

Field Measurements and Atmospheric Simulation Chamber Studies of Selected Biomass Burning Marker Compounds

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by

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&

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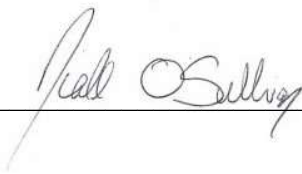
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Declaration

This is to certify that the work I am submitting is my own and has not been submitted for another degree, either at University College Cork or elsewhere. All external references and sources are clearly acknowledged and identified within the contents. I have read and understood the regulations of University College Cork concerning plagiarism and intellectual property.



Niall O'Sullivan

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Abstract

Biomass burning is a key contributor to ambient air pollution, which has significant impacts on climate and health. Biomass burning emits both solid particles and gaseous species known as volatile organic compounds (VOCs) which can undergo chemical oxidation reactions in the atmosphere with hydroxyl (OH) and nitrate (NO₃) radicals to produce secondary organic aerosols (SOA). While the particulate pollution has been well characterised, information on the VOCs associated with biomass burning is limited. To this end, a Time-of-Flight Chemical Ionisation Mass Spectrometer (ToF-CIMS) was deployed in Cork City, for the first comprehensive field study on the VOCs associated with residential burning of solid fuels (wood, peat, coal) in Ireland.

In the field study, a range of phenols and their nitro derivatives were detected during air pollution events caused by residential solid fuel burning. By following the evolution of these biomass burning markers through the night, evidence was found for the atmospheric conversion of phenol compounds to their analogous nitrophenols via gas-phase reaction with NO₃. Positive matrix factorisation was used to identify six different source categories for the VOCs which included fresh and atmospherically processed emissions from solid fuel burning, as well as oxidized emissions from local and regional background sources such as vehicles and agriculture.

A series of simulation chamber studies was also performed on the OH-initiated oxidation of two biomass burning marker compounds, 4-methylcatechol and guaiacol. The ToF-CIMS identified a large range of gas and particle products including polyphenols, nitrophenols, benzoquinones, ring scission species and accretion products, generating new information on the atmospheric degradation pathways. The results confirm the importance of both OH addition and H-atom abstraction reactions in initiating the oxidation processes and interestingly, in the case of guaiacol, loss of the methoxy group to form catechol which also underwent similar degradation pathways. A wide range of highly oxidized and nitro-containing species were identified in the particle phase which experienced further chemical processing, thus providing new insights into the mechanisms for the formation and atmospheric aging of SOA produced from biomass burning.

List of Abbreviations and Acronyms

ACSM	Aerosol chemical speciation monitor
AMS	Aerosol mass spectrometer
ATOFMS	Aerosol-time-of-flight mass spectrometer
BAM	Beta attenuation monitor
BBOA	Biomass burning organic aerosol
BC	Black carbon
BSQ	Big-segmented quadrupole
BVOC	Biogenic volatile organic compound
CCN	Cloud condensation nuclei
CIMS	Chemical ionisation mass spectrometer
COPD	Chronic obstructive pulmonary disease
CPC	Condensation particle counter
DBE	Double bond equivalent
DMA	Differential mobility analyser
DMS	Dimethyl sulfide
EC	Elemental carbon
EPA	Environmental Protection Agency
ERF	Effective radiative forcing
EUPHORE	European Photoreactor
FID	Flame ionisation detection
FIGAERO	Filter inlet for gases and aerosols
GC-MS	Gas chromatography mass spectrometry
GHG	Greenhouse gas

HOMs	Highly oxygenated organic molecules
HR-ToF-CIMS	High resolution time-of-flight chemical ionisation mass spectrometer
I-CIMS	Iodide CIMS
IHD	Ischaemic heart disease
IMR	Ion-molecule reactor
INP	Ice nucleating particle
IPCC	Intergovernmental Panel on Climate Change
LC-MS	Liquid chromatography mass spectrometry
MS	Mass spectrometry
MOVI	Micro orifice volatilisation impactor
NAC	Nitroaromatic compounds
NPF	New particle formation
OA	Organic aerosol
OC	Organic carbon
O/C	Oxygen to carbon ratio
OS _c	Oxidation state of carbon
OVOC	Oxygenated volatile organic compound
PAN	Peroxyacetyl nitrate
PCA	Principal component analysis
PM	Particulate matter
PMF	Positive matrix factorisation
PTFE	Polytetrafluoroethylene
PTR-MS	Proton-transfer-reaction mass spectrometer

RH	Relative humidity
SENEX	Southeast Nexus
SMPS	Scanning mobility particle sizer
SOA	Secondary organic aerosol
SOAS	Southern Oxidant and Aerosol Study
SSQ	Small-segmented quadrupole
TAG	Thermal desorption aerosol GC-MS
T _{max}	Temperature of maximum desorption signal
ToF	Time-of-flight
UK	United Kingdom
UPLC	Ultra-performance liquid chromatography
USA	United States of America
UV	Ultra-violet
VOC	Volatile organic compound
VUV	Vacuum ultra-violet
WHO	World Health Organisation

1. Introduction

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1.1 Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) are a class of organic compounds which exist in the gas phase at room temperature and are ubiquitous in the Earth's atmosphere. VOCs can be present at ppb or ppt concentrations in the troposphere and are derived from a multitude of sources, both biogenic and anthropogenic. Some of the most common groups of VOCs are alkanes, alkenes, halocarbons, carbonyls and aromatics (He et al., 2019). VOCs undergo a variety of reactions in the atmosphere, driven by atmospheric radicals (hydroxyl, nitrate and chlorine) and ozone (Williams and Koppmann, 2007). Some organic compounds, such as carbonyls, can also undergo direct photolysis by sunlight (Epstein et al., 2013). The reactions of VOCs have significant impacts on both climate and health, due to their propensity to form secondary organic aerosol (SOA) (Poschl, 2005; Hallquist et al., 2009). Aerosols are small solid or liquid particles suspended in air and can range in size from a few nanometres to tens of micrometres (Calvo et al., 2013). Organic aerosols (OA), both primary and secondary, are a major contributor to particulate matter (PM) pollution, most importantly the PM_{2.5} and PM₁ fractions. OA have been estimated to contribute up to 90% to PM_{2.5} concentrations (Jimenez et al., 2009), with SOA contributing up to 50% of total OA (Kanakidou et al., 2005). Thus, understanding the atmospheric chemistry of VOCs and SOA formation mechanisms is important to mitigate the effects of aerosols on both climate and health.

1.2 VOC Sources and Speciation

VOCs are derived from a wide variety of sources, incorporating both natural and anthropogenic activities. Biogenic VOCs (BVOCs) include species such as isoprene (C₅H₈), monoterpenes (C₁₀H₁₆) and sesquiterpenes (C₁₅H₂₄) and have been estimated to contribute up to 90% of global VOC emissions (Guenther et al., 1995). BVOCs are generally emitted from terrestrial ecosystems, however there are also significant

contributions to the global BVOC budget from the marine environment, particularly dimethylsulfide (DMS) which can undergo oxidation to form methanesulfonic acid as well as dimethylsulfoxide which are important atmospheric species (Ghahreman et al., 2019).

Anthropogenic VOCs are made up of many compound classes including alkanes, alkenes, aromatics and various oxygenated VOCs (OVOCs). They are commonly produced by combustion of fossil fuels in vehicles and industry, as well as biomass burning (Languille et al., 2020), and from their use as solvents (Williams and Koppmann, 2007). Biogenic species dominate global VOC emissions, however, in urban areas, anthropogenic species are often much more important due to the wide range of sources and human activities from which they are produced (Kanakidou et al., 2005). A specific class of VOCs which are produced from consumer and industrial products have been termed volatile chemical products (VCPs). VCPs originate from pesticides, paints, adhesives, cleaning agents, personal care products as well as a range of other sources (McDonald et al., 2018). VCPs have been shown to contribute up to half of petrochemical VOC emissions in major urban areas, while they are also a significant source of tropospheric ozone in urban environments (Coggon et al., 2021). In rural areas, anthropogenic VOC emissions primarily originate from biomass burning and agricultural activities (Calvo et al., 2013).

1.2.1 Biomass Burning Markers

Biomass burning is both a natural (wildfires) and anthropogenic process, with 90% of all biomass burning processes thought to be the result of human activity. Biomass burning emits a wide range of pollutants including particulate matter, carbon dioxide (CO₂), carbon monoxide (CO), nitrogen oxides (NO_x) and a plethora of VOCs (Koppmann et al., 2005; Chen et al., 2017). Wood burning leads to the pyrolysis of both lignin and cellulose, the primary components of wood which make up ~95% of its composition (Novaes et al., 2010). The most abundant product of cellulose pyrolysis is the anhydrous sugar, levoglucosan (Maduskar et al., 2018), which exists primarily in the particle phase and has been observed in numerous studies where biomass burning is a common contributor to organic aerosol (Pashynska et al., 2002; Kourtchev et al., 2008; Achad et al., 2018). Levoglucosan is therefore regularly used

as a particle phase molecular marker for biomass burning. Lignin is a polymer which contains three distinct aromatic ring substitution patterns, namely guaiacyl, syringyl and p-hydroxyphenyl, with the differences in distribution of the rings based on the variety of wood (Kawamoto, 2017). This leads to the emission of a variety of aromatic VOCs upon pyrolysis, including substituted methoxy phenols (e.g., guaiacol and syringol) as well as a range of substituted phenols (e.g., catechol and cresols) (Kawamoto, 2017), Figure 1.1.

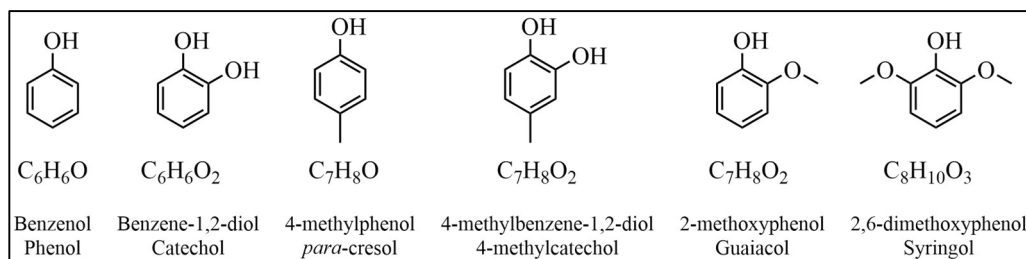


Figure 1.1 Selected biomass burning markers arising from lignin pyrolysis.

These species and their nitro derivatives have also been detected in the gas and particle phases in various studies of wood burning emissions (McDonald et al., 2000; Schauer et al., 2001; Akagi et al., 2012; Gilman et al., 2015). As a result, catechols and methoxyphenols are also considered to be important molecular marker compounds for biomass burning.

1.3 VOC Oxidation and Aerosol Formation

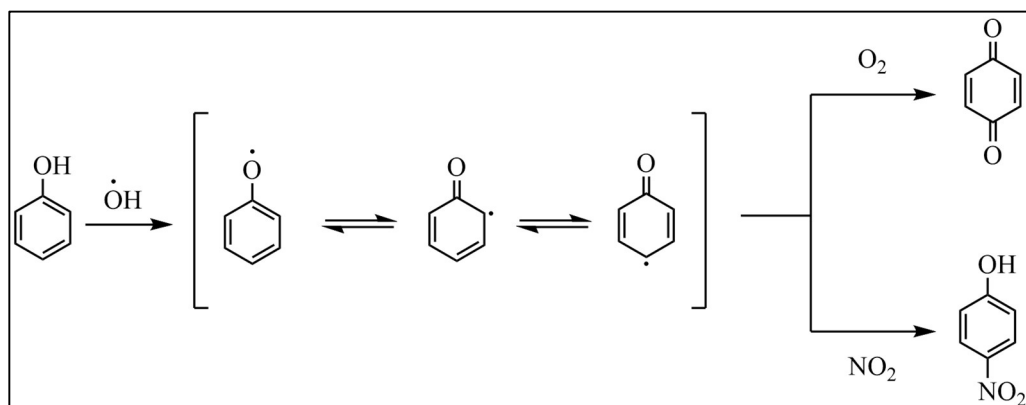
1.3.1 Oxidation pathways

Once emitted into the troposphere, VOCs can undergo chemical transformation via gas-phase reactions with hydroxyl (OH), nitrate (NO₃) and halogen (chlorine and bromine) radicals, as well as ozone (O₃) (Finlayson-Pitts and Pitts, 2000). Photolysis by sunlight is also possible for VOCs possessing a chromophore. OH radicals are the key driver of tropospheric chemistry and react readily with almost all biogenic and anthropogenic VOCs. They can be formed in the atmosphere from a variety of pathways including the photolysis of ozone and subsequent reaction of the excited

O^1D radical with water vapour (H_2O). Photolysis of formaldehyde (HCHO) and nitrous acid (HONO) are other significant sources of OH , particularly in more polluted environments. The tropospheric concentration of hydroxyl radicals depends on a number of variables, including sunlight intensity, concentration of precursors, nitrogen oxides (NO_x) and VOCs, but is generally around $1 \times 10^6 \text{ molecule cm}^{-3}$ during daylight hours (Heard and Pilling, 2003). Due to the highly reactive nature of hydroxyl radicals, they have a short atmospheric lifetime of $\sim 1 \text{ s}$. The reaction of OH with VOCs initiates a series of radical reactions in air which leads to the formation of VOC oxidation products and the regeneration of OH which helps to maintain the global budget of hydroxyl radicals (Heard and Pilling, 2003; Li et al., 2018).

Hydroxyl radicals readily react with organic compounds via two main reaction pathways, namely OH addition and hydrogen atom abstraction (H abstraction). The reaction pathway is highly dependent on the structure of the VOC. For aromatic compounds, the abstraction of a hydrogen atom directly from the ring is a highly energetically unfavourable pathway, e.g., for benzene, where reaction via OH addition is the major pathway ($\sim 95\%$) (Calvert et al., 2002). A summary of the possible reaction pathways for toluene is given in Scheme 1.1, where it is observed that as for all aromatics (C_xH_y), OH addition results in a cyclohexadienyl radical which can then undergo a variety of stabilisation reactions, with one of the most common pathways being reaction with O_2 to produce the hydroperoxyl (HO_2) radical and a stable molecule $\text{C}_x\text{H}_y\text{O}$, where a hydrogen atom has been replaced by a hydroxyl group. Another pathway involves addition of O_2 to the cyclohexadienyl radical to produce a peroxy radical $\text{RO}_2^\bullet$. This radical can undergo rearrangement resulting in a bicyclic radical, which upon reaction with O_2 , yields a bicyclic peroxy radical, $\text{BCPRO}_2^\bullet$. $\text{BCPRO}_2^\bullet$ can react with NO , yielding a bicyclic phenoxy $\text{BCPRO}^\bullet$ and NO_2 , or it can react with $\text{RO}_2^\bullet$ which also yields $\text{BCPRO}^\bullet$. $\text{BCPRO}^\bullet$ is then likely to undergo ring scission resulting in two products of smaller carbon chain lengths. Other pathways which involve the opening of the ring, but without breaking the carbon chain, are possible following the formation of a cyclohexadienyl radical, yielding products such as epoxides or dicarbonyls. It is often the result that the primary products of OH addition are more reactive than the precursor, and secondary or even tertiary chemistry can occur yielding highly oxidised species.

abstraction from phenol is outlined in Scheme 1.2, with benzoquinone and nitrophenol formation shown.



Scheme 1.2 Hydrogen abstraction mechanism from phenol showing benzoquinone and nitrophenol formation.

Hydroxyl radicals tend to dominate atmospheric chemistry during the daytime, however at night due to negligible photolysis and thus little to no OH production, nitrate radical chemistry can dominate. Nitrate radicals are formed via the reaction between ozone and nitrogen dioxide (Brown and Stutz, 2012) and while this reaction can also occur during the daytime, the nitrate radical is rapidly photolyzed by sunlight and does not reach significant concentrations until night-time. Most aromatic VOCs can react with NO₃ yielding organic nitrates, with these reactions generally proceeding via NO₃ addition to the aromatic ring, or via hydrogen abstraction from substituents on the ring, yielding RO• species which undergo further reaction to form stable molecules (Calvert et al., 2002).

The final major atmospheric oxidant is ozone, which reacts with unsaturated hydrocarbons via addition to the C=C bond. The resulting ozonide decomposes to yield a carbonyl and a Criegee intermediate which in turn can undergo a range of reactions, some of which produce OH radicals (Finlayson-Pitts and Pitts, 2000).

1.3.2 Aerosol Formation

VOC oxidation generates products with a higher oxygen to carbon ratio and lower volatility than the parent compound (Lanz et al., 2007; Aiken et al., 2008; Huffman et al., 2009; Grieshop et al., 2009). Once molecular volatility is low enough, the

oxidation products can partition into the particle phase forming aerosols. These aerosols are formed via reaction in the atmosphere rather than direct emission and are referred to as secondary organic aerosol (SOA) (Srivastava et al., 2022). Oxidised VOCs (OVOCs) can also undergo accretion reactions to form oligomers which partition readily into the particle phase (Kalberer et al., 2004). Partitioning into the particle phase may proceed via absorption of gas phase species onto fine atmospheric particles already in the atmosphere leading to growth of the primary particles, or via nucleation of sufficiently large OVOCs resulting in new particle formation (NPF). There has been some debate around the propensity with which OVOCs, particularly the class of compounds known as highly oxygenated organic molecules (HOMs), contribute directly to new particle formation. A study performed in Germany at a location significantly influenced by emissions from dairy farms, found significant correlations between sulfuric acid concentrations and new particle formation with little or no dependence on the concentration of HOMs. However as HOMs were present in all NPF events it could not be ascertained whether the absence of HOMs would have had an effect on NPF events (Kürten et al., 2016). A separate study in Switzerland however, found that NPF events were independent of sulfuric acid concentration once sufficient sulfuric acid was present, and significant correlations were observed between nucleation and the presence of HOMs (Bianchi et al., 2016).

Nucleation may also occur via condensation, whereby the gas phase concentration of a species increases until it reaches its saturation vapour pressure, at which point any excess amount of the species can condense homogeneously into the particle phase. This process is known as homomolecular nucleation, however it is not considered to be as important in aerosol growth as adsorption of sufficiently oxidised organic species onto the surface of pre-existing particles (Odum et al., 1996).

1.3.3 SOA complexity

SOA composition is a highly variable parameter, with dependencies on multiple atmospheric factors such as relative humidity (RH), concentration of NO_x during the aerosol formation process, the type of oxidant and light intensity (Pullinen et al., 2020; Chen et al., 2021, 2022). A range of studies have previously highlighted the impact of NO_x concentration on SOA yields, and although an enhancement is observed under

high NO_x conditions for some species (Ng et al., 2007a), it is more common for high NO_x concentrations to reduce SOA yields by forcing RO₂[•] species to react with NO rather than other RO₂[•] and HO₂, which tend to produce lower volatility products (Kroll et al., 2006; Sarrafzadeh et al., 2016). Relative humidity has also been shown to enhance SOA formation from several aromatic species (Healy et al., 2009; Chen et al., 2021), however increasing RH was found to reduce SOA yields from the long chain alkane n-dodecane (Lamkaddam et al., 2020).

The atmospheric oxidation of a single VOC can generate hundreds of oxidation products that partition into the particle phase (Walser et al., 2008). Recent studies investigating the photooxidation of anthropogenic and biogenic VOCs found significant differences in both aerosol yields and composition between mixed VOC experiments and single VOC experiments (Voliotis et al., 2022). The results obtained in these relatively straightforward laboratory studies highlight the complex nature of SOA. Given that there are often hundreds of VOCs in ambient air, it is clear that SOA in the real atmosphere will be even more complex and exhibit a very high degree of chemical variability.

1.4 Impacts on Climate and Health

1.4.1 Climate

Secondary organic aerosols have significant impacts on climate, due to their impact on the Earth's energy balance. The Intergovernmental Panel on Climate Change defined radiative forcing as “a measure of the influence a factor has in altering the balance of incoming and outgoing energy in the Earth-atmosphere system and is an index of the importance of the factor as a potential climate change mechanism” (IPCC, 2007). Radiative forcing can be simplified to the warming influence that a particular pollutant has on the Earth-atmosphere system. Pollutants alter the energy balance of the Earth by the absorption and scattering of solar radiation which can have net warming or cooling effects, also referred to as positive or negative radiative forcing effects. Figure 1.2 illustrates the effective radiative forcing (ERF) caused by different atmospheric components (IPCC, 2021).

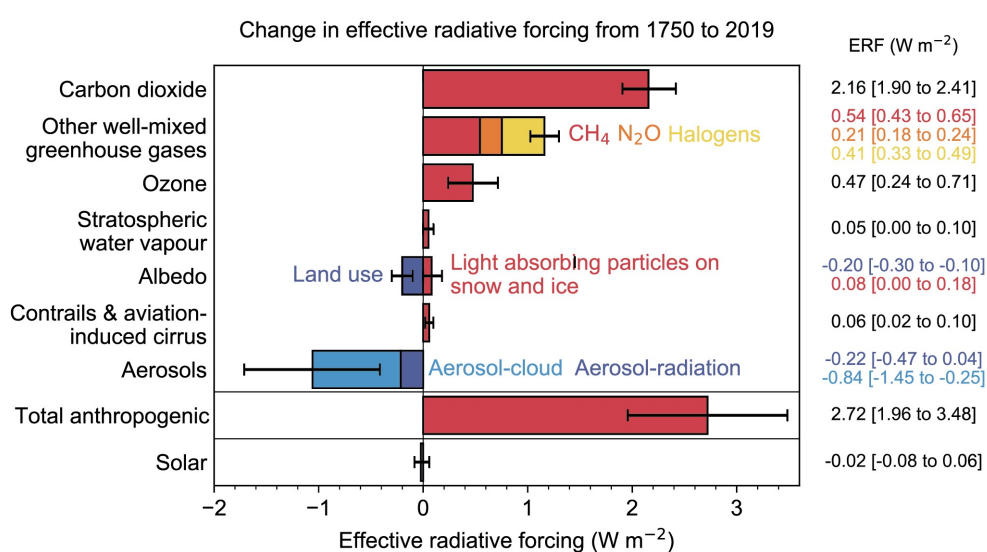


Figure 1.2 Changes in effective radiative forcing (ERF) caused by different atmospheric components between 1750 and 2019, adapted from IPCC, 2021.

Aerosols have a net cooling effect on the atmosphere, thus mitigating against the warming effects caused by other species, notably CO_2 and other greenhouse gases (GHGs). Figure 1.2 highlights both aerosol-radiation and aerosol-cloud interactions, which are also called the direct and indirect effects of aerosols. Aerosol-radiation interactions refer to the direct scattering and absorption of both incoming solar

radiation and radiation reflected by the Earth's surface which alters the amount of radiation reaching a particular location, thus resulting in a cooling effect (Andrews et al., 2011).

The indirect effect of aerosols, or aerosol-cloud interaction, refers to the fact that aerosols can act as cloud condensation nuclei (CCN) and ice-nucleating particles (INPs). Cloud condensation nuclei are surfaces upon which water vapour in the atmosphere can condense, with the ability of an aerosol to act as a CCN dependent on its composition. For example, inorganic salts such as sea salt, are far better condensation nuclei than organic species due to their higher solubility in water (Levy II et al., 2013). When increased concentrations of CCN are present, there is an increase in cloud albedo, which is a measure of the reflectivity of a cloud. Increased cloud albedo has a net cooling effect on the atmosphere due to the reflection of incoming solar radiation, with an estimate that cloud albedo has a net ERF of -0.9 W m^{-2} (Lohmann et al., 2010). Ice-nucleating particles promote the formation of ice crystals in clouds, which changes cloud properties such as radiative forcing and microphysical properties, while ice particles can also scavenge semi-volatile species and acidic trace gas species (Kanji et al., 2017). It has recently been shown that atmospheric aging of biomass burning aerosols increases their ability to act as INPs. This is because the aging process causes oxidation of the aerosol surface making it more hygroscopic and upon immersion in a cloud would be more likely to dissolve, thus exposing more ice-active sites for nucleation (Jahl et al., 2021).

Another indirect effect of aerosols on tropospheric temperature is their effect on precipitation in the troposphere. As aerosols reduce surface temperature via the direct effect, they reduce the need for precipitation to cool the troposphere to maintain energy balance. Precipitation is also reduced by aerosols which actively have a warming effect such as black carbon (BC) which reduces condensation and therefore precipitation (Levy II et al., 2013).

1.4.2 Health

Atmospheric aerosols and particulate matter (PM) have consistently been shown to have negative impacts on human health, due to their morphology and chemical

composition (Schraufnagel, 2020). They can affect the respiratory and cardiovascular systems and have also been linked with neurodegenerative diseases such as Alzheimer's and Parkinson's (Peters, 2023). A recent modelling study from the USA showed that exposure to SOA has a rate of mortality that is 6.5 times higher than that of PM_{2.5} exposure alone (Pye et al., 2021), thereby confirming that the chemical composition of fine (PM_{2.5}) and ultrafine (PM_{0.1}) particles has a significant impact on the health effects observed.

Recent estimates indicate that outdoor air pollution is responsible for upwards of three million premature deaths per annum globally (Lelieveld et al., 2019), while estimates regarding indoor pollution show similar results (Health Effects Institute, 2020). The World Health Organization (WHO) reports that the most common causes of mortality due to exposure to air pollution are ischaemic heart disease (IHD), stroke, chronic obstructive pulmonary disease (COPD) and lung cancer, with 24% of strokes and 43% of COPD cases worldwide attributable to air pollution (World Health Organization Regional Office for Europe, 2019).

PM enters the respiratory tract through inhalation as illustrated in Figure 1.3, with particle size playing a significant role in determining the depth to which a particle can penetrate the cardiovascular system (Morawska and Buonanno, 2021). Larger particles are generally deposited in the upper airway, with PM_{2.5} reaching the lungs and PM_{0.1} reaching the alveoli and potentially crossing the air-blood tissue barrier. Once particles cross into the bloodstream, they can be transported to any organ in the body, notably the liver, heart and central nervous system (Kreyling et al., 2006).

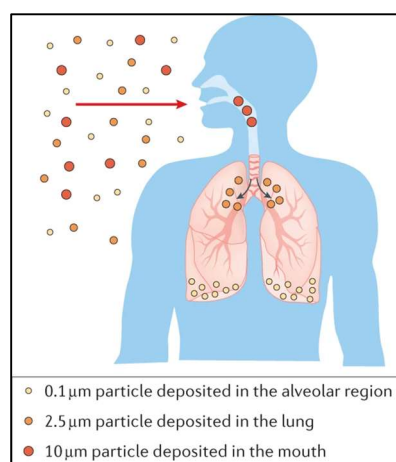


Figure 1.3 Schematic showing the regions of particulate deposition in the human respiratory system, adapted from Morawska et al 2021.

Inhalation of ultrafine particles (particles with aerodynamic diameter $\leq 0.1 \mu\text{m}$ (Kwon et al., 2020)) has been shown to result in tissue damage based on its composition, primarily related to the solubility of the particle. The water soluble fraction can cause oxidative stress and damage to DNA resulting in cell death due to hydroxyl radical formation via transition metal dependent pathways (Falcon-Rodriguez et al., 2016; Shen et al., 2022).

VOCs have also been shown to have adverse health effects, notably through the onset of pulmonary diseases such as asthma (Alford and Kumar, 2021). VOCs react with the epithelium lining (outer surface of organs and blood vessels) and the mucosa membrane (inner lining of organs) via reaction between these amine rich sites and CO bonds in VOCs (Alford and Kumar, 2021). Benzene and formaldehyde were found to have the most significant impact of any specific VOCs on pulmonary stress such as asthma, wheezing and throat irritation. In addition to triggering pulmonary stress, benzene is a known carcinogen to humans (Huff, 2007). Functionalised VOCs such as nitrophenols have also been found to have adverse effects on the endocrine system (Ahmed et al., 2015), while dinitrophenols have been observed to be highly toxic (Grundlingh et al., 2011). Both of these species were found to be among the most dominant nitroaromatic compounds (NACs) released from industrial sources in China (Lu et al., 2021).

1.5 Fate of VOCs and Aerosols in the Atmosphere

There are two primary removal methods for aerosols from the atmosphere, wet and dry deposition. Wet deposition involves two processes, in-cloud scavenging and below-cloud scavenging. In-cloud scavenging is the process of CCN and ICN formation, after which aerosols grow in size and eventually fall as precipitation, while below-cloud scavenging happens when aerosols in the atmosphere collide with falling precipitation and are collected by the precipitation as it falls (Jones et al., 2022).

Dry deposition is the removal of aerosols by physical processes, including impaction on different surfaces (forests, grasslands, and buildings) and gravitational settling. The degree of dry deposition by various mechanisms is highly dependent on particle diameter, with larger particles more efficiently removed by impaction while smaller particles are most efficiently removed by diffusion processes, such as Brownian diffusion (Farmer et al., 2021). Figure 1.4 illustrates the removal methods as a function of particle size, with the shaded regions corresponding to (a) diffusion processes (blue), (b) gravitational settling (yellow), (c) interception (orange) and (d) impaction (purple).

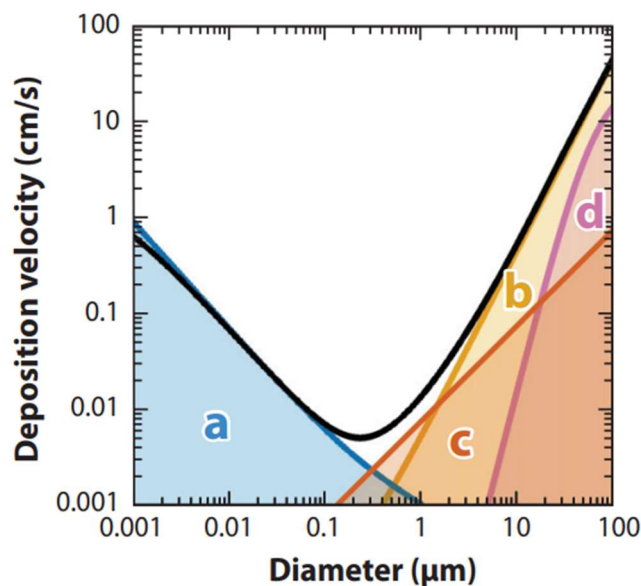


Figure 1.4 Particle deposition mechanisms as a function of particle size, adapted from Farmer et al (2021).

VOCs which do not partition into the particle phase due to their high vapour pressures even after oxidation, continue to be oxidised until they eventually form CO_2 (de Gouw and Warneke, 2007).

A summary of VOC processes and emissions is given in Figure 1.5 which highlights VOC sources, processing and sinks (Williams and Koppmann, 2007).

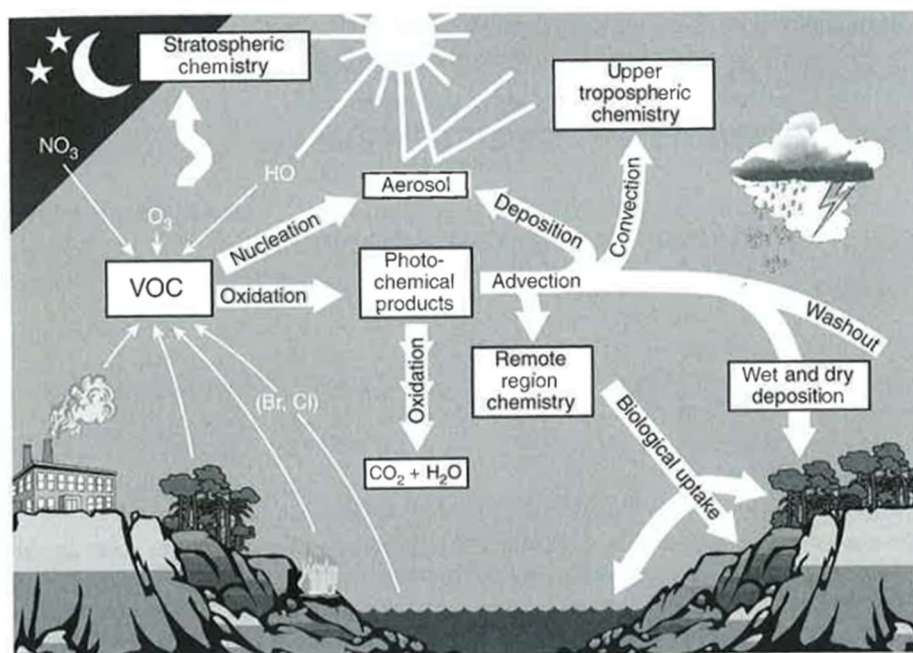


Figure 1.5 Summary of the chemistry and processes of VOCs in the atmosphere, adapted from Williams and Koppmann (2007).

1.6 Measurement Techniques

1.6.1 VOC Measurements

VOCs can be detected in the ambient atmosphere using a variety of different instruments, with mass spectrometry being the most widely used technique for measurements of chemical composition. Time-of-flight (ToF) mass spectrometers in particular provide an accurate and sensitive method for VOC detection, with Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) being especially efficient for online quantification purposes (de Gouw and Warneke, 2007). PTR-MS has been widely used for the detection of anthropogenic and biogenic hydrocarbons, as well as some

functionalized organic species (Herbig et al., 2009; Liu et al., 2017; Kammer et al., 2020). PTR-MS is not as effective for the measurement of OVOCs, especially for species with more than two oxygen atoms, however these species are readily detectable by Time-of-Flight Chemical Ionisation Mass Spectrometry (ToF-CIMS) (Riva et al., 2019b). Both methods operate using a reagent ion to transfer a charge to the analyte species, at which point it passes through at least one quadrupole and a range of ion lenses to focus the ion stream, before passing into a time-of-flight (ToF) chamber where the ions are pulsed, and the time taken to reach the detector is measured. The mass is determined based on the proportionality of the mass to charge ratio and time taken to reach the detector. These allow accurate mass measurements and in instruments with high resolving power, high resolution mass data can be obtained allowing the identification of multiple species at single unit masses.

PTR-MS operates using a drift tube and the hydronium ion (H_3O^+) to ionise the analyte, however, as mentioned, PTR-MS is not suitable for the detection of OVOCs where there are more than two oxygen atoms which is likely a result of the reduced volatility of these species and the low flow rates in PTR instruments (between 50 and 1000 sccm). On the other hand, ToF-CIMS allows for the detection of a wide range of VOCs due to the ability to switch reagent ions to efficiently detect the target species. Iodide (I^-) is a commonly used reagent ion due to its ability to detect OVOCs with two or more oxygen atoms, and this technique has been used in a variety of studies to detect OVOCs such as phenols and acids in both field measurements and simulation chamber experiments, as well as atmospheric trace gases such as nitric acid (HNO_3) (Lee et al., 2014; Riva et al., 2017; Thompson et al., 2017; Chen et al., 2020; Zhang et al., 2020; Salvador et al., 2021; Dörich et al., 2021). As well as iodide, other reagents can be used with the ToF-CIMS to detect different types of chemical species. For example, the use of nitrate (NO_3^-) CIMS allowed the first detection of HOMs (Ehn et al., 2014) and paved the way for more detailed studies on their role in aerosol formation (Jokinen et al., 2015; Richters et al., 2016; Molteni et al., 2018). Meanwhile, bromide (Br^-) CIMS has been used for the detection of atmospheric radicals allowing insights into radical generation during photooxidation processes (Sanchez et al., 2016).

Prior to the development of ToF analysers for online VOC detection, measurements were performed offline, using adsorbent materials to collect VOCs from ambient air, with subsequent analysis using various mass spectrometry techniques, primarily

thermal desorption gas chromatography mass spectrometry (GC-MS). Although GC-MS is able to identify and quantify a wide range of VOCs, the sample collection and analysis times can be long, with no high time resolution data available to monitor rapidly changing air masses (de Gouw and Warneke, 2007). On the other hand, one advantage of GC-MS over ToF-MS is the ability to separate, identify and quantify organic species with the same molecular formula (isomers), e.g. the monoterpenes, and both online and offline methods can therefore be used to provide complementary information on VOC composition.

1.6.2 Aerosol Measurements

The analysis of the chemical composition of organic aerosols has traditionally been carried out by extraction of material collected on quartz or Teflon filters, followed by offline analysis using liquid chromatography mass spectrometry (LC-MS), GC-MS or other analytical techniques (Edney et al., 2005; Reinnig et al., 2008; Kourtchev et al., 2011). Online characterisation of PM is possible with aerosol mass spectrometers (AMS) and the aerosol chemical speciation mass spectrometer (ACSM), however these instruments only provide bulk composition and offer no molecular identification. Nevertheless they are extremely useful instruments which have been used in numerous studies, especially in conjunction with positive matrix factorization (PMF) for source apportionment in a variety of locations (Canagaratna et al., 2007; Lin et al., 2017; Poulain et al., 2020).

Efforts to develop semi-real-time molecular level analysis of the particle phase led to the development of new measurement techniques. Particle impaction methods such as the MOVI (Micro Orifice Volatilisation Impactor) (Yatavelli et al., 2012) and TAG (Thermal Desorption Aerosol GC/MS-FID) (Williams et al., 2006) are two such methods, however they suffered from the same problem as most impaction methods, which is reduced particle collection efficiency. The development of the Filter Inlet for Gases and Aerosols (FIGAERO) (Lopez-Hilfiker et al., 2014) coupled to a CIMS instrument was a significant advancement in the semi-online analysis of organic aerosol. The FIGAERO utilises a moveable tray to analyse both gas and particle phase species separately. The operation of the FIGAERO is discussed in more detail in Chapter 2, but briefly, it collects particles on a PTFE filter while simultaneously

performing gas phase measurements, and after a selected time period, the gas phase sampling is stopped, and the organic aerosol collected on the filter is thermally desorbed and passed into the mass spectrometer for analysis. Use of the FIGAERO has allowed molecular identification of gas and particle phase organic species in a wide range of field and laboratory studies as well as providing key information regarding particle volatility, while recently it has been shown to be a useful tool for the offline analysis of previously collected ambient OA samples (Ye et al., 2019; Lee et al., 2020; Mehra et al., 2020; Salvador et al., 2021; Ye et al., 2021; Cai et al., 2023).

1.7 Chamber Studies of SOA formation

Laboratory studies are routinely performed to improve our understanding of the processes and reactions that govern atmospheric composition, air quality and climate. Over the last few decades, simulation chambers have emerged as one of the most useful tools for investigating the atmospheric oxidation of VOCs and formation of SOA due to their ability to provide an oxidizing environment where parameters such as light, relative humidity, NO_x and VOC concentration can all be controlled and monitored accurately (Doussin et al., 2023). Atmospheric simulation chambers are generally located indoors and use a range of lamps which emit in the UV-visible range to initiate photooxidation (Mentel et al., 2009; Healy et al., 2012; Voliotis et al., 2022). However, some outdoor simulation chambers also exist, such as the EUPHORE facility in Valencia, Spain (Martín-Reviejo and Wirtz, 2005), which uses natural sunlight to induce photochemistry.

Simulation chamber experiments of VOC oxidation typically involve the addition of the selected compound and oxidant (or a precursor) at the desired concentrations. Other gases such as nitrogen oxides or water vapour may also be added to the chamber. Reaction of VOCs with O₃ and NO₃ is performed in the dark, while for OH reactions, the UV-Visible lamps are turned on to photolyse a precursor to generate the OH radicals. Measurements of the gas-phase reactants and products is performed throughout the experiment using spectroscopy or spectrometry techniques, while the

growth and formation of SOA can be monitored using particle sizing instruments. Air samples can also be taken for further analysis offline. Simulation chambers have been used in a wide range of studies to measure SOA formation (Coeur-Tourneur et al., 2010; Healy et al., 2012; Fredrickson et al., 2022), to identify the major oxidation products of VOCs (Olariu et al., 2002, 2013; Lauraguais et al., 2014; Finewax et al., 2019; Voliotis et al., 2022), and also for the measurement of rate coefficients for VOCs with different atmospheric oxidants (Bejan et al., 2007; Olariu et al., 2000).

1.8 Overview

1.8.1 Aims of Research

The overall aim of this research is to:

- Identify the major VOCs present in ambient air in Cork City, Ireland during a winter field campaign and to elucidate their sources, with a particular focus on VOCs arising from the burning of solid fuels for home heating.
- Perform simulation chamber studies on the OH-initiated oxidation of two key VOCs identified during the field campaign to investigate the various reaction pathways that lead to the formation of oxidation products in both the gas and particle phases.
- Investigate the aging of the SOA formed in the simulation chamber experiments under both light and dark conditions to better understand how the composition of SOA changes in the atmosphere.

1.8.2 Overview of Thesis

Chapter 1 presents an introduction to volatile organic compounds (VOCs) and atmospheric aerosols, specifically; VOC sources in the atmosphere, atmospheric processing of VOCs to form secondary organic aerosol (SOA), the sinks of VOCs and SOA and their impact on both climate and health. Various techniques for the measurements of VOCs and SOA, both online and offline are also discussed.

Chapter 2 introduces the instrumentation used in this thesis, with specific focus on the time-of-flight chemical ionisation mass spectrometer (ToF-CIMS) which forms the basis for most of the work presented here. The atmospheric simulation chamber used in Chapter 4 and Chapter 5 is also described here, as well the experimental protocol used for simulation chamber experiments.

Chapter 3 presents the results from a field campaign performed in Cork City in winter 2019, during which the ToF-CIMS was deployed, along with other air quality monitoring instruments. There is a focus on the temporal profiles observed for selected

biomass burning marker compounds, including the species $C_7H_8O_2$, which is attributed to 4-methylcatechol and/or guaiacol. Positive matrix factorisation (PMF) is used to identify the major sources contributing to ambient VOC concentrations.

Chapter 4 presents results from a series of simulation chamber experiments on the OH-initiated oxidation of 4-methylcatechol where the FIGAERO-ToF-CIMS was used to identify the formation and evolution of the gas and particle phase products.

Chapter 5 focuses on results obtained using the FIGAERO-ToF-CIMS in a series of simulation chamber experiments on the OH-initiated oxidation of guaiacol. Mechanistic information is derived from the temporal evolution of the gas and particle phase products, and the aging of SOA was investigated under both light and dark conditions.

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2.1 ToF-CIMS

The principal instrument used in this work is a time-of-flight chemical ionisation mass spectrometer (ToF-CIMS), developed by ToFwerk AG, Switzerland and Aerodyne Research Inc, USA (Bertram et al., 2011). This instrument is used to detect gaseous species and especially VOCs but can be adapted to analyse the composition of SOA (Aljawhary et al., 2013). A schematic of the ToF-CIMS is shown in Figure 2.1. Air is sampled at a rate of 2 L min^{-1} through an inlet and flows into the ion-molecule reactor (IMR) where chemical ionisation of the analytes occurs. The ionised species subsequently pass through a critical orifice, a small-segmented quadrupole (SSQ) and a big-segmented quadrupole (BSQ). After passing through the BSQ, the ions are focused through a series of lenses before passing into the ToF chamber where they are separated based on their mass to charge ratio and finally detected. The instrument has three differentially pumped stages, with the pressure decreasing sequentially through the CIMS. The pressure in the IMR and SSQ can be varied to ensure optimum generation of analyte ions, with pressures of 150 mbar and 2 mbar respectively used for the field measurements presented in Chapter 3 and 120 mbar and 1.3 mbar respectively used for the chamber experiments performed in Chapter 4 and Chapter 5. The BSQ pressure of $\sim 1.6 \times 10^{-2}$ mbar is maintained by a turbo pump which is also used to deliver a pressure of $\sim 1 \times 10^{-6}$ mbar in the ToF chamber.

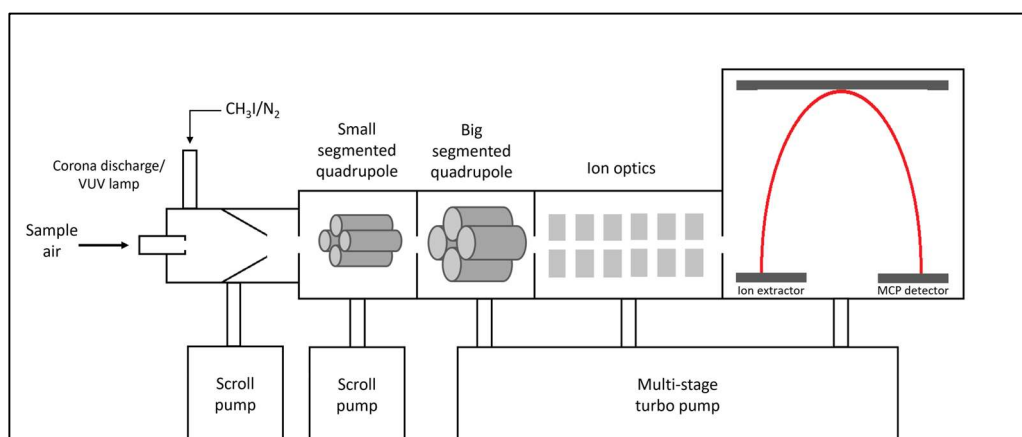


Figure 2.1 Schematic of the ToF-CIMS used in this work.

2.1.1 Ionisation Sources

The CIMS uses a soft ionisation process to produce analyte ions which undergo minimal fragmentation, thus enabling easy identification of the molecular formula. The ions are generated by passing high purity nitrogen (99.999%, BOC Gases Ireland Ltd.) over a permeation tube (VICI Metronics, USA) containing the reagent ion source in liquid form. The tube is heated to ensure that sufficient amounts of the reagent evaporate through the permeable material (polytetrafluoroethylene, PTFE) and is carried in the nitrogen flow. The permeation rate is proportional to temperature and flow rate of N₂ and these parameters were adjusted to reach the required concentration of reagent ion (Susaya et al., 2011). After passing through the ioniser, the reagent ions pass into the IMR, orthogonal to the analyte ions, where the neutral analyte molecules cluster with the reagent ions, generating charged analyte-reagent adducts which are readily detected by the CIMS. In this work, two different ionisation sources were used, a corona discharge and vacuum ultraviolet (VUV) source.

Corona discharge

A corona discharge is an electrical discharge formed between two electrodes, and when a charge of a few kilovolts or higher is applied, the air in between the two electrodes is ionised. The corona discharge used in this work is similar to that described in Zheng et al. (2015), Figure 2.2. It is important to minimise the contaminants in the air that passes through the corona discharge, especially oxygen and water due to the propensity of these species to generate O⁻ ions which can result in significant amounts of O₃ and NO₃ ions in the background mass spectra (Zheng et al., 2015). In addition to the work by Zheng et al. (2015) who measured sulfuric acid, a corona discharge coupled to a mass spectrometer was also used by Jost et al. (2003), to measure other atmospheric trace gases such as acetonitrile and sulfur dioxide, while Kürten et al. (2011) also measured sulfuric acid using a corona discharge CIMS (Jost et al., 2003; Kürten et al., 2011). The corona discharge was used as the ion source for the data presented in Chapter 3, however, due to the wide range of interferences from species such as O₂ and H₂O leading to high instrument backgrounds for species such as NO₃⁻ and O₃⁻, an alternative was sought.



Figure 2.2 Corona discharge and housing unit.

Vacuum ultraviolet

The vacuum ultraviolet (VUV) source for the ToF-CIMS was recently developed by Ji et al. (2020), who characterised the new source for use with iodide reagent. This source uses a Kr lamp which generates two emission lines centred at 116.486 nm and 123.582 nm respectively. During the characterisation of the system, methyl iodide (CH_3I) was used to generate I^- ions due to its large absorption cross section at the wavelengths produced by the Kr lamp, and its low ionisation potential (Ji et al., 2020). Ions were produced by absorption of the UV light by the CH_3I molecules producing cations and photoelectrons which then generate I^- ions after attaching to CH_3I . Characterisation of the VUV source showed that it gave similar spectral backgrounds to the ^{210}Po ion sources widely used in ToF-CIMS instruments, thus it was deemed a suitable replacement for the corona discharge which had been used to date. The VUV source was used for the data presented in Chapter 4 and Chapter 5. A picture of the VUV connected to the IMR is given in Figure 2.3.

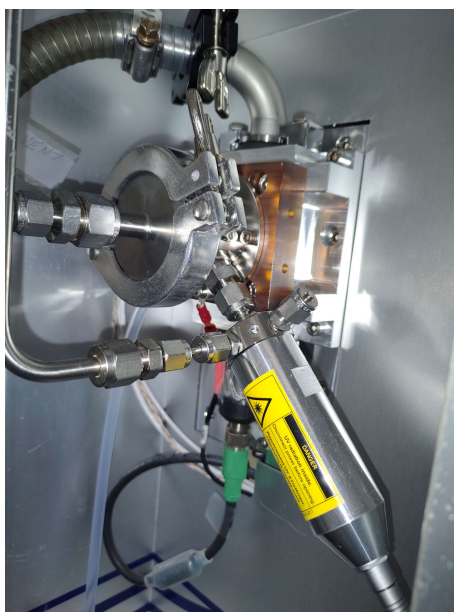


Figure 2.3 Vacuum ultra-violet light source connected to the IMR of the ToF-CIMS.

2.1.2 Reagent Ions

Iodide

The majority of this work was performed using iodide (I^-) as the CIMS reagent ion, generated from evaporation of methyl iodide in the permeation tube, heated at 35 °C. Iodide-CIMS (I-CIMS) has excellent capabilities for the detection of a range of compounds, notably multifunctional oxygenated organic compounds (Lee et al., 2014; Zhang et al., 2017; Riva et al., 2019b). Once the I^- ions have been generated and passed into the IMR, they react with neutral analyte ions to form negatively charged adducts:



Lee et al. (2014) found that iodide adducts are most likely to be formed with VOCs that have two or more oxygen atoms and the technique is not sensitive towards monofunctional alcohols, ketones or aldehydes and is also insensitive towards non-oxygenated VOCs. They also reported that iodide sensitivity to functional groups increases with polarity, in the order keto, hydroxy and acid groups (Lee et al., 2014). I-CIMS has been used for the detection of OVOCs in the field measurements described in Chapter 3 (with corona discharge ion source), as well as the simulation chamber experiments reported in Chapter 4 and Chapter 5 (with VUV ion source).

Benzene

Benzene has also been used as a reagent ion in atmospheric simulation chamber experiments presented in Chapter 4 and Chapter 5. The VUV initiated ionisation of benzene (C_6H_6) produces cations of benzene (C_6H_6^+) which can react with an analyte (A) to generate cations (A^+) via charge transfer while in some cases it also produced analyte ions which have undergone a proton transfer (AH^+) or in rare cases clustering with the reagent ($\text{C}_6\text{H}_6\text{A}^+$). Benzene CIMS has been used previously for the detection of a range of biogenic compounds such as isoprene, α -pinene and β -caryophyllene and was implemented in this work to explore the detection of ions which I-CIMS was not sensitive to (Kim et al., 2016; Lavi et al., 2018).

2.1.3 Data Analysis

All CIMS data was recorded at 1 Hz resolution, however prior to analysis pre-averaging was performed using the Tofware software package (Stark et al., 2015) (Tofware v3.2.0, Tofwerk and Aerodyne Research) which is a plug-in for the Igor Pro software (Igor Pro v7.0.8.1, Wavemetrics Inc, USA). Mass calibration as well as peak assignment and fitting were performed in Tofware. The instrument was generally operated with a resolution of $\sim 5500\ m/\Delta m$, allowing good peak separation during analysis. An example of the resolving power of the instrument is shown in Figure 2.4, where five different peaks at a single unit mass are well resolved and ready to be integrated.

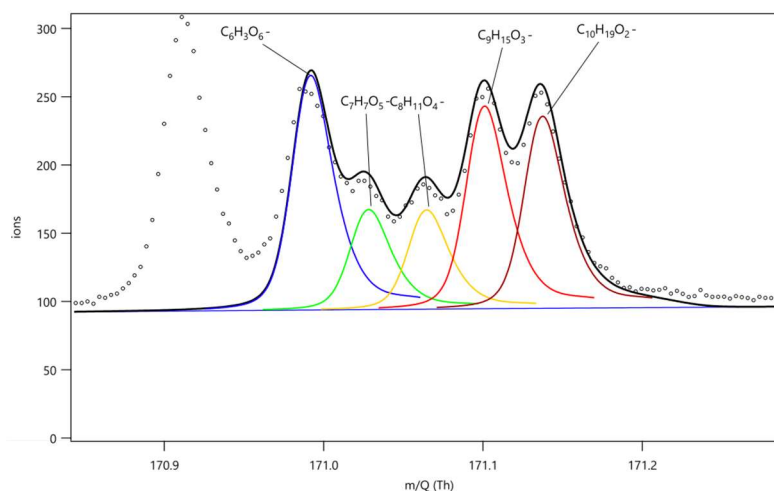


Figure 2.4 Mass resolving power of the ToF-CIMS.

Following peak fitting, normalisation by reagent ion, multiplication by a factor of 1×10^6 , and peak integration, data was exported from Tofware for further analysis and plotting, which was performed using various custom-built codes in the programming language R.

2.1.4 Filter Inlet for Gases and Aerosol (FIGAERO)

The FIGAERO was developed to allow the ToF-CIMS to detect gas and particle phase species near simultaneously (Lopez-Hilfiker et al., 2014). It has been used in a variety of field and simulation chamber studies to provide valuable insights into VOC oxidation and SOA formation (Gaston et al., 2016; D'Ambro et al., 2017; Chen et al., 2020; Thornton et al., 2020; Garofalo et al., 2021). A schematic of the FIGAERO is given in Figure 2.5

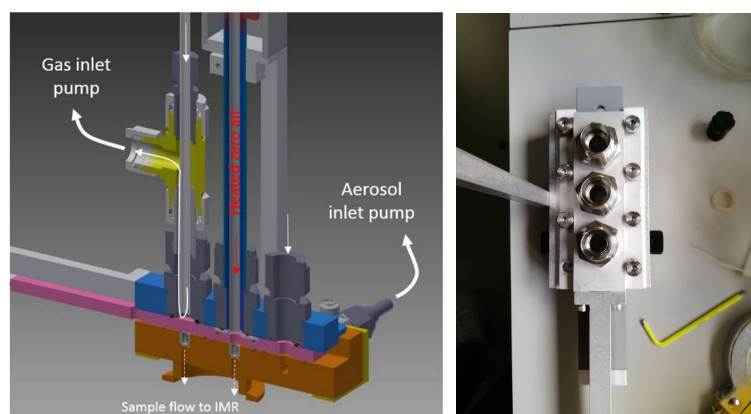


Figure 2.5 Schematic and picture of the FIGAERO inlet

The FIGAERO has three sampling lines (gas inlet, aerosol inlet and heated zero air) and two sample flows into the IMR. This sampling system is operated in different ways to allow two modes of operation, called “collect” and “desorb”. In the “collect” position, which is shown in the photograph above, the gas phase inlet is aligned with the IMR flow and gas phase species are continuously sampled by the CIMS. At the same time, the “aerosol inlet pump” is used to collect particles on a PTFE filter placed in the top sampling line. Once the gas phase analysis has been completed or sufficient particle mass has been collected on the filter, the FIGAERO is switched to “desorb” mode; the linear actuator is moved down, so that the filter now sits in the middle of the FIGAERO inlet and is aligned with the second sample flow to the IMR. High purity nitrogen is passed over the filter with a temperature ramp applied to the nitrogen

which passes through a heating block. The N₂ is heated from ambient temperature to 200 °C over a user defined time limit, which in this work was always 15 minutes. Once the temperature has been reached, the nitrogen is continuously passed over the filter at 200 °C for a further 15-minute period, known as the temperature soak period, to ensure complete desorption of all volatile material from the filter. This slow temperature ramping cycle results in semi-volatile material in the particle phase evaporating slowly from the filter, with evaporation rates related to molecular structure and volatility (Lopez-Hilfiker et al., 2014; Bannan et al., 2019). In the field campaign presented in Chapter 3 of this work, the FIGAERO inlet was operated on an hourly cycle incorporating 25 minutes of gas sampling and aerosol collection and a 35-minute aerosol analysis period, consisting of a 15-minute temperature ramp, a 15-minute temperature soak, and a cooling period of 5 minutes. The protocol for chamber experiments varied by experiment, with aerosol sampling periods variable based on SOA mass formation. In chamber experiments, ion signals were corrected for estimated mass loading based on the aerosol sampling flow, aerosol sampling duration and SOA mass in the chamber.

2.2 Other Instrumentation

2.2.1 Field Campaign

Gas analysers

Gas analysers were used for continuous monitoring of nitrogen oxides and ozone during the field campaign discussed in Chapter 3. Nitrogen oxides were monitored using a commercial chemiluminescence NO_x monitor (T200, Teledyne API). This instrument measures NO directly via titration with ozone and measuring the light emitted by the NO₂ that is produced. The instrument measures NO_x (NO and NO₂) by passing the sampled air over a heated molybdenum catalyst to convert NO₂ to NO which is then titrated with ozone, along with the NO originally in the air. In ambient air monitoring, the difference between the NO and NO_x concentrations is usually attributed to NO₂. Ozone was measured using a commercial monitor which operates on the principle of UV absorption at 254 nm (T400, Teledyne API).

Beta Attenuation Monitor (BAM-1020)

PM_{2.5} was monitored using a beta attenuation monitor, BAM-1020 (Met One Instruments Inc, USA). This model operates by collecting PM_{2.5} on a filter tape for 42 minutes at a rate of 16.7 L min⁻¹. PM mass concentration is then measured by beta attenuation which involves passing beta radiation through the filter tape and recording the amount of beta radiation absorbed by the collected particles, which is proportional to the amount of mass collected. Thus, PM_{2.5} concentration is reported hourly in units of $\mu\text{g m}^{-3}$.

2.2.2 Chamber experiments

Gas Analysers

Gas analysers for measuring NO_x and O₃ in the chamber experiments were the same models as those used in the field campaign (T200 and T400, Teledyne API). However, care was taken when analysing data recorded by the gas analysers during chamber experiments as a range of other species may contribute to the measured concentrations. For example, in experiments where HONO was used as the OH precursor, the thermal decomposition of HONO and other species contributes to the reported NO_x concentration, and it is incorrect to assume that the difference between the NO and NO_x concentrations is solely due to NO₂. As a result, it is more appropriate to consider the reported NO_x concentration to be the NO_y concentration, which is the sum of NO₂, HONO, HNO₃ and other nitrogen-containing species that may thermally decompose to produce NO (Finlayson-Pitts and Pitts Jr, 2000). In addition, the concentrations provided by the O₃ analyser during experiments where H₂O₂ was used were not deemed to be accurate as the OH precursor also absorbs strongly at 254 nm, thus giving false readings. Further interferences with measured O₃ concentrations are due to the formation of a plethora of organic species containing carbonyl groups. Carbonyl groups, especially those with significant conjugation, often absorb light in the UV region of 200 – 300 nm, varying with the specific structure of the organic species. These absorptions are due to both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in C=O bonds, thus the measured concentration of O₃ would be artificially inflated due to absorption of 254 nm radiation by these carbonyl containing compounds.

Scanning Mobility Particle Sizer (SMPS)

A scanning mobility particle sizer (SMPS model 3938, TSI Incorporated, USA) was used to measure the growth and evolution of SOA particles during chamber experiments. The SMPS system was operated using a sheath flow rate of 5 L min⁻¹ with a scanning time of 2 minutes, composed of 90 seconds of sampling and 30 seconds of purging, measuring particles from 10.7 to 469.8 nm. The SMPS system is composed of a model 3082 Electrostatic Classifier and a model 3750 Condensation Particle Counter (CPC). The electrostatic classifier separates particles using a differential mobility analyser (DMA) to generate monodisperse streams of aerosol based on electrical mobility which is inversely proportional to particle diameter. The size separated particles are then passed to the CPC, where particles are drawn through a heated saturator where butanol is vapourised and joined with the sample stream. The combined stream is then cooled by a condenser, leading to supersaturation of the butanol vapour and subsequent condensation. The particles in the stream act as condensation nuclei allowing larger particles to form, and once sufficient size is reached, the particles grow into large droplets which are counted by an optical detector. The SMPS system therefore allows for monitoring of particle formation and growth due to its ability to accurately measure both particle size and number concentration.

2.2.3 Data Analysis

Gas analyser and BAM data were recorded as .csv files which were subsequently imported and analysed using R. SMPS data was recorded using the TSI Aerosol Instrument Manager software (AIM v10.3.0.3, TSI Inc). and corrected with the AIM in-built functions for “*multiple charge correction*” and “*diffusion loss correction*”, as recommended by the manufacturer. The corrected SMPS data was exported from the AIM software as a .csv file, subsequently analysed and plotted in R. Various packages in R have been used for analysis and plotting, particularly the *Openair* package which was specifically designed for use with air pollution data (Carslaw and Ropkins, 2012).

2.3 Methodology

2.3.1 Atmospheric Simulation Chamber

Chamber Description

The atmospheric simulation chamber used for studies of the OH-initiated oxidation of 4-methylcatechol and guaiacol is described in detail elsewhere (Ashu-Ayem et al., 2012). Briefly, the simulation chamber consists of a cylindrical 2.65 m³ bag of Teflon foil, housed in an aluminium frame and operated at room temperature and atmospheric pressure, Figure 2.6.



Figure 2.6 Picture of the Atmospheric Simulation Chamber.

The chamber has aluminium end plates fitted with ports for addition of chemicals and extraction of air samples for analysis as well as a fan for internal mixing of reactants. The chamber is illuminated by a series of UV lamps (Philips) placed on the bottom of the chamber: 5 TL05 40 W lamps which emit entirely in the UVA region with an emission maximum around 370 nm; 5 Philips TLD08 18 W BLB lamps which also emit in the UVA region and have an emission maximum around 360 nm; 6 TUV T8 15 W lamps which emit in the UVC region and have an emission maximum at 253.7 nm.

Experimental Protocol

Prior to experiments, the chamber was flushed with clean, dry compressed air for a minimum of 12 hours at a flow rate of 100 L min⁻¹. Chamber background readings were recorded with all instruments for at least 30 minutes prior to any reagent addition.

For experiments performed in humid conditions, after the background was completed, compressed air was passed through a bottle containing deionised water and subsequently into the chamber at a flow rate of 10 – 15 L min⁻¹ until sufficient RH was attained in the chamber, monitored by a Vaisala temperature and humidity probe (DM70, Vaisala, Finland). Experiments performed under humid conditions generally had RH of ~ 40%, while dry experiments were performed with RH < 1%.

During photooxidation experiments, reagents were introduced from one side of the chamber, while instruments sampled chamber air from the other side. The fan was also used briefly following reagent addition to ensure homogenous mixing but was turned off during reaction to minimise wall losses. Experiments were performed in a batch manner, with addition of reagents prior to photochemical initiation of the experiment and no continuous addition performed. To ensure a constant volume in the chamber, clean, dry compressed air was added at the same rate as air was removed for instrument sampling.

The OH precursors used in these experiments were hydrogen peroxide (H₂O₂, 30% v/v, Sigma Aldrich) and nitrous acid (HONO), which was freshly prepared from the dropwise addition of 1% sodium nitrite (NaNO₂, Sigma Aldrich) in water to a 10% sulfuric acid (H₂SO₄) in water solution (Ng et al., 2007b). The experimental set up for HONO addition is given in Figure 2.7. Nitrogen gas was passed through the reaction vessel at a flow rate of 0.15 L min⁻¹ and subsequently into the chamber. The flow of N₂ was continued until sufficient total NO_x concentrations were reached in the chamber. It should be noted that the recorded NO_x concentration has contributions from HONO, NO and NO₂ as they are all produced from the reaction of NaNO₂ with H₂SO₄. H₂O₂ was added to the chamber by bubbling N₂ through a glass bulb containing H₂O₂ at a flow rate of 0.3 L min⁻¹, Figure 2.7.

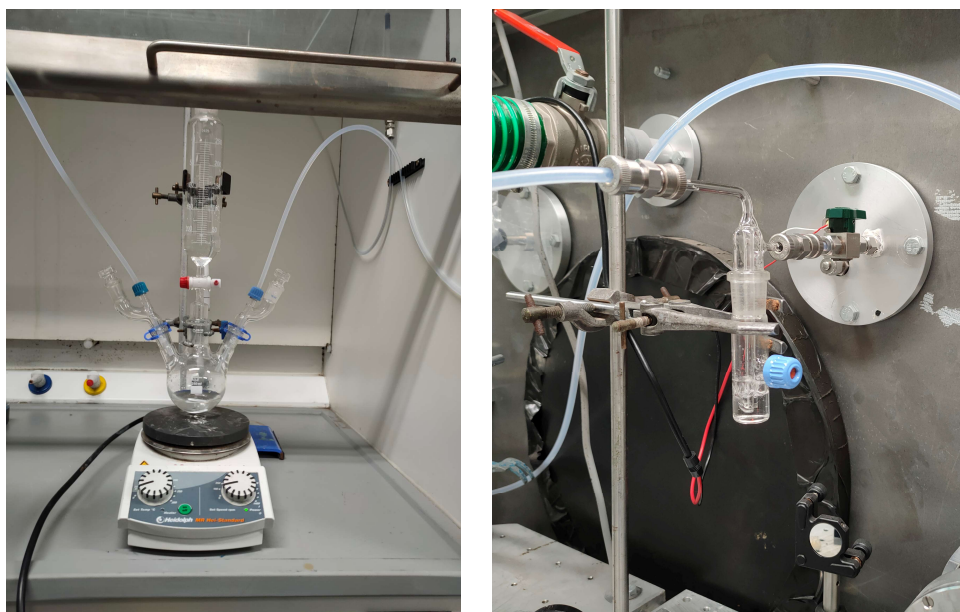


Figure 2.7 Experimental set-up for the addition of the OH precursors; HONO (left) and hydrogen peroxide (right).

Guaiacol ($\geq 98\%$, Sigma-Aldrich) was added to the chamber by passing N_2 at a flow of 0.5 L min^{-1} through a glass bulb containing a known amount of the pure liquid. Since 4-methylcatechol (4-MC) ($\geq 95\%$, Sigma-Aldrich) is a solid at room temperature, a solution of 1.65 mol L^{-1} of 4-MC in milliQ water was first prepared to assist with the addition of this compound to the chamber. Microlitre aliquots of the solution were added to the glass bulb and the contents added to the chamber using a flow of nitrogen as outlined above. A heat gun was used to gently warm the glass bulb to promote volatilization of the organic compounds. The set-up for addition of the organic compounds is shown in Figure 2.8.

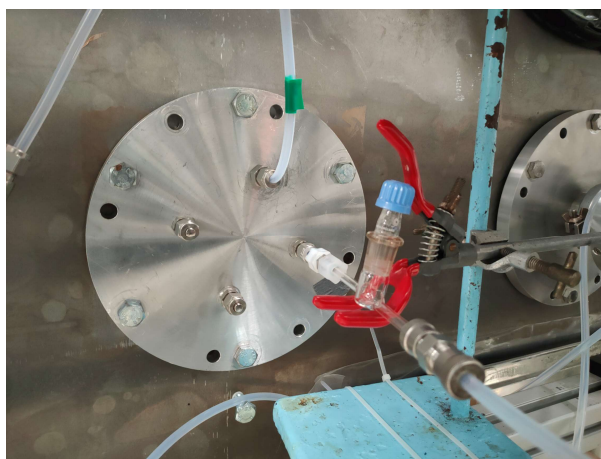


Figure 2.8 Sample injection port for simulation chamber photooxidation experiments.

The reagents were allowed to mix and reach steady concentrations before the reaction was initiated by turning on the lamps. Chamber blank experiments were performed regularly, where the same procedure was followed except for the addition of the VOC. The ToF-CIMS spectra obtained during these blank experiments were analysed, and the species observed in the blank experiments were ignored from analysis of experiments performed using 4-MC and guaiacol.

OH exposure

The estimated OH concentration during the experiments is calculated from the measured decay of the organic compound, which is in excess. A pseudo first-order kinetic plot yields a straight line with gradient $k[\text{OH}]$, where k is the known rate coefficient for reaction of OH with either 4-methylcatechol ($1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Olariu et al., 2000), or guaiacol ($5.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Lauraguais et al., 2015) and $[\text{OH}]$ is the steady state concentration of OH during the experiment in molecule cm^{-3} .

The OH exposure is a term used to assess the extent of aging that a species has experienced due to atmospheric processing with the OH radical over a period of time. It is calculated from the estimated OH concentration multiplied by the selected exposure time. To account for decay and dilution of the OH precursors in these experiments, calculations of the OH exposure estimates also incorporate the amount of OH precursor left in the chamber compared to the start of the reaction. In the atmosphere an average value of $[\text{OH}] = 1.1 \times 10^6 \text{ molecule cm}^{-3}$ is typically used (Li

et al., 2018), whereas in simulation chamber experiments, the estimated OH concentration is used.

SOA Yields

The yield of secondary organic aerosol (Y) from a given hydrocarbon is described as:

$$Y = \frac{\Delta M_0}{\Delta HC}$$

where ΔM_0 is the organic mass concentration and ΔHC is the corresponding concentration of hydrocarbon that has reacted (Odum et al., 1996).

2.3.2 FIGAERO Calibration

Calibrations to determine the vapour pressure of species thermally desorbed using the FIGAERO have been performed using a range of polyethylene glycol species (Bannan et al., 2019). This method involved making solutions (0.05 g L^{-1}) of tetra-, penta-, hexa- and octa-ethylene glycol, in acetonitrile and subsequently spotting $1 \text{ }\mu\text{L}$ of the solution on the PTFE filter of the FIGAERO and performing a desorption cycle. Three repeats of each solution were performed with the mean temperature of maximum ion signal (T_{max}) for each solution used for calibration. Between each desorption cycle, a blank desorption was performed to ensure that material from previous tests had been completely removed.

This method was found to produce highly reproducible results with little variance between desorption cycles for the same species. To investigate the effect of mixed solutions on T_{max} , a solution incorporating all of the glycol species was prepared to similar concentrations of each glycol. The T_{max} obtained from these desorptions were compared to those produced from the single species, with little to no effect observed.

The calibration plot relating FIGAERO T_{max} to vapour pressure for the polyethylene glycols is given in Figure 2.9. The literature vapour pressures have been taken from Krieger et al. (2018).

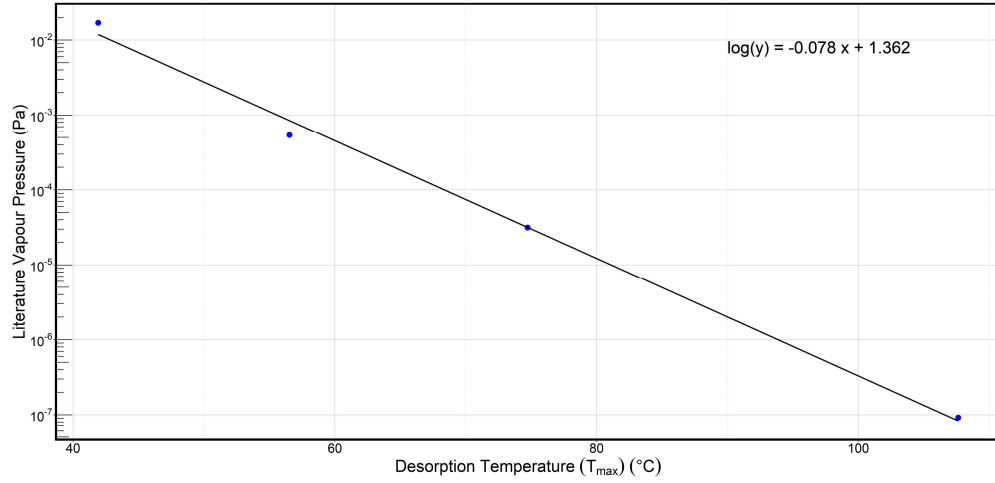


Figure 2.9 FIGAERO calibration plot comparing T_{max} to literature vapour pressures for a range of polyethylene glycol species.

It is noted that another study showed that atomised solutions of the polyethylene glycols showed improved performance than the Bannan et al. (2019) method, with the clusters of material observed during the syringe method removed. The clusters of material were found to influence the T_{max} value, while the atomisation process results in particles remaining as individual particles on the surface of the filter following aerosol collection (Ylisirniö et al., 2021). However due to limitations on instrumentation, this method could not be performed.

3. Characterisation of volatile organic compounds during wintertime air pollution in Cork City

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3.1 Introduction

Many urban centres in Ireland experience significant local air pollution events during winter due to the burning of solid fuels for home heating (Lin et al., 2019; Wenger et al., 2020). The first detailed studies of the chemical composition and sources of wintertime air pollution in Ireland were conducted in Cork City. In 2010, Hellebust et al. (2010) performed principal component analysis (PCA) and positive matrix factorisation (PMF) on ambient pollutant data incorporating NO, NO₂, O₃, PM_{2.5}, organic carbon (OC), elemental carbon (EC), SO₂ and particulate sulfate (SO₄²⁻) to identify and quantify the air pollution sources (Hellebust et al., 2010). Three major contributors to ambient particulate matter in the port of Cork City were identified, namely domestic solid fuel burning, road transport and industrial boilers, contributing 14%, 19% and 31% respectively. A further study analysed the biomass burning markers levoglucosan, mannosan and galactosan, present in PM_{2.5} samples to show that solid fuel home heating contributed 74.9% of the OC observed in February 2009 (Kourtchev et al., 2011). During the same winter period, an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) and High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-TOF-AMS) were used to quantify the contribution of different solid fuel types, i.e., coal, peat and wood to ambient PM_{2.5} levels (Dall'Osto et al., 2013). Biomass burning organic aerosol (BBOA) was the largest contributor (23%) to the total non-refractory organic mass, while in a follow-up analysis, PMF was used to attribute 61-70% of PM_{2.5} to primary emissions from traffic as well as urban and regional solid fuel burning, and 30-39% of PM_{2.5} to urban and regional secondary aerosol sources (Dall'Osto et al., 2014). These studies clearly show that extensive research has been carried out on the composition and sources of wintertime particulate pollution in Cork and other urban centres in Ireland. However, to date there have been no measurements of the large number of volatile organic compounds associated with these wintertime air pollution events.

ToF-CIMS, often in conjunction with the FIGAERO inlet for particle phase analysis, has been used in a variety of field campaigns to identify gas phase organic species in ambient air at various locations (Yatavelli et al., 2014; Lee et al., 2014; Bannan et al., 2015; Thompson et al., 2017; Lutz et al., 2019; Le Breton et al., 2019; Ye et al., 2021;

Salvador et al., 2021). The SENEX campaign discussed in Lee et al. (2014), was the first field deployment of an iodide HR-ToF-CIMS on an aircraft. A variety of different air masses and biomass burning plumes were experienced during 120 flights. Associated with the biomass burning plumes were the ion clusters $C_7H_8O_2I^-$, $C_7H_7NO_4I^-$, $C_7H_6O_2I^-$, $C_6H_6O_2I^-$ and $C_8H_8O_2I^-$ attributed to phenolic compounds and $HNCOI^-$ which was assumed to be isocyanic acid. In another study, Ye et al. (2021) also observed a range of compounds related to biomass burning, including monosaccharide derivatives ($C_6H_{10}O_5$ and $C_6H_{12}O_5$) as well as nitroaromatics and other phenolic derivatives. These species encompassed those observed by Lee et al. (2014), as well as nitrophenols ($C_6H_5NO_3$ and $C_6H_5NO_4$) and oxidation products of aromatic biomass burning products ($C_7H_8O_4$ and $C_7H_8O_5$) all clustered with iodide anions. Interestingly, some of the nitro-benzenediols ($C_6H_5NO_4$ and $C_7H_7NO_4$) observed in this study experienced double peaks in their diurnal profiles, one at noon and one in the evening which corresponded to the monosaccharide signal. The daytime peak was assumed to be associated with secondary formation due to photooxidation of aromatic species in the presence of NO_x .

The study performed by Salvador et al. (2021), measured gas and particle phase nitroaromatic compounds and found strong correlations between biomass burning emissions and the concentrations of nitroaromatics. Some of the most abundant species associated with biomass burning plumes in that study were nitrophenol ($C_6H_5NO_3$) and nitrocatechol ($C_6H_5NO_4$), while there were 14 other nitroaromatic compounds associated with biomass burning detected, including $C_7H_7NO_4$ and $C_8H_9NO_3$. In summary, numerous studies in various locations around the world have shown that phenolic species and their nitro derivatives are associated with biomass burning plumes.

Source identification of VOCs detected using the CIMS has been performed using positive matrix factorisation (PMF) which is a receptor model used to identify and quantify pollution sources using multivariate statistical techniques (Paatero and Tapper, 1994). PMF works by reducing matrices of speciated sample data into two simplified matrices, factor contributions, which when using CIMS data are mass spectra, and factor profiles, also known as time series. Factor profiles are interpreted in conjunction with other data such as meteorological data or ambient pollutant data to relate factors to specific sources (Norris et al., 2014). The equation for PMF is given

in Equation 3.1, where x is the speciated data matrix, of dimensions i (number of samples) and j (chemical species measured), p is the number of factors, f is the species profile for each source, g is the mass contributed by each factor to each individual sample and e_{ij} is the residual for each sample or species.

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad \text{Equation 3.1}$$

Previous studies utilising PMF with online VOC data have generally involved the use of proton transfer reaction mass spectrometry (PTR-MS) or offline analysis techniques using gas chromatography, and primarily focused on hydrocarbons rather than oxygenated species (Latella et al., 2005; Buzcu and Fraser, 2006; Lanz et al., 2008; Sauvage et al., 2009; Yuan et al., 2012). Some recent studies, however, have started to use ToF-CIMS measurements for PMF analysis of VOC sources. For example, PMF was applied to data collected by a nitrate (NO_3^-)-CIMS during the Southern Oxidant and Aerosol Study (SOAS) in 2013 (Massoli et al., 2018). This study identified a six factor PMF solution with three factors associated with terpenes and the other three factors related to isoprene, illustrating the capability of the ToF-CIMS to produce highly resolvable mass spectra for PMF analysis. Although phenolic species likely related to biomass burning were detected in that study, they were not included in the NO_3^- -CIMS PMF solution as they could not fit with any of the factors.

A similar study, performed using NO_3^- -CIMS in a boreal forest environment (Yan et al., 2016), produced a robust six factor PMF solution with day and night-time factors resolved. A distinction was observed between different oxidised monoterpene species which were attributed to separate O_3 -monoterpene and NO_3 -monoterpene night-time factors. Other studies have been published involving the use of PMF on ambient FIGAERO-I-CIMS measurements for source identification (Chen et al., 2020; Mehra et al., 2021). Mehra et al. (2021) used FIGAERO-CIMS measurements to identify an eight factor PMF solution to describe trends in organic aerosol in Beijing, with both anthropogenic and biogenic factors resolved. They observed both an afternoon and a morning factor which had strong contributions from nitroaromatic species. It was determined that both direct emission and nighttime chemistry with subsequent mixing of the boundary layer in the morning, were the main sources of the nitroaromatic species. Chen et al. (2020) used FIGAERO-CIMS in conjunction with aerosol mass spectrometry (AMS) to perform source apportionment in Georgia, USA. That study

did not experience any impact from biomass burning, with biogenic emissions, primarily derived from monoterpenes and isoprene, contributing the most to the PMF solution. A five factor PMF solution was resolved to describe organic aerosol with a nighttime factor composed of biogenic particulate organic nitrates accounting for 18% of the total organic aerosol measured during the campaign. The nighttime chemistry factor was observed to be primarily composed of monoterpene derived organic nitrates, however some isoprene derived products were also observed in that factor.

3.2 Aims

The overall aim of this work was to use the FIGAERO-I-CIMS, referred to as ToF-CIMS from here, to characterise the wide range of organic species present in ambient air in Cork City during winter and associate the organic compounds with the various pollutant sources. Temporal and diurnal trends in VOC concentrations have been elucidated to better understand the multitude of factors influencing ambient air quality in the city, with links between VOC concentrations, meteorological conditions and the key pollutants $\text{PM}_{2.5}$, NO_x and ozone also investigated. The high sensitivity and time resolution of the instrument has also been exploited to investigate atmospheric processing of the VOCs emitted during night-time pollution events. Finally, PMF analysis has been performed on the data to elucidate the key sources and processes which governed ambient VOC concentrations in Cork City during this wintertime period.

3.3 Methodology

A Time-of-Flight Chemical Ionisation Mass Spectrometer fitted with the Filter Inlet for Gases and Aerosols (FIGAERO-ToF-CIMS) was deployed in the atmospheric monitoring station located at the North Mall Campus of University College Cork, Ireland ($51^{\circ}54'00.5''\text{N}$ $8^{\circ}29'11.0''\text{W}$), from 26 January 2019 to 5 February 2019. The site is near the centre of the city and is a designated urban background location, with the city to the east and south-east and dense residential areas to the north and north-east, Figure 3.1. The monitoring station is equipped with a continuous particle monitor (BAM-1020B, Met One Instruments) for measuring $\text{PM}_{2.5}$ and automated gas analysers for measuring NO_x and O_3 (T200 and T400, Teledyne API). Some meteorological parameters (temperature, humidity, solar radiation) were measured on site, whereas wind speed and direction were taken from measurements at nearby Cork Airport by Met Éireann, Ireland's national meteorological service.

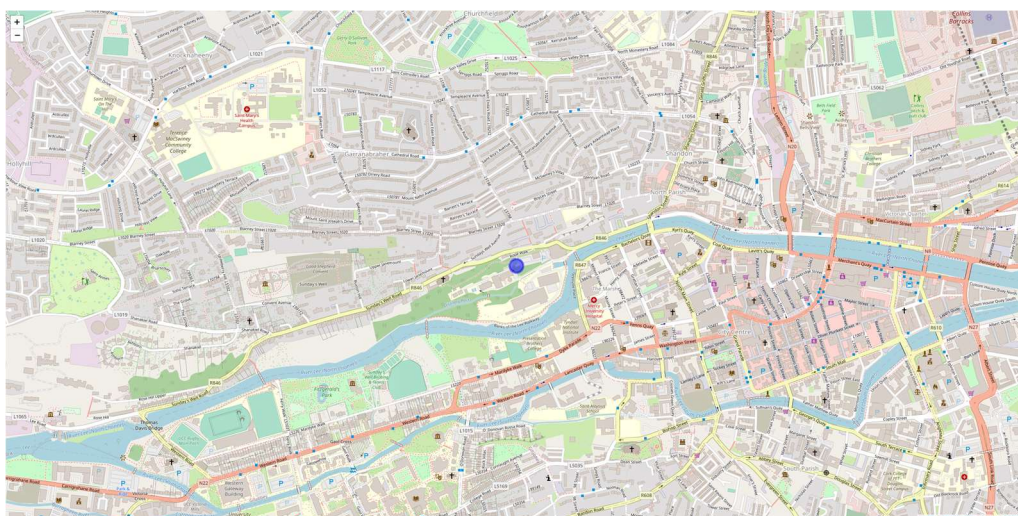


Figure 3.1 Map of Cork City showing location (blue marker) of monitoring site for winter 2019 field measurement campaign.

The ToF-CIMS was operated continuously in both gas and particle analysis modes, using iodide as the reagent ion, for 1-hour measurement cycles which consisted of continuous gas phase sampling for 25 minutes with simultaneous particle collection onto a PTFE filter, followed by a 35-minute thermal desorption cycle where heated nitrogen (99.999% purity, BOC Gases Ireland Ltd) was passed over the filter to desorb all organic material. The desorption cycle was composed of a 15-minute temperature ramp to 200°C , a 15-minute soaking period where the temperature was maintained at

200 °C to ensure complete removal of all volatile material and a 5-minute cooling procedure. The ToF-CIMS analysed the ambient gas phase by sub sampling at a rate of 2 L min⁻¹ from a larger flow of 22 L min⁻¹ using a 1.5 m stainless steel tube of ½” diameter which sampled from the roof of the monitoring station at a height of 3.5 m above ground level.

Ions were generated by passing a flow of nitrogen (99.999% purity, BOC Gases Ireland Ltd) over a permeation device containing methyl iodide held at a temperature of 35 °C and subsequently through a corona discharge at a flow of 2 L min⁻¹, maintained using a critical orifice, before entering the ion-molecule reaction (IMR) chamber, as described in Chapter 2. The IMR chamber was held at 60 °C to avoid condensation of semi-volatiles on the interior walls. The pressure in the IMR was maintained at 150 mbar, while the pressure in the small-segmented quadrupole (SSQ) was 2 mbar. Custom voltages were applied to the CIMS based on performance tests of instrument sensitivity to formic acid produced from a permeation tube and analysed using Thuner software. Instrument background mass spectra were obtained regularly by flowing dry zero air (BOC gases Ireland Ltd) into the IMR for a period of 5 minutes daily. These background spectra were subsequently subtracted from those obtained during the measurement periods.

CIMS data was analysed and background subtraction performed using Tofware v3.2.0 in Igor Pro 7.0.8.1 and fitted with high resolution peaks based on a mass calibration performed using peaks identified at 59.985292 Th, 144.915586 Th, 172.910501 Th and 380.713698 Th, which were assigned to CO₃⁻, (I)H₂O⁻, (I)CH₂O₂⁻ and (I)₃⁻ respectively, with a mean residual of 1 ppm, and a mass resolving power of ~ 5500 $m/\Delta m$, indicating a strong degree of confidence in all peaks within the mass calibration range and good peak separation. All ion signals were normalised by the sum of the iodide (I⁻) and iodide-water (I.H₂O⁻) clusters to account for any variance in the ion generation which affects clustering ability and therefore instrument sensitivity.

It was envisaged that the gas- and particle-phase detection capability afforded by the ToF-CIMS would enable investigation of the phase partitioning of organic compounds, thus helping to identify the species most associated with the various sources of particulate air pollution and especially residential solid fuel burning. Unfortunately, during data analysis it was discovered that the particle phase spectra

recorded by the CIMS were unreliable and consequently only results from the gas-phase are presented here. The data was deemed unreliable due to significant flow issues in the particle collection inlet, thus reducing particle collection efficiency. This issue was only resolved after the conclusion of the field measurement campaign, thus the data was removed from analysis.

To further aid identification of the sources of VOCs, Positive Matrix Factorisation (PMF) was performed on the dataset using the Source Finder (SoFi) software tool which was operated in Igor Pro using the multilinear ME-2 engine (Paatero and Tapper, 1994; Canonaco et al., 2013). Tofware was used to compute ion uncertainties for use in PMF which was performed using the SoFi v6.B run in Igor Pro v6.3.7.2. All PMF runs were performed without any constraining of the factors and no *a priori* information was provided to SoFi which could introduce bias into the PMF solutions. PMF was performed following some filtering of the VOC species to analyse with thresholds set so that only $C_xH_yO_zN_wS_v$ species were considered where x, y and z are all greater than 1.

3.4 Results and Discussion

3.4.1 Air Quality and Meteorology

PM_{2.5}, NO_x and O₃ concentrations showed considerable variation throughout the monitoring period. The time series for PM_{2.5} shows multiple pollution events with the highest hourly average concentration of approximately 190 µg/m³ occurring on the evening of 30 January 2019, Figure 3.2. A sustained period of elevated PM_{2.5} concentration was also observed around 3 February 2019.

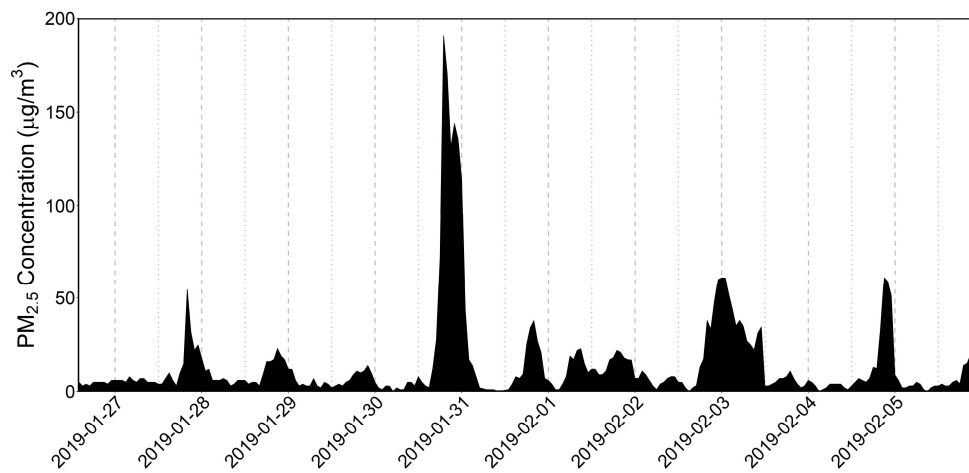


Figure 3.2 Time series of PM_{2.5} during the measurement campaign performed at the UCC North Mall campus during winter 2019.

The pollution events were found to occur primarily in the evening as indicated by the diurnal plot for PM_{2.5}. As shown in Figure 3.3, there is a clear increase in concentration which begins at approximately 17:00, reaching its maximum at 20:00 before undergoing gradual decay overnight. This type of diurnal profile is typical for wintertime in Cork City (Dall'Osto et al., 2013; Byrne et al., 2023) and other urban areas around Ireland (Wenger et al., 2020), where large evening peaks in pollution are experienced due to residential solid fuel burning.

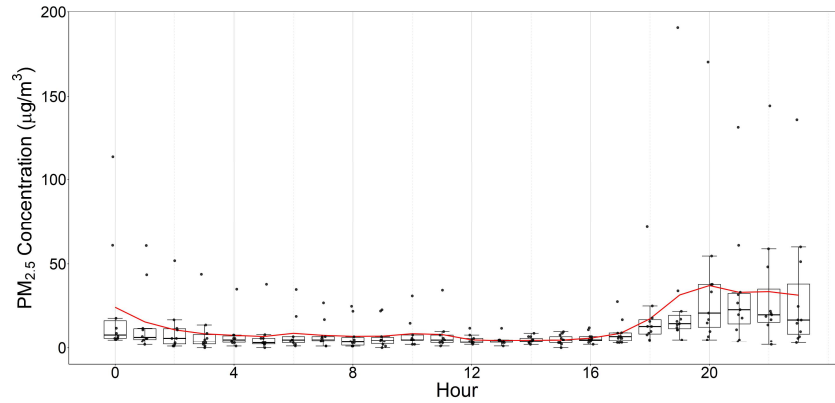


Figure 3.3 Diurnal time profile of $PM_{2.5}$ during the measurement campaign highlighting evening spikes in $PM_{2.5}$ mass concentration.

The bivariate polar plot of $PM_{2.5}$ mass concentration as a function of wind speed and direction, shown in Figure 3.4, clearly indicates that the highest concentrations of $PM_{2.5}$ occurred when there were low wind speeds originating from the north-east. Directly north and north-east of the monitoring site is a large residential area and combining this information with the diurnal pattern shown above, strongly suggests that the majority of the $PM_{2.5}$ pollution originates from the burning of solid fuels for home heating.

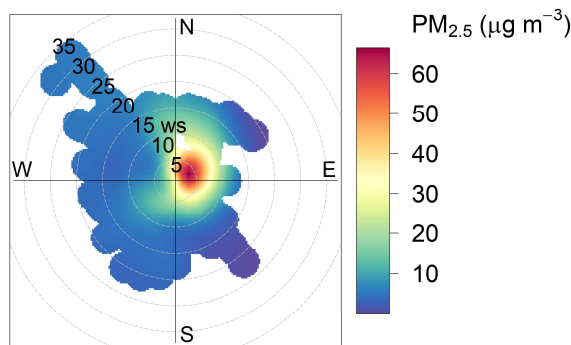


Figure 3.4 Bivariate polar plot of $PM_{2.5}$ mass concentration showing residential areas to the north-east of the monitoring site are the primary contributor to ambient $PM_{2.5}$ concentrations.

The relationships between $PM_{2.5}$ mass concentration, wind speed and direction, temperature and humidity are shown in Figure 3.5. The time series indicate that low wind speeds allowed $PM_{2.5}$ to accumulate, e.g., during the major pollution events on 30 January and 2 February, however once wind speed increased, the pollution dispersed rapidly on both occasions.

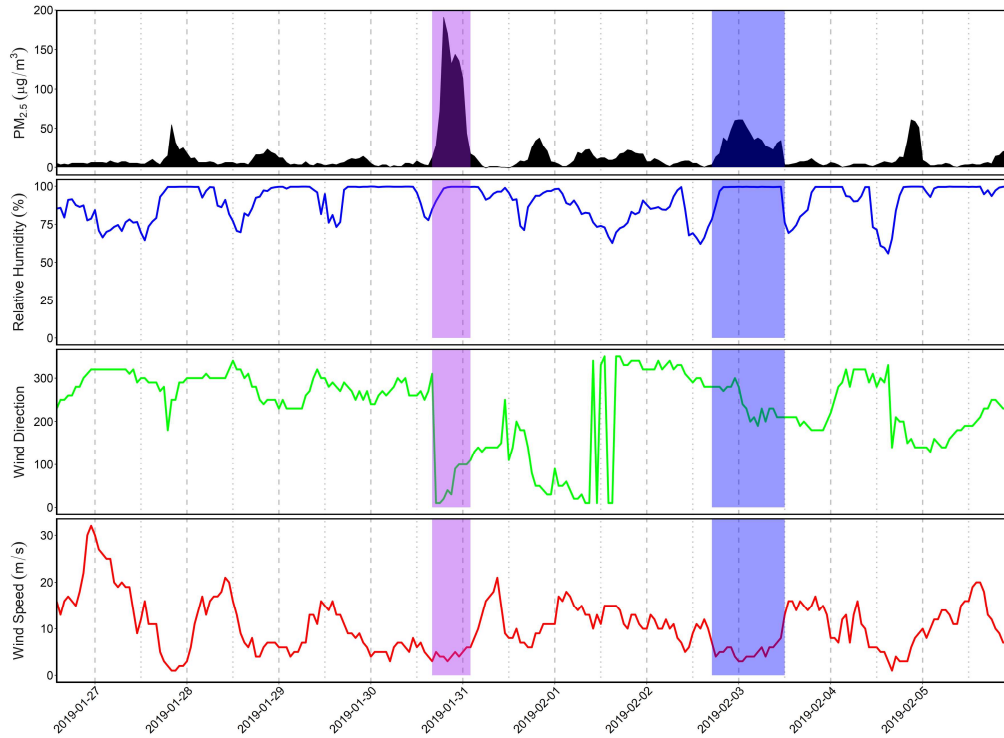


Figure 3.5 Time profile of $PM_{2.5}$ with relative humidity (blue) wind direction (green) and wind speed (red) highlighting the impact of wind on ambient $PM_{2.5}$ concentration. The coloured bars represent periods when wind speed was low allowing significant accumulation of $PM_{2.5}$.

The $PM_{2.5}$ mass concentration was also influenced by air temperature, with elevated levels observed on colder days, while warmer days had lower concentrations. This is illustrated in Figure 3.6, where the daily average $PM_{2.5}$ concentration is plotted as a function of air temperature, with wider segments indicating more data recorded at a specific temperature, while the $PM_{2.5}$ mass concentration is given by segment colour. The plot also shows that $PM_{2.5}$ was lower on days with higher precipitation, consistent with enhanced removal of airborne particles via wet deposition.

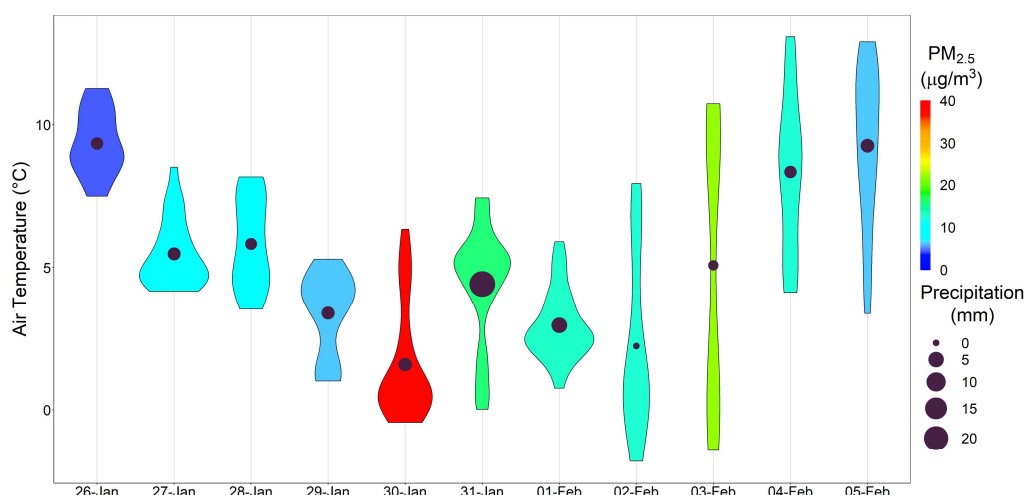


Figure 3.6 Violin plot of air temperature as a function of time, coloured by PM_{2.5} concentration, with precipitation levels also included.

The time series for NO_x and O₃ are given in Figure 3.7. The clear anti-correlation between NO₂ and O₃ is expected as ozone is depleted by reaction with NO, resulting in the formation of NO₂. Photodissociation of NO₂ during daylight hours produces NO and O^{*} which can react with O₂ to form O₃. Thus, in combustion plumes containing NO and NO₂, the O₃ concentration will decrease until the NO₂ is photochemically recycled yielding O₃ once again. Multiple depletions of O₃ were observed during the campaign with a corresponding increase in NO₂, such as on the evening of 28 January and very noticeably during the sustained pollution event on the 03 February.

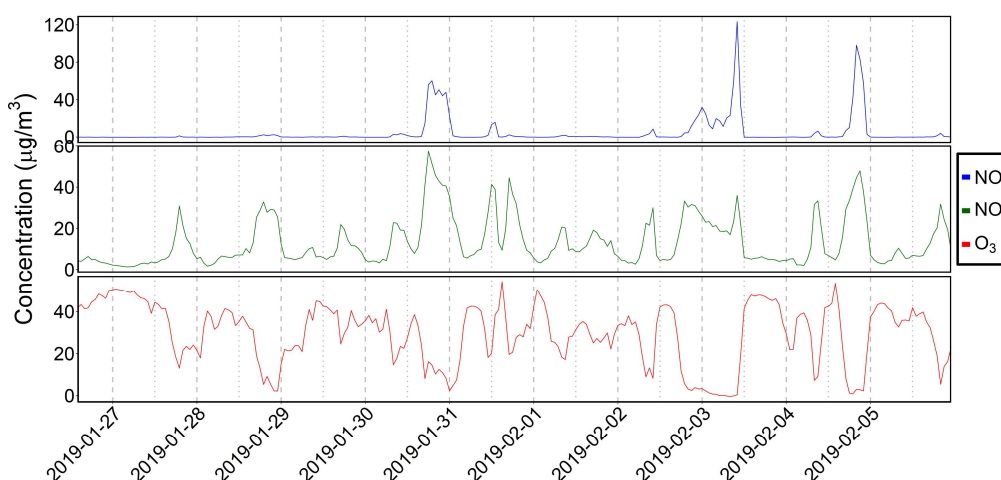


Figure 3.7 Time series of NO, NO₂ and O₃ during the winter 2019 measurement campaign.

The diurnal plots of O₃ and NO₂ further illustrate the relationship between these two pollutants, Figure 3.8. Reductions in O₃ concentration were observed during times

when the NO_2 increased due to morning and evening traffic patterns, as well as night-time solid fuel burning. The daytime peak in O_3 was due to the photochemical conversion of NO_2 into O_3 while the sunlight intensity was at its highest.

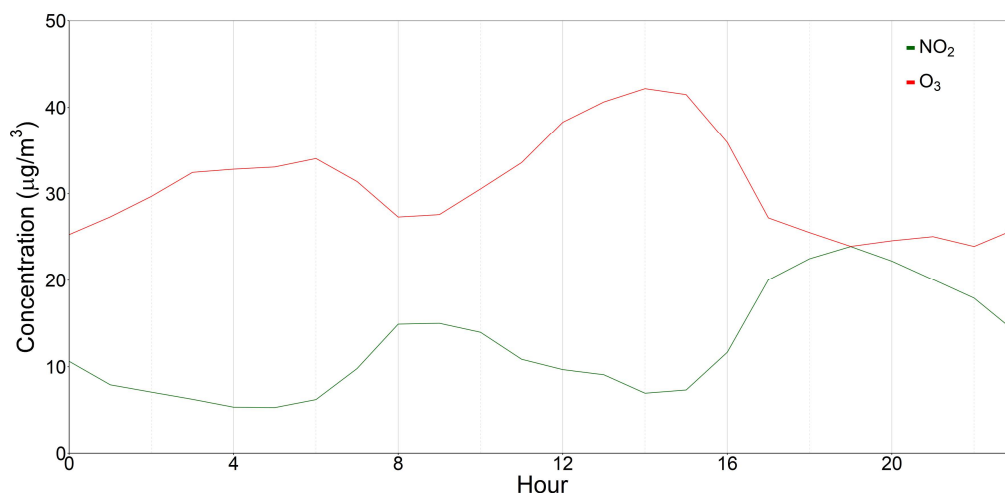


Figure 3.8 Diurnal time profiles of NO_2 and O_3 from the field measurement campaign showing the expected anti-correlation between the two species.

NO concentrations were low ($< 10 \mu\text{g}/\text{m}^3$) for most of the measurement period, likely due to this site being an urban background location which is not heavily influenced by primary traffic emissions. Most NO emitted by traffic in the city would have been converted to NO_2 by the time the air mass reached the monitoring station. Nevertheless, there were periods with elevated NO levels, most notably during the pollution events, where wind speed was low and NO_2 was also elevated. There were also a small number of spikes in NO concentration due to very local emissions from nearby vehicles, with the most significant of these being a very short-lived event on the 31 January (not seen in Figure 3.7, due to time averaging).

The bivariate polar plots of NO and NO_2 concentration shown in Figure 3.9 are quite different.

The NO plot indicates intense local sources, likely an idling truck or other vehicle close to the monitoring station. It should be noted that in cases of very low wind speed ($< 1 \text{ m/s}$) as observed for the NO bivariate polar plot, the actual direction of wind plays little to no role as there is little dispersion due to the wind. Thus, it only indicates that the source is local, but does not indicate direction. In contrast, the NO_2 plot is similar to that observed for $\text{PM}_{2.5}$. There was a strong influence from local solid fuel burning sources to the north-east and contributions from the east and south-east, most likely

due to road traffic. The mid-range concentrations originated from most directions and are also likely due to traffic emissions.

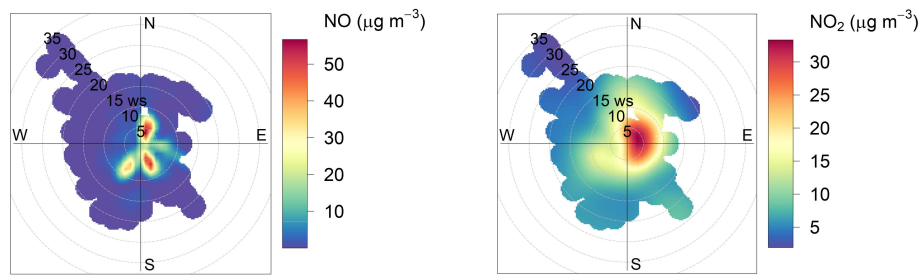


Figure 3.9 Bivariate polar plots of NO and NO₂ showing NO as a highly local pollutant while NO₂ has a more varied source profile.

The polar annulus plot for NO₂ concentration shown in Figure 3.10 provides more information about NO₂ diurnal trends and source direction, as it also incorporates the time of day. Although the short nature of the measurement period means that a large proportion of the plot is left empty (wind direction and time did not align during the short period), the results show that evening peaks in pollution mainly originated from the north and north-east, most likely corresponding to residential solid fuel burning, while peaks in the morning and late afternoon generally originated from a south-easterly direction which points towards a traffic source from the city.

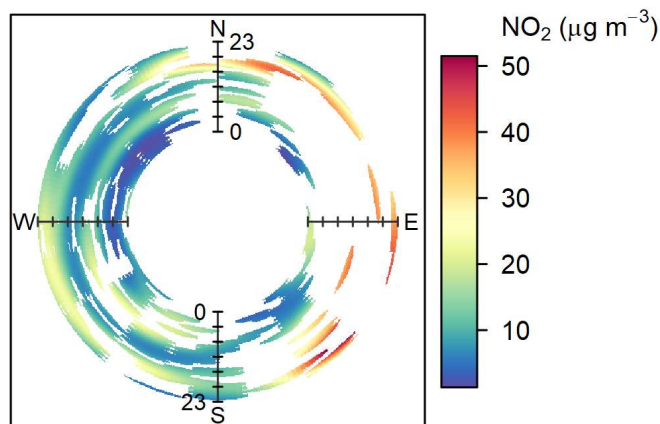


Figure 3.10 Polar annulus plot of NO₂ from the winter 2019 field measurement campaign highlighting the east and south-east as major sources of NO₂. Gaps in the plot are a result of wind direction measurements not aligning with NO₂ measurements during the relatively short field campaign.

3.4.2 Overview of CIMS Data

The CIMS records a mass spectrum every second and for this study, the spectra were averaged to 1 minute for analysis and subsequently to hourly resolution for time series plots. An averaged mass spectrum for gas-phase species detected across the entire campaign is given in Figure 3.11.

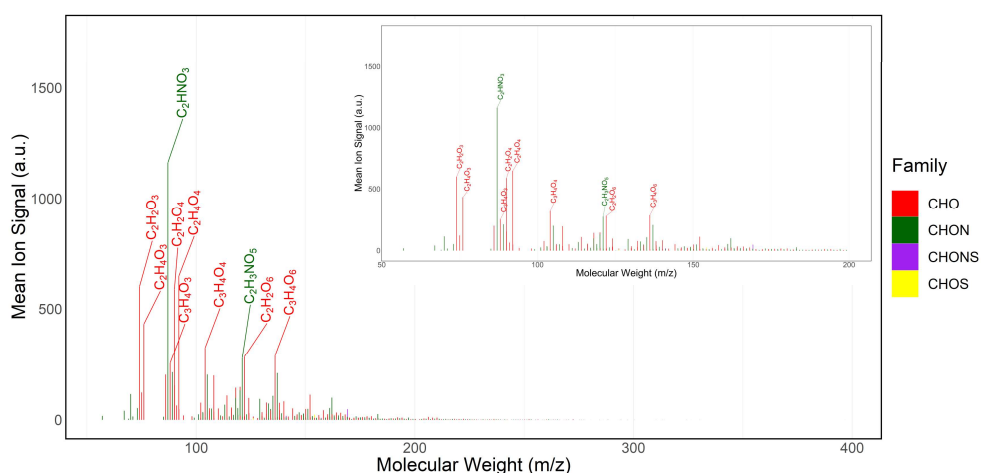


Figure 3.11 Average mass spectrum across the entire measurement campaign for species with $nC > 1$, $nH > 1$, $nO > 1$ and with I mass subtracted, with inset showing the same plot up to a m/z of 200 Th.

The average mass spectrum shows a prevalence of C₂ and C₃ species with high oxygen to carbon ratios, likely due to the strong affinity of I-CIMS for organic acids and reduced sensitivity to alcohols, ketones and aldehydes which contain only a single oxygen atom (Lee et al., 2014). To evaluate how the mass spectra varied across the entire campaign, the species were grouped by the number of carbon atoms in the respective organic compounds (nC) and plotted against both total ion counts and the relative ion contribution, Figure 3.12. Interestingly, there were a number of periods where increases in particulate pollution were also associated with increases in VOCs, most notably on 30 and 31 January, as well as 2 and 3 February. The pollution events on 30 and 31 January were characterised by significant increases in C₆ to C₈ species which are likely to be phenol derivatives produced by solid fuel burning, in line with previous studies of biomass burning emissions (Mohr et al., 2013; Lee et al., 2014; Salvador et al., 2021; Ye et al., 2021).

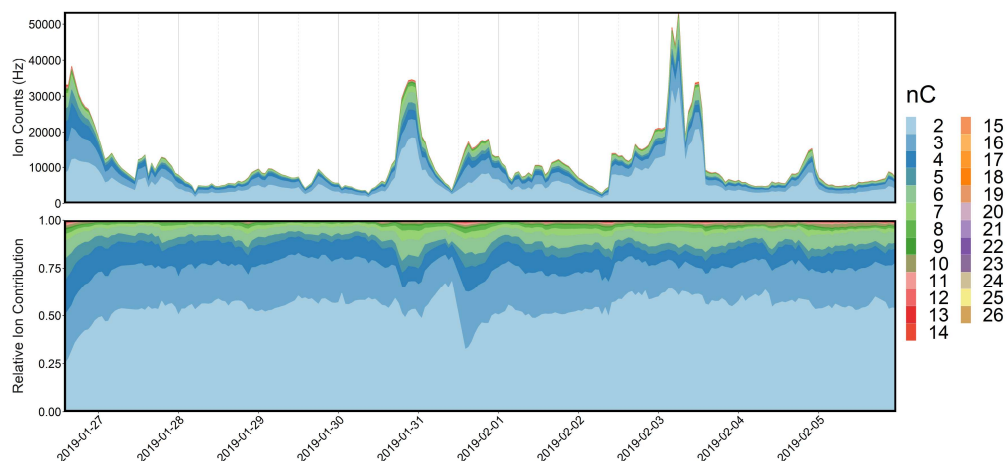


Figure 3.12 Time series of total ion counts and relative ion contribution of VOCs grouped by the number of carbons in each detected species.

While these plots highlight certain changes with the various air masses experienced during the campaign, simply looking at the number of carbon atoms in a molecule does not provide much molecular information; using the oxidation state of carbon atoms (OS_C), which is related to the oxygen to carbon ratio (O/C), hydrogen to carbon ratio (H/C) and nitrogen to carbon ratio (N/C), provides more information. The OS_C is given in Equation 3.2 (Kroll et al., 2011).

$$OS_C \approx 2 * O/C - H/C - 3 * N/C \quad \text{Equation 3.2}$$

The time series plot of the O/C ratio given in Figure 3.13 provides useful insight into the variation of VOC composition throughout the campaign. The pollution event observed on 30 January clearly shows a significant increase in species with O/C ratios between 0 and 2, which suggests that these are fresh VOC emissions which have not undergone any significant oxidation in the atmosphere. Similar, but often less pronounced, increases in low O/C species were also observed during other night-time local pollution events during the measurement period.

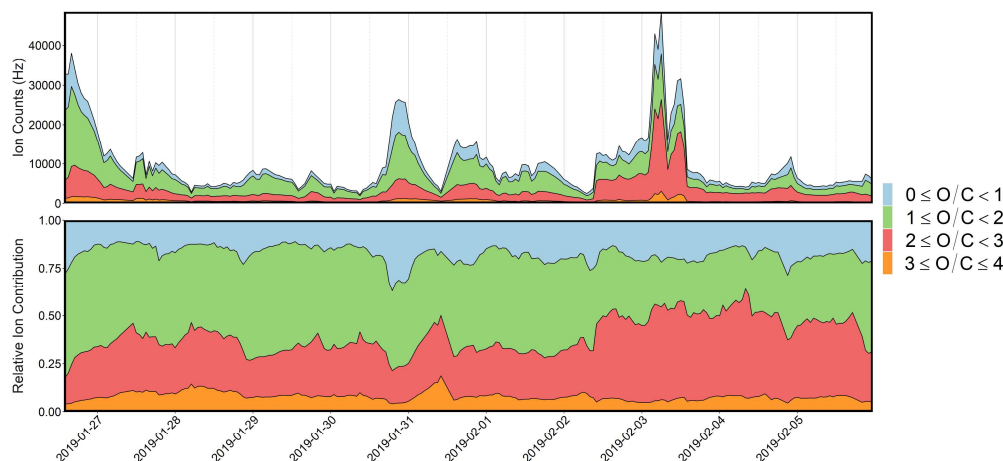


Figure 3.13 Time series and relative contribution time series of VOCs detected during the measurement campaign as a function of the oxygen to carbon ratio in each molecule giving an indication to the general degree of oxidation of all VOCs detected by the I-CIMS.

In contrast, the sustained pollution event observed during 2 and 3 February is characterised by a significant increase in species with an O/C ratio between 2 and 3. These findings are consistent with O/C ratios inferred from high resolution aerosol mass spectrometry data, with the lowest O/C ratios observed for primary emissions, while aged, oxygenated organic aerosols show the highest O/C ratios (Aiken et al., 2008; Canagaratna et al., 2015). It is important to note that due to I-CIMS sensitivity, at least one oxygen atom is required for a species to be detected, so these average O/C ratios are only indicative of the detected species and not the entire air mass which would be expected to have lower average O/C ratios due to ambient hydrocarbon concentrations.

The time series plot of OS_C values in Figure 3.14 shows similar results, where the sustained pollution event is characterised by an increase in species with OS_C between 2 and 4 indicating that these species have undergone atmospheric processing. The local pollution events contain species with low OS_C values as observed by the sharp increases in the green and red segments of the plot in the evening times, once again most notably on the 30 January. An interesting observation in both the O/C and OS_C plots is the large increase in more oxidised species immediately following the local pollution event on 30 January. While the total ion counts were quite low in this period, the contribution of species with higher O/C ratios increased noticeably, potentially

suggesting that night-time processing of the primary VOC species occurred to form more oxidised products.

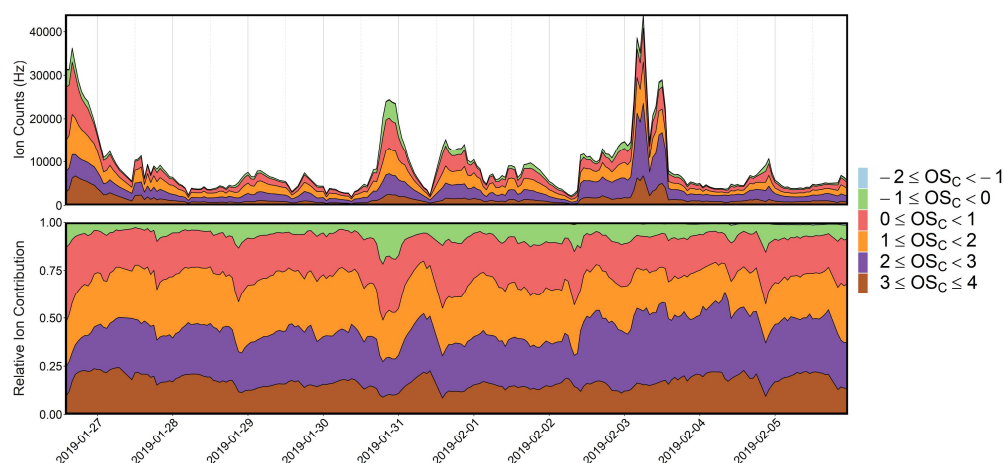


Figure 3.14 Time series and relative contribution time series of VOCs as a function of the average oxidation state of carbon in each molecule.

Comparison of pollution events

Comparisons between ToF-CIMS data collected during one of the local pollution events (from 15:00 on 30 January to 03:00 on 31 January) and the sustained pollution event (from 17:00 on 2 February to 11:00 on the 3 February) were made by generating difference mass spectra. The results are shown in Figure 3.15, where the y-axis is the difference in the mean concentration of species during the two periods, and the ion signals are coloured by the number of carbon atoms in the species. The majority of species which are significantly more concentrated in the local pollution event (positive y-axis) are C₅ to C₈, while the most abundant species during the sustained pollution event (negative y-axis) are in the C₂ to C₄ range, with some exceptions.

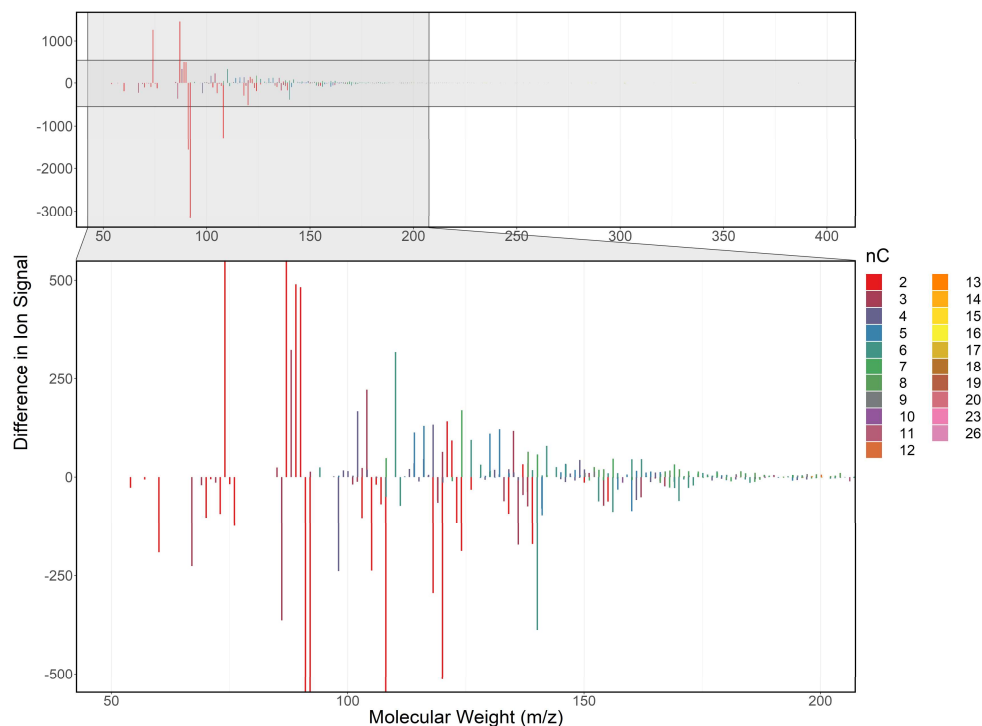


Figure 3.15 Difference in mass spectra observed during local (positive y-axis, 15:00 on 30 January to 03:00 on 31 January) and sustained pollution events (negative y-axis, 17:00 on 2 February to 11:00 on the 3 February), with bottom panel showing zoomed portion.

The prevalence of C_2 and C_3 species in the sustained pollution event suggest that this is a more aged air mass containing a range of smaller organic species produced via atmospheric oxidation of primary emissions. Meanwhile, the prevalence of C_5 to C_8 species during the local pollution events suggests significant concentrations of biomass burning markers. To better interpret the differences between the species detected in the pollution events, the OS_C is plotted against the number of carbon atoms present in the molecule (nC) in Figure 3.16, with data points coloured by the nature of the molecule and sized by the ratio of the mean signal in the local event to the mean signal in the sustained event. Thus, the largest and smallest data points represent the main local and advanced aging pollutant species respectively, with other data points representing species that did not change significantly between the two events.

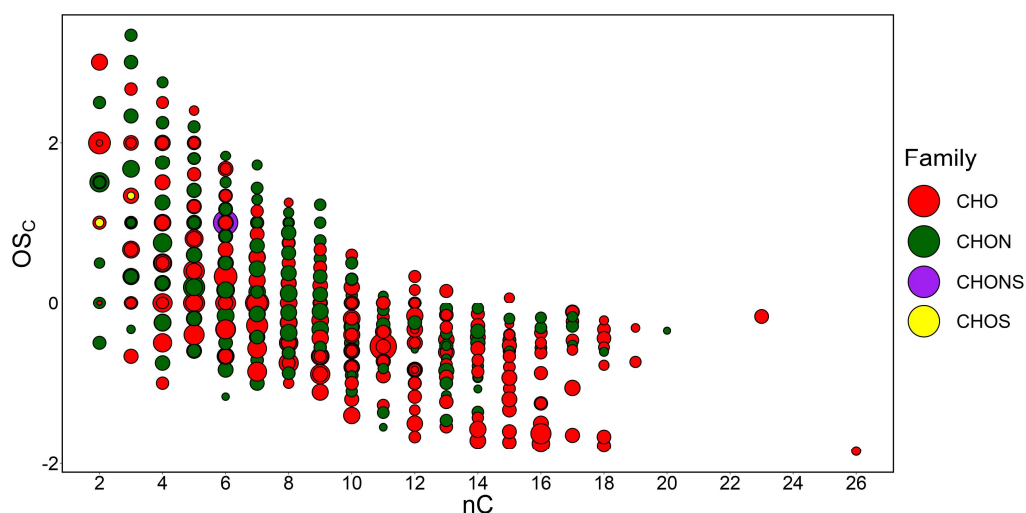


Figure 3.16 OS_C plot with data points sized by the ratio of VOC signal during the local pollution event to the sustained pollution event.

This plot once again highlights the prevalence of C_6 to C_8 species in local pollution events, which also have low OS_C values, indicating that these are likely fresh emissions with quite low O/C ratios. The smaller data points are centred between C_2 and C_4 as expected, with relatively high OS_C values offering further evidence that this sustained air pollution event has undergone significant aging giving rise to highly oxidized organic species.

To help illustrate the differences, the inverse plot is shown in Figure 3.17, where data are sized by the ratio of the mean signal during the sustained event to the mean signal during the local event. The shift to higher OS_C ratio species is more readily observed in this plot.

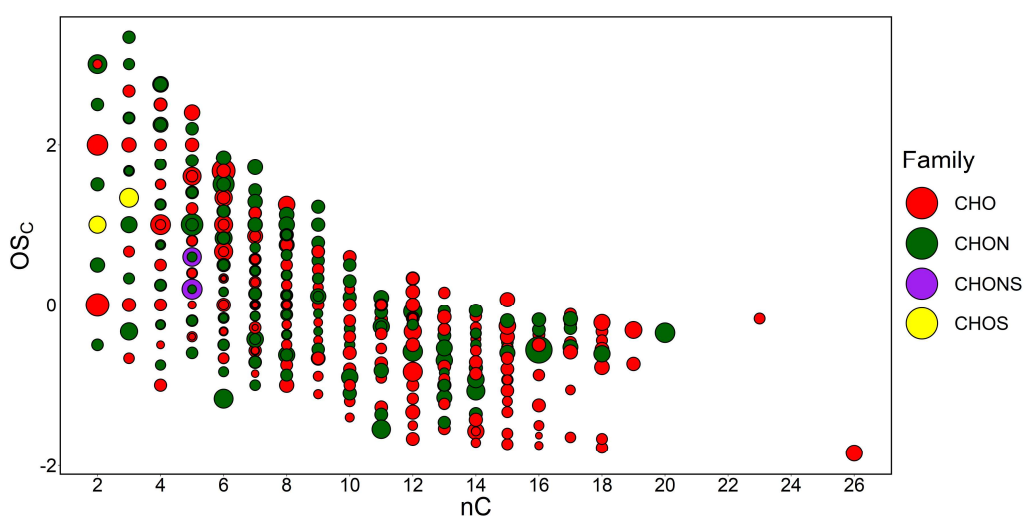


Figure 3.17 OS_C plot with data points sized by the ratio of VOC signal during the sustained pollution event to the local pollution event.

3.4.3 Gas Phase Acids

A range of common gas phase acids were detected during the measurement campaign, including, but not limited to, isocyanic acid (CHNO), nitrous acid (HONO), nitric acid (HNO₃) and formic acid (CH₂O₂). As shown in Figure 3.18, nitric acid, HONO and formic acid peaked in concentration during the sustained pollution event observed on 2 and 3 February.

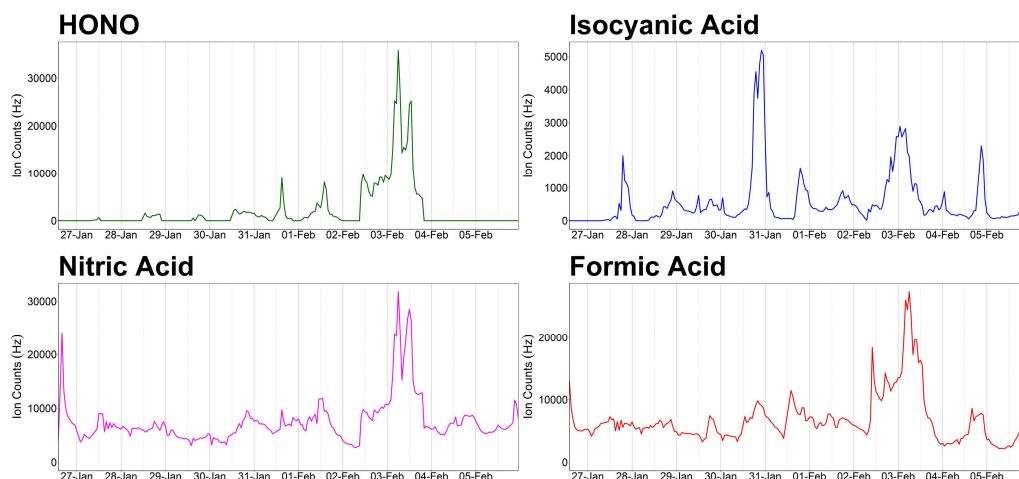


Figure 3.18 Time series of trace atmospheric gases, namely nitrous acid (HONO), isocyanic acid (CHNO), nitric acid (HNO₃) and formic acid (CH₂O₂). High instrument backgrounds were noted for HONO, which may affect its time trend even following background mass spectra subtraction.

The simultaneous appearance of large spikes in concentration of HONO and nitric acid during the early hours of 3 February, suggests that night-time heterogeneous hydrolysis of NO₂ is the likely source of these gaseous species (Tuite et al., 2021; Zhang et al., 2023). This assertion is supported by the prevailing conditions, which were characterised by low wind speed and near 100% relative humidity, Figure 3.5. Some smaller spikes in the concentration of these species were also observed during the daytime which may point towards traffic or photochemistry as potential sources. Interestingly, although HONO has previously been observed to be a product of biomass burning (Veres et al., 2010), it is not particularly high during the biomass burning pollution event and shows no correlation with ambient PM_{2.5} ($r^2 = 0.01$) in this study.

Formic acid and nitric acid were observed to be highly correlated ($r^2 = 0.78$), contrasting significantly with winter measurements performed in London during 2012 (Bannan et al., 2014), where there was no correlation between the two species ($r^2 =$

0.14) and formic acid was mainly attributed to traffic emissions due to strong correlations with both NO₂ and CO. The relatively weak correlation between NO₂ and formic acid in the current study ($r^2 = 0.36$) indicates that formic acid is primarily produced from secondary processes in the same manner as nitric acid (Veres et al., 2011). Nitric acid is generally formed via reaction between NO₂ and OH radicals and is therefore a good marker for photochemistry and secondary processes. Although the main source of formic and nitric acids in this study is likely photochemical processing, both species increased during local pollution events. This latter observation is consistent with a previous study which showed that formic acid is produced during smouldering phases of fires (Veres et al., 2010).

The time series for isocyanic acid is different to the other acids. A strong correlation with PM_{2.5} was observed ($r^2 = 0.9$), particularly during the evening pollution events, suggesting that it is a product of biomass burning, consistent with previous findings (Veres et al., 2010; Roberts et al., 2011). The diurnal plots given in 3.19 show that HONO, nitric acid and formic acid are more associated with the timing of the sustained pollution event, while isocyanic acid has a very similar pattern to PM_{2.5} (Figure 3.3).

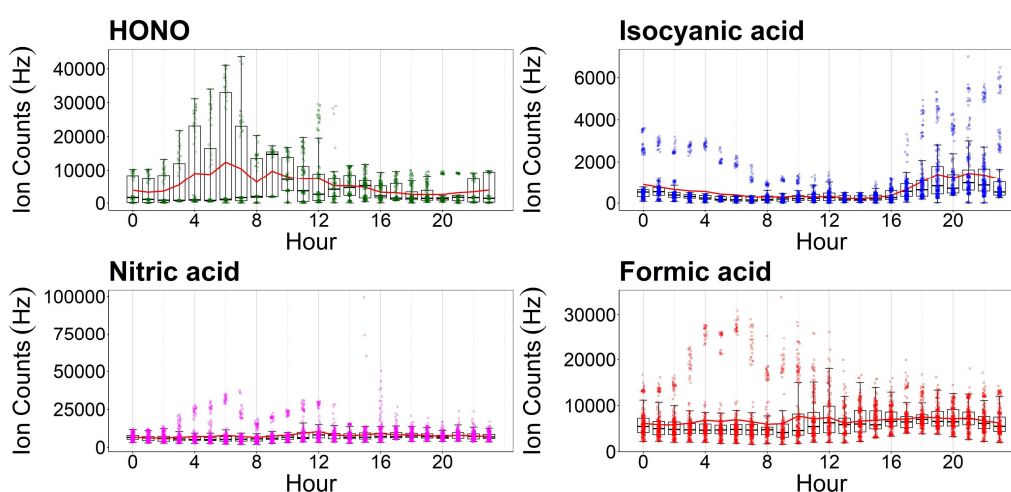


Figure 3.19 Diurnal profiles of nitrous acid, isocyanic acid, nitric acid and formic acid during the winter 2019 field measurement campaign.

Although the time series for HONO, nitric acid and formic acid in Figure 3.18 appear to be quite similar, the diurnal box plots illustrate some differences. Nitric acid shows some skewing due to the sustained pollution event, however these data are outside the interquartile range represented by the whiskers on the plots. There are also increases observed between 8:00 and 12:00 which likely correspond to nitric acid formation from the reaction of photochemically produced OH with NO₂ emitted from traffic. The

outliers observed at 15:00 and 16:00 could be related to traffic emissions, and when plotted with NO_x species, Figure 3.20, there are some periods of coincidence between NO_x and nitric acid, such as on the afternoon of 3 February, however this trend is not consistent throughout the campaign.

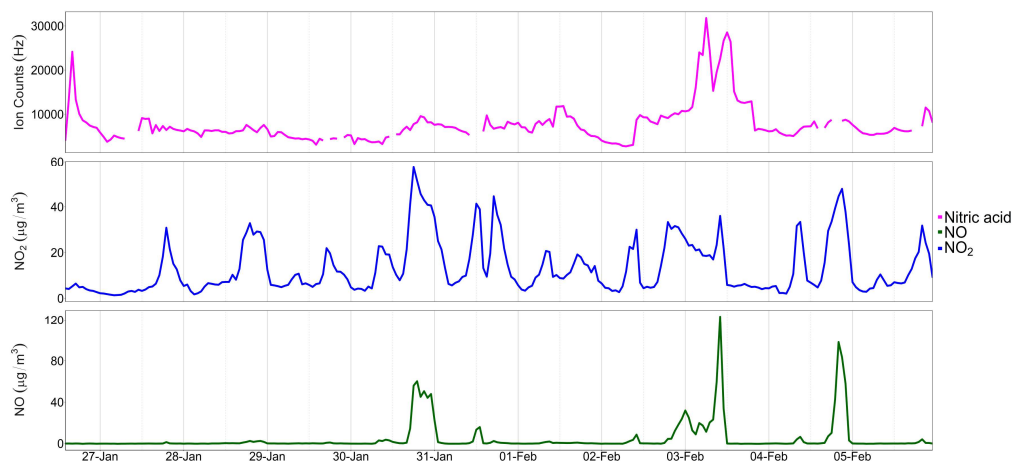


Figure 3.20 Time series of nitric acid with NO and NO_2 highlighting the lack of relationship between nitric acid and other NO_x trace gases during the field measurement campaign.

Formic acid also shows some outlier effect from the sustained pollution event and has morning increases which could potentially be a result of photochemical reactions beginning in daylight as formic acid is known to be a product of many VOC oxidation reactions. Formic acid is generally seen to have higher concentrations during the daytime, which is also an indicator that it is a product of photochemical induced reactions.

3.4.4 Biomass Burning Markers

A large number of C₆ to C₈ species were observed during the local PM_{2.5} pollution events which, based on a large number of studies (Schauer et al., 2001; Kahnt et al., 2013; Yee et al., 2013; Gaston et al., 2016; Bluvshstein et al., 2017), are attributed to a range of phenols, catechols and their nitrated derivatives which are produced from pyrolysis of lignin during wood burning (Liu et al., 2015). These are well established molecular markers for biomass burning. Several possible isomers for many of the proposed formulae are possible e.g., methylcatechol and guaiacol (C₇H₈O₂), both of which are found in biomass burning emissions.

Ion	Parent species	Attributed compounds	Reference
(I)C ₈ H ₁₀ O ₂ ⁻	C ₈ H ₁₀ O ₂	Creosol, dimethylcatechol	(Kahnt et al., 2013; Gaston et al., 2016)
(I)C ₈ H ₁₀ O ₃ ⁻	C ₈ H ₁₀ O ₃	Syringol, hydroxy-creosol	(Gaston et al., 2016)
(I)C ₈ H ₉ NO ₄ ⁻	C ₈ H ₉ NO ₄	Nitrocreosol, dimethyl-nitrocatechol	(Kahnt et al., 2013)
(I)C ₈ H ₉ NO ₅ ⁻	C ₈ H ₉ NO ₅	Nitrosyringol	(Bluvshstein et al., 2017)
(I)C ₇ H ₈ O ⁻	C ₇ H ₈ O	Cresols, anisole	(Schauer et al., 2001)
(I)C ₇ H ₈ O ₂ ⁻	C ₇ H ₈ O ₂	Methylcatechol, guaiacol	(Gaston et al., 2016)
(I)C ₇ H ₈ O ₃ ⁻	C ₇ H ₈ O ₃	Hydroxy-methylcatechol, hydroxy-guaiacol	(Yee et al., 2013)
(I)C ₇ H ₇ NO ₄ ⁻	C ₇ H ₇ NO ₄	Methyl-nitrocatechol, nitroguaiacol	(Gaston et al., 2016)
(I)C ₆ H ₆ O ₂ ⁻	C ₆ H ₆ O ₂	Catechol	(Gaston et al., 2016)
(I)C ₆ H ₆ O ₃ ⁻	C ₆ H ₆ O ₃	Hydroxy-catechol	(Yee et al., 2013)
(I)C ₆ H ₅ NO ₃ ⁻	C ₆ H ₅ NO ₃	Nitrophenols	(Gaston et al., 2016)
(I)C ₆ H ₅ NO ₄ ⁻	C ₆ H ₅ NO ₄	Nitrocatechols	(Gaston et al., 2016)

Table 3.1 Biomass burning markers detected by I-CIMS which are highly correlated with PM_{2.5}.

Three of the most prominent biomass burning markers are $C_8H_{10}O_2$, $C_7H_8O_2$ and $C_6H_6O_2$ as well as their nitro and hydroxy derivatives. All of these species are very highly correlated with $PM_{2.5}$, with some examples shown in Figure 3.21. This suggests that the night-time pollution events which produce the most extreme concentrations of $PM_{2.5}$ have significant contributions from wood burning, as observed during previous studies in Cork City (Dall'Osto et al., 2013).

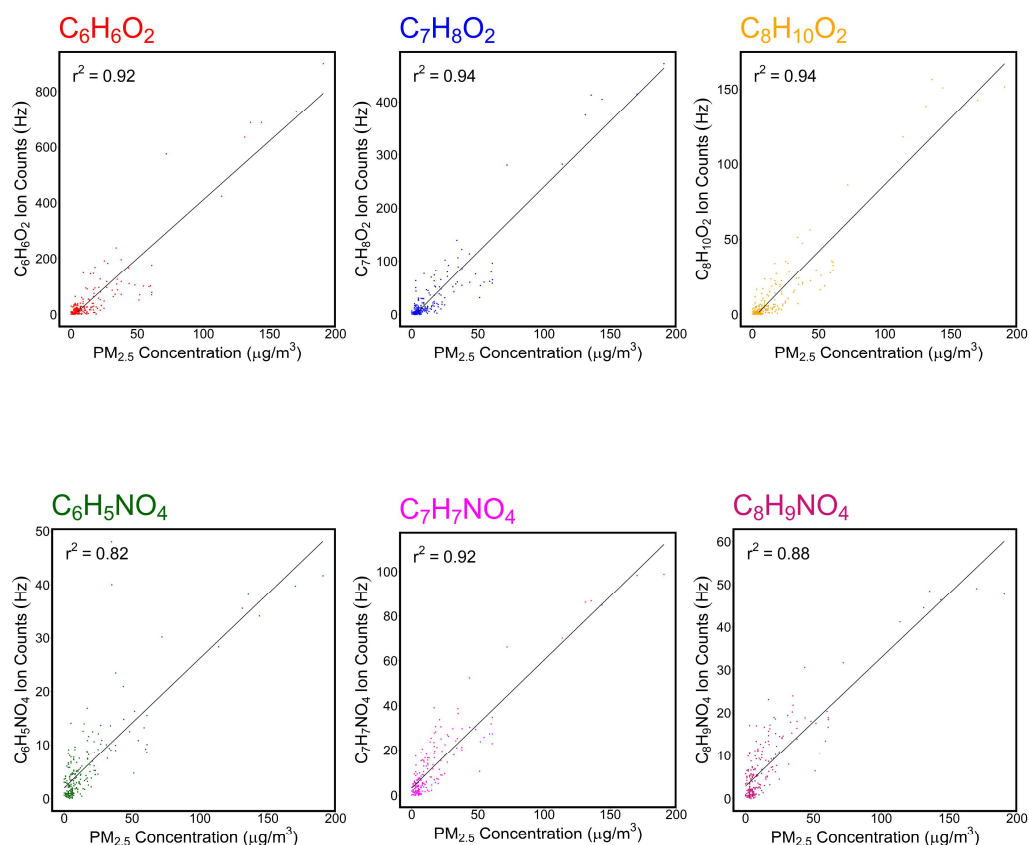


Figure 3.21 Scatter plots and correlation coefficients for $PM_{2.5}$ with selected biomass burning markers during the field measurement campaign, which are all assumed to be phenolic, with nitro derivatives for the aromatic species also plotted.

To further illustrate how these species correlate with $PM_{2.5}$, a time series comparison is given in Figure 3.22.

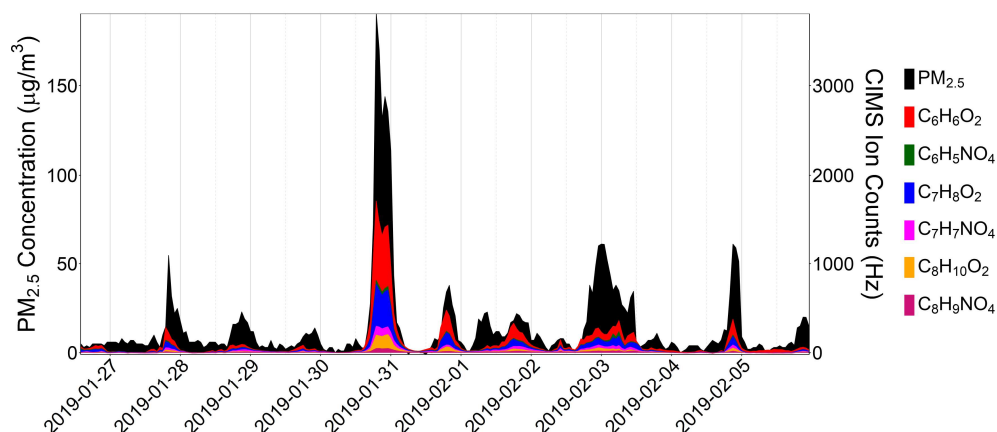


Figure 3.22 Time series of $PM_{2.5}$ and selected biomass burning marker compounds during the field measurement campaign in winter 2019.

As shown in Figure 3.22, the diurnal patterns for the main biomass burning markers are very similar to that shown by $PM_{2.5}$ and typical for residential solid fuel burning, however there are some interesting observations regarding the plots for $C_7H_7NO_4$ and $C_8H_9NO_4$. The increased daytime concentration of these species was not observed for the other species, which indicates another source, such as secondary photochemical production. Furthermore, the decay of the nitro species during the night is much slower than that observed for the other species, potentially indicating that they may also be produced via secondary chemistry at night-time.

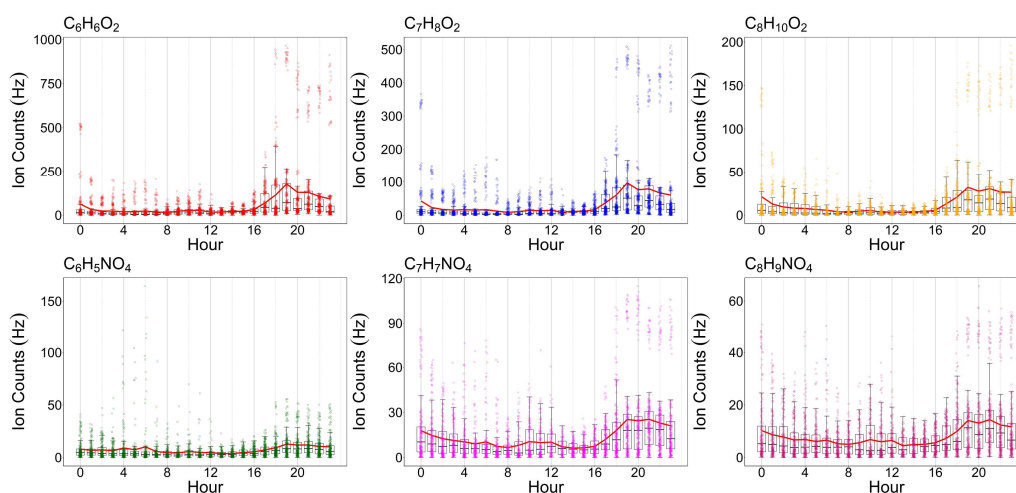


Figure 3.23 Diurnal time profiles during the field measurement campaign for the same VOC species which were seen to be highly correlated with $PM_{2.5}$ in Figure 3.21.

The bivariate polar plot for one of the species, $C_7H_8O_2$, is presented in Figure 3.24 and once again it is clear how similar this plot is to the $PM_{2.5}$ polar plot shown in Figure 3.4. The prevalence of this species from a very local, north-easterly origin highlights the dominance of wood burning in residential areas.

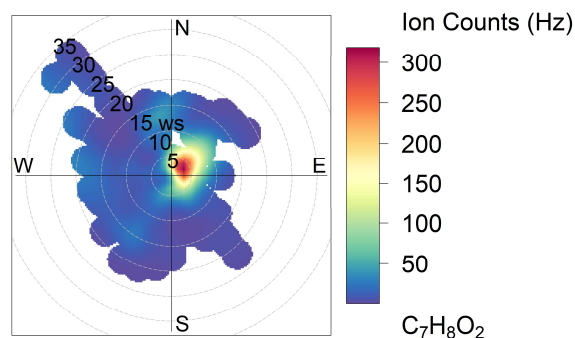


Figure 3.24 Polar plot of $C_7H_8O_2$ given as representative plot of the VOC species most highly correlated with $PM_{2.5}$ during the field measurement campaign.

Night-Time Processing of Biomass Burning Markers

As mentioned briefly above, the decay of $C_7H_7NO_4$ through the night was found to be slower than some of the other species which were also highly correlated with $PM_{2.5}$. In addition to being emitted directly by biomass burning, $C_7H_7NO_4$ could also be formed from atmospheric oxidation of the phenolic compound $C_7H_8O_2$ in the daytime via reaction with OH in the presence of NO_2 , or at night-time via reaction with the NO_3 radical (Lauraguais et al., 2014). The times series for $C_7H_7NO_4$ and $C_7H_8O_2$ are compared in Figure 3.25, along with those for two other nitroaromatics and their parent phenolic compounds.

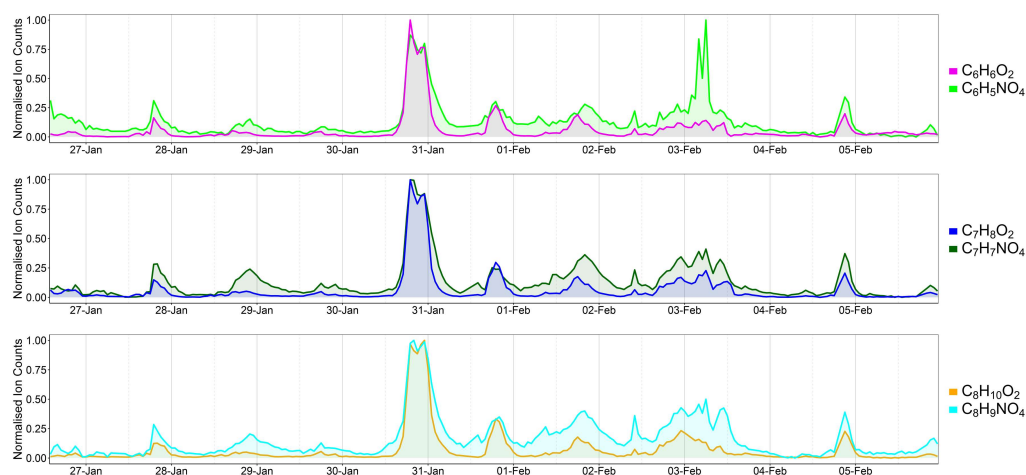


Figure 3.25 Time series of selected phenolic species and their nitro derivatives highlighting the slower decay of nitro-aromatic species.

It is clear that the nitroaromatics are primary emissions along with their related phenol compounds. Interestingly though, each of the nitroaromatics exhibited a slower decay and often a delayed maximum than their parent phenols during the night, suggesting that the nitro species were also being formed from atmospheric processing of the primary biomass burning emissions. This observation is consistent with numerous studies, where nitroaromatic compounds (NACs) have been detected in both primary and secondary biomass burning emissions (Iinuma et al., 2010; Wang et al., 2019; Salvador et al., 2021; Wang et al., 2020). Iinuma et al. (2010) identified methylnitrocatechols as biomass burning markers based on their strong linear correlations in the particle phase with levoglucosan. The study by Wang et al. (2019) found that secondary formation of NACs made a greater contribution than primary emissions, while similar results were observed in Wang et al. (2020), with significant increases in methylnitrocatechols observed during the night. However, there was a much more pronounced level of NAC formation observed in the latter studies than in the current, where formation is indicated by comparisons with other species rather than direct increase in concentrations.

A study in the UK using a similar instrument, MOVI-HR-ToF-CIMS, was unable to classify nitroaromatic species as having primary or secondary origin due to the site location, which was removed from the emission sources, however the NACs generally correlated very well with the BBOA AMS-PMF factor indicating they were mainly primary in origin (Mohr et al., 2013). Based on work by Yuan et al. (2016), it appears that the type of fuel being burned has a significant impact on the origin of NACs. In a field campaign where the predominant fuels were gas and oil, only 2% of NAC

concentrations were of primary origin (Yuan et al., 2016), suggesting that coal and wood burning which is common in the UK, is likely contributing to the observed NACs in the aforementioned study by Mohr et al. (2013). In Cork City wintertime pollution events are mainly due to the combustion of a mixture of solid fuels (coal, peat and wood) (Dall'Osto et al., 2013) and the time series shown in Figure 3.25 shows that these nitro compounds are both primary and secondary emissions.

Dark aging of VOCs has been repeatedly observed to contribute significantly to secondary organic nitrate, with reactions from both O_3 and NO_3 found to be significant (Kodros et al., 2020; Jorga et al., 2021). The Jorga et al. (2021) study estimated that up to 60% of secondary nitrate was organic in nature in a chamber study using ambient night air and exposing it to O_3 and NO_2 in the dark, and they found strong correlations with NO_3 and organic nitrate concentrations. Meanwhile, Ayres et al. (2015) have illustrated that it is not just biomass burning that can contribute to night-time secondary organic nitrate concentrations, as they studied the reactions of biogenic VOCs with the NO_3 radical and found that monoterpenes readily reacted with the nitrate radical yielding both gas and particle phase nitro species. They also found that particle phase C_{10} organic nitrate concentrations peaked during the night, with similar results seen during the SOAS campaign in the US (Ayres et al., 2015; Lee et al., 2016).

As shown in Figure 3.25, the phenol and related nitrophenol species tend to follow the same temporal pattern, however there is a very clear lag observed in the decay of the nitroaromatics when compared to their phenolic precursors. If atmospheric dilution was assumed to be the only loss process, then all of the primary-emitted species would have similar decay rates. However, the slower decay for each of the NACs points towards chemical conversion of the phenolic species to the corresponding nitrophenols. Plotting the ratio of the ion counts for the NAC to the parent phenol gives some indication as to when the processing may be occurring, Figure 3.26. The NAC to phenol ratio peaks during the night, typically several hours after the peak in primary emissions was observed.

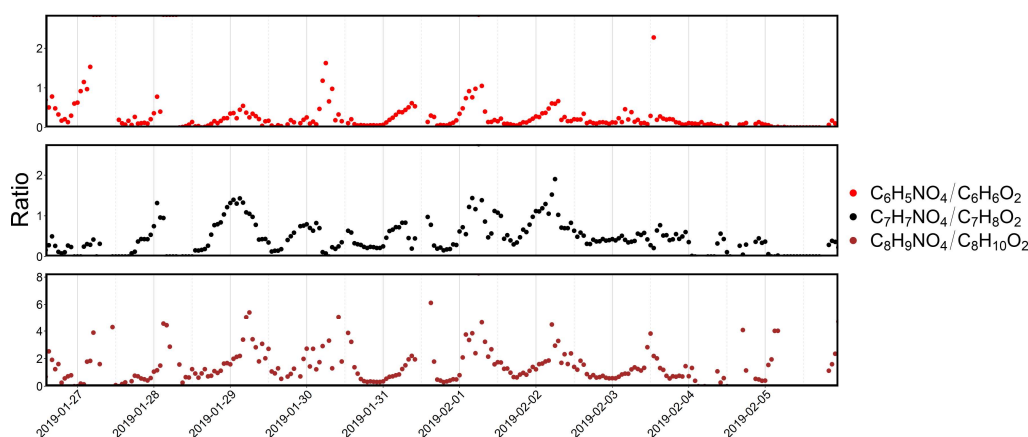


Figure 3.26 Time series of the ion counts ratio for NAC/phenol pairs illustrating that the nitro species dominate during the nighttime.

To further evaluate the trend, the mean diurnal cycle for these six biomass burning markers, as well as the ion ratios were plotted (Figure 3.27) in conjunction with the mean diurnal cycle of isocyanic acid (CHNO), which has negligible reactivity towards NO_3 radicals with $k_{\text{NO}_3} = 1.11 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Rosanka et al., 2020). Note that the sustained pollution event period has not been included in Figure 3.27 because it is not indicative of the general biomass burning trends and was found to skew the data. The traces have all been normalised by their respective maxima to scale all data between 0 and 1. As shown previously, isocyanic acid has a strong correlation with $\text{PM}_{2.5}$ ($r^2 = 0.9$) and follows a very similar trend to the C_6 - C_8 biomass burning markers. But because it is unreactive towards NO_3 and removal by dry deposition or uptake by particles is minimal, on the timescale of hours (Leslie et al., 2019), the decay of CHNO can be used as a proxy for the atmospheric dilution rate.

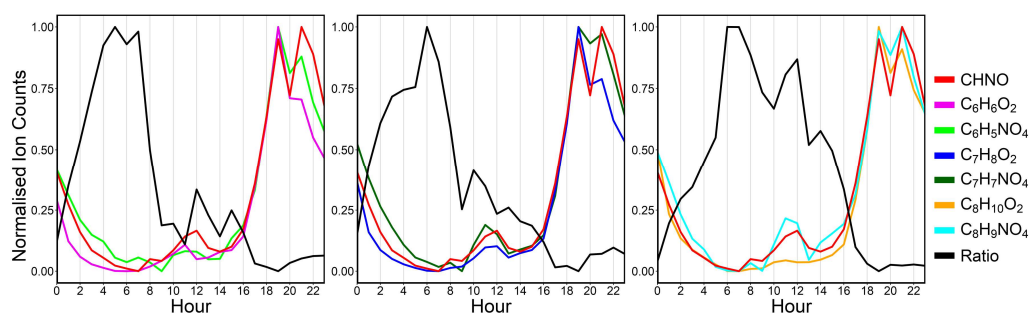


Figure 3.27 Normalised diurnal profiles of selected phenolic compounds and their nitro derivatives as well as isocyanic acid, illustrating nighttime formation of the nitro derivatives via NO_3 reactions.

As shown in each of the plots in Figure 3.27, the decay of the species seems to be in the order phenol > CHNO > NAC. Interestingly, the C_7 and C_6 phenolic species show

significantly faster decay than isocyanic acid, while the C₈ species is only marginally faster. Further analysis based on kinetic data is informative. If C₆H₆O₂ is assumed to be catechol ($k_{\text{NO}_3} = 9.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), C₇H₈O₂ is assumed to be methylcatechol ($k_{\text{NO}_3} = 1.47 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Olariu et al., 2004) and C₈H₁₀O₂ is assumed to be creosol ($k_{\text{NO}_3} = 2.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Yang et al., 2016), the relative decay rates for the phenolic species is in line with reactivity towards NO₃. This observation supports the assertion that the phenols undergo reaction with NO₃ to form their corresponding nitrophenol compounds. Evaluation of the first order decay rates for each species, calculated from the normalised plots given in Figure 3.27, over the time period 00:00 to 05:00, confirms this, Table 3.2. The nitro species have slower rates of decay than their potential precursors, with isocyanic acid having a rate of decay in between the precursor and product pairs for the C₆ and C₇ species. However, the C₈ species decay rates were only marginally different to the isocyanic acid, but the expected pattern was observed, with C₈H₁₀O₂ slightly faster than isocyanic acid, and C₈H₉NO₄ slightly slower, likely due to the slow reaction rate for creosol with the nitrate radical. Catechol was observed to have the fastest rate of decay with nitrocatechol having the slowest, suggesting that the conversion of catechol to nitrocatechol happens readily.

SPECIES	DECAY RATE (HOUR^{-1})
CHNO	0.57
C ₈ H ₁₀ O ₂	0.54
C ₈ H ₉ NO ₄	0.61
C ₇ H ₈ O ₂	0.64
C ₇ H ₇ NO ₄	0.44
C ₆ H ₆ O ₂	1.04
C ₆ H ₅ NO ₄	0.38

Table 3.2 First order decay rates for biomass burning markers from 00:00 to 05:00.

Each of the NAC/phenol ion ratios plotted in Figure 3.27 increase during the night, but then drop during the early morning. This could indicate nitrophenol photolysis by sunlight (Chen et al., 2011) as reaction with OH is considered to be slow. Interestingly there are also some small peaks during the middle of the day, which may be indicative

of another source of these species, potentially traffic or a photochemically driven reaction e.g., reaction of phenols with OH in the presence of NO₂.

3.4.5 Positive Matrix Factorisation

Initial analysis

PMF analysis was performed on the ToF-CIMS data to elucidate the key sources and processes which govern the ambient VOC concentrations measured in Cork City during the campaign. Initially, PMF was run to extract a maximum of 10 factors. Different solutions ranging from 1 factor solutions to 10 factor solutions were resolved, with each solution each repeated 10 times, producing 100 solutions overall. The Q/Q_{exp} data was explored to find the optimum number of factors to use. The output of Q/Q_{exp} for each of the 100 solutions is given in Figure 3.28, where the bars are coloured by the number of factors present in the solution.

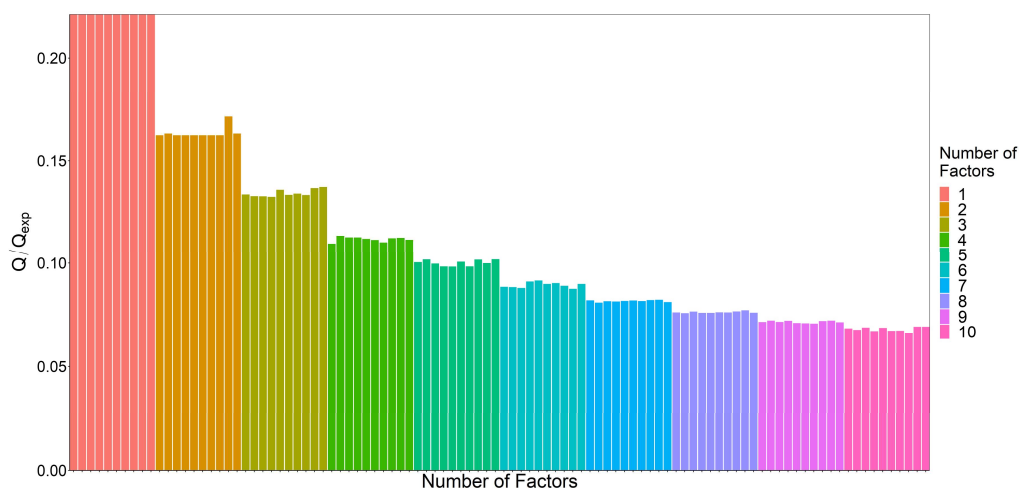


Figure 3.28 Q/Q_{exp} for each of the 100 PMF runs performed. A lower value of Q/Q_{exp} indicates that the run is closer to a fully explained PMF solution.

The results show that there is little difference in Q/Q_{exp} values for solutions with more than 6 factors, indicating that additional factors would likely only lead to splitting of already established factors without further explanation of the sources. Interpreting the absolute values of each factor as a function of the total sum of ions shows a similar result (Figure 3.29), with little to no increase in PMF performance beyond a 6-factor solution. Based on these two plots it was concluded that a 6-factor solution would offer the best explanation of the variance in VOCs observed during the campaign. To confirm this, further runs of PMF were performed using both profile normalisation (to remove sensitivity bias towards certain species) and resampling based on *fpeak* rotations to investigate the stability of the PMF runs. Interpretation of all of the various

runs of PMF lead to the choice of a single 6-factor PMF run as the best candidate for further analysis.

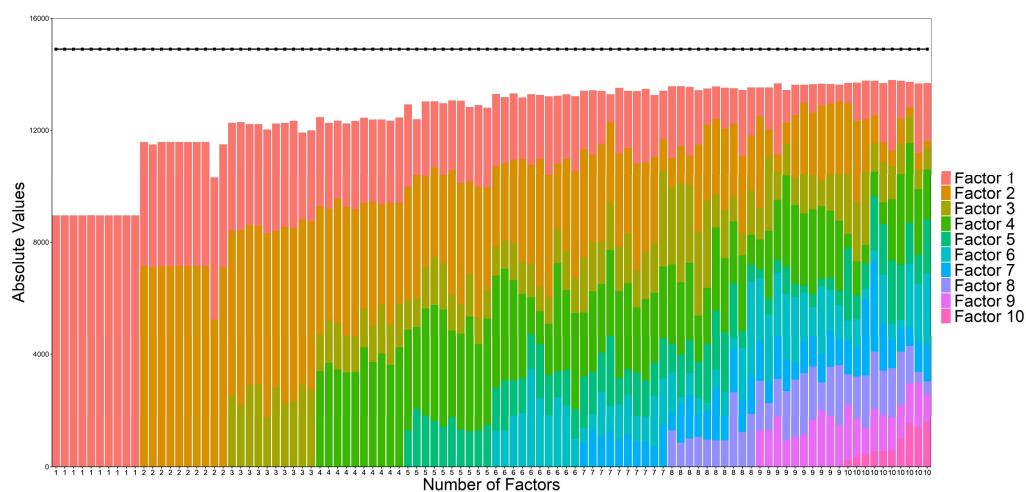


Figure 3.29 Absolute values of summed factor ion counts of the PMF runs compared to the total ion counts observed.

PMF Solution Results

The time series and average mass spectra for the chosen PMF solution are given in Figure 3.30, with some very clear patterns observed especially when compared to the PM_{2.5} time series. Note that while the PMF runs included all m/z values, the mass spectra plots are scaled to a maximum m/z of 200 Th as no significant signals were detected beyond this range.

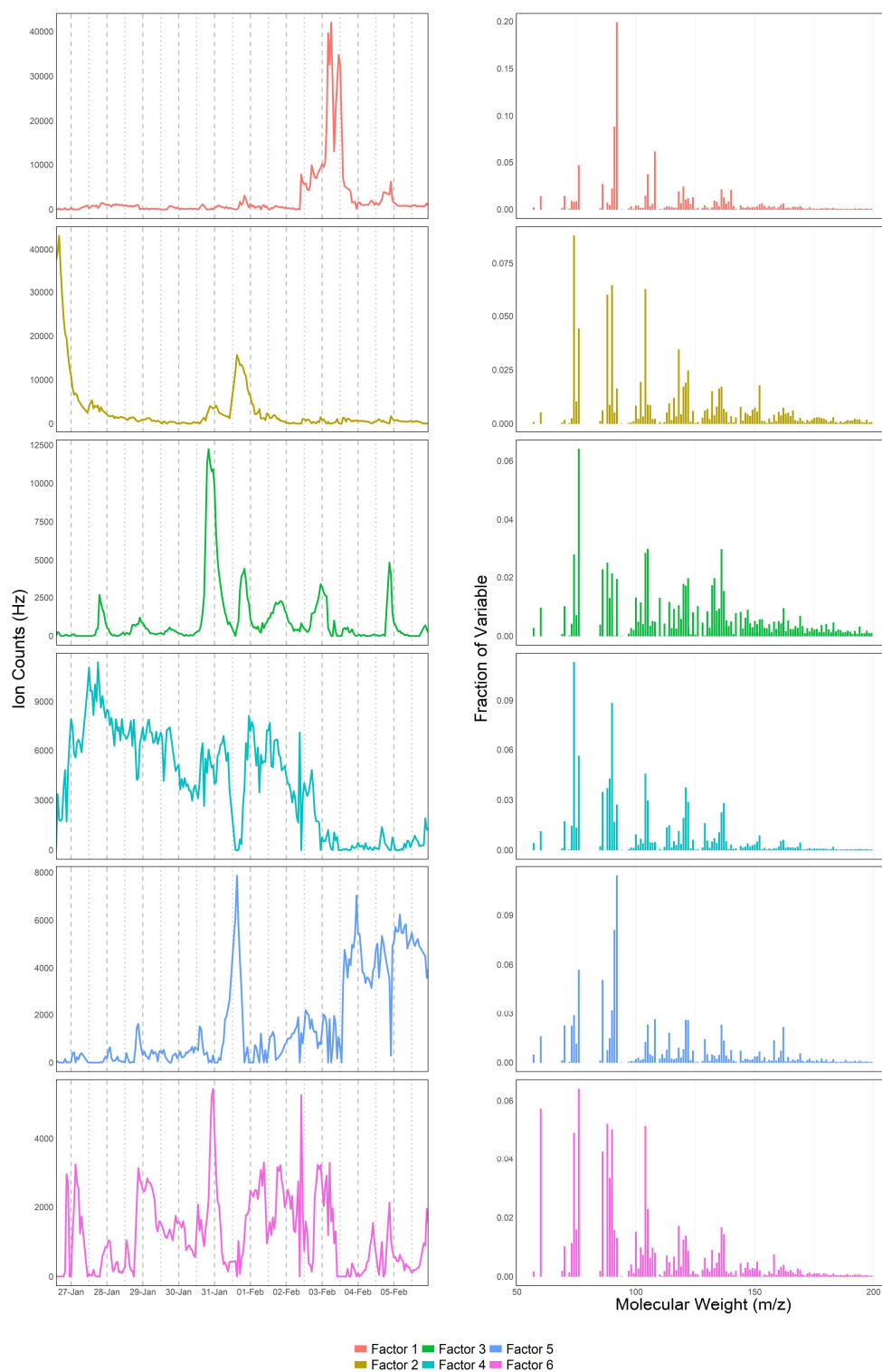


Figure 3.30 Time series of ion counts and average mass spectrum for each of the 6 factors resolved in the PMF solution.

The diurnal time series and polar plots for each of the factors resolved in the PMF solution are shown in Figure 3.31.

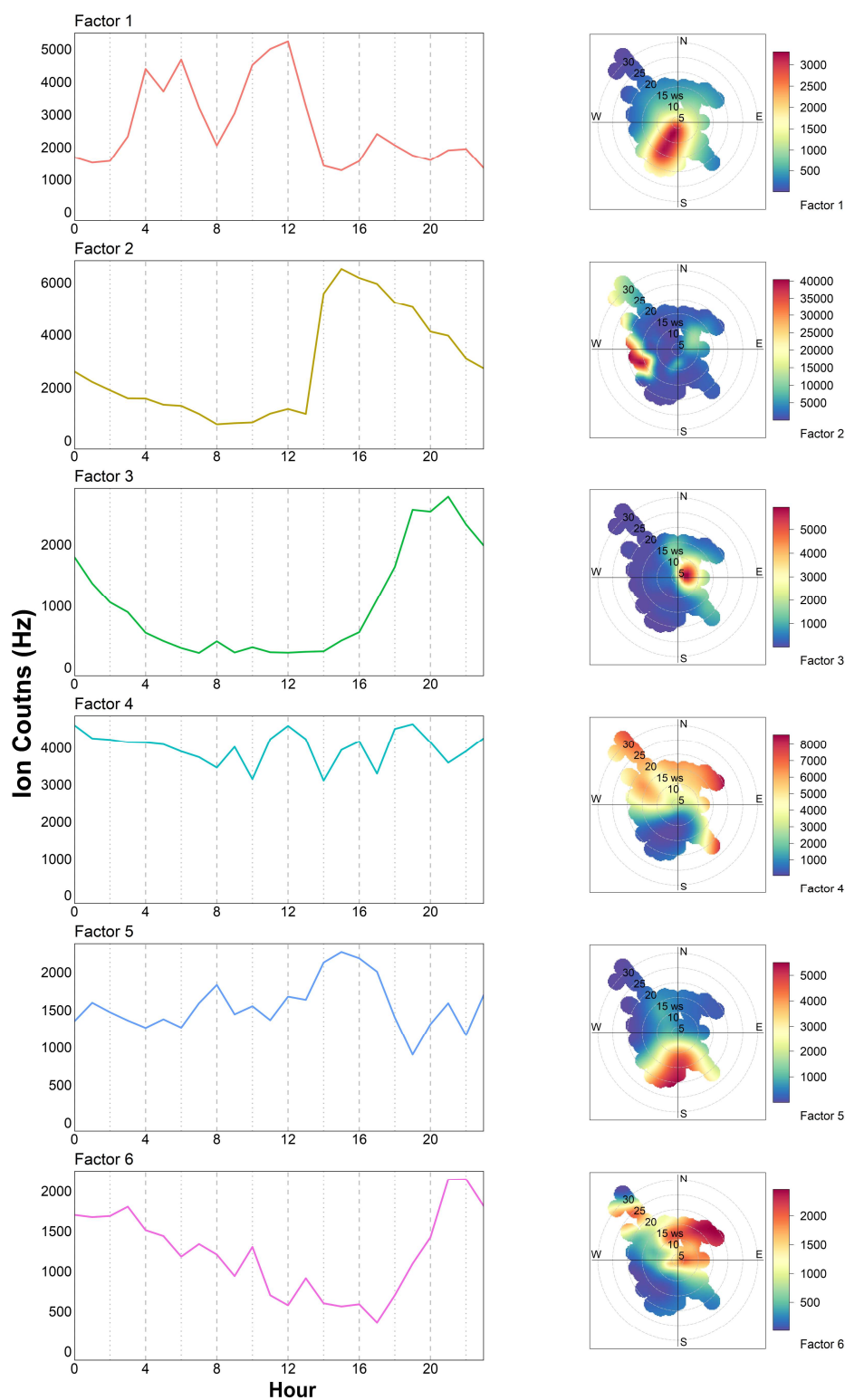


Figure 3.31 Factor diurnal time series and polar plots for each of the 6 factors resolved in the chosen PMF solution.

Table 3.3 gives the average molecular formulae for each of the observed factors, and some molecular ratios.

	<i>Average Molecular Formula</i>	<i>O/C</i>	<i>H/C</i>	<i>N/C</i>
Factor 1	C _{3.065} H _{4.153} O _{4.258} N _{0.337} S _{0.014}	1.389	1.355	0.11
Factor 2	C _{3.702} H _{4.816} O _{4.269} N _{0.224} S _{0.005}	1.153	1.301	0.06
Factor 3	C _{4.467} H _{5.748} O _{4.127} N _{0.344} S _{0.002}	0.924	1.287	0.077
Factor 4	C _{2.925} H _{3.637} O _{3.968} N _{0.339} S _{0.006}	1.356	1.243	0.116
Factor 5	C _{3.427} H _{4.364} O _{4.068} N _{0.340} S _{0.011}	1.187	1.274	0.099
Factor 6	C _{3.464} H _{4.686} O _{3.656} N _{0.308} S _{0.003}	1.055	1.353	0.089

Table 3.3 Average molecular formulae and molecular ratios for each factor in the chosen PMF solution.

Table 3.4 gives the formulas of the 10 most dominant species in each of the factors however, many of the species are common to all six factors due to the high sensitivity of I-CIMS towards low molecular weight acids.

Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
C ₂ H ₄ O ₄	C ₂ H ₂ O ₃	C ₂ H ₄ O ₃	C ₂ H ₂ O ₃	C ₂ H ₄ O ₄	C ₂ H ₄ O ₃
C ₂ H ₃ O ₄	C ₂ H ₂ O ₄	C ₂ H ₃ NO ₄	C ₂ H ₂ O ₄	C ₂ H ₃ O ₄	C ₂ H ₄ O ₂
C ₂ H ₄ O ₅	C ₃ H ₄ O ₄	C ₃ H ₄ O ₆	C ₂ H ₄ O ₃	C ₂ H ₄ O ₃	C ₃ H ₄ O ₃
C ₂ H ₄ O ₃	C ₃ H ₄ O ₃	C ₃ H ₄ O ₄	C ₃ H ₄ O ₄	C ₃ H ₂ O ₃	C ₃ H ₄ O ₄
C ₂ H ₃ NO ₄	C ₂ H ₄ O ₃	C ₂ H ₂ O ₃	C ₂ H ₃ NO ₃	C ₂ H ₂ O ₄	C ₂ H ₂ O ₄
C ₃ H ₂ O ₃	C ₄ H ₆ O ₄	C ₃ H ₄ O ₃	C ₂ H ₃ NO ₅	C ₂ H ₂ O ₃	C ₂ H ₂ O ₃
C ₂ H ₂ NO ₅	C ₃ H ₆ O ₃	C ₃ H ₂ O ₃	C ₃ H ₄ O ₃	C ₂ H ₄ O ₅	C ₃ H ₂ O ₃
C ₂ H ₂ O ₄	C ₂ H ₂ O ₆	C ₂ H ₂ O ₄	C ₃ H ₂ O ₃	C ₂ H ₃ NO ₅	C ₂ H ₃ NO ₃
C ₃ H ₄ O ₆	C ₄ H ₆ O ₃	C ₃ H ₃ NO ₅	C ₂ H ₃ NO ₄	C ₂ H ₂ O ₆	C ₃ H ₆ O ₃
C ₆ H ₄ O ₄	C ₂ H ₃ NO ₅	C ₂ H ₂ O ₆	C ₂ H ₂ O ₆	C ₂ H ₃ NO ₄	C ₂ H ₃ NO ₄

Table 3.4 Table of most abundant ions in each factor of the PMF solution.

To obtain more insight into the differences between the various factors, a similar table was prepared where all C₂ and C₃ species were ignored, Table 3.5. This results in only two factors containing very similar species (Factor 2 and Factor 6) and none of the factors have the same three most dominant species.

Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
C ₆ H ₄ O ₄	C ₄ H ₆ O ₄	C ₅ H ₈ O ₄	C ₄ H ₃ NO ₄	C ₄ H ₂ O ₄	C ₄ H ₆ O ₄
C ₆ H ₃ NO ₄	C ₄ H ₆ O ₃	C ₄ H ₄ O ₃	C ₄ H ₂ O ₄	C ₄ H ₃ NO ₄	C ₄ H ₄ O ₃
C ₄ H ₃ NO ₆	C ₅ H ₈ O ₄	C ₆ H ₆ O ₂	C ₄ H ₃ NO ₃	C ₁₀ H ₆ O ₂	C ₄ H ₈ O ₃
C ₄ H ₃ NO ₄	C ₄ H ₄ O ₄	C ₅ H ₆ O ₃	C ₄ H ₆ O ₄	C ₄ H ₃ NO ₃	C ₄ H ₆ O ₃
C ₆ H ₈ O ₄	C ₅ H ₈ O ₃	C ₄ H ₆ O ₃	C ₄ H ₄ O ₃	C ₆ H ₄ O ₄	C ₅ H ₈ O ₄
C ₄ H ₆ O ₄	C ₄ H ₂ O ₄	C ₄ H ₆ O ₄	C ₄ H ₆ O ₃	C ₆ H ₈ O ₄	C ₄ H ₈ O ₄
C ₄ H ₄ O ₃	C ₄ H ₄ O ₃	C ₆ H ₆ O ₃	C ₄ H ₂ O ₅	C ₄ H ₃ NO ₆	C ₆ H ₄ O ₂
C ₅ H ₃ NSO ₂	C ₄ H ₆ O ₅	C ₆ H ₁₀ O ₅	C ₄ H ₃ NO ₆	C ₆ H ₃ NSO ₃	C ₁₀ H ₆ O ₂
C ₆ H ₄ O ₅	C ₆ H ₈ O ₄	C ₅ H ₈ O ₃	C ₄ H ₄ O ₄	C ₆ H ₉ NO	C ₄ H ₃ NO ₃
C ₆ H ₃ NSO ₃	C ₄ H ₆ O ₆	C ₄ H ₅ NO ₅	C ₅ H ₈ O ₄	C ₄ H ₂ O ₅	C ₅ H ₈ O ₃

Table 3.5 Table of most abundant ions in each factor of the PMF solution when C₂ and C₃ species are ignored due to instrument bias towards these species.

PMF Solution Discussion

Assignment of Factors

The time series for Factor 1 shows no significant contribution to the total ion counts until 2 February at which stage it starts to increase and remains elevated throughout the duration of the sustained pollution event observed during the campaign. The polar plot highlights that this factor is dominant at lower wind speeds, once again highlighting that the sustained pollution event is a result of low wind speeds allowing the accumulation and subsequent oxidation of various VOCs. The average molecular formula for this factor C_{3.1}H_{4.2}O_{4.3}N_{0.3}S_{0.01} has the highest average O/C ratio for any of the factors, confirming that this factor can be attributed to highly oxidised species in an aged air mass.

Factor 2 shows two main peaks in its contribution to the total ion counts during the campaign, appearing on 26 and 31 January. The diurnal plot for this factor shows a sharp increase observed during early afternoon which then decays during the evening hours, Figure 3.31. The chemical species most associated with Factor 2 contain three or more oxygens, and the polar plot indicates a strong influence from the west at moderate wind speeds, suggesting a significant degree of transport. There is also some

influence from the north-west under high wind speed and while there appears to be several sources for this factor, the early afternoon peak, oxidised nature of the species and importance of wind speed all point towards Factor 2 being attributed to a regional source of atmospherically processed emissions from the western direction, which contains a combination of residential areas and agricultural land.

Factor 3 has a very similar time profile to $PM_{2.5}$, showing large peaks corresponding to evening pollution events and reaching its maximum at the same time as the $PM_{2.5}$ concentration, i.e., evening of 30 January. The strong correlation is illustrated in Figure 3.32.

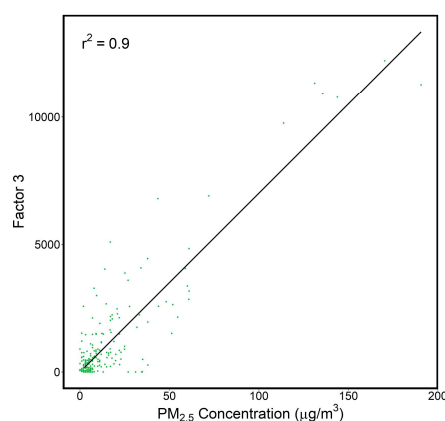


Figure 3.32 Scatter plot of Factor 3 with $PM_{2.5}$ concentration highlighting that this factor is the most closely associated with $PM_{2.5}$ concentration.

Factor 3 has the lowest O/C ratio of all factors, consistent with fresh biomass burning species which were observed during the evening pollution events. $C_6H_6O_2$, attributed to catechol, is one of the dominant species for Factor 3 and the very high correlation of the factor with the species $C_7H_8O_2$ and $C_8H_{10}O_2$ also suggests that this factor is a wood burning factor. The prevalence of these species indicates that this factor is similar to the factor assigned as “lignin” in a PMF study utilising FIGAERO-CIMS data (Kong and Pettersson, 2020). Interestingly, that study identified another biomass burning factor, labelled “cellulose” which had $C_6H_{10}O_5$ and $C_7H_{12}O_7$ as dominant species. $C_6H_{10}O_5$ corresponds to the molecular formula of levoglucosan (or its isomers) which is a widely known marker for wood burning (Fine et al., 2001, 2002; Iinuma et al., 2007). Although levoglucosan primarily exists in the particle phase and has not been detected by gas-phase CIMS before, it is interesting to note that the molecular formula is present in the 10 most abundant ions associated with Factor 3,

Table 3.5. This is further evidence that Factor 3 is wood burning factor which could be similar to a composite of the cellulose and lignin factors identified by Kong and Petersson (2020).

From the time series presented in Figure 3.30, it seems as though Factors 4 and 5 are the inverse of one another. The scatter plot of these two factors in Figure 3.33 highlights this, with the majority of the data occurring at the edges of the plot showing that when one factor is high the other is low, while there is an anti-correlation ($r^2 = -0.73$) observed between the two variables.

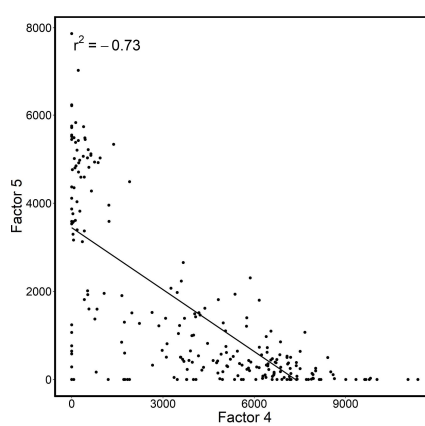


Figure 3.33 Scatter plot of Factor 4 and Factor 5 highlighting their anti-correlation.

A pattern such as this could imply that Factors 4 and 5 were created by the splitting of a factor. However, all PMF runs consistently generated these two factors as separate factors. Initial analysis of the time series of the factors offered no explanation as to their source but the fact that one of the factors is always present suggested that these two factors result from two different ambient backgrounds. The polar plots for the two factors offered the most reasonable explanation for the change in ambient background during the campaign, Figure 3.31. Factor 4 appears to be diffuse as it is observed at a variety of wind speeds and directions with no strong diurnal variation. Similarly, Factor 5 does not show a strong diurnal pattern, but it shows a dependence on southerly winds. Although there is no clear diurnal pattern observed, the small peaks at 8 am and in the later afternoon may highlight a traffic origin for some of the species in the factor, however upon comparison of the mass spectrum with those obtained for traffic emissions by Le Breton et al. (2019), no similarities were observed (Le Breton et al., 2019).

From the average molecular formulae calculated for the two factors, it is seen that Factor 5 has a slightly lower O/C ratio of 1.187 compared to 1.356 observed for Factor 4 which indicates the emissions from the southerly direction are less oxidised than those originating from the north. This is an indication that the VOCs in factor 5 are less aged than those in Factor 4, indicating that their source is closer to the measurement site.

Factor 6 shows a high degree of variation throughout the measurement period but has a diurnal profile with strong evening peaks pointing towards residential solid fuel burning as the source. However, a closer comparison of the diurnal profile with that of Factor 3 reveals some interesting differences.

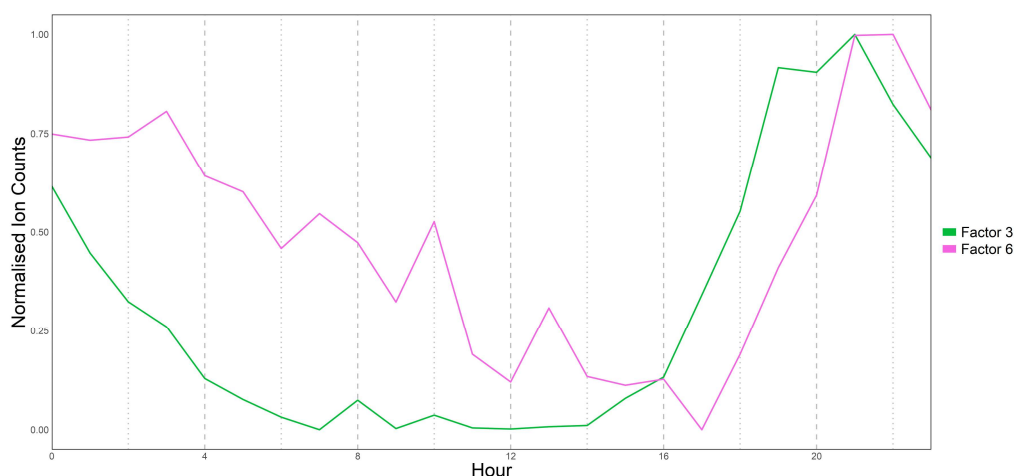


Figure 3.34 Normalised diurnal profiles of Factor 3 and Factor 6 illustrating their differences.

As shown in, Figure 3.34, Factor 6 peaks later than Factor 3 and does not decay as quickly. Indeed, the diurnal profiles for Factor 3 and Factor 6 are very similar to those of the phenols and their nitro products shown in Figure 3.27. Although nitroaromatics are not in the top 10 most abundant species in Factor 6, this factor does show a higher N/C ratio (0.089) than Factor 3 (0.077), as well as a higher O/C ratio (1.055 versus 0.924), consistent with night-time processing of the phenol biomass burning markers via reaction with NO_3 . Taking all of the observations and analysis into account, Factor 6 is assigned to atmospherically processed biomass burning emissions.

Contribution of Factors throughout the Campaign

The contribution of each factor to the total ion counts throughout the measurement period is shown graphically in Figure 3.35. Factor 2 clearly dominates at the beginning of the campaign with increases in both Factor 4 and Factor 6 during the evening. The predominant factor between the first evening and the pollution event observed on 30 January is Factor 4, indicating little to no change in ambient chemical composition between these days, however the pollution event on 30 January is very strongly characterised by increases in Factor 3 and in Factor 2. Factor 2 once again dominates on 31 January with some nighttime increases in Factor 6 also observed. The stagnant weather conditions on 2 February bring a significant period of dominance by Factor 1 with some hours having more than 90% of their air mass classified as being in this factor. Following this pollution event, Factor 5 becomes dominant as there appears to be a shift in the prevailing conditions, which as illustrated in Figure 3.31 is most likely a result of a change in the wind direction with Factor 5 originating to the south of the monitoring site.

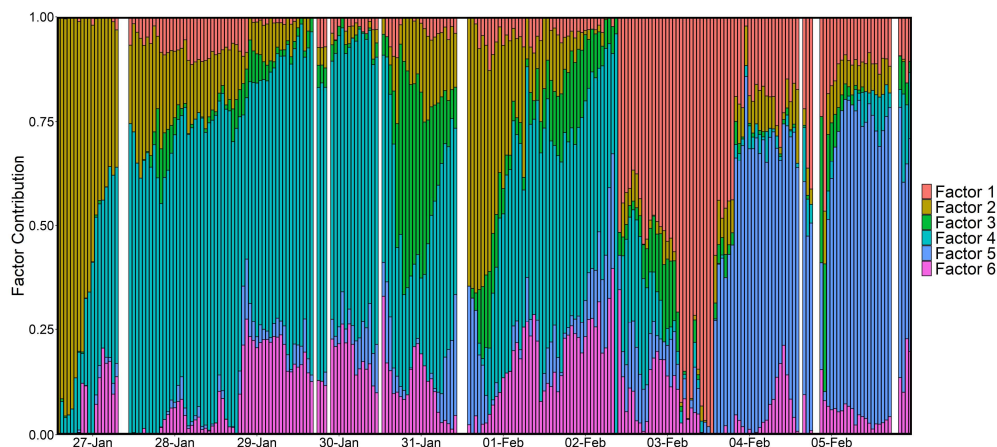


Figure 3.35 Factor contribution times series for entirety of measurement campaign.

It is clear from this figure that Factor 4 and Factor 5 contribute significantly to the total VOC concentration observed by the ToF-CIMS, suggesting that these factors are indicative of the background VOCs, with some wind dependence. As illustrated in Figure 3.36, these two factors combined to contribute 42.3% to the sum of the observed species throughout the whole campaign.

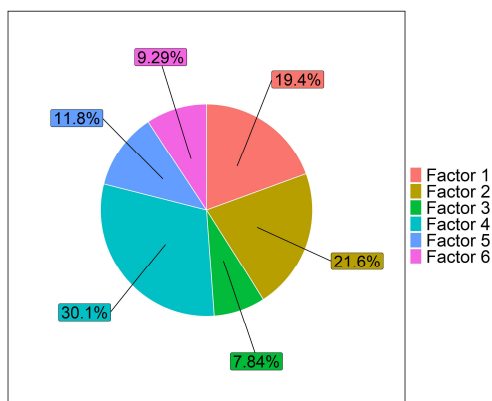


Figure 3.36 Pie chart showing the contribution that each factor makes to the total ion counts in the entire campaign.

Interestingly, Factor 3, which is highly correlated with $\text{PM}_{2.5}$ ($r^2 = 0.9$) and corresponds to the local wood burning events, only contributes 7.84% to the total observed organics. This indicates that despite the low contribution of wood burning emissions across the entire campaign, they are the most highly contributing towards PM illustrating how important it is to monitor and mitigate against these local domestic solid fuel burning pollution events.

Factor split of Biomass Burning Markers

The contribution of the six factors to the total ion counts for the selected biomass burning markers is shown in Figure 3.37. As expected, $\text{C}_6\text{H}_6\text{O}_2$, $\text{C}_7\text{H}_8\text{O}_2$ and $\text{C}_8\text{H}_{10}\text{O}_2$ primarily belong to Factor 3, with some contributions from other sources. The nitro species $\text{C}_6\text{H}_5\text{NO}_4$, $\text{C}_7\text{H}_7\text{NO}_4$ and $\text{C}_8\text{H}_9\text{NO}_4$ are also mostly associated with Factor 3, but have increased contributions from Factor 6, 9.29%, 22.7% and 14% respectively, compared to their non-nitro precursors. This was expected based on the potential for NO_3 chemistry illustrated in Figure 3.37. As shown in the pie charts, each of these species although dominated by Factor 3, also shows significant contributions from other factors.

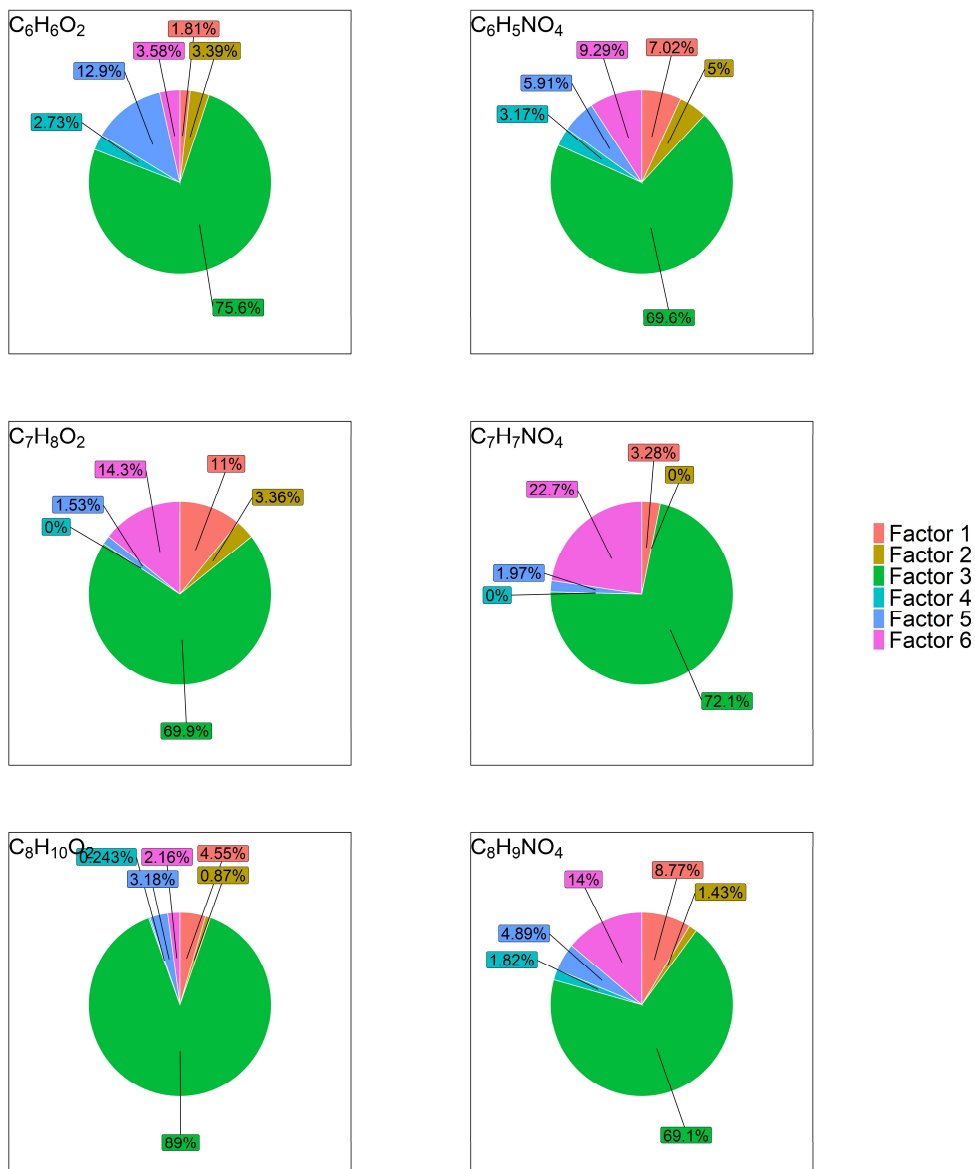


Figure 3.37 Pie charts of specific VOCs and the contribution of each factor to its concentration.

3.5 Conclusion

A field campaign was performed at an urban background location in Cork City during the winter of 2019, where an Aerodyne ToF-CIMS was used to continuously monitor gas phase organic species for a period of 12 days in conjunction with a suite of other monitors for atmospheric pollution. Strong diurnal patterns were observed for PM_{2.5} relating to local biomass burning events, which were characterised by large increases in species which are assumed to be phenolic in their nature and have strong links with wood and coal burning. Weather was also found to have significant impacts on PM_{2.5} concentrations, notably with reduced wind speeds allowing accumulation of PM_{2.5} while lower temperatures also resulted in increased residential solid fuel burning.

A range of gas phase acids were also observed, and found to have links with aqueous phase chemistry, as well as photooxidation of primary emissions. Atmospheric processing of biomass burning markers through the night was observed to occur resulting in the formation of nitro-aromatic compounds, consistent with other similar studies in urban areas. Analysis of the rate of decay of nitro-aromatic species, their potential precursors and the chemically inert species isocyanic acid, illustrated faster decay than would be expected, based solely on atmospheric dilution, for the phenol species, while the nitro-aromatic species were slower than would be expected. This highlighted the processing of the phenol species, likely by the NO₃⁻ radical, to form the nitro-aromatic compounds.

Positive matrix factorisation was performed, and a six-factor solution was found to best explain the variance in the dataset, with factors defined as aged VOCs, daytime aging of local emissions, wood-burning, residential background, city background and nighttime chemistry. The trends of the various factors have been accounted for, and no further factors could be extracted from the dataset. The major biomass burning species were found to primarily contribute to the wood-burning factor as expected, however interestingly it was observed that the nitro derivatives for the aromatic species were also found in the wood-burning factor suggesting that these species are primary in nature, rather than secondary. Nevertheless, for each of the nitro-analogues observed to form via nighttime chemistry, increased contributions to the nighttime

chemistry factor were observed, illustrating that although these species are mainly primary in their nature, they also have a significant secondary source.

Overall, this study presents the first online measurements of VOCs in Ireland and has highlighted the significant impact of residential solid fuel burning on VOC concentrations. A further winter study in which the FIGAERO operates properly is suggested to elucidate more information on the particle phase organic species, as well as studies in other seasons to investigate the seasonality of VOC emissions. A particular source of interest would be biogenic emissions and reactions during the summer which may contribute to secondary organic aerosol formation, as well as further investigations into the nighttime processing of VOCs.

4. Hydroxyl radical initiated oxidation of 4-methylcatechol

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4.1 Introduction

4-methylcatechol is an aromatic species, similar to various other catechols and phenols which are known products of wood combustion (Zhu et al., 2021). The atmospheric oxidation of 4-methylcatechol (4-MC) by OH radicals has not been extensively characterised as of yet, with only a few studies investigating the gas phase oxidation of this species. To date, there has been research into the ozone and nitrate reaction mechanisms and aerosol yields of 4-MC, while a study of hydroxyl initiated reactions at the air-water interface has also been performed but the gas phase hydroxyl initiated reactions have thus far been neglected (Coeur-Tourneur et al., 2010; Sun et al., 2019; Mayorga et al., 2021; Pillar and Guzman, 2017).

Reactions with ozone were investigated, and aerosol yields were reported to be in the range of 0.30 to 0.64 with a strong dependence on precursor concentration, while the reactions were computationally calculated to proceed via 1,3-cycloaddition resulting in primary ozonides and Criegee intermediates. Some of the computed products were calculated to have acute and chronic toxicity effects on both algae and fish highlighting the importance of understanding the mechanisms of oxidation of this species in the atmosphere (Coeur-Tourneur et al., 2010; Sun et al., 2019). Mayorga et al. (2021) investigated the reactions of various phenolic compounds, including 4-MC with the NO₃ radical and Pillar et al. (2017) performed experiments to determine the hydroxyl radical reactions of substituted phenols at the air-water interface, but did not exclusively investigate the gas phase hydroxyl radical chemistry of these compounds (Mayorga et al., 2021; Pillar and Guzman, 2017). The oxidation by NO₃ radicals was found to form secondary organic aerosol (SOA) with a yield of ~ 0.4, however the authors noted that their reaction system may not have been ideal for measuring SOA yields. The NO₃ radical reactions were found to yield a range of C₇ and also C₆ species indicating that despite the expectation that a methyl group would be a poor leaving group, some reactions occur via scission of this group from the aromatic ring. The major products of NO₃ reactions with 4-MC were found to be nitrophenol compounds, generally of the form C₇H₇NO_x, however a range of dinitro and trinitro products were also observed. A range of dimers were also detected in that work composed of both C₁₄ and C₁₂ species indicating that the C₆ species could oxidise further resulting in

these dimer products (Mayorga et al., 2021). The reactions performed using the hydroxyl radical at the air/water interface found sequential OH addition as well as ring scission leading to small organic acids to be significant reaction pathways, consistent with studies performed on similar species (Pillar et al., 2014; Pillar and Guzman, 2017).

Although the gas phase hydroxyl radical chemistry of 4-MC has not been extensively characterised, chamber photooxidation experiments have been performed on a range of similar species. Catechol ($C_6H_6O_2$), for example, has been studied under a variety of conditions. Finewax et al. (2018) investigated the reactions of the OH radical with catechol in the presence of NO_x where high SOA yields of 1.34 (OH reactions) and 1.5 (NO_3 reactions) were observed (Finewax et al., 2018). The dominant oxidation product was nitrocatechol ($C_6H_5NO_4$), suggesting that in the current study, methylnitrocatechols would be important oxidation products. Similar results were reported by Fredrickson et al. (2022), who also investigated catechol oxidation under both OH and NO_3 reaction conditions using a FIGAERO-CIMS. This study observed significant loss of nitrocatechol upon aging of the SOA, while a range of other species were detected in the particle phase, both with and without nitro functionality (Fredrickson et al., 2022). Nitrocatechols and methylnitrocatechols are important species to study due to their formation in the ambient atmosphere and contribution to brown carbon SOA. Vidović et al. (2018) have showed that they can readily form in the atmospheric condensed phase even under dark conditions, while Iinuma et al. (2010) observed methylnitrocatechols in significant concentrations in field samples with strong correlations with levoglucosan, highlighting their relationship with wood burning (Vidović et al., 2018; Iinuma et al., 2010). A computational study on phenol proposed that the dominant product of OH reaction would be catechol with only minor formation of nitrophenol, however the significant concentrations of nitro-aromatic species detected in field studies, such as by Mohr et al. (2013), may suggest that computational methods do not yet accurately predict the product distributions of hydroxyl initiated aromatic oxidation (Xu and Wang, 2013; Mohr et al., 2013).

Cresol (methyl-phenol) has also been studied, by both Olariu et al. and Schwantes et al. (Olariu et al., 2002, 2013; Schwantes et al., 2017). Olariu et al. (2002) investigated the OH reactions of *ortho*-, *meta*- and *para*-cresol in the presence of NO_x and found that the majority of products were explained by hydroxylated species, benzoquinones

and nitrophenols. This is consistent with the expectation that aromatic oxidation by the hydroxyl radical tends to proceed either via OH addition to the aromatic ring or by hydrogen abstraction (Olariu et al., 2002). Schwantes et al. (2017) also studied the oxidation of *ortho*-cresol and investigated the products of further oxidation than the primary products reported in the Olariu et al. (2002) study. They found that further oxidation yielded low volatility species while they also observed a plethora of ring scission species with carbon numbers of between 2 and 5. In the course of their work, they also investigated the reactions of 3-methylcatechol as this species is the primary OH addition product for *ortho*-cresol oxidation, and they observed significant formation of other hydroxylated products as well as some benzoquinone structures, but did not observe significant concentrations of methyl-nitrocatechols ($C_7H_7NO_4$). They also identified a range of decomposition products which were proposed to be products of a bicyclic intermediate pathway (Schwantes et al., 2017).

Studies on aromatic hydrocarbon such as benzene and toluene and other non-oxygenated hydrocarbons have also been performed and mechanisms have been derived for their atmospheric degradation in a range of studies. Zaytsev et al. (2019) investigated the OH oxidation of toluene and trimethylbenzene and found reactions can proceed via H-abstraction yielding aldehydes, or by OH addition yielding phenols, epoxides or bicyclic peroxy radicals which can undergo further decomposition to give ring scission species (Zaytsev et al., 2019). Priestley et al. (2021) performed photooxidation experiments on benzene in the Jülich Plant Atmospheric Chamber and found significant contributions from highly oxidised species with oxygen numbers between 9 and 11 while also detecting ring retaining phenol structures with oxygen numbers between 1 and 4, and a range of ring scission species. They also observed a number of R-NO_x species in experiments performed under NO_x conditions (Priestley et al., 2021). Xu et al. (2020) found similar results in a previous computational study, where hydroxyl initiated oxidation of benzene was simulated and proposed to result in a range of both ring opened and ring retaining species (Xu et al., 2020).

The results from these studies suggest that multiple pathways of oxidation of 4-MC are possible in hydroxyl initiated oxidation reactions, and significant yields of SOA are expected. It is anticipated that reactions will proceed primarily via OH addition, however the H-abstraction products, namely benzoquinones and nitrophenols are also expected to form and contribute to SOA formation.

4.2 Aims

The aims of this work were to characterise the gas and particle phase products of the hydroxyl initiated atmospheric photooxidation of 4-methylcatechol, a known product of biomass burning. The reagent decay and product formation were tracked using ToF-CIMS with both iodide and benzene reagent ions to elucidate the product formation pathways and the FIGAERO inlet was used to identify the major organic species in the particle phase. SOA formation and growth were monitored using a scanning mobility particle sizer (SMPS, TSI incorporated) and estimations on SOA yield were made using this data. The atmospheric processing of the SOA was also monitored with respect to time under both light and dark conditions to investigate how the organic species in the SOA evolved.

4.3 Materials and Methods

All photooxidation chamber experiments were carried out using the method described in Chapter 2. Briefly, all reagents were added to the chamber prior to the start of the reaction and allowed sufficient time to mix homogeneously before chamber irradiation. Because 4-MC is a solid, the compound was added to the chamber as a solution in milliQ water (1.6 mol L^{-1}). A known volume of this solution was added to a small glass bulb which was gently heated whilst flowing a stream of nitrogen (0.5 L min^{-1}) through the bulb and into the chamber. One μL of solution yielded approximately 15 ppb or $77.14 \mu\text{g m}^{-3}$ of 4-MC in the chamber. The OH precursors were added to the chamber at the same time as 4-MC, also using a stream of nitrogen. For experiments without added NO_x , N_2 was bubbled through aqueous hydrogen peroxide (30% v/v, Sigma Aldrich), while for reactions in the presence of NO_x , HONO was also added via the reaction of sulfuric acid and sodium nitrite. The reagents were monitored using the ToF-CIMS, while the NO_x analyser was also used to monitor HONO addition. Once sufficient concentrations of reagents were reached, their addition was stopped, and the chamber was given time to mix before photooxidation.

Following addition of 4-MC, a small residue was often observed in the glass vial, suggesting incomplete addition of the compound to the chamber. As a result, I-CIMS calibrations of 4-MC were performed under different humidity conditions to determine the concentration of reagent added in each experiment. Due to the differing chemistry of benzene ionisation which resulted in multiple ion clusters for the same species (protonated species, $\text{C}_x\text{H}_{y+1}\text{O}_z^+$ and charge transfer species, $\text{C}_x\text{H}_y\text{O}_z^+$) and instrument interferences, benzene-CIMS could not be accurately calibrated for 4-MC concentrations and no additional information of interest was found in these experiments. As such, they have been discarded from further discussion.

The ToF-CIMS was operated using the VUV source for ion generation as discussed in Chapter 2, with a reagent ion flow of 0.45 L min^{-1} .

To estimate mass loading on the FIGAERO filter, sampling duration and flow rate were measured, and the mass loading determined using the mass concentration reported by the SMPS at the start of the sampling period. This was used to correct for

different mass loadings in the same experiment as ion concentration is proportional to SOA mass loading.

Estimates of the OH concentration achieved during the experiments were derived from the measured decay of 4-MC assuming pseudo first-order conditions with 4-MC in excess and using a rate coefficient for the OH reaction of $1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Olariu et al., 2000).

SMPS data was collected over the particle diameter range of 12 to 400 nm using the Aerosol Instrument Manager v10.3.0.3. Data were corrected for wall losses and subsequently plotted using R v4.0.2.

4-Methylcatechol Calibration

To estimate 4-methylcatechol concentrations in the chamber, calibration experiments were performed, whereby different volumes of the 4-MC solution were added to the glass bulb and subsequently to the chamber in the standard method discussed above. The steady ion concentration recorded for each volumetric addition were then used to plot a calibration curve for 4-MC concentration, based on the relationship of the μL addition volume to the molar concentration of the solution, Figure 4.1.

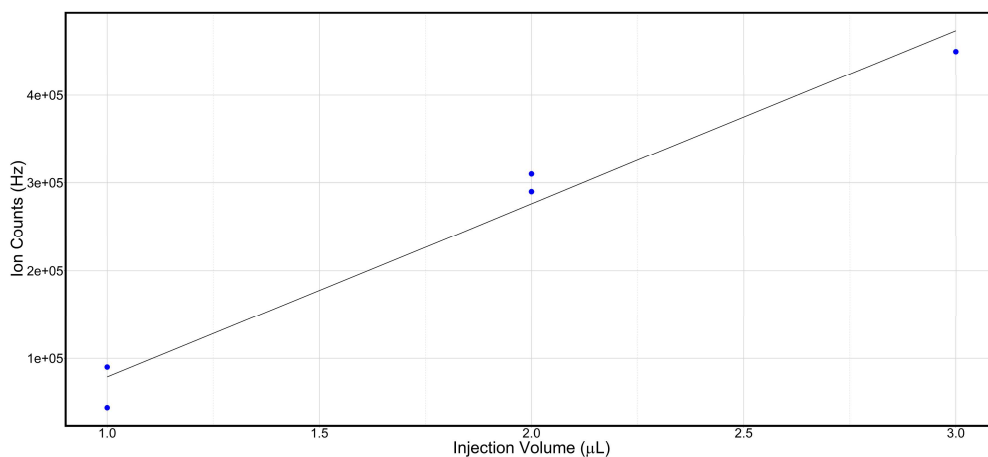


Figure 4.1 Calibration plot for 4-methylcatechol to calculate 4-MC concentrations in the atmospheric simulation chamber.

4.4 Results and Discussion

4.4.1 Reaction Parameters and Concentration Time Profiles

The OH-initiated oxidation of 4-MC was performed under a range of experimental conditions, with varying NO_x concentrations and relative humidity, different light conditions and ToF-CIMS reagent ions. The results obtained using benzene-CIMS did not provide an additional information and are not presented here. A summary of the experiments is presented in Tables 4.1, 4.2 and 4.3. The code used for experiment labels is as follows:

MC: 4-Methylcatechol.

I: Iodide CIMS reagent.

D/H: Dry or humid conditions.

NO_x: Indicates addition of NO_x (> 1 ppb).

UVA: Specifies only UVA lamps used in experiment.

DARK: Specifies experiments where UVA and UVC radiation was used to initiate the reaction between OH and 4-MC, however the lamps were switched off after a period of time and aging of the products were continuously monitored in the dark.

Experiment Code	4-Methylcatechol Concentration ($\mu\text{g}/\text{m}^3$)	Estimated OH Concentration ($\text{molecule}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$)	NO_x (ppb)	Relative Humidity (%)	SOA Corrected Mass ($\mu\text{g}/\text{m}^3$)	SOA Yield
MCID-1	70.71	9.88×10^6	< 1	< 1	34.76	0.49
MCID-2	61.07	1.38×10^7	< 1	< 1	16.28	0.27
MCID-3	95.78	9.12×10^6	< 1	< 1	32.40	0.34
MCID-4	73.93	3.72×10^7	< 1	< 1	19.79	0.27
MCID-5	28.29	1.74×10^7	< 1	< 1	0.33	0.01
MCIH-1	127.59	7.63×10^6	< 1	40	47.57	0.37
MCIH-2	23.14	1.26×10^7	< 1	60	14.52	0.63
MCIH-3	46.28	1.14×10^7	< 1	55	19.29	0.42
MCIH-4	21.60	1.87×10^7	< 1	44	5.322	0.25
MCIH-5	66.34	1.81×10^7	< 1	40	28.14	0.42
MCIH-6	24.69	1.93×10^7	< 1	40	10.21	0.41

Table 4.1 Experimental parameters for the OH-initiated oxidation of 4-MC performed without added NO_x

Experiment Code	4-Methylcatechol Concentration ($\mu\text{g}/\text{m}^3$)	Estimated OH Concentration ($\text{molecule}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$)	NO_x (ppb)	Relative Humidity (%)	SOA Corrected Mass ($\mu\text{g}/\text{m}^3$)	SOA Yield
MCID- NO_x -1	96.43	2.16×10^7	63	< 1	4.65	0.05
MCID- NO_x -2	133.39	1.52×10^7	55	< 1	71.35	0.53
MCID- NO_x -3	38.57	2.33×10^7	37	< 1	5.53	0.14
MCID- NO_x -4	25.07	2.26×10^7	43	< 1	4.39	0.18
MCID- NO_x -5	6.43	3.48×10^7	52	< 1	0.17	0.03
MCIH- NO_x -1	524.56	9.58×10^6	68	40	183.82	0.35
MCIH- NO_x -2	84.86	1.50×10^7	42	41	5.87	0.07
MCIH- NO_x -3	77.14	2.44×10^7	45	38	24.51	0.32
MCIH- NO_x -4	146.57	3.06×10^6	307	50	10.84	0.07
MCIH- NO_x -5	29.31	1.91×10^7	88	40	2.34	0.08
MCIH- NO_x -6	20.06	2.79×10^7	28	40	10.92	0.54

Table 4.2 Experimental parameters for the OH-initiated oxidation of 4-MC performed in the presence of NO_x .

Experiment Code	4-Methylcatechol Concentration ($\mu\text{g}/\text{m}^3$)	Estimated OH Concentration ($\text{molecule}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$)	NO_x (ppb)	Relative Humidity (%)	SOA Corrected Mass ($\mu\text{g}/\text{m}^3$)	SOA Yield
MCID- NO_x -UVA-1	131.8	1.09×10^6	181	< 1	< 1	< 0.1
MCID- NO_x -UVA-2	109.3	8.03×10^5	33	< 1	< 1	< 0.1
MCID- NO_x -UVA-3	154.3	7.03×10^5	62	< 1	< 1	< 0.1
MCID-Dark-1	33.43	2.01×10^7	0	< 1	4.79	0.14
MCID- NO_x -Dark-1	9.64	2.67×10^7	16.5	< 1	6.49	0.67
MCID- NO_x -Dark-2	12.86	3.13×10^7	32	< 1	3.03	0.24

Table 4.3 Experimental parameters for the OH-initiated oxidation of 4-MC performed using different light conditions, see text for details.

As shown in the tables above, the experiments performed using HONO and UVA lamps only, generated OH concentrations that were an order of magnitude lower than those where H₂O₂ and UVC lamps were also used. As a result, the decay of 4-MC during the UVA experiments was slow, NO was only partially consumed and the formation of ozone and SOA was minimal, Figure 4.2. Despite the slow reaction, the primary oxidation products such as C₇H₇NO₄, could be detected by CIMS.

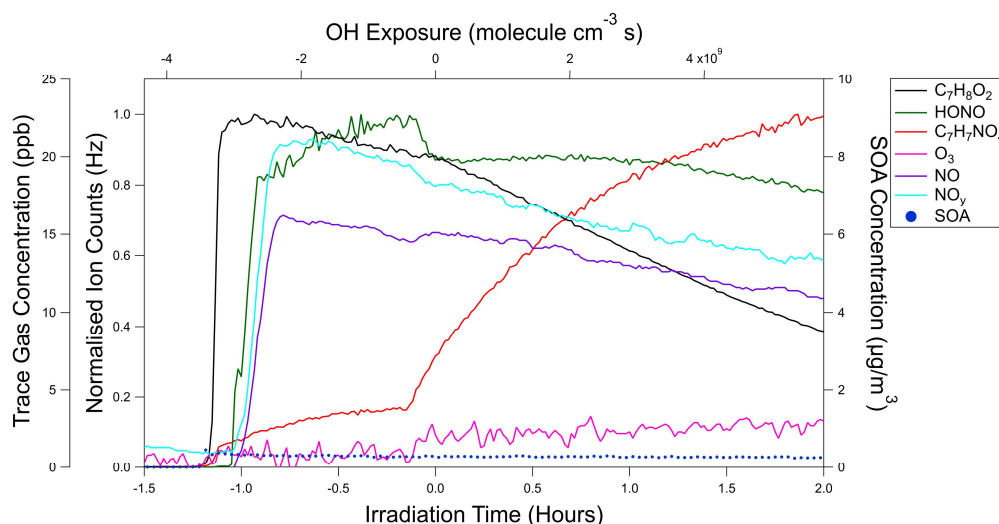


Figure 4.2 Summary plot of a 4-methylcatechol photooxidation experiment performed under UVA conditions (MCID-NO_x-UVA-2).

In contrast, when H₂O₂ and UVC lamps were used along with HONO and the UVA lamps, the decay of 4-MC was very rapid, Figure 4.3. The NO was also rapidly consumed, while substantial amounts of oxidation products, ozone and SOA were formed. In the following sections, detailed analysis of the CIMS data has been conducted to identify the nature of the oxidation products in both the gas and particle phase. The current knowledge on the atmospheric oxidation of aromatic compounds is used to interpret the results and provide insights into the reaction mechanisms for the OH-initiated oxidation of 4-MC.

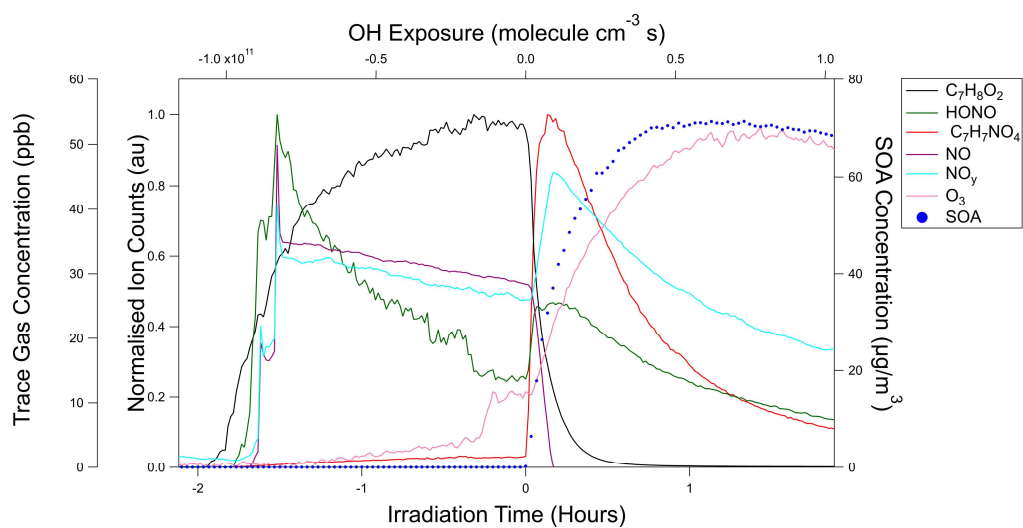


Figure 4.3 Summary plot of a 4-methylcatechol photooxidation experiment performed under UVC conditions (MCID-NO_x-2).

4.4.2 Gas Phase CIMS Analysis

Overview of different experimental conditions

NO_x experiments under UVA radiation

Table 4.3 shows that the estimated OH concentrations generated in the UVA radiation only experiments were close to the average ambient concentration of 1.0×10^6 molecule cm^{-3} , indicating that oxidation of 4-MC proceeded at a similar rate to that observed in the real atmosphere. In these experiments, the CIMS was able to detect the primary products of 4-MC and some secondary products. The change in the product composition was gradual, with C₇ species remaining the most dominant throughout each experiment. For the experiment plotted in Figure 4.4 the estimated OH exposure extends to almost 2×10^{10} molecule cm^{-3} s, corresponding to an equivalent atmospheric aging time of approximately 6 hours based on an average OH concentration of 1.0×10^6 molecule cm^{-3} (Heard and Pilling, 2003).

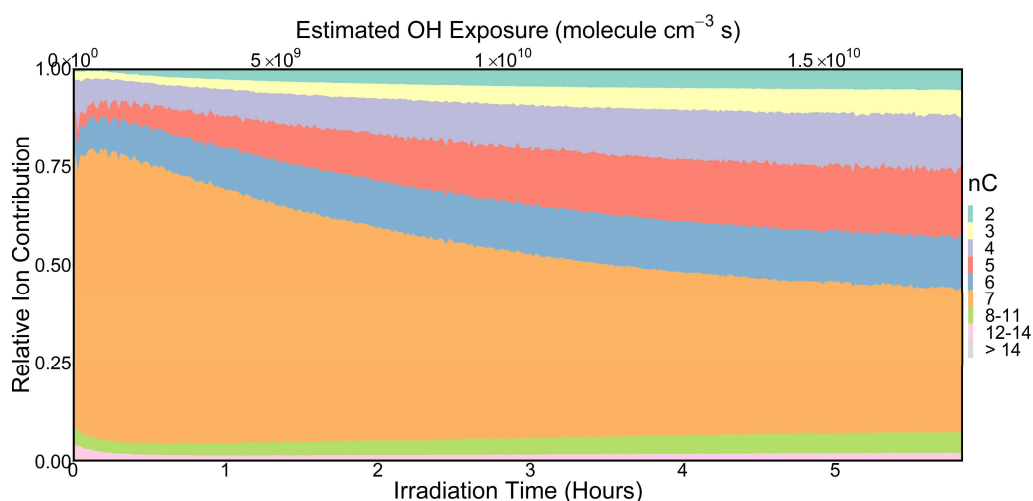


Figure 4.4 Time series of organic products grouped by carbon number for 4-MC photooxidation using UVA radiation (MCID-NO_x-UVA-1).

The time series shows an initial increase in C₇ species which contributed approximately 70% to the product composition initially, however as the reaction progressed, there was a marked increase in the contributions from C₂ - C₅ species, most likely corresponding to ring scission products arising from further oxidation. The slightly increased contribution from C₈ - C₁₁ species at longer reaction times may indicate the formation of gas phase accretion products from the ring scission species. Examination of the mass spectra for this experiment gives a clearer representation of the individual species which are contributing to the product distribution, Figure 4.5.

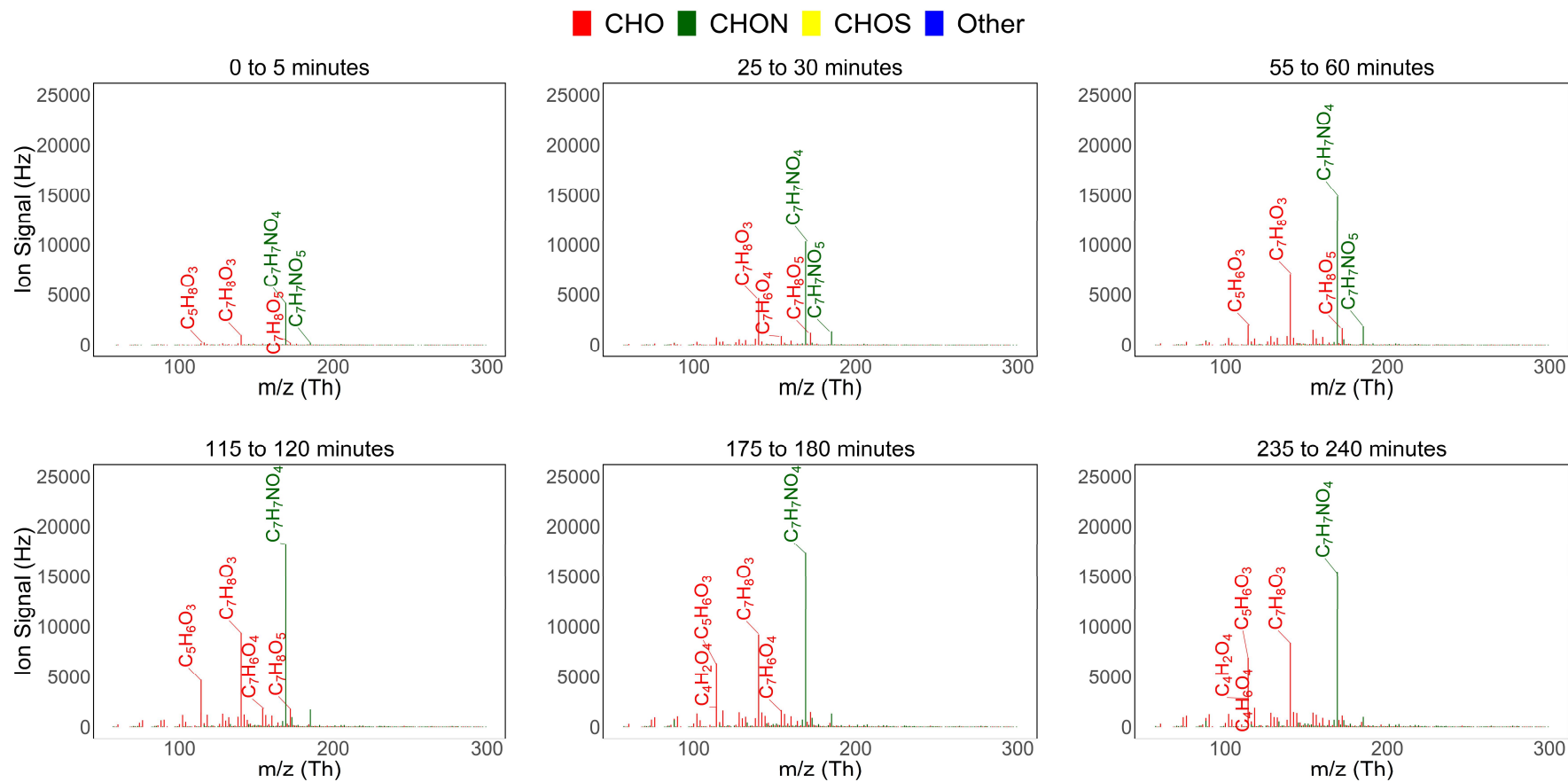


Figure 4.5 Average mass spectra for various 5-minute intervals during a 4-MC photooxidation experiment conducted in the presence of NO_x experiment under UVA conditions (MCID- NO_x -UVA-1).

As shown in Figure 4.5, the main species detected in the early stages of the reaction were $C_7H_8O_3$, $C_7H_7NO_4$, and $C_7H_8O_5$. The strong signal for $C_7H_7NO_4$, tentatively proposed to be methyl-nitrocatechol, differs from the work by Schwantes et al. (2017) in their study of 3-methylcatechol oxidation where they observed very little contribution from a $C_7H_7NO_4$ species (Schwantes et al., 2017). These primary species could be easily attributed to expected primary oxidation products arising from OH addition to the ring and H-atom abstraction from the -OH group. However, the observation of the highly oxygenated species $C_7H_8O_5$ during the early stages of the reaction may point towards other mechanistic pathways such as rapidly occurring autoxidation mechanisms or to epoxide formation (Bianchi et al., 2019; Yee et al., 2013). As the reaction proceeded, other species, including $C_7H_7NO_5$ and the ring scission product $C_5H_6O_3$ were observed in the mass spectra, indicating that further reactions were occurring, even at low OH concentrations, to produce secondary products. Nevertheless, $C_7H_7NO_4$ remained the most dominant peak in the mass spectra after a number of hours and higher OH concentrations are necessary to investigate the advanced oxidation of 4-MC. Proposed molecular structures for some of the species labelled in Figure 4.5 and the starting material are presented in Table 4.4 with all structures proposed tentatively based on the current knowledge of atmospheric reaction pathways.

Molecular Mass (g/mol)	Chemical Formula	Proposed Structure
124.12	C ₇ H ₈ O ₂	
169.13	C ₇ H ₇ NO ₄	
140.14	C ₇ H ₈ O ₃	
172.14	C ₇ H ₈ O ₅	
185.13	C ₇ H ₇ NO ₅	
154.12	C ₇ H ₆ O ₄	
114.10	C ₅ H ₆ O ₃	

Table 4.4 Proposed structures for primary oxidation products of 4-MC and NO_x oxidation (MCID-NO_x-UVA-1)

Analysis of the CIMS data by carbon number and family (CHO and CHON in particular), helps to visualise the evolution of the product composition with time, Figure 4.6. While it is clear that C₇ species were dominant throughout the reaction, Figure 4.6 highlights the large contribution of CHON compounds, even in the initial stages. This figure also shows that CHO species were dominant for products with 6 carbon atoms or less, suggesting that further OH reactions resulting in ring scission products are more likely to occur for species that do not contain a NO₂ group.

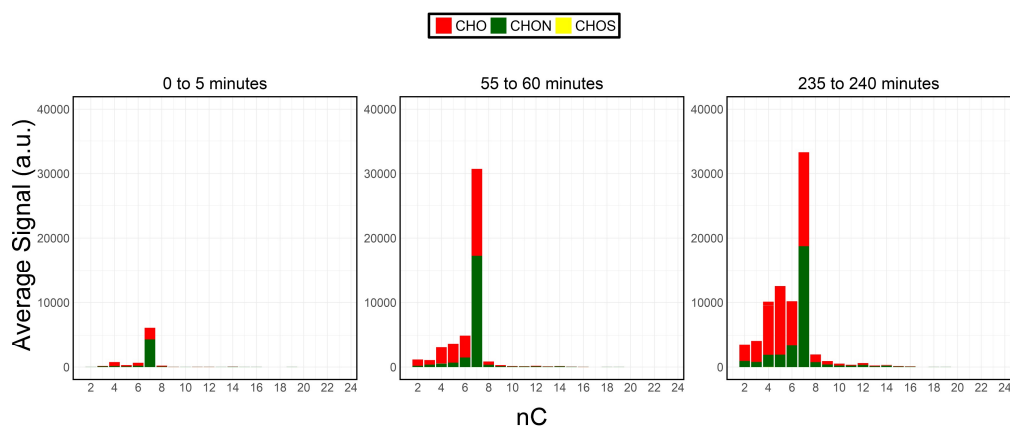


Figure 4.6 Distribution of oxidation products by carbon number and chemical family with respect to time under UVA conditions (MCID-NO_x-UVA-1).

Figure 4.7 shows the oxidation state of the carbon atom per molecule (OS_C) as a function of the number of carbon atoms in the molecule (Kroll et al., 2011) once again highlighting the lack of significant change in product composition with time.

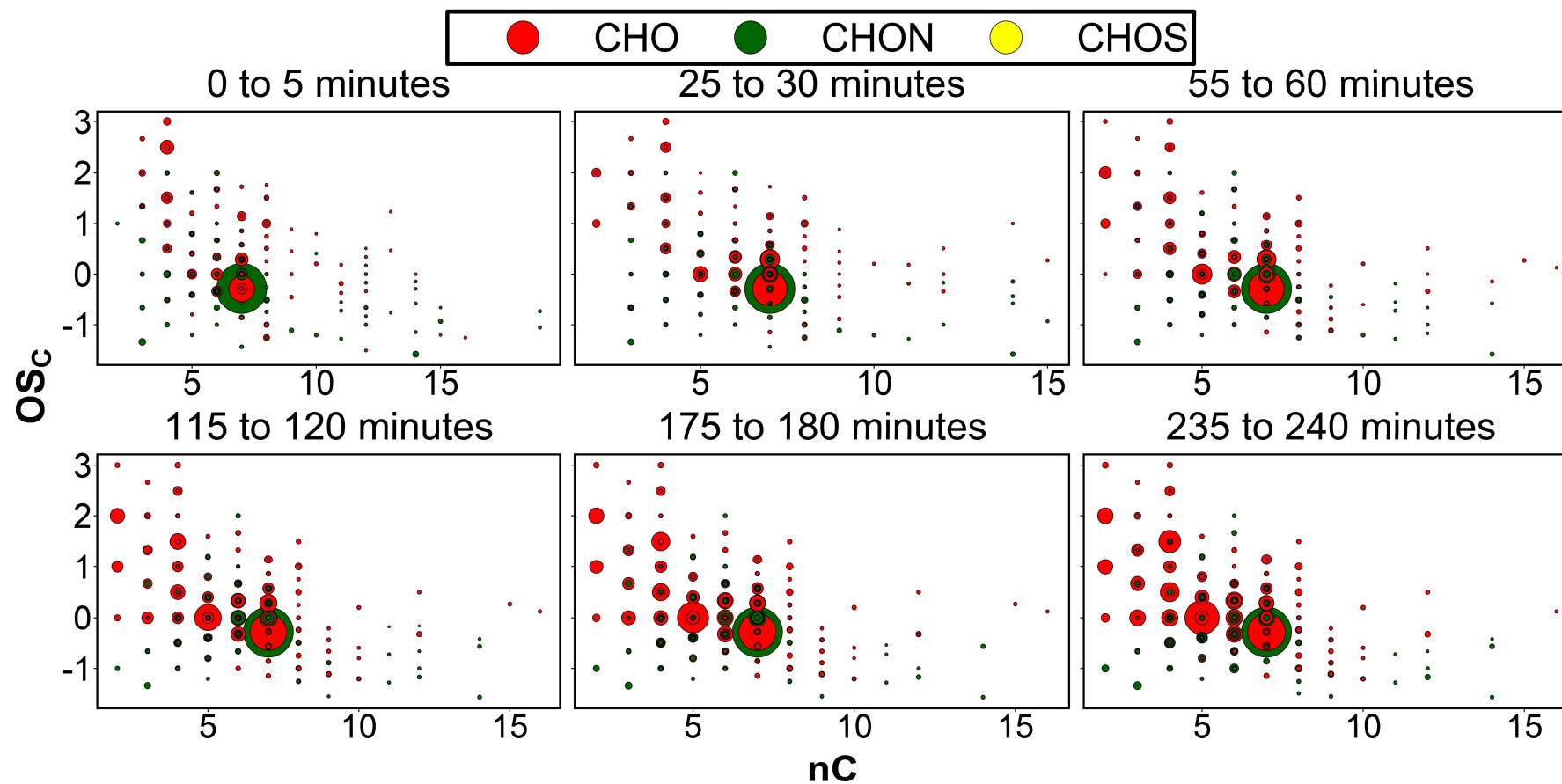


Figure 4.7 Plot of the OS_C as a function of nC under UVA and NO_x conditions (MCID- NO_x -UVA-1).

NO_x experiments under UVC radiation

When H₂O₂ and UVC radiation were used in addition to HONO and the UVA lamps, much higher OH concentrations ($1\text{--}5 \times 10^7$ molecule cm⁻³) were generated. The equivalent atmospheric aging time was up to 2 days in some experiments, providing significant insights into the advanced processing of 4-MC and its primary oxidation products.

The time series of organic products grouped by carbon number, Figure 4.8, initially shows a sharp increase in C₇ species, however smaller C₂–C₆ species, most likely produced by ring scission processes, became much more prevalent as the reaction progressed. An increase in species with more than 7 carbon atoms, was also observed, suggesting the formation of accretion products from ring scission species.

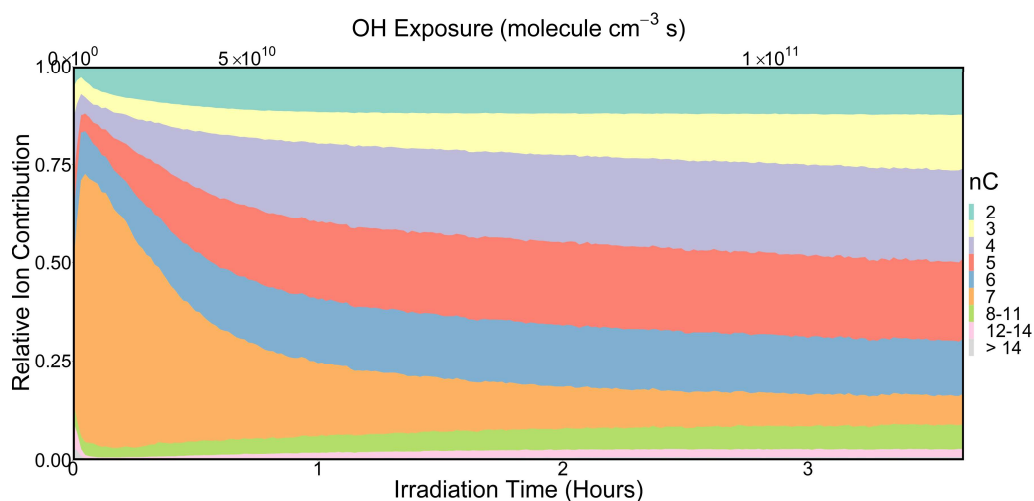


Figure 4.8 Time series of organic products grouped by carbon number for 4-MC photooxidation under UVC conditions (MCID-NO_x-1).

The mass spectra obtained after the same reaction time under UVA and UVC conditions show distinct differences, Figure 4.9.

The data displayed are averaged across the 5-minute intervals displayed above each panel. The panels where the relative ion contribution is the y-axis plot the ratio of the signal of each ion to the sum of all ions that are plotted, giving an indication of which are the most important ions in the spectra. One of the most striking differences between the two sets of data is the prevalence of ring opened CHO species under UVC radiation within the first 5 minutes of oxidation. Also of note is the apparent rapid decay of CHON species in the presence of UVC radiation, most likely due to the highly photolabile nature of the NO₂ group in these nitrophenolic species (Chen et al., 2011). To estimate the impact of the UVC radiation on the system compared to the UVA only reactions, investigations were performed on the decay rates of the same ions under both conditions. For the C₇H₈O₅⁻ ion for example, when comparing the decay rate in experiment MCID-NO_x-UVA-1 and experiment MCID-NO_x-1, the decay rate for the UVA experiment was 10.3 times slower than the UVC experiment, while the estimated OH concentrations were differed by a similar factor (1.09×10^6 and 9.9×10^7). A similar difference in decay rate of the precursor was found, where the UVA decay was 0.8 times UVC decay. With the additional losses due to losses to the particle phase in UVC experiments, it was deemed that UVC radiation had little effect on reagent decay or product formation.

The spread of contribution across a wide variety of ions observed in the latter stages of the UVC experiment is most likely due to the plethora of reaction pathways which are available for each product under the higher OH concentrations. Interestingly, in the third panel, a range of CHON species are observed to have higher concentrations under UVC conditions than under UVA, however these species are all present at higher masses than the initially dominant C₇H₇NO₄ ion, suggesting that more highly oxidised CHON species can form, however, these are likely due to incorporation of the NO₂ group at a later stage of oxidation rather than further OH reactions of C₇H₇NO_x species.

The change in the distribution of organic products by carbon number and chemical family over time is shown in Figure 4.10.

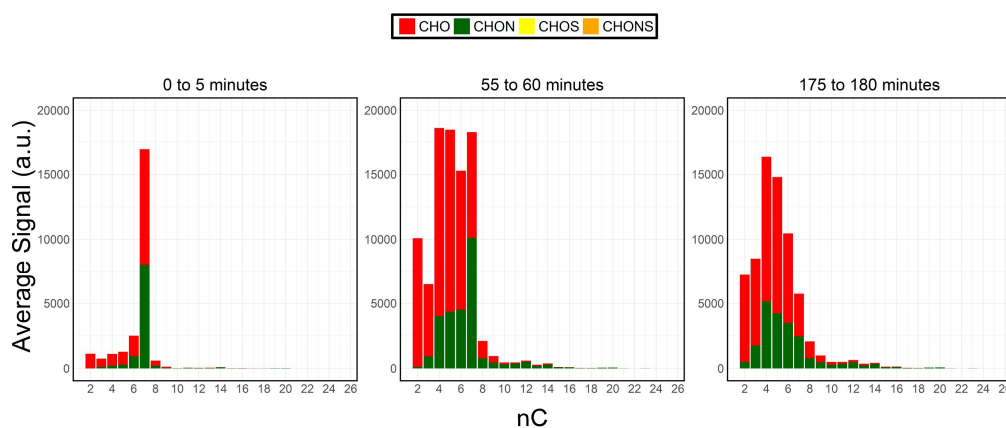


Figure 4.10 *Distribution of organic products by carbon number and chemical family with respect to time under UVC conditions (MCID-NO_x-1).*

As previously observed under UVA conditions, the C₇ species were the most significant during the initial stages of oxidation. However, due to the advanced processing with UVC radiation, the formation of smaller, ring-opened species was also observed in the first 5 minutes, with contributions from CHON species seen for all carbon numbers. This suggests that primary products containing NO₂ groups may undergo ring opening either via photolysis or further OH reaction, or that NO₂ could be incorporated during further oxidation of smaller chain species. Interestingly, when comparing the first and second panel in Figure 4.10, there is a change in the contribution to the C₇ signal, with the CHON species more dominant at the longer reaction times, likely due to lower reactivity of the nitro species compared to CHO products.

The oxidation state of the carbon atoms (OS_C) plotted as function of carbon number shows a very clear shift towards smaller chain species with high OS_C values as the reaction proceeds, Figure 4.11. Note that a number of shorter chain CHON species also appear in the later stages of the experiment, consistent with the data illustrated in Figure 4.10.

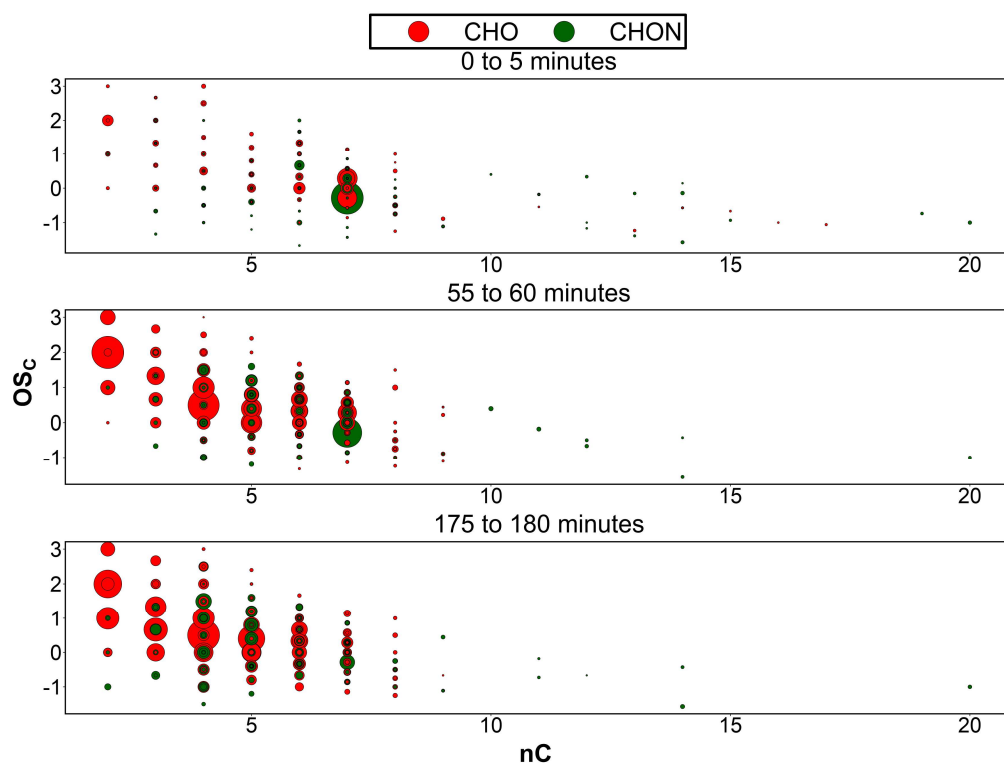


Figure 4.11 OS_C plotted as a function of the number of carbon atoms for an experiment performed under UVC conditions (MCID- NO_x -1).

Low NO_x conditions

In experiments performed using H₂O₂ as the OH precursor without the addition of NO_x, shows similar trends in the nC plots, where C₇ species are initially dominant, with increases in ring scission contributions with time, Figure 4.12.

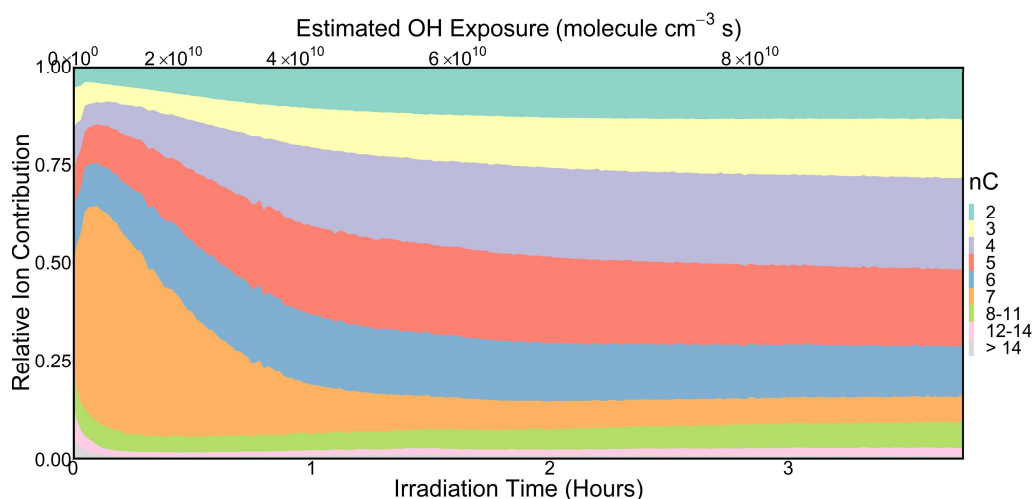


Figure 4.12 Time series of organic products grouped by carbon number for 4-MC photooxidation under low NO_x UVC conditions (MCID-1).

The contribution of CHON species was negligible as expected, while the CHO species were the same as those observed in the presence of NO_x. Comparison of the mass spectra for these types of experiments shows the prevalence of CHON species under high NO_x conditions and much smaller amounts of CHON species in the low NO_x conditions formed as a result of background NO_x in the chamber, Figure 4.13. The species that appear at lower masses ($m/z < 150$ Th) are very similar under both conditions, implying that the ring scission chemistry is not drastically altered in the presence of NO_x.

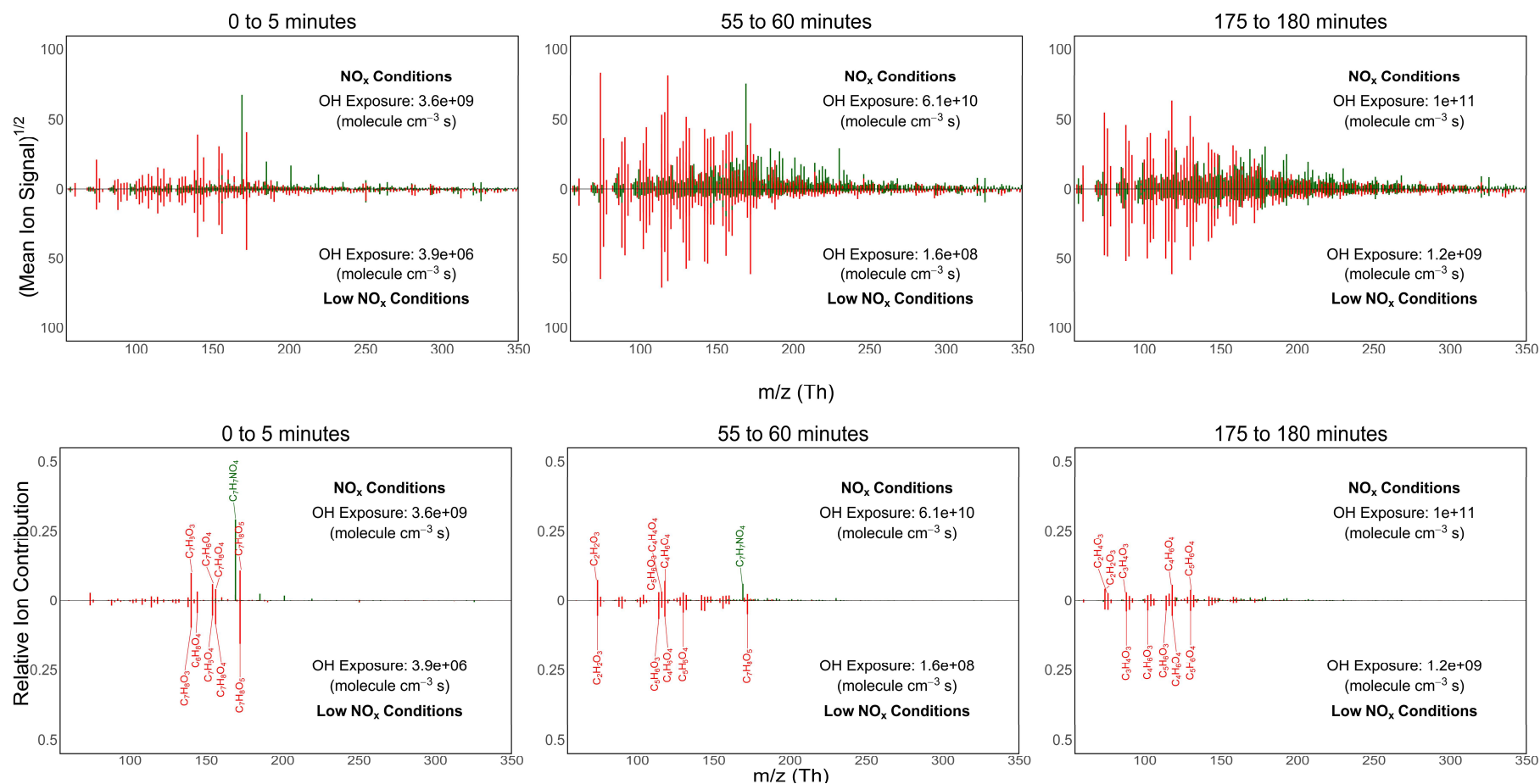


Figure 4.13 Comparison mass spectra taken at various 5-minute intervals during two 4-MC photooxidation experiment under low and high NO_x UVC conditions (MCID- NO_x -1 and MCID-1).

Examining the distribution of species by carbon number and family shows a similar pattern to what was observed previously in NO_x conditions, with an initial dominance of C_7 species, with smaller species becoming more influential with further oxidation, Figure 4.14.

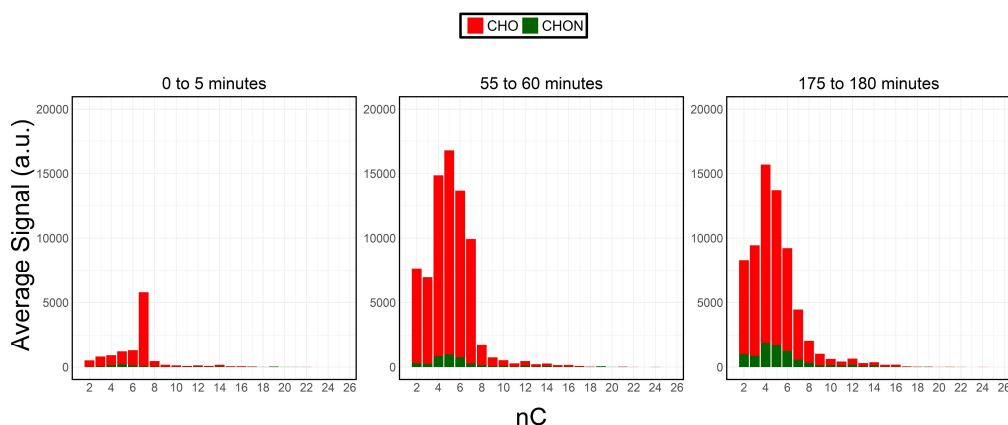


Figure 4.14 Distribution of organic products by carbon number and chemical family with respect to time under UVC low NO_x conditions (MCID-1).

The growth in contribution from CHON species with time is likely due to interaction with NO_x released from the walls of the chamber during irradiation of the chamber, with NO_2 concentrations, which represent all NO_x species excluding NO , reaching 3.8 ppb by the end of the experiment. The ToF-CIMS detected an increase in HONO as the experiment progressed, illustrated in Figure 4.15, however the signals observed for CHON species are still low compared to experiments where NO_x was added to the chamber.

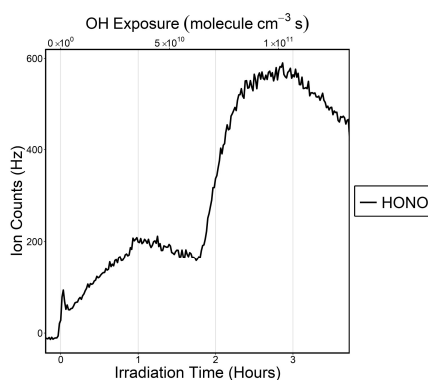
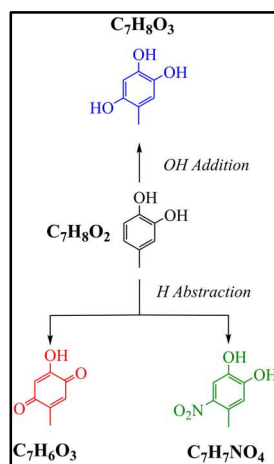


Figure 4.15 Time series of HONO evolution during a low NO_x experiment (MCID-1).

4.4.3 Mechanistic Discussion of 4-Methylcatechol Oxidation

Oxidation of aromatic hydrocarbons ($C_xH_yO_z$) is known to proceed primarily through two pathways, namely OH addition to the aromatic ring and hydrogen abstraction from the structure. OH addition tends to lead to increases in the number of oxygens in the structure with retention of the same number of carbons and hydrogens ($C_xH_yO_{z+1}$), with the products either being ring retaining or ring opened species, while H-abstraction results in the formation of phenoxy radicals, $RO^\bullet$. Phenoxy radicals can result in carbonyl formation, or in the presence of NO_x result in addition of NO or NO_2 to the compound. The formation of carbonyl compounds results in products with an extra oxygen atom and two less hydrogen atoms ($C_xH_{y-2}O_{z+1}$), while the incorporation of NO_2 functionality results in the loss of a hydrogen atom ($C_xH_{y-1}NO_{z+2}$).

It has been shown previously that toluene (C_7H_8) oxidation via H abstraction is unfavourable, contributing less than 10% (Zaytsev et al., 2019), while the same is true of aromatic species with OH groups, such as for the various cresol isomers (C_7H_8O), where Olariu et al. report yields of 64 – 73% for OH addition depending on the cresol isomer (Olariu et al., 2002). From these results, it was anticipated that hydroxyl initiated oxidation of 4-methylcatechol would primarily yield products from the OH addition pathways with some products from the H-abstraction route, with the primary products predicted to be $C_7H_8O_3$, $C_7H_6O_3$ and in the presence of NO_x , $C_7H_7NO_4$. These are illustrated in the simplified reaction scheme, Scheme 4.1.



Scheme 4.1 Summarised reaction pathways for 4-methylcatechol photooxidation.

As illustrated in Figure 4.8, for experiments performed under both UVA and UVC- NO_x conditions, all of these species evolved immediately following irradiation. Plotting time series for these species, Figure 4.16, shows that under UVC conditions

the individual species reach their respective maxima at different rates and also decay at different rates, which gives insight into their further reactivity, however they are all seen to form at the same time. Also observed in this plot is the more rapid decay of the precursor under UVC conditions.

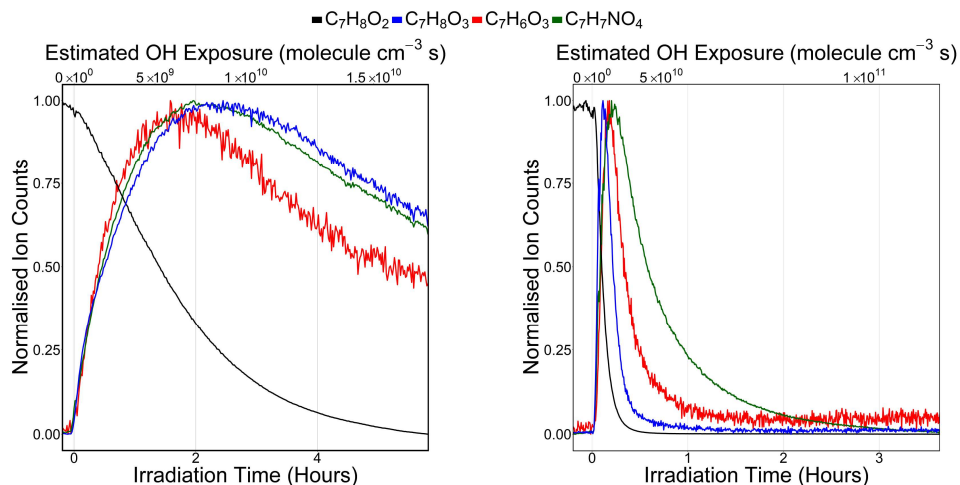
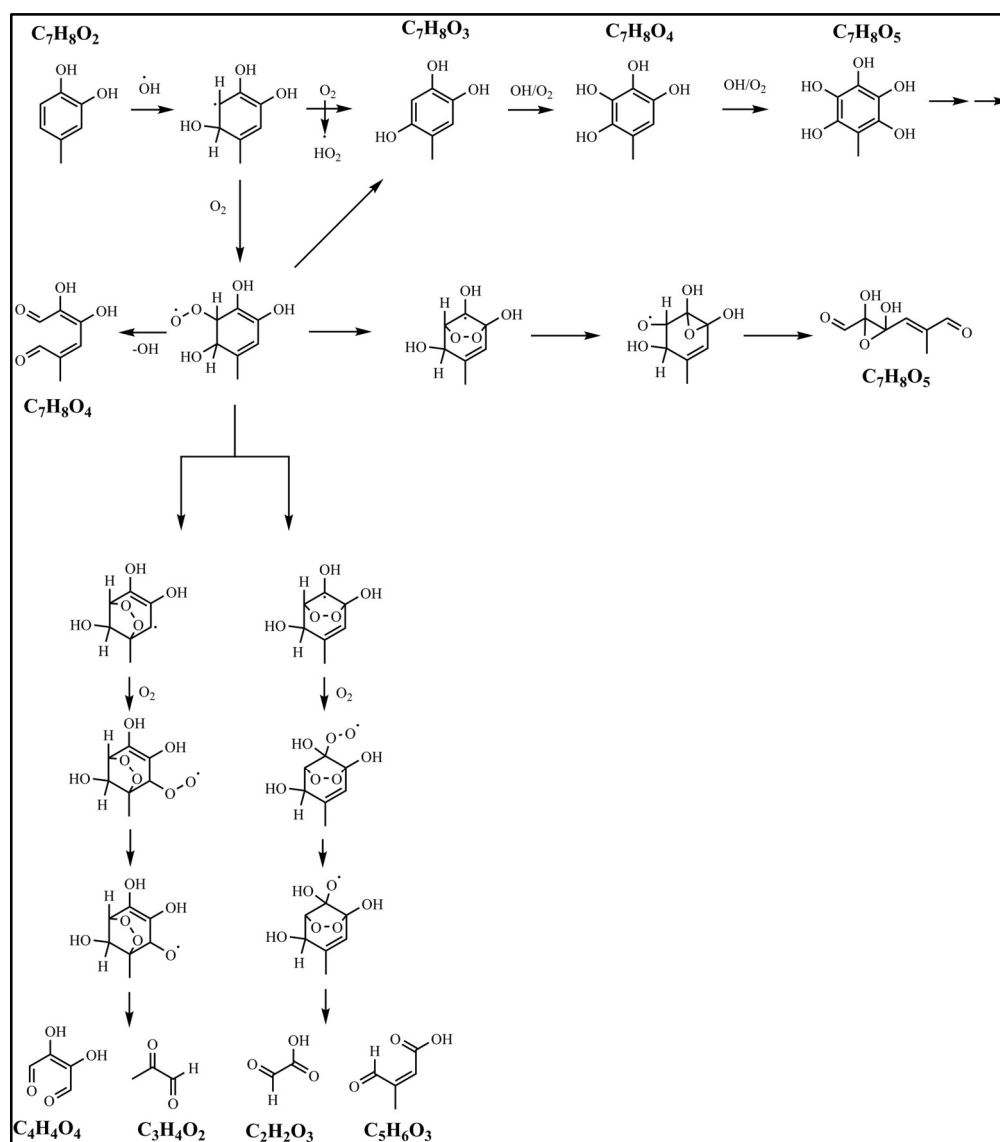


Figure 4.16 Time series of the primary oxidation pathway products for 4-MC photooxidation under UVA and UVC conditions (MCID-NO_x-UVA-1 and MCID-NO_x-1).

OH addition pathway

As discussed, one of the major oxidation pathways for 4-MC was the direct addition of OH to the aromatic ring resulting in the formation of the first hydroxyl species, C₇H₈O₃. This species underwent rapid formation under all conditions once photooxidation was initiated but it also underwent decay faster than would be expected for simple wall losses and it was thus concluded that this species could undergo further OH addition itself, resulting in a range of C₇H₈O_x species as well as other products. The sequential OH addition has been observed for other species previously, such as levoglucosan, cresol, phenol and various methoxyphenol compounds (Zhao et al., 2014; Schwantes et al., 2017; Mayorga et al., 2021; Yee et al., 2013). The addition of the OH group to the ring is a well-established mechanism in the literature and is presumed to proceed as outlined by Calvert et al. (2002) with the formation of an excited intermediate hydroxycyclohexadienyl radical species following OH[•] attack (Calvert et al., 2002). This radical can then undergo thermal stabilisation to the OH adduct with aromaticity restored, can undergo addition of O₂ resulting in the formation of peroxy radical species, or bimolecular reaction with O₂ resulting in the formation of the stable OH adduct as well as an HO₂[•] radical. The peroxy radical can undergo a

range of further reactions, including ring opening resulting in a dicarbonyl, dissociation to yield the OH addition species or it can form a bicyclic peroxy radical. This radical can subsequently undergo O₂ addition and react with NO yielding an alkoxy radical which can result in ring scission. Ring scission will yield either C₃ and C₄ products or C₂ and C₅ products depending on which bicyclic radical is initially formed. The bicyclic peroxy radical can also undergo epoxide formation and subsequent ring opening. A summary of the potential OH addition mechanism is given in Scheme 4.2.



Scheme 4.2 OH addition mechanism for 4-methylcatechol oxidation.

As illustrated, a multitude of species can be formed via the OH addition pathway, some of which have the same molecular formula, making it difficult to accurately assign structures to the species detected by the ToF-CIMS. This is especially true for the sequential OH addition species ($C_7H_8O_x$) where $O = 4$ or 5 , which are shown to have at least two potential structures. Time series under both UVA and UVC conditions are given in Figure 4.17 for most of the named species in Scheme 4.2 except for $C_3H_4O_2$ which is not readily detected due to I-CIMS poor sensitivity towards carbonyls.

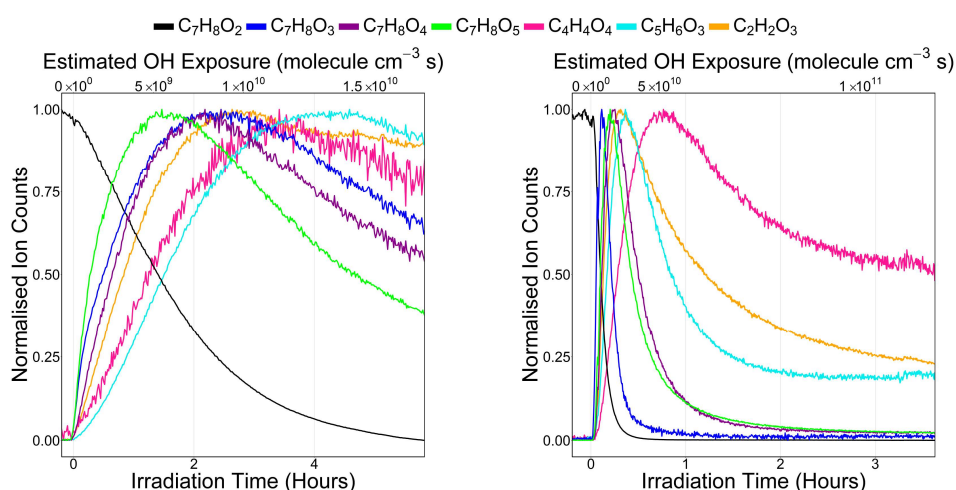
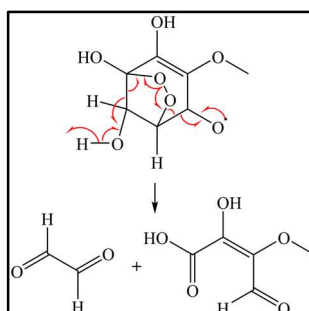


Figure 4.17 Time series of the OH addition pathway primary products for 4-MC photooxidation under UVA and UVC conditions (MCID-NO_x-UVA-1 and MCID-NO_x-1).

The rapid formation of $C_7H_8O_5$ seen in Figure 4.17, even under UVA conditions suggests that there is significant contribution to this signal from the epoxide structure given in Scheme 4.2 as it is highly unlikely that the third generation OH product would form so rapidly under low OH conditions. It is also seen that most of the species begin to evolve immediately, indicating that the rearrangement and O_2 reactions in the scheme all happen rapidly, thus most of these products can be referred to as primary. Under UVC conditions, the enhanced reactivity allows the decay of these species to be evaluated, with the ring scission species showing the slowest decay indicating that these species are continuously formed during the experiment and may not undergo further reaction or significant partitioning to the same degree as the C_7 species.

The ring scission products that form from the bicyclic peroxy radical intermediates are expected to form based on the interactions outlined in Scheme 4.3 below, yielding two carbonyl species, which are either a C_2 and a C_5 , or a C_3 and a C_4 species. The species

which form are dependant on the bicyclic species which form following the rearrangement of the O₂ group (Calvert et al., 2002).



Scheme 4.3 Ring opening pathway of bicyclic peroxy radicals.

Further Oxidation

Although the mechanism outlined in Scheme 4.2 suggests that multiple C₇H₈O_x species can form from a single oxidation step, there is also the possibility that sequential OH addition is taking place. The ToF-CIMS cannot elucidate the different isomers contributing to a given signal, however interpreting the signals for the sequential C₇H₈O_x suggests that sequential oxidation may be occurring, Figure 4.18. The evolution of the C₇H₈O₆ and C₇H₈O₇ species occurs later than the other species indicating that these are formed via further oxidation of the primary species, however as outlined in Scheme 4.2 these species could arise from the oxidation of any of the primary species.

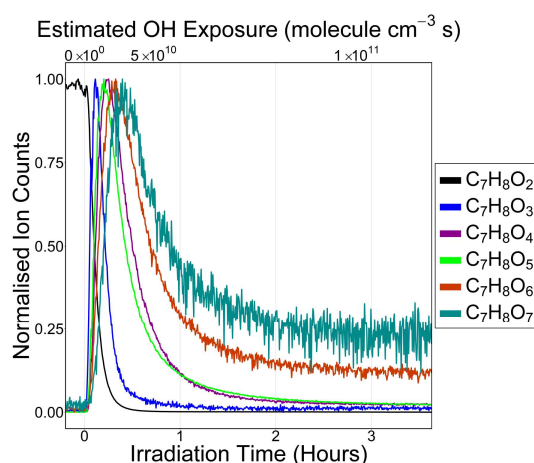


Figure 4.18 Time series of the sequential oxidation products for the OH addition pathway from 4-MC photooxidation (MCID-NO_x-1).

Further oxidation of the primary ring scission species is also observed. The C₅, C₄, C₃ and C₂ species outlined in Scheme 4.2 are all observed with at least one extra oxygen than the species given in the mechanism which suggests that either the primary ring scission species can undergo further oxidation themselves, or that ring scission during oxidation of the OH addition products results in these species. The species evolve later than the primary ring scission species, which supports the hypothesis that they are the result of further oxidation but the exact pathway from which they arise cannot be confirmed, Figure 4.19.

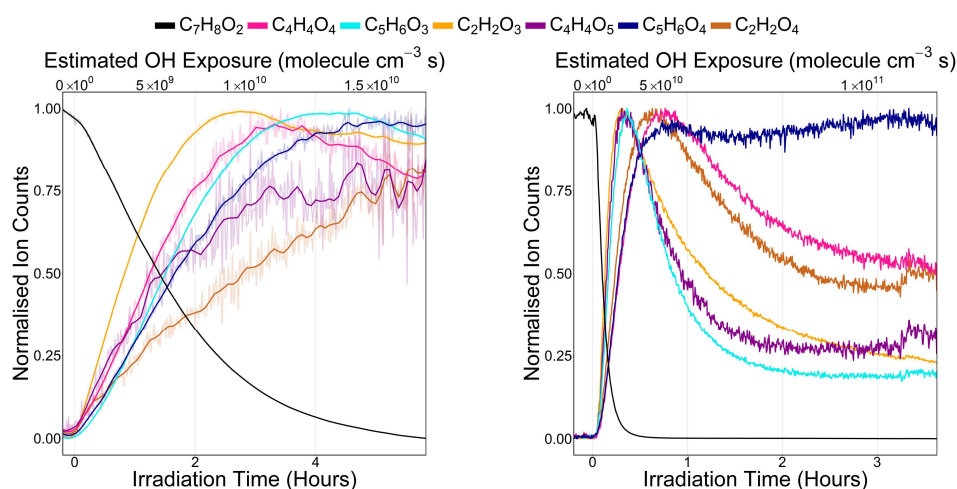


Figure 4.19 Time series of the sequential oxidation of ring scission species from the OH addition pathway from 4-MC photooxidation under UVA and UVC conditions (MCID-NO_x-UVA-1 and MCID-NO_x-1).

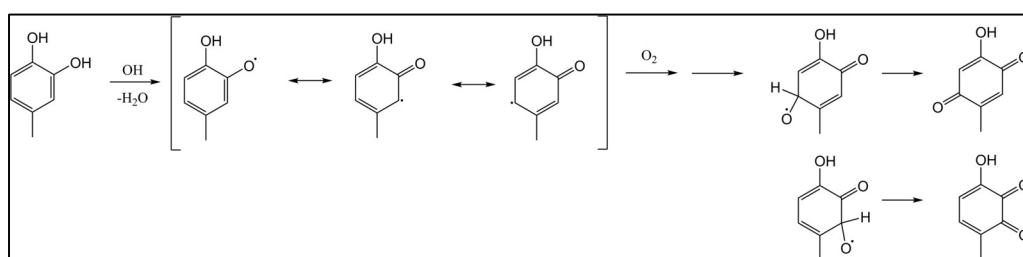
Under UVA conditions the secondary species do not show clear formation, with their signals being significantly noisy, however under UVC conditions, their formation is clearly observed, albeit slower than the primary species.

Hydrogen abstraction pathway

Low NO_x conditions

The other dominant pathway for aromatic OH oxidation in the atmosphere is hydrogen abstraction from the precursor. In theory, the hydrogen atom can be abstracted from anywhere in the molecule, however abstraction from the -OH group resulting in an RO[•] radical is the most likely pathway. A theoretical study on guaiacol (2-methoxy phenol) oxidation found that H-abstraction from the carbon atoms in the benzene ring was highly unfavourable in the gas phase while abstraction from the OH group was highly energetically favourable with an activation energy of 8.48 kcal mol⁻¹ (An et al.,

2019). Although guaiacol does not contain any methyl groups for direct comparison with this study, the low yield of the H-abstraction pathway from toluene of ~10% suggests that H-abstraction from the methyl group is unfavourable (Suh et al., 2003). Following the formation of the phenoxy radical (RO[•]), this species is likely to undergo rearrangements resulting in the formation of a carbonyl with a delocalised electron in the ring which under low NO_x conditions will likely result in O₂ addition and subsequent formation of a di-carbonyl, benzoquinone species. A proposed mechanism for this is outlined in Scheme 4.4, based on the mechanism outlined by Olariu et al. (2002) for the *ortho*, *meta* and *para* cresols (Olariu et al., 2002).



Scheme 4.4 Hydrogen abstraction pathway for 4-methylcatechol oxidation.

Benzoquinones are expected to be quite unreactive to further oxidation, however, it was observed that C₇H₆O_x species where x is greater than 3 formed, and often quite rapidly, Figure 4.20.

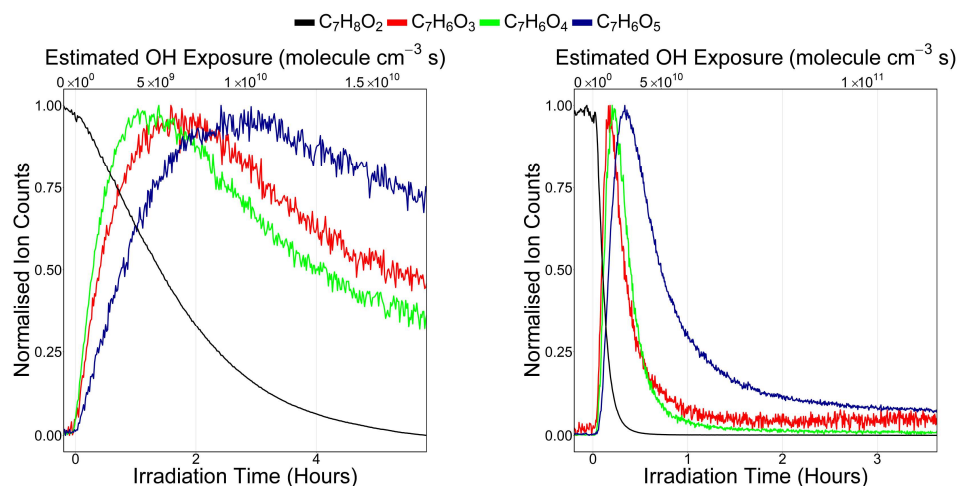


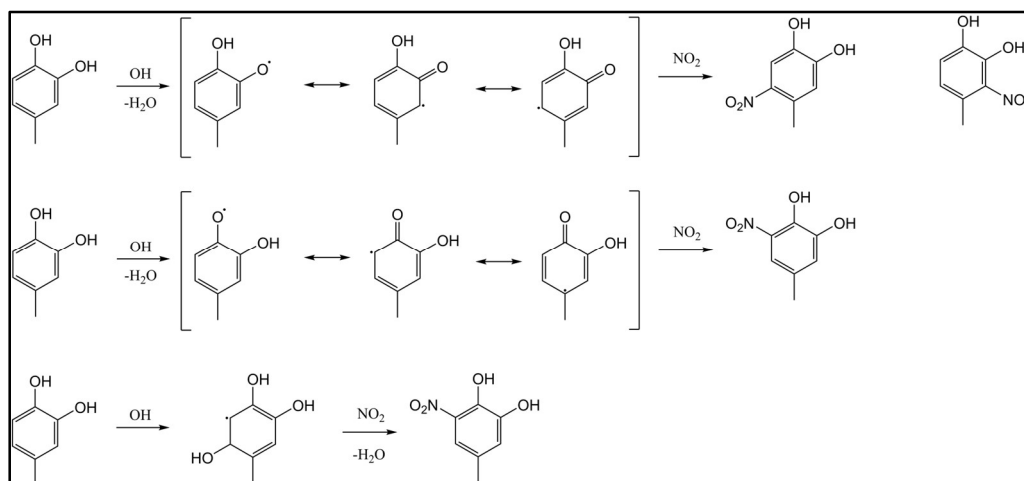
Figure 4.20 Time series of potential quinone species formed from the hydrogen abstraction pathway from 4-MC photooxidation under UVA and UVC conditions (MCID-NO_x-UVA-1 and MCID-NO_x-1).

The rapid formation of C₇H₆O₄ is surprising and suggests that it is not the product of OH addition to C₇H₆O₃, but rather an entirely different species. It is possible that abstraction proceeds from the methyl group resulting in O₂ addition to the [•]CH₂ group

and subsequent formation of an aldehyde which could undergo rapid oxidation to dihydroxybenzoic acid, however as this reaction would require prior formation of the aldehyde before acid formation it is not clear if this pathway is feasible. The formation of aldehydes and subsequent acid species from substituted catechols has been demonstrated at the air-water interface by Pillar et al (Pillar and Guzman, 2017).

High NO_x conditions

Under NO_x conditions, it has previously been reported that addition of O₂ to the phenoxy radical is a competitive process with NO₂ (Olariu et al., 2002). Addition of NO₂ results in the formation of methyl-nitrocatechols which retain aromaticity while the quinone structures lose aromaticity. Similar to the quinone species, NO₂ addition can occur at multiple sites giving rise to different isomers of the C₇H₇NO₄ species in Scheme 4.5. Given in Scheme 4.5 is also the mechanism for NO₂ addition via the OH addition mechanism.



Scheme 4.5 Methyl-nitrocatechol formation from 4-methylcatechol oxidation.

As observed for each of the previous pathways, species with increased numbers of oxygen than C₇H₇NO₄ were observed during the photooxidation experiments, Figure 4.21, and due to the low reactivity of R-NO₂ species towards OH, these are likely the result of NO₂ incorporation at further stages of C₇H₈O_x oxidation.

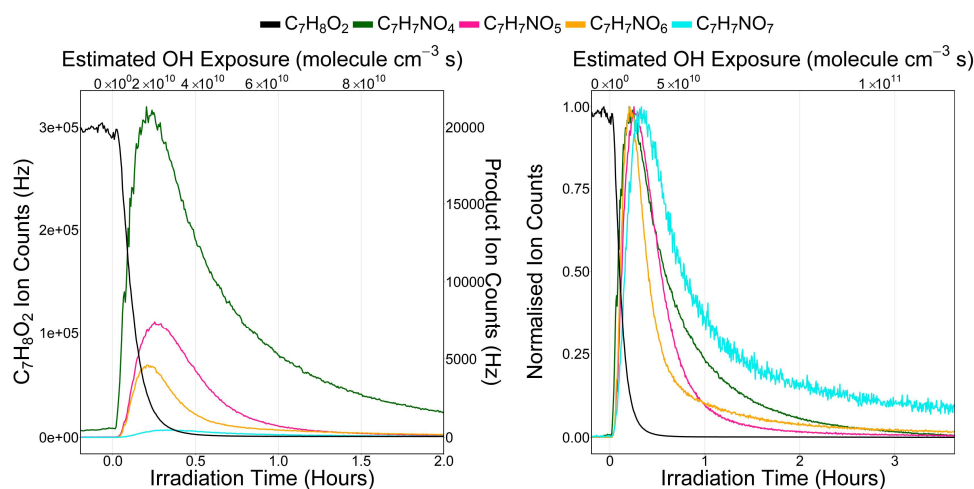


Figure 4.21 Scaled and normalised time series of $C_7H_7NO_x$ species formed from the hydrogen abstraction pathway of 4-MC photooxidation under UVC conditions (MCID- NO_x -1).

Further oxidation of H-abstraction products

Of particular interest in these experiments were a range of species containing more than one $-NO_2$ group which were detected under both UVA and UVC conditions, observed as secondary products from the primary NO_x species. Normalised plots are shown in Figure 4.22 for one of these secondary dinitro species with the primary NO_2 adduct as well as the precursor under both UVA and UVC conditions.

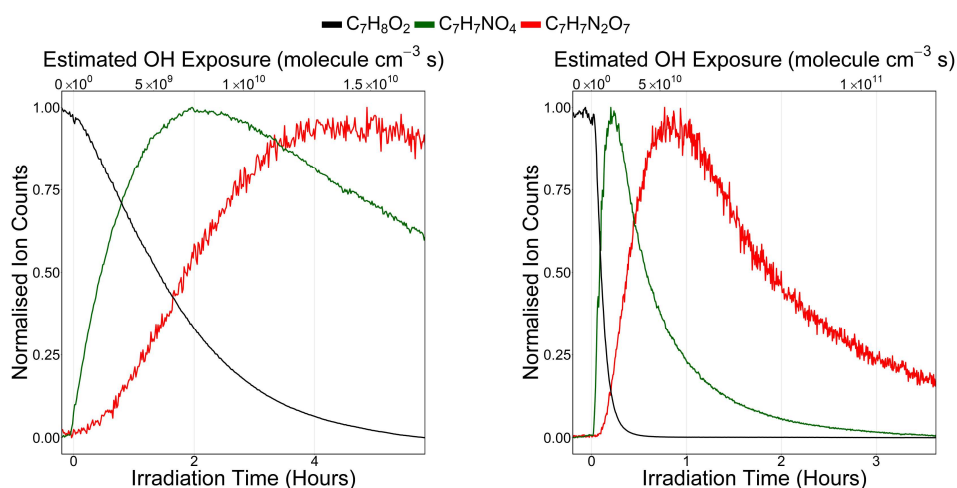


Figure 4.22 Evolution of dinitro species in the gas phase under both UVA and UVC conditions (MCID- NO_x -UVA-1, MCID- NO_x -1).

The formation of dinitrophenol compounds has been reported previously in the aqueous phase where it was hypothesised to be a result of UVA excitation of nitrophenols forming excited species which are long lived enough to undergo reaction

with $\bullet\text{NO}_2$ resulting in these dinitro species (Vione et al., 2005). The reaction may also be the result of hydrogen abstraction from a hydroxyl group of $\text{C}_7\text{H}_7\text{NO}_4$ resulting in a nitro-phenoxy radical, followed by NO_2 addition to the resonance stabilised radical as outlined by Yuan et al. (Yuan et al., 2016). Dinitro-phenols have been detected in the field in significant concentrations (Hofmann et al., 2008; Li et al., 2022) and are of particular importance due to their high toxicity (Grundlingh et al., 2011).

Several species which have molecular formulae indicative of NO_x incorporation into quinone species ($\text{C}_7\text{H}_5\text{NO}_x$) as secondary products were also detected in this work, albeit at low concentrations, Figure 4.23.

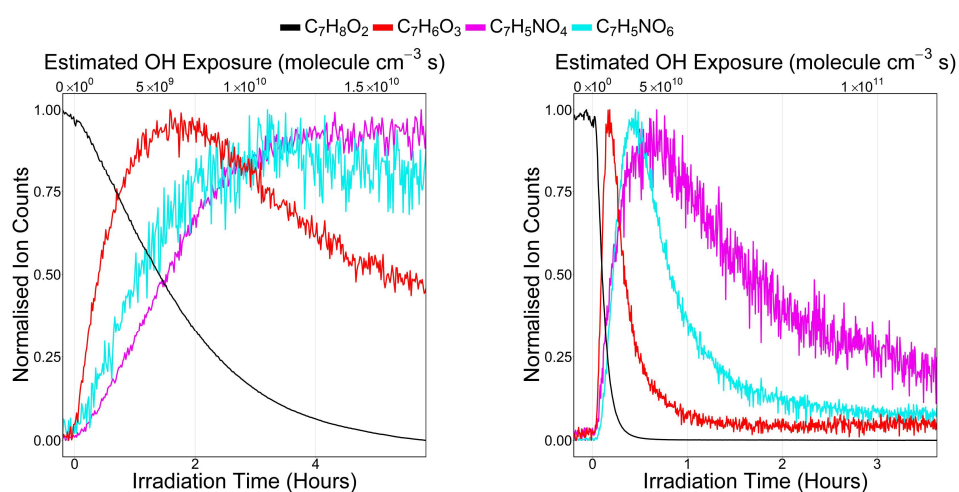


Figure 4.23 Normalised time series of $\text{C}_7\text{H}_5\text{NO}_x$ species under UVA and UVC conditions highlighting secondary chemistry of benzoquinone species (MCID- NO_x -UVA-1 and MCID- NO_x -1).

The exact mechanism of this type of reaction is not proposed but may involve NO or NO_2 addition to a radical subsequent to a hydrogen abstraction from the remaining hydroxyl group of $\text{C}_7\text{H}_6\text{O}_3$. These reactions could also indicate the influence of NO_3 chemistry resulting in R-ONO_2 species which could be the product of a reaction between $\text{C}_7\text{H}_6\text{O}_3$ and NO_3 , however previous studies predict that although addition of $-\text{ONO}_2$ to a radical ring species is possible, it generally results in intermediate species which decompose to form nitric acid (Bolzacchini et al., 2001; Harrison et al., 2005; Olariu et al., 2013). Products with R-ONO_2 structures have been reported for other atmospheric VOCs such as alpha-pinene however, so it is plausible that these species are formed but further work isolating these species would be necessary to characterise them fully (Perraud et al., 2010).

Dimers and Accretion products

As observed in various time series above (Figure 4.4, Figure 4.9, Figure 4.12), there are increases in species with between 8 and 11 carbon atoms throughout the photooxidation. These species are predicted to be the result of accretion reactions, between the various ring scission products formed during the oxidation process. Accretion products typically involve radicals ($\text{RO}^{\bullet}$ or $\text{RO}_2^{\bullet}$) reacting with themselves, other radicals or neutral molecules and yield products which are expected to have low volatilities and contribute to initial nucleation. They have been shown to play a critical role in the formation of SOA from α -pinene photooxidation (Shi et al., 2022). As observed in Figure 4.24, these species are seen to occur even in the presence of NO_x despite the expected suppression of RO_2 formation in the presence of NO_x .

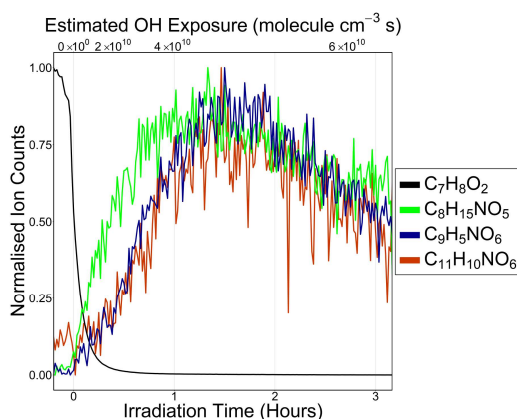


Figure 4.24 Normalised time series showing the evolution of gas phase C₈ to C₁₁ R- NO_x accretion products (MCIH- NO_x -2).

In addition to these C₈ to C₁₁ accretion products, a range of C₁₂ to C₁₄ accretion products were also detected in significant concentrations, Figure 4.10. These are likely to form from reactions between C₆ species, which may form via scission of the methyl group, and C₇ species which may be ring retaining species, or ring opened species such as the epoxide species previously proposed. A selection of these accretion products is shown in Figure 4.25.

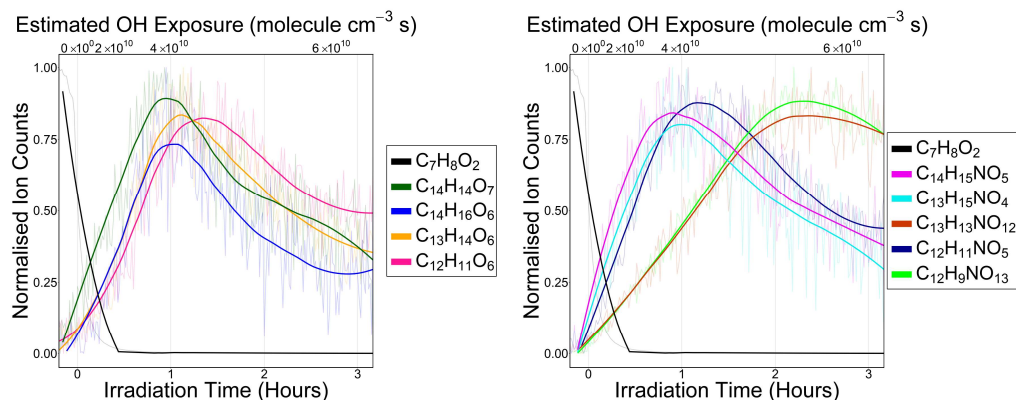


Figure 4.25 Normalised time series of the evolution of gas phase C_{12} to C_{14} accretion products from 4-MC photooxidation with a smoothing fit applied (MCIH- NO_x -2).

The time series illustrate that accretion products evolve almost immediately following irradiation, while there also appears to be secondary formation of more highly oxidised accretion products. It is unknown whether these result from accretion reactions between more aged species, or whether they are a result of aging of the primary accretion products. It is also highlighted that accretion reactions can happen for species with and without NO_x , however no dinitro accretion products were detected. The gas phase signals for these species generally experience significant noise due to their low concentrations, so to account for this a fit has been applied to the signals in Figure 4.25 with the actual data given as well.

4.4.4 Secondary Organic Aerosol Formation

Particle formation and growth

Secondary organic aerosol formation was only observed in experiments where UVC lamps were used. In these experiments, SOA was observed within the first few minutes of reaction, indicating that partitioning of low volatility products to the particle phase was a rapid process once sufficient oxidation was achieved. Subsequent particle growth in terms of both number and diameter was rapid, with particles generally reaching mean diameters of 30 - 40 nm within the first hour, Figure 4.26. Particle coagulation slowed with time, with number concentration falling and the diameter gradually increasing.

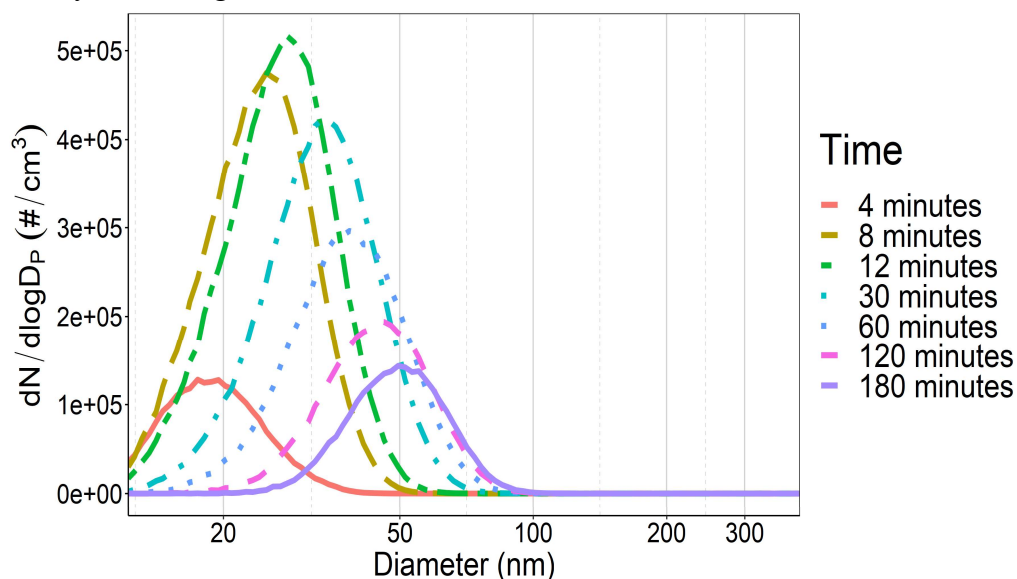


Figure 4.26 Particle growth during a 4-MC photooxidation experiment (MCID-NO_x-3).

SOA formation and growth can be visualised more clearly using so-called “banana plots”, where particle concentration is plotted as a function of time and diameter. Figure 4.27 illustrates a banana plot for an experiment where the wall-loss corrected data clearly shows the rapid initial growth of particle number and size, followed by a decrease in both growth rate and total particle number.

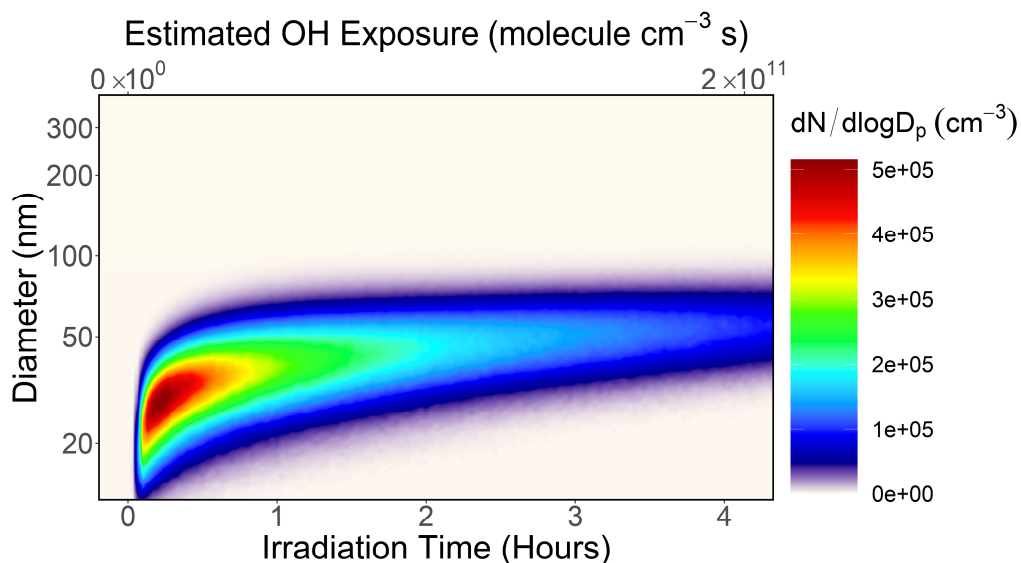


Figure 4.27 Banana plot of particle formation and growth for 4-MC photooxidation (MCID-NO_x-3).

When the data is plotted using the particle mass concentration rather than particle number concentrations, e.g., Figure 4.28, the particle mass shows a slower decay in concentration. This is explained by the coagulation of particles as the experiment progressed, which caused a reduction in particle numbers but an increase in mass concentration.

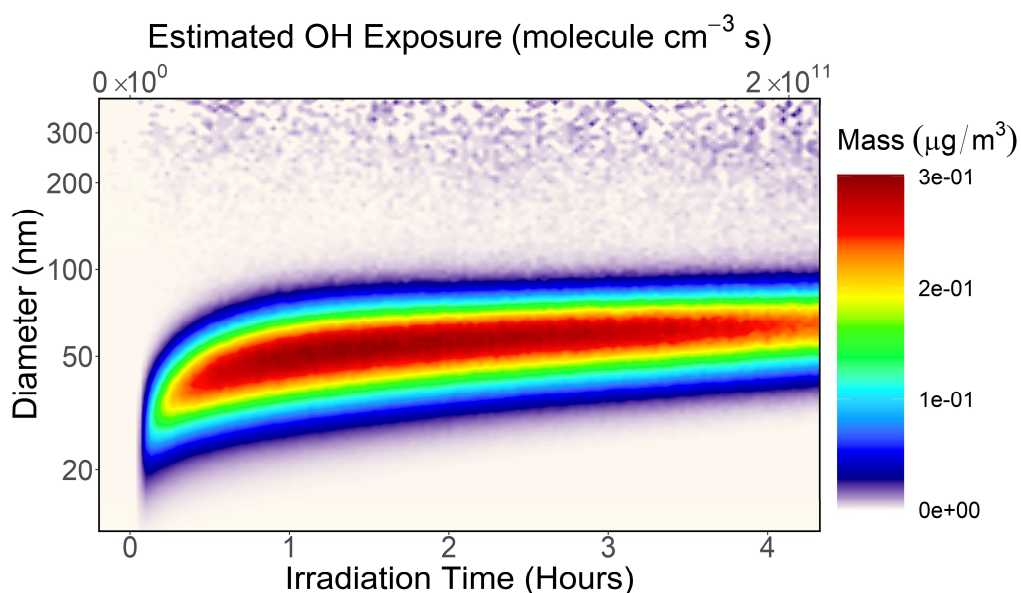


Figure 4.28 Banana plot of particle formation and growth expressed in terms of mass for 4-MC photooxidation (MCID-NO_x-3).

SOA Yields

SOA yields for dry, low NO_x photooxidation experiments were found to be in the range of 27-50% which are comparable to 4-MC ozonolysis experiments performed by Coeur-Tourneur et al. (2010) who reported yields of 20-64% and are also similar to SOA yields observed from ozonolysis of catechol reported by Olariu et al. (2003) (27-63%) and Coeur-Tourneur et al. (2009) (17-86%) (Coeur-Tourneur et al., 2009, 2010; Olariu et al., 2003).

The SOA yield for most high NO_x experiments was significantly lower than observed for the low NO_x experiments. For example, comparing experiments MCID-3 and MCID-NO_x-1 which have similar 4-MC starting concentrations (95.8 and 96.4 µg.m⁻³ respectively) but very different NO_x levels (< 1 ppb and 63 ppb respectively), the yield decreases drastically from 34% to 5%. The concentration of NO_x plays a crucial role in SOA formation by altering the reaction pathways for peroxy radicals produced during the hydrocarbon oxidation process (Kroll and Seinfeld, 2008). Under high NO_x conditions, the RO₂ + NO reaction tends to dominate and suppresses RO₂ + RO₂ and RO₂ + HO₂ pathways, which in turn suppresses the formation of less volatile oxidation products that are more likely to contribute to SOA formation and growth. While NO_x usually reduces SOA yield (Chen et al., 2022; Xu et al., 2015) it has also been shown that the SOA yield can also depend on the NO/NO₂ ratio (Chan et al., 2010). Since the determination of SOA yield was not the primary focus of this study, the hydrocarbon and NO_x conditions were not varied sufficiently to fully investigate the degree to which NO_x affected SOA formation.

Some previous studies on SOA formation from a variety of VOC precursors have found that relative humidity can increase both aerosol yield and particle diameter. In this study, it was difficult to interpret the SOA yield data under humid conditions due to changes in instrument sensitivity under humid conditions.

4.4.5 Particle Phase CIMS Analysis

Comparison of high and low NO_x experiments

A series of the 4-MC photooxidation experiments involved the use of the FIGAERO inlet with the ToF-CIMS to analyse the chemical composition of the particle phase via thermal desorption. A range of similarities were found between the gas and particle phase composition with many of what are assumed to be the same species, based on molecular formulae, being detected in both phases. This suggests that these species undergo partitioning between phases and may be involved in the initial nucleation processes resulting in particle formation. Comparison particle phase mass spectra between experiments performed under low and high NO_x conditions after similar degrees of aging are given in Figure 4.29.

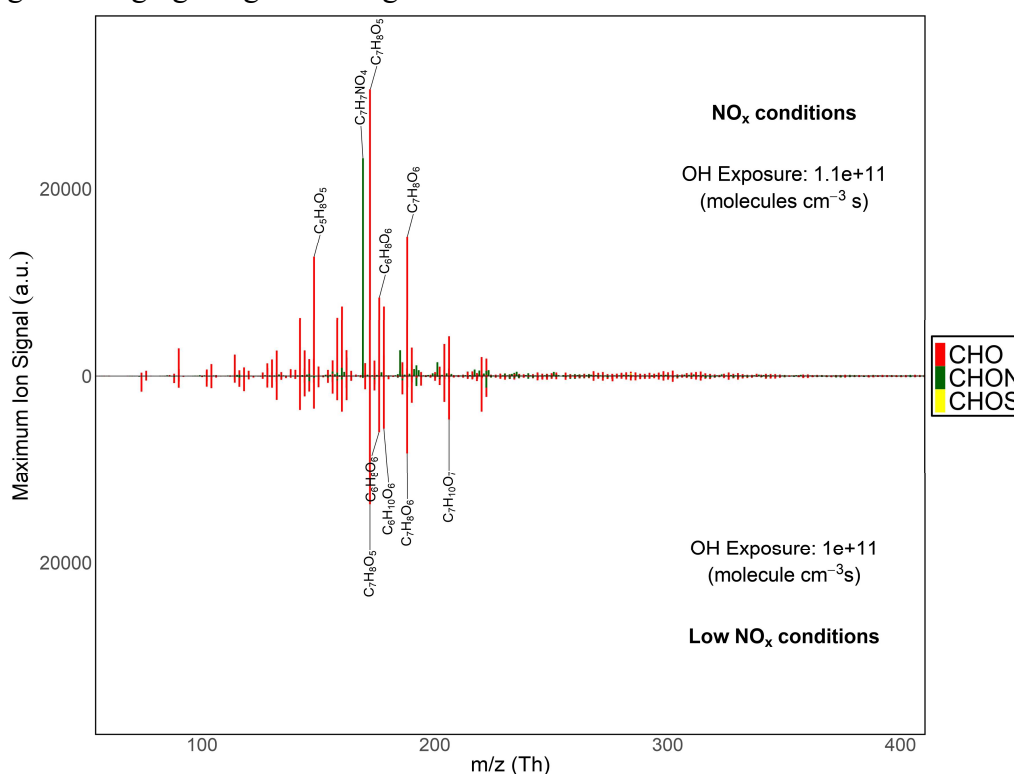


Figure 4.29 Comparison mass spectra for FIGAERO desorptions from 4-MC photooxidation experiments under high and low NO_x conditions (MCID-NO_x-2 and MCID-1).

There are clear contributions from many of the CHO and CHON species which were also observed in the gas phase suggesting that they partitioned between the two phases, such as C₇H₈O₅ and C₇H₇NO₄. The different NO_x concentrations were found to have little influence on the major CHO species, however there is a clear increase in the concentration of CHON species in the high NO_x experiment. Most of the same CHO

species are observed under both conditions, even the lower molecular weight ring scission species, at similar relative magnitudes. Higher molecular weight species, between 250 and 350 Th, are also quite similar in both spectra suggesting that similar accretion products form under both low and high NO_x conditions, with some CHON contributions observed in the NO_x experiment.

Table 4.5 illustrates the five peaks with the highest intensity in the desorption performed for MCID-NO_x-2 illustrated in Figure 4.29, with tentative structures suggested. Some of the molecular formulae observed suggest ring opening chemistry such as C₇H₈O₆ which is proposed to form via OH addition after saturation of the aromatic ring, yielding a ring-opened carboxylic acid. The C₅ and C₆ species both contain more hydrogen than would be expected, for conventional ring opening chemistry, suggesting that these form via ring scission of species which have lost their aromaticity and then undergo further reaction.

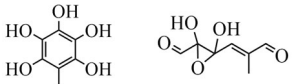
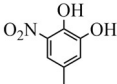
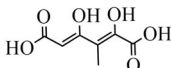
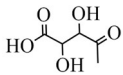
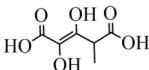
Molecular Mass (g/mol)	Chemical Formula	Proposed Structure
172.14	C ₇ H ₈ O ₅	
169.13	C ₇ H ₇ NO ₄	
188.13	C ₇ H ₈ O ₆	
148.11	C ₅ H ₈ O ₅	
176.12	C ₆ H ₈ O ₆	

Table 4.5 Major species and suggested structures for a FIGAERO desorption cycle performed during MCID-NO_x-2.

Interpreting the distribution of species by carbon number in both experiments, Figure 4.30, gives further insight into the key species governing the particle phase composition.

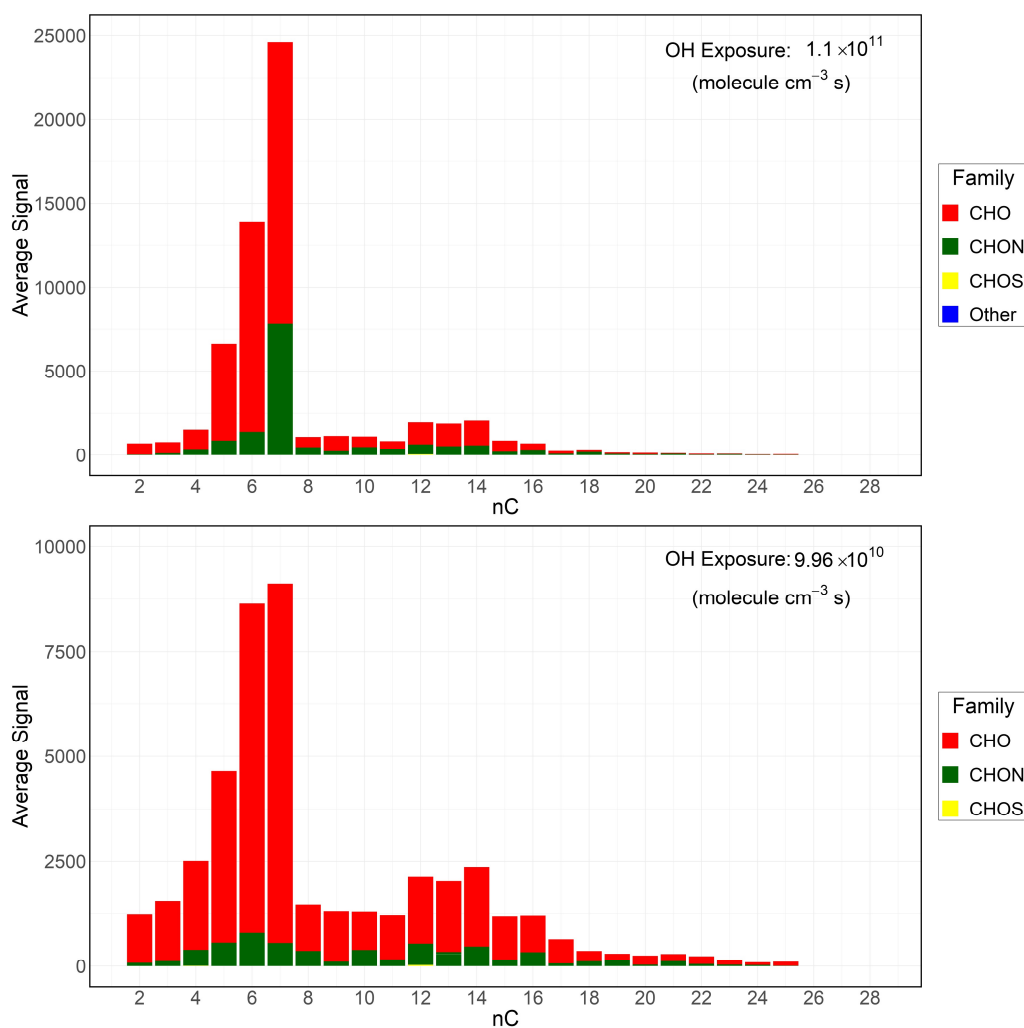


Figure 4.30 Distribution of organic products by carbon number and chemical family for FIGAERO cycles from experiments performed under high (top) and low (bottom) NO_x conditions (MCID- NO_x -2 and MCID-1).

Under both low and high NO_x conditions, C_7 species contribute the highest signal with significant contribution from C_7 CHON species, likely $\text{C}_7\text{H}_7\text{NO}_x$, under high NO_x conditions. However, there is also a large contribution from C_6 species in both low and high NO_x experiments, with similar CHON contributions in both. HONO evolution from the walls of the chamber under low NO_x conditions was discussed previously (Figure 4.15) and this likely contributes to some of the later stage oxidation processes, which may influence the formation of C_6 species as secondary accretion products between various ring scission products. They could also result from OH reactions with the precursor resulting in cleavage of the methyl group or potential ring opening and subsequent cleavage of one of the other carbon atoms. C_6 products have been observed in NO_3 reactions with 4-MC (Mayorga et al., 2021) while the C_7 NO_x aerosol phase species detected in that work were similar to the species observed here with significant contributions from suspected nitrophenol compounds, with

nitrophenols also detected in SOA derived from catechol (Fredrickson et al., 2022). Figure 4.30 also highlights the strong contribution of accretion products, specifically C_{12} , C_{13} , and C_{14} species to the particle phase. Accretion reactions are thought to contribute heavily to new particle formation so it follows that these would contribute significantly to the particle composition (Shi et al., 2022). Interestingly, while there are CHON contributions at most carbon numbers, they are predominant around C_7 , indicating that the nitroaromatics formed during the oxidation process do not react further to any significant extent to produce accretion or ring scission CHON species.

Interpreting the mass spectra as a function of the number of carbons, Figure 4.31, highlights the myriad of species which contribute to the species grouped together given in Figure 4.30.

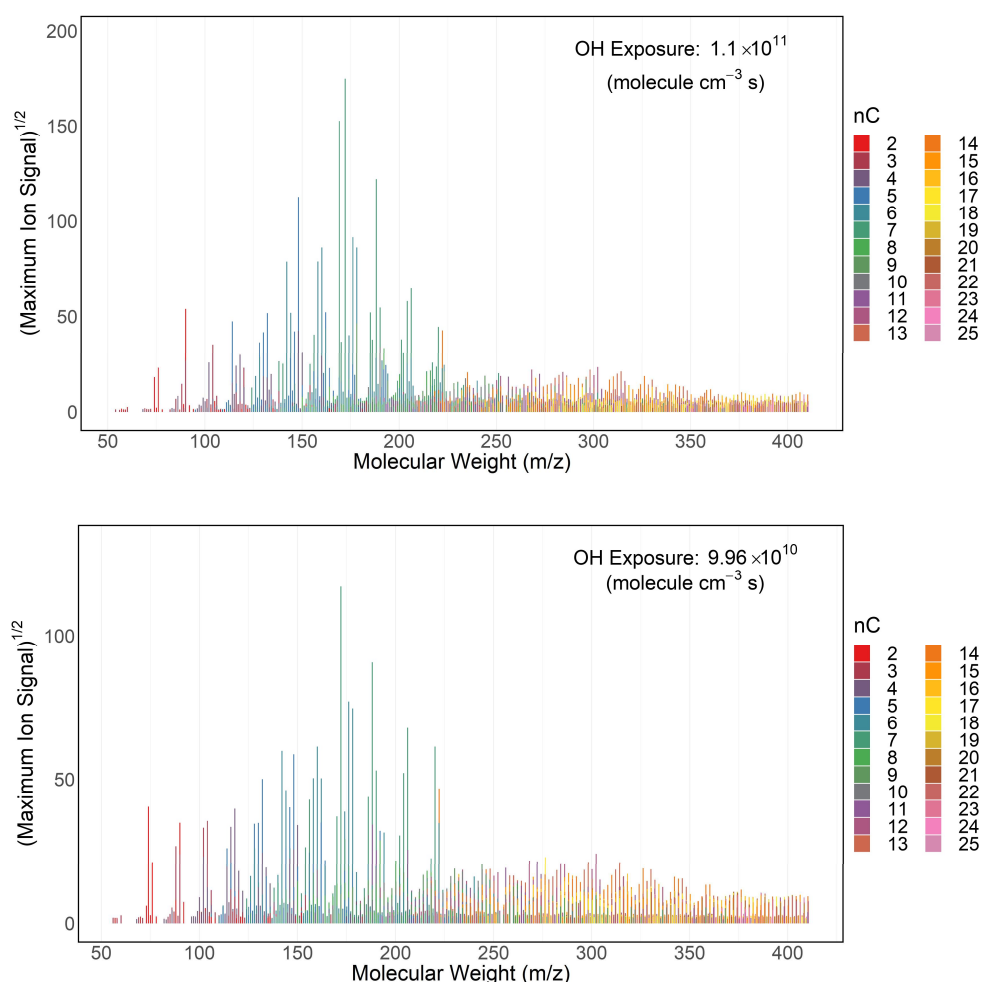


Figure 4.31 Particle phase mass spectra for organic species with signals coloured by the carbon number of a species for experiments performed under high (top) and low (bottom) NO_x conditions (MCID- NO_x -2 and MCID-1).

There are significant clusters of C_7 species between m/z ratios of 150 and 200 Th, corresponding to the numerous products containing OH and NO_2 groups in their structures. The prevalence of C_6 species as well $C_{12} - C_{14}$ species is also observed, showing that the significant contributions from these species to the distribution seen in Figure 4.30 are due to contributions from many species, rather than a single species.

Plotting the species from a desorption cycle as a function of other parameters such as the oxidation state of the carbon atoms, intensity of signal and the temperature of maximum desorption (T_{max}) for a given species, can also offer further insight into the nature of the particle phase, Figure 4.32. Here, only the 250 most intense peaks are plotted to highlight the most important species.

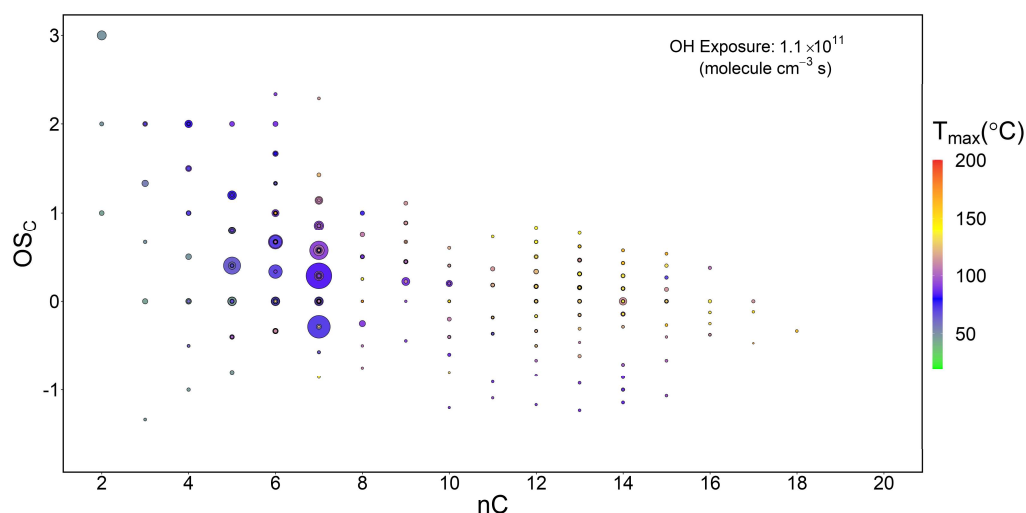


Figure 4.32 OS_C plot for a FIGAERO cycle for 4-MC photooxidation under NO_x conditions, with data points sized by maximum ion signal and coloured by T_{max} (MCID- NO_x -2).

T_{max} gives insights into the volatility of a given species as more volatile species will undergo complete evaporation from the filter at lower temperatures, while less volatile species will desorb at higher temperatures, based on the fact that evaporation rate is proportional to vapor pressure (Lopez-Hilfiker et al., 2014). When examining the C_7 species present, the colour scale indicates that species which are more highly oxidised desorb at higher temperatures as expected.

Chemical Families in the Particle Phase

Primary Oxidation Pathways

As highlighted in the mass spectra, Figure 4.29, many of the major particle phase products arise from the main oxidation pathways which were discussed in Section 4.4.3. Thermograms for some of the major CHO and CHON C_7 families i.e., $C_7H_8O_x$, $C_7H_7NO_x$, $C_7H_6O_x$ and $C_7H_5NO_x$ are plotted in Figure 4.33.

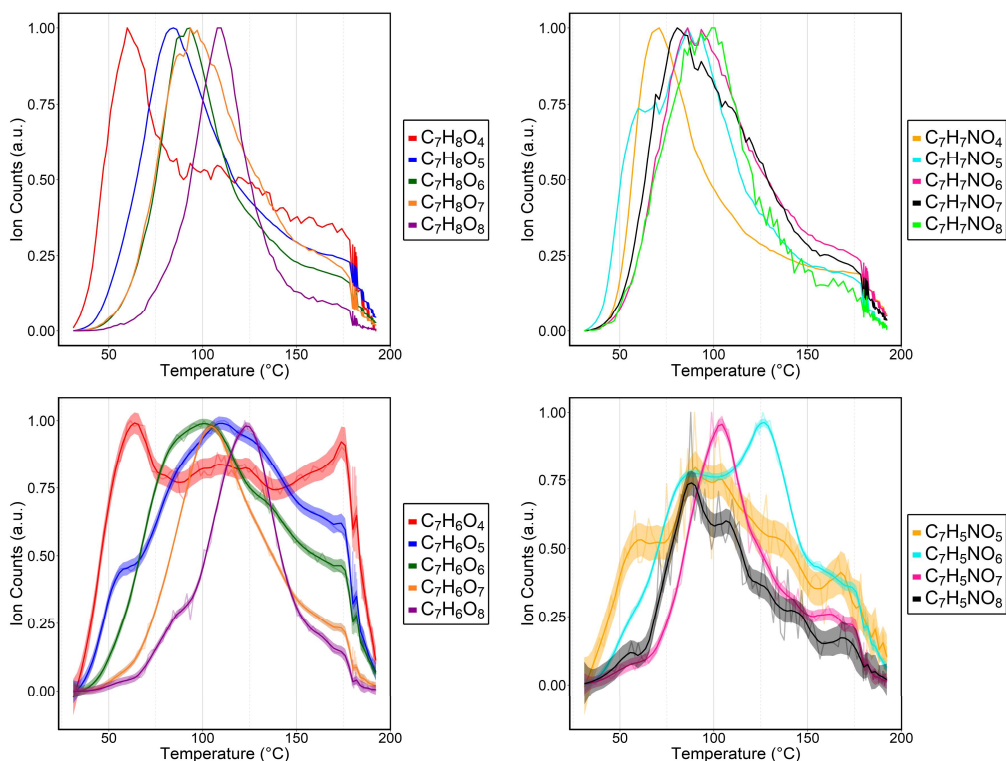


Figure 4.33 Normalised thermal desorption profiles from a FIGAERO cycle for some of the major reaction pathways in 4-MC photooxidation, including OH addition and H-atom abstraction as well as the NO_x families for these pathways. Thermograms were obtained after an estimated OH exposure of $1.3 \times 10^{11} \text{ molecule cm}^{-3} \text{ s}$ (MCID- NO_x -2).

As shown, most of the more highly oxidised species desorb at higher temperatures confirming what was observed in the OS_c plot, Figure 4.32, and consistent with previous work (Lopez-Hilfiker et al., 2014). It also observed that partitioning from the $C_7H_8O_x$ and $C_7H_6O_x$ species occurred at the second stage of oxidation, while for the $C_7H_7NO_x$ species, partitioning occurs at the primary oxidation product.

For the $C_7H_8O_x$ species, increasing the O/C ratio increases T_{max} , with $C_7H_8O_8$ having the highest T_{max} while $C_7H_8O_4$ has the lowest. Noticeably, the desorption of $C_7H_8O_4$ is not a normal distribution, as the signal tails off slowly. This may be due to

contributions to this ion signal from large oligomer species which thermally decompose at higher temperatures during the desorption cycle (Lopez-Hilfiker et al., 2015; Riva et al., 2019a). Comparatively the signal for the desorption of $C_7H_8O_8$ is a much narrower, almost Gaussian distribution which suggests only a single species contributes to this signal. The $C_7H_7NO_x$ species do not have as broad a range of T_{max} as the $C_7H_8O_x$ species with many of them clustered together. This suggests that the presence of the NO_2 group exerts more influence over molecular volatility than the degree of oxidation.

Like many of the species plotted, the $C_7H_7NO_5$ shows multiple distinct peaks, with peaks observed at approximately 55 °C and 85 °C, as well as some tailing. This signal can be somewhat deconvoluted to identify the different peaks under the desorption signal, Figure 4.34. Here, the distinct peaks under the curve were separated using the “Solver” plug-in in Microsoft Excel. The modelled data appears to be a good representation of the observed data and indicates that at least two distinct $C_7H_7NO_5$ species are present in the particle phase, with another possible contribution from the thermal decomposition of less volatile, higher molecular weight species e.g., accretion products.

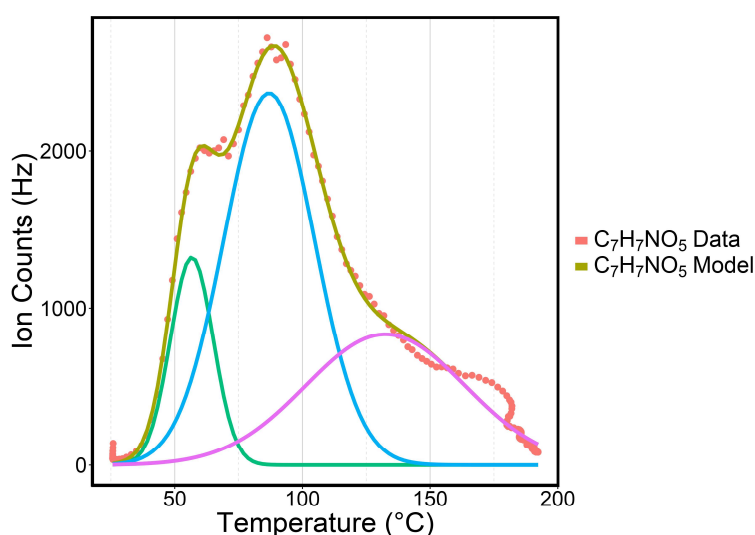


Figure 4.34 Deconvolution of the thermal desorption profile for $C_7H_7NO_5$ taken from a 4-MC photooxidation experiment (MCID- NO_x -2).

Accretion Products

Thermal desorptions of selected C₁₄ accretion products are given in Figure 4.35, illustrating both CHO and CHON species, and it is again seen that the more oxidised species have lower volatilities.

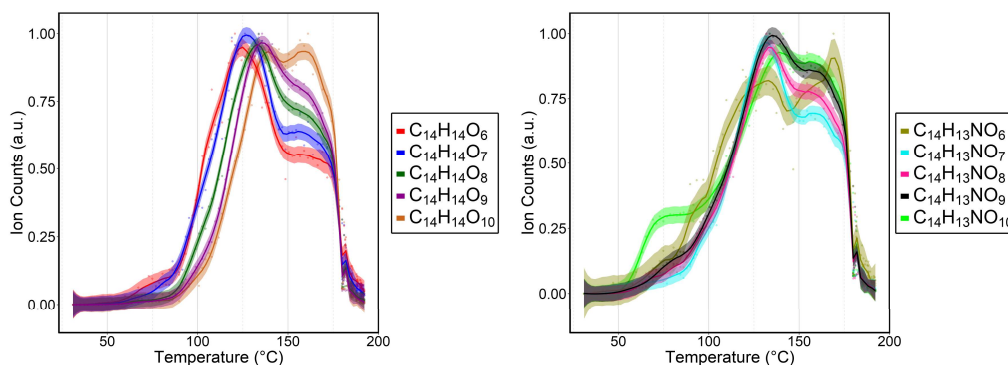


Figure 4.35 Thermal desorption profiles from a FIGAERO cycle for selected C₁₄ accretion products in 4-MC photooxidation, fitted with smoothing functions to reduce the signal noise. Thermograms were obtained after an estimated OH exposure of 1.3×10^{11} molecule cm⁻³ s (MCID-NO_x-2).

The multimodal desorption profiles highlight the different contributions to these ion signals, which may be a result of oligomer degradation or a result of significant differences in isomeric volatility based on molecular structure. Each of these species could form from a multitude of radical interactions, and thus have significantly different functional groups affecting their volatility. Accretion products have been found to contribute significantly to initial particle formation in numerous studies and are likely to play a key role in the initial nucleation reactions in this system (Shi et al., 2022; Lopez-Hilfiker et al., 2015).

In addition to these potentially ring retaining accretion products, a range of accretion products likely formed via interactions between ring scission products were also observed, Figure 4.36.

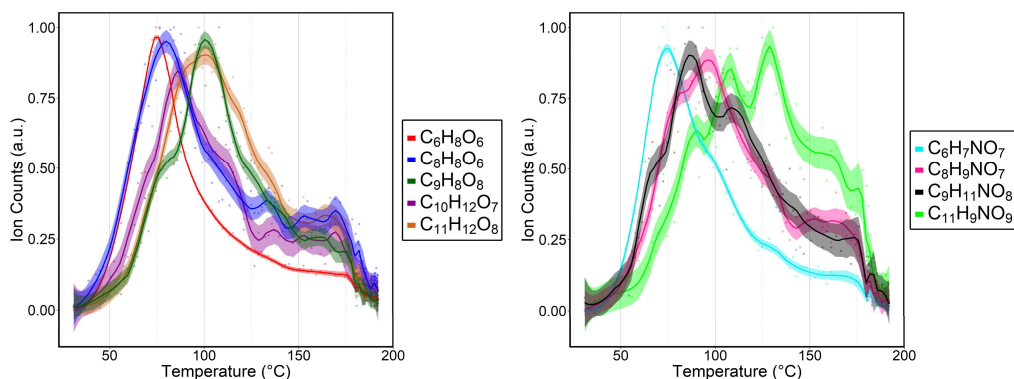


Figure 4.36 Thermal desorption profiles from a FIGAERO cycle for selected C₆ to C₁₁ accretion products in 4-MC photooxidation. Thermograms were obtained after an estimated OH exposure of 5.98×10^{10} molecule cm⁻³ s (MCIH-NO_x-2).

The species ranging from C₈ to C₁₁ and are likely formed from interactions between the myriad of C₂, C₃, C₄ and C₅ species observed in the gas phase. The large contribution of C₆ species to the particle phase may also be a result of accretion reactions. Both CHO and CHON accretion products are detected, suggesting that CHON species can undergo some degree of further processing, however the degree of CHON contribution to species which are not C₇ in nature is generally lower than CHO contribution (Figure 4.30).

Dinitro species

Similar to the gas phase, dinitro species are also observed in the particle phase, Figure 4.37.

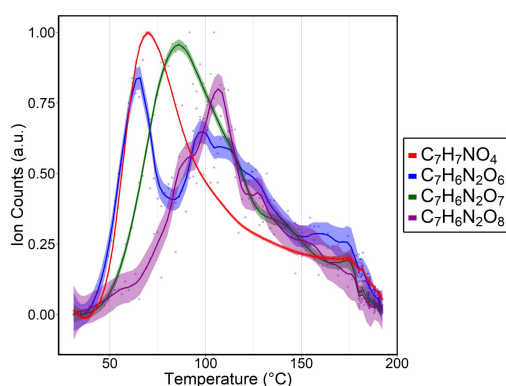


Figure 4.37 Thermal desorption profiles from a FIGAERO cycle for methyl-nitrocatechol and potential dinitro products in 4-MC photooxidation. Thermograms were obtained after an estimated OH exposure of 1.3×10^{11} molecule cm⁻³ s (MCID-NO_x-2).

The desorptions of the C₇ dinitro species occur with a shift in T_{max} when compared with the primary C₇H₇NO_x species, with a multimodal desorption profile observed for

$C_7H_6N_2O_6$. The first peak observed for this species evolves at a similar temperature as $C_7H_7NO_4$, with a later second peak. This may suggest minimal effect on volatility by the second $-NO_2$ functional group while there also may be oligomer thermal degradation contributing to the later peaks in T_{max} .

Dinitro and even trinitro species have been observed in the NO_3 initiated oxidation of similar species and as such it is not surprising that dinitro species are observed in this work. However, it is assumed that trinitro species thermally decompose as $R-N_3O_x$ species were not detected, and the late appearance of some of the species in Figure 4.37 are indicative of contribution from thermal degradation products (Yee et al., 2013; Kitanovski et al., 2014; Mayorga et al., 2021).

4.4.6 Aging of the Particle Phase

Light aging

To investigate how the composition of the particle phase changes with time and increased OH exposure, in experiments where sufficient SOA was formed, multiple collection and desorption cycles were performed to investigate changes in particle phase. Due to experiments investigating the aging of SOA requiring significant mass formation, some discussion here is based on low NO_x experiments which had higher SOA yields than NO_x experiments., particularly under dark conditions.

Changes to the Carbon Oxidation State

OS_C plots taken from different desorption cycles in a single photooxidation experiment show significant aging of the particle phase with increased exposure to OH radicals, Figure 4.38.

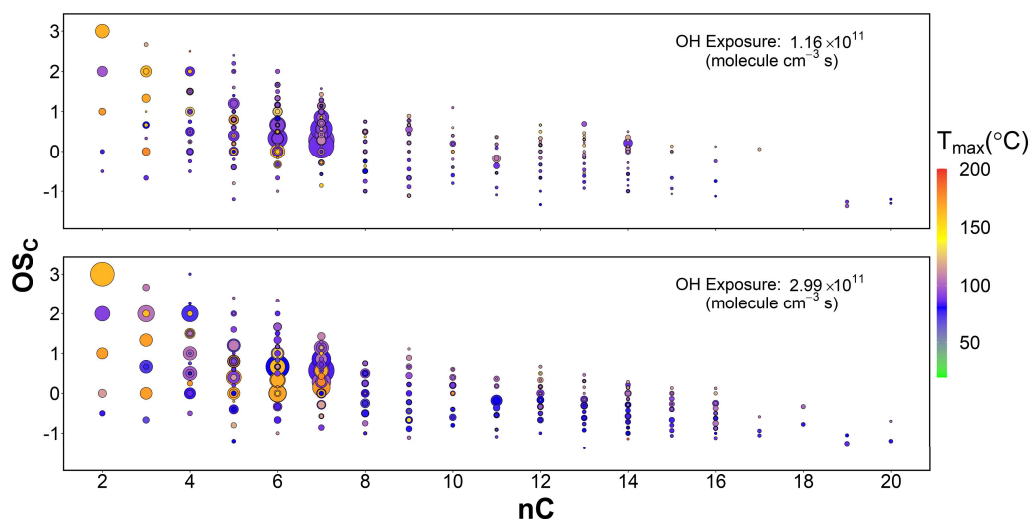


Figure 4.38 Comparative OS_C plots for two desorption cycles taken from the same 4-MC photooxidation experiment after different degrees of OH exposure (MCIH- NO_x -3).

There are numerous differences between the two plots, most notably the increased number of larger data points in the more aged plot. In the first plot, the most significant ions are centred around C_7 with some contribution from C_5 and C_6 species, however in the aged plot, there are more significant contributions from species with a higher OS_C and lower nC . The increase in contributions from more oxidised, smaller species demonstrates the significant aging of the particle phase which has occurred. This shift to smaller species becoming more important with increased OH exposure has been

seen previously observed, such as for α -pinene oxidation as reported by Chhabra et al. (Chhabra et al., 2015). It is interesting to note significant increases in $T_{\max}$ for a range of C_6 and C_7 species in the aged plot, likely due to thermal decomposition of larger oligomers. This effect of large oligomers on the desorption profile has been seen in other work such as in the NO_3 initiated oxidation of limonene by Faxon et al. (D'Ambro et al., 2017, 2022; Faxon et al., 2018; Lopez-Hilfiker et al., 2015).

There are noticeable increases in the signals for accretion products between both plots, potentially indicating that these species continue to form throughout the experiment, or it may suggest that they have increase stability and do not decay to the same scale as monomer species. This could have significant impacts on the toxicity of methylcatechol SOA as highly oxidised species are known to be highly toxic (Liu et al., 2023) and this data suggests that they are long-lived species in SOA.

Aging of Species of Interest

Interpreting how the signals of specific species change between various desorption cycles gives further insight into this behaviour, Figure 4.39.

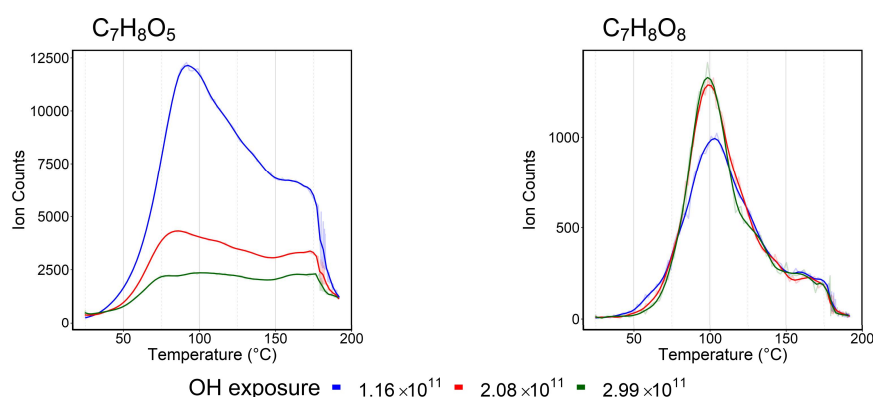


Figure 4.39 Thermal desorption profiles of selected $C_7H_8O_x$ species from different FIGAERO cycles from the same 4-MC photooxidation experiment, with data corrected for SOA mass loading on the PTFE filter (MCIH- NO_x -3).

$C_7H_8O_5$ shows significant decay with increased exposure to OH, where it is clearly observed that the highest recorded concentration for this species was in the earliest desorption with sequentially reducing concentrations observed. Significant change in $T_{\max}$ is also observed for the third desorption profile. All three desorptions show further contribution from other second species after 150 °C, however in the third desorption, this later signal has a higher intensity, indicating oligomer decomposition is the main source of $C_7H_8O_5$ ions at this stage in the experiment. $C_7H_8O_8$ however,

shows increases in concentration upon further OH exposure, which is common for many of the more oxidised species observed in these experiments. Unlike the $C_7H_8O_5$ desorption profiles, the $C_7H_8O_8$ profiles do not change shape drastically between desorption cycles with similar T_{max} observed for each profile. This suggests that this signal is primarily due to a single isomer which is continuously formed in the particle phase with further OH exposure.

The same trend is not observed for CHON species, and this is hypothesised to be a result of the photo-lability of the NO_2 group resulting in these species being more susceptible to photolytic degradation (Bejan et al., 2006; Chen et al., 2011; Yuan et al., 2016; W. Yang et al., 2021). As illustrated in Figure 4.40, even the more aged $C_7H_7NO_7$ species undergoes significant degradation between the first and final desorption cycle, while $C_7H_7NO_4$, the primary particle $C_7H_7NO_x$ species undergoes similar but more extensive degradation. Similar results were observed by Fredrickson et al. in their study of catechol oxidation, where nitrocatechol decay was observed with continuous chemical aging (Fredrickson et al., 2022).

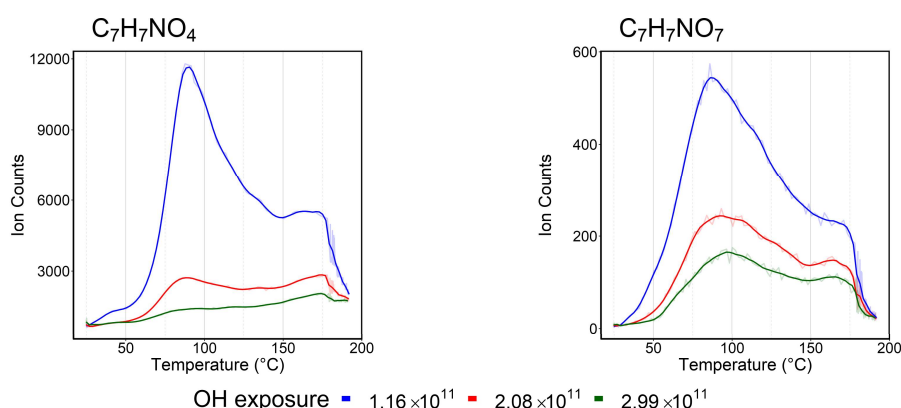


Figure 4.40 Thermal desorption profiles of selected $C_7H_7NO_x$ species from different FIGAERO cycles from the same 4-MC photooxidation experiment (MCIH- NO_x -3).

A range of other trends were observed for various species throughout the aging of the particle phase and a selection of these are shown in Figure 4.41.

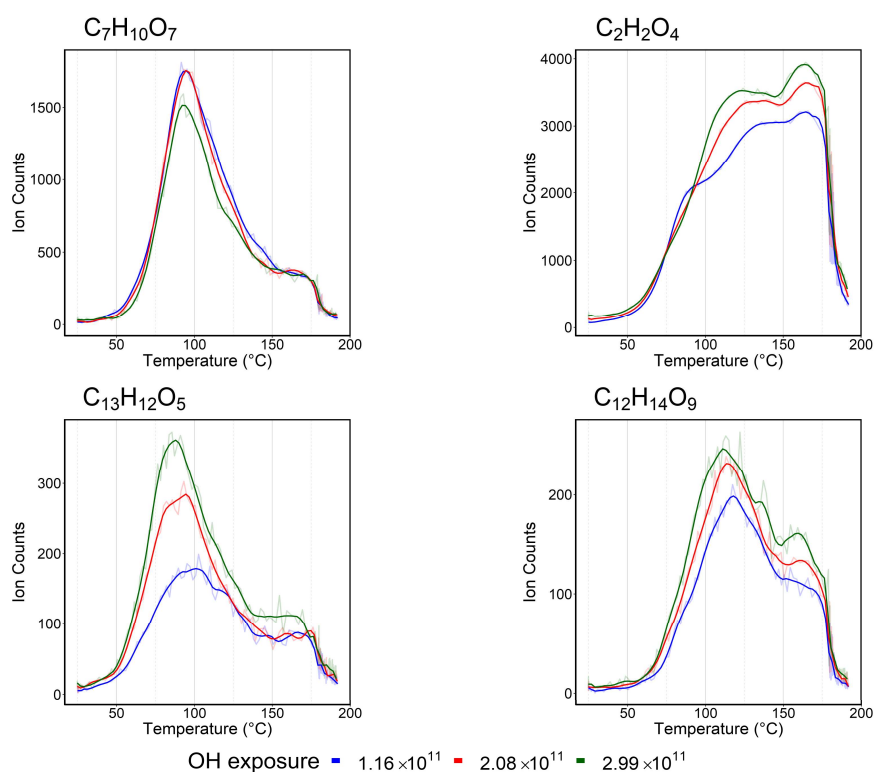


Figure 4.41 Thermal desorption profiles of selected species from different FIGAERO cycles from the same 4-MC photooxidation experiment (MCIH- NO_x -3).

The stability of certain species to further aging is observed, such as the $C_7H_{10}O_7$ species which shows little degradation upon further OH exposure. The $C_2H_2O_4$ signal undergoes significant changes with increased exposure, with the disappearance of the first peak (~ 90 °C) after the first desorption. The higher T_{max} degradation peaks also increase in magnitude with each successive desorption, suggesting that larger species undergoing thermal degradation to contribute to this signal are increasing in concentration with further OH processing. The C_{12} and C_{13} accretion products presented show increases in concentration with increased OH exposure, with the more oxidised $C_{12}H_{14}O_9$ species having a higher T_{max} than the C_{13} species.

Dark Aging

Effect on SOA formation

To investigate how particle growth and composition would change when OH production was ceased during an experiment, dark aging of the SOA was investigated by switching off the UV lights during an experiment while continuing to analyse the contents of the chamber using the ToF-CIMS. Significant changes were observed in particle formation, Figure 4.41, where there is a noticeable slowing of particle growth once the lights have been switched off. Figure 4.42 highlights how the width of the distribution remains relatively unchanged once the lights are switched off which contrasts with the previous particle growth plot given in Figure 4.28 where the distribution continued to narrow throughout the experiment. There is also a noticeable reduction in the degree of decay in particle number with the green and yellow regions of the plot extending further under dark conditions.

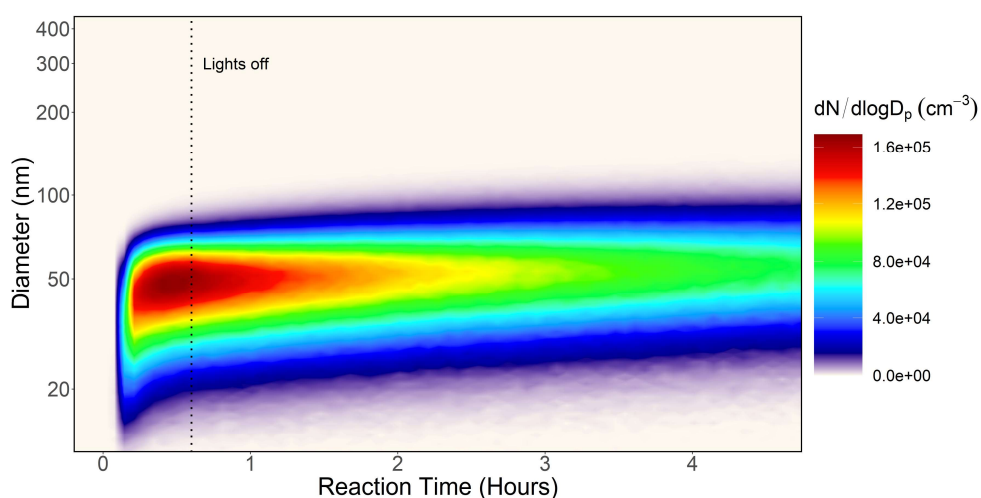


Figure 4.42 Banana plot of particle formation and growth for a 4-MC dark aging experiment (MCID-DARK-1).

Effect on aging of chemical species

In addition to the effect observed on the growth of SOA under dark conditions, changes were also observed in the FIGAERO data obtained during these experiments. The OS_C plots in Figure 4.43 illustrate reduced effects of dark aging on the oxidation state of the particle phase products, compared to the light aging in Figure 4.38.

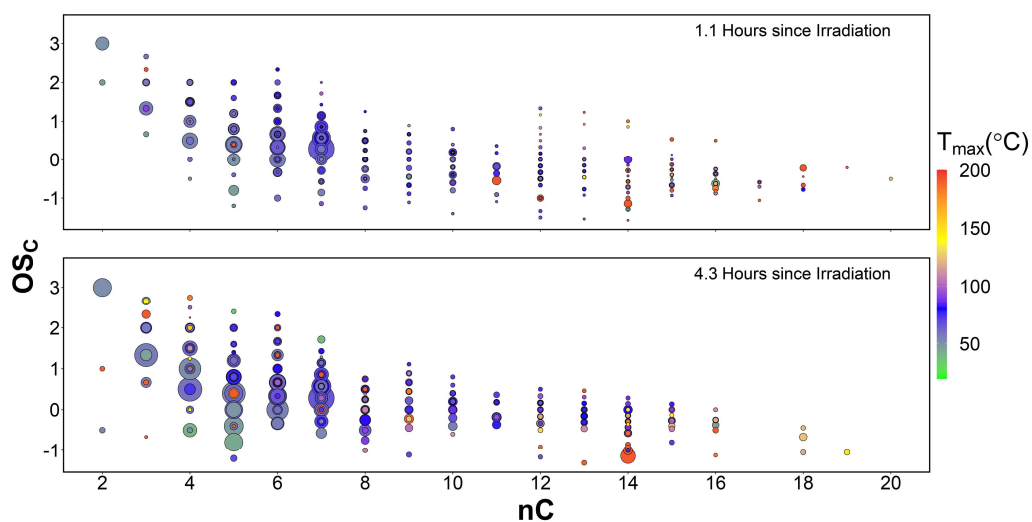


Figure 4.43 OSC plots for two desorption cycles performed in a dark experiment highlighting the minimal change in particle phase oxidation state in the dark. (MCID-DARK-1)

Plotting thermograms for various species in the dark conditions also shows the reduced effect compared to UV aged experiments, Figure 4.44.

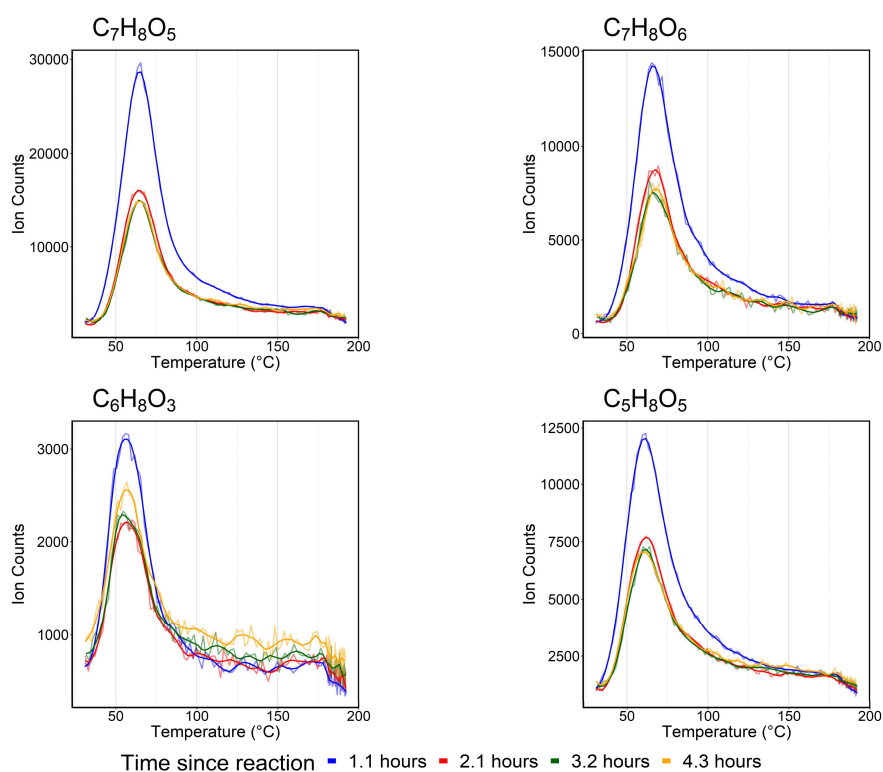


Figure 4.44 Thermal desorption profiles of selected species from different FIGAERO cycles from the same 4-MC dark aging experiment (MCID-NO_x-DARK).

Under light conditions, the primary particle phase species such as $C_7H_8O_5$ underwent decay with each successive desorption, however in the dark, the aging was slowed if not interrupted completely as there is little to no change between the second and fourth desorptions of the $C_7H_8O_5$ and $C_7H_8O_6$ species. Other species showed decay but to a lesser extent such as $C_5H_8O_5$, while the other species plotted, $C_6H_8O_3$ shows an initial decrease between the first and second desorptions, however increase from the second to third and once again from the third to the fourth. This suggests that there is some condensed phase processing of the SOA occurring in the dark even without exposure to hydroxyl radicals or light.

4.5 Conclusions

Atmospheric simulation chamber photooxidation experiments have been performed on 4-methylcatechol, a product of lignin pyrolysis, under a variety of atmospheric conditions with varying NO_x concentrations and relative humidity, with both gas and particle phase products reported using a FIGAERO-ToF-CIMS operated in iodide and mode. The aging of SOA by prolonged exposure to OH and light was also investigated and compared to dark aging.

4-methylcatechol was found to react via multiple reaction pathways, yielding a range of gas phase products, primarily C_7 in nature. Multiple gas phase reaction pathways were elucidated, including OH addition which yielded hydroxyl catechols, such as $\text{C}_7\text{H}_8\text{O}_3$. Sequential oxidation along the OH addition pathway was observed, with species up to $\text{C}_7\text{H}_8\text{O}_7$ detected in the gas phase. The OH addition pathway was also seen to rapidly produce more highly oxidised $\text{C}_7\text{H}_8\text{O}_x$ species such as $\text{C}_7\text{H}_8\text{O}_4$ and $\text{C}_7\text{H}_8\text{O}_5$ immediately after irradiation, suggesting that there are other species with the same molecular formulae as the sequential oxidation species. In addition to the C_7 species, a range of species with smaller carbon chains i.e., C_2 to C_5 species were also detected which are proposed to be the result of ring scission following the initial addition of the hydroxyl radical. Benzoquinones ($\text{C}_7\text{H}_6\text{O}_x$) and accretion products were also detected and are proposed to be the result of hydrogen abstraction from the hydroxyl groups in 4-MC yielding reactive phenoxy radicals, however these were observed in lower concentrations than the major species observed along the OH addition pathways. NO_x incorporation was observed along every major reaction pathway when experiments were performed in the presence of NO_x , with molecular formulae corresponding to methyl-nitrocatechols ($\text{C}_7\text{H}_7\text{NO}_4$) the most abundant products.

SOA formation and growth was swift under the high OH conditions generated using UVC radiation, beginning as soon as reactions were initiated by irradiation. SOA yields under dry, low NO_x conditions were found to be in the range of 27 – 50%, consistent with studies performed on similar compounds. The major particle phase species detected via thermal desorption using the FIGAERO inlet were found to occur via the same reaction pathways observed in the gas phase, however with a higher

degree of oxidation than the primary gas phase species. The first particle phase species observed along the OH addition pathway was the second OH addition product, $C_7H_8O_4$, with species up $C_7H_8O_8$ detected along this pathway. The primary CHON species detected, $C_7H_7NO_4$ partitioned readily and was among the most highly detected species in both the gas and particle phases when NO_x was present.

Substantial processing of the SOA was observed upon increased exposure to hydroxyl radicals, with both formation and decay of individual species observed. It was found that for many of the more oxidised species (e.g., $C_7H_8O_8$ and $C_{12}H_{14}O_9$) concentrations increased with further exposure to light and OH radicals, while some of the primary particle phase species (e.g., $C_7H_8O_5$ and $C_7H_7NO_4$) were found to undergo significant degradation in the aerosol phase. In the dark there was a reduction in the degree of aging of the SOA, however, increases in concentrations of certain species ($C_6H_8O_3$) were observed suggesting some condensed phase chemistry is occurring. Interruption of the aging process by turning off the lights was found to significantly impact the growth of SOA, with growth significantly reduced compared to experiments performed entirely under light conditions.

The aging of SOA can have significant impacts on the climatic effects, as increased oxidation of SOA results in aerosol with an elevated capacity to serve as cloud condensation nuclei (CCN) or ice nucleating particles (ICN). These particles can exert a substantial influence on cloud albedo and therefore the Earth's energy balance through radiative forcing (IPCC, 2021; Jahl et al., 2021; Lohmann et al., 2010). Additionally, enhanced oxidation of aerosol tends to augment their water solubility via the addition of hydroxyl or acid functional groups. Increased water solubility of aerosol particles can have adverse effects on cardiovascular health, while nitrophenol derivatives, another major product of this oxidation process, are recognized for their significant impact on human health (Ahmed et al., 2015; Falcon-Rodriguez et al., 2016).

Overall, this study has presented a comprehensive study on the major primary and secondary gas and particle phase products produced from hydroxyl-initiated oxidation of 4-methylcatechol. To better understand the oxidation pathways that govern this oxidation process and the oxidation products detected, structure-based analysis could be performed on both the gas and particle phase products, using offline analysis

techniques such as LC-MS or GC-MS. This would help to elucidate the major isomers which contribute to signals for molecular formulae observed along multiple reaction pathways, such as $C_7H_8O_5$ which can form via at least two pathways presented. It would be interesting to fully characterise the effect of the chamber lights on the 4-MC oxidation system, which could be done by performing OH initiated reactions in the dark, where the OH source could be ozonolysis of an alkene e.g., 2,3-dimethyl-butene. This should result in the same oxidation products that were observed in this study, however the UV radiation emitted by the chamber lamps in the system employed here may have had some influence on the identified reaction pathways. Dark OH reactions would also allow for more comprehensive investigations on the effect that light has on the aging of SOA, with photolysis removed as a loss mechanism. SOA yields and the relative effects of NO_x concentration and relative humidity could also be performed to fully characterise the atmospheric behaviour of 4-methylcatechol.

5. Hydroxyl radical initiated oxidation of guaiacol

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5.1 Introduction

Guaiacol (2-methoxyphenol, $C_7H_8O_2$) is an aromatic species directly emitted from lignin pyrolysis and which has been observed in both laboratory and field studies of biomass burning emissions (Mazzoleni et al., 2007; Simpson et al., 2005; Hays et al., 2002; McDonald et al., 2000). Kinetic studies of the atmospheric reactivity of guaiacol indicate that gas-phase reaction with both hydroxyl (OH) and nitrate (NO_3) radicals are expected to be the dominant loss processes in the troposphere (Lauraguais et al., 2015, 2016). Guaiacol also has the potential to form secondary organic aerosol (SOA), with SOA yields of 0.003 to 0.87 and 0.1 to 0.21 reported for the oxidation reactions initiated by OH (Lauraguais et al. 2014) and NO_3 (Meng et al. 2020), respectively.

There have been a range of studies on the atmospheric and aqueous phase oxidation pathways for guaiacol. Yee et al (2013) investigated the OH-initiated oxidation of guaiacol under low NO_x conditions and identified a range of ring-retaining and ring-opening products attributed to the OH addition pathway (Yee et al., 2013). Evidence for loss of the methoxy group was also obtained, however, the authors did not highlight products arising from hydrogen abstraction or accretion reactions, nor did they discuss in detail the oxidation products formed in the presence of higher NO_x concentrations. Lauraguais et al (2014) did report some of the primary products of OH oxidation under high NO_x conditions, such as nitroguaiacol ($C_7H_7NO_4$) and nitrocatechol ($C_6H_5NO_4$) (Lauraguais et al., 2014). Yang et al (2016) also identified these nitrophenol products in a study of the NO_3 -initiated oxidation of guaiacol, which primarily occurs via hydrogen abstraction from the -OH group, rather than addition to the aromatic ring. Interestingly, catechol and nitrocatechol were identified among the oxidation products suggesting that loss of the methoxy group can occur during NO_3 oxidation reactions (Yang et al., 2016). Meng et al. (2020) identified a range of nitrophenols, as well as dinitro compounds such as dinitrocatechol ($C_6H_4N_2O_6$) and dinitroguaiacol ($C_7H_6N_2O_6$) in the SOA formed during the NO_3 -initiated oxidation of guaiacol. A number of C_{13} and C_{14} products ($C_{13}H_{10}N_2O_8$ and $C_{14}H_{12}N_2O_8$) were also observed in the particle phase and attributed to dimers formed via association of nitrocatechols and nitroguaiacols (Meng et al., 2020).

Aqueous phase reactions of guaiacol have also been performed, with a focus on nitration. Kitanovski et al (2014) characterised the range of nitroaromatic compounds produced in a laboratory study of guaiacol photo-nitration and found that nitro- and dinitro-guaiacols were the predominant reaction products. The authors also identified significant concentrations of dinitroguaiacol in PM₁₀ field samples collected in Slovenia. The detection of dinitroguaiacol in ambient air is of particular importance due to the increased toxicity caused by the two nitro groups, as well as the enhanced contribution to atmospheric “brown” carbon (Kitanovski et al., 2014).

Recently, experiments investigating the multiphase nitration of guaiacol in simulated atmospheric aerosol via reaction with HONO was investigated by Kroflič et al (2021). Nitroguaiacol and nitrocatechol were formed, suggesting that both nitration and methoxy loss reactions were occurring. Increased relative humidity led to higher yields of 4-nitrocatechol from guaiacol and a new pathway of dark nitrophenol formation was also observed (Kroflič et al., 2021). This dark reaction was consistent with a previous study on dark aqueous phase reactions between HONO and various catechol species which produced nitrocatechols (Vidović et al., 2018).

None of the laboratory studies presented above followed the evolution of both the gas and particle phase species in real-time. However, Palm et al. (2020) utilised a FIGAERO-CIMS to elucidate key gas- and particle-phase products generated in a series of chamber experiments on the atmospheric oxidation of a mixture of phenolic compounds, including guaiacol. The experiments were designed to simulate the atmospheric processing of real wildfire emissions under high NO_x conditions and showed, among other things, that the primary products of guaiacol oxidation were nitroguaiacols. This detailed study showed that the FIGAERO-CIMS can provide unique insights into the complex multiphase chemistry associated with the atmospheric oxidation of phenolic compounds like guaiacol and improve our understanding of the oxidation mechanisms that lead to the formation and evolution of SOA.

5.2 Aims

The aims of this work were to perform detailed investigations of the reaction mechanisms for the OH-initiated oxidation of guaiacol (2-methoxy phenol) under high and low NO_x conditions. A FIGAERO-ToF-CIMS was used to elucidate the key gas-phase reaction pathways and to characterise the species formed in the particle phase. SOA formation and growth were monitored using a scanning mobility particle sizer (SMPS, TSI incorporated) and aging of the aerosol under both light and dark conditions was also studied to better understand the evolution of SOA in the atmosphere.

5.3 Materials and Methods

Guaiacol oxidation experiments were conducted in the same manner as for 4-methylcatechol, described in Chapter 4. Briefly, all reagents were added to the chamber and allowed sufficient time to mix homogeneously before the reaction was started via irradiation using a range of lamps emitting in the UVA and UVC spectral ranges. Hydroxyl (OH) radicals were generated from photolysis of H₂O₂, HONO or a mixture of both precursors, depending on the light and NO_x conditions selected for a particular experiment.

As guaiacol ($\geq 98\%$, Sigma-Aldrich) is a liquid, it was added to the chamber without any pre-treatment. Following addition of guaiacol, a small residue was often observed in the glass vial, suggesting incomplete addition of the compound to the chamber. As a result, a series of CIMS calibrations of guaiacol were performed under different humidity conditions to determine the concentration of reagent added in each experiment.

The ToF-CIMS was operated using the VUV source for ion generation as discussed in Chapter 2, with a reagent ion flow of 0.45 L min⁻¹.

To estimate mass loading on the FIGAERO filter, sampling duration and flow rate were measured, and the mass loading determined using the mass concentration reported by the SMPS at the start of the sampling period. This was used to correct for different mass loadings in the same experiment as ion concentration is proportional to SOA mass loading.

SMPS data was collected over the particle diameter range of 12 to 400 nm using the Aerosol Instrument Manager v10.3.0.3. Data were corrected for wall losses and subsequently plotted using R v4.0.2.

5.4 Results and Discussion

5.4.1 Reaction Parameters and Concentration Time Profiles

The OH-initiated oxidation of guaiacol was performed under a range of experimental conditions, with varying NO_x concentrations and relative humidity, different light conditions and CIMS reagent ions. A summary of the experiments is presented in Table 5.1. The code used for experiment labels is as follows:

G: Guaiacol.

I/B: Iodide or benzene CIMS reagent.

D/H: Dry or humid conditions.

NO_x: Indicates addition of NO_x (> 1 ppb).

UVA: Specifies only UVA lamps used in experiment.

DARK: Specifies experiments where UVA and UVC radiation was used to initiate the reaction between OH and guaiacol, however the lamps were switched off after a period of time and aging was continuously monitored in the dark.

Due to issues with some experiments where higher background particle counts were observed, a discussion of SOA yield is not presented. SOA yield was not the primary focus of this study and has already been characterised for OH reactions with guaiacol (Lauraguais et al., 2014); the chemical data elucidated from the CIMS is the main focus of this work.

Experiment Code	Guaiacol Concentration ($\mu\text{g}/\text{m}^3$)	Estimated OH Concentration (molecule cm^{-3})	NO_x (ppb)	Relative Humidity (%)	SOA Corrected Mass ($\mu\text{g}/\text{m}^3$)	SOA Yield
GID-1	441.6	3.90×10^7	0	< 1	60	0.14
GID-2	781.8	3.04×10^7	0	< 1	180	0.23
GIH-1	754.5	3.70×10^7	0	46	105	0.14
GID- NO_x -1	754.5	6.6×10^7	81	< 1	3.6	0.00
GID- NO_x -2	354.1	3.09×10^7	62	< 1	3.1	0.01
GIH- NO_x -1	942.5	7.40×10^7	55	48	61	0.06
GID- NO_x -UVA-1	629.0	6.64×10^6	39	< 1	0	0.00
GIH- NO_x -UVA-1	267.6	3.48×10^6	42	41	0	0.00
GID-DARK	343.2	2.63×10^7	0	< 1	265	0.77
GID- NO_x -DARK	435.1	7.16×10^6	33	< 1	107	0.25
GBD-1	232.1	2.75×10^7	0	< 1	26.4	0.11
GBD-2	754.5	2.64×10^7	0	< 1	105.2	0.14
GBH-1	685.9	2.20×10^7	0	45	17.1	0.02
GBD- NO_x -1	174.1	2.72×10^7	53	< 1	8.9	0.05
GBD- NO_x -2	217.6	1.1×10^7	97	< 1	0	0.00
GBD- NO_x -3	119.0	1.92×10^7	102	< 1	0	0.00
GBH- NO_x -1	754.5	3.04×10^7	51	39	35.1	0.05
GBH- NO_x -2	198.9	1.48×10^7	70	48	4.34	0.02

Table 5.1 Experimental parameters for the OH-initiated oxidation of guaiacol.

Experiments where UVA photolysis of HONO was the OH source yielded lower OH concentrations than experiments in which UVC radiation was used, resulting in slower chemistry and also suppression of SOA formation. A concentration time profile for one of these experiments is shown in Figure 5.1, with decay observed for guaiacol, HONO and NO under irradiation while NO_y species were seen to increase initially, however no increase in SOA mass was observed.

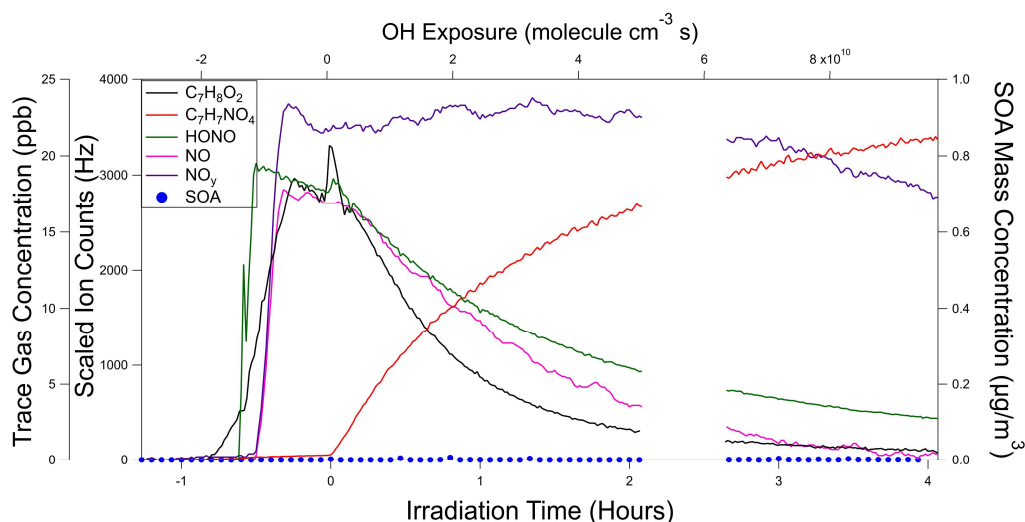


Figure 5.1 Summary plot for guaiacol and NO_x photooxidation performed under UVA conditions (GID-NO_x-UVA-1).

In most of the experiments, UVC radiation was used to generate higher OH concentrations and promote SOA formation. Under these conditions, faster decay of guaiacol was observed with significant SOA formation. SOA formation was found to be rapid, often starting within the first 5 minutes of irradiation, with rapid particle growth also observed. A concentration time profile for a typical experiment under NO_x conditions is shown in Figure 5.2.

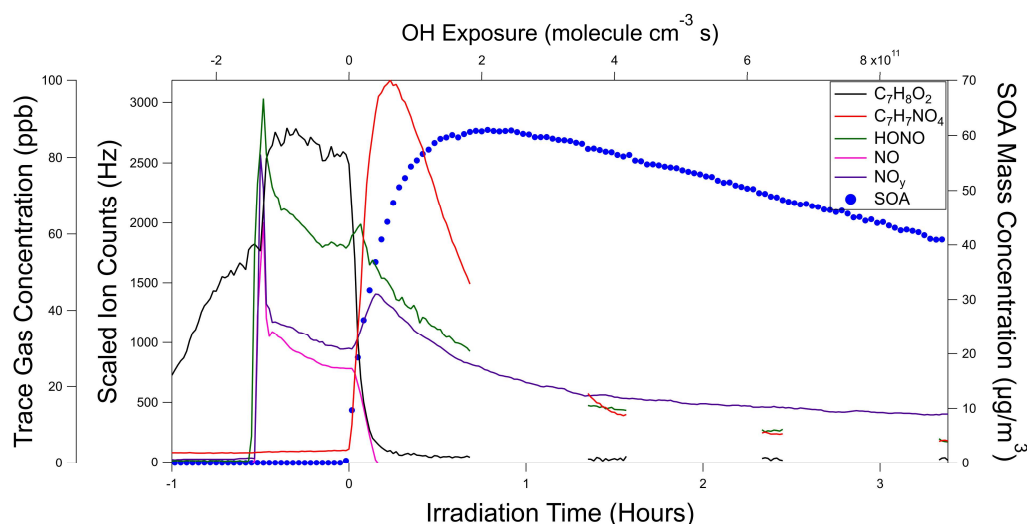


Figure 5.2 Concentration time profile for guaiacol and NO_x photooxidation under UVC conditions (GIH- NO_x -1).

Illustrated here, immediately after irradiation there is rapid decay seen in the traces for guaiacol and NO , with both species reaching the noise region within 30 minutes, while a more gradual decay in HONO is observed with an increase in the NO_y concentration, predicted to be primarily composed of NO_2 and nitric acid (HNO_3), formed as RO_2 species react with NO to form NO_2 and RO . SOA mass concentrations reached a maximum within the first hour of irradiation, demonstrating the rapid particle formation due to the influence of the UVC radiation resulting in highly oxidised, low volatility species forming and subsequently partitioning into the particle phase.

5.4.2 Gas Phase CIMS Analysis

Overview of different experimental conditions

NO_x experiments under UVA radiation

The reactions performed under UVA conditions are slower and therefore provide insight into the primary oxidation chemistry of guaiacol. Figure 5.3 illustrates the evolution in the product composition for one such UVA experiment as a function of the number of carbon atoms (nC) in each species (Note that species with one carbon atom (nC = 1) are not included due to strong interference from formic acid). As expected, C₇ species contribute significantly to the total, while there is also a large proportion of C₆ products, suggesting loss of the methoxy group which has previously been observed for guaiacol photooxidation (Yee et al., 2013; Lauraguais et al., 2014). Little to no change in composition is observed after 30 minutes, with C₇ and C₆ species remaining dominant throughout the experiment.

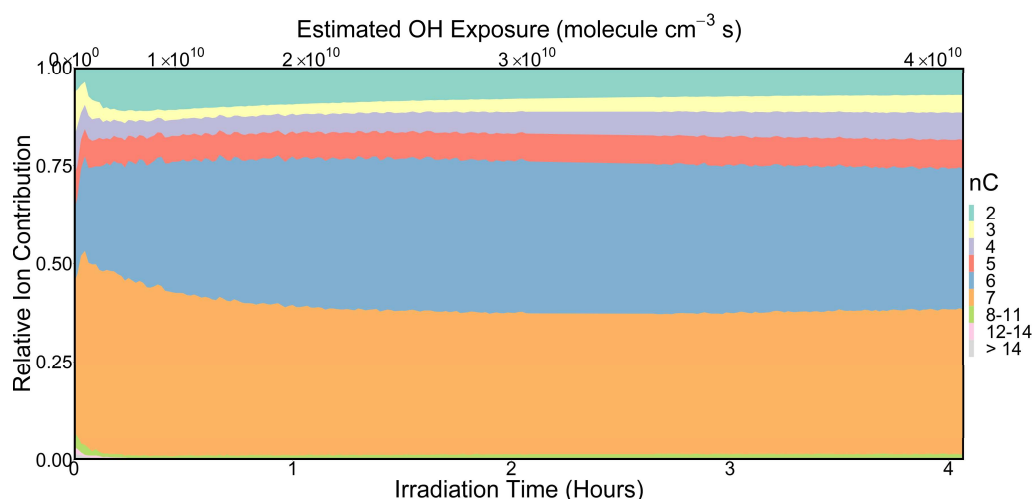


Figure 5.3 Time series of organic products grouped by carbon number for guaiacol photooxidation under UVA conditions (GID-NO_x-UVA-I).

An initial increase is observed for most groups of species and especially C₆ and C₇. As the reaction proceeds, the contribution of C₆ increases, with a corresponding decrease in the C₇ species, highlighting the importance of the products formed via methoxy loss. CIMS mass spectra averaged to 5-minute intervals at different stages of the reaction are shown in Figure 5.4 to highlight the molecular formula of key products and their temporal evolution.

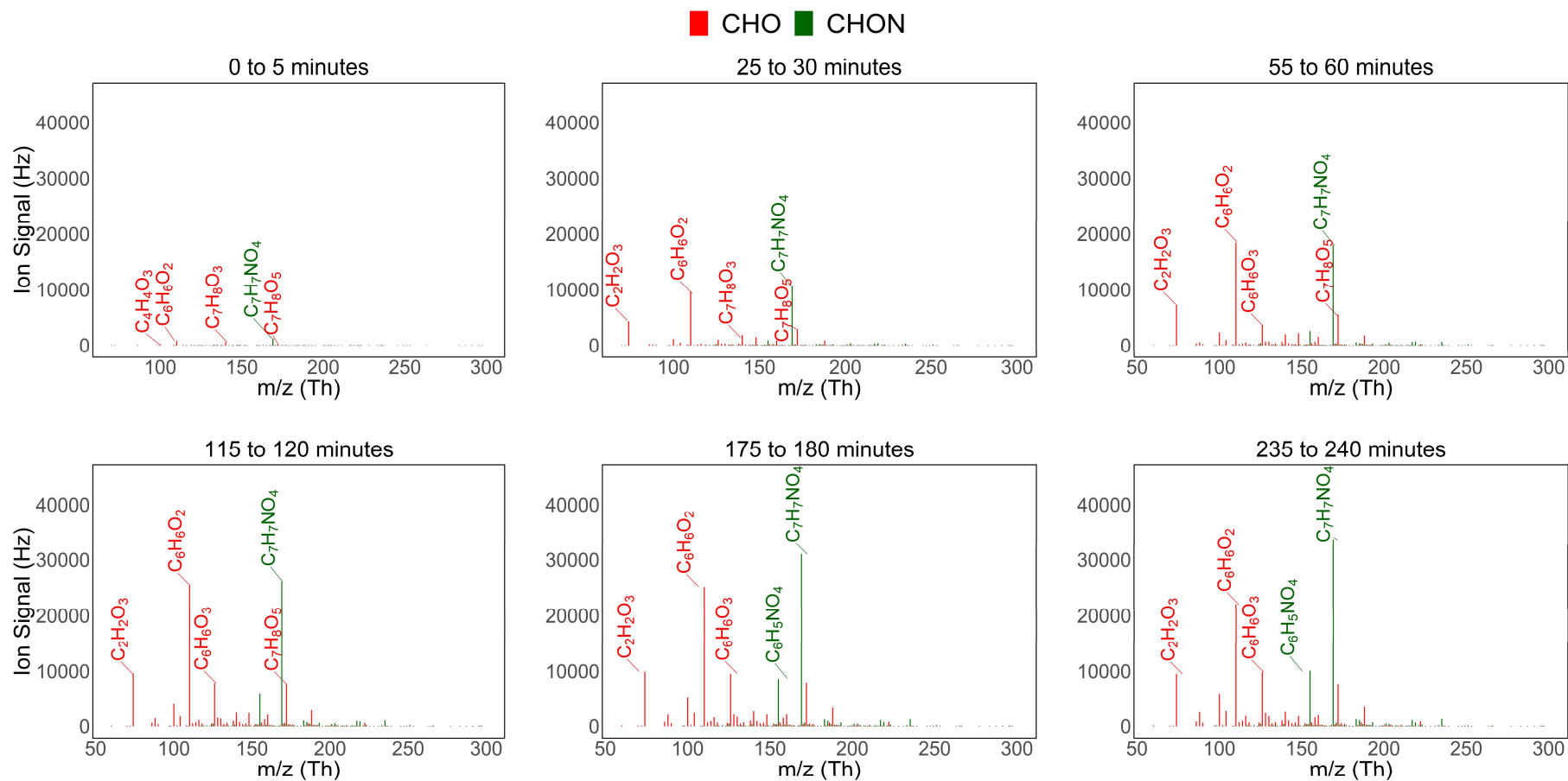


Figure 5.4 Average mass spectra for various 5-minute intervals during a guaiacol and NO_x photooxidation experiment under UVA conditions (GID-NO_x-UVA-1).

The five most intense signals (by ion counts per second) in each spectrum are labelled by molecular formula, with iodide (I^-) removed. Within the first few minutes of oxidation, the most dominant species are $C_7H_7NO_4$ and $C_6H_6O_2$, assigned to nitroguaiacol and catechol, respectively. Significant signals are seen for $C_7H_8O_x$ species likely formed via OH addition to guaiacol, while the presence of C_2 and C_4 species in the early stages of oxidation suggest ring scission chemistry is also occurring to some extent. The appearance of $C_6H_6O_3$ and $C_6H_5NO_4$ at later stages of the reaction likely result from further oxidation of $C_6H_6O_2$. Using the currently available knowledge on the atmospheric reaction pathways for guaiacol (Yee et al., 2013), molecular structures for the main products observed by CIMS are tentatively proposed in Table 5.2

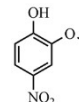
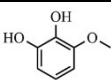
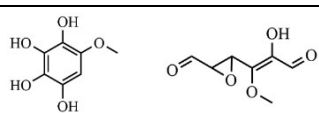
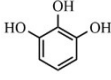
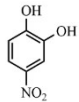
Molecular Mass (g/mol)	Chemical Formula	Proposed Structure
124.12	$C_7H_8O_2$	
169.13	$C_7H_7NO_4$	
110.11	$C_6H_6O_2$	
140.14	$C_7H_8O_3$	
172.14	$C_7H_8O_5$	
100.07	$C_4H_4O_3$	
126.11	$C_6H_6O_3$	
74.04	$C_2H_2O_3$	
155.11	$C_6H_5NO_4$	

Table 5.2 Proposed structures for gas-phase products observed by CIMS during the OH-initiated oxidation of guaiacol under high NO_x conditions (GID-NO_x-UVA-1).

Grouping the species by carbon number and chemical family helps to illustrate the change in the product distribution over time, Figure 5.5. C_7 and C_6 species are dominant in the early stages of oxidation, however the split between CHO and CHON

for C_7 and C_6 species are interestingly the opposite of each other, with CHON species dominating the C_7 distribution and CHO dominating the C_6 distribution. This may be due to any C_6 CHON species being secondary in nature as the methoxy group must be lost first before reactions can proceed to incorporate NO_x into the compounds, thus these products take longer to form, especially under the low OH conditions. The relative intensities of C_7 CHO and CHON species also changes with time, with CHON species continuously increasing throughout the experiment, with a similar increase observed for C_6 . This is potentially due to further reactions of CHO species resulting in ring scission to produce the C_2 to C_5 species observed, while CHON species do not undergo similar processes.

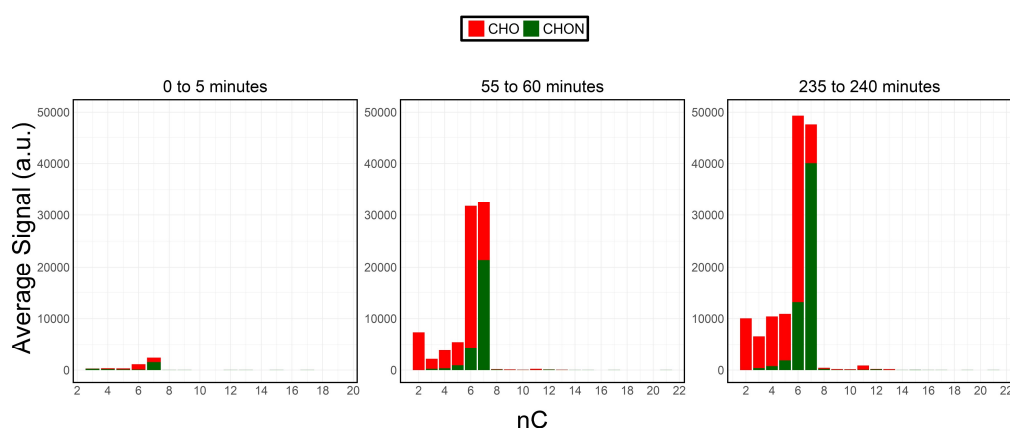


Figure 5.5 Distribution of oxidation products by carbon number and chemical family with respect to time under UVA conditions (GID- NO_x -UVA-1).

Figure 5.6 plots the oxidation state of the carbon, with data sized by mean ion intensity during each time period. It is clear that C_7 CHON and C_6 CHO species are the primary reaction products, however the growth of the C_6 CHON and C_2 CHO species with increased exposure to OH once again highlights the progression of the chemistry. As expected, further OH exposure leads to an increase in concentration of species with higher OS_C , however the UVA conditions do not allow for sufficient OH exposure to investigate the results of advanced aging.

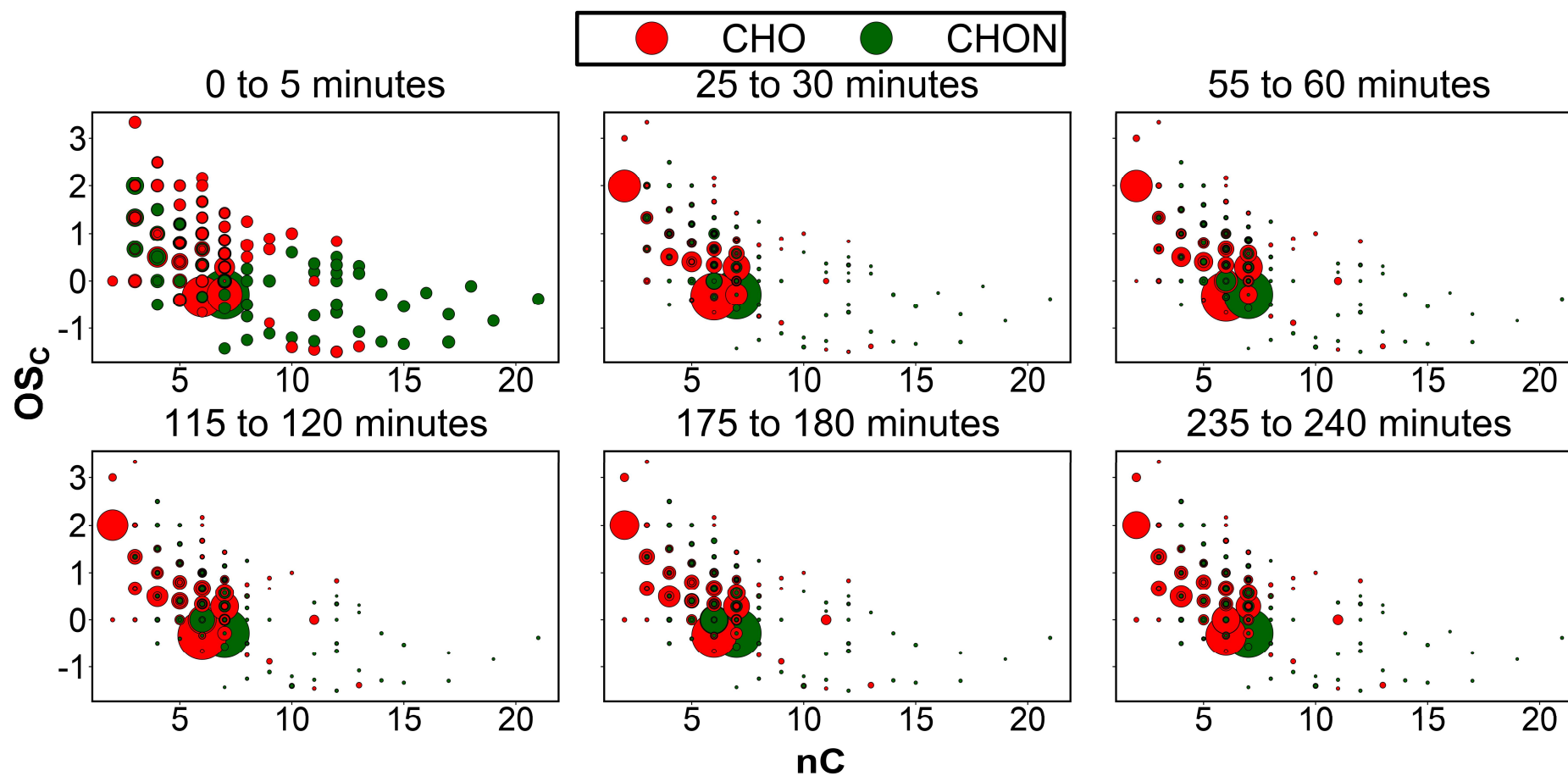


Figure 5.6 Plot of carbon oxidation state as a function of number of carbon atoms under UVA conditions and NO_x conditions (GID- NO_x -UVA-1).

NO_x experiments under UVC radiation

Experiments were also performed where UVA and UVC lamps were used to photolyse both HONO and H₂O₂. These experiments generated higher OH concentrations and allowed investigation into the advanced aging that takes place in the presence of NO_x.

The grouped by carbon time series for this experiment, Figure 5.7 once again shows the influence of the increased OH concentration under UVC conditions, with more drastic changes than what was observed in Figure 5.3. There is a clear initial spike in C₇ species followed by rapid decay, with corresponding increases in C₆, C₅, C₄ and C₃ species, while the relative contribution of C₅, C₄, C₃ and C₂ species continue to increase throughout the experiment.

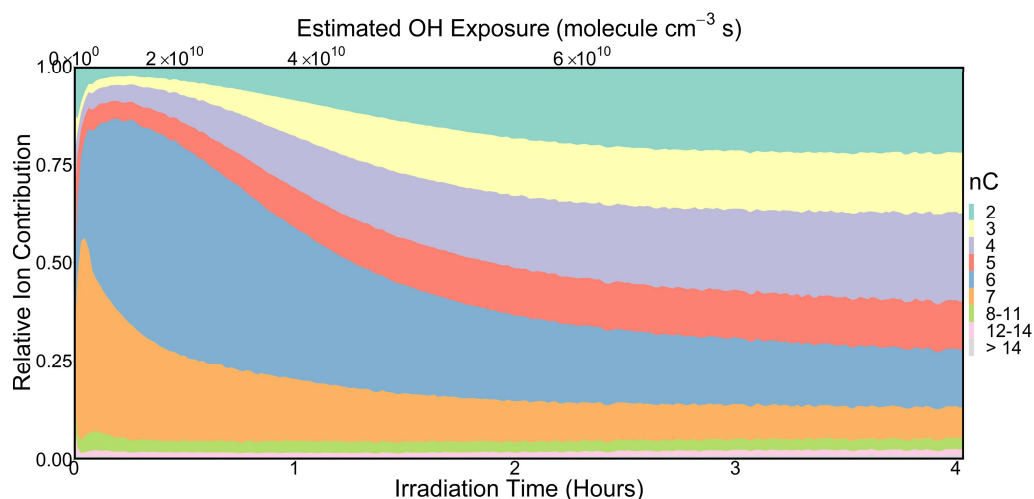


Figure 5.7 Time series of organic species grouped by carbon number for guaiacol photooxidation under UVC conditions (GID-NO_x-2).

Figure 5.8 plots mass spectra from experiments performed under UVA and UVC conditions after the same reaction times.

From the mass spectra, it is clear to see that while the intensity of the signals differs between the two conditions, generally the same species are observed under the different conditions. Of note is the significantly greater concentration of products under the UVC, high OH conditions which result in faster reactions and therefore greater yields in shorter time frames. Interestingly, by the third panel, oxidation has proceeded to such an extent in the high OH conditions that concentrations of all species have decreased significantly with no species representing even 10% of the air mass alone, which is a vast contrast to the earlier panels where the $\text{C}_6\text{H}_5\text{NO}_4$ signal contributes almost 25% alone. The wide spread of products in the third panel also highlights the multitude of reaction pathways which can be followed, resulting in a litany of oxidation products.

The mass spectra illustrate the significance of the NO_2 addition pathway in guaiacol oxidation as the two species which by far reach the highest concentration during this experiment are the first NO_2 addition products for the OH addition and methoxy loss pathways, namely $\text{C}_7\text{H}_7\text{NO}_4$ and $\text{C}_6\text{H}_5\text{NO}_4$. These spectra also show the rate of loss of these nitro products, particularly between the second and third panel as the ion signal for nitrocatechol ($\text{C}_6\text{H}_5\text{NO}_4$) has reduced by 50% in only 30 minutes. Predicted loss pathways for these nitro species are photolytic destruction due to the UV absorbing nature of the NO_2 group and partitioning into the particle phase, as the NO_2 group is deactivating towards further OH reaction.

It is interesting to note that the ring scission products of most importance after multiple hours of aging are primarily CHO species rather than CHON species, providing further evidence that further OH reactions of nitrophenol type compounds leading to more oxidised ring retaining and ring opening species are less likely to occur.

Classification of the organic species by nC and chemical family once again highlights the differences observed under higher OH conditions.

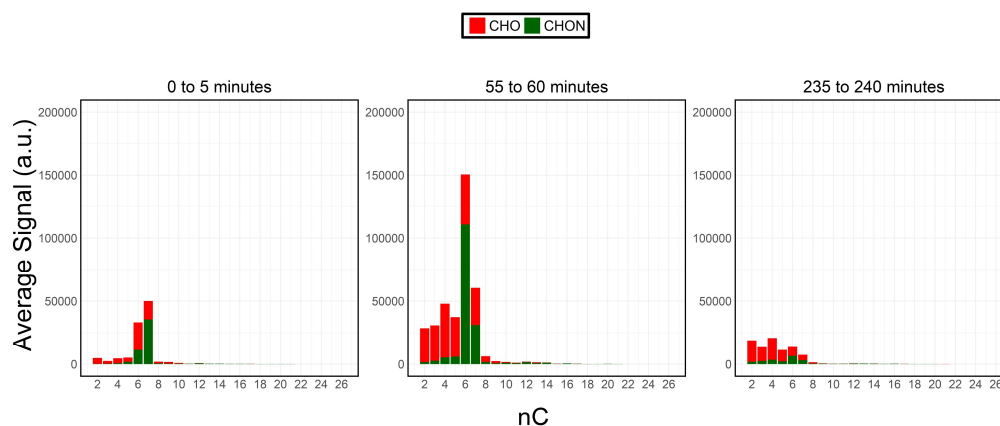


Figure 5.9 Distribution of organic species by carbon number and chemical family with respect to time under UV-C conditions (GID-NO_x-2).

As previously observed under UVA conditions, C₇ and C₆ species dominate initially with an inverse relationship in the CHO and CHON relative ratios. However, the advanced oxidation seen here results in C₆ CHON species becoming by far the highest concentration species with sufficient time, while the relatively low contributions from ring scission CHON species is also observed, with CHO species dominating the C₂ to C₅ distributions.

The OSc plots for this experiment, shown in Figure 5.10, show a shift towards an air mass dominated by more oxidised, smaller carbon chain species with respect to time, contrasting significantly with the UVA experiment plotted in Figure 5.7. The decline in C₇ and C₆ species at lower OSc values is pronounced in Figure 5.10, with increases in respective signals for C₇ and C₆ species with higher OSc ratios observed. This is most apparent when comparing the first and third panels, where the most significant red data point for a C₇ species in the first panel represents C₇H₈O₅, however by the fourth panel, this data point is smaller than the data point directly above it, representing C₇H₈O₆. Interestingly, despite the majority of ring scission species being CHO in nature, the increase in NO_x species containing 2 or 3 carbon atoms with an OSc between 1 and 3 that is observed, is indicative of peroxy acetyl nitrate (PAN) type compounds such as C₂H₃NO₅.

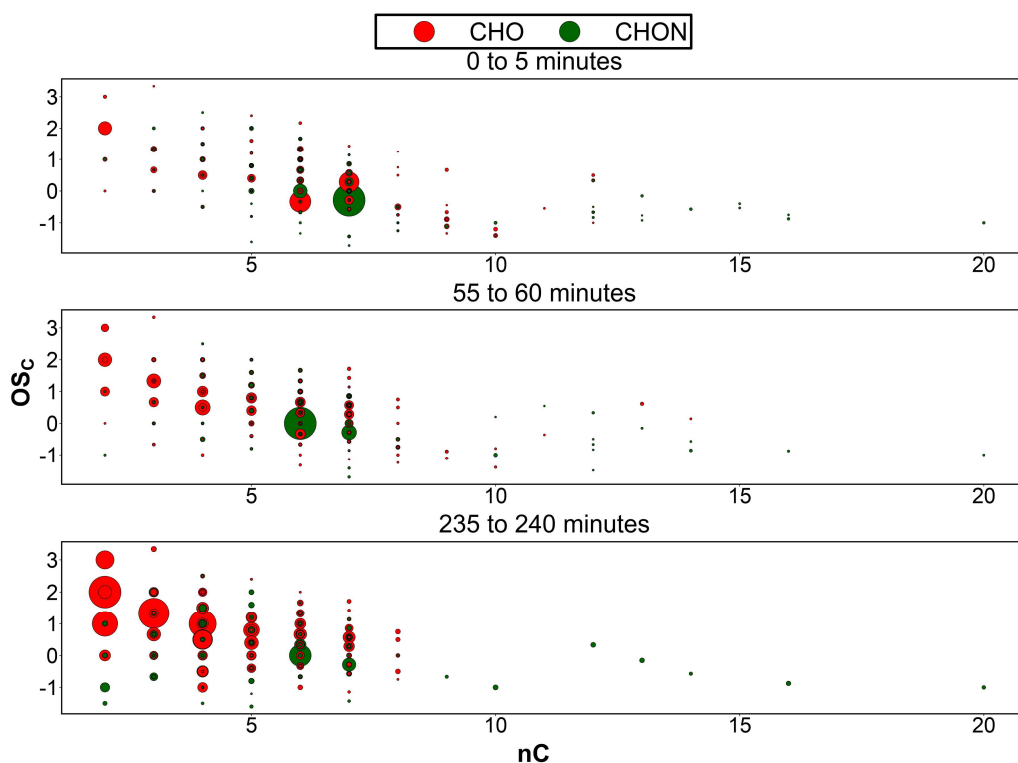


Figure 5.10 Plot of carbon oxidation state as a function of number of carbon atoms under UVC and NO_x conditions (GID-NO_x-2).

Low NO_x conditions

To elucidate the influence of NO_x chemistry on the oxidation of guaiacol, experiments were performed in low NO_x conditions for comparison, where photolysis of hydrogen peroxide (H₂O₂) by UVC radiation was the only source of hydroxyl radicals. These experiments yielded different results to the NO_x oxidation experiments, as expected, with the most obvious difference being the lack of significant contributions from NO_x species in these spectra, although some NO_x species are detected, likely due to of nitrous acid from the chamber wall reactions during the experiments (Pang et al., 2022; Luo et al., 2023).

Illustrated in Figure 5.11 are the comparison mass spectra between a UVC NO_x experiment (GID-NO_x-2) and a UVC low NO_x experiment (GID-2). Similar primary species are observed between the two experiments with the exception of the CHON species, and there are significant contributions from similar ring opening products due to the advanced oxidation between both experiments. The ring scission products are shown to evolve relatively quickly, and after one hour, most of the dominant ions are the result of ring scission pathways.

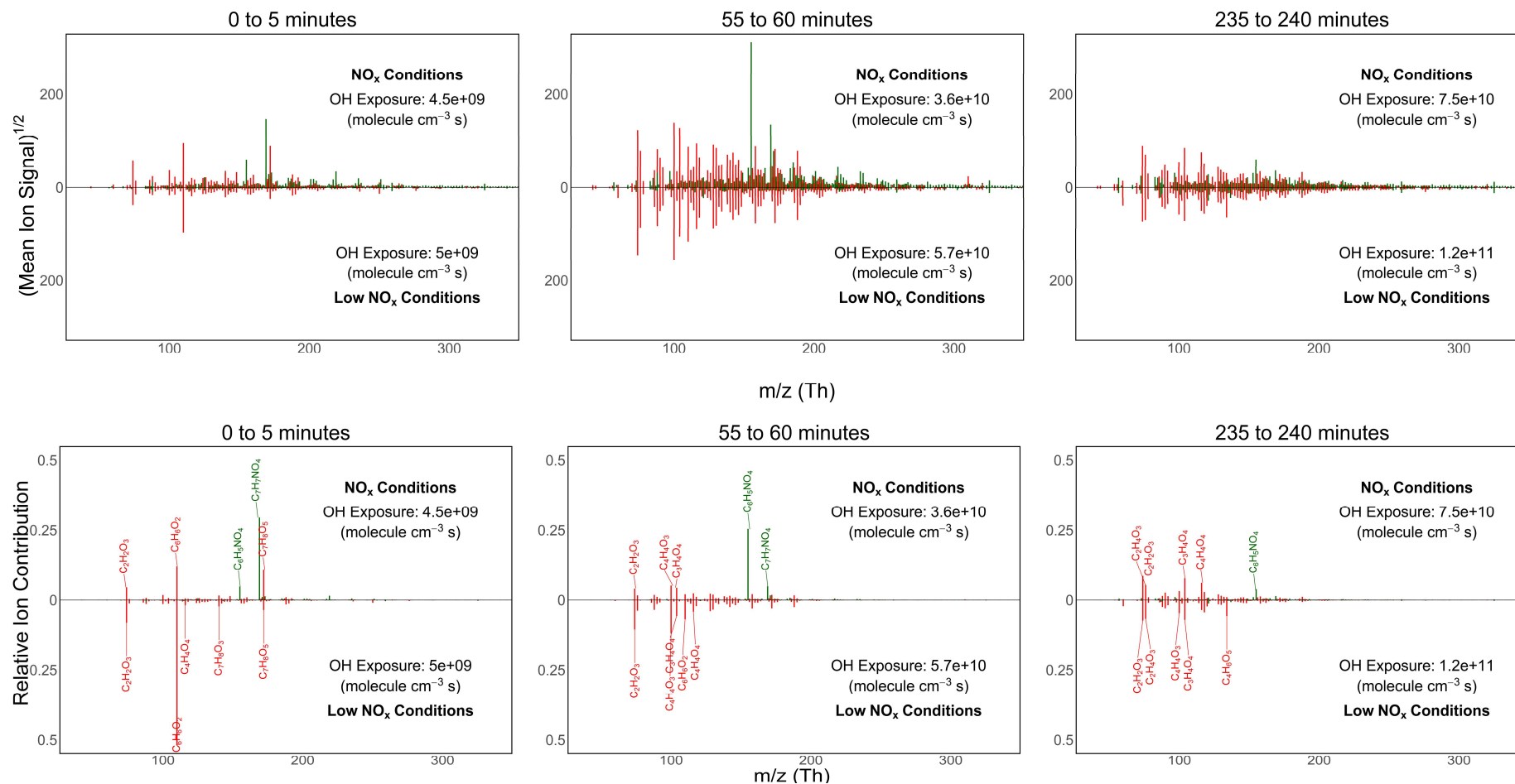


Figure 5.11 Comparison mass spectra from guaiacol photooxidation experiments under low and high NO_x conditions (GID-NO_x-2 and GID-2).

As previously, the increased OH concentrations from UVC radiation result in much more chemical aging of the air mass, with similar results shown in Figure 5.12 for the low NO_x experiment. Once again, species with low OS_C are initially dominant, but with sufficient time the ring scission species with higher carbon oxidation states become the most significant species. The evolution of CHON species is also observed after significant amounts of time as HONO evolves from the chamber walls, however, no evolution of the primary CHON species previously observed is seen, as the precursor is almost entirely reacted before HONO evolution plays a significant role in the chemistry.

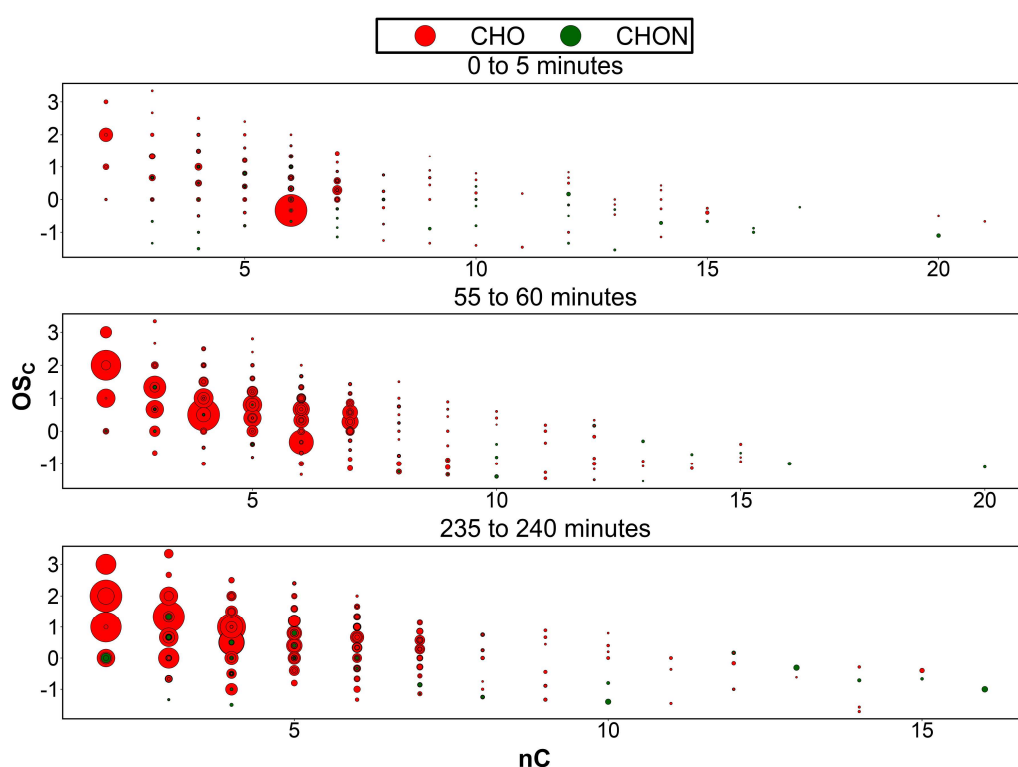
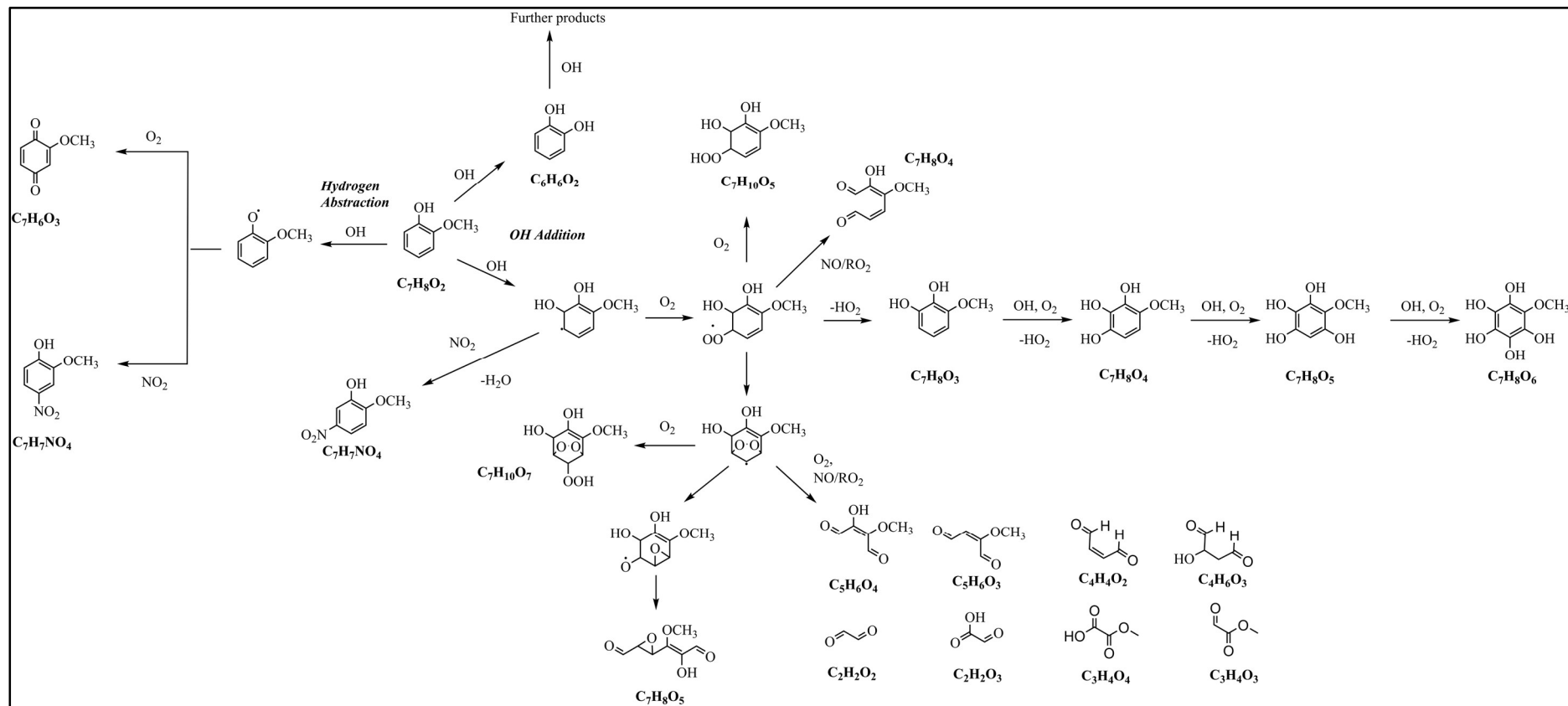


Figure 5.12 OS_C plots for guaiacol photooxidation in low NO_x conditions (GID-2).

5.4.3 Mechanistic Discussion of Guaiacol Oxidation

Oxidation of guaiacol is known to proceed primarily through two pathways, namely OH addition to the aromatic ring and hydrogen abstraction from the -OH group (Yee et al., 2013; Lauraguais et al., 2014; An et al., 2019). A simplified mechanism which incorporates these reaction pathways and expected reaction products is given in Scheme 5.1. The CIMS was able to detect many of the expected reaction products and follow their evolution during the oxidation process, providing useful information on their subsequent reactivity. Figure 5.13 shows the time series obtained for some of the main primary products, $C_7H_8O_3$, $C_6H_6O_2$, $C_7H_7NO_4$ and $C_7H_6O_3$ under UVA and UVC conditions. $C_7H_8O_3$ reaches its maximum before any of the other species and undergoes significant decay, even under UVA conditions, suggesting that this species is highly reactive. In contrast, $C_7H_6O_3$ takes the longest time to reach its maximum concentration under UVC conditions and has the slowest rate of decay, suggesting that this species may be more stable towards further reaction and partitioning to the particle phase. This observation supports the assignment of $C_7H_6O_3$ to a quinone, as indicated in Scheme 5.1. In the following discussion, the current mechanistic understanding of aromatic oxidation chemistry is used to help interpret the results obtained by CIMS and elucidate the key products and processes that govern the reaction system.



Scheme 5.1 Detailed reaction scheme for guaiacol photooxidation adapted from Yee et al, 2013.

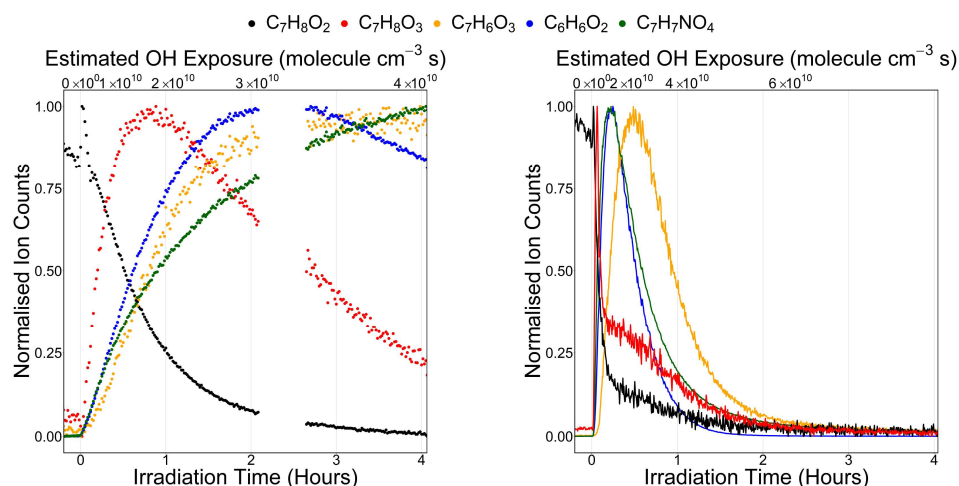


Figure 5.13 Normalised time series of selected primary products from guaiacol photooxidation under UVA and UVC conditions (GID-NO_x-UVA-1 and GID-NO_x-2).

OH Addition pathway

Methoxy retention

The results clearly show that one of the primary pathways for guaiacol photooxidation occurs via addition of a hydroxyl group to the aromatic ring, forming C₇H₈O₃. In accord with previous studies (Yee et al., 2013; An et al., 2019) this species is assigned to an isomer of methoxycatechol. As shown in Figure 5.13 and Figure 5.14, this species underwent rapid formation and significant decay under both UVA and UVC radiation, indicating that once formed, it undergoes further reaction with OH, e.g. to produce C₇H₈O₄, which in turn may also undergo reaction to produce C₇H₈O₅ and subsequently C₇H₈O₆. Sequential OH addition has been observed for various phenol compounds, including cresol, phenol and methoxyphenols (Zhao et al., 2014; Schwantes et al., 2017; Mayorga et al., 2021; Yee et al., 2013), as well as 4-methylcatechol (4-MC) in this work (see Chapter 4). As illustrated in Scheme 5.1, C₇H₈O₄ and C₇H₈O₅ can also be produced from other reaction pathways, thus making it difficult to accurately assign these ion signals to a specific species. It is also important to note that all of the attributed products are tentatively proposed based on the literature and known pathways for atmospheric oxidation (Calvert et al., 2002; Yee et al., 2013). As well as sequential OH addition, a range of other reaction pathways are possible for the adducts and radicals generated during the oxidation process, including epoxide formation and ring scission to produce dicarbonyls and other compounds with lower carbon numbers. All of the species in Scheme 5.1 were detected in the UVC experiments except C₂H₂O₂ and C₄H₄O₂, predicted to be glyoxal

and butenedial respectively, but this is assumed to be because of low I-CIMS sensitivity to these aldehydes. The time series for selected products generated via the OH addition pathway is shown in Figure 5.14.

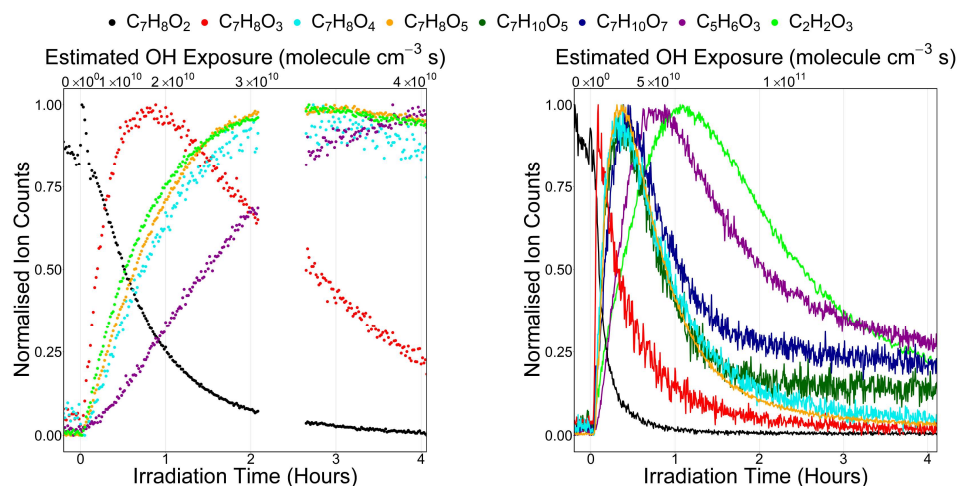


Figure 5.14 Normalised time series of selected products generated via the OH addition pathway under UVA and UVC conditions (GID-NO_x-UVA-1 and GID-2).

Interestingly, C₇H₁₀O₅ and C₇H₁₀O₇, assigned to hydroperoxide compounds by Yee et al. (2013), were not observed under UVA conditions, however both were observed under UVC conditions. Yee et al (2013) proposed that those species were derived from reaction of peroxy radicals with HO₂, however in this work the species were observed with similar yields under both low and high NO_x conditions, suggesting that they are not formed via the HO₂ pathway. It is proposed that they derive from autooxidation pathways via reaction with O₂. These C₇H₁₀O_x species, along with C₇H₈O₄ and C₇H₈O₅, all follow similar temporal trends in relation to their formation and decay, indicating that the pathways to produce these compounds are in competition with each other, as outlined in 5.1. As indicated above, C₇H₈O₄ and C₇H₈O₅ can also form via sequential OH addition and without structure-based analysis via offline mass spectrometry it is difficult to ascertain which of the isomers is formed. Interestingly, C₂H₂O₃ and C₅H₆O₃ evolve at different rates, noticeably under UVA conditions which suggests that there is a different pathway for C₂H₂O₃ formation.

Loss of aromaticity OH addition

A range of non-aromatic products were detected, primarily under UVC conditions. Some of these species retain all of the carbon, e.g. C₇H₁₀O₅ and C₇H₁₀O₇, while a large number of C₂ – C₅ compounds were also produced. Further analysis of the C₂H₂O₃

evolution revealed a similarity in the temporal trend of this species and C₅H₈O₅, Figure 5.15. These formulae have a combined molecular formula of C₇H₁₀O₈, however no C₇H₁₀O_x species were observed to form under UVA conditions. This may give some indication that under the conditions employed in those experiments, autooxidation with O₂ occurs leading to ring scission of the intermediates rather than retention of the carbon, forming C₇H₁₀O_x species. Autooxidation mechanisms giving rise to species with higher numbers of hydrogen atoms than expected in oxidation products have been proposed for benzene oxidation and may offer some explanation for the formation of these ring scission species (Priestley et al., 2021; Molteni et al., 2018). In Figure 5.15 a range of other ring scission products related to those presented in Scheme 5.1 are also plotted, which may arise from pathways involving ring scission rather than stabilisation of species which have lost their aromaticity.

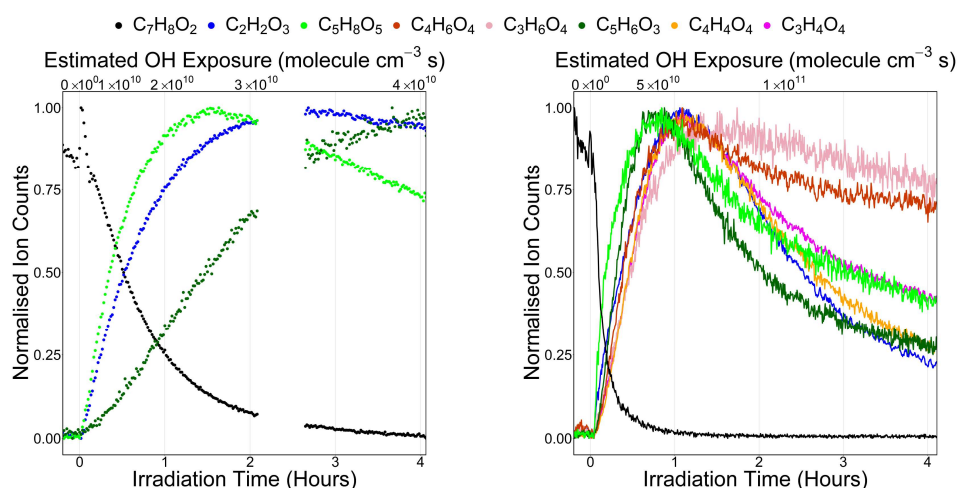
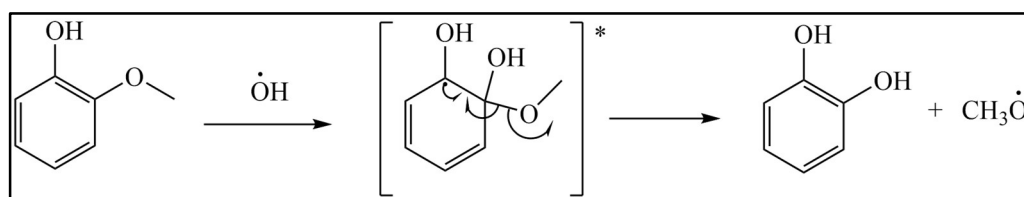


Figure 5.15 Normalised time series of ring scission species from the OH addition pathway under UVA and UVC conditions (GID-NO_x-UVA-1 and GID-2).

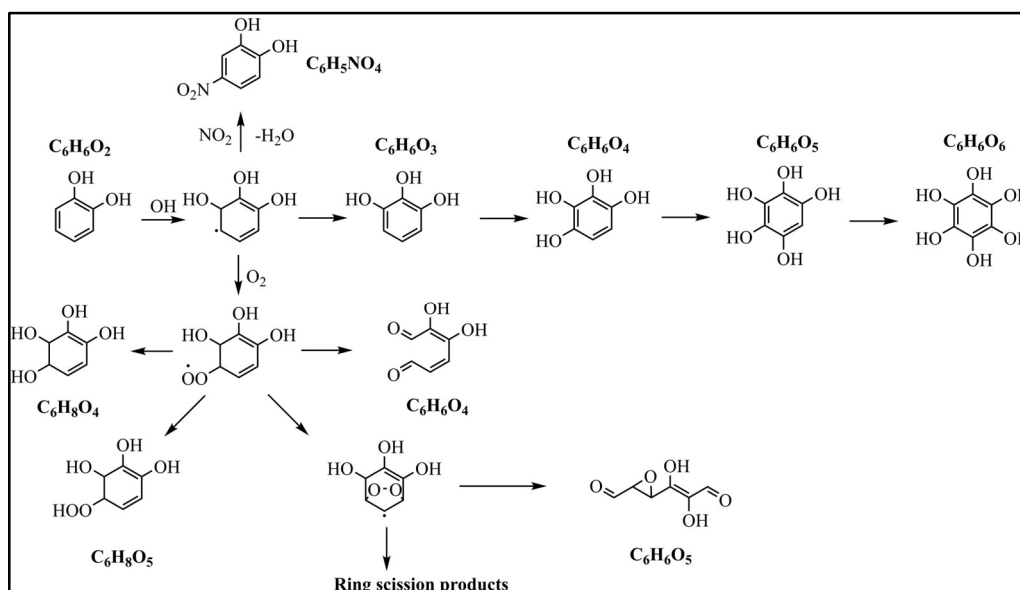
Methoxy loss

One of the primary oxidation pathways previously observed in guaiacol oxidation experiments is loss of the methoxy ($-\text{OCH}_3$) group resulting in the formation of catechol (Lauraguais et al., 2014; Yee et al., 2013). The proposed mechanism involves OH addition *ipso* to the methoxy group to form an energised radical which then rearranges to form catechol with the release of a methoxy ($\text{CH}_3\text{O}^\bullet$) radical, Scheme 5.2. The main fate of the methoxy radical is reaction with O_2 to produce formaldehyde and HO_2 .



Scheme 5.2 Proposed mechanism for the formation of catechol via the loss of the methoxy group from guaiacol.

The CIMS data shows that $\text{C}_6\text{H}_6\text{O}_2$ readily undergoes further reaction, to produce a range of $\text{C}_6\text{H}_6\text{O}_x$ and $\text{C}_6\text{H}_8\text{O}_x$ species, with $\text{C}_6\text{H}_5\text{NO}_x$ also observed in experiments performed under high NO_x conditions. Based on previous studies (Yee et al., 2013; Fredrickson et al., 2022), a proposed mechanism for the formation of C_6 products resulting from the reaction of $\text{C}_6\text{H}_6\text{O}_2$ with OH via the addition pathway is illustrated in Scheme 5.3.



Scheme 5.3 Proposed reactions and products arising from the OH-initiated oxidation of catechol via the addition pathway.

The CIMS data show that all of the proposed $C_6H_6O_x$ species were formed during the experiments, with the time series seemingly providing support for the sequential OH addition pathway, Figure 5.16. However $C_6H_6O_x$ species where $x > 2$ can also be formed via OH addition *ipso* to the methoxy group of $C_7H_8O_x$ species, e.g., $C_6H_6O_4$ could be produced from *ipso* OH addition to the methoxy group of $C_7H_8O_4$.

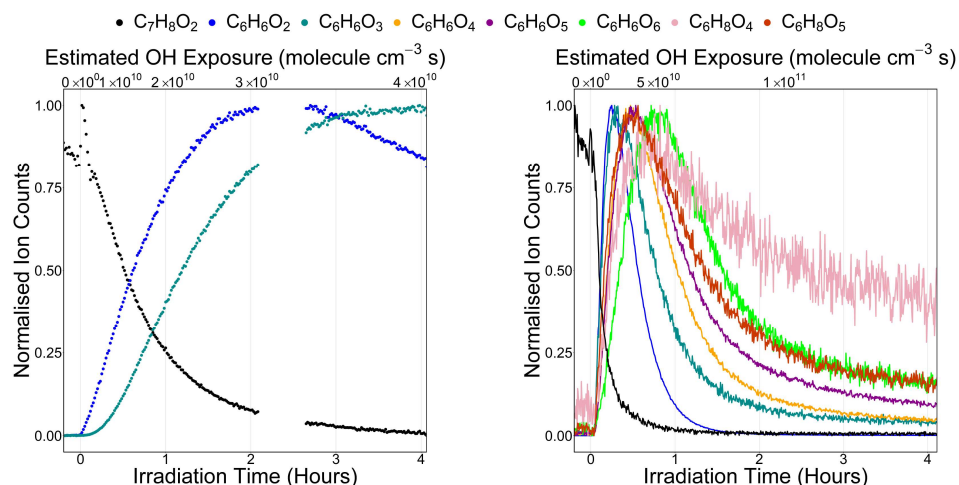


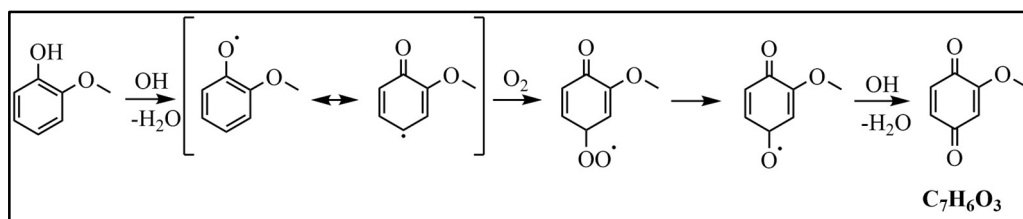
Figure 5.16 Absolute and normalised time series of methoxy loss products under UVA and UVC conditions (GID-NO_x-UVA-1 and GID-2).

The slower chemistry occurring under UVA conditions only generated one additional C_6 species, $C_6H_6O_3$, which has a characteristic time profile for a secondary product. The time series for the numerous species detected under UVC conditions highlights some interesting observations. $C_6H_6O_3$ is the first species detected after catechol, followed by three species ($C_6H_8O_5$, $C_6H_6O_4$ and $C_6H_6O_5$), which peaked together suggesting that their formation routes are competitive with each other. $C_6H_8O_4$ also appears at this time but peaks later in the reaction and has a very noisy signal, indicating that this is an unfavourable pathway. A C_6 epoxide could also correspond to the $C_6H_6O_5$ signal, and the formation of this species from the peroxy radical shown in Scheme 5.3 would compete with the other pathways. Interestingly, the Yee et al. (2013) study highlight the formation of a bicyclic ketone with the molecular formula $C_6H_6O_5$ as one of the primary products of guaiacol oxidation, however, the late appearance in this study indicates that it is more likely to be a catechol oxidation product.

Hydrogen abstraction pathway

Low NO_x conditions

Another possible oxidation pathway for guaiacol is H-atom abstraction followed by oxidation to produce C₇H₆O₃. This reaction pathway has been proposed theoretically (An et al., 2019) but previous experimental studies do not make reference to this pathway (Kitanovski et al., 2014; Lauraguais et al., 2014; Yee et al., 2013). It is however reported as a potential pathway in an experimental and theoretical study of NO₃ radical reactions with guaiacol (Yang et al., 2016). Theoretical calculations of the H-abstraction pathway suggest that abstraction from the hydroxyl group is the most favourable pathway with a Gibbs free energy of activation, $\Delta G^\ddagger$, of 8.48 kcal mol⁻¹ and a change in Gibbs free energy, ΔG , of -30.15 kcal mol⁻¹, making this site the most favourable for attack. Following delocalisation of the radical through the aromatic ring and subsequent reaction with O₂, further reaction with NO or RO₂, and finally a reaction with either OH or O₂ resulting in H₂O or HO₂ formation respectively, a methoxy quinone compound can form. This potential reaction scheme is outlined in Scheme 5.4.



Scheme 5.4 Hydrogen abstraction pathway of guaiacol oxidation.

Multiple C₇H₆O_x species are observed in the oxidation experiments, possibly resulting from H-atom abstraction of a more oxidised C₇H₈O_x product or further reaction (OH addition) of the methoxy quinone species. A time series for some of these species is shown in Figure 5.17, with a clear sequential oxidation pattern observed.

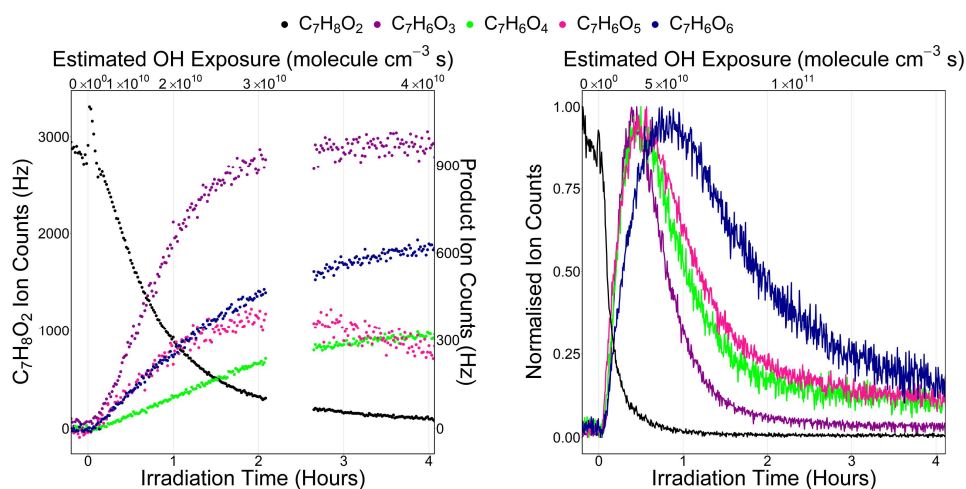


Figure 5.17 Scaled and normalised time series of $C_7H_6O_x$ species formed from the hydrogen abstraction pathway under UVA and UVC conditions (GID- NO_x -UVA-1 and GID-2).

Under UVA conditions there is a clear increase in $C_7H_6O_3$ immediately upon irradiation and there are also increases in $C_7H_6O_5$ and $C_7H_6O_6$ without significant time delay, while $C_7H_6O_4$ takes longer to evolve. The appearance of $C_7H_6O_5$ and $C_7H_6O_6$ before $C_7H_6O_4$ possibly indicates that an autooxidation reaction is responsible for the formation of these more highly oxidised species.

There were also a similar set of CIMS signals detected for $C_6H_6O_x$ species, suggesting that parallel chemistry may be occurring for catechol. For example, H-atom abstraction from catechol would lead to the formation of $C_6H_4O_3$. Time series for some of these species can be seen in Figure 5.18, showing a sequential formation with each OH addition.

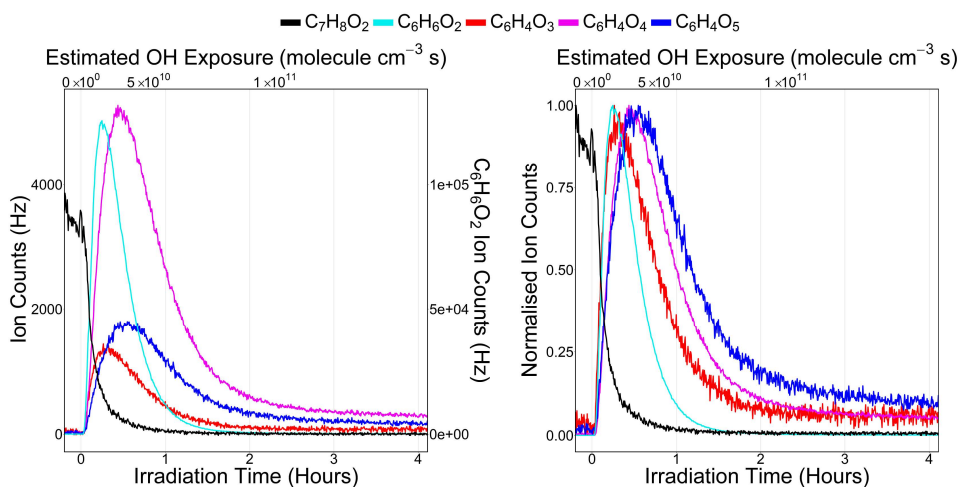


Figure 5.18 Scaled and normalised time series of $C_6H_4O_x$ species formed from the H-abstraction pathway of catechol oxidation under UVC conditions (GID-2).

NO_x conditions

As observed in other studies of guaiacol oxidation in the presence of NO_x, nitroguaiacols are some of the most dominant reaction products. There is some debate regarding the formation of the nitroguaiacols, and nitrophenol species in general, as they can originate via the OH addition or hydrogen abstraction reaction pathways (Olariu et al., 2002; Lauraguais et al., 2014), however regardless of their formation pathway, they are observed in abundance during high NO_x experiments. The primary CHON product is C₇H₇NO₄, with more highly oxidised C₇H₇NO_x species readily observed, Figure 5.19.

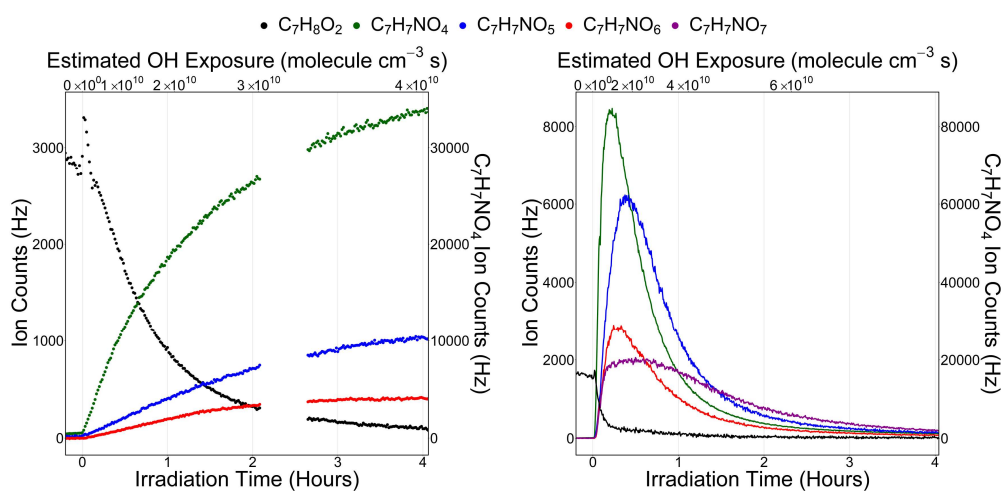


Figure 5.19 Scaled time series of C₇H₇NO_x species under UVA and UVC conditions (GID-NO_x-UVA-1 and GID-NO_x-2).

Under UVA conditions, C₇H₇NO₄ is observed immediately after irradiation, while the more highly oxidised species appear somewhat later. Under UVC conditions, the species are formed much more rapidly and react further. Interestingly, C₇H₇NO₇ does not decay in a similar manner to the other species, suggesting that for some time its rate of decay and formation are equal. This species could form from oxidation of C₇H₈O₅ or via some other pathway, with its primary loss pathway likely to be photolysis or partitioning to the particle phase. NO_x incorporation into the methoxy loss pathway and the hydrogen abstraction pathways was also observed, Figure 5.20.

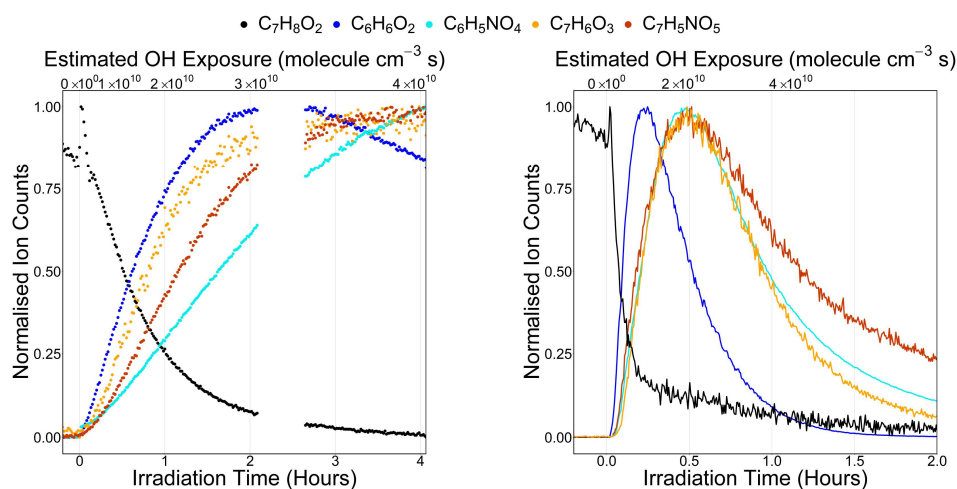


Figure 5.20 Time series of hydrogen abstraction, NO_x products formed from both guaiacol and catechol oxidation under UVA and UVC conditions (GID- NO_x -UVA-1 and GID- NO_x -2).

Accretion products

Hydroxyl radical oxidation of guaiacol was also found to result in the formation of a range of C_{12} , C_{13} and C_{14} compounds, which are likely the result of reactions between various C_6 and C_7 species formed during the oxidation process. The primary C_{12-14} species were only detected in the gas phase when benzene (C_6H_6) was the reagent ion as the clustering of iodide with these species is inefficient due to the high ratio of carbon to oxygen atoms. The time series for the C_{12-14} species were very similar to other primary products, with these accretion products forming almost immediately following irradiation, Figure 5.21. Also shown are some more highly oxidised C_{12-14} species which were detected in experiments where iodide was the reagent.

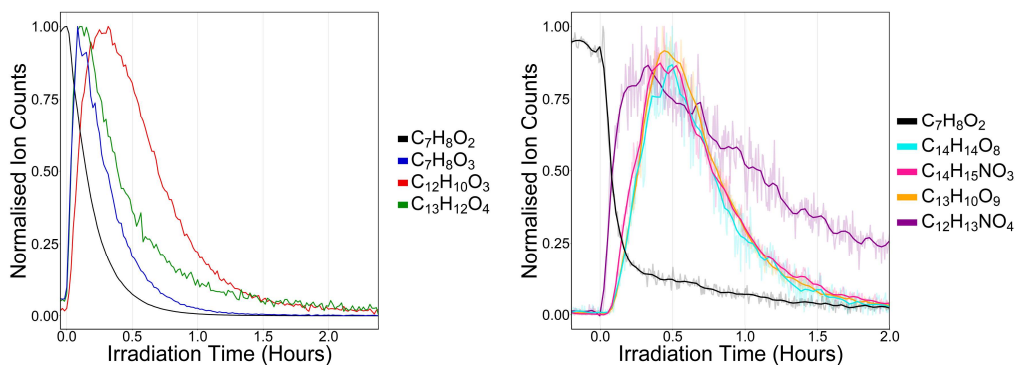
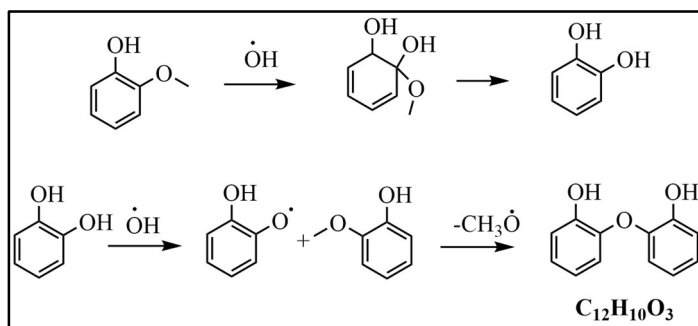


Figure 5.21 Comparison of accretion product formation between benzene and iodide experiments highlighting primary and more oxidised species (GBD-1 and GID- NO_x -2). Note that due to Benzene CIMS inability to detect the OH precursors, no estimation is made for OH exposure.

The formation of higher molecular weight products through accretion reactions has previously been observed during aromatic photooxidation (Priestley et al., 2021; Strollo and Ziemann, 2013; Ye et al., 2020). The reactions typically involve radicals ($\text{RO}\cdot$ or $\text{RO}_2\cdot$) reacting with themselves, other radicals or molecules. For example, a radical-radical reaction involving two $\text{RO}\cdot$ radicals would be expected to form a peroxy species ROOR . An example of a potential accretion reaction during the OH-initiated oxidation of guaiacol is shown in Scheme 5.5.



Scheme 5.5 Potential Dimer formation pathway.

In the proposed scheme above, $\text{C}_6\text{H}_6\text{O}_2$ is proposed to form via loss of the methoxy group following *ipso* addition to the methoxy group of guaiacol, and this diol may then undergo subsequent reaction with OH to form an $\text{RO}\cdot$ radical which may then attack a second guaiacol molecule *ipso* to the methoxy group, resulting in a dimer being formed through an oxygen bridge. A range of accretion products with 12, 13 or 14 carbon atoms were observed in these experiments, suggesting that any combination of C_6 and C_7 radicals can undergo reactions which result in dimer formation.

5.4.4 Gas Phase Photolysis of Nitrophenol Compounds

Nitrophenol compounds are known to be particularly photolabile due to the strong absorption capacity of the NO_2 functional group (Chen et al., 2011), with photolysis being the dominant pathway for degradation of nitrophenol compounds in the atmosphere (Bejan et al. 2006, Bejan et al. 2007; Roman et al. 2022; Sangwan and Zhu 2018; Zhao et al. 2010). Photolysis of these nitrophenol compounds can result in the release of HONO and the formation of a reactive intermediate species which may then undergo reaction with OH radicals. Since nitrophenol compounds underwent significant decay in the high NO_x experiments presented in this work, the HONO signals measured by CIMS have been evaluated. Figure 5.22 shows a marked

difference in the HONO decay for experiments under UVA and UVC conditions. Under UVA photolysis, the decay of HONO is quite smooth and has a relatively constant first order decay rate of $1.18 \times 10^{-4} \text{ s}^{-1}$, calculated using the following equation:

$$k = \ln \left(\frac{[\text{HONO}]_t}{[\text{HONO}]_0} \right) / t \quad \text{Equation 5.1}$$

where k is the rate of decay, $[\text{HONO}]_t$ is the concentration at time t and $[\text{HONO}]_0$ is the initial concentration. Under UVC conditions, there is a very clear change in the decay rate of HONO shortly after photolysis is initiated. The initial decay rate is $9.03 \times 10^{-3} \text{ s}^{-1}$, but after a few minutes of irradiation there is a sharp change as the decay rate decreases by an order of magnitude to $2.28 \times 10^{-4} \text{ s}^{-1}$. Since the light intensity was not changed during the experiments, it is safe to assume that the photolysis rate remained constant, indicating that the observed change in the HONO decay rate is due to a secondary source of HONO.

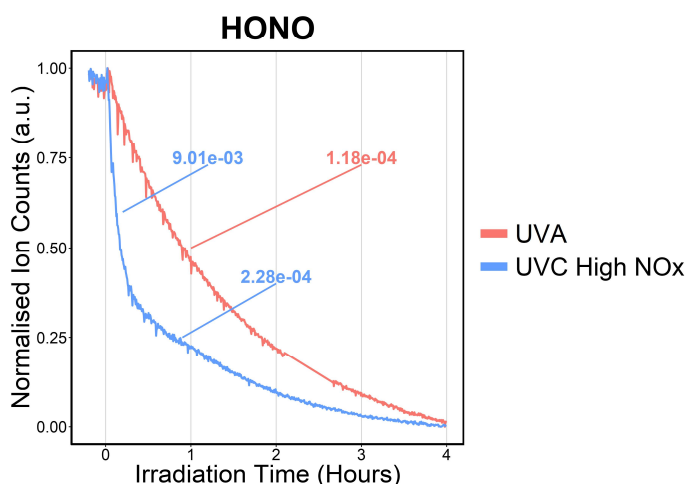
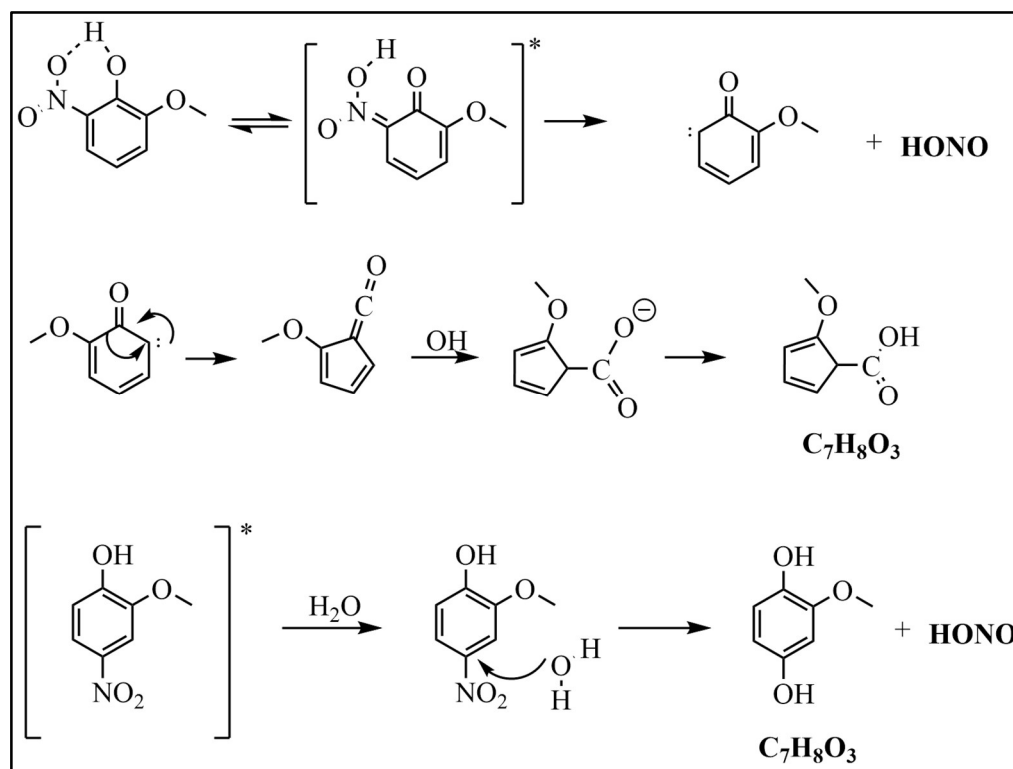


Figure 5.22 Normalised HONO decay rates under UVA and UVC experimental conditions (GID-NO_x-UVA-1 and GID-NO_x-2).

The HONO source is most likely photolysis of the nitroguaiacol ($\text{C}_7\text{H}_7\text{NO}_4$) and nitrocatechol ($\text{C}_6\text{H}_5\text{NO}_4$), the major gas phase nitrophenol compounds produced in these experiments. Nitrocatechol has previously been shown to readily photolyse under conditions similar to those used here (Roman et al., 2022) with nitroguaiacol expected to undergo a similar transformation. Potential reaction mechanisms for the photolysis of nitroguaiacol, based on the work conducted by Alif et al (1991) and Bejan et al (2006), is shown in Scheme 5.6 (Alif et al., 1991; Bejan et al., 2006). Bejan

et al. (2006) proposed that a hydrogen bonded stabilised intermediate can form when the NO₂ group is ortho to the OH group which can then undergo decomposition, releasing HONO and a radical which reacts further. Alif et al. performed photolysis of nitrophenol in solution and found that a range of products including catechol and cyclopentadiene carboxylic acids, formed after initial ketene formation.



Scheme 5.6 Potential mechanisms for the photolysis of nitroguaiacol.

Interestingly, both reaction mechanisms lead to the formation of products with the same molecular formula, C₇H₈O₃, which also corresponds to the formula of the first hydroxylated guaiacol discussed above. The time series for this species in experiments performed under different conditions is shown in Figure 5.23. Under UVA and high NO_x conditions, the formation of C₇H₈O₃ is followed by a relatively slow decay. Under UVC and high NO_x conditions, C₇H₈O₃ is formed very rapidly and initially undergoes a very rapid decay too. However, the decay rate subsequently slows, suggesting that a source of C₇H₈O₃, e.g., nitroguaiacol photolysis, becomes activated. Under UVC and low NO_x conditions, this source of C₇H₈O₃ is not present and the signal is most likely due to the hydroxylated product only.

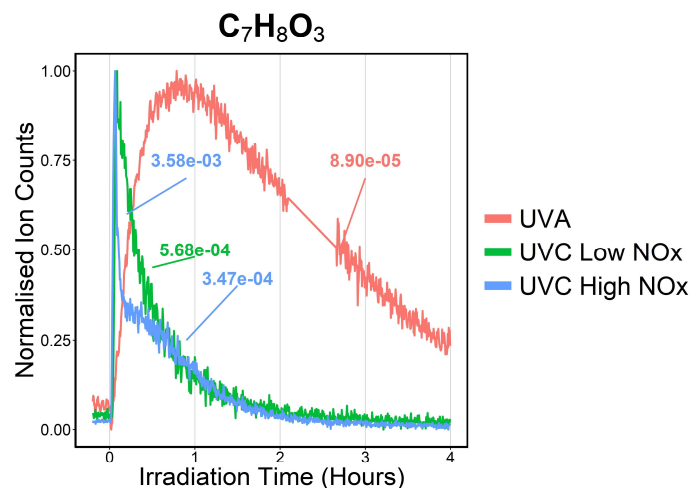


Figure 5.23 Time series of $C_7H_8O_3$ under various experimental conditions (GID- NO_x -UVA-1, GID-2 and GID- NO_x -2).

$C_6H_3NO_4$ also undergoes an unusual decay pattern, which may suggest that this species has another formation pathway, potentially the photolysis of the dinitro species $C_6H_4N_2O_6$ or $C_6H_4N_2O_7$ which were detected, with the normalised plot for these two species shown in Figure 5.24. Although the dinitro species do not have a trace which is as distinct as the other species there are significant increases in their concentrations upon irradiation, and their point of decay coincides with the point where the decay of $C_6H_3NO_4$ slows. Photolysis of the dinitro group could yield the loss of one of the nitro groups potentially leading to the formation of either nitrous (HONO) acid or nitric (HNO_3) acid. Adding either of these two compounds to the molecular formula $C_6H_3NO_4$ results in the two dinitro species detected, $C_6H_4N_2O_6$ and $C_6H_4N_2O_7$, offering further support for this theory.

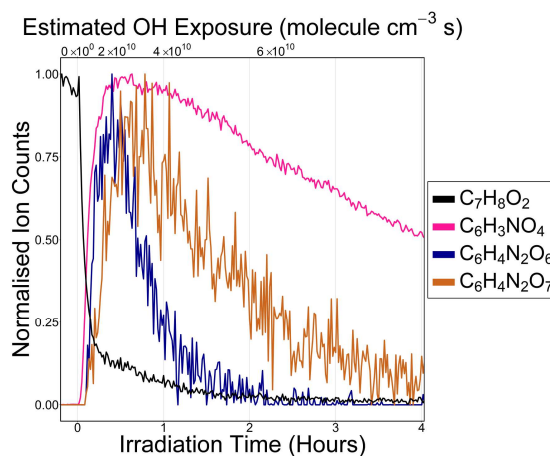


Figure 5.24 Potential photolysis of C_6 dinitro species resulting in the loss of a nitro group (GID- NO_x -2).

5.4.5 Secondary Organic Aerosol Formation

Particle Formation and Growth

Significant levels of SOA formation were observed in experiments where UVC radiation was used. A typical plot of particle formation and growth is shown in Figure 5.25. In this particular experiment, particles with a wide size distribution centring around 25 nm, are observed within the first 4 minutes of photooxidation. A more Gaussian distribution is observed after 20 minutes, with significant growth in particle size to around 70 nm in diameter. Further evolution over time results in significantly reduced particle number concentration and broader size distribution. The data presented in Figure 5.25 is consistent with rapid nucleation of highly oxidised products to produce a large number of small particles, followed by agglomeration to produce a smaller number of larger particles with higher mass.

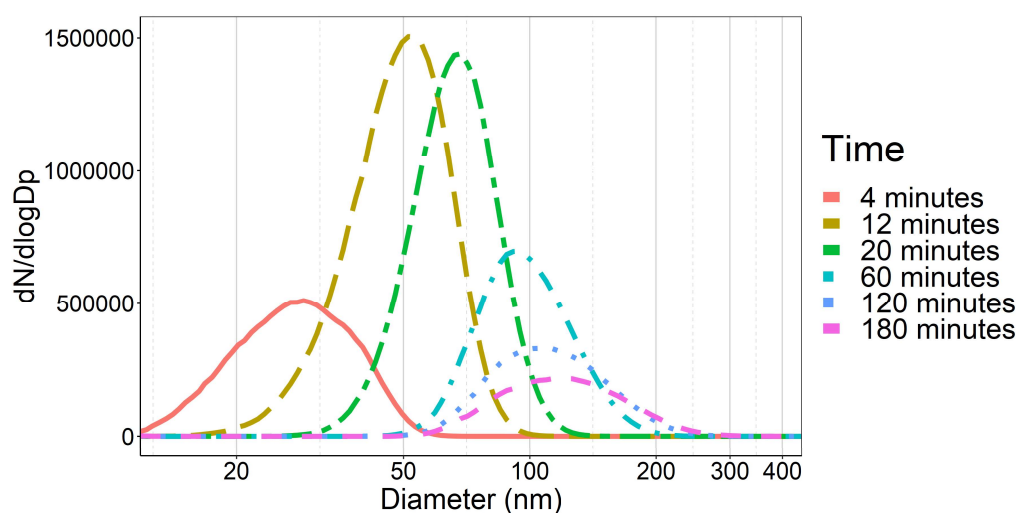


Figure 5.25 SMPS particle size distribution evolution with time (GID-2).

An alternative method of plotting particle growth is using so-called “banana plots”, where particle diameter is plotted against time, with the colour representing particle number concentration (Heintzenberg et al., 2007; Healy et al., 2012; Kerminen et al., 2018; Meng et al., 2020; Lin et al., 2022). Figure 5.26 illustrates a banana plot for same experiment as Figure 5.25 highlighting the rapid formation and growth with the highest concentration of particles, shown by the deep red, observed within the first 30

minutes. As time progresses, particle number decreases while the particles remain centred around 100 nm indicating little to no further growth at this point.

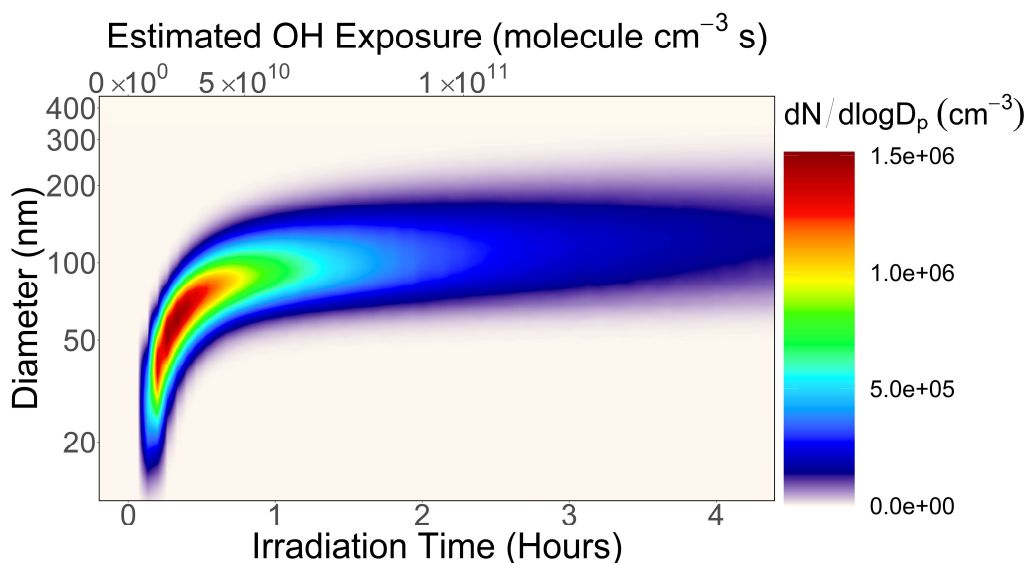


Figure 5.26 Banana plot showing particle growth and evolution for guaiacol photooxidation (GID-2).

5.4.6 Particle Phase Analysis

Particle Phase Product Analysis

Use of the FIGAERO inlet allows for molecular analysis of the particle phase by thermal desorption of SOA collected on a PTFE filter. Particle phase CIMS analysis was performed on all experiments where iodide was used as the reagent ion and sufficient particle formation occurred.

Comparison of mass spectra from experiments performed under high and low NO_x conditions which have undergone similar degrees of processing are given in Figure 5.27. Most of the major ions are observed under both experimental conditions.

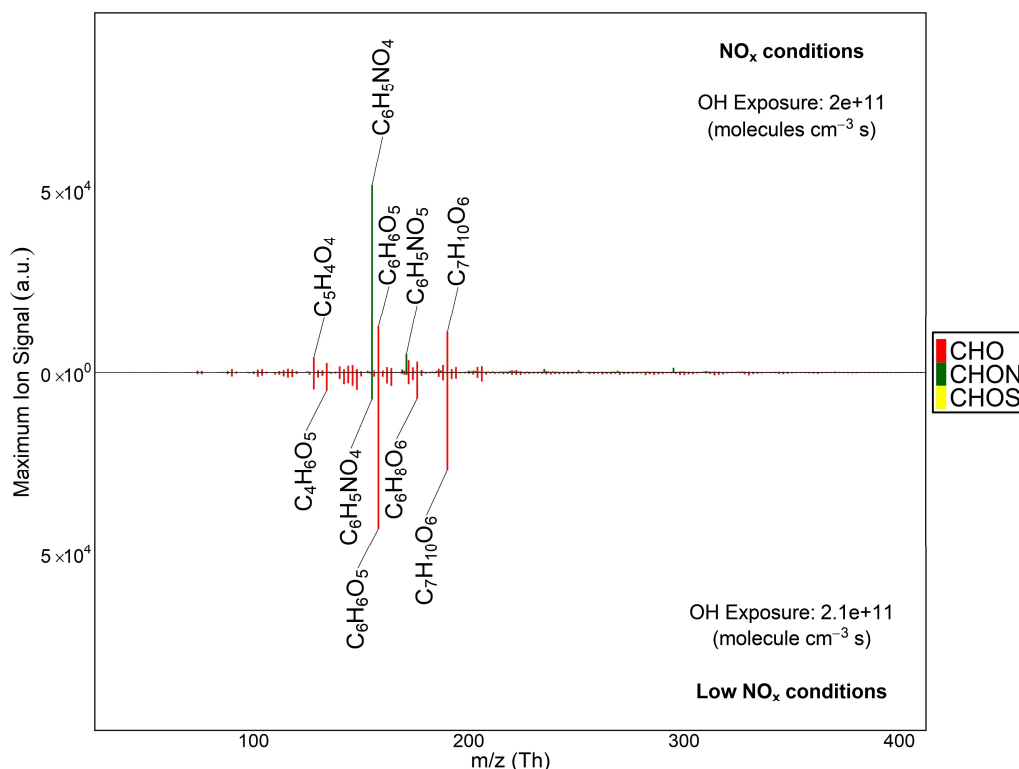


Figure 5.27 Comparison mass spectra for FIGAERO desorptions from guaiacol photooxidation experiments under high and low NO_x humid conditions (GIH-NO_x-1 and GIH-1).

Many of the gas-phase oxidation products are also observed in the particle phase. Species from the OH addition pathway, in addition to the methoxy loss pathway and ring scission species are observed, while C₇H₁₀O_x species are also observed in significant concentrations. It is noted that a signal for C₆H₅NO₄ is observed under low NO_x conditions, however this is most likely due to HONO desorption from the chamber walls, enhanced by higher relative humidity, as under dry conditions the same signal is not observed. Interestingly, in the high NO_x conditions, it appears that C₆ CHON species are more significant in the particle phase than the expected C₇H₇NO_x species which, although they were observed, were in much smaller quantities than their C₆ analogues. It is assumed that these species would have similar affinities for iodide ionisation, although it is acknowledged that the C₆ species have an extra hydroxyl group which could result in the C₆ species having a slightly better ability to cluster. It is also interesting that the high NO_x mass spectrum is dominated by a single large peak which was found to be almost four times as concentrated as the next most intense ion, while the low NO_x spectrum contains multiple dominant peaks from various oxidation pathways, with a wider distribution of products.

Table 5.3 illustrates the peaks with highest ion intensity in the particle phase with the molecular formula and proposed chemical structure based on the mechanisms previously discussed.

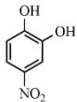
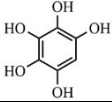
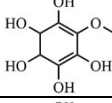
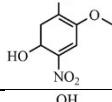
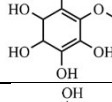
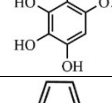
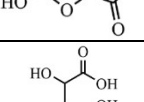
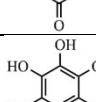
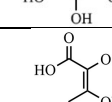
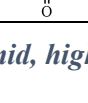
m/z (Th)	Chemical Formula	Proposed structure
155.11	$C_6H_5NO_4$	
158.11	$C_6H_6O_5$	
190.15	$C_7H_{10}O_6$	
171.11	$C_6H_5NO_5$	
176.12	$C_6H_8O_6$	
172.14	$C_7H_8O_5$	
128.08	$C_5H_4O_4$	
134.09	$C_4H_6O_5$	
188.14	$C_7H_8O_6$	
146.10	$C_5H_6O_5$	

Table 5.3 Major species detected in FIGAERO desorption under humid, high NO_x conditions (GIH- NO_x -1).

These results compare well with previous results from Lauraguais et al (2014). and Yee et al. (2013) who used gas chromatography with flame ionisation detection (GC-FID) and ultra performance liquid chromatography (UPLC) respectively for particle phase analysis (Lauraguais et al., 2014; Yee et al., 2013). Lauraguais et al. detected nitrocatechol ($C_6H_5NO_4$) and multiple isomers of nitroguaiacol ($C_7H_7NO_4$) as major NO_2 containing products while Yee et al. reported high yields of nitrocatechol as well as hydroxylated nitrocatechols ($C_6H_5NO_x$) and nitroguaiacols ($C_7H_7NO_5$ and $C_7H_7NO_6$). Yee et al. also reported significant yields of dinitrocatechol ($C_6H_4N_2O_6$),

however the signal obtained for this ion was relatively low in this work. Nitroguaiacol was detected in both gas and particle phases in this work, as well as hydroxylated nitroguaiacols, but these were not seen with the same magnitude as other C₇ species in the particle phase. The non-nitro products observed in the particle phase compare favourably with the products observed in low NO_x experiments performed by Yee et al. (2013), with significant contributions from C₇H₁₀O_x, C₇H₈O_x and C₆H₆O_x species as well as a range of C₅ and C₄ species which are very similar to the ions proposed in Table 5.3. These species are also detected in the high NO_x system employed by Yee et al. (2013), however they have significantly lower concentrations than in the low NO_x experiments.

A further study, investigating aqueous phase photo-nitration of guaiacol also identified a dinitro species as a primary product of guaiacol photo-nitration, in this case 4,6-dinitroguaiacol (Kitanovski et al., 2014). Once again, this ion was detected in the particle phase analysis presented here but not in significant quantities. One possible explanation for the lack of dinitro species in our work is thermal decomposition during the FIGAERO heating cycle, resulting in increased ion signals for other species which have the same molecular formula as the fragments.

The prevalence of nitrocatechol as the dominant CHON species detected in these experiments also compares favourably with the composition of SOA formed from the NO₃-initiated oxidation of guaiacol (Meng et al., 2020). Using liquid chromatography mass spectrometry (LC-MS) Meng et al. (2020) found nitrocatechol contributed 18% to the SOA mass, the most for any individual compound. The presence of dinitro species, including dinitro dimers such as C₁₄H₁₂N₂O₈, was also observed by Meng et al. (2020), again suggesting that these are an important class of species not detected by the FIGAERO-CIMS, either due to poor instrument sensitivity or thermal decomposition of the compounds.

Meng et al. (2020) also detected a range of compounds in the particle phase in minor amounts (relative abundance of ≤ 2% of the overall chromatogram signal) including C₆H₆O₂ and C₇H₈O₄ which were readily detected in the gas phase in this work but not in the particle phase. A range of trinitro species such as C₇H₅N₃O₇ and trimers such as C₂₀H₁₅N₃O₁₂ were also detected by Meng et al. (2020), which again were not detected

in this work. However, these latter products are much more likely to be formed during NO_3 reactions than the OH reactions studied in this work.

To further understand group contributions to the total organic aerosol, the distribution of products by carbon number and chemical family are plotted in Figure 5.28. Under high NO_x conditions, C_6 species contribute more than their C_7 counterparts, while under low NO_x conditions, the ratio of C_7 to C_6 species is increased. Under high NO_x conditions, C_6 CHON species are dominant, C_7 CHON species again do not contribute greatly to the distribution. There are also more significant contributions from accretion products under low NO_x conditions, likely due to enhanced reactions among $\text{RO}_2^\bullet$ species. Accretion reactions are thought to contribute significantly to particle nucleation (Shi et al., 2022), and addition of NO_x reduces the possibility of reactions among $\text{RO}_2^\bullet$ species typically leading to lower SOA yields than in the absence of NO_x . The ring scission species ($\text{C}_2 - \text{C}_5$) show similar distributions under both sets of conditions, with neither plot showing significant contribution from CHON species.

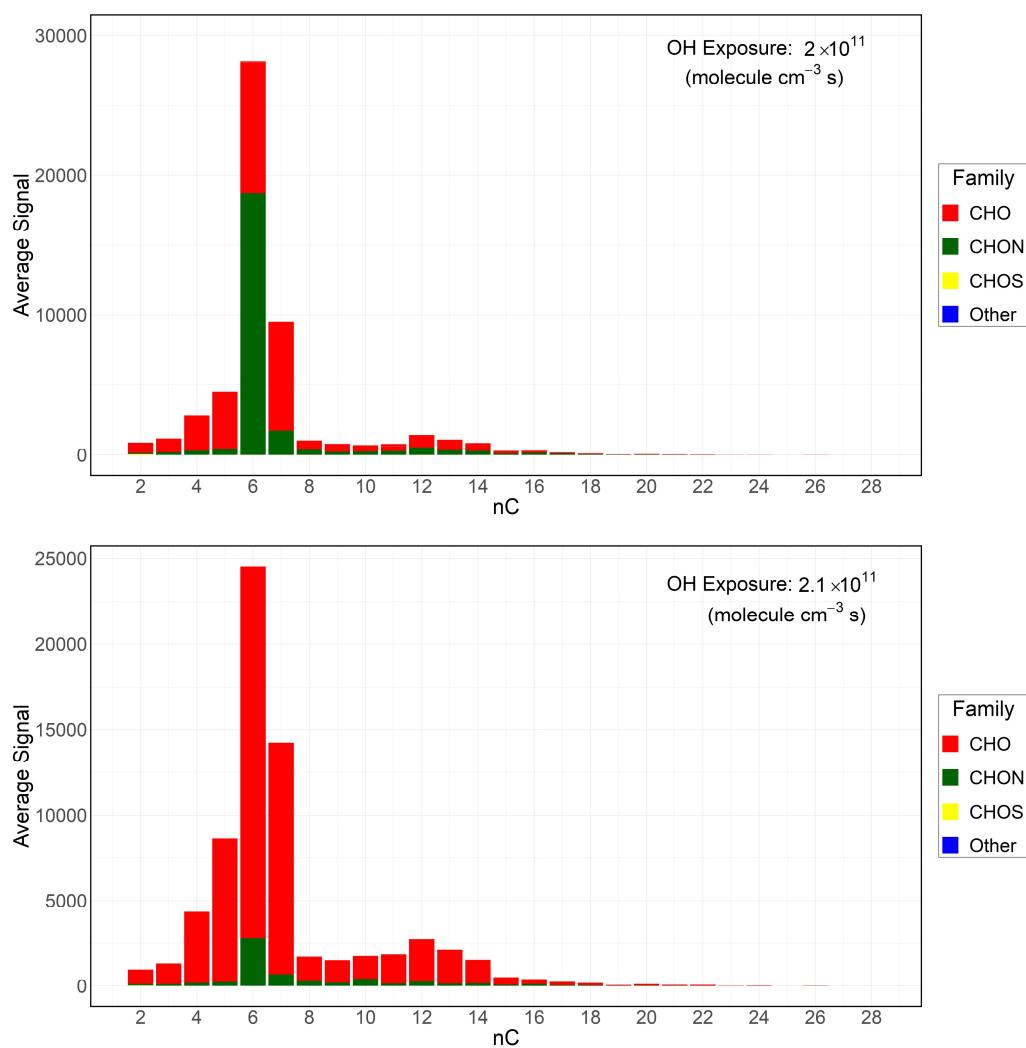


Figure 5.28 Distribution of organic products by carbon number and chemical family for FIGAERO cycles from experiments performed under high (top) and low (bottom) NO_x conditions (GIH- NO_x -1 and GIH-1).

Plotting the mass spectra as a function of just the number of carbon atoms, Figure 5.29, shows how multiple C_7 and C_6 species contribute, while also highlighting that many smaller species contribute to the ring scission signals observed in Figure 5.28.

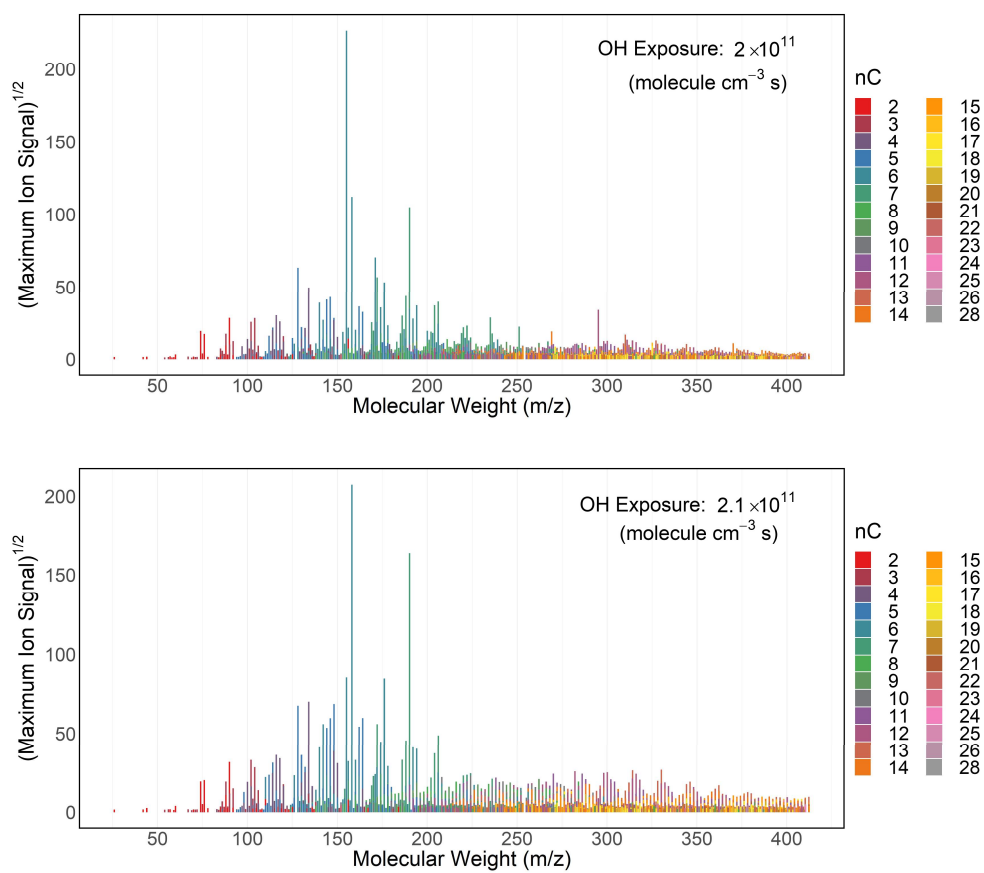


Figure 5.29 Mass spectra for organic species with signals coloured by the carbon number of a species for experiments performed under high (top) and low (bottom) NO_x conditions (GIH- NO_x -1 and GIH-1).

Chemical Families in the Particle Phase

Primary Oxidation Pathways

Thermograms obtained for the dominant C₆ and C₇ CHO families are given in Figure 5.30. As expected, the more oxidised species in each family have higher T_{max} values due to lower volatility. Some of the thermograms, e.g. for C₇H₈O₉ and C₆H₈O₈, have well defined Gaussian shaped peaks indicating that they correspond to a single species. However, many of the desorption profiles are non-Gaussian indicating that multiple isomers or molecular fragments arising from thermal degradation of higher molecular weight species could be contributing to the signals. This appears to be more common for species with the lowest degree of oxidation in each family. It is interesting to note that species with three and four oxygen atoms were observed in the C₆H₆O_x family but not for C₇H₈O_x, suggesting some differences in partitioning of the products due to molecular structure of the products.

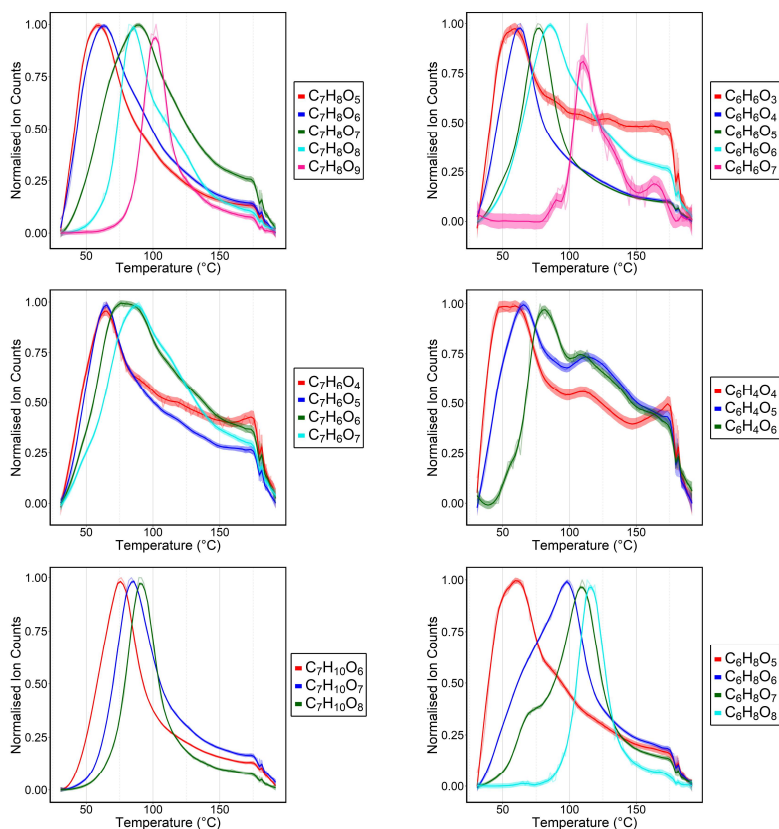


Figure 5.30 Thermal desorption profiles of major C₇ and C₆ CHO products observed in the particle phase. Thermograms were obtained after an estimated OH exposure of 7.0×10^{10} molecule cm⁻³ s (GID-1).

Thermograms obtained for the main CHON families, C₇H₇NO_x, C₇H₉NO_x, C₆H₅NO_x and C₆H₇NO_x are given in Figure 5.31. In general, the desorption profiles are broader

than those obtained for the CHO families and the degree of oxidation does not influence $T_{\max}$, with the exception of the $C_6H_7NO_x$ family, where the peak shifts to higher temperature for more oxidized species.

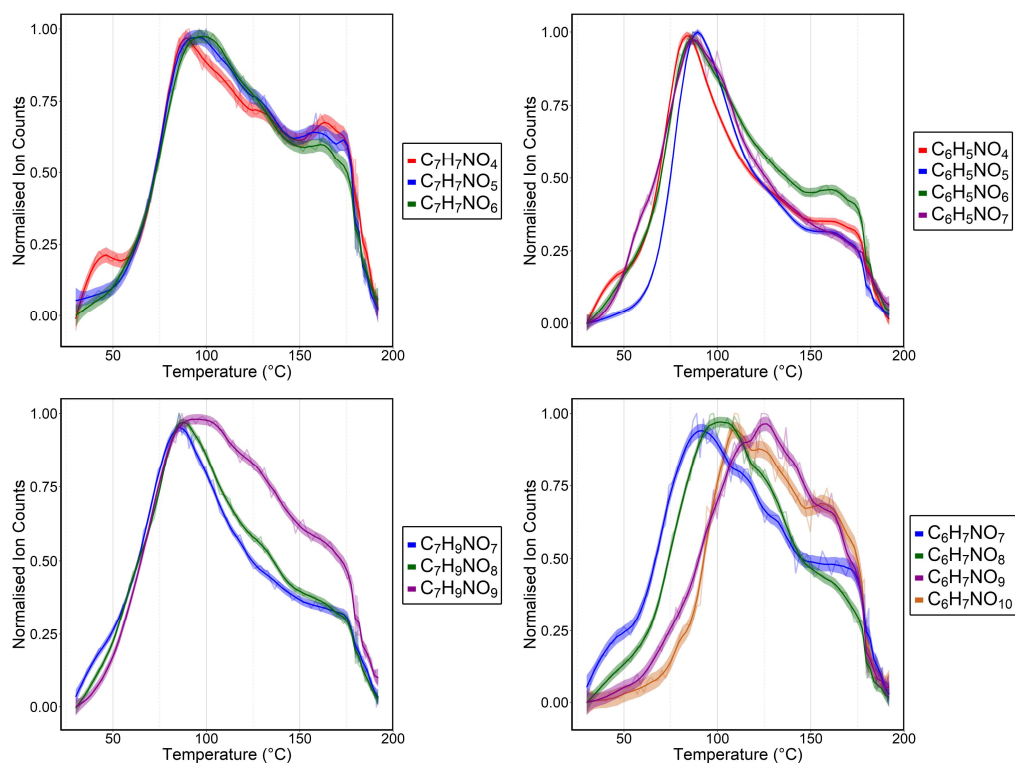


Figure 5.31 Thermograms of major C_7 and C_6 CHON species detected in the particle phase. Thermograms were obtained after an estimated OH exposure of 1.66×10^{11} molecule cm^{-3} s (GIH- NO_x -1).

Other Products

Thermograms for a selection of other products are given in Figure 5.32. The C_{12} - C_{14} families are attributed to accretion products arising from reactions of C_6 and C_7 species, while C_3 - C_5 are ring scission products. The C_8 - C_{11} species are likely formed from accretion of ring scission fragments. Many of the desorption profiles for the accretion products have several peaks, suggesting contributions from different isomers. The ring scission products also show multi-modal distributions, most noticeable for $C_5H_4O_3$, where a larger signal is observed for the oligomer thermal degradation product than for the first peak, likely corresponding to $C_5H_4O_3$ itself. Distortion of thermograms due to the thermal degradation of larger molecules has previously been observed in both field and simulation chamber experiments (Riva et al., 2019a; Lopez-Hilfiker et al., 2016). A recent study showed that a range of molecular properties can impact how readily a molecule will undergo thermal degradation, with

nO, the double bond equivalent (DBE) and $T_{\max}$ found to be determining factors (L. H. Yang et al., 2021).

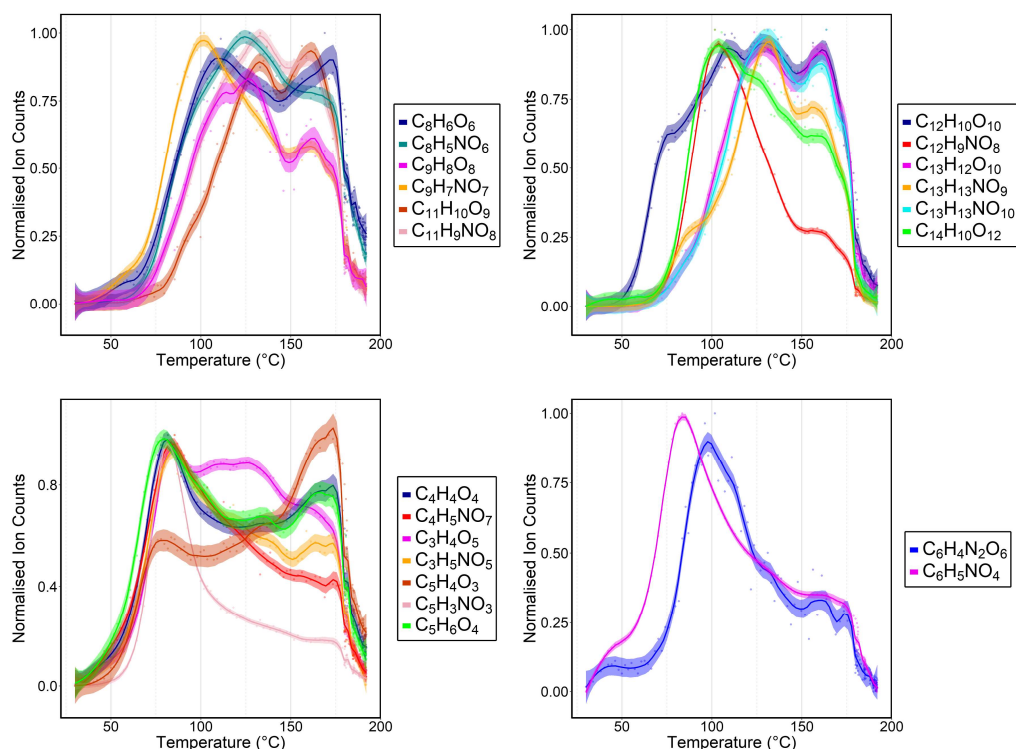


Figure 5.32 Thermograms of accretion and ring scission CHO and CHON particle phase species. Thermograms were obtained after an estimated OH exposure of $1.66 \times 10^{11} \text{ molecule cm}^{-3} \text{ s}$ (GIH- NO_x -1).

Figure 5.32 also shows the thermograms for $\text{C}_6\text{H}_5\text{NO}_4$ and $\text{C}_6\text{H}_4\text{N}_2\text{O}_6$ which are assumed to be nitrocatechol and dinitrocatechol respectively. The dinitro species has a slightly higher $T_{\max}$ and small interferences are also observed at higher temperatures, suggesting a possible contribution from the degradation of oligomeric species containing multiple nitro groups. Similar to this work, the study by Yee et al. (2013) highlighted the formation of dinitrocatechol at extremely high NO_x concentrations during guaiacol oxidation, however the study by Finewax et al. (2018) did not mention dinitro-catechol formation in their study of catechol oxidation. Dinitro-guaiacol species were observed by Kitanovski et al. (2014) in their study of aqueous phase photonitration of guaiacol, however these species were not detected in significant amounts in this work (Yee et al., 2013; Finewax et al., 2018; Kitanovski et al., 2014).

5.4.7 Aging of the particle phase

Light aging

In experiments where desorption cycles were performed over time, a change in the particle composition was observed. As the reaction progressed, the contribution of the primary particle phase species decreased while the accretion and ring scission products increased. In Figure 5.33 the oxidation state of carbon (OS_C) is plotted against the number of carbon atoms, coloured by the temperature at which the maximum ion counts are observed (T_{max}) and sized by the mean signal of each ion. The OS_C is calculated as per Kroll et al. (Kroll et al., 2011).

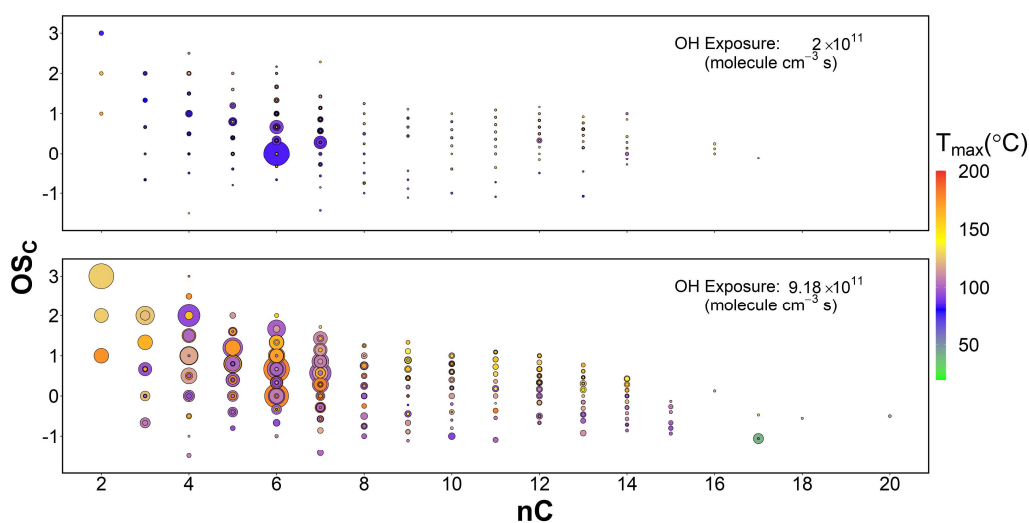


Figure 5.33 Comparative OS_C plots taken for desorption cycles at different stages of aging during guaiacol photooxidation (GIH- NO_x -1).

These plots indicate the degree to which an air mass is oxidised, while also demonstrating which chemical species have the highest concentrations in the particle phase. As shown in Figure 5.33, there are significant differences between the two plots. In the first desorption cycle, the particle phase is dominated by C_6 and C_7 species, proposed to be the primary particle phase products. Contrasting this, after approximately 4.5 times the degree of OH exposure, there is a marked difference in the primary contributors to the particle phase, with significant contributions observed from C_2 to C_5 species. These smaller species have significantly higher carbon oxidation states, demonstrating the significant aging which has occurred. It is also noticed that the T_{max} for these species has increased, suggesting that the species observed at later stages in the experiment are less volatile than those observed in the early stages of particle formation. This likely means the signals observed for smaller

species in the later stages of aging are the result of less volatile oligomer species thermally decomposing under the temperature ramping cycle of the FIGAERO.

To investigate this further, it is necessary to analyse the thermograms observed for individual species.

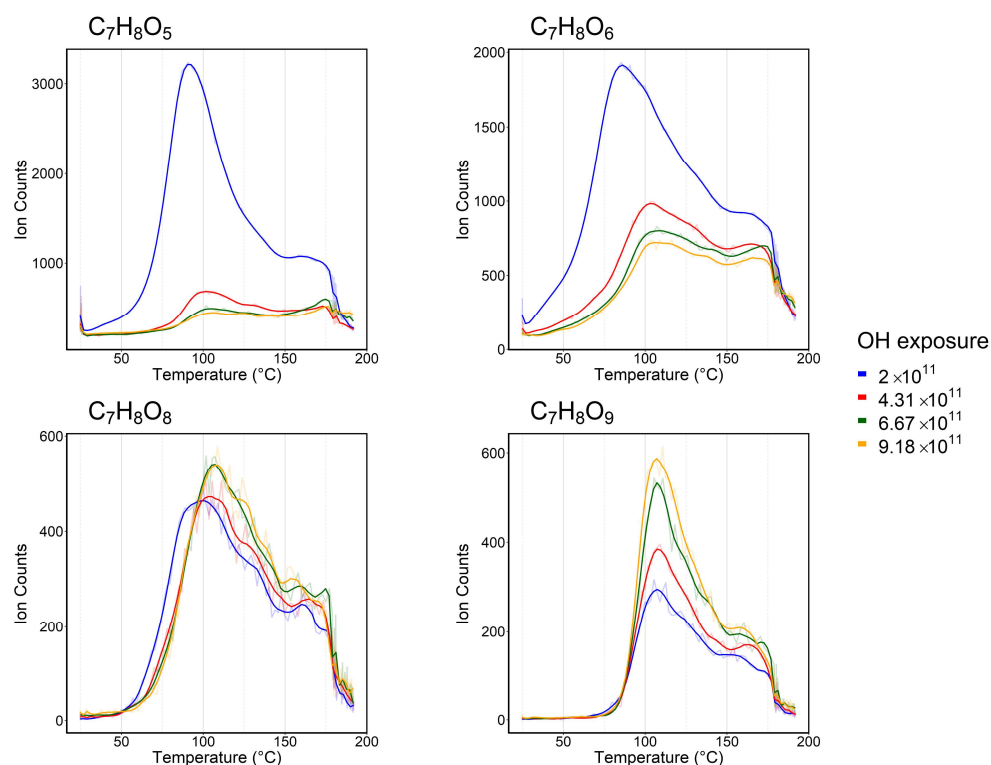


Figure 5.34 Successive desorption cycles for $C_7H_8O_x$ species showing decay of primary species with corresponding formation of more oxidised species in the particle phase (GIH- NO_x -1).

Figure 5.34 shows thermograms taken at various intervals for $C_7H_8O_x$ species, after corrections for SOA collected on the filter. There is a clear trend, where the primary particle phase products decrease in concentration while the more oxidised species increase in concentration with increasing OH exposure.

$C_7H_8O_5$ continuously decays through each successive desorption cycle, while the more highly oxidised $C_7H_8O_9$ increases suggesting that $C_7H_8O_5$ is undergoing continued oxidation in the particle phase. When examining the O_6 and O_8 species, similar trends are observed where the O_6 species decays to a lesser extent than the O_5 species, while the O_8 species increases to a lesser extent than the O_9 species. This is most likely due to their continued formation from $C_7H_8O_5$ oxidation, but they are then further oxidised towards the O_9 species. Although some shift in the T_{max} for these species is observed,

it is not significant enough to suggest that there is a change in the dominant isomer for these species with time.

CHON species in particular, were observed to undergo significant decay between desorption cycles with nitrocatechol ($C_6H_5NO_4$) undergoing more extensive decay than any other species observed in the particle phase, Figure 5.35. The significant loss of CHON species could be due to photolysis, widely observed for nitroaromatics (Bejan et al., 2006; Chen et al., 2011; Yuan et al., 2016; W. Yang et al., 2021).

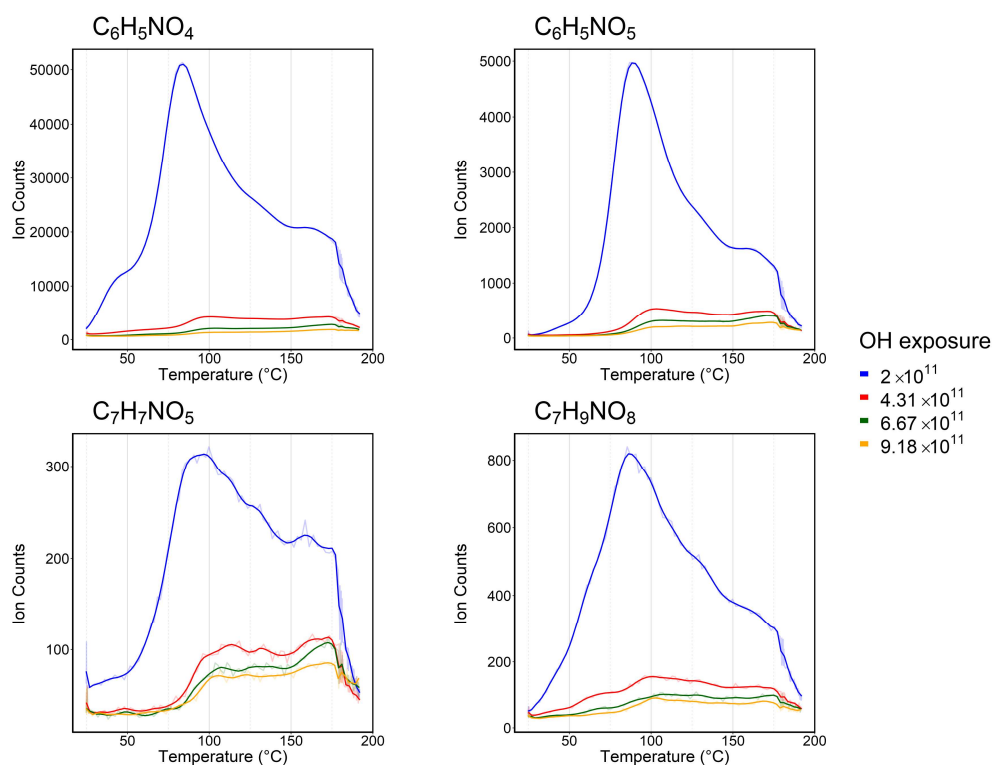


Figure 5.35 Successive desorption cycles for C_6 and C_7 CHON species highlighting their significant decay in the particle phase via photolysis (GIH- NO_x -1).

The increased formation of some accretion products as a result of processing in the particle phase was also observed in these experiments, Figure 5.36. This plot illustrates the C₈ and C₉ species increasing through successive desorption cycles. The thermogram shape remains relatively constant throughout each of the desorptions, suggesting little to no change in chemical structure. However, of the C₁₂ and C₁₃ species given in the plot, only the C₁₃ species increases in concentration, illustrating that not all species behave in the same manner.

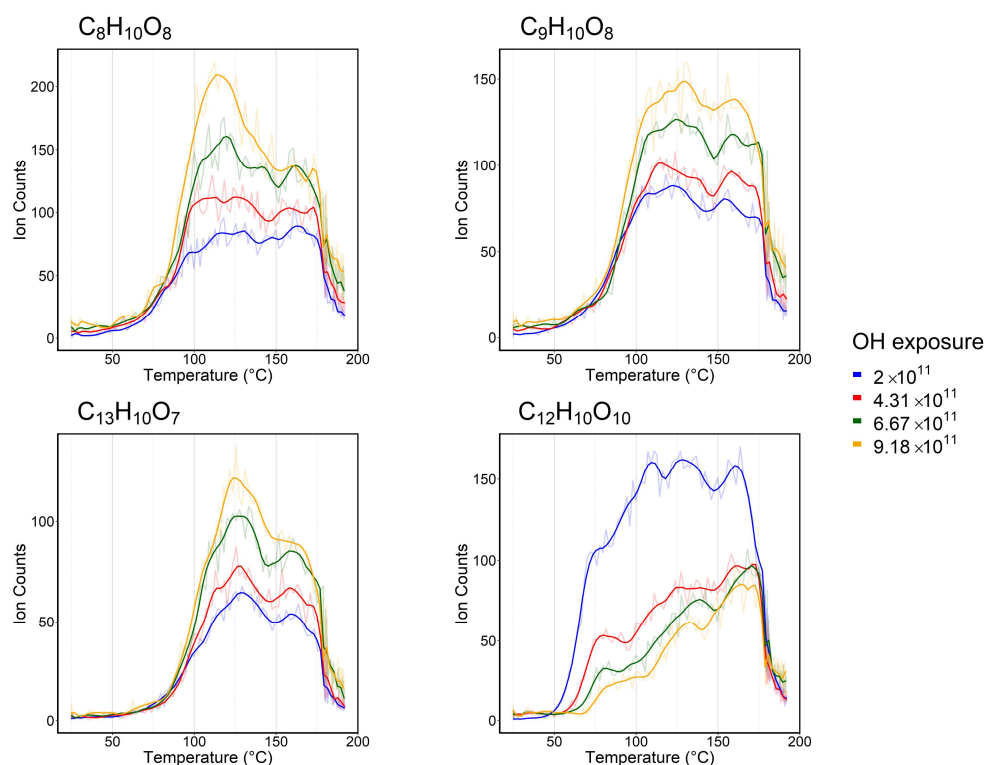


Figure 5.36 Successive desorption cycles for selected CHO accretion products showing both enhanced formation and decay for different species (GIH-NO_x-1).

Significant evolution of the signals for smaller species (C₂-C₄) was also observed, Figure 5.37.

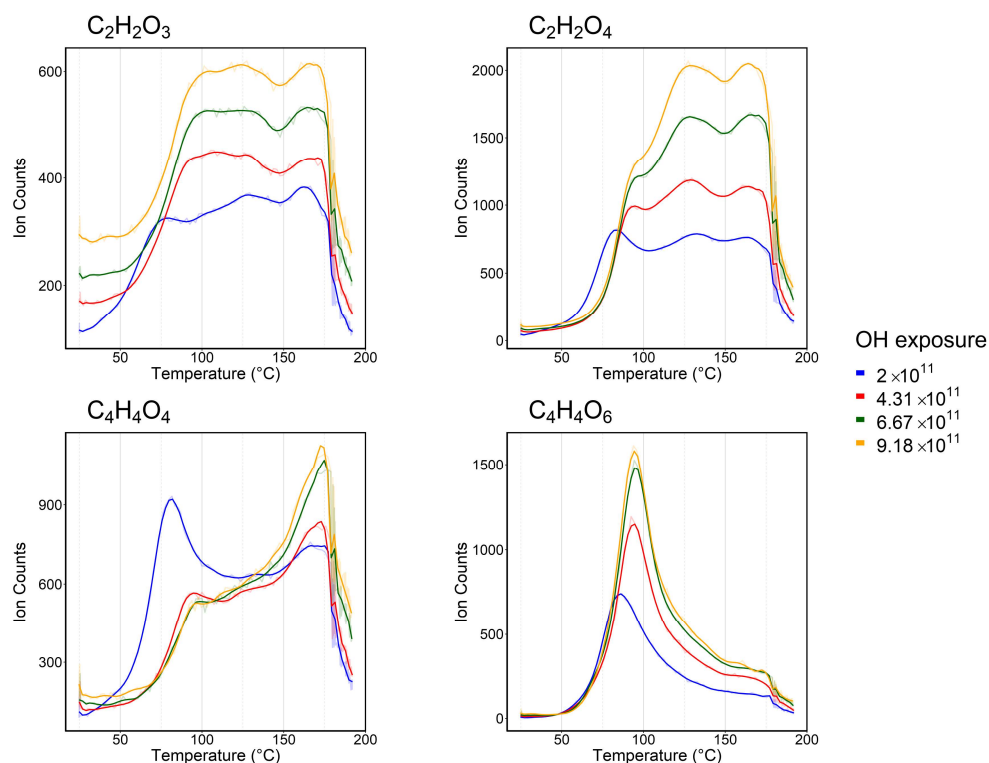


Figure 5.37 Successive desorption cycles for selected C_2 and C_4 CHO species illustrating enhanced formation in the particle phase (GIH- NO_x -1).

Here, each of these species reach their maximum ion signal in the final desorption, with the most prominent change in the $C_2H_2O_4$ signal, with this formula potentially corresponding to oxalic acid which is known as a tracer for aged air masses in the atmosphere (Carlton et al., 2007). Different trends are observed in the C_2 and C_4 species, with both of the C_2 species having an initial peak observed at approximately 70 °C in the first desorption cycle, but by the latter desorptions this peak is not present. This implies that the species responsible for the initial peak has been chemically processed and is no longer present, with the other peaks likely a result of oligomer decomposition. The C_4 species in Figure 5.37 show two different trends between each other, with the less oxidised $C_4H_4O_4$ species having a similar trend to the C_2 species, while $C_4H_4O_6$ appears to increase without significant change in the T_{max} value suggesting that the same species is increasing in concentration throughout the experiment.

There are noticeable changes in the shapes of the thermograms with each successive desorption, which is very noticeable for $C_2H_2O_4$ where a series of peaks are observed. Deconvolution of the final desorption profile reveals three distinct peaks under this thermogram, shown in Figure 5.38, where the data has been analysed to calculate an optimum model and Gaussian distributions subsequently fitted under the modelled data. Each of the three distributions is proposed to correspond to a different source of the $C_2H_2O_4$ molecular species, with the most likely source of the species at higher T_{max} being thermal decomposition of oligomers. The first signal is therefore likely the signal for oxalic acid.

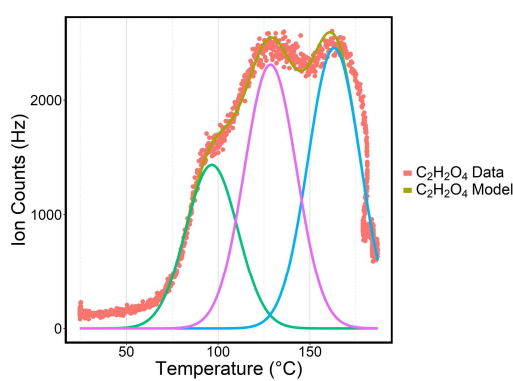


Figure 5.38 Deconvoluted $C_2H_2O_4$ thermogram observed for the 4th desorption cycle of Figure 5.37, showing multiple contributions to the $C_2H_2O_4$ signal (GIH-NO_x-1).

Dark aging

Dark aging of the SOA was investigated by switching off the UV lights while continuing to analyse the contents of the chamber using CIMS. Switching off the lights prevented further OH oxidation and photolysis of the gas- and particle-phase oxidation products and clearly affected the usual growth pattern of the particles. Figure 5.39 shows the banana plot for such an experiment which was carried out under dry conditions and in the presence of NO_x . Similar results were observed in both low and high NO_x conditions. When the lights are turned off there is no elongated tailing observed for the yellow, green or cyan regions as observed in experiments where the lights remain on, Figure 5.26. The particle number concentration decreases rapidly due to the lack of new particle production and the agglomeration of existing particles.

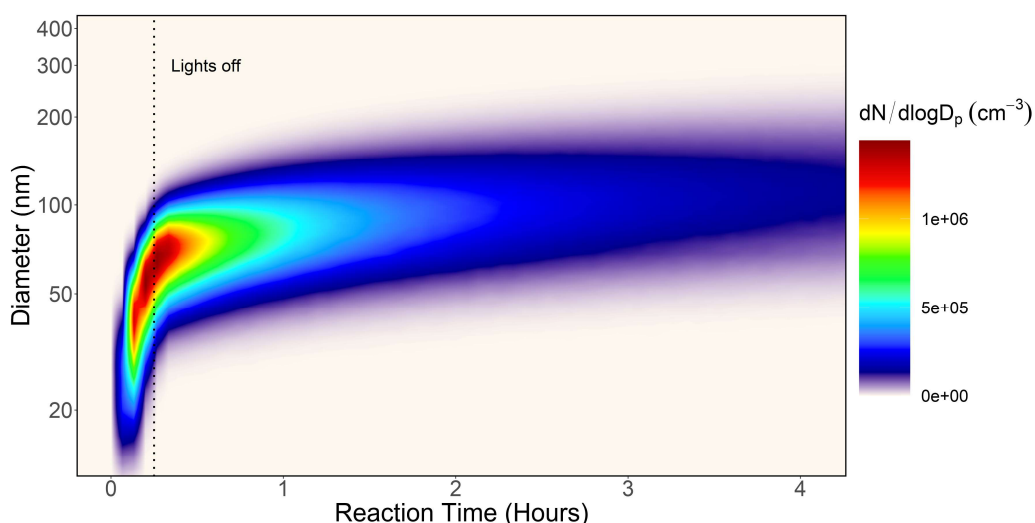


Figure 5.39 Banana plot for dry, high NO_x experimental conditions for dark aging experiment (GID- NO_x -DARK).

The OSc plots presented in Figure 5.40 show that dark aging only has a limited impact on the oxidation state of the products in the particle phase. The major species remain relatively unchanged even after several hours in the dark, however there are some more C_3 , C_4 and C_5 species present in the final desorption cycle. Analysis of the thermograms of specific species gives more insight into how they change under the dark conditions.

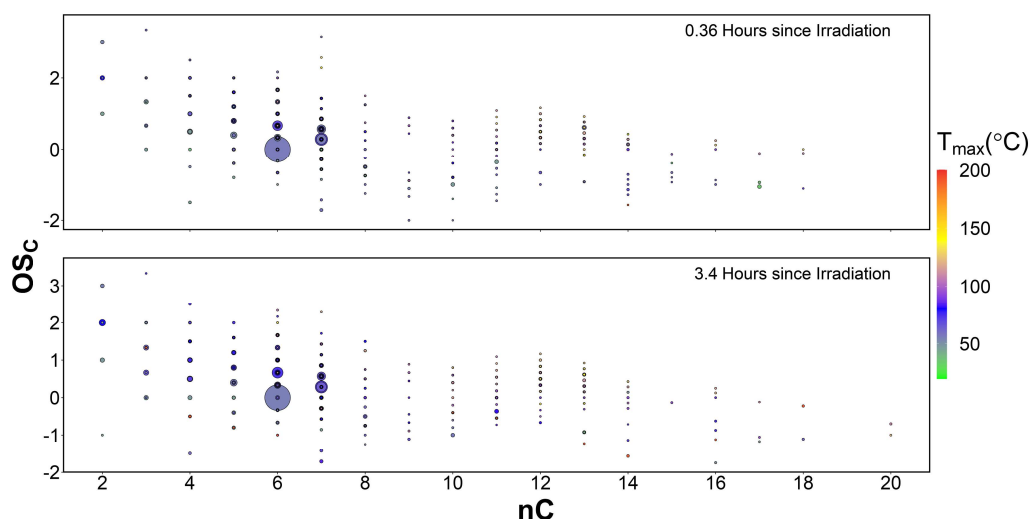


Figure 5.40 OSC plots taken for desorption cycles at different times since irradiation during a dark experiment showing little to no change in chemical composition (GID-NO_x-DARK).

Figure 5.41 shows that CHON compounds do undergo some losses in this dark system, however these losses are not as extensive as under the light conditions presented previously.

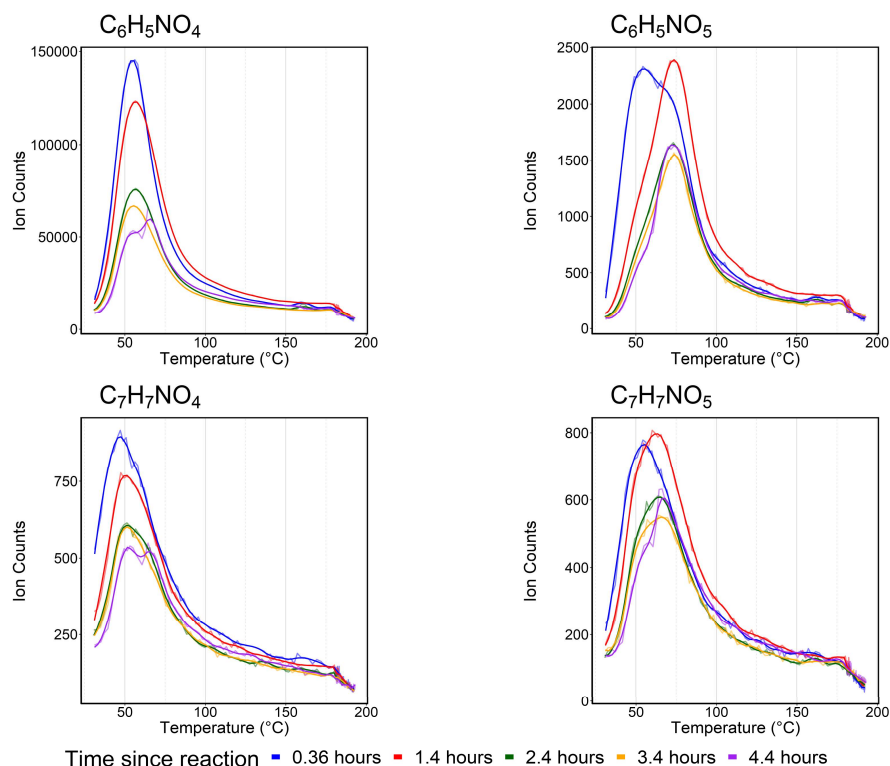


Figure 5.41 Successive desorption cycles for selected C₆ and C₇ CHON species under dark aging conditions (GID-NO_x-DARK)

These thermograms are also different to those obtained under light conditions. For example the losses observed for C₆H₅NO₄ are much lower than previously observed

(Figure 5.35), with successive desorptions still showing significant concentrations of this species without any major change in the desorption profile. However, the continuous decreases in sequential $C_6H_5NO_4$ concentrations are indicative of some processing of this species even in the dark, although this dark aging is not as extensive as photolysis.

Interestingly, the hydroxylated nitrocatechol, $C_6H_5NO_5$, does show some change in its desorption profile. Although it does not experience major losses in concentration, there is a change in the shape with the first desorption profile being indicative of at least two isomers being present, while the later desorptions suggest that the first isomer has undergone significant decay while the second isomer remains in significant quantities. This may indicate that one of the reaction pathways to form $C_6H_5NO_5$, e.g., OH addition to $C_6H_5NO_4$, has been stopped under the dark conditions, while the loss pathway of the first isomer is continuing.

The C_7 species which are plotted show similar trends to each other with minimal losses over time, although $C_7H_7NO_5$ undergoes a very slight shift in T_{max} , while the $C_7H_7NO_4$ species remains reasonably similar throughout. It is noticeable for each of the desorption profiles shown that there is no evolution of a second peak at higher desorption temperatures indicating that there are no thermal decomposition products contributing to the signals for these species. This may be an indication that advanced processing in the particles to form accretion products is reduced in dark conditions.

Analysis of some CHO species which were shown to undergo significant changes in light experiments and had significant influence from what are thought to thermal decomposition contributions also revealed changes under dark conditions, Figure 5.42.

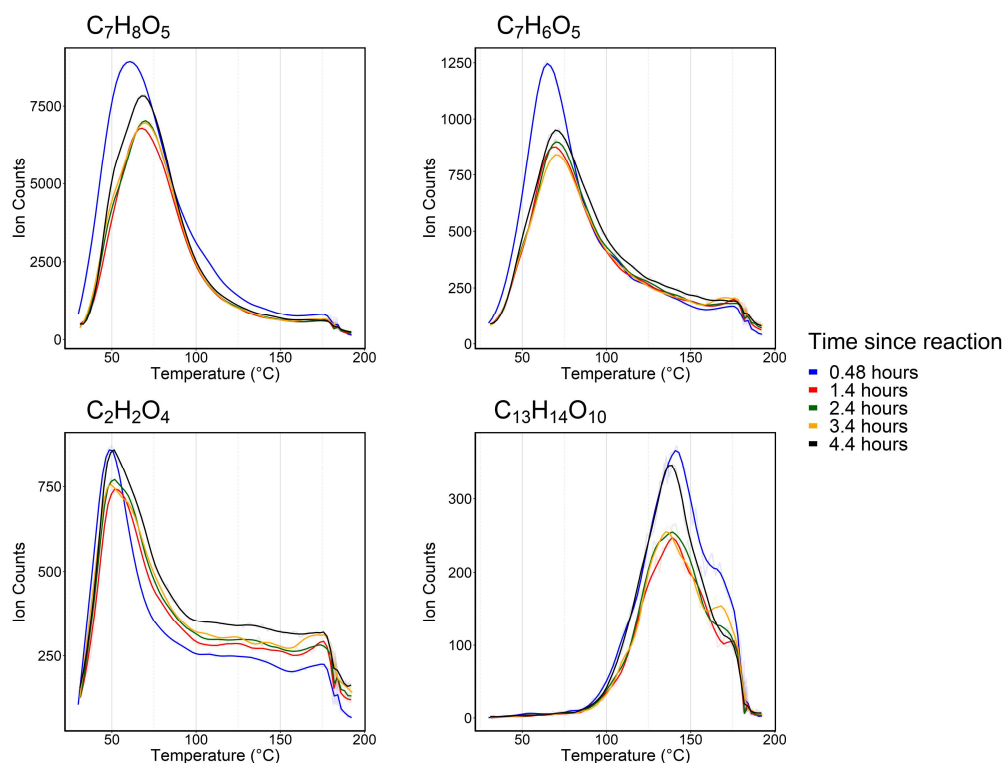


Figure 5.42 Successive desorption cycles selected CHO species under dark aging conditions (GID-DARK)

$C_7H_8O_5$ shows an interesting trend as it initially undergoes some decay but subsequently increases significantly in concentration in the final desorption, with the accretion product $C_{13}H_{14}O_{10}$ experiencing a similar effect. This may suggest some condensed phase processing resulting in the formation of these species via some unknown pathway. The $C_2H_2O_4$ signal in this plot is measurably different to that shown in Figure 5.37, with the signal decreasing through the first and second desorption cycles before reaching a relatively steady concentration before it increases slightly in the final desorption. There is also significant change in the T_{max} for the species between the two experiments, with $C_2H_2O_4$ having a T_{max} value of ~ 50 °C in Figure 5.42, while the profiles plotted in Figure 5.37 show no signal at this temperature. This may be an indication that under light conditions, all peaks observed in the thermograms are a result of thermal decomposition of oligomeric species. $C_7H_6O_5$ has a similar trend in concentration to $C_2H_2O_4$, with a decrease observed between the first two cycles and no major change observed for subsequent desorptions. Once again, there are again no significant contributions from fragments appearing at higher temperatures.

When considering particle phase accretion product formation for dark aging experiments, no evolution of species formed from ring scission products (C_8 , C_9 and C_{10} products) were observed at significant concentrations, unlike the UV aged experiments. Ring retaining accretion products (C_{12} , C_{13} and C_{14}) also show a different trend when aged under dark conditions compared to light conditions, Figure 5.43.

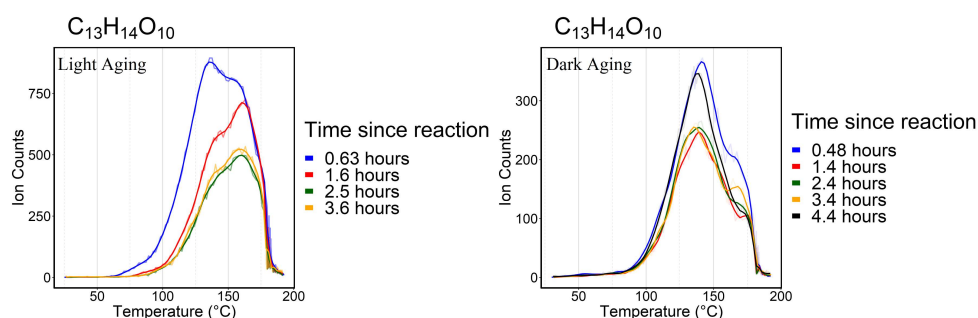


Figure 5.43 Comparison of $C_{13}H_{14}O_{10}$ aging under light and dark conditions (GIH-1 and GID-DARK).

In this figure, the same species are plotted from low NO_x experiments in both light and dark aging conditions and there are clear differences between the two plots. The light aging trace suggests the presence of two isomers, with the second isomer becoming the more dominant with time while the dark aging plot only has major contributions from one isomer which has a similar T_{max} to the first peak in the light aged plot (~ 130 °C). This suggests that these are similar species and the lack of a second isomer or fragment contributing to the dark aged signal is once again indicative that a significant proportion of the aging process is ceased in the dark and prevents oligomer formation. The increase in concentration of the species in the final desorption in the dark experiment is of particular interest, as it suggests condensed phase accretion reactions are occurring.

5.5 Conclusions

Atmospheric simulation chamber photooxidation experiments have been performed on guaiacol (2-methoxyphenol), a product of biomass burning, under a variety of atmospheric conditions with varying NO_x concentrations, light conditions and relative humidity. The gas and particle phase products have been characterised using a FIGAERO-ToF-CIMS operated in both iodide and benzene modes. Investigations into the aging of secondary organic aerosol (SOA) by prolonged exposure to OH and light were also performed and compared with aging in the dark.

Guaiacol was observed to react via multiple reaction pathways, yielding a range of gas phase products, primarily C_7 and C_6 in nature. Multiple gas phase reaction pathways were observed, including OH addition which yielded hydroxylated guaiacols such as $\text{C}_7\text{H}_8\text{O}_3$. Sequential oxidation of the OH addition species were observed in the gas phase up to the point of hydroxyl saturation of the aromatic ring, $\text{C}_7\text{H}_8\text{O}_6$. Other reaction pathways via OH addition were also observed, with the formation of hydroperoxides formed via autooxidation ($\text{C}_7\text{H}_{10}\text{O}_x$), ring opening species such as an epoxide ($\text{C}_7\text{H}_8\text{O}_5$) and a di-carbonyl ($\text{C}_7\text{H}_8\text{O}_4$) as well as a wide range of ring scission species with carbon numbers ranging from 2 to 5 detected. Interestingly, benzene diols were identified, proposed to form via methoxy loss from guaiacol after OH addition *ipso* to the methoxy group of guaiacol. The primary species along this pathway is $\text{C}_6\text{H}_6\text{O}_2$ proposed to be catechol, with all reaction pathways that were observed for guaiacol, also observed for catechol. In addition to products OH addition, species formed via hydrogen atom abstraction from the hydroxy group of guaiacol were also found. These included benzoquinones ($\text{C}_7\text{H}_6\text{O}_3$) and accretion products proposed to form from interactions between various phenoxy radicals arising from the oxidation reactions. Hydrogen abstraction products were also observed from catechol reactions, with NO_x incorporation along every major reaction pathway for both guaiacol and catechol in experiments performed under high NO_x conditions. The major product from guaiacol photooxidation under NO_x conditions was found to be nitrocatechol ($\text{C}_6\text{H}_5\text{NO}_4$), highlighting the importance of the methoxy loss pathway, as well as the influence of NO_x on the atmospheric chemistry of guaiacol.

SOA formation and growth was found to be rapid, beginning as soon as irradiation was initiated in experiments performed under the high OH conditions generated by UVC radiation. The major particle phase species detected via thermal desorption using the FIGAERO inlet were found to occur via the same reaction pathways observed in the gas phase, however with a higher degree of oxidation, with the first particle phase species observed along the OH addition pathway being $C_7H_8O_5$. In the gas phase, the most highly oxidised OH addition product was observed to be $C_7H_8O_6$, however in the particle phase species such as $C_7H_8O_9$ were detected, highlighting the prevalence of highly oxidised species in SOA. Similar to the gas phase, nitrocatechol was the species detected in the highest concentrations in the particle phase when NO_x was present. Biomass burning plumes contain significant concentrations of NO_x thus these results suggest nitrocatechol is the most important oxidation product for ambient photooxidation of guaiacol emitted by biomass burning processes.

Significant processing of the SOA was observed during photooxidation experiments, with both formation and decay of individual species observed. It was found that for many of the more oxidised species (e.g., $C_7H_8O_9$ and $C_2H_2O_4$) concentrations increased with further exposure to light and OH radicals, while some of the primary particle phase species (e.g., $C_7H_8O_5$ and $C_6H_5NO_4$) were found to undergo significant degradation in the aerosol phase with further processing. In the dark the degree of aging was found to be significantly reduced, however increases in concentrations of certain species ($C_{13}H_{14}O_{10}$) even under dark conditions suggest that some condensed phase chemistry can occur. Increased oxidation of SOA can result in aerosol that has a higher propensity for acting as cloud condensation nuclei (CCN) or ice nucleating particles (ICN) which have significant effect on cloud albedo and therefore the Earth's energy flux through radiative forcing (IPCC, 2021; Jahl et al., 2021; Lohmann et al., 2010). Increased oxidation of aerosol species tends to increase their water solubility, and more water soluble aerosol can also trigger irritations to the cardiovascular system, while nitrophenol derivatives are also known to have significant effects on human health (Ahmed et al., 2015; Falcon-Rodriguez et al., 2016).

Overall, this study has presented a comprehensive study on the major primary and secondary gas and particle phase products produced from hydroxyl-initiated oxidation of guaiacol. To further characterise the species detected in this work, some structure-based analysis could be performed on both the gas and particle phase products, using

offline analysis techniques such as LC-MS or GC-MS. Full structural characterisation of the oxidation products would allow more definite determination of the oxidation pathways that guaiacol undergoes. It would also help to elucidate the major isomers which contribute to signals for molecular formulae observed along multiple reaction pathways, such as $C_7H_8O_5$ which can form via at least two pathways presented. It would be interesting to fully characterise the effect of the chamber lights on the guaiacol oxidation system, which could be performed using a dark OH source, such as ozonolysis of an alkene e.g., 2,3-dimethyl-butene. In theory, this should result in the same products that were observed in this work, however the UV radiation emitted by the chamber lamps in the current study may have had some influence on the reaction pathways elucidated. Dark OH reactions would also allow for more comprehensive investigations on the effect that light has on the aging of SOA, as the chemistry would continue in the dark and photolysis of species such as the nitrophenols would be removed as a loss pathway. Investigations into mixed VOC chamber experiments would also be complementary and could offer significant insights into the behaviour of guaiacol in the atmosphere where multitudes of VOCs are found which could influence the oxidation pathways and SOA forming potential of guaiacol.

6. Conclusions

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6.1 Summary

In this work, a time-of-flight chemical ionisation mass spectrometer (ToF-CIMS) was used to investigate volatile organic compounds which are used as markers for biomass burning in the atmosphere. Field measurements were performed to investigate the presence of biomass burning markers in Cork City, and simulation chamber experiments were conducted to characterise the major oxidation products formed from the photooxidation of two biomass burning markers, namely 4-methylcatechol and guaiacol, both having the molecular formula $C_7H_8O_2$.

The ToF-CIMS was deployed at an urban background atmospheric monitoring site in Cork City during winter 2019 to monitor oxidised VOCs using iodide reagent CIMS. In conjunction with the ToF-CIMS, measurements of $PM_{2.5}$, NO_x and O_3 were also made to help characterise the sources of the observed VOCs. Strong diurnal patterns were observed for $PM_{2.5}$ with large evening peaks due to solid fuel burning for home heating. The $PM_{2.5}$ pollution peaks coincided with large increases in VOCs which are attributed to phenolic compounds from wood and coal burning. Based on the molecular formula, these VOCs were identified as catechols, methoxyphenols, functionalised phenols and nitro-aromatic compounds. In addition to nitro-aromatics being detected as primary products of biomass burning, they also appear to be produced by night-time chemical processing of the polluted air. Further analysis indicated that the reaction of phenol species with the nitrate radical is the most likely source for the secondary production of the nitro-aromatic compounds.

Positive matrix factorisation was performed on the VOC data from the field campaign. A six-factor solution was found to best explain the variance in the dataset, with factors attributed to aged VOCs, daytime aging of local emissions, wood-burning, residential background, city background and nighttime chemistry. The major biomass burning species, such as the catechols and phenols, were found to predominantly contribute to the wood-burning factor as expected. Interestingly, the nitro derivatives for the aromatic species were also found in the wood-burning factor which suggests that these species are predominantly primary in nature, rather than secondary. This work represents the first online measurements of VOCs in Ireland and highlighted the significant impact of residential solid fuel burning on VOC concentrations.

The atmospheric simulation chamber experiments elucidated the key oxidation pathways for the hydroxyl radical initiated degradation of 4-methylcatechol and guaiacol and identified the key oxidation products in both gas and particle phases. 4-methylcatechol was found to undergo reaction via both OH addition and H-atom abstraction with NO_x incorporation observed along all reaction pathways, with methyl-nitrocatechols (C₇H₇NO_x) among the most abundant products. Products formed via the OH addition pathway were dominant, with the C₇H₈O_x series of products among the most prevalent. Due to the high OH radical concentrations used, primary, secondary and in some cases tertiary products were observed in these experiments. A plethora of C₂ to C₅ ring scission species were detected, illustrating that cleavage of the aromatic ring is a major oxidation pathway. Accretion products arising from interactions between various intermediates, including ring scission species, were also observed as secondary products.

SOA was readily formed in experiments where sufficient OH radicals were generated using UVC radiation to photolyse H₂O₂. SOA yields under dry, low NO_x conditions were found to be in the range of 27 – 50%, consistent with studies performed on similar compounds. The main species detected in the particle phase species were the more oxidised forms of the primary gas phase products. The first particle phase species observed from the OH addition pathway was the secondary product, C₇H₈O₄, with species up to C₇H₈O₈ also detected along this pathway. Substantial processing of the SOA was observed upon increased exposure to hydroxyl radicals, with both formation and decay of individual species observed. Many of the more oxidised species increased in concentration with further exposure to light and OH radicals, while some of the primary particle phase species were found to undergo significant degradation in the aerosol phase.

Guaiacol was found to undergo similar oxidation pathways to 4-methylcatechol and also generated reaction products from the OH addition and H-atom abstraction pathways. The key difference between the chemistry of both compounds was the formation of numerous C₆ species in the guaiacol photooxidation system. These C₆ species were proposed to result from initial OH addition *ipso* to the methoxy group followed by loss of the methoxy group and formation of catechol (C₆H₆O₂), which subsequently underwent all of the same degradation pathways as guaiacol. This extra reaction pathway generated a complex system of reaction products, with nitrocatechol

($\text{C}_6\text{H}_5\text{NO}_4$) found to be the most abundant product in both the gas and particle phases when NO_x was present.

Similar to 4-methylcatechol, SOA formation from guaiacol photooxidation was rapid with significant processing of the major particle phase species observed. It was found that while most species underwent significantly less processing in the dark, some species such as the oligomer $\text{C}_{13}\text{H}_{14}\text{O}_{10}$, continued to form suggesting condensed phase chemistry was still occurring. The significantly reduced loss of nitro-aromatic species under dark conditions suggested photolysis of these species was their major degradation pathway.

The significant processing of SOA observed in this work highlights the importance of mitigating VOC emissions in the atmosphere, due to their reactivity and subsequent proclivity to form highly oxidised SOA. SOA with higher degrees of oxidation is known to enhance stress in humans due to increased reactive oxygen sites, while increased oxidation also enhances the ability of SOA to act as cloud condensation nuclei and ice-nucleating particles which have significant impacts on the climate.

6.2 Perspectives

This study has enhanced the understanding of the major OVOCs which dominate the atmosphere during wintertime in Ireland, while also providing new insights into the atmospheric chemistry of two atmospherically relevant biomass burning markers. Additional studies to further our understanding of these topics could be performed. In the context of the field measurement campaign:

- Another field campaign could be performed for a longer time-period in winter, in which the FIGAERO inlet is operational. This would provide new information on the partitioning of organic species associated with biomass burning as well as other sources in the atmosphere. The use of different reagent ions during the field campaign would also be useful for identifying a wider range of VOCs. For example, benzene or toluene reagent ions could be used to detect hydrocarbons from both biogenic and anthropogenic sources.
- Field campaigns performed using the FIGAERO inlet combined with the ToF-CIMS in other seasons as well as other locations in Ireland (i.e., agricultural, coastal, regional background) would provide much more information on the variety of sources and processes which govern the atmospheric chemistry VOCs.

In relation to the simulation chamber experiments performed on 4-methylcatechol and guaiacol, future work could involve:

- Chamber experiments performed entirely in the dark, using the ozonolysis of a suitable alkene as the OH source, to estimate the impact of UV radiation in the reaction systems.
- Chamber experiments performed on the nitrate radical initiated oxidation of the phenolic compounds to simulate nighttime processing of the biomass burning markers.
- Mixed VOC chamber experiments, whereby at least two VOCs are injected into the chamber to investigate how various VOCs and their oxidation products interact with each other. These experiments have significant atmospheric relevance, due to the complexity of the atmosphere and the many hundreds of VOCs which are present. Mixing both biogenic and anthropogenic VOCs for

these experiments would be of considerable interest, due to the dominance of BVOCs in the Earth's troposphere.

References

- Achad, M., Caumo, S., de Castro Vasconcellos, P., Bajano, H., Gómez, D., and Smichowski, P. (2018). Chemical markers of biomass burning: Determination of levoglucosan, and potassium in size-classified atmospheric aerosols collected in Buenos Aires, Argentina by different analytical techniques. *Microchemical Journal* 139:181–187. doi:10.1016/j.microc.2018.02.016.
- Ahmed, E., Nagaoka, K., Fayez, M., Abdel-Daim, M.M., Samir, H., and Watanabe, G. (2015). Suppressive effects of long-term exposure to P-nitrophenol on gonadal development, hormonal profile with disruption of tissue integrity, and activation of caspase-3 in male Japanese quail (*Coturnix japonica*). *Environ Sci Pollut Res Int* 22 (14):10930–10942. doi:10.1007/s11356-015-4245-9.
- Aiken, A.C., DeCarlo, P.F., Kroll, J.H., Worsnop, D.R., Huffman, J.A., Docherty, K.S., Ulbrich, I.M., Mohr, C., Kimmel, J.R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P.J., Canagaratna, M.R., Onasch, T.B., Alfarra, M.R., Prevot, A.S.H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J.L. (2008). O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry. *Environ. Sci. Technol.* 42 (12):4478–4485. doi:10.1021/es703009q.
- Akagi, S.K., Craven, J.S., Taylor, J.W., McMeeking, G.R., Yokelson, R.J., Burling, I.R., Urbanski, S.P., Wold, C.E., Seinfeld, J.H., Coe, H., Alvarado, M.J., and Weise, D.R. (2012). Evolution of trace gases and particles emitted by a chaparral fire in California. *Atmospheric Chemistry and Physics* 12 (3):1397–1421. doi:10.5194/acp-12-1397-2012.
- Alford, K.L. and Kumar, N. (2021). Pulmonary Health Effects of Indoor Volatile Organic Compounds—A Meta-Analysis. *Int J Environ Res Public Health* 18 (4):1578. doi:10.3390/ijerph18041578.
- Alif, A., Pilichowski, J.-F., and Boule, P. (1991). Photochemistry and environment XIII: Phototransformation of 2-nitrophenol in aqueous solution. *Journal of Photochemistry and Photobiology A: Chemistry* 59 (2):209–219. doi:10.1016/1010-6030(91)87009-K.
- Aljawhary, D., Lee, A.K.Y., and Abbatt, J.P.D. (2013). High-resolution chemical ionization mass spectrometry (ToF-CIMS): application to study SOA composition and processing. *Atmos. Meas. Tech.* 6 (11):3211–3224. doi:10.5194/amt-6-3211-2013.
- Alvarez-Idaboy, J.R., Mora-Diez, N., Boyd, R.J., and Vivier-Bunge, A. (2001). On the Importance of Prereactive Complexes in Molecule–Radical Reactions: Hydrogen Abstraction from Aldehydes by OH. *J. Am. Chem. Soc.* 123 (9):2018–2024. doi:10.1021/ja003372g.
- An, Z., Sun, J., Han, D., Mei, Q., Wei, B., Wang, X., and He, M. (2019). Theoretical study on the mechanisms, kinetics and ecotoxicity assessment of OH-initiated reactions of guaiacol in atmosphere and wastewater. *Science of The Total Environment* 685:729–740. doi:10.1016/j.scitotenv.2019.06.229.
- Andrews, E., Ogren, J.A., Bonasoni, P., Marinoni, A., Cuevas, E., Rodríguez, S., Sun, J.Y., Jaffe, D.A., Fischer, E.V., Baltensperger, U., Weingartner, E., Coen, M.C., Sharma, S., Macdonald, A.M., Leaitch, W.R., Lin, N.-H., Laj, P., Arsov, T., Kalapov, I., Jefferson, A., and Sheridan, P. (2011). Climatology of aerosol radiative properties in the free troposphere. *Atmospheric Research* 102 (4):365–393. doi:10.1016/j.atmosres.2011.08.017.

- Ashu-Ayem, E.R., Nitschke, U., Monahan, C., Chen, J., Darby, S.B., Smith, P.D., O'Dowd, C.D., Stengel, D.B., and Venables, D.S. (2012). Coastal Iodine Emissions. 1. Release of I₂ by *Laminaria digitata* in Chamber Experiments. *Environ. Sci. Technol.* 46 (19):10413–10421. doi:10.1021/es204534v.
- Ayres, B.R., Allen, H.M., Draper, D.C., Brown, S.S., Wild, R.J., Jimenez, J.L., Day, D.A., Campuzano-Jost, P., Hu, W., de Gouw, J., Koss, A., Cohen, R.C., Duffey, K.C., Romer, P., Baumann, K., Edgerton, E., Takahama, S., Thornton, J.A., Lee, B.H., Lopez-Hilfiker, F.D., Mohr, C., Wennberg, P.O., Nguyen, T.B., Teng, A., Goldstein, A.H., Olson, K., and Fry, J.L. (2015). Organic nitrate aerosol formation via NO₃ + biogenic volatile organic compounds in the southeastern United States. *Atmospheric Chemistry and Physics* 15 (23):13377–13392. doi:10.5194/acp-15-13377-2015.
- Bannan, T.J., Bacak, A., Muller, J.B.A., Booth, A.M., Jones, B., Le Breton, M., Leather, K.E., Ghalaieny, M., Xiao, P., Shallcross, D.E., and Percival, C.J. (2014). Importance of direct anthropogenic emissions of formic acid measured by a chemical ionisation mass spectrometer (CIMS) during the Winter ClearfLo Campaign in London, January 2012. *Atmospheric Environment* 83:301–310. doi:10.1016/j.atmosenv.2013.10.029.
- Bannan, T.J., Booth, A.M., Bacak, A., Muller, J.B.A., Leather, K.E., Le Breton, M., Jones, B., Young, D., Coe, H., Allan, J., Visser, S., Slowik, J.G., Furger, M., Prévôt, A.S.H., Lee, J., Dunmore, R.E., Hopkins, J.R., Hamilton, J.F., Lewis, A.C., Whalley, L.K., Sharp, T., Stone, D., Heard, D.E., Fleming, Z.L., Leigh, R., Shallcross, D.E., and Percival, C.J. (2015). The first UK measurements of nitryl chloride using a chemical ionization mass spectrometer in central London in the summer of 2012, and an investigation of the role of Cl atom oxidation. *Journal of Geophysical Research: Atmospheres* 120 (11):5638–5657. doi:10.1002/2014JD022629.
- Bannan, T.J., Le Breton, M., Priestley, M., Worrall, S.D., Bacak, A., Marsden, N.A., Mehra, A., Hammes, J., Hallquist, M., Alfarra, M.R., Krieger, U.K., Reid, J.P., Jayne, J., Robinson, W., McFiggans, G., Coe, H., Percival, C.J., and Topping, D. (2019). A method for extracting calibrated volatility information from the FIGAERO-HR-ToF-CIMS and its experimental application. *Atmospheric Measurement Techniques* 12 (3):1429–1439. doi:10.5194/amt-12-1429-2019.
- Bejan, I., Abd El Aal, Y., Barnes, I., Benter, T., Bohn, B., Wiesen, P., and Kleffmann, J. (2006). The photolysis of ortho-nitrophenols: a new gas phase source of HONO. *Physical Chemistry Chemical Physics* 8 (17):2028–2035. doi:10.1039/B516590C.
- Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P., and Benter, T. (2007). Investigations on the gas-phase photolysis and OH radical kinetics of methyl-2-nitrophenols. *Physical Chemistry Chemical Physics* 9 (42):5686–5692. doi:10.1039/B709464G.
- Berndt, T., Scholz, W., Mentler, B., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A. (2018). Accretion Product Formation from Self- and Cross-Reactions of RO₂ Radicals in the Atmosphere. *Angewandte Chemie International Edition* 57 (14):3820–3824. doi:10.1002/anie.201710989.
- Bertram, T.H., Kimmel, J.R., Crisp, T.A., Ryder, O.S., Yatavelli, R.L.N., Thornton, J.A., Cubison, M.J., Gonin, M., and Worsnop, D.R. (2011). A field-deployable, chemical ionization time-of-flight mass spectrometer. *Atmospheric Measurement Techniques* 4 (7):1471–1479. doi:10.5194/amt-4-1471-2011.

- Bianchi, F., Kurtén, T., Riva, M., Mohr, C., Rissanen, M.P., Roldin, P., Berndt, T., Crounse, J.D., Wennberg, P.O., Mentel, T.F., Wildt, J., Junninen, H., Jokinen, T., Kulmala, M., Worsnop, D.R., Thornton, J.A., Donahue, N., Kjaergaard, H.G., and Ehn, M. (2019). Highly Oxygenated Organic Molecules (HOM) from Gas-Phase Autoxidation Involving Peroxy Radicals: A Key Contributor to Atmospheric Aerosol. *Chem. Rev.* 119 (6):3472–3509. doi:10.1021/acs.chemrev.8b00395.
- Bianchi, F., Tröstl, J., Junninen, H., Frege, C., Henne, S., Hoyle, C.R., Molteni, U., Herrmann, E., Adamov, A., Bukowiecki, N., Chen, X., Duplissy, J., Gysel, M., Hutterli, M., Kangasluoma, J., Kontkanen, J., Kürten, A., Manninen, H.E., Münch, S., Peräkylä, O., Petäjä, T., Rondo, L., Williamson, C., Weingartner, E., Curtius, J., Worsnop, D.R., Kulmala, M., Dommen, J., and Baltensperger, U. (2016). New particle formation in the free troposphere: A question of chemistry and timing. *Science* 352 (6289):1109–1112. doi:10.1126/science.aad5456.
- Bluvshstein, N., Lin, P., Flores, J.M., Segev, L., Mazar, Y., Tas, E., Snider, G., Weagle, C., Brown, S.S., Laskin, A., and Rudich, Y. (2017). Broadband optical properties of biomass-burning aerosol and identification of brown carbon chromophores. *Journal of Geophysical Research: Atmospheres* 122 (10):5441–5456. doi:10.1002/2016JD026230.
- Bolzacchini, E., Bruschi, M., Hjorth, J., Meinardi, S., Orlandi, M., Rindone, B., and Rosenbohm, E. (2001). Gas-Phase Reaction of Phenol with NO₃. *Environmental Science & Technology* 35 (9):1791–1797. doi:10.1021/es001290m.
- Brown, S.S. and Stutz, J. (2012). Nighttime radical observations and chemistry. *Chem. Soc. Rev.* 41 (19):6405–6447. doi:10.1039/C2CS35181A.
- Buzcu, B. and Fraser, M.P. (2006). Source identification and apportionment of volatile organic compounds in Houston, TX. *Atmospheric Environment* 40 (13):2385–2400. doi:10.1016/j.atmosenv.2005.12.020.
- Byrne, R., Ryan, K., Venables, D.S., Wenger, J.C., and Hellebust, S. (2023). Highly local sources and large spatial variations in PM_{2.5} across a city: evidence from a city-wide sensor network in Cork, Ireland. *Environ. Sci.: Atmos.* 3 (5):919–930. doi:10.1039/D2EA00177B.
- Cai, J., Daellenbach, K.R., Wu, C., Zheng, Y., Zheng, F., Du, W., Haslett, S.L., Chen, Q., Kulmala, M., and Mohr, C. (2023). Characterization of offline analysis of particulate matter with FIGAERO-CIMS. *Atmospheric Measurement Techniques* 16 (5):1147–1165. doi:10.5194/amt-16-1147-2023.
- Calvert, J.G., Atkinson, R., Becker, K.H., Kamens, R.M., Seinfeld, J.H., Wallington, T.H., and Yarwood, G. (2002). The mechanisms of atmospheric oxidation of the aromatic hydrocarbons.
- Calvo, A.I., Alves, C., Castro, A., Pont, V., Vicente, A.M., and Fraile, R. (2013). Research on aerosol sources and chemical composition: Past, current and emerging issues. *Atmospheric Research* 120–121:1–28. doi:10.1016/j.atmosres.2012.09.021.
- Canagaratna, M.R., Jayne, J.T., Jimenez, J.L., Allan, J.D., Alfarra, M. r., Zhang, Q., Onasch, T.B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L.R., Trimborn, A.M., Northway, M.J., DeCarlo, P.F., Kolb, C.E., Davidovits, P., and Worsnop, D.R. (2007). Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. *Mass Spectrometry Reviews* 26 (2):185–222. doi:10.1002/mas.20115.

- Canagaratna, M.R., Jimenez, J.L., Kroll, J.H., Chen, Q., Kessler, S.H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L.R., Wilson, K.R., Surratt, J.D., Donahue, N.M., Jayne, J.T., and Worsnop, D.R. (2015). Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications. *Atmospheric Chemistry and Physics* 15 (1):253–272. doi:10.5194/acp-15-253-2015.
- Canonaco, F., Crippa, M., Slowik, J.G., Baltensperger, U., and Prévôt, A.S.H. (2013). SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data. *Atmospheric Measurement Techniques* 6 (12):3649–3661. doi:10.5194/amt-6-3649-2013.
- Carlton, A.G., Turpin, B.J., Altieri, K.E., Seitzinger, S., Reff, A., Lim, H.-J., and Ervens, B. (2007). Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments. *Atmospheric Environment* 41 (35):7588–7602. doi:10.1016/j.atmosenv.2007.05.035.
- Carslaw, D.C. and Ropkins, K. (2012). openair — An R package for air quality data analysis. *Environmental Modelling & Software* 27–28:52–61. doi:10.1016/j.envsoft.2011.09.008.
- Chan, A.W.H., Chan, M.N., Surratt, J.D., Chhabra, P.S., Loza, C.L., Crounse, J.D., Yee, L.D., Flagan, R.C., Wennberg, P.O., and Seinfeld, J.H. (2010). Role of aldehyde chemistry and NO_x concentrations in secondary organic aerosol formation. *Atmos. Chem. Phys.* 10 (15):7169–7188. doi:10.5194/acp-10-7169-2010.
- Chen, J., Li, C., Ristovski, Z., Milic, A., Gu, Y., Islam, M.S., Wang, S., Hao, J., Zhang, H., He, C., Guo, H., Fu, H., Miljevic, B., Morawska, L., Thai, P., Lam, Y.F., Pereira, G., Ding, A., Huang, X., and Dumka, U.C. (2017). A review of biomass burning: Emissions and impacts on air quality, health and climate in China. *Science of The Total Environment* 579:1000–1034. doi:10.1016/j.scitotenv.2016.11.025.
- Chen, J., Wenger, J.C., and Venables, D.S. (2011). Near-Ultraviolet Absorption Cross Sections of Nitrophenols and Their Potential Influence on Tropospheric Oxidation Capacity. *J. Phys. Chem. A* 115 (44):12235–12242. doi:10.1021/jp206929r.
- Chen, T., Chu, B., Ma, Q., Zhang, P., Liu, J., and He, H. (2021). Effect of relative humidity on SOA formation from aromatic hydrocarbons: Implications from the evolution of gas- and particle-phase species. *Science of The Total Environment* 773:145015. doi:10.1016/j.scitotenv.2021.145015.
- Chen, T., Zhang, P., Ma, Q., Chu, B., Liu, J., Ge, Y., and He, H. (2022). Smog Chamber Study on the Role of NO_x in SOA and O₃ Formation from Aromatic Hydrocarbons. *Environmental Science and Technology* 56 (19):13654–13663. doi:10.1021/acs.est.2c04022.
- Chen, Y., Takeuchi, M., Nah, T., Xu, L., Canagaratna, M.R., Stark, H., Baumann, K., Canonaco, F., Prévôt, A.S.H., Huey, L.G., Weber, R.J., and Ng, N.L. (2020). Chemical characterization of secondary organic aerosol at a rural site in the southeastern US: insights from simultaneous high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and FIGAERO chemical ionization mass spectrometer (CIMS) measurements. *Atmos. Chem. Phys.* 20 (14):8421–8440. doi:10.5194/acp-20-8421-2020.
- Chhabra, P.S., Lambe, A.T., Canagaratna, M.R., Stark, H., Jayne, J.T., Onasch, T.B., Davidovits, P., Kimmel, J.R., and Worsnop, D.R. (2015). Application of high-

- resolution time-of-flight chemical ionization mass spectrometry measurements to estimate volatility distributions of α -pinene and naphthalene oxidation products. *Atmos. Meas. Tech.* 8 (1):1–18. doi:10.5194/amt-8-1-2015.
- Coeur-Tourneur, C., Foulon, V., and Laréal, M. (2010). Determination of aerosol yields from 3-methylcatechol and 4-methylcatechol ozonolysis in a simulation chamber. *Atmospheric Environment* 44 (6):852–857. doi:10.1016/j.atmosenv.2009.11.027.
- Coeur-Tourneur, C., Tomas, A., Guilloteau, A., Henry, F., Ledoux, F., Visez, N., Riffault, V., Wenger, J.C., and Bedjanian, Y. (2009). Aerosol formation yields from the reaction of catechol with ozone. *Atmospheric Environment* 43 (14):2360–2365. doi:10.1016/j.atmosenv.2008.12.054.
- Coggon, M.M., Gkatzelis, G.I., McDonald, B.C., Gilman, J.B., Schwantes, R.H., Abuhassan, N., Aikin, K.C., Arend, M.F., Berkoff, T.A., Brown, S.S., Campos, T.L., Dickerson, R.R., Gronoff, G., Hurley, J.F., Isaacman-VanWertz, G., Koss, A.R., Li, M., McKeen, S.A., Moshary, F., Peischl, J., Pospisilova, V., Ren, X., Wilson, A., Wu, Y., Trainer, M., and Warneke, C. (2021). Volatile chemical product emissions enhance ozone and modulate urban chemistry. *Proceedings of the National Academy of Sciences* 118 (32):e2026653118. doi:10.1073/pnas.2026653118.
- Dall'Osto, M., Hellebust, S., Healy, R.M., O'Connor, I.P., Kourtchev, I., Sodeau, J.R., Ovadnevaite, J., Ceburnis, D., O'Dowd, C.D., and Wenger, J.C. (2014). Apportionment of urban aerosol sources in Cork (Ireland) by synergistic measurement techniques. *Science of The Total Environment* 493:197–208. doi:10.1016/j.scitotenv.2014.05.027.
- Dall'Osto, M., Ovadnevaite, J., Ceburnis, D., Martin, D., Healy, R.M., O'Connor, I.P., Kourtchev, I., Sodeau, J.R., Wenger, J.C., and O'Dowd, C. (2013). Characterization of urban aerosol in Cork City (Ireland) using aerosol mass spectrometry. *Atmos. Chem. Phys.* 13 (9):4997–5015. doi:10.5194/acp-13-4997-2013.
- D'Ambro, E.L., Hyttinen, N., Møller, K.H., Iyer, S., Otkjær, R.V., Bell, D.M., Liu, J., Lopez-Hilfiker, F.D., Schobesberger, S., Shilling, J.E., Zelenyuk, A., Kjaergaard, H.G., Thornton, J.A., and Kurtén, T. (2022). Pathways to Highly Oxidized Products in the Δ^3 -Carene + OH System. *Environ. Sci. Technol.* 56 (4):2213–2224. doi:10.1021/acs.est.1c06949.
- D'Ambro, E.L., Lee, B.H., Liu, J., Shilling, J.E., Gaston, C.J., Lopez-Hilfiker, F.D., Schobesberger, S., Zaveri, R.A., Mohr, C., Lutz, A., Zhang, Z., Gold, A., Surratt, J.D., Rivera-Rios, J.C., Keutsch, F.N., and Thornton, J.A. (2017). Molecular composition and volatility of isoprene photochemical oxidation secondary organic aerosol under low- and high- NO_x conditions. *Atmos. Chem. Phys.* 17 (1):159–174. doi:10.5194/acp-17-159-2017.
- de Gouw, J. and Warneke, C. (2007). Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrometry Reviews* 26 (2):223–257. doi:10.1002/mas.20119.
- Dörich, R., Eger, P., Lelieveld, J., and Crowley, J.N. (2021). Iodide CIMS and m/z 62: the detection of HNO_3 as NO_3^- in the presence of PAN, peroxyacetic acid and ozone. *Atmos. Meas. Tech.* 14 (8):5319–5332. doi:10.5194/amt-14-5319-2021.
- Doussin, J.-F., Fuchs, H., Kiendler-Scharr, A., Seakins, P., and Wenger, J. (Eds.) (2023). A Practical Guide to Atmospheric Simulation Chambers. Springer International Publishing, Cham.

- Edney, E.O., Kleindienst, T.E., Jaoui, M., Lewandowski, M., Offenberg, J.H., Wang, W., and Claeys, M. (2005). Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO_x/SO₂/air mixtures and their detection in ambient PM_{2.5} samples collected in the eastern United States. *Atmospheric Environment* 39 (29):5281–5289. doi:10.1016/j.atmosenv.2005.05.031.
- Ehn, M., Thornton, J.A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L.B., Jørgensen, S., Kjaergaard, H.G., Canagaratna, M., Maso, M.D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D.R., Wildt, J., and Mentel, T.F. (2014). A large source of low-volatility secondary organic aerosol. *Nature* 506 (7489):476–479. doi:10.1038/nature13032.
- Epstein, S.A., Tapavicza, E., Furche, F., and Nizkorodov, S.A. (2013). Direct photolysis of carbonyl compounds dissolved in cloud and fog droplets. *Atmospheric Chemistry and Physics* 13 (18):9461–9477. doi:10.5194/acp-13-9461-2013.
- Falcon-Rodriguez, C.I., Osornio-Vargas, A.R., Sada-Ovalle, I., and Segura-Medina, P. (2016). Aeroparticles, Composition, and Lung Diseases. *Front Immunol* 7:3. doi:10.3389/fimmu.2016.00003.
- Farmer, D.K., Boedicker, E.K., and DeBolt, H.M. (2021). Dry Deposition of Atmospheric Aerosols: Approaches, Observations, and Mechanisms. *Annual Review of Physical Chemistry* 72 (1):375–397. doi:10.1146/annurev-physchem-090519-034936.
- Faxon, C., Hammes, J., Le Breton, M., Pathak, R.K., and Hallquist, M. (2018). Characterization of organic nitrate constituents of secondary organic aerosol (SOA) from nitrate-radical-initiated oxidation of limonene using high-resolution chemical ionization mass spectrometry. *Atmos. Chem. Phys.* 18 (8):5467–5481. doi:10.5194/acp-18-5467-2018.
- Fine, P.M., Cass, G.R., and Simoneit, B.R.T. (2002). Organic compounds in biomass smoke from residential wood combustion: Emissions characterization at a continental scale. *Journal of Geophysical Research: Atmospheres* 107 (D21):ICC 11-1-ICC 11-9. doi:10.1029/2001JD000661.
- Fine, P.M., Cass, G.R., and Simoneit, B.R.T. (2001). Chemical Characterization of Fine Particle Emissions from Fireplace Combustion of Woods Grown in the Northeastern United States. *Environ. Sci. Technol.* 35 (13):2665–2675. doi:10.1021/es001466k.
- Finewax, Z., de Gouw, J.A., and Ziemann, P.J. (2019). Products and Secondary Organic Aerosol Yields from the OH and NO₃ Radical-Initiated Oxidation of Resorcinol. *ACS Earth and Space Chemistry* 3 (7):1248–1259. doi:10.1021/acsearthspacechem.9b00112.
- Finewax, Z., de Gouw, J.A., and Ziemann, P.J. (2018). Identification and Quantification of 4-Nitrocatechol Formed from OH and NO₃ Radical-Initiated Reactions of Catechol in Air in the Presence of NO_x: Implications for Secondary Organic Aerosol Formation from Biomass Burning. *Environmental Science & Technology* 52 (4):1981–1989. doi:10.1021/acs.est.7b05864.
- Finlayson-Pitts, B.J. and Pitts, J.N. (2000). CHAPTER 6 - Rates and Mechanisms of Gas-Phase Reactions in Irradiated Organic – NO_x – Air Mixtures., in *Chemistry*

- of the Upper and Lower Atmosphere, B.J. Finlayson-Pitts, J.N. Pitts, eds, Academic Press, San Diego, pp. 179–263.
- Finlayson-Pitts, B.J. and Pitts Jr, J.N. (2000). CHAPTER 11 - Analytical Methods and Typical Atmospheric Concentrations for Gases and Particles., in *Chemistry of the Upper and Lower Atmosphere*, Academic Press, San Diego, pp. 547–656.
- Fredrickson, C.D., Palm, B.B., Lee, B.H., Zhang, X., Orlando, J.J., Tyndall, G.S., Garofalo, L.A., Pothier, M.A., Farmer, D.K., Decker, Z.C.J., Robinson, M.A., Brown, S.S., Murphy, S.M., Shen, Y., Sullivan, A.P., Schobesberger, S., and Thornton, J.A. (2022). Formation and Evolution of Catechol-Derived SOA Mass, Composition, Volatility, and Light Absorption. *ACS Earth and Space Chemistry* 6 (4):1067–1079. doi:10.1021/acsearthspacechem.2c00007.
- Garofalo, L.A., He, Y., Jathar, S.H., Pierce, J.R., Fredrickson, C.D., Palm, B.B., Thornton, J.A., Mahrt, F., Crescenzo, G.V., Bertram, A.K., Draper, D.C., Fry, J.L., Orlando, J., Zhang, X., and Farmer, D.K. (2021). Heterogeneous Nucleation Drives Particle Size Segregation in Sequential Ozone and Nitrate Radical Oxidation of Catechol. *Environmental Science & Technology* 55 (23):15637–15645. doi:10.1021/acs.est.1c02984.
- Gaston, C.J., Lopez-Hilfiker, F.D., Whybrew, L.E., Hadley, O., McNair, F., Gao, H., Jaffe, D.A., and Thornton, J.A. (2016). Online molecular characterization of fine particulate matter in Port Angeles, WA: Evidence for a major impact from residential wood smoke. *Atmospheric Environment* 138:99–107. doi:10.1016/j.atmosenv.2016.05.013.
- Ghahreman, R., Gong, W., Galí, M., Norman, A.-L., Beagley, S.R., Akingunola, A., Zheng, Q., Lupu, A., Lizotte, M., Levasseur, M., and Leaitch, W.R. (2019). Dimethyl sulfide and its role in aerosol formation and growth in the Arctic summer – a modelling study. *Atmospheric Chemistry and Physics* 19 (23):14455–14476. doi:10.5194/acp-19-14455-2019.
- Gilman, J.B., Lerner, B.M., Kuster, W.C., Goldan, P.D., Warneke, C., Veres, P.R., Roberts, J.M., de Gouw, J.A., Burling, I.R., and Yokelson, R.J. (2015). Biomass burning emissions and potential air quality impacts of volatile organic compounds and other trace gases from fuels common in the US. *Atmospheric Chemistry and Physics* 15 (24):13915–13938. doi:10.5194/acp-15-13915-2015.
- Grieshop, A.P., Donahue, N.M., and Robinson, A.L. (2009). Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 2: analysis of aerosol mass spectrometer data. *Atmospheric Chemistry and Physics* 9 (6):2227–2240. doi:10.5194/acp-9-2227-2009.
- Grundlingh, J., Dargan, P.I., El-Zanfaly, M., and Wood, D.M. (2011). 2,4-Dinitrophenol (DNP): A Weight Loss Agent with Significant Acute Toxicity and Risk of Death. *Journal of Medical Toxicology* 7 (3):205–212. doi:10.1007/s13181-011-0162-6.
- Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P. (1995). A global model of natural volatile organic compound emissions. *Journal of Geophysical Research: Atmospheres* 100 (D5):8873–8892. doi:10.1029/94JD02950.
- Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, J.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T.F., Monod, A.,

- Prévôt, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R., and Wildt, J. (2009). The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* 9 (14):5155–5236. doi:10.5194/acp-9-5155-2009.
- Harrison, M.A.J., Barra, S., Borghesi, D., Vione, D., Arsene, C., and Iulian Olariu, R. (2005). Nitrated phenols in the atmosphere: a review. *Atmospheric Environment* 39 (2):231–248. doi:10.1016/j.atmosenv.2004.09.044.
- Hays, M.D., Geron, C.D., Linna, K.J., Smith, N.D., and Schauer, J.J. (2002). Speciation of Gas-Phase and Fine Particle Emissions from Burning of Foliar Fuels. *Environ. Sci. Technol.* 36 (11):2281–2295. doi:10.1021/es0111683.
- He, Z., Wang, X., Ling, Z., Zhao, J., Guo, H., Shao, M., and Wang, Z. (2019). Contributions of different anthropogenic volatile organic compound sources to ozone formation at a receptor site in the Pearl River Delta region and its policy implications. *Atmospheric Chemistry and Physics* 19 (13):8801–8816. doi:10.5194/acp-19-8801-2019.
- Health Effects Institute (2020). State of Global Air 2020.
- Healy, R.M., Chen, Y., Kourtshev, I., Kalberer, M., O'Shea, D., and Wenger, J.C. (2012). Rapid Formation of Secondary Organic Aerosol from the Photolysis of 1-Nitronaphthalene: Role of Naphthoxy Radical Self-reaction. *Environmental Science & Technology* 46 (21):11813–11820. doi:10.1021/es302841j.
- Healy, R.M., Temime, B., Kuprovskite, K., and Wenger, J.C. (2009). Effect of Relative Humidity on Gas/Particle Partitioning and Aerosol Mass Yield in the Photooxidation of p-Xylene. *Environ. Sci. Technol.* 43 (6):1884–1889. doi:10.1021/es802404z.
- Heard, D.E. and Pilling, M.J. (2003). Measurement of OH and HO₂ in the Troposphere. *Chem. Rev.* 103 (12):5163–5198. doi:10.1021/cr020522s.
- Heintzenberg, J., Wehner, B., and Birmili, W. (2007). 'How to find bananas in the atmospheric aerosol': new approach for analyzing atmospheric nucleation and growth events. *Tellus B* 59 (2):273–282. doi:10.1111/j.1600-0889.2007.00249.x.
- Hellebust, S., Allanic, A., O'Connor, I.P., Wenger, J.C., and Sodeau, J.R. (2010). The use of real-time monitoring data to evaluate major sources of airborne particulate matter. *Atmospheric Environment* 44 (8):1116–1125. doi:10.1016/j.atmosenv.2009.11.035.
- Herbig, J., Müller, M., Schallhart, S., Titzmann, T., Graus, M., and Hansel, A. (2009). On-line breath analysis with PTR-TOF. *J. Breath Res.* 3 (2):027004. doi:10.1088/1752-7155/3/2/027004.
- Hofmann, D., Hartmann, F., and Herrmann, H. (2008). Analysis of nitrophenols in cloud water with a miniaturized light-phase rotary perforator and HPLC-MS. *Analytical and Bioanalytical Chemistry* 391 (1):161–169. doi:10.1007/s00216-008-1939-6.
- Huff, J. (2007). Benzene-induced Cancers: Abridged History and Occupational Health Impact. *International Journal of Occupational and Environmental Health* 13 (2):213–221. doi:10.1179/oeh.2007.13.2.213.
- Huffman, J.A., Docherty, K.S., Aiken, A.C., Cubison, M.J., Ulbrich, I.M., DeCarlo, P.F., Sueper, D., Jayne, J.T., Worsnop, D.R., Ziemann, P.J., and Jimenez, J.L. (2009). Chemically-resolved aerosol volatility measurements from two megacity field studies. *Atmospheric Chemistry and Physics* 9 (18):7161–7182. doi:10.5194/acp-9-7161-2009.

- Linuma, Y., Böge, O., Gräfe, R., and Herrmann, H. (2010). Methyl-Nitrocatechols: Atmospheric Tracer Compounds for Biomass Burning Secondary Organic Aerosols. *Environmental Science & Technology* 44 (22):8453–8459. doi:10.1021/es102938a.
- Linuma, Y., Brüggemann, E., Gnauk, T., Müller, K., Andreae, M.O., Helas, G., Parmar, R., and Herrmann, H. (2007). Source characterization of biomass burning particles: The combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat. *Journal of Geophysical Research: Atmospheres* 112 (D8). doi:10.1029/2006JD007120.
- IPCC (2021). Climate Change 2021 – The Physical Science Basis: Working Group I Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, 1st ed. Cambridge University Press.
- IPCC (2007). Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. IPCC, Geneva, Switzerland.
- Jahl, L.G., Brubaker, T.A., Polen, M.J., Jahn, L.G., Cain, K.P., Bowers, B.B., Fahy, W.D., Graves, S., and Sullivan, R.C. (2021). Atmospheric aging enhances the ice nucleation ability of biomass-burning aerosol. *Science Advances* 7 (9):eabd3440. doi:10.1126/sciadv.abd3440.
- Ji, Y., Huey, L.G., Tanner, D.J., Lee, Y.R., Veres, P.R., Neuman, J.A., Wang, Y., and Wang, X. (2020). A vacuum ultraviolet ion source (VUV-IS) for iodide–chemical ionization mass spectrometry: a substitute for radioactive ion sources. *Atmospheric Measurement Techniques* 13 (7):3683–3696. doi:10.5194/amt-13-3683-2020.
- Jimenez, J.L., Canagaratna, M.R., Donahue, N.M., Prevot, A.S.H., Zhang, Q., Kroll, J.H., DeCarlo, P.F., Allan, J.D., Coe, H., Ng, N.L., Aiken, A.C., Docherty, K.S., Ulbrich, I.M., Grieshop, A.P., Robinson, A.L., Duplissy, J., Smith, J.D., Wilson, K.R., Lanz, V.A., Hueglin, C., Sun, Y.L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J.M., Collins, D.R., Cubison, M.J., E., Dunlea, J., Huffman, J.A., Onasch, T.B., Alfarra, M.R., Williams, P.I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J.Y., Zhang, Y.M., Dzepina, K., Kimmel, J.R., Sueper, D., Jayne, J.T., Herndon, S.C., Trimborn, A.M., Williams, L.R., Wood, E.C., Middlebrook, A.M., Kolb, C.E., Baltensperger, U., and Worsnop, D.R. (2009). Evolution of Organic Aerosols in the Atmosphere. *Science* 326 (5959):1525–1529. doi:10.1126/science.1180353.
- Jokinen, T., Berndt, T., Makkonen, R., Kerminen, V.-M., Junninen, H., Paasonen, P., Stratmann, F., Herrmann, H., Guenther, A.B., Worsnop, D.R., Kulmala, M., Ehn, M., and Sipilä, M. (2015). Production of extremely low volatile organic compounds from biogenic emissions: Measured yields and atmospheric implications. *Proceedings of the National Academy of Sciences* 112 (23):7123–7128. doi:10.1073/pnas.1423977112.
- Jones, A.C., Hill, A., Hemmings, J., Lemaitre, P., Quérel, A., Ryder, C.L., and Woodward, S. (2022). Below-cloud scavenging of aerosol by rain: a review of numerical modelling approaches and sensitivity simulations with mineral dust in the Met Office’s Unified Model. *Atmospheric Chemistry and Physics* 22 (17):11381–11407. doi:10.5194/acp-22-11381-2022.

- Jorga, S.D., Florou, K., Kaltsonoudis, C., Kodros, J.K., Vasilakopoulou, C., Cirtog, M., Fouqueau, A., Picquet-Varraut, B., Nenes, A., and Pandis, S.N. (2021). Nighttime chemistry of biomass burning emissions in urban areas: A dual mobile chamber study. *Atmos. Chem. Phys.* 21 (19):15337–15349. doi:10.5194/acp-21-15337-2021.
- Jost, C., Sprung, D., Kenntner, T., and Reiner, T. (2003). Atmospheric pressure chemical ionization mass spectrometry for the detection of tropospheric trace gases: the influence of clustering on sensitivity and precision. *International Journal of Mass Spectrometry, In Memoriam of Werner Lindinger* 223–224:771–782. doi:10.1016/S1387-3806(02)00963-6.
- Kahnt, A., Behrouzi, S., Vermeylen, R., Safi Shalamzari, M., Vercauteren, J., Roekens, E., Claeys, M., and Maenhaut, W. (2013). One-year study of nitro-organic compounds and their relation to wood burning in PM₁₀ aerosol from a rural site in Belgium. *Atmospheric Environment* 81:561–568. doi:10.1016/j.atmosenv.2013.09.041.
- Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A.S.H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., and Baltensperger, U. (2004). Identification of Polymers as Major Components of Atmospheric Organic Aerosols. *Science* 303 (5664):1659–1662. doi:10.1126/science.1092185.
- Kammer, J., Flaud, P.-M., Chazeaubeny, A., Ciuraru, R., Le Menach, K., Geneste, E., Budzinski, H., Bonnefond, J.M., Lamaud, E., Perraudin, E., and Villenave, E. (2020). Biogenic volatile organic compounds (BVOCs) reactivity related to new particle formation (NPF) over the Landes forest. *Atmospheric Research* 237:104869. doi:10.1016/j.atmosres.2020.104869.
- Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., and Wilson, J. (2005). Organic aerosol and global climate modelling: a review. *Atmospheric Chemistry and Physics* 5 (4):1053–1123. doi:10.5194/acp-5-1053-2005.
- Kanji, Z.A., Ladino, L.A., Wex, H., Boose, Y., Burkert-Kohn, M., Cziczo, D.J., and Krämer, M. (2017). Overview of Ice Nucleating Particles. *Meteorological Monographs* 58 (1):1.1-1.33. doi:10.1175/AMSMONOGRAPHIS-D-16-0006.1.
- Kawamoto, H. (2017). Lignin pyrolysis reactions. *J Wood Sci* 63 (2):117–132. doi:10.1007/s10086-016-1606-z.
- Kerminen, V.-M., Chen, X., Vakkari, V., Petäjä, T., Kulmala, M., and Bianchi, F. (2018). Atmospheric new particle formation and growth: review of field observations. *Environmental Research Letters* 13 (10):103003. doi:10.1088/1748-9326/aadf3c.
- Kim, M.J., Zoerb, M.C., Campbell, N.R., Zimmermann, K.J., Blomquist, B.W., Huebert, B.J., and Bertram, T.H. (2016). Revisiting benzene cluster cations for the chemical ionization of dimethyl sulfide and select volatile organic compounds. *Atmospheric Measurement Techniques* 9 (4):1473–1484. doi:10.5194/amt-9-1473-2016.
- Kitanovski, Z., Čusak, A., Grgić, I., and Claeys, M. (2014). Chemical characterization of the main products formed through aqueous-phase photolysis of guaiacol. *Atmos. Meas. Tech.* 7 (8):2457–2470. doi:10.5194/amt-7-2457-2014.

- Kodros, J.K., Papanastasiou, D.K., Paglione, M., Masiol, M., Squizzato, S., Florou, K., Skylakou, K., Kaltsonoudis, C., Nenes, A., and Pandis, S.N. (2020). Rapid dark aging of biomass burning as an overlooked source of oxidized organic aerosol. *Proceedings of the National Academy of Sciences* 117 (52):33028. doi:10.1073/pnas.2010365117.
- Kong, X. and Pettersson, J.B.C. (2020). Ordinal analysis applied to the results of positive matrix factorization of chemical ionization mass spectrometry data. *MethodsX* 7:101170. doi:10.1016/j.mex.2020.101170.
- Koppmann, R., von Czapiewski, K., and Reid, J.S. (2005). A review of biomass burning emissions, part I: gaseous emissions of carbon monoxide, methane, volatile organic compounds, and nitrogen containing compounds. *Atmospheric Chemistry and Physics Discussions* 5 (5):10455–10516. doi:10.5194/acpd-5-10455-2005.
- Kourtchev, I., Hellebust, S., Bell, J.M., O'Connor, I.P., Healy, R.M., Allanic, A., Healy, D., Wenger, J.C., and Sodeau, J.R. (2011). The use of polar organic compounds to estimate the contribution of domestic solid fuel combustion and biogenic sources to ambient levels of organic carbon and PM_{2.5} in Cork Harbour, Ireland. *Science of The Total Environment* 409 (11):2143–2155. doi:10.1016/j.scitotenv.2011.02.027.
- Kourtchev, I., Warnke, J., Maenhaut, W., Hoffmann, T., and Claeys, M. (2008). Polar organic marker compounds in PM_{2.5} aerosol from a mixed forest site in western Germany. *Chemosphere* 73 (8):1308–1314. doi:10.1016/j.chemosphere.2008.07.011.
- Kreyling, W.G., Semmler-Behnke, M., and Möller, W. (2006). Health implications of nanoparticles. *J Nanopart Res* 8 (5):543–562. doi:10.1007/s11051-005-9068-z.
- Kroflić, A., Anders, J., Drventić, I., Mettke, P., Böge, O., Mutzel, A., Kleffmann, J., and Herrmann, H. (2021). Guaiacol Nitration in a Simulated Atmospheric Aerosol with an Emphasis on Atmospheric Nitrophenol Formation Mechanisms. *ACS Earth and Space Chemistry* 5 (5):1083–1093. doi:10.1021/acsearthspacechem.1c00014.
- Kroll, J.H., Donahue, N.M., Jimenez, J.L., Kessler, S.H., Canagaratna, M.R., Wilson, K.R., Altieri, K.E., Mazzoleni, L.R., Wozniak, A.S., Bluhm, H., Mysak, E.R., Smith, J.D., Kolb, C.E., and Worsnop, D.R. (2011). Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nature Chemistry* 3 (2):133–139. doi:10.1038/nchem.948.
- Kroll, J.H., Ng, N.L., Murphy, S.M., Flagan, R.C., and Seinfeld, J.H. (2006). Secondary Organic Aerosol Formation from Isoprene Photooxidation. *Environ. Sci. Technol.* 40 (6):1869–1877. doi:10.1021/es0524301.
- Kroll, J.H. and Seinfeld, J.H. (2008). Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmospheric Environment* 42 (16):3593–3624. doi:10.1016/j.atmosenv.2008.01.003.
- Kürten, A., Bergen, A., Heinritzi, M., Leiminger, M., Lorenz, V., Piel, F., Simon, M., Sitals, R., Wagner, A.C., and Curtius, J. (2016). Observation of new particle formation and measurement of sulfuric acid, ammonia, amines and highly oxidized organic molecules at a rural site in central Germany. *Atmospheric Chemistry and Physics* 16 (19):12793–12813. doi:10.5194/acp-16-12793-2016.

- Kürten, A., Rondo, L., Ehrhart, S., and Curtius, J. (2011). Performance of a corona ion source for measurement of sulfuric acid by chemical ionization mass spectrometry. *Atmospheric Measurement Techniques* 4 (3):437–443. doi:10.5194/amt-4-437-2011.
- Kwon, H.-S., Ryu, M.H., and Carlsten, C. (2020). Ultrafine particles: unique physicochemical properties relevant to health and disease. *Exp Mol Med* 52 (3):318–328. doi:10.1038/s12276-020-0405-1.
- Lamkaddam, H., Gratien, A., Pangui, E., David, M., Peinado, F., Polienor, J.-M., Jerome, M., Cazaunau, M., Gaimoz, C., Picquet-Varrault, B., Kourtchev, I., Kalberer, M., and Doussin, J.-F. (2020). Role of Relative Humidity in the Secondary Organic Aerosol Formation from High-NO_x Photooxidation of Long-Chain Alkanes: n-Dodecane Case Study. *ACS Earth Space Chem.* 4 (12):2414–2425. doi:10.1021/acsearthspacechem.0c00265.
- Languille, B., Gros, V., Petit, J.-E., Honoré, C., Baudic, A., Perrussel, O., Foret, G., Michoud, V., Truong, F., Bonnaire, N., Sarda-Estève, R., Delmotte, M., Feron, A., Maisonneuve, F., Gaimoz, C., Formenti, P., Kotthaus, S., Haeffelin, M., and Favez, O. (2020). Wood burning: A major source of Volatile Organic Compounds during wintertime in the Paris region. *Science of The Total Environment* 711:135055. doi:10.1016/j.scitotenv.2019.135055.
- Lanz, V.A., Alfarra, M.R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A.S.H. (2007). Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra. *Atmospheric Chemistry and Physics* 7 (6):1503–1522. doi:10.5194/acp-7-1503-2007.
- Lanz, V.A., Hueglin, C., Buchmann, B., Hill, M., Locher, R., Staehelin, J., and Reimann, S. (2008). Receptor modeling of C₂-C₇ hydrocarbon sources at an urban background site in Zurich, Switzerland: Changes between 1993-1994 and 2005-2006. *Atmospheric Chemistry and Physics* 8 (9):2313–2332. doi:10.5194/acp-8-2313-2008.
- Latella, A., Stani, G., Cobelli, L., Duane, M., Junninen, H., Astorga, C., and Larsen, B.R. (2005). Semicontinuous GC analysis and receptor modelling for source apportionment of ozone precursor hydrocarbons in Bresso, Milan, 2003. Presented at the Journal of Chromatography A, pp. 29–39.
- Lauraguais, A., Bejan, I., Barnes, I., Wiesen, P., and Coeur, C. (2015). Rate Coefficients for the Gas-Phase Reactions of Hydroxyl Radicals with a Series of Methoxylated Aromatic Compounds. *J. Phys. Chem. A* 119 (24):6179–6187. doi:10.1021/acs.jpca.5b03232.
- Lauraguais, A., Coeur-Tourneur, C., Cassez, A., Deboudt, K., Fourmentin, M., and Choël, M. (2014). Atmospheric reactivity of hydroxyl radicals with guaiacol (2-methoxyphenol), a biomass burning emitted compound: Secondary organic aerosol formation and gas-phase oxidation products. *Atmospheric Environment* 86:155–163. doi:10.1016/j.atmosenv.2013.11.074.
- Lauraguais, A., El Zein, A., Coeur, C., Obeid, E., Cassez, A., Rayez, M.-T., and Rayez, J.-C. (2016). Kinetic Study of the Gas-Phase Reactions of Nitrate Radicals with Methoxyphenol Compounds: Experimental and Theoretical Approaches. *J. Phys. Chem. A* 120 (17):2691–2699. doi:10.1021/acs.jpca.6b02729.
- Lavi, A., Vermeuel, M.P., Novak, G.A., and Bertram, T.H. (2018). The sensitivity of benzene cluster cation chemical ionization mass spectrometry to select biogenic terpenes. *Atmospheric Measurement Techniques* 11 (6):3251–3262. doi:10.5194/amt-11-3251-2018.

- Le Breton, M., Psichoudaki, M., Hallquist, M., Watne, Å.K., Lutz, A., and Hallquist, Å.M. (2019). Application of a FIGAERO ToF CIMS for on-line characterization of real-world fresh and aged particle emissions from buses. *Aerosol Science and Technology* 53 (3):244–259. doi:10.1080/02786826.2019.1566592.
- Lee, B.H., D'Ambro, E.L., Lopez-Hilfiker, F.D., Schobesberger, S., Mohr, C., Zawadowicz, M.A., Liu, J., Shilling, J.E., Hu, W., Palm, B.B., Jimenez, J.L., Hao, L., Virtanen, A., Zhang, H., Goldstein, A.H., Pye, H.O.T., and Thornton, J.A. (2020). Resolving Ambient Organic Aerosol Formation and Aging Pathways with Simultaneous Molecular Composition and Volatility Observations. *ACS Earth Space Chem.* 4 (3):391–402. doi:10.1021/acsearthspacechem.9b00302.
- Lee, B.H., Lopez-Hilfiker, F.D., Mohr, C., Kurtén, T., Worsnop, D.R., and Thornton, J.A. (2014). An Iodide-Adduct High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer: Application to Atmospheric Inorganic and Organic Compounds. *Environ. Sci. Technol.* 48 (11):6309–6317. doi:10.1021/es500362a.
- Lee, B.H., Mohr, C., Lopez-Hilfiker, F.D., Lutz, A., Hallquist, M., Lee, L., Romer, P., Cohen, R.C., Iyer, S., Kurtén, T., Hu, W., Day, D.A., Campuzano-Jost, P., Jimenez, J.L., Xu, L., Ng, N.L., Guo, H., Weber, R.J., Wild, R.J., Brown, S.S., Koss, A., de Gouw, J., Olson, K., Goldstein, A.H., Seco, R., Kim, S., McAvey, K., Shepson, P.B., Starn, T., Baumann, K., Edgerton, E.S., Liu, J., Shilling, J.E., Miller, D.O., Brune, W., Schobesberger, S., D'Ambro, E.L., and Thornton, J.A. (2016). Highly functionalized organic nitrates in the southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets. *Proceedings of the National Academy of Sciences* 113 (6):1516–1521. doi:10.1073/pnas.1508108113.
- Lelieveld, J., Klingmüller, K., Pozzer, A., Burnett, R.T., Haines, A., and Ramanathan, V. (2019). Effects of fossil fuel and total anthropogenic emission removal on public health and climate. *Proceedings of the National Academy of Sciences* 116 (15):7192–7197. doi:10.1073/pnas.1819989116.
- Leslie, M.D., Ridoli, M., Murphy, J.G., and Borduas-Dedekind, N. (2019). Isocyanic acid (HNCO) and its fate in the atmosphere: a review. *Environ. Sci.: Processes Impacts* 21 (5):793–808. doi:10.1039/C9EM00003H.
- Levy II, H., Horowitz, L.W., Schwarzkopf, M.D., Ming, Y., Golaz, J.-C., Naik, V., and Ramaswamy, V. (2013). The roles of aerosol direct and indirect effects in past and future climate change. *Journal of Geophysical Research: Atmospheres* 118 (10):4521–4532. doi:10.1002/jgrd.50192.
- Li, M., Karu, E., Brenninkmeijer, C., Fischer, H., Lelieveld, J., and Williams, J. (2018). Tropospheric OH and stratospheric OH and Cl concentrations determined from CH₄, CH₃Cl, and SF₆ measurements. *npj Clim Atmos Sci* 1 (1):1–7. doi:10.1038/s41612-018-0041-9.
- Li, M., Wang, X., Zhao, Yanan, Du, P., Li, H., Li, J., Shen, H., Liu, Z., Jiang, Y., Chen, Jing, Bi, Y., Zhao, Yong, Xue, L., Wang, Y., Chen, Jianmin, and Wang, W. (2022). Atmospheric Nitrated Phenolic Compounds in Particle, Gaseous, and Aqueous Phases During Cloud Events at a Mountain Site in North China: Distribution Characteristics and Aqueous-Phase Formation. *Journal of Geophysical Research: Atmospheres* 127 (18):e2022JD037130. doi:10.1029/2022JD037130.

- Lin, C., Ceburnis, D., Hellebust, S., Buckley, P., Wenger, J., Canonaco, F., Prévôt, A.S.H., Huang, R.-J., O'Dowd, C., and Ovadnevaite, J. (2017). Characterization of Primary Organic Aerosol from Domestic Wood, Peat, and Coal Burning in Ireland. *Environ. Sci. Technol.* 51 (18):10624–10632. doi:10.1021/acs.est.7b01926.
- Lin, C., Ceburnis, D., Huang, R.-J., Xu, W., Spohn, T., Martin, D., Buckley, P., Wenger, J., Hellebust, S., Rinaldi, M., Facchini, M.C., O'Dowd, C., and Ovadnevaite, J. (2019). Wintertime aerosol dominated by solid-fuel-burning emissions across Ireland: insight into the spatial and chemical variation in submicron aerosol. *Atmospheric Chemistry and Physics* 19 (22):14091–14106. doi:10.5194/acp-19-14091-2019.
- Lin, X., Tang, X., Wen, Z., Long, B., Fittschen, C., Gu, X., Gai, Y., and Zhang, W. (2022). Direct observation of the particle-phase bicyclic products from OH-initiated oxidation of 1,3,5-trimethylbenzene under NO_x-free conditions. *Atmospheric Environment* 271:118914. doi:10.1016/j.atmosenv.2021.118914.
- Liu, F., Joo, T., Ditto, J.C., Saavedra, M.G., Takeuchi, M., Boris, A.J., Yang, Y., Weber, R.J., Dillner, A.M., Gentner, D.R., and Ng, N.L. (2023). Oxidized and Unsaturated: Key Organic Aerosol Traits Associated with Cellular Reactive Oxygen Species Production in the Southeastern United States. *Environ. Sci. Technol.* 57 (38):14150–14161. doi:10.1021/acs.est.3c03641.
- Liu, W.-J., Jiang, H., and Yu, H.-Q. (2015). Thermochemical conversion of lignin to functional materials: a review and future directions. *Green Chemistry* 17 (11):4888–4907. doi:10.1039/C5GC01054C.
- Liu, X., Huey, L.G., Yokelson, R.J., Selimovic, V., Simpson, I.J., Müller, M., Jimenez, J.L., Campuzano-Jost, P., Beyersdorf, A.J., Blake, D.R., Butterfield, Z., Choi, Y., Crounse, J.D., Day, D.A., Diskin, G.S., Dubey, M.K., Fortner, E., Hanisco, T.F., Hu, W., King, L.E., Kleinman, L., Meinardi, S., Mikoviny, T., Onasch, T.B., Palm, B.B., Peischl, J., Pollack, I.B., Ryerson, T.B., Sachse, G.W., Sedlacek, A.J., Shilling, J.E., Springston, S., St. Clair, J.M., Tanner, D.J., Teng, A.P., Wennberg, P.O., Wisthaler, A., and Wolfe, G.M. (2017). Airborne measurements of western U.S. wildfire emissions: Comparison with prescribed burning and air quality implications. *Journal of Geophysical Research: Atmospheres* 122 (11):6108–6129. doi:10.1002/2016JD026315.
- Lohmann, U., Rotstajn, L., Storelvmo, T., Jones, A., Menon, S., Quaas, J., Ekman, A.M.L., Koch, D., and Ruedy, R. (2010). Total aerosol effect: radiative forcing or radiative flux perturbation? *Atmospheric Chemistry and Physics* 10 (7):3235–3246. doi:10.5194/acp-10-3235-2010.
- Lopez-Hilfiker, F.D., Mohr, C., D'Ambro, E.L., Lutz, A., Riedel, T.P., Gaston, C.J., Iyer, S., Zhang, Z., Gold, A., Surratt, J.D., Lee, B.H., Kurten, T., Hu, W.W., Jimenez, J., Hallquist, M., and Thornton, J.A. (2016). Molecular Composition and Volatility of Organic Aerosol in the Southeastern U.S.: Implications for IEPOX Derived SOA. *Environ. Sci. Technol.* 50 (5):2200–2209. doi:10.1021/acs.est.5b04769.
- Lopez-Hilfiker, F.D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T.F., Carrasquillo, A.J., Daumit, K.E., Hunter, J.F., Kroll, J.H., Worsnop, D.R., and Thornton, J.A. (2015). Phase partitioning and volatility of secondary organic aerosol components formed from α -pinene ozonolysis and OH oxidation: the importance of accretion products and other low volatility compounds. *Atmos. Chem. Phys.* 15 (14):7765–7776. doi:10.5194/acp-15-7765-2015.

- Lopez-Hilfiker, F.D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T.F., Lutz, A., Hallquist, M., Worsnop, D., and Thornton, J.A. (2014). A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROsols (FIGAERO). *Atmos. Meas. Tech.* 7 (4):983–1001. doi:10.5194/amt-7-983-2014.
- Lu, C., Wang, X., Zhang, J., Liu, Z., Liang, Y., Dong, S., Li, M., Chen, J., Chen, H., Xie, H., Xue, L., and Wang, W. (2021). Substantial emissions of nitrated aromatic compounds in the particle and gas phases in the waste gases from eight industries. *Environmental Pollution* 283:117132. doi:10.1016/j.envpol.2021.117132.
- Luo, H., Vereecken, L., Shen, H., Kang, S., Pullinen, I., Hallquist, M., Fuchs, H., Wahner, A., Kiendler-Scharr, A., Mentel, T.F., and Zhao, D. (2023). Formation of highly oxygenated organic molecules from the oxidation of limonene by OH radical: significant contribution of H-abstraction pathway. *Atmospheric Chemistry and Physics* 23 (13):7297–7319. doi:10.5194/acp-23-7297-2023.
- Lutz, A., Mohr, C., Le Breton, M., Lopez-Hilfiker, F.D., Priestley, M., Thornton, J.A., and Hallquist, M. (2019). Gas to Particle Partitioning of Organic Acids in the Boreal Atmosphere. *ACS Earth and Space Chemistry* 3 (7):1279–1287. doi:10.1021/acsearthspacechem.9b00041.
- Maduskar, S., Maliekkal, V., Neurock, M., and Dauenhauer, P.J. (2018). On the Yield of Levoglucosan from Cellulose Pyrolysis. *ACS Sustainable Chem. Eng.* 6 (5):7017–7025. doi:10.1021/acssuschemeng.8b00853.
- Martín-Reviejo, M. and Wirtz, K. (2005). Is Benzene a Precursor for Secondary Organic Aerosol? *Environ. Sci. Technol.* 39 (4):1045–1054. doi:10.1021/es049802a.
- Massoli, P., Stark, H., Canagaratna, M.R., Krechmer, J.E., Xu, L., Ng, N.L., Mauldin, R.L.I., Yan, C., Kimmel, J., Misztal, P.K., Jimenez, J.L., Jayne, J.T., and Worsnop, D.R. (2018). Ambient Measurements of Highly Oxidized Gas-Phase Molecules during the Southern Oxidant and Aerosol Study (SOAS) 2013. *ACS Earth Space Chem.* 2 (7):653–672. doi:10.1021/acsearthspacechem.8b00028.
- Mayorga, R.J., Zhao, Z., and Zhang, H. (2021). Formation of secondary organic aerosol from nitrate radical oxidation of phenolic VOCs: Implications for nitration mechanisms and brown carbon formation. *Atmospheric Environment* 244:117910. doi:10.1016/j.atmosenv.2020.117910.
- Mazzoleni, L.R., Zielinska, B., and Moosmüller, H. (2007). Emissions of Levoglucosan, Methoxy Phenols, and Organic Acids from Prescribed Burns, Laboratory Combustion of Wildland Fuels, and Residential Wood Combustion. *Environ. Sci. Technol.* 41 (7):2115–2122. doi:10.1021/es061702c.
- McDonald, B.C., de Gouw, J.A., Gilman, J.B., Jathar, S.H., Akherati, A., Cappa, C.D., Jimenez, J.L., Lee-Taylor, J., Hayes, P.L., McKeen, S.A., Cui, Y.Y., Kim, S.-W., Gentner, D.R., Isaacman-VanWertz, G., Goldstein, A.H., Harley, R.A., Frost, G.J., Roberts, J.M., Ryerson, T.B., and Trainer, M. (2018). Volatile chemical products emerging as largest petrochemical source of urban organic emissions. *Science* 359 (6377):760–764. doi:10.1126/science.aaq0524.
- McDonald, J.D., Zielinska, B., Fujita, E.M., Sagebiel, J.C., Chow, J.C., and Watson, J.G. (2000). Fine Particle and Gaseous Emission Rates from Residential Wood Combustion. *Environ. Sci. Technol.* 34 (11):2080–2091. doi:10.1021/es9909632.

- Mehra, A., Canagaratna, M., J. Bannan, T., D. Worrall, S., Bacak, A., Priestley, M., Liu, D., Zhao, J., Xu, W., Sun, Y., F. Hamilton, J., A. Squires, F., Lee, J., J. Bryant, D., R. Hopkins, J., Elzein, A., Hapsari Budisulistiorini, S., Cheng, X., Chen, Q., Wang, Y., Wang, L., Stark, H., E. Krechmer, J., Brean, J., Slater, E., Whalley, L., Heard, D., Ouyang, B., F. Acton, W.J., Nicholas Hewitt, C., Wang, X., Fu, P., Jayne, J., Worsnop, D., Allan, J., Percival, C., and Coe, H. (2021). Using highly time-resolved online mass spectrometry to examine biogenic and anthropogenic contributions to organic aerosol in Beijing. *Faraday Discussions* 226 (0):382–408. doi:10.1039/D0FD00080A.
- Mehra, A., Wang, Y., Krechmer, J.E., Lambe, A., Majluf, F., Morris, M.A., Priestley, M., Bannan, T.J., Bryant, D.J., Pereira, K.L., Hamilton, J.F., Rickard, A.R., Newland, M.J., Stark, H., Croteau, P., Jayne, J.T., Worsnop, D.R., Canagaratna, M.R., Wang, L., and Coe, H. (2020). Evaluation of the chemical composition of gas- and particle-phase products of aromatic oxidation. *Atmos. Chem. Phys.* 20 (16):9783–9803. doi:10.5194/acp-20-9783-2020.
- Meng, L., Coeur, C., Fayad, L., Houzel, N., Genevray, P., Bouzidi, H., Tomas, A., and Chen, W. (2020). Secondary organic aerosol formation from the gas-phase reaction of guaiacol (2-methoxyphenol) with NO₃ radicals. *Atmospheric Environment* 240:117740. doi:10.1016/j.atmosenv.2020.117740.
- Mentel, T.F., Wildt, J., Kiendler-Scharr, A., Kleist, E., Tillmann, R., Dal Maso, M., Fisseha, R., Hohaus, T., Spahn, H., Uerlings, R., Wegener, R., Griffiths, P.T., Dinar, E., Rudich, Y., and Wahner, A. (2009). Photochemical production of aerosols from real plant emissions. *Atmospheric Chemistry and Physics* 9 (13):4387–4406. doi:10.5194/acp-9-4387-2009.
- Mohr, C., Lopez-Hilfiker, F.D., Zotter, P., Prévôt, A.S.H., Xu, L., Ng, N.L., Herndon, S.C., Williams, L.R., Franklin, J.P., Zahniser, M.S., Worsnop, D.R., Knighton, W.B., Aiken, A.C., Gorkowski, K.J., Dubey, M.K., Allan, J.D., and Thornton, J.A. (2013). Contribution of Nitrated Phenols to Wood Burning Brown Carbon Light Absorption in Detling, United Kingdom during Winter Time. *Environ. Sci. Technol.* 47 (12):6316–6324. doi:10.1021/es400683v.
- Molteni, U., Bianchi, F., Klein, F., El Haddad, I., Frege, C., Rossi, M.J., Dommen, J., and Baltensperger, U. (2018). Formation of highly oxygenated organic molecules from aromatic compounds. *Atmos. Chem. Phys.* 18 (3):1909–1921. doi:10.5194/acp-18-1909-2018.
- Morawska, L. and Buonanno, G. (2021). The physics of particle formation and deposition during breathing. *Nat Rev Phys* 3 (5):300–301. doi:10.1038/s42254-021-00307-4.
- Ng, N.L., Chhabra, P.S., Chan, A.W.H., Surratt, J.D., Kroll, J.H., Kwan, A.J., McCabe, D.C., Wennberg, P.O., Sorooshian, A., Murphy, S.M., Dalleska, N.F., Flagan, R.C., and Seinfeld, J.H. (2007a). Effect of NO_x level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes. *Atmospheric Chemistry and Physics* 7 (19):5159–5174. doi:10.5194/acp-7-5159-2007.
- Ng, N.L., Kroll, J.H., Chan, A.W.H., Chhabra, P.S., Flagan, R.C., and Seinfeld, J.H. (2007b). Secondary organic aerosol formation from m-xylene, toluene, and benzene. *Atmos. Chem. Phys.* 7 (14):3909–3922. doi:10.5194/acp-7-3909-2007.
- Norris, G., Duvall, R., Brown, S., and Bai, S. (2014). Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide.

- Novaes, E., Kirst, M., Chiang, V., Winter-Sederoff, H., and Sederoff, R. (2010). Lignin and Biomass: A Negative Correlation for Wood Formation and Lignin Content in Trees. *Plant Physiol* 154 (2):555–561. doi:10.1104/pp.110.161281.
- Odum, J.R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R.C., and Seinfeld, J.H. (1996). Gas/Particle Partitioning and Secondary Organic Aerosol Yields. *Environ. Sci. Technol.* 30 (8):2580–2585. doi:10.1021/es950943+.
- Olariu, R., Tomas, A., Barnes, I., and Wirtz, K. (2003). Atmospheric ozone degradation reaction of 1,2-dihydroxybenzene: Aerosol formation study., in *The European Photoreactor EUPHORE, Fourth Report 2001*, pp. 47–63.
- Olariu, R.I., Barnes, I., Becker, K.H., and Klotz, B. (2000). Rate coefficients for the gas-phase reaction of OH radicals with selected dihydroxybenzenes and benzoquinones. *International Journal of Chemical Kinetics* 32 (11):696–702. doi:10.1002/1097-4601(2000)32:11<696::AID-KIN5>3.0.CO;2-N.
- Olariu, R.I., Barnes, I., Bejan, I., Arsene, C., Vione, D., Klotz, B., and Becker, K.H. (2013). FT-IR Product Study of the Reactions of NO₃ Radicals With ortho-, meta-, and para-Cresol. *Environmental Science & Technology* 47 (14):7729–7738. doi:10.1021/es401096w.
- Olariu, R.I., Bejan, I., Barnes, I., Klotz, B., Becker, K.H., and Wirtz, K. (2004). Rate coefficients for the gas-phase reaction of NO₃ radicals with selected dihydroxybenzenes. *International Journal of Chemical Kinetics* 36 (11):577–583. doi:10.1002/kin.20029.
- Olariu, R.I., Klotz, B., Barnes, I., Becker, K.H., and Mocanu, R. (2002). FT-IR study of the ring-retaining products from the reaction of OH radicals with phenol, o-, m-, and p-cresol. *Atmospheric Environment* 36 (22):3685–3697. doi:10.1016/S1352-2310(02)00202-9.
- Paatero, P. and Tapper, U. (1994). Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* 5 (2):111–126. doi:10.1002/env.3170050203.
- Pang, J.Y.S., Novelli, A., Kaminski, M., Acir, I.-H., Bohn, B., Carlsson, P.T.M., Cho, C., Dorn, H.-P., Hofzumahaus, A., Li, X., Lutz, A., Nehr, S., Reimer, D., Rohrer, F., Tillmann, R., Wegener, R., Kiendler-Scharr, A., Wahner, A., and Fuchs, H. (2022). Investigation of the limonene photooxidation by OH at different NO concentrations in the atmospheric simulation chamber SAPHIR (Simulation of Atmospheric PHotochemistry In a large Reaction Chamber). *Atmospheric Chemistry and Physics* 22 (13):8497–8527. doi:10.5194/acp-22-8497-2022.
- Pashynska, V., Vermeylen, R., Vas, G., Maenhaut, W., and Claeys, M. (2002). Development of a gas chromatographic/ion trap mass spectrometric method for the determination of levoglucosan and saccharidic compounds in atmospheric aerosols. Application to urban aerosols. *Journal of Mass Spectrometry* 37 (12):1249–1257. doi:10.1002/jms.391.
- Perraud, V., Bruns, E.A., Ezell, M.J., Johnson, S.N., Greaves, J., and Finlayson-Pitts, B.J. (2010). Identification of Organic Nitrates in the NO₃ Radical Initiated Oxidation of α -Pinene by Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Environmental Science & Technology* 44 (15):5887–5893. doi:10.1021/es1005658.
- Peters, A. (2023). Ambient air pollution and Alzheimer's disease: the role of the composition of fine particles. *Proceedings of the National Academy of Sciences* 120 (3):e2220028120. doi:10.1073/pnas.2220028120.

- Pillar, E.A., Camm, R.C., and Guzman, M.I. (2014). Catechol Oxidation by Ozone and Hydroxyl Radicals at the Air–Water Interface. *Environmental Science & Technology* 48 (24):14352–14360. doi:10.1021/es504094x.
- Pillar, E.A. and Guzman, M.I. (2017). Oxidation of Substituted Catechols at the Air–Water Interface: Production of Carboxylic Acids, Quinones, and Polyphenols. *Environmental Science & Technology* 51 (9):4951–4959. doi:10.1021/acs.est.7b00232.
- Poschl, U. (2005). Atmospheric aerosols: composition, transformation, climate and health effects. *Angewandte Chemie (International ed. in English)* 44 (46):7520–40. doi:10.1002/anie.200501122.
- Poulain, L., Spindler, G., Grüner, A., Tuch, T., Stieger, B., van Pinxteren, D., Petit, J.-E., Favez, O., Herrmann, H., and Wiedensohler, A. (2020). Multi-year ACSM measurements at the central European research station Melpitz (Germany) – Part 1: Instrument robustness, quality assurance, and impact of upper size cutoff diameter. *Atmospheric Measurement Techniques* 13 (9):4973–4994. doi:10.5194/amt-13-4973-2020.
- Priestley, M., Bannan, T.J., Le Breton, M., Worrall, S.D., Kang, S., Pullinen, I., Schmitt, S., Tillmann, R., Kleist, E., Zhao, D., Wildt, J., Garmash, O., Mehra, A., Bacak, A., Shallcross, D.E., Kiendler-Scharr, A., Hallquist, Å.M., Ehn, M., Coe, H., Percival, C.J., Hallquist, M., Mentel, T.F., and McFiggans, G. (2021). Chemical characterisation of benzene oxidation products under high- and low-NO_x conditions using chemical ionisation mass spectrometry. *Atmos. Chem. Phys.* 21 (5):3473–3490. doi:10.5194/acp-21-3473-2021.
- Pullinen, I., Schmitt, S., Kang, S., Sarrafzadeh, M., Schlag, P., Andres, S., Kleist, E., Mentel, T.F., Rohrer, F., Springer, M., Tillmann, R., Wildt, J., Wu, C., Zhao, D., Wahner, A., and Kiendler-Scharr, A. (2020). Impact of NO_x on secondary organic aerosol (SOA) formation from α -pinene and β -pinene photooxidation: the role of highly oxygenated organic nitrates. *Atmospheric Chemistry and Physics* 20 (17):10125–10147. doi:10.5194/acp-20-10125-2020.
- Pye, H.O.T., Ward-Caviness, C.K., Murphy, B.N., Appel, K.W., and Seltzer, K.M. (2021). Secondary organic aerosol association with cardiorespiratory disease mortality in the United States. *Nat Commun* 12 (1):7215. doi:10.1038/s41467-021-27484-1.
- Reinmig, M.-C., Müller, L., Warnke, J., and Hoffmann, T. (2008). Characterization of selected organic compound classes in secondary organic aerosol from biogenic VOCs by HPLC/MSn. *Anal Bioanal Chem* 391 (1):171–182. doi:10.1007/s00216-008-1964-5.
- Richters, S., Herrmann, H., and Berndt, T. (2016). Highly Oxidized RO₂ Radicals and Consecutive Products from the Ozonolysis of Three Sesquiterpenes. *Environ. Sci. Technol.* 50 (5):2354–2362. doi:10.1021/acs.est.5b05321.
- Riva, M., Budisulistiorini, S.H., Zhang, Z., Gold, A., Thornton, J.A., Turpin, B.J., and Surratt, J.D. (2017). Multiphase reactivity of gaseous hydroperoxide oligomers produced from isoprene ozonolysis in the presence of acidified aerosols. *Atmospheric Environment* 152:314–322. doi:10.1016/j.atmosenv.2016.12.040.
- Riva, M., Heikkinen, L., Bell, D.M., Peräkylä, O., Zha, Q., Schallhart, S., Rissanen, M.P., Imre, D., Petäjä, T., Thornton, J.A., Zelenyuk, A., and Ehn, M. (2019a). Chemical transformations in monoterpene-derived organic aerosol enhanced by inorganic composition. *npj Clim Atmos Sci* 2 (1):1–9. doi:10.1038/s41612-018-0058-0.

- Riva, M., Rantala, P., Krechmer, J.E., Peräkylä, O., Zhang, Y., Heikkinen, L., Garmash, O., Yan, C., Kulmala, M., Worsnop, D., and Ehn, M. (2019b). Evaluating the performance of five different chemical ionization techniques for detecting gaseous oxygenated organic species. *Atmospheric Measurement Techniques* 12 (4):2403–2421. doi:10.5194/amt-12-2403-2019.
- Roberts, J.M., Veres, P.R., Cochran, A.K., Warneke, C., Burling, I.R., Yokelson, R.J., Lerner, B., Gilman, J.B., Kuster, W.C., Fall, R., and de Gouw, J. (2011). Isocyanic acid in the atmosphere and its possible link to smoke-related health effects. *Proceedings of the National Academy of Sciences* 108 (22):8966–8971. doi:10.1073/pnas.1103352108.
- Roman, C., Arsene, C., Bejan, I.G., and Olariu, R.I. (2022). Investigations into the gas-phase photolysis and OH radical kinetics of nitrocatechols: implications of intramolecular interactions on their atmospheric behaviour. *Atmos. Chem. Phys.* 22 (4):2203–2219. doi:10.5194/acp-22-2203-2022.
- Rosanka, S., Vu, G.H.T., Nguyen, H.M.T., Pham, T.V., Javed, U., Taraborrelli, D., and Vereecken, L. (2020). Atmospheric chemical loss processes of isocyanic acid (HNCO): a combined theoretical kinetic and global modelling study. *Atmos. Chem. Phys.* 20 (11):6671–6686. doi:10.5194/acp-20-6671-2020.
- Salvador, C.M.G., Tang, R., Priestley, M., Li, L., Tsiligiannis, E., Le Breton, M., Zhu, W., Zeng, L., Wang, H., Yu, Y., Hu, M., Guo, S., and Hallquist, M. (2021). Ambient nitro-aromatic compounds – biomass burning versus secondary formation in rural China. *Atmos. Chem. Phys.* 21 (3):1389–1406. doi:10.5194/acp-21-1389-2021.
- Sanchez, J., Tanner, D.J., Chen, D., Huey, L.G., and Ng, N.L. (2016). A new technique for the direct detection of HO₂ radicals using bromide chemical ionization mass spectrometry (Br-CIMS): initial characterization. *Atmospheric Measurement Techniques* 9 (8):3851–3861. doi:10.5194/amt-9-3851-2016.
- Sangwan, M. and Zhu, L. (2018). Role of Methyl-2-nitrophenol Photolysis as a Potential Source of OH Radicals in the Polluted Atmosphere: Implications from Laboratory Investigation. *The Journal of Physical Chemistry A* 122 (7):1861–1872. doi:10.1021/acs.jpca.7b11235.
- Sarrafzadeh, M., Wildt, J., Pullinen, I., Springer, M., Kleist, E., Tillmann, R., Schmitt, S.H., Wu, C., Mentel, T.F., Zhao, D., Hastie, D.R., and Kiendler-Scharr, A. (2016). Impact of NO_x and OH on secondary organic aerosol formation from β -pinene photooxidation. *Atmospheric Chemistry and Physics* 16 (17):11237–11248. doi:10.5194/acp-16-11237-2016.
- Sauvage, S., Plaisance, H., Locoge, N., Wroblewski, A., Coddeville, P., and Galloo, J.C. (2009). Long term measurement and source apportionment of non-methane hydrocarbons in three French rural areas. *Atmospheric Environment* 43 (15):2430–2441. doi:10.1016/j.atmosenv.2009.02.001.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., and Simoneit, B.R.T. (2001). Measurement of Emissions from Air Pollution Sources. 3. C₁–C₂₉ Organic Compounds from Fireplace Combustion of Wood. *Environ. Sci. Technol.* 35 (9):1716–1728. doi:10.1021/es001331e.
- Schraufnagel, D.E. (2020). The health effects of ultrafine particles. *Exp Mol Med* 52 (3):311–317. doi:10.1038/s12276-020-0403-3.
- Schwantes, R.H., Schilling, K.A., McVay, R.C., Lignell, H., Coggon, M.M., Zhang, X., Wennberg, P.O., and Seinfeld, J.H. (2017). Formation of highly oxygenated low-volatility products from cresol oxidation. *Atmos. Chem. Phys.* 17 (5):3453–3474. doi:10.5194/acp-17-3453-2017.

- Shen, J., Taghvaei, S., La, C., Oroumian, F., Liu, J., Jerrett, M., Weichenthal, S., Del Rosario, I., Shafer, M.M., Ritz, B., Zhu, Y., and Paulson, S.E. (2022). Aerosol Oxidative Potential in the Greater Los Angeles Area: Source Apportionment and Associations with Socioeconomic Position. *Environ. Sci. Technol.* 56 (24):17795–17804. doi:10.1021/acs.est.2c02788.
- Shi, X., Tang, R., Dong, Z., Liu, H., Xu, F., Zhang, Q., Zong, W., and Cheng, J. (2022). A neglected pathway for the accretion products formation in the atmosphere. *Science of The Total Environment* 848:157494. doi:10.1016/j.scitotenv.2022.157494.
- Simpson, C.D., Paulsen, M., Dills, R.L., Liu, L.-J.S., and Kalman, D.A. (2005). Determination of Methoxyphenols in Ambient Atmospheric Particulate Matter: Tracers for Wood Combustion. *Environ. Sci. Technol.* 39 (2):631–637. doi:10.1021/es0486871.
- Srivastava, D., Vu, T.V., Tong, S., Shi, Z., and Harrison, R.M. (2022). Formation of secondary organic aerosols from anthropogenic precursors in laboratory studies. *npj Clim Atmos Sci* 5 (1):1–30. doi:10.1038/s41612-022-00238-6.
- Stark, H., Yatavelli, R.L.N., Thompson, S.L., Kimmel, J.R., Cubison, M.J., Chhabra, P.S., Canagaratna, M.R., Jayne, J.T., Worsnop, D.R., and Jimenez, J.L. (2015). Methods to extract molecular and bulk chemical information from series of complex mass spectra with limited mass resolution. *International Journal of Mass Spectrometry* 389:26–38. doi:10.1016/j.ijms.2015.08.011.
- Strollo, C.M. and Ziemann, P.J. (2013). Products and mechanism of secondary organic aerosol formation from the reaction of 3-methylfuran with OH radicals in the presence of NO_x. *Atmospheric Environment* 77:534–543. doi:10.1016/j.atmosenv.2013.05.033.
- Suh, I., Zhang, R., Molina, L.T., and Molina, M.J. (2003). Oxidation Mechanism of Aromatic Peroxy and Bicyclic Radicals from OH–Toluene Reactions. *Journal of the American Chemical Society* 125 (41):12655–12665. doi:10.1021/ja0350280.
- Sun, J., Wei, B., Mei, Q., An, Z., Wang, X., and He, M. (2019). Ozonation of 3-methylcatechol and 4-methylcatechol in the atmosphere and aqueous particles: Mechanism, kinetics and ecotoxicity assessment. *Chemical Engineering Journal* 358:456–466. doi:10.1016/j.cej.2018.10.074.
- Susaya, J., Kim, K.-H., Cho, J.W., and Parker, D. (2011). The use of permeation tube device and the development of empirical formula for accurate permeation rate. *Journal of Chromatography A* 1218 (52):9328–9335. doi:10.1016/j.chroma.2011.11.007.
- Thompson, S.L., Yatavelli, R.L.N., Stark, H., Kimmel, J.R., Krechmer, J.E., Day, D.A., Hu, W., Isaacman-VanWertz, G., Yee, L., Goldstein, A.H., Khan, M.A.H., Holzinger, R., Kreisberg, N., Lopez-Hilfiker, F.D., Mohr, C., Thornton, J.A., Jayne, J.T., Canagaratna, M., Worsnop, D.R., and Jimenez, J.L. (2017). Field intercomparison of the gas/particle partitioning of oxygenated organics during the Southern Oxidant and Aerosol Study (SOAS) in 2013. *Aerosol Science and Technology* 51 (1):30–56. doi:10.1080/02786826.2016.1254719.
- Thornton, J.A., Mohr, C., Schobesberger, S., D'Ambro, E.L., Lee, B.H., and Lopez-Hilfiker, F.D. (2020). Evaluating Organic Aerosol Sources and Evolution with a Combined Molecular Composition and Volatility Framework Using the Filter Inlet for Gases and Aerosols (FIGAERO). *Accounts of Chemical Research*. doi:10.1021/acs.accounts.0c00259.

- Tuite, K., Thomas, J.L., Veres, P.R., Roberts, J.M., Stevens, P.S., Griffith, S.M., Dusanter, S., Flynn, J.H., Ahmed, S., Emmons, L., Kim, S.-W., Washenfelder, R., Young, C., Tsai, C., Pikelnaya, O., and Stutz, J. (2021). Quantifying Nitrous Acid Formation Mechanisms Using Measured Vertical Profiles During the CalNex 2010 Campaign and 1D Column Modeling. *Journal of Geophysical Research: Atmospheres* 126 (13):e2021JD034689. doi:10.1029/2021JD034689.
- Veres, P., Roberts, J.M., Burling, I.R., Warneke, C., de Gouw, J., and Yokelson, R.J. (2010). Measurements of gas-phase inorganic and organic acids from biomass fires by negative-ion proton-transfer chemical-ionization mass spectrometry. *Journal of Geophysical Research: Atmospheres* 115 (D23). doi:10.1029/2010JD014033.
- Veres, P.R., Roberts, J.M., Cochran, A.K., Gilman, J.B., Kuster, W.C., Holloway, J.S., Graus, M., Flynn, J., Lefer, B., Warneke, C., and de Gouw, J. (2011). Evidence of rapid production of organic acids in an urban air mass. *Geophysical Research Letters* 38 (17). doi:10.1029/2011GL048420.
- Vidović, K., Lašić Jurković, D., Šala, M., Kroflič, A., and Grgić, I. (2018). Nighttime Aqueous-Phase Formation of Nitrocatechols in the Atmospheric Condensed Phase. *Environmental Science & Technology* 52 (17):9722–9730. doi:10.1021/acs.est.8b01161.
- Vione, D., Maurino, V., Minero, C., and Pelizzetti, E. (2005). Aqueous Atmospheric Chemistry: Formation of 2,4-Dinitrophenol upon Nitration of 2-Nitrophenol and 4-Nitrophenol in Solution. *Environmental Science & Technology* 39 (20):7921–7931. doi:10.1021/es050824m.
- Voliotis, A., Du, M., Wang, Y., Shao, Y., Alfarra, M.R., Bannan, T.J., Hu, D., Pereira, K.L., Hamilton, J.F., Hallquist, M., Mentel, T.F., and McFiggans, G. (2022). Chamber investigation of the formation and transformation of secondary organic aerosol in mixtures of biogenic and anthropogenic volatile organic compounds. *Atmospheric Chemistry and Physics* 22 (21):14147–14175. doi:10.5194/acp-22-14147-2022.
- Walser, M.L., Desyaterik, Y., Laskin, J., Laskin, A., and Nizkorodov, S.A. (2008). High-resolution mass spectrometric analysis of secondary organic aerosol produced by ozonation of limonene. *Phys. Chem. Chem. Phys.* 10 (7):1009–1022. doi:10.1039/B712620D.
- Wang, H., Gao, Y., Wang, S., Wu, X., Liu, Y., Li, X., Huang, D., Lou, S., Wu, Z., Guo, S., Jing, S., Li, Y., Huang, C., Tyndall, G.S., Orlando, J.J., and Zhang, X. (2020). Atmospheric Processing of Nitrophenols and Nitrocresols From Biomass Burning Emissions. *Journal of Geophysical Research: Atmospheres* 125 (22):e2020JD033401. doi:10.1029/2020JD033401.
- Wang, Yujue, Hu, M., Wang, Yuchen, Zheng, J., Shang, D., Yang, Y., Liu, Y., Li, X., Tang, R., Zhu, W., Du, Z., Wu, Y., Guo, S., Wu, Z., Lou, S., Hallquist, M., and Yu, J.Z. (2019). The formation of nitro-aromatic compounds under high NO_x and anthropogenic VOC conditions in urban Beijing, China. *Atmospheric Chemistry and Physics* 19 (11):7649–7665. doi:10.5194/acp-19-7649-2019.
- Wenger, J., Arndt, J., Buckley, P., Hellebust, S., McGillicuddy, E., O'Connor, I., Sodeau, J., and Wilson, E. (2020). Source Apportionment of Particulate Matter in Urban and Rural Residential Areas of Ireland (SAPPHIRE) (No. 318), *EPA Research*.
- Williams, B.J., Goldstein, A.H., Kreisberg, N.M., and Hering, S.V. (2006). An In-Situ Instrument for Speciated Organic Composition of Atmospheric Aerosols:

- Thermal Desorption Aerosol GC/MS-FID (TAG). *Aerosol Science and Technology* 40 (8):627–638. doi:10.1080/02786820600754631.
- Williams, J. and Koppmann, R. (2007). Volatile Organic Compounds in the Atmosphere: An Overview., in *Volatile Organic Compounds in the Atmosphere*, John Wiley & Sons, Ltd, pp. 1–32.
- World Health Organization Regional Office for Europe (2019). Noncommunicable diseases and air pollution: WHO European high-level conference on noncommunicable diseases: time to deliver – meeting NCD targets to achieve Sustainable Development Goals in Europe: 9–10 April 2019, Ashgabat, Turkmenistan (No. WHO/EURO:2019-3641-43400-60937). World Health Organization Regional Office for Europe.
- Xu, C. and Wang, L. (2013). Atmospheric Oxidation Mechanism of Phenol Initiated by OH Radical. *The Journal of Physical Chemistry A* 117 (11):2358–2364. doi:10.1021/jp308856b.
- Xu, J., Griffin, R.J., Liu, Y., Nakao, S., and Cocker, D.R. (2015). Simulated impact of NO_x on SOA formation from oxidation of toluene and m-xylene. *Atmospheric Environment* 101:217–225. doi:10.1016/j.atmosenv.2014.11.008.
- Xu, L., Möller, K.H., Crounse, J.D., Kjaergaard, H.G., and Wennberg, P.O. (2020). New Insights into the Radical Chemistry and Product Distribution in the OH-Initiated Oxidation of Benzene. *Environmental Science & Technology* 54 (21):13467–13477. doi:10.1021/acs.est.0c04780.
- Yan, C., Nie, W., Äijälä, M., Rissanen, M.P., Canagaratna, M.R., Massoli, P., Junninen, H., Jokinen, T., Sarnela, N., Häme, S.A.K., Schobesberger, S., Canonaco, F., Yao, L., Prévôt, A.S.H., Petäjä, T., Kulmala, M., Sipilä, M., Worsnop, D.R., and Ehn, M. (2016). Source characterization of highly oxidized multifunctional compounds in a boreal forest environment using positive matrix factorization. *Atmospheric Chemistry and Physics* 16 (19):12715–12731. doi:10.5194/acp-16-12715-2016.
- Yang, B., Zhang, H., Wang, Y., Zhang, P., Shu, J., Sun, W., and Ma, P. (2016). Experimental and theoretical studies on gas-phase reactions of NO₃ radicals with three methoxyphenols: Guaiacol, creosol, and syringol. *Atmospheric Environment* 125:243–251. doi:10.1016/j.atmosenv.2015.11.028.
- Yang, L.H., Takeuchi, M., Chen, Y., and Ng, N.L. (2021). Characterization of thermal decomposition of oxygenated organic compounds in FIGAERO-CIMS. *Aerosol Science and Technology* 55 (12):1321–1342. doi:10.1080/02786826.2021.1945529.
- Yang, W., You, D., Li, C., Han, C., Tang, N., Yang, H., and Xue, X. (2021). Photolysis of Nitroaromatic Compounds under Sunlight: A Possible Daytime Photochemical Source of Nitrous Acid? *Environmental Science & Technology Letters* 8 (9):747–752. doi:10.1021/acs.estlett.1c00614.
- Yatavelli, R.L.N., Lopez-Hilfiker, F., Wargo, J.D., Kimmel, J.R., Cubison, M.J., Bertram, T.H., Jimenez, J.L., Gonin, M., Worsnop, D.R., and Thornton, J.A. (2012). A Chemical Ionization High-Resolution Time-of-Flight Mass Spectrometer Coupled to a Micro Orifice Volatilization Impactor (MOVI-HRToF-CIMS) for Analysis of Gas and Particle-Phase Organic Species. *Aerosol Science and Technology* 46 (12):1313–1327. doi:10.1080/02786826.2012.712236.
- Yatavelli, R.L.N., Stark, H., Thompson, S.L., Kimmel, J.R., Cubison, M.J., Day, D.A., Campuzano-Jost, P., Palm, B.B., Hodzic, A., Thornton, J.A., Jayne, J.T., Worsnop, D.R., and Jimenez, J.L. (2014). Semicontinuous measurements of

- gas–particle partitioning of organic acids in a ponderosa pine forest using a MOVI-HRToF-CIMS. *Atmospheric Chemistry and Physics* 14 (3):1527–1546. doi:10.5194/acp-14-1527-2014.
- Ye, C., Yuan, B., Lin, Y., Wang, Z., Hu, W., Li, T., Chen, W., Wu, C., Wang, C., Huang, S., Qi, J., Wang, B., Wang, C., Song, W., Wang, X., Zheng, E., Krechmer, J.E., Ye, P., Zhang, Z., Wang, X., Worsnop, D.R., and Shao, M. (2021). Chemical characterization of oxygenated organic compounds in the gas phase and particle phase using iodide CIMS with FIGAERO in urban air. *Atmospheric Chemistry and Physics* 21 (11):8455–8478. doi:10.5194/acp-21-8455-2021.
- Ye, Q., Wang, M., Hofbauer, V., Stolzenburg, D., Chen, D., Schervish, M., Vogel, A., Mauldin, R.L., Baalbaki, R., Brilke, S., Dada, L., Dias, A., Duplissy, J., El Haddad, I., Finkenzeller, H., Fischer, L., He, X., Kim, C., Kürten, A., Lamkaddam, H., Lee, C.P., Lehtipalo, K., Leiminger, M., Manninen, H.E., Marten, R., Mentler, B., Partoll, E., Petäjä, T., Rissanen, M., Schobesberger, S., Schuchmann, S., Simon, M., Tham, Y.J., Vazquez-Pufleau, M., Wagner, A.C., Wang, Y., Wu, Y., Xiao, M., Baltensperger, U., Curtius, J., Flagan, R., Kirkby, J., Kulmala, M., Volkamer, R., Winkler, P.M., Worsnop, D., and Donahue, N.M. (2019). Molecular Composition and Volatility of Nucleated Particles from α -Pinene Oxidation between $-50\text{ }^{\circ}\text{C}$ and $+25\text{ }^{\circ}\text{C}$. *Environ. Sci. Technol.* 53 (21):12357–12365. doi:10.1021/acs.est.9b03265.
- Ye, Z., Zhuang, Y., Chen, Yantong, Zhao, Z., Ma, S., Huang, H., Chen, Yanfang, and Ge, X. (2020). Aqueous-phase oxidation of three phenolic compounds by hydroxyl radical: Insight into secondary organic aerosol formation yields, mechanisms, products and optical properties. *Atmospheric Environment* 223:117240. doi:10.1016/j.atmosenv.2019.117240.
- Yee, L.D., Kautzman, K.E., Loza, C.L., Schilling, K.A., Coggon, M.M., Chhabra, P.S., Chan, M.N., Chan, A.W.H., Hersey, S.P., Crounse, J.D., Wennberg, P.O., Flagan, R.C., and Seinfeld, J.H. (2013). Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols. *Atmos. Chem. Phys.* 13 (16):8019–8043. doi:10.5194/acp-13-8019-2013.
- Ylisirniö, A., Barreira, L.M.F., Pullinen, I., Buchholz, A., Jayne, J., Krechmer, J.E., Worsnop, D.R., Virtanen, A., and Schobesberger, S. (2021). On the calibration of FIGAERO-ToF-CIMS: importance and impact of calibrant delivery for the particle-phase calibration. *Atmospheric Measurement Techniques* 14 (1):355–367. doi:10.5194/amt-14-355-2021.
- Yuan, B., Liggitto, J., Wentzell, J., Li, S.M., Stark, H., Roberts, J.M., Gilman, J., Lerner, B., Warneke, C., Li, R., Leithead, A., Osthoff, H.D., Wild, R., Brown, S.S., and de Gouw, J.A. (2016). Secondary formation of nitrated phenols: insights from observations during the Uintah Basin Winter Ozone Study (UBWOS) 2014. *Atmos. Chem. Phys.* 16 (4):2139–2153. doi:10.5194/acp-16-2139-2016.
- Yuan, B., Shao, M., de Gouw, J., Parrish, D.D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., and Hu, M. (2012). Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis. *Journal of Geophysical Research: Atmospheres* 117 (D24). doi:10.1029/2012JD018236.
- Zaytsev, A., Koss, A.R., Breitenlechner, M., Krechmer, J.E., Nihill, K.J., Lim, C.Y., Rowe, J.C., Cox, J.L., Moss, J., Roscioli, J.R., Canagaratna, M.R., Worsnop, D.R., Kroll, J.H., and Keutsch, F.N. (2019). Mechanistic study of the formation of ring-retaining and ring-opening products from the oxidation of aromatic

- compounds under urban atmospheric conditions. *Atmos. Chem. Phys.* 19 (23):15117–15129. doi:10.5194/acp-19-15117-2019.
- Zhang, B., Hu, X., Yao, L., Wang, M., Yang, G., Lu, Y., Liu, Y., and Wang, L. (2020). Hydroxyl radical-initiated aging of particulate squalane. *Atmospheric Environment* 237:117663. doi:10.1016/j.atmosenv.2020.117663.
- Zhang, X., Lambe, A.T., Upshur, M.A., Brooks, W.A., Gray Bé, A., Thomson, R.J., Geiger, F.M., Surratt, J.D., Zhang, Z., Gold, A., Graf, S., Cubison, M.J., Groessl, M., Jayne, J.T., Worsnop, D.R., and Canagaratna, M.R. (2017). Highly Oxygenated Multifunctional Compounds in α -Pinene Secondary Organic Aerosol. *Environ. Sci. Technol.* 51 (11):5932–5940. doi:10.1021/acs.est.6b06588.
- Zhang, X., Tong, S., Jia, C., Zhang, W., Wang, Z., Tang, G., Hu, B., Liu, Z., Wang, L., Zhao, P., Pan, Y., and Ge, M. (2023). Elucidating HONO formation mechanism and its essential contribution to OH during haze events. *npj Clim Atmos Sci* 6 (1):1–10. doi:10.1038/s41612-023-00371-w.
- Zhao, R., Mungall, E.L., Lee, A.K.Y., Aljawhary, D., and Abbatt, J.P.D. (2014). Aqueous-phase photooxidation of levoglucosan – a mechanistic study using aerosol time-of-flight chemical ionization mass spectrometry (Aerosol ToF-CIMS). *Atmos. Chem. Phys.* 14 (18):9695–9706. doi:10.5194/acp-14-9695-2014.
- Zhao, S., Ma, H., Wang, M., Cao, C., Xiong, J., Xu, Y., and Yao, S. (2010). Study on the mechanism of photo-degradation of p-nitrophenol exposed to 254 nm UV light. *Journal of Hazardous Materials* 180 (1):86–90. doi:10.1016/j.jhazmat.2010.03.076.
- Zheng, J., Yang, D., Ma, Y., Chen, M., Cheng, J., Li, S., and Wang, M. (2015). Development of a new corona discharge based ion source for high resolution time-of-flight chemical ionization mass spectrometer to measure gaseous H₂SO₄ and aerosol sulfate. *Atmospheric Environment* 119:167–173. doi:10.1016/j.atmosenv.2015.08.028.
- Zhu, J., Xu, J., Hu, H., Wang, X., Zhou, Y., and Jin, L. (2021). Novel detection of primary and secondary volatiles from cedar pyrolysis using in-situ pyrolysis double ionization time-of-flight mass spectrometry. *Chemical Engineering Science* 236:116545. doi:10.1016/j.ces.2021.116545.