

Title	Primary and secondary emissions from upland fires in Ireland
Authors	Felberbauer, Clara
Publication date	2023-04-26
Original Citation	Felberbauer, C. 2023. Primary and secondary emissions from upland fires in Ireland. MRes Thesis, University College Cork.
Type of publication	Masters thesis (Research)
Rights	© 2023, Clara Felberbauer. - https://creativecommons.org/licenses/by-nc-nd/4.0/
Download date	2026-10-30 06:43:59
Item downloaded from	https://hdl.handle.net/10468/14600

Ollscoil na hÉireann, Corcaigh
National University of Ireland, Cork



**Primary and Secondary Emissions from Upland Fires in
Ireland**

Thesis presented by
Clara Felberbauer, BSc
117112134
[0000-0001-9261-2773]
for the degree of
Master of Science

University College Cork
School of Chemistry

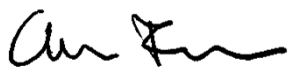
Head of School: Prof Anita Maguire

Supervisors: Dr Stig Hellebust and Dr Dean S. Venables

2023

Declaration

The work presented in this thesis was performed in the School of Chemistry and the Environmental Research Institute, University College Cork, during the academic years 2020 to 2022. This thesis is the independent work of the author and has not been submitted to any institution for the purpose of obtaining any other qualification.



Clara Felberbauer

Table of Contents

Declaration	2
Abstract	5
Acknowledgements	7
1 Introduction	8
1.1 Global fire activity	8
1.2 Wildfires, prescribed burns, and indigenous land management	9
1.3 Global wildfire trends	9
1.4 Fire and emissions characteristics	11
1.4.1 Fire behaviour	11
1.4.2 Burning Process	12
1.4.3 Emitted Species	13
1.5 Atmospheric Processing	15
1.6 Impacts of vegetation fires	17
1.6.1 Air quality and climate	17
1.6.2 Soil, water, and ecology	19
1.6.3 Human health	20
1.7 Irish context	21
1.7.1 Air quality and monitoring	21
1.7.2 Upland fires	22
1.7.3 FLARES project	23
1.8 Aim of work	24
2 Emission Factors for Irish wildfire fuels	25
2.1 Introduction	25
2.2 Methods	27
2.2.1 Fuel selection, sampling, and treatment	27
2.2.2 Setup, instrumentation, and experimental procedure	28
2.2.3 Filter Analysis	30
2.3 Results	31
2.3.1 Particulate Emissions	34
2.3.2 Gas phase products	37
2.3.3 Biomarkers	40

2.4	Uncertainty Analysis	42
2.5	Conclusion	44
3	Atmospheric Aging Experiments	47
3.1	Introduction	47
3.2	Methods	49
3.2.1	Setup and Instrumentation	49
3.2.2	Experimental Procedure	51
3.2.3	Calculations	53
3.3	Results	55
3.3.1	SOA Formation	55
3.3.2	Effects of atmospheric aging on particle size distribution	57
3.3.3	EC, OC and BC	59
3.3.4	NO _x chemistry	61
3.3.5	SO ₂	63
3.3.6	Biomarkers	64
3.3.7	Uncertainty Analysis	65
3.4	Conclusion	65
4	Field Measurements	67
4.1	Introduction	67
4.2	Opportunistic Sampling of Fire Events	67
4.2.1	Methodology	67
4.2.2	Fire events	68
4.2.3	Identification of potential biomarkers	69
4.3	Long-term monitoring campaign at a rural location	71
4.3.1	Methodology	72
4.3.2	Results	76
4.4	Conclusion	88
5	Conclusion and Outlook	90
6	Bibliography	92

Abstract

Emissions from wildfires have detrimental effects on air quality, climate change and human health. Despite frequent occurrence of wildfires and prescribed agricultural burns in upland areas, data on wildfire emissions in Ireland is scarce. This work was conducted as part of FLARES (Fire, Land and Atmospheric Remote Sensing of EmissionS), a project funded by the Irish Environmental Protection Agency (EPA) to improve the understanding of Irish upland fire emissions. Emission factors (EF) of typical Irish wildfire fuels (heather, gorse, purple moor grass) were measured for the first time. Emission factors were measured for a set of gases (carbon monoxide CO, carbon dioxide CO₂, methane CH₄, sulphur dioxide SO₂ and nitric oxides NO_x as NO), particulates and particulate fractions (fine particulate matter PM_{2.5}, total particulate matter TPM, black carbon BC, organic carbon OC, elemental carbon EC and total carbon TC) and molecular biomarkers (levoglucosan, mannosan, galactosan, 4-Nitrocatechol 4-NC, 4-Nitrophenol 4-NP and 4-Nitroguaiacol 4-NG).

Emission factors of measured gases were as follows: CO: 42 g/kg (heather), 27 g/kg (moor grass) and 80 g/kg (gorse); CO₂ 1167 g/kg (heather), 1558 g/kg (moor grass) and 1442 g/kg (gorse); SO₂: 1.38 g/kg (heather), 1.08 g/kg (moor grass) and 1.68 g/kg (gorse); NO_x as NO: 4.46 g/kg (heather), 5.51 g/kg (moor grass), and 6.85 g/kg (moor grass); CH₄: 0.21 g/kg (moor grass) and 0.38 g/kg (gorse). Particulate EFs resulted in EF of 4.71 g/kg (heather), 2.42 g/kg (moor grass) and 10.46 g/kg (gorse) for PM_{2.5}; 3.95 g/kg (heather), 4.26 g/kg (moor grass) and 14.33 g/kg (gorse) for TPM; 0.26 g/kg (heather), 0.21 g/kg (moor grass) and 0.50 g/kg (gorse) for BC; 1.28 g/kg (heather), 1.26 g/kg (moor grass) and 5.43 g/kg (gorse) for OC; 0.80 g/kg (heather), 0.81 g/kg (moor grass) and 2.23 g/kg (gorse) for EC; 2.09 g/kg (heather), 2.07 g/kg (moor grass) and 7.65 g/kg (gorse) for TC. EFs for biomarkers were 0.09 g/kg (heather), 0.18 g/kg (moor grass) and 0.19 g/kg (gorse) for levoglucosan; 0.01 g/kg (heather), 0.01 g/kg (moor grass) and 0.01 g/kg (gorse) for mannosan and 0.01 g/kg (heather), 0.01 g/kg (moor grass) and 0.02 g/kg (gorse) for galactosan; 0.78 mg/kg (heather), 0.42 mg/kg (moor grass) and 1.36 mg/kg (gorse) for 4-NC; 0.05 mg/kg (heather), 0.04 mg/kg (moor grass) and 0.07 mg/kg (gorse) for 4-NP and 0.25 mg/kg (heather), 0.15 mg/kg (moor grass) and 0.34 mg/kg (gorse) for 4-NG.

Combustion took place under flaming combustion conditions, reflected in high modified combustion efficiencies (MCE) of 0.95 to 0.98. Emissions for species like CO, PM_{2.5} and volatile organic compounds (VOCs) would be expected to be higher under real-world conditions where MCE is lower.

Secondary organic aerosol (SOA) formation from combustion emissions of the three fuels was studied under simulated day-time (UV lights and UV+OH precursor addition) and night-time conditions (dark + O₃ addition) in an atmospheric simulation chamber. SOA mass increased by 2-11% and was dependent on fuel type and oxidising conditions. Field and laboratory samples were analysed at the Leibniz Institute for Tropospheric Research (TROPOS) in Leipzig, Germany. Filter samples were analysed for the biomarkers levoglucosan, mannosan, galactosan, 4-nitrocatechol, 4-nitrophenol, and 4-nitroguaiacol.

Laboratory experiments were complemented by field studies. Ambient levels of PM_{2.5} and BC were measured during an 8-week field study in Glencree, rural Co. Wicklow, Ireland. Source apportionment of BC and analysis of biomarkers found no unambiguous signals that could be associated with wildfires. However, this dataset represents a valuable glance at air quality in a rural setting in Ireland. Despite the remote location and low population density in Glencree Valley, anthropogenic influences on air quality were significant, most notably from residential solid fuel burning. Monthly PM_{2.5} concentrations in Glencree (4.6 µg m⁻³) were lower than in nearby urban Tallaght (7.0 µg m⁻³), but less than expected based on the difference in population and local pollution sources. Other field observations included opportunistic sampling of the plume of a major wildfire at Killarney National Park, Co. Kerry, in April 2022.

Findings presented in this thesis contribute to the understanding of wildfire emissions in Ireland and highlight the influence of anthropogenic air pollution from solid fuel burning on rural locations.

Acknowledgements

First and foremost, I would like to thank my supervisors Dr Stig Hellebust and Dr Dean Venables for their constant support and guidance throughout the past two years. Thank you for always being approachable and ready to help. Your efforts, advice, and finally long hours of reading my thesis were greatly appreciated. I will always be grateful for your mentorship and the time at the CRAC lab.

Furthermore, I would like to thank the FLARES project team for all their work – Fiona Cawkwell, for leading the team through one and a half years of the project, Emma Chalençon, for her inputs and friendship, as well as everyone else for making this project come together. I would also like to acknowledge and thank the EPA for funding of the project.

An extended thanks to Germany, to everybody at TROPOS for welcoming me to Leipzig. Dankeschön to Falk Mothes for organizing this opportunity, and to Ricarda Gräfe, for her invaluable help in the chamber experiments and subsequent analysis. I would also like to acknowledge the ACTRIS funding, by which the laboratory work in Germany was made possible.

A huge thanks to Annie Hughes, who wrote her final year project on the thesis and whose analysis of the Glenree campaign was a great help. Our gratitude to the Glenree Centre for Peace and reconciliation who let us park our field monitoring equipment in Wicklow for two months. Thanks also to Wicklow Fire services for providing valuable on-the-ground experience and to our farmer contact in Kerry for offering his field for monitoring a prescribed burn.

A warm thanks to the CRAC lab, Niall O’Sullivan who analysed our field samples, Mehael Fenelly and Hayley Furnell who got me unstuck many a time, and to everyone for being the great CRAC that they are. I would also like to appreciate the equipment provided by the CRAC lab, and once again apologize about the van.

Last but not least, a thank you from the heart – to my family, boyfriend and friends for their never-ending support, I could not have done this without you.

1 Introduction

1.1 Global fire activity

“Something is always burning somewhere.” – Niels Andela, NASA scientist

At any given time, wildfires are burning on our planet Earth. While fires are an integral part of ecosystems that evolve with them, climate and land use change have led to increased threat from wildfires. Besides immediate threats from fires to people, property and ecosystems, landscape fires release large amounts of aerosols into the atmosphere. Air pollution from wildfires is detrimental to human health and greenhouse gases released from wildfires in turn exacerbate global climate change.

Global fire activity, like plant growth, follows a seasonal pattern. February is the main burning time for tropical regions across the globe, with about 3,000 fires observed on any given day. Most fires occur during the dry months (July, August, September) of the Northern Hemisphere where most of the planet’s land mass is found. Approximately 6,000 fires per day are detected by the NASA during these months in the temperate regions of the global North and South (NASA, 2008).

The NASA Moderate Resolution Imaging Spectroradiometer (MODIS) and the Visible Infrared Imaging Radiometer Suite (VIIRS) instruments provide Near Real Time (NRT) satellite imagery of global fire occurrence (Fire Information for Resource Management System - Fire Map). An example of the worldwide occurrence of fires for the first week of September 2020 is shown in Figure 1.1.

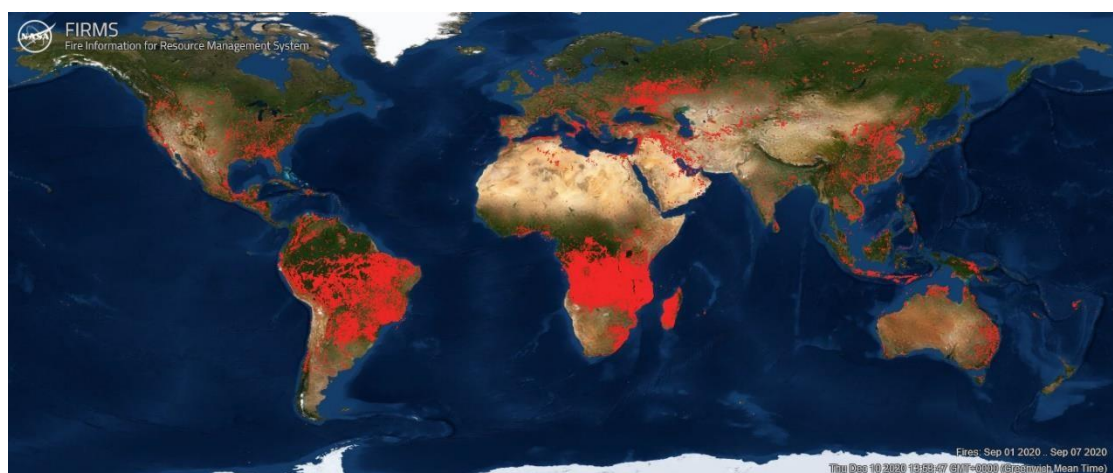


Figure 1.1: Global fire occurrence for the first week of September 2020 (NASA, 2020)

1.2 Wildfires, prescribed burns, and indigenous land management

A wildfire (also termed a wildland fire, bushfire, landscape or vegetation fire) is defined as any kind of “uncontrolled fire in a forest, grassland, brushland, or land sown to crops” (Encyclopaedia Britannica, 2020). Wildfires may be started naturally by phenomena such as lightning, volcanoes, comets, or coal-seam fires. Most fires, however, are of human origin: 84% of fires in the United States were found to be anthropogenic (1992 to 2012; Balch et al., 2017) and the global share is estimated to be 75% (WWF, 2020).

Prescribed burning, also called controlled or planned burning, is the practice of using fire on a predetermined plot of land in a controlled manner to achieve land management goals. In forestry, prescribed burns are used to prepare sites, manage forest understory, reduce fuel loads to prevent wildfires or control diseases (Grebner et al., 2013). In agriculture, fires are used to improve land and clear areas to be used as fields or pastures. Many indigenous peoples, including several Native American and Australian tribes, have a long history of using prescribed fire (Encyclopaedia Britannica, 2020). While wildfires occur during fire-favouring conditions, prescribed burns are often conducted outside the wildfire season, where high fuel moisture keeps burns at a lower intensity and easier to control (Urbanski, 2013).

1.3 Global wildfire trends

In the first two decades of the 21st century the area burned by wildfires globally decreased by a quarter (Andela et al., 2017). This decrease in fire has been linked to less fire in savannah and grassland ecosystems: With increased warming and drought conditions, fuel loads in African savannah ecosystems are reduced. At the same time, changes in land use reduce fuel loads (e.g., by grazing cattle) and cause landscape fragmentation, both suppressing fire occurrence (Wei et al, 2020, Andela & Van der Werf, 2014).

With climate and population changes, however, this trend is likely to reverse in the future (Carnicer et al., 2022). According to the 2022 report by the United Nations Environment Programme (UNEP) “Spreading like Wildfire: The Rising Threat of Extraordinary Landscape Fires”, the likelihood of catastrophic wildfires will increase under all emission scenarios by a factor of 1.31 to 1.57. The increased risk of wildfires is intrinsically, but not solely, linked to climate change, as well as changing

land use, land management practices and human population. Additionally, places which previously did not experience wildfires – such as drying peatlands and thawing permafrost (Rein & Huang, 2021) – are growing more affected. In Europe, fire weather, i.e., the frequency and duration of fire prone weather conditions, is projected to increase. This has potential to lead to the appearance of new fire-prone regions. Additionally, fire susceptibility is projected to increase in the major forested mountain areas, which are important biodiversity hotspots and important carbon sinks responsible for absorbing 10% of Europe's greenhouse gases (Carnicer et al., 2022).

In their 2022 report, UNEP comment on the under-preparedness of many governments to this challenge and urge policy makers to shift their focus and investments on preparing and mitigating wildfires.

Climate change increasingly exercises influence on fire weather, area burned and change in global fire regimes (IPCC, 2021). Extreme heatwaves and associated dry conditions resulted in increased wildfire activity and intensity during the summer months of 2022 in Western Europe. The total cumulative area burnt in the EU was 750,000 ha (January to September 2022), more than double the average from 2006 to 2021 (260,000 ha). EU countries affected most by area burnt as of August 2022 were Spain, Romania, and Portugal, but also countries outside the Mediterranean high-risk zone such as France, Slovenia, Czech Republic, Hungary, and Germany also saw significant increases in wildfire activity and area burnt (CAMS, 2022).

Increases in wildfire activity are intrinsically linked to air pollution and greenhouse gas effects. Carbon emissions from wildfires for 2022 were the highest in the past 15 years in the EU, and emissions in France and Spain were the highest in 20 years (CAMS, 2022). In July 2022, the Copernicus Atmospheric Monitoring Service (CAMS) warned of high ozone pollution levels caused by the heatwave and wildfires, which resulted in ozone concentrations exceeding 200 $\mu\text{g}/\text{m}^3$ in Portugal, Spain and Italy.

1.4 Fire and emissions characteristics

1.4.1 Fire behaviour

The key factors influencing wildland fire behaviour - fuel, weather, and topography are described in the “fire behaviour triangle” (Figure 1.2). The availability, arrangement and conditions of wildland fire fuels are fundamental to fire spread and intensity. Fuels may be characterized according to their size and respective combustibility – the smaller the fuel, the more quickly it reacts to temperature and moisture changes. Weather conditions fundamentally affect fuel and thus fire behaviour. Wind and precipitation control fuel moisture and fire spread. High temperatures and low humidity dry out fuels, making them more ignitable and they will burn more easily; precipitation and high humidity have the opposite effect. Topography also influences fires, which move more quickly up a steep slope as fuels are pre-heated by lower-lying fire. Furthermore, the orientation of the slope determines the effectiveness by which fuel is dried by the sun and influences the respective local microclimate.

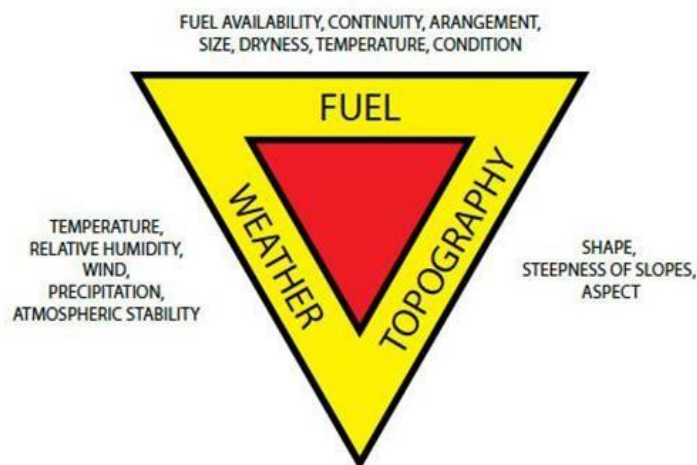


Figure 1.2: US Forest Service fire behaviour triangle

While fire intensity refers to the thermal energy released during the fire, fire severity describes the impact on the site. The same factors influencing fire intensity impact on fire spread, with an emphasis on biome/fuel type – i.e., a grassland fire moves much faster than fire in a forest. The temporal and spatial patterns in which fires appear on a landscape are called fire regimes (Leavell et al., 2017).

1.4.2 Burning Process

In essence, fire is an exothermic oxidation reaction which occurs when fuel reaches a high enough temperature to ignite. The combustion process of biomass is summarized by Koppmann et al. (2005) in three main phases:

1. Ignition phase – fine fuel is ignited by adjacent burning vegetation; larger fuel pieces are heated until they lose enough moisture to also catch fire. Volatile organic compounds (VOCs), organic species characterized by relatively low boiling point temperatures, evaporate during this phase. The length of this phase depends on fuel moisture, density, and size.
2. Flaming phase – transfer to this phase once fuel moisture is low enough. This phase is characterized by the decomposition of cellulose, hemicellulose, lignin, organic compounds, and trace minerals in the fuel. Through oxidization in the flame, hydrocarbons are volatilized, forming a char layer. In theory, complete combustion produces only carbon dioxide and water, but in nature combustion processes are incomplete and emit other products like carbon monoxide and organic compounds. Large amounts of VOCs are emitted into the atmosphere during wildfires due to high VOC content in plant material compared to fossil fuels. The type of organic compounds produced depends on fuel composition, temperature and temperature change over time. Emitted oxygenated compounds are quickly oxidized in the flame, forming stable VOCs. If the burning conditions are oxygen-rich, these reactions occur with the OH radical; if they are oxygen-depleted they react with the H radical, forming hydrocarbons of higher molecular weight.
3. Smouldering phase – oxidation of solid charcoal, flameless stage. The main product emitted is carbon monoxide, together with relatively high amounts of organic compounds emitted.

1.4.3 Emitted Species

Vegetation fires are a significant source of gaseous and particulate pollutants to the atmosphere (Andreae, 2019). The identities and quantities of pollutants released depend on fuel characteristics (i.e., chemical composition and moisture), burning conditions and atmospheric processing (Section 1.4.4). A good overview of particulate and gaseous emissions is given in Koppmann et al. (2005) and Urbanski et al. (2009). Chemical species emitted include the greenhouse gases carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), reactive compounds such as carbon monoxide, nitrogen oxides and volatile organic compounds as well as particulate matter (PM) (Urbanski et al., 2009). In addition to primary emissions (those released directly by the fire), wildfire smoke also undergoes chemical reactions in the atmosphere and can lead to a range of products and effects. These secondary effects include the formation of ground-level ozone (O_3) and secondary organic aerosol (SOA).

The major greenhouse gas emitted by wildfires is CO_2 . Carbon monoxide (CO), which is also emitted during wildfires, is not a GHG in itself but through atmospheric reaction with hydroxyl (OH) radicals contributes to tropospheric CO_2 and O_3 production and reduces stratospheric methane removal (Hungate and Koch, 2003). Methane is the second most important climate-forcing GHG after CO_2 and has a Global Warming Potential (GWP) of 84 (20-year average) or 28 (100-year average) compared to CO_2 (IPCC, 2013). Due to the long residence time of CH_4 in the atmosphere, variations in wildfire regimes have a direct impact on the global CH_4 balance (Koppmann et al., 2005).

Inorganic compounds emitted by wildfires include ammonia (NH_3), sulfur dioxide (SO_2), and nitrogen oxides (NO_x). Anthropogenic SO_2 is emitted by burning fossil fuels and by wildfires (Leino et al., 2014). SO_2 has adverse health effects such as respiratory disease (Brown et al., 2003). NO_x , i.e., nitric oxide (NO) and nitrogen dioxide (NO_2), are also released during the combustion process. NO_x plays a role in the formation of ground-level ozone, acid rain and particle formation. The difference in NO_x emissions is related to the amount of nitrogen contained in the fuel (Clements and McMahon, 1980) and to combustion conditions; oxidizing flaming conditions lead to higher emissions of N-compounds (Andreae and Merlet, 2001).

Wildfires are a significant source of particulate matter. The relative amounts of fine (diameter $<2.5\ \mu\text{m}$, $\text{PM}_{2.5}$) and coarse (diameter $<10\ \mu\text{m}$, PM_{10}) particulate matter released depends on combustion conditions (Hsieh et al., 2018), but fires release $\text{PM}_{2.5}$, which impairs visibility and has health and climate impacts. Further analysis of the optical, thermal, and chemical properties of particulate matter can provide information on the source and atmospheric processing state (Liang et al., 2020).

Organic Carbon (OC) and Elemental Carbon (EC) are two carbonaceous fractions of aerosol (i.e., particulate matter) with different chemical properties, origins, and climate impacts (Hussein et al., 2022). Elemental Carbon is primarily emitted during the incomplete combustion of carbon-containing fuels, while OC can be emitted directly from the fire or produced during atmospheric aging reactions. The distinction between OC and EC is based on the method of analysis used. Thermal-optical methods such as the Sunset OC-EC Aerosol Analyser used in this study measure EC and OC, while optical methods, such as the aethalometer, measure Black Carbon (BC) and Brown Carbon (BrC). While the light-absorbing properties and implications on global warming of BC are well-established, the importance of radiative forcing of BrC, the light-absorbing part of OC, has only recently been recognized (Kaskaoutis et al., 2021).

In addition to the gases and particulates mentioned above, a large variety of organic species is released during vegetation fires. Volatile organic compounds (VOCs) have been subject of much recent study (Amnuaylojaroen et al., 2019; Bousiotis et al., 2021; Gatzsche et al., 2017) due to their importance in the formation of ground-level ozone and secondary aerosols.

Source-specific, long-lived organic species can be used as chemical markers to identify impacts of biomass burning in smoke. Levoglucosan, along with its isomers mannosan and galactosan, is released during the pyrolysis of cellulose and hemicellulose above 300°C . Trace concentrations of levoglucosan can be found in live plant extracts but are much higher in products of burning process (Bhattacharai et al., 2019). Other biomarkers examined in this study are nitrophenol, nitroguaiacol and nitrocatechol. Most nitrated phenols have adverse effects on human and environmental health (Chow, 2006), and as a major component of Brown Carbon have effects on radiative forcing (Mohr et al., 2013).

1.5 Atmospheric Processing

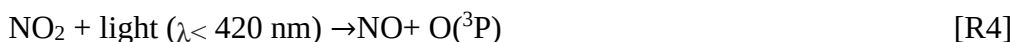
As wildfire smoke is released into the atmosphere, it undergoes complex physical and chemical changes known as atmospheric aging or atmospheric processing. These processes are governed by the identity and quantity of primary emissions released, as well as dilution processes, the concentrations of other species and radicals in the atmosphere and ambient conditions. The resulting changes can affect chemical composition, phase state, density, volatility, and morphology of emissions.

VOCs and their reaction products in the troposphere are removed physically (wet and dry deposition) and chemically by photolysis or reaction with oxidants. The major oxidants in the atmosphere are OH, O₃ and NO₃ for night-time reactions (with some contribution from Cl in marine environments). The OH radical is the most reactive of the oxidants, but O₃ occurs at much higher concentrations. During night-time, NO₃ plays a major role but quickly undergoes photolysis during the day (Finlayson-Pitts and Pitts, 2000).

One of the most fundamental conditions influencing atmospheric aging is the time of day, which affects the amount of irradiation that can drive reactions. Day-time tropospheric chemistry is driven by the generation of OH radicals from ozone (O₃) and sunlight (UV).

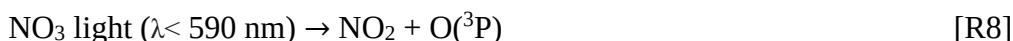


The production of OH is connected to the atmospheric nitrogen oxides cycle (NO_x). HO₂, which is produced in many reactions of trace gases with OH·, is converted back to OH· via reaction with NO. The NO₂ is photolyzed by UV radiation to produce a single oxygen atom that can react with ambient oxygen to reform O₃.



Very low OH concentrations are found at night when UV radiation is absent. Instead, nocturnal oxidation chemistry is usually driven by the NO₃ radical, which is

produced by the reaction of O_3 with NO_2 . The concentration of NO_3 is suppressed during the day because it is rapidly photolyzed by ambient light at visible wavelengths (Ball, 2014).



The importance of these reactions depends on VOC structure and ambient conditions. The resulting products are more oxidized, less volatile and more water soluble (Hallquist et al., 2009). At the same time, oxidation reactions can also lead to fragmentation of carbon chains, resulting in lower molecular weight (MW) and more volatile VOCs (Atkinson, 1998). Oxygen-to-carbon (O/C) ratios increase during atmospheric aging. O/C ratios are low for high concentration chamber experiments with high concentrations of precursors, but are expected to be higher under atmospheric conditions (Hallquist et al., 2009)

In terms of particle phase emissions, atmospheric aging can alter the properties of primary particles and result in the formation of secondary particles. Reactions leading to particles growth and formation include gas nucleation to form new particles (new particle formation), condensation on existing particles and coagulation between particles (particle growth), as well as aqueous phase reactions (Finlayson-Pitts and Pitts, 2000). Both increases and decreases have been reported in PM mass and organic carbon/elemental carbon (OC/EC) ratios for field and laboratory studies (Hodshire et al., 2019).

The changing chemistry of wildfire plumes has been observed in situ using airborne or stationary monitoring equipment (Paris et al., 2009; Yokelson et al., 2007). These atmospheric processes can also be simulated in atmospheric chambers (Kuang and Shang, 2020; Lim et al., 2019; Kalogridis et al., 2018), which are controlled environments where fuel amount, dilution ratios and reagents can be varied as required. Additionally, mathematical modelling approaches can be used to simulate atmospheric smoke processing (Trentmann et al., 2003; Konovalov et al., 2016). Most recently, Hodshire et al. (2021) used satellite data to observe atmospheric aging processes in biomass plumes.

1.6 Impacts of vegetation fires

While about a quarter of landscape fires globally are due to natural causes (WWF, 2020), wildfires – especially large-scale ones – present a severe, multi-layered disruption of natural and anthropogenic systems, posing a threat to human lives, health and property. Wang et al. (2020) calculated the socioeconomic cost of the 2018 California wildfires at \$148.5 billion, which is 1.5% of Californian annual gross domestic product. Expansion of the wildland-urban interface – areas where human developed land borders wildland areas – and anthropogenic climate change are increasing fire risk in these areas such as southern Europe (Ganteaume et al., 2021).

1.6.1 Air quality and climate

Wildfire emissions can significantly deteriorate air quality (Jaffe et al., 2020; Knorr et al., 2016). A study by Kalashnikov et al. (2022) concluded that air pollution from wildfire events had offset improvements made by air quality legislation in the US.

Depending on fire extent, intensity and wind direction, local residents (Figure 1.3) and first responders (Figure 1.4) can be exposed to severe levels of air pollution from direct wildfire emissions (Swiston et al., 2008; Magzamen et al., 2021).



Figure 1.3: Fire at Bray Head 2018 (picture courtesy of Aidan Dempsey, Wicklow Fire Services)



Figure 1.4: Fire fighters from Wicklow fire services at work (picture courtesy of Aidan Dempsey, Wicklow Fire Services)

Large wildfires can affect air quality in distant regions. In the summer of 2018, air monitoring stations in New York State registered a threefold increase in fine particulate matter (PM_{2.5}). A large smoke plume originating in southern Canada had travelled for thousands of kilometres (Hung, 2020).

Both particles and trace gases in vegetation fire plumes have significant effects on the atmosphere. During the dry months, thick haze layers are visible in large parts of the tropical and sometimes boreal boundary layers. In Ireland, smoke from fires in rural upland areas can affect urban and rural habituated areas. for example, during a large-scale upland fire in Galway in 2017 (Newstalk, 2017), and Bantry in February 2023 (Pers. Comm.).

Wildfires contribute to global warming through emission of greenhouse gases such as CO₂ and CH₄, as well as black and brown carbon aerosols. Aerosols influence the greenhouse effect directly through reflection (a cooling effect) or absorption (a warming effect) of sunlight. Aerosols indirectly influence weather and climate by acting as cloud condensation nuclei, by increasing cloud albedo (cloud albedo effect, cooling) and prolonging the lifetime of clouds (cloud lifetime effect), effectively suppressing rainfall.

On a global scale, the Copernicus Atmospheric Monitoring Service (CAMS) estimated that wildfires emitted 6450 million tonnes CO₂ eq. in 2021 (CAMS, 2021). Biomass burning is also the second largest global source of VOCs (Akagi et al., 2011).

Apart from direct emissions, CO₂ is slowly released from fire-killed plant necromass (Campbell et al., 2016; Mitchell, 2015). After posing a net source of CO₂ immediately after the fire, plant mass regrows and takes up CO₂ again, depending on the biome and severity of the fire (Kelly et al., 2021; Sun et al., 2016). About 20% of global fire emissions cannot be regained and pose a net source of CO₂ on a centennial time scale. This includes peat fires, deforestation fires and degradation fires (Zheng et al., 2021).

The Intergovernmental Panel on Climate Change (IPCC) reports an averaged combined land and ocean linear temperature rise of 0.85 [0.65 to 1.06] °C from 1880 to 2012 (IPCC, 2014). The increased risk of wildfire occurrence is linked to an increase in global temperature, increase in drought conditions and an increase in fire

weather (IPCC, 2021). In regions where climate change results in higher temperatures and less precipitation, this can lead to an increase in fire occurrence and intensity, as well as to an alteration in the distribution of fire-dependent and fire-influenced ecosystems (Liu et al., 2010). A decrease in snow coverage and earlier snow melting in spring can effectively prolong the fire season (Westerling et al., 2006). The IPCC 2014 synthesis report points out “increased damage from wildfires” as regional key risks for North America and Europe (IPCC, 2014).

The 2019 IPCC report states that climate change and human activity are playing an increasingly dominant role in wildfire regimes. While fire weather seasons have lengthened (1979-2013), the global area burnt has declined during recent decades due to a decline in savannah and grassland burning (IPCC, 2019), as well an increase in cropland area and anthropogenic fires suppression (Arora and Melton, 2018).

The latest 2021 IPCC report predicts an increase in fire weather with medium to high confidence for global warming of above 2°C compared to 1.5°C. For high CO₂ emissions scenarios, feedbacks between climate and the carbon cycle become larger but also more uncertain. Increases in wildfires in turn will have a detrimental effect on air quality, economic and health effects and further contribute to greenhouse gas emissions (Bowman, 2020).

1.6.2 Soil, water, and ecology

Large and intense wildfires can negatively affect water and soil quality. A river catchment after a large fire may have increased suspended sediment loads and associated elevated trace elements, which are of relevance if human communities depend on this watershed for their drinking water supply (Smith et al., 2011). When soil is burned during vegetation fires, CO₂ and organic compounds are released into the atmosphere (Otto et al., 2006). Large, hot fires can damage soil structure in affected areas (Tubridy, 2013).

By removing vegetation cover, wildfires also affect the amount of solar radiation reaching the ground. This impacts primary plant production, and mobilizes and transports soil nutrients from one local ecosystem to another (Andreae, 2019).

Many ecosystems, such as savannahs and temperate coniferous forests (Hoffmann et al., 2003) have evolved with wildfires and depend on them for their functioning, with

many plant species germinating, reproducing or establishing with fire. Well-managed prescribed fires can imitate these effects and contribute to a functioning ecosystem and prevention of extreme wildfire events in such ecosystems (Pausas and Keeley, 2019).

Conversely, fire management policies in North America, Australia and the Mediterranean have long solely focussed on fire suppression. The famous “Smokey Bear campaign” has assured US citizens since 1944 that only they can prevent forest fires (Hesseln, 2018). Similarly, bushfires in Australia are currently mainly managed through suppression (Mariani et al., 2022). In contrast, in many European Forests, much more intensely managed, excess undergrowth is removed and utilized, reducing the fuel for extreme wildfires (Oberle, 1969). Some prescribed burns are being discussed and conducted as a way of alleviating fire risk in Australia and the United States, but may face barriers in terms of negative perceptions, availability of funding and experience as well as environmental regulations and weather conditions (Miller et al, 2020).

These examples illustrate that wildfires are not merely destructive in their nature. Some ecosystems have evolved with and depend on them, while in others they represent a disturbance. Similarly, prescribed burns can be a useful landscape management tool and even alleviate the risk of larger fires, as well as be a damaging force when used in the wrong context (Knapp et al, 2009).

1.6.3 Human health

In addition to direct injury through fires by exposure to flames or heat, wildfires are harmful to human health through emission of air pollutants. Air pollution is the single biggest environmental risk to human health (WHO, 2021). Direct and indirect emissions from wildfires detrimental to human health include particulate matter, carbon monoxide, nitrogen dioxide, sulphur dioxide and ozone. While carbon monoxide typically affects the area closest to the fire, particulate matter and ozone can be transported over long distances (Xu et al., 2020).

For the pollutants mentioned above, WHO air quality guidelines exist based on a strong body of research exist for these pollutants. For other species released by wildfires, i.e. Black Carbon/Elemental Carbon and ultrafine particles, evidence

health effects is not sufficient and WHO recommend monitoring and reduction (WHO, 2021).

There is strong evidence associating wildfire smoke with respiratory diseases such as asthma and an increased risk in respiratory infections as well as overall mortality (Reid et al., 2016). Children are a vulnerable group due to their sensitive developing lungs and higher respiratory rate compared to adults. Additionally, experiencing wildfires in their immediate vicinity is a traumatic experience and may impact on children's mental health (Hauptmann, 2020). A recent study by Milton and White (2020) on Australian bushfires suggests that PM from wildfire smoke may be more neurologically damaging than ambient PM from other sources.

Globally, it is estimated that wildfires and volcanoes combined directly caused around 2,400 deaths between 1998 and 2017 (UNISDR and CRED, 2018). In comparison the number of premature deaths related to wildfire smoke is estimated between 260,000 - 600,000 (Johnston et al., 2010). Increasing wildfire risk is connected to human health risks with ongoing global warming, and yet another good reason to urgently cut global carbon emissions (Xu et al., 2020).

1.7 Irish context

1.7.1 Air quality and monitoring

Air pollution is the most pressing environmental risk to human health based on disease burden (WHO, 2021). The major air pollutants of concern in Ireland are particulate matter (PM), which is mostly produced by residential solid fuel combustion, and nitrogen oxides (NO_x), which is largely associated with transport emissions. High emission solid fuels – wood, coal, and peat – accounted for about 10% of residential heating in Irish households in 2021, with a higher percentage being used in rural areas (CSO, 2021). High PM levels are of concern in many populated areas, where the local population is exposed to multiple sources (EPA, 2021).

Although significant improvements have been made on air quality in recent decades, air pollution from PM_{2.5} is the cause of an estimated 1,300 premature deaths per year in Ireland. World Health Organisation (WHO) air quality guidelines were exceeded at 38 of 67 monitoring stations in 2020 (EPA, 2021).

Ireland has a national air quality monitoring network of 111 national and local monitoring stations as of April 2023 (Figure 1.5), most of which are located in towns and urban areas. Upland fires, on the other hand, generally occur removed from population settlements of all sizes, including those with air quality monitoring facilities. As a result, there are currently limited opportunities to directly measure the impacts of wildfires on nearby air quality through the current Irish monitoring network.

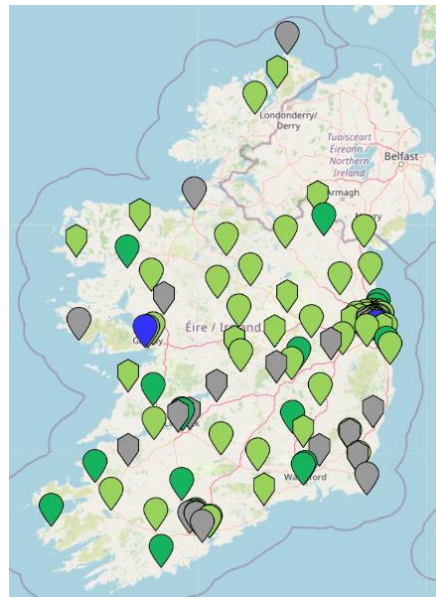


Figure 1.5: Air quality monitoring network in Ireland (EPA, 2023).

1.7.2 Upland fires

Due to its influence by the Atlantic and the Gulf stream, Ireland experiences a unique temperate maritime climate with high humidity. Most of the country is characterized by agricultural land (67.7% - mainly pastures) and wetlands (14.9%). Forest cover (9.5%) is among the lowest in Europe (CORINE, 2018). This is reflected in fire activity: FLARES found only 4% of fires to occur in forested land (coniferous forest), and most fires occur in areas dominated by grass and shrub vegetation (Cawkwell et al., under review).

Essentially all vegetation fires in Ireland are of anthropogenic origin. Such fires may be started on purpose, maliciously, or occur by accident. Planned burning, also called prescribed burning of agricultural areas is a widely used practice in Ireland. It is mainly used to clear marginal agricultural land from unwanted vegetation and promote new plant growth, which may be associated with an increased income from

the reared livestock (Carroll et al., 2021). To limit accidental spread of fires and damage to wildlife, it is illegal to burn land from March 1st to August 31st under Section 40 of the Wildlife Act, 1976 (amended by Section 46 of the Wildlife Act, 2000). A description on the history, culture and contemporary practice of upland fires can be found in Carroll et al. (2021).

In this thesis, the term ‘upland fires’ is used in an Irish context, referring to both wildfires and prescribed burning.

Fires, whether accidental or deliberate, usually occur during times of low humidity and prevailing winds drying out the vegetation. Fire services personnel have also noted that wildfire conditions often occur during periods of easterly winds as opposed to more common south-westerly winds (Irish Fire Services, pers. comm.).

Although relatively small when compared to fires in other parts of the world, fires in Ireland can reach considerable size and impact in relation to the size of the country and local ecological habitats. Additionally, wildfires were found to often occur in areas of ecological importance (Cawkwell et al, under review). One example is the Killarney National Park Fire 2021, which burned for three days and is described in this work.

1.7.3 FLARES project

To address many of the unknowns around Irish wildfires, the Irish Environmental Protection Agency (EPA) funded the FLARES (Fire, Land and Atmospheric Remote sensing of EmissionS) project. The research was conducted by the Environmental Research Institute (ERI), the Department of Geography and the School of Chemistry at University College Cork in collaboration with Randbee Consultants (Portugal) and EO Analytics (Dublin, Ireland). The research presented in this thesis was carried out as part of the FLARES project. The full project report will be accessible on the EPA Ireland website after publication.

The aim of FLARES was to systematically collect and collate data on controlled and uncontrolled wildland fires in Ireland; estimate total area burnt, calculate total emissions, and assess impacts on air quality, climate, and ecosystems.

Total emissions from wildfires (E_x) were calculated from the area burnt (A), the fuel loading (FL), the combustion completeness (CC), i.e., percentage of fuel burnt, and a fuel-specific Emission Factor (EF_x in g pollutant per kg fuel burnt) – Equation 1.1.

$$E_x = A * FL * CC * EF_x \quad (Eq. 1.1)$$

Areas burnt were estimated from different Earth Observation (EO) products and are described in Cawkwell et al. (under review). Literature values were used for fuel loading and combustion completeness. Derivation of Emission Factors for Irish wildfire fuels, simulation of atmospheric processing from smoke of these fuels, and field measurements at real-world fire events are described in this work.

Irish wildfire data prior to FLARES was limited and inadequately organized. Under the Paris

Agreement, all member states must report annual GHG emissions to the United Nations Framework Convention on Climate Change (UNFCCC), which includes emissions from wildfires. By providing a much-improved estimate of the area and land type burnt, as well as emission factors specific to Irish wildfires, FLARES contributed to improving estimates of national GHGs from wildfires for Ireland.

1.8 Aim of work

The aim of this work is to characterize and quantify primary and secondary emissions from upland fires in Ireland. Chapter 2 describes the first measurement of emission factors from burning vegetation specific to the Irish flora. Direct (primary) emissions for three typical Irish upland fire fuels were measured. In Chapter 3, experiments investigating the atmospheric processing of combustion emissions of these fuels are described, focussing on secondary organic aerosol (SOA) formation. Experiments were conducted in an atmospheric simulation chamber under three different reaction conditions, simulating day-time and night-time atmospheric aging. Field measurements of real-world fire events and rural air quality are described in Chapter 4. Finally, in Chapter 5, results on wildfire emissions and air quality are summarized and an outlook on future work is given.

2 Emission Factors for Irish wildfire fuels

2.1 Introduction

The amount of a particular pollutant emitted during combustion is an essential quantity for understanding how wildfires affect atmospheric composition and associated impacts on air quality, human health, and climate.

The relationship between the mass of a fuel burned and the emitted combustion products is commonly described by a fuel-specific Emission Factor, EF_x which is the mass of pollutant emitted in grams of pollutant x emitted (M_x) per kg mass of dry fuel burned (M_{fuel}) (Andreae & Merlet, 2001, Equation 2.1)

$$EF_x = \frac{M_x}{M_{fuel}} [g/kg] \quad (Eq. 2.1)$$

Quality and quantity of pollutants emitted depend on fuel type as well as combustion conditions. An important characteristic in this context is combustion completeness, i.e., whether the process is dominated by flaming or smouldering combustion. This can be described via the Modified Combustion Efficiency (MCE, Ward & Min Hao, 1991), which is the relative concentration of C_{CO_2} to $C_{CO_2} + C_{CO}$ (Equation 2.2)

$$MCE = \frac{C_{CO_2}}{C_{CO_2} + C_{CO}} \quad (Eq. 2.1)$$

High MCE values ($MCE > 0.95$) are associated with flaming combustion conditions, whereas lower MCE values (< 0.95) are indicative of smouldering combustion conditions. The MCE is a defining factor for the type and quantity of emissions released. Products of flaming combustion are more oxidised than those of the smouldering stage. Particulate emissions are released during both stages but have different physical and optical properties.

Concentrations of emissions can be measured directly in the field, where they are expressed as emission ratios (ER, concentration ratio of species in the plume in relation to CO or CO₂ to background concentration), which can then be converted to EFs. Field measurements are difficult to conduct and may be strongly influenced by factors outside of experimenter control. Sampling of prescribed or experimental burns is easier to plan (Miranda et al., 2005), but due to differing fire conditions (prescribed

burns are usually conducted during wetter weather conditions which make them easier to control) there may be a significant difference in emissions characteristics. For example, Liu et al. (2017) measured on average two times higher EFs for PM₁ (particulate matter <1 µm) from wildfires than from prescribed fires. Alternatively, emission factors can be measured directly from a known amount of fuel burnt in a controlled laboratory facility. This has the advantage of being able to control and manipulate conditions; however factors such as fuel moisture, oxygenation and fuel spread will not be fully representative of a real fire. As a result, MCE during laboratory experiments tends to be higher compared to actual wildfires and prescribed burns, and associated emissions are dominated by flaming combustion (Andreae, 2019).

Emissions Factors for a wide range of pollutants and fuels exist in the literature. The most recent review by Andreae (2019) follows earlier reviews by Andreae & Merlet (2001) and Akagi et al. (2011). Andreae's updated version groups EFs for fuels by biome (Savannah and grassland, Tropical Forest, Temperate Forest, Boreal Forest, Peat Fires and Open Agricultural Residue Burning). The largest number of studies exists for arid regions of Africa, Australia and the Americas (Abdulraheem et al., 2020; Yokelson et al., 2011). Other studies report on temperate (e.g. Yokelson et al., 2007), boreal (Bertschi et al., 2003) and tropical forests (Yokelson et al., 2011; Andreae et al., 1988).

Despite the large number of studies, no EFs for vegetation commonly found in Irish upland habitats have been previously reported. Studies closest to Ireland in geography and habitat include studies on the Mediterranean region and Iberian Peninsula by Alves et al. (2011) and Vicente et al. (2011), as well as on European conifers and peat by Iinuma et al. (2007) on. In Ireland, however, less than 5% of the burned area from 2015-2021 was coniferous forest (Cawkwell et al., under review). Additionally, the Irish climate is classed as temperate oceanic on the Köppen climate classification system, which is different to the majority of EFs defined in the literature.

The FLARES project represents the first measurement of EFs for fuels characteristic of Irish upland fires (Cawkwell et al., under review). The aim of this chapter is to describe the methodology and resulting Emission Factors for prominent Irish wildfire fuels for a range of important GHGs and air pollutants.

2.2 Methods

2.2.1 Fuel selection, sampling, and treatment

From a workshop with experienced personnel in the Irish fire services, three main fuels were selected as representative of wildfires in upland habitats - gorse (*Ulex sp.*), heather (*Calluna and Erica spp.*) and purple moor grass (*Molinia caerulea*).

Upland fires in Ireland are commonly referred to as ‘gorse fires’, in indication of the importance of this species to upland burning. Due to its thorny branches and leaves, gorse is difficult to remove. Land owners conduct prescribed burns to manage upland areas for livestock grazing. Ireland is home to two gorse species — common gorse (*Ulex europaeus*/ Irish: Aiteann gallda) and western gorse (*Ulex gallii*/Aiteann gaelach). Both are similar evergreen thorny shrubs with yellow flowers. *U. europaeus*, which was selected for this study, is common in the uplands whereas *U. gallii* is a lowland species. Three common heather species are native to Ireland: ling (*Calluna vulgaris*/Fraoch Mór), bell heather (*Erica cinerea*/Fraoch Cloigíneach) and cross-leaved heath (*Erica tetralix*/Fraoch Naoscaí). Purple moorgrass (*Molinia caerulea*/Fionnán) is a widespread deciduous species found in seasonally or permanently wet soils. It forms dense tussocks of dried leaves that under the right conditions provide rapidly burning fuel.

Fuel samples (Figure 2.1) were collected in early June 2021. Heather and *Molinia* samples were collected in Gneeves Bog, an upland area in Millstreet, Co Cork, Ireland. *U. europaeus* samples were collected near Kinsale, Co Cork.



Figure 2.1: (left to right): Gorse (*Ulex*), heather (*Calluna*) and purple moor grass (*Molinia caerulea*) fuel samples.

Samples of gorse, heather, and purple moor grass were collected, air-dried, and shipped to Germany three weeks prior to experiments. Heather and gorse were sampled as green branches. Purple moor grass was collected from dried tussocks to represent realistic fuel conditions. Fuel moisture for all fuels was determined using a TESTO606-1 (Testo SE, Germany) handheld meter. Grass fuel humidity was additionally determined by establishing the gravimetric difference before and after desiccation in a dry oven for 24 h.

2.2.2 Setup, instrumentation, and experimental procedure

Experimental burns were performed at the Leipzig Biomass Burning Facility (LBFF), a facility managed by the Leibniz Institute for Tropospheric Research (TROPOS) in Leipzig, Germany. The LBFF is regularly used in combination with the Atmospheric Chemistry Department Chamber (ACD-C, setup described in Section 3.2.1) and was modified as described below for the EF experiments.

The set-up of the combustion experiments is illustrated in Figure 2.2. Fuels were burned in a conventional residential-type wood stove. A fraction of the smoke was drawn from the stove pipe through a heated transfer line into a Dekati Diluter DI-1000 diluter (Dekati, Finland) and mixed with a flow of clean air (D1 in Figure 2.2). If necessary to stay within instrument measurement ranges, the diluted smoke sample was diluted via a second step (D2) using mass flow controllers and fed into instruments via stainless steel transfer lines. All calculated EFs were corrected for D1 and D2 dilutions as appropriate.

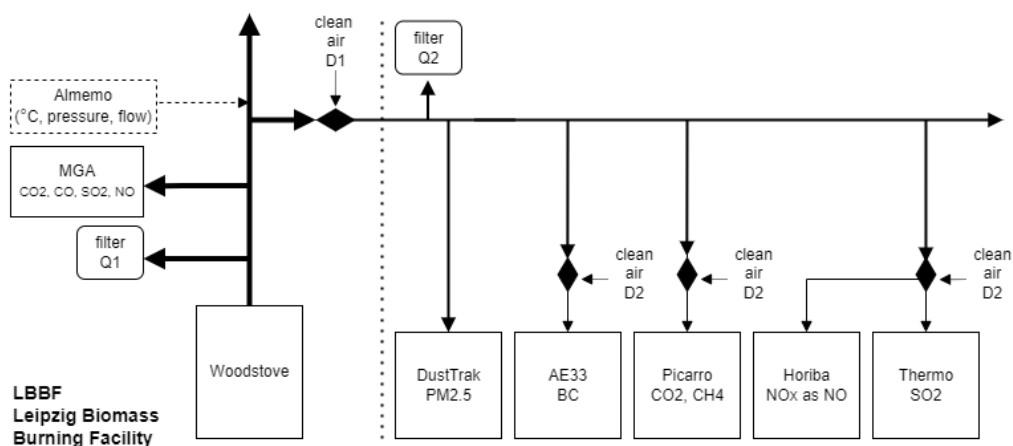


Figure 2.2: Flow and instrumentation scheme for EF experiments at the TROPOS Leipzig Biomass Burning Facility.

Instrumentation by measured parameter, manufacturer and time resolutions are listed in Table 2.1, and displayed in Figure 2.2.

Table 2.1 Instrumentation used for emission factor experiments

Instrument	Manufacturer	Parameter	Sampling Interval
Almemo sensors	Ahlborn	temperature, pressure, flow	10 s
MultiGasAnalyzer MGA 12	Dr Foedisch	CO ₂ , CO, SO ₂ , NO	20 s
Aethalometer AE33	Magee Scientific	BC	60 s
DustTrak II Aerosol Monitor 8532	TSI	PM _{2.5}	10 s
G2401 Cavity Ringdown Spectrometer	Picarro	CO ₂ , CO, CH ₄	around 1 s
APNA-370 Ambient NO _x monitor	Horiba	NO, NO ₂ , NO _x	180 s
Pulsed Fluorescence SO ₂ Analyser	Thermo Environmental Instruments	SO ₂	60 s

At the stove pipe, temperature, flow velocity and pressure of the smoke were measured by Ahlborn Almemo sensors as well as CO₂, CO, SO₂ and NO by a Dr Foedisch MGA 12 MultigasAnalyser, which was calibrated by a zero adjustment with ambient air at the start of each experiment day. After respective dilutions, a Picarro G2401 Cavity Ringdown Spectrometer optically measured CO₂, CO and CH₄ concentrations. Gas analysers were used to measure NO, NO₂ and NO_x (Horiba APNA 370 analyser) and SO₂ (Thermo Environmental Instruments Inc. Pulsed Fluorescence SO₂ Analyser).

Black carbon (BC) was measured by a Magee Scientific Aethalometer AE33. The AE33 uses a dual-spot measurement at seven different wavelengths (370, 470, 520, 590, 660, 880 and 950 nm), allowing source appointment of BC as originating from fossil fuel combustion or biomass burning based on the spectral profile (Zotter et al., 2017). A TSI Condensation Particle Counter Model 3750 optically measured particle number, size, volume, and distribution, while PM_{2.5} concentrations were measured optically with a Dusttrak II Aerosol Monitor 8532 using the appropriate inlet, which was cleaned and oiled according to the user manual prior to each experiment. Filter samples were collected on quartz filters (ø 47 mm, Munktel MK360 by Ahlstrom-Munksjo) at a flow rate of 30 L/min. Samples were taken directly at the stove pipe (Q1 in Figure 2.2) and after D1 (Q2) to check for dilution losses.

Triplicate experiments were performed for each EF experiment using with an approximate fuel mass of 50 g. A portion of the fuel was placed in the wood stove and ignited with a propane lighter. The fuel was fed in small doses to sustain stable, low flaming conditions. After 2-4 min, the end of each burn was noted when no visible flame was observable.

Exact masses of fuel, cold ashes and unburnt material fraction were weighed for each experiment. The total initial fuel mass was used in the EF calculation.

Additionally, a longer burn was performed for each fuel to measure EFs under more stable burning conditions. These burns were approx. 15 minutes long and fuel masses of 200 to 450 g ($\pm$ 50 g) were burnt.

2.2.3 Filter Analysis

Filters were analysed for: A) gravimetric TPM mass (Q1 only); B) Elemental and Organic Carbon (EC/OC); C) monosaccharide anhydrides (levoglucosan, mannosan and galactosan) which function as biomass burning markers; D) a series of organic compounds (4-nitrophenol, 4-nitrocatechol, 4-nitroguaiacol and vanillic acid) which were identified as potential biomass burning markers during the field campaign (Section 4.3.3).

Filters for gravimetric analysis were pre-baked at 110°C for 24 h. This method was chosen instead of the commonly used 800°C / 3 h baking to avoid cracking and losses of filter material. Gravimetric analysis was only conducted for filters at Q1 during emission factor experiments. All other methods described below apply to all filters (Sections 2.3, 3.3 and 4.4.2).

Monosaccharide anhydrides were analysed using high-performance anion-exchange chromatography/pulsed amperometric detection (HPAEC-PAD). 2 filter spots ($\varnothing$ 14 mm) were cut out and added to 1ml ultra-pure water. After 2 h of shaking, the fluid was filtrated with a 0.45 μ m syringe filter (IC Acrodisc; PALL) and analysed via high-performance anion-exchange chromatography/pulsed amperometric detection (HPAEC-PAD).

The biomarkers 4-nitrophenol, 4-nitrocatechol, 4-nitroguaiacol and vanillic acid were identified using an ultrahigh-performance liquid chromatography (LC) system (Vanquish Horizon, Thermo Fisher Scientific) coupled with a high resolution Orbitrap mass spectrometer (Q Exactive Plus, Thermo Fisher Scientific, MS resolution 70k, negative polarisation mode, calibration range 0.024 - 400 μ g/l). A spot (field samples

ø 30mm, laboratory samples ø 34mm) was cut from each filter for extraction; extraction medium and limit of detection (LOD) can be found in Table 2.2.

Table 2.2 Extraction medium, manufacturer, and limit of detection (LOD) for biomarkers.

	Vanillic acid	4-Nitrophenol	4-Nitrocatechol	4-Nitroguaiacol
manufacturer	Aldrich	Fluka	Fluka	Sigma-Aldrich
purity of standard	97.0%	99.5%	98.0%	97.0%
Limit of Detection	0.391 µg/L	0.391 µg/L	0.391 µg/L	0.391 µg/L

Determination of OC/EC was conducted from a 1.5 cm² filter punch analysed in a Sunset Laboratory OCEC Carbon Aerosol Analyzer Model 4L. The instrument distinguishes OC and EC by two-step process of thermal desorption of OC at a lower temperature in an oxygenfree atmosphere and desorption at higher temperature and subsequent oxidization of EC. Both species are detected as CO₂ by a non-dispersive infrared (NDIR) detector system.

2.3 Results

The following EF were determined in this study (Table 2.3): carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄); sulfur dioxide (SO₂), nitric oxide (NO), total particulate matter (TPM), fine particulate matter (PM_{2.5}), Black Carbon (BC), Organic Carbon (OC), Elemental Carbon (EC) and Total Carbon (TC); levoglucosan, mannosan, galactosan, 4-Nitrocatechol (4-NC), 4-Nitrophenol (4-NP), 4-Nitroguaiacol (4-NG). For comparison with literature values, Table 2.3 also lists average EF for field studies of the ‘Savannah and Grassland’ biome as compiled by Andreae (2019). This category was deemed most suitable for comparison due to similar fuel characteristics, and the large number of studies recorded. Uncertainties related to EF_{CO2} are discussed in Section 2.4.

Table 2.3: Emission factors for heather, purple moor grass and gorse established during FLARES in comparison to Andreae (2019) 'Savannah and Grassland' biome. SD = standard deviation, (Andreae, 2019)

	Heather (<i>Calluna sp</i>)		Purple Moor Grass (<i>M. caerulea</i>)		Gorse (<i>U. europeus</i>)		Savannah and Grassland (Andreae, 2019)	
<i>parameter</i>	<i>average</i>	<i>SD</i>	<i>average</i>	<i>SD</i>	<i>average</i>	<i>SD</i>	<i>average</i>	<i>SD</i>
MCE	0.97	0	0.98	0	0.95	0	0.94	0.02
CO	42	6	27	2	80	7	69	20
CO ₂	1167	51	1558	54	1442	87	1660	90
CH ₄	NA	NA	0.21	0.06	2.52	0.38	2.70	2.20
SO ₂	1.38	0.46	1.08	0.58	1.68	0.39	0.47	0.44
NO _x as NO	4.46	0.39	5.51	0.35	6.85	0.56	2.50	1.30
PM _{2.5}	4.71	1.13	2.42	0.47	10.46	1.41	6.70	3.30
TPM	3.95	0.78	4.26	0.58	14.33	0.15	8.70	3.10
BC	0.26	0.10	0.21	0.07	0.50	0.05	0.53	0.35
OC	1.28	0.16	1.26	0.37	5.43	0.81	3.00	1.50
EC	0.80	0.25	0.81	0.19	2.23	0.44	0.53	0.35
TC	2.09	0.36	2.07	0.28	7.65	0.39	3.20	1.50
Levoglucosan	0.09	0.02	0.18	0.06	0.19	0.02	0.05	NA
Mannosan	0.01	0.00	0.01	0.01	0.01	0.00	NA	NA
Galactosan	0.01	0.00	0.01	0.01	0.02	0.00	NA	NA
4-NC**	0.78	0.23	0.42	0.13	1.36	0.37	NA	NA
4-NP**	0.05	0.02	0.04	0.00	0.07	0.00	NA	NA
4-NG**	0.25	0.04	0.15	0.05	0.34	0.12	NA	NA

all EF in g/kg except **in mg/kg

Fire-integrated Modified Combustion Efficiency (MCE) values ranged from 0.97 to 0.99, indicating flaming conditions for all experiments. The MCE values were derived from MGA measurements, and uncertainties discussed in Section 2.4 apply to these values.

The highest MCE values (0.98) were observed in the grass experiments, a fine fuel type with low humidity, allowing for quick, flaming combustion. The MCE values were slightly lower for the woodier fuels heather (0.96) and gorse (0.95). The relatively low moisture content of the dried fuels and the high burning efficiency of the woodstove promoted flaming combustion. Other laboratory studies report similar MCEs under comparable conditions. For example, Chen et al. (2007) measure MCE 0.98-0.99 for flaming-phase combustion of wildfire fuels.

McMeeking et al. (2009) comment that $MCE > 0.95$ is unlikely for real-world wildfires; however, Korontzi et al. (2003) report $MCE > 0.975$ for a field study on grassland fires. Andreae (2019) reports an average MCE of 0.94 ± 0.02 for the ‘Savannah and Grassland’ biome field studies. It is therefore probable that MCEs for Irish wildfires would be lower than those measured in the laboratory for the same fuels. Similar observations have been made by Stockwell et al. (2014), who found a MCE of 0.961 for combustion of grass fuels in the laboratory. Assuming lower MCE for real fires, they recalculated EFs for a range of species at a lower average MCE (0.938 from African savannah field measurements) using a linear regression approximation.

The EF_{CO_2} values measured in the burn chamber experiments were 1167 g/kg for heather, 1442 g/kg for gorse and 1558 g/kg for purple moor grass. The EF_{CO} values ranged from 27 g/kg for moor grass to 80 g/kg for gorse fuels, while heather emitted 42 g/kg (Figure 2.3).

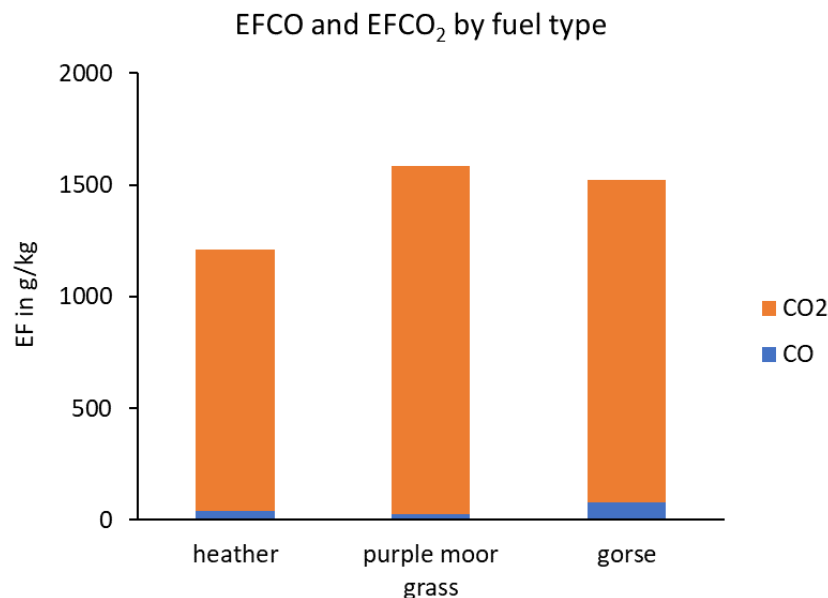


Figure 2.3: EF for CO_2 and CO by fuel type.

The EF_{CO} for all species and EF_{CO_2} for grass compare well with the literature; Andreae (2019) give an average of 1655 g/kg CO_2 (N=32) and an average of 69 g/kg CO (N=20) in the ‘Savannah and Grassland’ category. The EF_{CO_2} for heather and gorse are lower than the ‘Savannah and Grassland’ average by 2 SD and 4 SD, respectively. As Savannah and Grassland fuels have a higher moisture content and lower MCE, this

relative shift in CO to CO₂ is to be expected. Similar EF_{CO2} have been reported by Pallozzi et al. (2018) for Mediterranean conifers (985 - 1480 g/kg) and Alves et al. (2011a) for pine and undergrowth from wildfires in Portugal (1200 g/kg).

2.3.1 Particulate Emissions

Gravimetric determination of total particulate matter (TPM) yielded three times higher average EFs for gorse (14.33 g/kg) compared to grass (4.26 g/kg) and heather (3.95 g/kg) (Figure 2.4). Gorse is high in VOCs, which results in increased particle formation. Irish fire services personnel reported that gorse burned with large flames owing to its high oil content (pers. comm.).

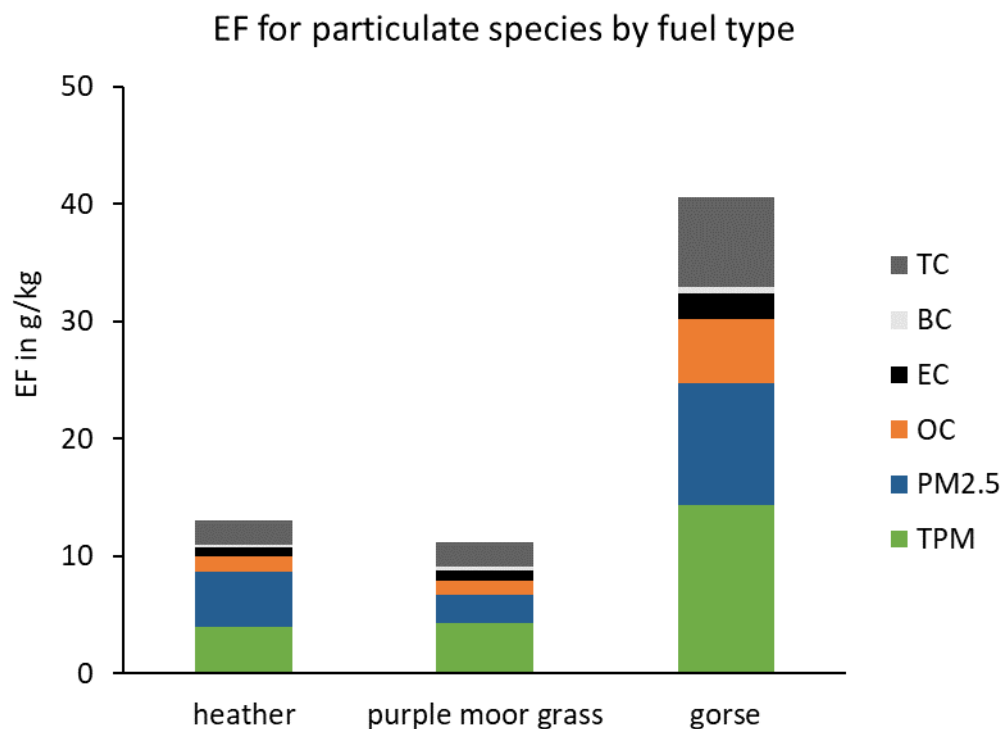


Figure 2.4: EF for particulate species by fuel type

The EF_{TPM} values are in agreement with values reported in the literature. An EF_{TPM} value of 14.0 g/kg was reported by Alves et al. (2011) for field measurements of mixed vegetation from wildfires in Portugal – mainly evergreen species like *Pinus pinaster* and *Eucalyptus globulus*, along with other shrubs, grasses, and some deciduous species. The measured EF_{TPM} from grass and heather are on the lower end of the scale. Sinha et al. (2003) report EF_{TPM} from 4.8 g/kg to 13.0 g/kg for savannah and grassland field measurements, and Andreae (2019) calculated an average of 8.7 g/kg for the ‘Savannah and Grassland’ category. Higher PM emissions from gorse are likely due

to high VOC content and slightly lower MCE. Higher PM emissions would be expected during a real-world fire situation at lower MCE.

As expected from the TPM results, $EF_{PM_{2.5}}$ were highest for gorse (10.46 g/kg) followed by heather (4.71 g/kg) and grass (2.42 g/kg). The measured $EF_{PM_{2.5}}$ were not in perfect accordance with EF_{TPM} (Table 2.1); in fact, uncorrected $EF_{PM_{2.5}}$ were in fact lower than EF_{TPM} by a factor of 2. For these kind of combustion processes, it would be expected that most particles emitted are small ($PM_{2.5}$ and smaller).

The following factors may contribute to this difference 1) additional losses in transfer lines, which were also observed seen between Q1 and Q2 filters. As the instrument measuring $PM_{2.5}$ (TSI DustTrak) is further down in the system than the filters, it is possible that additional particle mass was lost in this manner. $PM_{2.5}$ concentrations were corrected for loss within transfer lines via loss ratio of TC as quantified from the discrepancy between Q1 and Q2 filters. 2) Differences in measurement method: TPM is determined gravimetrically, while the DustTrak is an optical instrument. 3) TPM may have included some ash content.

Overall, $EF_{PM_{2.5}}$ are in good accordance with the literature, studies summarized by Andreae in the savannah and grassland category range from 3.1 g/kg (Andreae et al., 1998) to 16.8 g/kg (Holder et al., 2016).

The measured EF_{OC} and EF_{EC} for gorse were four and three times higher respectively than for heather and moor grass (Table 2.3), which is consistent with overall higher PM emissions and VOC content. OC/TC and EC/TC ratios are illustrated in Figure 2.5. OC made up 60-70% of TC, and gorse was on average about 10% higher in OC than grass and heather fuels.

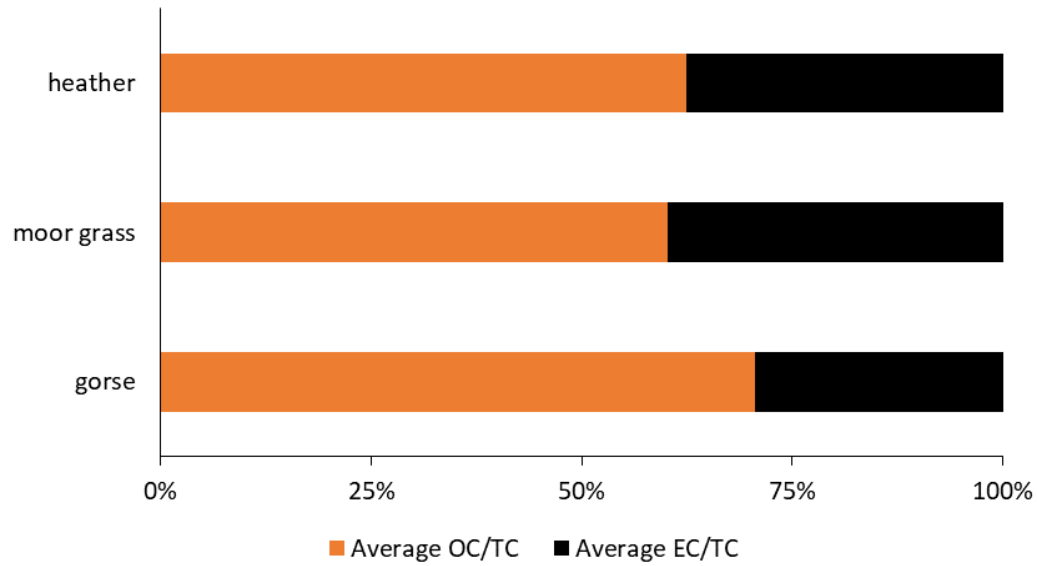


Figure 2.5: Ratios of OC, EC and TC for gorse, moor grass and heather fuel experiments.

Comparison of OC and EC concentrations from filters taken at directly at the stove pipe (Q1) and after dilution D1 (Q2) revealed average decreases of 44% for OC and 10% for EC. It is likely differences arise from dilution-caused re-partitioning of semivolatile OC from the particle phase to the gas phase, thereby reducing the OC content of particles. Loss to the gas phase is not expected for EC, which is a refractory material. Thus, the loss in EC is indicative of particle loss in the transfer lines.

The measured EF_{BC} were highest in gorse (0.50 g/kg), followed by heather (0.26 g/kg) and grass (0.21 g/kg). These values are in accordance with the literature: Andreae (2019) reports 0.53 ± 0.35 g/kg for ‘Savannah and Grassland’ studies. Low EF_{BC} for grass- and shrublands were similarly reported by Lawson et al. (2015) (0.16 g/kg for Australian coastal shrubland) and Ward & Hardy (1991) (0.16 g/kg, Savannah). On average 5% of TPM mass consisted of Black Carbon (BC).

Like $EF_{PM2.5}$, EF_{BC} were corrected for particle loss in the system using filter losses, in this case using the EC loss (average 10%) as BC and EC are both measure the same species with different methods. On average EF_{EC} are higher than EF_{BC} by a factor of 4, possibly due to reasons discussed for $EF_{PM2.5}$. Furthermore, the Aethalometer measuring BC was subject to an additional dilution step (D2). While all emission factors were corrected for dilution effects, this introduces further uncertainty. Other possible differences in $EF_{PM2.5}$ and EF_{BC} that are unaccounted for will be investigated further, however it was not possible to do so within the scope of this work.

2.3.2 Gas phase products

Methane (CH_4) emission factors were measured for purple moor grass and gorse, but a blockage in the Picarro inlet during the measurements precluded methane measurements for heather experiments.

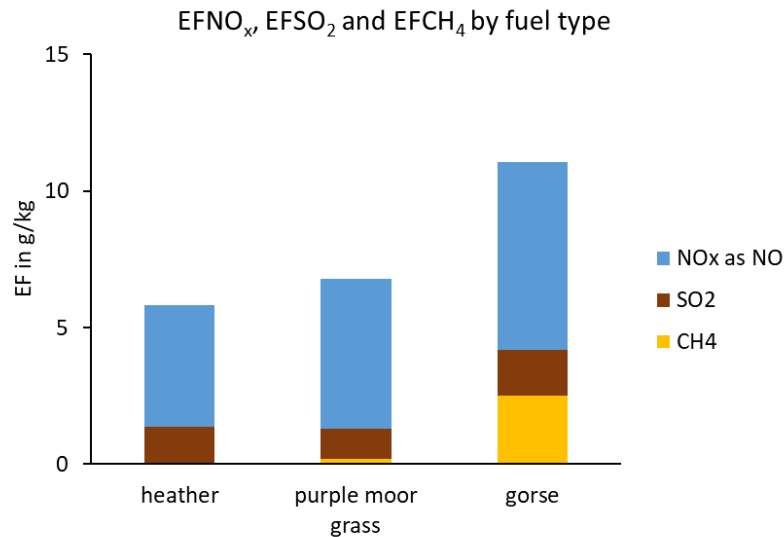


Figure 2.6: EF for gases (NO_x as NO, SO₂, CH₄) by fuel type

The measured EF_{CH_4} for gorse (2.52 g/kg) were about 12 times higher than for purple moor grass (0.21 g/kg) (Figure 2.6). The value for gorse is close to average field measurements reported by Andreae (2019) for ‘Savannah and Grassland’ field studies (2.70 g/kg), as well as by Akagi et al. (2011) for Savannah (1.94 g/kg) and Chaparral (2.51 g/kg) (Table 2.4). Lawson et al. (2015) reported a value of 3.8 g/kg for Australian coastal shrubland; Urbanski et al. (2009) 2.1 g/kg for grass and shrubland in the Southeast and Midwest US and Alves et al (2010) 1.5 g/kg for Mediterranean shrubland, further confirming that EF_{CH_4} for gorse are in good accordance with values reported for similar shrubland vegetation. The EF_{CH_4} for grass fuels measured during FLARES are comparatively low. Scholes et al. (1996) reported values from 1.7 to 3.4 g/kg in grasslands; Holder et al. (2017) 1.4 g/kg for Kentucky blue grass, and Yokelson et al. (2003) 2.19 g/kg for savannah grass. The EF_{CH_4} from our study is closest to Sinha et al. (2004) who report 0.5 g/kg for Dambo grassland, a type of wetland habitat in Malawi. Sinha et al. (2003) note that EF_{CH_4} for Savannah fires are low compared to fires of woody materials.

If we again assume lower MCE for real fire conditions, the FLARES emission factors are expected to underestimate wildfire EF_{CH_4} , because more CH_4 is emitted during

smouldering combustion (Volkova et al., 2014; Stockwell et al., 2014). Methane emissions from wildfires are especially climate relevant as CH₄ released in wildfires, unlike CO₂, is not sequestered back as vegetation regrows (Sinha et al., 2003).

Table 2.4: Literature values for EFCH₄ (g/kg)

<i>EFCH₄ (g/kg)</i>	<i>Vegetation type</i>	<i>Source</i>
2.52	gorse	this study
0.21	purple moor grass	this study
0.5	Dambo grassland	Sinha et al. (2004)
1.4	Kentucky blue grass	Holder et al. (2017)
1.5	Mediterranean shrubland	Alves et al (2010)
1.94	savanna	Akagi et al. (2011)
2.1	Southeast and Midwest US shrubland	Urbanski et al (2009)
2.19	savanna grass	Yokelson et al. (2003)
2.51	Chaparral	Akagi et al. (2011)
2.7	savanna and grassland	Andreae (2019)
3.8	Australian coastal shrubland	Lawson et al (2015)
1.7 - 3.4	grassland	Scholes et al. (1996)
1.8 - 2.3	savanna	Scholes et al. (1996)

The measured EF_{SO₂} are 1.68 g/kg for gorse, 1.38 g/kg for heather and 1.08 g/kg for purple moor grass, respectively (Table 2.5). These values are slightly higher than the values reported for ‘Savannah and Grassland’ (0.47 ± 0.44 g/kg) by Andreae (2019) but are similar to Vakkari et al. (2019) for Southern African savannah and grassland fires (1.1 g/kg). However, Vakkari et al. (2019) explain their elevated SO₂ as associated with industrial influences. Flaming combustion leads to the formation of more oxygenated compounds such as SO₂ (Yokelson et al., 1997) thus the high MCE during FLARES experiments may contribute to high EF_{SO₂}.

Table 2.5: Literature values for EF_{SO_2} (g/kg)

EF_{SO_2} (g/kg)	Vegetation type	Source
1.68	gorse	this study
1.38	heather	this study
1.08	purple moor grass	this study
0.47 ± 0.44	savanna and grassland	Andreae (2019)
1.1	savanna and grassland, South Africa	Vakkari et al. (2019)

The measured EF_{NO_x} as NO are 4.46 g/kg for heather, 5.51 g/kg for purple moor grass and 6.85 g/kg for gorse. While these values are higher than what is reported Andreae (2019) for the ‘Savannah and Grassland’ biome by (2.49 ± 1.30 g/kg), Stockwell et al. (2014) reported EF_{NO_x} (Table 2.6). 4.23 g/kg for laboratory experiments with savannah grass adjusted to field conditions. Like SO_2 , NO_x is emitted under flaming conditions (Yokelson et al., 1997). Mebust et al. (2011) found an average 30% decrease in NO_x for a reduction in MCE from 0.95 to 0.90, which gives a possible explanation for the relatively high NO_x emissions with high MCE during FLARES experiments reported here.

Table 2.6: Literature values for EF_{NO_x} (g/kg)

EF_{NO_x} (g/kg)	Vegetation type	Source
6.85	gorse	this study
5.54	heather	this study
4.46	purple moor grass	this study
2.49 ± 1.30	savanna and grassland	Andreae (2019)
4.23	savanna grass (laboratory experiments adjusted to field conditions)	Stockwell et al. (2014)

The EF_{NO_x} and EF_{SO_2} were measured at two points in the system, directly at the stove pipe via a Dr Foedisch MGA, and after two dilutions (D1 and D2 in Figure 2.2) via a Horiba NO_x monitor and a Thermo SO_2 analyzer. Upon checking Horiba instrument flows after experiments, it was discovered that the instrument flow was irregular, which is likely to have negatively influenced measurements. Furthermore, both instruments recorded values as averages over long measurement intervals, i.e., 1 min for SO_2 and 3 min for NO_x , respectively, and most EF experiments lasted fewer than 3 min. Real-time measurements of these instruments were recorded visually via video,

however manual transcription and analysis of this data was out of the scope of this work. Instead, MGA measurements were used for determination of EF_{NO_x} and EF_{SO_2} .

2.3.3 Biomarkers

Monosaccharide anhydrides

Filter samples were analysed at TROPOS Leipzig for the organic compounds levoglucosan, mannosan and galactosan. The EFs for levoglucosan were lowest for heather (0.09 g/kg) and higher for purple moor grass (0.18 g/kg) and gorse (0.19 g/kg) despite gorse being a woodier fuel (Table 2.7). Heather had the highest amount of unburnt fuel left after experiments, which might explain the low EF for levoglucosan.

Table 2.7: Literature EF for levoglucosan, mannosan and galactosan.

<i>levoglucosan</i>	EF (g/kg)		<i>Vegetation type</i>	<i>Source</i>
	<i>mannosan</i>	<i>galactosan</i>		
0.09	0.01	0.01	heather	this study
0.18	0.01	0.01	purple moor grass	this study
0.19	0.01	0.02	gorse	this study
1.11	0.17	0.5	rice straw	Li et al. (2020)
1.41	0.36	0.74	maize straw	Li et al. (2020)
2.58	0.51	1.02	wheat straw	Li et al. (2020)
0.05			Australian grasslands	Wang et al. (2017)
0.41			grass	Oros et al. (2006)
2.75			Australian Eucalypt forests	Reisen et al. (2018)

The EFs for levoglucosan found in this study were in agreement with those reported in the literature (Table 2.7): a field study of Australian grasslands by Wang et al. (2017) report 0.05 g/kg while Oros et al. (2006) found 0.41 g/kg for grass. On the high end of the spectrum, Reisen et al. (2018) reported 2.75 g/kg for field measurements of flaming (>80%) combustion in Australian Eucalypt forests.

The relative amounts of levoglucosan and its isomers depend heavily on factors such as fuel characteristics, (e.g. softwood or hardwood (Fabbri et al., 2009); branches, wood, leaves etc (Vicente et al., 2011; Sullivan et al., 2008)), and combustion conditions, including flaming/smouldering phase, temperature and combustion appliance (Vicente & Alves, 2018). Kuo et al. (2008) observed high variability between levoglucosan yields in samples of different species. They identified temperature as the most influential factor affecting levoglucosan levels in char, and

highest yields were found in low-temperature samples (150-350 °C). Vicente et al. (2011) found a low correlation between MCE and levoglucosan emissions. Variations of levoglucosan between experiments of the same fuel ranged from 11-3%, likely a reflection of differences in the factors mentioned above.

As expected, mannosan and galactosan levels were significantly lower than levoglucosan (0.01 and 0.01 g/kg for heather; 0.01 and 0.01 g/kg for purple moor grass; 0.01 and 0.02 g/kg for gorse, respectively). This is similarly reported in other studies (Li et al., 2020; Fabbri et al., 2009). Li et al. (2020) calculated EFs for fresh smoke samples from rice (levoglucosan 1.11, mannosan, 0.17 galactosan 0.50 g/kg), maize (levoglucosan 1.41, mannosan 0.36, galactosan 0.74 g/kg) and wheat straw (levoglucosan 2.58, mannosan 0.51, galactosan 1.02 g/kg).

Other potential biomarkers

On average, EFs for 4-nitrocatechol, 4-nitroguaiacol and 4-nitrophenol were highest in gorse (1.21, 0.30 and 0.07 mg/kg, respectively), followed by heather (0.77, 0.25 and 0.05 mg/kg) and grass (0.37, 0.13 and 0.04 mg/kg). Vanillic acid was not found in the samples.

Table 2.8: EF in literature for 4-nitrocatechol, 4-nitroguaiacol and 4-nitrophenol

<i>4-nitrocatechol</i>	<i>EF (mg/kg)</i>		<i>Vegetation type</i>	<i>Source</i>
	<i>4-nitrophenol</i>	<i>4-nitroguaiacol</i>		
0.78	0.05	0.25	heather	this study
0.42	0.04	0.15	moor grass	this study
1.36	0.07	0.34	gorse	this study
0.32-3.97	0.04-0.59		various fuels*	Wang et al. (2017)

*leaves, branches, corncob, corn stalk, and wheat straw

Wang et al. (2017) found that the ratio of nitrated phenol emissions to PM_{2.5} increased with MCE. The basis of PM_{2.5} estimated EF for a variety of fuels (leaves, branches, corncob, corn stalk, and wheat straw) ranged from 0.32-3.97 mg/kg for 4-nitrocatechol and 0.04-0.59 mg/kg for 4-nitrophenol, which is in accordance with our study (Table 2.8).

2.4 Uncertainty Analysis

Uncertainties are introduced across the measurement process. Emission factors are calculated from the amount of pollutant released by kg fuel burnt. If we assume that the uncertainty of the gravimetric fuel measurement is negligible compared to the other parameters, the largest uncertainties are within the flow measurements and dilutions, followed by uncertainties in the instrument or quantitative analysis method. Thus, uncertainties increase with increasing dilution steps. Flow measurements within the stove pipe were measured with an uncertainty of 3%, which applies to all EF measurements. As uncertainties for dilution factors D1 and D2 were not known, a maximum upper limit of 15% uncertainty was assumed as it was deemed unlikely that deviations would be greater. Similarly, a 5% uncertainty was assumed for instruments where uncertainties were not known, as this is a value commonly reported by manufacturers of online analytical instruments.

Every increment in percent uncertainty introduced in any step is directly reflected in the overall EF uncertainty. Total relative uncertainty was calculated (Equation 2.3) as described by Harvey (2020) where the relative compounding uncertainty u_R of the result R is a function of the respective uncertainties of measurements A , B and C (u_A , u_B and u_C).

$$u_R = \sqrt{\left(\frac{u_a}{A}\right)^2 + \left(\frac{u_b}{B}\right)^2 + \left(\frac{u_c}{C}\right)^2} \quad \text{Eq. 2.3}$$

Uncertainties are summarized in Table 2.9. The u_R for EFs are calculated as by Eq 2.3 from the respective instrument uncertainty, the F0 flow uncertainty and the dilution uncertainties at D1 and D2 if applicable. Relative uncertainties for EF range from 6-22%, which is overall lower than SD between experiments.

Table 2.9 Relative uncertainties for instrument measurements at different points in the system

Instrument	Uncertainty Instrument	Source	D1	D2	u_r EF	applies to species
MGA	5%	assumed max.			6%	CO ₂ , CO, NO, SO ₂
Q1 filter	5%	assumed max.			8%	OC, EC, TC, all biomarkers
DustTrak	5%	assumed max.	x		16%	PM _{2.5}
Picarro	5%	assumed max.	x	x	22%	CH ₄
AE33	1.1%	Andrea et al. (2020)	x	x	21%	BC
Instrument	Uncertainty Instrument	Source				
Flow (F0) - Almemo sensor	3%	Ahlborn Almemo manual				
Dilution D1 Dekati	15%	assumed max.				
Dilution D2 mass flow controller	15%	assumed max.				

Standard deviation (SD) between experiments ranged from 1% to 53%, indicating high burn-to-burn variability and large overall uncertainty for EFs for most species measured as shown in Table 2.10.

Table 2.10 Standard deviations between EF experiments

experiment	CO	CO ₂	CH ₄	SO ₂	NO	TPM	PM _{2.5}	BC	OC	EC	TC
EFH1	34	1138	NA	0.78	3.95	4.90	4.96	0.34	1.42	1.18	2.60
EFH2	38	1103	NA	1.10	4.32	3.97	4.26	0.15	1.25	0.57	1.82
EFH3	47	1187	NA	1.78	4.53	2.99	3.61	0.26	1.18	0.66	1.84
EFHL	49	1240	NA	1.87	5.03	NA	6.27	0.39	NA	NA	NA
EF heather	42	1167	NA	1.38	4.46	3.95	4.71	0.26	1.28	0.80	2.09
SD heather %	15%	4%	NA	33%	9%	20%	24%	37%	8%	33%	17%
EFGR1	26	1568	0.20	0.24	5.83	4.21	2.02	0.14	1.16	0.64	1.81
EFGR2	24	1639	0.22	1.01	5.42	3.57	1.90	0.28	0.87	1.07	1.94
EFGR3	30	1492	0.29	1.22	5.81	5.00	3.05	0.15	1.75	0.71	2.46
EFGR4	27	1532	0.13	1.87	4.97	NA	2.71	0.28	NA	NA	NA
EF grass	27	1558	0.21	1.08	5.51	4.26	2.42	0.21	1.26	0.81	2.07
SD grass %	7%	3%	27%	53%	6%	14%	20%	33%	29%	23%	14%
EFGO1	86	1540	2.17	2.31	7.81	14.18	9.71	0.58	4.41	2.82	7.23
EFGO2	71	1388	2.60	1.62	6.51	14.53	11.45	0.43	6.39	1.79	8.18
EFGO3	73	1329	2.19	1.24	6.40	14.27	8.55	0.51	5.48	2.07	7.55
EF GOL	88	1512	3.11	1.57	6.69	NA	12.11	0.48	NA	NA	NA
EF gorse	80	1442	2.52	1.68	6.85	14.33	10.46	0.50	5.43	2.23	7.65
SD gorse %	9%	6%	15%	23%	8%	1%	13%	11%	15%	20%	5%

Although TROPOS Leipzig have extensive experience with biomass burning and smoke aging experiments, the setup described in Section 2.2.2 was the first time this setup was used for EF determination, leading to procedural uncertainty regarding the flow measurements within the system. It was not possible to quantify this uncertainty exactly, but if we assume a 5% error in flow measurements, this leads to a 5% uncertainty in EF, because flow translates directly to volume. Again this is lower than most burn-to-burn variabilities.

Additionally, upon calibration a year after the experiments it was discovered that the MGA CO₂ measurements were about 45% too high. The long time between the experiments and re-calibration, and the fact that the MGA instrument was configured for measuring flue gases at much higher CO₂ and CO concentrations add to the uncertainty of these values. A correction factor of 0.45 was applied to CO₂ values. Although measured values are associated with high uncertainty, they are within the range of reported literature, e.g. ‘Savannah and Grassland’ category reported in Andreae (2019).

Other uncertainties include specific instrument and method errors, as well as errors in fuel mass. The latter is higher for “long” experiments (EFHL, EFGOL, EFGRL), during which more fuel was burn. As these experiment runs were originally intended to only test instrument performance under more stable conditions, fuel mass was not recorded as precisely as for the other experiments ($\pm 50\text{g}$).

Despite the abovementioned uncertainties, EF for most species measured are in broad agreement with literature values.

2.5 Conclusion

From a global perspective, wildfires are a major source of climate-relevant gases and aerosols. While fires in Ireland happen on a relatively small scale, fire regimes are predicted to change (IPCC, 2014). Of particular concern are fires in the wildland urban interface, which put communities adjacent to upland areas at risk (Irish Fire Services, pers. comm.). With this trend continuing, accurate data on wildfire emissions are becoming more important.

Emission Factors for a range of pollutants were measured for fuels common in Irish wildfires. The selected fuels were gorse (*Ulex sp.*), heather (*Calluna and Erica spp.*) and purple moor grass (*Molinia caerulea*), which were identified as significant fuels for upland fires in Ireland. To our knowledge, this is the first time emission factors have been reported for natural vegetation fires in an Irish context. Literature examples of fuels from similar climates are rare, and the values reported here will also be relevant to similar biomes and temperate maritime climates, such as Britain and northern European coastal areas.

A difference in emissions factors was observed between the different fuel species. In general, emission factors for gorse, although at a slightly lower MCE, were higher than for heather and grass. Moor grass emissions were overall lowest, except for CO₂, which is in accordance with the highest MCE values observed for this fuel.

As emission factors during this study were determined in laboratory experiments, combustion conditions do not fully reflect real-world fire situations. The wood burning stove used during these experiments is likely to lead to differences regarding the size and temperature of the fire, fuel humidity during and oxygenation conditions. Modified combustion efficiency was very high (0.95-0.98) during the FLARES emission factor experiments. This resulted in higher EFs for CO₂, and lower EF for CO, carbonaceous gases and aerosols than would be expected in real-world fires. Other studies have used open-fire setups, which in terms of air flow and fuel volume may be closer to real-world conditions; this was not possible due to the logistics of the facility.

Combustion efficiency, i.e., the proportion of fuel burnt during an experiment, differed depending on the fuel type. For grass experiments, all the fuel was burnt and converted to ash. For heather experiments, the amount of unburnt material ranged from 4-26% of the total fuel mass, and for gorse burns from 2-14%. For the calculation of Emission Factors, the total amount of fuel weighed out and put in the stove was used. It was observed at the site of the Army Barracks fire that stems and branches of heather were left blackened but unburnt. As gorse is a similarly coarse fuel, it can be assumed that some percentage of it would be left unburnt as well, whereas dry grass could be expected to burn completely. For this study, using the whole fuel mass was deemed reasonable, as in practicality an emission factor that can be estimated from the total amount of biomass available and the amount of biomass burnt visible from GIS data is required.

Despite uncertainties regarding the emission factors, resulting values are in relatively good agreement with the literature. The greatest uncertainty in the calculation of total wildfire emissions for Ireland relates to the amount of biomass available as fuel. Little data is available on standard fuel masses, even more so in an Irish context. Creation of such a dataset would be helpful for improved emissions estimations.

The FLARES project (EPA 2019-CCRP-MS.65) estimates Irish national GHG emissions of 60,000-200,000 t CO₂-eq/year between 2015 and 2021 (Cawkwell et al., under review). Although only accounting for 0.1 to 0.2% of annual national Irish GHG emissions, wildfire emissions are considerably higher than previously estimated in the National Inventory Report (NIR). This improvement was achieved by establishment of a fire-events database and burnt area delineation as described in (Cawkwell et al., under review) and providing suitable emissions factors for Irish wildfire fuels. The FLARES study also shifted the focus of Irish wildfires away from forest fires. This land cover class previously was the only one covered in the NIR, but was found to only represent a small fraction of fires in Ireland.

3 Atmospheric Aging Experiments

3.1 Introduction

Wildfires emit large amounts of gases and aerosols into the atmosphere. In addition to immediately released primary emissions, secondary aerosols are formed through atmospheric processing. These can have significant impacts air quality, climate, and human health.

Increases in atmospheric particulate matter are due to formation of secondary inorganic aerosols (SIA) and secondary organic aerosol (SOA), sometimes occurring as new particle formation events. Secondary Inorganic Aerosol is formed through gas and condensed phase reactions that produce sulphate, nitrate and ammonium ions from SO_2 , NO_2 and ammonia (NH_3) in the gas phase. The formation of SOA on the other hand is more complex but SOA frequently accounts for a substantial portion of the tropospheric aerosol burden (Kroll and Seinfeld, 2008).

Formation of SOA occurs via physiochemical pathways from primary organic aerosol (POA) and gas-phase volatile organic compounds (VOCs) (Rodelas et al., 2019). These reactions are complex due to the enormous number of potential VOCs — Goldstein & Gallaby (2007) estimate there are between 10,000 and 100,000 different VOCs in the atmosphere. This complexity is further increased by the many different gas-to-particle conversion pathways which can lead to SOA formation and growth (Hallquist et al., 2009). The formation of SOA from VOCs has been subject to numerous studies (e.g. Majdi et al., 2019; Fredrickson et al., 2022; Kourtchev et al., 2016; Mutzel et al., 2016).

Production of SOA is governed by dilution and oxidization processes (Ahern et al., 2019). The partitioning of aerosols between gas and particle phase is determined by compound volatility. In a smoke plume, volatility may decrease, causing VOCs to partition into the particle phase, forming SOA and contributing to TPM. On the other hand, dilution may cause particles to evaporate, thereby decreasing TPM. This evaporation produces VOCs, which can again act as SOA precursors, and may re-condense with increased plume age (Hodshire et al., 2019). The SOA are less volatile and more hygroscopic than POA (Wang et al., 2022). Oxidation reactions include the heterogenous uptake of oxidants (OH , O_3 and NO_3) by liquid-phase organics, as well

as oxidation of gas phase compounds form low-vapor-pressure products that can form SOA (Rudich et al., 2007). Additionally, a large fraction of atmospheric aerosols is semivolatile, and mass transfer can easily shift to the liquid or gas phase (Shrivastava et al., 2006).

Atmospheric chamber experiments are a well-established experimental approach to study trace gas and aerosol chemistry, including secondary particle formation. An in-depth review of the history of atmospheric simulation experiments can be found in Hidy (2019). The earliest atmospheric simulations go back to experiments by Tyndall and Wilson in the late 19th century; which explored photochemical reactions by irradiation of gases, and by Wilson in the same period investigating cloud formation. After growing concern about air pollution, major “smog chamber” facilities were established in the USA during the 1960s. The 1980s saw much work on NO_x chemistry and VOCs in these chambers. Reviews of chamber experiments include those of Glasius & Goldstein (2016); Hallquist et al. (2009); Kroll & Seinfeld (2008a); Lim et al. (2019) and Lim et al. (2010).

Simulating atmospheric aging in laboratory experiments poses a complex challenge. The setup of an atmospheric processing chamber consists of an enclosed reactor space made from a non-reactive material such as Teflon film, stainless steel, or borosilicate glass. Chambers have systems to control and monitor dilution and sample flows, irradiation, temperature, and relative humidity. Limitations of chamber experiments arise from wall losses, i.e. losses of pollutants and radicals on chamber walls, as well as the challenges of accurately simulating real-world conditions (Chu et al., 2022). To reduce the effects of walls on the chemical and physical processes taking place in the chamber, atmospheric simulation chambers strive to have the largest practicable volume. Chamber volumes may range from 1 m³ for small benchtop reactors to almost 300 m³ for large outdoor facilities (Hidy, 2019).

Atmospheric aging processes have been studied on a wide range of fuels in laboratory experiments. Lim et al. (2019) focused on wildfire fuels of the western US – pine and fir species, as well as peat, dung and rice straw. Stockwell et al. (2014) burned grasses, rice straw, peat and temperate and boreal coniferous canopy fuels, as well as some non-wildfire fuels, while Kalogridis et al. (2018) experimented with boreal coniferous fuels typical of Siberian forests.

Field measurements of wildfire plumes have shown increased oxidation of aerosols with increasing plume age, as indicated by increases in O:C ratios (Hodshire et al., 2019). Additionally, such studies have shown the oxidation and decay of levoglucosan with increased plume age (Cubison et al., 2011). In terms of SOA increase, Hodshire et al. (2019) discuss significant discrepancies in laboratory and field studies, most prominently an average net increase in SOA observed during laboratory studies (Hennigan et al., 2011). In contrast, field observations vary from significant mass enhancement (Wigder et al., 2013), to small increases or even net losses (Brito et al., 2014; Capes et al., 2008). Possible explanations for these differences include variations in emissions, dilution differences, chamber and transfer line losses, and differences in baselines (Hodshire et al., 2019).

The goal of this chapter is to explore the atmospheric aging of fresh emissions from typical fuels of Irish upland fires during day-time and night-time conditions. The study was carried out as series of atmospheric simulation chamber experiments at the Leibniz Institute for Tropospheric Research (TROPOS), Leipzig. In particular, the objectives were to study the extent to which the PM mass per air volume changes following atmospheric processing and to investigate whether SOA formation contributes significantly to the total particle emissions of Irish wildfires. Day-time and night-time atmospheric processing reactions were simulated.

3.2 Methods

3.2.1 Setup and Instrumentation

Atmospheric aging experiments were performed in the Atmospheric Chemistry Department Chamber (ACD-C) at TROPOS Leipzig. A detailed description of the chamber can be found in Kroflič et al. (2021).

ACD-C is an inflatable cylindrical Teflon aerosol chamber with a volume of 19 m³, and a surface/volume ratio of 2 m⁻¹. The chamber is temperature and humidity-controlled. UV lamps simulate solar irradiation at $J(\text{NO}_2) = 2.6 \times 10^{-3} \text{ s}^{-1}$. Sampling ports at the bottom of the chamber are connected to a range of instruments. The smoke sample is drawn into the chamber via the Dekati (dilution factor 8.53 at 20 °C) from the LBBF described in Section 2.2.2. A schematic overview of the setup is given in Figure 3.1.

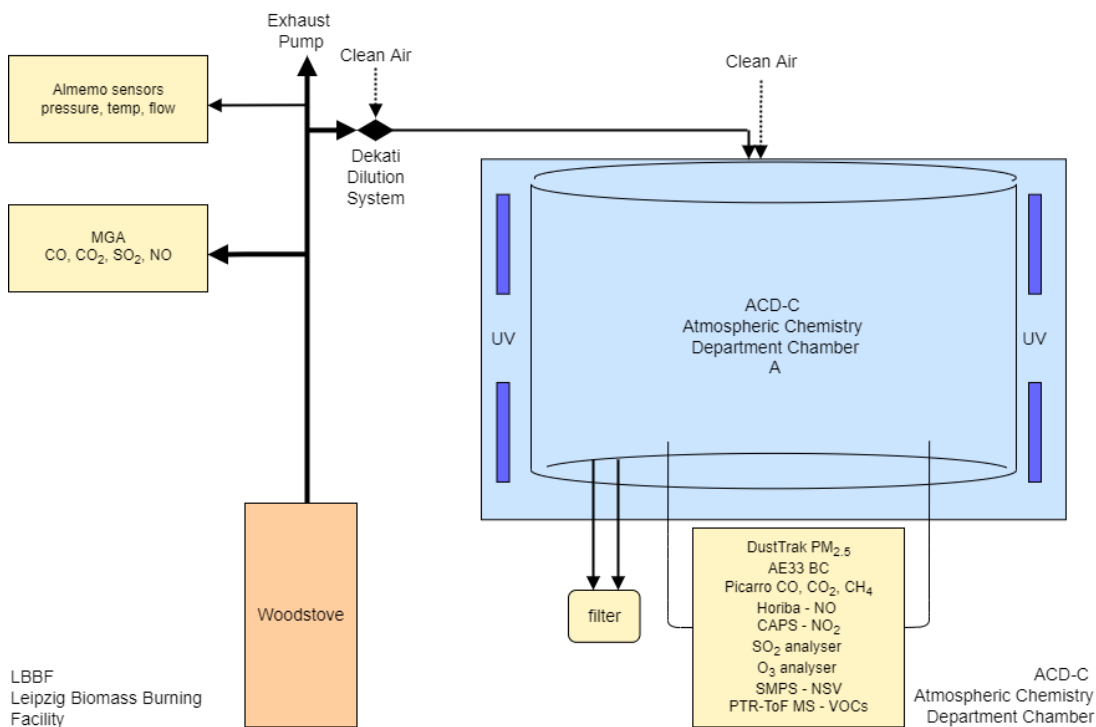


Figure 3.1: Schematic of LBFF and atmospheric simulation chamber ACD-C at TROPOS Leipzig.

Instrumentation used for this series of experiments is listed in Table 3.1 and included a scanning mobility particle sizer (SMPS), a condensation particle counter (TSI Model 3750), a handheld PM_{2.5} monitor (Dusttrak II Aerosol Monitor 8532 from TSI, Inc. USA), an aethalometer (Magee Scientific AE33) to determine BC and BrC, and filter holders for PTFE and quartz filters for offline analysis of OC/EC and biomarkers. Gas concentrations were measured by a cavity ringdown spectrometer (Picarro G2401 for CO₂, CO and CH₄), and gas analysers (Horiba APNA 370 for NO, NO₂ and NO_x; Aerodyne CAPS for NO₂ and Thermo Scientific model 49i UV photometric analyser for O₃). Additionally, an Ionicon proton transfer reaction time-of-flight mass spectrometer (PTR ToF – MS) with a mass resolution of 8000 was used to track OH concentrations and measure VOCs during some experiments.

Table 3.1: Instrumentation chamber experiments.

Instrument	Manufacturer	Parameter	Sampling Interval
Almemo sensors	Ahlborn	temperature, pressure, flow	10s
MultiGasAnalyzer	Dr Foedisch	CO ₂ , CO, SO ₂ , NO	20s
Aethalometer AE33	Magee	BC	60s
DustTrak II Aerosol Monitor 8532	TSI	PM _{2.5}	10s
G2401 Cavity Ringdown Spectrometer	Picarro	CO ₂ , CO, CH ₄	around 1s
APNA-370 Ambient NO _x monitor	Horiba	NO, NO ₂ , NO _x	180s
Pulsed Fluorescence SO ₂ Analyser	Thermo Environmental Instruments	In SO ₂	60 s
CAPS NO ₂ sensor	Aerodyne	NO ₂	1s
UV Photometric O ₃ Analyzer 49i	Thermo Fisher Scientific Inc.	O ₃	
Condensation Particle Counter Model 3750	TSI	particle size, number, volume	
PTR-TOF MS	Ionicon		

3.2.2 Experimental Procedure

For each fuel, three types of atmospheric aging experiments were conducted:

- A) simulated daytime aging with UV lights
- B) simulated daytime aging under reactive conditions with UV lights + generation of OH radical
- C) simulated night-time aging (no lights) + addition of O₃.

In scenario A (day-time UV experiments), two sets of UV lights (300-550 nm, 12 W m⁻²) were switched on to simulate daytime aging (Note: This generated some OH from precursors in the injected sample even if no additional OH precursors were added to the chamber). In scenario B, 0.1 µL/hr 7.5% H₂O₂ solution was injected into the chamber in addition to the sample to generate higher OH radical concentrations with UV lights. For scenario C (night-time), no lights were switched on in the chamber. A concentration of 180 ppb O₃ in the chamber was produced by flowing 2.5 l/min O₂ over a UV lamp prior to injecting the sample.

Table 3.1 gives an overview of chamber experiments performed during FLARES. An initial chamber blank experiment without smoke injection was performed to establish baseline conditions (BLANK). Experiments are named after the type of fuel (gorse GO, grass GR, heather H) and the oxidation conditions (day-time scenario A “UV”, day-time scenario B “OH” and night-time scenario C “O₃”). E.g., for day-time UV grass experiments the experiment code is GR_UV. Experiments GO_UV2, GR_UV2, GO_UVOH2 were repeats due to instrument issues with the Picarro analyser.

Table 3.1: Atmospheric aging experiments performed during FLARES

	Fuel	oxidant	concentration	Day/night	Reaction time h	Smoke injection min	# filter BLANK	# filter DARK	#filter REACTION	fuel mass g	comments
NA	BLANK	BLANK + UV		NA	4	NA	NA	1	2	NA	issues Picarro
moor grass	GR_UV	UV		day	4	2.5	1	1	2	125	issues Picarro
moor grass	GR_UV_2	UV		day	4	2.5	1	1	2	125	
moor grass	GR_OH	UV + H ₂ O ₂ (OH)	0.1 µl/hr	day	4	2.5	1	1	2	125	
moor grass	GR_O3	O ₃	180 ppb	night	4	2.5	1	1	2	125	
heather	H_UV	UV		day	4	2.5	1	1	2	150	
heather	H_OH	UV + H ₂ O ₂ (OH)	0.1 µl/hr	day	4	2.5	1	1	2	200	
heather	H_O3	O ₃	180 ppb	night	4	2.5	1	1	2	175	
gorse	GO_OH	UV + H ₂ O ₂ (OH)	0.1 µl/hr	day	4	2.5	1	1	2	150	issues Picarro
gorse	GO_OH_2	UV + H ₂ O ₂ (OH)	0.1 µl/hr	day	4	2.5	1	1	2	125	
gorse	GO_UV	UV		day	4	5	1	1	2	300*	issues Picarro
gorse	GO_UV_2	UV		day	4	2.5	1	1	2	200	issues Picarro
gorse	GO_O3	O ₃	180 ppb	night	4	2.5	1	1	2	150	issues Picarro

* fuel mass not exact

Prior to each experiment, the chamber was purged overnight with 200 L/min of dry, clean air. Relative humidity was adjusted to a target value of 65% using a HPLC pump and ultrapure H₂O, and temperature was adjusted to 21°C. Once desired starting conditions were reached, the inflow of clean air into the chamber was stopped.

A fuel parcel (approx. 25 g) was placed in a wood burning stove and ignited with a propane lighter. Additional fuel parcels of the same mass were added periodically to keep the fire burning steadily. Once a stable smoke temperature was reached, fire emissions were injected into the chamber for a period of 2.5 min at a flowrate of 5.7 L/min (dilution ratio 8.53 at 20 °C). The concentrations of OH radical in the chamber were tracked by monitoring the decline of d9-Butanol, of which 1.4 µl were injected into the chamber, via PTRToF-MS. After a reaction time of 4 h, the experiment ended, and the chamber was flushed.

It is important to note that 4 h processing time does not equate to the same amount of simulated time in the atmosphere. The equivalent of simulated to atmospheric aging

time can be established through comparison of photochemical age defined by OH exposure (OH clock method; Barmet et al., 2012)

Filter samples were collected on quartz (sampled at 30 L/min) and PTFE filters (40 L/min). Samples were taken before smoke injection (“BLANK”), after smoke injection (“DARK”), and after 4 h reaction time (“REACTION”). After taking the “BLANK” filters, the chamber was re-inflated with clean air to make up for the volume loss. Duplicate samples were taken for “REACTION” filters.

3.2.3 Calculations

The extent of formation of SOA was estimated from the increase in particle mass per m^3 . For the sake of this study it was assumed that all secondary aerosol formed is organic and resulting from oxidation of volatile organic compounds in the injected sample. Formation of SIA cannot be ruled out as filters were not analysed for inorganic ions, but contributions are likely small.

Particle mass enhancement was calculated from SMPS data. Particle volumes were converted to mass concentrations assuming an average aerosol density of 1.5 g/cm^3 (Pitz et al 2003). Wall loss corrections were applied as described below. Particle mass increase (Equation 3.1) was estimated by the difference between the initial amount of particle mass upon smoke injection ($\text{PM}_{\text{initial}}$) and the maximum amount of PM mass observed in the chamber (PM_{max}).

$$\text{PM}_{\text{increase}} = \text{PM}_{\text{max}} - \text{PM}_{\text{initial}} \quad \text{Eq 3.1}$$

Wall losses of particles and SOA precursors are inherent to chamber experiments; inert materials and large chamber volumes help to reduce wall effects but cannot eliminate them. Wall losses were estimated by two different methods:

1. Loss rates were measured during the stabilisation period prior to the oxidation regime. The measured loss rates were then applied to the subsequent measurements during the experiment.
2. Unaccounted losses were estimated from the initial and final concentration of EC collected on filter samples.

In the first method, wall losses were calculated by assessing the average total particle volume losses (SMPS data) in the 15 min period between the smoke injection into the

chamber and the start of UV reactions during day-time experiments (Figure 3.2). Total particle volume decreases prior to initiating oxidation chemistry can be attributed to wall losses and leaks. The negative slope was applied to particle volume concentrations. Day-time average decreases were applied to night-time experiments as under these conditions O_3 was already present in the chamber and aging reactions started immediately. The maximum amount of PM mass (PM_{max}) occurred within the first hour of simulated aging for all experiments. Subsequent losses in the chamber - likely attributable to wall losses and dilution effects - resulted in a net mass loss of particles at the end of the experiment (Figure 3.2).

Loss rates were higher after reaction start (Figure 3.2). This is possibly due to differences in particle sizes, as larger particles form during the oxidation phase, which deposit more quickly.

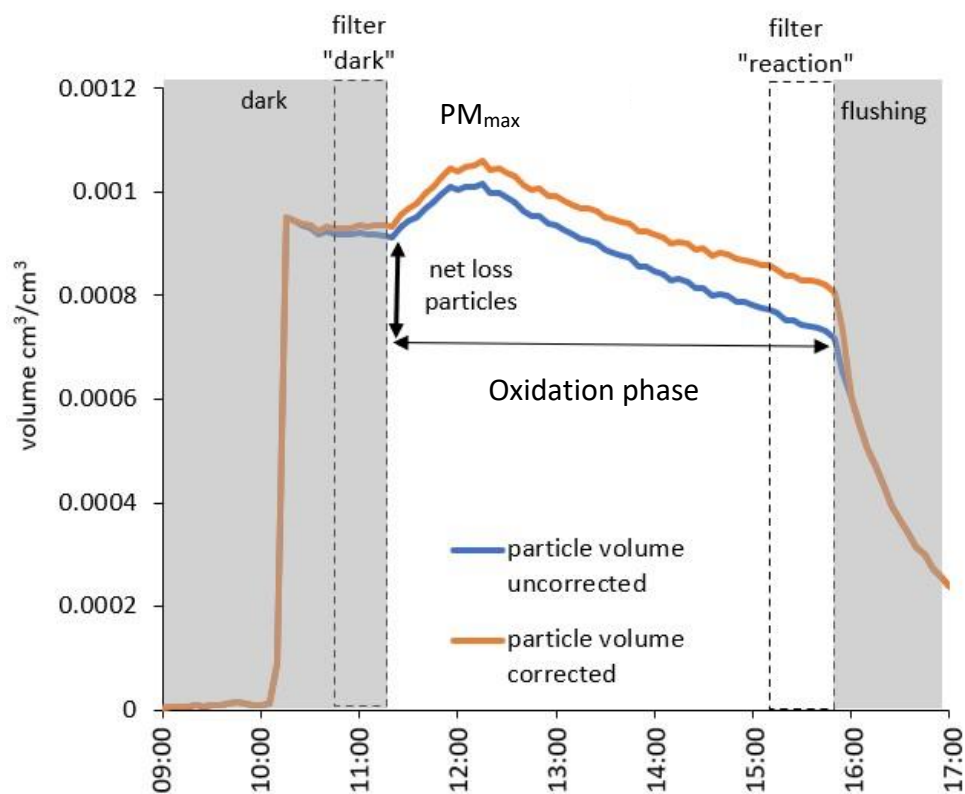


Figure 3.2: Time profile for total particle volume and wall-loss corrected total particle volume; slope for wall loss correction for between smoke injection (1) and reaction start (2).

For the second method, the difference in EC concentrations of filters before (“DARK”) and after 4 h reaction (“REACTION”) was calculated. As EC is a refractory primary pollutant and is not lost to reactions or evaporation, the losses on the filters are attributable to combined wall losses and dilution effects. EC losses ranged from 0 to 30%.

Both methods were found to be in satisfactory agreement when applied to calculated PM masses (SMPS data), resulting in up to 2% difference in resulting PM mass yields.

3.3 Results

3.3.1 SOA Formation

SOA formation in the chamber under different aging regimes were investigated for increases in PM mass concentration based on SMPS measurements. Upon exposure to UV light and/or oxidants during simulated day-time and night-time aging, average particle volume and surface increased, while particle number decreased (Figure 3.3). The values presented below are corrected by the EC method.

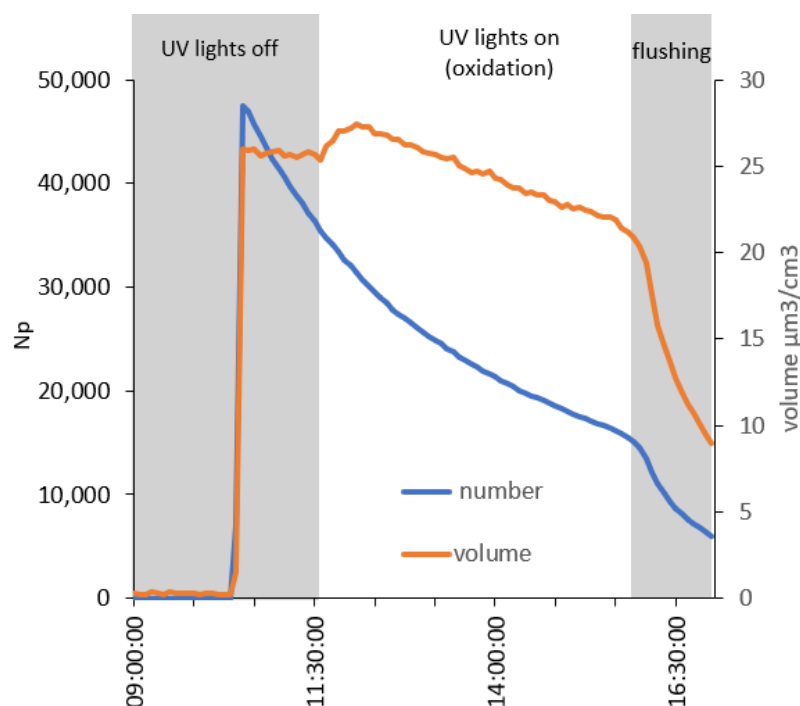


Figure 3.3: Time profiles of the particle number concentration and mass concentration for day-time aging experiment (CH_GO_OH)

Average secondary PM enhancement ratios were 1.08 for day-time UV, 1.07 for daytime UV + OH, and 1.08 for night-time experiments, respectively. Overall PM mass increase was modest (ratio of 1.07 ± 0.05). For example, Heringa et al. (2011) found organic matter increases from wood log burner experiments as high as 4.1 ± 1.4 after five hours of photooxidation; Tiitta et al. (2016) reported average SOA enhancement of 2.0 for dark and UV aging.

Enhancement of PM mass varied between fuels. Average increases of 3% were measured for heather experiments, and 7% increases for grass. The PM in gorse burning emissions, a fuel with high VOC content, was observed to increase by 10% upon atmospheric aging. It must be noted that fuel masses were higher for gorse experiments (Figure 3.4).

Secondary PM yields were high for dark aging experiments. Kodros (2020) report significant increases of secondary aerosols with night-time aging under NO_2 and O_3 (NO_3 precursors) addition.

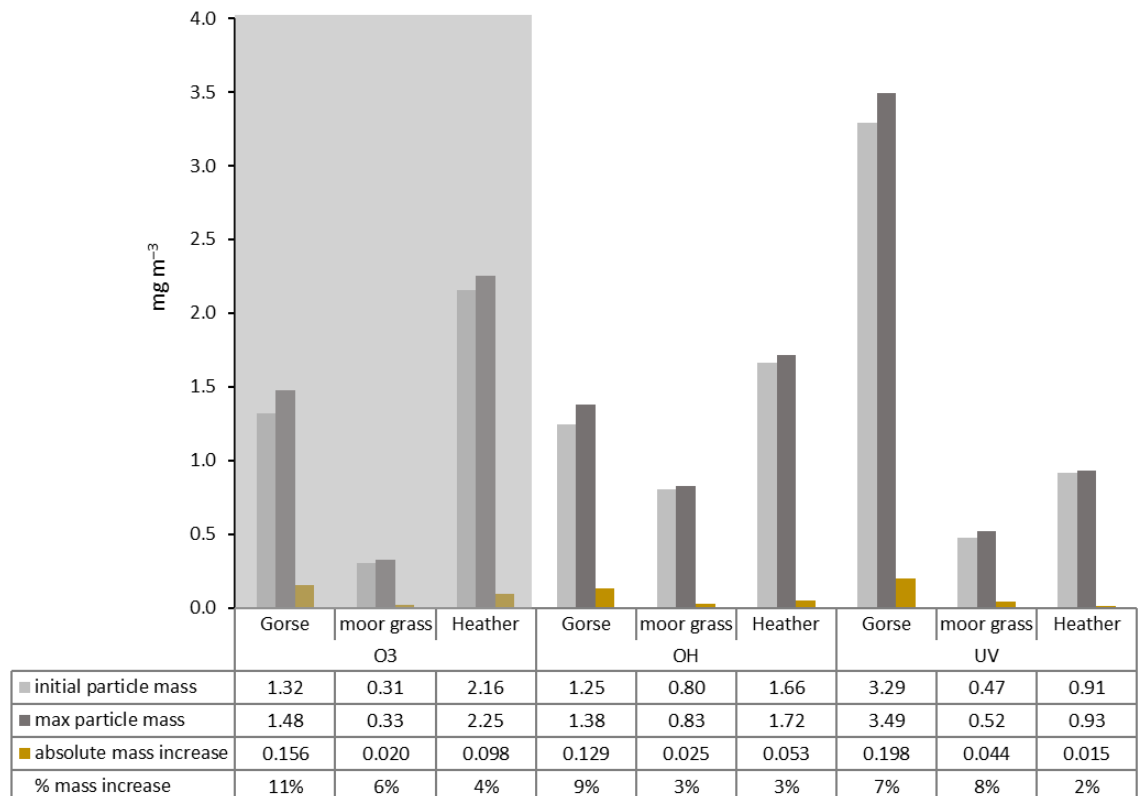


Figure 3.4: Relative and absolute increase in particle mass by fuel type and aging conditions.

3.3.2 Effects of atmospheric aging on particle size distribution

Initial particle size distributions and characteristics for grass, heather and gorse fuels are summarized in Table 3.2. Observations of initial particles were made within the first few minutes upon smoke injection. Differences between fuels in initial particle diameter (D_p) and number (N_p) were observed between fuels. It should be noted that the amounts of fuel burnt differ between experiments and were higher for heather and gorse fuels.

Table 3.2: Size distribution and characteristics of initial particles for grass, heather, and gorse fuels

fuel	experiment	fuel (g)	smoke injection (min)	Size Mode of number	Particle diameter at Mode (nm)	total number (particle/cm ³ /1000)	total surface (μm ² /cm ³)	total volume μm ³ /cm ³	total mass (μg/cm ³ * 100000)
grass	GR_UV	125	2.5	86285	28	50	515	14	2.16
	GR_UV_2	125	2.5	72490	25	43	472	14	2.03
	GR_OH	125	2.5	71365	30	48	873	28	4.25
	GR_O3	125	2.5	82603	23	42	366	10	1.53
	average			78185	27	46	557	17	2.49
	sd			6405	3	4	191	7	1.04
heather	H_UV	150	2.5	117307	39	67	1087	32	4.77
	H_OH	200	2.5	115348	39	70	1290	40	6.07
	H_O3	175	2.5	142629	42	86	1817	59	8.82
	average			125095	40	74	1398	44	6.56
	sd			12424	1	8	308	11	1.69
gorse	GO_UV	300	5	248967	62	144	4382	131	19.65
	GO_OH	150	2.5	106565	58	59	1712	50	7.50
	GO_O3	150	2.5	105890	71	49	1390	36	5.35
	GO_UV_2	200	2.5	141312	66	77	2164	61	9.18
	GO_OH_2	125	2.5	96513	54	47	1022	26	3.90
	average**			139850	62	58	1572	43	6.48
	sd**			56653	6	12	420	13	2.02

*assumed aerosol density = 1.5 g/cm³

**omitting GO_UV experiment

Temporal analysis of particle size distribution patterns in all experiments shows initial high numbers of small particles (70,000 – 25,000), at diameters between 23 to 71 nm (Aitken mode). With progressing reaction time, two distinct particle size distribution patterns could be observed: A) unimodal distribution and B) bimodal distribution.

During most simulated day and night-time experiments, initially emitted small particles coagulated to form large particles over time. This is indicated by a shift in particle diameters from smaller to larger particles, as well as a decrease in particle numbers during the experiment. This presents itself as a unimodal distribution, and is illustrated in Figure 3.5 (2D plot) and Figure 3.6 (time-resolved 3D plot).

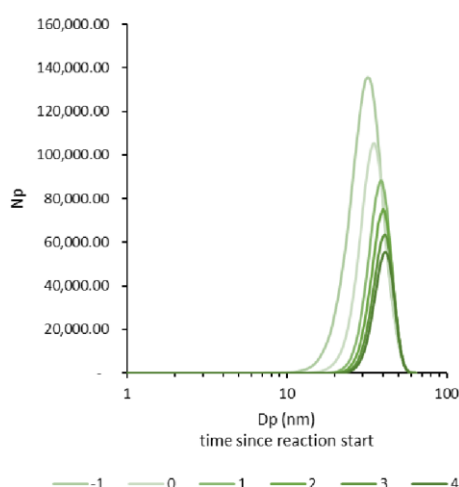


Figure 3.5: Unimodal particle size distribution over 4 h of experiment time in 2D (example: GO_UV2).

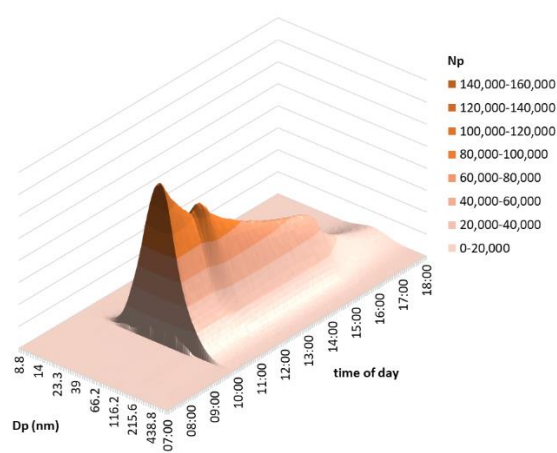


Figure 3.6: Unimodal particle size distribution over 4 h of experiment time in 3D (example: GO_UV2).

Figure 3.7 shows the time profile of chamber reactions under day-time UV aging of grass fuel emissions. As during other experiments, particle coagulation was observed. Additionally, new particle formation (NPF) due to rapid gas-to-particle nucleation reactions were observed. NPF in our experiments was observed after around 60 min, which is in accordance with the 30-60 min reported by Hennigan et al. (2012). The mass of the new size mode is small relative to that of the primary emissions. The NPF peak occurs at about 10 nm vs 20 nm for other fuels, which is a factor of 2 in diameter, but a factor of 8 in volume and mass. NPF was visible as a bimodal distribution (Figure 3.7 and Figure 3.8).

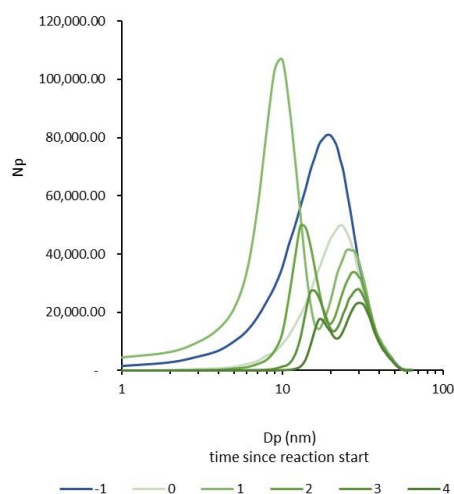


Figure 3.7: Bimodal distribution in particle sizes for grass fuel day-time (UV) aging (GR_UV).

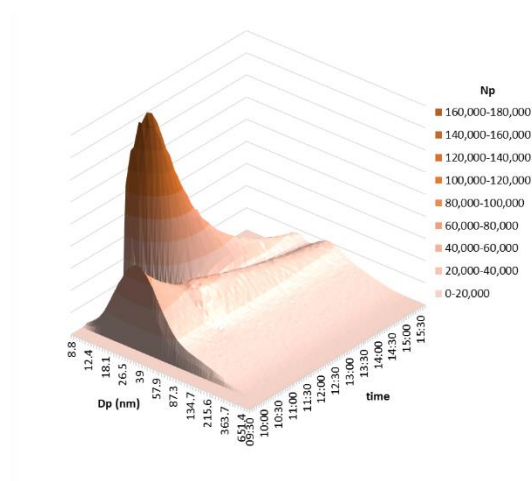


Figure 3.8: Bimodal distribution of particles - Particle number and diameter over 4h experiment aging time for UV day-time aging of grass fuel experiment (GR_UV2).

Similar to observations by Hosseini et al. (2010), NPF was only observed in some experiments, namely day-time aging (UV and UV+OH) of grass fuels. This is likely due to recognizably lower initial D_p and N_p of grass fuels; conditions which favour nucleation over condensation reactions as a sink for low volatility compounds (Curtius, 2009).

3.3.3 EC, OC and BC

While initial OC/EC ratios varied throughout experiments (Figure 3.9), the major fraction of both fresh and aged carbonaceous aerosol was organic, which is in accordance with the literature (e.g. Gupta, 2022).

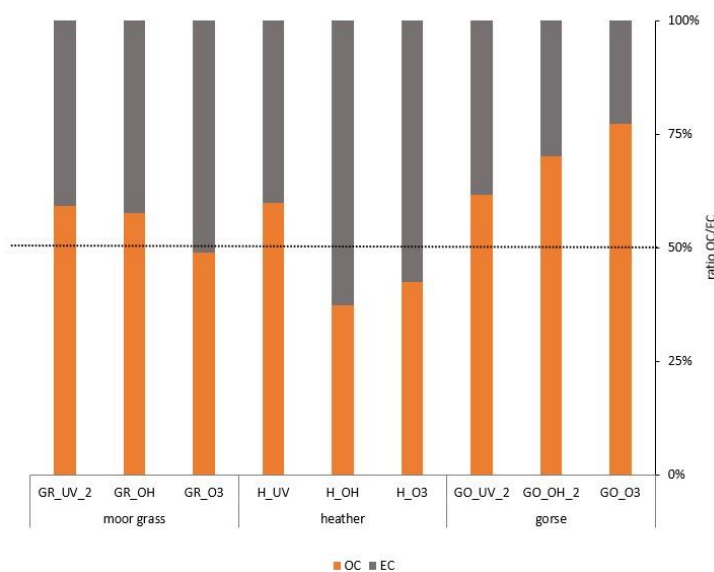


Figure 3.9: Initial OC/EC ratios for chamber experiments by fuel.

Formation of SOA would be expected to be reflected in an increase of OC formed during the reaction relative to EC, which is a non-reactive primary pollutant. A comparison of filter samples before and after 4 h reaction time revealed a decrease in both EC and OC over all experiments. EC losses ranged between 5-30%, which can be attributed to particle loss. OC concentrations of most aged samples were lower than initial OC concentrations even when corrected for EC losses as described in Section 3.2.3. This points towards additional losses, e.g. dilution, which could not be fully accounted for, as described above (Section 3.2.3). Similar decreases in particles were visible in SMPS and BC measurements. As is evident from Figure 3.2, maximum particle concentrations were reached relatively early, thus if filters samples had been taken at that stage in the experiment, an increase in OC concentrations would have been observed.

Black Carbon as measured by the aethalometer at 880 nm (BC6) was relatively stable for most experiments. Ratios of different wavelengths can be indicative of changes in BC and BrC. A comparison of BC at 370 nm (BC1) at 880 nm (BC6) showed relatively steady values, indicating modest SOA formation. A notable exception is one day-time aging gorse fuel experiment (GO_UV), for which the BC1/BC6 ratio increased upon start of photooxidation reaction (Figure 3.10). Twice the amount of fuel was used for this experiment, which could contribute to this observation. The regular spikes in

Figure 3.10 are likely artefacts related to the dual spot or loading correction of the instrument.

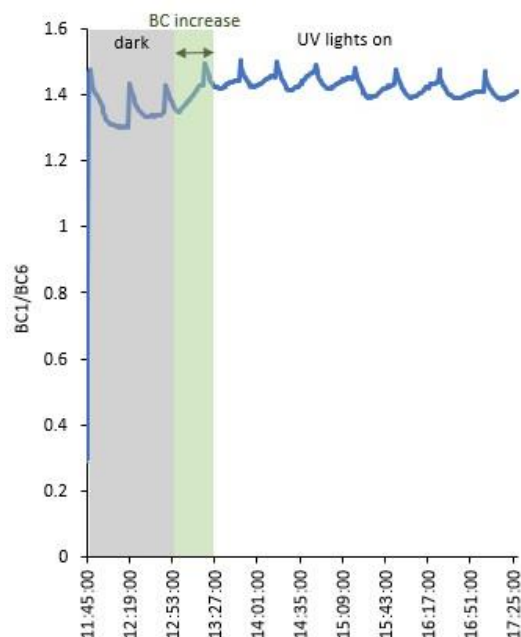


Figure 3.10: BC1/BC6 value for day-time aging gorse fuel experiment (GO_UV).

3.3.4 NO_x chemistry

NO_x plays a role in day-time and night-time SOA formation. Rapid conversion of NO to NO₂ and subsequent formation of O₃ upon reaction start was observed for all day-time experiments (UV and UV +OH; Figure 3.11). Note that the sharp downward lines in the NO₂ profiles in Figure 3.11 are artefacts.

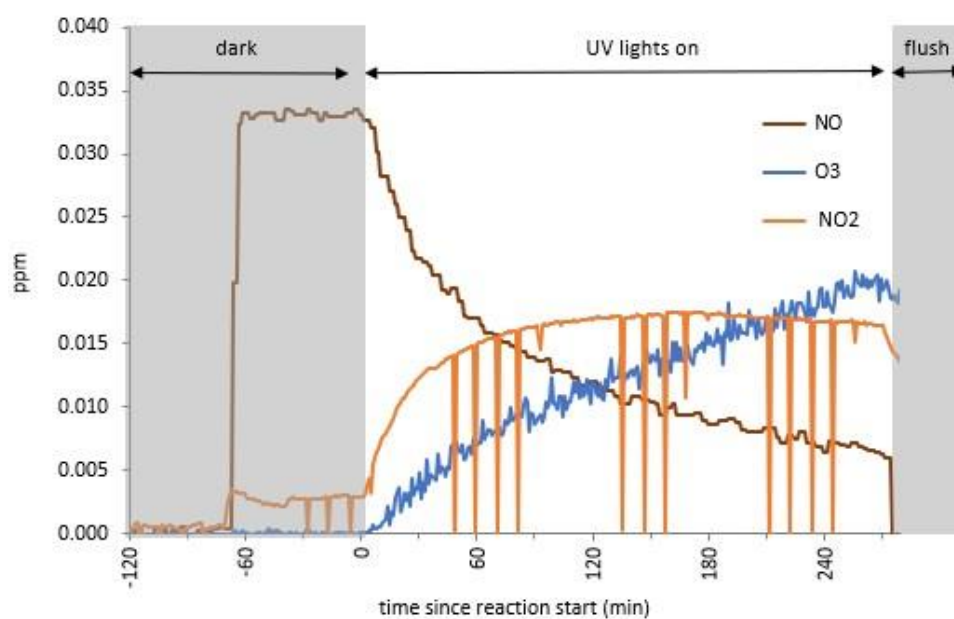


Figure 3.11: Rapid conversion of NO to NO₂ and subsequent O₃ formation (example: H₂UV)

NO₂ formation was more rapid and O₃ production was higher for gorse fuels compared to grass and heather, likely due to higher VOC content of this fuel. Addition of H₂O₂ led to about three times higher O₃ production in grass fuels (Figure 3.13) compared to UV only experiments (Figure 3.12). The higher reaction rates UV+OH experiment thus represent a longer period of atmospheric aging.

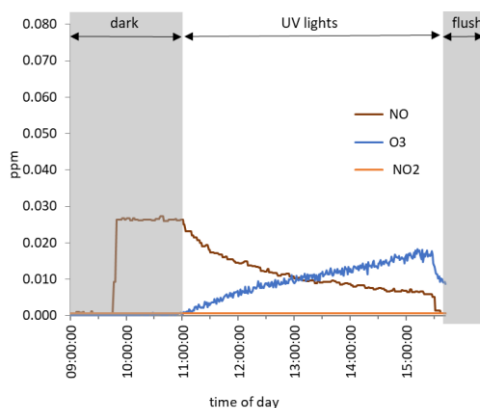


Figure 3.12: O₃ production for grass fuels; UV reaction

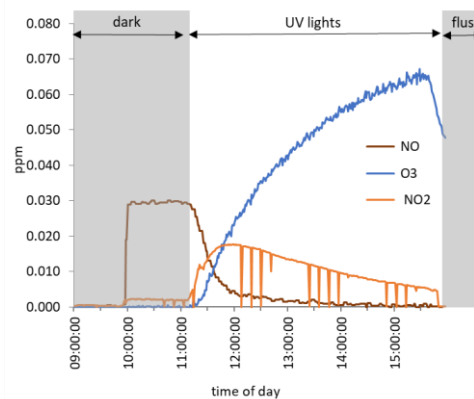


Figure 3.13: O₃ production for grass fuels;
UV+OH reaction

Under night-time aging conditions, high initial O₃ concentrations (180 ppb) led to an increase in NO₂, caused by the reaction between O₃ and NO (Figure 3.14). O₃ concentrations decreased rapidly as a result, forming the NO₃ radical, as described in Section 1.3.

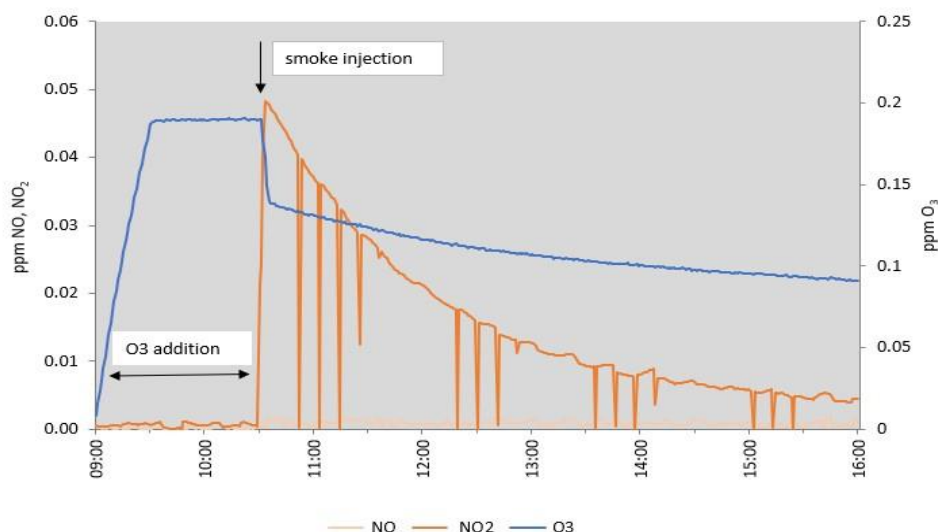


Figure 3.14: Rapid NO₂ formation under night-time reactions (O₃ addition).

3.3.5 SO₂

Reaction products of SO₂ have been shown to contribute to SOA mass (Vivanco et al., 2009; Zhao et al., 2018). Initial emissions of SO₂ were stable for grass and heather fuels, but highly variable for gorse experiments, even where the same amount of fuel mass was burnt (initial SO₂ concentrations differed by a factor of 6 for GO_OH and GO_O3).

A decrease in SO₂ was observed during all experiments. SO₂ particles formation pathways include particle growth via sulfuric acid, condensation and dry deposition, wet deposition, and wall losses. High NO_x and RH conditions have been shown to promote SOA formation through sulphate formation from SO₂ (Liu et al., 2019).

Observed SO₂ decreases were notably faster under day-time (UV and UV+OH) than night-time conditions (Figure 3.15 and Figure 3.16), which points towards rapid reaction with the OH radical and subsequent incorporation into the particle phase. This is in accordance with a study on urban air quality by Khoder (2002), who found higher sulphur and nitrogen conversion ratios for day-time vs night-time.

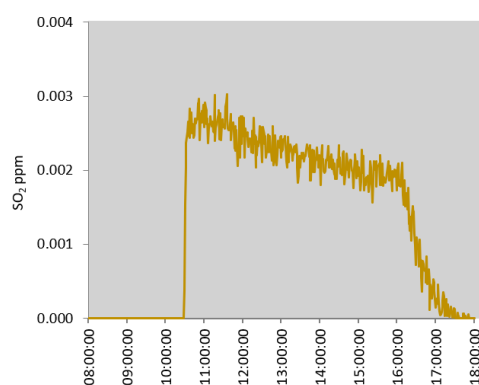


Figure 3.15: Gradual SO₂ decrease under night-time conditions (example: GR_O3).

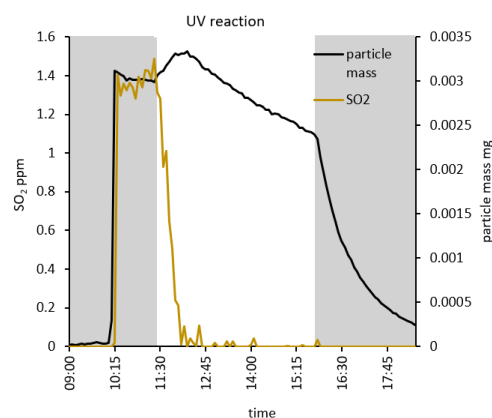


Figure 3.16: Rapid SO₂ decrease under day-time conditions (example: GO_OH).

While SO_x are hygroscopic species and could contribute to the particle phase as secondary inorganic aerosols (SIA), concentrations have not been measured during these experiments. The contribution of SIA is likely to be small due to low initial concentrations of SO₂.

3.3.6 Biomarkers

Figure 3.17 shows concentrations of fresh (“dark”) and aged (“reaction”) monosaccharide anhydrides. Almost all monosaccharide concentrations on aged filter samples were lower than fresh ones.

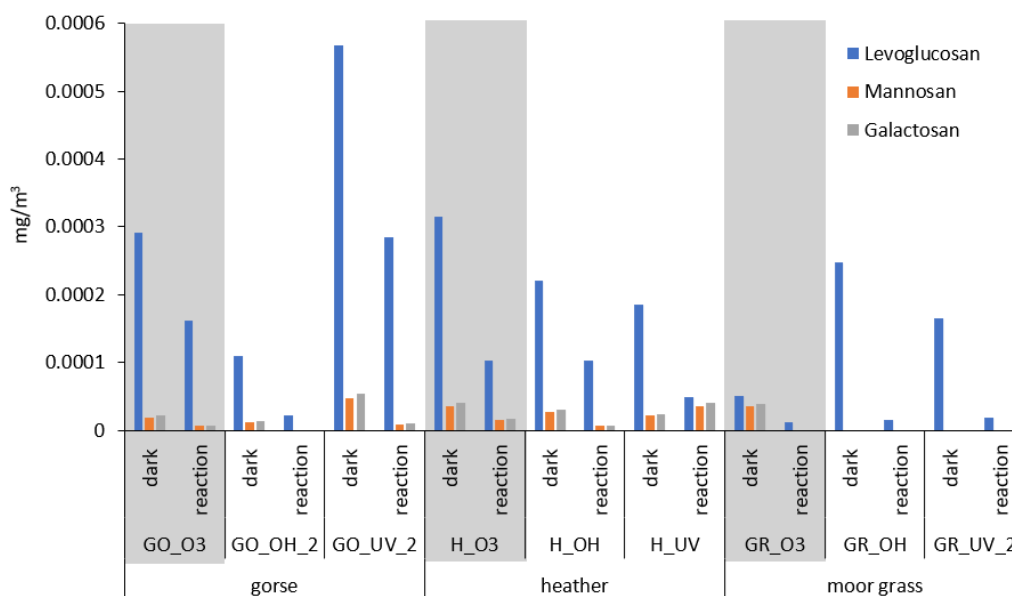


Figure 3.17: Monosaccharide anhydride concentrations for atmospheric aging experiments before (“dark”) and after (“reaction”) 4 h of atmospheric processing.

Concentrations of 4-Nitrocathol, 4-Nitrophenol and 4-Nitroguaiacol for fresh (“DARK”) and aged (“REACTION”) smoke samples are displayed in Figure 3.18. Initial concentrations of biomarkers would be expected to be similar for night-time experiments, but varied, possibly due to different fuel amounts. As for other species measured on filter samples, these concentrations represent only a “snapshot” in time. Some biomarkers were formed during daytime experiments from VOC and nitrogen compounds, a reaction which did not take place during night-time experiments. All concentrations below are corrected to account for EC losses as described in Section 3.2.3.

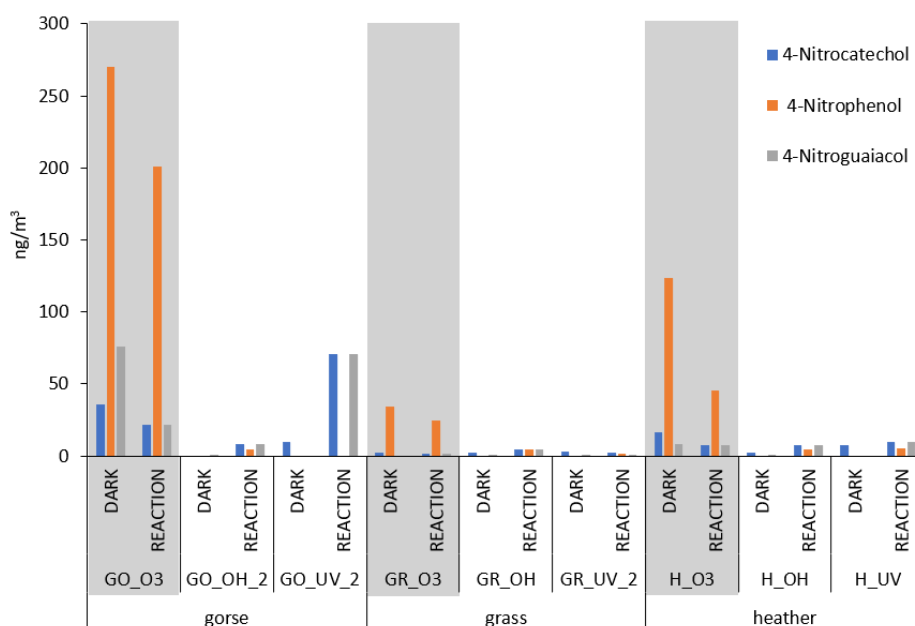


Figure 3.18: Concentrations of 4-Nitrocatechol, 4-Nitrophenol and 4-Nitroguaiacol for atmospheric aging experiments before ("dark") and after ("reaction") 4 h of atmospheric processing.

3.3.7 Uncertainty Analysis

Uncertainty in the chamber is mainly introduced through 1) flow and dilutions 2) wall losses in the chamber and 3) instrument errors. Uncertainties regarding dilution D1 were discussed in Section 2.4 and apply to the chamber as well. Again, an upper limit of 15% is assumed. Wall losses are described in Section 3.2.3 and ranged between 0 and 30% based on EC filter calculations. The instrument uncertainty, if not known, is assumed to be 5%, which leads to an overall maximum uncertainty of 16%. Calculation of compounding uncertainties is given in Section 2.4, Equation 2.3.

3.4 Conclusion

Atmospheric aging experiments for Irish upland fire fuels were conducted at the Atmospheric Chemistry Department Chamber (ACD-C) at TROPOS Leipzig. Smoke aging experiments were conducted under day-time (UV and UV+ OH) and night-time (O_3) conditions to investigate chemical changes. Experiments focussed specifically on particle size distribution, mass enhancement, formation of secondary organic aerosols and chemical aging of biomass burning markers.

Particle emissions, distribution, number, size, volume and particle mass were estimated from SMPS data. Initial high numbers of small particles were observed to grow into larger particles over 4 h of simulated aging in the chamber. An initial

increase in PM mass after 30 - 60 min was observed for all experiments. Nucleation reactions leading to new particle formation were observed under day-time (UV; UV+OH) experiments for grass fuels. Low initial particle concentrations favoured nucleation reactions over condensation reactions, forming new particles which were observed from a size of approx. 10 nm.

Overall Organic Aerosol (OA) mass enhancement was low to moderate. Secondary OA as estimated by total mass increase (SMPS data) ranged from 2 - 11%. Low SOA formation and particle increase are likely due to low emissions of primary organic aerosols (Donahue et al., 2012), high MCE and low VOC content of fuels. Additionally, the amounts of fuel burnt were small (125 - 300 g) and the smoke sample in the chamber was highly diluted.

Due to losses in the chamber, a net decrease in particles and BC was observed for SMPS and AE33 measurements over the 4 h experiment. This is reflected in concentrations measured on filter samples, which were taken several hours after maximum particle concentrations were reached. Concentrations of monosaccharide anhydrides were subsequently lower on almost all aged filter samples.

Biomarkers (4-nitrocatechol, 4-nitrophenol and 4-nitroguaiacol) increased during daytime aging and decreased during night-time aging conditions.

Reactions producing sulfates and nitrates were observed in all chamber experiments. It is likely that these pathways contributed to secondary aerosol formation, although with a small contribution to particle mass due to low initial concentrations.

The results of these experiments illustrate the importance of fuel type on SOA formation. Grass is low in VOCs (Stockwell et al., 2015); it seems logical that a grass-dominated upland fire would result in less SOA formation than in an area with vegetation which is higher in VOCs, such as gorse shrubs, or forests. Similarly, it can be assumed that real-world fire conditions with lower MCEs (Andreae, 2019) would see more SOA formation. Overall SOA formation was low to moderate, ranging from 7-11% PM mass increase in night and day-time aged smoke. Greatest particulate mass enhancement was observed for gorse experiments due to high VOC content and larger fuel mass burnt.

4 Field Measurements

4.1 Introduction

Air quality in Ireland is monitored by a network of 111 local and national stations managed (April 2023) by the Irish Environmental Protection Agency (EPA). Despite an increasing wildland fire – urban interface, most fires occur in upland areas. These events may have significant impacts on the air quality of rural communities, they are unlikely to be captured by the national monitoring network, as most EPA stations are situated in cities and larger towns.

While air quality in Ireland is generally good, it can be severely impacted by residential solid fuel burning especially during the cold season. The EPA-funded SAPPHIRE project found that residential heating accounted for 60-80% of wintertime $PM_{2.5}$ levels in three medium-sized Irish towns (Wenger et al., 2020). Similarly, Heffernan (2022) observed high levels of $PM_{2.5}$ from residential solid fuel burning in Enniscorthy, Co Wexford.

A field measurements were conducted aiming to identify and quantify impacts of wildfire emissions on atmospheric composition. The field measurement strategy involved A) sampling of a prescribed burn in an upland area, B) opportunistic sampling of wildfire events and C) a 2-month field study in a rural background location with a history of wildfires.

However, the option A above could not be carried out because adverse weather conditions prohibited the planned sampling of a prescribed burn in an upland area in Co Kerry during the 2021 legal burning season (September 1st to February 28th).

4.2 Opportunistic Sampling of Fire Events

4.2.1 Methodology

Due to the unpredictable nature of upland fires, a “rapid response” approach was taken to sample fire events in spring 2021. Media were monitored for reports of fire events within reasonable driving distance of Cork City. Two fire events was sampled in this way; these were i) Cobh and ii) Killarney and they are described below.

The instrumentation used for opportunistic sampling was limited as it needed to be handheld and easily deployable. A DustTrak II Aerosol Monitor 8532 with a $PM_{2.5}$

inlet was used to measure particulate matter levels in the smoke plume. Additionally, 10 L Tedlar gas sampling bags were filled in the vicinity of the fire. Due to rapidly changing wind directions and safety considerations, it was not possible to continuously sample within the smoke plume. Tedlar bag samples were analysed for molecular markers of biomass burning; the method is described in Section 4.2.3.

4.2.2 Fire events

Cobh, Co Cork

A small-scale gorse fire close to a residential area in Cobh, Co. Cork, was sampled on May 6th, 2021. While not a typical upland fire due to the location, the vegetation included grass and gorse. In addition to natural vegetation, rubbish such as tyres deposited in the area was also observed to burn (Figure 4.1). Although fire services contained the fire relatively quickly, the smoke plume reached a nearby housing estate, affecting residents' air quality. Grab-sample style DustTrak PM_{2.5} measurements reached extreme levels (up to 6930 $\mu\text{g m}^{-3}$) in the smoke plume 30 -100 m from the fire. It is important to note that these measurements only represent a snapshot of concentrations in the plume and do not represent a maximum or average for the whole fire event.



Figure 4.1 Burning vegetation and rubbish in Cobh, Co. Cork.

Killarney, Co Kerry

A major fire occurred from April 23rd - 25th 2021 at Killarney National Park, an area of great natural beauty and ecological value (Figure 4.2). Measurements of PM_{2.5} were made approximately 200 — 500 m downwind of the fire front in the Gap of Dunloe in the evening of April 25th. Due to the steep terrain and safety considerations, it was not possible to take samples closer to the fire. As a result, maximum downwind concentrations sampled in Killarney (874 $\mu\text{g m}^{-3}$) were lower than in Cobh. Tedlar bag samples for biomarker analysis (Section 4.2.3) were taken in the smoke plume and at a background location. While the smoke plume impacted residents in the immediate vicinity, it did not reach Killarney town during this specific event.



Figure 4.2 Smoke plume over the Gap of Dunloe, Killarney, Co. Kerry

4.2.3 Identification of potential biomarkers

Tedlar bag samples from wildfire events were analysed to identify potential biomass burning markers for Irish upland fires. A total of 9 samples were taken at the Killarney fire, and one sample was taken in Cobh.

Contents of gas sampling bags were analysed using an Aerodyne ToF-CIMS (Time-of-Flight Chemical Ionisation Mass Spectrometer) to determine composition of

organic gases. Analysis of gaseous samples was carried out by Niall O’Sullivan from the UCC CRAC group.

The ToF-CIMS was operated in iodide mode, i.e. iodide was used as the reagent ion with I^- anions generated by passing a flow of nitrogen over a heated permeation tube containing methyl iodide and using a vacuum ultra-violet lamp source to ionise the methyl iodide. Iodide ions enter the ion molecule reactor (IMR) orthogonal to the analyte stream and in this region the I^- ions cluster with the analyte molecules to form MI^- clusters. The instrument has a resolving power of $\sim 5000\text{ m}/\Delta m$. Mass calibration of mass spectra was based on peaks from NO_3^- , $(I)H_2O^-$, $(I)CH_2O_2^-$, $(I)HNO_3^-$, I_2^- and $(I)_4HNO^-$, all of which were consistently above the noise level and had no interferences from other ions. All CIMS data was processed in Tofware 3.2.3 / Igor 7.08.

The instrument was set to sample clean, dry compressed air for 30 s before switching to sampling the Tedlar bags. The analytical focus was on signals that increased when moving from the compressed air to the bag samples.

An example of an averaged mass spectrum collected from a Tedlar bag sample is shown in Figure 4.3. The background signal was calculated from the average signal observed while sampling the compressed air minus the average signal per ion detected while sampling from the bag. Thus, the plot highlights the species which showed the greatest increase in signal from the clean air supply to the bag sample.

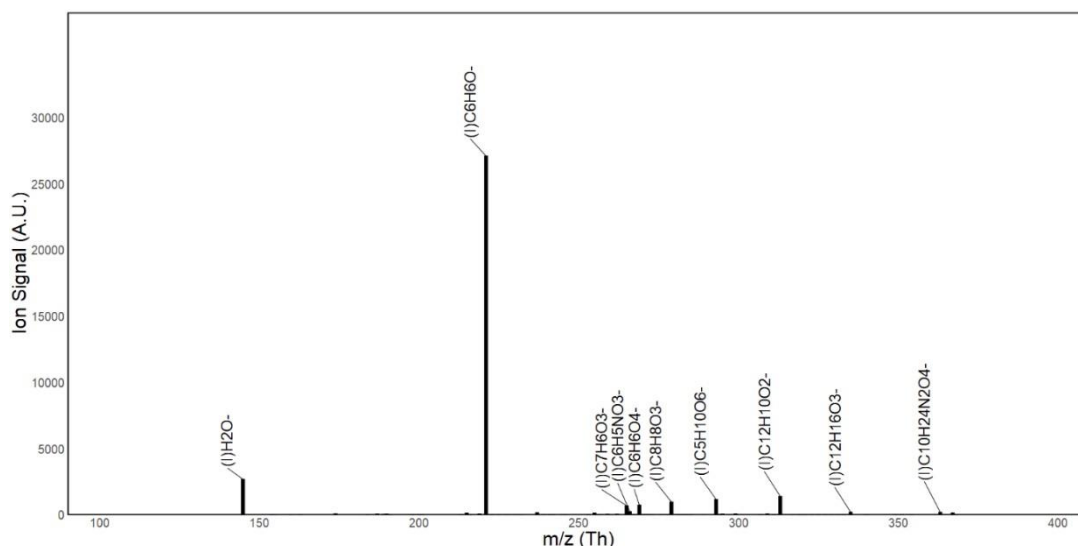


Figure 4.3: ToF-CIMS spectrum of biomarkers from opportunistic sampling of fire events.

(I) $\text{C}_6\text{H}_6\text{O}^-$ was identified as the predominant peak in all samples. This molecular formula corresponds to phenol, which is associated with solid fuel burning as it is produced in pyrolysis of lignin (Soongprasit et al., 2020).

A series of $\text{C}_6\text{H}_6\text{O}_x$ species where x ranges from 2 to 4 were detected in the bag samples, originating from either the burning process or early-stage atmospheric processing. In two of the bag samples, the presence of (I) $\text{C}_6\text{H}_5\text{NO}_3^-$ (nitrophenol), was detected. This nitro species is most likely associated with phenol, but it is again unclear whether this species is a primary product of burning or due to the oxidation of phenol in the presence of NO_x (Wang et al., 2020).

As a result of the analysis of all the tedlar bag samples collected from wildfire plumes, the following species were chosen as potential biomass burning markers for wildfires: levoglucosan $\text{C}_6\text{H}_{10}\text{O}_5$ (based on strong signals for other biomass burning markers); nitrocatechol $\text{C}_6\text{H}_5\text{NO}_4$ (based on signal for $\text{C}_6\text{H}_5\text{NO}_3$); vanillic acid $\text{C}_8\text{H}_8\text{O}_4$ (based on signal for $\text{C}_8\text{H}_8\text{O}_3$), nitroguaiacol $\text{C}_7\text{H}_7\text{NO}_4$ (based on strong signals for other biomass burning markers) and nitrophenol. The most likely isomers of these species are 4-Nitrophenol, 4-Nitrocatechol and 4-Nitroguaiacol. Filter samples from the two-month long field monitoring campaign (Section 4.4), as well as from chamber and emission factor experiments were analysed for these species. More details on analysis method are given in Section 2.2.3.

4.3 Long-term monitoring campaign at a rural location

An 8-week field campaign was conducted in a rural location in Co Wicklow, using UCCs mobile air quality monitoring laboratory. The field campaign was run from March 31st to May 31st, 2021 and aimed to:

- 1) assess how Irish upland fires affect air quality at a rural location
- 2) gather information about the chemical composition and characteristics of smoke plumes from Irish upland fires
- 3) assess how closely the simulated burns match those observed in the environment.

4.3.1 Methodology

Location

Glencree Valley in Co Wicklow was selected as a suitable monitoring location based on fire activity in the preceding five years as identified by the FLARES fire events data base (Cawkwell et al., under review; (Figure 4.3, left). Glencree Valley is part of the Enniskerry municipality and is located in the northern Wicklow Mountains, 25 km south-east of Dublin City (population 1.4 million) and 20 km west of Bray, Co Wicklow (population 30,000) (Figure 4.4, right). Few houses are located in the valley itself; the nearest towns are Glencullen (9 km north-east, population 238), Enniskerry (13 km west, population 1,889) and Manor Kilbride (19 km west, population 272). The R115 Regional ‘Old Military Road’ runs through the area, and receives local and tourist traffic, especially on weekends (Hughes, 2022).

The UCC mobile monitoring unit was deployed at the Glencree Centre for Peace and Reconciliation, which provided road and electricity access.

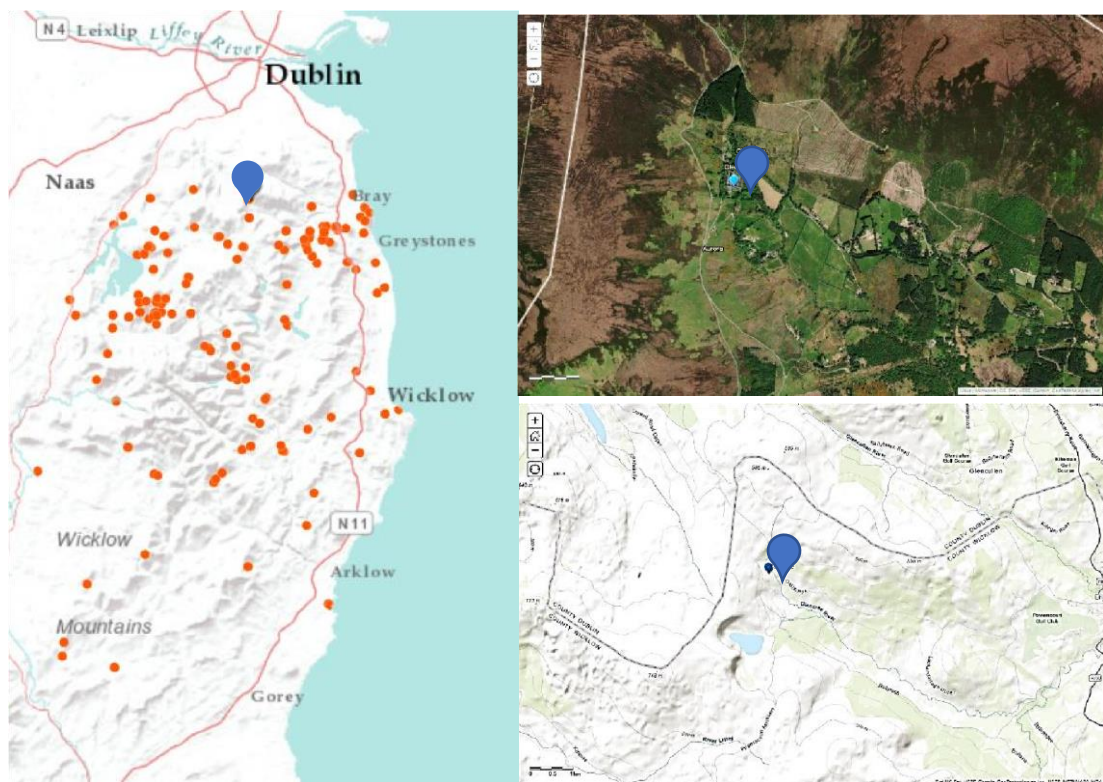


Figure 4.4 LEFT: Location of monitoring site in Glencree Co Wicklow (blue marker and historic fire events 2015-2020 (red) RIGHT: Satellite image (top) and topographic map (bottom) of Glencree Valley.

Instrumentation

The UCC mobile air quality monitoring unit (Figure 4.5) consists of a trailer with field instrumentation to measure levels of particulate matter, carbonaceous aerosol optical properties and chemical tracers specific to biomass burning (Table 4.1).

Table 4.1: Instrumentation used during field monitoring campaign.

Instrument	Manufacturer	Parameter	Sampling Interval
Aethalometer AE33	Magee	BC	1 s
High Volume Aerosol Sampler DHA-80	Digitel	PM _{2.5}	24 h
PurpleAir PA-II-SD	PurpleAir	PM _{2.5}	120 s
Aranet4 air quality sensor	Aranet	CO ₂	15 min
COzIR	GSS	CO ₂	0.5 s
EL-USB-CO Carbon Monoxide Data Logger	Lascar Electronics	CO	5 s
passive sampling tubes	Draeger, Gradko	NO ₂	2 weeks
Portable Weather Station NOMAD	Casella	wind speed and direction	5 min

A Magee AE33 Aethalometer continuously measured black carbon (BC) concentrations by optical attenuation over seven wavelengths (370, 470, 520, 590, 660, 880 and 950 nm). Based on the spectral signal of BC, The BC measured was attributed to either fossil fuel burning or biomass burning sources. The contribution of each fuel source was quantified based on the Sandradewi Aethalometer model (Sandradewi, 2008) using the values for the Angstrom exponents determined by (Zotter et al. 2017), i.e. $\alpha_{\text{fossil}} = 0.9$ and $\alpha_{\text{biomass}} = 1.68$. The percentage contribution of biomass burning towards BC is expressed as BB% and indicates burning of plant-based material, including residential solid fuels (wood, peat, coal) and upland vegetation.

Particulate matter in size fractions from 0.3 μm to 10 μm in diameter, including PM_{2.5} and PM₁₀, were measured in real time using a PurpleAir PA-II-SD system (PurpleAir, California, USA). The PurpleAir units measure PM mass using laser particle counter sensors (Plantower PMS5003, Plantower, China). PurpleAir measurements have been found to be well correlated with reference methods (Ardon-Dryer et al., 2020) (Stavroulas et al., 2020) but tend to overestimate PM_{2.5} levels and need to be calibrated (Johnson et al., 2019). The sensors produce two data streams, “CF_1” and “atm”, based on two different calibrations. In our study, PurpleAir CF_1 data streams were used, which use an algorithm provided by the manufacturer Plantower based on indoor particle density to calculate PM mass (FAQ about PurpleAir, 2022). The raw data from the PurpleAir sensors overestimate the PM_{2.5} levels compared to reference instrumentation by a factor of approximately 1.8. Therefore, a correction factor of 0.57

based on a linear correlation between co-located PA-II and Beta Attenuation Monitor (BAM) measurements in Cork City, Ireland was applied to CF₁ values (Byrne et al., 2023).

Filter samples of ambient air were collected over 24 h (11 am to 10.59 am) by a DHA-80 High Volume Aerosol Sampler (DIGITEL, Switzerland) equipped with a PM_{2.5} inlet. Air was sampled at 500 L min⁻¹ on 150 mm PallFlex Tissuquartz filters (Pall, USA). Filters were analysed at TROPOS Leipzig for OC/EC content and potential wildfire biomarkers (levoglucosan, mannosan, galactosan; vanillic acid, 4-nitrophenol, 4-nitroguaiacol and 4-nitrocatechol as described in Section 4.3.3). Analysis methods of filter samples are described in detail in Section 2.2.3.

Additional low-cost sensors were deployed to measure CO₂ and CO. CO₂ was recorded by two infrared sensors, an Aranet4 indoor air quality sensor in 15 min intervals, and a GSS COzIR CO₂ sensor in 30 s intervals. CO was measured with an EL-USB-CO Carbon Monoxide Data Logger. Passive NO₂ sampling tubes (Draeger and Gradko) were deployed for two weeks each. Data from these sensors was not included in the analysis as it was only available for limited time periods (CO₂ from Aranet4; NO₂) or were below the limit of detection (CO).

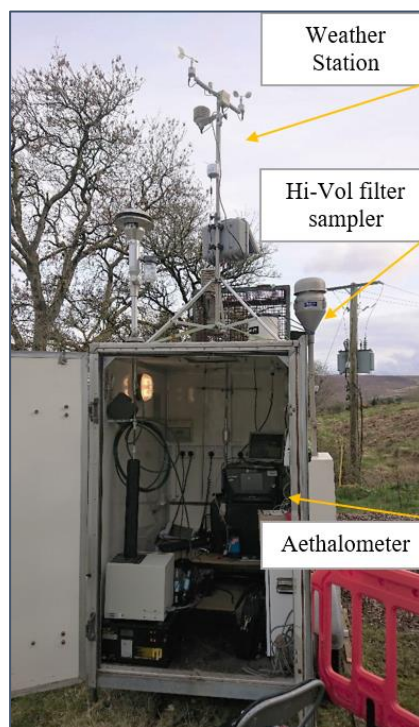


Figure 4.5: UCC mobile monitoring setup in Glencree, Co Wicklow.

Wildfire Impact Assessment

The potential impact of nearby wildfires on the monitoring location was assessed by comparing changes in atmospheric composition ($\text{PM}_{2.5}$, BC, OC/EC, biomarkers) with fire events within a 15 km buffer zone. Based on the topography of the area, more distant fires were considered unlikely to have a significant impact on the monitoring site. Cleaning of the data and a first analysis was conducted by Annie Hughes as part of her final year undergraduate project (Hughes, 2022).

Information on fire activity for the period of the field campaign was obtained from the FLARES fire events database, which was compiled from media and fire services records, information from EFFIS (European Forest Fire Information Systems) and FIRMS (Fire Information for Resource Management Systems) and burn scar data from Landsat-8 and Sentinel-2 GIS data sets. The GIS methods are described in detail in (Cawkwell et al., under review).

To assess possible impacts of wildfires on air quality at the monitoring location, atmospheric composition and meteorological data were analysed on days with fire events. The data was examined:

- 1) to identify divergences from typical diurnal $\text{PM}_{2.5}$ and BC patterns which could point towards a singular pollution source.
- 2) to analyse elevated (>50%) BB% levels during non-typical peak times to establish if pollution was likely caused by fossil fuel or biomass burning.
- 3) to assess whether the average wind direction during the day matched the general direction of a known fire event.
- 4) to confirm whether divergences in $\text{PM}_{2.5}$ levels reported by a nearby EPA air quality monitoring station (Tallaght, residential area, 10 km NNW) and the pollution event was specific to the monitoring area or a feature of the regional air masses or typical daily cycle

The FLARES fire database was examined via a matrix based on the four criteria mentioned above. It is important to note that fulfilling the four criteria above made the interception of wildfires at the monitoring site possible but not certain.

4.3.2 Results

Air quality in Glencree

Typical 24h profiles of PM_{2.5} and BC levels displayed two diurnal peaks on weekdays, one in the morning and one in the evening (Figure 4.6a). The reason for this repeating pattern becomes evident when considering the relative contribution of biomass burning to the black carbon fraction of PM_{2.5} (Figure 4.6b). Employing the BC source apportionment model described by Zotter et al. (2017), morning peaks in Glencree could be attributed to vehicle traffic. Evening peaks on the other hand were shown to predominantly originate from residential solid fuel burning (wood, turf, coal), which is common practice in rural Ireland (CSO, 2021). Average PM_{2.5} concentrations were higher in the evenings, indicating that air quality at the sampling location was more heavily impacted by residential solid fuel burning than traffic emissions.

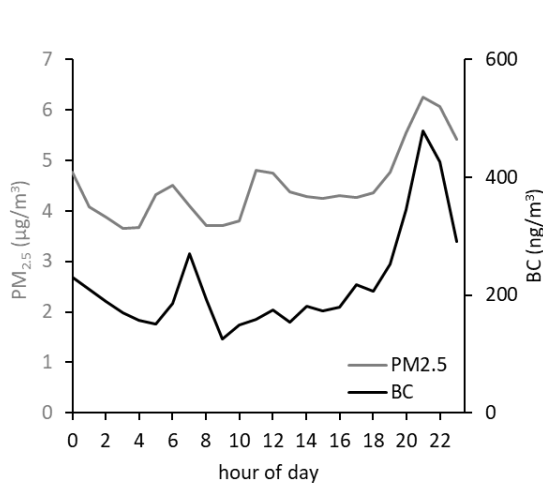


Figure 4.6a: PM_{2.5} and BC concentrations on weekdays in Glencree

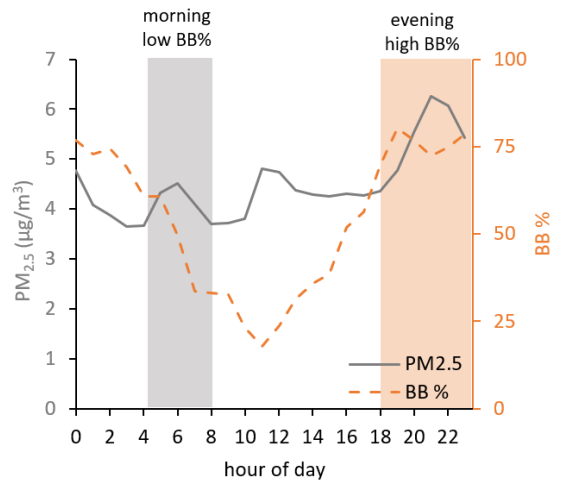


Figure 4.6b: PM_{2.5} and BB% on weekdays in Glencree

The impact of solid fuel use on air quality also reflects in monthly BC and PM_{2.5} trends. Average concentrations of BC decreased from $0.3 \mu\text{g m}^{-3}$ in April to $0.2 \mu\text{g m}^{-3}$ in May; similarly, PM_{2.5} average concentrations declined by 60-70% April and May. This monthly downward trend is likely related to an increase in ambient temperature (averages: April 6.4°C , May 8.7°C) marking the end of the heating season. Additionally, seasonal increase in the height of the planetary boundary layer can further decrease ground level concentrations (Chan and Wood, 2013).

Average concentrations of $\text{PM}_{2.5}$ during the monitoring period (31 March – 31 May 2021) were $4.6 \mu\text{g m}^{-3}$. The short-term (24 h) WHO air quality guideline of $15 \mu\text{g m}^{-3}$ was exceeded once during monitoring period (21/4/2021) (WHO, 2021).

Comparison with Urban Locations

The $\text{PM}_{2.5}$ levels measured at Glencree Valley were compared to measurements from nearby urban EPA air quality monitoring stations at Tallaght, Co. Dublin (Station 44; distance: 10 km, population 64,000) and Newbridge, Co. Kildare (TNO3953; distance: 34 km; population 22,000) (Figure 4.7).

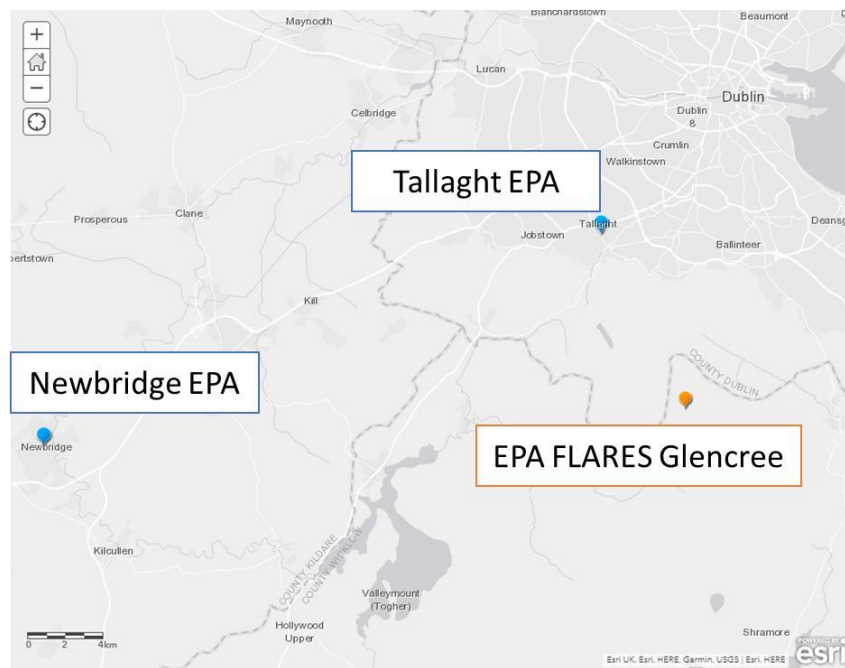


Figure 4.7: FLARES (orange) and EPA (blue) monitoring station locations.

Tallaght, Co Dublin: Average $\text{PM}_{2.5}$ concentrations were higher in Tallaght ($7.0 \mu\text{g m}^{-3}$) than in Glencree ($4.6 \mu\text{g m}^{-3}$) for data available during the monitoring period (8/4/2021 to 14/5/2021). Both locations exhibited similar time profiles of $\text{PM}_{2.5}$, especially over periods of prolonged elevated concentration (Figure 4.8). This implies that despite the marked differences in population size and traffic levels, rural Glencree is impacted by similar anthropogenic sources of pollution as urban Tallaght. The observed similarity in pollution levels over both short (24 h) and extended periods (days and weeks) can in part be attributed to similar patterns of residential fuel and vehicle use patterns, and to being similarly impacted by long-range transport of particulate matter affecting air composition on a larger regional scale.

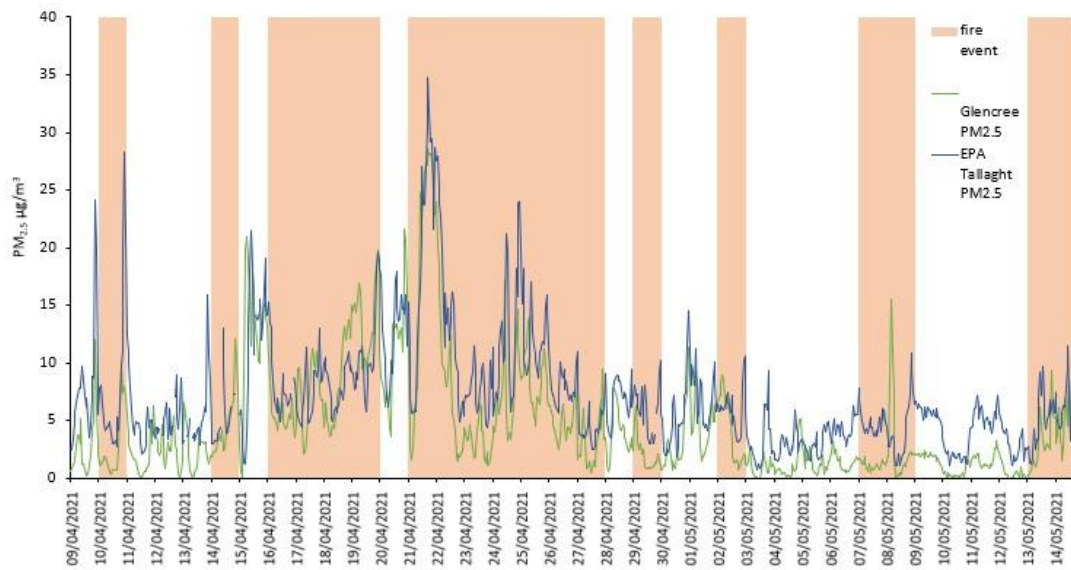


Figure 4.8 PM_{2.5} hourly averages in Tallaght, Co. Dublin (EPA monitoring station) and Glencree, Co. Wicklow. Dates with fire events within the 15km zone around Glencree are marked in red.

Figure 4.9 shows hourly data for times in which wind direction was the same for both locations during the sampling period. PM_{2.5} levels for Glencree and Tallaght correlate most strongly in the NE wind direction ($R^2=0.71$). This is possibly due to pollution originating from Dublin, which is located to the NE of both Tallaght and Glencree. Medium correlation from SW direction, which is the predominant wind direction in Ireland, is likely due to the influence of Irish regional background air. Correlation was lowest for winds from the SE ($R^2=0.05$), which are air masses influenced by air masses coming from continental Europe.

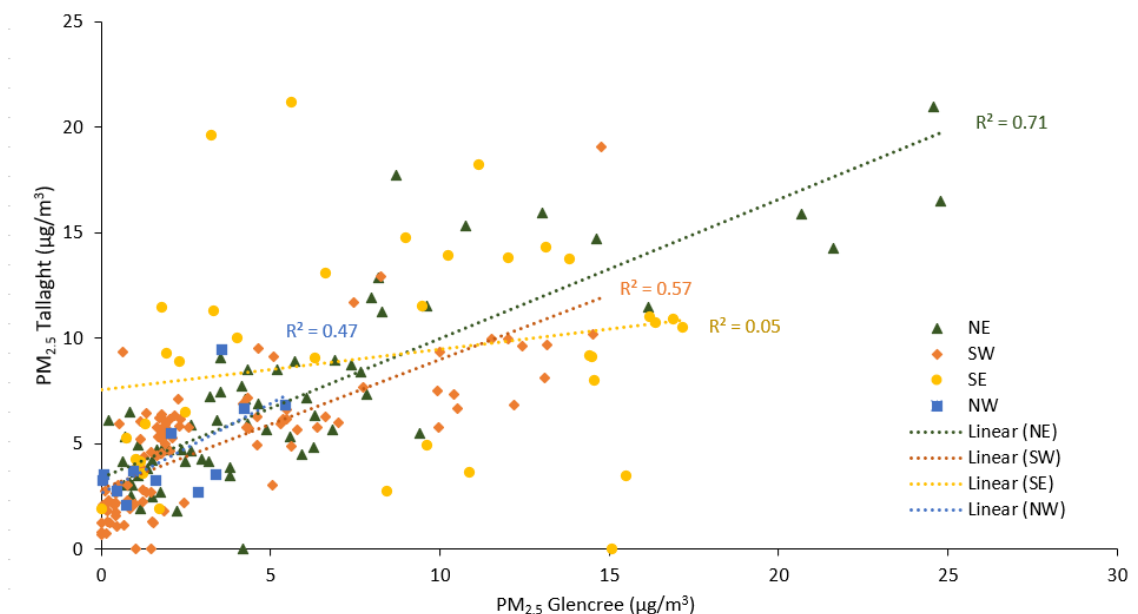


Figure 4.9: Correlation plot of PM_{2.5} Glencree vs Tallaght by wind direction.

Much like Glencree, Tallaght showed distinct morning and evening elevated $PM_{2.5}$, although the timing of the peaks differed slightly (Figure 4.10).

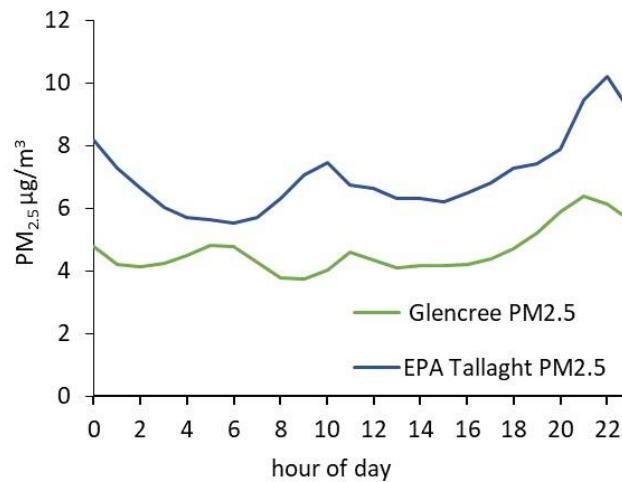


Figure 4.10 $PM_{2.5}$ averaged over monitoring period for Glencree (rural) and Tallaght (urban) EPA station

Newbridge, Co Kildare: Although $PM_{2.5}$ trends do not follow the same pattern as Glencree and Tallaght, average values during the sampling period were similar ($4.6 \pm 8.9 \mu g m^{-3}$ for Glencree and $5.6 \pm \mu g m^{-3}$ for $PM_{2.5}$ in Newbridge). Over prolonged periods, $PM_{2.5}$ values were higher in the rural Glencree location than at the Newbridge site (Figure 4.11).

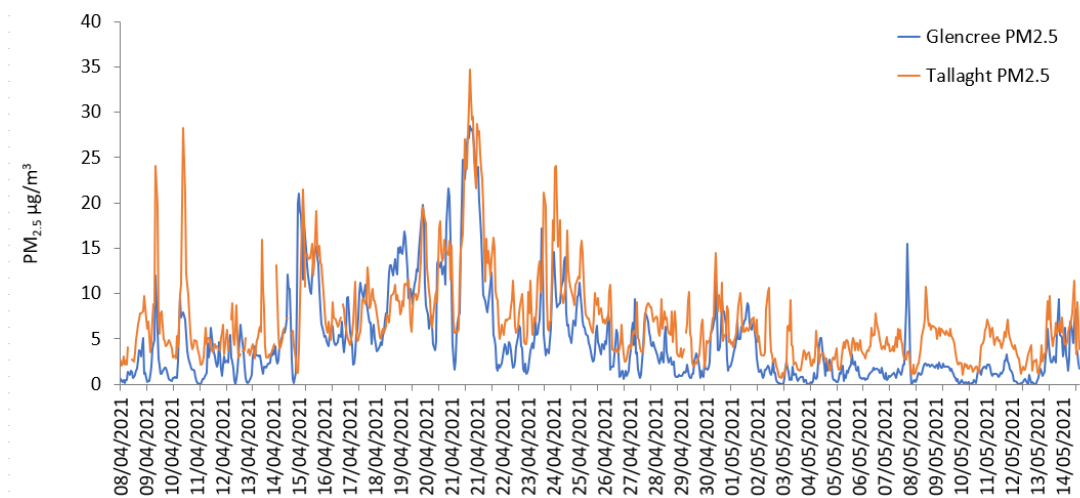


Figure 4.11: $PM_{2.5}$ hourly averages in Newbridge, Co. Kildare (EPA monitoring station) and Glencree.

These findings are consistent with $PM_{2.5}$ trends for rural locations reported in the EPA Air Quality Report 2020. A comparison of EPA monitoring stations in cities, towns and rural Ireland 2010-2020 revealed that mean annual average $PM_{2.5}$ was highest in rural locations for all years except 2010, 2019 and 2020. Similarly, $PM_{2.5}$ levels in big towns are on average higher than in the largest cities Dublin and Cork (EPA, 2021).

Chapter 4

Solid fuel use is common in Ireland (CSO); additionally, at the time of the study legislation banning bituminous coal (“smoky coal ban”) applied only to towns with populations greater than 15,000 (Solid Fuel Regulations 2012-2020, 2022). This regulation was updated in October 2022 to regulate all solid fuels nationwide. Tallaght, as part of Dublin, and Newbridge, due to their population size, were designated “Low Smoke Zones”, where the smoky coal ban was applicable.

Another factor in which may have contributed to PM_{2.5} levels in Glencree is the topography of the valley which could trap emissions.

It is likely that use of bituminous (“smoky”) coal along with other smoky residential fuels such as turf and wood in rural locations is responsible for decreases in air quality in the Glencree area.

Wildfire Impact Assessment

From March 31st to May 31st 2021, fires occurred on 29 days within a 15 km radius (Figure 4.12). Out of these, 19 days were in April, 9 in May and 1 in March. None of these fires occurred closer than 5 km to the monitoring site.

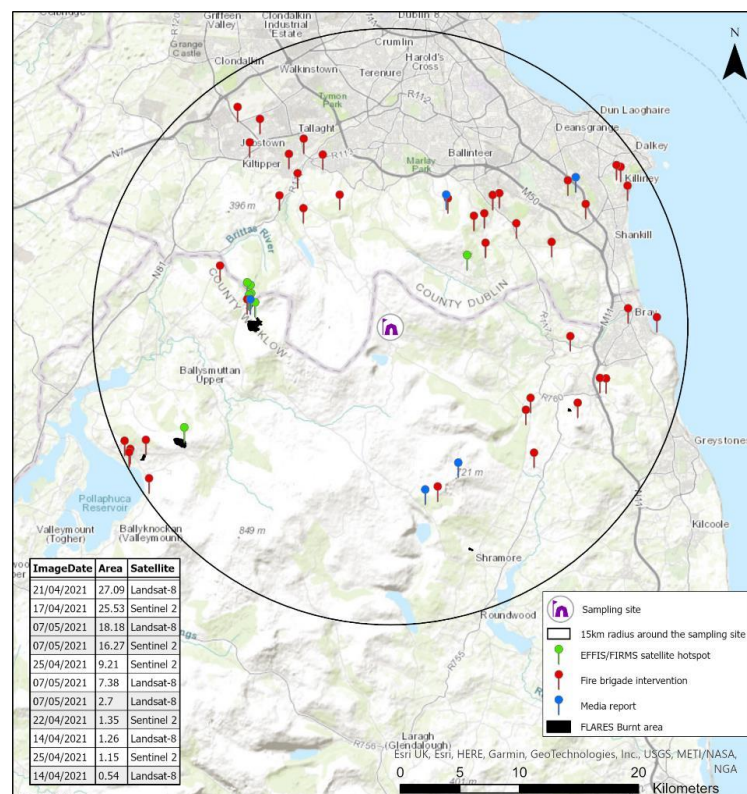


Figure 4.12: Fires around field sampling site in Glencree, Co Wicklow from March 31st to May 31st, 2021. Map courtesy of Emma Chalençon, UCC Geography Department.

Based on the criteria described in Section 4.3.1, fire events potentially impacting on the monitoring site were identified. Only 32 out of 83 fire database entries fulfilled at least 3 criteria, and 20 fulfilled 4 criteria. Entries fulfilling more than 3 criteria were examined more closely.

01/4/2021 The data suggests possible wildfire influence with a large, rapid increase in BC originating from biomass burning observed in the early morning, deviating from the diurnal pattern (Table 4.2, Figure 1). This event coincided with a fire reported at Old Long Hill (53.1598°N, 6.18629°W), and another fire at Ballyremon Commons (53.135°N, 6.18365°W), locations which match the SE wind from the direction of the fire. No PM_{2.5} data is available for this day.

16/4/2021 Elevated PM_{2.5} and BC levels from 9:00 to 16:00 were observed outside the usual diurnal pattern (Table 4.2, Figure 2a and 2b). Wind direction during this period coincided with a day-time fire at Kilbride Army Camp (distance approx. 7.5 km; 53.2043°N, 6.3976°W). The FLARES team was informed of the event but arrived only when the fire had already been extinguished.

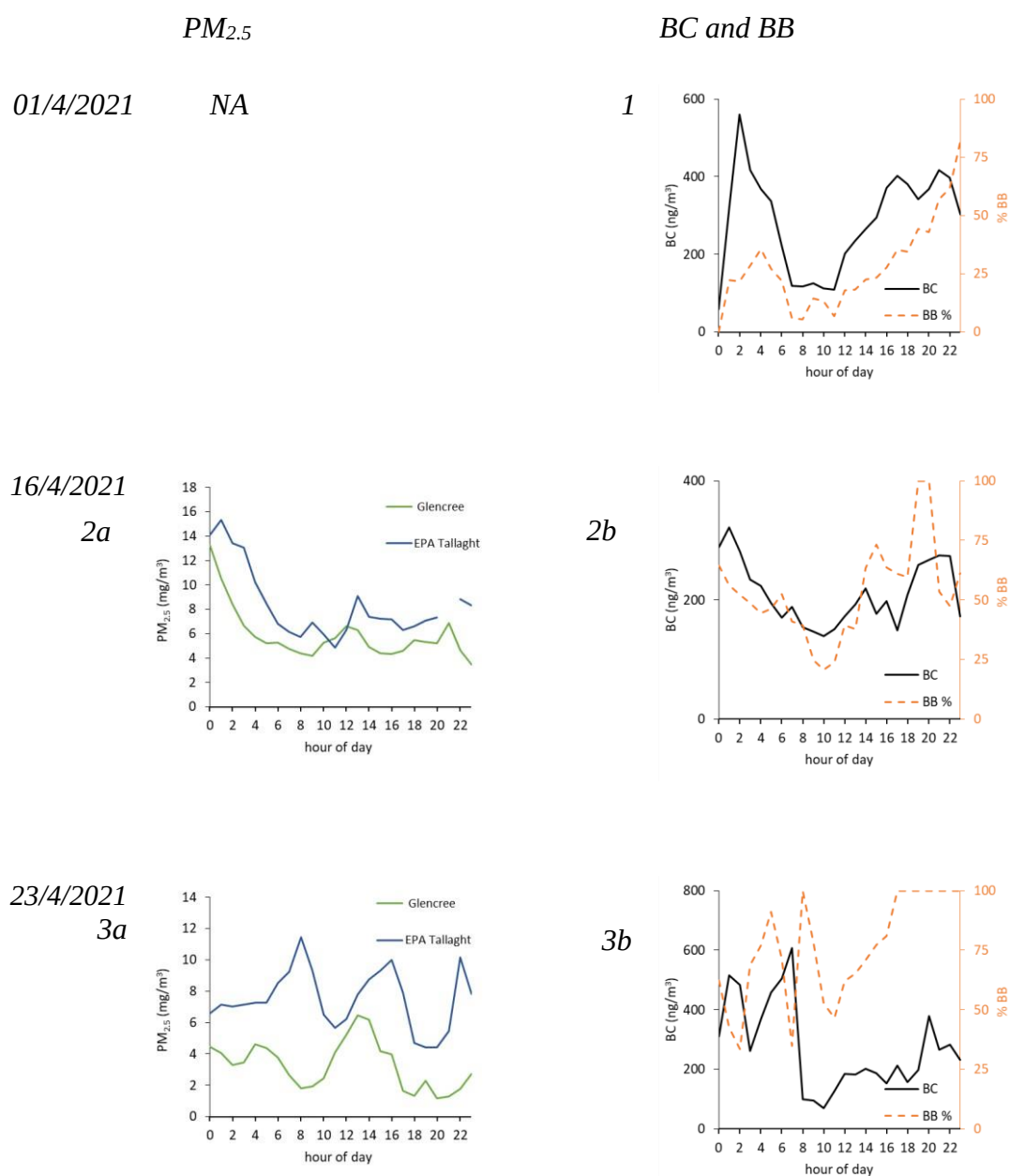
23/4/2021 A rise in PM_{2.5} and BC with high BB% was seen in the early morning hours, and increased PM_{2.5} levels were observed during the middle of the day (Table 4.2, Figure 3a and 3b). Elevated PM_{2.5} peaks were mirrored in Tallaght about 3 h later. BB% was high in the morning and increased during the afternoon. Three fire events were reported for this day but did not coincide with the average wind direction for the day.

24/4/2021 A sharp peak in PM_{2.5} as well as a BC double peak attributable to biomass burning were observed from 6:00 to 14:00 (Table 4.2, Figure 4a and 4b). Four separate fire events were reported for this day. However, no fires occurred in the SE wind direction from the monitoring site.

26/4/2021 Elevated PM_{2.5} and a high BB% BC peak was observed around 11:00-15:00 in Glencree and Tallaght (Table 4.2, Figure 5a and 5b). One of four events – a fire at Hazelgrove (53.2752°N, 6.3981°W) – is in agreement with the NW wind direction during that day.

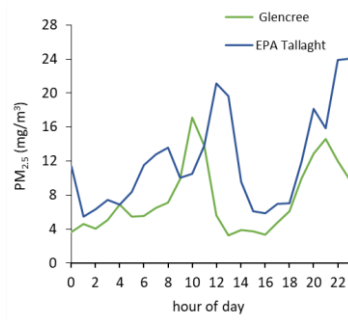
29/4/2021 Elevated $PM_{2.5}$ and a high BB% BC peak around 2 am in Glencree and Tallaght (Table 4.2, Figure 6a and 6b). A fire at Old Long Hill (53.1598°N, 6.18629°W) was reported that day, but the average wind direction at Glencree was NE, and not SE where the fire was located.

Table 4.2 $PM_{2.5}$, BC and BB% on days with potential wildfire influence in Glencree

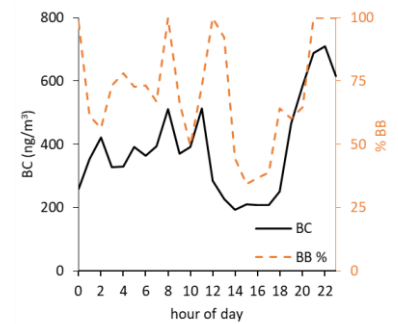


24/4/2021

4a

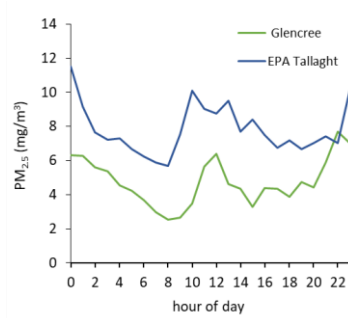


4b

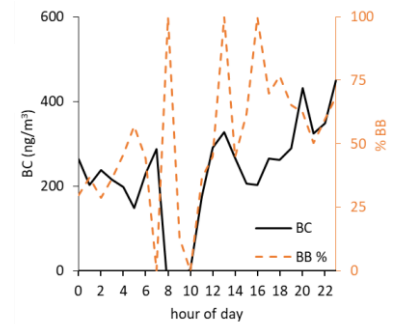


26/4/2021

5a

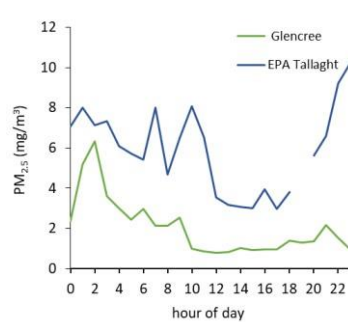


5b

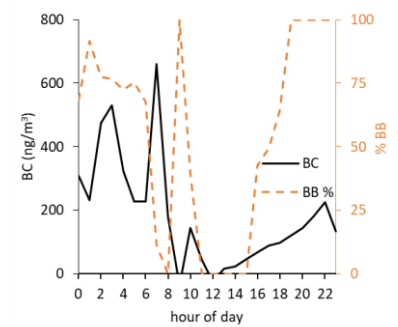


29/4/2021

6a



6b



Overall, it was not possible to unambiguously establish the impact of wildfire emissions on the monitoring site from this analysis. Wildfire influence was likely as described above on 1/4/2021 and 26/4/2021 based on BB% patterns and coinciding wind directions. Some $PM_{2.5}$ levels at the times of potential wildfires exceeded maximum $PM_{2.5}$ from residential heating (23/4/2021, 24/4/2021, 29/4/2021).

Filter Analysis

OC/EC/TC

The OC, EC and TC content of $PM_{2.5}$ during the sampling period are displayed in Figure 4.13. Levels of OC/EC/TC varied strongly on a day-to-day basis, with daily averages higher in April (OC 1047 $ng\ m^{-3}$, EC 170 $ng\ m^{-3}$, TC 1217 $ng\ m^{-3}$) than in May (OC 363 $ng\ m^{-3}$, EC 107 $ng\ m^{-3}$, TC 470 $ng\ m^{-3}$), most likely attributable to a higher level of domestic heating during April.

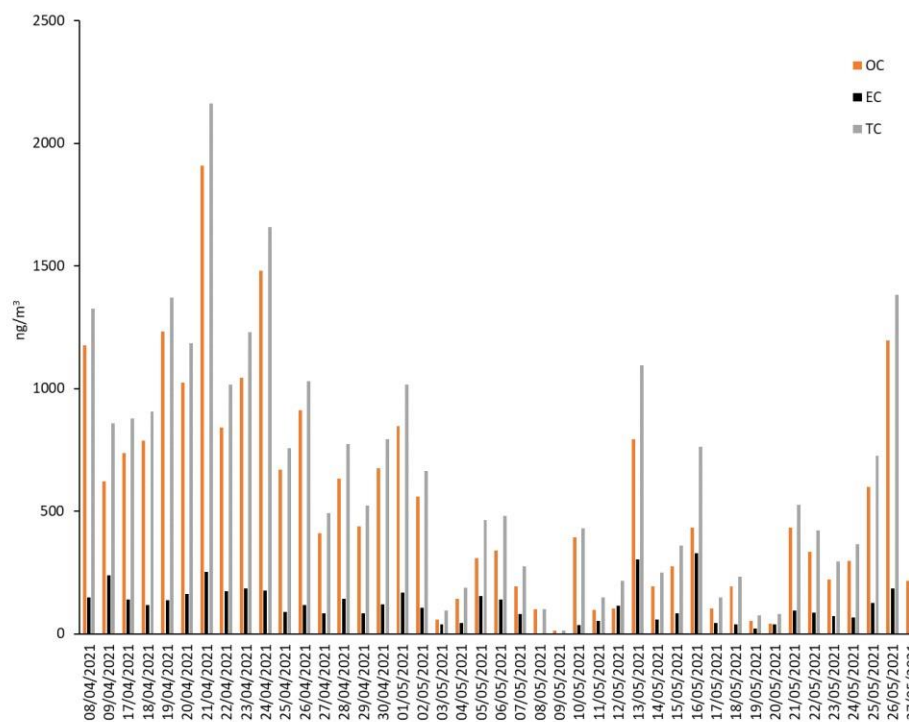


Figure 4.13: OC/EC/TC content of 24 h $PM_{2.5}$ filter samples in Glenree

Similarly, the relative contribution of OC was almost twice as high in April compared to May. The OC/EC ratios for Glenree over the measurement period are displayed in Figure 4.14.

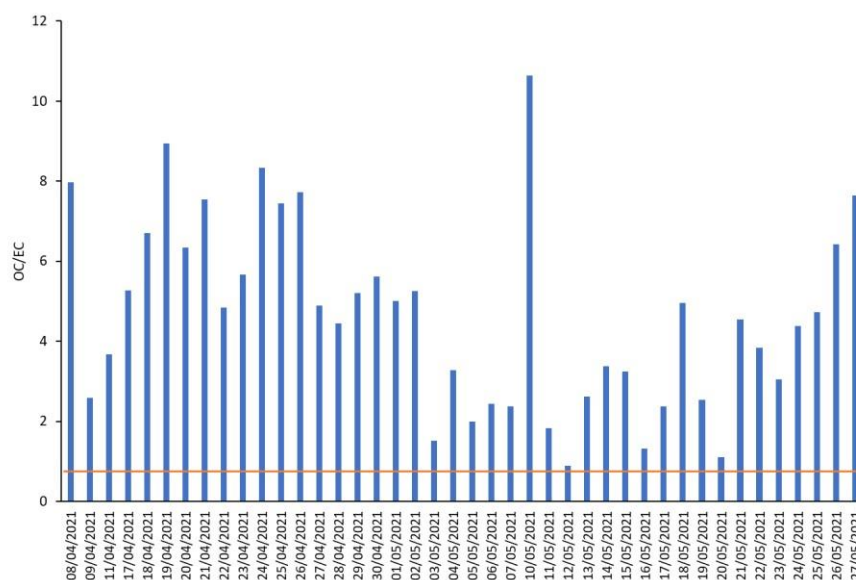


Figure 4.14: OC/EC ratios for Glenree over the measurement period.

Monosaccharide anhydrides

Average values for monosaccharide anhydrides during the sampling period were 1.5 ng m^{-3} ($0.3\text{--}7.1 \text{ ng m}^{-3}$) for levoglucosan, 0.3 ng m^{-3} ($0.04\text{--}1.58 \text{ ng m}^{-3}$) for mannosan and 0.1 ng m^{-3} ($0\text{--}0.49 \text{ ng m}^{-3}$) for galactosan. Like $\text{PM}_{2.5}$, average monosaccharide anhydride levels were higher in April than in May, again pointing towards increased influences of biomass burning on air quality during April.

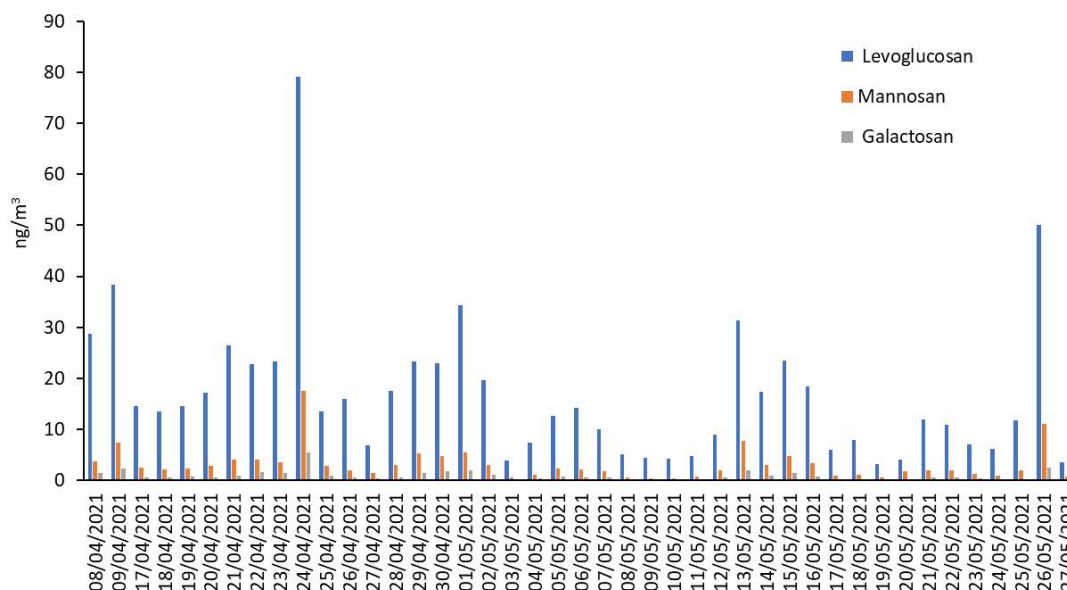


Figure 4.14: 24 h monosaccharide anhydride averages in Glencree during the monitoring period.

Ambient levels of anhydrosugars fluctuate with season and are generally higher during the cold months due to increased heating with lignin-containing fuels (Golly et al., 2019; Heffernan, 2022; Kourtchev et al., 2011). The concentrations found in Glencree during spring were low, and ambient levels were similar to those reported by Yttri et al. (2011) at a Nordic rural background site (Table 4.3). Heffernan (2022) found high concentrations ($68.56\text{--}265.01 \text{ ng m}^{-3}$ and 265.01 ng m^{-3} during day-time and night-time respectively) at a road-side location in urban Dublin. Kourtchev et al. (2011) measured average levoglucosan levels of 9.3 ng m^{-3} during summer measurements and $74\text{--}289 \text{ ng m}^{-3}$ during the colder seasons in Cork Harbour.

Table 4.3: Levels of monosaccharide anhydrides from this study and in the literature

Location	Source	time of year	levoglucosan ng m ⁻³	mannosan ng m ⁻³	galactosan ng m ⁻³
Irish rural backgrounds site	this study	spring (April)	6.8-79.2	1.4-17.6	0.3-5.5
		spring (May)	3.3-50.1	0.4-11.1	0.0-2.5
Nordic rural background site	Yttri et al. (2011)	summer	2.1 - 9.8	0.39 - 1.3	0.06 - 0.35
Irish urban port	Kourtchev et al. (2011)	summer	9.3		
		winter	74 - 289		
Irish urban site (Dublin)	Heffernan (2022)	winter	68.56 (day)		
			265.01 (night)		

Other Biomarkers

Figure 4.15 displays 24 h average concentrations of 4-nitrocatechol, 4-nitrophenol and 4-nitroguaiacol in Glencree. No traces of vanillic acid were found in the samples. In line with monosaccharide anhydride and PM_{2.5} results, average biomarker concentrations were higher in April (0.15 ng m⁻³ 4-nitrocatechol, 0.12 ng m⁻³ 4-nitrophenol, 0.01 ng m⁻³ 4-nitroguaiacol) than in May (0.05 ng m⁻³ 4-nitrocatechol, 0.10 ng m⁻³ 4-nitrophenol, 0.001 ng m⁻³ 4-nitroguaiacol). Average concentrations over the full monitoring period were highest for 4-nitrophenol (0.10 ng m⁻³), followed by 4-nitrocatechol (0.08 ng m⁻³) and 4-nitroguaiacol (0.004 ng m⁻³).

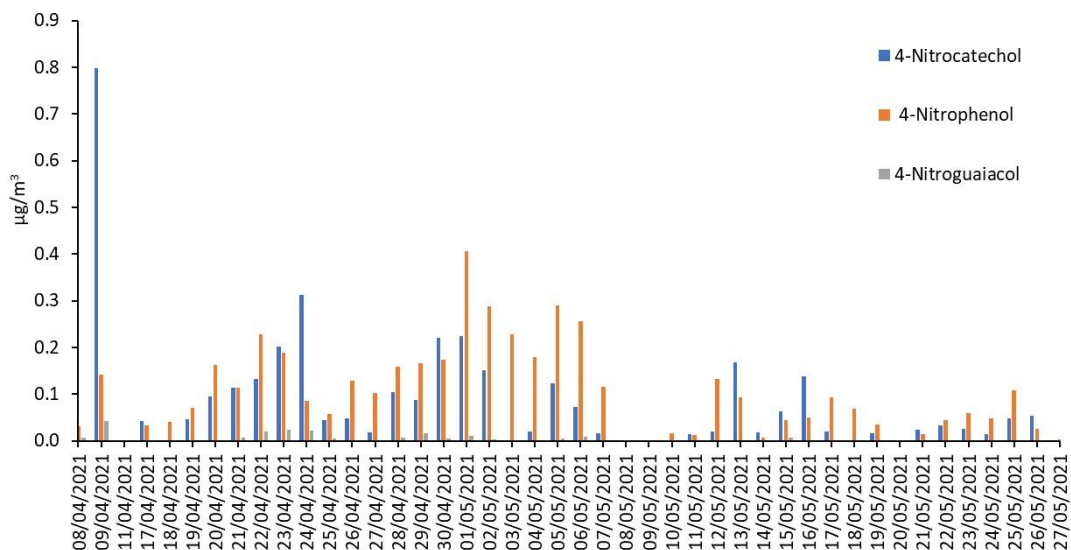


Figure 4.15: 24 h averages for biomarkers (4-nitrocatechol, 4-nitrophenol and 4-nitroguaiacol) in Glencree during the monitoring period

Levels of these biomarkers found in Glencree were low compared to the literature (Cecinato et al., 2005; Kitanovski et al., 2020 – Table 4.4).

Table 4.4: Levels of biomarkers from this study and in the literature

ng m ⁻³	Irish rural backgrounds site, this study		Rome, Italy, Cecinato et al. (2005)	Mainz, Germany, Kitanovski et al. (2020)	Thessaloniki, Greece, Kitanovski et al. (2020)
	<i>spring (April)</i>	<i>spring (May)</i>		<i>winter</i>	<i>winter</i>
4-nitrocatechol	0.00-0.80	0.00-0.22		0.05 – 3.90	5.89 – 36.33
4-nitrophenol	0.03-0.23	0.00-0.41	17.8 ± 5.6	0.24 – 1.27	0.75 – 3.80
4-nitroguaiacol	0.00-0.04	0.00-0.01			

Table 4.5 summarizes the average concentrations of species observed during the Wicklow field campaign.

Table 4.5 Average concentrations Glencree/Wicklow campaign over the period March 31st to May 31st 2021.

species	Apr	stdev	May	stdev	all	stdev	unit
PM*	6.2	4.3	2.1	1.4	4.6	4.0	µg m ⁻³
BC	258	120	162	103	210	122	ng m ⁻³
OC	912	381	316	275	618	493	ng m ⁻³
EC	148	48	93	79	131	85	ng m ⁻³
TC	1060	414	410	334	748	554	ng m ⁻³
Levogluconan	23.68	16.05	12.68	10.91	1.51	1.27	ng m ⁻³
Mannosan	4.34	3.70	2.36	2.40	0.28	0.28	ng m ⁻³
Galactosan	1.33	1.19	0.59	0.65	0.08	0.09	ng m ⁻³
4-Nitrocatechol	0.15	0.19	0.05	0.06	0.08	0.13	ng m ⁻³
4-Nitrophenol	0.12	0.06	0.10	0.11	0.10	0.09	ng m ⁻³
4-Nitroguaiacol	0.01	0.01	0.00	0.00	0.00	0.01	ng m ⁻³

*from 08/04/2021-14/5/2021

4.4 Conclusion

The FLARES field monitoring strategy consisted of a two-month long monitoring campaign in a rural background location in combination with a rapid response approach during which samples were taken at real-world fire events. The 8-week monitoring campaign was conducted in spring 2021 in Glencree, Co Wicklow, and measured ambient levels of PM_{2.5}, BC and biomarkers.

The Wicklow upland area around Glencree has historically experienced frequent wildfires and prescribed burns (Cawkwell et al., under review). No burns happened closer than 5 km from the site during the monitoring period. Data analysis revealed possible impacts of wildfires on atmospheric composition but unambiguous evidence for wildfire influence could not be established, but overall the evidence suggests that wildfires did not impact the air quality at the monitoring location significantly. Occasions where an increase in PM_{2.5} levels was potentially attributable to nearby wildfires suggested that, while the contributions to atmospheric particle levels in the monitoring location was difficult to quantify, it was generally low over the monitoring period. The extent of wildfire influence during the monitoring period would be complemented by further analysis of the biomarker data in the future. An alternative approach to quantifying wildfire impact on populated areas would be to interview residents of towns and villages near upland areas about past experiences of wildfire smoke, and install low-cost sensors, e.g. PurpleAir, in those locations.

This field campaign provides valuable observations of air quality in a rural location in Ireland, a type of site that is largely invisible to the EPA air quality monitoring network. Analysis of PM_{2.5} and biomass burning contribution to BC levels showed two-peak diurnal patterns, which were attributed to traffic (morning peak) and residential solid fuel heating (evening peak). This ties in with observations of made previously in Ireland and highlights the importance of monitoring and managing air quality in rural locations.

Atmospheric levels of PM_{2.5} were measured using low-cost optical scattering devices (PurpleAir). Data quality from low-cost sensors comes with limitations compared to reference-grade methods, such degradation over time, influence of relative humidity

and temperature. Nevertheless, the data can be seen as indicative and useful in pointing out the trends described above. The application of a correction factor developed in Ireland (Byrne et al, 2023) furthermore improves the quality of the data.

A comparison between Glencree (a sparsely populated rural valley setting) and the EPA national monitoring site in Tallaght, Dublin (population 76,000 in 2016), revealed two main findings. Firstly, air quality in Glencree was greatly influenced by anthropogenic air pollution, much of it originating from local emissions. Average $PM_{2.5}$ levels during the monitoring period were only about a third lower in Glencree despite a difference in population of three orders of magnitude. Additionally, diurnal patterns showed impacts of traffic and residential fuel burning on the location. Residential fuel burning emissions are one of the largest contributors to air pollution from PM in Ireland (EPA, 2021). Air quality legislation, such as the smoky coal ban, up until October 2022 has only applied to locations with a population greater than 15,000 residents (“low smoke zones”).

Secondly, pollution levels in Glencree and Tallaght followed similar trends, underlining the impact of local emissions and of transboundary pollution. Two temporal patterns were observed in both locations:

- i) the local and highly regular (on the scale of hours to days) fluctuations attributable to solid fuel burning and local traffic
- ii) the synoptic scale variation in air masses and long-range transported air pollution that elevates the $PM_{2.5}$ levels across a wide area over longer timeframes (days to weeks) and which is evident in both locations.

These results highlight the importance and effectiveness of air quality regulations, and the need to monitor a range of sites, including non-urban locations.

5 Conclusion and Outlook

The work presented in this thesis as part of the FLARES project aimed to deepen the understanding of Irish upland fires and associated emissions of gases and aerosols. To this end, primary and secondary emissions of Irish wildfire fuels were studied in burn chamber experiments at TROPOS Leipzig. Additionally, a two-month field campaign, along with opportunistic sampling of wildfire plumes, was undertaken to establish the effect of wildfires on rural air quality.

Emission factors (EFs) of gas and particle phase products for three typical vegetation types that feature in Irish wildfires (heather, gorse, purple moor grass) were measured. To our knowledge, this is the first time EFs have been determined for these plant species in controlled experiments. Due to the lack of data for fuels from similar habitats, the EF established in this study are a valuable contribution to the body of literature on emission factors.

The uncertainties in measurements have been addressed and discussed. Owing to experimental uncertainties in the measurement of CO₂ emissions during the burn experiments (Section 2.4), we recommend the use of Andreae (2019) standard values for EFCO₂. Other emission factors generated in this study for common Irish plant species generally compare well with the literature for similar vegetation in other habitats.

As experiments were conducted under laboratory conditions, limitations related to the accurate simulation of a wildfire apply. The use of a conventional wood burning stove with dry fuels promoted flaming combustion conditions, resulting in high modified combustion efficiency (MCE) and low emissions of species like carbon monoxide (CO), particulate matter (PM) and volatile organic compounds (VOCs).

Secondary organic aerosol formation (SOA) from the combustion products was studied in atmospheric simulation chamber experiments. Particle mass enhancement was modest and varied between experiments (1.07 ± 0.05), likely due to low emissions of primary organic aerosol (POA) and high MCE.

A two-month continuous field monitoring campaign to measure atmospheric PM_{2.5}, BC and biomarkers was carried out in between March 31st and May 31st 2021 in a

rural location (Glencree Valley, Co Wicklow) with the aim of assessing air quality and wildfire impacts. The results of this field monitoring campaign represent a valuable dataset of air quality measurements from a rural Irish area. While Ireland's air quality network is constantly expanding, most stations are located around urban or town locations. Studies by Heffernan (2022) and Wenger et al. (2020) have highlighted air quality issues in small to medium-sized towns arising from residential heating.

PM_{2.5} levels in rural Glencree were found to follow similar temporal trends as nearby suburban Tallaght, located in the Greater Dublin Area. Although average PM_{2.5} was lower in Glencree, levels were higher than expected for a very low population density location. It is apparent that both locations are subject to similar anthropogenic influences, namely traffic and solid fuel use, and that air quality in a rural location might not be as pristine as one might initially assume. Our results highlight the importance and effectiveness of air quality regulations, as well as the need for greater monitoring of rural locations to better understand air quality issues in the Irish countryside.

Due to the large amounts of data produced during the chamber and field experiments, not all measurements are presented in this report. A more detailed analysis of the composition of wildfire emissions and chamber experiments will be conducted in due course.

Estimates produced by the FLARES project, based in part on the emission factors reported in Chapter 2, found that upland fires in Ireland released between 60,000 and 200,000 tCO₂ eq/year between 2015 and 2021 (Cawkwell et al., under review). Although wildfires account for only 0.1 to 0.2% of annual national Irish GHG emissions, emissions are significantly higher than previously estimated. These observations contribute to a more accurate reporting of GHG emissions required for the National Inventory Report as per Article 13.7a of the Paris Agreement (UNFCCC, 2015). In addition to climate impacts, FLARES highlighted the impact of wildfires to upland habitats. FLARES found that 30-50% of burnt area each year occurs on areas protected for its ecological value (Cawkwell et al., under review). These results highlight the need for further control of wildfires outside the prescribed burning period, and for proper management plans for Ireland's protected areas.

6 Bibliography

- Abdulraheem, K. A., Adeniran, J. A., Aremu, A. S., Yusuf, M. N. O., Adebisi, J. A., Sadiku, N. A., Olofintoye, O. O., Ismail, A., and Sonibare, J. A.: Emission factors of some common grass species in West Africa, *Environ Monit Assess*, 192, <https://doi.org/10.1007/s10661-020-08725-0>, 2020.
- Ahern, A. T., Robinson, E. S., Tkacik, D. S., Saleh, R., Hatch, L. E., Barsanti, K. C., Stockwell, C. E., Yokelson, R. J., Presto, A. A., Robinson, A. L., Sullivan, R. C., and Donahue, N. M.: Production of secondary organic aerosol during aging of biomass burning smoke from fresh fuels and its relationship to VOC precursors, *Journal of Geophysical Research: Atmospheres*, 124, 3583–3606, <https://doi.org/10.1029/2018JD029068>, 2019.
- Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, *Atmos Chem Phys*, 11, 4039–4072, <https://doi.org/10.5194/acp-11-4039-2011>, 2011.
- Alves, C., Vicente, A., Nunes, T., Gonçalves, C., Fernandes, A. P., Mirante, F., Tarelho, L., Sánchez de la Campa, A. M., Querol, X., Caseiro, A., Monteiro, C., Evtyugina, M., and Pio, C.: Summer 2009 wildfires in Portugal: Emission of trace gases and aerosol composition, *Atmos Environ*, 45, 641–649, <https://doi.org/10.1016/j.atmosenv.2010.10.031>, 2011a.
- Alves, C. A., Vicente, A., Monteiro, C., Gonçalves, C., Evtyugina, M., and Pio, C.: Emission of trace gases and organic components in smoke particles from a wildfire in a mixed-evergreen forest in Portugal, *Science of the Total Environment*, 409, 1466–1475, <https://doi.org/10.1016/j.scitotenv.2010.12.025>, 2011b.
- Amnuaylojaroen, T., Macatangay, R. C., and Khodmanee, S.: Modeling the effect of VOCs from biomass burning emissions on ozone pollution in upper Southeast Asia, *Heliyon*, 5, e02661, <https://doi.org/10.1016/J.HELİYON.2019.E02661>, 2019.
- Andela, N., Morton, D. C., Giglio, L., Chen, Y., van der Werf, G. R., Kasibhatla, P. S., Defries, R. S., Collatz, G. J., Hantson, S., Kloster, S., Bachelet, D., Forrest, M., Lasslop, G., Li, F., Mangeon, S., Melton, J. R., Yue, C., and Randerson, J. T.: A human-driven decline in global burned area, *Science* (1979), 356, 1356–1362, <https://doi.org/doi:10.1126/science.aal4108>, 2017.
- Andela, N., & van der Werf, G. R.: Recent trends in African fires driven by cropland expansion and El Nino to La Nina transition. *Nature Climate Change*, 4(9), 791–795. doi:10.1038/nclimate2313, 2014.
- Andreae, M. O.: Emission of trace gases and aerosols from biomass burning - An updated assessment, *Atmos Chem Phys*, 19, 8523–8546, <https://doi.org/10.5194/acp19-8523-2019>, 2019.
- Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, *Global Biogeochem Cycles*, 15, 955–966, <https://doi.org/https://doi.org/10.1029/2000GB001382>, 2001.
- Andreae, M. O., Browell, E. v., Garstang, M., Gregory, G. L., Harriss, R. C., Hill, G. F., Jacob, D. J., Pereira, M. C., Sachse, G. W., Setzer, A. W., Silva Dias, P. L., Talbot, R. W., Torres, A. L., and Wofsy, S. C.: Biomass-burning emissions and associated haze layers over Amazonia, *Journal of Geophysical Research: Atmospheres*, 93, 1509–1527, <https://doi.org/10.1029/JD093ID02P01509>, 1988.

- Andreae, M. O., Andreae, T., Annegarn, H., Beer, J., Cachier, H., le Canut, P., Elbert, W., Maenhaut, W., Salma, I., Wienhold, F., Andreae, M. O., Andreae, T. W., Annegarn, H., Beer, J., Cachier, H., Elbert, W., Maenhaut, W., Wienhold, F. G., and Zenker, T.: Airborne studies of aerosol emissions from savannah fires in southern Africa: 2. Aerosol chemical composition, Africa: 2. Aerosol chemical composition. *Journal of Geo-physical Research: Atmospheres*, 103, 119–151, <https://doi.org/10.1029/98JD02280>, 1998.
- Ardon-Dryer, K., Dryer, Y., Williams, J. N., and Moghimi, N.: Measurements of PM_{2.5} with PurpleAir under atmospheric conditions, *Atmos Meas Tech*, 13, 5441– 5458, <https://doi.org/10.5194/AMT-13-5441-2020>, 2020.
- Arora, V. K. and Melton, J. R.: Reduction in global area burned and wildfire emissions since 1930s enhances carbon uptake by land, *Nat Commun*, 9, <https://doi.org/10.1038/s41467-018-03838-0>, 2018.
- Atkinson, R.: Gas-phase degradation of organic compounds in the troposphere, *Pure and Applied Chemistry*, 70, 1327–1334, <https://doi.org/10.1351/PAC199870071327>, 1998.
- Bailey, R. G.: *Fire Regimes in Different Regional Ecosystems and Their Management Implications*, 2005.
- Balch, J. K., Bradley, B. A., Abatzoglou, J. T., Chelsea Nagy, R., Fusco, E. J., and Mahood, A. L.: Human-started wildfires expand the fire niche across the United States, *Proc Natl Acad Sci U S A*, 114, 2946–2951, <https://doi.org/https://doi.org/10.1073/pnas.1617394114>, 2017.
- Ball, S.: Atmospheric chemistry at night, <https://doi.org/10.1039/c2cs35181a>, 2014.
- Barmet, P., Dommen, J., Decarlo, P. F., Tritscher, T., Praplan, A. P., Platt, S. M., Prévôt, A. S. H., Donahue, N. M., and Baltensperger, U.: Atmospheric Measurement Techniques OH clock determination by proton transfer reaction mass spectrometry at an environmental chamber, *Atmos. Meas. Tech*, 5, 647–656, <https://doi.org/10.5194/amt-5-647-2012>, 2012.
- Bates, J. T., Fang, T., Verma, V., Zeng, L., Weber, R. J., Tolbert, P. E., Abrams, J. Y., Sarnat, S. E., Klein, M., Mulholland, J. A., and Russell, A. G.: Review of Acellular Assays of Ambient Particulate Matter Oxidative Potential: Methods and Relationships with Composition, Sources, and Health Effects, <https://doi.org/10.1021/acs.est.8b03430>, 2019.
- Bertschi, I., Yokelson, R. J., Ward, D. E., Babbitt, R. E., Susott, R. A., Goode, J. G., and Hao, W. M.: Trace gas and particle emissions from fires in large diameter and belowground biomass fuels, *Journal of Geophysical Research: Atmospheres*, 108, <https://doi.org/10.1029/2002jd002100>, 2003.
- Bhattarai, H., Saikawa, E., Wan, X., Zhu, H., Ram, K., Gao, S., Kang, S., Zhang, Q., Zhang, Y., Wu, G., Wang, X., Kawamura, K., Fu, P., and Cong, Z.: Levoglucosan as a tracer of biomass burning: Recent progress and perspectives, <https://doi.org/10.1016/j.atmosres.2019.01.004>, 15 May 2019.
- Bousiotis, D., Brean, J., Pope, F. D., Dall’osto, M., Querol, X., Alastuey, A., Perez, N., Petäjä, T., Massling, A., Nøjgaard, J. K., Nordstrøm, C., Kouvarakis, G., Vratolis, S., Eleftheriadis, K., Niemi, J. v, Portin, H., Wiedensohler, A., Weinhold, K., Merkel, M., Tuch, T., and Harrison, R. M.: The effect of meteorological conditions and atmospheric composition in the occurrence and development of new particle formation (NPF) events in Europe, *Atmos. Chem. Phys*, 21, 3345–3370, <https://doi.org/10.5194/acp-21-3345-2021>, 2021.

Brito, J., Rizzo, L. v., Morgan, W. T., Coe, H., Johnson, B., Haywood, J., Longo, K., Freitas, S., Andreae, M. O., and Artaxo, P.: Ground-based aerosol characterization during the South American Biomass Burning Analysis (SAMBBA) field experiment, *Atmos Chem Phys*, 14, 12069–12083, <https://doi.org/10.5194/acp-14-12069-2014>, 2014.

Brown, T. P., Rushton, L., Muggleston, M. A., and Meehan, D. F.: Health effects of a sulphur dioxide air pollution episode, *J Public Health Med*, 25, 369–371, <https://doi.org/10.1093/PUBMED/FDG083>, 2003.

Byrne, R., Ryan, K., Venables, D. S., Wenger, J. C., and Hellebust, S.: Highly local sources and large spatial variations in PM_{2.5} across a city: evidence from a city-wide sensor network in Cork, Ireland, *Env Sc Atm*, 2023

Campbell, J. L., Fontaine, J. B., and Donato, D. C.: Carbon emissions from decomposition of fire-killed trees following a large wildfire in Oregon, United States, *J Geophys Res Biogeosci*, 121, 718–730, <https://doi.org/10.1002/2015JG003165>, 2016.

CAMS: Wildfires wreaked havoc in 2021, CAMS tracked their impact, <https://atmosphere.copernicus.eu/wildfires-wreaked-havoc-2021-cams-tracked-theirimpact>, 6 December 2021.

CAMS: Europe's summer wildfire emissions highest in 15 years, <https://atmosphere.copernicus.eu/europes-summer-wildfire-emissions-highest-15years>, 6 September 2022.

Capes, G. Johnson, B., McFiggans, G., Williams, P.I., Haywood, J., and Coe, H.: Aging of biomass burning aerosols over West Africa: Aircraft measurements of chemical composition, microphysical properties, and emission ratios, *J. Geophys. Res.*, 113, D00C15, [doi:10.1029/2008JD009845](https://doi.org/10.1029/2008JD009845), 2008.

Carnicer, J., Alegria, A., Giannakopoulos, C., Giuseppe, F. di, Karali, A., Koutsias, N., Lionello, P., Parrington, M., and Vitolo, C.: Global warming is shifting the relationships between fire weather and realized fire-induced CO₂ emissions in Europe, *Sci Rep*, 12, <https://doi.org/10.1038/s41598-022-14480-8>, 2022.

Carroll, M. S., Edgeley, C. M., Nugent, C., Carroll, M. S., Edgeley, C. M., and Nugent, C.: Traditional use of field burning in Ireland: history, culture and contemporary practice in the uplands, *Int J Wildland Fire*, 30, 399–409, <https://doi.org/10.1071/WF20127>, 2021.

Cawkwell, F., Chalencon, E., Felberbauer, C., Hellebust, S., Martin, B., Postma, T., Serbin, G., and Venables, D.: Quantifying burnt areas, habitats burned, and emissions from wildfires in Ireland 2015-2021 (EPA 2019-CCRP-MS.65), Johnstown Castle, Co Wexford, under review.

Cecinato, A., Palo, V. di, Pomata, D., Concetta, M., Scianò, T., and Possanzini, M.: Measurement of phase-distributed nitrophenols in Rome ambient air, *Chemosphere*, 59, 679–683, <https://doi.org/10.1016/j.chemosphere.2004.10.045>, 2005.

Chan, K. M. and Wood, R.: The seasonal cycle of planetary boundary layer depth determined using COSMIC radio occultation data, *J. Geophys. Res. Atmos*, 118, 422–434, <https://doi.org/10.1002/2013JD020147>, 2013.

Chen, L. W. A., Moosmüller, H., Arnott, W. P., Chow, J. C., Watson, J. G., Susott, R. A., Babbitt, R. E., Wold, C. E., Lincoln, E. N., and Wei, M. H.: Emissions from laboratory combustion of wildland fuels: Emission factors and source profiles, *Environ Sci Technol*, 41, 4317–4325, <https://doi.org/10.1021/es062364i>, 2007.

- Chowdhury, S., Pozzer, A., Haines, A., Klingmüller, K., Münzel, T., Paasonen, P., Sharma, A., Venkataraman, C., and Lelieveld, J.: Global health burden of ambient PM_{2.5} and the contribution of anthropogenic black carbon and organic aerosols, *Environ Int*, 159, 107020, <https://doi.org/10.1016/J.ENVINT.2021.107020>, 2022.
- Chu, B., Chen, T., Liu, Y., Ma, Q., Mu, Y., Wang, Y., Ma, J., Zhang, P., Liu, J., Liu, C., Gui, H., Hu, R., Hu, B., Wang, X., Wang, Y., Liu, J., Xie, P., Chen, J., Liu, Q., Jiang, J., Li, J., He, K., Liu, W., Jiang, G., Hao, J., and He, H.: Application of smog chambers in atmospheric process studies, *Natl Sci Rev*, 9, <https://doi.org/10.1093/nsr/nwab103>, 2022.
- Clements, H. B. and McMahon, C. K.: Nitrogen oxides from burning forest fuels examined by thermogravimetry and evolved gas analysis, *Thermochim Acta*, 35, 133–139, [https://doi.org/10.1016/0040-6031\(80\)87187-5](https://doi.org/10.1016/0040-6031(80)87187-5), 1980.
- CSO: Household Environmental Behaviours - Energy Use Quarter 3 2021: <https://www.cso.ie/en/releasesandpublications/er/hebeu/householdenvironmentalbehaviours-energyusequarter32021/>, last access: 18 August 2022.
- Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W. H., Apel, E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T., Rierner, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J., Wisthaler, A., and Jimenez, J. L.: Atmospheric Chemistry and Physics Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies, *Atmos. Chem. Phys*, 11, 12049–12064, <https://doi.org/10.5194/acp-11-12049-2011>, 2011.
- Curtius, J.: Nucleation of atmospheric particles, *Eur. Phys. J. Conferences*, 1, 199–209, <https://doi.org/10.1140/epjconf/e2009-00921-0>, 2009.
- DAFM: Prescribed Burning Code of Practice, n.d.
- Donahue, N. M., Robinson, A. L., Trump, E. R., Riipinen, I., Kroll, J. H., Donahue, N. M., Robinson, A. L., Trump, E. R., Riipinen, I., and Kroll, J. H.: Volatility and Aging of Atmospheric Organic Aerosol Contents, *Top Curr Chem*, https://doi.org/10.1007/128_2012_355, 2012.
- Elias, S.: Changes in Terrestrial Environments, Threats to the Arctic, 323–365, <https://doi.org/10.1016/B978-0-12-821555-5.00015-2>, 2021.
- Encyclopedia Britannica: “prescribed fire,” <https://www.britannica.com/science/prescribed-fire>, 11 February 2020.
- EPA: Air Quality in Ireland 2020, Air quality in Europe 2021, 2021.
- EPA: AirQuality.ie, <https://airquality.ie/>, 2022.
- Fabbri, D., Torri, C., Simoneit, B. R. T., Marynowski, L., Rushdi, A. I., and Fabiańska, M. J.: Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene lignites, *Atmos Environ*, 43, 2286–2295, <https://doi.org/10.1016/j.atmosenv.2009.01.030>, 2009.
- Finlayson-Pitts, B. J. and Pitts, J. N.: Chemistry of the upper and lower atmosphere: theory, experiments, and applications, 2000.
- 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.: Formation and Evolution of Catechol-Derived SOA Mass, Composition, Volatility, and Light Absorption, *ACS Earth Space Chem*, 6, 1067– 1079, <https://doi.org/10.1021/ACSEARTHSPACECHEM.2C00007>, 2022.
- Ganteaume, A., Barbero, R., Jappiot, M., and Maillé, E.: Understanding future changes to fires in southern Europe and their impacts on the wildland-urban interface, *Journal of Safety Science and Resilience*, 2, 20–29, <https://doi.org/10.1016/J.JNLSSR.2021.01.001>, 2021.
- Gatzsche, K., Iinuma, Y., Tilgner, A., Mutzel, A., Berndt, T., and Wolke, R.: Kinetic modeling studies of SOA formation from α -pinene ozonolysis, *Atmos Chem Phys*, 17, 13187–13211, <https://doi.org/10.5194/ACP-17-13187-2017>, 2017.
- Glasius, M. and Goldstein, A. H.: Recent Discoveries and Future Challenges in Atmospheric Organic Chemistry, *Environ Sci Technol*, 50, 2754–2764, <https://doi.org/10.1021/ACS.EST.5B05105>, 2016.
- Goldstein, A. and Gallaby, I.: Known and Unexplored Organic Constituents in the Earth's Atmosphere, *Environ Sci Technol*, 41, 2007.
- Golly, B., Waked, A., Weber, S., Samake, A., Jacob, V., Conil, S., Rangognio, J., Chrétien, E., Vagnot, M. P., Robic, P. Y., Besombes, J. L., and Jaffrezo, J. L.: Organic markers and OC source apportionment for seasonal variations of PM_{2.5} at 5 rural sites in France, *Atmos Environ*, 198, 142–157, <https://doi.org/10.1016/j.atmosenv.2018.10.027>, 2019.
- Wildlife Act, 1976: <https://www.irishstatutebook.ie/eli/1976/act/39/enacted/en/print>, last access: 21 June 2022.
- Solid Fuel Regulations 2012-2020: <https://dcenr.maps.arcgis.com/apps/webappviewer/index.html?id=fcee728a0ee1427d9a3973a090a9f292>, last access: 20 August 2022.
- Grebner, D. L., Bettinger, P., and Siry, J. P.: Common Forestry Practices, 255–285 pp., <https://doi.org/10.1016/b978-0-12-386901-2.00011-7>, 2013.
- 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.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys*, 9, 5155–5236, 2009.
- Propagation of Uncertainty: [https://chem.libretexts.org/Courses/BethuneCookman_University/B-CU%3A_CH345_Quantitative_Analysis/Book%3A_Analytical_Chemistry_2.1_\(Harvey\)/04%3A_Evaluating_Analytical_Data/4.03%3A_Propagation_of_Uncertainty](https://chem.libretexts.org/Courses/BethuneCookman_University/B-CU%3A_CH345_Quantitative_Analysis/Book%3A_Analytical_Chemistry_2.1_(Harvey)/04%3A_Evaluating_Analytical_Data/4.03%3A_Propagation_of_Uncertainty), last access: 4 October 2022.
- Heffernan, E.: Spatial and temporal variation of ambient carbonaceous aerosol in Ireland and strategies for effective monitoring of source contributions, PhD, University College Cork, Cork, 2022.
- Hennigan, C. J., Miracolo, M. A., Engelhart, G. J., May, A. A., Presto, A. A., Lee, T., Sullivan, A. P., McMeeking, G. R., Coe, H., Wold, C. E., Hao, W. M., Gilman, J. B., Kuster, W. C., de Gouw, J., Schichtel, B. A., Collett, J. L., Kreidenweis, S. M., and Robinson, A. L.:

Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber, *Atmos Chem Phys*, 11, 7669–7686, <https://doi.org/10.5194/ACP-11-7669-2011>, 2011.

Hennigan, C. J., Westervelt, D. M., Riipinen, I., Engelhart, G. J., Lee, T., Collett, J. L., Pandis, S. N., Adams, P. J., and Robinson, A. L.: New particle formation and growth in biomass burning plumes: An important source of cloud condensation nuclei, *Geophys Res Lett*, 39, <https://doi.org/10.1029/2012GL050930>, 2012.

Heringa, M. F., DeCarlo, P. F., Chirico, R., Tritscher, T., Dommen, J., Weingartner, E., Richter, R., Wehrle, G., Prévôt, A. S. H., and Baltensperger, U.: Investigations of primary and secondary particulate matter of different wood combustion appliances with a high-resolution time-of-flight aerosol mass spectrometer, *Atmos Chem Phys*, 11, 5945–5957, <https://doi.org/10.5194/ACP-11-5945-2011>, 2011.

Hidy, G. M.: *Atmospheric Chemistry in a Box or a Bag*, *Atmosphere* (Basel), 10, <https://doi.org/10.3390/atmos10070401>, 2019.

Hodshire, A. L., Akherati, A., Alvarado, M. J., Brown-Steiner, B., Jathar, S. H., Jimenez, J. L., Kreidenweis, S. M., Lonsdale, C. R., Onasch, T. B., Ortega, A. M., and Pierce, J. R.: Aging Effects on Biomass Burning Aerosol Mass and Composition: A Critical Review of Field and Laboratory Studies, *Environ Sci Technol*, 53, 10007–10022, <https://doi.org/10.1021/acs.est.9b02588>, 2019.

Hodshire, A. L., Ramnarine, E., Akherati, A., Alvarado, M. L., Farmer, D. K., Jathar, S. H., Kreidenweis, S. M., Lonsdale, C. R., Onasch, T. B., Springston, S. R., Wang, J., Wang, Y., Kleinman, L. I., Sedlacek, A. J., and Pierce, J. R.: Dilution impacts on smoke aging: Evidence in Biomass Burning Observation Project (BBOP) data, *Atmos Chem Phys*, 21, 6839–6855, <https://doi.org/10.5194/ACP-21-6839-2021>, 2021.

Hoffmann, W. A., Schroeder, W., and Jackson, R. B.: Regional feedbacks among fire, climate, and tropical deforestation, *Journal of Geophysical Research: Atmospheres*, 108, <https://doi.org/10.1029/2003JD003494>, 2003.

Holder, A. L., Hagler, G. S. W., Aurell, J., Hays, M. D., and Gullett, B. K.: Particulate matter and black carbon optical properties and emission factors from prescribed fires in the southeastern United States, *Journal of Geophysical Research: Atmosphere*, 121, 3465–3483, <https://doi.org/10.1002/2015JD024321>, 2016. Holder, A. L., Gullett, B. K., Urbanski, S. P., Elleman, R., O'Neill, S., Tabor, D., Mitchell, W., and Baker, K. R.: Emissions from prescribed burning of agricultural fields in the Pacific Northwest, *Atmos Environ*, 166, 22–33, <https://doi.org/10.1016/J.ATMOSENV.2017.06.043>, 2017.

Hosseini, S., Li, Q., Cocker, D., Weise, D., Miller, A., Shrivastava, M., Miller, J. W., Mahalingam, S., Princevac, M., and Jung, H.: Particle size distributions from laboratory-scale biomass fires using fast response instruments, *Atmos Chem Phys*, 10, 8065–8076, <https://doi.org/10.5194/acp-10-8065-2010>, 2010.

Hsieh, Y. P., Bugna, G., and Robertson, K.: Thermochemical Properties of PM_{2.5} as Indicator of Combustion Phase of Fires, *Atmosphere* 2018, Vol. 9, Page 230, 9, 230, <https://doi.org/10.3390/ATMOS9060230>, 2018.

Hughes, A.: Final Year Project Report, Investigating the potential sources and the contributing factors to air quality emissions in Glencree, Co. Wicklow, University College Cork, Cork, 2022.

Hungate, B. A. and Koch, G. W.: GLOBAL CHANGE | Biospheric Impacts and Feedbacks, in: Encyclopedia of Atmospheric Sciences, Elsevier, 876–886, <https://doi.org/https://doi.org/10.1016/B978-0-12-382225-3.00472-2>, 2003.

Hussein, T., Li, X., Bakri, Z., Alastuey, A., Arar, S., Al-Hunaiti, A., Viana, M., and Petäjä, T.: Organic and Elemental Carbon in the Urban Background in an Eastern Mediterranean City, *Atmosphere (Basel)*, 13, <https://doi.org/10.3390/atmos13020197>, 2022.

Iinuma, Y., Brüggemann, E., Gnauk, T., Müller, K., Andreae, M. O., Helas, G., Parmar, R., and Herrmann, H.: Source characterization of biomass burning particles: The combustion of selected European conifers, African hardwood, savannah grass, and German and Indonesian peat, *Journal of Geophysical Research: Atmospheres*, 112, 8209, <https://doi.org/10.1029/2006JD007120>, 2007.

IPCC: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge, United Kingdom and New York, NY, USA, 2013.

IPCC: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, IPCC, Geneva, 151-pp pp., 2014.

IPCC: Climate Change and Land: an IPCC special report on climate change, desertification, land degradation, sustainable land management, food security, and greenhouse gas fluxes in terrestrial ecosystems, 2019.

IPCC: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge, United Kingdom and New York, USA, <https://doi.org/https://dx.doi.org/10.1017/9781009157896>, 2021.

Jaffe, D. A., O'Neill, S. M., Larkin, N. K., Holder, A. L., Peterson, D. L., Halofsky, J. E., and Rappold, A. G.: Wildfire and prescribed burning impacts on air quality in the United States, *J Air Waste Manage Assoc*, 70, 583–615, <https://doi.org/10.1080/10962247.2020.1749731>, 2020.

Johnson, K., Gantt, B., and Clements, A.: PurpleAir PM_{2.5} performance across the U.S., https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=539776&Lab=CEMM, 9 December 2019.

Johnston, F., Henderson, S., Chen, Y., Tanderson, J., Marlier, M., DeFries, R., Kinney, P., Bowman, D., and Brauer, M.: Estimated Global Mortality Attributable to Smoke from Landscape Fires, *Environ Health Perspect*, 120, <https://doi.org/10.1289/ehp.1104422>, 2010.

Kalashnikov, D. A., Schnell, J. L., Abatzoglou, J. T., Swain, D. L., and Singh, D.: Increasing co-occurrence of fine particulate matter and ground-level ozone extremes in the western United States, *Sci Adv*, 8, 9386, <https://doi.org/10.1126/2022.04.033>, 2022.

Kalogridis, A. C., Popovicheva, O. B., Engling, G., Diapouli, E., Kawamura, K., Tachibana, E., Ono, K., Kozlov, V. S., and Eleftheriadis, K.: Smoke aerosol chemistry and aging of Siberian biomass burning emissions in a large aerosol chamber, *Atmos Environ*, 185, 15–28, <https://doi.org/10.1016/j.atmosenv.2018.04.033>, 2018.

- Kaskaoutis, D.G., Grivas, G., Stavroulas, I., Bougiatioti, A., Liakakou, E., Dumka, U.C., Gerasopoulos, E. and Mihalopoulos, N.: Apportionment of black and brown carbon spectral absorption sources in the urban environment of Athens, Greece, during winter. *Science of The Total Environment*, 801, p.149739, 2021.
- Kelly, J., Ibáñez, T. S., Santín, C., Doerr, S. H., Nilsson, M.-C., Holst, T., Lindroth, A., and Kljun, N.: Boreal forest soil carbon fluxes one year after a wildfire: Effects of burn severity and management, *Glob Chang Biol*, 27, 4181–4195, <https://doi.org/10.1111/gcb.15721>, 2021.
- Khoder, M. I.: Atmospheric conversion of sulfur dioxide to particulate sulfate and nitrogen dioxide to particulate nitrate and gaseous nitric acid in an urban area, *Chemosphere*, 49, 675–684, [https://doi.org/10.1016/S0045-6535\(02\)00391-0](https://doi.org/10.1016/S0045-6535(02)00391-0), 2002.
- Kitanovski, Z., Shahpoury, P., Samara, C., Voliotis, A., and Lammel, G.: Composition and mass size distribution of nitrated and oxygenated aromatic compounds in ambient particulate matter from southern and central Europe implications for the origin, *Atmos Chem Phys*, 20, 2471–2487, <https://doi.org/10.5194/acp-20-2471-2020>, 2020.
- Knapp, E. E., Estes, B. L., & Skinner, C. N.: Ecological effects of prescribed fire season: a literature review and synthesis for managers, 2009.
- Knorr, W., Dentener, F., Hantson, S., Jiang, L., Klimont, Z., and Arneth, A.: Air quality impacts of European wildfire emissions in a changing climate, *Atmos Chem Phys*, 16, 5685–5703, <https://doi.org/10.5194/ACP-16-5685-2016>, 2016.
- Kodros, J.: Rapid dark aging of biomass burning as an overlooked source of oxidized organic aerosol, *Proceedings of the National Academy of Sciences*, 117, 33028– 33033, <https://doi.org/https://doi.org/10.1073/pnas.2010365117>, 2020.
- Konovalov, I. B., Berezin, E. v., and Beekmann, M.: Effect of photochemical selfaction of carbon-containing aerosol: Wildfires, *Izvestiya - Atmospheric and Ocean Physics*, 52, 263–270, <https://doi.org/10.1134/S0001433816030063>, 2016.
- Koppmann, R., von Czapiewski, K., and Reid, J. S.: 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, 10455–10516, <https://doi.org/10.5194/acpd-5-10455-2005>, 2005.
- Korontzi, S., Ward, D. E., Susott, R. A., Yokelson, R. J., Justice, C. O., Hobbs, P. v., Smithwick, E. A. H., and Hao, W. M.: Seasonal variation and ecosystem dependence of emission factors for selected trace gases and PM_{2.5} for southern African savannah fires, *Journal of Geophysical Research: Atmospheres*, 108, <https://doi.org/10.1029/2003jd003730>, 2003.
- 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.: 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*, <https://doi.org/10.1016/j.scitotenv.2011.02.027>, 2011.
- Kourtchev, I., O'Connor, I. P., Giorio, C., Fuller, S. J., Kristensen, K., Maenhaut, W., Wenger, J. C., Sodeau, J. R., Glasius, M., and Kalberer, M.: Effects of anthropogenic emissions on the molecular composition of urban organic aerosols: An ultrahigh resolution mass spectrometry study, *Atmos Environ*, 89, 525–532, <https://doi.org/10.1016/J.ATMOSENV.2014.02.051>, 2014.

- Kourtchev, I., Giorio, C., Manninen, A., Wilson, E., Mahon, B., Aalto, J., Kajos, M., Venables, D., Ruuskanen, T., Levula, J., Loponen, M., Connors, S., Harris, N., Zhao, D., Kiendler-Scharr, A., Mentel, T., Rudich, Y., Hallquist, M., Doussin, J.-F., Maenhaut, W., Bäck, J., Petäjä, T., Wenger, J., Kulmala, M., and Kalberer, M.: Enhanced Volatile Organic Compounds emissions and organic aerosol mass increase the oligomer content of atmospheric aerosols, *Nature Scientific Reports*, <https://doi.org/10.1038/srep35038>, 2016.
- Kroflić, A., Anders, J., Drventić, I. D., Mettke, P., Böge, O., Mutzel, A., Kleffmann, J., and Herrmann, H.: Guaiacol Nitration in a Simulated Atmospheric Aerosol with an Emphasis on Atmospheric Nitrophenol Formation Mechanisms, *ACS Earth Space Chem*, 5, 1083–1093, <https://doi.org/10.1021/acsearthspacechem.1c00014>, 2021.
- Kroll, J. H. and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, *Atmos Environ*, 42, 3593–3624, <https://doi.org/10.1016/j.atmosenv.2008.01.003>, 2008.
- Kuang, Y. and Shang, J.: Changes in light absorption by brown carbon in soot particles due to heterogeneous ozone aging in a smog chamber, *Environmental Pollution*, 266, <https://doi.org/10.1016/j.envpol.2020.115273>, 2020.
- Kuo, L. J., Herbert, B. E., and Louchouart, P.: Can levoglucosan be used to characterize and quantify char/charcoal black carbon in environmental media?, *Org Geochem*, 39, 1466–1478, <https://doi.org/10.1016/J.ORGGEOCHEM.2008.04.026>, 2008.
- Lawson, S. J., Keywood, M. D., Galbally, I. E., Gras, J. L., Caine, J. M., Cope, M. E., Krummel, P. B., Fraser, P. J., Steele, L. P., Bentley, S. T., Meyer, C. P., Ristovski, Z., and Goldstein, A. H.: Biomass burning emissions of trace gases and particles in marine air at Cape Grim, Tasmania, *Atmos Chem Phys*, 15, 13393–13411, <https://doi.org/10.5194/acp-15-13393-2015>, 2015.
- Leavell, D., Berger, C., Fitzgerald, S., and Parker, B.: Oregon State University - Fire Science Core Curriculum, 2017.
- Leino, K., Riuttanen, L., Nieminen, T., Maso, M. D., Väänänen, R., Pohja, T., Keronen, P., Järvi, L., Aalto, P. P., Virkkula, A., Kerminen, V.-M., Petäjä, T., and Kulmala, M.: Biomass-burning smoke episodes in Finland from eastern European wildfires, *Boreal Environment Research*, 19, 275–292, <https://doi.org/10.2/JQUERY.MIN.JS>, 2014.
- Li, J., Li, J., Wang, G., Zhang, T., Dai, W., Ho, K. F., Wang, Q., Shao, Y., Wu, C., and Li, L.: Molecular characteristics of organic compositions in fresh and aged biomass burning aerosols, *Science of The Total Environment*, 741, 140247, <https://doi.org/10.1016/J.SCITOTENV.2020.140247>, 2020.
- Liang, L., Engling, G., Cheng, Y., Liu, X., Du, Z., Ma, Q., Zhang, X., Sun, J., Xu, W., Liu, C., Zhang, G., and Xu, H.: Biomass burning impacts on ambient aerosol at a background site in East China: Insights from a yearlong study, *Atmos Res*, 231, <https://doi.org/10.1016/J.ATMOSRES.2019.104660>, 2020.
- Lim, C., Hagan, D. H., Coggon, M. M., Koss, A. R., Sekimoto, K., de Gouw, J., Warneke, C., Cappa, C. D., and Kroll, J. H.: Secondary organic aerosol formation from the laboratory oxidation of biomass burning emissions, *Atmos Chem Phys*, 19, 12797–12809, <https://doi.org/10.5194/acp-19-12797-2019>, 2019.

Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, *Atmos Chem Phys*, 10, 10521–10539, <https://doi.org/10.5194/ACP-10-10521-2010>, 2010.

Liu, S., Jiang, X., Tsona, N. T., Lv, C., and Du, L.: Effects of NO_x, SO₂ and RH on the SOA formation from cyclohexene photooxidation, *Chemosphere*, 216, 794–804, <https://doi.org/10.1016/J.CHEMOSPHERE.2018.10.180>, 2019.

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.: Airborne measurements of western U.S. wildfire emissions: Comparison with prescribed burning and air quality implications, *J Geophys Res*, 122, 6108–6129, <https://doi.org/10.1002/2016JD026315>, 2017.

Liu, Y., Stanturf, J., and Goodrick, S.: Trends in global wildfire potential in a changing climate, *For Ecol Manage*, 259, 685–697, <https://doi.org/10.1016/j.foreco.2009.09.002>, 2010.

Magzamen, S., Gan, R. W., Liu, J., O'Dell, K., Ford, B., Berg, K., Bol, K., Wilson, A., Fischer, E. v., and Pierce, J. R.: Differential Cardiopulmonary Health Impacts of Local and Long-Range Transport of Wildfire Smoke, *Geohealth*, 5, e2020GH000330, <https://doi.org/10.1029/2020GH000330>, 2021.

Mahowald, N., Lindsay, K., Rothenberg, D., Doney, S. C., Moore, J. K., Thornton, P., Randerson, J. T., and Jones, C. D.: Desert dust and anthropogenic aerosol interactions in the Community Climate System Model coupled-carbon-climate model, *Biogeosciences*, 8, 387–414, <https://doi.org/10.5194/bg-8-387-2011>, 2011.

Majdi, M., Sartelet, K., Maria Lanzafame, G., Couvidat, F., Kim, Y., Chrit, M., and Turquety, S.: Precursors and formation of secondary organic aerosols from wildfires in the Euro-Mediterranean region, *Atmos Chem Phys*, 19, 5543–5569, <https://doi.org/10.5194/ACP-19-5543-2019>, 2019.

McMeeking, G. R., Kreidenweis, S. M., Baker, S., Carrico, C. M., Chow, J. C., Collett, J. L., Hao, W. M., Holden, A. S., Kirchstetter, T. W., Malm, W. C., Moosmüller, H., Sullivan, A. P., and Cyle E., W.: Emissions of trace gases and aerosols during the open combustion of biomass in the laboratory, *Journal of Geophysical Research Atmospheres*, 114, <https://doi.org/10.1029/2009JD011836>, 2009.

Mebust, A. K., Russell, A. R., Hudman, R. C., Valin, L. C., and Cohen, R. C.: Characterization of wildfire NO_x emissions using MODIS fire radiative power and OMI tropospheric NO₂ columns, *Atmos Chem Phys*, 11, 5839–5851, <https://doi.org/10.5194/ACP-11-5839-2011>, 2011.

Milton, L. A. and White, A. R.: The potential impact of bushfire smoke on brain health, *Neurochem Int*, 139, <https://doi.org/10.1016/j.neuint.2020.104796>, 2020.

Miranda, A. I., Ferreira, J., Valente, J., Santos, P., Amorim, J. H., and Borrego, C.: Smoke measurements during Gestosa - 2002 experimental field fires, *Int J Wildland Fire*, 14, 107–116, <https://doi.org/10.1071/WF04069>, 2005.

Mitchell, S.: Carbon Dynamics of Mixed- and High-Severity Wildfires: Pyrogenic

CO₂ Emissions, Postfire Carbon Balance, and Succession, in: *The Ecological Importance of Mixed-Severity Fires*, Elsevier, 290–309, <https://doi.org/10.1016/B978-0-12-802749-3.00010-4>, 2015.

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.: Contribution of nitrated phenols to wood burning brown carbon light absorption in Detling, United Kingdom during winter time, *Environ Sci Technol*, 47, 6316–6324, <https://doi.org/10.1021/ES400683V>, 2013.

Mutzel, A., Rodigast, M., Iinuma, Y., Böge, O., and Herrmann, H.: Monoterpene SOA – Contribution of first-generation oxidation products to formation and chemical composition, *Atmos Environ*, 130, 136–144, <https://doi.org/10.1016/J.ATMOSENV.2015.10.080>, 2016.

Newstalk: Warning of “massive amounts of pollution from Galway fire”, <https://www.newstalk.com/news/warning-of-massive-amounts-of-pollution-fromgalway-fire-536759>, 2017.

Oberle, M.: Forest fires: suppression policy has its ecological drawbacks. *Science*, 165(3893), 568–571, 1969.

Oros, D. R., Abas, M. R. bin, Omar, N. Y. M. J., Rahman, N. A., and Simoneit, B. R. T.: Identification and emission factors of molecular tracers in organic aerosols from biomass burning: Part 3. Grasses, *Applied Geochemistry*, 21, 919–940, <https://doi.org/10.1016/J.APGEOCHEM.2006.01.008>, 2006.

Otto, A., Gondokusumo, R., and Simpson, M. J.: Characterization and quantification of biomarkers from biomass burning at a recent wildfire site in Northern Alberta, Canada, *Applied Geochemistry*, 21, 166–183, <https://doi.org/10.1016/j.apgeochem.2005.09.007>, 2006.

Palozzi, E., Lusini, I., Cherubini, L., Hajiaghayeva, R. A., Ciccioli, P., and Calafapietra, C.: Differences between a deciduous and a conifer tree species in gaseous and particulate emissions from biomass burning, *Environmental Pollution*, <https://doi.org/10.1016/j.envpol.2017.11.080>, 2018.

Paris, J. D., Stohl, A., Nédélec, P., Arshinov, M. Y., Panchenko, M. v., Shmargunov, V. P., Law, K. S., Belan, B. D., and Ciais, P.: Wildfire smoke in the Siberian Arctic in summer: Source characterization and plume evolution from airborne measurements, *Atmos Chem Phys*, 9, 9315–9327, <https://doi.org/10.5194/ACP-99315-2009>, 2009.

Pausas, J. G. and Keeley, J. E.: Wildfires as an ecosystem service, *Front Ecol Environ*, 17, 289–295, <https://doi.org/10.1002/fee.2044>, 2019.

FAQ about PurpleAir: <https://www2.purpleair.com/community/faq#hc-what-is-the-difference-between-cf-1-and-cf-atm>, last access: 19 August 2022.

Reid, C. E., Brauer, M., Johnston, F. H., Jerrett, M., Balme, J. R., and Elliott, C. T.: Critical Review of Health Impacts of Wildfire Smoke Exposure, *Environ Health Perspect*, 124, 1334–1343, <https://doi.org/10.1289/EHP.1409277>, 2016.

Rein, G., & Huang, X.: Smouldering wildfires in peatlands, forests and the arctic: Challenges and perspectives. *Current Opinion in Environmental Science & Health*, 24, 100296, 2021.

Reisen, F., Meyer, C. P., Weston, C. J., and Volkova, L.: Ground-Based Field

Measurements of PM_{2.5} Emission Factors From Flaming and Smoldering Combustion in Eucalypt Forests, *Journal of Geophysical Research: Atmospheres*, 123, 8301–8314, <https://doi.org/10.1029/2018JD028488>, 2018.

RTE: Killarney National Park wildfire burns for third night, <https://www.rte.ie/news/ireland/2021/0425/1211931-killarney-national-park-fire/>, 2021.

Rudich, Y., Donahue, N. M., and Mentel, T. F.: Aging of Organic Aerosol: Bridging the Gap Between Laboratory and Field Studies, *Annu Rev Phys Chem*, 58, <https://doi.org/10.1146/annurev.physchem.58.032806.104432>, 2007.

Sandradewi, J., Prévôt, A.S.H., Weingartner, E., Schmidhauser, R., Gysel, M., and Baltensperger, U.: A study of wood burning and traffic aerosols in an Alpine valley using a multi-wavelength Aethalometer, *Atmos Environ*, 42, 101–112, <https://doi.org/10.1016/j.atmosenv.2007.09.034>

Scholes, R. J., Ward, D. E., and Justice, C. O.: Emissions of trace gases and aerosol particles due to vegetation burning in southern hemisphere Africa, *Journal of Geophysical Research: Atmospheres*, 101, 23677–23682, <https://doi.org/10.1029/95JD02049>, 1996.

Shrivastava, M. K., Lipsky, E. M., Stanier, C. O., and Robinson, A. L.: Modeling semivolatile organic aerosol mass emissions from combustion systems, *Environ Sci Technol*, 40, 2671–2677, <https://doi.org/10.1021/ES0522231>, 2006.

Sinha, P., Hobbs, P. v., Yokelson, R. J., Bertschi, I. T., Blake, D. R., Simpson, I. J., Gao, S., Kirchstetter, T. W., and Novakov, T.: Emissions of trace gases and particles from savannah fires in southern Africa, *Journal of Geophysical Research: Atmospheres*, 108, <https://doi.org/10.1029/2002jd002325>, 2003.

Sinha, P., Hobbs, P. v., Yokelson, R. J., Blake, D. R., Gao, S., and Kirchstetter, T. W.: Emissions from miombo woodland and dambo grassland savannah fires, *Journal of Geophysical Research: Atmospheres*, 109, 11305, <https://doi.org/10.1029/2004JD004521>, 2004.

Smith, H. G., Sheridan, G. J., Lane, P. N. J., Nyman, P., and Haydon, S.: Wildfire effects on water quality in forest catchments: A review with implications for water supply, <https://doi.org/10.1016/j.jhydrol.2010.10.043>, 5 January 2011.

Soongprasit, K., Sricharoenchaikul, V., and Atong, D.: Phenol-derived products from fast pyrolysis of organosolv lignin, *Energy Reports*, 6, 151–167, <https://doi.org/10.1016/J.EGYR.2020.08.040>, 2020.

Stavroulas, I., Grivas, G., Michalopoulos, P., Liakakou, E., Bougiatioti, A., Kalkavouras, P., Fameli, K. M., Hatzianastassiou, N., Mihalopoulos, N., and Gerasopoulos, E.: Field evaluation of low-cost PM sensors (Purple Air PA-II) Under variable urban air quality conditions, in Greece, *Atmosphere (Basel)*, 11, <https://doi.org/10.3390/atmos11090926>, 2020.

Stockwell, C. E., Yokelson, R. J., Kreidenweis, S. M., Robinson, A. L., Demott, P. J., Sullivan, R. C., Reardon, J., Ryan, K. C., Griffith, D. W. T., and Stevens, L.: Trace gas emissions from combustion of peat, crop residue, domestic biofuels, grasses, and other fuels: configuration and Fourier transform infrared (FTIR) component of the fourth Fire Lab at Missoula Experiment (FLAME-4), *Atmos. Chem. Phys*, 14, 9727–9754, <https://doi.org/10.5194/acp-14-9727-2014>, 2014.

Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, *Atmos. Chem. Phys.*, 15, 845–865, <https://doi.org/10.5194/acp-15-845-2015>, 2015.

Sullivan, A. P., Holden, A. S., Patterson, L. A., McMeeking, G. R., Kreidenweis, S. M., Malm, W. C., Hao, W. M., Wold, C. E., and Collett, J. L.: A method for smoke marker measurements and its potential application for determining the contribution of biomass burning from wildfires and prescribed fires to ambient PM_{2.5} organic carbon, *Journal of Geophysical Research Atmospheres*, 113, <https://doi.org/10.1029/2008JD010216>, 2008.

Sun, Q., Meyer, W. S., Koerber, G. R., and Marschner, P.: A wildfire event influences ecosystem carbon fluxes but not soil respiration in a semi-arid woodland, *Agric For Meteorol.*, 57–66, <https://doi.org/10.1016/j.agrformet.2016.05.019>, 2016.

Swiston, J. R., Davidson, W., Attridge, S., Li, G. T., Brauer, M., and van Eeden, S. F.: Wood smoke exposure induces a pulmonary and systemic inflammatory response in firefighters, *European Respiratory Journal*, 32, 129–138, <https://doi.org/10.1183/09031936.00097707>, 2008.

Tiitta, P., Leskinen, A., Hao, L., Yli-Pirilä, P., Kortelainen, M., Grigonyte, J., Tissari, J., Lamberg, H., Hartikainen, A., Kuusalo, K., Kortelainen, A. M., Virtanen, A., Lehtinen, K. E. J., Komppula, M., Pieber, S., Prévôt, A. S. H., Onasch, T. B., Worsnop, D. R., Czech, H., Zimmermann, R., Jokiniemi, J., and Sippula, O.: Transformation of logwood combustion emissions in a smog chamber: Formation of secondary organic aerosol and changes in the primary organic aerosol upon daytime and nighttime aging, *Atmos Chem Phys*, 16, 13251–13269, <https://doi.org/10.5194/ACP-16-13251-2016>, 2016.

Trentmann, J., Andreae, M. O., and Graf, H. F.: Chemical processes in a young biomass-burning plume, *Journal of Geophysical Research: Atmospheres*, 108, <https://doi.org/10.1029/2003jd003732>, 2003.

Tubridy, M.: A Study to Identify Best Management of Upland Habitats in County Wicklow, Roundwood, Co Wicklow, 2013.

United Nations Framework Convention on Climate Change, Paris Agreement, 12/2015, <https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement>, 2015.

UNISDR and CRED: Economic Losses, Poverty and Disasters 1998–2017, 2018.

Urbanski, S. P.: Combustion efficiency and emission factors for wildfire-season fires in mixed conifer forests of the northern Rocky Mountains, US, *Atmos Chem Phys*, 13, 7241–7262, <https://doi.org/10.5194/acp-13-7241-2013>, 2013.

Urbanski, S. P., Hao, W. M., and Baker, S.: Chemical Composition of Wildland Fire Emissions, *Developments in Environmental Science*, 8, 79–107, [https://doi.org/10.1016/S1474-8177\(08\)00004-1](https://doi.org/10.1016/S1474-8177(08)00004-1), 2009.

Vakkari, V., Beukes, J. P., Josipovic, M., and van Zyl, P. G.: Observations of ozone formation in southern African savannah and grassland fire plumes, *Atmospheric Environment*, 223, <https://doi.org/10.1016/j.atmosenv.2019.117256>, 2019.

Vicente, A., Alves, C., Monteiro, C., Nunes, T., Mirante, F., Evtyugina, M., Cerqueira, M., and Pio, C.: Measurement of trace gases and organic compounds in the smoke plume from a wildfire in Penedono (central Portugal), *Atmos Environ*, 45, 5172–5182, <https://doi.org/10.1016/j.atmosenv.2011.06.021>, 2011.

- Vicente, E. and Alves, C.: An overview of particulate emissions from residential biomass combustion, <https://doi.org/10.1016/j.atmosres.2017.08.027>, 1 January 2018.
- Vivanco, M., Santiago, M., Diego, C., and Borrás, E.: Effect of SO₂ concentration on SOA formation in a photoreactor from a mixture of anthropogenic hydrocarbons and HONO, 2009.
- Volkova, L., Meyer, C. P., Murphy, S., Fairman, T., Reisen, F., and Weston, C.: Fuel reduction burning mitigates wildfire effects on forest carbon and greenhouse gas emission, *Int J Wildland Fire*, 23, 771–780, <https://doi.org/10.1071/WF14009>, 2014.
- 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.: Atmospheric Processing of Nitrophenols and Nitrocresols From Biomass Burning Emissions 1, *Journal of Geophysical Research: Atmospheres*, 125, e2020JD033401, <https://doi.org/10.1029/2020JD033401>, 2020.
- Wang, H., Guo, S., Wu, Z., Qiao, K., Tang, R., Yu, Y., Xu, W., Zhu, W., Zeng, L., Huang, X., He, L., and Hallquist, M.: Secondary organic aerosol formation from straw burning using an oxidation flow reactor, *J Environ Sci (China)*, 114, 249–258, <https://doi.org/10.1016/j.jes.2021.08.049>, 2022.
- Wang, X., Meyer, C. P., Reisen, F., Keywood, M., Thai, P. K., Hawker, D. W., Powell, J., and Mueller, J. F.: Emission Factors for Selected Semivolatile Organic Chemicals from Burning of Tropical Biomass Fuels and Estimation of Annual Australian Emissions, *Environ Sci Technol*, 51, 9644–9652, <https://doi.org/10.1021/acs.est.7b01392>, 2017.
- Ward, D. E. and Hardy, C. C.: Smoke emissions from wildland fires, *Environ Int*, 17, 117–134, [https://doi.org/10.1016/0160-4120\(91\)90095-8](https://doi.org/10.1016/0160-4120(91)90095-8), 1991.
- Ward, D. E. and Min Hao, W.: Projection of emissions from burning of biomass for use in studies of global climate and atmospheric chemistry, 1991.
- Ward, D. S., Kloster, S., Mahowald, N. M., Rogers, B. M., Randerson, J. T., and Hess, P. G.: The changing radiative forcing of fires: global model estimates for past, present and future, *Atmos Chem Phys*, 12, 10857–10886, <https://doi.org/10.5194/acp-12-10857-2012>, 2012.
- Wei, F., Wang, S., Fu, B., Brandt, M., Pan, N., Wang, C., & Fensholt, R. (2020). Nonlinear dynamics of fires in Africa over recent decades controlled by precipitation. *Global Change Biology*, 26(8), 4495–4505. doi:10.1111/gcb.15190
- Wenger, J., Arndt, J., Buckley, P., Hellebust, S., McGillicuddy, E., O'Connor, I., Sodeau, J., and Wilson, E.: Source Apportionment of Particulate Matter in Urban and Rural Residential Areas of Ireland (SAPPHIRE), 2020.
- van der Werf, G. R., Randerson, J. T., Giglio, L., van Leeuwen, T. T., Chen, Y., Rogers, B. M., Mu, M., van Marle, M. J. E., Morton, D. C., Collatz, G. J., Yokelson, R. J., and Kasibhatla, P. S.: Global fire emissions estimates during 1997–2016, *Earth Syst Sci Data*, 9, 697–720, <https://doi.org/10.5194/essd-9-697-2017>, 2017.
- Westerling, A. L., Hidalgo, H. G., Cayan, D. R., and Swetnam, T. W.: Warming and earlier spring increase Western U.S. forest wildfire activity, *Science* (1979), 313, 940–943, <https://doi.org/10.1126/science.1128834>, 2006.

- WHO: WHO global air quality guidelines. Particulate matter (PM_{2.5} and PM₁₀), ozone, nitrogen dioxide, sulfur dioxide and carbon monoxide. Executive summary., Geneva, 2021.
- Wigder, N. L., Jaffe, D. A., and Saketa, F. A.: Ozone and particulate matter enhancements from regional wildfires observed at Mount Bachelor during 2004–2011, *Atmos Environ*, 75, 24–31, <https://doi.org/10.1016/J.ATMOSENV.2013.04.026>, 2013.
- WWF: Fires, Forests, and the Future - A crisis raging out of control?, 2020.
- Xu, R., Yu, P., Abramson, M. J., Johnston, F. H., Samet, J. M., Bell, M. L., Haines, A., Ebi, K. L., Li, S., and Guo, Y.: Wildfires, Global Climate Change, and Human Health, *N Engl J Med*, 2020.
- Yokelson, R. J., Susott, R., Ward, D. E., Reardon, J., and Griffith, D. W. T.: Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy, *Journal of Geophysical Research: Atmospheres*, 102, 18865–18877, <https://doi.org/10.1029/97JD00852>, 1997.
- Yokelson, R. J., Bertschi, I. T., Christian, T. J., Hobbs, P. v., Ward, D. E., and Hao, W. M.: Trace gas measurements in nascent, aged, and cloud-processed smoke from African savannah fires by airborne Fourier transform infrared spectroscopy (AFTIR), *J. Geophys. Res*, 108, 8478, <https://doi.org/10.1029/2002JD002322>, 2003.
- Yokelson, R. J., Karl, T., Artaxo, P., Blake, D. R., Christian, T. J., Griffith, D. W. T., Guenther, A., and Hao, W. M.: The tropical forest and fire emissions experiment: Overview and airborne fire emission factor measurements, *Atmos Chem Phys*, 7, 5175–5196, <https://doi.org/10.5194/acp-7-5175-2007>, 2007.
- Yokelson, R. J., Burling, I. R., Urbanski, S. P., Atlas, E. L., Adachi, K., Buseck, P. R., Wiedinmyer, C., Akagi, S. K., Toohey, D. W., and Wold, C. E.: Trace gas and particle emissions from open biomass burning in Mexico, *Atmos Chem Phys*, 11, 6787–6808, <https://doi.org/10.5194/acp-11-6787-2011>, 2011.
- Yttri, K. E., Simpson, D., Nojgaard, J. K., Kristensen, K., Genberg, J., Stenström, K., Swietlicki, E., Hillamo, R., Aurela, M., Bauer, H., Offenberg, J. H., Jaoui, M., Dye, C., Eckhardt, S., Burkhardt, J. F., Stohl, A., and Glasius, M.: Source apportionment of the summer time carbonaceous aerosol at Nordic rural background sites, *Atmos Chem Phys*, 11, 13339–13357, <https://doi.org/10.5194/ACP-11-13339-2011>, 2011.
- Zhao, D., Schmitt, S. H., Wang, M., Acir, I. H., Tillmann, R., Tan, Z., Novelli, A., Fuchs, H., Pullinen, I., Wegener, R., Rohrer, F., Wildt, J., Kiendler-Scharr, A., Wahner, A., and Mentel, T. F.: Effects of NO_x and SO₂ on the secondary organic aerosol formation from photooxidation of α -pinene and limonene, *Atmos Chem Phys*, 18, 1611–1628, <https://doi.org/10.5194/ACP-18-1611-2018>, 2018.
- Zheng, B., Ciais, P., Chevallier, F., Chuvieco, E., Chen, Y., and Yang, H.: Increasing forest fire emissions despite the decline in global burned area, *Sci Adv*, 7, <https://doi.org/10.1126/SCIADV.ABH2646>, 2021.
- Zotter, P., Herich, H., Gysel, M., El-Haddad, I., Zhang, Y., Mocnik, G., Hüglin, C., Baltensperger, U., Szidat, S., and Prévôt, A. S. H.: Evaluation of the absorption Ångström exponents for traffic and wood burning in the Aethalometer-based source apportionment using radiocarbon measurements of ambient aerosol, *Atmos Chem Phys*, 17, 4229–4249, <https://doi.org/10.5194/ACP-17-4229-2017>, 2017.