Emissions from Residential Solid Fuel Combustion and Implications for Air Quality and Climate Change

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Declaration

The candidate confirms that the work submitted is his own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated in section 1.3. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to work of others.

Acknowledgements

First and foremost I would like to thank my supervisors Professor Jenny Jones, Professor Alan Williams, Dr Amanda Lea-Langton and Professor Piers Forster for their support throughout my studies. Huge thanks to all of my co-authors and everyone in our research group, most notably Farooq Atiku, Dougie Philips, Ben Dooley, Patrick Mason, Yee-Sing Chin and Paula McNamee. Special thanks also go to Dr Rob Johnson and Arigna Fuels who kick-started the project and kept me on my toes in the first few months. Many thanks also to Dr Bijal Gudka and Dr Leilani Darvell for guidance and advice. I am very grateful to University of Leeds technical and laboratory staff too for their support and patience. They are Ed Woodhouse, Dr Simon Lloyd, Dr Adrian Cunliffe, Sara Dona, Karine Alves Thorne, Dave Instrell, Bob Harris and Sam Burdon. Not to forget LEMAS who were very helpful and supportive with my electron microscopy escapades.

Many thanks also to the EPSRC Doctoral Training Centre in Low Carbon Technologies (EP/G036608), as well as the DTC centre managers, James McKay, Emily Bryan-Kinns, Rachel Brown and David Haynes for everything they've done for me over the past four years. Many thanks also go to colleagues in other departments, most notably Professor Dominic Spracklen and Mr Edward Butt in Earth & Environment. Thanks also to Jes Sig Andersen and Dr Guy Coulson for hosting me in Denmark and New Zealand where I learned an enormous amount about the topic. The Supergen Bioenergy Hub and SHARE network deserves a special mention due to their kind support, guidance and financial contributions (EP/J017302).

Finally I would like to thank my family and friends, who have supported me every step of the way throughout my combined nine years at University, and who can finally stop asking 'haven't you finished yet?'

Abstract

Small scale biomass burning stoves and boilers are growing in popularity in the UK and abroad, owing in part to renewable heat incentives and policies. However, combustion in domestic scale appliances is often inefficient and uncontrolled in comparison to larger systems, leading to high emissions factors of gaseous pollutants such as CO, NO_x and PAH, as well as fine particulate matter (PM). Evidence is presented from 105 source apportionment studies from 31 developed countries showing that the impact of residential solid fuel (RSF) combustion on air quality is more wide spread that previously thought. Wood burning contributes to up to 95% of wintertime ambient PM in some rural communities in New Zealand, which is used as a case study throughout this work. Modelling work has shown that emissions from heating stoves may be underestimated in global climate models (GCMs) and UK residential wood consumption is forecast to increase by a factor of 14 between 1990 and 2030. By 2030, annual emissions of black carbon (BC) from UK wood stoves and fireplaces are predicted to exceed 3000 tonnes which is higher than the traffic sector. BC is the most important component of RSF radiative forcing, accounting for over 77% total warming effect. Model inventory and literature emission factors (EFs) for over 150 pollutants have been compared and contrasted, and compiled into a new RSF emissions inventory.

Results are presented from experimental work on the emissions testing of a 6 kW_{th} multi-fuel stove and three high quality cook stoves, burning a range of over 25 conventional and novel fuels including wood, coal, agricultural residues and torrefied wood briquettes. Despite a large resource of agricultural residues being available with lower EFs than open burning, their suitability as a residential solid fuel is uncertain. For example, straw briquettes had a measured density less than half that of wood logs and reed briquettes showed evidence of ash melting in the stove bed due to a high sodium, silica and chlorine content. It was found that PM and CO emissions were correlated to the content and composition of volatile matter within the fuel and NO_x is linearly dependent on fuel nitrogen content. Mean whole cycle PM EFs ranged from 2.1 g kg^{-1} for wood logs to 4.2 g kg^{-1} for coal and 0.5 g k^{-1} for smokeless fuel. Torrefaction of wood has the potential to significantly reduce emissions, with PM EFs 49% lower than wood logs. However, emissions from all fuels were highly dependent on the duration of the flaming phase of combustion, during which EFs may be a factor of 5-9 higher than the smouldering phase. Heat treatment such as torrefaction removes 10-15% of volatiles, shortening the flaming phase and removing key species involved in the chemical soot formation pathways, which are discussed in detail.

The physical and optical properties of collected particulate samples collected were also examined using electron microscopy and spectroscopy, which are useful for GCMs. Flaming phase particles had a high average EC/TC ratio (>0.9), a high carbon:oxygen ratio (93:5.4) and an Ångström Absorption Exponent (AAE) near 1 (0.9-1.2). After emission, it was found that particles undergo a significant increase in branching and oxygenation (C:O 88:10). The morphology of particles was also found to change following the injection of plasma into the flue, which is evaluated as a promising retrofit abatement technology.

Graphical abstract

Cross section of a wood log before being split and bagged.

‘To poke a wood fire is more solid enjoyment than almost anything else in the world’

Charles Dudley Warner

Contents

List of Figures

List of Tables

List of Abbreviations

A/F	Air-to-Fuel ratio
AAE	Ångström Absorption Exponent
AAS	Atomic Absorption Spectroscopy
AGWP	Absolute Global Warming Potential
AMS	Aerosol Mass Spectrometer
AOD	Aerosol Optical Depth
ASE	Accelerated Solvent Extraction
ATN	Attenuation
ATOFMS	Aerosol Time-of-Flight Mass Spectrometer
BC	Black Carbon
BEIS	Department for Business, Energy & Industrial Strategy
BrC	Brown Carbon
BS	British Standard or Black Smoke
BTX	Benzene, toluene and xylene
CAU	Census Area Unit
CCA	Copper Chromium Arsenate
CCN	Cloud Condensation Nuclei
CHNS	Carbon, Hydrogen, Nitrogen and Sulphur (ultimate analysis)
CMB	Chemical Mass Balance
CO	Carbon monoxide
CPD	Cyclopentadiene
DECC	Department for Energy and Climate Change (UK). *Note this department has recently changed to BEIS*
DEFRA	Department for Environment, Food and Rural Affairs (UK)
DMS	Differential Mobility Spectrometer
DUKES	Digest of United Kingdom Energy Statistics
EC	Elemental Carbon
EDS or EDX	Energy-dispersive X-ray spectroscopy
EELS	Electron Energy Loss Spectroscopy
EI	Emissions Index (EF)
ELVOC	Extremely low volatility organic compounds
EMEP/EEA	European Monitoring and Evaluation Programme / European Environment Agency
EPA	Environmental Protection Agency (USA)
EPC	Energy Performance Certificate
ESP	Electrostatic Precipitator
FTIR	Fourier Transform Infrared spectrometer
GAINS	Greenhouse gas – Air pollution Interactions and Synergies
GCV	Gross Calorific Value
HACA	Hydrogen Abstraction Acetylene Addition
HAPINZ	Health and Air Pollution in New Zealand study
HCB	Hexachlorobenzene
HCN	Hydrogen cyanide
HGF	Hygroscopic Growth Factor
HHV	Higher Heating Value (=GCV)
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IPCC	Intergovernmental Panel on Climate Change
LEMAS	Leeds Electron Microscopy and Spectroscopy centre
LII	Laser-Induced Incandescence
LPG	Liquefied petroleum gas

MAC	Mass absorption cross-section
MBIE	Ministry of Business, Innovation and Employment (NZ)
MC	Moisture Content
MC	Moisture Content
MCE	Modified Combustion Efficiency
MCS	Microgeneration Certification Scheme
MSF	Manufactured Solid Fuel
NAEI	National Atmospheric Emissions Inventory (UK)
NCV	Net Calorific Value
NES	National Environmental Standard (NZ)
NMVOC	Non-Methane Volatile Organic Compounds
NO_x	Oxides of nitrogen ($NO + NO_2$)
NSPS	National Source Performance Standard (USA)
NZFFA	New Zealand Farm Forestry Association
NZHHA	New Zealand Home Heating Association
OC	Organic Carbon
OECD	Organization for Economic Cooperation and Development
OGC	Organic Gaseous Carbon
OGC	Organic gaseous carbon
PAC	Polycyclic Aromatic Compounds
PAH	Polycyclic Aromatic Hydrocarbons
PCA	Principle Component Analysis
PCBs	Polychlorinated biphenyls
PCDD/F	Polychlorinated Dibenzo-p-Dioxins and -Furans
PM	Particulate Matter
PMF	Positive Matrix Factorisation
POA	Primary Organic Aerosol
POP	Persistent organic pollutant
ppm	Parts Per Million
Py-GC/MS	Pyrolysis gas chromatography mass spectrometry
RH	Relative Humidity
RHI	Renewable Heat Incentive (UK)
RSF	Residential Solid Fuels
RWC	Residential Wood Combustion
SDFGV	Specific Dry Flue Gas Volume
SEM	Scanning Electron Microscopy
SIA	Stove Industry Alliance
SOA	Secondary Organic Aerosol
SP^2	Single particle soot photometer
SSA	Single Scattering Albedo
SSF	Solid Smokeless Fuel
TC	Thermocouple
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TPES	Total Primary Energy Supply
UNFCCC	United Nations Framework Convention on Climate Change
WBT	Water Boiling Test
WHO	World Health Organisation
WSOC	Water Soluble Organic Carbon

Chapter 1

Motivation and Background

1.1 Context

The research questions relating to residential solid fuel (RSF) combustion for cooking and heating can be broadly separated into three categories. Firstly, what are the emissions and how are they affected by fuel properties and technology types. Secondly, what effect do emissions have on air quality and health. Thirdly, to what extent can biomass RSFs offset greenhouse gas (GHG) emissions from fossil fuel combustion and what are the impacts of biomass emissions on climate change.

Climate Change

In November 2016, 197 parties to the UNFCCC agreed to strengthen the global response to the threat of climate change. The aim of the Paris Agreement is to limit global temperature increase to 2°C above pre-industrial levels, and to pursue efforts to limit the rise to 1.5°C. In order to achieve this, CO_2 concentrations will need to stabilise at approximately 430-480 ppm according to IPCC scenario RCP2.6 (IPCC, 2014). Current CO_2 concentrations as measured at the Mauna Loa Observatory, Hawaii are 405 ppm. Models suggest that the 1.5-2.0°C target will not be met with current practices, leading to a warming of up to 4°C and irreversible effects on the planet including sea level rise, desertification, species loss and famine. Hence to achieve the target, a reduction in GHG emissions of 41-72% is required by 2050 relative to 2010 (IPCC, 2014). The UK has legally binding targets to ensure 15% of energy and 12% of heat come from renewable sources by 2020, and to reduce GHG emissions by 80% by 2050, relative to 1990 levels.

Globally, the residential and commercial buildings sector accounted for 19% of global GHG emissions in 2010 (Lucon *et al.* 2014). A large proportion of emissions in this sector are attributable to inefficient combustion in cookstoves, heating stoves and open fires. Biomass used in the residential and commercial sectors accounts for over 90% of final energy consumption in some low income countries (see chapter 9). Within OECD nations, energy used for heating accounted for 37% of final energy consumption in 2009 (Beerepoot and Marmion 2012) and is expected to grow by 79% over the period 2010 – 2050 (Lucon *et al.* 2014). Despite this, the residential and commercial buildings sector above all others was highlighted as having the greatest potential for the most cost-effective emissions reductions through energy efficiency measures and renewable space heating technologies (UNEP 2009; IEA 2013). Bioenergy has been identified as one such technology and wood fuel for household heat is one of the major drivers of bioenergy uptake, accounting for 54% of total UK renewable heat generation (see section 7.5).

Air Quality

Solid fuel combustion for cooking and heating releases hundreds of pollutants into the air including both gas- and particle-bound species. A description of the formation and health effects of these species is given in Chapter 2. The health effects of smoke inhalation are more pronounced in developing countries where widespread use of cookstoves leads to high exposure rates. As described in chapter 9, this leads to 4 million premature deaths per year. The key research question here is how to reduce this exposure through clean cooking technologies and fuel switching, without increasing GHG emissions. As shown in figure 1-1, the traditional pathway to reduced emissions is a move away from biomass fuels to higher energy content and lower emitting fossil fuels (kerosene, LPG etc.) and eventually to highly efficient minimal emission fuels (natural gas, electricity).

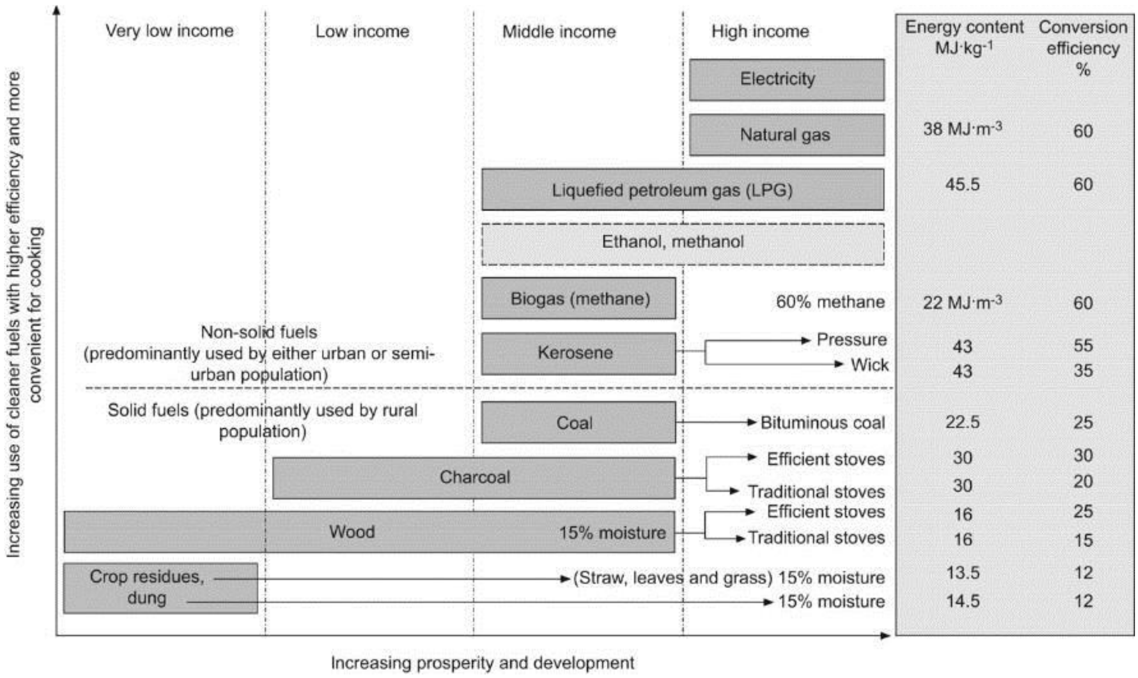


Figure 1-1. The household energy ladder. Source: Kurmi et al. (2012)

Even within high income countries, there is still a large reliance on solid fuels for space heating, particularly where there is limited access to natural gas infrastructure. Wood fuels also tend to be cheaper than electricity, LPG and kerosene, especially in the UK. However, RSF combustion technologies are still relatively simple and there is a greater potential for user error than with other heating systems. There is also a natural affinity for the aesthetics of a wood fire and a desire to reduce fossil fuel consumption. Aside from open fireplaces, most appliances are closed systems venting directly to atmosphere so the health effects are less pronounced than for cookstoves. However, evidence is presented in Chapter 2 that these appliance contribute up to up to 95% of winter time ambient air pollution in some communities, and up to 70% of emitted pollution re-enters the home. Chafe et al. (2015) found that there were an estimated 20,000 annual premature deaths in Europe in 2010 due to wood and coal fires, up 23% of 1990 levels. With a number of countries in Europe failing air quality standards, there is a need to better understand emissions from RSF combustion.

1.2 Aims and Objectives

The overarching aim of this work is to investigate the impact of fuel properties and operating conditions on emissions from RSF appliances, and to assess the impact of those emissions on air quality, climate and atmospheric chemistry. Key aims include:

Aim 1: Review published information on RSF emissions and impacts.

Objective 1a: Identify the key pollutants from RSF combustion and critically compare standard test methods.
Objective 1b: Develop and compile an emissions inventory database for emissions factors from the literature and from models.
Objective 1c: Quantify the contribution of RSF combustion to ambient air pollution around the world.

Aim 2: Measure and compare emissions factors for different fuels and appliances.

Objective 2a: Characterise a wide range of fuels and identify which properties lead to higher emissions.
Objective 2b: Conduct combustion and emission tests for a wide range of fuels and appliances including heating stoves and cooking stoves
Objective 2c: Link findings in order to improve understanding of the mechanisms involved in pollutant formation.
Objective 2d: Evaluate the emissions reduction potential of a novel abatement device.

Aim 3: Investigate the physical and optical properties of emitted particles.

Objective 3a: Capture soot particles from different fuels and combustion conditions and investigate their morphology and composition using electron microscopy.
Objective 3b: Measure the optical properties of particles and identify contributing factors.

Aim 4: Model RSF combustion emissions in the UK and associated impacts on climate.

Objective 4a: Compare and contrast activity data and emissions for RSF used in air quality & climate models.
Objective 4b: Develop a new inventory for UK RSF combustion and put into international context.
Objective 4c: Assess climate impacts by feeding inventory data into a climate model.

1.3 Thesis structure

In accordance with the requirements of the University of Leeds, this work consists of four published journal articles (Chapters 4, 5, 6 and 7) with a critical literature review (Chapter 2) and a discussion (Chapter 10). An additional manuscript is presented in Chapter 8 which has been submitted but not yet published. Three additional manuscripts are in preparation for submission and data from these is presented in Chapters 9 and 10.6.

Declaration of authorship:

<table>
<tr><td>Chapter
4</td><td>Reference
E.J.S. Mitchell., A. Williams, A.R. Lea-Langton, J.M. Jones., R. Johnson, P. Layden. (2015). The Impact of Fuel Properties on the Emissions from the Combustion of Biomass and other Solid Fuels in a Fixed Bed Domestic Stove. <i>Fuel Processing Technology</i> 142, 115-123.</td></tr>
<tr><td colspan="2">Declaration of authorship
This paper was written entirely by the author, with support from AW and co-authors. All figures and tables were my own. PL and RJ provided fuels and the stove used in experiments. AL-L and JMJ provided supervisory guidance and helped set up the first test lab.</td></tr>
</table>

<table>
<tr><td>Chapter
5</td><td>Reference
F.A. Atiku, E.J.S. Mitchell, A.R. Lea-Langton, J.M. Jones, A. Williams, K.D. Bartle. (2016). The Impact of Fuel Properties on the Composition of Soot Produced by the Combustion of Residential Solid Fuels in a Domestic Stove. <i>Fuel Processing Technology</i>, 151, 117-125.</td></tr>
<tr><td colspan="2">Declaration of authorship
This paper was written by the author, AW and FA. Contribution greater than 50%. This work began with a focus on the composition of soots derived from model compounds – all results relating to the model compounds were done by FA. However as the paper grew and more data was generated, the focus became on the stove-derived soots (my own) and the model compounds had a lesser role. This paper is a follow-on to chapter 4 above – filters generated through this work were analysed for EC and OC composition. Tables 2, 3 and 4 are my own. Figures 1, 2, 3, 4, 5, 6, 7 are my own. I re-plotted and re-analysed the data for figs 8 and 9 and table 1 but the original data was by FA. AL-L and JMJ provided supervisory guidance. KB provided expertise on the interpretation of py-GC/MS results.</td></tr>
</table>

<table>
<tr><td>Chapter
6</td><td>Reference
D. Phillips, E.J.S. Mitchell, K. Parmar, A. R. Lea-Langton, A. Williams. (2016). The use of conservation biomass feedstocks as potential bioenergy resources in the United Kingdom. <i>Bioresource Technology</i>, 212, 271-279.</td></tr>
<tr><td colspan="2">Declaration of authorship
This paper was written by the author, DP, and AW. This work began as a DTC mini project where my involvement was small (DP lead). However, several experiments needed repeating/expanding and additional tests needed to be done (stove experiments) in order to have sufficient material for a publication. Tables 2, 3, 5 and 6 are my own. All of the figures are my own and the critical analysis is my own. KP contributed py-GC/MS results in table 4 and bark proximate/ultimate analysis in table 3. DP contributed the resource analysis in the introduction (table 1), proximate/ultimate analysis of 5 fuels, and editing of the text. AL-L and JMJ set up the project and provided supervisory guidance.</td></tr>
</table>

<table>
<tr><td>Chapter 7</td><td>Reference
E.J.S. Mitchell, G. Coulson, E. Butt, P.M. Forster, J M. Jones, A.R. Lea-Langton, A. Williams. 2017. Heating with Biomass in the UK: Lessons from New Zealand. <i>Atmospheric Environment</i> 152, 431-454.</td></tr>
<tr><td colspan="2">Declaration of authorship
This paper was written entirely by the author. All tables, figures and analysis are my own. This paper received a great deal of interest and was featured in the New Scientist (Issue 3111, 4th Feb 2017) (https://www.newscientist.com/article/2119595-wood-burners-london-air-pollution-is-just-tip-of-the-iceberg/). GC provided some of the unpublished data referenced in table 4 and general guidance. EB contributed some background knowledge and papers to reference, as well as links to the GAINS database which I used extensively. PF, JMJ and AW provided supervisory guidance.</td></tr>
</table>

<table>
<tr><td>Chapter 8</td><td>Reference
J.M. Jones, E.J.S Mitchell, A. Williams, E. K. Barimah, G. Jose, K.D. Bartle, N. Hondow, A.R. Lea-Langton. (2017) Examination of Combustion Generated Smoke Particles at Source Using Different Sampling Methods: Effects on Atmospheric Light Absorption. <i>Submitted for publication.</i></td></tr>
<tr><td colspan="2">Declaration of authorship
This paper is currently in review for publication. It was written and initiated by the author, JMJ and AW. EB and GJ conducted the spectrometer measurements and AAE determination. NH provided TEM and EELS expertise. Interpretation and discussion was conducted by the author and AW.</td></tr>
</table>

<table>
<tr><td>Chapter 9</td><td>Reference
E.J.S Mitchell, Y. Ting, J. Allan, A.R. Lea-Langton, D.V. Spracklen, G. McFiggans, H. Coe, A. Williams, J M. Jones. Emissions from Improved Cookstoves in Sub-Saharan Africa. <i>In preparation for Environmental Science and Technology</i></td></tr>
<tr><td colspan="2">Declaration of authorship
This paper is currently in preparation for publication. The results included here (Chapter 9) were carried out exclusively by the author with support from YT and JA. AL-L, DS, GM, HC, AW and JMJ set up the project and provided supervisory guidance.</td></tr>
</table>

<table>
<tr><td>Chapter 10.6</td><td>Reference
B Gudka, J M. Jones, A. Williams, A.R. Lea-Langton, E.J.S Mitchell, G Stammers, G. Finnerty, J. Gane and J. Oladipo. (2017). The Kinetics of the Rapid Washing of Waste Wood and the Impact on Emissions. <i>In preparation for Bioresource Technology.</i></td></tr>
<tr><td colspan="2">Declaration of authorship
This paper is currently in preparation for publication and is led by BG. My contribution was to the waste wood briquetting and combustion trails. Few results are included here (Chapter 10.6) were carried out exclusively by the author and BG.</td></tr>
</table>

<table>
<tr><td>Chapter 11.4 (Appendix IV)</td><td>Reference
E.J.S Mitchell, B. Gudka, C. Whittaker, I. Shield, J M. Jones, A. Williams. (2017) The Impact of Agronomy on the Potential of Agricultural Residues for Small Scale Domestic Heating. <i>In preparation for Energy & Fuels.</i></td></tr>
<tr><td colspan="2">Declaration of authorship
This paper is currently in preparation for publication. The results included here (Chapter 11.4) were carried out exclusively by the author with support from BG.</td></tr>
</table>

1.4 List of Publications

In addition to the aforementioned publications, the following articles have been published but are not included in the thesis:

E. W. Butt, A. Rap, A. Schmidt, C.E. Scott, K.J. Pringle, C.L. Reddington, N.A.D. Richards, M.T. Woodhouse, J. Ramirez-Villegas, H. Yang, V. Vakkari, E.A. Stone, M. Rupakheti, P.S. Praveen, P. Beukes, M. Josipovic, P. Van Zyl, **E.J.S. Mitchell**, S. Sallu, P.M. Forster, and D.V. Spracklen. (2015) The impact of emissions from residential combustion on atmospheric aerosol, human health and climate. *Atmos. Chem. Phys.*, 16, 873-905.

G. Coulson, E. Somervell, **E.J.S. Mitchell,** I. Longley, G. Olivares. (2017). Ten years of woodburner research in New Zealand: A review. *Air Quality and Climate Change [currently under review]*

J.M. Jones, A.B. Ross, **E.J.S. Mitchell**, A.R Lea-Langton, A. Williams, K.D. Bartle. (2017) Organic Carbon Emissions from the Co-firing of Coal and Wood in a Fixed Bed Combustor. *Fuel*, 195, 226-231.

A list of conference papers presented during the PhD is given below:

E.J.S. Mitchell, A.R. Lea-Langton, J.M. Jones, A. Williams. (2013) Impacts of Wood Burning on Climate. *Clean Air Society of Australia and New Zealand (CASANZ) Conference*. Wellington, New Zealand. November 2013.

E.J.S. Mitchell, A.R. Lea-Langton, J.M. Jones, A. Williams. (2014) Impact of Feedstock Parameters on Airborne Emissions from Small-Scale Biomass Combustion and their Associated Impacts on Air Quality and Climate. *International Bioenergy Conference*. Manchester, UK. 11-13 March 2014.

E.J.S. Mitchell, J.M. Jones, A.R. Lea-Langton, A. Williams, A. Harvey, K. Zhang. (2014) Emissions Control from Domestic Biomass Combustion. *Annual Assembly of the Supergen Bioenergy Hub*. European Bioenergy Research Institute (EBRI), Aston University, Birmingham, UK. 5th November 2014.

E.J.S. Mitchell, A.R. Lea-Langton, J.M. Jones, A. Williams. (2015) Emissions from Domestic Biomass Combustion and Implications for Air Quality and Climate Change. *23rd European Biomass Conference and Exhibition (EUBCE)*. Vienna, Austria. 1-4 June 2015.

E.J.S. Mitchell, D. Philips, K. Parmar, A.R. Lea-Langton, J.M. Jones, A. Williams. (2015) The Characterisation of Peat Grown Willow and Silver Birch as Potential Bioenergy Feedstocks. *1st Chemistry in Energy Conference*. Heriot-Watt University, Edinburgh, UK. 20-22 July 2015.

E.J.S. Mitchell, A.R. Lea-Langton, J.M. Jones, A. Williams. (2015) The Impact of Residential Solid Fuel Properties on Elemental and Organic Carbon Emissions. *11th International Conference on Carbonaceous Particles in the Atmosphere*. Berkeley, California, USA. 10-13 August 2015.

K. Zhang, **E.J.S. Mitchell**, Lea-Langton, A., Harvey, A., Jones, J. and Williams, A. (2015) Abatement of Smoke Emissions from Domestic Stove Combustion using Novel Plasma

Device. *1st International Biomass Emissions Conference*. University of Leeds, Leeds, UK. 14-15 September 2015.

E.J.S. Mitchell, A.R. Lea-Langton, J.M. Jones, A. Williams. (2016) Atmospheric Chemistry Implications of Residential Solid Fuel Combustion. *Chemistry in the Urban Atmosphere: Faraday Discussion*. London, United Kingdom. 6-8 April 2016.

E.J.S. Mitchell, Emissions from Biomass Heating Systems. In: *SUPERGEN Bioenergy Hub: Renewable Heat - The Role of Bioenergy*. All Energy Conference and Exhibition, Glasgow, United Kingdom. 4-5 May 2016.

A.R Lea-Langton, D.V. Spracklen, S.R. Arnold, L.A. Conibear, J. Chan, **E.J.S. Mitchell**, J.M. Jones, A. Williams. (2017). Air Quality Impacts from Cookstove Emissions. *International Bioenergy Conference*. Manchester, UK. 22-23 March 2017.

1.5 References

CHAFE, Z., M. BRAUER, M. HÉROUX, Z. KLIMONT, T. LANKI, R. O. SALONEN and K. R. SMITH. 2015. *Residential heating with wood and coal: Health Impacts and Policy Options in Europe and North America.* Copenhagen, Denmark: World Health Organisation (WHO).

IEA. 2013. *Tracking Clean Energy Progress 2013. IEA Input to the Clean Energy Ministerial.* Paris: OECD/IEA.

IPCC 2014. 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. *In:* 'CORE WRITING TEAM', R. K. P. A. L. A. M. (ed.). Geneva, Switzerland: IPCC.

KURMI, O. P., LAM, K. B. H. & AYRES, J. G. 2012. Indoor air pollution and the lung in low- and medium-income countries. *European Respiratory Journal,* 40**,** 239-254.

LUCON, O., D. ÜRGE-VORSATZ, A. ZAIN AHMED, H. AKBARI, P. BERTOLDI, L.F. CABEZA, N. EYRE, A. GADGIL, L.D.D. HARVEY, Y. JIANG, E. LIPHOTO, S. MIRASGEDIS, S. MURAKAMI, J. PARIKH, C. PYKE and M. V. VILARIÑO. 2014. Buildings. *In:* O. EDENHOFER, R. PICHS-MADRUGA, Y. SOKONA, E. FARAHANI, S. KADNER, K. SEYBOTH, A. ADLER, I. BAUM, S. BRUNNER, P. EICKEMEIER, B. KRIEMANN, J. SAVOLAINEN, S. SCHLÖMER, C. VON STECHOW, T. ZWICKEL AND J.C. MINX, ed. *Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.* Cambridge, UK. and New York, USA.: Cambridge University Press.

UNEP. 2009. *Buildings and Climate Change: Summary for Decision-Makers.* Paris: UNEP DTIE.

Chapter 2

Critical Literature Review

2.1 RSF Combustion: History, Policy and Practice

The link between the household burning of solid fuels and poor air quality can be traced back as far as pre-historic times. Samples of mummified lung tissues from ancient civilisations in Egypt and elsewhere have showed evidence of anthracosis (blackening of the lungs) which it is believed was caused by exposure to RSF smoke from cooking and heating in confined indoor environments (Mosley, 2014). The Romans Horace (65 BC – 8 AD) and Seneca (4 BC – 65 AD) described the smoke from domestic wood burning as 'oppressive' in Rome where it blackened buildings and forced people to regularly venture out of the city in the search for clean air. Nevertheless, little was done to reduce emissions from residential wood burning. By the medieval period, increasing consumption of coal was beginning to affect air quality in Europe. One of the first connections comes from medieval Britain, when in 1306, Edward I Longshanks (1239-1307) banned coal burning in homes. Small amounts of coal collected from surface mines has been burned throughout the centuries alongside wood, but Edward's ban was one of the first pieces of evidence of it causing adverse health effects. Due to urbanisation and population growth in London, there was a high demand for and limited supply of wood for cooking and heating (Brimblecombe, 1976). As a result, coal was shipped to London from Northeast England and Southeast Scotland where it was gathered from beaches due to seams being close to the surface there. This 'Sea Coal' had a high sulphur content and there are reports of a sulphur stench filling the air of London, as well as clouds of dark smoke which irritated the eyes and lungs. Hence a ban was introduced with penalties of heavy fines, torture or even execution, but burning continued nonetheless.

A number of later monarchs also expressed their frustration at smoke from sea coal in the capital. In 1661, John Evelyn (1620-1706) wrote a letter to the then king, Charles II, describing sea coal smoke as "noxious", unhealthy and damaging to the city of London. His work *Fumifugium* (1661) goes on to suggest removing certain polluting industries such as lime kilns out of the city, and advocates the burning of low smoke fuels in domestic fires:

> *As the famous proverb goes, 'there is no smoke without fire'; nor is there any fire without smoke, and so it might be suggested that we use materials on our fires which burn clear and easily.*

The ensuing Industrial Revolution saw a phenomenal increase the consumption of coal and the industrial sector quickly became the biggest contributor to ambient air pollution in the UK. The great smogs of London have been described or portrayed in the works of Charles Dickens, Charles Darwin and Monet and were often so severe in the winter that visibility was limited to just a few meters. In December 1952, a high pressure anticyclone system and wintertime atmospheric temperature inversion led to a five day smog so intense that it caused the deaths of several thousand people and brought the city of London to a standstill. The event was directly linked to domestic burning of coal, as well as industrial sources, and led to the Clean Air Act of 1956.

The Clean Air Act banned emissions of 'black smoke' in urban areas termed 'smoke control areas' and placed fines on offenders. Historically the Act is based on visible emissions and the 1993 revision states that "*If, on any day, smoke is emitted from a chimney of any building within a smoke control area, the occupier of the building shall be guilty of an offence*." The penalty is a fine of up to £1000. Exemptions are available if the emitter has been found to be using an appliance or fuel that has been approved. A fuel is exempt if it has a sulphur content of less than 2% and the smoke emission rate is less than 5g hour^{-1} when tested to BS 3841 (total gravimetric PM). An appliance ≤44 kW is exempt if the smoke emission is 5 g hour^{-1} + 0.1 g per 0.3 kW when tested to BS PD 6434:1969.

Additional emissions limits are placed on appliances at the European level. European Technical Specification DD CEN/TS 15883:2009 describes methods for the measurements of NO_x, OGC and PM used by member states; principally NS 3058/ NS 3059 in Norway, DIN-plus in Germany and BS PD 6434 in the UK. There are significant differences in the test procedures used in these standards which complicates comparative studies (see chapter 7). Key differences include the draught, fuel, reporting units, dilution, filter temperatures, and sampling durations & equipment. The standard EN 13240 addresses many of these issues by specifying numerous parameters relating to the design and performance of appliances. It requires appliance efficiency to be greater than 50% and CO emissions to be less than 1.0% (ref. 13% O_2). However, emissions of PM, NO_x and OGC are left to national legislation. A new standard is currently being developed in Europe, EN 16510 *Part 2-1: Roomheaters*, which does aim to standardise test methods across Europe for the aforementioned pollutants, but is still a draft for development at the current time.

A number of authors have noted that these standards may not be fully representative of real-world emissions, primarily due to user operating conditions such as start-up, overloading and fluctuating burn rates, as well as the use of non-standard fuels (Ancelet et al., 2010, Xie et al., 2012, Wöhler et al., 2016). The number of variables is reduced in standard test methods in order to provide robust and reproducible results which are comparable between appliance types. Standardised operating variables include the fuel (species and size), the draught (natural or forced) and the test conditions (number of burn rate categories and duration). Full details of these parameters for seven international standards are given in Table 7-2. The methods typically require 2-4 burn rate categories (low, nominal, high, safety), whereas under-real world conditions there may be many more categories. Hence emissions test standards for stoves are arguably less representative of real-world emissions than standards used in other sectors such as vehicles. For vehicular emissions, incremental European exhaust emission standards have been implemented since 1992, which follow strict laboratory test protocols that have been designed to simulate emissions under a range of driving conditions (Sileghem et al., 2014). In recent years, test cycles such as the New European Drive Cycle (NEDC) have come under a great deal of scrutiny for a number of reasons, including the Volkswagen emissions scandal. Test standards for stoves have received much less scrutiny (Tissari et al., 2007). Wilton (2012) found that real-world emissions from in-situ stoves were typically a factor of 2 higher than those determined under laboratory conditions, whereas Tissari et al. (2007) and Scott (2005) found the factor can be as high as 3-5. A statistical analysis of 390 tests of in-situ stoves was carried out by Coulson et al. (2015). It found that geometric mean PM_{10} emission factors from older and modern stoves were 9.8 g kg^{-1} and 3.9 g kg^{-1} with standard deviations of ± 2.4 g kg^{-1} and ± 3.8 g kg^{-1} respectively.

Emissions limits also apply to biomass heating systems under the Renewable Heat Incentive (RHI). In order to be eligible for RHI payments, a biomass burning appliance must be fitted with a boiler capability and must be emissions certified through the Microgeneration Certification Scheme (MCS). Stoves and fireplaces are therefore not eligible, with the exception of some efficient pellet stoves. The MCS limits include an efficiency of 75%, CO concentrations of less than 1% (ref 13% O_2), and emissions factors of 30 g GJ^{-1} for PM and 150 g GJ^{-1} for NO_x. A detailed comparison of standard test methods and emission limits in presented in chapter 7, Table 7-2.

From a safety perspective, a stove or fireplace must be installed by competent persons in accordance with Buildings Regulations Document J. This document specifies the vent size requirements for homes with wood burners. For an open fire, the vent size needs to be at least 50% of the cross sectional area of the flue. For stoves, the vent must be 550 mm^2 per kW appliance output rated above 5 kW. The requirement is 850 mm^2 per kW for modern well sealed homes with a permeability less than 5 $m^3\ h^{-1}\ m^{-2}$. Only HETAS registered personnel are entitled to carry out such work and issue an installation certificate. Document J also specifies the requirements for chimney/flue installation and positioning. The height of the chimney outlet must be ≥1 m above the height of 2.3 m adjacent or adjoining buildings for solid fuel installations, in accordance with standard BS EN 15287-2:2008.

2.2 Pollutant Emissions and Formation

This chapter explores what are the emissions from RSF combustion, how they are formed and what impact they have on air quality, atmospheric chemistry and climate change.

2.2.1 Particulate matter

Particulate matter (PM) is a mixture of solid and liquid phase particles with various morphologies and compositions that are suspended in a flue gas or in the atmosphere. A variety of instrumental methods are available to measure PM but typically total particulate is measured gravimetrically using Teflon, glass fibre or quartz filter papers. Size-segregated PM is a useful indicator of adverse health impacts as smaller particles are more easily inhaled than larger particles and penetrate further into the lungs. PM is classified into three categories from an air quality and emissions perspective; particles smaller than 10 µm (PM_{10}), 2.5 µm ($PM_{2.5}$) and 1.0 µm (PM_1). $PM_{2.5}$ is defined as particles which pass through a size-selective inlet with a 50% efficiency cut-off at 2.5 µm aerodynamic diameter (BS EN ISO 23210:2009). Studies have shown that combustion generated soot particles are in the most part below $PM_{2.5}$ and even PM_1 (Nussbaumer, 2003). The residential combustion category accounted for 52% of $PM_{2.5}$ emissions in the European Union in 2013 (Guevara, 2016).

Biomass PM is a mixture of ash and soot with adsorbed organic species such as polycyclic aromatic hydrocarbons (PAH). Soot contains organic carbon (OC) and black carbon (BC), also referred to as elemental carbon (EC). OC, EC and BC are measured by thermal-optical methods and play an important role in aerosol-climate interactions. The particles are most often internally mixed with a core of black carbon and organics adsorbed to the surface (Reid et al., 2005b). More efficient burning of biomass, such as in automated pellet boilers, leads to higher relative levels of inorganics such as KCl in the particulate matter (see section 2.2.1.3). However, uncontrolled and inefficient burning, such as in log stoves, leads to higher levels of organics in the aerosol.

2.2.1.1. Organic Carbon and Brown Carbon

Biomass OC aerosols are a highly complex mixture of thousands of species (Allan et al., 2010) and comprise 50-70% of the mass of $PM_{2.5}$ (Hays et al., 2002). OC is part of the overall organic aerosol mass (OA) also known as organic matter (OM). The typical ratio of OM:OC is 1.6 to

2.1 (Turpin and Lim, 2001). Organic aerosols may be categorised as either primary organic aerosol (POA) or secondary organic aerosol (SOA). The emission of OA is strongly dependent on the burning conditions and phase of combustion, as well as the fuel properties (Weimer et al., 2008). However, emissions factors in the order of 4 g kg^{-1} have been reported from RSF use (Saud et al., 2012).

Ageing and SOA formation

After emission to the atmosphere, the size and morphology of wood smoke aerosol particles increases and there is a change in composition (Cahill, 2010) (see section 2.7). Aerosol mass spectrometry studies have observed a change in the ratio of mass fragments m/z 60 and m/z 44. The former has been associated with $C_2H_4O_2^+$ and anhydrosugars and is a marker of biomass burning (see appendix I). Ageing causes a reduction in this mass fragment due to oxidation of POA. Mass fragment 44 (CO_2^+) is associated with aged OA and SOA and has been correlated with changing particle physical and optical properties. Therefore the ratio of m/z 44 to m/z 60 increases with ageing and increased SOA formation (Grieshop et al., 2009a, Heringa et al., 2011, Lack et al., 2013, Gilardoni et al., 2016).

SOA are formed as gas phase volatile organic compounds (VOCs) undergo chemical transformations to less volatile compounds, before condensing and nucleating and becoming part of the solid particulate phase (Seinfeld and Pandis, 2006). It follows that POA are defined as the organic vapour compounds which are present in the hot flue gas of stoves and boilers, which have not yet condensed to the particulate phase. However, distinguishing between POA and SOA is complicated by the fact that organic vapours can form part of an internally mixed soot particle and therefore be considered primary (Reid et al., 2005b, Seinfeld and Pandis, 2006).

SOA can substantially increase the total particle emissions from RSF combustion, with ratios of SOA:POA of 1.5-6.0 being reported (Saleh et al., 2013, Grieshop et al., 2009b). Aging of wood smoke produces an increase in PM mass by a factor of 3-7 when SOA is included (Bruns et al., 2016). Other mass enhancement factors for biomass burning have been reported at 1.8-3.0 (Bian et al., 2017), 1.42 ± 0.36 (Ortega et al., 2013) and 4.1 ± 1.4 (Heringa et al., 2011). Residential wood combustion is therefore an important contributor to ambient OA concentrations in many areas of the world and there is a need to better understand wood burning SOA formation (Hallquist et al., 2009).

The formation mechanisms of SOA are complex and dependent on the VOC mix, meteorological conditions and co-emitted species such as NO_x. Details of formation mechanisms are described elsewhere (Dusek, 2000, Gelencser, 2004, Seinfeld and Pandis, 2006, Yee et al., 2013). Briefly, emitted VOCs undergo oxidation through reactions with OH,

NO_3 and O_3 radicals produced by photolysis (see chapter 2.6.3) (Grieshop et al., 2009b). The semi-volatile oxidation products then undergo condensation and nucleation into the particle phase. Key aromatic precursor species include benzene, toluene and xylene (BTX) and BTX with methyl- and ethyl- substituted groups. The key compounds present in the SOA formed from these species are given in Forstner et al. (1997) and include the predominant species 2,4-dimethylphenol, 2,5-furandione, 2-furaldehyde, benzaldehyde, benzoic acid and 2-methyl-4-nitrophenol. Nitrophenols are important light-absorbing secondary products formed by OH addition on toluene and reaction with NO_2 via *o*-, *m*-, or *p*-cresol (Mohr et al., 2013, Gelencser, 2004). VOCs emitted from coal combustion include alkenes such as octane and decene which oxidise to heptanal/nonanal and heptanoic acid/nonanoic acid (Gelencser, 2004). For residential wood combustion, oxidation products of phenol, naphthalene and benzene comprise up to 80% of observed SOA (Bruns et al., 2016), with further contributions from lignin pyrolysis products syringol and guaiacol (Yee et al., 2013). In addition, aldehydes may also undergo photooxidation to carboxylic acids.

The gas-particle partitioning of the oxidation products has also been the focus of a great deal of research. Vapour phase products must be high molecular weight ($>C_7$), low volatility and low vapour pressure; ensuring concentrations exceed saturation. This allows the products to condense onto existing primary particles (soot or ash) or to form new particles by nucleation. Both pathways will increase the PM mass, OC:EC ratio and O:C ratio over time, but the latter will also result in increased particle number concentrations. However, gas-particle partitioning is better described by absorption partitioning kinetic models, which take into account temperature, humidity, NO_x, meteorological data and data from smog chamber studies (Seinfeld and Pandis, 2006, Dusek, 2000). Evidence is also presented for aqueous phase SOA formation from wood burning, which is thought to be an important route since WSOC accounts for more than half of wood burning emissions (Gilardoni et al., 2016). The fractional aerosol yield Y is defined as $\Delta M_0/\Delta ROG$ where ΔM_0 is the SOA mass concentration produced from given amount of reactive organic gas reacted. Yields ranged from 25-37% for syringol and 46-50% for guaiacol, to 24-50% for phenol and 30-75% for naphthalene (Yee et al., 2013, Bruns et al., 2016, Chan et al., 2009). The average SOA yields for the wood and coal emissions profiles are 20% and 31% respectively (Dusek, 2000). In the heating season, winter time low temperatures favour partitioning of semi-volatile VOCs into the aerosol phase and stable meteorological conditions favour the accumulation of precursors.

Brown carbon

Brown carbon (BrC) is defined as the light-absorbing fraction of OC aerosols, such as tar-like compounds from combustion (Andreae and Gelencsér, 2006, Alexander et al., 2008). The most strongly absorbing BrC species are extremely low volatility organic compounds (ELVOCs), nitrated phenols and O- and N-heterocyclic PAH (O-PAHs and N-PAHs) (Saleh et al., 2014, Mohr et al., 2013, Lin et al., 2016, Martinsson et al., 2015). ELVOCs consist of 18-20+ carbon atoms which are largely unsaturated and contain nitrogen (Di Lorenzo et al., 2017). Other absorbing components include benzaldehydes, benzoic acids and some carboxylic acids (Gelencser, 2004). Polycarboxylic acids are also a principle component of WSOC from wood burning (Decesari et al., 2001). Brown carbon emissions factors of 1.1 g kg^{-1} and 8.6 g kg^{-1} for anthracite and bituminous coal burning respectively (Sun et al., 2017). BrC PAH emission factors of 0.97 mg kg^{-1} and 1.7 mg kg^{-1} have been reported for pine and peat respectively, with methylpyrenes and methylfluoranthenes dominating (Samburova et al., 2016). Brown carbon has been detected in the form of 50-300 nm spherical 'tar balls' which are emitted in high numbers from smouldering combustion of biomass and account for a significant proportion of anthropogenic carbonaceous aerosol emissions (Chakrabarty et al., 2010, USEPA, 2012). Hence BrC plays a significant role in the global climate system and accounts for 19% of absorption by anthropogenic aerosols (Feng et al., 2013). Brown carbon absorbs strongly in the low visible (blue) and near-UV wavelengths (~ 380-450 nm), which is significant as up to 40% of solar irradiance is found between 400 nm and 600 nm wavelengths (Sun et al., 2007, Lin et al., 2016). Pandey et al. (2016) found that the organic fraction of PM can contribute as much as 45% of visible light absorption by biomass particulate.

2.2.1.2. Black Carbon and Elemental Carbon

Black carbon (BC) has been the focus of a great deal of aerosol research in recent years (Lamarque et al., 2010, Myhre et al., 2013, Zha et al., 2014, Reid et al., 2005a, Reid et al., 2005b). An in-depth review of BC sources and impacts was carried out by Bond et al. (2013). Black carbon is characterised by strong absorbance of visible light, insolubility in water and an aggregate appearance of carbon spherules (Petzold et al., 2013). An estimated 5-20% of biomass PM consists of elemental carbon (Naeher et al., 2007). The category "residential-commercial combustion" was estimated as the largest anthropogenic source of BC emissions in 2005 by UNEP and WMO (2011), at 2.7 Mt yr^{-1}. Bond et al. (2013) reported a BC emissions factor of 1.09 g kg^{-1} for a domestic wood boiler.

The definitions of black, elemental, brown and organic carbon are dependent on the method used to quantify them (Lack et al., 2014). The elemental carbon (EC) definition refers to the carbonaceous fraction of an aerosol which is thermally stable and there is less emphasis on light absorption properties. In contrast, refractory black carbon (rBC) is measured using only optical methods such as laser induced incandescence (LII) with a single particle soot photometer (SP^2). Light absorbing carbon (LAC) is the sum of BC and BrC and total carbon (TC) is the sum of

OC and EC. The NAEI database also includes black smoke (BS) which was measured in ambient air across the UK Automatic Urban and Rural Network (AURN) up until the year 2008/9. Black smoke is measured in accordance with BS 1747-11: 1993, also known as ISO 9835: 1993, and is defined as *strongly light-absorbing particulate material suspended in the ambient atmosphere*. BS is measured on PM collected on filters (typically cellulose) with minimum pore size 0.1 µm using a smoke stain reflectometer. In 2008, the black smoke samplers were replaced with aethalometers which measure BC on quartz filters (Butterfield et al., 2009).

Thermal and thermal-optical determination of EC, BC and OC is usually carried out on a particulate sample collected on a high temperature filter (quartz). The samples are then heated according to a specific program which features a number of temperature stages in different atmospheres. The objective is to remove the volatile OC fraction without leaving OC charring artefacts which could be mistaken for EC, before fully oxidising the EC at a temperature greater than 470°C (Petzold et al., 2013, Lack et al., 2014). The exact temperature programme used for the analysis is dependent on the choice of protocol. The most commonly used protocols are European Supersites for Atmospheric Aerosol Research (EUSARR), National Institute for Occupational Safety and Health (NIOSH) Method 5040 and Interagency Monitoring for Protected Visual Environments (IMPROVE) protocols. An example is given in Figure 2-1.

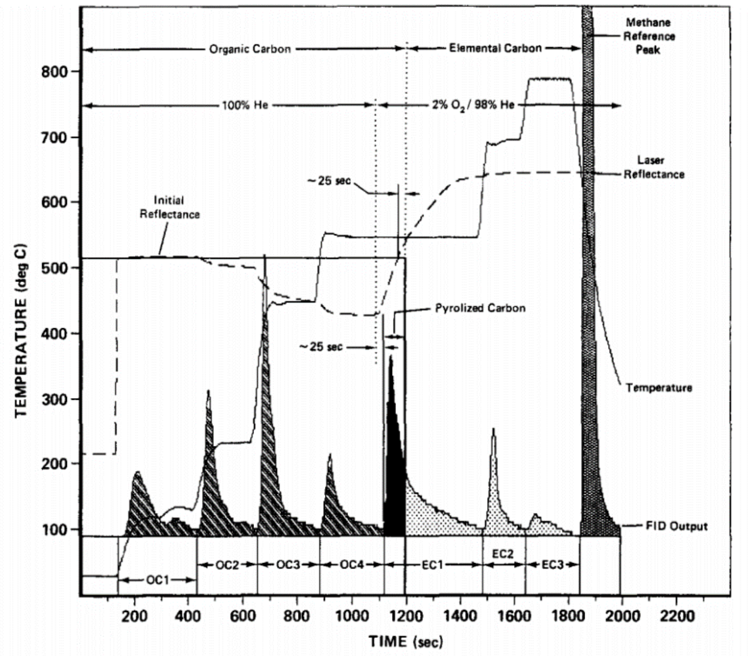


Figure 2-1. Example of a thermogram from thermal-optical analysis of EC and OC content. Source: (Chow et al., 1993)

A number of other measurement options are available including photoacoustic spectrometry, aethalometers, reflectometers, laser-induced incandescence (LII) and Raman spectroscopy. The latter is a highly accurate measure of graphitic carbon (Gelencser, 2004).

As described in Chapters 3 and 5, EC has been measured in this work using a thermogravimetric analyser (TGA). One source of uncertainty in this method is that charring of the OC fraction may occur during pyrolysis, leading to an overestimate of EC. An optical correction is applied using a laser in thermal-optical measurements (Chow et al., 1993, US EPA, 2012). Hence thermal-optical methods may be more accurate than the TGA method. However, they are limited by soot loadings on the filters, whereby high soot masses can restrict light attenuation through the filter (Schmid et al., 2001). Thermal-optical analysis using the Sunset Laboratories analyser is limited by EC particle loadings of ~60 µg cm^{-2} and OC loadings of 400 µg cm^{-2}. In chapters 4-6, the dilution tunnel was not yet installed so the majority of EC loadings were above the 60 µg cm^{-2} limit, reaching up to 268 µg cm^{-2}. Glass fibre filters were also used in the early work, which have a lower melting temperature and must be subject to a different thermal programme. Therefore, the simplified TGA method was used as an estimate of EC/OC based on volatility. Similar methods have been used by (Fermo et al., 2006) and (Huang et al., 2006). Other potential sources of error in thermal analysis techniques include the catalytic effects of metals and metal oxides such as potassium (see section 2.2.1.3) and interferences with other non-carbonaceous components and with the filter matrix (Bond et al., 2013). However, a disadvantage of refractory BC measurements (eg. SP2) is the particle size range for detection, which is not the case for the TGA method. The range for incandescence is 70-500 nm for the SP2 (Slowik et al., 2007). There is also a difference in EC/OC determination between source emissions measurements and ambient air measurements. Fresh PM sampled during emissions testing will contain higher EC and OC concentrations and lower carbonate carbon than ambient PM (Chow et al., 1993, Schmid et al., 2001, Andreae and Gelencser, 2006).

There is a need for reduced uncertainty in the estimation of EC/OC within RSF PM samples, as any error is propagated with errors in the $PM_{2.5}$ sampling method, as well as with natural variations in EC/OC with fuel type, appliance type and operating conditions. Kupiainen and Klimont (2007) found that the share of BC and OC within PM ranged from 5-20% and 37-52% respectively for wood burning stoves. The OC/PM fraction for wood burning fireplaces varied more considerably from 45-75%. The combined error was found to cause an uncertainty of -30% to +17% in BC emissions estimates and -10% to +23% in OC emissions in Europe, compared to the central RAINS model estimates.

2.2.1.3. Inorganics and ash

Ash constitutes as much as 5-10% of dry mass of some biomass fuels such as agricultural residues. When the fuel is combusted, many of the more volatile metals are released which then cool and condense into aerosols. The fly ash contains significant amounts of K, Ca, Na and Zn with lesser amounts of Mn, Mg, Fe, Al, S, P and Cl (Wiinikka et al., 2007). PM from some feedstocks such as contaminated land-grown biomass and waste wood may also contain small quantities of As and Pb. Coal tends to have more Al, Fe and Ti than biomass which is higher in Si, K and Ca (Demirbas, 2004). Potassium plays perhaps the most significant role in inorganic aerosol formation (Jones et al., 2014).

Salt particles such as KCl and K_2SO_4 are present in varying proportions in biomass smoke, but dominate the organic ash fraction of particulate matter. PM sampled from larger automated biomass boilers may be proportionally higher in salt particles than PM sampled from small batch-fed wood stoves (Weimer et al., 2008). This is due to the high organic content of wood stove PM which is a direct result of the poor burning conditions. K has been shown to be one of the most abundant volatile elements in biomass smoke, with emissions factors of 27 mg kg^{-1} being reported (Hedberg et al., 2002). The same study observed maximum Cl emissions factors of 10.6 mg kg^{-1} and found that wood burning $PM_{2.5}$ had highly different elemental composition to other sources of $PM_{2.5}$ such as road dust.

In general, the fine particulates from biomass combustion are generally formed by condensation of volatile vapours. In the case of KCl, the salt can form aerosol either by reaction with SO_2 to form a sulphate or nucleation to form a solid KCl particle (Zeuthen, 2007):

$$2\mathrm{KCl}_{(g)} + \mathrm{SO_2}_{(g)} + \mathrm{H_2O}_{(g)} + 1/2\mathrm{O_2}_{(g)} \xrightarrow{\text{high temperature}} \mathrm{K_2SO_4}_{(g)} + 2\mathrm{HCl}_{(g)}$$

$$\mathrm{KCl}_{(g)} \xrightarrow[\text{on } \mathrm{K_2SO_4} \text{ seeds during cooling}]{\text{heterogeneous nucleation}} \mathrm{KCl}_{(s)}$$

In addition to KCl, inorganic ash PM may contain other alkali salts of potassium or sodium sulphates, phosphates and carbonates (Bølling et al., 2009). Agricultural and other non-woody biomass fuels may have a higher phosphorous content compared to heartwood (Porbatzki et al., 2011). The theoretical formation, condensation and nucleation of potassium chloride, sulphate and phosphate is complex and highly dependent on temperature in the combustion chamber and flue (Wiinikka et al., 2007). For example, a distinct peak in the amount of KCl salt and K_3PO_4 particles may be observed at temperatures approaching 600°C (Zeuthen, 2007).

2.2.1.4. Soot formation pathways

The routes and mechanisms by which soot is formed from coal and biomass combustion has been described in detail previously. This subchapter presents an overview of current research and knowledge.

Polycyclic Aromatic Compounds (PAC) play a key role in the formation of soot particles, which are primarily EC and have an ‘onion-skin’ appearance of graphitic layers due to the way in which they are formed (Bockhorn, 1994). Three routes have been proposed for soot formation following pyrolysis and combustion of solid fuels, which are summarised in Figure 2-2.

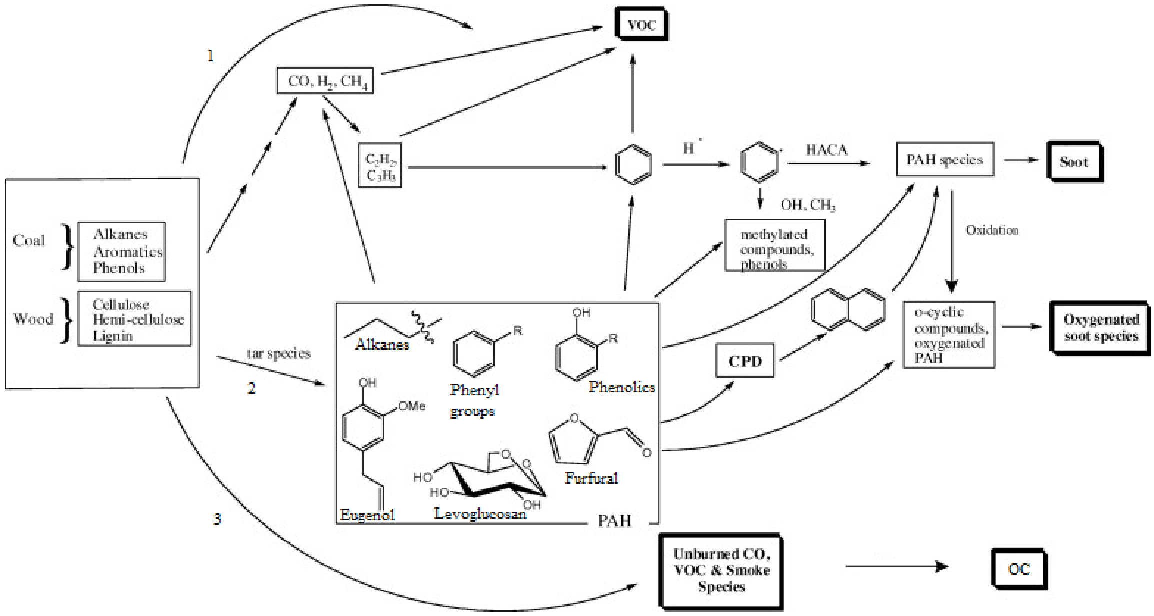


Figure 2-2. Proposed routes for the formation of VOC, PAH and soot. Adapted from (Fitzpatrick et al., 2009) and Fitzpatrick et al. (2007).

In route 1, pyrolysis of biomass cellulose and hemicellulose yields CO and light hydrocarbons which reform to produce larger compounds such as benzene (Fitzpatrick et al., 2007). These molecules then go to form PAH species via the hydrogen-abstraction-acetylene-addition (HACA) mechanism and hence primary soot particles by nucleation and coagulation of larger aromatic structures (Bockhorn, 1994, Kholghy et al., 2016). In reaction route 2, pyrolysis of cellulose yields furfural and pyrolysis of lignin yields anisole, eugenol and phenolic compounds. These then go on to form the reactive intermediate cyclopentadiene (CPD) by the loss of CO at temperatures greater than 700°C (Atiku et al., 2017, Fitzpatrick et al., 2008, Fitzpatrick et al., 2007, Lea-Langton et al., 2015, Khachatryan et al., 2006). Pyrolysis of CPD yields benzene, toluene, indene and naphthalene which can form further soot via the HACA mechanism. Increased oxygen availability has been correlated with suppression of both CPD and PAH formation; indicating that better fuel air control can reduce soot emissions (Fitzpatrick et al., 2008). The route 3 pathway involves slippage of combustion intermediates into the atmosphere which go on to form the OC and BrC fraction of PM. A number of these species are unique to a specific fuel type and hence can be used as tracers, as detailed in section 2.5.

The soot formation mechanism for coal proceeds by a similar pathway to biomass, including the partial pyrolysis of phenols and alkylphenols to CPD and naphthalene (Fitzpatrick et al., 2009). PAH are also involved in coal soot formation although the composition and relative proportions of PAH is different to biomass, with higher concentrations of some species with high sooting tendencies. HACA is a less important route for coal than for biomass because coal has a much higher aromatic carbon content than wood, where aromaticity is limited to the lignin fraction (20-25% dry basis). Pyrolysis of coal yields aliphatics (such as the n-decane model compound) and higher molecular weight PAHs (>3 ring) which may go on to form soot directly (Ross et al., 2011, Fitzpatrick et al., 2009).

Soot formation in fuel rich mixtures can be simplified by the reaction below (Warnatz et al., 2006)

$$\mathrm{C}_n\mathrm{H}_m + k\mathrm{O}_2 \rightarrow 2k\mathrm{CO} + \frac{m}{2}\mathrm{H}_2 + (n-2k)\mathrm{C}_s$$

According to the theoretical thermodynamic equilibrium, solid carbon (C_s) or soot should appear where the ratio C:O is approximately 1. However, the soot limit has been detected as low as 0.4, depending on the fuel type, which indicates that soot formation is controlled by kinetics via oxygen/local mixing conditions and time-temperature history (Mansurov, 2005, Warnatz et al., 2006, Koziński and Saade, 1998). The soot-forming temperature window has been identified as 1000-2000K (Warnatz et al., 2006), but potassium exerts a catalytic effect by lowering the volatilsation temperature of BC (Gelencser, 2004)

2.2.2 CO, NO_x and SO_x

Carbon monoxide is a well-known product of incomplete combustion and is released primarily in the smouldering phase of a fire. Domestic stoves can be a significant source of CO in urban areas, with emissions factors of 130 g kg^{-1} and higher having been recorded (McDonald et al., 2000). On an energy basis, the EEA/EMEP database reports emissions factors of 26 g GJ^{-1} for a natural gas boiler compared to 2000-5000 g GJ^{-1} for wood and coal combustion.

Similarly, NO_x is a regulated pollutant formed during combustion which is both an irritant and can react to form smog (Naeher et al., 2007). There are three primary sources of NO_x; thermal, prompt and fuel. At the low temperatures that are observed in domestic stoves and boilers, fuel-NO_x is the primary source, with NO predominating. During combustion, the nitrogen is released from inorganic nitrate and ammonium ions and proteins (Williams et al., 2012). The NO_x emissions factor depends on the N content of the fuel, which is highly variable between feedstocks (Olanders and Gunners, 1994) but Bond et al. (2013) reports a factor of 3 g kg^{-1}. The fuel-bound nitrogen may be converted to HCN, NH_3, N_2O or NO; depending on the combustion conditions and the ratio of O/N in the fuel (Aho et al., 1993). HCN is highly toxic and N_2O is a potent greenhouse gas, but they are mostly converted during combustion to NH_3 and N_2 respectively (Winter et al., 1999). The phase of combustion also impacts heavily on the emission of nitrogen species. Up to 75% of the fuel nitrogen is released as volatile-nitrogen during the devolatilisation stage; but N_2O has been shown to peak just after the flame is extinguished, indicating that it is destroyed by the flame (Winter et al., 1999).

Most woody biomass fuels have a very low sulphur content (<0.5% dry basis) and hence low SO_x emissions (Demirbas, 2004). However, some coals and lignites can have sulphur contents of up to 11% (though usually much less) and manufactured solid fuels up to 2%. SO_2 emissions factors of 0.1-0.3 g kg^{-1} and 8.8 g kg^{-1} have been reported for wood and coal respectively (Ross et al., 2002). Most sulphur in coal is present as pyritic sulphur (FeS_2) and organic sulphur. The majority of fuel sulphur is converted to SO_2 with lesser amounts of SO_3, H_2S and K_2SO_4 (Glassman et al., 2015). The formation route for SO_2 from pyrite (FeS2) can be either from decomposition at temperatures of around 300°C to FeS and S or oxidation at temperatures of around 500°C to form Fe_2O_3 and S. Sulphuric acid H_2SO_4 also dissociates above 500°C. The elemental sulphur from both reactions is then rapidly oxidised to SO_2 (Wu, 2005).

2.2.3 Organic gaseous emissions

Methane is an intermediate in the conversion of fuel-bound carbon and hydrogen to carbon dioxide and water. In wood burning stoves, CH_4 emissions are a sign of too low combustion temperatures or a lack of available oxygen (Van Loo and Koppejan, 2007). CH_4 concentrations have been measured as high as 30 ppm in the flue gas of log stoves (Olsson et al., 2003); and emission factors of up to 15 g kg^{-1} have been reported (Bond et al., 2013). Globally, the most recent estimate for the contribution of biomass and biofuel burning to methane emissions is 32 to 39 Tg(CH_4) yr^{-1} which includes 14 to 17 Tg(CH_4) yr^{-1} from traditional biofuel burning (Ciais, 2013).

In the UK, a volatile organic compound (VOC) is defined as any organic compound having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101.3 kPa.

Many hundreds of organic compounds and hydrocarbons are released during the devolatilisation stage of combustion. High VOC and tar emissions are associated with the low temperature and poor mixing conditions associated with wood stoves (Williams et al., 2012). A non-methane VOC (NMVOC) emissions factor of 23.6 g kg^{-1} has been reported for wood burning stoves (Bond et al., 2013). VOCs include most organic compounds with less than about 12 C atoms including non-methane hydrocarbons (e.g propane, pentane, hexane, cyclohexane, acetylene, BTX) and oxygenated VOCs (alcohols, aldehydes, ketones, ethers, esters and organic acids). Aldehydes and ketones are oxidation products of VOCs. They contain a carbonyl group and are of the form RCHO and $R_1(CO)R_2$ respectively (Stockwell et al., 2011). Cerqueira et al. (2013) found that there were significant variations in the concentration of aldehydes in wood smoke depending on which wood species were burned and in which phase samples were taken. Formaldehyde emissions as high as 2 g kg^{-1} (dry fuel) were recorded for oak, and as low as 0.5 g kg^{-1} for pine. Similar results were obtained by (Hedberg et al., 2002). 1,3-Butadiene is a VOC listed as a probable carcinogen by the WHO. Emission factors up to 1 g kg^{-1} are reported for wood stoves (Tissari et al., 2007).

Polycyclic aromatic hydrocarbons (PAH) are a group of organic semi-volatile Polycyclic Aromatic Compounds (PAC) and are usually treated separately from other hydrocarbons due to their carcinogenic effects (Van Loo and Koppejan, 2007, Garra et al., 2015). The US EPA has classified 16 PAHs as priority pollutants based on their toxicity and risk of human exposure, which are listed in Table 2-1. Of these, seven are believed to be probable carcinogens (*) (Bojes and Pope, 2007). Two key mechanisms have been proposed to describe the formation of PAH during wood combustion, which are both highly dependent on temperature (Orasche et al., 2013). The first is that breakdown products of lignin condense and form polycyclic aromatic rings. The second is thought to be the major route, which is via cyclopentadienyl radicals from the partial pyrolysis of phenols, again derived from lignin (Fitzpatrick et al., 2009). CO is thermally eliminated from the phenols via the phenoxy radical to form cyclopentadiene; which then reacts and self-combines to form the PAH naphthalene. A PAH emissions factor of 43 mg kg^{-1} has been reported by Lohmann et al. (2006), with naphthalene dominating.

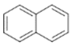
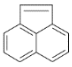
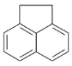
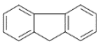
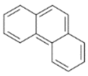
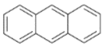
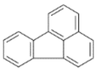
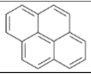
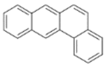
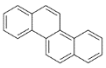
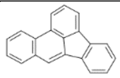
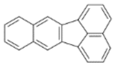
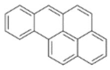
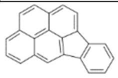
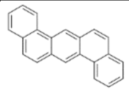
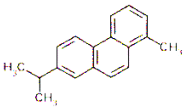
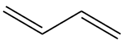
PAH species	Emissions factor (mg kg^{-1})	Probable carcinogen
Naphthalene 	8.2	
Acenaphthylene 	6.6	
Acenaphthene 	0.6	
Fluorene 	2.82	
Phenanthrene 	6.8	
Anthracene 	1.7	
Fluoranthene 	3.5	
Pyrene 	3.2	
Benz[a]anthracene 	0.81	*
Chrysene 	0.74	*
Benzo[b]fluoranthene 	0.33	*
Benzo[k]fluoranthene 	0.23	*
Benzo[a]pyrene 	0.56	*
Indeno[123-c,d]pyrene 	0.38	*
Dibenzo[ah]anthracene 	0.06	*
Benzo[g,h,i]perylene 	0.32	*
ΣPAHs	43	
Retene 	0.02-0.5	
1,3 butadiene 	8-209	*

Table 2-1. Emissions factors for the 16 EPA priority PAH plus retene and 1,3-butadience from domestic wood burning. Expanded from Lohmann et al. (2006).

The burning of coal and wood in the residential sector is a significant source of PAH in the UK (Wenborn et al., 1999, Lee et al., 2005) and abroad (see sections 2.5 and 11.1). Contributions of up to 77% of benzo[a]pyrene have been reported in some communities (Pietrogrande et al., 2015).

2.2.4 Chlorinated emissions

The burning of residential solid fuels including wood and coal is a major contributor to dioxin and furan emissions across Europe (Maasikmets et al., 2016, Quaß et al., 2000). Contributions include 50% in Austria (Hübner et al., 2005), 53% in Estonia (Maasikmets et al., 2016), 6% in Turkey (Saral et al., 2014) and 58% in Portugal (Quina et al., 2011). In addition, coal burning in stoves was found to be a greater source than wood burning in Turkey.

Despite the majority of RSF users burning ‘pure wood’, there are major uncertainties in variation in fuel types used in households and how representative laboratory fuels may be of real-life conditions (Lohmann et al., 2006). For example, many households with a wood burning stove may burn waste paper, card and wood materials, as well as self-sourced wood logs which may not be properly seasoned. The burning of household waste or treated wood, despite being tightly prohibited, has the potential to be a significant source of polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/F) in the UK as it is in other countries. Studies have shown that the burning of treated wood, as well as waste paper and cartons, can increase the emissions of PCDD/Fs by many orders of magnitude (Launhardt et al., 1998, Wasson et al., 2005). However, certain novel feedstocks such as grasses and reeds that are used to produce solid biofuel pellets or briquettes are naturally high in chlorine compared with virgin wood, and dioxin emissions have been found to be proportional to the fuel Cl content (Olsson et al., 2003, Chandrasekaran et al., 2013a). Nevertheless, waste and treated wood remains the leading source of PCDD/Fs within the residential sector. Treatments include copper chromium arsenate (CCA), creosote (coal and wood tars), pentachlorophenol (PCP) and coatings such as varnish and polyvinyl chloride (PVC).

There are over 200 PCDD/F compounds, as shown in Figure 2-3, many of which are toxic, mutagenic, persistent and accumulate in the food chain (Lavric et al., 2004, Zhang et al., 2017).

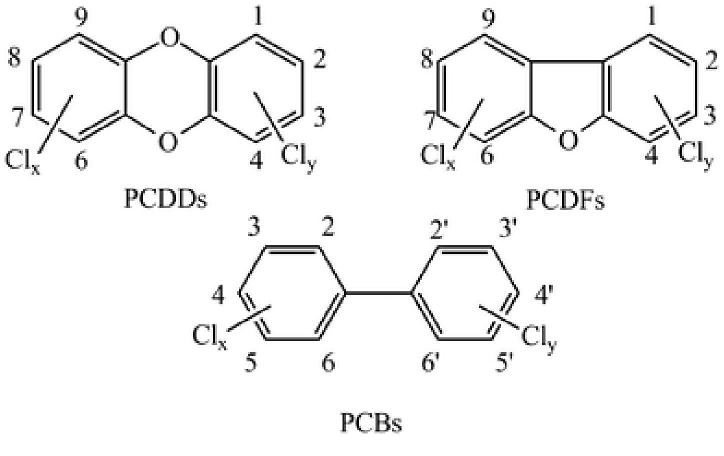


Figure 2-3. Structure of PCDD/Fs and PCBs. Source: (Zhang et al., 2017)

Measurements of dioxins and furans is done by high resolution gas chromatography mass spectrometry (HRGC/HRMS) following the European standard EN 1948-3:2006 or US EPA Method 23. Concentrations and emission factors are reported in units of international toxic equivalent (I-TEQ) which weights the compounds by their WHO-defined toxicity. The formation mechanisms of PCDD/Fs from biomass combustion are discussed in Chagger et al. (1998). Briefly, the two suggested routes are de novo synthesis at temperatures of 300-325°C in the presence of a copper or iron catalyst; and chlorination and aromatisation of aliphatic compounds via molecular chlorine from HCl. In the former, an increased metal release rate has been observed above 400°C and catalytic copper may be present in significant concentrations in certain feedstocks such as CCA-treated wood (Helsen et al., 1999). Chlorine is released as gaseous HCl during both the devolatilisation and smouldering stages of combustion (Chandrasekaran et al., 2013b). HCl is also released from the reaction of KCl with SO_2 to form K_2SO_4 (Zeuthen et al., 2007). Under oxidising conditions, organic compounds react to form phenols and a phenoxy radical, which reacts with HCl to form dioxins and furans (Chandrasekaran et al., 2013b). Other POPs released from residential combustion include polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs) and hexachlorobenze (HCB) (Lee et al., 2005).

2.3 Variation in Emission factors

Emissions factors are influenced by fuel properties including the type, shape and density of the fuel, and by operating conditions including the type of appliance and user error in operating the stove. Emission factors are typically presented as milligrams of pollutant released per kilogram of fuel burned (mg kg^{-1}), or on the basis of fuel energy input (mg MJ^{-1}). Some studies report EFs in mg m^{-3} at a reference oxygen content (typically 11% or 13% O_2) and standard temperature and pressure (STP, 0°C, 1013 mbar). Emissions factors are rarely reported in units of mass per unit delivered or useful energy (mg MJ_d^{-1}), although this is becoming commonplace for emissions testing of cookstoves following the Water Boiling Test protocol (see chapter 9).

2.3.1 Impact of fuel properties on emissions

Coal-based residential solid fuels include anthracite, bituminous coal and brown coal or lignite. Anthracite is the highest rank coal and is considered a smokeless fuel. Bituminous lump coal is often the cheapest fossil fuel RSF and a number of manufacturers in the UK source the fuel from Poland. Lignite is typically burnt in the form of briquettes in stoves and open fires and has been identified as a source of dioxins and other pollution in Ireland, Germany and Eastern Europe (Thuβ et al., 1995). The burning of peat for home heating is also common in parts of

Ireland and Eastern Europe. Peat is essentially a very low grade coal but has a high ash content. Peat is available as air dried peat turf or milled and pressed into briquettes. Manufactured solid fuels (MSF) are commercially available briquettes usually made from carbonaceous residues from the refining industry, or coal which has been heated to over 700°C to remove volatiles (Saral et al., 2014). As a category, MSF consists of 82.5% solid smokeless fuel (SSF), 1.5% coke and 16% petroleum coke in the UK. SSF is defined by the Clean Air Act 1993 as having PM emissions of less than 5 g hour^{-1} and is suitable for use in smoke control areas.

Biomass-based RSFs include agricultural residues, energy crops, charcoal and wood in the form of logs, chips, pellets, briquettes and waste wood. As described in chapter 7, over 90% of wood consumers in the UK burn logs. In recent years, a growing number of briquettes have become available, marketed as *heat logs* or *synthetic logs*. Such briquettes are commonly made from pressed sawdust residues with are thermally extruded to form briquettes. Wood pellets and chips are not typically burned in stoves and fireplaces but are common in larger units (>50 kW) and more modern single house boiler systems. According to the Domestic Wood Use Survey (DECC, 2016), the second most commonly used type of wood fuel is waste wood (22% of users). The burning of waste is generally prohibited in the UK under the Environmental Permitting Regulations, although exemptions apply such as the burning of untreated wood and garden residues. Environmental Waste Exemption U4 allows the burning of plant tissue, vegetable waste, bark, cork, untreated sawdust and wooden packaging (usually wood pallets) in appliances <400 kW for heat and power. The burning of municipal solid waste (including plastics, rubber) and treated wood is prohibited. Coatings, preservatives and glues found in treated wood products can release a number of toxins including POPs and heavy metals (see section 2.4).

The properties of biofuels are substantially different to those of fossil fuels, as shown in Table 2-2. As the table shows, biomass has a significantly lower carbon content and a much higher oxygen and water content, which means it has a lower gross calorific value (GCV) or higher heating value (HHV). This means that more of the fuel must be burned for the same delivered energy output, which is something that is not accounted for by using emissions factors with units of g kg^{-1}.

Fuel sample	Coal	Wood (oak)	Straw (wheat)	Generic Biomass
Ultimate analysis:				
C	81.5	50	41.8	
H	4	6	5.5	
N	1.2	0.3	0.7	
S	3	–	–	
Cl	–	–	1.5	
O (diff.)	3.3	42.4	35.5	
Proximate analysis:				
Moisture (% ar)	4.8	6.5	7.3	
Volatiles (% db)	2.5	78.6	64	
Fixed carbon (% db)	43.6	21.5	23.4	
Ash (% db)	8.3	0.5	12.7	
General properties:				
Fuel density (kg m^{-3})	~1300			~500
Particle size	~100 µm			~3 mm
C content (wt% db)	65–85			42–54
O content (wt% db)	2–15			35–45
S content (wt% db)	0.5–7.5			Max 0.5
SiO_2 (wt% ash db)	40–60			23–49
K_2O (wt% ash db)	2–6			4–48
Al_2O_3 (wt% ash db)	15–25			2.4–9.5
Fe_2O_3 (wt% ash db)	8–18			1.5–8.5
Ignition T (K)	490–595			418–426
HHV (MJ kg^{-1})	23–28			14–21

ar – As received basis; db – Dry basis

Table 2-2. Comparison of typical coal and biomass properties. Adapted from Demirbaş (2003) and Demirbas (2004).

Coal is has a complex three dimensional structure of aromatic rings (benzene-, naphalene-) which are bridged by aliphatic chains containing hydroxyl groups (Levine et al., 1982). Some typical properties of commonly used coal and peat in the residential sector are presented in Table 2-3.

	Age (million years)	Carbon content (%)	Bulk density (kg m^{-3})
Anthracite	350+	86-98%	800-929
Bituminous coal	100-300	46-86%	673-913
Lignite	60	46-60%	641-865
Peat	<50	<60%	1000

Table 2-3. Typical properties of RSF coals. Adapted from (Speight, 2012)

Some coals have a high reactivity due to their porous nature, high surface area (>100 m^2 g^{-1}) and high oxygen content (up to 20% for low rank coals). Peat is characterised by a low carbon content and a moisture content of over 75%. It can also contain a relatively high amount of nitrogen compared to other fuels at up to 2%, and has been found to have higher emissions factors than traditional biomass fuel (Iinuma et al., 2007). Among the largest sources of peat are Finland, Ireland and Indonesia.

Wood fuel can be broken down into two key types; softwoods (gymnosperms) and hardwoods (angiosperms). The latter are more slow growing and have a different composition of cellulose, hemicellulose and lignin to the former. The structure of these polymers are shown in Figure 2-4. Cellulose is a polymer made up of a chain of C6 sugars, mostly D-glucose, linked by β-1,4-glycosidic bonds. Hemicellulose is a heteropolysaccharide and is made up of C5 sugars, such as xylose, mannose and galactose, present in branched chains. In contrast, lignin is made up of highly cross-linked aromatic polymers; mainly *p*-Coumaryl, coniferyl and sinapyl alcohols. Gymnosperm lignin consists mainly of coniferyl alcohol derivatives (guaiacyl- type) and angiosperm lignin consists mainly of sinapyl alchol derivatives (syringyl- type). Coumaryl alcohol is a precursor of anisyl- type lignin which is dominant in herbaceous biomasses (Nolte et al., 2001). Lignins are complex polymers that provide the structural rigidity of biomass. Typical cellulose contents of hardwoods and softwoods are 38-51% and 33-42% respectively, whereas typical lignin contents are 21-31% and 27-32% respectively (Rovio et al., 2008). The thermal breakdown temperatures of cellulose, hemicellulose and lignin are 315-400°C, 220-315°C and 160-900°C (Yang et al., 2007).

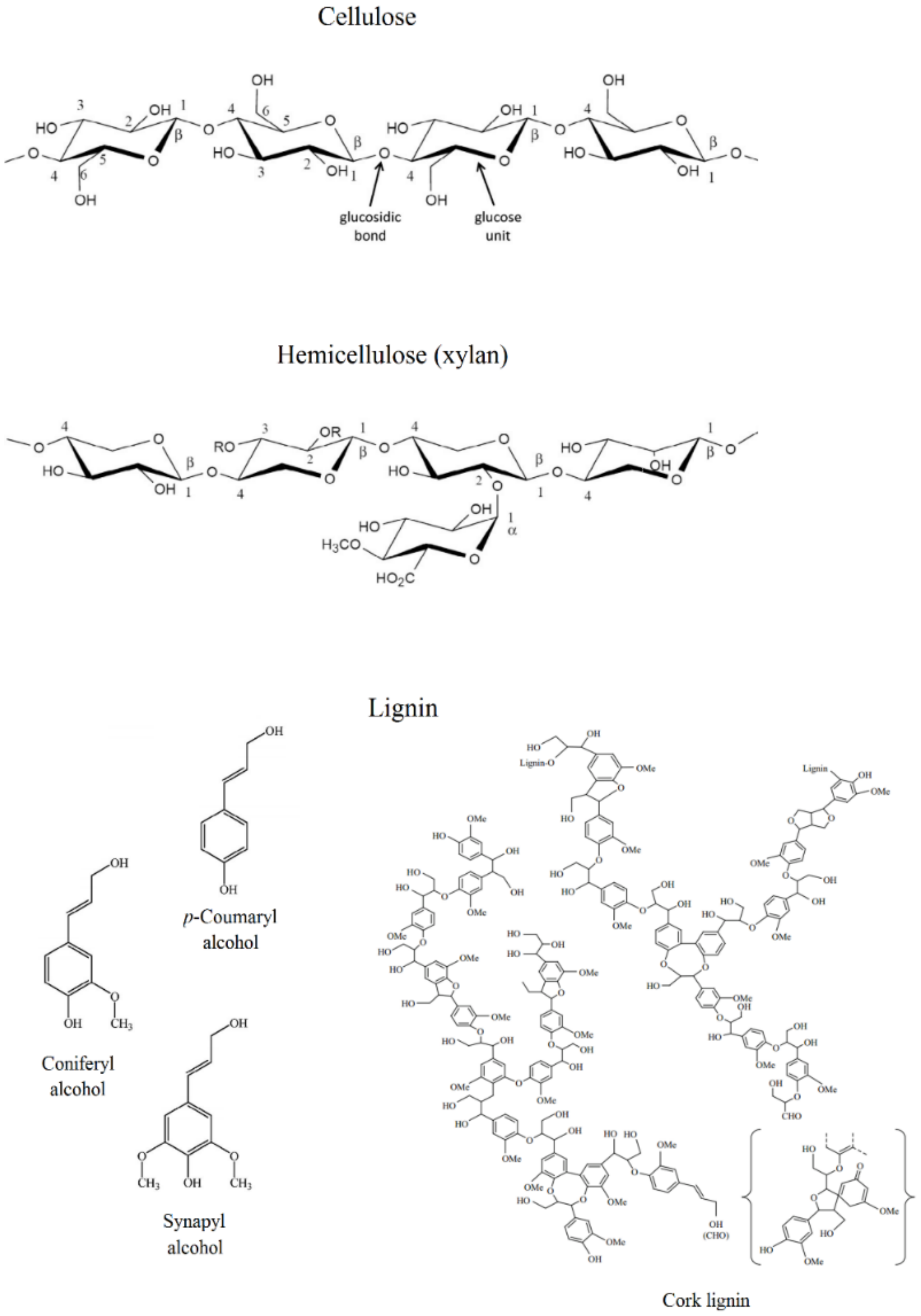


Figure 2-4. Structure of cellulose, hemicellulose and lignin. Adapted from (Anca-Couce, 2016) and (Chen, 2014)

The UK National Atmospheric Emissions Inventory (NAEI) emissions factor database lists 8 solid fuels under the category 1.A.4.bi *Residential stationary combustion*, which are listed in table 2-4. The NAEI is regularly updated and improved as new data become available and the factors presented here are correct for the year 2014 (accessed January 2017). See Chapter 3.9.

Abr	Unit	Anthra-cite	Char-coal	Coal	Coke	Peat	Pet Coke	SSF	Wood
CO_2	g kg^{-1}	878		719	859	370	891	790	
CH_4	g kg^{-1}	2.00	6.00	15.70	5.80	3.84	0.34	5.80	3.69
NO_x	g kg^{-1}	4.37	3.00	3.56	3.99	0.62	3.42	3.79	0.88
CO	g kg^{-1}	158.5	210.0	140.2	144.8	69.5	2.3	137.5	53.2
NMVOC	g kg^{-1}	1.70	3.00	14.00	4.90	7.07	4.90	4.90	7.07
SO_2	g kg^{-1}	14.4	0.11	25.9	14.4	0.11	142.4	16.0	0.11
N_2O	g kg^{-1}	0.14	0.03	0.12	0.12	0.02	0.02	0.12	0.05
NH_3	g kg^{-1}	0.99		0.99	0.99				0.99
PM_{10}	g kg^{-1}	1.87	7.90	9.29	1.71	7.90	3.05	1.62	8.24
$PM_{2.5}$	g kg^{-1}	1.13	7.69	9.15	1.68	7.69	3.00	1.60	7.69
BS	g kg^{-1}	5.6	1.00	40.0	5.60	1.00	0.25	5.60	1.00
As	mg kg^{-1}	0.47	0.03	0.47	0.47	0.03	0.92	0.47	0.03
Br	mg kg^{-1}	1.32	0.01	1.32		0.01	0.14		0.01
Cd	mg kg^{-1}	0.03	0.08	0.03	0.03	0.08	0.30	0.03	0.08
Ca	mg kg^{-1}	53.4	9.5	523.3		9.5			9.5
Cr	mg kg^{-1}	0.90	0.90	0.90	0.90	0.90	3.14	0.90	0.90
Cu	mg kg^{-1}	0.21	0.10	0.21	0.21	0.10	1.11	0.21	0.10
Pb	mg kg^{-1}	2.85	0.91	2.85	2.85	0.91	0.78	2.85	0.91
Mg	mg kg^{-1}	17.3	1.6	169.8		1.6			1.6
Mn	mg kg^{-1}								
Hg	mg kg^{-1}	0.11	0.03	0.11	0.11	0.03	0.36	0.11	0.03
Ni	mg kg^{-1}	0.46	0.98	0.46	0.46	0.98	258.65	0.46	0.98
K	mg kg^{-1}	14.3	44.5	140.2		44.5			44.5
Se	mg kg^{-1}	0.42	0.09	0.42	0.42	0.09	1.71	0.42	0.09
Na	mg kg^{-1}	17.1	10.5	167.1		10.5			10.5
Sn	mg kg^{-1}	0.14	0.14	0.14		0.14	13.76		0.14
V	mg kg^{-1}	0.11	0.03	0.11	0.11	0.03	682.2	0.11	0.03
Zn	mg kg^{-1}	2.49	1.25	2.49	2.49	1.25	5.38	2.49	1.25
AcN	mg kg^{-1}	0.11	3.10	5.24	0.11	3.10	0.11	1.11	3.10
AcNy	mg kg^{-1}	0.15	78.60	7.15	0.15	78.60	0.15	1.52	78.60
AnT	mg kg^{-1}	0.04	6.50	1.85	0.04	6.50	0.04	0.39	6.50
B(a)A	mg kg^{-1}	0.04	5.00	1.79	0.04	5.00	0.04	0.38	5.00
Benzene	mg kg^{-1}	75.4	107.0	617.9	217.4	252.3		217.4	252.3
B(a)P	mg kg^{-1}	0.03	1.30	1.55	0.03	1.30	0.03	0.33	1.30
B(b)F	mg kg^{-1}	0.001	1.50	0.07	0.001	1.50	0.001	0.01	1.50
B(ghi)P	mg kg^{-1}	0.02	1.00	0.82	0.02	1.00	0.02	0.17	1.00
B(k)F	mg kg^{-1}	0.0005	0.50	0.02	0.0005	0.50	0.0005	0.0049	0.50
Chry	mg kg^{-1}	0.03	3.80	1.67	0.03	3.80	0.03	0.36	3.80
Db(ah)A	mg kg^{-1}	0.04	0.02	1.79	0.04	0.02	0.04	0.38	0.02
FlA	mg kg^{-1}	0.06	6.90	2.98	0.06	6.90	0.06	0.63	6.90
Fl	mg kg^{-1}	0.33	8.30	16.21	0.33	8.30	0.33	3.45	8.30
I(123cd)P	mg kg^{-1}	0.02	0.09	1.19	0.02	0.09	0.02	0.25	0.09
Nap	mg kg^{-1}	2.55	90.30	123.34	2.55	90.30	2.55	26.23	90.30
Phen	mg kg^{-1}	0.14	24.40	6.56	0.14	24.40	0.14	1.39	24.40
Pyr	mg kg^{-1}	0.06	7.30	2.98	0.06	7.30	0.06	0.63	7.30
PCBs	µg kg^{-1}	3.60	1.99	3.60	3.60	1.99		3.60	1.99
PCDD/F	ngI-TEQ kg^{-1}	27.5		24.1	23.8		28.6	24.1	11.9
HCB	ng kg^{-1}			18.7					74.5
HCl	mg kg^{-1}	2350		2350					
HF	mg kg^{-1}	90		90					

Table 2-4. RSF emissions factors for different fuels listed in the NAEI database 2014. Source: NAEI (http://naei.defra.gov.uk/)

The table shows a substantial variation in emission factors between fuel types, as a result of the different compositions of the fuels. The key properties affecting emissions are the volatiles content and composition, which are involved in soot formation, and the levels of N, S, K and Cl in the fuel (Jones et al., 2014, Williams et al., 2012). It is well known that the elemental composition of biomass affects the combustion properties of the fuels, with slagging and fouling problems having been encountered in high temperature large scale systems (Ryu et al., 2006). The alkali index and relative acid to base ratio are useful indicators of the slagging propensity of biomass, as is the silica content which is high in herbaceous biomasses. Emissions of CO, CH_4 and other organics is influenced by the temperature of the bed, calorific value, shape factors, and particle density (Yang et al., 2005). Smaller particle size results in a higher burn rate due to higher surface area and more rapid devolatilisation, which causes higher EC and PM emissions. Morán et al. (2015) measured the emissions from a number of agricultural residues against traditional white wood pellets. The study found that HCl and NO_x emissions were highest for rye straw due to high fuel Cl and N content; concluding that only high quality wood fuels can be recommended due to forthcoming CO emissions restrictions from the Ecodesign Directive. (Chandrasekaran et al., 2013b) also found emissions of PM, NO_x, CO, SO_2 and PCDD/Fs to be higher from herbaceous biomass than woody biomass. Fuel properties also influence the size and morphology of emitted particulate matter (Chakrabarty et al., 2006), as discussed in section 2.7. Further discussion of the variation in emissions factors is given in section 2.3.3.

2.3.2 Impact of combustion conditions on emissions

Appliance type and design has a significant effect on emissions. More modern well-desgined stoves offer better fuel-air mixing and higher efficiencies, together with lower emissions than traditional cast-iron heating stoves. Chandrasekaran et al., (2013b) found that appliance operation has a greater influence on emissions than fuel type.

Solid biofuels also have a much higher volatile content than coal and therefore show distinct phases of combustion; as volatiles are burned before the remaining fixed carbon. It has been shown that emissions factors vary substantially depending on in which phase of combustion the measurements are taken (Tissari et al., 2008). Weimer et al. (2008) found that there were greater differences in emissions factors between the different combustion phases of the same fuel than between different fuels in the same phase. Exposure studies have also shown that the body reacts differently to biomass smoke depending on the phase of combustion (Stockfelt et al., 2012).

Ignition phase

Start-up phase emissions are known to be significant from stoves and particularly boilers where low ignition temperatures result in PM emissions equivalent to several hours of operation at nominal load (Win and Persson, 2014). Start-up phase emissions are largely exempt from standard test methods for biomass burning appliances, whereas they are included for vehicular emissions testing. BS EN 13240 necessitates a separate ignition and pre-test period in order to bring the appliance up to temperature following the manufacturer's instructions. Typically a combination of firelighters and kindling (newspaper, small sticks) is used to start the fire although there is considerable variation between operators (Wöhler et al., 2016).

The first stages of combustion are drying and pyrolysis. Small pieces of biomass ignite and larger pieces undergo radiative heating. During heating the moisture in the larger biomass is out-gassed and large quantities of highly volatile organics are released, including aromatics and ethers (Koppmann et al., 2005). During the low temperature phase, the decomposition of hemicellulose and lignin gives rise to methanol, aldehydes and formic and acetic acids. As the temperature increases to over 250°C the vast majority of the fuel is thermally decomposed and aromatic compounds such as benzene, toluene and phenols are emitted (Elsasser et al., 2013). The aromatic content in the biomass smoke is determined by the amount of precursors in the fuel and the flame temperatures. Oxygenated aliphatics are also present but are typically limited to C_1 or C_2 chain lengths due to the high rate coefficients of longer chain alkyl radicals.

Flaming phase

In this phase, the thermal breakdown of the biomass releases volatile hydrocarbons which are then rapidly oxidised in the flame. Koppmann et al. (2005) states that predicting the emission of gaseous compounds from first principles is near impossible due to the complexity of mixing in the flame, cracking and oxidation reactions as well as the inhomogeneity of the fuel. During the flaming phase, gaseous compounds are oxidised by reactions with radicals which are similar to the VOC chemistry in the troposphere (Weimer et al., 2008). In the case of domestic stoves, the excess air ratio can be as high as 200% and the reactions are initiated by OH radicals. Tissari et al. (2009) found that as much as 90% of PM emissions are emitted during the flaming phase.

Smouldering phase

Flameless smouldering combustion consists of the solid phase oxidation of fixed carbon or char, which is typically 20-30% of the as received fuel for biomass (Table 2-2). The formation rate of VOCs during this phase is relatively low but there is no flame for full oxidation. The major emissions during this phase are CO where there is a limited oxygen supply to the bed. Elsasser et al. (2013) also found high levels of m/z 44 compounds during this phase which it is thought could be a result of CO_2 from decarboxylation of organic acids, or oxidation of black carbon and OA (Alfarra et al., 2007).

In the literature, smouldering burning of biomass is often referred to for open burning and wildfires. In this work smouldering is a distinct mode of combustion, rather than a phase within the natural combustion cycle. It is characterised by low combustion efficiencies (MCE) and high emissions of organics, brown carbon and CO (McMeeking et al., 2009). For stoves, the smouldering phase is particularly important at night when operators often close the air dampers on stoves to prolong the heat output, leading to rich combustion and high equivalence ratios. As a result, significant diurnal variations in PM concentrations have been observed in wood burning communities (Ancelet et al., 2014). Increases in OA concentrations of up to 70% observed between the hours of 18:00 and 01:00 (Alfarra et al., 2007) and biomass burning can contribute up to 90% of OA during these hours (Florou et al., 2017). Favez et al. (2009) found that the spectral signature of aerosols in such communities also shows a diurnal pattern, most likely due to brown carbon from wood burning. NO_x and CO reduce at night following at peak in the evening around 20:00 (Sandradewi et al., 2008).

2.3.3 Emissions inventories

A number of emission factor (EF) inventories are used in the different parts of the world to represent RSF combustion. In the UK, the principal emissions factor inventory is the National Atmospheric Emissions Inventory (NAEI) which is regularly updated and improved. In 2003, a report to DEFRA was published which scrutinised NAEI EFs for the residential sector (Hobson et al., 2003). The report found that there were significant differences in the emissions profiles of solid fuel heating appliances which may be a significant source of error in the NAEI data. Current NAEI emissions factors are given in Table 2-4. In addition to the NAEI used in the UK, some of the most widely used inventories in air quality and climate models include the European Monitoring and Evaluation Programme (EMEP), the Intergovernmental Panel on Climate Change Emissions Factor DataBase (IPCC EFDB), the Greenhouse gas - Air pollution Interactions and Synergies (GAINS) and the United States Environmental Protection Agency (USEPA). The differences between these inventories and the implications are discussed in Chapter 7.2. In addition to this, a comprehensive review of RSF emissions factors for stoves and fireplaces has been conducted and an emissions inventory has been developed. The inventory features emissions factors for 110 pollutants for multiple appliance and fuel types from 51 studies. This is a large file and is therefore included as an electronic supplement to this thesis. The average emissions factors for PM, CO and NO_x from the inventory are presented in Figure 2-5.

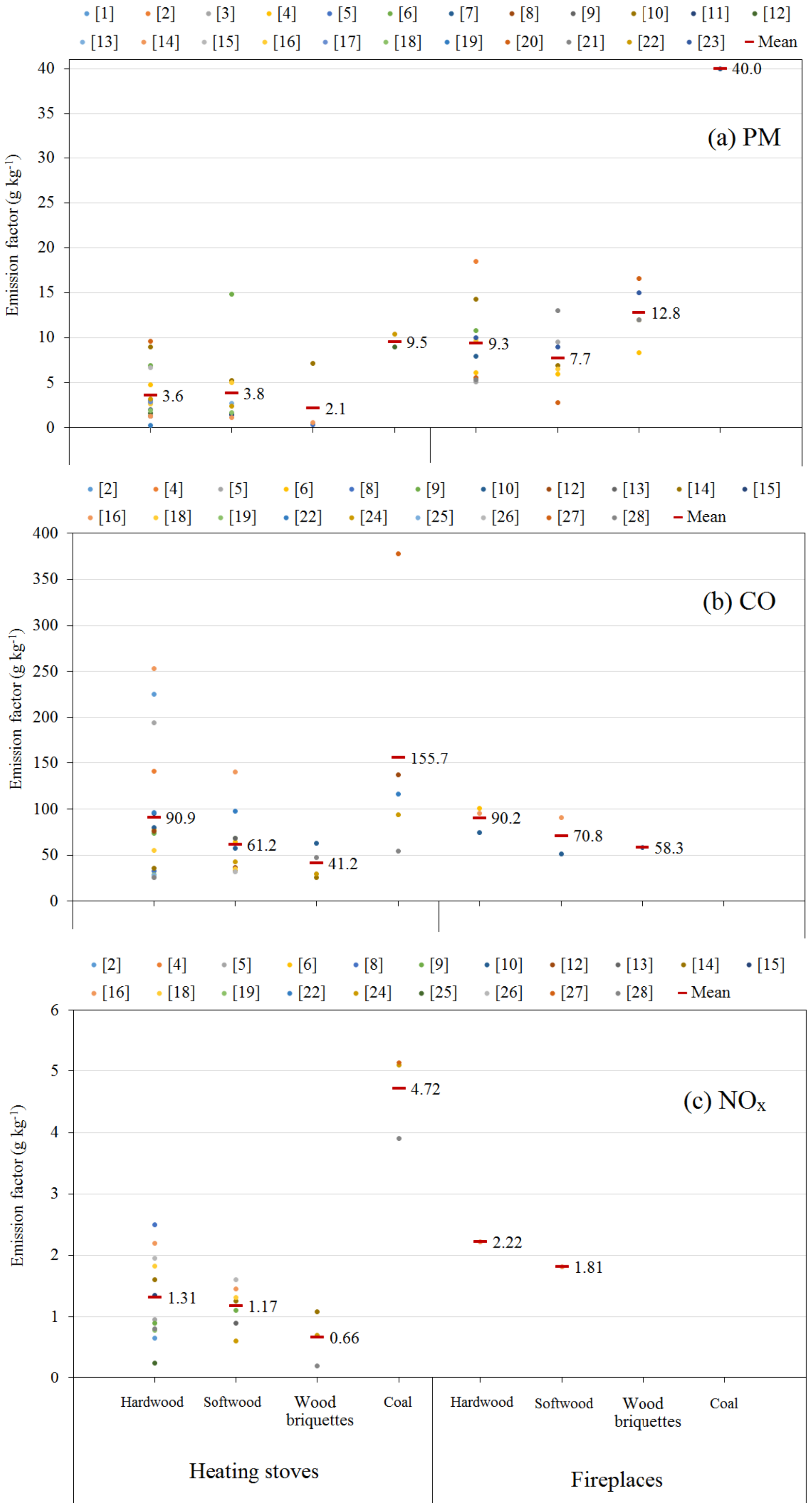


Figure 2-5. Average emissions factors for heating stoves and fireplaces from the literature

[1] Hedberg et al. (2002), $PM_{2.5}$
[2] Larson and Koenig (1994), PM
[3] Schauer et al. (2001), $PM_{2.5}$
[4] McDonald et al. (2000), PM
[5] Johansson et al. (2004)
[6] Evtyugina et al. (2014), Calvo et al. (2015) and Vicente et al. (2015), $PM_{2.5}$
[7] Lee et al. (2005), PM_{10}
[8] Lamberg et al. (2011), $PM_{2.5}$
[9] Tissari et al. (2007), $PM_{2.5}$
[10] Gonçalves et al. (2011), Gonçalves et al. (2012) and Fernandes et al. (2011)
[11] Fine et al. (2004), $PM_{2.5}$
[12] Šyc et al. (2011), PM
[13] Pettersson et al. (2011), PM
[14] Kistler et al. (2012)
[15] Tissari et al. (2008), PM_{10}
[16] Ozgen et al. (2014), PM
[17] Jordan and Seen (2005), PM
[18] Orasche et al. (2012), PM
[19] Tschamber et al. (2016), PM
[20] Gullett et al. (2003), PM
[21] Hildemann et al. (1991), PM
[22] Butcher and Ellenbecker (2012), PM
[23] Dasch et al (1982), PM
[24] Ross et al. (2002), PM
[25] Koyuncu and Pinar (2007)
[26] Reda et al. (2015) and Czech et al. (2016)
[27] Hobson et al. (2003)
[28] Truesdale et al. (1984)

2.4 Air Quality and Health Impacts

The emissions from household solid fuel combustion are known to be hazardous to health and historically this has been the reason for the development of many aspects air quality legislation in developed countries; including smoke control areas, emissions limits and standard test methods for appliances and fuels. Evidence for the impact of RSF burning on air quality is derived using a number of methods which are discussed in section 11.1.

On a global scale, biomass combustion emits more particulate matter and gaseous air pollutants than the combustion of fossil fuels, which is typically done under more controlled conditions (Straif et al., 2013). This is due to large scale use of solid biofuels for cooking in developing countries. More than 3 billion people worldwide rely on biomass fuels for their primary energy supply; and this is projected to stay relatively constant in the future (Anenberg et al., 2013). However, there are large differences in the number of people using solid biofuels for cooking and heating depending on the country of interest, and the rurality of the user within that country. Such wide-scale use of basic and inefficient combustion devices has profound health implications for the populations of developing countries, through exposure to biomass smoke (Anenberg et al., 2013, Naeher et al., 2007, Bølling et al., 2009). The World Health Organisation (WHO, 2013) identified indoor smoke from the combustion of solid fuels as one of the top 10 risks for worldwide burden of disease. It accounts for 2.7% of the global burden of disease and 2-4 million premature deaths per year. In developed countries, emissions from most sources including traffic are reducing but emissions from residential wood combustion are increasing at the detriment of respiratory and cardiovascular health (Sigsgaard et al., 2015). In addition, RSF emissions often have a greater impact than some other pollution sources because they are emitted in urban populated areas at low heights which do not allow sufficient mixing and dilution before exposure (Thuβ et al., 1995). As much as 70% of emitted smoke can re-enter the home and homes of neighbours (Zelikoff et al., 2002). Exposure is also higher in suburban areas where there are greater concentrations of stoves and fireplaces providing solid fuel space heating, rather than gas or electric heating systems (Titos et al., 2017).

Comprehensive reviews of the health effects of emissions from RSF combustion have been carried out previously, finding that exposure to wood smoke causes acute and chronic physiologic responses including lung and heart disease and reduced lung capacity (Sigsgaard et al., 2015, Chafe et al., 2015, Naeher et al., 2007, Kocbach Bølling et al., 2009, Zelikoff et al., 2002). A summary of some the most high impact species is presented in Table 2-5, together with the WHO guideline concentration for ambient air.

Among the greatest exposure concerns are fine particulate ($PM_{2.5}$), PAH, NO_2 and CO. CO and NO_x bind to haemoglobin reducing the oxygen carrying capacity of bloodstream. Indoor CO concentrations over 40 times the WHO limit (Table 2-5) have been reported in wood burning homes (Zelikoff et al., 2002). $PM_{2.5}$ levels have been directly correlated with premature mortality due to cardiopulmonary disorders, and many PAH species are carcinogenic and mutagenic (Bojes and Pope, 2007, Yim and Barrett, 2012). In ISO 7708:1995 *Particle Size Fraction Definitions for Health-Related Sampling*, $PM_{2.5}$ is categorised under the 'high-risk respirable convention'. In addition to the direct effect of $PM_{2.5}$, adsorption of organics to the surface of fine particulates may also act as a carrier for carcinogens deep into the lungs (Allan et al., 2010). The relative lung penetration of different size fractions of RSF PM is shown in Figure 2-6.

Species	2005 WHO Guideline values		Health effects
	Concentration	Time	
Carbon Monoxide CO	10 mg m^{-3*}	8 hour	Binds to haemoglobin reducing oxygen uptake, asphyxiant, relatively long lived
Nitrogen oxides NO_x	For NO_2: 40 µg m^{-3} 200 µg m^{-3}	 Annual 1 hour	Irritant, reacts with hydrocarbons to form O_3. NO_2 is more toxic than NO, exacerbating asthma and bronchitis
Ozone O_3	100 µg m^{-3}	8 hour	Irritant, formed by secondary reactions in photochemical smog
PAH	1 ng $m^{-3\,*}$	Annual	Mutagenic, potent carcinogens
NMVOC	Benzene 5 µg m^{-3} * 1,3-butadiene 2.25µg m^{-3*}	Annual Annual	Varied. Irritant, carcinogenic, mutagenic, teratogenic
Dioxins and furans (PCDD/Fs)	0.1 ng m^{-3**}	6 hours	Carcinogenic, mutagenic, persistent. Liver cell damage, neurotoxicity
$PM_{2.5}$	10 µg m^{-3} 25 µg m^{-3}	Annual 24 hour	Inflammation, irritation, cardiopulmonary disorders. See also ISO 7708:1995
Ammonia NH_3			Extreme concentrations can cause irreversible pulmonary damage but small amounts are unlikely to have severe effects
Sulphur oxides SO_x	20 µg m^{-3} 500 µg m^{-3}	24 hour 10 min	Coughing, aggravation of asthma and bronchitis. Combines with water to form sulfuric acid H_2SO_4 leading to acid rain
Hydrogen chloride (HCl)	60 mg m^{-3**}	30 min	Irritation of the throat and asthma-like symptoms
Heavy metals	Pb 0.5 µg m^{-3*} As 6 ng m^{-3*} Cd 5 ng m^{-3*} Ni 20 ng m^{-3*}	Annual Annual Annual Annual	Kidney damage, foetal abnormalities, bioaccumulation, neurotoxicity

*EU Air Quality Directive 2008/50/EC, for reference
**EU IED Directive 2010/75/EU, for reference

Table 2-5. Guideline concentrations and health effects of RSF pollutants.

Over 90% of RSF PM mass has been found to be in the ultrafine fraction (< 1 µm) (Bari et al., 2011). The health effects of the particulate depend on the composition which is determined by a combination of the appliance type, burning conditions and fuel type. PM_1 from wood burning stoves has been shown to induce cytotoxic, genotoxic and inflammatory responses in cells (Tapanainen et al., 2011, Hannigan et al., 2005). Fine PM is also associated with the highest particle number concentrations which can cause cardiovascular disorders including atherosclerosis (Araujo and Nel, 2009). Particles exhibiting the highest DNA damage were found to contain high levels of PAH, although a link has also been made between PM zinc content and increased toxicity (Dilger et al., 2016).

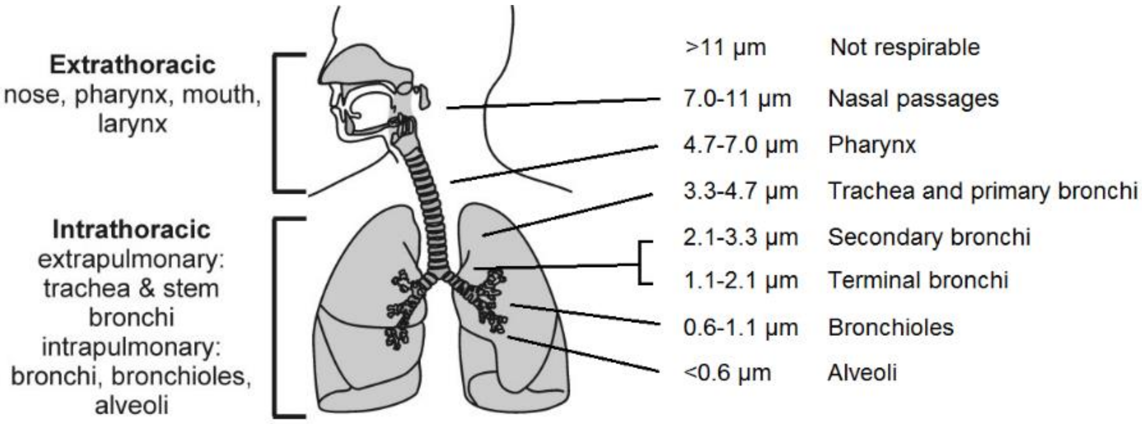


Figure 2-6. Lung penetration of different size fractions of particulate matter. Adapted from (Geiser and Kreyling, 2010) and (Tager, 2012)

It is understood that Zn^{2+} and ZnO promote the formation of reactive oxygen species (ROS) which induce cell oxidative stress and toxicity (Torvela et al., 2014b, Uski et al., 2015). A major constituent of ROS is semiquinone-type radicals (Khachatryan et al., 2006). Wood PM has been found to contain up to 80 times more ROS per unit mass of particles than cigarette and diesel smoke, with low temperature rich conditions being the most conducive (Miljevic et al., 2010). PM from wood heating appliances has been shown to be less cytotoxic than oil-fired heating systems (Kasurinen et al., 2015) but the overall PM emissions are higher, leading to reduced air quality if switch is made from oil to wood (Moshammer et al., 2009). A limited number of studies indicate that PM from herbaceous biomasses incite a more severe genotoxic response that from wood (Kasurinen et al., 2016). The type of appliance and efficiency also impacts on the toxicological properties of biomass PM, whereby PM toxicity reduces with increased efficiency (Uski et al., 2014, Longhin et al., 2016). Tapanainen et al. (2011) found that wood PM from a traditional heater induced a 3-fold higher cell death and DNA damage rate than wood PM from an efficient pellet stove.

PM from bituminous coal has also been linked to lung cancer and cardiovascular diseases (Shao et al., 2016, Junninen et al., 2009, Chafe et al., 2015, Straif et al., 2013). In addition to zinc, iron, cadmium and lead are important components in the oxidative capacity of coal PM (Shao et al., 2013). Combusted-generated iron nanoparticles in the form of magnetite Fe_3O_4 induce oxidative cell damage and have recently been linked with Alzheimer's disease (Maher et al., 2016). Fe emission factors are not included in inventories discussed in section 2.3.3, but the fraction of Fe in coal PM is 4 times greater than biomass PM (Watson et al., 2001). Conversely, the Zn fraction in wood PM is 3 times greater than coal PM. In addition to metals that are naturally present in solid fuels, additional heavy metals may be released such as from the burning of treated and waste wood. Copper chromated arsenate (CCA) has been used as a timber preservative since the 1930's and although strongly prohibited and discouraged, evidence of CCA treated wood burning has been presented across the world. Arsenic concentrations up to 110 ng m^{-3} have been reported in wood burning communities, which is up to 100 times typical background levels (see Table 2-5) (Ancelet et al., 2012). CCA-treated wood burning has also been noted in the US (Maykut et al., 2003), with extreme examples of 300 ng m^{-3} indoor air leading to pathological arsenic exposure with neurological and physical symptoms including seasonal alopecia (Peters et al., 1984). Up to 14% of the arsenic in the raw fuel is emitted into the air during combustion (Wasson et al., 2005).

Soot carbon has been identified as the main transport medium for PAH in ambient air (Fernández et al., 2002). Assuming that all adsorbed PAH are taken up when inhaled, the PAH exposure risk factor can be up to 7 times higher in wood burning communities than background sites (Sarigiannis et al., 2015b). An increased exposure to PAH has been observed in the indoor environments of homes burning wood and coal. Gustafson et al. (2008) found that PAH concentrations were 3-5 times higher than in reference homes, with phenanthrene being the most abundant species but benzo(a)pyrene having the highest cancer potency. Over 95% of benzo(a)pyrene levels in wintertime ambient air have been attributed to domestic wood burning in some communities (Freeman and Cattell, 1990). Jakovljević et al. (2016) recorded an increase in B(a)P, fluoranthene and pyrene concentrations in the heating season in a Croatian village, with an associated 10-fold increase in mutagenicity. During the wood heating season, an average of 44% of total PAHs in ambient air are carcinogenic (Bari et al., 2011), though the composition may change depending on fuel type. Increased PAH emissions have been observed from the burning of treated wood with coal tar creosote (Wenborn et al., 1999). Emitted PAH may also be nitrogenated (N-PAHs) which are potent mutagens (Hannigan et al., 2005). In addition to PAH, other known or suspected carcinogens arising from RSF combustion include benzene, toluene, xylene, 1,3-butadiene, formaldehyde and acetaldehyde. Gustafson et al. (2007) observed indoor air benzene concentrations to be twice and high in homes with wood burners compared to those without.

2.5 Source apportionment and attribution of RSF emissions

Calculation of the contribution of residential solid fuel combustion to ambient PM is complex in urban and suburban atmospheres due to mixing with pollution from other sources. Typical categories used in source apportionment studies include traffic, road dust, brake wear, crustal matter, and industrial sources. With regard to RSF, the majority of source apportionment studies refer to biomass burning (including wildfires) or residential wood combustion. A wide range of methods are used to apportion PM and other emissions to this source, and a description of these methods is given in section 11.1. These include tracer methods such as black carbon, carbon isotopes, levoglucosan, potassium and PAH. Many of these tracers can be combined to create an emissions profile for wood and coal burning, which can be used in models such as positive matrix factorisation (PMF) and chemical mass balance (CMB). A comparison of the source profiles for residential wood and coal combustion are available (Watson et al., 2001).

A comprehensive review of source apportionment studies for RSF was carried out and the results are shown in Table 2-6. As shown in the table, some of the areas most affected by residential wood burning include Tasmania, Australia; Thessaloniki, Greece; the Po Valley, Italy; Hastings and Alexandra, New Zealand; Roveredo, Switzerland; and Libby MT, Rochester NY and Puget Sound WA in the USA. In these areas, the contribution of RWC to ambient air quality has been well documented. The contributions include 95% of $PM_{2.5}$ in Launceston, Tasmania, 96% of OC in the Po Valley, Italy, and 62% of PAH in Seiffen, Germany. In some areas such as the Czech Republic, Ireland, East Germany, and Poland a significant contribution from residential coal burning has been observed. The winter contributions include 70% of PM_{10} in Krakow, 81% of $PM_{2.5}$ in Zonguldak, Turkey, and 43% of OC in Ústí nad Labem, Czech Republic. As a result of the financial crisis in Greece, there has been wide scale uptake of solid fuels for space heating to replace more expensive gas, electric and oil based systems. The health impacts of this can be severe in the wintertime, with increased mortality, chronic bronchitis and respiratory and cardiac admissions (Sarigiannis et al., 2015a, Saraga et al., 2015). Despite the recognised contribution of wood burning to air pollution in certain areas such as Scandinavia and Alpine/mountainous areas, table 2-6 is one of the first compilations showing the global distribution and scale of RSF pollution. The source apportionment studies presented reveal the impact of real-world emissions on ambient air quality. As described in section 2.1, real-world emissions may be significantly higher and more variable than emissions derived under standard laboratory conditions due to user variables (Wöhler et al., 2016). The studies also show the seasonality of RSF emissions. For example, RSF was found to contribute to 28% of OC in the summer in Cork, Ireland, versus 80% in the winter (Kourtchev et al., 2011). From a modelling perspective, there is therefore a need to better quantify RSF activity data and emission factors; both in-situ and under real-world conditions simulated in the laboratory.

Country	City	Species	Season	Class	RSF contr. (%)	Method	Reference
Australia	Huon Valley, Tasmania	$PM_{2.5}$	Winter	Urban/rural	77	PMF	Reisen et al. (2013)
	Launceston	PM_{10}	Winter	Urban	95	^{14}C and levoglucosan	Jordan et al. (2006)
	Brisbane	PM_{10}	Annual	Urban	7	CMB, TTFA and MLR	Chan et al. (1999)
	Griffith University, Brisbane	$PM_{2.5}$	Annual	Suburban	15	CMB, TTFA and MLR	Chan et al. (1999)
Austria	Vienna	OC	Winter	Mixed urban	31-40	Anhydrosugars	Caseiro et al. (2009)
	Vienna	OC	Summer	Mixed urban	5-6	Anhydrosugars	Caseiro et al. (2009)
	Graz	OC	Winter	Mixed urban	38-59	Anhydrosugars	Caseiro et al. (2009)
	Graz	OC	Summer	Mixed urban	8-15	Anhydrosugars	Caseiro et al. (2009)
	Salzburg	OC	Winter	Mixed urban	34-70	Anhydrosugars	Caseiro et al. (2009)
	Salzburg	OC	Summer	Mixed urban	7-10	Anhydrosugars	Caseiro et al. (2009)
	Vienna	PM_{10}	Winter	Mixed urban	7-10	Anhydrosugars	Caseiro et al. (2009)
	Vienna	PM_{10}	Summer	Mixed urban	1-2	Anhydrosugars	Caseiro et al. (2009)
	Graz	PM_{10}	Winter	Mixed urban	12-19	Anhydrosugars	Caseiro et al. (2009)
	Graz	PM_{10}	Summer	Mixed urban	4-6	Anhydrosugars	Caseiro et al. (2009)
	Salzburg	PM_{10}	Winter	Mixed urban	10-20	Anhydrosugars	Caseiro et al. (2009)
	Salzburg	PM_{10}	Summer	Mixed urban	2-4	Anhydrosugars	Caseiro et al. (2009)
	Sonnblick	OC	Winter	Rural	5.8-11	14C, levoglucosan and cellulose	Gelencsér et al. (2007)
	Sonnblick	EC	Winter	Rural	0.5-4.8	14C, levoglucosan and cellulose	Gelencsér et al. (2007)
	Sonnblick	OM	Winter	Rural	23	Levoglucosan	Puxbaum et al. (2007)
Belgium	Borgerhout	PM_{10}	Winter	Urban	8.6 ± 4.3	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Ghent	PM_{10}	Winter	Urban	9.2 ± 4.9	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Mechelen	PM_{10}	Winter	Suburban	11.3 ± 5.4	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Hamme	PM_{10}	Winter	Rural	21.9 ± 15.8	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Lier	PM_{10}	Winter	Rural	10.6 ± 6.3	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Retie	PM_{10}	Winter	Rural	9.9 ± 5.8	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Houtem	PM_{10}	Winter	Rural	9.3 ± 12.0	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Borgerhout	OC	Winter	Urban	36 ± 11	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Ghent	OC	Winter	Urban	40 ± 13	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Mechelen	OC	Winter	Suburban	43 ± 12	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Hamme	OC	Winter	Rural	60 ± 22	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Lier	OC	Winter	Rural	43 ± 12	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Retie	OC	Winter	Rural	43 ± 12	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Houtem	OC	Winter	Rural	40 ± 53	Monosaccharide anhydrides	Maenhaut et al. (2012)
	Antwerp	PM_{10}	Winter	Urban	5.83 ± 1.84	Levoglucosan	Cordell et al. (2016)
	Ghent	OC	Winter	Urban	35	Monosaccharide anhydrides	Zdráhal et al. (2002)
Canada	Golden, BC	$PM_{2.5}$	Winter	Rural valley	31	PMF	Jeong et al. (2008)
	Edmonton, Alberta	PM_1	Winter	Suburban	17.1	PMF	Bari et al. (2015)
Chile	Temuco	PM_{10}	Winter	Urban	87		Sanhueza et al. (2012)

	Santiago	$PM_{2.5}$	Winter	Urban	10-40	CO tracer and chemical model	Saide et al. (2016)
	Valdivia	PAH	Winter	Urban	90	PAH by GC-MS	Bravo-Linares et al. (2016)
	Southern cities in Chile	$PM_{2.5}$	Winter	Urban	90	CO tracer and chemical model	Saide et al. (2016)
Czech Republic	Mladá Boleslav	PM_1	Winter	Urban	49	PMF	Hovorka et al. (2015)
	Prague	$PM_{2.5}$	Winter	Urban	39	Monosaccharide anhydrides	Saarikoski et al. (2008)
	Prague	OC	Winter	Urban	79	Monosaccharide anhydrides	Saarikoski et al. (2008)
	Ostrava	$PM_{2.5}$	Winter	Urban	42	PMF	Vossler et al. (2016)
	Ústí nad Labem	OC	Winter	Urban	5	CMB	Schladitz et al. (2015)
	Ústí nad Labem	OC (coal)	Winter	Urban	43	CMB	Schladitz et al. (2015)
	Ústí nad Labem	EC	Winter	Urban	57	PMF	Schladitz et al. (2015)
	Ústí nad Labem	$PM_{2.5}$	Winter	Urban	31	PMF	Schladitz et al. (2015)
	Brno	OC	Winter	Urban	24.1-34.2	Monosaccharide anhydrides and monocarboxylic acids	Křůmal et al. (2015)
	Brno	EC	Winter	Urban	16.6-17.7	Monosaccharide anhydrides and monocarboxylic acids	Křůmal et al. (2015)
	Šlapanice	OC	Winter	Rural	20.2-51.7	Monosaccharide anhydrides and monocarboxylic acids	Křůmal et al. (2015)
	Šlapanice	EC	Winter	Rural	14.7-45.8	Monosaccharide anhydrides and monocarboxylic acids	Křůmal et al. (2015)
Denmark	Vindinge	$PM_{2.5}$	Winter	Rural	10	Gaussian plume dispersion model	Glasius et al (2008)
	Copenhagen	PM10	Winter	Urban	4.0	Anhydrosugars	Caseiro and Oliveira (2012)
	Copenhagen	PM10	Winter	Rural	3.4	Anhydrosugars	Caseiro and Oliveira (2012)
Estonia	Tartu	PM2.5	Annual	Urban	40	Receptor model / CMB	Orru et al. (2010)
Finland	Kuopio	$PM_{2.5}$	Winter	Suburban	16	PMF	Tuomi et al. (2015)
	Kurkimäki	VOCs and benzene	Winter	Rural	26-48 and 35-62	CMB with VOC and PAH	Hellén et al. (2008)
	Helsinki	$PM_{2.5}$	Autumn	Urban	25	Monosaccharide anhydrides	Saarikoski et al. (2008)
	Helsinki	OC	Autumn	Urban	58	Monosaccharide anhydrides	Saarikoski et al. (2008)
	Helsinki	$PM_{2.5}$	Winter	Urban	18-29 and	Monosaccharide anhydrides	Saarnio et al. (2012)
	Helsinki	$PM_{2.5}$	Winter	Suburban	27-66	Monosaccharide anhydrides	Saarnio et al. (2012)
	Helsinki	OA	Winter	Suburban	50	Multilinear engine algorithm	Aurela et al. (2015)
France	Paris	$PM_{2.5}$	Winter	Urban BG	10-30	Aethalometer	Favez et al (2009)
	Lens	PM_{10}	Winter	Urban BG	25	PMF	Waked et al. (2014)
	Puy de Dôme	OC	Winter	Rural	7.1-14	14C, levoglucosan and cellulose	Gelencsér et al. (2007)
	Puy de Dôme	EC	Winter	Rural	0.6-6.5	14C, levoglucosan and cellulose	Gelencsér et al. (2007)
	Lille	PM_{10}	Winter	Urban	11.57 ± 3.38	Levoglucosan	Cordell et al. (2016)
	Puy de Dôme	OM	Winter	Rural	21	Levoglucosan	Puxbaum et al. (2007)
	Marseille	OA	Winter	Urban	48	AMS and PMF of offline filter extracts	Bozetti et al. (2017)
	Lille	PM_{10}	Winter	Urban	7.8-15.4	Levoglucosan	Cordell et al. (2016)
Germany	Dettenhausen	PM_{10}	Winter	Rural	59	PMF	Bari et al. (2010)

	Augsburg	PM$_{10}$	Winter	Urban	25	CMB	Gu et al. (2013)
	Seiffen	OA	Winter	Rural	20	PMF	Poulain et al. (2011)
	Seiffen	PAH	Winter	Rural	62	PMF	Poulain et al. (2011)
	Schauinsland	OC	Winter	Rural	12-23	14C, levoglucosan and cellulose	Gelencsér et al. (2007)
	Schauinsland	EC	Winter	Rural	1-10	14C, levoglucosan and cellulose	Gelencsér et al. (2007)
	Schauinsland	OM	Winter	Rural	21	Levoglucosan	Puxbaum et al. (2007)
	Duisburg	PM$_{2.5}$	Autumn	Urban	13	Monosaccharide anhydrides	Saarikoski et al. (2008)
	Annaberg-Buchholz	PM$_{2.5}$	Winter	Rural town	30	PMF	Schladitz et al. (2015)
		EC	Winter	Rural town	55	PMF	Schladitz et al. (2015)
		OC	Winter	Rural town	22	CMB	Schladitz et al. (2015)
		OC (coal)	Winter	Rural town	33	CMB	Schladitz et al. (2015)
Greece	Thessaloniki	PM$_{10}$	Winter	Urban	8-12	CMB	Argyropoulos et al (2012)
	Thessaloniki	OM	Winter	Urban BG	39	CMB	Manoli et al. (2015)
	Athens	OA	Winter	Urban	43	PMF	Florou et al. (2017)
	Patras	OA	Winter	Urban	60	PMF	Florou et al. (2017)
Hungary	K-Puszta	OC	Winter	Rural	33-56	14C, levoglucosan and cellulose	Gelencsér et al. (2007)
	K-Puszta		Winter	Rural	2.7-13	14C, levoglucosan and cellulose	Gelencsér et al. (2007)
	K-Puszta	OM	Winter	Rural	47	Levoglucosan	Puxbaum et al. (2007)
Ireland	Tivoli Docks, Cork	EC	Summer	Urban BG	20	PMF	Healy et al. (2010)
		OC	Summer	Urban BG	21	PMF	Healy et al. (2010)
		PM$_{2.5}$	Summer	Urban BG	5	PMF	Healy et al. (2010)
		OC	Summer	Urban BG	28	PCA–MLR	Kourtchev et al. (2011)
		OC	Winter	Urban BG	80	PCA–MLR	Kourtchev et al. (2011)
		PM$_{2.5}$	Summer	Urban BG	6	PCA–MLR	Kourtchev et al. (2011)
		PM$_{2.5}$	Winter	Urban BG	28	PCA–MLR	Kourtchev et al. (2011)
		PM$_{2.5}$	Winter	Urban BG	46-50	PMF	Dall'Osto et al. (2014)
Italy	Lombardy	OC	Annual	Mixed	20-50	PMF and anhydrosugars	Piazzalunga et al. (2011)
	Lombardy	PM$_{10}$	Annual	Mixed	5-25	PMF and anhydrosugars	Piazzalunga et al. (2011)
	Po Valley	PAH	Winter	Rural	77% of BaP	CMB	Pietrogrande et al. (2015)
	Po Valley	OC	Winter	Rural	35	CMB	Pietrogrande et al. (2015)
	Milan	PM$_{10}$	Winter	Urban BG	14	PMF	Bernardonia et al. (2011)
	Oasi Le Bine	OC	Summer	Rural	10	CMB	Perrone et al. (2012)
	Oasi Le Bine	OC	Winter	Rural	85-96	CMB	Perrone et al. (2012)
	Oasi Le Bine	PM$_{2.5}$	Summer	Rural	3	CMB	Perrone et al. (2012)
	Oasi Le Bine	PM$_{2.5}$	Winter	Rural	27-31	CMB	Perrone et al. (2012)
	Propata	EC	Winter	Rural	53±9	Optical measurement	Massabò et al. (2015)
	Propata	OC	Winter	Rural	61±5	Optical measurement	Massabò et al. (2015)
	Genoa	EC	Winter	Urban BG	16±7	Optical measurement	Massabò et al. (2015)
	Genoa	OC	Winter	Urban BG	15±5	Optical measurement	Massabò et al. (2015)
Japan	Tokyo	PM$_{10}$	Winter	Suburban	24-28	14C	Uchida et al. (2010)
	Tokyo	PM$_{10}$	Summer	Suburban	39-42	14C	Uchida et al. (2010)
	Tokyo	PM$_{10}$	Winter	Urban	12.7	CMB	Okamoto et al. (1990)
Luxembourg	PM$_{10}$ is dominated by the fine fraction (<1µm) in the winter months (Sep-Feb) due to domestic heating						Buchholz et al. (2014)

Netherlands	Amsterdam	PM$_{2.5}$	Winter	Urban	11	Monosaccharide anhydrides	Saarikoski et al. (2008)
	Wijk aan Zee	PM$_{10}$	Winter	Urban	1.3-4.1	Levoglucosan	Cordell et al. (2016)
	Cabauw	OA	Annual	Rural	0-23	PMF	Schlag et al. (2016)
	Wijk aan Zee	PM$_{10}$	Winter	Urban	2.74 ± 1.45	Levoglucosan	Cordell et al. (2016)
	Amsterdam	PM$_{10}$	Winter	Urban	4.78 ± 1.90	Levoglucosan	Cordell et al. (2016)
New Zealand	Auckland (KLD)	PM$_{2.5}$	Winter	Suburban	69	Ion beam analysis and PMF	Trompetter et al. (2010)
	Hastings	PM$_{2.5}$	Winter	Urban	91	Ion beam analysis and PMF	Trompetter et al. (2010)
	Masterton	PM$_{2.5}$	Winter	Rural	80	Ion beam analysis and PMF	Trompetter et al. (2010)
	Upper Hutt	PM$_{2.5}$	Winter	Urban	63	Ion beam analysis and PMF	Trompetter et al. (2010)
	Christchurch	PM$_{2.5}$	Winter	Urban	79	Ion beam analysis and PMF	Trompetter et al. (2010)
	Auckland (KLD)	PM$_{2.5}$	Summer	Suburban	13	Ion beam analysis and PMF	Trompetter et al. (2010)
	Hastings	PM$_{2.5}$	Summer	Urban	9	Ion beam analysis and PMF	Trompetter et al. (2010)
	Masterton	PM$_{2.5}$	Summer	Rural	45	Ion beam analysis and PMF	Trompetter et al. (2010)
	Upper Hutt	PM$_{2.5}$	Summer	Urban	25	Ion beam analysis and PMF	Trompetter et al. (2010)
	Christchurch	PM$_{2.5}$	Summer	Urban	26	Ion beam analysis and PMF	Trompetter et al. (2010)
	Nelson	PM$_{2.5}$	Annual	Urban	77	Ion beam analysis and PMF	Ancelet et al. (2015)
	Nelson	PM$_{10}$	Annual	Urban	48	Ion beam analysis and PMF	Ancelet et al. (2015)
	Wainuiomata	PM$_{2.5}$	Winter	Suburban	48	PMF	Davy et al. (2012)
	Alexandra	PM$_{10}$	Winter	Urban	86-91	PMF	Ancelet et al. (2014)
	Masterton	PM$_{10}$	Winter	Rural	89-90	PMF	Ancelet et al. (2012)
Norway	Hurdal	EC	Winter	Rural	7-12	^{14}C & monosaccharide anhydrides	Yttri et al. (2011)
	Oslo	EC	Winter	Urban BG	6-11	^{14}C & monosaccharide anhydrides	Yttri et al. (2011)
	Hurdal	OC	Winter	Rural	27-41	^{14}C & monosaccharide anhydrides	Yttri et al. (2011)
	Oslo	OC	Winter	Urban BG	25-39	^{14}C & monosaccharide anhydrides	Yttri et al. (2011)
	Oslo	PM$_{2.5}$	Winter	Urban	27	PMF	Laupsa et al. (2009)
Poland	National average	PM$_{10}$	Annual	Nationwide	50		Juda-Rezler et al. (2011)
	Nowa Huta, Krakow	PM$_{10}$ (coal)	Winter	Urban	70	AMS	Mira-Salama et al. (2008)
	Krakow	PM$_{10}$ (coal)	Winter	Urban	50	CMB and C-PMF	Junninen et al. (2009)
	Krakow	B(a)P (coal)	Winter	Urban	90	CMB and C-PMF	Junninen et al. (2009)
Portugal	Aveiro	OC	Winter	Urban	52-69	14C, levoglucosan and cellulose	Gelencsér et al. (2007)
	Aveiro	EC	Winter	Urban	4-12	14C, levoglucosan and cellulose	Gelencsér et al. (2007)
	Nationwide average	PM$_{10}$	Annual		18	MM5/CHIMERE air quality model	Borrego et al. (2010)
	Foros de Arrão	PM$_{2.5}$	Winter	Rural	17	PMF	Canha et al. (2014)
	Porto	PM$_{10}$	Winter	Rural	3	Anhydrosugars	Caseiro and Oliveira (2012)
	Porto	PM$_{10}$	Winter	Urban	3	Anhydrosugars	Caseiro and Oliveira (2012)
	Aveiro	OM	Winter	Urban	68	Levoglucosan	Puxbaum et al. (2007)
	Azores	OM	Winter	Rural	18	Levoglucosan	Puxbaum et al. (2007)
Slovakia		High contribution to PM$_{10}$ from local residential heating across the country					Krajčovičová et al. (2014)
Slovenia	Maribor	Substantial winter emissions from residential wood burning					Kitanovski et al. (2012)
South Korea	Seoul	PM$_{2.5}$	Summer	Urban	12.1	PMF	Heo et al. (2009)
	Jeju Island	PM$_{2.5}$	Spring	Rural	25	PMF	Han et al. (2006)

	Incheon	$PM_{2.5}$	Annual	Urban	6.1	PMF	Choi et al. (2013)
Spain	Grenada	TC	Winter	Suburban	41-47	Aethalometer and levoglucosan	Titos et al. (2017)
	Huelva, Seville	OA	Winter	Urban	15	PMF	Diesch et al. (2012)
Sweden	Tanumshede	$PM_{2.5}$	Winter	Rural	25	PMF	Molnar and Sallsten (2013)
	Hagfors		Winter	Rural			Gustafson et al. (2007)
	Lycksele	$PM_{2.5}$	Winter	Rural town	70	PMF and levoglucosan	Hedberg et al (2006)
	Lycksele	PM_{10}	Winter	Rural town	36-82	PMF	Krecl et al. (2008)
	Vavihill	OC % of TC	Winter	Rural	32	Levoglucosan and 14C	Genberg et al. (2011)
	Vavihill	EC % of TC	Winter	Rural	7	Levoglucosan and 14C	Genberg et al. (2011)
Switzerland	Zurich	OM	Summer	Urban backgrd	10	AMS & PMF	Lanz et al. (2007)
	Zurich	OM	Winter	Urban backgrd	35-40	AMS & CMB/PMF	Lanz et al. (2008)
	Roveredo	OM	Winter	Rural valley	94	^{14}C	Alfarra et al (2007)
	Zurich	OC	Winter		41	^{14}C	Szidat et al. (2006)
	Zurich	EC	Winter		20-30	^{14}C	Szidat et al. (2006)
	Zurich	OC	Summer		10	^{14}C	Szidat et al. (2006)
	Zurich	EC	Summer		4-8	^{14}C	Szidat et al. (2006)
	Zurich	BC	Winter	Urban	24±11	Aethalometer	Herich et al. (2011)
	Payerne	BC	Winter	Rural	33±12	Aethalometer	Herich et al. (2011)
	Magadino-Cadenazzo	BC	Winter	Rural	30±11	Aethalometer	Herich et al. (2011)
	Alpine regions	EC	Rural	Winter	42-49	14C, levoglucosan and water soluble ionic species	Zotter et al. (2014)
							Gianini et al. (2013)
Turkey	Zonguldak	$PM_{2.5}$ (coal)	Winter	Urban	81	PAH ratios	Akyüz et al. (2008)
	Bogazici Univ,	PAH	Winter	Rural	19	CMB	Hanedar et al. (2011)
	Bursa	PAH	Winter	Urban	22.8	PAH ratios	Esen et al. (2008)
	Bursa	PAH (coal)	Winter	Urban	5.7	PAH ratios	Esen et al. (2008)
UK	LDN and BMX	Concentrations generally very low compared to the rest of Europe and with other studies					Harrison et al. (2012)
	London	OA	Winter	Urban BG	38	AMS and PMF	Young et al (2015)
	London	OA	Winter	Urban BG	11	AMS and PMF	Young et al (2015)
	London	OA	Annual	Urban BG	34	AMS and PMF	Young et al (2015)
	London	POA	Annual	Urban BG	43	AMS and PMF	Young et al (2015)
	London	PM_{10}	Annual 3 year	Urban BG	7-10	Aethalometer & levoglucosan	Fuller et al. (2014)
	London	PM_{10}	Winter	Urban BG	10	Aethalometer	Fuller et al. (2014)
	London	PM_{10}	Summer	Urban BG	2	Aethalometer	Fuller et al. (2014)
	London	BC	Winter	Urban BG	23	Aethalometer	Fuller et al. (2014)
	London	BC	Summer	Urban BG	11	Aethalometer	Fuller et al. (2014)
	North Kensington	OC	Winter	Urban BG	15	CMB	Yin et al. (2015)
	Harwell	OC	Winter	Rural	28	CMB	Yin et al. (2015)
	North Kensington	$PM_{2.5}$	Winter	Urban BG	4	CMB	Yin et al. (2015)
	Harwell	$PM_{2.5}$	Winter	Rural	7	CMB	Yin et al. (2015)

	North Kensington, London	BC	Winter	Urban	26±13	PMF, SP2, aethalometer	Liu et al. (2014)
	Holme Moss, West Yorkshire	BC	Winter	Rural	45	PMF	Liu et al. (2011)
	Leicester	PM_{10}	Winter	Urban	3.21 ± 2.36	Levoglucosan	Cordell et al. (2016)
USA	Truckee Meadows, Nevada	$PM_{2.5}$	Winter	Urban valley	11-51	CMB	Chen et al. (2012)
	Fresno, CA	OA	Wnter	Urban valley	33	AMS and PMF	Young et al (2015)
	Fresno, CA	$PM_{2.5}$ and OC	Winter	Urban valley	18% and 41%	Anhydrosugars	Gorin et al. (2006)
	Fresno, CA	$PM_{2.5}$	Winter	Urban valley	29-31	CMB	Chow et al. (2007)
	Underhill, Vermont	$PM_{2.5}$	Winter	Rural	12.5-24.3	PMF	Polissar et al. (2001)
	Underhill, Vermont	$PM_{2.5}$	Summer	Rural	6.1-13.7	PMF	Polissar et al. (2001)
	Pasadena	$PM_{2.0}$	Annual	Urban	9.6	CMB	Schauer et al. (1996)
	Pasadena	OA	Annual	Urban	19.3	CMB	Schauer et al. (1996)
USA	Downtown LA	$PM_{2.0}$	Annual	Urban	5.7	CMB	Schauer et al. (1996)
	Downtown LA	OA	Annual	Urban	12.3	CMB	Schauer et al. (1996)
	West LA	$PM_{2.0}$	Annual	Urban	10.8	CMB	Schauer et al. (1996)
	West LA	OA	Annual	Urban	22.0	CMB	Schauer et al. (1996)
	Rubidoux	$PM_{2.0}$	Annual	Urban	1.3	CMB	Schauer et al. (1996)
	Rubidoux	OA	Annual	Urban	5.0	CMB	Schauer et al. (1996)
	Libby, Montana	$PM_{2.5}$	Winter	Rural	81	CMB	Ward et al. (2010)
	Seattle (multiple)	$PM_{2.5}$	Annual	Suburban	7-31	PMF	Kim and Hopke (2008a)
	Olympic N.P, WA	$PM_{2.5}$	Annual	Rural	13	PMF	Kim and Hopke (2008b)
	Portland, OR	$PM_{2.5}$	Annual	Urban	27	PMF	Kim and Hopke (2008b)
	Fairbanks, Alaska	$PM_{2.5}$	Winter	Urban	62.7-81.2	CMB	Ward et al. (2012)
	Central LA & Riverside	OC	Annual	Urban	9-10	PMF	Heo et al. (200)
	Waterbury, VM	$PM_{2.5}$	Annual	Rural	28-46	CMB and others	Sexton et al. (1985)
	Boise, Idaho	$PM_{2.5}$	Winter	Urban	62-94	14C and DMP Isomers	Benner et al. (1995)
	Fairbanks, Alaska	$PM_{2.5}$	Annual	Urban	31-66	14C	Busby et al. (2016)
	Fairbanks, Alaska	$PM_{2.5}$	Annual	Urban	20-61	Levoglucosan	Busby et al. (2016)
	Fairbanks, Alaska	$PM_{2.5}$	Annual	Urban	65-68	CMB	Busby et al. (2016)
	Rochester, NY	$PM_{2.5}$	Winter	Urban	17.30%	Aethalometer, levoglucosan & K	Wang et al. (2011)
	BH, Seattle	$PM_{2.5}$	Annual	Urban	24-31%	CMB model	Wu et al. (2007)
	Montana	$PM_{2.5}$	Winter	Rural	55.5-77.0%	CMB and ^{14}C	Ward and Lange (2010)

Table 2-6. Results of source apportionment studies for RSF burning in the literature.

2.6 Climate Change Impacts

The impact on atmospheric chemistry and climate change of many of the pollutants released from biofuel combustion have been studied individually, but cross-links between many of them and the link with inefficient burning have not been well investigated.

2.6.1 Direct impacts

Perturbations made by anthropogenic emissions the Earth’s energy budget are measured by radiative forcing (RF) which is the net balance between incoming solar irradiance and outgoing thermal infrared energy. Positive values lead to an increase in global average surface temperature and negative values lead to a decrease. Domestic biomass combustion contributes to a number of components of radiative forcing, including CO_2, CH_4, CO, NMVOCs, NO_x, SO_2, BC and OC. Figure 2-7a shows the most recent IPCC estimate of the RF contribution of each of these components. Figure 2-7b shows the estimates of climate forcing for selected source categories, including that from residential solid fuel combustion.

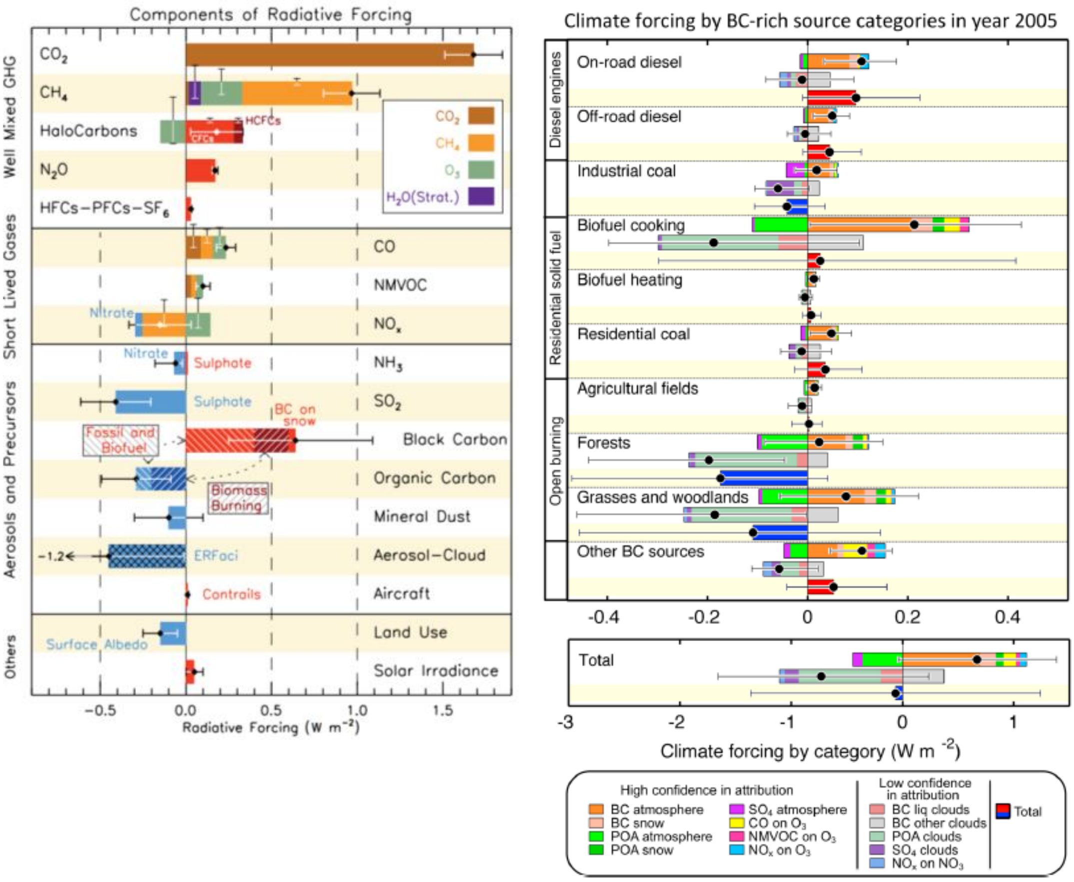


Figure 2-7. a) IPCC’s components of global radiative forcing for the period 1750-2011 (Myhre et al., 2013). b) Total climate forcing for BC-rich source categories, assuming year 2000 indefinite emissions rates (Bond et al., 2013)

Figure 2-7b shows a substantial contribution of fossil, biofuel and biomass burning to BC and OC radiative forcing. Domestic or residential wood burning falls under the category of "biofuel" in the IPCC reports, which is often reported together with fossil fuel burning. Biomass burning is typically used as an umbrella term for wildfires and open burning sources. Particularly noteworthy are both the magnitude of the positive forcing of the BC component and the associated uncertainty which, for the first time, show BC to be the second most important component of radiative forcing. Despite the high emissions of BC and other components from domestic sources, Figure 2-7. b shows the forcing of biofuel heating and residential coal to be relatively low in comparison to other sources including diesel engines and wildfires. However, there is a high uncertainty in the activity data and emissions factors used to develop these estimates, as shown by the large error bars, and the biofuel heating category is also often highly localised and seasonal. Forcing from these species occurs entirely within the first year after emission. The importance of emissions from biofuel cooking are self-evident in Figure 2-7. b. A strong warming effect from BC is offset by a strong cooling effect by POA to yield a small net positive forcing. However, the uncertainty error bar is vast and dwarfs many of the other categories entirely.

Figure 2-7b shows that black carbon is one of the strongest contributors to RSF positive forcing. This is due to a strong absorption of visible light, as well as indirect effects such as lowering of the albedo of snow and ice. BC has a low chemical reactivity in the atmosphere and is primarily removed by wet or dry deposition (Bond et al., 2013). Therefore the impact of BC emissions to atmosphere is determined by its optical properties (Reid et al., 2005a). There is a great deal of uncertainty in the extent to which the cooling effect of biomass aerosols offsets the warming due to BC (see figure 2-7a). The ratios of POA:BC and SO_2:BC of a particular emissions source are a useful gauge whether the source will have a positive or negative associated radiative forcing. Figure 2-8 shows these ratios for several emissions sources.

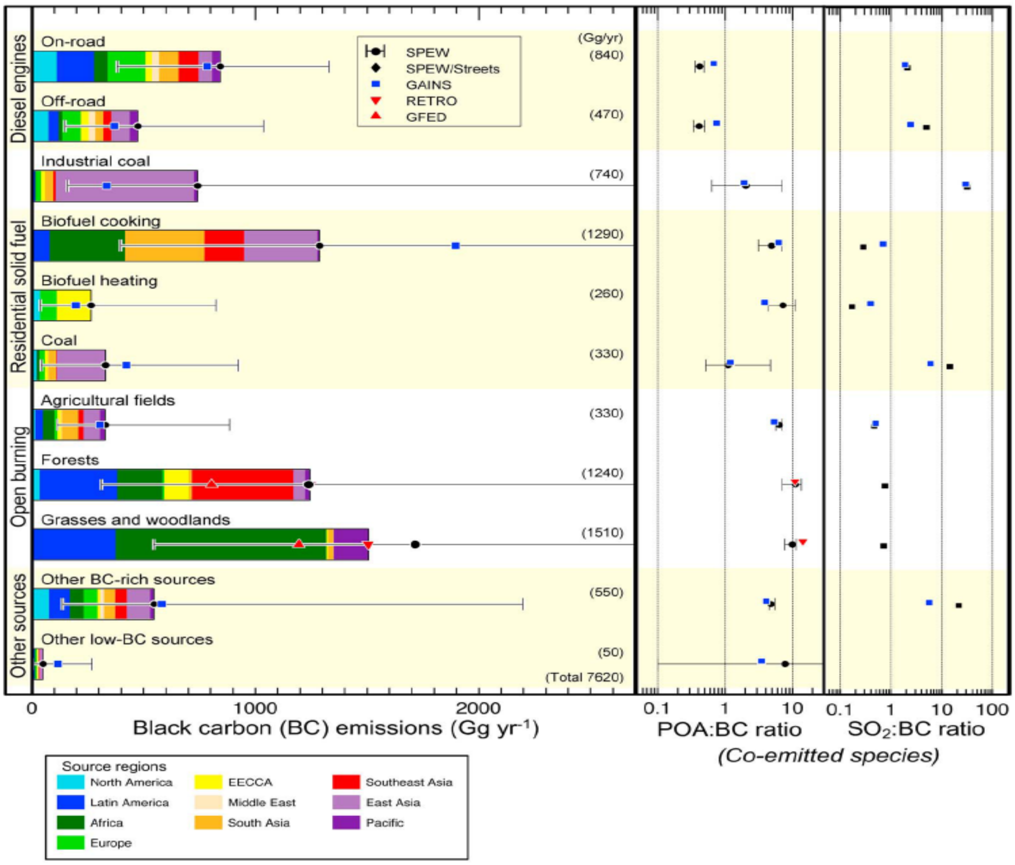


Figure 2-8. Black carbon and co-emitted species by region and source in 2000. Source: (Bond et al., 2013)

As the figure shows, the residential solid fuel sector features the largest difference between the emissions estimates from the SPEW and GAINS databases. Emissions from biofuel heating are 35% higher in SPEW than GAINS; owing to differences in activity data and emissions factors. However, both agree that biofuel cooking is one of the largest sources of BC, dominated by Asia and Africa. In 2000, emissions from this source were estimated at 1290 Gg yr^{-1}, compared to 330 Gg yr^{-1} for residential coal burning and 260 Gg yr^{-1} for biofuel heating. It is also interesting that within the biofuel heating category, the largest source region is Eastern Europe, Caucasus and Central Asia (EECCA), followed by Europe and North America. This clear spatial variation is believed to cause 'hotspots' of atmospheric BC, which can result in local scale direct radiative forcing in the order of +10 W m^{-2} (Bond et al., 2013). One study estimated the radiative forcing due to BC over an urban site in India to be as high as +23.4 W m^{-2} (Panicker et al., 2010). On a global scale, RSF combustion exerts an annual mean direct radiative forcing of -66 to + 21 mW m^{-2}, with high sensitivities to BC/OC/SO_2 ratios and particle size distributions (Butt et al., 2016).

The POA:BC ratio is higher for wood cooking than wood heating. This is believed to be due to the assumption that the technology used for heating is larger and more developed; giving more efficient combustion (depending on the operation). Therefore the radiative forcing per unit fuel burned is technology dependent, as shown in Figure 2-9.

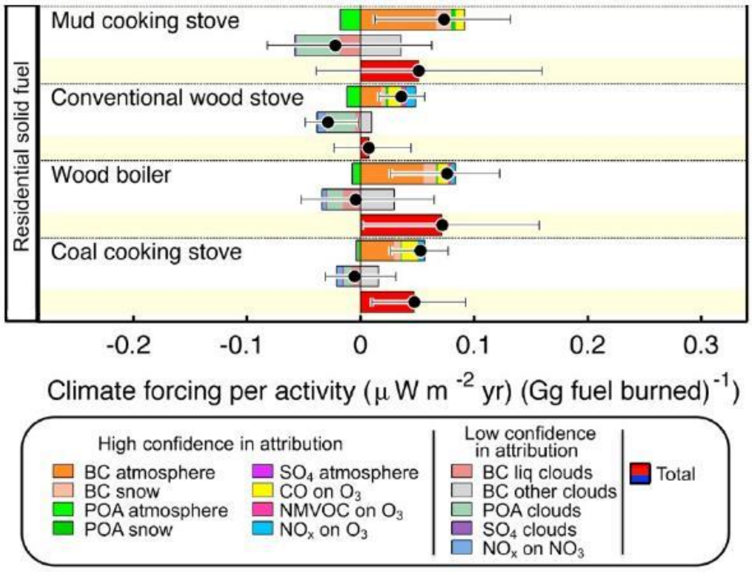


Figure 2-9. Radiative forcing per unit activity for RSF combustion. Adapted from (Bond et al., 2013).

RF per unit emission of a particular species is also referred to as absolute global warming potential (AGWP) for a given time period. Figure 2-9 shows that a greater warming effect is exerted on the climate by cooking stoves and boilers than traditional wood stoves, although there is a large uncertainty in the total net impact on climate. This is due to a combination of uncertainties in activity data, emissions factors and climate sensitivity. Chung and Seinfeld (2002) found the average atmospheric lifetime of BC to be 4 – 10 days, with an average of 6.4 days. Bond et al. (2013) showed a similar range in the reported lifetime, varying from 3.31 to 10.6 days, with an average of 6.2 days. Chung and Seinfeld (2005) found that the climate sensitivity of BC direct radiative forcing was 0.6 K W^{-1} m^{-2}. Similarly, extrapolation of the findings of Tripathi et al. (2005) yields a lower atmospheric warming of 0.09 K day^{-1} (µg m^{-3})$^{-1}$ BC. The 20- and 100-year GWPs of BC are 4470 and 1000-2000 respectively (Boucher, 2013).

The largest impact contribution to RSF radiative forcing is from the aerosol fraction, notably BC and OC. Mixing state can affect the key properties of the aerosols, such as polarity, hygroscopicity, optical properties and ability to act as cloud condensation nuclei (CCN) (Boucher et al., 2013). Biomass PM adsorbs pyrolysis products such as organic acids to the surface of particles, which classifies them as internally mixed particles with higher oxygen functionalities. This makes biomass PM more hygroscopic and more active as CCN (Jones et al., 2005). This can lead to cloud whitening through increased cloud droplet number, as well as increased cloud lifetime (Yu, 2000). This has a profound cooling effect, although uncertain. OC and inorganic aerosols also have a cooling effect due to their light scattering nature.

2.6.2 Indirect climate impacts

The indirect effects on climate such as cloud and cryosphere interactions can be significant. After emission, carbonaceous aerosols can either be deposited on the surface of snow and glaciers via dry deposition or washed out with precipitation. Particles can also act as nuclei in ice and cloud formation and can be deposited as part of the snow accumulation (Ingvander et al., 2013).

A review of the impacts of BC over the Himalayas was conducted by the Government of India (INCCA, 2011). It found that a reduction in glacier area of over 20% in the past 40 years coincided with a warming trend of 0.25 K decade^{-1} and a three-fold increase in aerosol optical depth (AOD). Long range transport of these species, particularly from wildfires, may be accelerating Artic summer melt due to direct heating from Arctic haze as well as a reduction in the albedo of snow and ice (Treffeisen et al., 2007).

Evidence has also been put forward that anthropogenic emissions of BC during the industrial revolution caused surface radiative forcings of up to and above 35 W m^{-2} over the European Alps, which substantially accelerated glacial retreat (Painter et al., 2013). It has been noted that any assessment of the impact of BC on glaciers will need to include the contribution that BC makes to regional climate change, as well as direct effects on the glacier (Xu et al., 2009). The deposition pathways of carbonaceous aerosols are known to be highly complex in glaciated upland areas. However, the presence of these aerosols throughout the glacier system has been recorded, as shown in Figure 2-10.

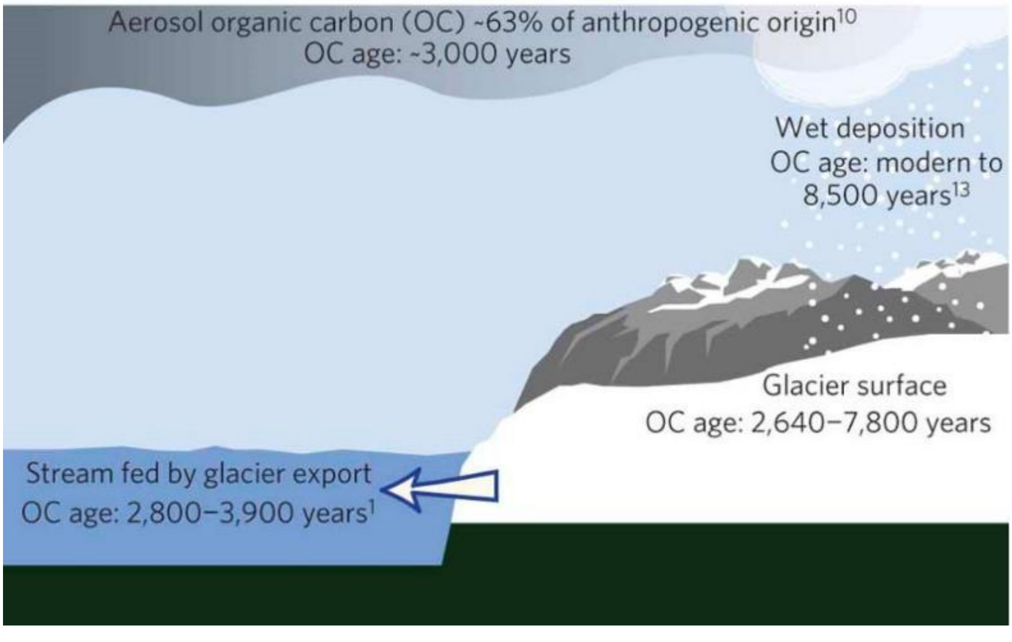


Figure 2-10. The glacier organic carbon cycle. Source: (Stubbins et al., 2012)

As shown in the figure, it is estimated that 63% of aerosol organic carbon is derived from anthropogenic activities; with 33% originating from industrial sources and 30% from biomass combustion (Jurado et al., 2008). Analysis of dissolved organic matter throughout the glacial system was carried out by Stubbins et al. (2012). High numbers of condensed aromatic peaks were observed compared with river water, as well as high abundances of aliphatics including fatty acids. Many of these compounds are directly attributable to RSF combustion. Yasunari et al. (2010) and Yasunari et al. (2013) directly modelled the impact of BC from biomass and biofuel combustion on the Indo-Gangetic Plain. It was found that BC concentrations in the region could reduce the surface albedo of Tibetan glaciers by more than 5% and increase annual discharges by more than 33%. However, the deposition rate is one of the most crucial uncertainties. Despite this, Flanner et al. (2007) have shown that the local efficacy (temperature response to a given forcing) of BC/snow is more than three times greater than that of CO_2 because of the strong effect of the BC on snow melting rates, which amplifies the snow-albedo feedback. Domestic burning in the Indo-Gangetic plain for heating and cooking may also be having a substantial impact on regional climate through the formation of atmospheric brown clouds (ABCs) (Ramanathan et al., 2008, Bonasoni et al., 2010). Recent works have suggested that Asian ABCs may be having a global impact on climate, increasing the poleward heat transport and rainfall during the Asian monsoon (Wang et al., 2014, INCCA, 2011). This effect is known as the Elevated Heat Pump (EHP) effect which modifies the energy balance over the Himalayan region (Lau et al., 2006, Lau et al., 2010).

RSF PM may also act as nuclei in cloud and ice nucleation, particularly as the majority of particles are below $PM_{2.5}$ and PM_1 (Nussbaumer, 2003). Increased number of nuclei can cause an increase in cloud albedo effect through increased cloud extent, droplet number and lifetime (Boucher et al., 2013). This causes a negative RF and a cooling effect, which may have contributed towards the recently observed lower than expected rise in global average surface temperature. A comprehensive review of ice nucleation in clouds has been carried out by (Murray et al., 2012). The study highlighted the importance of carbonaceous combustion aerosol as ice nuclei, but also the lack of publications in this area. At the time of study, the authors found only one laboratory study using particles from biomass combustion rather than combustion of liquid fuels. Petters et al. (2009) suggested that the internally mixed nature of biomass PM and the organic coating may inhibit ice nucleation. However, this is dependent on the phase of combustion and particles with a higher ash content correlated with increased ice nucleation.

Several feedbacks also exist between the radiative forcing components of biomass smoke. For example, black carbon on snow and ice has been found to amplify glacial melting, creating a negative feedback loop where glaciers create rock flour and dust aerosols at an accelerated rate which ultimately help to melt the glacier. This may also been a source of fine quartz and feldspar which are known to be effective cloud and ice forming nuclei (Prospero et al., 2012, Atkinson et al., 2013).

2.6.3 Impacts on atmospheric chemistry

The emission of CH_4 and VOC, as well as CO, affect the oxidative capacity of the atmosphere by reacting with HO_x radicals (Koppmann et al., 2005). However, methane is also a potent greenhouse gas with a 20-year and 100-year global warming potential (GWP) of 72 and 25 respectively (Forster, 2007). These values include the direct effects of methane being a strong absorber in the infra-red, as well as indirect effects such as the interaction with ozone and stratospheric water vapour. The global atmospheric lifetime of methane is approximately 8.7 years, whilst the perturbation lifetime is 12 years (Denman et al., 2007). This is of consequence because large one-time emissions, such as mass use of stoves on a particularly cold winter's day, reduce the oxidative capacity of the atmosphere by suppressing the OH radical and increase background CH_4:

$$\mathrm{CH_4 + OH \longrightarrow CH_3 + H_2O}$$

The methyl radical (CH_3) formed readily reacts with oxygen to form the methylperoxy radical (CH_3O_2). CH_3O_2 may then react with either HO_2 or NO. Through the HO_2 pathway, methyl hydroperoxide is formed:

$$\mathrm{CH_3 + O_2 + M \longrightarrow CH_3O_2 + M}$$

$$\mathrm{CH_3O_2 + HO_2 \longrightarrow CH_3OOH + O_2}$$

CH_3OOH is considered to be a HO_x reservoir as it can photolyse to release OH or it can react with OH to form HCHO and another OH radical (Seinfeld and Pandis, 2006).

The emission of organic compounds from combustion is a well-documented precursor of tropospheric ozone and photochemical smog, particularly in urban areas due to vehicular emissions (Pugliese et al., 2014). Tropospheric ozone also has a positive associated radiative forcing as shown in figure 2-9, where O_3 RF is broken down by the contribution of its precursor compounds.

Two of the most important precursors in ozone formation in the troposphere are VOCs (including methane) and NO_x. During the day, NO and NO_2 react with O_3 via photolysis with no net increase in either species. However, when VOCs are present, a hydrocarbon (RH) may produce an organic peroxy radical (RO_2) by reaction with OH, which then reacts with OH (Pugliese et al., 2014):

$$\mathrm{OH + RH + O_2 \longrightarrow H_2O + RO_2}$$

$$\mathrm{RO_2 + NO \longrightarrow RO + NO_2}$$

RO may then react via several routes but the following is typical, creating two ozone molecules:

$$\mathrm{RO + O_2 \longrightarrow R'CHO + HO_2}$$

$$\mathrm{HO_2 + NO \longrightarrow OH + NO_2}$$

$$\mathrm{RH + 4O_2 \longrightarrow R'CHO + 2O_3 + H_2O}$$

A key parameter in the ability of a polluted atmosphere to form tropospheric ozone is the ratio of VOC:NO_x. In effect there is a competition between the two species for the OH radical (Seinfeld and Pandis, 2006). The second order rate coefficient for the reaction of OH with NO_2 is approximately 1.7×10^4 ppm^{-1} min^{-1} which is around 5.5 times that of average VOCs. Hence NO_x tends to be removed from the polluted atmosphere faster than VOCs (Seinfeld and Pandis, 2006). Greater VOC:NO_x ratios lead to higher mixing ratios of peroxy radicals and increased production of ozone due to more prompt conversion of NO to NO_2 via the HO_2 radical, as above. Biomass burning emits both NOx and VOCs. However, NO_x emissions are similar to or lower than that of coal, whereas VOC emissions are much higher (Ross et al., 2002, Koppmann et al., 2005). In this way, domestic wood-burning could contribute to a higher VOC:NO_x ratio and hence higher levels of tropospheric ozone. Despite this, it may be argued that the impact of the seasonality of residential biomass burning may be to some extent offset by the reduction in photolysis reactions. I.e., wood burning emissions show a distinct peak in the wintertime when there is a trough in sunlight intensity and hence in photo-dissociation.

Aldehydes also play a key role in atmospheric chemistry, being a significant source of free radicals via photolysis. The simplest aldehyde, formaldehyde, may undergo two photolysis reactions in the lower troposphere (Stockwell et al., 2011):

$$\mathrm{CH_2O + hv \rightarrow H_2 + CO}$$

$$\mathrm{CH_2O + hv \rightarrow H^{\cdot} + HO_2^{\cdot}}$$

In highly polluted areas, the latter reaction can be as significant a source of HO_x radicals as ozone photolysis. Higher molecular weight aldehydes such as CH_3CHO acetaldehyde can react with OH in the polluted atmosphere to form peroxyacetyl nitrate (PAN). PAN is a major carrier of NO_2 (Brich et al., 1984). It is more stable and long-lived at lower temperatures, like those in the upper troposphere, and as such can be transported to clean atmospheres where it may then thermally degrade or photolyse.

The role of NO_x in tropospheric ozone formation has been discussed alongside VOCs in the preceding chapter. During the day, the cycle of NO_2 photolysis and the reaction of NO and O_3 produces no net change in either NO_x or O_3 (Pugliese et al., 2014):

$$\mathrm{NO_2} + hv \longrightarrow \mathrm{NO} + \mathrm{O}$$

$$\mathrm{O} + \mathrm{O_2} + \mathrm{M} \longrightarrow \mathrm{O_3} + \mathrm{M}$$

$$\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2} + \mathrm{O_2}$$

However, net production of O_3 can occur in the presence of VOCs, which can affect air quality as described in Table 2-5. Biomass smoke has also been shown to have a strong interaction with tropospheric reservoir molecules such as hydrogen peroxide (H_2O_2), peroxyacyl nitrates (PAN) and nitrous acid (HONO) (Seinfeld and Pandis, 2006). Nitrous acid can be directly released by some sources such as wildfires or it can form via heterogeneous reaction involving NO_2 and H_2O (Akagi et al., 2011). HONO acts as a reservoir for both HO_x and NO_x as it photodissociates in the morning to release OH and NO (Kim et al., 2014).

2.7 Physical and Optical Properties of RSF particulate matter

As discussed in section 2.6.1, particulate and carbonaceous aerosol emissions have the greatest impact on climate within the RSF category, but carry the greatest uncertainty. Therefore an understanding of the physical and optical properties of emitted particles is crucial for climate models to predict the absorption or scattering of radiation, and propensity to form clouds via CCN.

Biomass burning aerosols are most often agglomerates of internally mixed particles with a core of black carbon and KCl, coated with organic compounds (Reid et al., 2005b, Kocbach et al., 2006), as shown in Figure 2-11. Internally mixed aerosol particles may feature both solid and liquid fractions, which are determined by the relative humidity.

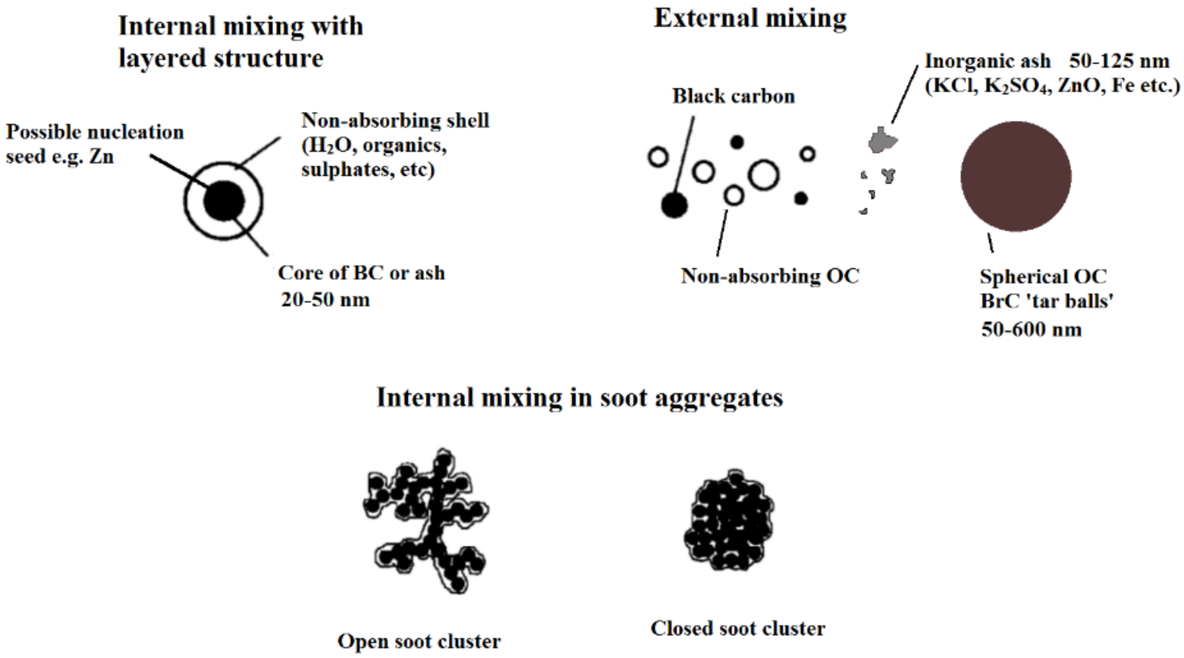


Figure 2-11. Mixing states of soot particles. Adapted from (Martins et al., 1998) and (Bølling et al., 2009)

As shown in Figure 2-11, primary BC particles are 20-50 nm in diameter which then chain and agglomerate into clusters with a wide range of sizes (0.1-2.0 µm) (Torvela et al., 2014a). Clustering increases with ageing and open chains collapse into tightly packed near-spherical structures which are more strongly absorbing (Martins et al., 1998). Ageing also causes an increase in the scattering of BC particles by as much as a factor of 24 (He et al., 2015). Knox et al., (2009) however found that the mass absorption cross section (MAC) of coated BC particles does not change significantly with ageing, whereas denuded samples without coatings showed an increase in MAC, which could be due to an increase in the size of the BC particles. The changing humidity of ambient air may affect the solid-liquid transition of biomass burning aerosols, which has an impact on their morphology and light-scattering properties (Freney et al., 2010, Naoe et al., 2009, Gelencser, 2004). A non-absorbing shell of water, organics etc can cause a lensing effect whereby the BC particle can absorb more radiation than an uncoated BC particle (Gelencser, 2004). Pure EC particles are hydrophobic even at relatively high humidity but thin coatings can increase hygroscopicity. Hydration alters the size soot particles and increases absorption, as well as increasing the polarity. Hygroscopic growth factor (HGF) accounts for the effect of humidity on geometric size of particles and is defined as the ratio between dry particle diameter and particle diameter at a low relative humidity (RH, %). Values as low as 1.04 (85% RH) have been cited for freshly emitted biomass burning particles but this can increase up to 1.5 after ageing (Vu et al., 2015a). A number of factors influence the HGF of particles including particle size, degree of oxygenation and polarity but it is believed aerosol composition plays the greatest role (Gelencser, 2004). In general, a higher water soluble fraction and an increased shell thickness of a BC particle causes an increase in the single scattering albedo (SSA) (Naoe et al., 2009). This implies that the internally mixed nature of biomass PM may result in a more negative radiative forcing than PM from other sources such as diesel engines. However, the net radiative forcing is still believed to be strongly positive. For example, optical measurements of biomass burning particles in Colorado showed that internal mixtures of BC and particulate organic matter enhanced absorption by up to 70% (Lack et al., 2012).

Inorganic ash particles such as potassium chloride, potassium sulphate and potassium phosphate generally have high hygroscopic growth factors and are often water soluble (Bølling et al., 2009). Ash particles are also usually modelled with a spherical morphology when in fact microscopy studies have shown such particles have a granular structure with crystal faces (Freney et al., 2010), which changes their optical properties (Reid et al., 2005a). Phosphates released during combustion may bind potassium in the combustion chamber into the coarse particle mode. In this way, the addition of phosphates such as $Ca(H_2PO_4)_2$ have been used as sorbents to reduce industrial PM emissions (Zeuthen et al., 2007). However, the fine fraction of the PM may contain elevated levels of potassium due to nucleation of potassium phosphate. The formation of sulphates from the reaction of inorganic ash constituents is also of consequence because sulphate aerosols such as K_2SO_4 are known to have a significant cooling effect on the atmosphere due to light scattering (Boucher et al., 2013). The sulphur content of most biomass fuels is generally very low but can be significant for fuels such as lignite. The zinc content in biomass, however, is relatively high and zinc oxide particles may act as nuclei in particle formation (Torvela et al., 2014a).

Particle size distribution is a key physical property of RSF PM and influences the surface area, toxicity and radiative transfer properties of the particles. Number size distribution is typically measured on a log scale, as shown in Figure 2-12. Fine PM can be separated into nucleation mode (<30 nm), Aitken mode (30-100 nm), accumulation mode (100-1000 nm) and coarse mode (>1 µm) particles. RSF combustion is a substantial contributor to the nucleation mode in many parts of the world. The median particle diameters for flaming wood and smouldering wood and coal were found to be 50-70 nm, 30-40nm and 30-80 nm respectively, depending on fuel type, appliance type, time-temperature history and dilution (Vu et al., 2015b, Lighty et al., 2000). Poor burning conditions and the burning of high moisture fuels results in larger particles, up to 140 nm in diameter (Chakrabarty et al., 2006).

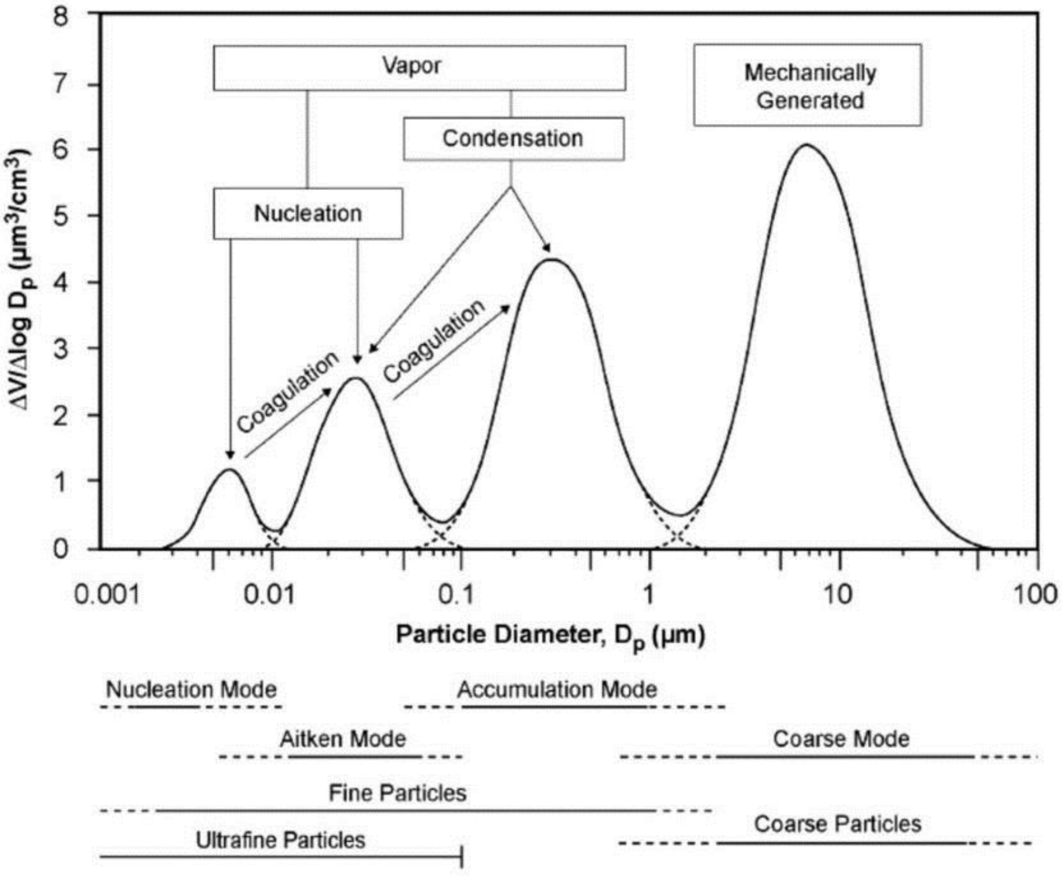


Figure 2-12. Particle size distribution for aerosols. Source: (Araujo and Nel, 2009)

In addition to the physical properties of RSF aerosol, a large body of information is available on their optical properties. The net effect of an aerosol on radiative transfer can be gauged by the extinction coefficient b_{ext} which is the sum of absorption coefficient b_{abs} and scattering coefficient b_{scat}. The value of b_{abs} (Mm^{-1}) is the absorption coefficient of a bulk PM sample. Single scattering albedo (*SSA*) is the ratio of aerosol scattering coefficient to the extinction coefficient $b_{scat}/b_{abs}+b_{scat}$ (0-1, dimensionless) and ranges from 0.17 for a diesel engine (Bond and Bergstrom, 2006) to 0.16 for a wood stove and 0.89 for coal burning (Frey et al., 2014). Values up to 0.99 have been reported for peat burning (Pokhrel et al., 2016).

The mass absorption cross section (MAC σ_{abs}) (m^2 g^{-1}) is a wavelength dependent measure of light absorption of an aerosol, normalised to the mass of particles (Bond and Bergstrom, 2006). The MAC of biomass PM varies with fuel type, combustion conditions, ageing and composition. Carbonaceous aerosol particles are generally not homogenous and therefore do not have a constant refractive index, but models have been used to predict absorption by model BC and BrC particles, as shown in Figure 2-13.

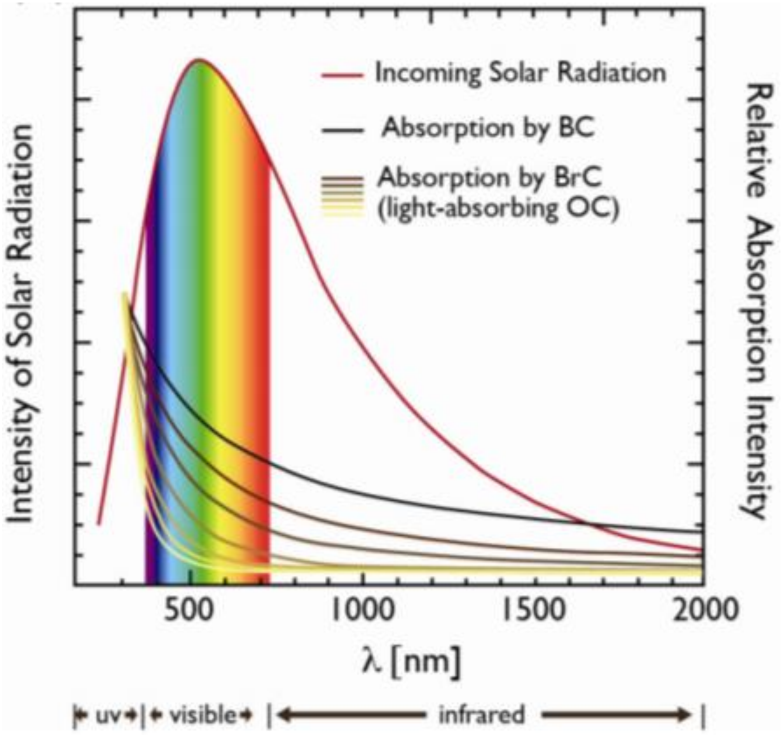


Figure 2-13. Light absorption by carbonaceous aerosols. Source: (USEPA, 2012).

BC accounts for 86% of the total amount of radiation absorbed by wood smoke across the solar spectrum, but OC more strongly absorbs UV radiation and therefore may affect the photochemistry of the troposphere (Kirchstetter and Thatcher, 2012). Since MAC is a wavelength-dependent property, it is often reported at 550 nm, near to the peak intensity of incoming solar radiation. Other gas species which contribute to urban haze such as NO_2 have a small contribution to total light extinction coefficient; often less than 5% (Chan et al., 1999)

MAC_{550nm} values as high as 58 m^2 g^{-1} have been reported (Martins et al 1998), but a typical range is 5.2-19.3 m^2 g^{-1}, with an average of 12.1 ± 4.0 m^2 g^{-1} (Gelencser, 2004). The MAC of tar balls is typically 50% that of black carbon particles (Jacobson, 2012) and the mass scattering cross section (σ_{scat}) for general OC is 4-7 m^2 g^{-1} (Gelencser, 2004). Absorption emissions index (EI_{abs}) use a useful parameter defined as MAC per unit mass of fuel burned (m^2 kg^{-1}). Average values of 0.65 m^2 kg^{-1}, 48 m^2 kg^{-1} and 0.16 m^2 kg^{-1} are reported for lignite, bituminous coal and MSF coal briquettes respectively (Bond et al., 2002). For biomass, $EI_{abs,520nm}$ values of 9.12 m^2 kg^{-1}, 7.98 m^2 $kg^{-1}$and 1.14 m^2 kg^{-1} were reported for total LAC, BC and BrC respectively from the burning of birch logs in a wood stove (Martinsson et al., 2015). Some studied have also calculated radiative forcing from RSF PM emissions per unit energy delivered by the appliance. For example, (Frey et al., 2014) calculated +20±49 mW m^{-2} MJ^{-1} for a masonry heater burning birch logs.

Within climate models, aerosol optical depth (AOD) expresses the attenuation of solar irradiance through a vertical atmospheric column. AOD can be estimated by the product of MAC and aerosol mass load per surface area of the column (Gelencser, 2004). AOD is therefore a critical parameter in radiative transfer models, combining mass concentration and optical properties of a particular aerosol mix. In atmosphere with high levels of RSF burning, absorption has been correlated with water soluble organic carbon (WSOC) and tracers such as levoglucosan (Hecobian et al., 2010). The absorption Ångström wavelength exponent $Å_{abs}$, AAE, or α (dimensionless), is a measure of the wavelength-dependence of AOD. Industrial and vehicular sources emit highly carbonaceous aerosols black in colour have α values close to 1, whereas low temperature inefficient combustion sources emit larger amounts of organics and tars, giving the particles a brown to yellow appearance and α values of 5 or more. $Å_{abs}$ values are also dependent on particle size (Moosmüller et al., 2011). The Ångström exponent is calculated by linear regression of the natural log of light attenuation versus wavelength

$$b_{abs} = a\,\lambda^{-Å_{abs}} \qquad\qquad \frac{b_{abs}(\lambda_1)}{b_{abs}(\lambda_2)} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-Å_{abs}}$$

Where b_{abs} is the absorption coefficient at wavelength λ and a is a constant. Typically 2-5 wavelengths are used to determine $Å_{abs}$ in the UV, visible and near-infrared. Ambient measurements of $Å_{abs}$ show a seasonal and diurnal variation in RSF burning communities, with values of 1.0-1.2 in summer and 1.3-2.0 in winter (Sandradewi et al., 2008, Favez et al., 2009). $Å_{abs}$ values for fresh and aged PM measured directly from RSF technologies vary significantly, as shown in Table 2-7.

The value of $Å_{abs}$ for biomass burning PM is typically 1-3 and closer to 1 for coal burning. (Sun et al., 2017) reports a value of 0.96-1.73 for several samples of bituminous coal, whereas the values for reduced-volatile briquettes ranged from 2.1-3.2. More extreme values (4-12) are associated with brown carbon and tar from smouldering biomass combustion (Lin et al., 2016, Massabò et al., 2015, Feng et al., 2013, Kirchstetter et al., 2004). The exponent is therefore dependent on fuel type and propensity of the fuel to form soot, as well as technology and combustion conditions such as burning rate and modified combustion efficiency (MCE) (Bond et al., 2002, Bond, 2001, Pokhrel et al., 2016). Higher values (6.2-8.3) have also been found to correlate with aged biomass smoke containing SOA and HULIS (Hecobian et al., 2010). There is a need for better understanding of the variation in the Ångström exponent because it is used in BC source apportionment studies using aethalometers (see section 2.5 and appendix 11.1), though it may not be as accurate as other methods due to variations in $Å_{abs}$ for different PM sources and interferences with BrC (Harrison et al., 2013, Lack and Langridge, 2013). A linear trend has been observed between $Å_{abs}$ and OC/EC ratio, hence high values of $Å_{abs}$ are associated with high OC emissions from inefficient combustion (Favez et al., 2009, Pokhrel et al., 2016).

$\mathrm{Å}_{abs}$ is also related to temperature and heating rate of the fuel due to pyrolysis and release of absorbing organic vapours including WSOC and tracers such as monosaccharide anhydrides (Rathod et al., 2017, Hecobian et al., 2010).

Sample	λ (nm)	$\mathrm{Å}_{abs}$	Fuel	Technology	Reference
PM	370-950	2.5-2.7	Birch logs, ignition phase (high BrC)	Heating stove	(Martinsson et al., 2015)
PM	370-950	1.0-1.2	Birch logs, whole cycle	Heating stove	
PM	370-950	1.38	Oak	Heating stove	(Saleh et al., 2013)
PM	370-880	>1-3	Beech	Heating stove	(Harrison et al., 2013)
PM	370-880	1.5-2.5	Black poplar	Heating stove	
PM	370-880	2-3.0	Oak	Heating stove	
PM	450-1000	1.0-2.8	Coal	Stove	(Bond et al., 2002)
$PM_{2.5}$	350-550	3 ± 1	Mixed (wood, agri residues, dung cake)	Cookstove	(Pandey et al., 2016)
OC	350-550	6.3 ± 1.8	Mixed (wood, agri residues, dung cake)	Cookstove	
PM	370-950	1.48	Pine	Open burn	(Saleh et al., 2013)
PM	370-950	2.15	Galberry	Open burn	
PM	405-870	1.0-3.5	Mixed (wood, agri residues, brush)	Open burn	(Hopkins et al., 2007a)
PM	405-660	7.7 ± 0.4	Peat	Open burn	(Pokhrel et al., 2016)
PM	370-950	1.3-2.0	Mixed, strong wood influence	Winter ambient	(Sandradewi et al., 2008)
PM	370-950	1.15-1.4	Mixed, strong wood influence	Winter ambient	(Favez et al., 2009)
PM	370-520	1.1	Fossil fuel (coal, traffic)	Winter ambient	(Titos et al., 2017)
PM	370-520	1.8-2.2	Biomass burning	Winter ambient	
BrC	405-532	4.2	Pine	Open burn	(Chakrabarty et al., 2010)
BrC	405-532	6.4	Alaskan duff	Open burn	
BrC	350-990	3.0-7.4	Mixed, strong wood influence	Winter ambient	(Kirchstetter and Thatcher, 2012)

Table 2-7. Comparison of reported values for absorption Ångström exponent from the literature.

A number of studies have used scanning and transmission electron microscopy (SEM and TEM) with electron energy loss spectroscopy (EELS) and Energy Dispersive X-Ray Spectroscopy (EDX) to investigate the physical of optical properties of RSF particulate matter. For carbonaceous particles, two useful parameters derived from these techniques include the O:C ratio of the particles and the relative proportion of hybridised *s* and *p* orbitals. The ratio of sp^2 to sp^3 bonding is useful for characterising amorphous versus graphitic carbon. Sp^2 bonding is characteristic of anisotropic crystalline (graphitic) structure whereas sp3 is characteristic of highly isotropic crystalline (amorphous) carbon such as diamond (Fitzpatrick et al., 2008, Daniels et al., 2007). Sp^2 hybridisation is also correlated with absorbance at visible wavelengths and Raman spectroscopy is a sensitive measure of the degree of graphitisation of soot (Nordmann et al., 2013, Bond and Bergstrom, 2006, Sze et al., 2001). The amount of disorder within soot particles increases with the oxygen content of the fuel and the sp^2 bonded carbon content is generally low relative to fossil fuels (Yang et al., 2016, Moffet et al., 2010). A comparison of sp^2 bonding percentages and carbon-to-oxygen ratios was presented for biomass burning by (Hopkins et al., 2007a) and for coal burning by (Bond et al., 2002). As shown in table Table 2-8, coal soot is generally less oxygenated than biomass soot and has a higher percentage of graphitic carbon. Biomass soot is more amorphous and is much more oxygenated, particularly after ageing. Smouldering biomass PM (BrC and tar balls) has by far the lowest sp^2 hybridisation at 5-10%, and C:O ratios of 55:45 (Laskin et al., 2015, Hopkins et al., 2007b).

A summary of typical optical properties of particles generated through RSF combustion is presented in Table 2-8.

	Biomass		Coal
	Fresh	Aged	Fresh
σ_{abs} 550nm (m^2 g^{-1})	0.54 ± 0.2	0.45 ± 0.2	4.1 ± 1.7
σ_{scat} 550nm (m^2 g^{-1})	3.6 ± 1.0	3.6 ± 1.1	0.5
SSA	0.87 ± 0.06	0.89 ± 0.06	0.38 ± 0.23
HGF (80%RH)	1.1 ± 0.1	1.2 ± 0.2	1.0-1.1
Ångström (Å)	2.2 ± 0.2	6.2-8.3	1.3 ± 0.1
% sp^2	31-60	10-41	56-79
C:O	78:22	65:35	84:16

Sources: Reid et al. (2005a), Bond et al. (2002), Frey et al. (2014), Ye et al. (2011) (Hopkins et al. (2007b)

Table 2-8. Overview of optical properties of RSF particulate matter

2.8 References

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Chapter 3

Experimental Design

Initial experiments were conducted without a dilution tunnel, directly below a laboratory extraction system as shown in Chapter 4, Figure 4-1. In these experiments, the stove was mounted on a test trihedron, placed directly underneath the laboratory extraction system. The extraction setting was varied in order to apply small draught, as detailed in Chapter 4. The flue gas composition was measured by a Testo 340 and particulate matter by a Richard Oliver Smoke Meter (total gravimetric PM) and a cyclone set (PM_{10} and $PM_{2.5}$).

In subsequent experiments, the test rig was moved to a different laboratory where a dilution tunnel and additional equipment were installed. The test laboratory was designed by the author in accordance with published standards and with the help of supervisors, University of Leeds Estate Services and an external contractor. The final experimental setup is shown in Figures 3-1 to 3-3.

The appliance is placed on a balance inside a heat resistant test trihedron. The purpose of the test trihedron is to restrict access to the hot stove in accordance with health and safety requirements. It also allows the entire unit to be wheeled in and out of the laboratory before and after testing. There are two key benefits of the design, whereby the dilution tunnel and flue are fixed in position but the appliance can be easily changed. Firstly, the flexible hood design allows an appliance of any size to be tested; including biomass boilers, wood burning and multifuel stoves, and developing world cookstoves using a dedicated firebox. Secondly, sampling cables, connections and fittings do not need to be changed for each appliance, making testing more time and cost efficient, as well as being consistent.

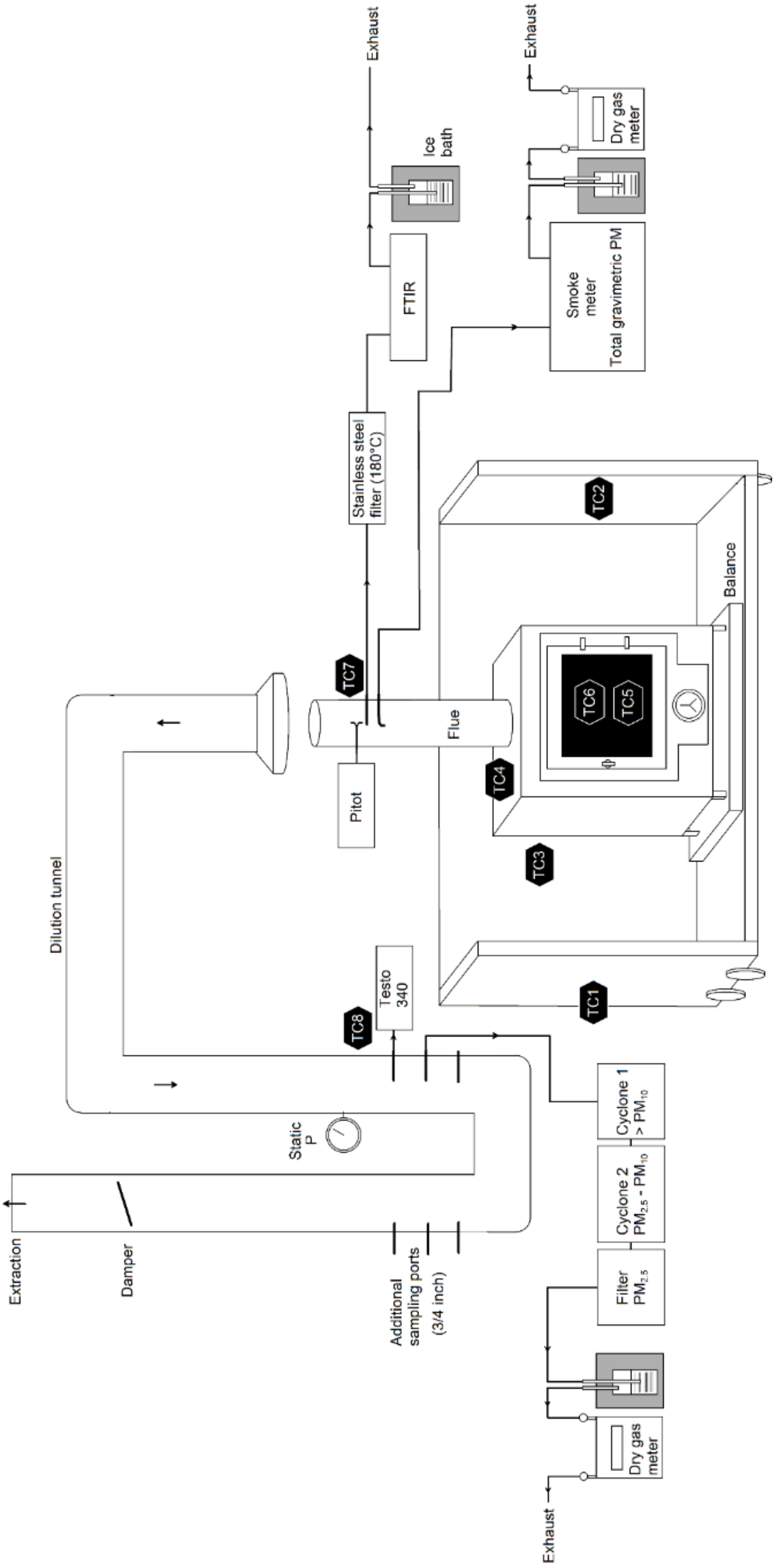

Figure 3-1. Final test assembly.

Figure 3-2. Photograph of laboratory testing of a heating stove

Figure 3-3. Photograph of laboratory testing of a cookstove.

3.1 Temperature, burning rate and flow rate measurements

Temperature

As shown in Figure 3-1, an array of K-type thermocouples was installed to monitor the temperature of the stove and sampling points. The signals were interpreted and recorded using the PicoLog software. Thermocouples one to three (TC1-3) measure the temperature of the centre left, right and rear of the test trihedron. TC4, TC5 and TC6 measure the stove surface, fuel bed and flame temperatures respectively. TC7 and TC8 measure the gas temperature at the sampling points in the flue and dilution tunnel.

Burning rate

Appliances were placed on a KERN DE 300K5DL platform balance which allows fuel mass loss rate to be recorded during the combustion cycle. The accuracy in the measurements is ±10 g. Measurements were recorded manually at 2-5 minute intervals depending on the particular test, although in later experiments online measurements were taken using the *KERN Balance Connection* software.

Flue gas flow rate

Flue gas velocity and flow rate were calculated by measuring the dynamic pressure change in the flue, using a Wöhler DC100 pressure computer. Both S-type and Prandtl-type (L-type) pitot tubes were used. The velocity at the measurement point v_i (m s^{-1}) is calculated as described in BS EN ISO 16911-1:

$$v_i = K\sqrt{\frac{2\overline{\Delta p_\iota}}{\rho}}$$

$\overline{\Delta p_\iota}$	is the average dynamic pressure measured at the point *i* (Pa)
K	is the coefficient of the Pitot tube which includes the Pitot calibration factor and constant values relating to Pitot design. This is 0.84 for S-type and 1.00 for Prandtl-type Pitots
ρ	is the density of the wet gas at the measurement point (kg m^{-3})

Combustion efficiency

The modified combustion efficiency (MCE) is a simple but useful parameter often used to assess smouldering/flaming tendency of a combustion process. MCE is defined by the CO and CO_2 concentrations, where Δ indicates background corrected values;

$$MCE = \frac{\Delta CO_2}{\Delta CO + \Delta CO_2}$$

3.2 Dilution tunnel sampling

The dilution tunnel design and general test procedures used are in accordance with BS EN 13240 and NS 3058 (detailed in DD CEN/TS 15883). The designs are shown in Figure 3-4 and Figure 3-5. The combination allows the primary combustion products to measured in the flue section (BS 13240) and the diluted products to be brought to within the measurement range of PM analysers.

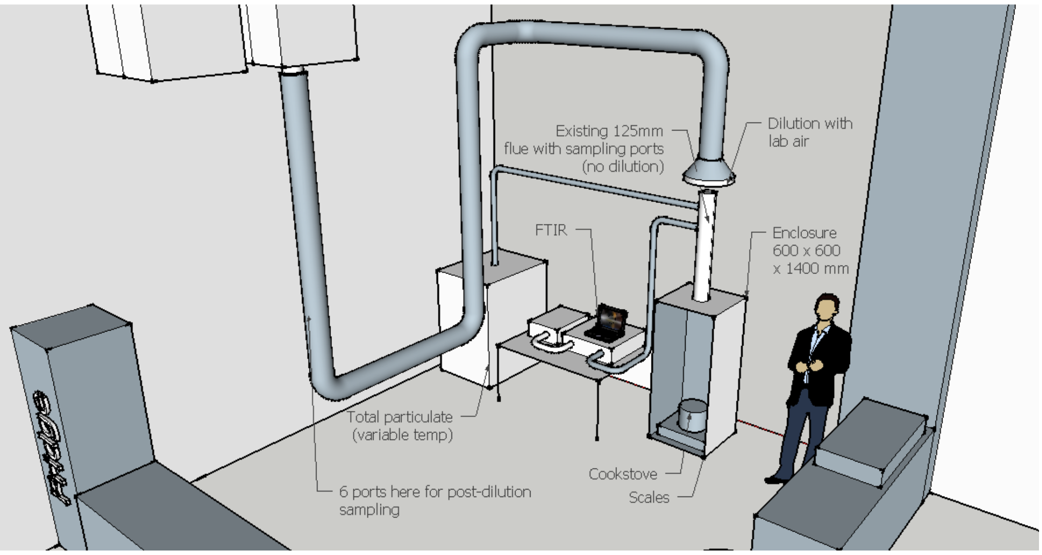

Figure 3-4. Computer model of the laboratory during the design stage

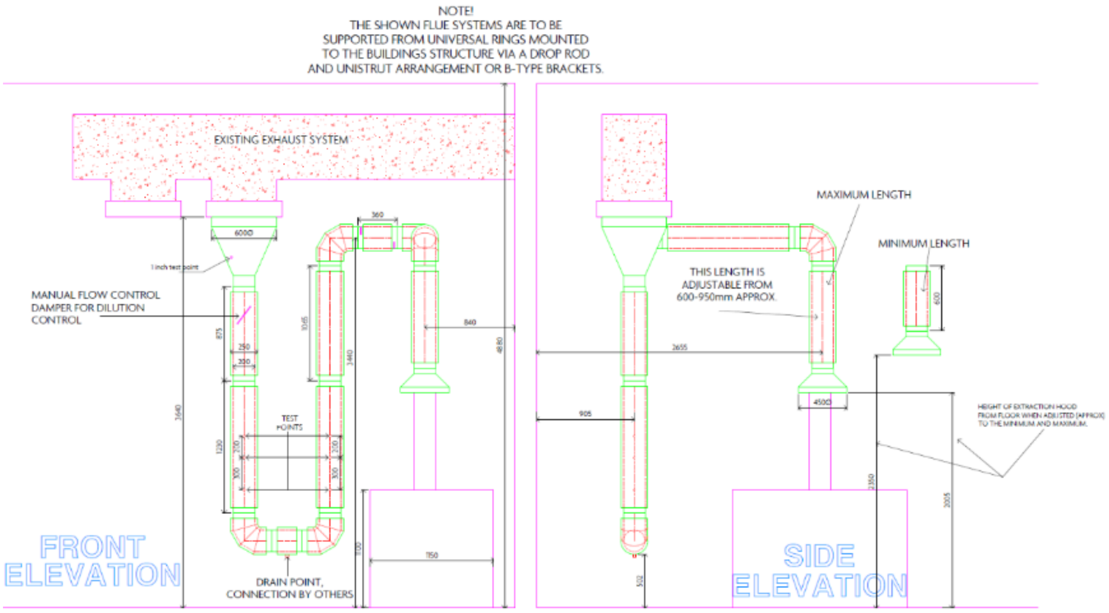

Figure 3-5. Dilution tunnel design by A1 Flue Systems on behalf of Glen Wilson Ltd.

The flow rate through the dilution tunnel can be carefully controlled and maintained using a combination of the laboratory extraction setting (two settings) and a damper placed at the end of the dilution tunnel. The static pressure is displayed on the dilution tunnel exterior. Dilution is made with ambient laboratory air and so a baseline background should be made, particularly for particulate measurements such as DMS, AMS and SP^2. Some studies have used filtered air for injection, particularly where an ageing chamber is used to investigate SOA formation (Orasche et al., 2012, Fine et al., 2002, Fine et al., 2001, Lamberg et al., 2011). By varying the static pressure, the dynamic pressure, velocity and flow rate in the duct increase linearly, as shown in Figure 3-6. The dynamic pressure is used to achieve isokinetic sampling as described in Chapter 3.4.

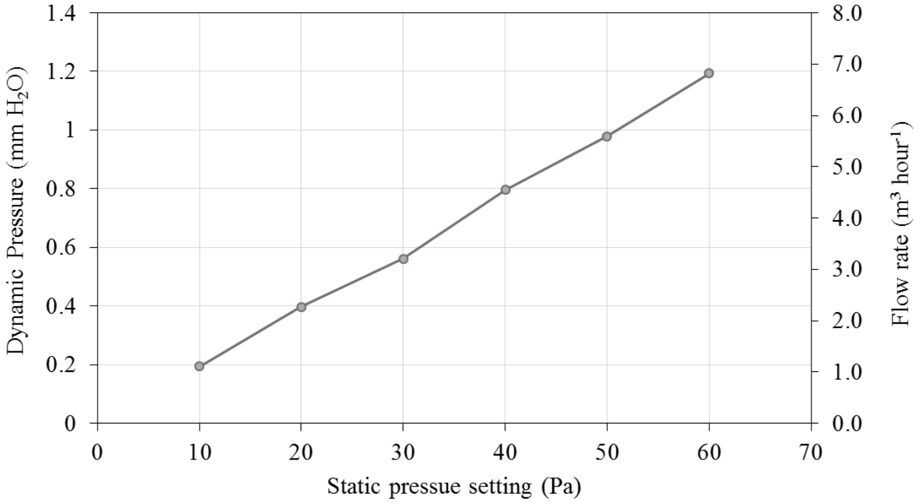

Figure 3-6. Variation of dilution tunnel flow rate with static pressure setting.

3.3 Gas sampling

Testo 340

Initial experiments were conducted using a Testo 340 analyser which allows the measurement of O_2, CO_2, CO, NO and NO_2 simultaneously. The sampling rate is 1.0 l min^{-1} and concentrations can be measured online using the Testo *easyEmission* software, with a variable resolution as low as 30 seconds. Measurements are made via pre-calibrated electrochemical sensors using the principle of ion selective potentiometry. The measurement range and accuracy are specified in the technical data supplied with the instrument. Generally they are ±0.2 vol.% for O_2 and CO_2, ±5% for NO and NO_2 and ±10% for CO at the concentrations observed in these experiments. The instrument features an automatic dilution system to protect the sensors. This feature was commonly activated in the early experiments due to high concentrations of CO which occasionally exceeded the 10,000 ppm limit of the instrument, leading to additional errors. In the later experiments, the Testo was used in the dilution tunnel (Figure 3-1) and was used to calculate the dilution ratio through the CO and CO_2 concentrations CO_{Testo}/CO_{FTIR} and $CO_{2,Testo}/CO_{2,FTIR}$.

FTIR analyser

Later experiments were conducted using a Gasmet DX4000 Fourier Transform Infrared (FTIR) analyser for the principle gas measurements. Briefly, an infrared beam is passed via beam splitter to both a fixed mirror and a moving mirror, which are then reflected back through a sample to a detector (Peltier-cooled mercury cadmium telluride detector at 180°C). The two signals are then recombined into an interferogram, which is converted into spectra using a Fourier transform (Bacsik et al., 2004). Given known wavelengths at which molecules absorb light, selective and quantitative analysis of up to 50 gas species can be made using this instrument. The formation of specific libraries tends to be iterative for given applications such as RSF combustion due to wide variations in gas composition with fuel type and appliance type. The reference library used in these experiments began with the standard 16 gases H_2O, CO_2, O_2, CO, NO, NO_2, N_2O, NH_3, SO_2, HCl, HF, CH_4, C_2H_6, C_2H_4, C_3H_8, C_6H_{14}. The library has been amended a number of times over the course of the experiments with the help of Quantitech Ltd., with later additions including HCN, CHOH, C_6H_6, C_2H_2, acetic acid and furfural. The reasons for this include certain gases being out of range of the instrument, a desire to measure a new gas, and known interferences between species (such as NO_2 and hydrocarbons – see discussion section). The Gasmet DX4000 is factory calibrated for measured gases which are then valid for the life of the instrument, according to the manufacturer. Those factors that would affect the calibration (pathlength, wavelength, source etc.) are either fixed or closely controlled. The instrument is serviced annually and a new water vapour calibration is conducted by the service engineer. The experimental error associated with this instrument is presented in Table 3-1 for twelve key gases.

O_2	2.4%	CO	6.5%	NO	5.6%	NO_2	6.7%	SO_2	9.2%	CHOH	4.0%
HCl	11.3%	NH_3	9.3%	CO_2	5.0%	H_2O	6.0%	HF	19.4%	CH_4	6.1%

Table 3-1. Measurement uncertainties for the DX4000 FTIR. Source: MCERTS Product Conformity Certificate, Sira Certification Service (2016).

Prior to FTIR analysis, flue gas is drawn through a 0.1 µm sintered steel filter at 180°C and then through a Teflon coated heated line into the analyser via a pump and separate ZrO_2 cell, which is used for O_2 calibration of the instrument. The rated sampling rate is 2-10 l min^{-1}. The steel filter is a useful addition to the sampling train because it allows the collection of high temperature PM (EC and ash only). After the analysis, the hot gas is sent to exhaust via an impinger ice bath, which allows the collection of condensate and water soluble organic carbon (WSOC).

3.4 Particulate sampling

Total gravimetric PM

Total particulate matter concentration was measured gravimetrically using a Richard Oliver smoke meter and 55 mm filters (Li et al., 2007). The instrument was extremely useful for this work because the heated filter housing on the front of the instrument (shown in white in Figure 3-7) allowed filters to be changed rapidly and hence PM samples can be collected over specific periods of interest within the combustion cycle. For example, ignition, fuel addition, bed agitation etc.

In the first batch of tests, 25 l of flue gas through two back-to-back glass fibre filter papers at a rate of 5 l/min. Three filters were taken in the flaming phase, and three in the smouldering phase. In the later tests, a separate gas meter was fitted to the exhaust line of the instrument, having passed through an impinger ice bath. This was due to uncertainties in the accuracy of the instruments built in gas meter. Samples were drawn from a 4mm nozzle in the flue via a Teflon coated heated line at 120°C. Care was taken to clean the inner pipework of the instrument with acetone between test periods in order to minimise particle cross contamination between fuels. The heated line was cleaned with compressed air.

Figure 3-7. Smoke meter used in the tests.

Initial testing used Whatman GF/F filters which have been used extensively for PM collection and subsequent analysis. However, as the research progressed it became apparent that these filters are not suitable for high temperature BC/OC analysis. Therefore quartz filters were used in the later tests, following advice from Sunset Laboratories, Tony Hansen, Griša Močnik and Andre Prevot. Further discussion of the effects of filter choice is given in chapter 10.

Cyclones

Experiments followed a method based on USEPA Method 201a and BS ISO 25597 for the determination of PM_{10} and $PM_{2.5}$ size fractions. Briefly, in the standard methods a probe featuring a set of cyclones, pitot tube and thermocouple is inserted directly into the flue. Flue gas is drawn through a pre-selected nozzle into the cyclone separators and then through a heated probe into a set of impingers, before a dry gas meter. A schematic is shown in Figure 3-8.

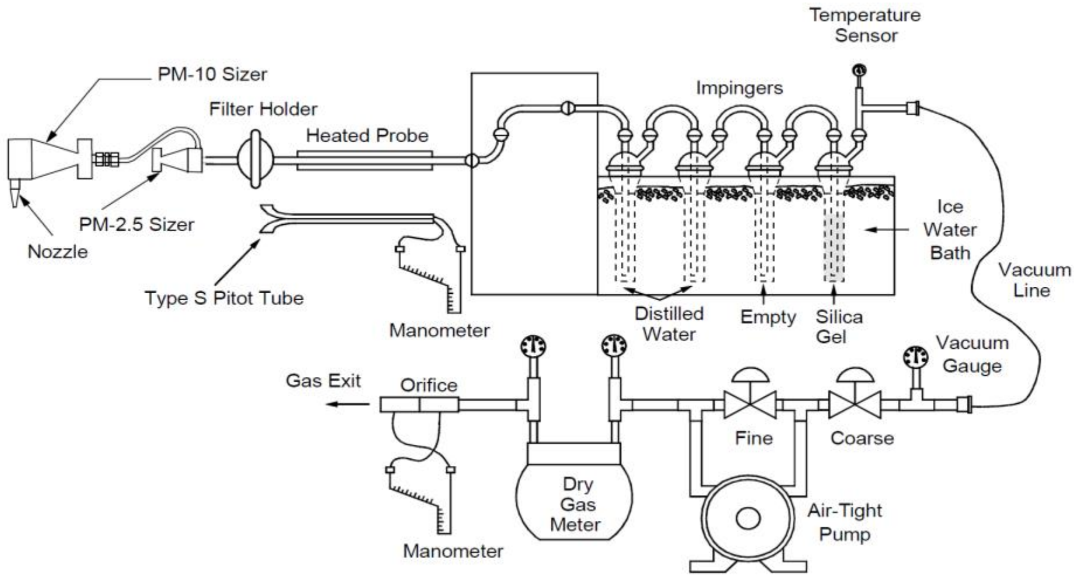

Figure 3-8. Schematic of the PM_{10} and $PM_{2.5}$ sampling train. Source: USEPA Method 201a.

However, due to the small flue size of the test rig it was necessary to mount the cyclones externally to the flue. In the standard methods, the cyclones are inserted into the flue for a period of around 30 minutes for temperature equilibration. Due to the cyclones being mounted externally, a heated jacket and PID controller was used in lieu, as shown in Figure 3-9.

Figure 3-9. Images showing the setup of the cyclone separators and heating system.

As discussed in Chapter 4, the system is designed for industrial stack monitoring using isokinetic sampling. The sampling velocity through the nozzle is varied to match the velocity in the flue. As shown in Figure 3-9, initial testing was done in the flue without dilution and it was found that the particle size is highly dominated by the fine fraction (see chapters 4, 8 and 9). In the final test assembly (Figure 3-1), samples were drawn into the cyclones from the dilution tunnel. The design calculations in BS ISO 25597 yielded a nozzle size of 9 mm for a static pressure setting of 40 Pa (see Figure 3-6).

Impactors

There are two British Standard methods available to measure PM_{10} and $PM_{2.5}$. These are BS ISO 25597 (high concentrations, cyclones) and BS EN ISO 23210 (low concentrations, impactors). During the commissioning of the system, an 8 stage Andersen impactor was used but the system was unheated and condensation became a problem. During the testing of the plasma abatement device (see chapter 10), a Dekati three stage cascade impactor was used to determine PM_{10}, $PM_{2.5}$ and PM_1 at a flow rate of 30 l min^{-1}. The device was heated but flue gas was undiluted and there were issues with overloading.

Differential Mobility Spectrometer (DMS)

Two experiments were carried out using a Cambustion DMS500 MKII fast aerosol mobility size spectrometer to measure particle size distribution in the flue. Results are presented in chapter 9. Samples were drawn from the flue and were diluted automatically by the instrument using compressed air. The DMS uses a unipolar corona discharge to apply a charge to particles which is proportional to its surface area. The charged particles are then introduced into a classifier column lined with electrometer detectors. Particles travel different distances down the column depending on their size and electrical mobility, allowing a particle size distribution to be generated. Measurements are taken at 180°C and there is a pre-cyclone on the instrument to remove particles greater than 2.5 µm. Hence the instrument can be operated in 1.0 µm mode or 2.5 µm mode, but the former was used in these experiments. The instrument was calibrated by manufacturer (Cambustion, Cambridge, UK) shortly before the experiments commenced (9th August 2016) using H_2SO_4 (15 nm), NaCl (49.6 nm) and NaCl (100 nm) aerosols. An autozero baseline was taken at the beginning of each day using laboratory air. There were no other particle sources operating in the laboratory at the time of testing. The choice of calibration file (.dmd) is dependent on the aerosol type and morphology, rather than a specific application. In this work, the inversion matrix used was derived from propane soot as a model for non-spherical agglomerate soot particles. This calibration file was recommended by the manufacturer for solid fuel testing (Cambustion, 2016). A detailed study on the reproducibility of the instrument was carried out by Cambustion (2017).

Additional analysers

In addition to the above instruments, during the cookstove testing an Aerosol Mass Spectrometer (AMS) was used to measure size-resolved particle composition including SO_4, NO_3, NH_4 and organics. A single particle soot photometer (SP^2) was also used to measure particle incandescence (black carbon) and scattering (organic coatings) online. Both of these instruments were installed, calibrated and operated by colleagues at the University of Manchester and results are therefore not included here. Results will be presented in a forthcoming publication, led by the University of Manchester.

3.5 Appliances and Operating Conditions

Details of the heating stove used in these experiments is given in Chapter 4 subsection 4.2.2. It is a Waterford Stanley Oisin multifuel stove rated at 5.7 kW and 79% thermal efficiency. This appliance was chosen because it is typical of a mid-range domestic stove which meets the requirements to burn both wood and coal type fuels. It features a raised grate and single stage primary air supply, as shown in Figure 3-10. The stove is not 'DEFRA approved' and not exempt for use in smoke control areas under the Clean Air Act.

Figure 3-10. Heating stove used in the experiments.

No other heating appliances have been tested in this work so that the impact of fuel properties on emissions can be evaluated with the appliance kept constant. Three developing world cookstoves have been tested, details of which are given in chapter 9**Error! Reference source ot found.**. These appliances are improved cookstoves, designed to reduce fuel useage and emissions. They include a Gyapa charcoal stove, CarbonZero wood stove and a WorldStove Lucia-type pyrolytic stove.

In chapters 4-6, the operating conditions used were chosen to mimic real-life conditions in the laboratory. As described in Chapters 2.1 and 2.3.2, the measurement protocol and operating conditions have a significant effect on appliance performance and emission factors. Standard laboratory testing under BS EN 13240 requires an ignition phase and pre-test period before the test batch of fuel is added. Hence, the ignition and pre-test (cold start) emissions are not included. In chapters 4-6, single batch testing was carried out with no re-loading. This was done in order to assess the effects of ignition and combustion phase on emissions throughout the test cycle, and to derive phase-specific emission factors. Fuel loading was determined using the nominal rating of the stove and the fuel calorific value. Three to five repeat tests were carried out on each fuel type after the stove had returned to room temperature and the ash removed. In subsequent work (agricultural residues, waste wood and cookstove testing), a number of batches of fuel were added and each reload acted as a repeat test. The number of reloads varied from 3-5 for agricultural residues up to 27 for cookstove testing.

3.6 Post analysis of particles

EC and OC

Elemental carbon (EC) and organic carbon (OC) were determined thermogravimetrically using a Shimadzu TGA. A filter cutting was folded and placed directly on the TGA hang-down for maximum accuracy. As described in Chapter 5, the sample was purged with nitrogen at a rate of 50 ml min^{-1} before the temperature was raised to 550°C at a rate of 5°C min^{-1} to release volatile OC (Huang et al., 2006). After a 10 min hold time, the atmosphere was switched from N_2 to air which derived fixed carbon that we assume is analogous to EC. The TGA is calibrated regularly by the analytical laboratory manager using fixed mass weights and an automatic calibration programme on the instrument. The accuracy of this instrument is ±0.001 mg. As described in Chapter 2, there are three standard protocols for determination of BC(EC) and OC: NIOSH, IMPROVE and EUSARR. Several quartz filters taken during the emissions testing of straw briquettes (see Appendix IV) were sent to Sunset Laboratories, Netherlands, where the NIOSH protocol was used to determine EC and OC.

Py-GC/MS

The composition of the OC fraction (defined here as pyrolysed gases at 550°C) was determined directly using pyrolysis gas chromatography mass spectrometry (py-GC/MS). The details of this analysis are given in Chapter 5. Briefly, a CDS 5200 series pyroprobe was used to liberate OC from the filter onto an adsorbent trap (Tenax TA) at 40 °C. The gaseous products (H_2, CO, CO_2, CH_4 etc) are vented. The trap is then desorbed at 300 °C in a flow of helium onto the chromatographic column (RTX 1701 60 m capillary column, 0.25 mm id, 0.25 μm film thickness) within the Shimadzu 2010 GC-MS instrument. For all GC-MS studies, the chromatogram peaks were assigned using the NIST2008 Mass Spectral Library Database and previous analysis from the literature (e.g. Fitzpatrick et al., 2007).

PAH

Accelerated solvent extraction (ASE) was used to extract the PAH from the filter PM samples, using toluene as a solvent. The solvent was then condensed using a nitrogen blower. PAH analysis was performed with a Perkin Elmer Clarus GC-MS using a deuterated pyrene recovery standard. EPA-16 PAH species were identified by the *m/z* ratios using the NIST2008 database and the literature.

Electron Microscopy

Scanning Electron Microscopy (SEM) analysis was carried out using a Carl Zeiss EVO MA15 microscope. Particle composition was analysed by energy dispersive spectroscopy (EDS) using an Oxford Instruments X-Max silicon drift detector with an 80 mm^2 crystal. Samples were gold coated for 8 minutes to enhance conduction.

Transmission electron microscopy (TEM) was carried out on two samples with the help of the Leeds Electron Microscopy and Spectroscopy centre (LEMAS). The first sample was eluted from a filter matrix through agitation in acetone and examined with a FEI CM200 TEM. The second was sampled directly onto holey carbon grids placed into the flue of the stove, as described in chapter 8. Samples we examined by a FEI Titan3 Themis TEM operating at 80kV and fitted with a Gatan One-View CCD and Quantum ER electron energy loss spectrometer (EELS). As the electron beam passes through the sample, it is affected by the structure and composition of the particles present. This was used to determine the ratio of sp^2 to sp^3 carbon and the carbon to oxygen ratio, as described in chapter 2.

3.7 Fuels

3.7.1 Overview of fuels used in all studies

A full list of all the fuels used in the study is given in Table 3-2 and their physical appearance is shown in Figure 3-11. Papers 1 and 2 (Chapters 4 and 5) fuels were mostly commercially available solid fuels, typical of the mix used in the UK and Ireland. Not all fuels were included in the published work and these have been included in supplementary material in the appendices. Paper 3 (chapter 6) fuels were sourced from various RSPB reserves and were biomass arisings from conservation practices including habitat management. Additional fuels were used during the cookstove testing, which are described in Chapter 9, and in other work detailed in chapter 10.6.


Commercial hardwood logs
Dimensioned pine
Reed briquettes
Wheat/Barley Straw
Sugarcane Bagasse
High bark logs
Synthetic logs
Torrefied spruce
Waste wood
Peat turf
Lumpwood charcoal
Bituminous coal
50:50 biomass blend
Peat briquettes
Lignite
MSF
Smokeless fuel

Figure 3-11. Photographs of fuels used in the experiments

Cat	Fuel	Description	Technology	Chapter
1	Mixed hardwood logs	Commercially available, seasoned	Heating stove	4, 5
	Birch logs	Source from Ireland and Humberside. Seasoned	Heating stove	4, 5, 6
	Ash logs	Sourced from Lancashire. Seasoned	Heating stove	6, 9
	Hazel logs	Sourced from Lancashire. Seasoned	-C-	6
	Willow logs	Sourced from Humberside. Seasoned	Heating stove	4, 6
	Willow billets	Sourced from Humberside. Seasoned	Heating stove	4, 6, 11
	Willow charcoal	Sourced from Humberside. Seasoned	Heating stove	6
	Pine	Dimensioned CLS pine lumber	Heating stove	4, 8, 9
	Spruce log	Source: Aberdeenshire, Seasoned	-C-	
	Synthetic logs	2 commercial large wood briquettes. Calor/FuelExpress	-C-	9
	Wood pellets	Commercial white wood pellets	Heating stove, cookstove	4, 11
	Lumpwood charcoal	Commercial Namibian lumpwood charcoal	Cookstove	4, 11
	Oak	Dry oak sticks and branches. High bark content	Cookstove	4, 11
	Oak WET	High MC oak sticks and branches. High bark content	Cookstove	4, 11
2	Waste wood	Milled & briquetted waste wood	Heating stove	9
	Washed waste wood	Milled, washed & briquetted waste wood	Heating stove	9
3	Torrefied spruce	Torrefied spruce briquettes from Andritz AG.	Heating stove	4, 5
	Torrefied willow	Torrefied willow briquettes from Rothamsted/ECN	-C-	9
	Torrefied olive	Torrefied olive briquettes from Arigna Fuels	-C-	4, 9, 11
4	Peat turf	Air-dried Irish bog peat	Heating stove	4, 7
	Peat briquettes	Commercially available, Bord na Mona	Heating stove	4, 5
	Lignite	Commercially available briquettes, Arigna Fuels	Heating stove	4, 11
	Bituminous coal	Polish lump coal from Arigna Fuels	Heating stove	4, 5
	Biomass/coal blend	50% olive stove, 50% coal-derived residues from Arigna Fuels	Heating stove	4, 5
	Low smoke fuel	Cosyglo. Commercially available, Arigna Fuels.	Heating stove	4, 5
	Smokeless fuel	Ecobrite. Commercially available, Arigna Fuels.	Heating stove	4, 5
5	Reed briquettes	Source brackish water Humberside. Briquetted externally	Heating stove	6
	Reed char	As above, charred instead of briquetted	-C-	6
	Wheat straw	4 wheat straws with different treatments. Briquetted	Heating stove	4, 9, 11
	Barley straw	3 barley straws with different treatments. Briquetted	Heating stove	9
	Bagasse	Brazilian sugarcane bagasse, dried and briquetted.	-C-	9
	Miscanthus briquette	Commercially available, University of Bath	-C-	9
	Sunflower husk	Agricultural residue for comparison. Not briquetted	-C-	4, 11
6	Multi-fuel stove deposit	Soot deposit recovered from the flue of a multi-fuel stove in a home	Deposit	4
	Wood stove deposit	Soot deposit recovered from the flue of a Morso wood stove in a home	Deposit	4

Categories: 1: wood fuels, 2: waste wood, 3: torrefied fuels, 4: peats and coals, 5: herbaceous biomasses, 6: soot deposits. -C- indicates characterisation and fuel analysis but no emissions testing.

Table 3-2. List of fuels used in different sections of the work.

3.7.2 Fuel Characterisation

Sample preparation

Biomass fuels were shredded using a Retsch SM100 cutting mill to a size of <1 mm, and were then milled using a SPEX 6770 cryogenic grinder to achieve a very fine particle size require for analysis. Mineral fuels were milled using a Retsch PM100 ball mill. All samples were sieved to ensure a particle size of 90 µm or less. Unless otherwise stated, wood logs were milled and analysed including the bark.

Briquetting

Most samples were briquetted externally before testing, however a small number were briquetted in house. An MTI electromotion hydraulic press was used to produce 60 mm diameter briquettes (height 20 mm) waste wood and washed waste wood (see chapter 11). The pressure applied was 20-30 MPa. Straw briquettes were manufactured by Business Support Associates Ltd using an RUF press with a pocket diameter of 75mm and the pressing pressure was 20 MPa. Twenty percent moisture was added to the samples (based on as received weight) and allowed to equilibrate for 6 days. A binder was then added consisting of 10% solid pre-gelled wheat starch (based on as received weight) and briquetted immediately after mixing.

Proximate analysis

Proximate analysis on mineral fuels was carried out according to BSO ISO 17246; whereby moisture is determined by drying in a nitrogen oven at 105 °C for over an hour, volatile content is determined by heating out of contact with air at 900 °C for 7 minutes, and ash is determined by heating in air at 815°C. For the biomass fuels, proximate analysis was carried out according to BS EN 14774-3 for moisture, BS EN 15148 for volatile matter and BS EN 14775 for ash. The principle is the same for solid biofuels as mineral fuels, but the moisture is determined in air and the ashing temperature is 550 °C. Tests were repeated in triplicate and an average reported.

Ultimate analysis

Ultimate analysis (CHNS) was carried out in triplicates on a CE Instruments Flash EA1112. Oxygen was calculated by difference in accordance with BS ISO 17247. Samples were prepared by weighing 2.5 mg of 90 µm sample into a tin capsule and crimping. A vanadium pentoxide catalyst was added to the high carbon low volatile fuels as a combustion aid. Microanalytical standards used were antropine, 2,5-Bis(5-tert-butyl-2-benzoxazolyl)thiophene (Bbot), dl-methionine, l-cystine and sulphanilamide. Reference materials used were olive stone and coal standard (Elemental Microanalysis B2170 and B2306). Samples are combusted in a high temperature (1000°C) oxygen-rich atmosphere and the resulting gases are detected using gas chromatography and thermal conductivity detection. The lower limits of detection for sulphur and nitrogen on this instrument are 0.05% and 0.1% respectively.

Bomb calorimetry

Calorific value was determined by bomb calorimetry using a Parr 6200 calorimeter. 0.5 mg of raw sample was placed into a crucible, close to but not touching a fuse wire between two electrodes, and placed inside the 'bomb' container. 10 cm^3 of deionised water is placed in the bottom of the container to absorb the combustion gases. The 'bomb' is then filled with oxygen to a pressure of 30 bar and placed in a 2 litre bucket of deionised water at room temperature. The 'bomb' is then ignited and the calorific value is determined by the raise in temperature of the water. After combustion, the 'bomb' is removed and left for 10 minutes to ensure good partitioning of combustion gases into the water matrix.

Trace elements

Chloride, fluoride, bromide, sulphate and phosphate anions were determined via ion chromatography (IC) of the washings following bomb calorimetry. This method is in accordance with Method A of BS EN 15289:2011. The instrument used was a Dionex DX-100 IC. This method was used for chlorine content determination in all sample except those in Chapter 6, where the Cl content was determined externally by combustion and mercuric nitrate titration in the School of Chemistry, University of Leeds.

Trace metal contents of samples were determined by atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) of digestates. Microwave digestion of 0.2 g of raw sample in 10 ml HNO_3 was used in all tests. The AAS instrument used was a Varian 240fs AAS using an acetylene burner and a nitrous oxide-acetylene burner for elements such as calcium. The latter requires an ioniser suppressant which was achieved using a KCl solution. The ICP-MS instrument was a Perkin Elmer SCIEX Elan DRC-e. For ICP-MS analysis, digestates were diluted by a factor of 5000 and were made on a mass basis rather than volume, in order to minimise errors as much as possible. Ultra-high purity deionised water was used for dilutions. Samples are dried, dissociated and ionised by injection into an argon plasma and the resulting ions are detected by a mass spectrometer.

Thermogravimetric analysis

Thermogravimetric Analysis (TGA) was carried out on a TA Instruments Q5000 analyser. A sequential program was used to simulate proximate analysis in ambient air. The temperature program involved a drying stage at 105°C and a volatile stage at 900°C in nitrogen for all fuels, before an ashing stage. The ashing temperature was 550°C for biomass fuels and 815°C for mineral fuels, as recommended in the relevant British standards. The temperature profile is shown in Figure 3-12.

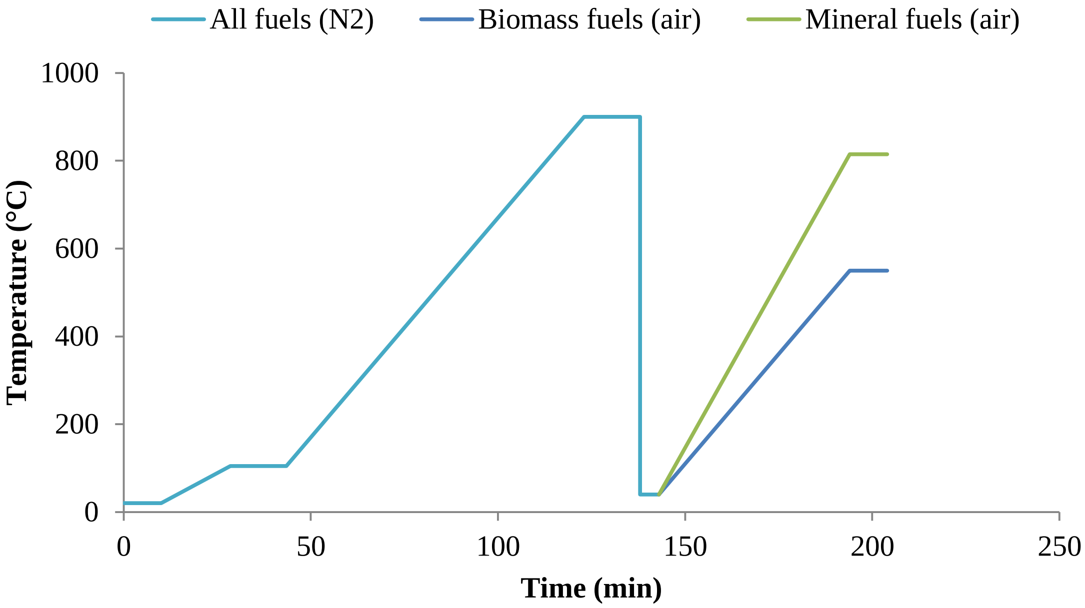

Figure 3-12. Temperature programme for thermogravimetric analysis of all fuels.

3.8 Emission factor calculations

Pollutant concentrations are typically measured and reported in units of parts per million (ppm) or in mg m^{-3} at standard reference conditions. A number of variables must be corrected to standard conditions including the flue gas temperature, pressure, moisture content and oxygen content. The correction is shown below

$$C = C_i \times \frac{273 + T_g}{273 + T_{ref}} \times \frac{P}{1013} \times \frac{21 - O_{2,ref}}{21 - O_{2,i}} \times \frac{100}{100 - MC}$$

where:

C	is the corrected pollutant concentration of the (ppm or %)
C_i	is the measured pollutant concentration at the actual oxygen concentration
T_g	is the measured flue gas temperature (°C)
T_{ref}	is the reference temperature, 0°C for STP and 20°C for NTP
P	is the sum of barometric pressure and static pressure (hPa or mbar) [note that static pressure << barometric]
$O_{2,i}$	is the measured dry oxygen content
$O_{2,ref}$	is the reference oxygen concentration, typically 11% or 13%
MC	is the measured moisture content of the flue gas (%)

$$C_{mg/m3} = C_{ppm} \times \frac{M_{mol}}{V_{mol,std}}$$

where C is the corrected pollutant concentration in mg m^{-3} or ppm and $V_{mol,std}$ is the standard volume of 1 mole of an ideal gas at STP, 22.4 litres. M_{mol} is the molecular weight of the pollutant of interest, 46 g mol^{-1} for NO_2, 28 g mol^{-1} for CO etc.

Once concentrations are corrected to standard conditions, a variety of methods exist for the calculation of emission factors or emission indices, depending on the combustion source and availability of data during the experiments, as well as the requirements for a given standard. For example, the Clean Air Act exemption requires a PM emission factor of less than 5 g $hour^{-1}$, whilst the RHI and Ecodesign requirements are given in mg MJ^{-1} fuel input and in mg m^{-3} respectively. Perhaps the most commonly reported unit in the literature is milligrams of pollutant emitted per kilogram of fuel burned (mg kg^{-1}).

3.8.1. Emissions factors for vehicle testing

This method originates from calculating the emission index for vehicular emissions testing, but uses the same principles as other methods to convert from mg m^{-3} to g kg^{-1} or g GJ^{-1}. The equation used is:

$$EI = C \times (1 + A/F_m) \times 1000$$

where C is the concentration of a pollutant in mg m^{-3} and A/F_m is the air to fuel ratio at the time of sampling. For solid fuel emissions testing, A/F_m is determined from the stoichiometric air to fuel ratio (calculated from the fuel CHNS analysis) and the measured oxygen content, via the relationship:

$$A/F_m = A/F_{stoic} \times \frac{(100 + \lambda_e)}{100}$$

where λ_e is the excess air ratio determined by the oxygen content of the flue gas relative to 21% in atmosphere. For particulate, EI is calculated using following formula:

$$EI = \frac{C}{1.16} \times (1 + A/F_m)$$

where the terms are the same as above and 1.16 is the density of the sampled flue gas. This method is useful where the mass burning rate of fuel is not known.

3.8.2. Emission factors for industrial air pollution sources

Generally industrial sources are also not able to directly measure fuel burning rates and the so the conversion from mg m^{-3} to g kg^{-1} or g GJ^{-1} is made using the specific dry flue gas volume (SDFGV) per unit fuel input. SDFGV in m^3 GJ^{-1} or m^3 kg^{-1} is again calculated from the stoichiometry of combustion using a given CHNS content for a particular fuel (wood, coal, straw etc.)

$$EI = \frac{C \times SDFGV}{1000}$$

where C and $SDFGV$ are at 0°C, 1013 mbar and the same defined oxygen concentration. SDFGV can be calculated directly for a given fuel using the ultimate analysis results, following the method of Harker and Backhurst (1981) and Ozgen et al. (2014). SDFGV can also be taken from tables which are available in the literature such as in (AEA, 2012) for the UK/DEFRA and (Gibbs, 1998) for the USEPA. The advantage of this method is that it is relatively simple, however it does not directly measure fuel burn rate and does not account for variations in the fuel properties which may impacts on emissions factors such as moisture content. Due to the correction to a reference oxygen concentration, this method is not suitable in cases where there is very high excess air, as described in further detail in chapter 10.

3.8.3. Emissions factors for small scale combustion sources

The carbon balance method

Here, the conversion to g kg^{-1} or g GJ^{-1} is made using a carbon balance method, as described in the Water Boiling Test (WBT) for cookstove testing and references therein (GACC, 2014). This method is also used for derivation of emissions factors for open biomass burning, e.g. forest fires and land clearance. The principle of the method is that all the fuel carbon is converted to combustion products CO_2, CO, PM and THCs (total hydrocarbons including VOCs). The ratio between pollutant concentration and carbon concentration is used in lieu of the reference oxygen level correction used in other methods. Full details and equations for this method are given in the WBT.

The total flow method

In this method, all pollutant emissions from an appliance are collected in a hood or stack and the fuel burning rate and flue gas flow rate are directly measured. The emission index is then calculated as follows

$$EI = \int_{t_0}^{t} \frac{C_i \times Q}{m}\, dt$$

where C_i is the concentration of species i (mg m^{-3}), Q is the flow rate measured in the duct, m is the mass of fuel burned from time t_0 to t. A comparison and discussion of the advantages and disadvantages of these methods is given in chapter 10.

3.9 Modelling work

Chapter 7 presents modelling work carried out using the GAINS (Greenhouse gas–Air pollution Interactions and Synergies) model (http://gains.iiasa.ac.at/models). The GAINS model and its predecessor, RAINS, have been used in the formation of national and international air quality and climate policy across Europe for over 20 years (Kellly, 2006, Amann et al., 2011). GAINS was developed by the International Institute for Applied Systems Analysis (IIASA; Laxenburg, Austria) as a tool to evaluate the potential of emission control strategies to reduce greenhouse gases and/or improve local and regional air quality. Full details of the GAINS model projections, assumptions and data sources are available in the literature (Amann, 2015, Amann et al., 2011, Amann et al., 2013, Klimont et al., 2016, Kupiainen and Klimont, 2007). In summary, 5-yearly activity data is derived exogenously from the TSAP (Thematic Strategy on Air Pollution, (Amann, 2015)) and IEA (International Energy Agency) statistical data for the period 1990-2010, which is consistent with national reporting such as the NAEI activity data in the UK. Future projections to 2030 are derived from the IEA/OECD Energy Technology Perspectives and the IEA World Energy Outlook, which account for population, economic and sectoral growth rates in individual countries. The projections are part of the ECLIPSE (Evaluating the CLimate and Air Quality ImPacts of ShortlivEd Pollutants) project - European Commission 7th Framework funded project 282688 (http://eclipse.nilu.no/). The most recent version, V5, has been used in this work under the current legislation (CLE) scenario. ECLIPSE_V5_CLE assumes efficient enforcement of committed legislation, with some deviations where data is available (Stohl et al., 2015). Three other scenarios are available, but there is little effect on RSF category activity data in the UK and New Zealand. The CLE 'base' scenario is comparable with the greenhouse gas emissions pathway for a 6°C warming by 2100 (similar to IPCC scenario RCP 6.0).

The advantages of using GAINS to assess the impacts of emissions from RSF combustion have been demonstrated by a number of studies (UNEP/WMO, 2011, Winther and Nielsen, 2011, Klimont et al., 2016, Yttri et al., 2014, Stohl et al., 2015, Denier van der Gon et al., 2015).

Residential sector solid fuel heating technology types are represented in GAINS as heating stoves (HS), open fireplaces (FP), single house boilers <50 kW (SHB) and medium commercial boilers <50 MW (MB). In the UK and New Zealand, additional emissions sources include cooking stoves and outdoor sources (firepits, chimneas, barbeques, pizza ovens, garden incinerators). However, GAINS activity data/emissions for the former are negligible for solid fuels in both countries, and the latter is also negligible although perhaps underrepresented (Bari et al., 2015, Kabir et al., 2010). Nevertheless, the focus of the study presented in Chapter 7 is on the biggest contributors to PM emissions; heating stoves and fireplaces.

In any given year, the national emissions *E* (kt year^{-1}) of pollutant *i* in country *c* are given by

$$E_{i,c} = (A_c \times EF_i)_{HS} + (A_c \times EF_i)_{FP} + (A_c \times EF_i)_{SHB} + (A_c \times EF_i)_{MB}$$

where A_c is the activity data (amount of fuel energy input, PJ) and EF_i is the technology- and fuel-specific emission factor of pollutant *i* (kt PJ^{-1} or g MJ^{-1}). The net radiative forcing for each country c is then calculated for the year after emission for both coal-type and biomass-type RSFs by

$$RF_c = \sum_{i=1}^{i} (E_{i,c} \times RFPUE_i)$$

where $RFPUE_i$ is the radiative forcing per unit emission (µW m^{-2})(kt year^{-1})$^{-1}$ during the first year after emission. Values of $RPUE_i$ are taken from (Bond et al., 2013), tables C1 and C4, as described in Chapter 7. A key assumption in this work is that CO_2 emissions from biomass combustion are offset by CO_2 absorption during the growth of the tree. A number of studies have shown this not to be the case (see Chapters 2.6 and 10.4), but the focus of this work is on climate impacts from short-lived species from the point of emission.

In Chapter 7, emissions factors, activity data and annual emissions were taken from the GAINS model (using ECLIPSE_v5_CLE, as above) in Feb-June 2016, and hence do not include the revisions made after the DECC/BEIS *Domestic Wood Use Survey* was published in April 2016. The same is true of NAEI data, whereby all emissions factors and activity data used in this work were taken before the NAEI was updated to include revised wood consumption estimates and associated historical emissions. Subsequent updates to the NAEI since the preparation of this work may reduce the differences presented in Figure 7-13, due to the inclusion of survey data. When the NAEI was accessed in Spring/Summer 2016, activity data was available up to the year 2013. Bottom-up emissions inventory calculations used 2013 census data for New Zealand and 2013/14 survey data (published 2016 by DECC/BEIS) for the UK.

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Chapter 4

The Impact of Fuel Properties on Emissions Factors

The Impact of Fuel Properties on the Emissions from the Combustion of Biomass and other Solid Fuels in a Fixed Bed Domestic Stove

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Abstract

Experimental results are presented on the emissions from a single combustion chamber stove burning wood, coal and processed fuels. This technique was used to permit comparisons to be made of the influence of different fuel types without it being influenced by the effects of secondary combustion. Measurements were made of CO, NO_x and fine particulates during the major phases of combustion, namely flaming and smouldering. Measurements of the particulates were made in two ways: firstly using a gravimetric total particulate measurement and secondly using a cyclone technique to give $PM_{2.5}$ and PM_{10} size fractions. Smoke emissions from the different fuels were very dependent on the phase of combustion especially for the total particulate results, where flaming phase emissions were much higher than in the smouldering phase. It was found that the particulate emission factors for the wood fuels were dependent on the volatile content whilst the coals followed a different pattern. NO_x was linearly dependent on the fuel-N content for all the fuel types, but the relationship for biomass is different from that for coal. CO emissions were very dependent on the combustion phase.

Key words: solid fuels, stove combustion, pollutants

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Supplementary data associated with this article can be found in section 11.2. This material has not been published.

4.1 Introduction

A number of countries have introduced energy policies in order to reduce greenhouse gases. In the case of heating applications this has led to an increase in the use of wood burning stoves and boilers particularly in Europe, although coal burning appliances are still widely used in many parts of the world. The use of solid biofuels has been the fastest growing energy source in the UK in the last two decades and a similar situation applies across the EU. In many cases these appliances use a single combustion chamber originally designed for the combustion of coal and often the combustion process is poorly controlled. More recently stoves designed specifically for biomass fuels and employing better fuel preparation have reduced the extent of the emissions. Nevertheless there are still concerns about the health effects particularly from fine particles and NO_x [1-5] as well as from the influence of black carbon and organic compounds on climate change [6,7].

In the UK the Renewable Heat Incentive (RHI) [7] has been promoted for both domestic and commercial application which advocates the use of low carbon technologies including the use of biomass fuels. Similar schemes operate in many parts of Europe; in Ireland a combination of higher prices and policies such as the Greener Homes Scheme has resulted in a greater use of wood for domestic heating. The UK Clean Air Act and RHI [8] place emission limits on small appliances when tested to standard methods (BS PD 6434 and BS EN 303-5). A variety of emissions limits or test standards operate around the world. In the EU there is the proposal to bring in much tighter legislation by 2022 (Eco-design) for solid fuel local space heaters, with particulate emissions and NO_x varying according to fuel type. The emphasis on emissions is currently directed to both fine particulates and NO_x. Many of the particles produced are below 1 µm in diameter which are the most hazardous to health [1]. Wood burning is also associated with high emissions of organics such as polycyclic aromatic hydrocarbons (PAH) which are known to be mutagenic and carcinogenic [2- 4]. Consequently a number of research programmes have looked in detail at the emissions from wood-fuelled appliances [3, 9-18] and there is also interest in pre-processing the fuels to reduce emissions.

In this paper we have used a fixed grate multi-fuel stove with a single combustion chamber. This type of stove has the advantage of giving information on the emissions directly released from the primary combustion of the fuel enabling the effects of different fuel types to be studied. Thus we have studied a range of fuels, two woods, a torrefied fuel, a peat, a biomass/coal blend and two smokeless fuels. This design is still widely used in many countries for domestic heating. Measurements were made of the particulate and gaseous emissions during a single combustion cycle for a number of fuels used typically in the UK and Ireland in order to obtain insight into the effects of the different phases of combustion, flaming and smouldering, on pollutant formation. A flue gas sample dilution tunnel was not used because of the diverse fuels studied and so information was obtained only on the primary products formed.

4.2 Experimental Methods

4.2.1. Fuels used

A total of eight fuels were studied which are listed in Table 4-1. They consist of three groups; (1) two woods, these having similar moisture levels to avoid the complications resulting from too many variables, (2) a pre-treated biomass fuel and (3) coal or coal derived fuels, these being included for comparison purposes. Biomass fuels were shredded using a Retsch SM100 cutting mill to a size of <1 mm, and were then milled using a SPEX 6770 cryogenic grinder to achieve a very fine particle size required for analysis. The mineral fuels were milled using a Retsch PM100 ball mill. All samples were sieved to ensure a particle size of 90 µm or less. The wood logs were milled and analysed including the bark.

Proximate analysis on the coal and smokeless fuels was carried out according to BSO ISO 17246. For the biomass fuels, proximate analysis was carried out according to BS EN 14774-3 for moisture, BS EN 15148 for volatile matter and BS EN 14775 for ash. These are the same as for mineral fuels, but the moisture was determined in air rather than nitrogen, and the ashing temperature is 550°C rather than 815°C. The 50:50 blended fuel was tested both ways for comparison purposes. Ultimate analysis (CHNS) was carried out on a CE Instruments Flash EA1112. Gross calorific values (GCV) were determined on a weight % dry basis by bomb calorimetry using a Parr 6200 Calorimeter. Cl and P were determined via ion chromatography of the washings following bomb calorimetry. This method is in accordance with Method A of BS EN 15289:2011. The P and Ca values were determined by means of nitric acid digestion and ICP-MS, and K values were determined using atomic absorption spectroscopy (AAS) since it is more accurate than ICP-MS. The data obtained are given in Table 4.2. VM denotes volatile matter and FC the fixed carbon content.

Fuel No.	Fuel type	Physical Description
1	Domestic firewood (A)	Commercially available seasoned mixed hardwood. ~200mm long; diam.~70mm
2	Domestic firewood (B)	Air dried hardwood (Silver Birch) logs, ~200mm long; diam. ~70mm
3	Torrefied wood briquettes	Torrefied spruce wood (bark-free). Briquettes approx. 70mm diameter. From Andritz AG. Torrefaction temperature approx. 280-295°C.
4	Peat briquettes	Briquettes of pressed peat. Length ~185 mm diam. ~ 70 mm
5	Bituminous coal	Premium grade bituminous coal (Poland) supplied in lumps ~ 100mm
6	Biomass/coal blend	Briquetted blend of 50% olive stone/50% low sulphur petroleum coke, coal and anthracite. Approx. 80 mm diameter
7	Low smoke fuel	Cosyglo (supplied by Arigna Fuels). Anthracite based commercially available product, 84x65x35mm briquettes.
8	Smokeless fuel	Ecobrite (supplied by Arigna Fuels). Anthracite based commercially available product, 50x50x30mm briquettes.

Table 4-1. Fuel types used in the study.

Fuel No	1	2	3	4	5	6	7	8
Fuel type	Wood A	Wood B	Torrefied briq	Peat briq	Coal	Biomass Blend	Low smoke	Smoke-less
VM (% db)	84.2	79.3	72.1	64.4	39.7	14.0	23.4	8.2
Ash	0.1	0.9	1.0	4.9	4.2	6.7	5.5	5.2
FC	15.8	20.5	27.6	33.4	57.9	80.1	72.1	86.9
MC (% ar)	8.4	7.8	4.6	7.1	7.2	2.7	6.3	3.4
C (% daf)	53.3	51.6	54.7	59.1	82.1	74.3	78.0	81.6
H	6.1	5.9	5.8	5.0	4.8	3.6	3.9	3.4
N	0.4	0.6	0.1	1.6	1.9	1.7	1.6	1.7
S	0.03	0.02	0.04	0.4	0.4	2.1	0.4	2.0
Cl (% db)	0.03	0.02	0.04	0.11	0.06	0.05	0.05	0.02
P (ppm db)	3591	4142	4059	3750	3608	4815	3980	3629
Ca	18386	11978	8766	27244	5923	10261	16375	5867
K	583	3487	1280	89	265	11168	723	767
Zn	140	823	55	47	1	0	21	0
GCV (MJ kg^{-1} db)	19.5	18.8	23.0	20.6	36.3	27.6	34.5	33.3

ar = as received; db = dry basis; daf = dry ash free

Table 4-2. Proximate, ultimate and analyses and gross calorific values (GCV) for the fuels used.

4.2.2. Combustion Experiments

A fixed bed stove (Waterford Stanley Oisin) was used which meets the current designs to use multiple fuels. The appliance is nominally rated as having a maximum non-boiler thermal output of 5.7 kW and an efficiency of 79% but in these experiments the unit was run at approximately full load. A diagram of the unit and the flue and sampling arrangements are shown in Fig. 4-1.

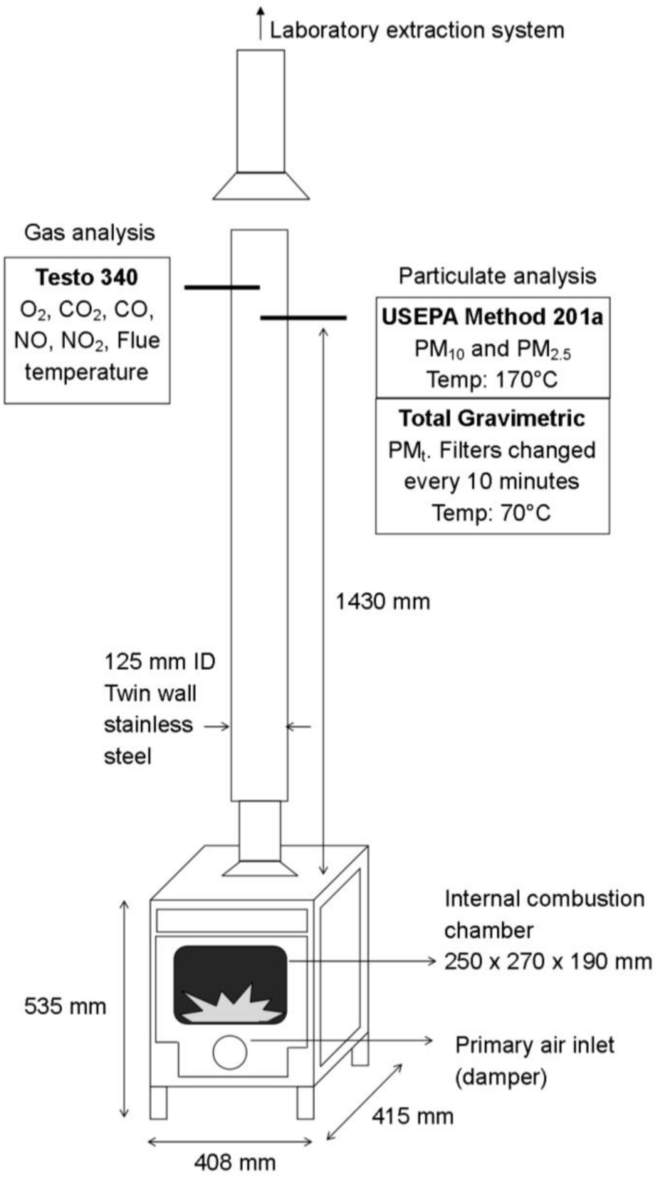

Figure 4-1. Diagram showing the equipment arrangement.

The internal dimensions of the combustor are 250 x 270 x 190 mm (height x width x depth) with a deflector plate across the top section. The geometry of the combustion chamber was unchanged in all the experiments. There is a single primary air supply under the grate which is manually controlled via a damper. The dimensions of the grate which determines the distribution of the air flow as well as the movement of the fuel particles and ash in the burning bed is shown in Fig. 4.2.

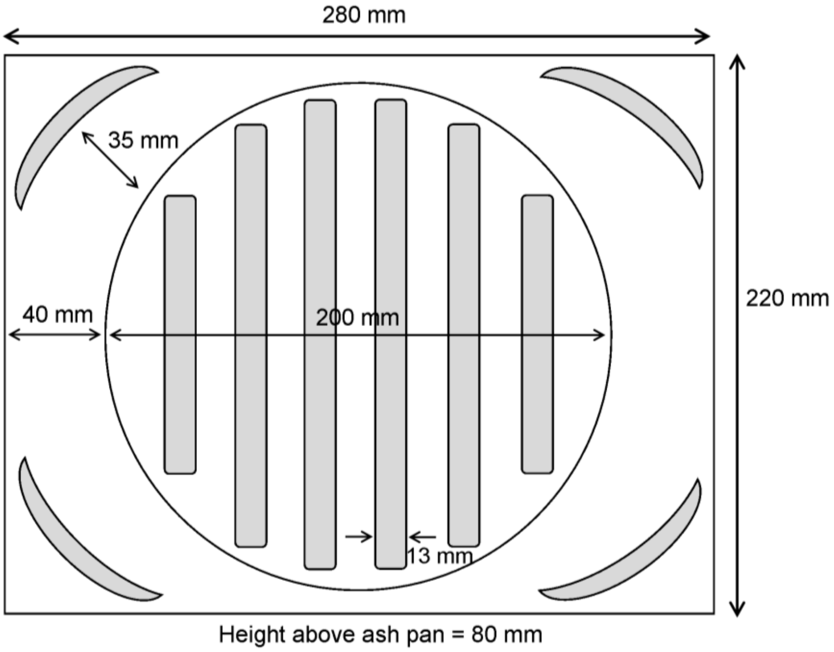

Figure 4-2. Diagram showing the grate arrangement

The stove was mounted on an electronic balance and the general arrangement of the test equipment was largely in accordance with BS EN 13240. Each run was started using the stove at room temperature to replicate a cold start. Sampling was undertaken by means of ports in the flue positioned 1.43 m above the stove as shown in Fig 4-1. The insulated flue had an internal diameter of 125 mm. The stove was directly underneath a laboratory extraction system which applied a continuous draught of 12 Pa as required for the nominal heat output test in BS EN 13240.

A weighed batch of fuel which was in the range of 2-3 kg was used for each run, with no re-loading being undertaken; this mass was chosen on the basis of BS13240 and the nominal heat output and efficiency. As far as possible the fuels were placed on the grate in a similar way each time with a uniform level bed layer. The sizes of the fuels were given in Table 4-1. All of the briquetted fuels were approximately the same size and logs of a similar size were selected but in this case there was a greater variation. There are some small deviations from the strict application of the standard method (such as the diameter of the flue) but in these experiments using a small stove the objective is to compare fuels using combustion of a single batch of fuel. The primary air flow was adjusted on the basis to give approximately 100% excess air for the coal-based fuels and 150% for the biomass fuels as recommended by the manufacturer for this stove. Ignition was undertaken by means of a known mass of fire-lighters which were arranged in the same position on the grate for each experiment. The early part of the ignition phase is influenced by this process and these results are not included. Flue gas samples were taken when ignition was complete and combustion established. Their composition was measured using a Testo 340 instrument for O_2, CO_2, CO, NO, NO_2, as well as the flue gas temperature. The accuracy of the gas composition measurements was ± 5%. Flue gas velocity and flow rate were measured using a Wöhler DC100 computer for pressure measurements and an S-type pitot tube, in accordance with BS EN ISO 16911-1.

The particulate content in the combustion gases was measured in two ways. In the first, PM_{10} and $PM_{2.5}$ were determined using a cyclone set (US EPA Method 201a and BS ISO 25597). Here a sampling probe consisting of cyclones, a pitot tube and a thermocouple is inserted directly into the flue. Flue gas is drawn through the sampling nozzle into the cyclone separators and then through a heated line into a set of impingers to collect water and other condensables, and then to a dry gas meter. The cyclones were mounted externally to the flue at a controlled temperature of 170°C. As far as possible isokinetic sampling was used but with the low flow rate in the flue (<1.5 m s^{-1}) this was difficult and is not necessary for relatively small particulate sizes [19]. Sampling was carried out for a period of typically 20 minutes for each fuel. The filters were stored at 5°C prior to analysis.

In the second method, total particulate matter (PM_t) was determined using a gravimetric method which required 25 L of sampled gas passed through a Whatman GF/F glass microfibre (0.7µm) filter paper, with a second one used as a backing filter paper. The gas was taken via a heated line at 120°C and passed through the filter papers which were in a holder mounted in a furnace at 70°C. The furnace arrangement permitted the gases to be cooled to this temperature and permitted the condensation of semi-volatile organic compounds. The filter temperature was chosen to be the same as that recommended in the dilution tunnel standard [BS 3841]. Three repeat measurements were taken in each combustion phase for each fuel and the arithmetic mean average reported. Each sample was taken for five minutes before the filter papers were changed. All filter papers were stored in a desiccator for 24 h prior to measurement. Particulate matter was examined using a Hitachi SU8230 scanning electron microscope (SEM). Samples were platinum coated.

Values of elemental carbon (EC) and total carbon (OC) were determined using a thermo-gravimetric method (TGA) which yields time-weighted-average measurements. The Total Carbon (TC) is the sum of EC and OC. This method was adopted because in this study there was a very high particle loading on the filters which rendered them unsuitable for thermal/optical analytical methods. Thus we used a TGA with a nitrogen carrier gas and we assume that OC is equivalent to the volatile content (105°C – 550°C in N_2) and EC is equivalent to the fixed carbon content (550°C in air). It allows accurate comparisons to be made between the different soot samples.

4.3 Experimental Results

4.3.1 Fuel Properties

Thermogravimetric analyses (TGA) were made on all the fuels. The heating rates used were those employed for the determination of the proximate analysis based on the BS methods. The TGA results obtained are shown in Fig 4-3 together with the heating profiles employed.

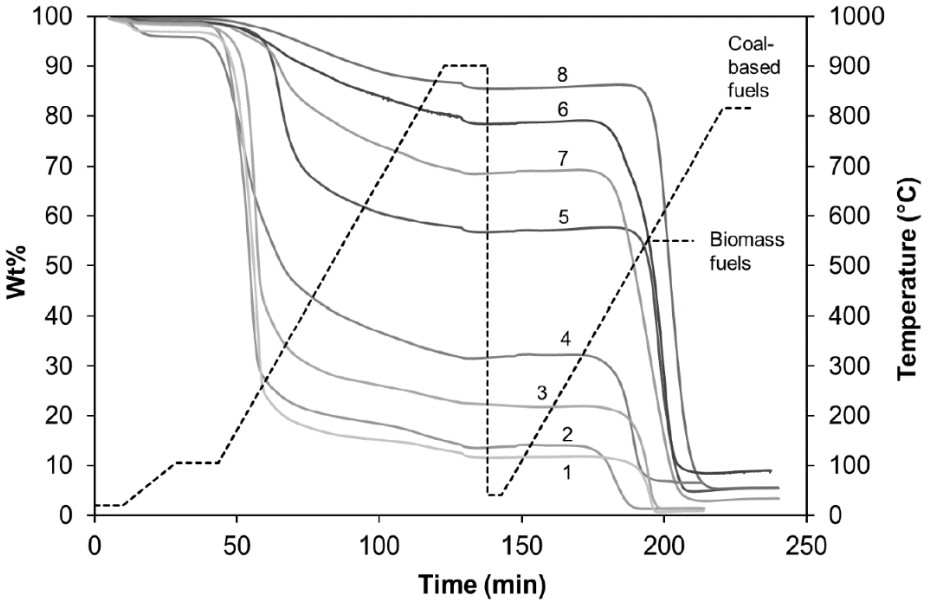

Figure 4-3. TGA results for the fuels studied. 1: wood A; 2: wood B; 3: torrefied wood briquettes; 4: peat briquettes; 5: coal; 6: coal/biomass blend; 7: lowsmoke fuel; 8; smokeless fuel. Temperature ---

The Proximate, Ultimate, and gross calorific value (GCV) results for each fuel measured in the conventional way presented in Table 4-2 are consistent with the TGA plots. There were difficulties in the measurement of some of the quantities because of their inhomogeneous nature, for example, the wood samples contained bark whilst the biomass/coal mixture contained components of greatly differing VM content. However the trends are important and are clearly identified. Of particular note in Fig. 4-3 and Table 4-2 is the trend in the volatile content with the woods having the highest values and the smokeless fuel having the lowest value.

Batch combustion in a fixed bed follows three major stages. Ignition occurs first once the surface material of the fuel devolatilises and forms a gaseous flame. Once this flame is established the ‘flaming phase’ takes place characterised by the combustion of volatile products and their decomposition products (secondary pyrolysis products) as luminous diffusion flames. Thirdly the smouldering phase occurs which is characterised by heterogeneous char combustion and limited visible gas phase combustion. Elasser et al. [17] have recently identified four combustion phases but in the present work we have used the simpler classification of the two major phases, flaming and smouldering because of the difficulty of distinguishing between the other phases.

Measurements were made of the mass burning rates for all fuels and these are shown in Fig.4-4. These are consistent with the TGA results shown in Fig 4-3. The initial maximum value is followed by a decline with occasional slight increases due to the movement of the fuel in the bed. The time during a combustion cycle at which samples are taken for particulate analysis was found to have a substantial influence on the emissions data. It is interesting to note that the high volatile wood fuels release a high concentration of highly carbonaceous dark smoke during flaming combustion. In contrast the torrefied fuel burns more slowly and has a more uniform rate of heat release and of smoke emission.

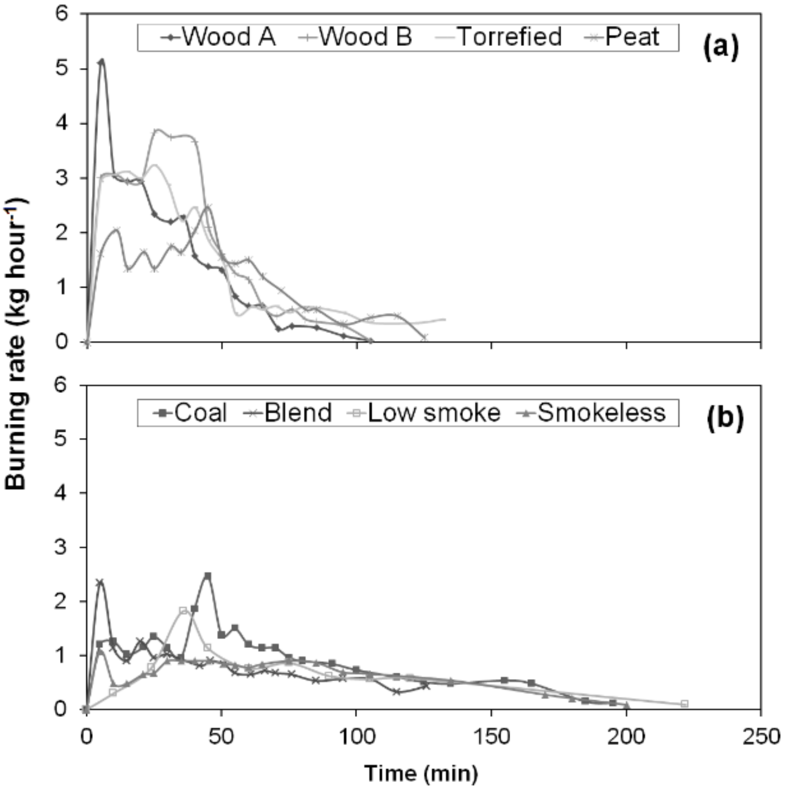

Figure 4-4. Variation of burning rate with time for each of the fuels. (a) fuels 1-4; (b) fuels 5-8.

The average burning rates for the flaming and smouldering phases for all the fuels are given in Table 4-3.

Fuel	Average burning rate (kg hour^{-1})	
	Flaming	Smouldering
1	2.37	0.27
2	2.59	0.32
3	2.59	0.47
4	1.61	0.36
5	1.31	0.43
6	1.05	0.58
7	0.99	0.42
8	0.77	0.54

Table 4-3. Average burning rates during flaming and smouldering phases for the different fuels.

As expected the flaming rates are approximately proportional to the volatile content (VM) since they are dependent on the volatile matter released whilst the smouldering rate is proportional to the Fixed Carbon (FC) values given in Table 4-2. The flue temperatures reflected the burning rates and approximately followed the same pattern with time and their values ranged from 150-350°C.

4.3.2 NO$_x$ and SO$_x$ emissions

NO$_x$ measurements were made throughout the combustion cycle. NO$_x$ emission factors were calculated for both flaming and smouldering phases on the basis of 13% O$_2$ content in the combustion gases. These values are given in Table 4-4 where the errors are ±10%.

	ppm at 13% O$_2$		mg MJ^{-1}		
Fuel	Flaming	Smouldering	Flaming	Smouldering	Average over whole cycle
1	88	40	152	67	110
2	98	54	175	93	142
3	74	32	134	56	85
4	274	190	504	345	438
5	184	105	274	153	204
6	216	237	367	401	390
7	219	161	345	253	287
8	195	167	292	249	259

Table 4-4. NO$_x$ emissions factors for the different combustion phases.

The NO$_2$ content was always less than 5 mol% for the biomass- and 15 mol% for the coal-based fuels. The emission factors vary significantly with the fuel-N content; the values for the nitrogen content of the biomass fuels (<0.6wt% daf) is much lower than for the coal and peat samples. Plots are given for the emission factors for both phases in Fig. 4-5.

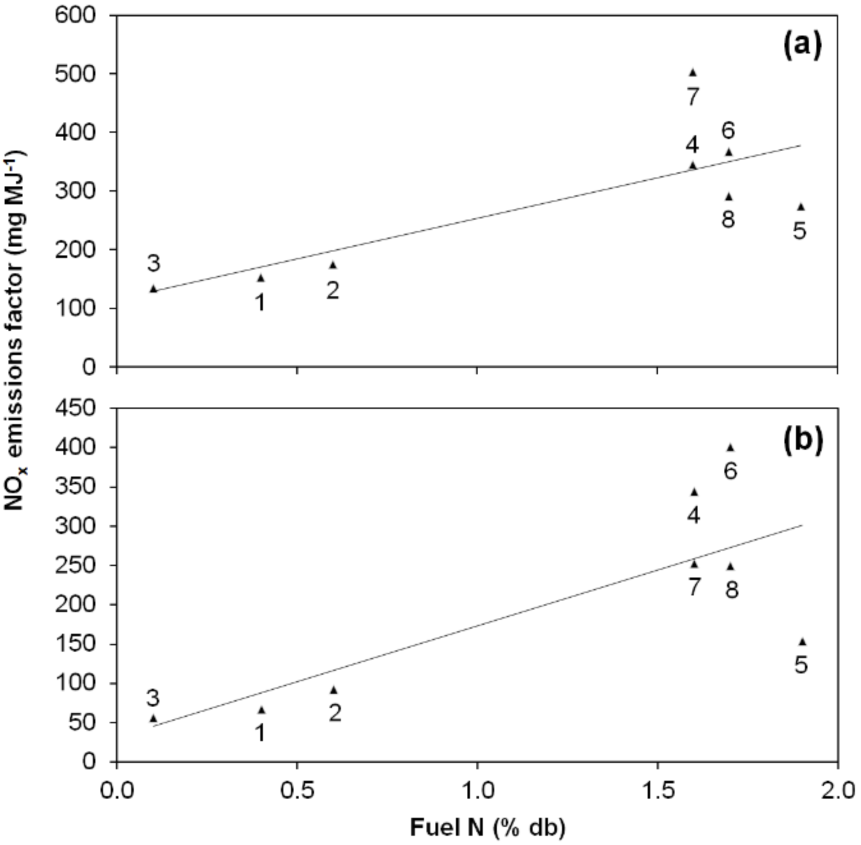

Figure 4-5. NO_x emissions for each fuel plotted against fuel nitrogen content for (a) flaming, and (b) smouldering phases.

It is seen that the NO_x emissions factors for each fuel is dependent on the phase of combustion, that is, whether it is flaming or smouldering, although the effect is not large. The variation with fuel-N content is interesting because they are only dependent on the fuel-N content and not on the fuel type. It is well known that NO_x emissions from coal combustion [20] and from biomass combustion [21] are a function of the fuel-N content but this not been shown that the emissions from all these fuels follow the same linear relationship for combustion in a stove. This probably arises because the fuel-N present in all these fuels consists mainly of cyclic N-compounds and so the formation of NO. A similar situation will also holds for the conversion during the smouldering period where the common feature is the char-N. The NO_x emissions predominantly resulted from fuel-NO_x because relatively small amounts of thermal NO_x are formed in the residence times available in either the flaming or smouldering phase. The evidence for this comes from (a) on the basis of a calculated residence time of 0.2 s and an average combustion chamber temperature of 1500K then the computed NO_x yield is 1ppm using the method used by us previously [22], (b) CFD calculations for a similar wood furnace but at a higher temperature gave a value of 25 ppm [23].

The sulphur content varies between 0.02% for the wood fuels to 2.0% for the smokeless fuel (no. 8) whilst the 50:50 test fuel (no. 6) has a sulphur content of 2.1% which has implications for SO_x emissions. The consequence is that the equilibrium SO_2 concentrations are about 50 ppm for the woods whilst the values from the coal based fuels are in the range of 350 to 1500 ppm. The wood ash was studied using energy-dispersive X-ray spectroscopy (EDX) and this showed relatively low unburned carbon content and a high presence of Si, Ca and K. Some of the SO_2 is retained by the ash forming calcium compounds and the flue gases contained less than the calculated equilibrium amount and typically 10ppm SO_2 was found experimentally.

4.3.3 Particulate Matter Emissions

The PM emissions factors for each fuel are dependent on the fuel studied also on whether the fuel is flaming or smouldering. A typical plot of the fuel burning rate and the total particulate emission (PM_t) from the combustion of the torrefied wood (fuel 3) as measured by the gravimetric method is shown in Fig. 4-6(a). The distinction between the flaming and smouldering phases is best done by direct visual observation and it coincides with a change in the CO and NO_x emissions as shown in Fig. 4-6(b).

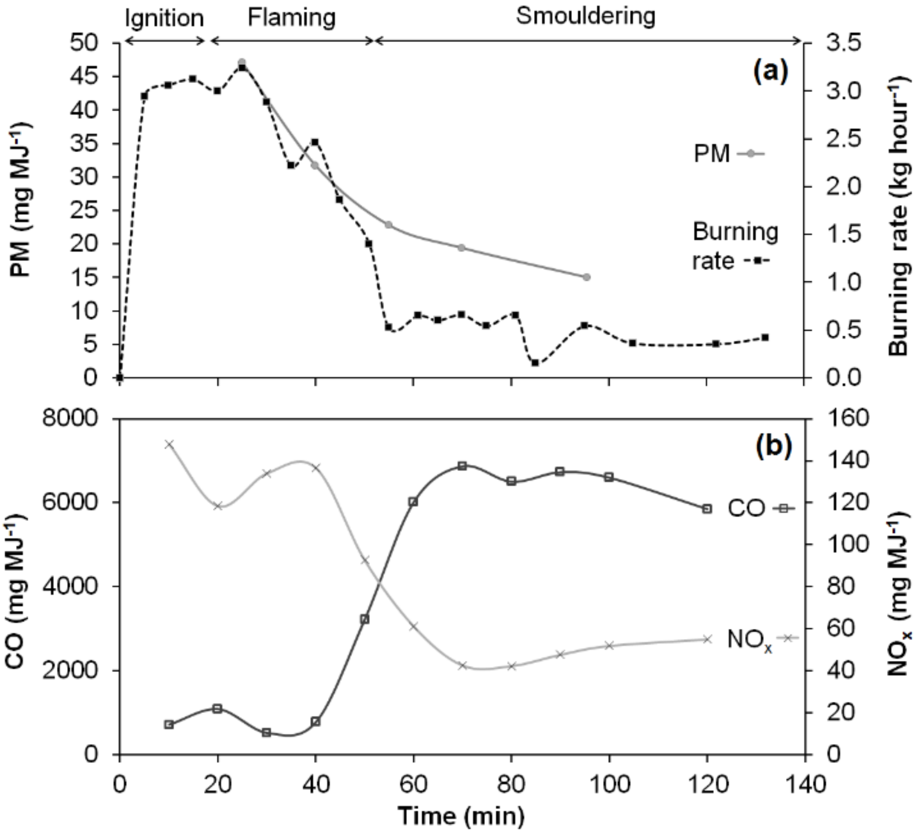

Figure 4-6. The variation of (a) the burning rate, ■, and emission factors for PM, ●, and (b) emissions factors for CO, □, and NO_x, ×, for the burning of torrefied wood briquettes (fuel no. 3).

The change is gradual and often complicated by random movement of the burning fuel bed despite keeping the combustion conditions as similar as possible. This can result in errors in defining the phases of combustion.

Particulate samples were taken periodically during the combustion cycle and the weight of the sample determined at the points shown in Fig. 4-6. Each point represents a sample taken over a 5 min period. The total particulate measured for each combustion phase is the average of the values in that region. It was found that the particulate samples consist of two components: a carbonaceous black smoke which deposits on the first filter paper and a yellowish material containing potassium that is collected on the second (backing) filter paper. The material on the second filter paper must have a particle size less than 0.7 µm. It was also noticed that the smoke on the first filter paper of the second sample taken just after the peak of devolatilisation was brownish in colour, in contrast to all the other samples which were black. This brown soot is tar-like ‘brown carbon’ rather than particulate as is the case with the black soot.

The PM_t emissions factors measured by the gravimetric method for the different fuels are given in Table 4-5 for the different combustion phases. They are presented in terms of mg m^{-3} at 70ºC which is the temperature at which they were measured.

	mg m^{-3} (as measured, 70°C)		
Fuel	Flaming phase	Smouldering phase	Average over whole cycle
1	81	10	45
2	145	21	83
3	37	9	23
4	151	14	83
5	515	26	271
6	151	44	97
7	66	22	44
8	29	11	20

Table 4-5. PM_t emissions factors for the two combustion phases as determined by the gravimetric method for all of the fuels.

The results show a substantial difference between PM emission rates in the flaming and smouldering phases. Average figures over the whole of the combustion cycle are also presented. There is also a difference in the ranking of the fuels, depending on the basis used for comparison. The results on an energy basis are shown in Fig 4-7.

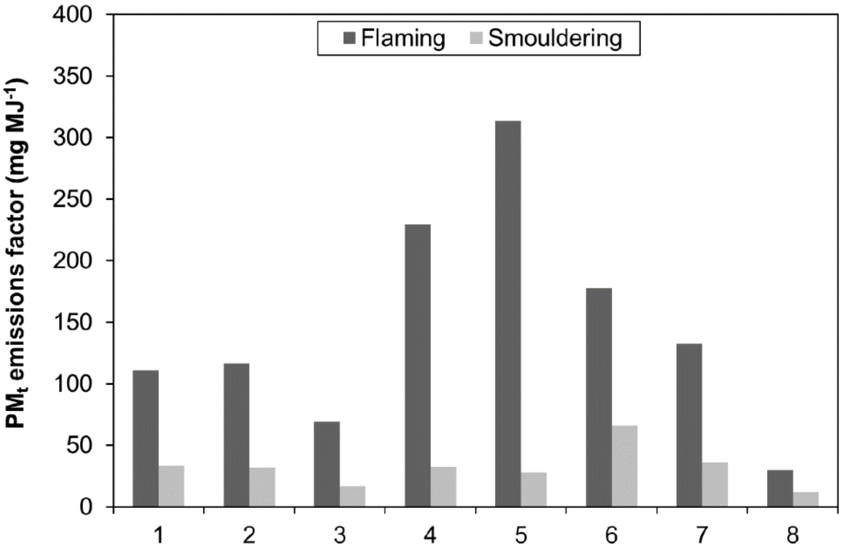

Figure 4-7. Comparison of total particulate (PM$_t$) emissions factors from the flaming and smouldering phases using the gravimetric method for the different fuels (fuels 1-8).

The trends are quite marked since the PM released during the flaming phase are much greater than for smouldering but the differences are much reduced in the case of the 'smokeless' fuels, torrefied wood and the smokeless coal. The experimental errors in these values are ± 10%. The PM emissions in both phases for the two woods (no's.1 and 2) are similar on a thermal basis whilst the value for the torrefied wood (no. 3) is much smaller. The coal (no.5) gives the highest value with the peat (no.4) and the blend (no.6) giving intermediate values. The low smoke fuel (no.7) is similar to the wood and the smokeless fuel (no.8) is similar to the torrefied woods.

The size fractions PM$_{10}$ and PM$_{2.5}$ were determined for some of the fuels using the cyclone method as well and the results for the flaming phase are presented in Table 4-6.

	Emissions factor (mg MJ^{-1})		
	Cyclones		Gravimetric
Fuel	PM$_{10}$	PM$_{2.5}$	Flaming Phase
Wood A	95	91	111
Torrefied briquettes	40	32	69
Peat briquettes	214	210	230
Coal	189	185	313
Smokeless fuel	15	14	30

Table 4-6. PM$_{10}$ and PM$_{2.5}$ emissions factors for selected fuels by the cyclone method at 170°C and comparison with the gravimetric method at 70°C.

It is shown in Table 4-6 that there are significant differences in the emissions factors reported by the two methods. Four fuels have been selected, a wood, a torrefied wood, a peat and a smokeless coal, which have significant differences in their volatile content. The major factor resulting in the difference in the particulate emission factor by the two methods is in the choice of particulate collection temperature. The cyclone method which is at 170°C would largely collect elemental carbon (EC) whilst the Gravimetric Method at the lower temperature of 70°C will also collect involatile organic matter such the PAH compounds (i.e. TC which is the sum of EC and OC.). Here we have taken the values for $PM_{2.5}$ (assumed to be mainly produced in the flaming phase) as well as the values form the gravimetric from the flaming phase (taken from Table 5 but shown here for comparison purposes). In principle this should give values for Elemental Carbon (EC)/Total Carbon (TC). In the case of wood (no.1) this method gives a value of 0.8±0.1, in the case of the torrefied wood (no.3) and the peat (no.4) both give 0.9 ± 0.1, and for the smokeless fuel (no.8) a value of 0.5 ±0.1. The significance of these values is discussed later.

The results from the cyclone tests also show that a very small amount of PM greater than 2.5 µm was collected for any of the fuels. This is consistent with observations which show that the majority of particles are below $PM_{2.5}$ and even PM_1 for example, as shown in references [9, 18]. These soot particles are fragile and can easily fragment once they enter the atmosphere. This has been verified by electron microscopy studies of the particles on the filter papers. The individual particles were between 50 nm and 90 nm but are aggregated in the form of chains. Larger particles can be formed by the formation of loosely bound carbonaceous aggregates and this is much more marked with the coal particulates than for the biomass particulates. As a result there is a visible difference between the soot collected from mineral-based fuels and woody fuels.

Plots were made of the average total particulate against volatile matter (given in Table 2) and this is shown in Fig. 4-8. The origin is set at 9% VM because it is the value for cokes which do not produce smoke during combustion [24]. The data consist of two main groups. The woods (nos. 1-3) lie on one line, the coal based fuels (5-8) lie on a different line and produce more smoke. The single point for peat (no. 4) lies in an intermediate position.

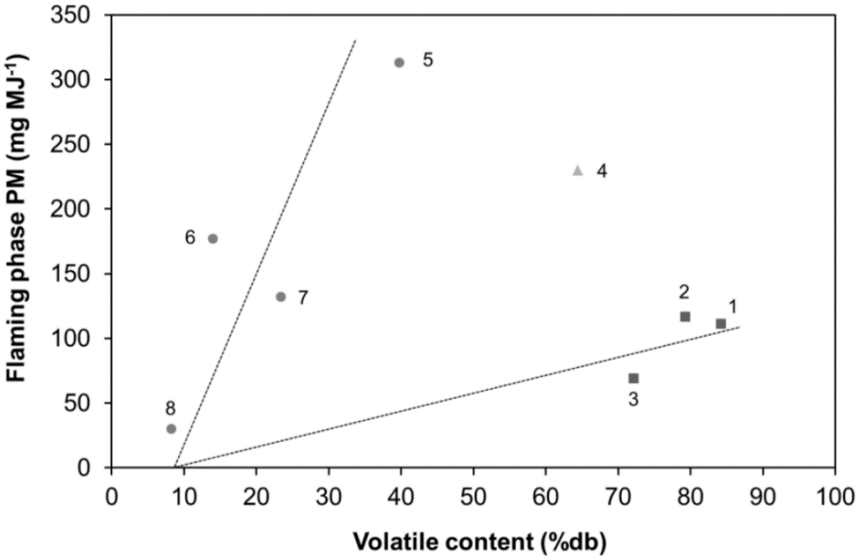

Figure 4-8. Plot of the average flaming phase particulate emission (PM) against the volatile content (VM) for the fuels.

As is well known the total particulate mass from the combustion of biomass and coal consists of both carbonaceous soot and inorganic aerosols, the contribution of the latter from coal combustion is relatively small. In the case of the combustion of wood no 1 the grate losses were measured and it was found that 1.0 g of ash was left from the initial 3.0 kg of fuel and the unburned carbon in the ash was less than 10 wt%. Using the data in Table 2 it is seen that some of the ash in the original fuel is lost and if this is mainly due to evaporation of the potassium salts-into the of combustion air, it would give a concentration of aerosol of 10-20 mg/MJ. This is consistent with the results of other research e.g. [18]. Thus in this work with a single stage combustor the carbonaceous soot is the dominant particulate emitted. The plot in Fig. 8 is therefore that of the carbonaceous particulate matter and it can be seen that the plot for the biomass fuels (nos. 1,2 and 3) and the coal-based fuels lie on different lines. Peat (no.4) which is partially coalfield has a degree of coalification intermediate position between the coal and the biomass, which it has in the plots in Fig 8. These results are consistent with the concept that the formation of soot from coal and from biomass follows different routes [25,26].

Values for EC/TC were determined for five fuels, the two woods (nos. 1 and 2), the torrefied fuel (no. 3), the coal (no. 5) and the smokeless fuel (no. 8) during the combustion process. The data obtained are shown in Fig. 4-9.

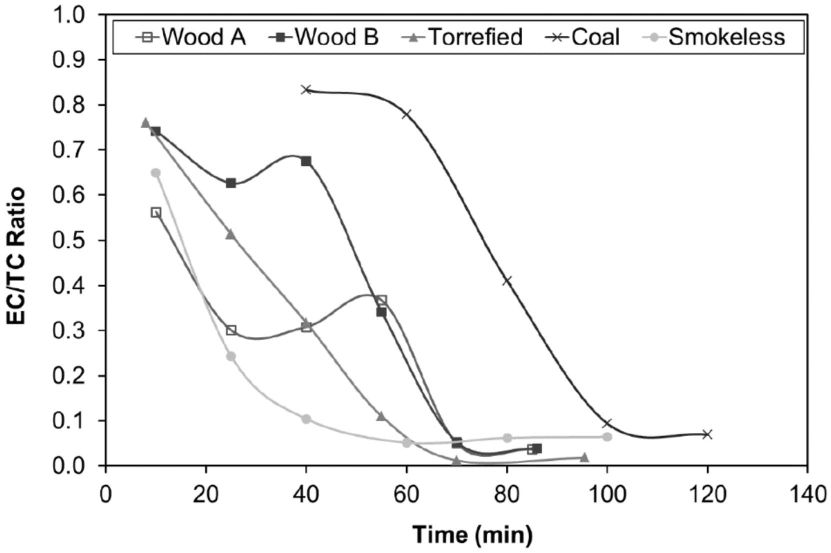

Figure 4-9. Plot of EC/TC for (a) wood A (no. 1), ☐, (b) wood B (no.2), ■, (c) torrefied wood (no.3), ▲, (d) coal (no. 5), ×, and smokeless fuel (no. 8), ●.

The CO can be produced by the incomplete combustion of the volatiles in the flaming phase or from the combustion of the char in the smouldering phase; in both cases the CO is oxidised by the excess air to form CO_2 in the later stages of the combustor. In the case of rich homogeneous gaseous hydrocarbon flames there is a correlation between CO concentrations and soot yield (and also PAH because the formation routes are linked) and this is the case in the flaming phase. We find this is not the case since the CO emission during the smouldering phase is higher during the smouldering phase than the flaming phase-as shown by comparing Table 4-5 with Table 4-7. There is also considerable fluctuating combustion behaviour during the combustion process as observed by many others e.g. [17], this being due to the settling movement during the combustion of the fuel particles of char. The average concentrations during the different combustion phases for the different fuels are listed in Table 4-7. It is also interesting to note that the CO emission from the torrefied fuel is much lower than any of the other fuels. See table 4-8.

	ppm at 13% O_2		mg MJ^{-1}		
Fuel	Flaming	Smouldering	Flaming	Smouldering	Average over whole cycle
1	4817	14372	5041	14648	9845
2	2000	8112	2172	8507	4706
3	708	5553	781	5972	4084
4	2989	8779	3341	9688	5985
5	2334	12229	2113	10804	6941
6	2785	7417	2885	7629	6169
7	5078	15495	4863	14806	11143
8	2775	9068	2518	8186	6853

Table 4-7. CO emissions factors for the different combustion phases.

The level of CO emitted is dependent on the time temperature history above the burning bed and is characteristic of this type of unit. In particular the concentrations will be reduced if a secondary combustion chamber is fitted.

These values for CO, smoke and NO_x should be compared with the limits set in the UK [8] and in Europe [27] for small boilers. In the UK the RHI limits for new stoves (fitted with boilers, which is not the case here) are 30 g GJ^{-1} for particulate matter and 150g GJ^{-1} NO_x. In the EU, whilst no limits have been agreed at present for small stoves or space heaters, values have been agreed for small boilers < 59 kW where the limit for CO is 3000 mg m^{-3} at 10% O_2; organic compounds 100 mg m^{-3} and particulate matter 150 mg m^{-3}. Values have not been specified for NO_x. In order to achieve these limits for particulate emission a secondary combustion chamber would be necessary.

4.4 Discussion

4.4.1 The general features of biomass combustion

The factors determining combustion behaviour of biomass are: (1) the geometrical shape of the fuel, the porosity and the tendency of the fuel to undergo fragmentation. Here some fuels are in lump form of various sizes and others are briquetted. The external surface area of the fuel particle determines the rate of initial devolatilisation as well as the subsequent progress of the flame front into the particle and combustion of the char formed. These determine the burning rate and consequently the temperature in the combustion chamber, (2) the chemical composition - C, N and ash content and volatile content, and (3) the supply of air and operating conditions especially the fuel load which determines the fuel/air ratio.

The general features of the combustion of biomass and coal are generally understood [5,25,26,28] and there are many similarities such as the major steps of devolatilisation and char burn out. But there are some significant differences particularly in relation to the formation of smoke from biomass [25] compared with coal [26]. Many research groups have measured emission factors for various types of furnaces and it is not possible to list them all here. But only a few research groups have measured emission factors for both biomass and coal in the same appliances. The emission factors are approximately in accord with those observed in our previous work using biomass or coal and indeed co-firing [10,11], although for a slightly different furnace with a continuous feed and a secondary combustor. Such furnaces with continuous operation and a secondary combustion chambers will emit lower levels of particulate matter, CO and organic material.

	Polish coal (Wujek) [15]	Lump pine wood
CO	2990 (6941)	2400 (4706)
NO_x	162 (204)	32 (142)
Particulate	294 (169)	116 (78)

Table 4-8. Comparison of previous results [10,11] mg MJ^{-1} with average results in this work given in parenthesis.

4.4.2 NO_x Formation

The formation of NO_x can only be formed by the oxidation of fuel-N groups at the temperatures found here. The combustion of coal results in the formation of HCN [29]. In the case of biomass the fuel nitrogen compounds form both HCN and NH_3, but in the case of wood the majority of the product is HCN [22]. Consequently the straight line relationship shown in Fig. 4-5 might be expected since the chemical mechanism is similar and the rate of release of these compounds is determined by the mass burning rates; it is clear from Fig. 4-4 that they are not too dissimilar.

4.4.3 Particulate, organics and CO formation

The routes leading to the formation of smoke from biomass [25] and from coal [26] are different. In the former, pyrolysis of the different constituents, cellulose and lignin can form soot via the HACA (hydrogen abstraction acetylene addition) route or via aromatic compounds respectively. Coal mainly forms soot from the PAH and tar compounds released from the coal structure. However one feature is common and that is here they are burning in the form of large particles which burn out slowly. It is seen from Fig 4-4 that soot is released from both the flaming and most of the smouldering phases and it seems that volatiles or their secondary products are being released throughout the whole combustion cycle; indeed the amount of soot released is approximately proportional to the total mass of fuel burned. There are fragments of incompletely combusted fuel in the ash in both the case of biomass or coal based fuels as indicated in electron microscope photographs. Thus the mechanism we have previously put forward [5,10,11] and which is summarised in Fig 4-10 would apply to both phases of combustion and for all the fuels studied here. The route via aromatic species would be dominant during the flaming phase and the smouldering route would be largely based on a HACA route [5].

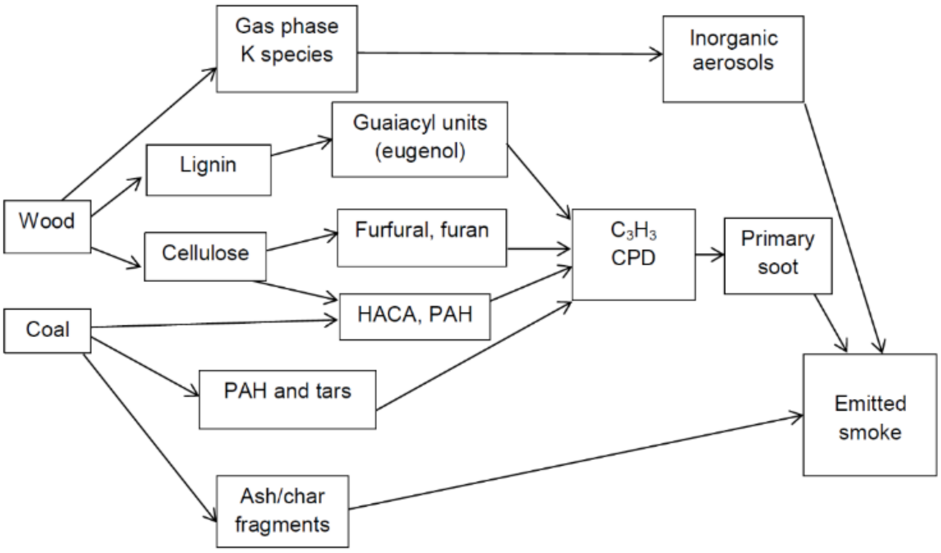

Figure 4-10. The routes to the formation of smoke from biomass or coal, or a blend.

The smoke consists of carbonaceous particulates some of which have formed chains and agglomerated together with KCl aerosol and fragments of char. The data on size distribution shows that from this stove the majority of the particulate is below 2.5 µm. The formation of organic compounds such as PAH is an integral part of the soot forming mechanism and the ratio of the elemental carbon (EC) to the organic carbon (OC) is determined by the combustion chemistry of the volatiles produced by a particular solid fuel. The amount of OC bound to the EC particles depends on the initial VM and on the temperature history in the later stages of the furnace, as does the amount in the gas phase. The formation of CO follows a pattern depending on the phase of combustion. The initial stages of combustion involve devolatilisation from the outer layer of the particle releasing volatiles that then form both smoke and CO, both eventually forming CO_2 if the time-temperature conditions permit but the residence in most small units preclude this happening. In the smouldering phase the outer layer of the fuel particle will consist of char with some unreacted fuel decomposing in the core of the particle. The char will readily burn with the incoming oxygen producing greater quantities of CO and smaller amounts of smoke-as observed. The KCl will be equally released during both phases of combustion. Torrefaction of biomass has been found to reduce particulate emissions from combustion by approx. 40% compared to the source material, achieved by the reduction in volatile content.

Many researchers have stressed the importance of the ratio of Black Carbon (BC) to Organic Carbon (OC) in the combustion of carbonaceous fuels, when evaluating the impact on climate. Here we assume that effectively BC is equivalent to the elemental carbon (EC). The data in

Fig. 4-9 shows that the values of EC/TC vary during the combustion cycle. In the operation of a real combustor it would be refuelled before it reaches the full extent of the smouldering stage and so here we have taken mean values of EC/TC from the flaming stage. These values are: Wood A (no.1), 0.4; Wood B (no. 2), 0.6, Torrefied wood (no.3,) 0.4 and Coal (no.5), 0.8. In addition here we determine the averaged total particulate at two temperatures, namely at 170°C and 70°C. At the former temperature most of the OC would be lost giving a value of EC whilst at 70°C most of it would be collected giving a value of the total amount of EC and OC which is effectively total carbon, TC. Here we find that for the main part of the combustion for wood A that EC/TC = 0.8 and for the torrefied wood and peat is 0.9; a smokeless fuel (no. 8) gave a value of 0.5. This method using selective condensation of the organic fraction depends on the volatility (and VM content) of the organic fraction released and varies from wood, torrefied wood and smokeless coal. Measurements obtained using a similar combustion arrangement but using Aerosol Time of Flight Mass Spectrometry (ATOFMS) gave values of EC/TC of 0.4 for flaming and 0.3 smouldering for a soft wood [30]. A similar log fuelled combustion system although with two-stage combustion was found to give a value of EC/TC of 0.47 [31].

4.5 Conclusions

1) Eight fuels which included woods, torrefied fuels, coal and smokeless coal and which have substantial differences in their volatile content were burned as lumps in a single combustion chamber residential stove. The total particulate matter emissions ($PM_{t)}$ associated with coal based fuels followed a linear relationship with the volatile content, the wood based fuels followed a different linear relationship whilst the single peat result was intermediate between the two classes. The torrefied fuel gave the lowest emission of the fuels studied. This arises because of the difference in the mechanism of soot formation of these fuels.

2) A linear relationship was found between the fuel-nitrogen content and the NO_x emitted for all fuels whether wood-based or coal-based. The wood fuels and torrefied wood briquettes showed the lowest NO_x emissions (< 100 ppm at 13% O_2) due to the lowest fuel-bound nitrogen content. The levels of NO_x emissions from the coal-based fuels were approximately twice that of the wood fuels.

3) A cyclone set was used to determine the $PM_{2.5}$ and PM_{10} size fractions. It was found that the majority of particles are below $PM_{2.5}$ for all fuels whether wood-based or coal based. This was confirmed with SEM imaging and is consistent with the observations of other researchers.

Acknowledgements

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Chapter 5

The Impact of Fuel Properties on the Composition of Emitted Soot

The Impact of Fuel Properties on the Composition of Soot Produced by the Combustion of Residential Solid Fuels in a Domestic Stove

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Abstract

Soot is formed from the incomplete combustion of biomass and conventional fossil fuels. It consists largely of a carbonaceous core termed Elemental Carbon (EC) with adsorbed volatile organic species, commonly termed Organic Carbon (OC). Estimation of the ratio of BC/OC is critical as climate models have recognised the Global Warming Potential (GWP) of BC as the second most important climate forcing agent after carbon dioxide. This paper presents values of EC, OC and EC/TC (where TC = EC + OC) for three different soot types: Firstly, soots collected on filters from the combustion of eight fossil fuel and biomass residential solid fuels (RSF), burned in a 6 kW heating stove. Secondly, chimney soot deposits taken from 'real-life' stoves installed in domestic homes; and finally wick burner soots generated from biomass model compounds; namely eugenol, furfural and anisole. Values of the EC/TC ratios for wood logs, torrefied briquettes, coal and smokeless fuel are given. These ratios are highly dependent on burning conditions; namely the flaming and smouldering phases. The results of this study suggest that EC and OC emissions from various solid fuels differ substantially in composition and relative proportion, which is useful information for climate models.

Keywords: biomass, combustion, emissions, particulate matter

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Supplementary data associated with this article can be found in Appendix III (section 11.3). This material has not been published.

5.1 Introduction

The Global Warming Potential (GWP) of combustion gases such as carbon dioxide and methane has been well researched [1]. There is increasingly interest in the GWP associated with the particulate and aero-sol fractions of combustion emissions. Soot formed by the incomplete combustion of fossil or bio-fuels consists of agglomerated chains of carbonaceous spherules of elemental carbon (EC) with condensed organic compounds (OC). OC is also known as the volatile fraction or solvent extractable fraction. Black Carbon (BC) consists of the light absorbing fraction of the carbonaceous aerosols which mainly consists of EC, but they are not exactly the same. Watson et al. [4] found that despite being well correlated they are not measures of the same properties of particulate matter.

The organic fraction also contains light absorbing brown carbon (BrC), which is mostly associated with relatively involatile organic compounds such as tars [5]. EC and OC emissions and light absorption properties of residential solid fuel combustion generated particulate matter are determined by type of fuel and the combustion conditions, and a need for a better understanding of these effects has been highlighted [6,7]. The ratio of BC/OC is of interest in terms of the effect of soot particles on climate change [1,2,3]. This is because BC has a net positive radiative forcing (warming effect) and OC has a net negative radiative forcing (cooling effect). The global 100 year GWP for BC and OC fractions are 900 and —46 [1]. Some studies suggest that biomass particles can exhibit higher ratios of OC to BC (or EC) in comparison with conventional fuels [2,3].

Exposure to soot particles importantly also leads to adverse health effects [8–12]. Many of the health impacts are associated with the adsorbed volatile species in the soot OC fraction, and it is known that oxy-PAH species, such as semiquinones can damage cell tissue [9].

Extensive research has been made into the mechanism of soot formation during the combustion of hydrocarbon and soot forming mechanisms have been postulated, for example, references [13–18]. The mechanism of soot formation from biomass combustion however involves additional routes arising from the oxygenated components in biomass. Recently models have been proposed for the formation of soot from wood combustion [17,18] in which the role of the aromatic lignin components has been emphasised.

Studies have been made of the emission of BC (and EC) as well as OC from the combustion of biomass, and especially wood fuel, for example [6,10,11,19–22]. There are considerable differences between the values obtained by the various groups and a number of standard methods have been recommended including optical examination of collected samples [4,23,24], but they do not give detailed insight into their formation mechanism. Ross et al. [25] measured the solvent extractable organic fraction and concluded that a range of compounds were present which could be divided into three classes. These are: weakly bound compounds easily desorbed and easily extractable in solvents, more strongly bonded surface material that are probably large three-dimensional PAH or polyyne compounds, and highly developed ordered soot, i.e. elemental carbon. An aerosol time of flight mass spectrometer (ATOFMS) has also been used [26–28] but the interpretation of these results raises issues about the meaning of BC, EC and OC.

Small biomass stoves are widely used throughout the world and contribute significantly to ambient air pollution and feedstock parameters significantly influence the emissions of NO_x, CO and particulate matter. The soots studied in this work are sampled from the flue gases and also from deposits in chimneys from multi-fuel and wood burning domestic stoves. Previous work has identified the main pyrolysis products during the first stages of biomass combustion to include eugenol, furfural and anisole [17] so these species are investigated as model compounds. The results from real systems are complicated by the fact that the organic material consists of the precursors to the formation of soot as well as incompletely combusted fuel. The smoke also contains small quantities of inorganic matter and it is known that the fuels studied here are a major source of non-soil K, Si, Ca, Fe, Ti and Cl.

In this paper we have measured the properties of the soot emitted in terms of the effect on global warming. In particular we have made measurements on the values of BC and OC from a domestic stove using a range of fuels and obtained novel measurements on their variation with time. The results from practical systems have been compared with data obtained from laboratory studies using model compounds that are produced during the combustion of biomass. We have also considered the relationship between BC, OC and the inorganic fraction of the particulate matter.

5.2 Experimental Methods

A fixed bed stove (manufactured by Waterford Stanley Oisin) which meets the current designs for use with multiple fuels was used for the main experiments and which has been described previously and an outline diagram given [22]. In this text it is referred to as the ‘Stove’. Essentially it consists of a rectangular box 259 mm high, 270 mm wide and 190 mm deep with a grate at the bottom and a deflector plate across the top section; no secondary air was added. The deflector plate effectively divided the unit into a primary and secondary zones with volumes of 8×10^{-3} m^3 and 1.4×10^{-3} m^3 respectively. The residence times in each zones are 0.9 and 0.2

s. The Stove is nominally rated as having a maximum non-boiler thermal output of 5.7 kW and in these experiments the unit was run at approximately maximum load. The mass of a typical charge is 2.7 kg.

The draft in the flue was provided partly by natural convection and partly by the extraction system, their combined effect was to produce a static pressure in the flue of 12 Pa, as specified in Section 6.4 of BS EN 13240; 2001. Soot samples were collected from the flue gases onto a pre-weighed filter paper at specific times as before and analysed ex situ [22]. Importantly the filter papers were maintained at a temperature of 70 °C during sampling as set out in BS 3841–3: 1994, as before. Other samples were obtained from soot deposits in chimneys of multi-fuel (coal and/or wood) and wood-burning domestic stoves, these are referred to as the 'Multi-fuel Stove' and 'Wood Stove' in the text. These soot samples were exposed to flue temperatures of about 200-300 °C., and they were allowed to cool in air before collection.

Soot samples were obtained from model wood pyrolysis products, namely, eugenol, furfural, anisole and also from n-decane using a wick burner. This type of burner was used because organic compounds with high boiling points cannot easily be vaporised and burned in the gas phase in diffusion or premixed burners because they thermally de-compose at their boiling point. A technique recently used by us [27] and others [29,30] is to use carefully controlled combustion using diffusion flames burning on a wick. The burner has been previously described [27] and had a wick diameter of 2.0 mm and wick height kept at 7.0 mm. These diffusion flame soots were collected onto a glass surface at a known height above the flame. They were stored under argon prior to analysis to minimise secondary reactions.

Thermogravimetric analysis (TGA) was used to measure the OC, EC and ash fractions of the soot [31,32] by means of a Stanton Redcroft instrument. The samples were stored in a desiccator prior to analysis. The OC mass fraction was determined by heating the soot samples in nitrogen to 550 °C, ensuring that a steady mass was achieved. During this heating period, continuous FTIR characterisation was conducted on the evolved material using a Thermo Scientific Nicolet iS10 model analyser. The gas was switched to air and the temperature was increased to 600 °C and held until no further mass loss was observed, this represented the EC. The mass remaining after the OC and EC were measured represented the ash fraction. Huang et al. [32] found that most OC is released at a relatively low temperature of 550 °C during pyrolysis, while EC is released at higher temperatures via combustion.

The soot samples were also analysed for OC by using Py-GC-MS at selected temperatures or by ramped temperature pyrolysis for detailed analysis of the OC. The system used was a Shimadzu 2010 GC-MS linked to a CDS 5200 series pyrolyser operating in trap mode. In this, the sample was heated at temperature of 100 °C to a maximum of 600 °C and desorbed separately into the GC-MS in order that chromatograms could be obtained. After pyrolysis the resulting products (C_4-C_{20}) are trapped onto an adsorbent trap (Tenax TA) at 40 °C by operating the CDS pyrolyser in adsorbent mode. The trap is then desorbed at 300 °C in a flow of helium onto the chromatographic column. The gaseous products (H_2, CO, CO_2, CH_4 etc) are not trapped onto Tenax TA and are vented. The CDS 5200 pyrolysis unit was connected to a Shimadzu 2010 GC-MS. The products were separated on an Rtx 1701 60 m capillary column, 0.25 mm id, 0.25 pm film thickness, using a temperature program of 40 °C, static time 2 min, ramped to 250 °C at a ramp rate of 4 °C min^{-1} with a static time of 30 min; the column head pressure at 40 °C was 2 bar. For all GC-MS studies, the chromatograms were assigned on the basis of the NIST Mass Spectral Library Database, from previous literature and by known retention times, as described before [18].Micro-pyrolysis of soot samples was undertaken using a CDS 5200 series micro-pyrolyser in which the samples were directly heated at a nominal heating rate of 20 °C ms^{-1} to a hold temperature of 600 °C and the values of EC and TC determined by the mass loss. Elemental analysis of the soot samples was undertaken by digestion in concentrated nitric acid (0.1 g in 10 ml 69% HNO_3) and atomic absorption mass spectrometry (Varian 240 fs AAS).

5.3 Experimental Results

5.3.1 BC/OC measurements

Samples of deposited soot taken from the flues of the Multi-fuel and Wood Stove units and from the diffusion flames of the model fuels (eugenol, furfural, anisole and n-decane) were analysed by TGA and the values of OC, EC and ash (inorganic material) determined. Typical plots are shown in Fig. 5-1 together the method used to define EC, OC and ash.

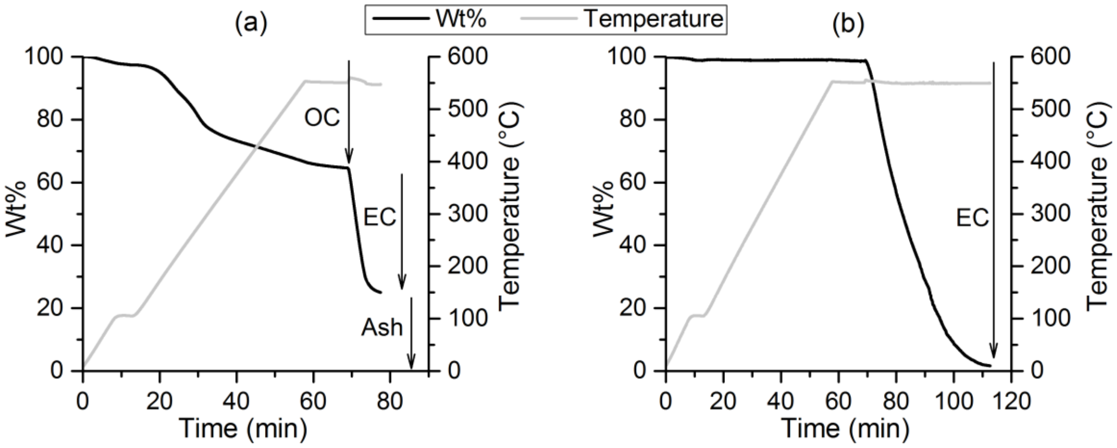

Figure 5-1. Thermogravimetric analysis of (a) deposit from inside a multi-fuel stove chimney and (b) soot deposit from a eugenol flame.

The OC is defined by the temperature it is collected at; here the filter temperature is set at 70 °C as before [22] as required by BS 3841–2: 1994 so that low boiling point material is not collected. In the equivalent soot measurement for diesel engines this temperature is set at 52 °C. Data obtained for EC/TC in this way are given in Table 1 for fuels numbered 1–6. TC is taken as the sum of EC and OC. Values of EC/TC were also determined for these samples using the Micro-pyrolysis method previously described, and these values are also given in Table 5-1.

		EC/TC	
#	Soot sample	TGA	Micro-pyrolysis
1	Multi-fuel stove, chimney deposit	0.60	0.66
2	Wood Stove, chimney deposit	0.65	0.65
3	Eugenol diffusion flame	0.99	0.98
4	Furfural diffusion flame	0.99	0.95
5	Anisole diffusion flame	0.99	0.97
6	n-Decane diffusion flame	1.00	0.98

Table 5-1. Soot EC/TC determined by TGA and comparison with micro-pyrolysis method.

A range of fuels, numbered 7–14 in Table 5-2, were burned in the stove and samples of smoke were taken on filter papers at a number of known times. Sampling times for each filter sample were every 5 min.

		VM	EC/TC			OC mg MJ^{-1}			EC mg MJ^{-1}		
No	Fuel	% db	Flam	Smo	Avg	Flam	Smo	Avg	Flam	Smo	Avg
7	Wood A	84.2	0.42	0.12	0.30	40.1	7.7	27.1	30.2	1.1	18.5
8	Wood B	79.3	0.69	0.13	0.46	17.1	3.4	11.6	45.8	0.5	27.7
9	Torrefied briquettes	72.1	0.67	0.17	0.37	4.9	1.3	2.8	11.5	0.3	4.8
10	Peat Briquettes	64.4	0.34	0.19	0.28	135.2	5.8	83.4	37.6	1.6	23.2
11	Coal	39.7	0.85	0.47	0.62	40.6	2.5	17.7	240.5	4.0	98.6
12	Biomass blend	14.0	0.43	0.20	0.25	24.4	11.7	14.3	18.7	3.1	6.2
13	Low smoke fuel	23.4	0.47	0.30	0.38	55.2	7.2	31.2	39.2	4.9	22.0
14	Smokeless fuel	8.2	0.38	0.19	0.23	13.7	2.8	5.0	7.9	0.6	2.1

Smo: smouldering

Table 5-2. Volatile matter, EC/TC, OC and EC for fuels 7–14.

Since the values of OC/EC vary with time, the data obtained are complex and only one example, for the torrefied fuel (fuel no. 3), is given in Fig. 5-2. Data for EC and OC for the samples collected on the filter papers during the combustion of two woods of different composition, a torrefied fuel, a biomass blend, coal and a smokeless fuel are shown in Fig. 5-3. The points at which the measurements were made are indicated. It should be noted that the differences in the burning rates of the fuels are determined by the size of the fuel particles (that is the surface area) as well as the combustion air requirements.

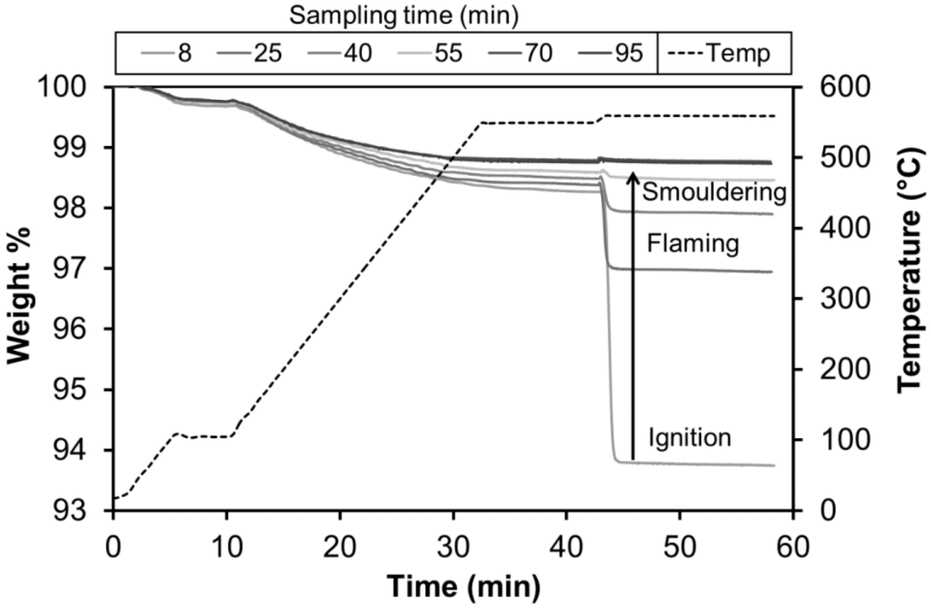

Figure 5-2. Combined TGA plots for all the sample filters taken throughout the burning cycle of torrefied wood. The arrow shows the large reduction in the EC with time.

The detailed compositions of these fuels, which have been used for a previous study, have been given [22]. However their volatile contents are given again in Table 2 because of their significance to this work; the moisture content of the wood was about 8 wt%, the torrefied wood about 5 wt%, the coal and the peat about 7 wt% and the other fuels between 2 and 6 wt% [22].

It is clear from Fig. 3 that both EC and OC and EC/TC vary with time in a way that depends on the fuel type. For the wood logs, the composition of the soot is highly dependent on the phase (flaming or smouldering) of combustion. Flaming combustion promotes the formation of highly carbonaceous soot, dominated by EC. Smouldering combustion forms mostly organic compounds and tars, which condense to form a brown organic aerosol deposit called ‘brown carbon’ [5]. Values of EC/TC are given in Table 2 for samples numbered 7–14.

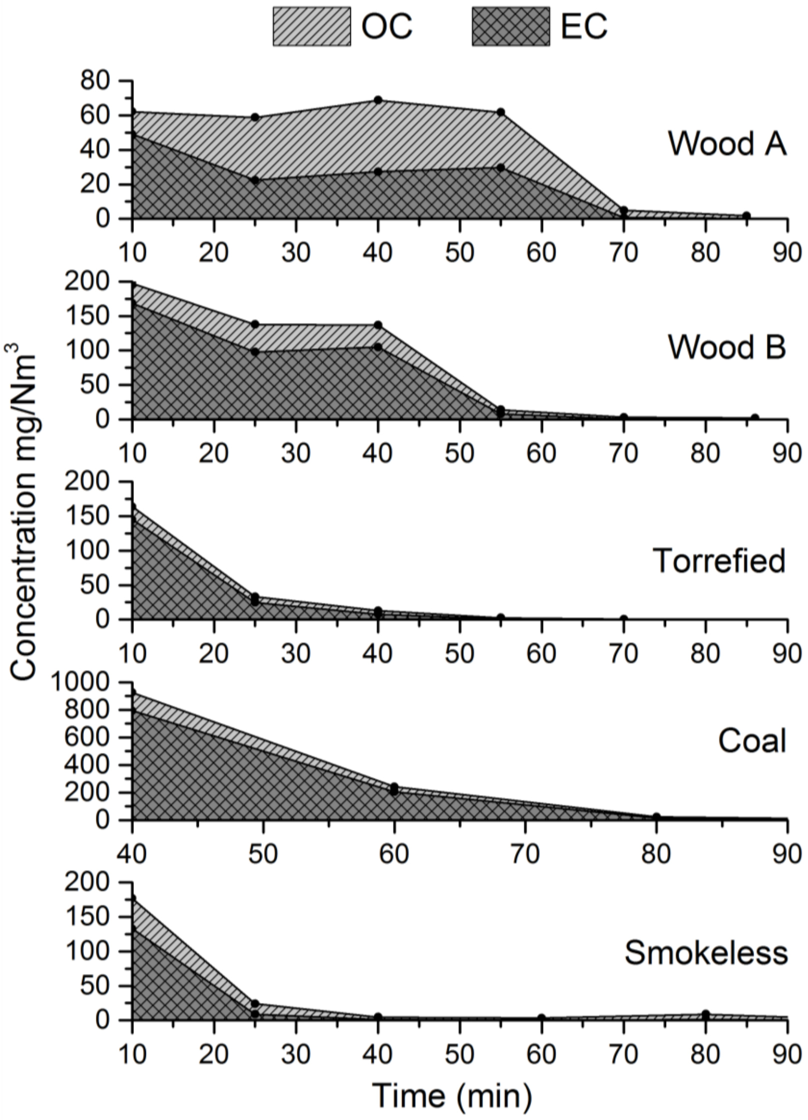

Figure 5-3. Composition of samples collected on the filter papers as a function of time during the combustion of: wood A; wood B; torrefied fuel; coal and a smokeless fuel. Experimental results: ●.

The inorganic content for soot samples from the Stove studies for Woods A (fuel no 7), B (no 8), Torrefied wood (no 9), Coal (no 10) and Smokeless fuel (no 11) were determined and are shown in Fig. 5-4. The inorganic content again varied with time but typically at a midpoint of the combustion cycle, namely after 30 min, was about 25% of the total particulate material for all fuels.

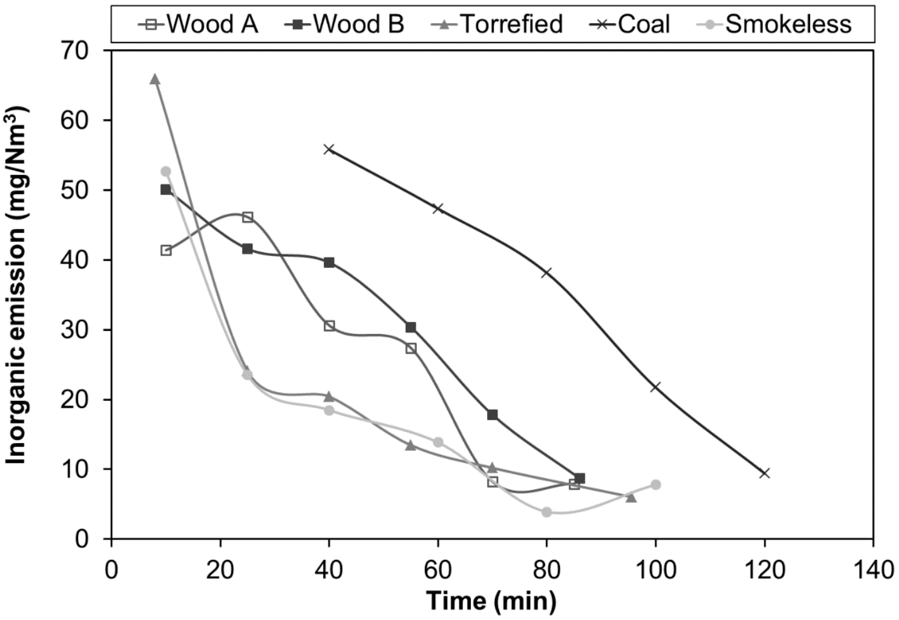

Figure 5-4. Inorganic content collected in in the filters (mg/Nm^3) as a function of time for Wood A (fuel 7), Wood B (fuel 8), Torrefied wood (fuel 9), Coal (fuel 10) and Smokeless Fuel (fuel 11).

Samples of soot deposits were taken from the Multi-fuel and Wood stoves and examined by TGA (cf Fig. 1). There was a considerable amount of ash present in these samples (cf Fig. 1.), the highest for the Multi-fuel stove at 21 wt%; the ash content from the Wood Stove was lower. The values obtained are shown in Fig. 5-5 together with a typical value for the flue gases during the combustion of all the fuels during the flaming phase.

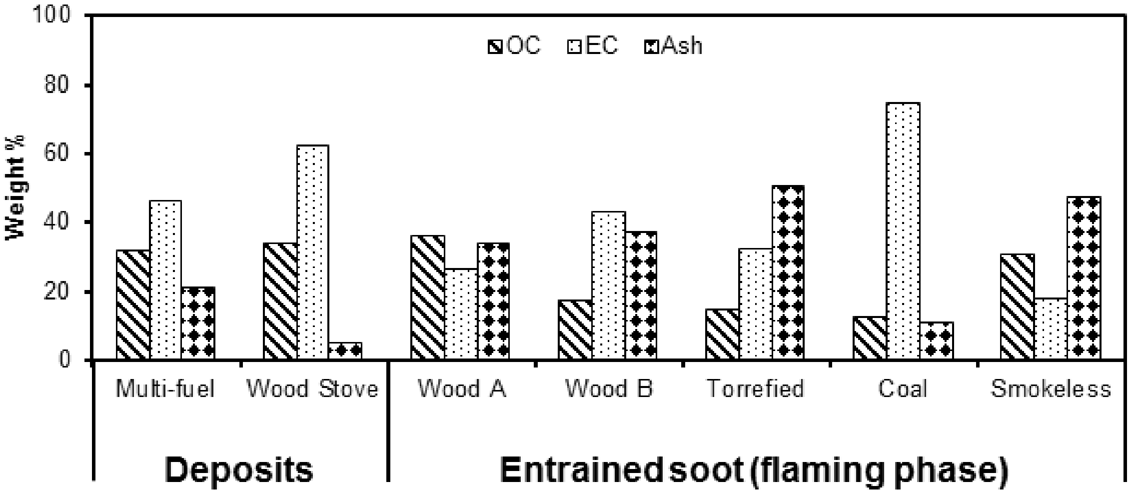

Figure 5-5. Composition (wt %) of OC, EC and ash for the soot deposits and in the flue gases during the flaming phase for the different fuels.

These ash levels are lower than this average during the later stages of combustion. The inorganic content of the deposited soot samples from the flues was analysed by AAS. The results are presented in Table 5-3.

	1	2
	Multi-fuel stove, chimney deposit	Wood Stove, chimney deposit
K	7317	5215
Na	8459	1500
Fe	5435	8897
Mn	296	941
Ca	8505	14169
Al	6957	1647
Cu		76
Zn	293	403
Mg	2368	1923
Pb	350	357
Ti	14	2

Table 5-3. Inorganic analysis of the two soot deposit samples (mg kg^{-1}).

The results show significant differences in the content of Na, Mn, Ca and Al. The model fuels were all pure liquids and soot deposits from them did not contain inorganic material.

5.3.2 Nature of the soot samples and the associated OC

Experimental data were obtained on the black and the brown soot samples resulting from the combustion of wood sample A during the stove studies. SEM images of soot on the filter obtained from the combustion of Wood A during (a) flaming combustion, which has a high BC, and (b) smouldering combustion, which has high OC and the formation of brown carbon (BrC). It is seen from Fig. 5-6 (a) that the BC samples consist of spherical particles with basic units of about 55 nm diameter but largely consisting of chains of agglomerates up to1000 nm in size. The OC/BrC sample shown in Fig. 5-6 (b) is an amorphous tar-like material; fibres from the filter are also apparent in this image. TGA analysis of this tar showed that it consisted of 83 wt% volatile material and 17 wt% fixed carbon on a dry ash free basis.

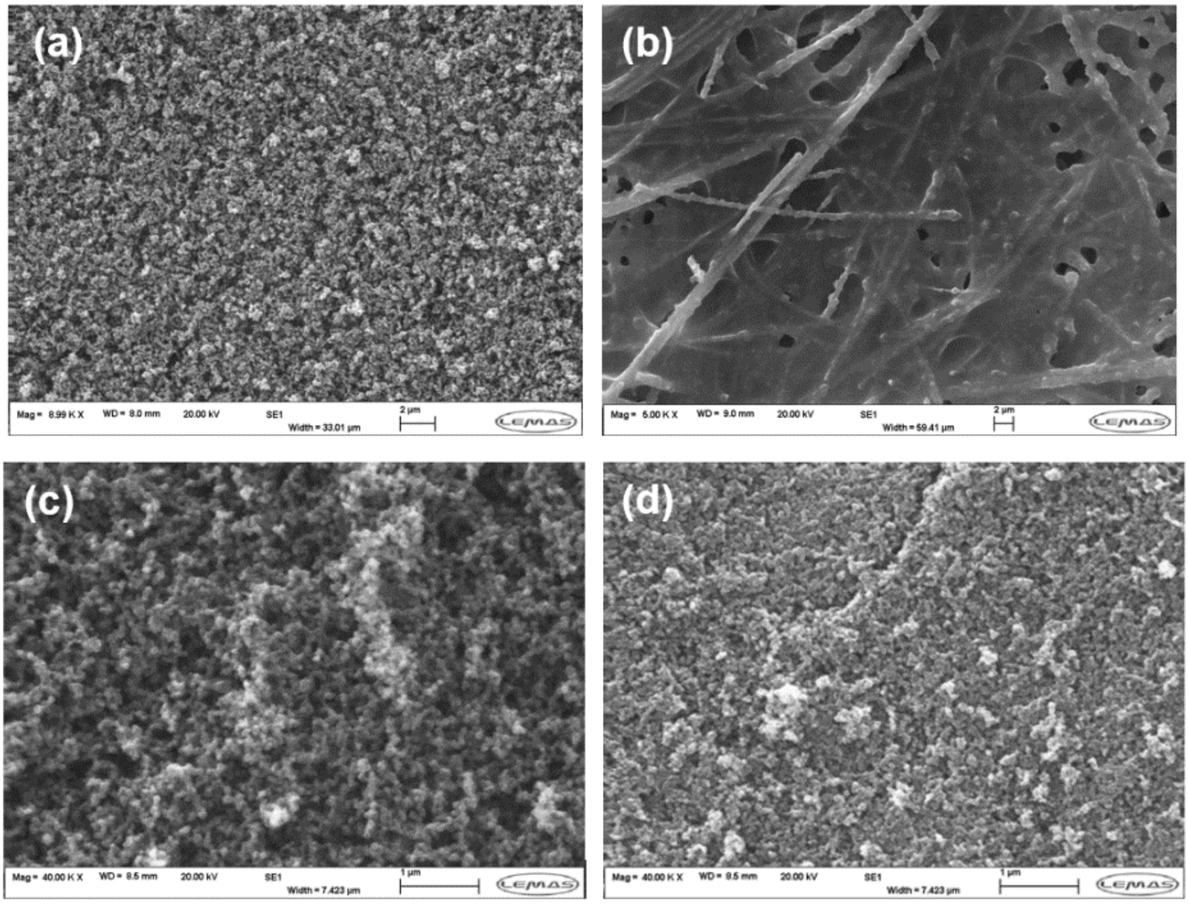

Figure 5-6. SEM images of (a) wood soot collected during flaming combustion (high BC), (b) wood soot collected during smouldering combustion (high OC and BC), (c) anisole soot, and (d) n-decane soot.

These filter samples of the black carbon and brown carbon were analysed by Py-GC-MS at 300°C using the method given earlier. The results are shown in Fig. 5-7 (a) and (b). It should be noted that these samples are those in the temperature window of the filter temperature, 70 ˚C, and the Py-GC-MS pyrolysis temperature of 300 °C; the same samples were heated to 400 and 500 °C with only little evolution of further material. But there is much less material evolved compared with other studies where higher temperatures were used. For example, Fitzpatrick et al. [17] used a temperature of 1000 °C whilst Song and Peng [31] used temperatures up to 700 °C.

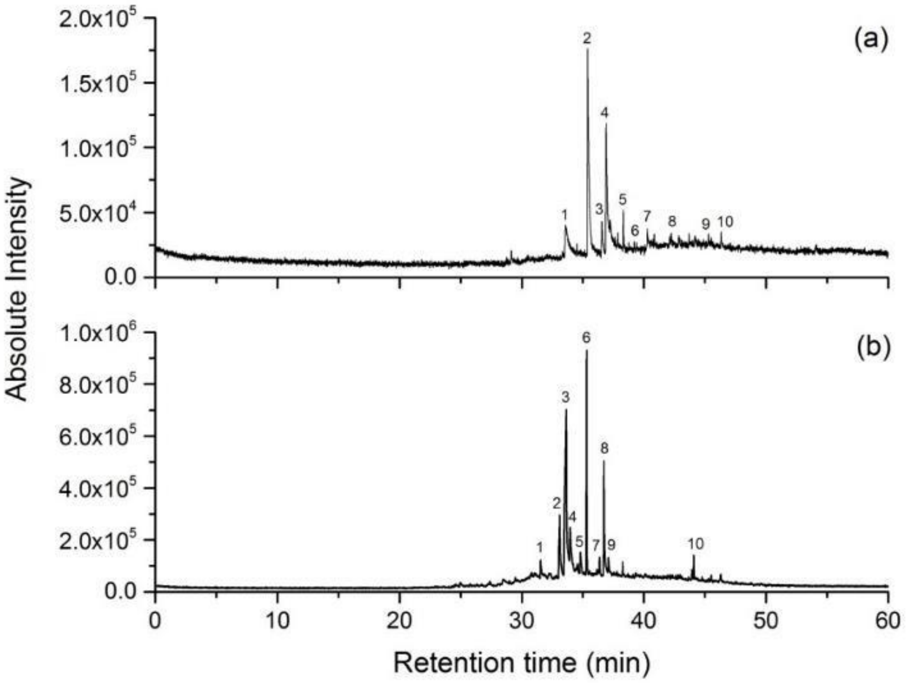

Figure 5-7. Py-GC-MS chromatogram of compounds desorbed at 300°C from: (a), black smoke. Key: 1. levoglucosan; 2: 1,6 anhydro-alpha-D-glucofuranose; 3; tetrabenzyl glucose; 4; methoxy eugenol; 5: kauran (diterpenoid alcohol); 7: cyclohexane, 1-(1-tetradecylpentadecyl)-; and (b), brown smoke. Key: 1. 1-(4-hydroxy-3-methoxyphenyl)-2-propanone; 2. alpha-D-glucopyranose; 3. levoglucosan; 4. 4-ethoxymethyl-2-methoxyphenol; 5. unidentified; 6. 1, 6 anhydro-alpha-D-glucofuranose; 7,8, methoxy eugenol; 9, 3-hexenoic acid; 10, naphthalenone (or dihydroxynaphthalene)

In the chromatograms in Fig. 5-6 the important components are identified in the key. The apparently raised baseline between 25 and 50 min in the chromatogram reproduced in Fig. 5-7 results from the overlapping signals from very many unresolved low-concentration components of the tar thermally desorbed at 300 °C; by analogy with the large number of compounds present in wood pyrolysis products [17, 33,34] and carbon based materials [31] not one constituent of the baseline signal is present at sufficient concentration to be detected individually. There is still controversy concerning the mechanism which leads to the observed composition of cellulose pyrolysis products, but there is general agreement [34,35] that two competing routes operate, with production on the one hand of gas and char, and on the other liquid (primary) tars predominantly made up of levoglucosan, along with smaller amounts of other sugars. Secondary reactions give rise to anhydrosugars, furans, ketones and carboxylic acids among which compounds acetol and hydroxyacetaldyde are prominent [35].

The sugars which contribute markedly to the chromatograms of the brown and black tars evidently originate from cellulose and hemicellulose and represent the primary pyrolysis products sampled at an early stage. These oligosaccharides mostly rapidly decompose, but significant amounts are weakly adsorbed on the carbonaceous particles and are desorbed at 300 °C. The difference in quantity and distribution of the products in the tars then depends on the extent of further decomposition, as well as on their chemical composition and the nature of the carbon particle surface. Thus levoglucosan was present in brown smoke at a considerably higher concentration than in black smoke, but the compound at highest concentration in both was 1.6-anhydro-alpha-Dglucofuranose. There is strong evidence [31,35] that the nature and composition of cellulose pyrolysis products is influenced by the phenolic compounds produced by decomposition of lignin; methoxybenzene is present at high concentration in both black and brown smoke.

Samples were taken from the deposited soot in the chimney flue from the Multi-fuel stove. These consist of soot that has been subject to heat after deposition and their nature is different from the samples taken on filters. Their only role in terms of particulate emissions is if they fragment and are entrained in the flue gases. The Multi-fuel stove soot showed two phases of mass loss: with most loss up to ~320 °C then a slower rate of OC release up to the final temperature. These two phases may correlate with the phases of weakly bound and strongly bound material [25]. A Py-GC-MS examination was made of these deposited soot samples and an example is shown in Fig. 5-8(a) pyrolysed at 400 °C. It contained a prominent series of peaks attributed to the alkane/alkene pairs extending from C12 to C25 with a maximum at C18 and thought to arise from alkyl radicals generated by beta-bond scission of long chain alkyl aromatics. With increasing pyrolysis temperature, 500 °C and 600 °C (results shown in Fig. 5-7 (b) and (c)) the series was extended to lower carbon numbers, and was superposed on a partially unresolved background of many peaks including those from 1 to 4 ring PAH substituted with (mainly methyl) short-chain alkyl groups and identified by selective-ion monitoring MS. This behaviour is typical of the pyrolysis products of the higher MW aromatic-based constituents of heavy hydrocarbon such as asphaltenes [36]. The lower MW compounds are much more prominent in the 600 °C product.

Overall, the results of characterisation of the soot from the chimney flue of the Multi-fuel stove are consistent with the deposition in the flue of the highest MW fraction of a hydrocarbon oil fuel. These are mixed with the phenolic components of the biomass tar from lignin.

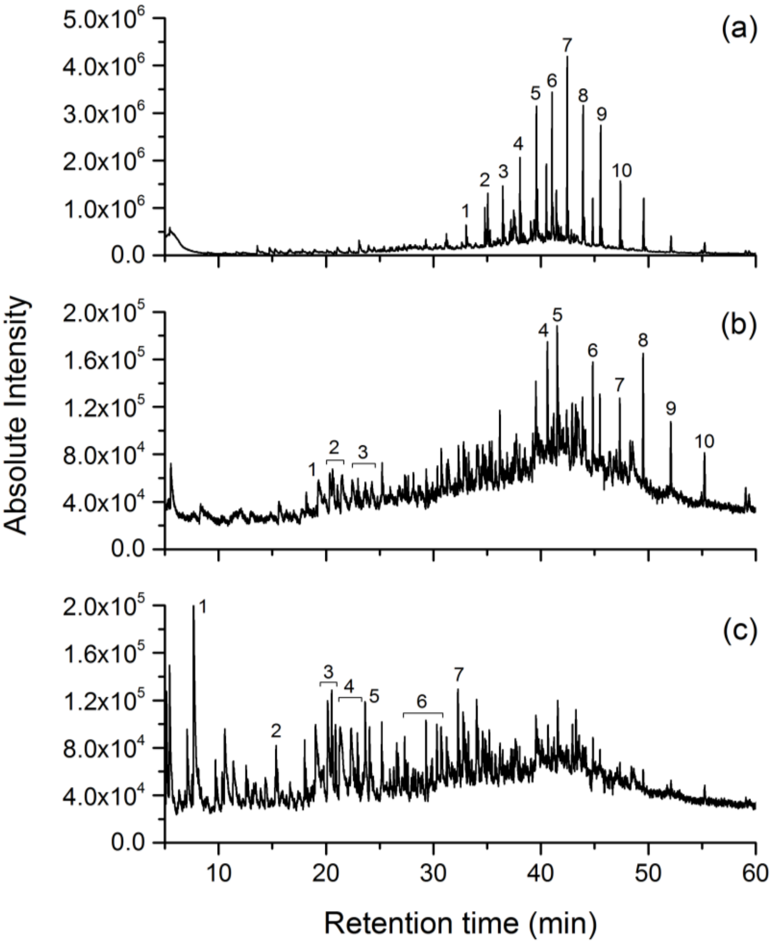

Figure 5-8. Py-GC-MS chromatograms of soot from the multi-fuel stove at: **(a)** 400°C; 1. 3-10 alkanes; 2. phenanthrene; **(b)** 500°C; 1. phenol ; 2. methyl phenols; 3. dimethyl phenols; 4. fluoranthene; 5. pyrene; 6. unknown; 7-10, alkanes; (c) 600°C; 1. toluene; 2, phenol; 3. methyl phenols; 4. dimethyl phenols; 5. methylnapthalenes, 6. dimethyl naphthalenes; 7. napthalenol.

Soot samples from the diffusion flame combustion of furfural, anisole, eugenol and n-decane were obtained using the diffusion flame burner and collected on an uncooled glass plate (at about 100 °C) at known distances above the flame. These deposits were of a hard particulate nature except for the eugenol soot which was a fluffy, typically aromatic type of soot. Examples of the soots are shown in Fig. 5-6 (c) for anisole and Fig. 5-6 (d) for n-decane. In the former case the sample consisted of chains of soot with the diameter of the individual particles being 48 ± 10 nm, which is similar to wood (58 ± 10 nm); n-decane soot had smaller diameter particles, namely 37 ± 10 nm.

Py GC-MS analysis was made of these samples collected from eugenol at heights of 5 and 10 cm above the flame and the results are given in Fig. 5-9 (a) and (b). It is clear the sample obtained nearer the flame contains many eugenol decomposition products but by the time the samples reach 10 cm from the flame only the major species remain.

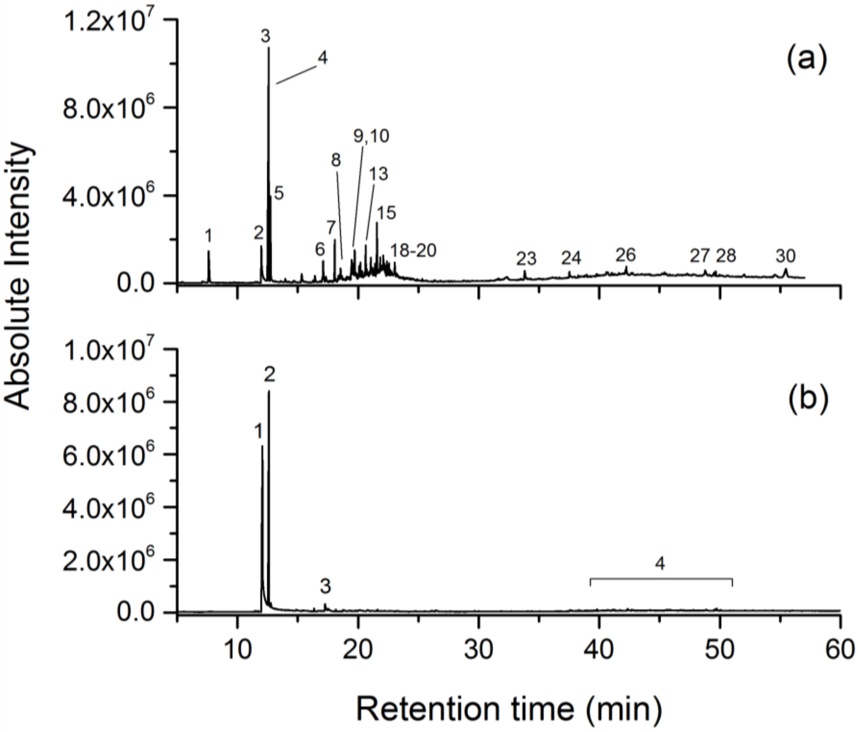

Figure 5-9. Py-GC-MS chromatogram of compounds desorbed at 300ºC from eugenol soot (a) collected 5cm above the flame: 2. toluene; 3. furfural; 4. 3,5-dimethyl-octane, 5. methoxy-benzene; 6. 1-ethenyl-3-methoxy- benzene; 7 to 29, aromatic and aliphatic hydrocarbons; 30. D-allose, and (b). Soot collected 10cm above the flame: 1. furfural; 2, methoxy-benzene; 3. 1-ethenyl-3-methoxy benzene. From 20 -59 min: small quantities of aromatic aliphatic hydrocarbons.

The most notable difference between the diffusion flame samples and the stove samples is the very high values for EC measured for the soot from the former. In the present configuration with soot samples which remain at an elevated temperature and in an unconstrained flow of combustion products there is little opportunity for the OC to condense on the soot samples. Consequently the Py-GC-MS are of very small samples and the amount of identifiable material at low temperatures desorption is limited, as is seen from the Py-GC-MS.

A major issue is the choice of the desorption temperature used for the Py-GC-MS studies. The soots derived from the wood burning stove contained high levels of methoxyphenols and dimethoxyphenols at pyrolysis temperature of 400 °C (cf Fig. 5-8). These species are associated with the lignin part of the wood structure. These phenolic species were present at 500 °C but by 600 °C mainly aromatics were seen for the same sample. Song and Peng [31] used a pyrolysis temperature of up to 700 °C to investigate soots and charcoals, concluding that the higher temperatures were most appropriate and finding that the products were dominated by aromatic compounds. They also found oxygen-containing pyrolytic products in all the samples analysed, but suggested that these arose from thermal decomposition of the carbonaceous solid particles.

5.4 Discussion

5.4.1 Factors determining the ratio of EC/TC

Because of the importance of black carbon and organic carbon in atmospheric chemistry a number of test protocols have been established initially based on emissions from diesel engines [23]. In the present studies single batch combustion of biomass has been adopted and it is seen from Figs. 5-4 and 5-5 that both the organic and inorganic emissions vary considerably with time. This can occur in a continuously fired unit although the effect would be less pronounced. The relative proportions of elemental carbon (EC) and co-emitted organic carbon (OC) depend on the nature of the combustion phase, flaming or smouldering.

A main issue is the amount of OC associated with the soot particle. This will contain some PAH species involved in the growth of the soot particle as well as adsorbed volatile components from the surrounding gases, the latter is very much dependent on the temperature time history of the soot particle. The measured OC also depends on the method in which it is determined particularly the filter temperature and temperature at which it is desorbed for examination. The soot collected from the diffusion flames of model pyrolysis compounds onto a deposition plate at a temperature of about 200 °C contain very little OC (cf Table 5-1). This is in agreement with earlier work with sooting laminar ethene-air flames [37] that showed there was little OC deposited on heated plates but by using water-cooled plates there was a considerable deposition of PAH and other hydrocarbon species. Results obtained by Ferge et al. [26] who used an ATOFMS are in good agreement with those presented here: for instance, hydrocarbon diffusion flames had an EC/TC ranging between 79.9 and 94.4. Maricq [38] found similar results from hydrocarbon diffusion flames.

In our previous work we used an ATOFMS for investigation of EC/TC ratio in both eugenol and n-decane soot using the method of Ferge et al. [26] and found that samples of post flame gases gave EC/TC values of 0.52 ± 6 and 0.88 ± 5 respectively. Using the same technique values have also obtained for burning wood. For softwood pine, these values were: 0.61 during flaming combustion and 0.62 during smouldering combustion. Similarly EC/TC values for burning willow were 0.50 for flaming combustion and 0.65 for smouldering combustion [8]. In all these experiments the samples were taken to the ATOFMS through a sampling probe at about 100 °C.

The emissions factors for EC and OC reported in this study are within the ranges reported for a traditional log wood stove [6]. This study reported flaming phase emissions factors for BC and OC as 72 ± 66 mg MJ^{-1} and 14 ± 10.5 mg MJ^{-1} respectively; comparable to 30- 46 mg MJ^{-1} and 17-40 mg MJ^{-1} respectively in this study for the two wood fuels. The difference in values reflects the importance of combustion conditions and also the variability in EC and OC between biomass fuels. This has also been found in other studies [6]. Schmidl et al. [19] looked at the composition of soot from different types of woods using direct sampling from the flue gases. The EC/TC values reported were in the range of 0.15–0.30 for the woods (larch, spruce, beech and oak) and 0.43 for the briquettes. The high OC fraction suggests poor combustion conditions, the higher values for briquettes were attributed to their disintegration under burning conditions giving better access to air. These values are similar to those obtained here during the different combustion stage and are given in Table 5-2. Peat combustion was associated with the highest average OC emission factor, 84 mg MJ^{-1}. This is consistent with the findings of Pokhrel et al. [7].

Some extremely detailed studies have been undertaken recently by the Zimmerman group [11,20] and by Calvo et al. [39] using a dilution tunnel methods and the soot samples were collected on unheated filters. Generally their results for a number of woods are consistent with those found here given in Table 5-2 for the flaming phases. Chen et al. [40] have made measurements using similar methods from coal combustion in fixed beds and found that EC/TC has a value about 0.75 for bituminous coals and 0.44 for anthracite (a low volatile ‘smokeless’ fuel). These values follow the same trends as those given in Table 5-2 although it should be noted that with a dilution tunnel the cooling time-temperature history of the soot particle is determined by mixing patterns during the dilution process. This is of importance where standard test methods are used to collect particulate. The Ecodesign regulations 2015/1185 implementing Directive 2009/125/EC allow three different methods to be used to measure particulate emissions from solid fuel space heaters. These include measurement directly in the flue using a heated filter; measurement over the full burn cycle using a dilution tunnel; and measurement over a 30 min period using a filter at ambient temperature or an electrostatic preciptitor. Although each method has it's own specific requirements, the results of this study suggest that the first and third methods may underestimate the OC fraction if sampling is carried out only at high temperatures, or only during the flaming phase.

5.4.2 Chemical composition of soot pyrolysis products

In this work it was observed that the graph of weight loss against time/temperature for the multifuel soot had three types of region: an initial low-temperature region in which, a second, generally more extensive section; and a final rapid weight loss during oxidation in air. These correspond to the three types of material which were identified by Ross et al. [25] as constituents of soot or BC: weakly-bound material, easily thermally desorbed, and extractable by solvents; more strongly-bound material less easily desorbed; and finally highly developed soot which is burned in the final phase of the TGA. In the case of biomass combustion the weakly bound constituents consist of the lower MW PAH soot precursors which arise from the early products of soot growth such as naphthalene and anthracene which are volatile and easily lost [25,41]. The major components are those from the decomposition of cellulose such as oligosaccharides, levoglucosan and furfural; and from the decomposition of the sugars and lignin such as eugenol may be converted into marker compounds. Any differences between the soots lie in the relative amounts of different products, the sampling method and analytical method employed. Further weight loss regions then arise from the desorption of higher MW analogues involved in the soot forming routes.

5.4.3 The inorganic components

The inorganic components of the fuels examined are given in Table 5-4 which is taken from [15].

Fuel No Fuel type	7 Wood A	8 Wood B	9 Torrefied Fuel	11 Coal	13 Smokeless fuel
ash	0.1	0.9	1.0	4.2	5.2
S %db	0.03	0.02	0.04	0.4	2.0
Cl %db	0.03	0.02	0.04	0.06	0.02
P ppm db	3,591	4,142	4,059	3,608	3,629
Ca ppm db	18,386	11,978	8,766	5,923	5,867
K ppm db	583	3,478	1280	265	767
Zn ppm db	140	823	55	1	0

Table 5-4. Inorganic content of the sampled samples (from [15])

The relationship between the experimentally determined flue gas contents and the initial fuel composition is complex. Coal gave the highest amount of inorganic material which is greater than that from Woods A and B whilst the lowest are the torrefied and smokeless fuels. The coal is expected to give a high level because of the high ash content, the woods have a lower ash content. The torrefied fuel has a similar ash content to the woods but it has a lower potassium content. The smokeless fuel surprisingly gives the lowest level of inorganic content in the flue gases despite a high ash content and high levels of all the metals. This presumably arises from the fact that smokeless fuel is thermally pre-treated and this process binds the inorganic species to the largely carbonaceous char matrix. However if the data are considered on an emission/MJ basis the results show that the emissions from the woods are similar to the coal whilst the torrefied wood and the smokeless fuels are lower. In comparison to the ‘real life’ wood stove soot deposits, the Multi-fuel stove soot deposits were higher in sodium, aluminium, titanium and magnesium. However zinc and calcium were approximately twice as high in the wood stove soot sample.

5.5 Conclusions

Measurements were made of the emissions of OC, EC and EC/TC resulting from the combustion of a number of fuels in a fixed bed domestic stove. There are considerable differences between fuels with the smokeless fuels and torrefied wood giving lower levels of total EC and OC. Average EC/TC ratios for wood logs, torrefied briquettes, coal and smokeless fuel were 0.46, 0.37, 0.62 and 0.23 respectively. Coal soot showed the highest EC/TC. Combustion conditions were also found to be a key variable, whereby the EC/TC ratio is a function of whether it is flaming or smouldering combustion. For the wood fuels, the EC/TC ratio was 3–5 times lower during the smouldering phase than the flaming phase. The inorganic components of the particulate were dependent on the fuel as well as the combustion conditions. Analysis of the OC composition of all three categories of soot samples was carried out by pyrolysis GC-MS. A significantly higher levoglucosan response was observed in the brown carbon from wood soot.

The chimney soot deposit sample from the ‘real life’ wood stove showed similar pyrolysis products. Soots collected from the combustion of biomass model compounds had very low OC content, with EC/TC ratios ranging from 0.95 to 0.99.

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5.6 References

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Chapter 6

Emissions from Non-Traditional Feedstocks

The Use of Conservation Biomass Feedstocks as Potential Bioenergy Resources in the United Kingdom

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Abstract

A number of countries have introduced energy policies to reduce the emission of carbon dioxide which, in the case of bio-heat, has resulted in increased use of small wood burning stoves and boilers, particularly in Europe. There are issues surrounding the supply of sustainable wood feedstock, prompting a desire to utilise local biomass resources. This includes biomass generated through the management of natural woodlands in nature reserves and conservation areas. These management practices can also extend to other areas, such as raised bog wildernesses and estuary Reed beds. We term the biomass from this resource as conservation biomass. This study is concerned with the viability of this resource as a fuel within the United Kingdom, and combustion tests were carried out using a small domestic stove. It was concluded that there is as much as 500 kt y^{-1} that could be used in this way.

Keywords: biomass; conservation biofuels; combustion; emissions

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Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2016.04.057. In addition to this, further supplementary material on the combustion properties of agricultural residues is presented in appendix IV (section 11.4).

6.1 Introduction

European policies and targets for reducing emissions of carbon dioxide have led to an increase in the use of biomass in stoves and boilers throughout Europe. As a consequence, there are potential problems surrounding the availability of sustainable supplies of wood feedstock in Europe. With the requirement of large quantities of imported biomass for electricity generation in the UK (DUKES, 2015), coupled with the desire to achieve security of supply, there is a growing necessity to use local biomass resources. Sustainable bio-heat remains a challenge in many European countries. Thus, small-scale combustion applications may have to be increasingly used, although with appropriate attention to environmental and sustainability issues (Gerssen-Gondelach et al., 2014).

In 2014, the UK used approximately 4.9 Mt of fuel wood (DUKES, 2015) of which 354 kt of wood pellets and briquettes were produced using locally grown woods and recycled Grade A wood (Forestry Statistics, 2015). For small scale bio-heat, alternative feedstocks from local sources are an attractive option for both consumer and supplier; however, there are issues about where this is sourced. Particular areas of the countryside are designated with a protected status to ensure that their high value nature and wildlife is not altered or destroyed. Special Areas of Conservation (SACs) and Special Protection Areas (SPAs) within the UK represent a significant expanse of land, covering a range of environments such as forests, moorlands and wetlands.

Although the UKs woodlands have been historically managed, a declining use of wood products has resulted in many forested areas becoming neglected, negatively impacting upon biodiversity and their long-term ecology (Read et al., 2009). The biodiversity of an area can be preserved through a passive management approach, but inaction can result in the suppression of important habitat values and, as a result, can be detrimental to conservation. Therefore, active management, such as small scale felling within previously managed woodlands, or the removal of invasive species, can become an environmental necessity. UK sites with significant nature conservation value, such as Sites of Special Specific Scientific Interest (SSSIs), are currently undermanaged, with less than half of the reported areas undergoing positive conservation management. Consequently, management practices hold a great environmental importance (Bernes et al., 2014; Ditlhogo et al., 1992; DEFRA, 2014).

This study aims to examine fuel characterisations for some potential biomass feedstocks produced from conservation management processes for use in bioenergy production. The resources considered include a variety of native broadleaved wood species and harvested common reeds, sourced from Areas of Outstanding Natural Beauty (AONB), SSSIs, and dedicated nature reserves.

In addition to the existing unmanaged woodland located within the UK, there are other conservation areas that require regular upkeep, namely Reed beds, which are predominantly located on the UK's wetlands. In total, there are 5 kha of Reed beds located within the UK, which require intensive management to safeguard their preservation. The regular cutting of the Reeds is necessary ensuring the correct conditions for rare breeding and migratory birds are achieved, thus improving biodiversity. Cutting the Reeds is a common management practice; however they are often openly burned (Ditlhogo et al., 1992). The inefficient combustion is associated with high emissions of pollutants (Lemieux et al., 2004). In addition, open burning releases CH_4, N_2O and carbonaceous aerosols which are important drivers of climate change (Jacobson, 2014). The practice of harvesting Reeds over a prolonged period of time increases the density of the grown Reeds, but also decreases their shoot thickness (Cowie et al., 1992). Estimates of the above-ground biomass production in the existing literature indicates that Reeds can produce 14–15 t ha^{-1} annually, suggesting that undertaking the required management practices of Reed bed conservation could result in a potentially significant source of local biomass resource (Kuhlman et al., 2013; Kobbing et al., 2014).

Region	SAC		SPA	
	No. Sites	Area (ha).	No. Sites	Area (ha).
England	230	1,068,476[‡]	81	1,054,353
Scotland	236	939,727[‡]	152	1,205,988
Wales	85	590,864	17	172,149
England/Scotland*	3	112,564	1	43,637
England/Wales*	7	95,132	3	209,247
Northern Ireland	54	85,831[‡]	16	114,052
Total	615	2,892,594	270	2,799,426

*Areas that cross the border, [‡]includes Sites of Community Importance (SCIs)

Table 6-1. Areas of Special Conservation and Special Protection in the UK.

Other estimates indicate that the productivity in wetlands can be as low as 10% of this figure, similarly in grasslands it can be as low as 6 t ha^{-1} (Wichtmann and Schafer, 2007) while coppiced woodlands can achieve a productivity of 2–5 t ha^{-1} (Hytonen and Issakainen, 2001). As a result, the variability in conservation sites gives rise to a wide variety of different biomass forms that could be utilised in the production of bioheat (Kuhlman et al., 2013; Kask et al., 2013/2014; Wichtmann et al., 2014; Ranjitkar et al., 2014; Sommersacher et al., 2015).

Consequently, conservation management practices can produce a considerable amount of biomass wastes that are currently disposed of by open burning. This product is therefore available on a sustainable basis as a byproduct of management actions aimed at conserving habitats and their incumbent wildlife. However the amount available of this biomass is dependent upon the proportion left in situ to maintain the health of the habitat, a figure which can vary from 10% to 100% (Welfe et al., 2014). This data enables us to estimate an approximate value for the availability of 'conservation' biomass later in this paper.

Thus this study aims to examine the potential and fuel characterisation for some of these biomass feedstocks produced from conservation management processes. The resources considered include a variety of native broadleaved wood species and harvested common Reeds, sourced from Areas of Outstanding Natural Beauty (AONB), SSSIs, and dedicated nature reserves.

6.2 Materials and methods

6.2.1. Source of the fuels

The sources of all of the conservation fuel in the UK are set out in Table 6-1. We have studied typical samples in particular locations described below and the samples studied are listed in Table 6-2. In addition to the raw (unprocessed) biomass samples, charcoal (biochar) produced from the peat grown Willow has been investigated, whilst both biochars and briquettes had been produced using the harvested Reed. The separate carbonising (charring) and briquetting processes were undertaken for us using traditional heated kiln methods.

The Humberhead Peatlands National Nature Reserve is considered the largest area of raised bog wilderness in lowland Britain and is located in South Yorkshire. The site is classified as both a SAC and a SPA due to its habitat and consequent role as a breeding site. Both the peat grown Willow and Silver Birch samples were sourced from a natural regenerated woodland area, which spans 200 ha. As the site has developed naturally, there is no uniformity in the tree ages, ranging from young saplings to well established specimens. Of the samples analysed, those taken from this site were the stem wood of juvenile Willow and Silver Birch trees. The woodland is established on peat soil, in an area that has historically undergone extensive peat extraction for use as a fuel. The composition of peat is dependent upon an array of environmental conditions. As a result, peats tend to have higher contents of N, S, Al and Ca, whilst the Ca content can vary greatly from site to site.

Type	Sample name	Site Type	Sample Type
Woods	Ash (*Fraxinus excelsior*)	Woodland (AONB[3])	Heartwood, Bark
	Birch (*Betula pendula*)	Peat (SAC[1])	Heartwood, Bark, homogenised
	Hazel (*Corylus avellana*)	Woodland (AONB[3])	Heartwood, Bark
	Willow (*Salix caprea*)	Peat (SAC[1])	Homogenised
	Willow (*Salix caprea*)	Floodplain (SSSI[2])	Heartwood, Bark
	Willow SRC (*Salix viminalis*)	Short Rotation Coppice	Homogenised
	Willow Billets (*Salix* spp)	Tidal Estuary	Heartwood, Bark
	Willow Char 1	Peat (SAC[1])	Traditional thermal kiln
	Willow Char 2	Peat (SAC[1])	Traditional thermal kiln
Herbaceous	Reed Raw (*Phragmites australis*)	Tidal Estuary	Common reed as harvested
	Reed Char 1	Tidal Estuary	Traditional thermal kiln
	Reed Char 2	Tidal Estuary	Traditional thermal kiln
	Reed Washed	Tidal Estuary	Lightly washed in room temp. distilled water
	Straw raw (*Triticum* spp)	Agricultural land	Wheat straw as harvested
	Washed straw	Agricultural land	Lightly washed in room temp. distilled water
	Peat turf	Peatland in Ireland	Cut bog peat, air dried.

[1]Special Area of Conservation, [2]Site of Specific Scientific Interest, [3]Area of Outstanding Natural Beauty

Table 6-2. Description of samples used in the study.

Alternatively, the Ash and Hazel wood samples, as described in Table 6-2, were sourced from an AONB. Their extraction was part of a thinning regime to improve access throughout the woodland, resulting in the samples originating from the stem wood of older, more established trees. The Willow samples, sourced from the Floodplain and Tidal Estuary sites, were produced following pollarding and the removal of branches as a management tool to help maintain the local habitat.

The Reeds were sourced from Blacktoft Sands as part of a regular, mechanised cutting regime of the Reed beds. This process is required to maintain an appropriate habitat for the conservation of the visiting birds. Common Reed grows predominantly in saturated marsh areas. This means that the surrounding environmental conditions, such as nutrient availability and the depth and salinity of the water, impact the growth and composition of the biomass. Other than the Reed briquettes and chars, the biomass samples used in this research were delivered with no additional processing following harvesting. On receipt of the harvested samples, they were stored in a covered, outdoor fuel store in separate, breathable containers.

6.2.2. Fuel characterisation

Prior to analysis, the fuels and chars were milled using a Retsch SM100 cutting mill and a Retsch PM100 ball mill before being milled to <90 µm in a SPEX 6770 cryogenic grinder to produce a homogeneous flour from each fuel. This type of equipment was used because of the high silica content of the Reeds. The bark was separated from the majority of the wood fuels and analysed separately. However in the case of Birch and Willow, the fuel logs were homogenised as received, including the bark.

Proximate analysis of the samples was undertaken using thermal gravimetric analysis (TGA) using a TA Thermogravimetric Analyzer Q5000 and using 3 mg sample sizes and standard procedures. The temperature was raised to 105 °C (to give the moisture loss), then 900 °C (to give the loss of volatile matter) in nitrogen, before being cooled to 550 °C and combusted in air, to give the ash content. In addition to calculating the proximate values, TGA also gives a detailed overview of the thermochemical behaviour during the process; this data was obtained from single runs.

The Ultimate analysis (C, H, N) was carried out using a CE Instrument Flash EA1112, the experiments being carried out in duplicate; the oxygen was calculated by difference as given in BS ISO 17247. The higher heating value (HHV) was calculated using data from the Ultimate analysis by means of the following equation (Friedl et al., 2005), on a dry ash free basis:

$$\mathrm{HHV} = \frac{3.55\mathrm{C}^2 - 232\mathrm{C} - 2230\mathrm{H} + 51.2(\mathrm{C} \times \mathrm{H}) + 131\mathrm{N} + 20600}{1000}$$

where C, H, N are the mass% of carbon, hydrogen and nitrogen, respectively, all on a dry basis. The inorganic content of the fuels was determined after digestion via atomic absorption spectroscopy (AAS), using a Varian 240 fs AAS. The chlorine contents of the fuels were determined using a single mercuric nitrate titration.

6*.2.3. Pyrolysis analysis*

Pyrolysis gas chromatography mass spectrometry (Py–GC–MS) was performed using a CDS 5000 series pyrolyser coupled to a Shimadzu 2010 GC–MS. Approximately 2 mg of biomass fuel was pyrolysed at 500 °C. The products were separated on an Rtx 1701 60 m capillary column, 0.25 id, 0.25 lm film thickness, using a temperature program of 40 °C, a hold time of 2 min, ramped to 250 °C, and a hold time of 15 min. Assignments of the main peaks were made from mass spectral detection by using a NIST05a MS library. Only the peaks with a high degree of certainty (over 90%) are included.

6.2.4. Domestic stove combustion tests

A Waterford Stanley Oisin Multifuel stove was used to study combustion of all the fuels is shown in Fig. 6-1 and is rated as having a maximum thermal output of 5.7 kW and an efficiency of 79%. There is one primary air supply which is manually controlled via a damper, which is shown in Fig. 6-1. The general arrangement of the stove and measurement equipment was in accordance with BS EN 13240, as described previously (Mitchell et al., 2015). The stove was mounted on an electronic scale and sampling ports were installed in the 125 mm diameter flue at a height of 1.43 m.

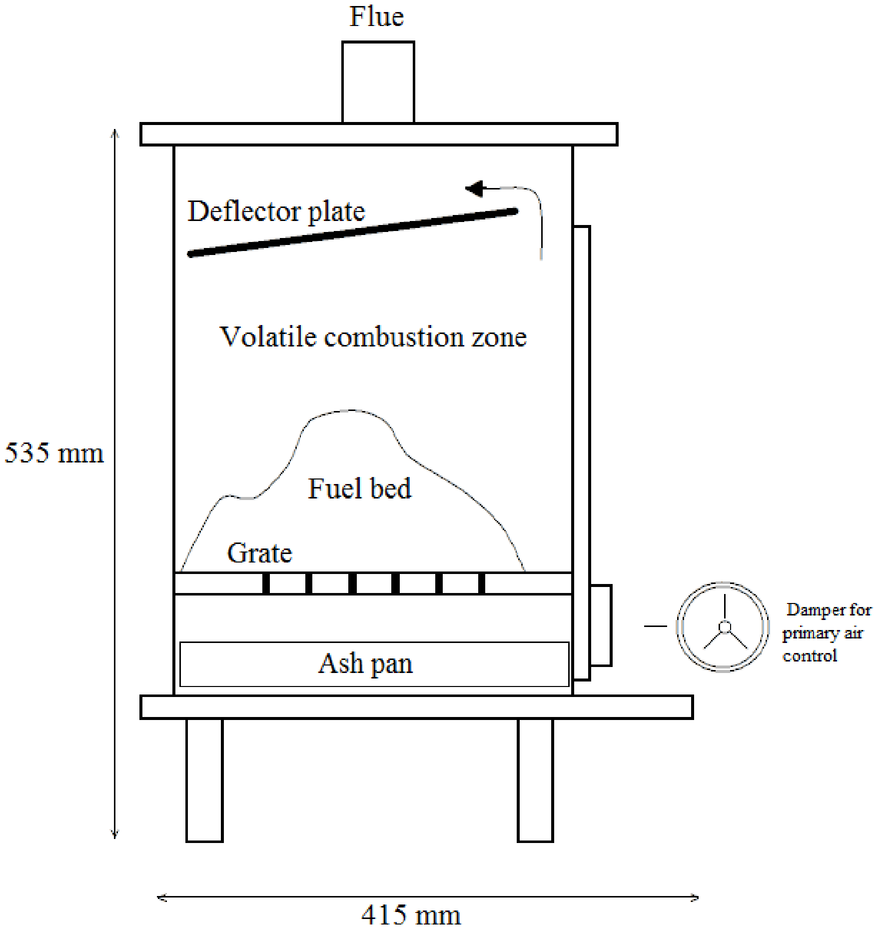

Figure 6-1. Diagram of the stove.

One batch of a known mass of fuel was tested on each run, with no re-loading. The total energy content of each load was fixed at 25 ± 5 MJ. The damper was adjusted to give approximately 150% excess air, as recommended by the appliance manufacturer, which was kept constant for all fuels. Flue gas composition was monitored using a Testo 340 analyser for O_2, CO_2, CO, NO, NO_2 and flue gas temperature. Particulate matter (PM) was determined using a gravimetric method in which 25 L of flue gas was passed through two Whatman GF/F glass microfibre (0.7 lm) filter papers held at 70 °C. Samples were taken at 10 min intervals in order to monitor the change in emissions over time. The emissions factors were calculated in g per kg of fuel burned and are reported as the arithmetic mean of three runs.

Scanning electron microscope (SEM) analysis was carried out using a Hitachi SU8230 scanning electron microscope. Particle composition was analysed by energy dispersive spectroscopy (EDS) using an Oxford Instruments X-Max silicon drift detector with an 80 mm^2 crystal. Samples were iridium coated. Experiments were not carried out with blends of the different fuels. But it is possible to estimate emissions of NO_x and PM on the basis of an ‘additivity’ rule, that is, the emission of the blend is approximately the sum of the emissions of the individual components on a pro rata basis (Sommersacher et al., 2015; Mitchell et al., 2015).

6.3 Results and Discussion

6.3.1. Fuel Characterisation

The proximate, ultimate, and higher heating value (HHV) results for a number of fuels, woods, bark, Reeds, a briquetted Reed, straws and biochars from woods and Reeds are given in Table 6-3. These show a large variation in their properties. Compared to the raw fuel, the briquetted Reed showed a lower volatile content and a higher ash content which is probably due to the processing conditions.

Sample	C % daf	H % daf	N % daf	O % daf	Volatile % db	FC % db	Ash % db	HHV MJ/kg db	K ppm db	Fe ppm db	Na ppm db	Mg ppm db	Mn ppm db	Al ppm db	Ca ppm db	Cl % db
Ash Bark	50.5	5.9	0.6	42.4	85.6	5.3	9.1	18.21	2215	78	260	977	44	664	43813	0.06
Ash Wood	47.7	6.1	0.1	46	90	9.5	0.5	18.84	956	0	201	365	2	847	1876	0.04
Birch Bark	54.6	5.9	0.7	38.3	80.6	17.8	1.6	21.77	2235	172	98	687	290	332	4313	0.09
Birch Wood	45.8	5.7	0.3	48.1	92.5	7	0.5	18.02	740	62	185	833	129	1155	3123	0.05
Birch (H)	48.4	6.5	0.2	44.7	91.2	7.4	1.4	19.04	621	25	905	504	140	142	1105	0
Hazel Bark							10.2	15.59	1531	49	630	605	131	995	35805	0.17
Hazel Wood	48.1	6.1	0.3	45.3	91.2	7.4	1.4	18.83	680	26	183	353	23	521	2443	0.09
Willow Bark 1	53.4	5.5	1.8	38.7	73.3	20	6.7	19.9	6666	0	104	898	5	516	9036	0.11
Willow Wood 1	45.8	5.8	0.2	48	89	10.2	0.8	18	3295	24	446	743	7	577	3046	0.06
Willow Bark 2	47.6	5.3	1.1	45.5	74.9	19.9	5.2	17.94	5247	79	474	2465	135	817	14213	0.16
Willow Wood 2	48.6	6.1	0.2	45	89.9	9.1	1	19.12	1063	0	383	469	15	482	1911	0.11
Willow SRC	48.4	6.3	0.4	44.6	88.2	9.7	2.1	18.9	2223	51	677	587	25	225	5487	0
Willow (H)	47.6	6.3	0.5	45.2	88.1	9.4	2.5	18.51	2656	52	851	851	10	95	6773	0.07
Willow Char 1	90.2	2.3	0.5	6.9	11.5	84.5	4	32.33	5480	51	745	1780	88	339	13445	0.25
Willow Char 2	76.3	4.6	0.9	18	38.6	56.2	5.2	29.26	4840	26	1291	1455	271	160	13869	0.26
Reed Briquette	45.4	5.7	0.5	33.9	79.5	6.2	14.3	18.02	2003	126	9841	1523	58	404	2643	0.18
Reed Char 1	80	1.6	1	4.2	11	75.9	13.1	28.1	2294	283	4227	1121	145	510	1189	0.17
Reed Char 2	73.6	2.2	1	8.6	12.1	73.5	14.4	26.48	1910	331	3859	1261	153	454	1360	0.12
Reed Raw	44.9	6.1	0.4	43.8	85.3	10.1	4.6	17.82	576	50	1954	601	45	391	774	0.09
Reed Washed									391	43	3913	783	35	561	235	0.11
Straw	44.3	6.2	0.5	43	82.3	12	5.7	17.62	6431	26	1589	717	44	369	3626	0.06
Straw Washed	43.5	6.1	0.4	42.3	81.2	11.3	7.5	17.25								0.11
Peat turf	61.3	2.4	2.2	29.1	67	31.3	1.7	26.02	137	9392	1395	1955			25250	0.29

Table 6-3. Ultimate (daf), Proximate (db), HHV and inorganic composition (db) of the fuels

Unlike the Reed char samples, the two Willow chars significantly differed from one another due to different reaction conditions. A higher proportion of the volatiles (38.6%) remained in char 2, compared with Willow char 1 (11.5%) and the two Reed chars (11.0% and 12.1%). The carbonisation process increases the HHVs of the conservation biomass feedstocks, as shown in Table 6-3, producing results comparable to bituminous coal. Significant differences were also observed between the wood and bark samples. In all cases, the bark contained higher values for elemental and fixed carbon, nitrogen and HHV than the heartwood. The peat turf sample was found to contain high levels of both moisture (>30%) and fuel nitrogen (2.2%). The heartwood samples of the peat-grown Willow (Thorne Moor) contained 0.5% nitrogen, whereas the Willow analysed from non-peated sites contained 0.2–0.4% nitrogen. This highlights the importance of the nitrogen content of the soil on the biomass composition.

The variation in fuel types is demonstrated by the Van Krevelen diagram shown in Fig. 6-2. Of particular note is the fact that the barks are more carbonaceous, that is more aromatic, than the woods. These have a higher HHV when considered on a daf basis. On average the bark content was about 13 wt%.

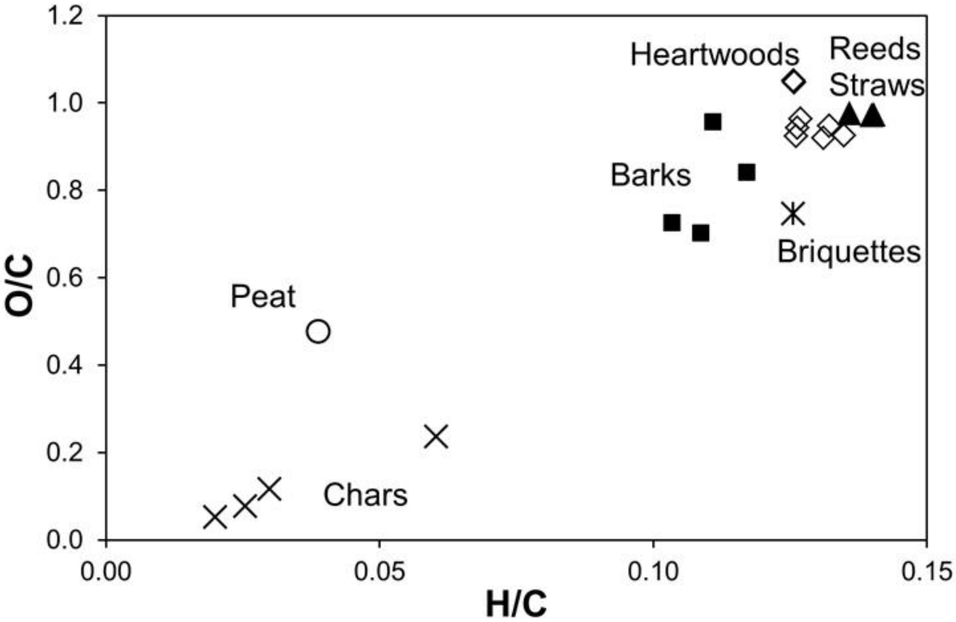

Figure 6-2. Van Krevelen diagram for the fuels

The differences in the inorganic content of the fuels are shown in Table 6-3. The herbaceous feedstocks generally contained higher levels of Na, Mg and Cl whereas the wood fuels generally contained more K and Ca. The inorganic content of the Reed samples are principally affected by their growing conditions in brackish estuarine water; the Reed briquette had a higher level of sodium compared to both the untreated Reed and the Reed chars. Both of the Reed chars contained significantly higher trace elements. The exceptions to this were the Reed briquettes which contained high levels of Na, Mg and Ca. It is believed that this is due to possible contamination from binding agents during the briquetting process. The briquettes were produced from biomass sourced from the same site as the raw Reeds analysed within this study. Additionally, washing the Reed for 15 min was found to reduce the content of K, Fe, Mn and Ca.

The barks contained substantially higher levels of all inorganics, particularly Ca and K. The existence of metallic elements within wood can often be directly related to the surrounding environment of the tree, with its roots often absorbing the existing available inorganics, before distributing them throughout the remainder of the tree. Fe is found at higher concentrations in the bark, but levels were much lower than the other inorganics. Bark can be contaminated by inorganic impurities, such as soil and sand. Calcium was found to be the dominant inorganic species in the analysed wood fuels, particularly prominent in the bark of the ash and hazel samples. These samples were both sourced from the same woodland area, suggesting that the sites soil may have been calcium rich. Interestingly, in both the ash and hazel samples the calcium content of the heartwood was comparable to the other wood species analysed; however the calcium concentrations within their bark is considerably higher.

Similar to the Reed, the carbonisation process was found to concentrate the inorganics in the Willow chars. The example peat turf sample used was found to contain relatively high levels of Fe, Na and Ca, which suggests that the peat-grown wood species assimilate particular inorganics during growth. This could mean that potential combustion issues related to the inorganic content of peat could also be witnessed when using peat-grown wood fuels, similarly to that of nitrogen content and the consequent emissions of NO_x.

The thermogravimetric data obtained for the woods, barks and two wood charcoals are shown Fig. 6-3(a) and the data for the straws, Reeds and chars are shown in Fig. 6-3(b). Individual information for the different fuels is not indicated, but the general trends are clear. From Fig. 6-3(a) it is clear that there is a significant difference in the rate of devolatilisation between the woods and the barks, this resulting from the high lignin and high inorganic content of the bark, which lowers the volatile content and increases the ash content. It is seen from Fig. 6-3(a) that most fuels decompose rapidly at temperatures above 300 °C, whereas bark decomposition occurs in three stages. For example the weight derivative for pyrolysis stage of hazel bark shows three distinct peaks at 340 °C, 489 °C and 661 °C. The first peak is at a comparable temperature for volatile loss in the other fuels, but the additional two peaks were not seen on any other fuel.

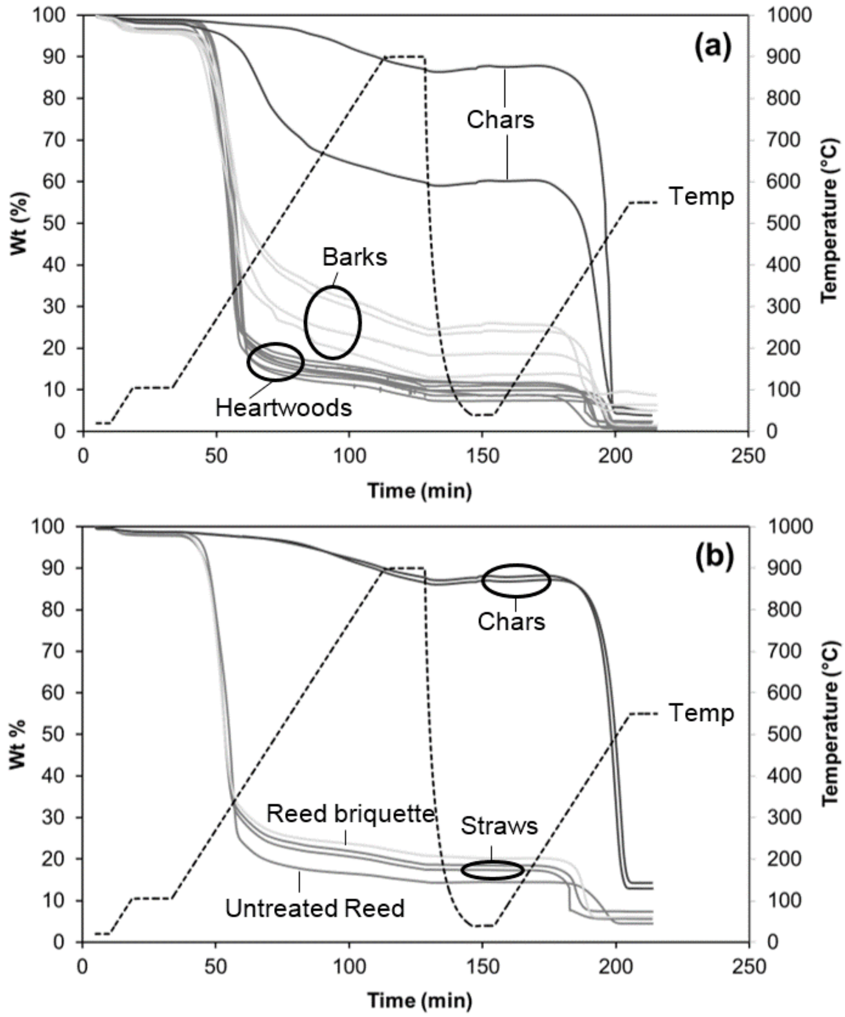

Figure 6-3. TGA results for (1) the woody biomasses and (b) the herbaceous biomasses.

From Fig. 6-3(b) it is seen that there are differences between the straws and the untreated Reed, whilst both are different to the woods in Fig. 6-3(a). This behaviour is consistent with that observed in other studies (Amaral et al., 2014; Mitchell et al., 2015). The Reed briquette contains a binder which changes the rates of devolatilisation. The properties of the chars in Fig. 6-3(a) and (b) behave in a way compatible with their composition (cf Table 6-3).

6.3.2. Pyrolysis GC-MS analysis

Pyrolysis GC–MS chromatograms for the woods and their barks are shown in Supplementary **Error! Reference source not found.** and **Error! Reference source not found.** respectively. milar measurements were made for the heartwood and bark of the peat grown Silver Birch samples, however these are not shown here. The corresponding peaks are a result of the decomposition of the cellulose and lignin components and follow the pattern previously seen for pine (Fitzpatrick et al., 2008).

Generally the heartwoods exhibit the same fingerprint while the bark differs greatly. Similar compounds were found in both heartwood and barks materials for all trees, but there are differences in the abundance of certain species; different patterns are shown for the cellulose and hemicellulose derived compounds and those from lignin. These differences have been quantified by using ratios of certain key species; it should be noted that many of the complex species cannot be quantitatively determined so the ratio method overcomes this difficulty.

The species examined are firstly acetic acid (hydroxyl acetaldehyde) designated in Supplementary information, and furfural (F), both of which are decomposition products of cellulose. The other species, such as furan, are in small concentrations, whilst the major decomposition species CO, H_2 and CO_2 are not seen by GC–MS. The second group are the lignin decomposition species. Previous work suggests that the lignin decomposition species are largely responsible for the smoke formation in the flame (Fitzpatrick et al., 2008) so it is of interest to examine these more closely. They have been designated as guaiacyl (G) and syringyl (S) where S/G defines the lignin core, eugenol (E) which we use as a marker of the lignin deposition products. The lignin decomposition indicators are defined as A, B and C; these are the methoxy, allyl, vinyl or propenyl phenolic compounds of various types depending on the biomass. Some of the barks, such as hazel bark, generate much higher molecular weight compounds – and in this case heneicosane, a C_{21} n-alkane which is a waterproofing agent. The two Willow heartwoods from different sites exhibit the same fingerprint; however the two Willow barks do not. This might be attributed to site conditions. In particular, the potassium and calcium contents are significantly different and weathering can also affect the bark composition. The values of the ratios of these compounds are given in Table 6-4.

	F/a	E/F	S/G	A/E	B/E	C/E
Ash wood	6.8	1.7	1.1	0.6	1.6	1.0
Birch wood	7.6	1.9	3.6	1.0	1.3	1.6
Hazel wood	7.1	0.8	3.1	2.5	2.50	4.3
Willow wood	7.0	2.0	1.8	0.7	0.6	1.5
Ash bark	0.6	4.1	1.5	0.6	0.8	0.6
Birch bark	0.6	2.3	0.5	0.8	0.4	0.6
Hazel bark	0.2	1.6	0.3	0.7	1.1	2.6
Willow bark (no 1)	0.2	2.1	0.05	0.6	0.1	0.2

Table 6-4. Relative abundance of compounds in heartwood and bark samples.

A number of issues are clear. The thermal decomposition of the cellulose from woods, as given by F/a, are to the barks; in the latter there is an extensive conversion to acetic acid, presumably aided by the high levels of the metals present. The values of S/G are different, the lower values for the bark is more like values for a grass, the wood being a more interconnected lignin The values of E/F show the higher level of lignin in the bark, in line with the ultimate analysis, and associated with this is the curious variations of the lignin decomposition products. The amount of the lignin decomposition products A, B and C are similar with the woods but vary considerably with the barks. It is clear that these types of pyrolysis GC–MS analyses give an insight into the chemistry. However, as seen previously (Mitchell et al., 2015), the best indicators of smoke forming tendency are C/H ratio and the volatile content.

6.3.3. Domestic stove tests

Three fuels were combusted in the stove; these were Ash wood logs, Reed briquettes and lump wood Willow charcoal. These are representative of the range of fuels available; log wood is a reasonably good biomass fuel, charcoal is a relatively expensive processed fuel and the Reed briquette is typical of a low grade fuel. These combustion experiments were made on a batch basis in order to observe how the emissions of PM, NO_x and CO change over time in one cycle. The results are shown in Fig. 6-4.

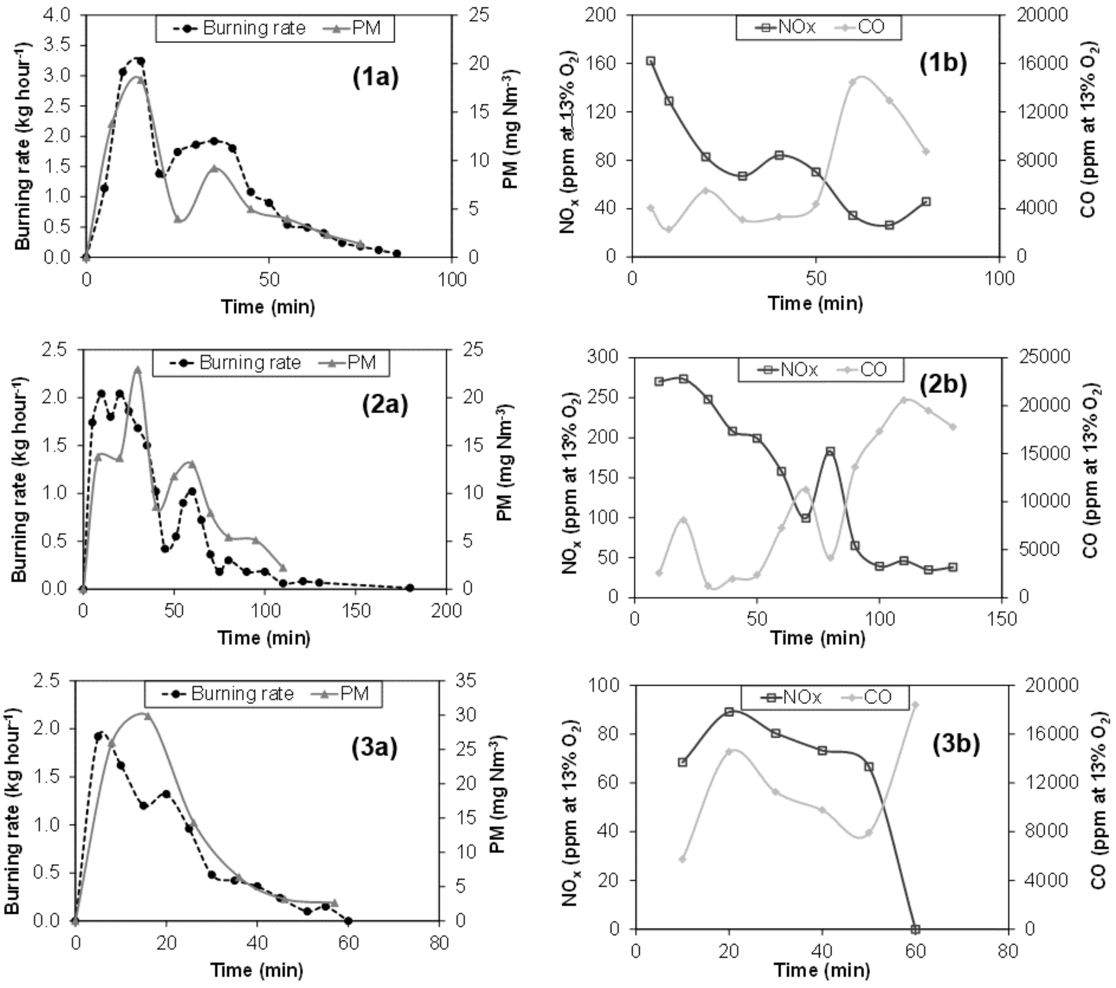

Figure 6-4. Plots of (a) burning rates and PM emissions and (b) NO_x and CO emissions for: (1) Ash logs, (2) Reed briquettes and (3) Willow char during combustion in a domestic stove.

The results are generally consistent with those observed previously by us using a similar stove (Mitchell et al., 2015) and with the predictive model of Sommersacher et al. (2012). The profiles show substantial differences in the combustion properties of the fuels. The average burning rate for the Willow char (0.73 kg h^{-1}) was much lower than the Ash wood logs (1.22 kg h^{-1}) and the Reed briquettes (0.82 kg h^{-1}). However, the average value for the Reed briquettes was slightly skewed by a very long smouldering time compared to the wood logs. In one of the tests the briquettes were still visibly glowing and exuding heat after 4.5 h; this is a desirable feature compared with logs.

The Willow char, due to a combination of its relatively small size and its lower overall mass (for the same energy content), had the shortest total run time. As a result of the carbonisation process and reduction in volatile content, the char showed a rapid decrease in burning rate and concentrations of particulate matter (PM) following ignition. The duration of the chars flaming phase was shorter than that of the other fuels, lasting less than 20 min. This is significant with regards to the emission of PM as, during the flaming phase, large quantities of carbonaceous soot are produced from the volatiles. There is a gradual increase in the PM emissions rate as the combustion approaches the peak of the flaming phase, which is proportional to the volatile content of the fuel (Mitchell et al., 2015), before decreasing as it moves into the smouldering phase.

The relative duration of the smouldering phase for the charcoal is much higher than the other fuels, as the small amount of remaining volatiles (approximately 11%) are rapidly driven off. Consequently, the total PM emissions are lower than that of the wood logs and Reed briquettes, where the volatile combustion is more dominant. Fig. 6-4 also shows a small secondary peak in both the PM emissions and burning rate for both the Ash logs and Reed briquettes. This is due to the fragmentation of the fuel and increase in burning rate. This causes an increase in NO_x and CO formation. NO_x emissions are strongly correlated with flaming combustion (dominated by NO), accordingly reducing over the course of the run. NO_x emissions were much higher for the Reed briquettes than for Ash logs, which is consistent with the higher fuel- nitrogen content as shown in Table 6-3 as is expected (Sommersacher et al., 2012; Mitchell et al., 2015; Amaral et al., 2014; Fournel et al., 2015). Willow char however does not follow that pattern: it has similar nitrogen content to the Reed briquettes, but during the combustion test it had slightly lower NO_x emissions. This is probably due to the fact that the wood char present reduces the NO to N_2.

As expected, CO shows a strong negative correlation with flaming combustion (Mitchell et al., 2015). There is a rapid increase in the concentration of CO when the smouldering phase commences, indicating that the CO emissions are chiefly determined by the relative duration of the smouldering phase for each fuel. CO emissions are lowest for the wood logs, which have the highest volatile content. Of these, the highest was the Willow char, which had only a 20 min flaming phase. A summary of the emission factors derived here for flaming conditions are compared with those for the open burning of biomass given in the literature in Table 6-5. These emission factors are used because this condition is similar to open burning combustion.

Biomass type	PM	NO_x	CO	CH_4
Common reed [32]	36.2	6.0 – 10.2	31.4 – 62.6	1.2 – 2.0
Temperate forest [33]	5.2 - 20.2	1.5 - 3.5	57 - 121	1.5 - 6.3
Stove–Ash wood logs [this study]	1.9	2.2	103.6	-
Stove-Reed briquette[this study]	1.4	4.7	255.7	-
Stove– willow charcoal [this study]	1.2	3.5	319.5	-

Table 6-5. Emission factors (g kg^{-1}) for the open burning of two biomass types compared with those for a domestic stove from this study (McMeeking et al., 2009: Akagi et al., 2011).

The data in Table 6-5 shows that a substantial reduction of PM emissions is achievable when the fuel is burned in a domestic appliance, compared to open burning, a current practice associated with the under-utilised conservation biomass feedstocks (Lemieux et al., 2004; McMeeking et al., 2009; Akagi et al., 2011). NO_x emissions are largely unchanged compared to open burning, as is the CO emission for the wood logs. The CO emission factors for the Reed briquettes and Willow char are higher than the reported values for open burning. This will be due to differences in fuel type since the Reed briquette tends to form a char after the early stages of combustion and the behaviour thereafter is similar to charcoal fuel; chars form carbon monoxide more easily because combustion occurs on the carbonaceous surface. A further difference between stove and open burning is that air entrainment into the plume formed in the latter case reduces the carbon monoxide concentration (Akagi et al., 2011).

Overall the environmental impact from burning in stoves is less than for open burning and of course energy is made available for heating, cooking and potentially for electricity generation. The benefit from burning Reeds is not as advantageous however.

6.3.4. Ash analysis

There were significant differences in the properties of the residual ash resulting from the combustion tests. These are summarised in Fig. 6-5 and are separated into two categories; under-gate and over-grate losses from the different fuels. The under-grate losses are defined as that which can pass through the grate spacing of 13 mm and are dominated by fine ash particles. The over-grate losses are those that are too large to pass through and consisted mostly of unburnt fuel particles.

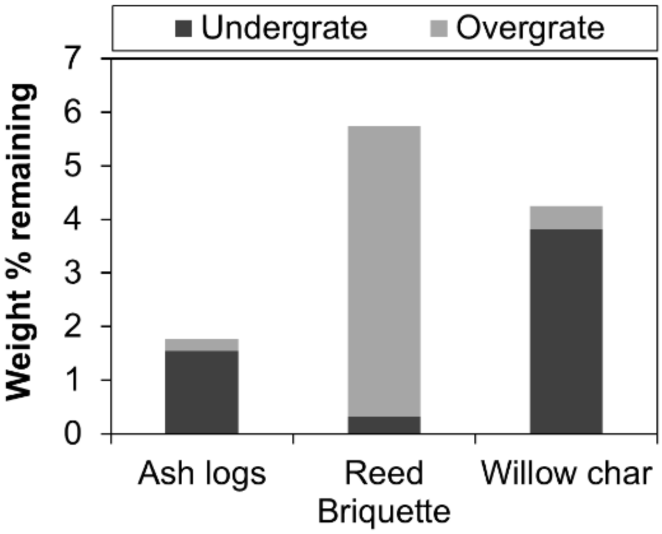

Figure 6-5. Ash losses (over-grate and under-grate) after combustion for three fuels studied.

Fig. 6-5 shows that the total ash losses are lowest for the Ash wood logs and highest for the Reed briquettes. This is consistent with the ash contents, given in Table 4, which are 0.5 wt%, 6.2 wt % and 4 wt% for the Ash logs, Reed Briquette and Willow Char, respectively. Unlike the other fuels, the majority of the ash losses for the Reed Briquettes are over-grate, which is attributed to them largely retaining their size and shape after combustion. In this case, the over-grate losses contain a significant amount of fused clinkers which, on average, represented 5–10% of the total mass of residual ash; the largest example of clinker measured approximately 40 mm in length. As shown in Table 6-3, the Reed contains higher levels of ash, especially silica, with the amount varying between seasons.

The ash content can be higher in the summer months, influencing their slagging and fouling behaviour (Kask et al., 2014). The characteristic ash melting temperatures for *P. australis* have been reported as low as 800 °C for sintering, 1100 °C for softening and 1200 °C for melting, but these values depend on the source of the Reeds as well as the part of the plant where the sample is taken (Patuzzi et al., 2012). In order to confirm the reasons for the observed ash fusion, samples of the Reed briquette ash and the wood log ash were analysed by SEM EDX and the results are given in Table 5-6.

Element (wt%)	Reed briquette	Ash wood
C	6.8	19.3
O	44.7	44.3
Na	12.4	1.5
Mg	2.4	2.4
Al	0.2	-
Si	22.8	-
P	0.5	0.6
S	-	2.5
K	3.4	11.8
Ca	6.2	17.6
Fe	0.7	-
Total:	100.0	100.0

Table 6-6. Bed ash analysis.

The results show that there was a high proportion of silica in the Reed briquette ash. There was also a relatively high proportion of sodium and aluminium in comparison to the constituents of the wood log ash. The relative carbon content of the wood ash was higher, indicating a poorer burnout efficiency. In addition, the proportion of potassium and calcium was higher in the wood ash, which is consistent with the results of the inorganic analysis of the raw fuel. These results are consistent with previous studies (Kask et al., 2013/2014; Sommersacher et al. 2012; Bostrom et al., 2012) where it has been shown that the ratio of Si/(Ca + Mg) is important. The general trend is that as the content of Ca and Mg increases, the ash fusion temperatures also increase and thus reduce the tendency for slag formation; this is observed with the wood sample here. In the case of the Reeds, silica melts are observed, a result of the high silica content in the Reed and also due to possible contamination from sand and soil.

Due to their high inorganic content and ash melting tendency, Reed chars may not be suitable for residential combustion. They may be blended with other fuels, otherwise, chars made from wetland biomass such as Reed could be converted into biochar, improving soil productivity and carbon sequestration on agricultural lands (Cui et al., 2016).

6.3.5 Implications for the supply of biomass

There is little or no openly published information in the way that biomass is harvested from Conservation Areas in the United Kingdom, nor how much biomass produced in this way could be used as an indigenous energy resource. In order to estimate this values for the yield (2 t ha^{-1}) and the productivity (10%) given in the Introduction have been used on an overall average basis. Additionally, the suitability of the biomass as a fuel has been considered and estimated that 50% of the biomass is suitable as a fuel. Thus this gives on average a value of 0.1 t ha^{-1} that can be utilised. From the total area of Special Conservation and Special Protection given Table 6-1 this give a useable biomass yield of approximately 500 kt Mt y^{-1}. It is clear that these sources can provide a significant amount of biomass although the errors in this estimation are at least a factor of 2. However in some cases such as Reed the fuel may need upgrading by blending thus increasing the yield. These materials can be blended with good quality biomass and be suitable for domestic use, but would not be suitable for power stations. The quality of the biomass obtained is highly variable and is geographically dispersed in the UK, but the amount of available conservation material is considerable. Fuel improvements can be undertaken by washing, carbonising or through torrefaction before blending the product with higher quality materials to make pellets or briquettes.

The increased ash contents of the bark samples, when compared to their corresponding heartwood, pose questions about the necessity for debarking. Increased concentrations of ash could have detrimental impacts during combustion, however due to the higher contents of carbon-rich lignin within the bark, debarking would result in a reduction of energy content. Peat-grown woods were found to contain marginally higher levels of nitrogen, iron and calcium than non-peat woods. It is recommended that all of the tree, including its bark, should be used if possible.

Pyrolysis GC–MS showed the woods were very similar. It was found that greater amounts of lignin derived aromatic hydrocarbons exist within the bark which, during combustion, could prompt increased levels of soot formation. The high volatile levels of the untreated Ash wood logs resulted in them having the highest burning rate and PM emissions of the three fuels, during the stove combustion tests. Conversely, using wood-based biomass chars reduces particulate emissions, however the increased carbon content results in higher emissions of CO. In comparison to the other fuels, the Reed briquettes had intermediate levels of CO and PM emissions, although their levels of NO_x where the highest.

Maintaining biodiversity in conservation sites will require continual management and, as such, useable conservation biomass resource will continue to be produced. As current practices for dealing with conservation biomass include open burning, which has been shown to produce high levels of PM emissions, alternative ways of dealing with the resource should be identified.

6.4 Conclusions

1) In the United Kingdom there is a considerable biomass resource available as a result of conservation management techniques, with about 500 kt y^{-1} that can be used as a domestic fuel.
2) This is more environmentally acceptable than the current open burning option since the utilisation in domestic stoves provides usable heat and reduces emissions.
3) The biomass resource contains a significant amount of a low grade material such as Reeds and soil contaminated wood.
4) The lower grade material such as Reeds could be blended with higher grade saleable fuel for domestic heating as briquettes or pellets.

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Chapter 7

The Impact of Residential Solid Fuel Combustion on Climate Change

Heating with Biomass in the United Kingdom: Lessons from New Zealand

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Graphical abstract:

A delivery of wood logs to a home in South Island, New Zealand.

Keywords: Residential solid fuels, emissions inventories, climate.

Abstract

In this study we review the current status of residential solid fuel (RSF) use in the UK and compare it with New Zealand, which has had severe wintertime air quality issues for many years that is directly attributable to domestic wood burning in heating stoves. Results showed that RSF contributed to more than 40 µg m^{-3} PM_{10} and 10 µg m^{-3} BC in some suburban locations of New Zealand in 2006, with significant air quality and climate impacts. Models predict RSF consumption in New Zealand to decrease slightly from 7 PJ to 6 PJ between 1990 and 2030, whereas consumption in the UK increases by a factor of 14. Emissions are highest from heating stoves and fireplaces, and their calculated contribution to radiative forcing in the UK increases by 23% between 2010 and 2030, with black carbon accounting for more than three quarters of the total warming effect. By 2030, the residential sector accounts for 44% of total BC emissions in the UK and far exceeds emissions from the traffic sector. Finally, a unique bottom-up emissions inventory was produced for both countries using the latest national survey and census data for the year 2013/14. Fuel- and technology-specific emissions factors were compared between multiple inventories including GAINS, the IPCC, the EMEP/EEA and the NAEI. In the UK, it was found that wood consumption in stoves was within 30% of the GAINS inventory, but consumption in fireplaces was substantially higher and fossil fuel consumption is more than twice the GAINS estimate. As a result, emissions were generally a factor of 2-3 higher for biomass and 2-6 higher for coal. In New Zealand, coal and lignite consumption in stoves is within 24% of the GAINS inventory estimate, but wood consumption is more than 7 times the GAINS estimate. As a result, emissions were generally a factor of 1-2 higher for coal and several times higher for wood. The results of this study indicate that emissions from residential heating stoves and fireplaces may be underestimated in climate models. Emissions are increasing rapidly in the UK which may result in severe wintertime air quality reductions, as seen in New Zealand, and contribute to climate warming unless controls are implemented such as the Ecodesign emissions limits.

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7.1 Introduction

Globally, 9.18 $GtCO_2eq$ was emitted from the residential and commercial buildings sector in 2010; accounting for approximately 19% of global greenhouse gas emissions and 33% of black carbon (BC) emissions (Lucon *et al.* 2014). A significant proportion of emissions in this sector are attributable to inefficient combustion in cookstoves, heating stoves and open fires. Approximately 3 billion people worldwide, mostly in developing nations, rely on biomass and other solid fuels as their primary source of energy (Bonjour 2013), which has significant health impacts due to exposure to air pollutants (Butt *et al.* 2016; Lelieveld *et al.* 2015). Within the OECD, energy used for heating accounted for 37% of final energy consumption in 2009 (Beerepoot and Marmion 2012) and is expected to grow by 79% over the period 2010 – 2050 (Lucon *et al.* 2014). Despite this, the residential and commercial buildings sector above all others was highlighted as having the greatest potential for the most cost-effective emissions reductions through energy efficiency measures and renewable space heating technologies (UNEP 2009; IEA 2013).

Biomass (mainly wood logs and pellets) has been identified as a key option to decarbonise the residential sector and consumption has been increasing in recent years, largely owing to a combination of bioenergy support initiatives, higher energy prices, aesthetics, and climate change consciousness (Eisentraut and Brown 2014). Consequently there has been an impact on health due to deteriorated air quality in many areas, particularly in wintertime. For example, an estimated 20,000 and 9,200 premature deaths occurred in Western Europe and high-income North America in 2010 due to residential heating with wood and coal; an increase of 23% and 18% respectively on 1990 estimates (Chafe *et al.* 2015). Fuel switching from oil and gas fuels to residential solid fuels (RSF) can also exacerbate air quality issues, particularly at a local scale. Moshammer *et al.* (2009) estimated that if all homes in an Upper Austria study region switched from oil to wood-fired heating systems, there would be an increase in the annual average PM_{10} concentration of 3-5 $\mu g\ m^{-3}$, leading to approximately 170 additional premature deaths per year.

Small scale combustion of solid fuels in heating stoves and fireplaces is often uncontrolled and unabated, leading to high emissions factors for gaseous and particulate pollutants. Methane (CH_4) and non-methane volatile organic compounds (NMVOCs) are byproducts of too low combustion temperatures or lack of available oxygen in the combustion chamber (Van Loo and Koppejan 2007). Emissions are generally much higher for biomass fuels than for coal, but also depend on combustion conditions which are characterised by the modified combustion efficiency (MCE). A high value of MCE denotes efficient flaming combustion and low carbon monoxide (CO) to carbon dioxide (CO_2) ratios. A low value of MCE denotes inefficient smouldering combustion, with high levels of CO and organic carbon (OC). The latter which may contain tars, phenolics, acetic acid, aldehydes and polycyclic aromatic hydrocarbons (PAH). Low values of MCE are common in older log wood stoves or where there are poor operating procedures such as overloading or poor inlet air control. Nitrogen oxides (NO_x) and to a lesser extent nitrous oxide (N_2O) and ammonia (NH_3) are in the most part formed via the conversion of fuel-bound nitrogen and proteinaceous compounds at the low temperatures observed in stoves and fireplaces (Williams *et al.* 2012). Hence they are proportional to the nitrogen content of the fuel. The same is true of sulphur dioxide (SO_2) emissions which are dependent on the levels of sulphur, calcium, potassium and chlorine in the fuel. The sulphur content of wood is typically very low (<0.1 %), so coal-based sources are more significant.

Particulate matter below 10 µm in diameter (PM_{10}) and below 2.5 µm in diameter ($PM_{2.5}$) are among the most useful indicators of the health impacts of RSF use (Naeher *et al.* 2007; Straif, Cohen and Samet 2013). Many studies have shown that PM from RSF combustion is predominately in the fine and ultrafine fraction, which penetrate deep into the lungs and can cause cardiopulmonary disorders and cancer (Allan *et al.* 2010). The constituents of $PM_{2.5}$ include black carbon (BC), organic carbon (OC) and ash. BC is characterised by strong absorbance of visible light, insolubility in water and a microscopic appearance of aggregated carbon spherules. Radiative forcing (the net change in irradiance causing either cooling or warming) via BC arises both directly, via light absorption, and indirectly via darkening of ice and snow. There is also a cooling effect via cloud interaction, but this is uncertain and direct absorption of radiation in the atmosphere is the largest term (Bond *et al.* 2013; Boucher *et al.* 2013; Seinfeld and Pandis 2006). Organic carbon aerosol can be primary (POA) or secondary (SOA) formed in the atmosphere by VOC oxidation products. Recent research has shown that the contribution of residential wood burning to organic aerosol loadings may be up to a factor of 3 higher when SOA is included (Bruns *et al.* 2015). The organic fraction is often adsorbed to the surface of BC or ash particles and is among the most harmful to health, having irritant, carcinogenic, mutagenic, teratogenic qualities (Naeher *et al.* 2007; Jones *et al.* 2014). POA has a net negative radiative forcing in the atmosphere and in clouds, with a slight positive effect on ice and snow. There is also a slight positive radiative forcing from the small fraction of OA that absorbs radiation, especially in the UV range, which is termed ‘brown carbon’ (Saleh *et al.* 2014). Interestingly, the negative radiative forcing of fossil fuel POA is almost twice that of biomass (Bond *et al.* 2013), which may be linked to the higher degree of oxygenation of biomass soot (Jones, Ross and Williams 2005). Finally, inorganics are present in the ash fraction of PM, mainly as alkali salts (KCl, K_2SO_4 and K_3PO_4) with smaller amounts of trace elements and heavy metals including Zn, Pb, Cd and aluminosilicates (Molnár *et al.* 2005). Small scale unabated burning of waste wood and treated timber may also release arsenic. Elevated As concentrations have been attributed to this source in New Zealand (Ancelet, Davy and Trompetter 2015) and the USA (Peters *et al.* 1984)

Residential wood burning is often assumed to be carbon neutral and one of the cheapest ways to reduce greenhouse gas emissions. In this study we assume that wood burning is indeed CO_2 neutral, and investigate the emissions and climate impacts of other pollutants, given that assumption. A comparison is made between the United Kingdom, where residential wood burning is being promoted and growing rapidly; and New Zealand, where wood burning stoves have been widely used for many years and are causing severe wintertime pollution in some areas.

7.2 Review of residential solid fuel (RSF) use in the UK and New Zealand

7.2.1 RSF in the UK

The UK has legally binding targets to ensure 15% of energy comes from renewable sources by 2020, and to reduce greenhouse gas emissions by 80% by 2050, relative to 1990 levels. For the residential and heating sectors, the Renewable Energy Strategy 2009 set a target of 12% of heat to come from renewables by 2020 (corresponding to approximately 260 PJ). Fuel switching to electricity and biomass was identified as a key pathway to achieve this (DECC 2012a), but residential biomass use was noted to have the potential for significant air quality impacts (DECC 2012b). The UK's greenhouse gas emissions have reduced by approximately 30% since 1990, but residential sector emissions have reduced by just 20% (DECC 2015a). Hence the residential sector share of total GHG emissions has increased from 21% to 24%.

Official figures show that in total, RSF consumption in the UK has reduced by 87% since 1970. This reduction has been driven by a move away from coal-fired boilers to more efficient and less polluting gas & electric heating central heating systems, as shown in Figure 7-1a and Figure 7-1b.

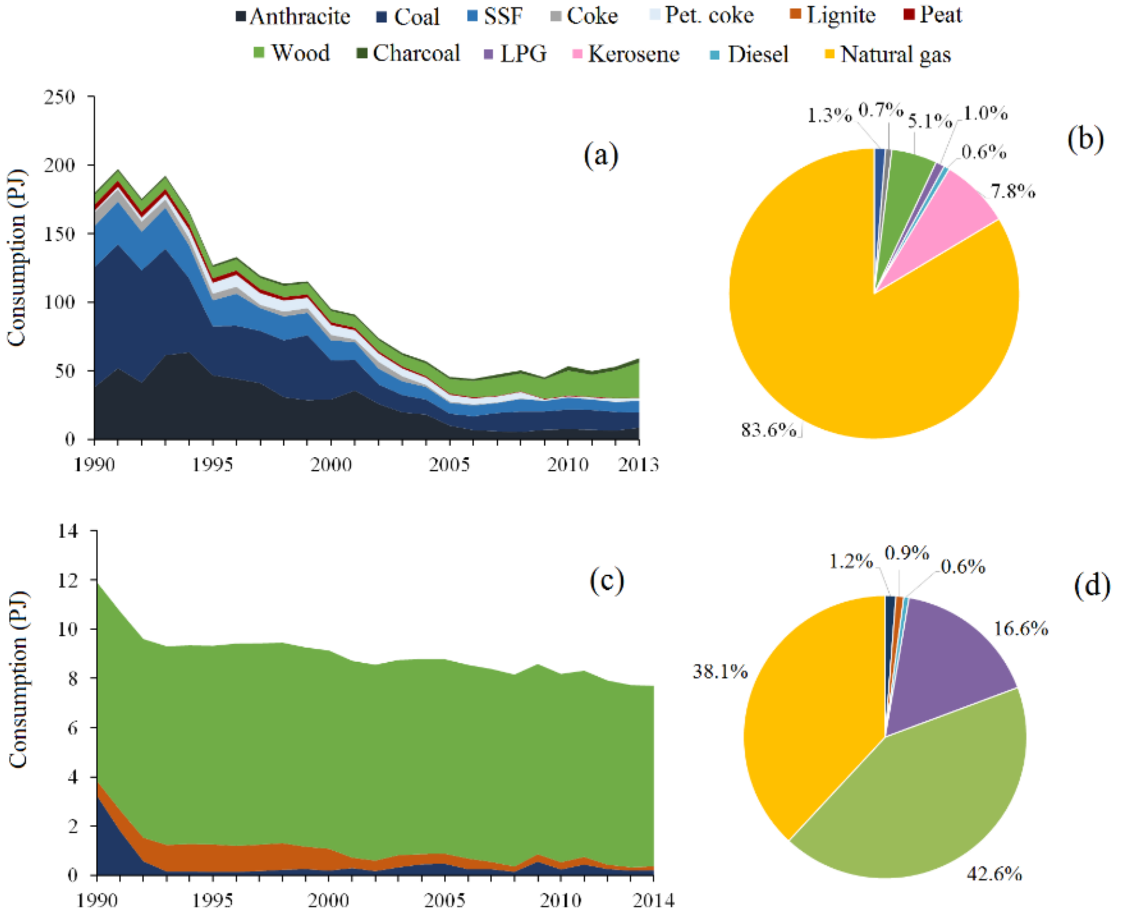

Figure 7-1. Breakdown of officially reported RSF consumption in the residential sectors of the UK (a) and New Zealand (c). Consumption of all fuels including gas and liquid is shown in (b) for the UK and (d) for New Zealand. Data sources: NAEI, DUKES (DECC 2015a), EUROSTAT (2016), MBIE (2015).

Fuel switching from coal to gas has been driven by increased availability of North Sea gas and associated national grid infrastructure, as well as national policy aimed at reducing the number of smog events such as those seen in the 1950s, 1960s and 1970s. Air quality legislation such as The Clean Air Act of 1956 (revised 1993) has dramatically reduced the demand for coal since its inception, by prohibiting the emission of visible smoke.

In the year 2014, natural gas accounted for 83.6% of total residential energy consumption. Although solid biomass contributed just 5.1% of total UK non-electric energy consumption, it dominated the RSF category and represents the largest renewable energy source in the sector. Biomass use has increased more quickly in the EU28 residential sector, having increased from 929 PJ in 1990 to 1606 PJ in 2014, an increase of 73% (EUROSTAT 2016). Other technologies such as solar thermal, biogas and air & ground source heat pumps are gaining popularity, thanks in part to government incentive schemes such as the domestic renewable heat incentive (RHI), but biomass heating systems are the largest contributor to renewable heat production. Biomass produced 55% of renewable heat paid for under the domestic RHI between April 2014 and February 2016 (DECC 2016b). Of the total number of accreditations for biomass systems, 58% replaced oil / kerosene fired heating systems which are among the most expensive to run. It should be noted, however, that log heating stoves are not eligible for and hence not included in the RHI statistics. Pellet stoves and boilers are eligible, but must meet emissions, sustainability and metering criteria; and the home must provide an Energy Performance Certificate (EPC) or a Green Deal Advice Report.

Woodfuel for household heat is one of the major drivers of bioenergy uptake in the UK, and is strongly correlated to gas and oil prices (Adams *et al.* 2011). However due to relatively high capital costs and a need to develop supply chains, UK policies supporting biomass have, until recently, mostly targeted medium and large scale applications. Sites with relatively high heat demands that are not connected to the national gas grid were found to be the most likely to implement biomass for heat within the residential/commercial sector. This includes agricultural buildings, hotels and schools/higher education institutions (Carbon Trust 2012). Such schemes are generally 100-1000 kW biomass boilers using pellets or wood chip which can be delivered in bulk. Larger systems also commonly have combustion optimisation features such as lambda sensors for oxygen feedback, secondary/tertiary air injection and flue gas abatement technologies. In the most part, heating stoves and fireplaces do not feature such control technologies which leads to more inefficient combustion and higher emissions of pollutants per unit fuel input.

Very little data is available on heating stoves and household RSF consumption in the UK, primarily due to difficulties in monitoring and regulating such small scale emissions sources. In an attempt to better understand the consumption of wood in UK homes, the Department for Energy and Climate Change (DECC) conducted a nationwide survey in 2015 (DECC 2016a). In summary, the survey found that 7.5% of respondents used wood fuel, and over 90% of those used logs in heating stoves and fireplaces, rather than pellets, chips or briquettes. A similar trend was found across Europe, where 90% of residential biomass used is in the form of hardwood logs (Wöhler *et al.* 2016). The DECC survey also found that previous estimates of domestic wood consumption were a factor of 3 lower than the 68 PJ total for 2013. It should be noted that the data shown in figure 1 do not include these revisions. According to data from the Stove Industry Alliance (SIA), sales of heating stoves were 200,000 in 2014, up 21% on 2005 levels (SIA 2016). Approximately two thirds of these were multi-fuel stoves, although research showed that 77% were used to burn wood only. Sales growth was strongest for low emission DEFRA exempt appliances, which are approved for use in smoke control areas (see section 7.2.3). In the future, sales are expected to grow for stoves which meet the European Ecodesign emissions limits, which emit up to 80% less particulate matter than older stoves.

It has been known for many years that RSF combustion contributes to UK air pollution, particularly in rural communities (Lohmann, Northcott and Jones 2000; Lee *et al.* 2005). Yet there are very few studies on biomass burning source apportionment compared with other countries in Europe and North America, for example. Several studies have recently found that domestic wood burning is an increasingly important source of particulate matter. Fuller *et al.* (2014) estimated the contribution of wood burning to annual PM_{10} in London to be 1.1 $\mu g\ m^{-3}$ and Crilley *et al.* (2015) estimated the contribution to black carbon to be 15-30%. Young *et al.* (2015) found the contribution to organic aerosol to be up to 38% during the winter. These emissions rival those of the traffic sector, causing dangerous air pollution and counteracting traffic emissions reduction policies in London (Robinson 2015).

7.2.2 RSF in New Zealand

New Zealand is traditionally viewed as a good example of a low carbon economy, particularly regarding electricity and heat supply. The contribution of renewables to total primary energy supply (TPES) in New Zealand was 38.3% in 2012, the third highest in the OECD. In contrast, the contribution in the UK was 4.5%; the fifth lowest in the OECD (OECD 2014). Of the renewable contribution to TPES, 80% came from geothermal and hydro power in 2014. Nationwide, woody biomass supplied 58.3 PJ, up 52% since 1990 and of this, 13% (7.34 PJ) was consumed in the residential sector.

In contrast to the UK, RSF consumption in New Zealand has been relatively constant since 1990, and the fuel mix is dominated by wood, as shown in Figure 7-1c and Figure 7-1d. In comparison to the UK, there is a greater reliance on LPG (16.6%) and low grade coal/lignite, as well as wood (42.6%). There is also comparatively low uptake of kerosene/heating oil and patent fuels (manufactured solid fuels, including smokeless fuel and coke). Coal consumption is constrained largely to the west and south of the country where it is mined. The RSF mix has remained largely unchanged for many years, as shown in Figure 7-1c, although total consumption has been reducing gradually at an average rate of 85 TJ $year^{-1}$ between 1995 and 2014. New Zealand's Bioenergy Strategy 2010 (BANZ 2010) set out targets for 25% of consumer energy to come from bioenergy by 2040 (currently 8.5%), as well as a 60% increase in the country’s use of biomass for heat. This includes substitution of coal or gas heating.

Both UK and New Zealand homes are often highly energy inefficient in comparison to other OECD countries, due to relatively poor insulation and heating patterns (Howden-Chapman *et al.* 2009). In New Zealand there is a tradition of heating just one room of the house using unflued gas and electric heaters, as well as open fires and heating stoves burning RSF. Homes using solid fuel heating stoves were found to be warmer on average than homes using other heating methods (French *et al.* 2007). Wood heating is also one of the cheapest options for homeowners due to the plentiful supply. New Zealand has a large domestic source of wood fuel, mainly as Radiata pine from the forestry industry. The bioenergy strategy, together with the New Zealand Home Heating Association (NZHHA), NZ Farm Forestry Association (NZFFA) and the Energy Efficiency and Conservation Authority (EECA), are pushing to increase the supply of wood fuels for export. A consequence of this surplus is lower prices for home owners. However, fuel poverty and excess winter mortality are similar in both the UK and NZ at 10-14% and 18-19% respectively (Howden-Chapman *et al.* 2009). Energy used for space heating accounts for the largest share of residential energy consumption in both countries. The share is 34% in New Zealand (Isaacs *et al.* 2010), but is much higher in the UK at 62% (Palmer and Cooper 2014). Although total consumption of biomass in the residential sector is higher in the UK, proportionally it is much higher in NZ, as shown in Table 7-1.

	NZ	UK	Unit	Ref
Solid biomass consumption in residential sector	7.34	54.67	PJ	(EUROSTAT 2016); (MBIE 2015)
Number of dwellings (million)	1.781	27.914		(DCLG 2016); (StatisticsNZ 2016)
Population (million)	4.509	64.596		ONS, (StatisticsNZ 2015)
Average biomass consumption per dwelling	4.12	1.96	GJ household $^{-1}$	
Average biomass consumption per person	1.63	0.85	GJ person $^{-1}$	

Table 7-1. Comparison of residential biomass consumption in the UK and NZ, 2014.

As shown in the table, average residential biomass consumption per dwelling is over twice as high in New Zealand as the UK. However, accurate reporting of RSF consumption in both countries is confounded by huge uncertainties and variation in the data, especially in comparison to metered fuels such as gas, electricity and LPG (Isaacs *et al.* 2010). Daily wintertime wood consumption estimates vary from 277 MJ day^{-1} in Christchurch to 486 MJ day^{-1} in Nelson, Rotorua and Taumarunui (Wilton 2012). An average value of 360 MJ day^{-1} was used by Kuschel *et al.* (2012). The calculated wood fuel use in the DECC survey is 154 MJ day^{-1} for an open fire and 128 MJ day^{-1} for a heating stove; significantly lower than the New Zealand estimates. Analysis of data from the U.S finds that the average household wood consumption in homes that use wood as their primary source of heating is 238 MJ day^{-1} versus 76 MJ day^{-1} in homes where wood is only used for secondary heating (USEIA 2014). Despite the uncertainty, the officially reported consumption of woody biomass in the NZ residential sector reduced by approximately 9% from 1990 to 2014, as shown in Figure 7-1c. This is arguably a result of efficiency improvements and new emissions limits for heating stoves.

7.2.3. Emissions Limits and Standard Test Methods

Three key standards exist for the testing of heating stoves in Europe, NS 3058/ NS 3059 in Norway, DIN-plus in Germany and BS PD 6434 in the UK. There are significant differences in the test procedures used in these standards (Seljeskog *et al.* 2013), as shown in Table 7-2. In addition, RHI emissions limits apply to eligible boilers in the UK, which include an efficiency of 75%, CO concentrations of less than 1% (ref 13% O_2), and emissions factors of 30 g GJ^{-1} for PM and 150 g GJ^{-1} for NO_x (approx. 0.54 g kg^{-1} and 2.7 g kg^{-1} respectively). The European standard EN 13240 also requires appliance efficiency to be greater than 50% and CO emissions to be less than 1.0% (ref. 13% O_2). However, emissions of PM, NO_x and OGC are left to national legislation. Recently, the Ecodesign of Energy-related Products Directive (2009/125/EC) regulation 2015/1185 was published which has the specific aim of reducing emissions of PM, OGCs and CO from this source by 27 kt $year^{-1}$, 5 kt $year^{-1}$ and 399 kt $year^{-1}$ respectively by 2030. This will be done via the implementation of emissions limits for open- and closed-fronted heaters from the year 2022, as shown in Table 7-2.

As the table shows, there are significant differences in the requirements of standard test methods around the world. Historically, regulation has emphasised total (non-size segregated) particulate matter emissions, although in recent years CO and thermal efficiency have been added, followed by NO_x and organic gaseous carbon (OGC). There are significant differences in the test procedures used in these standards which complicates comparative studies. Key differences include the draught, fuel, reporting units, dilution, filter temperatures, and sampling durations & equipment. One of the highest impact variables is the use of a dilution tunnel, whereby a greater proportion of the condensable organic fraction is captured compared to hot-sampling. This alone can increase PM emissions factors by orders of magnitude (Seljeskog *et al.* 2013; Coulson, Bian and Somervell 2015). In addition, emissions factors may be increased further if atmospheric ageing of emitted smoke is taken into account (Bruns *et al.* 2015; Bruns *et al.* 2016), though it may be argued that OGC measurement may be used as a proxy for SOA formation.

	Country	**Europe**	**Europe**	**Germany /Austria**	**Norway**	**UK**	**USA**	**Australia / New Zealand**
Test parameters	**Standard**	Ecodesign regulation 2015/1185	EN 13240	DIN-plus	NS 3058	BS PD 6434 / BS 3841	NSPS / ASTM E2515, E2780 – 10 / EPA Method 28WHH	AS/NZS 4012, 4013 and 4014
	Location		Chimney	Chimney	Dilution tunnel	ESP/Dilution tunnel	Dilution tunnel	Dilution tunnel
	Draught		Forced 12 PA	Forced 12 PA	Natural	<1.25 Pa (natural)	<1.25 Pa (natural)	<1 Pa (natural)
	Sampling T		70°C	70°C	35°C	70°C	<32°C	15-32°C
	Fuel	Range of Biomass / fossil fuels. Wood logs must be beech, birch or hornbeam	Range of Biomass / fossil fuels. Wood logs must be beech, birch or hornbeam	As specified in EN 13240	Dimensioned spruce (49 x 49 mm), 16-20% MC	Coal, lignite, patent fuels, peat and wood	"Crib wood" dimensioned (38 x 89 mm) Douglas Fir, 15-25% MC. Cordwood alternative available	Dimensioned (100 x 50 mm) Radiata pine, 16-20% MC in New Zealand. Hardwood in Aus
	Weight of test fuel	Dependent on choice of PM measurement method	As per manufacturer's instruction	As specified in EN 13240	112 ± 11 kg m^{-3} firebox volume	15 kg	112 ± 11 kg m^{-3} firebox volume	
	Test condition	Dependent on choice of PM measurement method	3 categories: Nominal, slow and safety tests	As specified in EN 13240	4 burn rate categories	2 burn rate categories: nominal and low (plus intermediates if necessary), repeated 5 times	3 Method 28 burn rate categories	3 burn rates: high, medium and low
	Test duration	Dependent on choice of PM measurement method	Min. refuelling interval 1.5 hours for wood at nominal	30 minutes		Time between first re-fuel and a trough in radiation heat output	Load time 1060 s m^{-3} firebox volume	
	Include ignition/ start-up?	Dependent on choice of PM measurement method	No	No	No – 1 hour pre-test	No – provided no "undue trouble to the user"	No – kindling, newspaper and pre-burn fuel	No
	Units	mg m^{-3} at 13% O_2	mg Nm^{-3} at 13% O_2	mg Nm^{-3} at 13% O_2	g kg^{-1}	g hour^{-1}	g hour^{-1}	g kg^{-1}
Emissions limits	**PM**	2.4 / 5.0		75	10	5	4.5 reducing to 2.0	1.5
	CO	1500	< 1%	1500			Optional?	
	OGC / THC (as C)	120		120				
	NOx (as NO_2)	200 / 300		200				
	Efficiency	65%	50%	75%			63% (non-catalytic)	65%

Table 7-2. Comparison of standard test conditions for heating stoves in different countries. Expanded from Seljeskog *et al.* (2013)

New Zealand's National Environmental Standards (NES) feature five standards for ambient air quality. The NES standards for CO, NO_2 and PM_{10} are 10,000 µg m^{-3} (8 hour mean), 200 µg m^{-3} (1 hour mean) and 50 µg m^{-3} (24 hour mean) respectively. Most breaches of this standard are attributed to domestic heating with wood; with 24 hour PM_{10} concentrations of more than 200 µg m^{-3} having been recorded in some towns (Coulson *et al.* 2013). Hence New Zealand has introduced a design standard for wood burners installed in urban areas. The NES standard for wood burners centres on PM_{10} emissions and an emissions limit of 1.5 g kg^{-1} dry fuel burned is required when tested to AS/NZ 4013. An efficiency of 65% is also required when tested to AS/NZ 4012 using fuels certified under AS/NZ 4014. AS/NZS 4013:2014 is a revised version of AS/NZS 4013:1999, and initial tests showed that the revised method is more representative of real-world conditions and gave emissions factors 2.5 times larger than the previous method (Todd and Greenwood 2006).

A comprehensive review of particulate emissions due to RSF burning in New Zealand was carried out by Wilton (2012), who noted that real-world emissions of NES compliant appliances were typically twice as high as those determined under laboratory conditions as described above. Real-world emissions have been found to be substantially higher in New Zealand (Ancelet *et al.* 2010; Xie, Mahon and Petersen 2012), as well as in Europe (Wöhler *et al.* 2016) and the USA (USEPA 2016); primarily due to user operating conditions such as start-up, fuel properties, overloading and fluctuating burn rates. A statistical analysis of PM_{10} emissions factors from in-situ wood stove tests in New Zealand was carried out by Coulson, Bian and Somervell (2015). The study found that geometric mean emission factors for older and low-emission stoves were 9.8 ± 2.4 g kg^{-1} and 3.9 ± 3.8 g kg^{-1} (dry wood) respectively. The distribution was found to be log-normal and hence the use of geometric, rather than arithmetic, mean emission factors are recommended.

A new standard for PM emissions from wood stoves was introduced in the city of Nelson in 2006, requiring 1g kg^{-1} rather than the NES standard of 1.5 g kg^{-1}. As a result of this implementation, PM_{10} and BC were found to be decreasing at an average rate of 0.5 µg m^{-3} and per year and 100 ng m^{-3} per year respectively (Ancelet, Davy and Trompetter 2015). Stove replacement programs have been found to achieve similar benefits in other countries. For example, Noonan *et al.* (2011) noted a 70% reduction in indoor $PM_{2.5}$ concentrations in a rural community in the USA, due to replacing old and inefficient wood stoves. Rule 4901 was passed in the San Joaquin Valley, California, in 1992 which limited emissions from RSF burning during periods of poor air quality, and required new wood burners to meet EPA/NSPS certified. As a result, $PM_{2.5}$ concentrations reduced in the area by 11-15% (Yap and Garcia 2015). In Europe, it is estimated that replacing current RSF technologies with more efficient wood pellet stoves could reduce concentrations of OC and EC by more than 50% in large parts of the continent (Fountoukis *et al.* 2014).

Due to regular breaches of NES air quality standards by RSF burning, a number of health impact studies have been carried out in New Zealand. Perhaps the most comprehensive was the Health and Air Pollution in New Zealand (HAPINZ) study (Kuschel *et al.* 2012). It found that RSF burning was attributable to 56% of premature deaths due to anthropogenic PM_{10} in 2006, making it the leading cause. This equated to 655 premature deaths, 334 admissions due to cardiac and respiratory illness, and 817,600 restricted activity days. The estimated cost due to these impacts was NZD $2.385 billion. In addition, it was noted that basing the report on PM_{10} rather than $PM_{2.5}$ led to an underestimate of the attribution of health impacts to transport and RSF emissions because these sources make a greater contribution to fine PM. For example, studies have shown that over 90% of the mass of emissions from wood combustion are below $PM_{2.5}$ (Bond *et al.* 2004; Nussbaumer 2003; McDonald *et al.* 2000; Young *et al.* 2015).

7.3 Methods

The New Zealand national census is a useful means of collecting data on qualitative RSF use. Question 16 requires the resident to "*mark as many spaces as you need to show which of the following are ever used to heat this dwelling*." The UK census is more focussed on the type of central heating used at a property (gas, electric, oil, solid fuel, other, or no central heating). Information on fuels used for supplementary heating is limited to sub-national housing surveys and studies into fuel poverty in off-grid homes by organisations such as the Office of Fair Trading (OFT 2011), the Office of Gas and Electricity Markets (OFGEM) and the Department of Energy and Climate Change (DECC) (Palmer and Cooper 2014). The New Zealand census also has the advantage of being held every 5 years, whereas the UK census is held every 10 years. Additionally, data is available at three different resolutions: census area unit (CAU); ward; and territorial authority. CAU represents the finest resolution, with some urban grid cells less than 1 km^2 in area. A number of models and inventories offer activity data, emissions data and emissions factors for the residential sectors of both countries. Studies have shown that several models in Europe underestimate pollutants such as wintertime OC when compared with observations, which is most likely due to residential wood burning (Aas *et al.* 2012). The use of revised emissions factors for RSF combustion was found to increase total $PM_{2.5}$ emissions in Europe by 20% (Denier van der Gon *et al.* 2015).

7.3.1. A Top-Down Estimate of BC Concentrations in New Zealand

A top-down approach was used to estimate black carbon concentrations due to RSF combustion in New Zealand. Emissions of PM_{10} and corresponding monthly atmospheric concentrations in 2006 were taken from the HAPINZ study (Kuschel *et al.* 2012). BC concentrations were calculated by multiplying PM_{10} concentrations by the ratio of BC/PM_{10}. To define this ratio for New Zealand both spatially and temporally, 31 separate datasets containing simultaneous measurements of PM_{10} and BC were analysed from 10 locations across New Zealand. The wintertime BC concentrations were then calculated for each census area unit (CAU) in New Zealand and were mapped using ArcGIS.

7.3.2. Emissions and Climate Impacts Using the GAINS Model

In order to assess the impacts of RSF emissions, the GAINS model (http://gains.iiasa.ac.at/models/) was used to provide detailed activity and emissions data broken down by fuel and technology type, in both the UK and New Zealand. The version of the model used was ECLIPSE version 5 for UNFCCC Annex 1 nations. Several scenarios are available but here we use the current legislation (CLE) scenario (Stohl *et al.* 2015), which assumes efficient enforcement of committed legislation, with some deviations. For the residential sector, it is not known whether this scenario includes legislation such as Ecodesign in Europe. The residential sector in GAINS is broken down into four key technologies: commercial boilers (<50 MW), single house boilers (<50 kW), heating stoves and fireplaces. There are minor contributions from open pits and cookstoves, but these are small in comparison to the other technologies and are not considered in this work. Each technology is then also broken down by fuel type. For the UK, fuels include hard coal (grade 1), derived coal (coke, briquettes etc.), agricultural residues and fuelwood. For New Zealand, the split is between hard coal (grade 1), brown coal/lignite (grade 1), and fuel wood.

Emissions data is available for 12 pollutants in GAINS: carbon dioxide, methane, oxides of nitrogen, carbon monoxide, non-methane volatile organic compounds, sulphur dioxide, ammonia, nitrous oxide, PM_{10}, $PM_{2.5}$, black carbon and organic carbon. For some pollutants, the full breakdown by fuel and technology was not available. These included CO_2, NO_x, CO, SO_2, NH_3 and N_2O. For these species, the breakdown was calculated by multiplying the GAINS activity data by the GAINS emissions factors for each fuel for the general residential/domestic sector (fuel specific but not technology specific). These are given in Table 7-3. The net CO_2 emissions factor is assumed to be zero for biomass, in order to investigate the climatic effects of non-CO_2 species. In the case of CO, emissions factors were not available in this version of GAINS. Therefore emissions factors were taken from the EMEP/EEA database (EEA 2013) in this case, again using GAINS activity data. Full BC and OC emissions were available for the UK (in GAINS Europe) but not for New Zealand. The New Zealand emissions were calculated from PM_{10} emissions data, using the ratio of the GAINS BC and PM_{10} emissions factors for the UK.

The climate impacts were calculated by multiplying the emissions for each RSF source by the Absolute Global Warming Potential (AGWP) for each pollutant. The units of AGWP are radiative forcing per unit emission over one year, and are taken from (Bond *et al.* 2013). The values for CO_2 and N_2O were taken from the IPCC AR5 report (Myhre *et al.* 2013).

Table 7-3 shows the net radiative forcings for each pollutant, which includes direct and indirect effects on a global scale. Cloud effects for species such as BC and particulate organic carbon are included in these net factors. See Bond et al. (2013) for the full breakdown. The values used here are also central estimates. For BC, the net lower and net upper estimates are 83% lower and 144% higher than the central estimate respectively. For biomass OC, the errors are -65% to +84%.

Parameter	Net Forcings (μW m^{-2}) (Gg yr^{-1})$^{-1}$	Emissions factors (t PJ^{-1})			
		Brown Coal /lignite	Hard coal, grade 1	Derived coal (coke etc)	Biomass
CO_2	0.0917	99,500	94,300	100,000	0
CH_4	2.2				
NO_x	-6.2	70	118	110	68
CO	0.48	5000	5000	5000	4000
NMVOC	0.78				
SO_2	-9.0	1239	616	541	4
NH_3	0	8	8	0.5	8.2
N_2O	24.3	1.4	1.4	1.4	4
BC	74.3				
OC (fossil fuel)	-16.9				
OC (biomass)	-12.5				

Table 7-3. GAINS emissions factors for the general residential sector used to calculate technology-specific emissions where the data was unavailable.

7.3.3. A Bottom-Up Emissions Inventory Calculation and Comparison

Finally, a bottom-up emissions inventory was produced for both countries using unique activity data and emissions factors. This allowed the comparison of activity data, emissions, and climate impacts between this study and the GAINS model, alongside several other international climate models. An extensive review of RSF sector emissions factors was carried out. The most comprehensive and fuel/technology specific factors were found to be those of the EMEP/EEA database and these were selected for the modelling work (EEA 2013).

Activity data in New Zealand was derived following the method of the HAPINZ study (Kuschel *et al.* 2012). The method uses 2006 census data for the number of homes in each census area unit, multiplied by average daily wintertime consumption factors for wood and coal, multiplied by average PM_{10} emissions factors for each species. These emissions are then constrained to inventories which have been produced for regional councils. Finally, these peak wintertime values are assigned an annual distribution in order to account for the high seasonal variability of RSF use. In this work, the updated 2013 census data (StatisticsNZ 2015) has been used, with the same wintertime consumption factors of 20 kg day^{-1} for wood and 16 kg day^{-1} for coal. The annual distribution is presented in Figure 7-2.

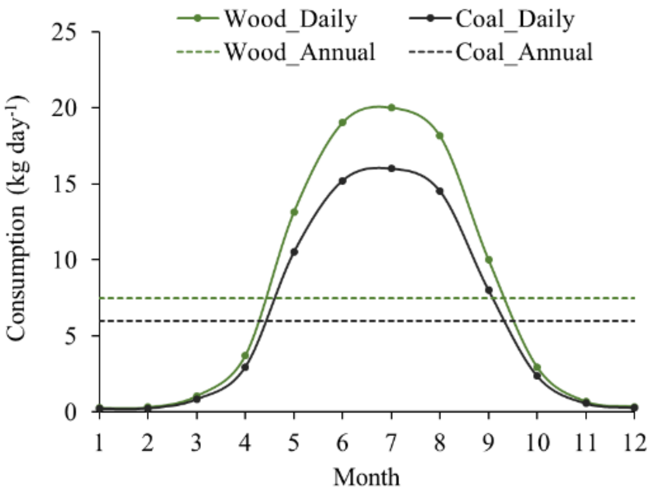

Figure 7-2. Model factors for average daily and annual household consumption of wood and coal, in households using each fuel.

The distinction between different grades of coal is not possible with this method, because the census does not differentiate bituminous coal from lignite or anthracite; which are known to have substantially different emissions factors (Lee *et al.* 2005; Mitchell *et al.* 2016). Activity data in the UK was derived from the recent DECC Wood Consumption Survey for wood (DECC 2016a) and the DECC Sub-National Residual Fuel Consumption Statistics (DECC 2015b) for coal and derived coal / manufactured solid fuel (MSF). The former also has data on the number of homes using coal, but the focus is on wood users who use coal as well as wood.

7.4 Results

4.1. Top-down Calculation of 2006 BC Concentrations in New Zealand

Analysis of datasets featuring simultaneous PM_{10} and BC measurements was conducted in several wood burning communities across New Zealand in order to determine the ratio of BC/PM_{10}. The results are given in Table 7-4. In addition to Table 7-4, a study from a suburban town near Wellington found that the contribution of wood burning to ambient $PM_{2.5}$ and BC averaged over a two year period was 2.9 μg m^{-3} and 846 ng m^{-3} respectively (Davy *et al.* 2012). Hence the ratio of BC/$PM_{2.5}$ was 28.8%, which is similar to the BC/PM_{10} ratio observed in other locations. Applying these factors to the HAPINZ data yields the wintertime concentrations of BC in New Zealand, and the results are given in Figure 7-3.

The results show that the majority of the country has very low wintertime BC concentrations, typically below 1000 ng m^{-3} and below 500 ng m^{-3} in many rural areas. The highest concentrations were in the city of Nelson, specifically Toi Toi, Wahsington and Bronte districts which had mean winter BC concentrations over 10 μg m^{-3}. Also in the highest 10% were Richmond, Arrowtown, Alexandra, Milton, North beach Christchurch, Kaiapoi Christchurch. Many of these regions are known to have poor wintertime air quality as shown in Table 7-4.

.

				Concentration ($\mu g\ m^{-3}$)		Ratio (%)	
Town	Class	Region	Season	PM_{10}	BC	BC/PM_{10}	Data Source
Rangiora,	S	ChC	W	660.0	9.4	1.9	NIWA, unpublished
Waikuku,	S		W	4.3	1.3	41.9	
Kaiapoi and	S		W	863.5	1.4	0.3	
Woodend	S		W	306.5	1.2	0.8	
Dunedin	U	Dnd	A	112.7	32.3	30.6	
Dunedin	U		A	99.6	25.4	29.6	
Dunedin	U		A	192.6	68.5	43.8	
Dunedin	U		A	242.7	55.6	29.6	
Dunedin	U		A	56.2	18.9	37.7	
Green Island	S		W	84.3	12.8	21.0	
Dunedin	U		W	32.9	2.9	11.0	
Dunedin	U		W	20.2	3.3	17.6	
Takapuna	S	Auk	S	14.3	1.9	13.6	GNS Science, unpublished
Takapuna	S		W	18.1	4.0	22.2	
Queen Street	U		S	17.2	3.8	22.1	
Queen Street	U		W	18.5	5.3	28.6	
Khyber Pass	U		S	17.0	4.0	23.9	
Khyber Pass	U		W	19.7	6.0	30.8	
Penrose	S		S	15.9	1.8	11.1	
Penrose	S		W	18.3	3.3	18.4	
Henderson	S		S	11.8	1.2	10.4	
Henderson	S		W	16.5	3.4	20.5	
Alexandra	R	COt	W	19	4.9	25.7	(Ancelet *et al.* 2014)
Alexandra	R		W	33	6.6	19.9	
Alexandra	R		W	17	4.4	25.8	
Alexandra	R		W	29	5.5	19.1	
Masterton	R	Wrp	W	25	3.1	12.6	(Ancelet *et al.* 2012)
Masterton	R		W	32	3.7	11.6	
Nelson	U	Nln	W			12.7	(Grange *et al.* 2013)
Nelson	U	Nln	W	21	2.9	12.7	(Ancelet, Davy and Trompetter 2015)
Auckland, Masterton, Nelson, Alexandra	U	Mixed	W			14.1	(Trompetter *et al.* 2013)
	U	**NZ**	**W**			**24.6**	
	S	**NZ**	**W**			**16.7**	
	R	**NZ**	**W**			**19.1**	

Chc: Christchurch; DnD: Dunedin; Auk: Auckland; COt; Central Otago; Wrp: Wairarapa; Nln: Nelson

Table 7-4. Ratio of BC/PM_{10} in urban (U), suburban (S) and rural (R) locations in the winter (W) and the summer (S) in New Zealand.

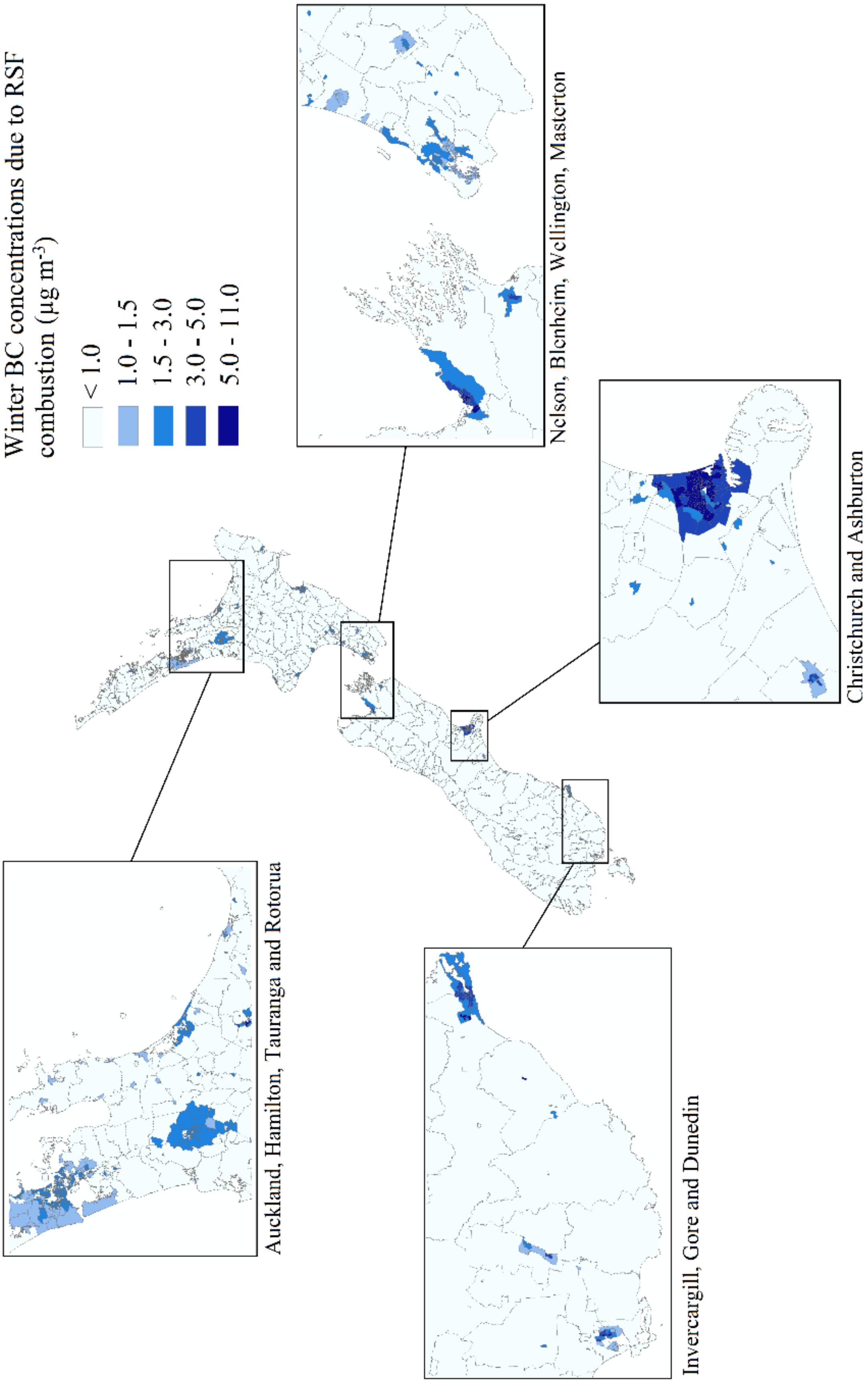

Figure 7-3. Wintertime concentrations of black carbon due to residential solid fuel burning in New Zealand in 2006.

7.4.2. Emissions and Climate Impacts Using the GAINS Model

Activity data for RSF combustion in the residential sector from the GAINS database is presented in Figure 7-4.

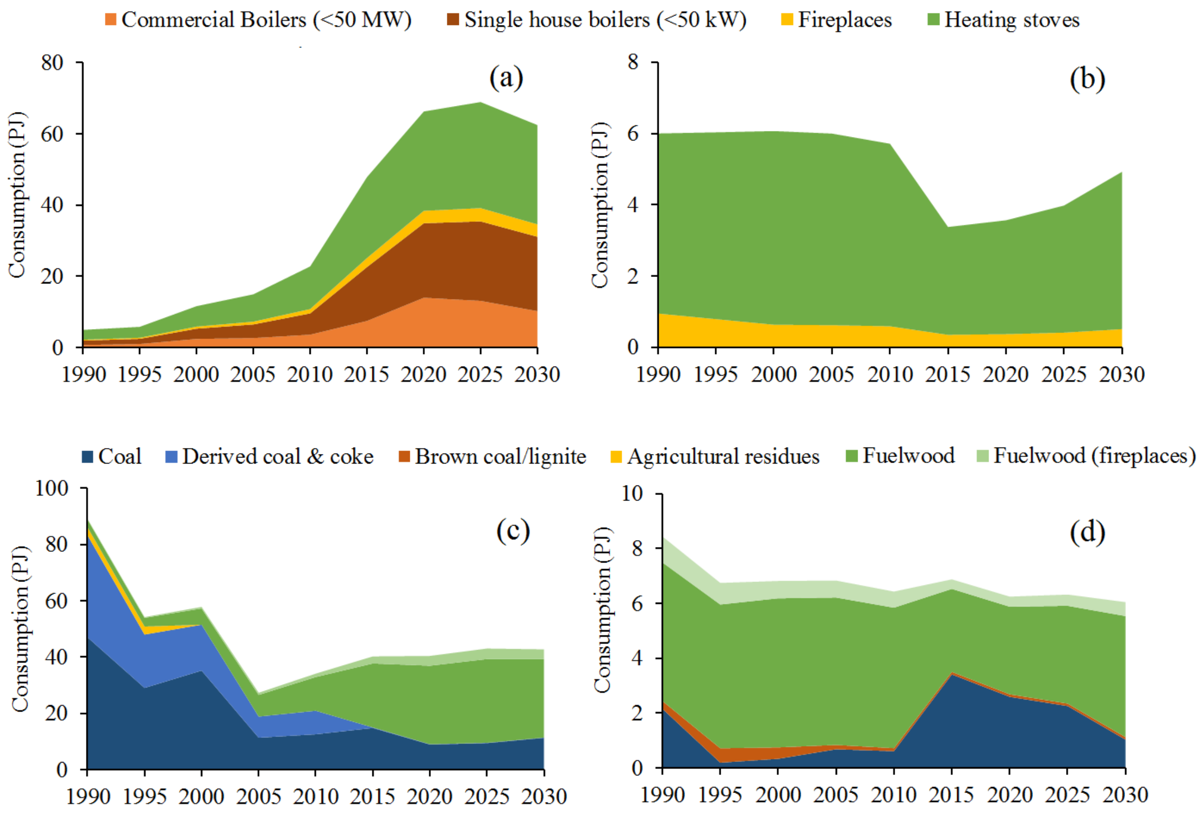

Figure 7-4. Breakdown of activity data for RSF combustion by technology and fuel type according to the GAINS database, 1990 - 2030. Top: wood fuel consumption by technology type in (a) the UK and (b) New Zealand. Bottom: breakdown of fuel consumption in heating stoves and fireplaces in (c) the UK and (d) New Zealand.

In the UK, the model shows that consumption of wood in the residential sector is increasing rapidly and will continue to do so to 2025. Heating stoves account for the largest proportion of wood use (47% in 2015), and this is largely due to a switch from coal and derived coal to biomass, as shown in Figure 7-4c. The model forecasts coal consumption in stoves to continue to reduce to 2030, yet wood consumption in stoves and fireplaces is estimated to increase by almost a factor of 4 between 2005 and 2030. It should be noted that GAINS only includes wood consumption in fireplaces and hence does not account for fossil fuel consumption in this technology. A small amount of agricultural residues is consumed in stoves between 1990 and 200, but is negligible compared to other fuels. In New Zealand, the model shows that consumption of wood remained comparatively constant between 1990 and 2010 at approximately 6 PJ. Wood consumption is dominated by heating stoves, with commercial and single house boilers consuming negligible amounts throughout the timeframe. Between 2010 and 2015 there is a 41% reduction in wood consumption and a six-fold increase in hard coal (grade 1) consumption, suggesting a large fuel switching programme in stoves in New Zealand. Lignite consumption remains relatively low (< 0.5 PJ) throughout the period.

Fuel- and technology-specific emissions data is available in the GAINS database for certain pollutants in the RSF sector, but not all. The missing values have been calculated using GAINS emissions factors and the activity data given in Figure 7-4c and Figure 7-4d, as detailed in section 3.2. The results for heating stoves and fireplaces are given in Figure 7-5 for the United Kingdom and Figure 7-6 for New Zealand. The UK results show that emissions are highly dependent on the type of fuel used and the activity data for each. Emissions generally follow the same trend as the activity data in Figure 7-4c, whereby the total reduces to a low in 2005 as coal consumption reduces, before increasing to 2030 as wood consumption increases. CO_2 and SO_2 emissions are negligible for biomass burning compared to fossil fuel burning and reduce considerably over the period. NO_x and CO emissions are also dominated by fossil fuel combustion and increase by just 27% and 42% respectively from 2005 to 2030. CH_4 emissions are more strongly correlated with wood burning and increase from 3 kt year^{-1} in 1990 to 7 kt year^{-1} in 2030. NMVOCs are also highly dominated by wood combustion throughout the period and total residential sector emissions increase by a factor of 3.3 between 2005 and 2025. This is the largest increase of all pollutants. In 2015, heating stoves accounted for 74.6% of NMVOC emissions from wood combustion in the UK residential sector. Organic carbon (OC) emissions followed a similar trend, except for negligible emissions from derived coal. Particulate emissions are also dominated by wood combustion from the year 2001 onwards. PM_{10} emissions from wood combustion increase in by a factor of 10 in heating stoves and 14 in fireplaces respectively from 1990 to 2030. Similar trends are found in single house boilers and commercial boilers over the period. $PM_{2.5}$ emissions account for more than 96% of PM_{10} emissions, indicating that the majority of the emitted particles are in the fine fraction. Black carbon emissions are shown in Figure 7-5k. BC emissions from wood combustion in stoves increased from 0.27 kt year^{-1} in 1990 to 2.8 kt year^{-1} in 2030. Emissions from coal reduced over the period and fell below those of wood in the year 2004.

Emissions in New Zealand also follow the same trend as the activity data, shown in Figure 7-4d. Coal consumption peaks at 3.4 PJ in 2015, with corresponding emissions peaks of 331 kt year^{-1} for CO_2 and 2.2 kt year^{-1} for SO_2. Although consumption of lignite remains low over the modelling period, the fuel contributes significantly to SO_2 emissions, peaking at 0.65 kt year^{-1} in 1995; 82% of total emissions from stoves and fireplaces. Emissions of CH_4 and NMVOCs are more dominated by wood combustion and reduce by a factor of 3 between 1990 and 2030. Emissions of CO, NH_3 and N_2O are relatively evenly split between fossil fuels and biomass and stay largely consistent at 30 kt year^{-1}, 0.5 kt year^{-1} and 0.025 kt year^{-1} respectively. Emissions of $PM_{2.5}$ and OC emissions reduce linearly at rates of 68 t $year^{-1}$ and 23 t $year^{-1}$ respectively. The increased coal consumption has a greater impact on BC emissions, becoming the leading source of BC between 2014 and 2027. Despite this, BC emissions reduce by 42% over the modelling period. A summary of the activity and emissions data for heating stoves and fireplaces in the year 2015 is given in Table 7-5 for both New Zealand and the UK. Total emissions of black carbon in stoves and fireplaces in 2015 were 3.26 kt in the UK and 0.60 kt in New Zealand. This equates to 0.117 kg $dwelling^{-1}$ and 0.337 kg $dwelling^{-1}$ respectively.

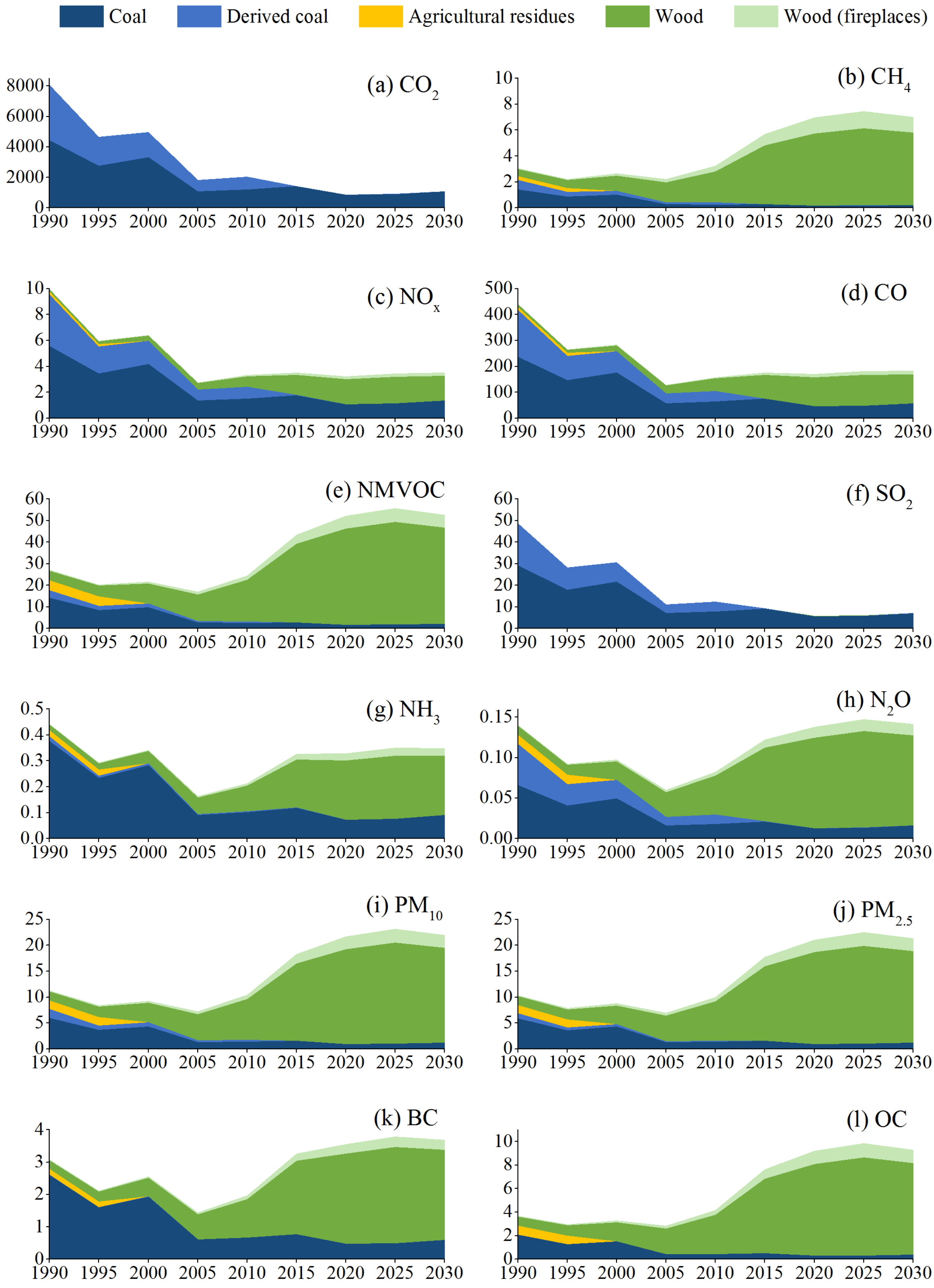

Figure 7-5. Emissions of selected climate-relevant species (kt year^{-1}) from heating stoves and fireplaces in the UK, 1990 to 2030. (a) CO_2; (b) CH_4; (c) NO_x; (d) CO; (e) NMVOC; (f) SO_2; (g) NH_3; (h) N_2O; (i) PM_{10}; (j) $PM_{2.5}$; (k) BC; (l) OC.

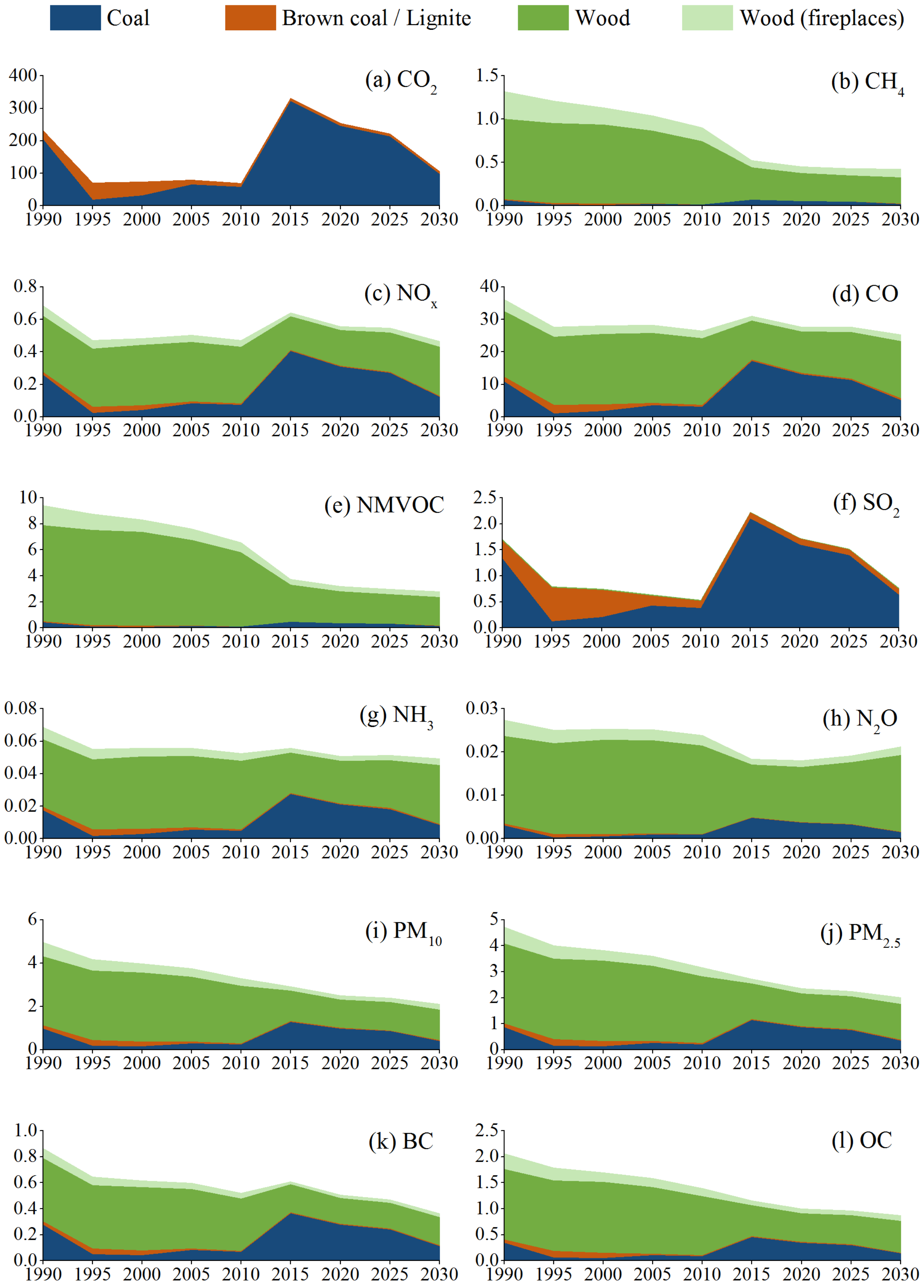

Figure 7-6. Emissions of selected climate-relevant species (kt year^{-1}) from heating stoves and fireplaces in New Zealand, 1990 to 2030. (a) CO_2; (b) CH_4; (c) NO_x; (d) CO; (e) NMVOC; (f) SO_2; (g) NH_3; (h) N_2O; (i) PM_{10}; (j) $PM_{2.5}$; (k) BC; (l) OC.

		UK, 2015				NZ, 2015			
		Biomass		Fossil fuel		Biomass		Fossil fuel	
Parameter	Unit	Fire-place	Stove	Fire-place	Stove	Fire-place	Stove	Fire-place	Stove
Activity data	PJ	2.52	22.71		15.01	0.35	3.03		3.50
CO_2	kt year^{-1}				1416				331
CH_4	kt year^{-1}	0.88	4.54		0.27	0.09	0.37		0.07
NO_x	kt year^{-1}	0.17	1.55		1.78	0.02	0.21		0.41
CO	kt year^{-1}	10.10	90.86		75.04	1.39	12.11		17.52
NMVOC	kt year^{-1}	4.29	36.34		2.73	0.42	2.88		0.45
SO_2	kt year^{-1}	0.011	0.10		9.23	0.001	0.013		2.22
NH_3	kt year^{-1}	0.02	0.19		0.12	0.003	0.025		0.03
N_2O	kt year^{-1}	0.010	0.09		0.02	0.001	0.012		0.005
PM_{10}	kt year^{-1}	1.82	14.89		1.55	0.21	1.41		1.31
$PM_{2.5}$	kt year^{-1}	1.76	14.42		1.53	0.20	1.36		1.17
BC	kt year^{-1}	0.22	2.27		0.77	0.02	0.21		0.37
OC	kt year^{-1}	0.81	6.35		0.49	0.09	0.60		0.47

Table 7-5. GAINS pollutant emissions inventory for RSF combustion in stoves and fireplaces in the United Kingdom and New Zealand, 2015.

The climate impacts of the emissions profiles given in figures 7-5 and 7-6 were then calculated for the years 2010 and 2030 and the results are presented in figure 7-7.

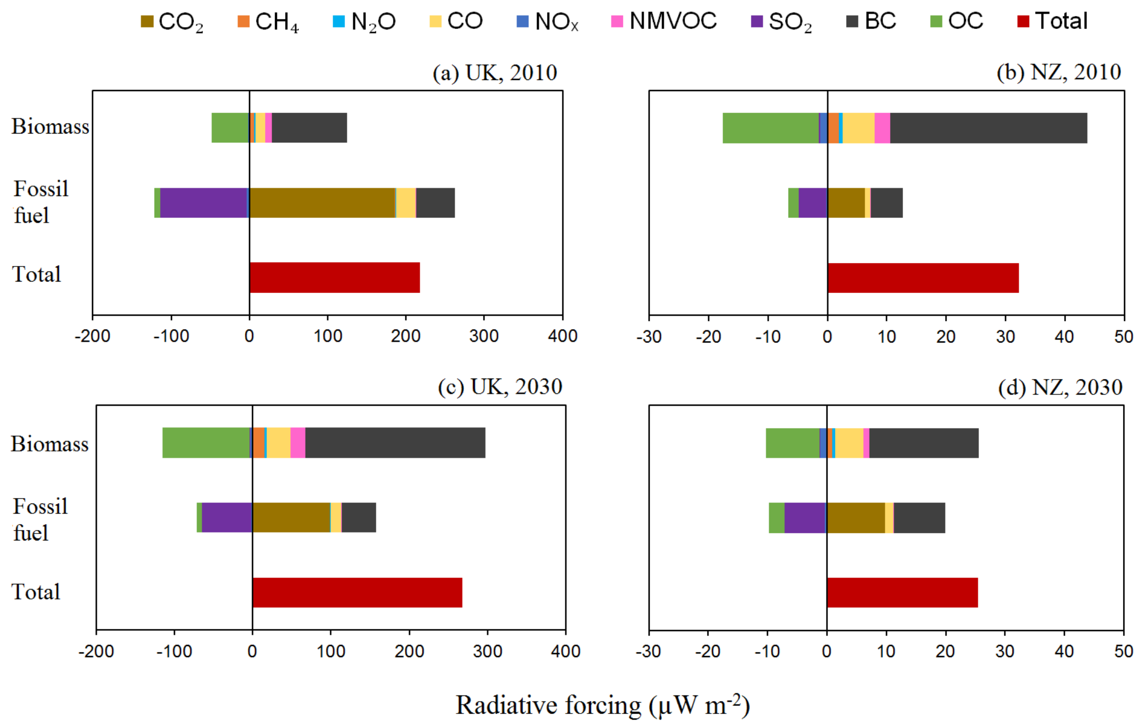

Figure 7-7. Breakdown of radiative forcing due to biomass and fossil fuel RSF combustion in heating stoves and fireplaces in: (a) UK in 2010; (b) NZ in 2010; (c) UK in 2030; (d) NZ in 2030.

The results show that carbon dioxide from fossil fuel combustion was the largest contributor to radiative forcing in the UK residential sector in 2010. The contribution from biomass burning was approximately half that of fossil fuel, with black carbon being the most important warming species. SO_2 from coal and derived coal combustion offset some of the warming by -110 µW m^{-2}, giving a net positive radiative forcing of 218 µW m^{-2} for the UK in 2010. In contrast, by 2030 biomass has a larger warming impact than fossil fuel combustion. Black carbon from wood burning in stoves and fireplaces causes a radiative forcing of 97 µW m^{-2} in 2010. Despite some offset by organic carbon, the total net radiative forcing increases by 23% to 268 µW m^{-2}.

In New Zealand, net radiative forcing reduces by 21% between 2010 and 2030. Forcing due to biomass burning in stoves and fireplaces is a factor of 4.3 lower than that of fossil fuel burning in 2010. By 2030, net forcing due to coal burning has increased by 40% relative to 2010, and is just 33% lower than that of biomass burning. Black carbon remains the most important forcing agent in both scenario years, accounting for 77% of the total warming effect of combined biomass and fossil fuel burning in 2010; and 76% in 2030. However, in the intervening years, forcing due to coal combustion exceeds that of biomass combustion by a factor of 2.4, due to a surge in coal consumption. This results in a slight increase in total net forcing (shown in red) in 2015, but an overall reducing trend across the modelling period. In the UK, total net forcing reduces rapidly from 1990 to 2005 but then increases at an average rate of 3.6 µW m^{-2} due to increased wood burning.

As discussed in section 3.2, the net AGWP factors used to create figure 10 are central estimates and carry a substantial uncertainty. Error bars have not been included here because the uncertainties in global radiative forcing due to anthropogenic pollution are substantial and beyond the scope of this study (Bond et al., 2013). There are also errors associated with the activity data (up to factor of 3 for the UK according to recent survey results) and with the emissions factors used. For BC and PM_{10}, emissions factors for wood burning stoves vary by ±30% between inventories (see table 7-6). The combined uncertainties are substantial and hence values reported here should be treated as estimates.

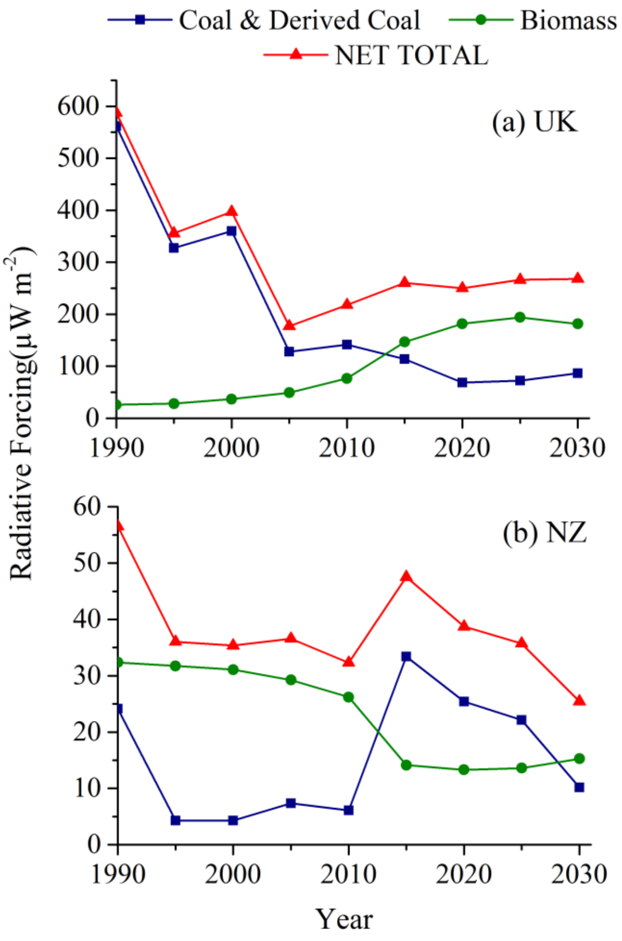

Figure 7-8. Total climate forcing due to wood and coal combustion in heating stoves and fireplaces in the UK (a) and New Zealand (b).

7.4.3 A Bottom-Up Emissions Inventory Calculation and Comparison

A bottom-up approach was used in order to create emissions inventories for both countries, which can be compared with established inventories. In the UK, activity data for wood was derived from the DECC Wood Consumption Survey (DECC 2016a). It found that the proportion of homes using wood for heating varies regionally. The proportion was lowest in London and the North East at 3.9% and 4.0% respectively, and highest in Northern Ireland and the South East at 18.4% and 15.8% respectively. The survey also asked wood users whether they used any additional fuels as well as wood. It found that the proportion of households using coal as well as wood was below 3% across much of the UK. The exception was in Northern Ireland where 10.1% of wood fuel users also used coal, which reflects the high consumption of mixed RSF in the region. Conversely, despite 15.8% of respondents in the South East using wood, just

1.7% of those also used coal; indicating that wood dominates the RSF mix. Activity data for coal and derived coal was derived from the DECC Sub-National Residual Fuel Consumption Statistics (DECC 2015b). The results are shown in Figure 7-9. It was found that coal consumption was highest in the East Midlands at 2.62 PJ and lowest in London at 0.22 PJ. Consumption of manufactured solid fuel (derived coal, smokeless fuel, briquettes etc) was also highest in the East Midlands at 1.98 PJ, closely followed by Yorkshire and the Humber at 1.93 PJ. Consumption in London was 0.25 PJ.

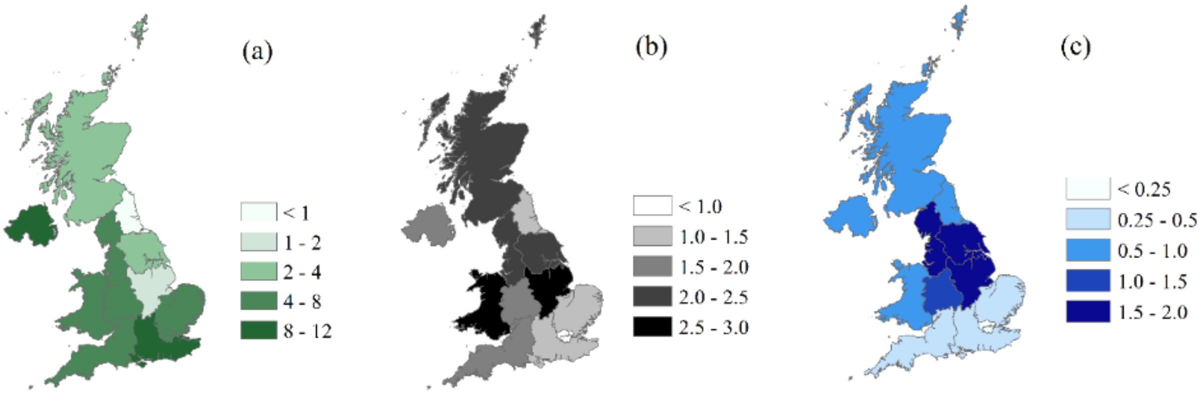

Figure 7-9. UK activity data (PJ) for (a) wood; (b) coal and (c) manufactured solid fuel.

In New Zealand, activity data for both wood and coal was derived from the 2013 National Census (StatisticsNZ 2015) using the methodology of the HAPINZ study (Kuschel *et al.* 2012). As shown in Figure 7-10, the census data shows that the proportion of households using wood is far higher in New Zealand than in the UK. Over 90% of homes in many rural wards such as Taihape, Opuha and Glenmark use wood for heating. Coal consumption is much more dependent on location. The proportion of homes using coal for heating is below 5% across much of the country, particularly North Island. The proportion is highest in wards located in the west and south of South Island, including Northern Ward, Grey District (76%), Inangahua (69%) and Mataura (65%).

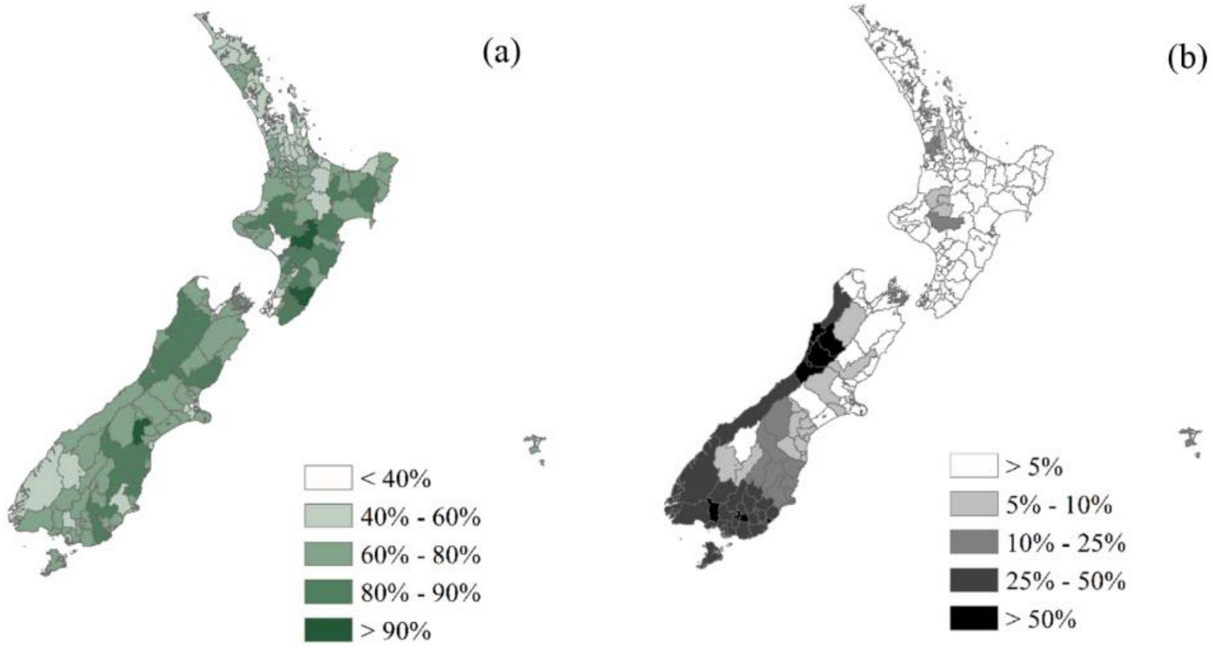

Figure 7-10. Proportion of households in New Zealand using a) wood; and b) coal; in 2013.
Data Source: (StatisticsNZ 2015)

In order to produce an inventory, an in-depth review of RSF sector emissions factor inventories was carried out. Emissions factors applying to heating stoves and fireplaces were compared between the following inventories: the EMEP/EEA air pollutant emission inventory guidebook (EEA 2013), U.S Environmental Protection Agency AP-42 (USEPA 1995), GAINS (http://gains.iiasa.ac.at/models/), the IPCC emissions factor database (EFDP) (www.ipcc-nggip.iges.or.jp/EFDB/), and the UK National Air Emissions Inventory (NAEI) (http://naei.defra.gov.uk/). The results are shown in table 7-6 for wood and coal. Inventories such as GAINS, the IPCC EFDP and NAEI offer emissions factors for other residential solid fuels such as charcoal, peat, anthracite, coke and lignite.

		EMEP				USEPA		GAINS			IPCC				NAEI		This study				
		Heating stoves		Fireplaces		Heating stove	Fireplace	Heating Stoves		Fireplaces	Heating stove	Fireplace	Residential		Residential		Heating stoves		Fireplaces		Residential
Pollutant	Unit	Wood	Coal	Wood	Coal	Wood	Wood	Wood	Coal	Wood	Wood	Wood	Wood	Coal	Wood	Coal	Wood	Coal	Wood	Coal	MSF
Carbon Dioxide	g GJ^{-1}						94444		94300				112000	94600		21789		94600		94600	24459
Methane	g GJ^{-1}					833		200	30	350	932		300	267-2650	205	476	200	476	350	476	149
Nitrogen oxides	g GJ^{-1}	50	100	50	60	78	72		80		120	110	100	100^{-1}80	49	108	50	100	50	60	113
Carbon Monoxide	g GJ^{-1}	4000	5000	4000	5000	6411	7017				10000	11000	5000	2000-3600	2956	4249	4000	5000	4000	5000	3517
Non Methane VOC	g GJ^{-1}	600	600	600	600		6361	1600	300	1700			600	200	393	424	600	600	600	600	148
Sulphur Dioxide	g GJ^{-1}	11	900	11	500	11	11		726						6	785	11	900	11	500	1096
Nitrous Oxide	g GJ^{-1}						8		1.4			9	4	1.5	3	4	3	4	3	4	3
Ammonia	g GJ^{-1}	70	5	74	5				8						55	30	70	5	74	5	30
PM$_{10}$	g GJ^{-1}	760	450	840	330	850	961	655	455	720					458	281	760	450	840	330	56
PM$_{2.5}$	g GJ^{-1}	740	450	820	330			635	450	698					427	277	740	450	820	330	55
Black Smoke	g GJ^{-1}														56	1212					144
Black Carbon	g GJ^{-1}	74	29	57	32			100	130	86							117	130	101	95	5
Organic Carbon	g GJ^{-1}					1472	0.4	280	160	320							326	160	376	117	20
Lead	mg GJ^{-1}	27	100	27	100										51	86	27	100	27	100	76
Cadmium	mg GJ^{-1}	13.0	1.0	13.0	0.5	0.61									4.4	0.9	13.0	1.0	13.0	0.5	2
Mercury	mg GJ^{-1}	0.6	5.0	0.6	3.0										1.7	3.3	0.6	5.0	0.6	3.0	5
Arsenic	mg GJ^{-1}	0.2	1.5	0.2	1.5										1.7	14.2	0.2	1.5	0.2	1.5	16
Chromium	mg GJ^{-1}	23	10	23	10	0.03									50	27	23	10	23	10	38
Copper	mg GJ^{-1}	6	20	6	20										5.6	6.4	6	20	6	20	11
Nickel	mg GJ^{-1}	2	10	2	10	0.39									54	14	2	10	2	10	1263
Selenium	mg GJ^{-1}	0.5	2.0	0.5	1.0										5	13	0.5	2.0	0.5	1.0	19
Zinc	mg GJ^{-1}	512	200	512	200										69	75	512	200	512	200	89
Calcium	mg GJ^{-1}														525	15856					
Tin	mg GJ^{-1}														7.5	4.2					417
Vanadium	mg GJ^{-1}														1.7	3.3					3303
Magnesium	mg GJ^{-1}														89	5145					
Sodium	mg GJ^{-1}														583	5064					
Beryllium	mg GJ^{-1}														0.36	40					4
Potassium	mg GJ^{-1}														2472	4250					
Manganese	mg GJ^{-1}					4.72															
Benzo[a]pyrene	mg GJ^{-1}	121	250	121	100	111									72	47	121	250	121	100	8.4
Benzo[b]fluoranthene	mg GJ^{-1}	111	400	111	170	167									83	2	111	400	111	170	0.4
Benzo[k]fluoranthene	mg GJ^{-1}	42	150	42	100	56									28	0.6	42	150	42	100	0.1
Indeno[123-cd]pyrene	mg GJ^{-1}	71	120	71	80										5	36	71	120	71	80	6.4
Benz[a]anthracene	mg GJ^{-1}					556									278	54					
Anthracene	mg GJ^{-1}					389									361	56					
Benzene	mg GJ^{-1}					54									14	19					
Benzo[ghi]perylene	mg GJ^{-1}					111									56	25					
Fluorene	mg GJ^{-1}					667									461	491					
Dibenz[ah]anthracene	mg GJ^{-1}														1	54					
Acenapthylene	mg GJ^{-1}					5889									4367	217					
Napthalene	mg GJ^{-1}					8000									5017	3738					
Pyrene	mg GJ^{-1}					667									406	90					
Phenanthrene	mg GJ^{-1}					2167									1356	199					
Acenapthene	mg GJ^{-1}					278									172	159					
Fluoranthene	mg GJ^{-1}					556									383	90					
Chrysene	mg GJ^{-1}					333									211	51					
Total PAH	mg GJ^{-1}																2389	7576	2389	7576	950
Polychlorinated biphenyls	µg GJ^{-1}	0.06	170	0.06	170										111	109	0.06	170	0.06	170	109
Dioxins	ng I-TEQ GJ^{-1}	800	1000	800	500										662	731	800	1000	800	500	742
Hexachlorobenzene	µg GJ^{-1}	5	0.62	5	0.62										4	1	5	0.62	5	0.62	
Hydrogen Chloride	g GJ^{-1}															71					

Table 7-6. Summary of emissions factors applying to residential solid fuel combustion in stoves and fireplaces in five inventories, and those chosen for this study.

As the table shows, not all pollutants are accounted for in all inventories. The most extensive is the NAEI database, but these factors apply to the residential sector in general and are not technology specific. The most comprehensive fuel- and technology-specific factors were found to be those of the EMEP/EEA database and these were selected as the basis for the modelling work. EMEP/EEA emissions factors are largely consistent with other inventories. However, the PM_{10} emissions factor for wood burning in stoves in EMEP/EEA is 16% higher than in GAINS and 66% higher than in NAEI. Despite this, BC emissions are 26% lower than in GAINS for wood stoves and a factor of 4.5 lower than in GAINS for coal stoves. Also in comparison with GAINS,

Table 7-6 shows that EMEP/EEA may over-estimate emissions of cadmium, zinc and indeno[1,2,3-cd]pyrene from wood burning, as well as copper and total PAHs from coal burning. There may be an underestimate of emissions of arsenic, nickel, selenium and PCBs. In comparison to stoves, emissions factors for fireplaces are very similar for wood combustion in the EMEP/EEA inventory. However, for coal burning NO_x, SO_2, PM_{10}, cadmium, mercury, PAH and PCDD/F are lower for fireplaces than stoves. Furthermore GAINS does not provide emissions factors for coal burning in fireplaces, whereas EMEP/EEA does. It should be noted, however, that the EMEP/EEA factors apply to ‘solid fuels other than biomass’ and are not specific to a certain fuel type such as bituminous coal.

Factors for CO_2, CH_4, N_2O, OC and total PAH were not included in the EMEP/EEA inventory. The value for CO_2 was taken from the IPCC EFDP inventory. Methane emissions factors were taken from GAINS for wood burning and the NAEI for coal burning. N_2O and derived coal / MSF emissions factors were also taken from NAEI. Finally, BC and OC emissions factors were calculated from EMEP/EEA $PM_{2.5}$ emissions factors, applying the ratio of BC or OC to $PM_{2.5}$ as given in the GAINS database. Values for ΣPAH were taken from Lee *et al.* (2005).

Combining the activity data in Figure 7-9 and Figure 7-10 with the emissions factors in Table 7-6 yields the emission inventories for both countries. The results are presented for the UK in Figure 7-11 and for New Zealand in Figure 7-12. The totals for both countries are presented in Table 7-7.

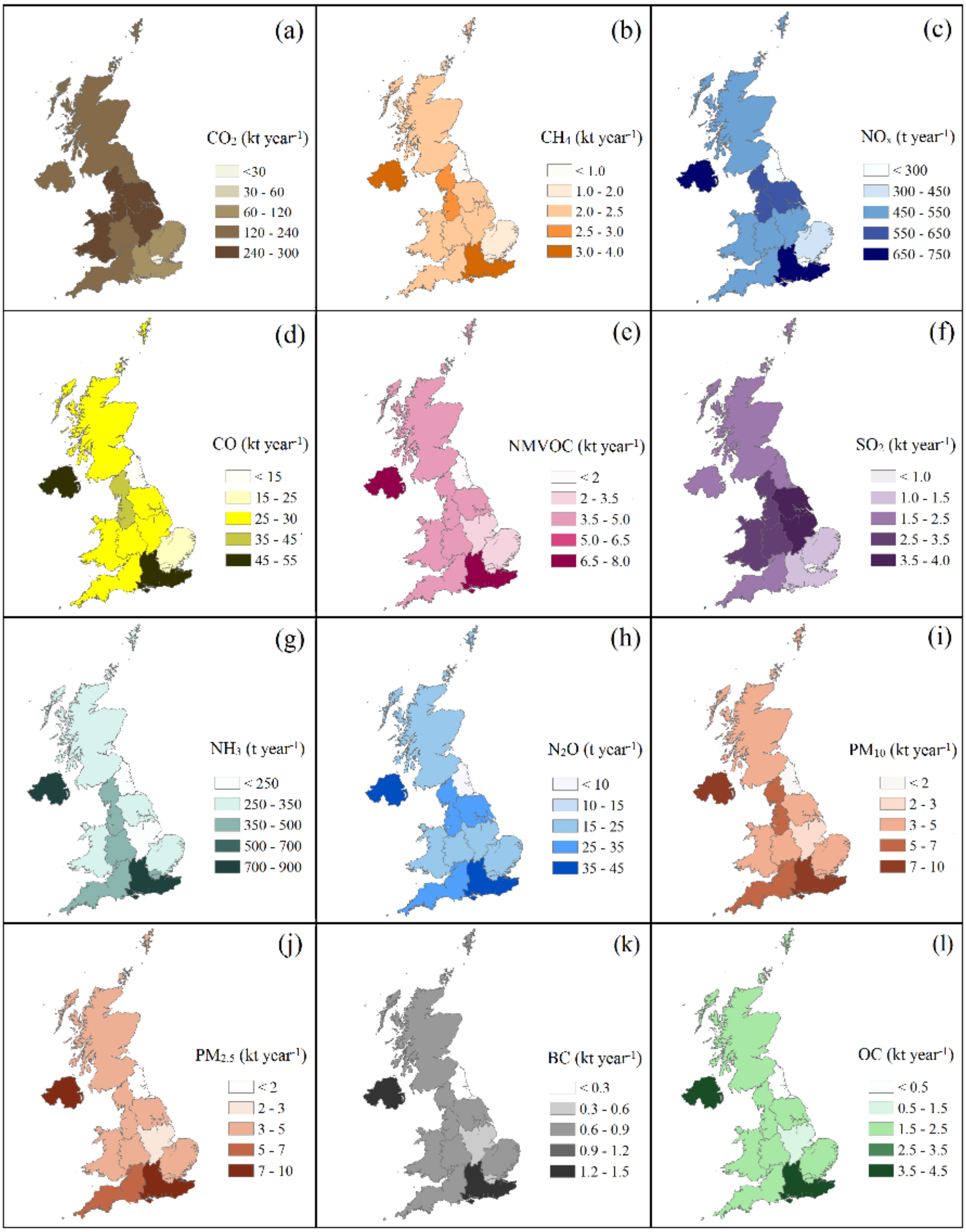

Figure 7-11. Distribution of emissions from stoves and fireplaces in the UK in 2014.

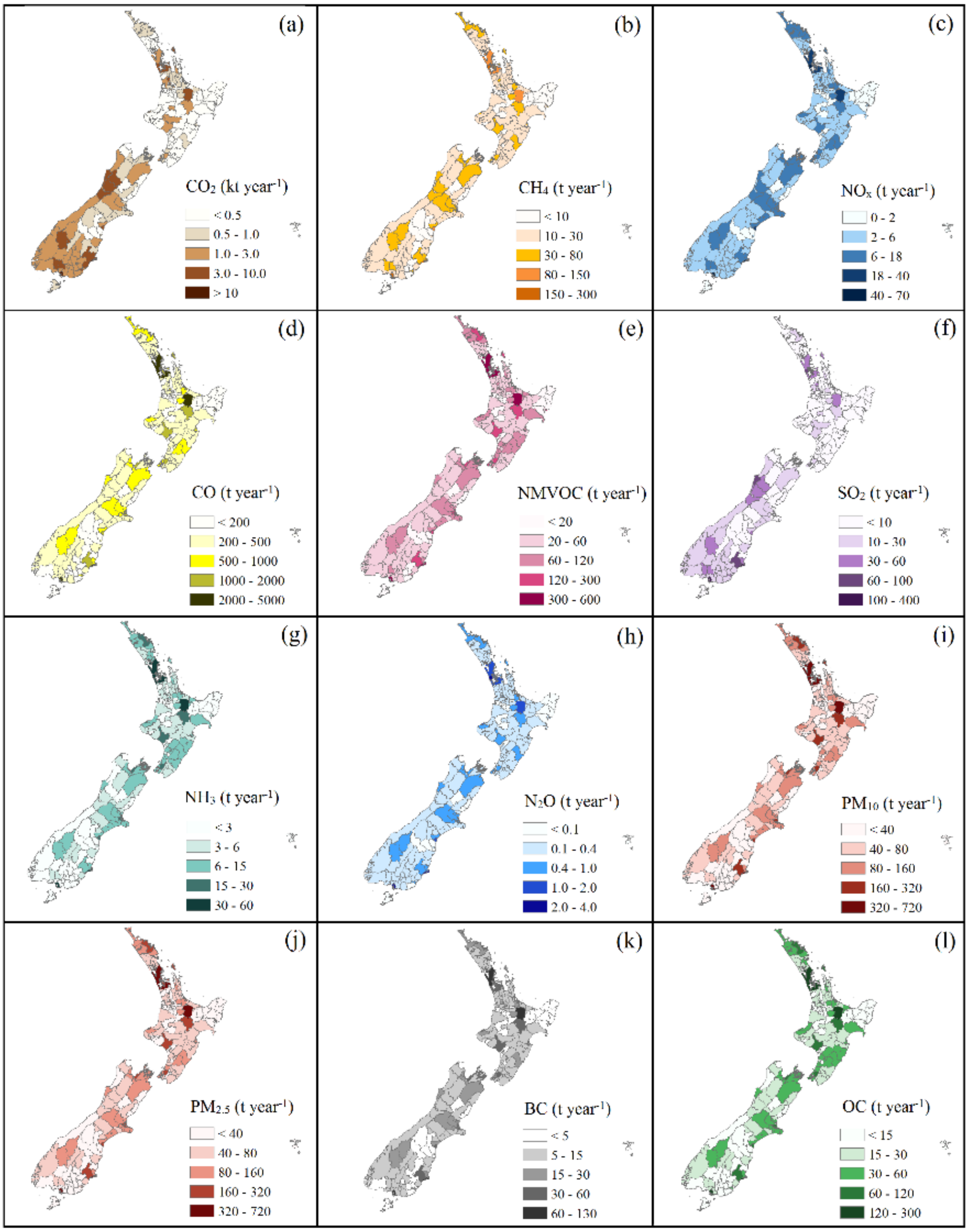

Figure 7-12. Distribution of emissions from stoves and fireplaces in New Zealand in 2013.

		UK, 2013/14					NZ, 2013	
		Wood		Coal		MSF	Wood	Coal
Parameter	Unit	Fire-places	Stoves	Fire-places	Stoves	Stoves + Fire-places	Stoves + Fire-places	Stoves + Fire-places
Activity data	PJ	32.80	29.51	10.79	9.71	10.99	26.72	4.34
CO_2	kt year^{-1}			1021	918	269		415
CH_4	kt year^{-1}	11.5	5.9	5.1	4.6	1.6	5.3	0.1
NO_x	kt year^{-1}	1.6	1.5	0.6	1.0	1.2	1.3	0.4
CO	kt year^{-1}	131.2	118.0	53.9	48.5	38.6	106.4	21.9
NMVOC	kt year^{-1}	19.7	17.7	6.5	5.8	1.6	16.0	2.6
SO_2	kt year^{-1}	0.4	0.3	5.4	8.7	12.0	0.3	3.9
NH_3	kt year^{-1}	2.4	2.1	0.05	0.05	0.3	1.9	0.02
N_2O	kt year^{-1}	0.10	0.09	0.04	0.04	0.03	0.08	0.02
PM_{10}	kt year^{-1}	27.6	22.4	3.6	4.4	0.6	20.2	2.0
$PM_{2.5}$	kt year^{-1}	26.9	21.8	3.6	4.4	0.6	19.7	2.0
BC	kt year^{-1}	3.3	3.4	1.0	1.3	0.05	3.1	0.6
OC	kt year^{-1}	12.3	9.6	1.3	1.6	0.2	8.7	0.7
Lead	t year^{-1}	0.89	0.80	1.08	0.97	0.84	0.72	0.44
Cadmium	t year^{-1}	0.43	0.38	0.01	0.01	0.02	0.35	0.004
Mercury	t year^{-1}	0.02	0.02	0.03	0.05	0.05	0.01	0.02
Arsenic	t year^{-1}	0.01	0.01	0.02	0.01	0.18	0.01	0.01
Chromium	t year^{-1}	0.75	0.68	0.11	0.10	0.42	0.61	0.04
Copper	t year^{-1}	0.20	0.18	0.22	0.19	0.12	0.16	0.09
Nickel	t year^{-1}	0.07	0.06	0.11	0.10	13.88	0.05	0.04
Selenium	t year^{-1}	0.02	0.01	0.01	0.02	0.21	0.01	0.01
Zinc	t year^{-1}	16.79	15.11	2.16	1.94	0.98	13.62	0.88
B[a]P	t year^{-1}	3.97	3.57	1.08	2.43	0.09	3.22	1.10
B[b]F	t year^{-1}	3.64	3.28	1.83	3.88	0.004	2.95	1.76
B[k]F	t year^{-1}	1.38	1.24	1.08	1.46	0.001	1.12	0.66
I[123-cd]P	t year^{-1}	2.33	2.09	0.86	1.16	0.07	1.89	0.53
ΣPAHs	t year^{-1}	78.4	70.5	81.7	73.5	10.4	63.5	33.2
PCB	g year^{-1}	2.0	1.8	1834	1650	1199	1.6	746.1
Dioxins	g I-TEQ year^{-1}	26.2	23.6	5.4	9.7	8.1	21.3	4.4
HCB	g year^{-1}	164.0	147.5	6.7	6.0		133.0	2.7

B[a]P: Benzo[a]pyrene; B[b]F: Benzo[b]fluoranthene; B(k)F Benzo[k]fluoranthene; I[123-cd]P: Indeno[123-cd]pyrene

Table 7-7. Pollutant emissions inventory for RSF combustion in the United Kingdom and New Zealand, 2013/14.

In the UK, the results show that emissions are highly dependent on regional fuel consumption. Emissions of CO_2 and SO_2 are highest in regions with the highest fossil fuel combustion, including the North of England and Wales. All other emissions are highest in Northern Ireland and the South East, where wood fuel consumption in highest. Emissions remain consistently low in the North East, where consumption of RSF is low across all fuel types. The national totals for activity data and emissions in Table 7-7 may be compared with the GAINS estimates in Table 7-5. It can be seen that wood consumption in stoves is within 30% of the GAINS inventory estimate. However, wood consumption in fireplaces is higher by more than 30 PJ compared to GAINS. Combined fossil fuel consumption is 31.49 PJ, more than twice the GAINS estimate. The higher activity data also corresponds to higher emissions. For biomass, the majority of emissions are higher by a factor of 2-3. The exceptions are NH_3 and SO_2 which are significantly higher than in GAINS, and NMVOCs which are within 8% of the GAINS estimate. For fossil fuel, there is a greater differences between the two inventories. The majority of emissions estimates are higher by a factor of 2-6 than in GAINS. The exceptions are CH_4 and OC emissions which are significantly higher. This is because the CH_4 emissions factor for coal stoves in the NAEI is 476 g GJ^{-1} versus 30 g GJ^{-1} in GAINS.

In New Zealand, regional fuel consumption also has a large impact on emissions. CO_2 and SO_2 emissions are far higher in South Island than in North Island, particularly in Greymouth, Grey District. Emissions from wood burning are more uniformly distributed across the country, and are strongly correlated to the larger population areas. Emissions of CH_4, NMVOCs, CO, particulate matter, BC and OC are consistently high in wards such as Rotorua, Nelson and Waitakere ward which includes the Auckland suburban areas of Waitakere and Henderson. Emissions are also highest in the wards which include Invercargill and Dunedin, where BC emissions over 100 tonnes $year^{-1}$ have been calculated. This corresponds to annual BC emissions of 5.6 kg $dwelling^{-1}$ and 3.8 kg $dwelling^{-1}$ in the two wards respectively. Comparing activity data, the results show that fossil fuel consumption in the GAINS model is within 24% of the calculated consumption. However calculated national wood consumption is higher than the GAINS estimate by a factor of 7.9. This has a significant impact of total national emissions. Calculated emissions from fossil fuel combustion are in the most part higher by a factor of 1-2 than in GAINS, except for NMVOCs and N_2O which are higher by a factor of 5.8 and 4.0 respectively. Calculated emissions from biomass burning range from 4.8 times higher for NMVOCs to 67.9% higher for ammonia. Importantly, black carbon emissions are 13.5 times higher, which has significant implications for climate.

7.5 Discussion and Implications for the UK

Analysis of HAPINZ data (Kuschel et al. 2012) found that the contribution of domestic heating to wintertime PM10 concentrations was highest in Alexandra, Arrowtown and Milton at 45-50 µg m-3; up to 2.5 times higher than the WHO recommended annual mean. Calculated average winter BC concentrations were also highest in these areas, peaking at 10 µg m^{-3}. The nationwide average was 1.8 µg m^{-3} and typically 4-7 µg m^{-3} in urban/suburban areas which is typical of the winter concentrations reported by the studies shown in Table 7-4. These concentrations are comparable with those in highly polluted regions of India and Asia, which have resulted in localised radiative forcing over urban areas of up to 23 Wm^{-2} (Panicker *et al.* 2010; Peng *et al.* 2016). It is therefore recommended that a full radiative transfer modelling exercise be carried out over urban areas in New Zealand in order to fully understand the climate impacts of wood burning stoves.

Emissions of NVMOCs, BC, OC and particulate matter are highly dominated by heating stoves because of the lower efficiency of combustion. This is in agreement with Denier van der Gon *et al.* (2015) who found the residential wood combustion is the largest source of organic aerosols in Europe. Lower combustion temperatures and larger fuel particle size promote pyrolysis conditions which are conducive to higher emissions of organics (Williams *et al.* 2012; Jones *et al.* 2014). The NVMOC emissions factor for coal combustion in heating stoves (300 g GJ^{-1}) is more than a factor of 5 lower than for wood (1600 g GJ^{-1}) in the GAINS database. In contrast, the factor is the same (600 g GJ^{-1}) for both wood and coal combustion in the EMEP/EEA database, and very similar in the NAEI database. Specific NO_x emissions factors by technology were not available in GAINS but the factor for biomass in the general residential sector is almost half that of coal, as shown in Table 7-3. NO_x emissions are influenced by the nitrogen content of the fuel (Mitchell *et al.* 2016) and the temperature of combustion (Jones *et al.* 2014). The same is true of SO_x emissions. Fuel-bound sulphur is typically very low in wood and biomass fuels, but can be as high as 2% in manufactured solid fuel (Van Loo and Koppejan 2007). However, the use of binders or additives such as calcium carbonate during the production of MSF briquettes can help retain a proportion of the sulphur in the ash. Figure 7-6f shows that lignite contributes to SO_2 emissions, particularly between 1995 and 2000. The GAINS emissions factor for lignite in heating stoves is 558 t PJ^{-1} versus 616 t PJ^{-1} for hard coal, which is consistent with the relative sulphur contents reported by Beamish, Barakat and St. George (2001). New Zealand has several billion tonnes of lignite resources in the Southland and Otago regions which may contribute to RSF emissions in the future.

Emissions of PM_{10} and $PM_{2.5}$ increase substantially from 2005 to 2030 in the UK, largely due to the increase in wood burning. The PM_{10} emissions factor for wood burning in heating stoves is 44% higher than that of coal burning in the GAINS database. This is corroborated by the EMEP/EEA and NAEI databases which find PM_{10} emissions from wood burning are 64% and 63% higher respectively than coal, on an energy basis. However, PM_{10} emissions are higher for coal on a mass basis. For example, the NAEI reports emissions factors of 9.3 g kg^{-1} and 8.2 g kg^{-1} for coal and wood respectively. This is in good agreement with Coulson, Bian and Somervell (2015) who found emissions factors from in-situ wood stoves exhibit a log-normal distribution with a mean of 9.8 g kg^{-1} (± 2.4 g kg^{-1}). The 95% confidence interval for PM_{10} emissions from conventional heating stoves burning wood and similar wood waste in the EMEP/EEA database is 6.8-27.3 g kg^{-1} (380-1520 g GJ^{-1}) with a mean of 13.7 g kg^{-1}. The range of the 95% confidence interval is lower for fossil fuel at 7.5-15.8 g kg^{-1}. The HAPINZ study used factors of 8 g kg^{-1} for wood and 25 g kg^{-1} for coal (Kuschel *et al.* 2012). The most important component of particulate matter for climate change is black carbon and this is presented at a percentage in the EMEP/EEA database. The 95% confidence interval is 2-20% for wood (average 10%) and 2-26% for coal (average 6%). In comparison, fractions reported in GAINS are 16% for wood and 29% for coal. Analysis of several studies by Winther and Nielsen (2011) found the BC fraction to vary from 10% in wood fireplaces to 15% in wood stoves and 35% in wood boilers. The fraction was much higher for coal at 45%.

The results show that the net impact on climate of heating stoves and fireplaces in both the UK and New Zealand is strongly warming, and black carbon is the most important component of radiative forcing, particularly where consumption of wood exceeds that of coal. A comparison of the BC emissions reported here is made with several international climate models, and is shown in Figure 7-13. The figure also shows projected emissions under different scenarios from RSF combustion until the year 2100. The suffix _calc denotes that BC has been calculated from PM_{10} data. In the UK, most scenarios predict a gradual reduction in BC emissions over the period. However, the GAINS and NAEI data show that after 2004 there has been a significant increase in BC emissions, which will continue until 2025. In New Zealand, all model scenarios suggest a large reduction in BC emissions from 2010 onwards. The BC emissions estimate of this study is approximately 40% higher than the highest estimate made by the PEGASOS model, but significantly higher than all other models. The BC emissions factors used here are similar to that of the GAINS database so it is most likely the activity data which carries the largest uncertainty.

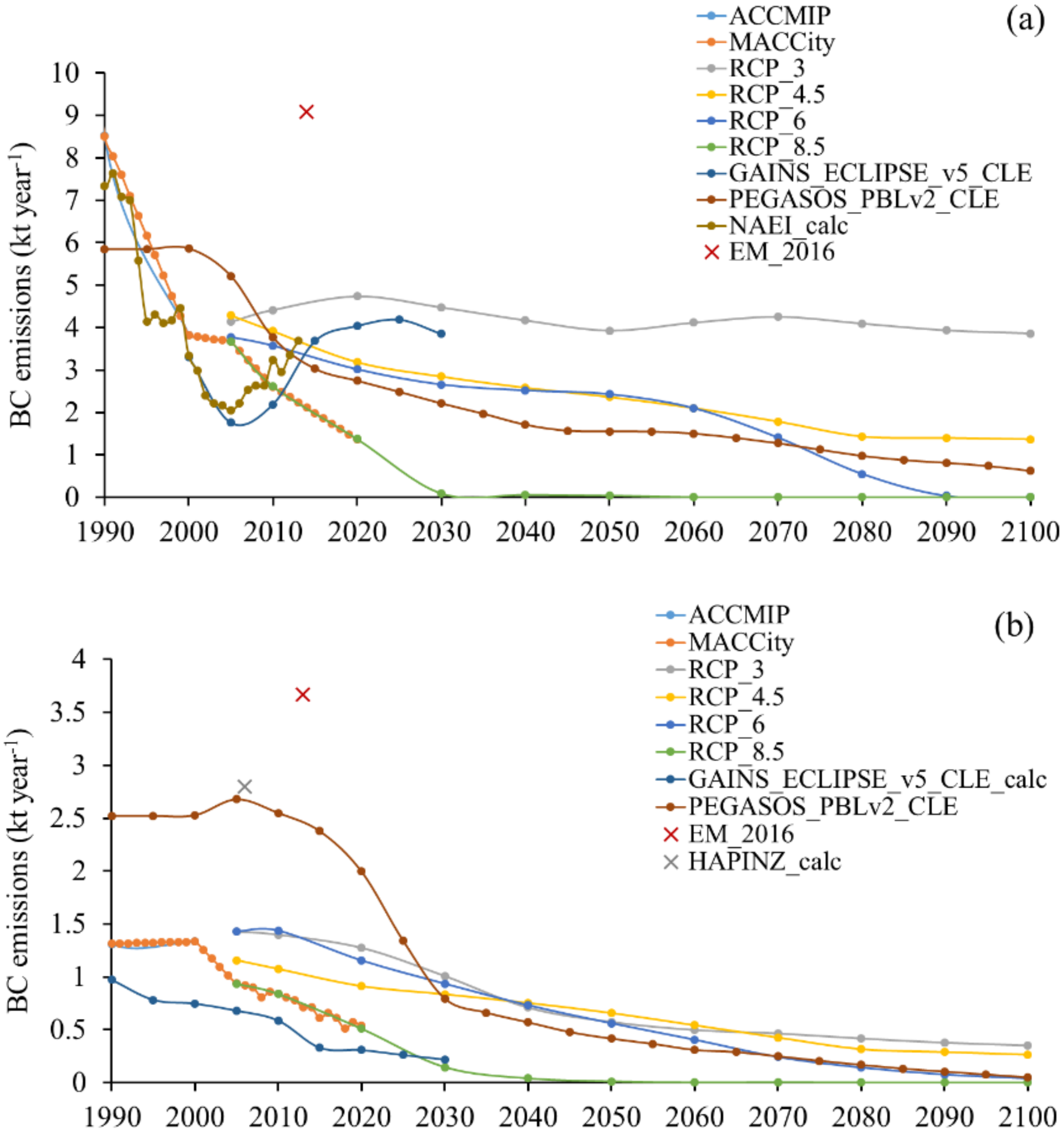

Figure 7-13. Comparison of model predictions of BC emissions from the residential sector in (a) the UK; and (b) New Zealand; for the years 1990 – 2100.

Figure 7-13a also shows that the calculated UK BC emissions are approximately three times higher than most climate models predict. This is in agreement with the findings of the recent DECC Domestic Wood Use Survey, which found that DUKES has previously underestimated wood consumption by a factor of three (DECC 2016a). Denier van der Gon *et al.* (2015) also found that previous inventories in Europe underestimated emissions from wood RSF by a factor of 2-3. If BC emissions were to increase at the same rate as $PM_{2.5}$, as given in the NAEI inventory between 2005 and 2013, then emissions would be over 6.7 kt year^{-1} by 2030; an increase of 84% on 2013 emissions. In context, emissions from passenger cars (UNFCCC section 1.A.3.b.i) were 1.7 kt in 2015, reducing to 0.4 kt in 2030 according to GAINS (ECLIPSE version 5, CLE scenario).

The GAINS model predicts a reduction in BC emissions across most UNFCCC sectors, but an increase in the residential sector (section 1.A.4.b.i). In fact, by 2030 the residential sector accounts for 44% of total BC emissions and 40% of total OC emissions across all sectors in the UK. This is comparable to Denmark, where residential wood combustion is prevalent (Winther and Nielsen 2011). The high contribution of RSF to BC and OC is largely due to increased use of wood in heating stoves as shown in Figure 7-4. The contribution of other technologies in the residential sector to BC, OC and total $PM_{2.5}$ is comparatively low, as shown in Figure 7-14a. In 2025, heating stoves and fireplaces account for 77% of BC emissions, 90% of OC emissions, and 85% of total residential sector $PM_{2.5}$ emissions. This is a result of lower combustion efficiencies, lower MCE and higher emissions factors for small scale biomass technologies. However, larger technologies such as single house biomass boilers (< 50 kW) and commercial biomass boilers (<50 MW) make a larger contribution to NO_x emissions due to higher combustion temperatures and formation of thermal NO_x (Williams *et al.* 2012). As shown in Figure 7-14b, heating stoves and fireplaces account for just 42% of NO_x emissions in 2025.

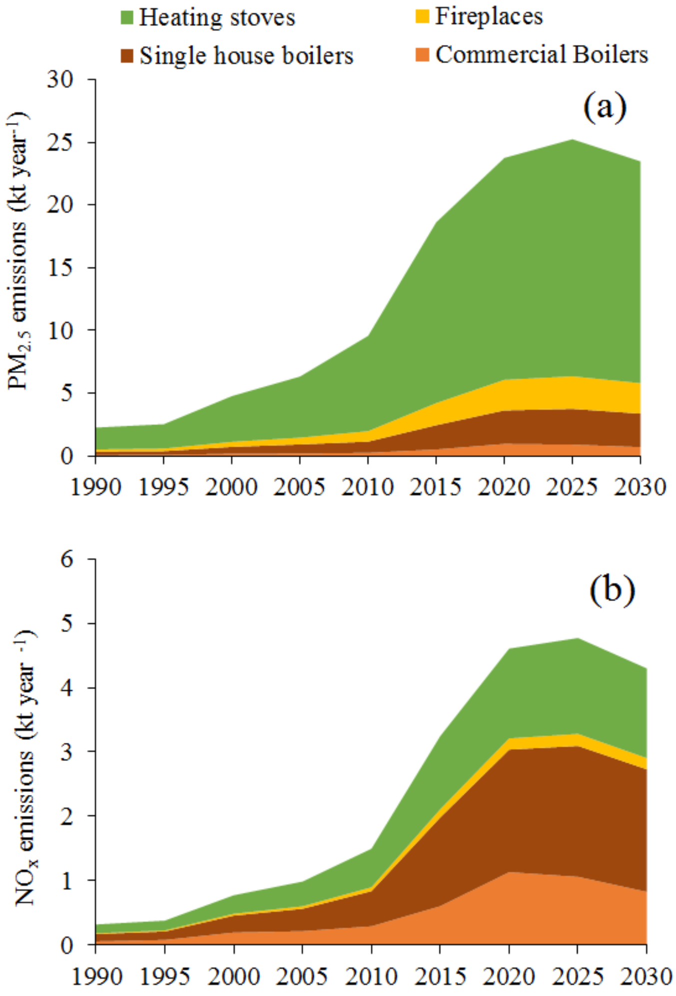

Figure 7-14. Breakdown of UK residential sector emissions from wood combustion by technology for (a) $PM_{2.5}$ and (b) NO_x, according to the GAINS model, 1990-2030.

As discussed in section 7.2.2, there is good comparability between residential heating sectors in New Zealand and the UK in terms of fuel poverty and energy efficiency of homes. However, space heating accounts for a greater proportion of residential energy consumption in the UK than New Zealand. Both average wood consumption per household, and average wood consumption per day are twice as high in New Zealand as in the UK. This may be linked to the limited availability or higher cost of alternative heating fuels, particularly as New Zealand has a large domestic supply of wood, whereas the UK does not and may rely on wood imports in the future. In addition, the climates of the two countries are comparable, but distinct. The latitude of New Zealand ranges from 34° to 47° South, whereas mainland UK covers 50° to 58° North. Being closer to the equator, the far north of New Zealand has a sub-tropical climate and typical winter daytime maximum air temperatures are 12-17°C. The South Island is generally cooler and more mountainous, with maximum winter daytime temperatures of 5-12°C. Average winter daily maximum temperatures in the UK are similar but generally lower, ranging from 5-7°C in northern Scotland to 7-10°C in southern England. Both countries also commonly experience smog episodes during winter anticyclones and atmospheric temperature inversions (Kossmann and Sturman 2004; Milionis and Davies 2008). Such events are typically correlated with lower temperatures and higher emissions from home heating.

The UK also has 60 million more inhabitants and 26 million more homes than New Zealand, and currently 7.5% of UK households burn wood compared to >50% of NZ households (see section 7.2.1). Due to the higher density of housing, small increases in emissions may have a greater impact in the UK. For example, a 1% increase in the number of UK homes burning wood would lead to over 30,000 extra tonnes of wood (dry basis) being burned per year, assuming the factors given in table 7-1.

7.6 Policy Implications

A high degree of uncertainty remains in RSF activity data estimates, due to inherent difficulties in monitoring this highly variable emissions source. Bottom-up inventories using the latest census, survey and sales data hold the potential to reduce uncertainty.

Implications for air quality and health

Biomass burning stoves and boilers have the potential to significantly reduce greenhouse gas (mainly CO_2) emissions from the residential sector, but care must be taken to ensure that this is not done at the detriment of air quality, particularly in the winter time. The UK is facing a number of legal challenges over European air quality breaches. Hence an increase in residential wood burning could impede efforts to reduce national emissions of NO_x, NMVOCs, NH_3, $PM_{2.5}$ and CH_4 through planned revisions to the National Emission Ceilings (NEC) Directive 2001/81/EC. The improvement of emissions inventories for residential wood burning was identified as one of the key areas for improvement in receptor modelling studies and "*substantially more information*" is needed in this area "*before abatement policies can be formulated*" (AQEG 2012).

Although a range of low-emission appliances are available through the RHI, uptake remains low, particularly where there is an option to install a cheaper more traditional wood burning stove. The Ecodesign Regulations in Europe have the potential to increase uptake of such appliances and significantly reduce emissions in the future. The regulations also help to minimise variation between standard test methods across Europe, but significant differences remain internationally such as in standard fuels and sampling methods. Before Ecodesign is implemented, voluntary eco-labelling of new appliances such as Flamme Verte (France), Nordic Swan (Scandinavia) and Burnwise (NSPS, USA) may help to reduce emissions. If emissions from older appliances are to be reduced without replacement, then policies may target fuel switching to pellets/briquettes or pretreated fuels (torrefied biomass or washed wood), as well as 'No Burn Days' and retrofitting of abatement technologies.

Implications for climate change

As described in section 7.2.1, the UK must achieve targets of 12% renewable heat by 2020, 15% total renewables by 2020, and 80% emissions reductions by 2050. In order to achieve this, the Committee on Climate Change (CCC) has developed a series of quadrennial 'carbon budgets' with specific targets enshrined into law. The fifth carbon budget (2015-2035) sets a target of installing 400,000 extra biomass boilers for space heating (not including district heating), equating to 36 PJ and GHG savings of 1.3 $MtCO_2$-equivalent.

Current policy incentivising residential biomass uptake explicitly targets biomass boilers (CCC targets and RHI policy) and there is little or no support for stoves. This is because heat generated must be metered in order to be eligible for RHI payments. A coinciding benefit is that boilers tend to have lower emissions factors than stoves and must meet RHI emissions and efficiency criteria. Consumption of wood pellets is also more easily audited than wood logs, where there is a large 'grey' or informal market consisting of self-sourced fuel and waste wood (Bitterman and Suvorov 2012). However, the DECC Domestic Wood Consumption Survey and subsequent revisions to DUKES highlight the importance of small scale unmetered residential wood combustion (RWC) in the renewable energy mix, as shown in table 7-8.

	DUKES 2014 (year 2013)	DUKES 2016 (year 2013)	DUKES 2016 (year 2015)
Renewable heat	35%	63%	54%
Total renewable energy	5.4%	14.2%	10.7%

Table 7-8. Revised contributions of domestic wood combustion to renewable heat and total renewable energy generation in the UK. Data source: DUKES 2016 Chapter 6, table 6.6, (DECC, 2016a).

The revisions mean that the UK moves from level 3 (RWC <10% renewables) to level 2 (RWC 10-30% renewables), according to European 20-20-20 reporting standards (Bitterman and Suvorov 2012). As a result it is recommended that the UK conduct a RWC survey every 3-4 years instead of 5-10 years and errors in the reporting should be ±10% rather than ±30%.

7.7 Conclusions

Here we present one of the first detailed inventories of black carbon concentrations from RSF combustion in New Zealand. Concentrations were higher than 10 µg m^{-3} in some suburban areas of Christchurch, Dunedin, and Nelson. In comparison, BC concentrations due to wood burning in London are estimated to be 0.17-0.33 µg m^{-3} (see section 2.1). This has significant implications for air quality and climate and serves as an example of the BC concentrations that can be expected in similar sized UK towns and cities, should RSF use in stoves and fireplaces continue to increase without emissions controls. As is the case in New Zealand, residential wood combustion (RWC) may become the largest source of ambient wintertime PM_{10} and BC in the UK. Model predictions show a 14-fold increase in the consumption of wood in the UK residential sector between 1990 and 2030 and heating stoves alone account for 40-55% of this. As a result, emissions of CH_4, NMVOCs, PM_{10}, $PM_{2.5}$ and OC increase significantly and total net radiative forcing increases by 23% between 2010 and 2030. Due to the reduction in coal use and the increase in wood use, black carbon surpasses carbon dioxide to become the most important component of RSF radiative forcing, with wood burning BC alone accounting for over 50% of the total positive radiative forcing in 2030.

A unique bottom-up emissions inventory was produced for both countries using the latest census data for New Zealand and survey data for the UK. One recommendation from New Zealand is that conducting a survey of fuels used for home heating every 3-5 years helps to reduce uncertainty in activity data which is important for renewable energy targets, emissions inventories and air quality and climate models. Activity data was multiplied by emissions factors derived from a critical analysis of 5 inventories, which highlighted the uncertainty in emissions factors in this subcategory. In order to reduce uncertainty in emissions factors, it is recommended that standard test methods be modified to replicate real-world emissions, and in-situ testing be carried out as has been done in New Zealand. More than ten years of research has been conducted on RSF emissions and associated air quality impacts in New Zealand, whereas UK research has largely focussed on other sectors. The relative success of imposing additional emissions limits on wood burners has also been demonstrated, such as in Nelson where PM_{10} and BC are reducing (see section 7.2.3). In terms of BC, OC and climate, a deeper understanding of the impact of ‘brown’ fraction of organic carbon is required, as well as the impact of high SOA formation from aged wood smoke.

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Chapter 8

Optical Properties of Particulate Matter from RSF Combustion

Examination of Combustion Generated Smoke Particles at Source using Different Sampling Methods: Effects on Atmospheric Light Absorption

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Abstract

The role of black carbon particles (BC) in climate change is important and the major sources are from combustion processes. Particles with a higher content of organic carbon (OC) compounds as well as Brown Carbon (BrC) absorb heat to a greater degree rather than reflecting it. The BC/OC ratio is important in atmospheric chemistry. Measurements are often made with samples taken on filter papers from flue gases by thermo or optical methods. Here soot samples are taken from a biomass stove and from model compounds such as furfural and anisole. The Absorption Angstrom Exponents (AAE) are obtained from these samples together with Py-GC-MS information. The results are linked to the combustion of biomass.

Keywords: optical properties, biomass, soot, particulate, Angstrom

This work has been submitted for publication.

8.1 Introduction

The emission of smoke from the combustion of biomass in domestic stoves or cook stoves results in significant environmental problems. This is because the major components are black carbon (BC) aerosol and organic carbons (OC) such as PAH, which together with the Greenhouse Gases are the dominant absorber of visible light [1-6]. The PAH may be condensed onto the soot particles or be present as organic aerosols (OA), or in the vapour phase; tar balls are intermediate between soots and PAH. It has been proposed that BC is the second most important contributor to positive radiative forcing after that from carbon dioxide [3] whilst both BC and OC have a significant health impact [7,8]. The way in which these are produced in the combustion system plays a major role although chemical reactions in the atmosphere play an important secondary role; this paper is only concerned with the role of the combustion processes. The experimental measurement of the extent of emission of BC and OC is often undertaken by means of collection of a portion of the exhaust gases directly on a filter paper or by using a diluted sample in a dilution tunnel.

Samples can be taken above the flue or, in the case of cookstoves or wild fires, immediately above the source before the smoke disperses into the atmosphere. Soot formed by the incomplete combustion of fossil or bio-fuels consists of agglomerated chains of carbonaceous spherules of elemental carbon (EC) with condensed organic compounds (OC). OC is also known as the volatile fraction or solvent extractable fraction. But in certain cases involatile condensed partially combusted cellulose (such as levoglucosan) and lignin components (such as polyphenols) can form organic aerosols (OA) which can play a role [9]. The nature of the soot particle emitted depends on the fuel being burned, the conditions under which it is formed [3,7-10] and the post-flame conditions. Newly-formed soot results from the combination of molecules approximately the size of pyrene which may be either planar ('protographenes') or non-planar ('protofullerenes'); these can continue to grow by surface growth via ethyne or PAH species depending on the flame environment. Later in the flame the soot particles age and anneal [11,12], agglomerate and as the post-flame cools, become associated with condensed hydrocarbon species such as large PAH [11] and unreacted sugars, their amount depending on the degree of completeness of the gas phases combustion.

The major problem arising from the combustion of biomass is the use in small combustion units rather than large power plant where careful combustion control and flue gas treatment reduces smoke emissions. Fixed bed combustion undergoes three phases of combustion, initial ignition and flaming combustion stage mainly of the pyrolysed volatiles, and then via a transitional stage through to a smouldering phase. The flaming stage produces BC and associated soot-forming PAH precursors, the transitional and smouldering phases produces largely CO together with brown carbon (BrC). Brown carbon is defined as the light absorbing fraction of organic carbon aerosols, such as tar-like biomass decomposition products resulting from the pyrolysis of incompletely combusted biomass material trapped within the core of the burning biomass.

On a global scale, the largest source of BC is open burning of forests and savannas together with cook stoves in Africa, India and Asia [3]. Here flaming phase combustion combines with brown carbon from incompletely combustion biomass such as trees; this is not the case with grasses. Another major source comes from the developed countries in North America, Northern Europe and New Zealand. Each of these combustion systems undergoes different combustion characteristics. Here again the sources are from flaming phase combustion during initial lighting and from re-loading of the fuel. Much depends on the fuel particle size; pellet burners using automatic feeding together with some aspect of flue gas clean-up produce lower levels of all pollutants.

Current atmospheric radiative models include contributions from both black carbon and organic carbon. BC is the dominant absorber of visible light although the term BC is subject to various interpretations [4,5]. In these models OC was treated as purely scattering but it can absorb at shorter visible and UV wavelengths due to the presence of brown carbon (BrC) [6]. Brown Carbon results from the incomplete combustion of cellulose decomposition products and largely arises from uncontrolled burning of biomass in bush or forest fires. But it is also produced from biomass stoves, especially cookstoves. Atmospheric radiation models use the parameters single scattering albedo (SSA) and absorption angstrom exponent (AAE) and these contain information on aerosol absorption [2,6]. They are obtained by making measurements in the atmosphere using filter paper sampling or optical attenuation measurements. It has been suggested that SSA and AAE can be parameterized based on the modified combustion efficiency (MCE), the ratio of [CO_2]/[CO and CO_2] which is effectively a measure of incomplete combustion. However Pokhrel et al. [6] have provided evidence that EC/OC provides a better correlation.

Although optical diagnostic methods have been widely used a number of methods have been devised to measure EC/TC (BC/OC) both from samples taken at source from the flue gases or the environment [9,10,14-17]. Basically there are two methods: analysing samples which have been collected on filter papers or by using *in situ* optical methods which are usually laser based. Collected soot samples have been analysed by thermo-gravimetric means coupled with analysis of the released organic compounds, or by solvent extraction, or by optical means using the filter paper samples. In the present experiments samples are taken from the flue gases from a single burn (batch) stove and collected onto a filter paper in a sampling system. Some samples were obtained from a diluted flue gas which had been diluted by a factor of 12 in a dilution tunnel. In addition samples of soot were collected directly onto holey carbon coated electron microscope grids.

8.2 Experimental Methods

The major source of the samples was a fixed bed stove (Waterford Stanley Oisin) rated as having a maximum non-boiler thermal output of 5.7 kW and has previously been described [9]. The stove was mounted on an electronic balance to give the mass rate of burn. Wood and straw were used as fuels. Total particulate matter (PM) in the flue gases was determined using a gravimetric method which required sampled gas passed through a preconditioned Munktell 360 Microquartz filter paper, with a second one used as a backing filter paper. The gas was taken via a heated line at 125°C and passed through the filter papers which were in a heated block at 70°C. Three repeat measurements were taken during the flaming phase for each fuel and the average taken. Some measurements were made using a dilution tunnel. All filter papers were stored in a desiccator for 24 h prior to measurement using a TGA for pine soot or by a thermos-optical method undertaken by Sunset Laboratories Inc. for straw.

Secondly samples were obtained from a wick burner using model wood pyrolysis products, namely, furfural and anisole and also soot from n-decane. The wick burner is not an ideal combustor but is the only way of burning high boiling point liquids and was operated under carefully controlled combustion conditions previously described [16]. The wick burner soot samples were collected directly onto a glass filter surface held at 20cm above the flame.

The Absorption Angstrom Exponents (AAE) of the filter papers were determined using a Perkin Elmer Lambda 950 UV-Vis-NIR Spectrophotometer over the range of 400-1200nm. The Absorption Angstrom Exponent is defined as:

$$b_{abs} = a\lambda - AAE$$

where b_{abs} is the absorption coefficient and the constant, ‘a’, is independent of wavelength. For small spherical soot particles AAE equals 1. The constant ‘a’ is dependent on the thickness of the absorbing sample.

Thermogravimetric analysis (TGA) was used to measure the OC, EC and ash fraction fractions as previously described [9] for the pine samples, and a thermo-optical method (-undertaken by Sunset Laboratories Inc. for the straw samples. Py-GC-MS was used in conjunction with sequential temperature pyrolysis for detailed analysis of the OC. The chromatograms were assigned on the basis of the NIST Mass Spectral Library Database, from previous literature and by known retention times [9]. Soot sampling was undertaken directly onto the TEM grids, by impaction. The holey-carbon film grids were inserted into the flue for a measured time between 1-3 minutes depending on sample location and loading. The soot samples we examined by a FEI Titan3 Themis transmission electron microscope (TEM) operating at 80kVand fitted with a Gatan One-View CCD and Quantum ER electron energy loss spectrometer. Care was taken such that electron energy loss spectroscopy (EELS) was conducted at the sample orientation independent angle [17], and on a region of sample entirely over a hole in the carbon film filling the area of the selected area aperture to eliminate any carbon signal from the TEM support grid.

8.3 Results

8.3.1. Results from filter experiments

Samples of soot were obtained from the combustion of pine and straw under three stages of combustion, and from furfural and anisole burning on a wick burner and collected on a filter paper. Fig. 8-1 shows a typical example of absorption spectrum of Pine wood soot in the wavelength range of 400 to 1200nm. Using Originlab software, the absorption spectrum was fitted with an exponential function described in eqn (1) to determine the AAE value. This procedure was ultilised to determine AAE values for various samples. Thicker samples show band spectra for PAH and possible nitro-phenols.

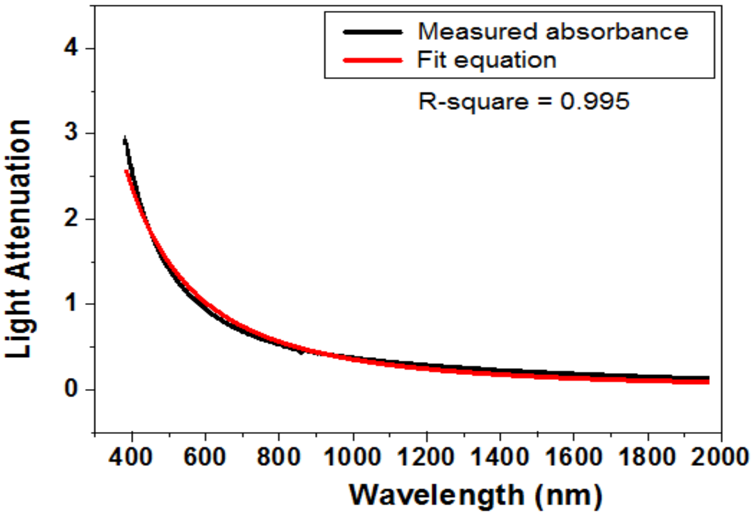

Figure 8-1. Typical Absorption Angstrom Exponent determination (Pine wood soot)

The Absorption Angstrom Exponents were calculated from equation (1) and are summarised in Table 8-1 together with the colour of the filter deposit, the modified combustion efficiency, MCE (the ratio of [CO_2]/[CO and CO_2]) and the values EC/TC.

It is seen the value for AAE for anisole, an aromatic compound which gives a ‘pure’ soot, is 1. Furfural which produces more oxygenated OC has a slightly higher value (1.2) consistent with previous experiments. The values for flaming combustion for wood is close to unity but for smouldering combustion the values are higher, again consistent with the formation of brown carbon [15-18].

Fuel	AAE	Colour of the filter	Modified combustion efficiency (MCE),	EC/TC
Anisole	1.01	Fluffy black	1	0.98
Furfural	1.18	Black	1	0.98
Pine wood, flaming	0.99	Black	0.93	0.5
Pine wood, transition	1.91	Brown	0.65	0.3
Pine wood, smouldering	3.33	Yellowish	0.63	0.1
Barley straw, flaming	0.51	Black with blue-grey tinge	0.79	0.78
Wheat straw, flaming	1.16	Grey-brown	0.87	0.26

Table 8-1. Summary of the Absorption Angstrom Exponent, and sample properties

8.3.2. Results from Py-GC/MS Experiments

Earlier work, particularly from diesel emissions, suggested that all the PAH was associated with the soot particles largely because samples taken on filters collected both the soot together with some surface PAH as well as condensed high molecular weight PAH. It is now believed that much of the latter is in the form of organic aerosols (OA). Identifications are given here of PAH collected on filters from the combustion of pine and straw in a stove. The major species types and some of the species identified in the OC [17, 18] are shown in Table 8-2.

Pyrolysis Temp °C	Wood Stove: using pine	Anisole	Furfural
400°C	Methoxyphenols methyl-furans, levoglucosan, sugars	Alkanes, aromatics phenanthrene; fluoranthene;: pyrene,	Alkanes, oxygenates including carboxylic acids and esters
500°C	Phenols, methyl phenols, furans, methoxyphenols dimethoxyphenols, anisole	2-4 ring aromatics from HACA	No significant peaks Methoxyphenols, traces of carboxylic acids
600°C	Traces of organic acids, aldehydes; aromatics, methyl phenols	No significant peaks	No significant peaks

Table 8-2. Major Species types identified in the Soot Organic Carbon Fraction.

8.3.3. Microscopy Studies of Soot Samples Extracted from the Flame Gases from Pine Combustion

TEM photographs obtained from the combustion of pine in the stove are shown in Figs 8-2 to 8-4. It is seen from Figs 8-2 and 8-3 that soot produced from the flue gases for both flaming and smouldering combustion are not significantly different. Particle size studies using a DMS instrument showed that are 20 nm and 100 nm particles present in a bi-modal distribution.

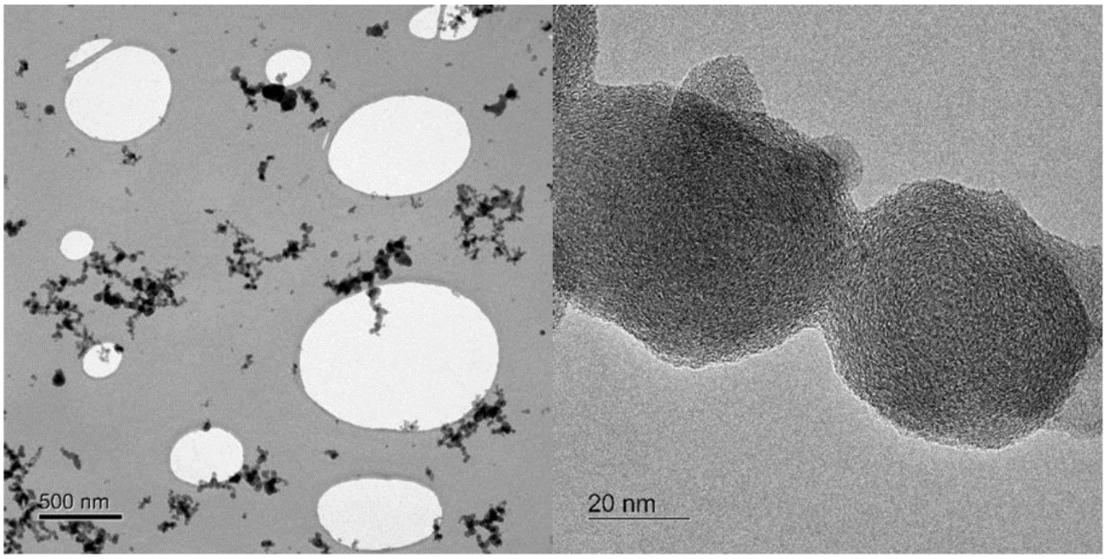

Figure 8-2. Pine soot: flaming phase, flue gas sample.

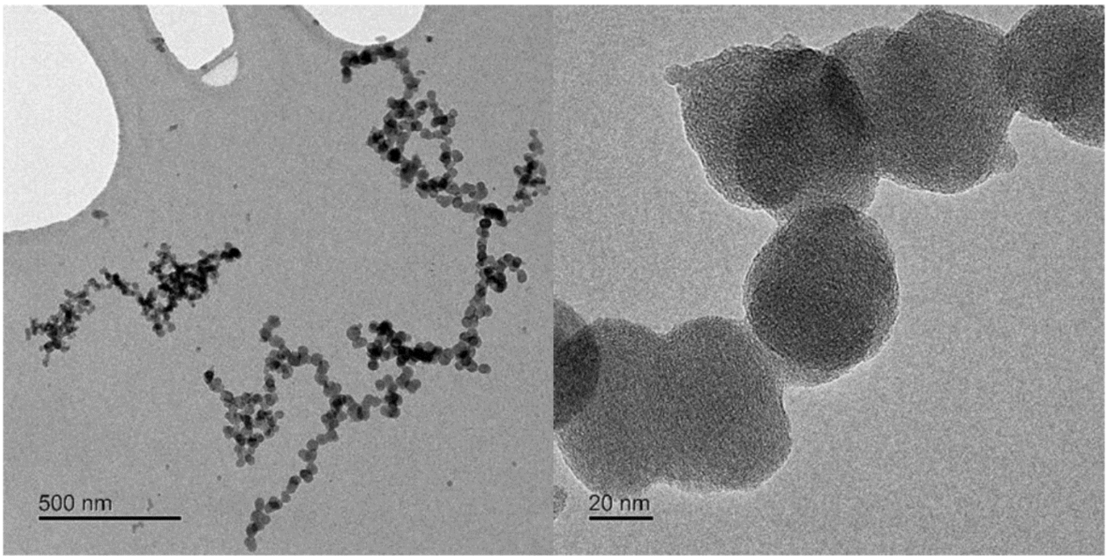

Figure 8-3. Pine soot: smouldering phase, flue gas sample.

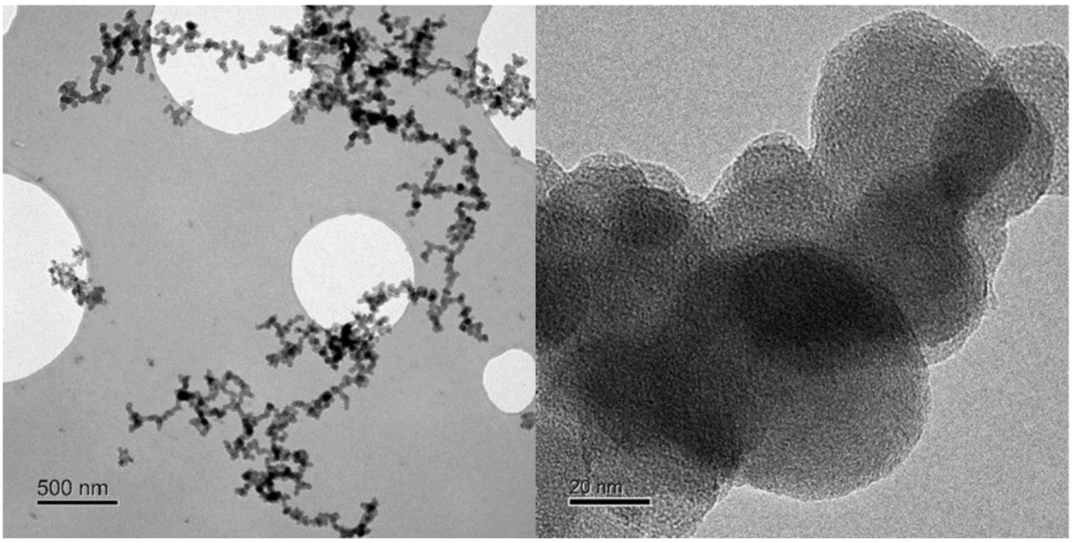

Figure 8-4. Pine soot: flaming phase, dilution tunnel sample.

If a dilution tunnel is used with a dilution factor of 12 there is increased branching and agglomeration of particles in the dilution tunnel (see 500 nm scale images) compared to freshly emitted particles. Clearly the degree of agglomeration is not just a feature of the combustion process but the process of dilution of the flue gases that is always present in combustion systems [19]. Electron energy loss spectroscopy (EELS) analysis of the structures of the soot samples were made, and the results for SP^2 and C:O are given in Table 8-3. It is seen that a distinct nitrogen peak was found for the samples, increasing for the smouldering case. The dilution tunnel has a marked effect on the sizes of the soot chains, these samples also show increased oxygenation and the SP^2 content is slightly lower for dilution tunnel samples.

	%SP^2	C (%)	N (%)	O (%)
Flaming	66.5 (n=10)	93.3 (n=8)	1.3 (n=8)	5.4 (n=8)
Smouldering	64.3 (n=8)	92.4 (n=7)	1.7 (n=7)	5.9 (n=7)
Dilution tunnel	60.5 (n=10)	88 (n=4)	1.6 (n=4)	10.4 (n=4)

n = number of spectra used to generate each average value in the table

Table 8-3. Summary of the EELS results.

The presence of both O and N in soot [20,21] and PAH is known [22,23] but not usually included in soot forming models. Newly formed soot and PAH have abundant free electrons that enables them to react with both O$_2$ and NO present in the flame zone under appropriate reaction conditions. The oxygenated interface promotes wetting via OC. Nitrated phenols are a significant constituent of biomass burning secondary organic aerosol. They contribute to the light absorbing fraction of organic carbon (brown carbon) [23]. But the major contribution is from PAH [11,24-28] which is discussed later.

8.4 Discussion

As a consequence of the adverse effects of smoke resulting from the combustion of biomass extensive studies have been made of the influence of both domestic fires and wild fires on both the local environment and the global climate. Most of this work has been directed towards atmospheric pollution and the consequences, and less has been directed towards investigations of the source, the combustion processes, and means to control the problem.

Much is now known about the mechanism of formation of soot largely based on studies of the combustion of hydrocarbon fuels in the gas phase [11,27,28]. As shown in Fig. 8-5 the volatile PAH first formed consists of lower MW PAH soot precursors which arise from the primary radical products from cellulose such as acetylene, the HACA route [27,28], or react through CPDyl. Other devolatilisation products of the fuel may also be present, for example, the resinous constituents of coniferous wood may be converted into marker compounds including retene (1-methyl-7-isopropylphenanthrene). Biomass soot formation includes a major route from lignin decomposition which forms large amounts of oxygenated compounds such as methoxyphenols such as eugenol.

Soot formation from larger particles of biomass in bed combustion is complicated by the heterogeneous nature of the fuel if the particle size causes non-uniform temperatures, that is, it is sufficiently large to be controlled by heat transfer (if the Biot number is large). This is not an important issue during the flaming phase of combustion which occurs mainly in the gaseous phase but is significant during the smouldering phase in fixed (and fluidised) bed combustion and wild fires. This will determine the extent of the emission of BC but particularly influence the nature of the OC released and the relative amount to BC.

In typical hot flames in combustion appliances the cellulose decomposes to give species that can enter the HACA route to soot together aromatic derived species from lignin that readily generate soot precursors. The soot forming mechanism is given below in Fig. 8-5. It should be noted that the formation of Brown Carbon would form an additional route which involves incomplete combustion because of the fuel particle size.

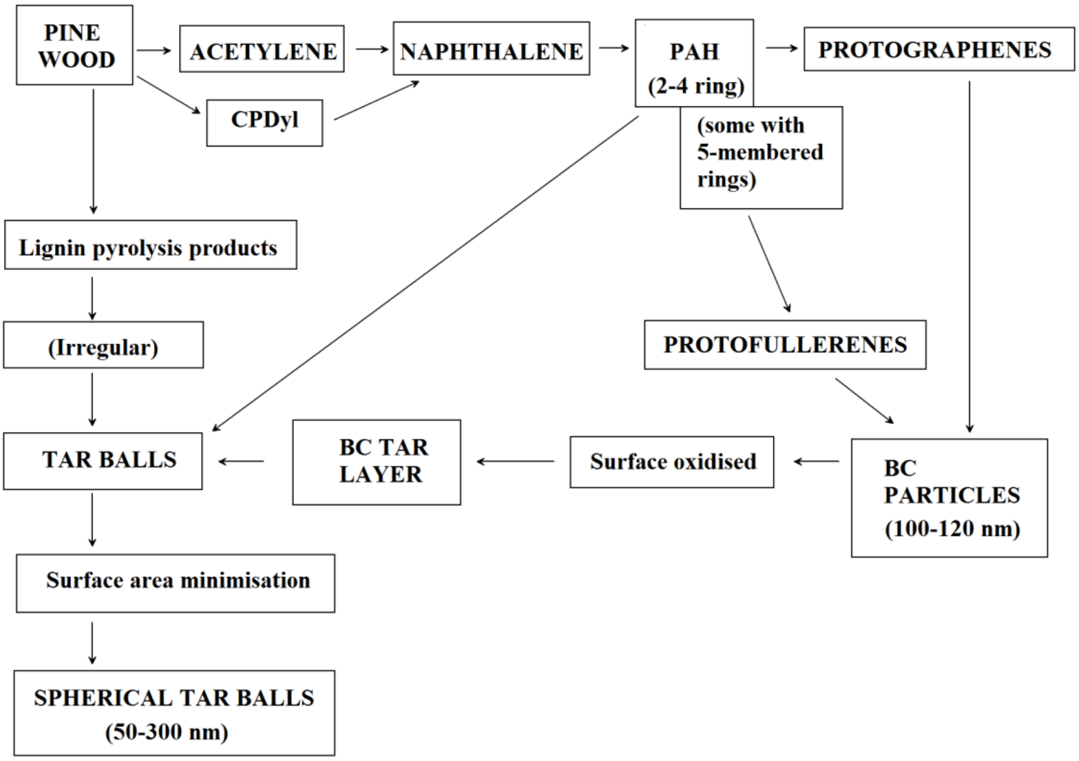

Figure 8-5. Outline mechanism of the formation of soot and tar balls.

The values obtained for AAE in Table 8-1 may be related to the degree of incomplete combustion as given by MCE, that is the amount of organic compounds lost but these can include readily volatile/ gaseous species such as low molecular weight aldehydes which are in the gas phase and are readily oxidised. The other option is to relate AAE to EC/TC (or to (TC-EC)/TC) and this has a more realistic meaning since (TC-EC) refers to non-volatile material remaining on the filter paper. In order to fully interpret this knowledge of the range of OC produced during the combustion process is required, and this is done in some cases [18, 24]. We have previously classified these compounds into three classes of material as constituents of soot or BC: weakly-bound material, easily thermally desorbed, and extractable by solvents; more strongly-bound material less easily desorbed; and finally highly developed soot [18].

Brown Carbon consists largely of independent particles of large molecular weights formed by incomplete combustion and will be collected by filter paper sampling. The question arises as to the relationship with EC/TC. It is likely that Brown Carbon consists of two classes of components, largely sugar-derived pyrolysis products arising from the incomplete combustion of cellulose and large PAH compounds including some nitro-polyphenols. The former being formed from partially pyrolysed biomass in the centre of large biomass particles mainly during the smouldering phase-from which the partially reacted products can escape. The second group result from the reaction of some of the large stable PAH with nitric oxide or dioxide in the flame zone. Further reactions occur in the atmosphere.

The values of EC/TC depend on the way in which they are determined, in particular whether they are measured by purely gravimetric methods, part-optical/part gravimetric or entirely optical using laser techniques such as ATOFMS or related techniques. Previously we have used an ATOFMS [29] for investigation of EC/TC ratio in both wood smoke and model fuels. In this method C_nH_y peaks with three or more carbon atoms and low hydrogen content are assigned to EC like polymeric carbonaceous fractions, while C_nH_y peaks with higher relative hydrogen content are assigned to fragmented organic compounds, or more "OC-like" polymeric fractions. We have also obtained [29] EC/TC values for burning wood using ATOFMS. For softwood, these values were: 0.61 during flaming combustion and 0.62 during smouldering combustion. Values obtained for model compounds are similar as those obtained in other studies as described in reference [29].

In the present work we report values of EC/TC for flaming and smouldering conditions (Table 8-1) obtained using filter paper sampling where there is a significant difference between the values for flaming and smouldering conditions. Other studies, for example [30] also show that when using the filter sampling method there is a significant difference between 'good' combustion, that is, in flaming combustion, and 'poor' combustion, that is, in smouldering combustion and cases where the large size of the fuel causes internal pyrolysis prior to combustion.

This is in contrast to the ATOFMS methods and is clearly linked to the fact that the filter paper sampling method collects the entire sample, i.e. carbonaceous particles together with inherent PAH as well as independent OC, the amount depending on the filter temperature [18]. The ATOFMS method measures only the inherent PAH and consequently there is a similarity between EC/TC for both flaming and smouldering since the soot forming reactions are the same in both, as in Fig 8-5.

In summary, pine wood soot consists of a carbonaceous core surrounded by a layer of high molecular weight PAH used as building bricks for the growth of the particle. Other PAH molecules with lower boiling points may condense on the core depending on the temperature in the exhaust gases and may evaporate off when in the atmosphere over a period of time. The total amount of PAH available to be involved in the condensation and re-evaporation processes depends on the availability of oxygen and the degree of mixing. Since this varies at least in fixed bed combustion during the flaming phase and the smouldering phase because of the different volatiles release mechanism (homogeneous verses heterogeneous) there is scope for a more active means of combustion control. Firstly by using pre-treated fuels such as torrefied fuels [9] with an optimised structure (pelleted particles), better control of fuel/air ratio, as well as the placement of the air supply.

However there is another issue and that relates to the optical properties of the BC in the environment and this is indicated here by the Absorption Angstrom Exponents. This is largely due to Brown Carbon and whilst this can be minimised by the methods outlined above, much of this is formed by uncontrolled wild fires and here the only method of control is by reducing them.

8.5 Conclusions

1. The mechanism leading to the formation of black carbon is a fairly well established gas phase route and is linked to the volatile content of the fuel and to the combustion of cellulose.
2. Brown Carbon is optically different to BC and the mechanism of formation is due to low temperature pyrolysis in large particles of biomass.
3. Lignin produces a range of PAH including large molecules which can form OA
4. The values of EC/TC depend on the method by which they are measured, this has implications in climate models: the optical effects (AAE) depend on a combination of 2 and 3.
5. Whilst soot chains are formed in the combustion gases their exact structure is dependent upon further flame gas quenching or dilution processes.

8.6 References

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Chapter 9

Emissions from Improved Cookstoves

Emissions from Improved Cookstoves in Sub-Saharan Africa

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Summary and justification

Residential solid fuel (RSF) combustion incorporates both heating and cooking sectors and although the focus of this thesis is on heating stoves, serious consideration should also be given to cooking. Exposure to biomass smoke in developing world households is a serious health concern and a number of studies and organisations have trialled stove replacement programs with improved cookstoves. Recent evidence (Mortimer et al., 2017) has suggested that the use of improved cookstoves does not reduce health impacts to the extent that laboratory testing suggests. Therefore, there is a need to better understand and characterise the emissions from improved cookstoves and their impacts. In this work, emissions testing was carried out on three improved cooking stoves typically used in Africa. These included a wood stove, a charcoal stove and a gasifier-type stove. Online measurements were made of particle size distribution and composition using a DMS, SP^2, AMS and total gravimetric method. Gas composition was measured by online FTIR yielding information on emissions relevant to both health (CO, NO_x, SO_2, VOCs) and climate (CH_4, CO_2, N_2O). This work is currently being written up for publication so the below is a short introduction to the topic, together with some of the key results obtained and discussion of how the results link to the preceding chapters of this thesis. The principal investigator for this project was Professor Dominic Spracklen and the experimental work was carried out by the author in collaboration with Y. Ting and J. Allan from the University of Manchester, UK.

9.1 Introduction

Currently 2.7 billion people worldwide rely on solid biomass fuels for cooking and 1.2 billion people are without access to electricity. Exposure to biomass smoke during cooking is among the top 10 risks for worldwide burden of disease (Romieu and Schilman, 2013). According to IEA model projections, nearly all regions across the world show a reduction in the number of people without access to clean cooking facilities between 2014 and 2030, with the exception of Africa (IEA, 2016b). Here, the figure increases from 793 million to 823 million people as population rise outpaces the switch to clean cooking. Africa also has the greatest share of residential energy derived from solid biomass out of all regions, including southern Asia, with an estimated 628 gigatonnes of biomass consumed in African cookstoves in 2015 (IEA, 2016a).

$PM_{2.5}$ and NO_x emissions across Africa are projected to increase by 15% and 50% by 2040 according to the IEA's New Policies scenario, thereby failing the UN Sustainable Development Goal 7 on clean cooking. The NO_x increase is driven principally by the transport sector, but cookstoves account for around half of the increase in $PM_{2.5}$ (IEA, 2016a). Cookstoves also account for approximately 30% and 70% of global black carbon and organic carbon emissions respectively (Bond et al., 2004), although there are strong regional differences. For example, cookstoves in Africa account for approximately 70% and 80% of BC and OC emissions. Such high regional emissions can not only affect local air quality but also regional meteorology (Wang et al., 2014) and climate (MacCarty et al., 2008). There is also growing evidence that organic carbon emissions contribute to light absorption as well as scattering in the atmosphere. OC coatings also affect the optical properties of emitted internally mixed black carbon particles, through coatings and lensing effects (Liu et al., 2015, Saliba et al., 2016)

RSF fuel types used in developing countries consist mostly of hardwoods and charcoal, but also dung cake, agricultural residues and a growing number of briquettes (Qi et al., 2016). Fuel types used are largely location-dependent. For example in Uganda, 86% of rural households use mainly firewood for cooking whereas just 15% use firewood in urban areas, where charcoal is preferred (UBOS, 2010). Average daily consumption of firewood and charcoal in Maputo, Mozambique was estimated at 5.5 kg day^{-1} and 2.7 kg day^{-1} respectively (Brouwer and Falcão, 2004). This is significantly lower than the wintertime wood consumption for heating stoves; 7.1 kg day^{-1} and up to 20 kg day^{-1} in the UK and New Zealand respectively (see chapter 7). Despite a smaller amount of fuel being consumed, the health effects of RSF combustion in developing countries is far more significant than in developed countries due to direct exposure to air pollutants in an indoor environment (Anenberg et al., 2013).

Fuelwood use in cookstoves is unsustainable in many areas of Sub-Saharan Africa, including Uganda where additional forest plantations may be required to meet demand sustainably (Zanchi et al., 2013). The rate of deforestation across Africa is four times the world average and 40% higher than in South America, with African forest area reducing at an average rate of 2.8 million hectares per year (FAO, 2016) – an area the size of Equatorial Guinea. Charcoal production is often inefficient with typical yields ranging from 8-20% (Yonemitsu et al., 2014, Girard, 2002). The charcoal industry is also unregulated in many areas and there is anecdotal evidence of a "charcoal mafia" system, which threatens conservation efforts in regions such as the Democratic Republic of Congo. Inefficient charcoal production is a major source of methane and VOCs which have implications for atmospheric chemistry and climate (Adam, 2009, Bailis et al., 2005). Emissions factors for charcoal production can be far in excess of those of burning the end product, as shown in Table 9-1.

	Retort kiln [a]	Earth mound kiln [b]
CO_2	3024 - 4132	1058 - 3027
CO	122 - 149	143 - 333
NMVOC	6.65 - 9.35	60.1 - 124.0
CH_4	19.7 - 84.3	32.2 - 61.7
PM	7.7 - 10.7	25.0 - 41.2
NO_x	0.73 - 2.47	0.021 - 0.130
N_2O		0.068 - 0.30

Table 9-1. Emissions factors (g kg^{-1} charcoal produced) for selected pollutants during the production of charcoal from mixed wood in A: improved retort kilns (Sparrevik et al., 2015) and B: traditional earth mound kilns (Pennise et al., 2001)

9.2 Materials and methods

9.2.1. Fuel sources

A commercially available Namibian charcoal was used with the Gyapa stove, which meets the standard requirements for barbeque charcoal in the UK (BS EN 1860-2:2005). The improved wood stove was operated with two hardwoods and a straw. The hardwoods were dry willow (*Salix sp.*) and dry and wet oak (*Quercus robur*). The straw was grain-free wheat (*Triticum sp.*). Willow and oak sticks were similarly sized, with diameters ranging from 2mm to 26mm and length ranging from 89-181mm. The LuciaStove was operated with wood pellets were 6mm in diameter with a maximum length of 23mm. Characterisation of the fuels is presented in Table 9-2. The nitrogen content of the oak fuels (0.7-1.1%) were higher than previously used samples which have a lower bark content. The oak and willow used here were sticks and branches and therefore had a higher NO_x content.

Fuel	% db				% ar	% db basis			CCV
	C	H	N	S	MC	VM	FC	Ash	MJ/kg db
Oak (dry)	50	5.8	0.7	0.04	5.1	87.1	11.5	1.4	19.929
Oak (wet)	50.5	5.78	1.09	0.06	27.9	82.1	16.3	1.6	20.196
Willow (dry)	47.4	6.2	0.4	0.04	5.6	82.6	15.7	1.7	18.902
Wheat Straw	50.3	5.5	0.5	0.06	12.0	70.0	14.2	3.7	20.002
Charcoal	76.72	1.73	0.59	0.04	3.1	16.0	70.7	13.4	28.227
Wood pellets	50.68	5.97	0.18	0.02	6.5	85.5	14.1	0.4	20.178

Table 9-2. Characterisation of the fuels used in the cookstove project.

9.2.2. Cookstove appliances

Three ‘improved’ cookstove designs were tested; a charcoal stove, a wood stove and a pyrolytic stove, as shown in Figure 9-1. Gyapa is a widely used fuel-efficient charcoal stove which originated in Ghana. Almost 500,000 units have been sold across Africa (www.gyapa.com). Gyapa features a 50mm thick ceramic liner and raised grate designed with 20mm air holes and a 105mm door used to vary primary air supply. CarbonZero is an improved rocket-type wood cooking stove which uses over 50% less firewood compared to the traditional threestone fire (www.co2balance.com). Trials have taken place in Kenya, Tanzania, Rwanda and Uganda. The ceramic liner is thicker than the Gyapa stove at 78mm and the 150mm fuel/air inlet has no primary air control. A 60mm high metal fuel feed support was used in this opening. The final stove is the LuciaStove (http://worldstove.com/stoves) which was tested with wood pellets. A firelighter (typically kerosene) is used to ignite the top of fuel bed, which causes a pyrolysis front to move down through the bed, releasing vapours. The volatile gases are pushed through a lower ring of holes and drawn up the side of the fuel bed before being re-injected and combusted in a gas-like ring flame. Due to this process, not all of the fuel is fully combusted. A nitrogen-enriched biochar remains which may be useful as a fertiliser and as a form of carbon sequestration. A number of LuciaStove designs of varying size and complexity have been developed and one of the simplest and smallest designs has been used here. Trials have been conducted in Ethiopia, Zambia and others which show a good performance against a standard TLUD design.

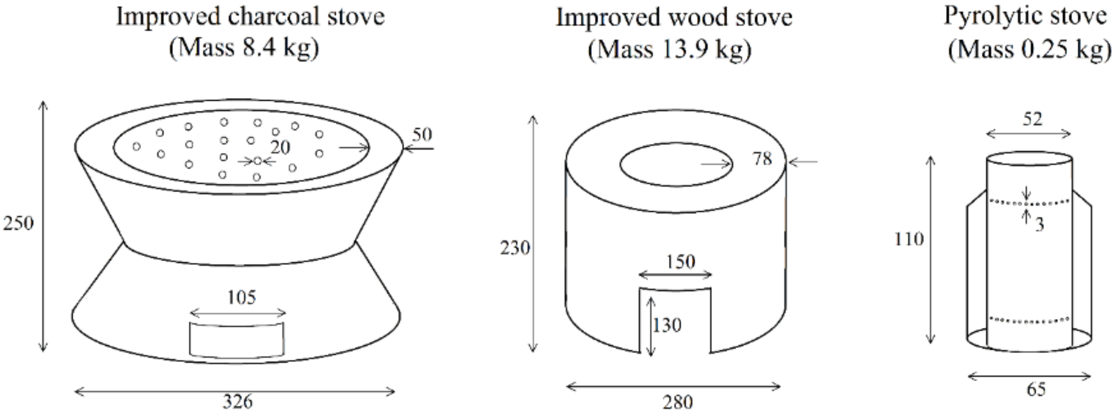

Figure 9-1. Dimensions of the stoves used in the study (not to scale)

9.2.3. Combustion and emission experiments

The test assembly used was modified for cookstove testing from that used previously for heating stoves (see chapters 3-6). Each cookstove was placed on a heat-resistant surface atop an electronic platform scale (Kern DE 300K5DL). Combustion tests were carried out inside a custom-made firebox, measuring 750mm by 750mm with a height of 1330mm. The firebox was designed to provide symmetrical inflow of air through 130mm high inlets, which permits axisymmetric entrainment of air to the bed and to the diffusion flame/hot gases above the main combustion zone. A 1m flue section, 125mm in diameter, allowed for sampling of the primary combustion products. Sampling at this point represents the pollution to which a user would be exposed standing directly above the cookstove. The smoke generated was then drawn into a dilution tunnel (200mm diameter) and mixed with ambient laboratory air, simulating ambient concentrations to which neighbours and passersby would be exposed. The static pressure and flowrate in the dilution tunnel was fixed for each test and the dilution ratio (measured by the difference in CO concentration) varied from 3-6 depending on the appliance type and combustion conditions. The experimental setup is shown in Figure 9-2.

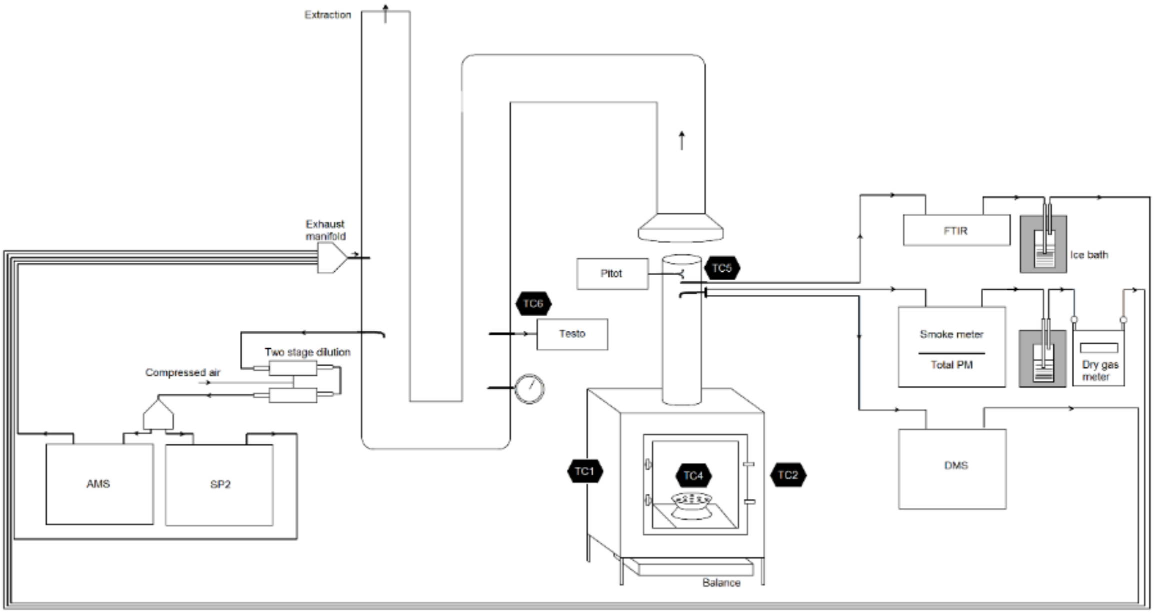

Figure 9-2. Schematic showing experimental set-up

Details of the gas and particle analysers are given in Chapter 3. Sampling for the DMS, FTIR and gravimetric PM were conducted in the flue, pre-dilution. Sampling for the Testo, AMS and SP2 were done in the dilution tunnel, post-dilution. Two Dekati DI-1000 diluters utilising compressed air were placed in series before the AMS and SP2, giving a three stage dilution effect.

The thermocouples (TC1-6) were redeployed to measure temperatures of the flue gases and firebox. TC4 was placed above the centre of each cookstove to measure the temperature to which a cooking pot would be exposed. Note that no cooking pot was used in the experiments as is done in the water boiling test.

9.3 Results

Here are presented a short overview of some of the key results from the study. Results are presented in depth in an article which is currently being written up for publication.

9.3.1. Stove performance indicators

Stove performance can be assessed by the power input, fuel consumption and useful temperature output. These are presented in Figure 9-3 and Figure 9-4. Despite the power output of the Lucia WorldStove being a lot smaller than the other stoves, a temperature of over 500°C was maintained at the pan supports for almost an hour. The average burning rate was just 50 g hour^{-1}. whereas the average burning rates for charcoal, wet oak and dry oak were 0.32, 0.67 and 1.06 kg hour^{-1} respectively.

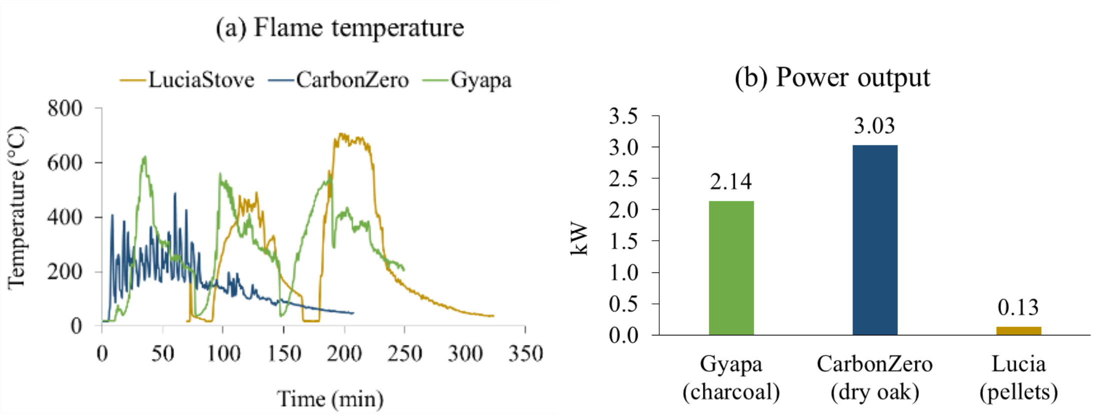

Figure 9-3. A) Temperature variation at the pan supports for the three stoves. B) Average power outputs for each stove.

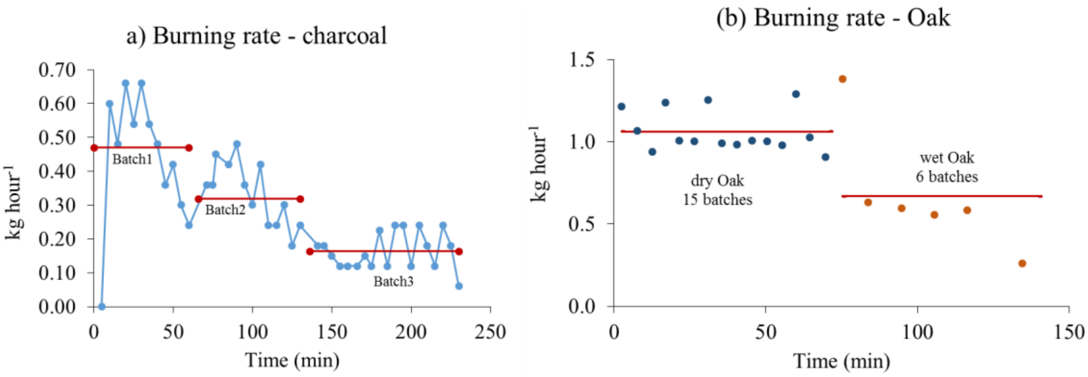

Figure 9-4. Burning rates of the Gyapa charcoal stove and the CarbonZero wood stove

9.3.2. Comparison of emissions factors

The temperatures, burning rates and fuel types had a large impact on the emissions factors across all of the tests. As in previous chapters of this thesis, an attempt was made to standardise emissions to STP and a reference oxygen concentration of 13%, using the correction factor $(21-O_{2,ref})/(21-O_{2,meas})$. However, as shown in Figure 9-5, the oxygen concentration rarely falls below 18-19% for any cookstove, whereas the heating stove reaches as low as 10%. This is due to substantial dilution with ambient air entrained from the open base of the firebox. Therefore the oxygen correction methods are no longer possible because the correction factor is far too at concentrations close to 21%. Hence results presented here are given at the measured oxygen concentration.

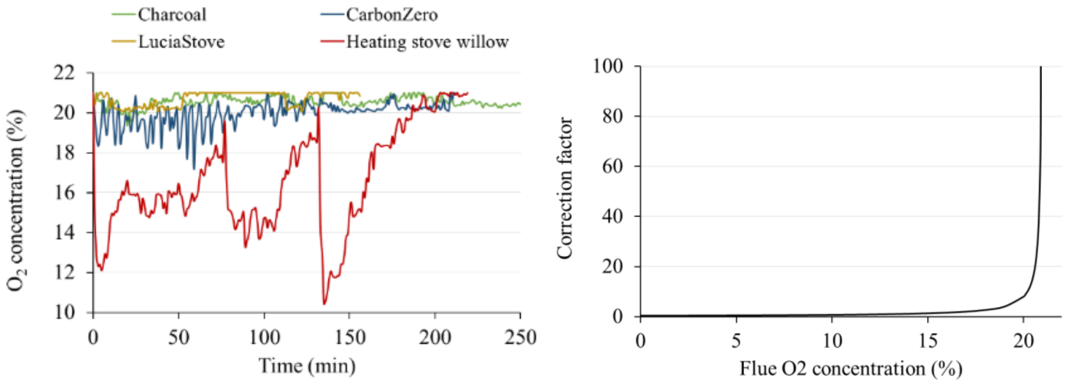

Figure 9-5. Flue gas oxygen concentrations for the different stoves and calculated oxygen correction factor.

Pollutant concentrations and emissions factors showed the same dependency on combustion conditions as in previous work (flaming, smouldering and MCE), as shown in Figure 9-7 and Figure 9-6. Emissions of NO and SO_2 are strongly correlated with flaming combustion and high burning rates, whereas CO and CH_4 are correlated with smouldering and low MCE. However, due to the regular reloading of the wood stove appliance, the duration of the smouldering phase was not as long as in previous work using a multifuel stove. The most striking change in the CarbonZero stove oak emissions profile is when wet wood (>27% MC) was used rather than dry wood (<6% MC). A reduction in NO_x emissions was offset by a two-fold increase in methane emissions. Despite this, peak CH_4 and CO concentrations were far higher for charcoal than for wood. As described in chapters 2 and 4, CO emissions are proportional to the carbon content of the fuel and PM emissions are proportional to the volatile content. Burning charcoal instead of wood reduces emissions of and exposure to PM but this is offset by a three-fold increase in CO emissions.

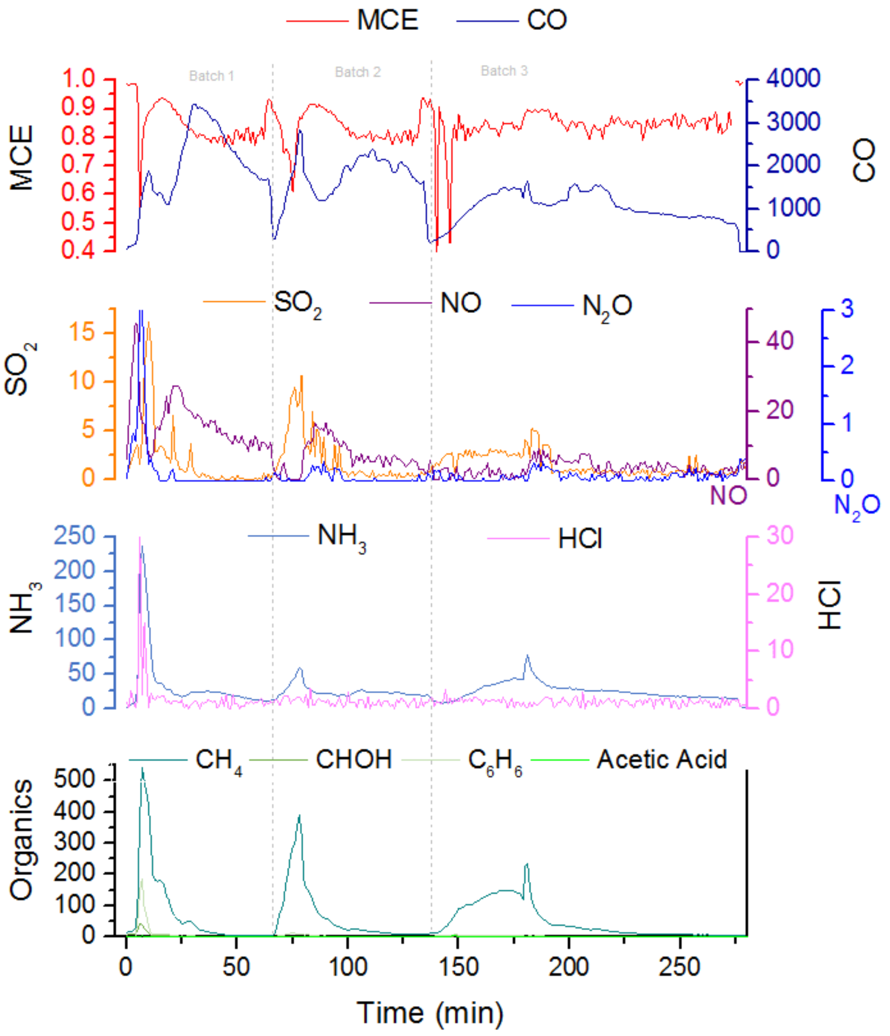

Figure 9-6. Emissions profile for the Gyapa stove burning charcoal.

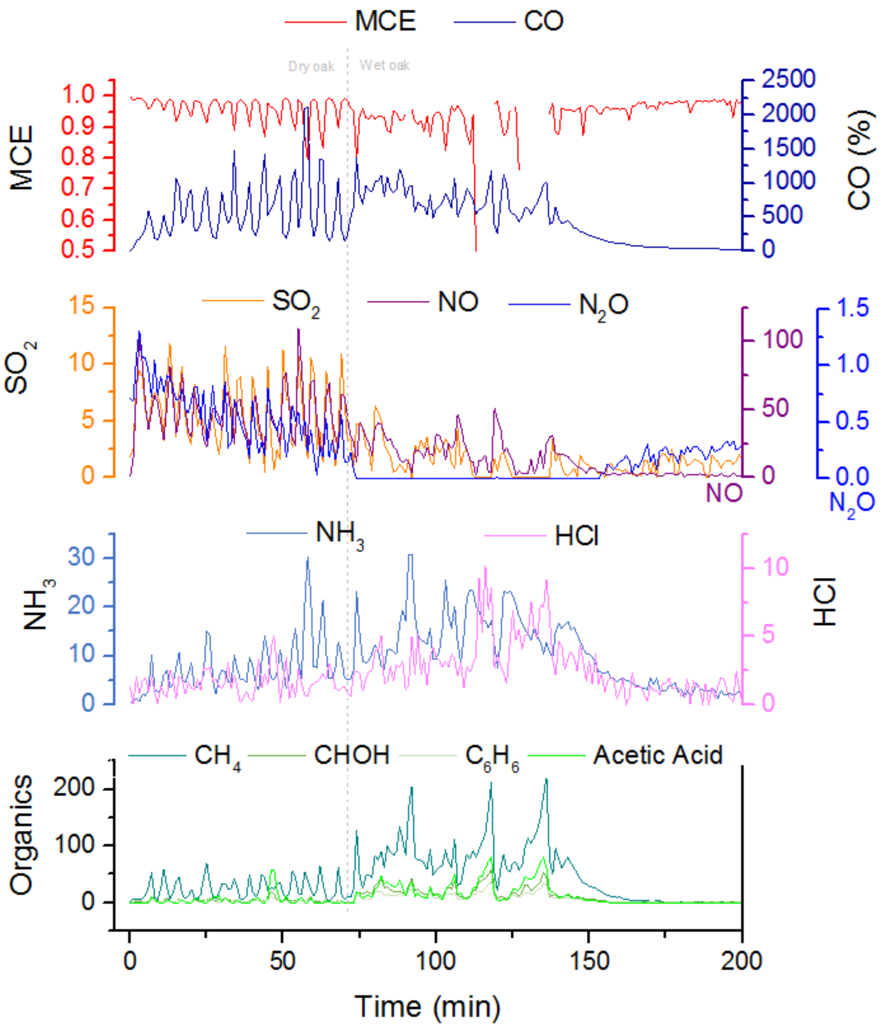

Figure 9-7. Emissions profile for the CarbonZero stove burning dry and wet oak.

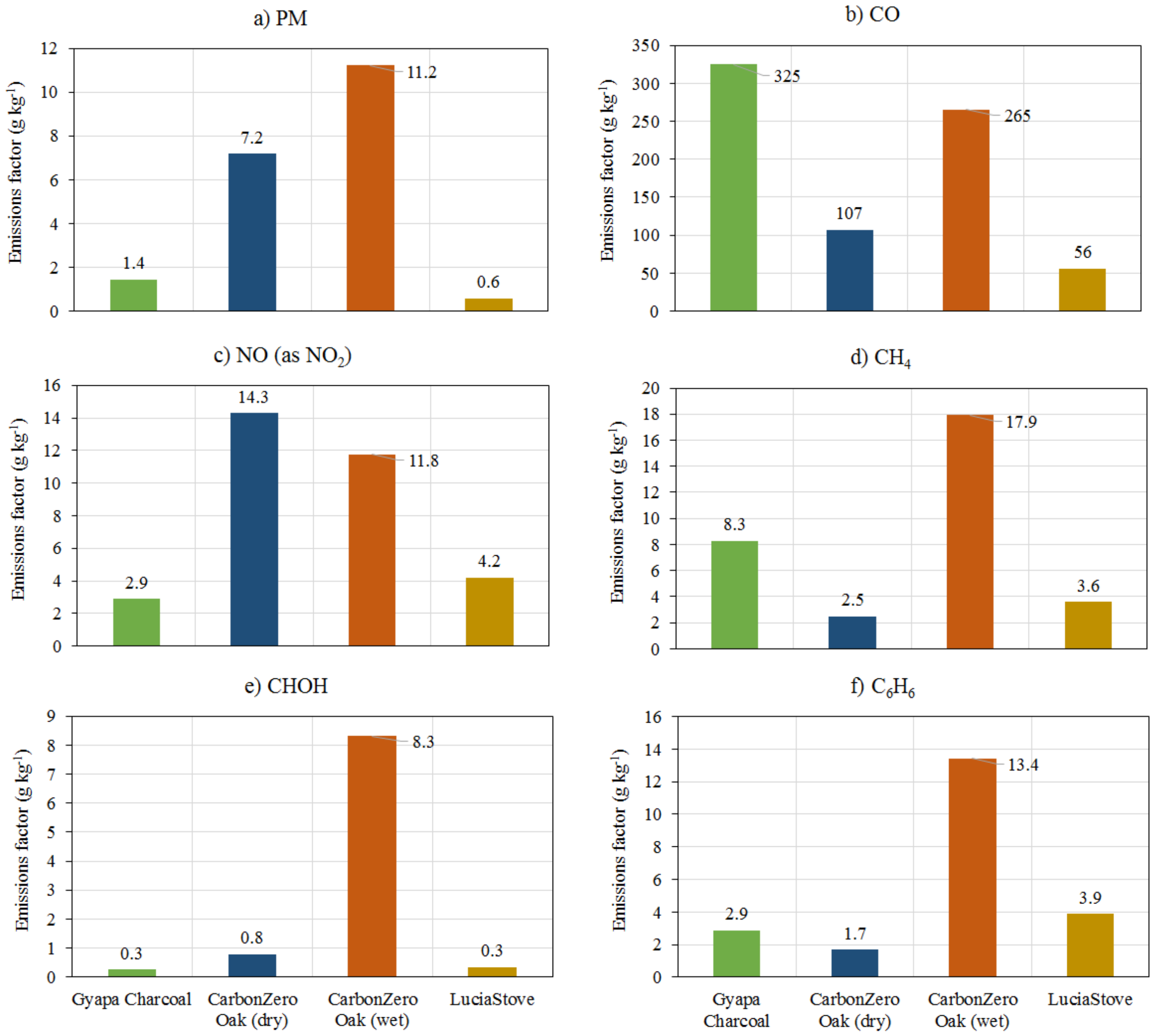

Figure 9-8. Emissions factors for charcoal, dry wood, wet wood and the gasifier stove.

Results showed that emissions factors of methane, formaldehyde and benzene were a factor of 2-10 higher for wet wood than for dry wood burned in the CarbonZero stove. The dry wood had the highest emissions of NO (14.3 g kg^{-1}) which is similar to the emissions factors of other high nitrogen fuels such as peat (see chapter 4). The charcoal stove sowed far lower emissions of PM, NO and formaldehyde than the wood stove, but emissions of CO and CH_4 were significantly higher. The Lucia WorldStove had the lower emissions factors for nearly all pollutants due to the higher efficiency of the gas flame.

9.3.3. Particle size distribution and composition

Particle size distribution in the range 6-1000 nm was measured using a differential mobility spectrometer (DMS) as described in chapter 3. Analysis of the results revealed a dependence of particle size on fuel type and stove type, as shown in Figure 9-9. Each series represents an averaging time (sec for [a] and min for all others) with the combustion cycle of a single batch of fuel.

The DMS results reveal a biomodal particle size distribution for dry wood with peaks at 20 nm and 105 nm. The time series show that the relative height of these peaks are determine by the sampling period within the combustion cycle. During char burnout, the smaller 20 nm particles dominate whereas during flaming combustion the 105 nm dominate. This is confirmed by the charcoal particle size distribution which has a single, skewed, particle size distribution at 20 nm. Data from the SP2 and AMS confirmed that the 105 nm particles are primarily carbonaceous soot particles and over 90% of the BC was emitted during the flaming phase. Organic matter (OM) dominates during the smouldering phase but were not observed on the DMS due to the high temperature (180°C).

The particle size distribution for wet wood burning was an intermediate between the bimodal distribution for wet wood, with a geometric mean in the range 30-40 nm. Large peaks were observed in the OM content of the particles generated from wet wood burning, which correlates well with a drop in the MCE and temperature, as well as an increase in the CO and CH_4 emissions.

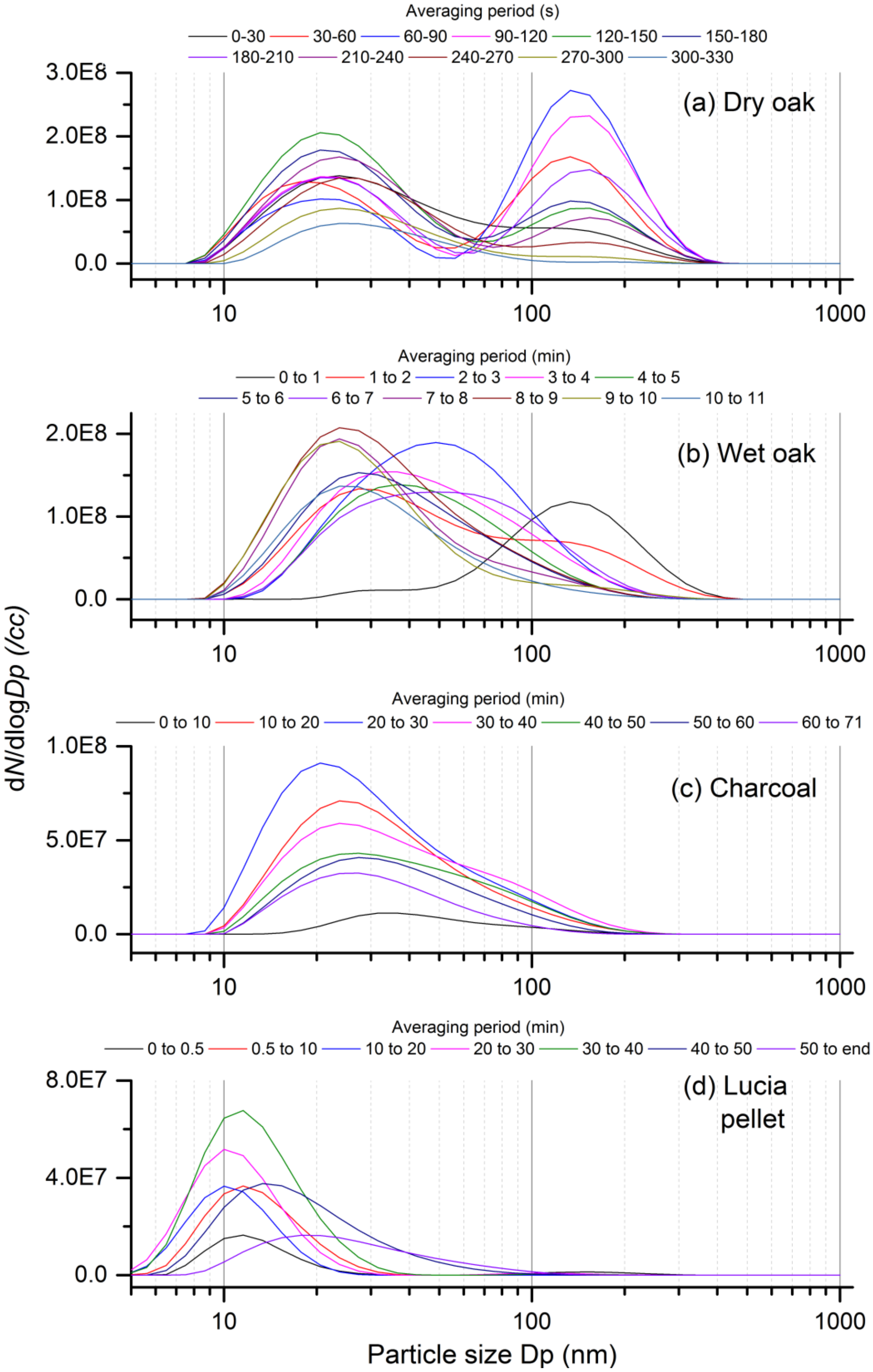

Figure 9-9. Particle size distributions for dry oak, wet oak, charcoal and the Lucia stove.

9.4 Conclusions

- RSF burning in cookstoves poses a greater health burden that RSF burning in heating stoves due to higher exposure in the indoor environment.
- IEA projections show an increase in $PM_{2.5}$ emissions from cookstoves in Africa without stove interventions, but recent evidence has shown such interventions are not achieving the health benefits that are required.
- Evidence is presented from the emissions testing of improved African cookstoves, using a test assembly designed by the author which was modified from earlier work described in this thesis.
- It was found that wood fuel emits the highest levels of PM and wet wood emits high levels of organics and methane.
- Compared with dry wood, using charcoal reduces PM emissions by a factor of 5 but increases CO emissions by a factor of 3
- Gasifier-type stoves emit the lowest levels of all pollutants and was the most effective use of fuel i.e. the flame was sustained for longest with the smallest fuel input

9.5 References

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Chapter 10

Overview and Discussion

10.1 Emissions inventories and source apportionment (Aim 1)

Emissions factors and total emissions rates have been compared and contrasted between 4 commonly used inventory databases (NAEI, IPCC, EMEP and GAINS), as well as 7 future model scenarios, and the results are discussed in chapter 7. Considerable gaps and uncertainties were identified between the inventories, particularly for trace metals, PAH and chlorinated species. Emissions factors of $PM_{2.5}$, NO_x and CO varied by a factor of 1.9, 2.4, 3.4 between inventories and the NAEI (2013) consistently showed the lowest EFs. A unique emissions inventory was also produced using EFs reported in the literature. The inventory features over 110 pollutants from over 50 studies and reports wide variations in emissions factors depending on appliance type and fuel type. The average values are reported below in chapter 10.2, along with a comparison of measured values.

Emissions from heating and cooking are often seen as a problem only in developing countries. Although it is true that indoor exposure is often higher in these regions, leading to severe health impacts, ambient air quality can be equally poor during cold periods in wealthier nations. Evidence of the impact of RSF combustion in developed nations has been assessed through a review of source apportionment studies. Over 105 studies from 31 countries have measured the contribution of RSF burning to ambient PM_{10}, $PM_{2.5}$, BC, OC and PAH. These are reported in Table 2-6. The contributions are very high in some areas such as Switzerland, New Zealand and the rural USA, often accounting for over 90% of $PM_{2.5}$. These locations can serve as examples of the air quality impacts that may be expected in similar sized UK towns and cities, should wood burning in inefficient stoves and fireplaces continue to increase.

10.2 The impact of fuel properties on emissions (Aim 2)

In this work, an emissions testing laboratory was set up and developed for RSF fuel and appliance testing. Emissions testing has been carried on using a domestic 6 kW multifuel stove. No other heating stoves were used here in order to assess the impact of fuel properties on emissions with the appliance variable kept constant. However, additional cookstove appliances have been tested (see chapter 11.5) which provide useful information for heating stoves. For example, the emissions reduction potential of gasifier stoves.

10.2.1 Fuel properties

The impact of fuel properties on emissions has been evaluated as described in chapters 4 and 6 and the preceding sections of this chapter. A full list of fuels tested is given in table (3-1) and includes characterisation of over 35 fuels. The key properties influencing emissions factors are the levels of nitrogen, sulphur, chlorine and potassium. The latter affect fuel reactivity (Qin and Thunman, 2015). High nitrogen fuels such as waste wood and peat lead to high NO_x emissions factors and high sulphur fuels such as coal and MSF lead to high emissions on SO_2, depending on the level of CaO blended into the fuel which may bind S into the ash fraction. The quantity and composition of the fuel volatile fraction is the most important factor in PM emissions factors. As detailed above, heat treated fuels with low volatile contents such as torrefied fuel, charcoal and smokeless fuels have reduced sooting tendencies and therefore lower PM emissions factors, although there is an increase in CO emissions. Inorganics in the bark may also affect combustion properties and the merits of de-barking wood fuels is described in Chapter 6. Generally, increased bark contents increase emissions of PM, VOC and CO and increase the risk of ash melting (Filbakk et al., 2011, Qin and Thunman, 2015). Typical barks contents in this work ranged from 7.1% for spruce to 25.4% for oak, depending on age and location of the sample within the tree.

Generally the emission factors are similar between wood types, which is consistent with previous studies (Kistler et al., 2012, Orasche et al., 2012). Larger differences are apparent between hardwoods, softwoods and herbaceous biomasses due to differences in lignin composition and inorganic constituents such as potassium and silica. The potential of novel RSF fuels such as torrefied material and agricultural residues (chapter 6) have been assessed. Torrefied spruce briquettes had 38% lower PM emissions, 40% lower NO_x emissions and 13% lower CO emissions than traditional seasoned hardwood logs. Khalil et al., (2013) found even more substantial emission reductions using torrefied material. PM_1, CO and OC emission factors were reduced by factors of 2, 1.5 and 3 respectively for torrefied spruce compared to raw spruce. The study found increased NO_x emissions from torrefied material compared to non-torrefied material, which is linked to the increased fuel nitrogen content. The reduction observed in Chapter 4 may therefore be due to the comparison of hardwood with torrefied softwood, which has a lower fuel-N content, so further work should be conducted to evaluate the impact of torrefaction on NO_x emissions.

Chapter 6 found that the high silicia, chlorine, sodium and ash fraction of reeds and straws lead to sintering at relatively low temperatures compared to wood fuels. Reed also showed high PM and NOx emissions and a high ash content and is therefore unsuitable for residential applications. Work is ongoing to assess the potential of other agricultural residues including wheat straw, barley straw, miscanthus and sugarcane bagasse, but characterisation results show promising properties compared to reed. A number of issues were identified during the briquetting of these fuels, largely due to the low density. Briquette size and density varies significantly between feedstocks, both commercially made and laboratory made, as shown in Figure 10-1. Commercial systems are usually extrusion based large hollow briquettes or ‘synthetic logs’. Laboratory made briquettes were formed using a mechanical press and die as described in chapter 3.

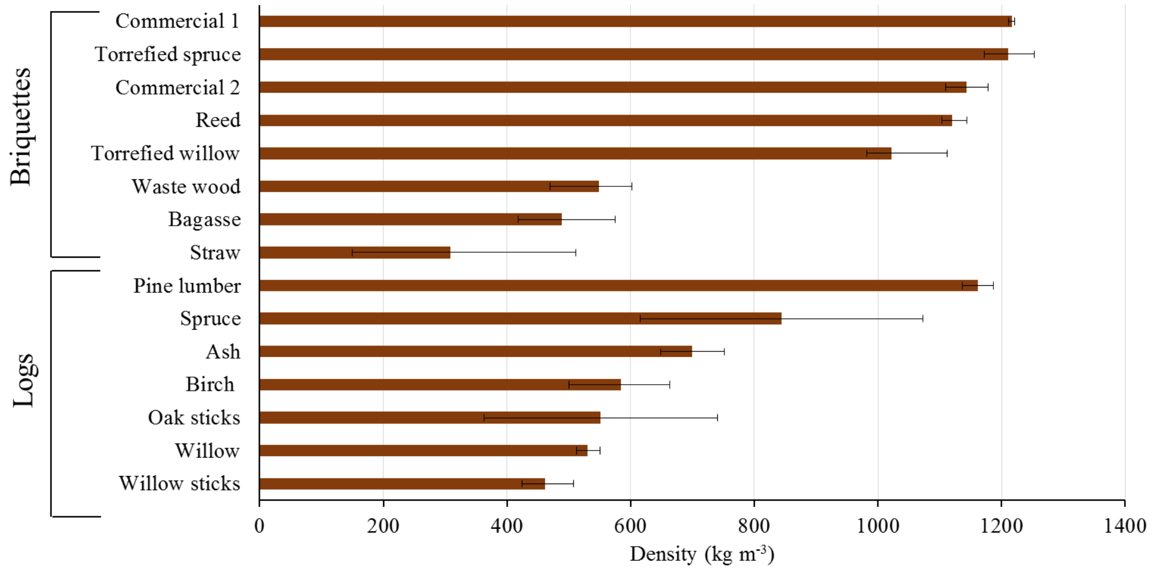

Figure 10-1. Density measurements for biomass fuels

The commercially made extruded sawdust briquettes or ‘synthetic logs’ were in the range 1000-1200 kg m^{-3}, whereas the density of the mechanically pressed waste wood, straw and bagasse briquettes was halved. The log fuels had densities ranging from 500-850 kg m^{-3}, with the exception of pine lumber which had a density similar to that of extruded briquettes. This may be why the PM emission factors observed in appendix 2 were lower for pine. Higher density materials have higher thermal conductivities (Mason et al., 2016) but delayed release of volatiles and ensuing soot formation.

Standards exist for the specifications of wood logs and wood briquettes. For the former, BS EN 14961-5, is concise and primarily focussed on log moisture and size. The latter, BS EN 14961-3, is more detailed and sets requirements for the size and composition of the briquettes, as detailed in Table 10-1. The standard also requires that additives be stated, which may include binders such as wheat, corn and potato starch as well as slagging inhibitors or combustion aids.

Studies have shown that briquettes manufactured from agricultural residues have great potential as a cost-effective fuel replacement for more highly emitting fossil fuels such as coal (Rezania et al., 2016). Briquettes and manufactured solid fuels also reduce emissions of $PM_{2.5}$, EC, OC and CO by 90% or more compared to raw fuels when burned in cookstoves, thereby reducing exposure and health impacts of RSF combustion (Li et al., 2016).

Property	Requirement
Diameter	To be specified
Moisture	≤ 15% (ar)
Ash	≤ 3% (db)*
Density	≥ 1000 kg m^{-3}
Additives	≤ 2% (db)
NCV (ar)	≥ 14.9 MJ kg^{-1} (ar)*
N	≤ 1% (db)
S	≤ 0.04% (db)
Cl	≤ 0.03% (db)
As	≤ 1 mg kg^{-1} (db)
Cd	≤ 0.5 mg kg^{-1} (db)
Cr	≤ 10 mg kg^{-1} (db)
Cu	≤ 10 mg kg^{-1} (db)
Pb	≤ 10 mg kg^{-1} (db)
Hg	≤ 0.1 mg kg^{-1} (db)
Ni	≤ 10 mg kg^{-1} (db)
Zn	≤ 100 mg kg^{-1} (db)

*variable depending on wood source

Table 10-1. Requirements for wood briquettes under BS EN 14961-3: 2011

Life cycle impacts are also considerably lower than traditional fuels, as the feedstock is a by-product and does not require additional land or put strain on forestry resources (Wang et al., 2017). However, evidence presented here (chapter 6) and in the literature shows that there may be increased NO_x and SO_x emissions for certain feedstocks compared to wood logs and briquettes so more research is required in this area to identify optimal feedstocks (Roy and Corscadden, 2012).

10.2.2 Moisture content

Despite advice to the contrary, many wood fuel users burn improperly seasoned wood with a high moisture content (>20%). According to a recent survey, one quarter of users store wet logs for less than the recommend 12-24 months to allow for sufficient drying (Wöhler et al., 2016). From the literature, emissions factors of carbonaceous aerosols can be up to a factor of 5 higher for wet wood versus dry wood (Magnone et al., 2016). This was confirmed in this work (Chapter 9) where experiments were conducted burning wet (>30%) and dry (<10%) oak. It was found that adding wet wood causes an immediate drop in temperature and increases in emissions factors of PM, CO, methane, formaldehyde and benzene by factors of 1.6, 2.5, 7.2, 10.4 and 7.9 respectively. There is also a change in the NO/NO_2 ratio which has implications for air quality. There are also higher emissions of OC and PAH by a factor of up to 4. Evidence from the literature suggests that the relationship between MC and PM is typically parabolic as shown in Figure 10-2.

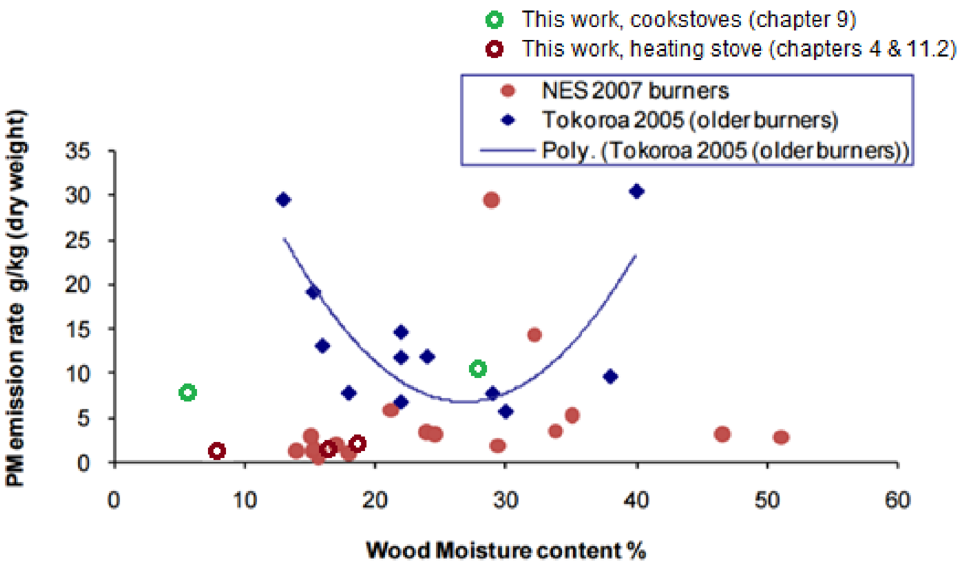

Figure 10-2. Relationship between PM emissions factors and wood fuel moisture content. Source: (Wilton and Bluett, 2007).

High MC promotes low temperature combustion (250–500°C) where methane, aldehydes, methanol, furanes and aromatic compounds such as BTX and phenols are emitted. The duration of this low temperature phase increases with increasing moisture content (Koppmann et al., 2005). Conversely, extremely low MC promotes rapid devolatilisation and vapour combustion which promotes the formation of elemental carbon (soot) particles in greater numbers from the mechanisms outlined above.

10.2.3 Gaseous emissions

Nitrogen Oxides

It was found that NO_x emissions were linearly dependent on the fuel nitrogen content across multiple fuel types. The highest nitrogen contents were observed in peat turf (2.5% db), coal (1.9%) and high bark wood fuels (1.1%) fuels which had the highest NO_x emissions (2.1-2.6 g kg^{-1}, 7.4 g kg^{-1} and 9.0 g kg^{-1} for hardwood, coal and peat respectively). These values were higher than the literature inventory averages, 1.3 g kg^{-1}, 4.7 g kg^{-1} for hardwood and coal respectively (see figure 2-5). The results suggest that the NAEI database values (0.88 g kg^{-1}, 3.56 g kg^{-1} and 0.62 g kg^{-1}) may be underestimated.

The key factor in NO_x emissions formation is the fuel-N. Of 17 biomass types reported by Kistler et al. (2012), very few had a nitrogen content above 0.3%, resulting in NO_x emissions factors of 1-2 g kg^{-1}. However, pine needles were found to have a fuel-N content of 0.9% and a NO_x emissions factor of 2.3 g kg^{-1} (132 mg MJ^{-1}). It is hypothesised in Chapter 4 that all NO_x formed is from conversion of the fuel nitrogen due to the low temperatures observed. However, emissions testing of beech logs (0.2% N) in a larger 30 kW boiler (Orasche et al., 2012) resulted in maximum NO_x EFs of 10.2 g kg^{-1} (668 mg MJ^{-1}). Given the low fuel-N content, this suggests NO_x formation by other means. Thermal NOx formation requires temperatures of 1300°C or more but the bed temperature is these experiments rarely exceeded 800-900°C as shown in figure 9-3 (Glarborg et al., 2003). The final possible NO_x formation route is the prompt NO_x mechanism whereby atmospheric N_2 reacts with fuel-derived CH radicals, forming HCN and NO (Williams et al., 2012). However, this mechanism is not thought to play as significant a role in NO_x formation from biomass combustion as it does from fossil fuel combustion (Van Loo and Koppejan, 2007). An estimated fuel-N to NO_x conversion factor of 0.23-0.55 is reported and the excess air ratio and temperature were found to have a greater impact on NO_x formation than fuel-N (Skreiberg et al., 1997). Hence a detailed modelling study is recommended in order to corroborate results obtained here. NO_x emissions typically consist of 90% NO and 10% NO_2 which was confirmed in this work (Chapter 4). For coal, wood and most other fuels the NO_2 constituted less than 5% of the total NO_x measured by the Testo. Later measurements using FTIR were confounded by an interference of NO_2 spectra with hydrocarbons and discussions on ongoing with the instrument manufacturer to address this.

N_2O concentrations peaked at 20-30 ppm and emissions factors of 38 mg kg^{-1} were calculated for burning willow (0.4% N, db) which is in good agreement with (Maasikmets et al., 2016). There are very few other studies reporting N_2O emissions factors from RSF combustion, but EFs as high as 120 mg kg^{-1} have been reported (Kinsey et al., 2012). Due to the higher global warming potential of N_2O (310, 100-year), it is recommended that further testing be undertaken to measure N_2O emissions factors.

Carbon monoxide

Given the WHO guideline concentration of 10 mg m^{-3}, it may be concluded that dangerous levels of CO are emitted from RSF combustion across multiple fuel types. CO concentrations of up to 4% (at 13% O_2 and STP) were observed during the smouldering phases of high carbon fuels such as charcoal and smokeless fuels. Emissions factors ranged from 92-184 g kg^{-1} for hardwood and 228-384 g kg^{-1} for coal and smokeless fuel. These results are slightly higher than the average literature inventory values (91 g kg^{-1} and 156 g kg^{-1} for hardwood and coal) but the range reported is very large (25-250 g kg^{-1} and 50-370 g kg^{-1} respectively). See Chapter 2.3. The NAEI emissions factors are 53 g kg^{-1} and 145 g kg^{-1} respectively so again these may be considerably underestimated in air quality models. The increased CO emissions from heat treated fuels such as charcoal and smokeless fuels is of concern because it may in-part offset benefits of reduced particulate emissions. This is especially true in high exposure environments such as developing world cookstoves. CO emissions were a factor of three higher for the charcoal cookstove than the wood stove tested in this work (see chapter 9).

The timing of sampling within the combustion cycle has a significant impact on emissions (Kortelainen et al., 2015). For example CO concentrations up to 2800 ppm (20% O_2) are present in the flue of smokeless fuel even 200 minutes after ignition. For wood fuels, a test may be abandoned when there is no visible flame, but for wood B, CO was emitted at up to 1500 ppm (20% O_2) for up to an hour after the flame was extinguished.

Methane

It is widely understood that CH_4 is released from inefficient combustion, but it is not generally thought to be a significant component in the radiative forcing of RSF combustion. However, modelling work in Chapter 7 has shown that CH_4, CO and VOCs together contribute to 21-35% of radiative forcing due to wood stove emissions. CH_4 accounts for 5-8% assuming an emissions factor of 200 g GJ^{-1} (3.6 g kg^{-1}) reported by GAINS for wood burning stoves. However, as Table 7-6 shows, emission factors up to 833 g GJ^{-1} and 932 g GJ^{-1} are reported by the USEPA and IPCC inventories. Assuming all other EFs are kept constant, this increases the share of CH_4 radiative forcing to 18-29%. As shown in Table 2-4, the NAEI emission factor for methane range from 3.69 g kg^{-1} for wood to 5.8 g kg^{-1} for smokeless fuel and 15.7 g kg^{-1} for bituminous coal. However, efficient operation of stove such as air-starvation (rich burning), overloading and using wet fuel can result in dramatically increased CH_4 emissions. EFs of up to 14-25 g kg^{-1} (Larson and Koenig, 1994) and even 91 g kg^{-1} have been reported (Johansson et al., 2004). The latter study found that upgrading from older inefficient stoves to modern low-emission stoves can reduce methane emissions by up to 9000 times. In this work, CH_4 emissions from a charcoal cookstove and wood cookstove were found to be 8.3 g kg^{-1} and 2.5 g kg^{-1} respectively. A dramatic 7-fold increase in CH_4 emissions was observed when wet wood (28% MC) was burned instead of dry wood. These results show that methane emissions may be underestimated in models and in laboratory studies which may not be representative of real world conditions. Emissions of GHGs such as CH_4 from wood burning stoves may confound efforts to reduce emissions, particularly in the short term as CH_4 has a 20-year GWP of 56.

10.2.4 Particulate Emissions

Particulate matter

PM poses one of the greatest health concerns arising from inhalation of RSF combustion smoke, as described in Chapter 2, and for this reason PM, PM_{10} and $PM_{2.5}$ are the key species of interest in test standards and emissions limits. PM emission factors were found to be dependent on volatile content and heat treated fuels such as torrefied wood, charcoal and smokeless fuel were found to have the lowest emission factors due to the lowest volatile contents. Coal was an exception to the rule due to the different composition of the fuel and higher propensity to form highly carbonaceous soot particles (see chapter 10.3).

Emissions factors ranged from 1.5-2.1 g kg^{-1} for hardwood and 4.2-11.3 g kg^{-1} for coal to 0.9-1.5 g kg^{-1} for torrefied and smokeless fuel. For the cookstove, the values were 1.4 g kg^{-1} and 7.2 g kg^{-1} for charcoal and wood stoves respectively. These results correlate well with the average literature inventory values (3.6 g kg^{-1} and 9.5 g kg^{-1} for hardwood and coal) but as with CO EFs, the range reported is very large (0.2-10 g kg^{-1} and 8-40 g kg^{-1} for wood and coal respectively). See Chapter 2.3.3. The NAEI (2013) emissions factors are 8.24 g kg^{-1} and 9.29 g kg^{-1} respectively for wood and coal so unlike the other pollutants, they may be overestimated in this inventory. The NAEI EF for smokeless fuel 1.62 g kg^{-1} matches well with these results.

As with CO and the other pollutants, emissions factors for PM are highly dependent on the timing of sampling. If PM sampling is carried out over the entire combustion cycle with two in-series filters using a dilution tunnel, the choice of when to end sampling significantly affects the final result. For example, in the example shown in Figure 10-3, sampling for an extra 40 minutes at the end of the test will capture a negligible amount of particulates, but a considerable amount of CO. It is believed that this is one of the reasons for the different results reported by different standard test methods as described in chapter 7. In the German DIN-plus method, a Wöhler SM96 probe is inserted into the flue without dilution, 3 minutes after the start of the test run. The probe then samples at 9 l min^{-1} for 30 minutes and hence is not isokinetic. The probe features a heating and a cooling chamber and samples at 70°C. In contrast, the Norwegian NS3058 method samples from a dilution tunnel through two filters held at 35°C over the entire test cycle.

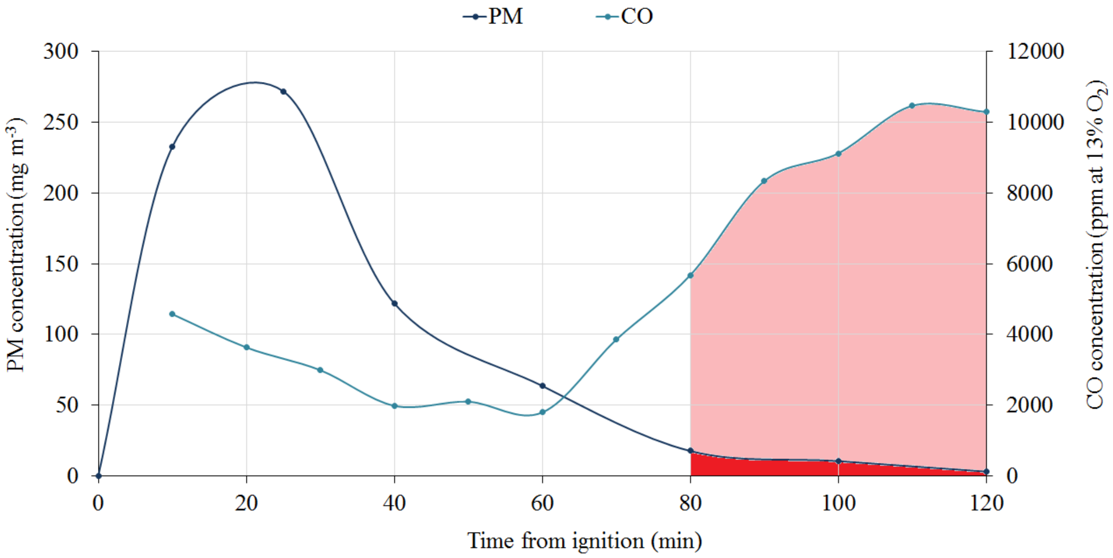

Figure 10-3. Emissions profile for peat briquettes showing the effect of sampling timing on emissions.

One of the major results in this work is evidence of the substantial variation in instantaneous emission factors throughout the combustion cycle (see chapter 4). Statistical analysis of these emissions factors reveals a very wide spread of values, as shown in appendix II (Table 11-7). Figure 10-4 shows the mean whole cycle emission factors with standard deviation across all tests for each fuel type.

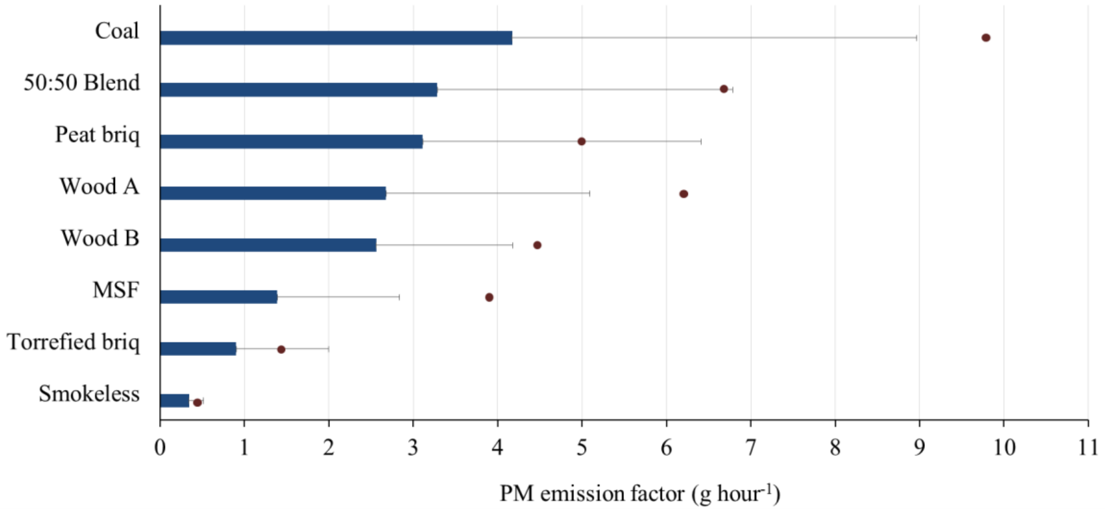

Figure 10-4. Average whole-cycle PM emission factors in grams per hour. Error bars show the standard deviation. Red points show flaming phase emission factors.

Emission factors are reported here in grams per hour, calculated using the average grams per kilogram emission factors and burning rates reported in chapter 4. The results show that only the manufactured solid fuel, torrefied briquettes and smokeless fuel meet the 5 g hour^{-1} limit given by the Clean Air Act within a reasonably high degree of confidence. The large standard deviations observed here are consistent with previous works (e.g. Bond et al., 2002) and reflect the inherent uncertainty and variability in emissions from this source (Coulson et al., 2015). Such high variability in performance and operating conditions lead to lower reproducibility and repeatability compared to some other sources of air pollution. A comprehensive investigation into emission factor variability was conducted by Fachinger et al., (2017). The study found that experimental- and fuel- related variabilities led to EF uncertainties of 30% for a wood log stove and 5% for a pellet stove, thereby verifying the user as a major source of error (Wöhler et al., 2016). In this work, it was found that most of the uncertainty is associated with the flaming phase. The standard deviation in flaming phase EFs for wood A, wood B and coal were 2.4, 1.3 and 4.8 g kg^{-1} respectively, compared to 0.16, 0.19 and 0.38 g kg^{-1} for the smouldering phase.

BC and OC

As shown in chapter 7, BC and OC are the most important components of radiative forcing from RSF combustion. Models show that residential solid fuel combustion will account for 44% and 80% of all BC emissions in the UK and Europe in 2030 respectively (see Chapter 7 and Wilnhammer et al. (2017)) The ratio of BC (or EC) to TC gives a good indication of the warming or cooling effect of the particles. It was found that EC/TC ratios are dependent on the fuel types and combustion conditions, whereby high volatile and highly sooting fuels give high EC/TC ratios (0.69 for wood and 0.85 for coal). The ratios are lower for smokeless fuels and torrefied fuels and during the smouldering phase where OC emissions dominate.

For hardwood, EC and OC emissions factors measured in this work were 0.35-0.87 g kg^{-1} and 0.22-0.76 g kg^{-1} respectively. These are in good agreement with the literature inventory values for EC, which are 0.2-1.8 g kg^{-1} (Oros and Simoneit, 2001), 0.3-1.7 g kg^{-1} (Tissari et al., 2007) and 0.3-1.5 g kg^{-1} (Heringa et al., 2011). OC values were in good agreement with Tissari et al. (2007) (0.2-2.3 g kg^{-1}) and Heringa et al. (2011) (0.36-0.73 g kg^{-1}) but were significantly lower than the values reported by Oros and Simoneit (2001) (4.2-25.4 g kg^{-1}) and McDonald et al. (2000) (1.1-3.6 g kg^{-1}). EC and OC emission factors are not reported in the NAEI inventory, but are given in the EMEP and GAINS inventories (see chapter 7). The values for BC are 1.3 g kg^{-1} (EMEP) and 1.8 g kg^{-1} (GAINS). The value for OC is 5.0 g kg^{-1} (GAINS).

For coal, EC and OC emissions factors were measured at 3.6-8.0 g kg^{-1} and 0.6-1.47 g kg^{-1} respectively. Literature values for EC ranged from 0.17-0.47 g kg^{-1} (Oros and Simoneit, 2000) to 0.76-5.4 g kg^{-1} (Bond et al., 2004). OC emissions factors ranged from 0.4-4.3 g kg^{-1} (Bond et al., 2004) to 0.1-5.5 g kg^{-1} (Chen et al., 2009) and 2.0-10.4 g kg^{-1} (Ross et al., 2002). The EMEP and GAINS values for BC are 0.96 and 4.3 g kg^{-1} respectively, and the values for OC is 5.3 g kg^{-1} in GAINS. The measured values in this study are generally in good agreement with the literature and inventories but they also highlight the range of uncertainty in EC and OC emission factors (a factor of 10 a more) and a need for more work to reduce this uncertainty.

10.2.5 Particle Composition

Inorganics

The inorganic aerosol emissions were not directly measured in this work due to known interferences from the filter media. Of particular interest was potassium in the aerosol, as K is known to play an important role in aerosol formation (see chapter 2) and fuel/soot reactivity (Qin and Thunman, 2015, Trubetskaya et al., 2016). However, after correspondence with the filter manufactures it was not possible to obtain the K composition, which varied significantly between individual filters. Certification from Whatman shows that the QM-H brand filters have Al, Fe, Mg, Na and Zn contents of 50, 30, 25, 40 and 5 ppm respectively. In later work, PM was collected by other means including the FTIR probe steel filter and by impaction onto a steel plate or TEM grid inserted into the flue. Future work will assess the elemental composition of this particulate and how it varies with fuel type and throughout the combustion cycle. SEM/EDX and TEM/EELS was carried out on the particulate as described in chapters 4/5 and 8 respectively. The latter revealed particles were up to 90% carbon with traces of O, Ca, Cu and Mg, as well as S for the MSF fuels. There was, however, interference from the filter which gave a Si peak. TEM/EELS of pine soot revealed oxygen contents of 5-10% and nitrogen contents of 1.3-1.7% (see chapter 8). This is believed to be the first time N has been detected in this way and has been possible due to the enhanced power and sensitivity of the new TEM within LEMAS. Future work will be carried out to identify the nitrogen containing compounds present, be they nitrated phenols, PAH or nitrates, which are thought to be important components of brown carbon (see chapter 2 and appendix 1). Improved understanding of the composition and optical properties of light absorbing organic carbon will help to improve model predictions of aerosol optical depth over polluted atmospheres.

Inorganic emissions may also be estimated by mass balance, knowing the composition of the fuel and ash residues, but this method has the potential for large errors due to inhomogeneous fuels. Results are presented in Chapter 5 of the inorganic content of soot deposits recovered from the flues of an in-situ multi-fuel and wood burning stove. Assuming these samples are analogous to coal and wood soot respectively, inorganic EFs are calculated using the PM emissions factors given above. The results are given in table 10-2.

	K	Na	Fe	Mn	Ca	Al	Cu	Zn	Mg	Pb	Ti
Multi-fuel stove	30.7	35.5	22.8	1.2	35.7	29.2		1.2	9.9	1.5	0.06
Wood Stove	11.0	3.2	18.7	2.0	29.8	3.5	0.16	0.8	4.0	0.75	0.004

Table 10-2. Estimated emissions factors for inorganics in soot (mg kg^{-1})

In comparison to the NAEI inventory (Table 2-4) all EFs for coal burning are several times lower. However, this could be due to the choice of PM emission factor, which is higher in the NAEI. EFs for inorganics in the wood soot are comparable to the NAEI database, especially for Zn, Na and K (1.25, 10.5 and 44 g kg^{-1}). However, interestingly Ca, Cu and Mg are larger which suggests that these EFs may be underestimated. In addition, Fe and Al are not included in the NAEI, whereas evidence is presented in Chapter 2 that these species affect the oxidative potential of PM and particulate Fe has been linked to disorders such as Alzheimer’s disease. It is also interesting to note the dramatically increased vanadium emissions factors for MSF combustion, due to blending of petroleum coke into briquettes.

OC & PAH

The composition of the organic fraction of particulate matter was also determined by pyrolysis GC-MS, as described in chapter 5. Soot samples collected on filters were pyrolysed in a helium atmosphere and then analysed by GC-MS. This is believed to be one of the first studies using this technique. Fuel samples were also pyrolysed directly at different temperatures to simulate the heating conditions in the stove. Pyrolysis of high brown carbon and black carbon samples yielded levoglucosan and anhydrosugar compounds as well as methoxyphenols and methoxy eugenol in different proportions. Anhydrosugars and organic acids are breakdown products of cellulose and hemicellulose and have been widely used in source apportionment studies. A number of lignin pyrolysis products were also identified including methoxyphenols, furfural, eugenol and PAH such as pyrene and fluoranthene. The ratios of these species is also useful for source apportionment as detailed in Chapter 2 and appendix 1. The relative proportions of lignin-specific compounds guaiacol, syringol and anisole can be used to determine between hardwood, softwood and herbaceous biomasses. It was found that these compounds are released at temperatures of 500°C and up and affect fuel soot yields (Trubetskaya et al., 2016). Lower temperature pyrolysis of softwood (torrefied spruce briquettes) was found to release resin acid and coniferyl alcohols which are particularly useful tracers for softwoods. The ratio of PAH species is also used in fuel-specific source apportionment (see table 11-2) and may be particularly useful when combined with carbon isotope measurements. Measured PAH ratios are presented in table 9-4 for wheat straw briquettes, which were found to agree with published ratios. A key finding here, however, was that the ratio varies with combustion conditions (flaming or smouldering). The ratio varies more significantly for some species such as phenanthrene and anthracene than it does for fluoranthrene and pyrene. Few low MW PAH species were detected which is most likely due to the filter collection temperature of 70°C.

10.2.6 Soot formation mechanisms & the impact of torrefaction

A number of the abovementioned compounds are also involved in the chemical mechanisms for the formation of soot particles, or elemental carbon. The findings of the studies presented in this thesis have been linked back to previous work investigating the soot formation from biomass model compounds. See for example (Fitzpatrick et al., 2009). The findings from these studies and others have been collated, re-analysed and published in a new study (Jones et al., 2017). The study showed that soot formation via the hydrogen abstraction carbon addition (HACA) mechanism is insufficient to explain the higher soot concentrations observed during coal combustion. It is believed that the cyclopentadiene (CPD) mechanism contributes to additional soot formation, as well as condensation reactions of smaller PAHs such as naphthalene. DMS measurements described in appendix VI revealed a bimodal particle size distribution for wood burning, with peaks at 20-30nm and 100-110 nm. The latter is correlated with high burn rates, high MCE and high EC particle content. It is therefore believed that these particles are formed primarily by the HACA mechanism. The smaller particles peak in abundance during the char burnout phase. Here, temperatures are higher and cellulose/hemicellulose has been liberated so soot formation is largely by phenolic lignin-breakdown products, via the CPD mechanism. For coal, low MW PAHs released may go on to form soot particles directly. Both particle sizes have been identified in soot samples using electron microscopy (see appendix V).

A major finding of this study is that torrefaction as a pretreatment has significant potential to reduce emissions from residential wood combustion. Torrefaction causes decomposition and deacetylation of hemicellulose, a slight loss of cellulose, and demethoxylation of lignin as well as an overall increase in aromaticity (Neupane et al., 2015, Akinrinola, 2014). Solid state FTIR analysis conducted by (Normark et al., 2016) of torrefied spruce wood showed that compared to the raw fuel, there is a reduction in the content of carbohydrate-related bands in the 1030-1060 cm^{-1} region which are linked to hemicellulose. Approximately 40% of hemicellulose is lost at torrefaction temperatures of 250°C (Barta-Rajnai et al., 2016). There is also a loss of nitrogen and a reduction in char reactivity (Jones et al., 2012), which could lead to lower soot formation. Several studies report lower yields of low MW species (acetic acid etc) from pyrolysis/combustion of torrefied material, but higher yields of levoglucosan. There are also conflicting reports over the impact of torrefaction on the yields of furfural, guaiacol, eugenol and vanillin. Although these species are involved in the CPD soot formation mechanism, it is believed that the lower volatile content and reduced reactivity lead to reduced soot formation by the dominant HACA mechanism. Interestingly though, there is a reduction in the yield of 1,2-cyclopentanedione (Chang et al., 2012). These findings have been confirmed by py-GC/MS analysis (see chapter 11.3.3) and are promising for the potential of torrefaction as a pre-treatment for the residential sector. This is the subject of further work (see chapter 10.4).

10.3 Physical and optical properties of emitted particles (Aim 3)

Electron microscopy and spectroscopic techniques have revealed significant differences in the morphology, composition and optical properties of emitted soot particles. The results of this analysis are presented in chapters, 5, 8 and 11.3. A novel technique was used in this study to assess light absorption of PM collected on filters across a full spectrum of wavelengths, whereas previous studies have only used 2-4 wavelengths. As described in appendix I (chapter 11.1.1), correction factors must be applied to filter-based measurements of particle optical properties such as those presented in chapter 8.3. This is done in order to compensate for filter loading and scattering effects which may skew the results. For example, the corrected black carbon concentration can be related to the un-corrected BC concentration BC_i by the formula $BC_{corrected} = (1 + k\ ATN)BC_i$, where k is the loading correction factor and ATN the light attenuation at a given wavelength (Virkkula et al., 2007). The factor k is dependent on the sampling system and aerosol type, as well as the filter substrate and the wavelength used in the in the reflectometer or transmissometer measurements (de la Sota et al., 2017). Samples were taken on quartz fibre filters in chapter 8.3, and the Ångström exponent derived using transmissometry. Under these conditions, a k factor of 1.3 ± 0.9 was proposed by Davy et al. (2017) for ambient measurements. A detailed comparison of published correction factors for the Ångström exponent for different aerosol types is given in Collaud Coen et al., (2010). A correction factor of 1.09 (1.00-1.27) was recommended for wood burning aerosol (e.g. Thessaloniki, Greece). Pandey et al. (2016) applied a factor of 1.5 ± 0.15 for cookstove aerosols collected on Teflon filters, but the authors noted that there is a need for improved factors for such high OC sources. Corrections are not applied in Chapter 8, but will be applied to the revised version of the paper before publication.

As shown in Chapter 5, 8 and appendix III, freshly emitted soot during flaming wood combustion consisted of short open chains of carbon spherules which are highly spherical. This particulate has a high EC/TC ratio (0.42-0.65; chapter 5.3) and is associated with high modified combustion efficiencies (0.80-0.95; Chapter 9, appendix IV). DMS data (Chapter 9) showed that individual spherules are 20-110 nm in diameter and chains are less than 1 µm. There are very few particles in the range 2.5-10 µm (Chapter 4) and those that are present are largely fuel fragments and ash released from disturbance of the bed, which are readily removed from the atmosphere. Fossil fuel (coal and MSF) soot particles were found to be more granular in shape than wood soot particles (appendix III), which were multi-cored in the case of pine soot confirming reports in the literature (Trubetskaya et al., 2016). Flaming phase particles had a high average EC/TC ratio (>0.9) and the Angstrom Absorption Exponent (AAE), $\%SP^2$ and C:O values for these particles were 0.9-1.2, 66.5% and 93:5.4 respectively (Chapter 8). Flaming phase soot particles were found to absorb strongly in the visible wavelengths such as at 550 nm which is the wavelength at peak intensity of solar irradiance.

Ageing and cooling of the particles on dilution into the atmosphere increases the chain length and cross branching, with agglomerates forming up to 2.5 µm. An increase in the dilution factor also increases the fine particle concentration due to nucleation and coagulation of sulphate and nitrate aerosols (Lipsky et al., 2002, Vu et al., 2015, Singh et al., 2014). Condensation of water and organics onto the surface of the particles occurs which acts as a transport medium for PAH, and causes a lensing effect. This increases absorption as described in chapter 2.7. The %SP^2 and C:O ratio for diluted particles were 60.5% and 88:10 respectively, showing an increase in oxygenation of the particles after cooling. This has implications for the polarity and hygroscopicity of the particles, whereby increased oxygenation increases propensity to form CCN (see section 2.7).

Lower temperature combustion at low MCEs increases the OC fraction of the PM. The particles also appear as 'sticky' closed clusters up to 200 nm in diameter which readily agglomerate. Low MCE and smouldering combustion is also conducive to brown carbon formation in the form of tar balls. Although tar balls have not been directly observed in this study, tar 'smears' have been observed on filters (Chapter 5). This material would go on to form tar balls after emission to the atmosphere. Py-GC/MS of filter samples (Chapter 5) found that brown carbon consists of methoxyphenols, nitrophenols, sugars and extremely low molecular weight VOCs, confirming reports in the literature (Budisulistiorini et al., 2017). Optical analysis of filters (Chapter 8) found that brown carbon PM was found to absorb strongly in the UV and low-visible wavelengths, with an AAE of 1.9-3.3 which is consistent with the literature (see Chapter 2). A summary of soot particle formation and properties in presented in figure 10-5. Existing knowledge is shown in blue and that which has been added to is shown in red, together with the relevant section of this thesis. Bockhorn (1994) introduced the key chemical mechanisms for soot particle formation and growth in hydrocarbon flames, but little emphasis was given to solid fuel sources and the impact of fuel properties. Several studies have applied this theory to biomass and coal combustion (e.g. Ross et al., 2002, Fitzpatrick et al., 2009, Atiku et al., 2017) but few have combined this knowledge with the the physical and optical properties of the particles, as shown in Figure 10-5. Aside from dedicated aging chamber studies (e.g. Grieshop et al., 2009), few studies have measured changes in the individual particle properties with aging. The focus of these studies is also often on bulk properties such as particle number concentration and organic content measured with AMS. As described above, high resolution TEM/EELS was used in Chapter 8 and revealed increased branching and oxygenation of particles after emission. The increased oxygenation can in-part be linked to condensation of organic vapours, which may contain brown carbon compounds. The brown carbon analysis results described above may be useful for aerosol modelling studies through better understanding of BrC AAE and composition.

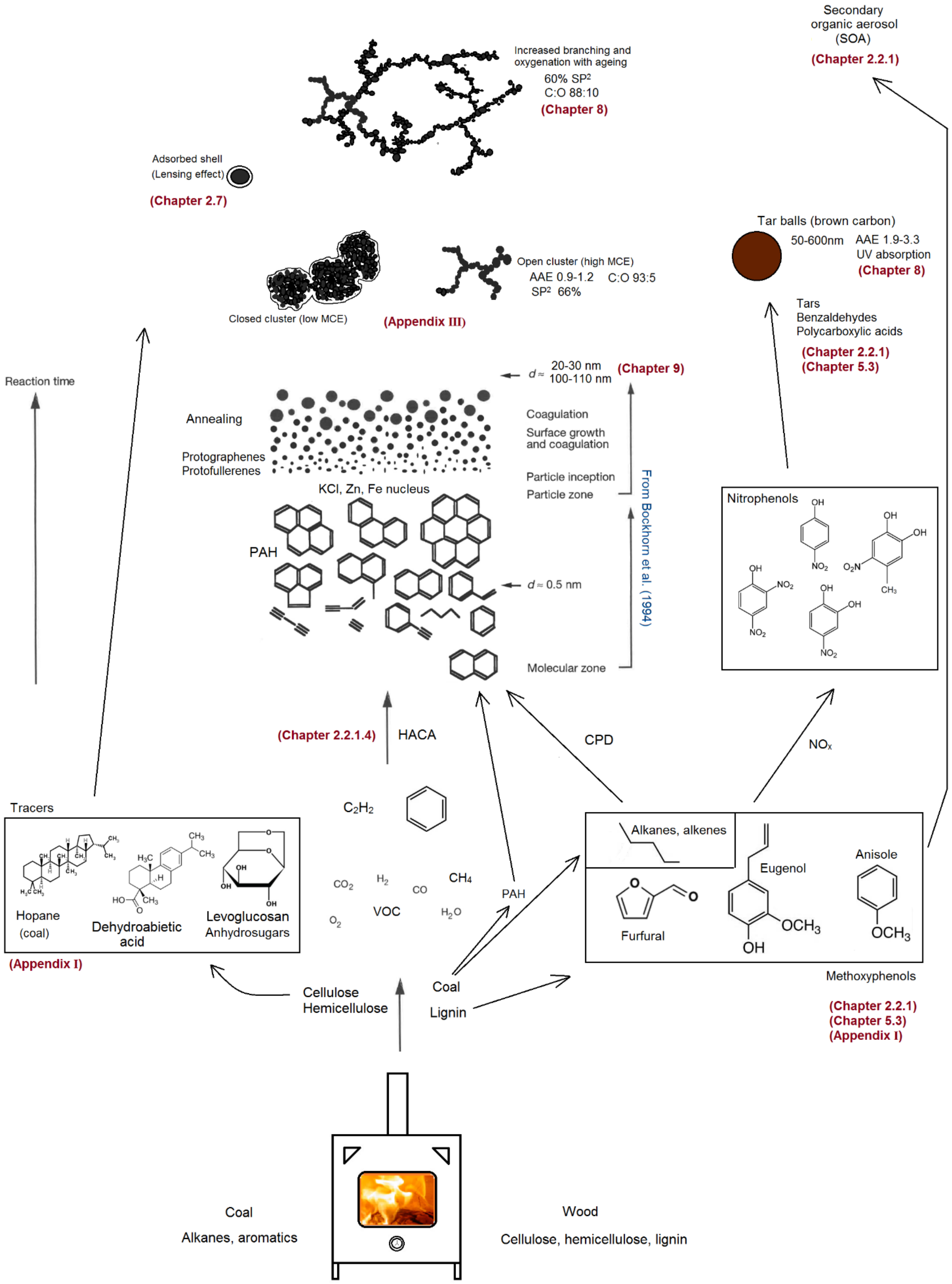

Figure 10-5. Soot formation mechanisms for RSF combustion. Expanded and updated from (Bockhorn, 1994)

10.4 Climate Impacts of RSF Combustion in the UK (Aim 4)

The modelling study presented in Chapter 7 assessed uncertainties in activity data and emissions factors for RSF combustion in the UK. Industry data showed stove sales increased by 21% between 2005 and 2016 and recent findings from a government survey found that residential wood combustion was underestimated by a factor 3. Revisions increased the share of residential wood combustion (RWC) to >10% of renewable energy and >50% of renewable heat generation in the UK, making the sector a key part of the UK's 20-20-20 targets. Models predict UK RWC to increase by a factor of 14 between 1990 and 2030, with heating stoves and fireplaces dominating, and a corresponding increase in $PM_{2.5}$ emissions. Due to a wide scale reduction in coal and fossil fuel use and an increase in wood use, the most important components of radiative forcing from RSF combustion are BC and OC followed by VOCs and CH_4.

According to the GAINS model (see Chapters 3 and 7), activity data for UK residential sector LPG and natural gas burning were 15.2 PJ and 1274 PJ in 2015, reducing slightly to 11.6 PJ and 1123 PJ in 2030. Hence residential gas and liquid fuel combustion contribute to significant GHG emissions and radiative forcing, as shown in table 10-3.

	2015		2030	
	CH_4	CO_2	CH_4	CO_2
Gas	392	16,803	154	14,171
LPG	0.4	1228	0.5	1103

Table 10-3. Radiative forcing from natural gas and LPG burning in the UK residential sector (μW m^{-2})

The table shows that radiative forcing due to CH_4 and CO_2 emissions from natural gas burning are 66 to 78 times higher than all RSF burning in the UK. Radiative forcing from LPG burning alone is 4.7 times higher than RSF burning. It is therefore important to contextualise the results presented in Chapter 7 and highlight the strong requirement for GHG emissions reductions in the UK residential sector. In addition, these factors only account for emissions from the point of combustion and do not account for upstream emissions. For gas, upstream emissions can be very significant due to extraction, processing and leakages. Methane leakages from the UK gas grid network alone were estimated at 1.9-10.8% and 200 kt in 2010 (Hammond and O' Grady, 2017, Dodds and McDowall, 2013). Using the same factors as above, this leads to an additional 440 μW m^{-2} of radiative forcing, twice that of RSF burning in the UK. Upstream emissions from wood log processing and life cycle analysis (LCA) of wood logs has not been included in this work because it is beyond the scope. A number of LCA models exist (e.g. SimaPro) to model these impacts and there has been a substantial amount of research conducted on sustainability of biomass for heat and power (e.g. Thornley, 2017, Thornley et al., 2015, Welfle et al., 2017). In neglecting the upstream emissions from wood processing, we assume in Chapter 7 that wood is carbon (CO_2) neutral until the point of emission and investigate the climate impacts of the many pollutants emitted, which is highly uncertain as shown. A recent report by Chatham House (Brack, 2017) highlighted the need for better understanding of the carbon cycle and to ensure that wood burnt in stoves in fireplaces is certified and sourced from forests which are continuously replaced. Biomass for home heating has the potential to significantly reduce greenhouse gas emissions from the residential sector, through replacement of gas, kerosene and LPG.

Stoves and fireplaces are the cheapest and simplest RSF combustion technologies to provide space heating. This can offset the demand for natural gas, LPG or kerosene to an extent, but other fuels may be required for water heating and for cooking. For example, Mitchell (2012) found that some off-grid homes use up to 7 different fuel types in the home, and Baker (2011) found that 64% of households in England that use kerosene as their primary heating fuel also rely on solid fuels for supplementary heating. Nevertheless, natural gas remains the largest source of GHG emissions in the UK residential sector, as shown in figure 10.6.

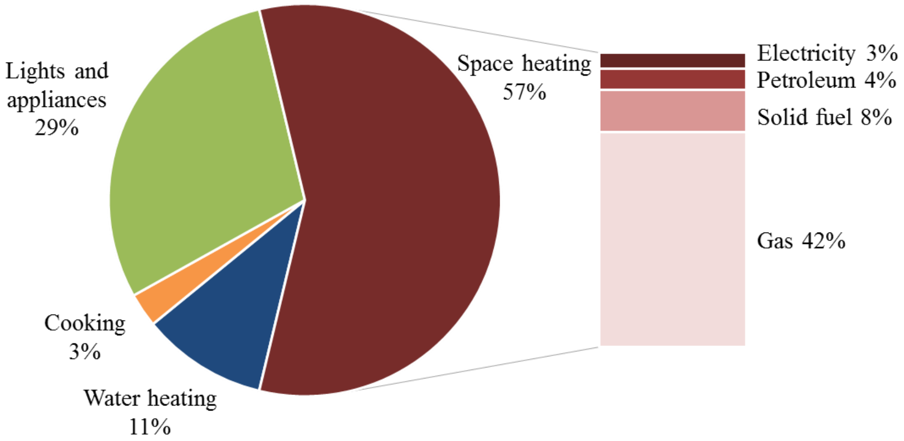

Figure 10-6. The proportion of domestic energy consumption used for space heating by fuel type in the UK in 2015. Data source: (BEIS, 2016)

Some 1037 PJ of natural gas was consumed for space heating in the UK in 2015, representing 42% of total domestic energy consumption. Any potential GHG savings arising from switching from gas to biomass need to consider the upstream emissions as described above. Pierobon et al. (2015) found that the upstream emissions account for 40% of life cycle GHG emissions for wood combustion in stoves. However, the extent to which BC and OC are included in LCA models is unclear (e.g. Cespi et al. (2014)), and could lead to significantly higher GHG impacts from the point of combustion (see chapters 2.6 and 7). Nevertheless, Cespi et al. (2011) found that modern, automated pellet stoves had the lowest life cycle GHG impacts of all RSF technologies considered, despite the energy penalty from pelletisation (Welfle et al., 2017). This was verified by Solli et al. (2009) who calculated LCA impacts of wood stoves in the range 80-110 g CO_2e kWh^{-1}.

As shown in Chapter 7, wood consumption in heating stoves is forecast to increase from 12.0 PJ in 2010 to 29.8 PJ in 2025. If we assume that this increase completely offsets consumption of other fuel types, the emissions savings can be calculated as shown in table 10-4.

Fuel type	Life cycle GHGs (gCO_2e kWh^{-1})	Reference	Emissions savings (kt CO_2e)
Wood stove (new)	80	Solli et al. (2009)	[Ref emissions, 0]
Wood stove (old)	110		148
Natural gas	204	BEIS (2016)	613
LPG	230		742
Heating oil	260		890
Coal	359		1380
Petroleum coke	358		1375

Table 10-4. Life cycle greenhouse gas savings achievable for new wood stoves compared to common residential fuel types for the period 2010-2025.

Hence the greatest GHG savings can be achieved through substitution of coal and smokeless fuels. However, as shown in Chapter 7, consumption of these fuels has reduced considerably since 1990 and is low compared to gas, LPG and heating oil. If 10% of natural gas consumption (103.7 PJ) was substituted with wood, this would require approximately 6800 kt of wood logs (assuming an 85% conversion efficiency), but could save 3572 $ktCO_2e$ of GHG emissions.

However, there is a large body of evidence (Chapter 2.5) showing the impact that inefficient biomass use in simple stoves and fireplaces can have on air quality in communities around the world. The technology exists to reduce these emissions (modern Ecodesign-ready appliances, gasifier stoves, abatement technologies) but there is little incentive to adopt them at the domestic scale at the present time.

10.5 Abatement of emissions

There is a clear need to reduce emissions from RSF combustion in many parts of the world in order to achieve air quality and climate benefits. This includes the UK, where emissions from wood burning are increasing and are beginning to offset the benefits of emissions reductions in other sectors such as traffic (Fuller et al., 2013).

Emissions reductions can also be achieved via optimisation of fuel properties and pre-treatments. Results have been presented of the benefits of using torrefied fuel (see above) and heat-treated low-volatile fuels such as smokeless fuels. Washing is also a promising technique for low grade feedstocks such as waste woods, reeds and straws. Washing removes inorganic elements such as K, Cl, S, Fe, Mg and P which increases the ash melting temperature of the fuel and reduces HCl and SO_2 emissions (Gudka et al., 2016). Washing can also be combined with other pre-treatments such as torrefaction, steam explosion or hydrothermal carbonisation (Zhang et al., 2016). The use of additives and binders also has the potential to reduce emissions from biomass briquettes. Pilot studies from larger scale plants have shown additives can reduce SO_2 and NO emissions by binding sulphur as $CaSO_4$ and promoting the conversion of fuel-N to N_2 rather than NO_x (Daood et al., 2014, Glarborg et al., 2003). Additives include Fe-, Ca- and Al_2SiO_5- based mixtures. Up to 30% lower PM emissions and 98% less sintering has been observed from burning agricultural resides blended with additives compared to the raw fuel (Fournel et al., 2015). Commercially available additives are also available in the form of ‘soot reducers’ which are added to the fire and claim to reduce tar build up in the flue. These are blends of NH_4Cl and $CuCl_2$. NH_4Cl decomposes into NH_3 and HCl when heated in flame and the copper has a catalytic effect (Nicholls and Staples, 1932).

At the simplest level, emissions reductions can be achieved through education programs promoting behavioural changes and optimised operating conditions (Kennedy and Basu, 2013, Wöhler et al., 2016). For example, discouraging the burning of wet wood, treated waste or municipal solid waste, not overloading the stove and not air-starving the stove overnight. Emissions reductions can also be achieved via appliance design and efficiency optimisation (Kortelainen et al., 2015). Policies necessitating the replacement of older stoves with modern Eco-design ready equivalents can reduce $PM_{2.5}$ emissions factors by 50-60% (Wilnhammer et al., 2017). However, some studies find that the Ecodesign Directive alone is insufficient to achieve the potential reductions from changeout programs, reducing emissions by just 6% in Finland (Savolahti et al., 2014). If all stoves were replaced with modern equivalents that meet performance standard criteria, emissions could be reduced by up to 95% (Winijkul and Bond, 2016), but evidence is reported in Chapter 7 that real-world emissions are typically twice as high as those measured under laboratory conditions. $PM_{2.5}$ emissions can be reduced by up to 90% by replacing a log wood stove with an automated pellet stove or gasifier stove (see figure 11-28 and EMEP/GAINS inventories). However pellet stoves are often associated with higher costs and lower aesthetic qualities, so additional incentives may be required or pellet-log hybrids (Lamberg et al., 2017). A variety of retrofit abatement technologies are also available (see chapter 10.6.4) including filters, catalysts and ESPs but adoption in generally very low compared to other pollution sources such a vehicles which have had catalytic converter and diesel particle filters for many years. Catalysts and filters are more common in the USA and can achieve $PM_{2.5}$ emissions reductions up 68% (Ward et al., 2017).

10.6 Future research directions

In addition to the published results and supplementary material presented in the preceding chapters of this thesis, a number of further studies have been developed in collaboration with partners from the Supergen Bioenergy Hub and others. This chapter outlines the aims, objectives and findings of these studies which have not yet been published. In summary, the need for further research has been identified in the following key areas:

- Experimental assessment of the impact of variation in standard test methods on emissions factors and recommendations for a standard that is representative of real-world emissions
- Emissions reduction potential of Eco-design ready stoves under real-world conditions
- The role of inorganic emissions and ash in soot formation and toxicology
- Improved understanding of the formation mechanisms of brown carbon and the chemical composition of BrC and WSOC (nitrated phenols etc).
- Improved understanding of secondary organic aerosol (SOA) formation from RSF combustion in polluted urban atmospheres. See for example (Tiitta et al., 2016) and (Corbin et al., 2015).
- Improved source apportionment using combined methods such as carbon isotopes, PAH ratios and anhydrosugars.
- Life cycle analysis of RSF combustion climate impacts including upstream emissions
- Emissions abatement by fuel pre-treatment and upgrading (torrefaction, washing, additives)
- Emissions abatement by retrofit technologies (catalysts, filters, ESPs and non-thermal plasma)

10.6.1 Waste Wood

A journal article is under preparation entitled *The Kinetics of the Rapid Washing of Waste Wood and the Impact on Emissions.* This project is led by Dr Bijal Gudka and is in partnership with Veolia UK.

Samples of mixed waste wood were milled and homogenised before being pressed into briquettes and combusted in the same stove described in previous chapters. Three distinct subcategories of waste wood were used; standard waste wood, washed waste wood and waste wood blended with an additive. In the study, results are presented of the impact of a rapid washing process on the fuel properties. The nature of the material leached out has also been examined. The contribution of the author to this work is the inorganic analysis of the raw fuel and briquetting of the samples, as well as the combustion testing and emissions measurements. Images showing of the combustion testing of waste wood briquettes are shown in Figure 10-7, as well as the combustion of chipboard waste.

Figure 10-7. Photos of the waste wood emissions tests for (a) homogenised briquettes and (b) chipboard with *fraxinus* sp.

Characterisation analysis showed that the chlorine, nitrogen and ash content of the homogenised waste wood 0.6%, 3.6% and 3.9-4.5% respectively (dry basis), far higher than the values for virgin wood reported in the previous chapters. The high nitrogen content may be due to the glues and binders used in chipboard. The chipboard alone was found to have a nitrogen content of up to 5%.

K	Na	Fe	Mn	Ca	Al	Cu	Zn	Mg
602	493	613	89	3886	661	34	289	494

Table 10-5. Trace metal content of the homogenised waste wood (ppm dry basis).

The inorganic analysis shows that the waste wood does not have significantly higher trace metal content than virgin wood. The low Cu content suggests that there was not a significant amount of CCA treated waste wood in the high grade waste wood fuel stream. Cr and As were not measured by the author, but colleagues reported As concentrations in the range 2-50 ppm. The highest observed As content in other samples in this work was 3.6 ppm in the reed briquettes.

Typical concentrations (at 13% O_2 at STP) of NO and N_2O were 600 ppm and 70 ppm respectively which were three times that of the straws shown above. This is a result of the higher fuel nitrogen content in the waste wood. The FTIR library was adapted during these tests to include HCN, which is known to be emitted from waste burning. Concentrations ranged from 40 to 200 ppm and averaged 90 ppm (13% O_2, STP). CH_4 and NH_3 peaked at 2500 ppm and 2000 ppm respectively, and HCl was consistently above 100 ppm whereas for the straws above HCl rarely exceeded 50 ppm. The washed and additive samples were found to have significantly lower NH_3, HCl and SO_2 emissions which was consistent with the leachate analysis showing that these compounds have been removed by washing.

10.6.2 PAH and Carbon Isotope Analysis

Polycyclic aromatic hydrocarbons (PAH) are emitted in significant quantities from RSF combustion and have profound implications for health, as described in chapter 2. The PAH content of PM samples collected at different times on filters has been determined by accelerated solvent extraction in toluene and GC/MS, as described in chapter 3. The results for barley straw 424 briquettes are presented in Figure 10-8. The emissions profile for this fuel is shown in section 11.4 . The timing for the flaming and smouldering samples are 31-35 minutes and 19-25 minutes respectively.

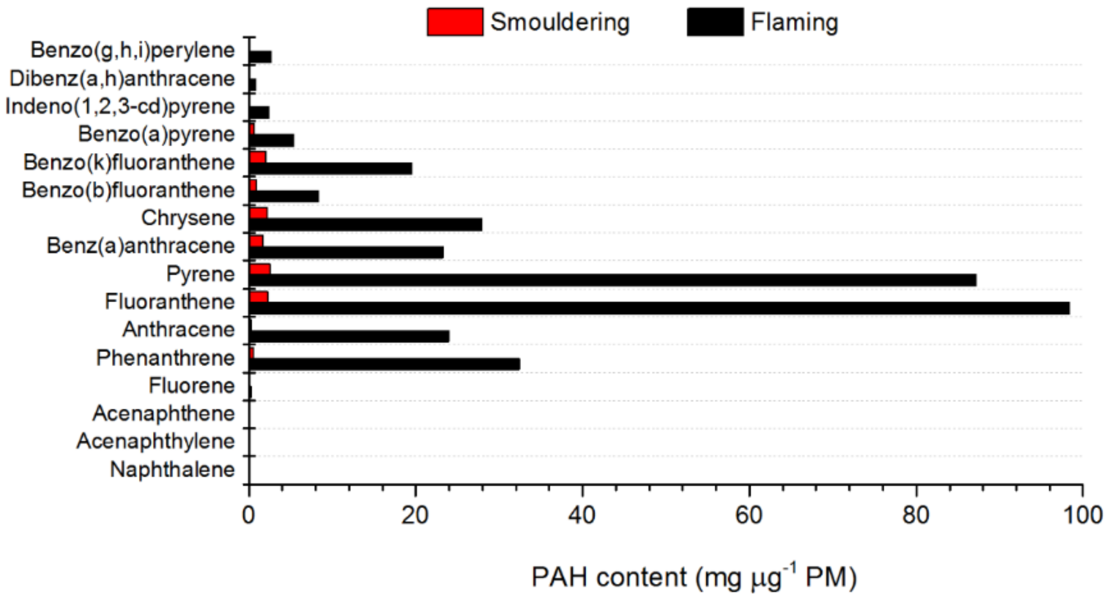

Figure 10-8. PAH content of PM from the combustion of barley straw 424 briquettes.

As shown the PAH content of the flaming phase sample (high EC) is much higher than the smouldering sample. The dominant PAH are the high MW PAH pyrene and fluoranthene. This may be due to the temperature of soot collection which was 70°C in this work. We have shown in previous work (supplied as a supplement to this thesis) than lighter two-ring PAH species such as naphthalene may remain in the gas phase at these temperatures and not be collected (Jones et al., 2017). The relative ratios of different PAH species may also be useful for source apportionment as described in appendix I, section 11.1. The ratios for the species listed above from barley straw are presented in Table 10-6. These results are in good agreement with the values reported for straw in appendix 1, although the ratio of anthracene to anthracene plus phenanthrene of 0.38 is slightly out of the 0.015-0.25 range reported. It is also interesting to note the impact of flaming versus smouldering on these ratios, particularly for indeno(1,2,3-cd)pyrene/benzo(ghi)perylene and phenanthrene/anthracene. These ratios were a factor of 2 and 10 greater in the smouldering sample than the flaming respectively.

	RET/ (RET+ CHR)	ANT/ (ANT+ PHE)	BaA/ (BaA+ CHR)	FLA/ (FLA+ PYR)	IcdP/ (IcdP+ BghiP)	BaP/ BghiP	PHE/ (PHE+ANT)	1,7-DMP/ (1,7 + 2,6-DMP)
Smol	-	0.33	0.43	0.47	0.83	29.0	0.67	-
Flam	-	0.43	0.45	0.53	0.48	2.1	0.58	-
Avg	-	0.38	0.44	0.50	0.66	15.5	0.62	-

Table 10-6. Source apportionment PAH ratios for barley straw 424.

In addition to temperature, a number of factors are known to influence PAH composition of RSF PM. Analysis is currently underway to analyse the impact of these parameters on PAH composition in filter soot (70°C), FTIR filter soot (180°C) and impinger water condensate (<10°C). The analysis is being conducted by Dr Aaron Eveleigh through a collaboration with University College London. Measurement of the carbon isotope fractionation ($\Delta^{13}C$) is also being made which is useful for source apportionment, as described in appendix I. It is has be proven in the past that isotope ratios depend on combustion conditions and fuel types (Chanton et al., 2000). Primary wood smoke PM is richer in ^{13}C than aged PM and SOA and wood smoke PAH is ^{13}C heavy in certain species compared to vehicular PM (O'Malley et al., 1994, Garbaras et al., 2015).

10.6.3 Particle Toxicity

Toxicity of RSF combustion generated particles is also highly dependent on fuel type and combustion conditions, as described in chapter 2. Experiments are currently underway to assess the impact of filter-bound particulate on laboratory grown cell cultures. These experiments are taking place in the Faculty of Biological Sciences, University of Leeds through a collaboration with Professor Mike Routledge.

The genotoxicity (ie DNA damage induction) of collected particulate is determined using the alkaline single cell gel electrophoresis (aka Comet) assay (Olive and Banath, 2006). This gives information about the comparative toxic hazard associated with particulates from different RSF fuels, appliance types and combustion conditions. Correlations may be determined between MCE and toxicity of particles, which is largely related to the PAH content.

10.6.4 Emissions Abatement Technologies

10.6.4.1. Abatement Options Available

A number of options have been trialled to try and reduce or minimise emissions from RSF combustion in afflicted areas. Non-technological solutions include recommended “no-burn days” which are being used in the San Francisco Bay Area, the South Coast Air Basin (Orange Country), and in New South Wales, Australia. Public notices are disseminated through local newspapers, radio and television as well as “check before you burn” apps which supply users with the air quality index on any given day. A proposed blanket ban on residential open fires in Paris was announced in December 2014 but was repealed after a matter of days.

Voluntary eco-labelling of new appliances such as Flamme Verte (France), Nordic Swan (Scandinavia) and Burnwise (NSPS, USA) may help to reduce emissions by encouraging users to invest in a lower emission stove. However, there is little incentive. Tighter emissions limits for appliances have been applied in some areas as bye-laws, for example in the New Zealand as described in chapter 7. National and international emissions limits may also be tightened periodically, following the example of the EURO drive cycle limits for vehicles. The Ecodesign regulations aim to reduce emissions of PM, OGC and CO by 27, 5 and 399 kt year^{-1} through policy measures alone but the limits apply only to new appliances. Where stove change-out programs or scrappage schemes are available, significant emissions reductions can be achieved. For example, one initiative in Montana, USA, replaced 1200 stoves and indoor $PM_{2.5}$ concentrations reduced by 71% (Noonan et al., 2012). This led to the New Source Performance Standards for Residential Wood Heaters (NSPS) which require PM emissions of less than 2.0 g hour^{-1}.

Technologically, emissions control systems for residential appliances are either non-existent or very simplistic in comparison to larger scale emissions sources. Air pollution control systems for industrial combustion include selective non-catalytic NO_x reduction, flue gas desulphurisation and recirculation, scrubbers, bag filters, electrostatic precipitators (ESPs) and even activated carbon injection. Most systems also feature online gas analysis for Environmental Permitting requirements and oxygen feedback systems to optimise the air-to-fuel ratio. Very few if any of these technologies are commonly used at the residential scale, primarily due to financial rather than technological constraints. Indeed, the technology has been proven for small scale systems but they still lag behind other emissions source such as traffic which have used catalytic converters and diesel particle filters for many years. Some medium scale sources do feature control technologies such as commercial & single house pellet/chip boilers. Here the control systems are most often lambda sensors for O_2 feedback and ceramic filters, cyclones or ESPs for particulate control.

Detailed reviews of available abatement devices and their operating principles are given by Lim et al. (2015), Obernberger (2011) and AEA (2010). A selection of example retrofit technologies is briefly outlined. A number of European appliance suppliers offer micro-ESPs which may be fitted to the flue and claim PM_1 removal efficiencies of 96% of more. The ESP is also an approved standard method for determining PM emissions for solid fuels via BS 3841-2:.1994. In the USA, catalytic stoves have been available for many years. Retrofit ceramic or steel honeycomb catalysts are available to buy off the shelf and online and use a platinum or palladium catalyst. Example devices made by Condar Co. retail at USD $150-200 and have a lifespan of 2-5 years. Emissions during the ignition phase are vented straight to atmosphere via a bypass flue system while the catalytic converter temperature is raised to the required 200-

260°C. The catalyst converts pollutants to benign species and recovers the process heat. The final example listed here is the Barbas Energa stove (http://barbasbellfires.com/en/fireplaces/energa) ceramic foam filter. The manufacturers claim tests revealed a reduction in PM concentrations from 40 mg m^{-3} to < 5 mg m^{-3} using the filter. The appearance of these technologies in shown in figure 10-9.

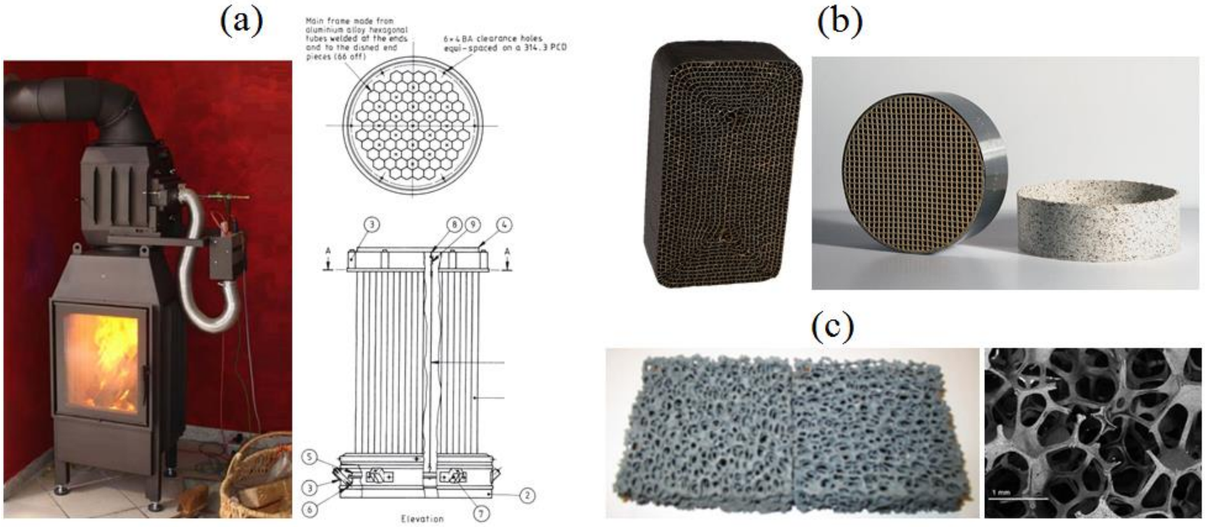

Figure 10-9. Retrofit abatement technologies for stoves: (a) electrostatic precipitator, (b) Condar steel/ceramic catalysts, (c) Barbas Energa ceramic filter.

In addition to retrofit technologies, reduced emissions factors can be achieved by appliance design and by fuel switching, as proven in the preceding chapters of this thesis. Optimal appliance designs feature automated combustion control systems such as pellet stoves and gasifier stoves. A log gasifier stove has a two part combustion chamber where the fuel is pyrolyzed before the resulting gases are combusted, resulting in lower emissions factors. A comparison of the emissions reduction potential of modern appliances and control systems in shown in Figure 10-10. The figure uses emissions factors from the EMEP and GAINS databases as described in Chapter 7.

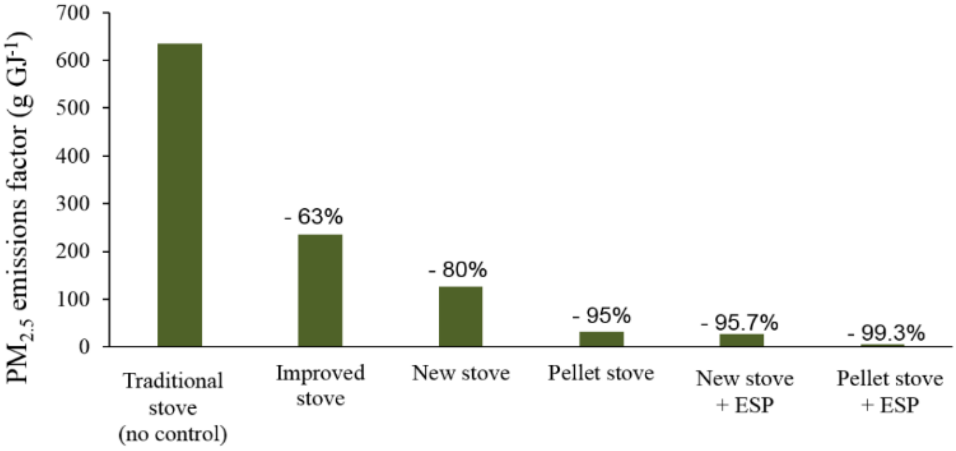

Figure 10-10. Achievable reductions in emissions factors using modern stoves and control systems.

Finally, indoor air quality in RSF burning homes may be improved using commercially available air purifiers. One study found a reduction of 60% in $PM_{2.5}$ and 75% in levoglucosan concentrations through the use of HEPA filters (Potera, 2011).

10.6.4.2. Experimental testing of a novel plasma device

In this work, a novel plasma emissions abatement device was tested and the impacts on gas composition and particle size was evaluated. This work was carried out with Dr Kui Zhang and Professor Adam Harvey from Newcastle University, in a collaboration initiated through the Supergen Bioenergy Hub.

Non-thermal plasmas can generate positive and negative ions, ozone, and plasma activated species at low temperatures and ambient pressure. Injection of these species into the flue gas of a stove or boiler can oxidise pollutants such as organics into benign species that are vented to atmosphere. The ions also apply a charge to the soot particles which makes them agglomerate into larger particles which are more easily removed and are less respirable. The ioniser used in this work was designed and constructed by Kui Zhang at Newcastle University and tested by the author at the University of Leeds. It has the advantage of being relatively low power (5-15 W), low cost and quiet in operation. It also requires less maintenance or cleaning than a honeycomb catalyst or ESP which may pose a fire risk if used after the recommended life span.

The device consists of a simple wire mesh electrode to which a voltage is applied, ionising the air. By connecting the outlet of the ioniser to the flue with a quartz tube, air is drawn through the device and into the flue through the pressure difference. In dry air, the ioniser generates-, O_2^+, O_2^-, $O_2(a1\Delta_g)$, $O({}_3P)$, $O({}_1D)$, O_3, $N_2(A_3\Sigma u_+)$, $N2(B_3\Pi_g)$, $N({}_4S)$ and $N({}_2D)$. In humid air or flue gas, the ioniser also generates hydroxyl radicals H, OH, HO_2 and H_2O_2. A diagram showing the interaction of these species with stove flue gas is shown in Figure 10-11. The device was found to impact on VOC, NOx and PM emissions as shown in Figure 10-12 and Figure 10-13.

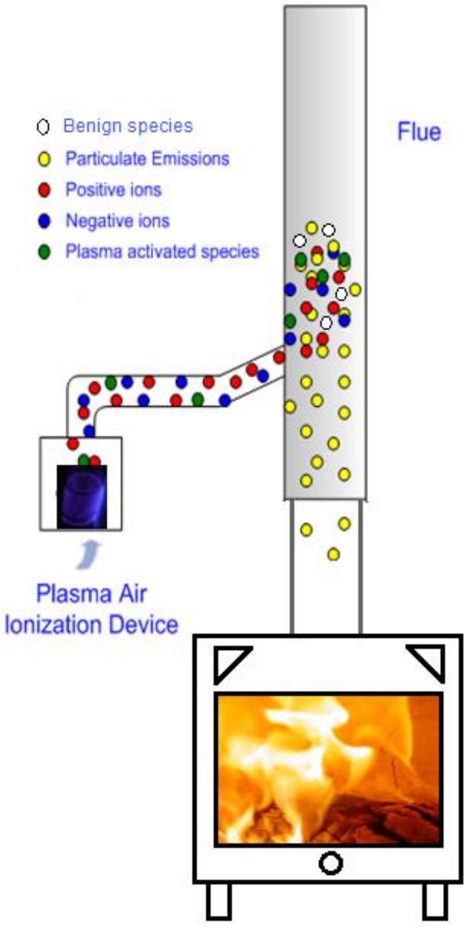

Figure 10-11. Interaction of non-thermal plasma device with flue gas.

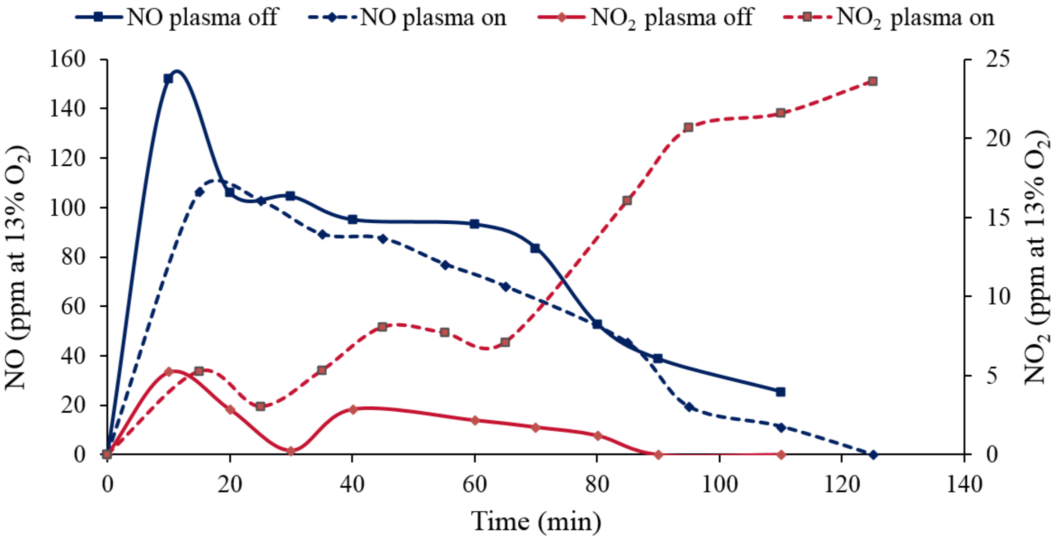

Figure 10-12. Effect of plasma on NO_x emissions.

Gas analysis showed a slight reduction in NO emissions and an increase in NO_2 emissions. This is believed to be primarily due to oxidation by ozone, which has a fast reaction rate with NO as shown in Table 10-7.

Reaction	k_{298} (cm^6 $molecule^{-2}$ s^{-1})
$NO + O_3 \longrightarrow NO_2 + O_2$	1.8×10^{-14}
$NO + O \longrightarrow NO_2$	1.0×10^{-31}
$CO + O \longrightarrow CO_2$	1.16×10^{-36}

Table 10-7. Reaction rate coefficients from the NIST chemical kinetics database.

No impact was observed on CO emissions which are substantial from RSF appliances. This is because the reaction rate for the oxidation of CO is very low, as shown. The plasma also had an impact on particulate as shown in Figure 10-13. The proportion of fine particles reduced and the proportion of course particles above 10 microns increased. SEM analysis revealed that the soot chains also appeared more clustered and agglomerated after plasma injection. However, this may be due to natural variation in soot morphology over the combustion cycle, as described in appendix II, so further work is required to confirm this. The impinger water condensate was much lighter in colour after exposure to the plasma, indicating that some of the condensable organics had been oxidised in the flue.

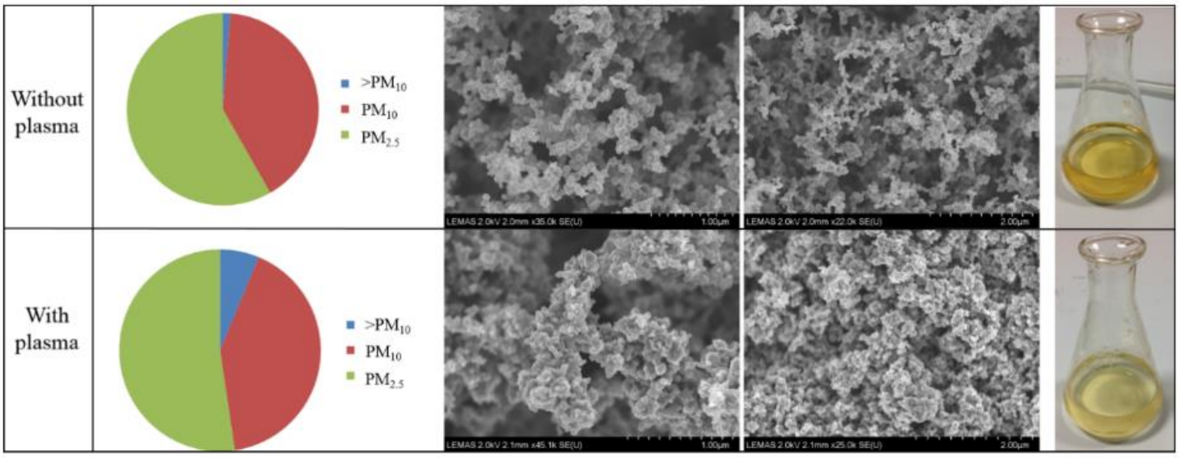

Figure 10-13. Effect of plasma on particle size distribution, particle morphology and impinger condensate

In summary, these preliminary results show that plasma air ionisation has great potential to reduce emissions from wood burning stoves. However, further work is required to confirm the gas phase reactions taking place and quantify the reductions that can be achieved. The author has also entered into discussions on the formation of a patent for a self-powered emissions reduction system. The design uses the heat of the stove to generate electricity which is used to power the ioniser and/or an ESP. A Peltier module has been purchased and testing is underway.

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Chapter 11

Appendices

11.1 Appendix I. Source Apportionment of RSF Combustion

A variety of methods are available for the source apportionment of residential solid fuel smoke in atmospheric plumes. This appendix outlines some of the most commonly used methods and the theory behind them.

11.1.1 Multiwavelength aethalometers

An aethalometer is an instrument that measures the attenuation of specific wavelengths of light through a quartz fibre filter. The filter is held on a spool which allows the instrument to measure black carbon concentration in ambient air in real-time.

The wavelength used for black carbon measurements is typically 880 nm, with additional measurement at 370 nm in two-wavelength aethalometers. The latter is interpreted as an indicator of aromatic organic compounds. Seven wavelength aethalometers also measure at 470 nm, 520 nm, 590 nm, 660 nm and 950 nm for more detailed studies of aerosol optical properties (Arnott et al., 2005, Sandradewi et al., 2008c).

The BC concentration on the filter (µg m^{-3}) is given by

$$BC = \frac{b_{abs}}{\sigma_{abs}} = \frac{1}{\sigma_{abs}} \frac{A}{Q} \frac{\Delta ATN}{\Delta t}$$

σ_{abs} = mass absorption efficiency / wavelength-dependent light absorption cross section (m^2 g^{-1}) = $K \times \lambda^{-Å_{abs}}$, where K is a constant, λ is the wavelength (nm) and Å is the Ångström exponent.
b_{abs} = absorption coefficient (m^{-1}) Defined with the Beer-Lambert law.
A = spot area (cm^2)
Q = flow rate (l min^{-1})
ΔATN = change in attenuation in time Δt = -100 ln(I/I$_0$)

Qualitative source apportionment can be achieved using multi-wavelength aethalometers using the difference between BC determined at 370 nm and 880 nm, Delta-C = BC$_{370nm}$ – BC$_{880nm}$. Wood smoke BC is thought to absorb UV light (370 nm) more effectively than IR light (880 nm). Hence higher values of Delta-C can serve as an indicator of wood burning and have been found to peak at evenings and weekends in the winter months (Wang et al., 2011a, Wang et al., 2011b)

More quantitative wood burning source apportionment has been achieved by relating the wavelength-dependent absorption coefficient b$_{abs}$ to the source-specific Ångström exponent Å, as shown in the equations below: (Herich et al., 2011, Sandradewi et al., 2008b, Favez et al., 2009)

$$\frac{b_{abs}(\lambda_1)_{FF}}{b_{abs}(\lambda_2)_{FF}} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-\text{Å}_{FF}}$$

$$\frac{b_{abs}(\lambda_1)_{wb}}{b_{abs}(\lambda_2)_{wb}} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-\text{Å}_{wb}}$$

$$b_{abs}(\lambda) = b_{abs}(\lambda)_{FF} + \, b_{abs}(\lambda)_{wb}$$

However, there are known issues with source apportionment using aethalometers, such as interferences from loading effects, thermal stability issues and sample matrix effects. Some studies emphasise that the ratio is mostly indicative and should not necessarily be used for empirical apportionment of wood-smoke in PM (Harrison et al., 2013). However it can be used in conjunction with other tracers and a number of corrections to data have been proposed, such as filter loading bias (Weingartner et al., 2003, Virkkula et al., 2007, Cheng and Yang, 2015).

11.1.2 Positive matrix factorisation

Positive Matrix Factorisation is a commonly used technique for source apportionment and is derived from receptor modelling. Correlation matrices are developed whereby rows typically represent emissions profiles of various sources and columns represents the scores of each emissions profile factor (Gianini et al., 2013, Paatero and Tapper, 1994). This approach is similar to principal component analysis (PCA), except with a least-squares regression analysis applied rather than eigenvector analysis (Kourtchev et al., 2011). PMF has been shown to have several advantages over other techniques such as PCA, including non-negativity and a lack of the need for prior information on emissions sources (Gianini et al., 2012). Several versions of PMF software are available including PMF2 and the USEPA PMF. Comparative studies have shown that generally the different models agree well, but some uncertainties are apparent due to differences in the least-square regression algorithms and non-negativity constraints used (Kim and Hopke, 2007). The wood smoke source profile was found to have one of the lowest correlations between the two models, reflecting the high uncertainty in this area (Larsen and Baker, 2003).

11.1.3 Carbon isotope analysis

Carbon isotope source apportionment is used to differentiate between biogenic/contemporary and fossil fuel derived combustion sources to carbonaceous aerosol. During growth, biomass material absorbs atmospheric CO_2 through photosynthesis. The CO_2 contains a known abundance of the carbon radioisotope ^{14}C and when the material is cut or harvested, the isotope decays with a half-life of 5,370 years (Heal, 2014). As this is relatively short in geological terms, a particulate sample from residential coal burning would be more depleted in ^{14}C that a particulate sample of wood burning. Therefore the ratio of ^{14}C abundance in a sample to that of contemporary carbon yields the proportion of contemporary to fossil carbon in the particulate sample. A study by (Ward et al., 2006) found that 78-82% of ^{14}C in the ambient PM of Libby, Montana, was attributable to residential wood burning. Recent work has also allowed the determination of ^{14}C in specific fractions of carbonaceous aerosol such as EC and OC (Szidat et al., 2004).

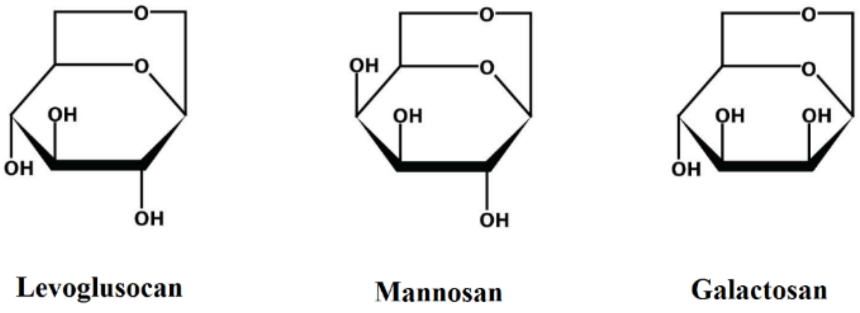
In addition to ^{14}C, measurement of ^{13}C abundances may be useful in determining the degree of photochemical processing of organic aerosols in the atmosphere. It is hypothesized that secondary organic aerosols are depleted in ^{13}C compared to primary particulate and SOA precursors (Szidat et al., 2004). Carbon isotopes may also be used for the source apportionment of other climate and health relevant pollutants from wood burning, such as methane, CO and PAH (Currie et al., 1994a). Unlike vehicular particulate samples, wood smoke PAH has been found to be ^{13}C heavy in benz(a)anthracene relative to fluroanthene and pyrene, and also ^{13}C depleted in chrysene and benzofluoranthene. These findings by (O'Malley et al., 1994) were used to identify residential wood burning as the dominant source of PAH in St John's Harbour and Conception Bay, Newfoundland. Similar techniques may be applied for source apportionment of coal burning PAH (McRae et al., 1999), although the author noted that the fuel conversion technology and temperature influences the ^{13}C content of the emitted PAH. The same is true of biomass burning. Methane emitted from smouldering fires where the combustion efficiency is low (high OC, CO) were found to be depleted in ^{13}C compared to high temperature flaming combustion (high EC, CO_2) (Chanton et al., 2000). The biomass fuel type can also impact on the ^{13}C signature of emitted carbonaceous aerosol, VOC and hydrocarbons (Gensch et al., 2014). Compound specific ^{13}C analysis within anhydrosugars (levoglucosan, mannosan and galactosan) has been highlighted as a promising technique for source apportionment of fuel type and combustion conditions for biomass burning (Sang et al., 2012). Radiocarbon analysis has been found to be a relatively precise and accurate technique in source apportionment, but high costs may be prohibitive to routine work (Jordan et al., 2006)

11.1.4 Chemical Mass Balance

Chemical Mass Balance analysis (CMB) is also a receptor model that uses variance least squares regression analysis and provides a sum of linear products of source profile contributions (Friedlander, 1973, Ward et al., 2012). CMB is a fully constrained model and a prior knowledge of emissions sources and profiles is required (Chow and Watson, 2002). CMB may combine many other tracers such as anhydrosugars, trace elements and carbon isotopes and hence may be very useful in rural communities where winter wood burning is known to be a significant source of air pollution (Gianini et al., 2013). CMB is particularly useful for source apportionment of the organic fraction of particulate matter and numerous studies have used this technique to for OC, OM, VOC and individual species (Schladitz et al., 2015, Yin et al., 2015, Hellén et al., 2008, Chow and Watson, 2002). The benefits of CMB include allowing errors to be assigned to each source profile contribution and free software is available from the USEPA. Drawbacks include an inability to identify unknown emissions sources and a lack of detailed secondary aerosol effects (Viana et al., 2008b). Detailed emissions inventories are crucial for CMB, and it has been shown that fuel-specific profiles can be used to differentiate between biomass types such as hardwood and softwood (Chow et al., 2007). A example profile for general wood smoke is given in (Hannigan et al., 2005).

11.1.5 Monosaccharide anhydrides

Cellulose makes up 40-50% of the mass of wood and during pyrolysis, it is converted into solid phase char, solid/liquid phase tars and gas phase compounds such as aldehydes and CO. Water soluble monosaccharide anhydrides (MA's) such as levoglucosan are present in the tar of the fine particle fraction of PM (Zhang et al., 2011). Their structure is shown in Figure 11-1 .



Levoglusocan **Mannosan** **Galactosan**

Figure 11-1. Structure of levoglucosan, mannosan and galactosan

Levoglucosan (1,6-anhydro-β-d-glucopyranose) has been the most widely used as a tracer for biomass burning due to its relatively stable properties in the atmosphere (Bai et al., 2013, Fraser and Lakshmanan, 2000) and reasonably large emission rates (Simoneit et al., 1999, Nolte et al., 2001). As with other tracers, quantitative source apportionment with levoglucosan is marred by the dependency of emissions factors on fuel type and burning conditions. The mass fraction of levoglucosan in PM ($f_{\text{levoglucosan}}$) can vary from 3% to more than 20% (Hedberg et al., 2006) and emissions factors can vary from 1 mg kg^{-1} in efficient pellet or chip boilers to more than 5000 mg kg^{-1} in older inefficient stoves and fireplaces burning high moisture wood logs (Jordan and Seen, 2005). However, where knowledge of local wood types being burned is available, levoglucosan fractionation in total OC and PM can be used to estimate the contribution of biomass burning:

$$PM_{wb} \text{ or } OC_{wb}\ (\mu g\ m^{-3}) = \text{levoglucosan}\ (\mu g\ m^{-3}) \times f_{\text{levoglucosan, PM or OC}}$$

For example, (Caseiro and Oliveira, 2012) used weighted-average values of $f_{\text{levoglucosan, PM}}$ of 10.7 for Northern European locations and 7.61 for Portugal, reflecting differences in the fuel mix in those locations. (Puxbaum et al., 2007) used an average values of 7.35 (OC) for a mixture of hardwood and softwood, (Caseiro et al., 2009) used a weighted average of 6.1 (OC) and 9.1 (OM) for a fuel mix of 15% beech and 85% spruce, and (Sang et al., 2013) used a value of 10.0 (OC) for a calculated fuel mix of crop residues, hardwood and softwood.

The levoglucosan stereoisomers, mannosan (1,6-anhydro-β-d-mannopyranose) and galactosan (1,6-anhydro-β-d-galactopyranose) are also useful indicators of biomass burning, though they are not emitted in such high quantities (Simoneit, 2002). Unlike levoglucosan, mannosan and galactosan are derived from hemicellulose. Hemicelluloses are heterogeneous polysaccharides which contain xylose, mannose, galactose and arabinose as well as glucose. Hemicellulose decomposes at 225-325°C whereas cellulose decomposes at 325-375°C (Zhang et al., 2011). Therefore higher ratios of levoglucosan to mannosan and galactosan indicate lower temperature combustion and higher inefficiency in stoves.

The ratio of levoglucosan to mannosan (lev/man) and mannosan to galactosan (man/gal) can be used to distinguish between the types biomass contributing to the aerosol loading. For example, as shown in Table 11-1, crop residues such as cereal straws have been associated with high ratios of lev/man, whereas the ratio for softwood is much lower. Lev/man ratios are highest for lignite and galactosan emissions are very low, indicating a loss of hemicellulose with increasing coalification (Fabbri et al., 2009).

Biomass	Lev/Man	Man/Gal	OC/Lev
Crop residues	32.6 ± 19.1	1.2 ± 1.1	17.2 ± 9.2
Softwood	4.0 ± 1.0	3.9 ± 2.1	8.5 ± 6
Hard wood	21.5 ± 8.3	1.5 ± 0.3	7.1 ± 3.9
Lignite	54.0		

Table 11-1. Average ratios of anhydrosugars and OC for different biomass types. Values are averages from a literature survey by (Sang et al., 2013) and (Fabbri et al., 2009).

However as shown in the table, there are reasonably large uncertainties associated with this method so a combination of cellulose- and hemicellulose-derived MA's with other chemical tracers is recommended, such as methoxyphenols derived from lignin pyrolysis (Gaston et al., 2016) and trace elements (Hedberg et al., 2006). Furthermore, it has been demonstrated that levoglucosan may react with the hydroxyl radical OH, with the products contributing to SOA formation and atmospheric acidity (Bai et al., 2013). A correction for this was made by (Sang et al., 2013), using a standard exponential decay rate model, allowing the ageing of biomass smoke plumes to be taken into account.

MA's are typically measured by extraction of aerosol filters in dichloromethane followed by derivatisation and GC-MS, or HPLC (Dye and Yttri, 2005). However, recently other methods have been used for quantification of MA's which does not require extensive sample preparation or derivatisation, such as high-performance anion-exchange chromatography (Iinuma et al., 2009, Saarnio et al., 2010) and soft ionisation time-of-flight mass spectrometry (Gaston et al., 2016). Aerosol mass spectrometers often attribute the *m/z* 60 mass fragment to monosaccharide anhydrides and a correlation has been observed between this and brown carbon aerosol absorption (Lack et al., 2013).

11.1.1. Inorganics and trace elements

Inorganics and trace elements are typically used within source profiles in chemical mass balance source apportionment studies (Chow et al., 2007). The majority of inorganics are present in very low concentrations in biomass PM and the differences between wood species tend to be small, largely depending on the soil and environmental conditions where the tree was grown (Kleeman et al., 1999). Certain elements such as potassium, chlorine and zinc are abundant in biomass burning particulate matter and high concentrations of these species in ambient PM may indicate a source of biomass burning (Hedberg et al., 2006). Potassium and chlorine each make up 2-5% of woody biomass fine particulate mass and hence are useful tracers (Reid et al., 2005). However again they are subject to large variations in emissions factors, with higher emissions generally being correlated with higher temperature efficient combustion (Khalil and Rasmussen, 2003) and herbaceous rather than woody biomasses (Turn et al., 1997). Despite this, the Zn and K content of biomass burning particulate is not as dependent on burning conditions as monosaccharide anhydrides (Hedberg et al., 2006). Source apportionment using these species is also subject to interferences from other sources of fine particle K and Cl and from the choice of measurement method. Techniques such as XRF yield a measurement of total potassium whereas others only measure water soluble potassium, such as ion chromatography or atomic absorption spectrometry following agitation of a filter in distilled water (Calloway et al., 1989). Nevertheless, much of the potassium released through the combustion of biomass is in the form of water soluble inorganic salts KCl and K_2SO_4 (Sandradewi et al., 2008a). Aerosol mass spectrometers measure K+ ions generated from the volatilsation of these compounds, which is a destructive technique, and more qualitative than others due to incomplete volatilsation (Weimer et al., 2008).

Potassium is one of the most extensively used inorganic tracers. Despite potassium being ubiquitous in the environment, elevated concentrations above known background levels may be indicative of biomass burning. In affected areas, a linear correlation has been observed between levels of water soluble K in ambient PM and residential wood burning (Chow et al., 2007). Dust from crustal matter has a known K/Fe ratio and any K measured in PM in excess of that ratio may be attributed to wood smoke (Calloway et al., 1989, Currie et al., 1994b). Although K emissions factors from softwood are generally lower than hardwood and crop residues, potassium alone is not thought to be a suitable tracer for detailed source apportionment between fuel types. Nevertheless, the ratio of potassium to levoglucosan has been shown to be useful in this regard (Urban et al., 2012). (Puxbaum et al., 2007) found that a ratio below 0.2 is indicative of residential heating with wood, whereas a ratio above 0.5 is indicative of open burning of straws and grasses. However, the k/levoglucosan ratio presented by (Caseiro et al., 2009) ranged from 0.59 to 1.11 which was significantly higher than values reported in the literature. The authors argued that despite the higher values, the correlation between the two species remained strong, and higher temperature combustion in more modern appliances results in higher inorganic content in the particulate (fly ash potassium salts). Urban et al. (2012) also found that the ratio is lower for smouldering (0.24) versus flaming (1.01) combustion. Nonetheless the results reflect the uncertainties associated with this method. The ratio of potassium to elemental carbon has also been used to distinguish between fuel types, with ratios of 0.20 and 0.95 reported for herbaceous and lignocellulosic biomass PM respectively (Turn et al., 1997). In addition to potassium, herbaceous biomass particulate is characterised by high Cl. (Turn et al., 1997) found that chlorine emissions factors were 10 times higher for herbaceous biomass fuels than wood fuels, whereas zinc emissions factors were 25-30 times higher for wood fuels. Despite this, few studies use zinc in source apportionment as other factors are known to contribute to zinc loading, including mobile sources such as brake wear (Chow and Watson, 2002).

Certain elements may also be used to identify waste and waste wood burning in ambient particulate matter. Copper chromium arsenate (CCA) has been used as a wood preservative for many years and often it is burned in log stoves as a free source of fuel. However, this can be severely detrimental to health. Measurements of ambient PM in Seattle, USA, revealed high levels of arsenic and statistical analysis revealed a Pearson correlation coefficient of 0.84 between arsenic and biomass burning, suggesting prevalent waste wood burning (Maykut et al., 2003). A similar correlation has been observed in wood burning regions of New Zealand, where annual average inorganic arsenic levels have been measured at over 3 times the national air quality guidelines limit (Ancelet et al., 2015). As was found to be largely confined to the fine particle fraction, but more research in this area is required.

11.1.2. Polycyclic aromatic hydrocarbons

PAH are produced from a number of combustion sources and are present in solid, liquid and gaseous environmental media. Emissions are known to be high for low temperature combustion sources such as stoves and fireplaces (Katsoyiannis et al., 2011) and ΣPAH emissions factors of 250 ± 25 mg kg^{-1} and 43 ± 9 mg kg^{-1} have been reported for coal and wood burning respectively (Lee et al., 2005). Measurements of twenty or more PAH species can be made simultaneously by GC-MS and the relative abundances of certain species over others can be used to determine the source (Khalili et al., 1995). In the particle phase, lower molecular weight (202-228 g mol-1) species dominate the PAH profile of wood smoke irrespective of combustion conditions and fuel type (Hays et al., 2003). However, total emissions factors are much higher for higher moisture fuel and appliances with a poor air supply, and also shorter-chain PAHs such as fluorene are enriched where combustion temperatures are low (Viana et al., 2008a). Acenaphthylene, anthracene, benzo(a)pyrene, naphthalene, phenanthrene and retene are the major components of wood smoke PAH (Khalili et al., 1995). The former is released from both hardwood and softwood, as well as coal, combustion and has been extensively studied due to its carcinogenic properties (Bari et al., 2009, Hays et al., 2003). Retene (1-methyl-7-isopropylphenanthrene) is present in relatively high proportions in softwood smoke and has been used as a tracer for many years (Ramdahl, 1983). It is formed from resin acids typical of softwood burning (Benner et al., 1995), and is very low in hardwood particulate matter (Fine et al., 2002). It is, however, semivolatile and may be partially lost in the atmosphere (Schauer and Cass, 2000)

Source profiles for PAH emissions are useful in receptor modelling and clear geographical and seasonal differences in the ratios of certain species have been identified, depending on the pollution source. Elevated levels of fluoranthene, pyrene and benzo(a)pyrene were identified in rural areas of Croatia during the winter, owing directly to residential heating with wood and coal (Jakovljević et al., 2016). The heating season in Harbin, China was characterised by an increase in the ratio of IcdP/(IcdP + BghiP) and a decrease in ratio of the FL/(FL+PYR), which was attributable to domestic coal burning in the region (Ma et al., 2010). Despite some interferences due to summer wildfires and photodegradation, the wood heating season is also characterised by higher ratios of BaA/(BaA + CHR) and ANT/(ANT + PHE) (Tobiszewski and Namieśnik, 2012). Detailed PAH diagnostic ratios can even be used to differentiate between biomass types, as shown in Table 11-2.

Waste wood	Charcoal	Agricultural residues (open	Grasses	Straw (wheat, barley,	Wood	Softwood	Hardwood	Coal	Anthracite	Bituminous coal	Lignite / brown coal	
-	-	-	-	-	-	0.83-0.96	0.054-0.450	0.30-0.45	-	0.30-0.58	-	RET/(RET+CHR)
0.017-0.23	0.08-0.21	0.15-0.26	0.13–0.23	0.015-0.25	-	0.10-0.26	0.02-0.25	>0.10	0.29	0.098-0.40	0.00–0.16	ANT/(ANT+PHE)
0.45-0.73	0.37	0.66-0.73	0.44–0.49	0.35-0.51	0.43-0.59	0.35-0.64	0.40-0.74	0.35-0.46	0.22-0.49	0.29-0.59	0.39–0.49	BaA/(BaA+CHR)
0.45-0.90	0.33-0.44	0.73-0.78	0.53–0.63	0.13-0.65	>0.5	0.38-0.79	0.47-0.88	>0.50	0.51-0.62	0.28-0.72	0.59–0.85	FLA/(FLA+PYR)
0.30-0.68	0.667	0.56	0.52–0.69	0.15-0.95	0.42-0.62	0.49-0.69	0.074-0.59	0.48-0.56	0.44–0.57	0.31-0.62	-	IcdP/(IcdP + BghiP)
-	-	-	-	-	-	-	-	0.9–6.6	-	-	-	BaP/ BghiP
-	-	-	-	-	0.84	-	-	0.85	-	-	-	PHE/ (PHE + ANT)
-	-	-	-	-	-	0.90	0.71	0.65-0.68	-	-	0.62	1,7/(1,7 + 2,6-DMP)

Table 11-2. PAH diagnostic ratios for typical solid residential solid fuels (Yunker et al., 2002, Tobiszewski and Namieśnik, 2012, Yan et al., 2005, Akyüz and Çabuk, 2008, Galarneau, 2008, Dvorská et al., 2011)

The ratio of 1,7- to 2,6-dimethylphenanthrene (DMP) is a relatively sensitive source apportionment indicator for several fuel types (Benner et al., 1995). Values below 0.5 suggest vehicular emissions, between 0.6 and 0.7 suggest coal burning, and values between 0.7 and 0.9 suggest wood burning (Yunker et al., 2002). However, practical application of diagnostic ratios in regions with a complex mix of PAH sources and sinks has proven difficult and a prior knowledge of sources is useful (Katsoyiannis et al., 2011, Dvorská et al., 2011).

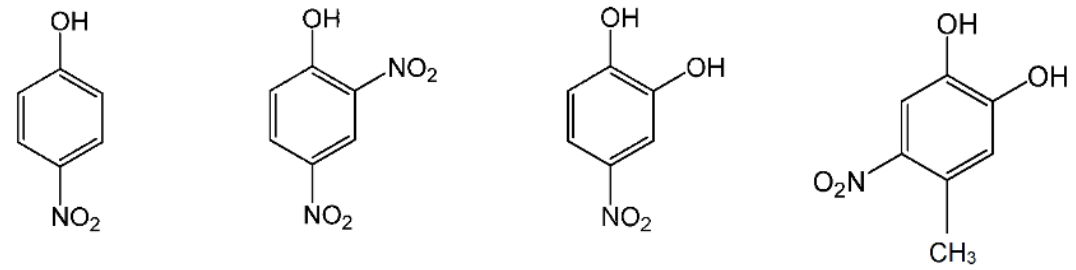
11.1.3. Other tracers and markers

An extensive review of organic markers for different types of biomass combustion was conducted by (Simoneit, 2002). It was found that differences in pyrolysis products from different parts of the biomass (cellulose, hemicellulose and lignin) made the most useful tracers. These are discussed below.

The relative proportions of pyrolysis products from the lignin types (guaiacyl-, syringyl- and anisyl-) can be used for fuel specific source apportionment in areas of mixed biomass burning (Gaston et al., 2016, Simoneit et al., 1993). Guaiacyl- lignins are typical of softwood, whereas a combination of guaiacyl- and syringyl- lignin is typical of hardwood, and anisyl- lignin is typical of herbaceous biomass (Nolte et al., 2001). Pyrolysis of guaiacyl- lignin yields guaiacol (2-methoxyphenol), eugenol (4-Allyl-2-methoxyphenol) and vanillin (4-hydroxy-3-methoxybenzaldehyde) which, together with resin acids and coniferyl alcohols, may be used for source apportionment of softwood burning (Mazzoleni et al., 2007, Nolte et al., 2001). Pyrolysis of syringyl- lignin yields syringol (2,6-Dimethoxyphenol), syringaldehydes, syringyl organic acids and synapyl alcohols (Simpson et al., 2005). Guaiacol is emitted in approximately equal amounts from hardwood and softwood burning, but syringol emissions factors are up 250 times higher for hardwood than softwood burning (McDonald et al., 2000). Specifically propionylsyringol and butyrylsyringol have been identified as particularly useful hardwood tracers (Schauer and Cass, 2000, Oros and Simoneit, 2001b). For softwood, coniferyl alcohol and resin acids such as abietic acid and dehydroabietic acid are particularly useful stable and non-volatile tracers (Bergauff et al., 2009, Schnelle-Kreis et al., 2007, Simoneit, 2002, Oros and Simoneit, 2001a).

Methoxyphenols are semi-volatile pyrolysis products of lignin and are present in relatively high concentrations in both the gas and particle phases of biomass smoke (Chow et al., 2007, Mazzoleni et al., 2007). Accounting for up for 21% of the fine particle mass (McDonald et al., 2000), more than thirty species of methoxyphenols have been identified for biomass burning (Hawthorne et al., 1988). Methoxyphenols have unique tracer properties for biomass burning source apportionment and are relatively easily extracted and analysed. They are advantageous over tracers such as K, CH_3Cl, 14C and anhydrosugars which may be sensitive to variable background concentrations and atmospheric degradation, or require expensive and time consuming analysis (Hawthorne et al., 1988, Simpson et al., 2005, Hoffmann et al., 2007).

Nitrated phenols are a significant constituent of biomass burning secondary organic aerosol. They contribute to the light absorbing fraction of organic carbon (brown carbon) (Mohr et al., 2013) and have been used as biomass burning tracers. Compounds such as 4-methyl-5-nitrocatechol have been found to be present in higher concentrations than methoxyphenols in wood burning regions during the winter, and are evidence of aged, oxidised biomass SOA (Iinuma et al., 2010, Kahnt et al., 2013). The high polarity and stability of nitrophenols makes them one of the most abundant organic compounds in rainwater, which may be problematic as they are phytotoxic and may contribute to forest decline (Harrison et al., 2005). Traffic is believed to be the major source, although wood and coal burning are known to contribute significantly (Kahnt et al., 2013). Emissions factors for nitrophenols range from 1.4-4.6 mg kg^{-1} for peat burning to 12-31 mg kg^{-1} for softwood burning (Iinuma et al., 2007). The most abundant species in wood burning nitrophenols is believed to be 2-nitroguaiacol, although Orasche et al. (2012) found that emissions of 2,6-Dimethoxy-4-nitrophenol were 4 times higher for hardwood burning than softwood burning. The main formation routes for nitrophenols in SOA are believed to be OH oxidation of phenols (Harrison et al., 2005). Formation routes for nitrocatechols in SOA are by photo-oxidation of benzene, toluene and m-cresol (3-methylphenol) in the presence of NO_x (Iinuma et al., 2010, Lin et al., 2015).



4-nitrophenol **2,4-dinitrophenol** **4-nitrocatechol** **4-methyl-5-nitrocatechol**

Figure 11-2. Example structures of common nitrophenols and nitrocatechols. Adapted from (Lin et al., 2015).

Halogenated methane compounds such as methyl bromide and methyl chloride (chloromethane, CH_3Cl) are also useful components in the wood burning source profile for CMB modelling (Edgerton et al., 1986, Turn et al., 1997). Aside from uses in industry or as a refrigerant, biomass burning is a key anthropogenic source of methyl chloride. Natural sources lead to relatively high background concentrations but elevated concentrations have been observed in wintertime ambient air in wood burning communities (Khalil and Rasmussen, 2003, Hawthorne et al., 1988). CH_3Cl emissions factors range from 20.27 ± 1.68 mg kg^{-1} for synthetic logs to 39.99 ± 15.14 mg kg^{-1} for fireplace combustion of hardwood (McDonald et al., 2000). Emissions do not vary with combustion temperature as significantly as elemental tracers (Khalil and Rasmussen, 2003), but emissions factors may be much higher for open burning or burning of high halogen fuels such as waste or agricultural residues (Lemieux et al., 2004). Many of tracers for herbaceous biomass burning are the same as those of woody biomass and hence are not suitable as unique tracers. However, the relative proportions of some species such as PAH and potassium can be useful. In addition, a small number of unique tracers have been identified for herbaceous biomass burning which include anisic acid (p-methoxy-benzoic acid), triterpenoids and sterols such as campesterol (Simoneit, 2002).

For peat, lignite and coal, unique tracers are dependent on the coal rank and burning conditions. The organic fraction of coal smoke is dominated by *n*-alkanes, *n*-alkenes and aromatics such as picene (Dibenzo[a,i]phenanthrene, benzo(a)chrysene), as well as the ratio of hopane to homohopane (Oros and Simoneit, 2000). Lignite smoke is characterised by dominance of C31-hopanes, divanillyl, lignans, di- and tri-terpenoids (Simoneit, 2002). There is also an increase in phenolic emissions with decreasing coal rank. Several studies from the Republic of Ireland offer useful information on source apportionment in regions where the RSF fuel mix is not as dominated by wood as it is much of central Europe, North America, Australia and New Zealand. The fuel mix in Ireland consists of hardwood and softwood logs, peat turf and peat briquettes, manufactured solid fuels (petroleum coke, smokeless fuels), bituminous coals and anthracite (Mitchell et al., 2016). In addition to wood, peat and coal combustion also contribute to potassium, anhydrosugar and PAH concentrations which can hinder fuel specific source apportionment. Speciation can be achieved though additional profiles for peat and coal combustion in PMF models (Dall'Osto et al., 2014), and using PAH and monosaccharaide anhydride ratios. Levoglucosan to manosan ratios of 3.7, 3.1 and 8.6 were found for ash wood logs, bituminous coal and peat briquettes respectively (Kourtchev et al., 2011).

11.1.4. References

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11.2 Appendix II. Supplementary Material for Chapter 4

11.2.1. Theoretical gas composition and ash analysis

The stoichiometric air-to-fuel ratios and theoretical flue gas compositions have been calculated at three separate excess air ratios ε and the results are presented in Table 11-3. The calculations follow the method of Harker and Backhurst (1981).

ε	Parameter	1	2	3	4	5	6	7	8
	A/F_{stoic}	7.05	7.00	9.06	8.16	11.63	10.65	11.49	11.21
0	H_2O	21.4	20.8	16.5	16.1	11.9	9.8	10.1	8.5
	CO_2	15.3	15.7	16.2	16.6	16.5	17.5	17.1	17.9
	SO_2 (ppm)	7	5	0	417	358	1793	753	1185
	N_2	84.7	84.3	83.8	83.4	83.5	82.3	82.8	82.0
	O_2	-	-	-	-	-	-	-	-
100	H_2O	11.6	11.2	8.7	8.5	6.1	5.1	5.2	4.4
	CO_2	7.4	7.6	7.9	8.1	8.0	8.6	8.4	8.8
	SO_2 (ppm)	3	2	0	203	174	877	367	580
	N_2	81.6	81.4	81.2	81.0	81.1	80.5	80.7	80.4
	O_2	11.0	11.0	10.9	10.9	10.9	10.8	10.9	10.8
150	H_2O	9.4	9.1	7.1	6.9	4.9	4.1	4.2	3.5
	CO_2	5.9	6.0	6.3	6.4	6.4	6.8	6.7	7.0
	SO_2 (ppm)	3	2	0	161	138	698	292	462
	N_2	81.0	80.9	80.7	80.5	80.6	80.1	80.3	80.0
	O_2	13.1	13.1	13.0	13.0	13.0	12.9	13.0	12.9

Table 11-3. Theoretical flue gas compositions (%) for the fuels used in Chapter 4.

The primary air flow was adjusted using the damper on the front of the stove to achieve 100% excess air for the coal-based fuels and 150% for the biomass fuels. This was done on the recommendation of the manufacturer of the appliance. As shown in Table 11-3, considerable SO_2 emissions are expected from the combustion of the relatively high sulphur manufactured solid fuels. However, as eluded to in Chapter 4, it is believed that part of the sulphur is bound in the ash through the addition of binders calcium compounds. The ash was examined under SEM and EDS analysis was used to determine the elemental composition. The results are shown in Figure 11-3. Note that the SEM images included here (top row) are not the same positions used for the EDS spectra. The images are included to show the diversity of the smokeless fuel ash and the lignin structure of a wood ash particle. The latter indicates low temperature combustion and therefore the gaseous products will be dominated by cellulose and hemicellulose breakdown products.

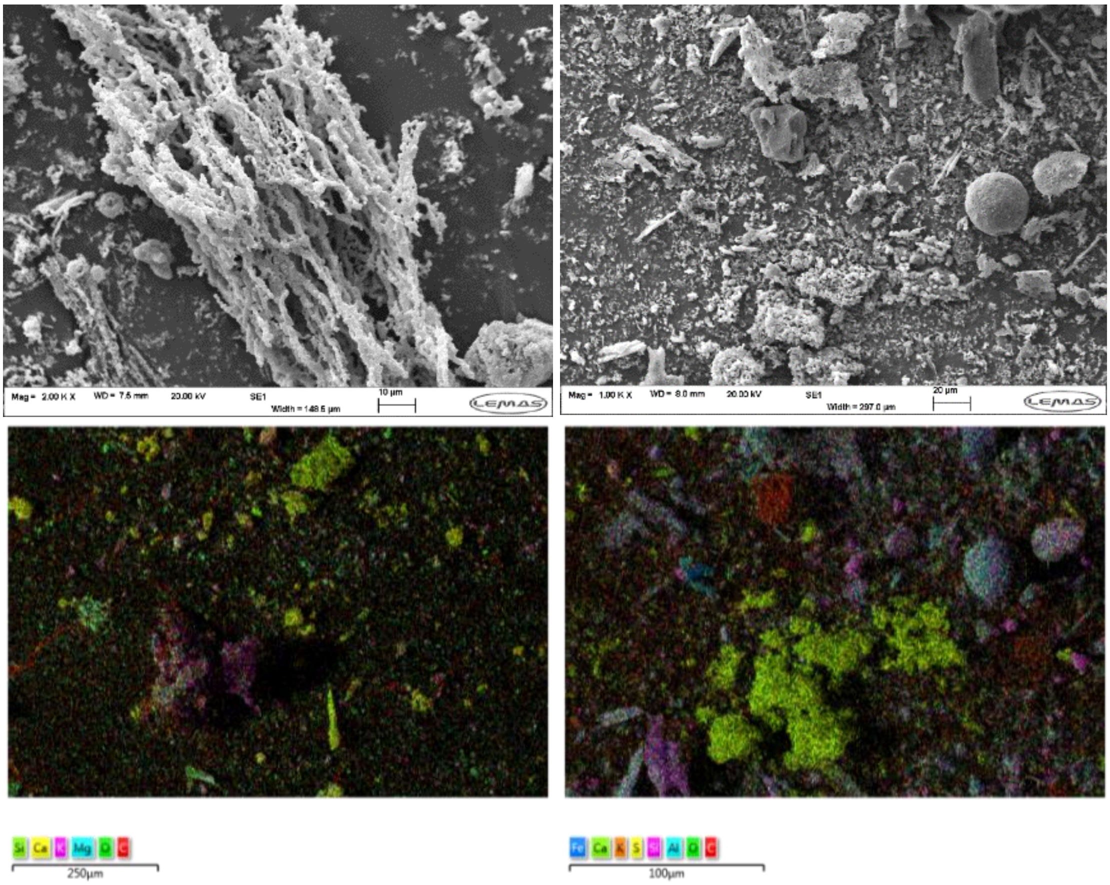


Figure 11-3. SEM/EDS images of wood ash (left) and smokeless fuel ash (right).

From the EDS analysis, the wood ash showed a relatively low carbon content and a high presence of Si, Ca and K; whereas the Ecobrite ash showed high levels of C, Fe, Al and S, as well as Si and Ca. There was also a substantial variation in the amount and carbon content of ash residues following each test. The losses can be categorised into an undergrate (< 13 mm diameter) fraction and an overgrate fraction. Those losses are presented in Figure 11-4.

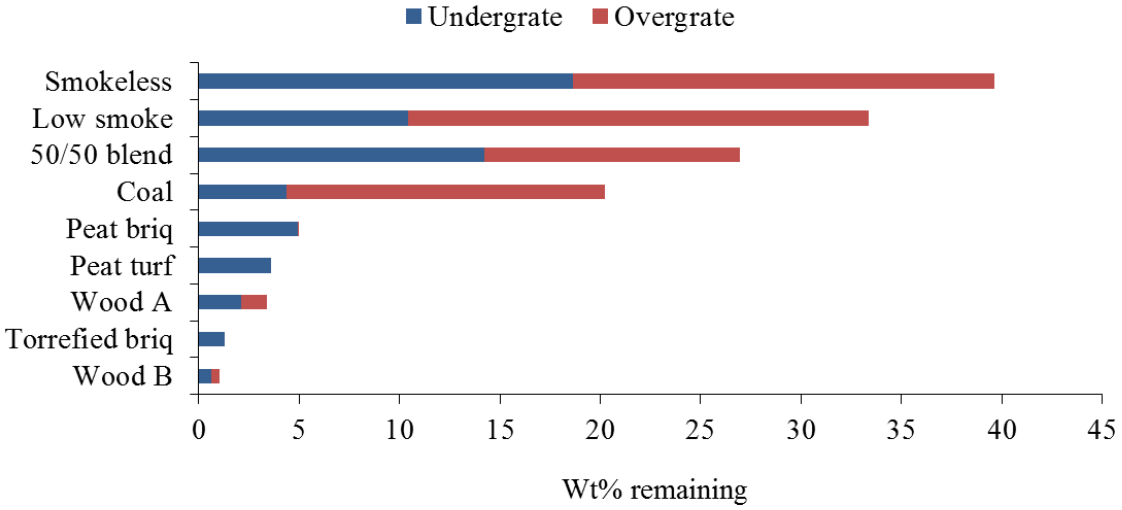


Figure 11-4. Average undergrate and overgrate losses for each fuel.

The overgrate losses are carbonaceous fuel residues that have not fully combusted. Overgrate losses were found to increase with the carbon content of the fuel and were significant for the coal- and coke- based fuels. This may be a result of the batch testing carried out in these experiments, whereby the maximum achievable temperature may not have been reached. Subsequent testing included a number of fuel reloads.

Additional metal analysis was available for the fuels described in Chapter 4, and the results are presented below.

		1	2	3	4	5	6	7	8	Peat turf
Li	mg kg^{-1} db	2.5	0.4	0.2	0.0	8.1	6.1	8.4	8.8	0.4
Be	mg kg^{-1} db	0.0	0.0	0.0	0.0	1.6	0.2	0.2	0.2	0.0
B	mg kg^{-1} db	32.5	7.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Na	mg kg^{-1} db	1003	995	938	1130	991	1271	1272	999	1014
Mg	mg kg^{-1} db	308	835	473	1794	632	1493	1614	482	1420
Al	mg kg^{-1} db	3545	1304	685	808	6444	3349	9553	5000	554
Ti	mg kg^{-1} db	2178	4326	4721	1890	2317	2851	2551	3135	2732
V	mg kg^{-1} db	0.5	0.5	0.3	1.0	35.2	328.5	125.3	220.8	0.7
Cr	mg kg^{-1} db	17.4	17.3	16.9	18.5	23.5	19.9	20.8	21.7	15.3
Mn	mg kg^{-1} db	41.3	15.4	78.1	16.8	8.7	6.8	24.3	11.6	8.0
Fe	mg kg^{-1} db	948	891	1675	7397	6916	3428	8278	4641	6823
Co	mg kg^{-1} db	0.2	2.5	0.2	0.4	8.9	1.6	1.9	2.7	0.5
Ni	mg kg^{-1} db	26.5	25.5	26.1	29.3	64.9	121.2	71.3	110.1	26.6
Cu	mg kg^{-1} db	249.3	7025	43.8	53.6	67.6	52.3	83.4	55.8	60.3
Se	mg kg^{-1} db	14.8	0.0	8.4	2.5	8.7	16.4	5.2	0.0	2.1
Br	mg kg^{-1} db	274.7	221.2	194.0	403.5	259.3	278.9	367.7	391.5	538.2
Cd	mg kg^{-1} db	0.1	1.3	0.2	0.0	0.0	0.2	0.0	0.0	0.0
Sn	mg kg^{-1} db	9.7	10.1	9.9	8.1	9.2	10.8	9.7	7.9	8.9
I	mg kg^{-1} db	13.0	9.6	9.2	43.8	20.3	15.8	21.3	22.2	61.7
Ba	mg kg^{-1} db	50.5	35.6	75.7	251.9	42.6	132.7	253.9	191.9	63.1
Hg	mg kg^{-1} db	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.3
Pb	mg kg^{-1} db	9.1	13.7	4.6	7.9	216.9	13.7	87.4	23.0	13.2

Table 11-4. Additional trace element analysis for fuels 1-8.

The manufactured solid fuels (6-8) show a high content of vanadium and nickel which is consistent with petroleum coke – derived materials. This is consistent with the higher emissions factors reported in Chapter 2 and has health implications for the emitted particulate (Bell et al., 2009). Vanadium is not present in as high quantities in coal (fuel 5), but it did contain the highest concentrations of Be, Al and Pb. The peat briquettes and peat turf contained relatively high levels of Fe, I and Mg.

11.2.2. Experimental Uncertainty

The average emission factors for PM, CO and NO_x for all fuels are presented in Table 11-5, Table 11-6, and Table 11-7. Also included is the number tests conducted and the number of individual data points used to generate each average value.

		Phase value			Whole cycle average		
Fuel	Parameter	Ignition	Flaming	Smouldering	Mean	Median	SD
1	EF (g kg^{-1})	44.5	51	216	117	80	104
	EF (mg MJ^{-1})	2492	2866	12093	6546	4465	5848
	N_{data}	2	20	14	35		
	N_{tests}	2	5	4	5		
	SD		39	93			
2	EF (g kg^{-1})	44.9	58	202	100	72	89
	EF (mg MJ^{-1})	2594	3353	11632	5778	4129	5129
	N_{data}	2	18	27	27		
	N_{tests}	2	4	4	4		
	SD		44	89			
3	EF (g kg^{-1})	16	41	226	138	150	178
	EF (mg MJ^{-1})	722	1851	10330	6307	6840	8142
	N_{data}	2	15	18	18		
	N_{tests}	2	4	3	4		
	SD		45	178			
4	EF (g kg^{-1})	97.7	52	171	101	82	74
	EF (mg MJ^{-1})	5101	2706	8906	5284	4295	3843
	N_{data}	2	21	15	37		
	N_{tests}	2	4	3	4		
	SD		36	57			
5	EF (g kg^{-1})	128.3	52	224	158	91	142
	EF (mg MJ^{-1})	3809	1534	6648	4678	2714	4220
	N_{data}	2	22	36	60		
	N_{tests}	2	4	3	4		
	SD		24	148			
6	EF (g kg^{-1})	129	70	194	141	122	78
	EF (mg MJ^{-1})	4814	2602	7213	5256	4545	2911
	N_{data}	2	24	33	59		
	N_{tests}	2	4	3	4		
	SD		37	58			
7	EF (g kg^{-1})	134.5	113	473	325	262	222
	EF (mg MJ^{-1})	4330	3642	15231	10459	8426	7135
	N_{data}	2	18	27	46		
	N_{tests}	2	4	3	4		
	SD		60	166			
8	EF (g kg^{-1})	142.3	44	210	157	116	140
	EF (mg MJ^{-1})	4427	1375	6525	4895	3602	4347
	N_{data}	2	17	37	55		
	N_{tests}	2	4	3	4		
	SD		27	142			

Table 11-5. CO emission factor variation for all fuels.

The latter represents the number of individual emission factors derived at regular intervals within one test. The whole cycle emission factors and variation is represented by the mean, median and standard deviation. The duration of each phase is also shown in Table 11-7.

		Phase value			Whole cycle average		
Fuel	Parameter	Ignition	Flaming	Smouldering	Mean	Median	SD
1	EF (g kg^{-1})	3.4	1.2	0.8	1.1	0.9	0.7
	EF (mg MJ^{-1})	192.6	64	45	60	48	41
	N$_{data}$	2	21	15	37		
	N$_{tests}$	2	5	5	5		
	SD (g kg^{-1})		0.7	0.4			
2	EF (g kg^{-1})	4.6	2.5	2.2	2.5	2.6	1.2
	EF (mg MJ^{-1})	264.2	141	128	142	148	72
	N$_{data}$	2	18	8	27		
	N$_{tests}$	2	4	3	4		
	SD (g kg^{-1})		0.7	2.0			
3	EF (g kg^{-1})	3.2	2.2	1.3	1.7	1.5	1.0
	EF (mg MJ^{-1})	148.0	98	60	80	70	44
	N$_{data}$	2	15	18	34		
	N$_{tests}$	2	4	3	4		
	SD (g kg^{-1})		0.7	1.0			
4	EF (g kg^{-1})	9.2	6.9	4.6	6.0	5.8	2.2
	EF (mg MJ^{-1})	480.0	361	239	313	305	114
	N$_{data}$	2	21	15	38		
	N$_{tests}$	2	4	3	4		
	SD (g kg^{-1})		2.0	1.5			
5	EF (g kg^{-1})	13.0	6.9	5.7	6.3	6.4	2.4
	EF (mg MJ^{-1})	386.3	204	169	187	189	71
	N$_{data}$	2	22	41	65		
	N$_{tests}$	2	4	3	4		
	SD (g kg^{-1})		2.3	1.9			
6	EF (g kg^{-1})	9.1	5.2	6.6	6.1	5.4	2.8
	EF (mg MJ^{-1})	338.2	194	245	227	201	103
	N$_{data}$	2	24	33	59		
	N$_{tests}$	2	4	3	4		
	SD (g kg^{-1})		2.2	2.9			
7	EF (g kg^{-1})	11.8	8.3	6.5	7.2	7.4	2.5
	EF (mg MJ^{-1})	381.2	267	208	231	238	81
	N$_{data}$	2	18	34	53		
	N$_{tests}$	2	4	3	4		
	SD (g kg^{-1})		2.7	2.1			
8	EF (g kg^{-1})	10.8	6.5	6.4	6.5	6.3	2.3
	EF (mg MJ^{-1})	336.1	203	200	203	197	71
	N$_{data}$	2	17	42	60		
	N$_{tests}$	2	4	3	4		
	SD (g kg^{-1})		2.3	2.2			

Table 11-6. NO_x emission factor variation

		Phase value			Whole cycle average		
Fuel	Parameter	Ignition	Flaming	Smouldering	Mean	Median	SD
1	EF (g kg^{-1})	1.22	2.82	0.64	2.09	1.79	2.23
	EF (mg MJ^{-1})	68.3	158.0	35.6	117.2	100.3	124.8
	N_{data}	1	8	4	12	12	12
	N_{tests}	1	3	3	3	3	3
	SD (g kg^{-1})		2.44	0.16			
	Duration (min)	15	40	50			
2	EF (g kg^{-1})	2.44	2.40	0.45	1.50	1.45	1.35
	EF (mg MJ^{-1})	141.0	138.3	26.2	86.6	83.9	78.0
	N_{data}	1	7	6	13	13	13
	N_{tests}	1	4	3	4	4	4
	SD (g kg^{-1})		1.26	0.19			
	Duration (min)	15	50	55			
3	EF (g kg^{-1})	3.29	1.51	0.36	1.13	0.88	0.92
	EF (mg MJ^{-1})	150.2	68.9	16.3	51.4	40.4	42.0
	N_{data}	1	6	3	9	9	9
	N_{tests}	1	3	2	3	3	3
	SD (g kg^{-1})		0.90	0.07			
	Duration (min)	15	40	125			
4	EF (g kg^{-1})	7.53	3.10	0.62	2.48	1.79	2.62
	EF (mg MJ^{-1})	392.9	161.8	32.5	129.5	93.4	137.0
	N_{data}	1	6	2	8	8	8
	N_{tests}	1	3	2	3	3	3
	SD (g kg^{-1})		3.01	0.11			
	Duration (min)	15	60	60+			
5	EF (g kg^{-1})	12.00	7.48	0.84	4.16	1.94	4.78
	EF (mg MJ^{-1})	356.2	222.0	24.9	123.5	57.7	141.9
	N_{data}	1	12	12	24	24	24
	N_{tests}	1	5	5	5	5	5
	SD (g kg^{-1})		4.85	0.38			
	Duration (min)	15	60	120			
6	EF (g kg^{-1})	13.88	4.27	1.51	3.04	2.48	1.92
	EF (mg MJ^{-1})	516.2	158.8	56.2	113.3	92.4	71.5
	N_{data}	1	5	4	9	9	9
	N_{tests}	1	3	3	3	3	3
	SD (g kg^{-1})		1.64	0.77			
	Duration (min)	15	40	75			
7	EF (g kg^{-1})	13.52	1.46	0.78	1.46	0.70	1.76
	EF (mg MJ^{-1})	435.4	46.9	25.2	46.9	22.5	56.8
	N_{data}	1	19	5	24	24	24
	N_{tests}	1	4	3	4	4	4
	SD (g kg^{-1})		1.76	0.59			
	Duration (min)	15	65	115			
8	EF (g kg^{-1})	10.60	0.56	0.40	0.50	0.45	0.25
	EF (mg MJ^{-1})	329.9	17.6	12.3	15.5	14.0	7.7
	N_{data}	1	11	7	18	18	18
	N_{tests}	1	4	4	4	4	4
	SD (g kg^{-1})		0.30	0.09			
	Duration (min)	15	30	155			

Table 11-7. PM emission factor variation.

11.2.3. Additional fuels

Emissions testing was carried out on additional fuels as well as those given in chapter 4, using the same test assembly. These included Irish peat turf, German lignite briquettes (RWE Union) and UK commercially available wood briquettes or ‘heat logs’. The manufactures of briquettes 1 and 2 were FuelExpress and Calor respectively and both were purchased from hardware shops. They are thermally extruded, densified ‘synthetic logs’ with a slightly higher calorific value, as shown in table 11-8.

		Peat turf	Pine lumber	Lignite briquette	Wood Briquette 1	Wood Briquette 2
MC	% ar	34.4	7.0	13.7	6.7	7.9
VM	% db	65.3	86.1	50.6	90.1	84.8
Ash	% db	3.8	0.2	4.3	1.3	0.7
FC	% db	30.9	13.7	45.1	8.6	14.5
C	% db	56.22	49.2	64.91	49.7	50.56
H	% db	4.86	6.5	4.01	5.78	5.92
N	% db	2.51	0.09	0.72	0.24	0.16
S	% db	0.51	< 0.02	0.32	0.02	< 0.02
O	% db	32.1	44.1		43.0	42.7
GCV	MJ kg^{-1} db	22.358	19.262	24.965	19.818	20.105
Cl	% db	0.29	< 0.01	0.03	0.01	0.01
K	mg kg^{-1} db	137	271	189	1313	446
Na	mg kg^{-1} db	1395	34	2422	51	25
Fe	mg kg^{-1} db	9392	94	3535	97	53
Mn	mg kg^{-1} db	8	64	56	90	39
Ca	mg kg^{-1} db	25250	784	11507	3442	711
Al	mg kg^{-1} db	805	186	705	183	49
Zn	mg kg^{-1} db	48	42	37	38	
Mg	mg kg^{-1} db	1955	379	4364	344	189

Table 11-8. Characterisation of additional commonly used or commercially available fuels.

In comparison to the wood fuels, peat turf and lignite briquettes have a higher carbon, chlorine, sodium, iron and calcium content. The nitrogen content of the peat turf is also much higher than the other fuels, which has implications for NO_x emissions given the linear relationship shown in Chapter 4. Pine lumber has been added here for two reasons. Firstly, to provide a softwood for comparison with the traditional hardwood logs and secondly, to provide a uniformly dimensioned fuel in order to improve reproducibility. Burning a uniformly cut dimensioned fuel is also a requirement of a number national test standards, as described in Chapter 7.

The burning rates and emissions factors for lignite briquettes, peat turf and pine were calculated in the same way as for the other fuels, and the results are presented in Table 11-9.

		Burning rate (kg hour^{-1})	g kg^{-1}			mg MJ^{-1}		
			PM	CO	NO_x	PM	CO	NO_x
Lignite briquettes	Flam	1.52	4.0	92	8	161	3690	326
	Smo	0.45	1.0	380	5	38	15197	201
	Avg	0.81	3.0	274	6	120	10958	247
Peat turf	Flam	2.16	3.9	60	8	145	2690	350
	Smo	0.30	1.0	157	7	43	7023	303
	Avg	1.19	2.4	109	7	102	4856	326
Pine	Flam	1.71	1.0	48	1.1	51	2478	59
	Smo	0.32	0.2	155	0.5	10	8024	26
	Avg	1.30	0.4	97	0.9	21	5015	46

Table 11-9. Emissions factors for lignite, peat turf and pine.

The peat and lignite show similar emissions factors for PM and CO to those shown in Chapter 4. The NO_x emissions factors were low for the pine and high for the peat turf which is as expected given the fuel nitrogen contents. The relationship follows the linear trend shown in Chapter 4. PM emissions are also proportional to the volatile content, but depend on the rate of release of volatiles (or burning rate) and the compositions of the volatile organic fraction. For example, as shown by the TGA results in Chapter 4, during devolatilisation the mass loss rate for wood B (5.76 wt% min^{-1}) is a factor of ten greater than for the smokeless fuel (0.54 wt% min^{-1}). The PM emissions factors for the pine are slightly lower than expected which may be due to an instrumental error in the gravimetric filter measurement.

The flue gas temperatures also reflect the differences in the combustion conditions between the fuels. These are presented in Figure 11-5. There is a clear distinction in the flue gas temperature profiles between the biomass fuels, peat/lignite fuels and coal/coke fuels. Biomass (green) shows a distinct peak in flue temperature, correlated with burning rate, due to combustion of volatiles and formation of soot and EC particles. Flue temperatures are lower for the coal- and coke- fuels and show a slow increase and decay, though more of the heat is radiated into the room rather than being lost in the flue. Interestingly, the peat fuels show an intermediate profile.

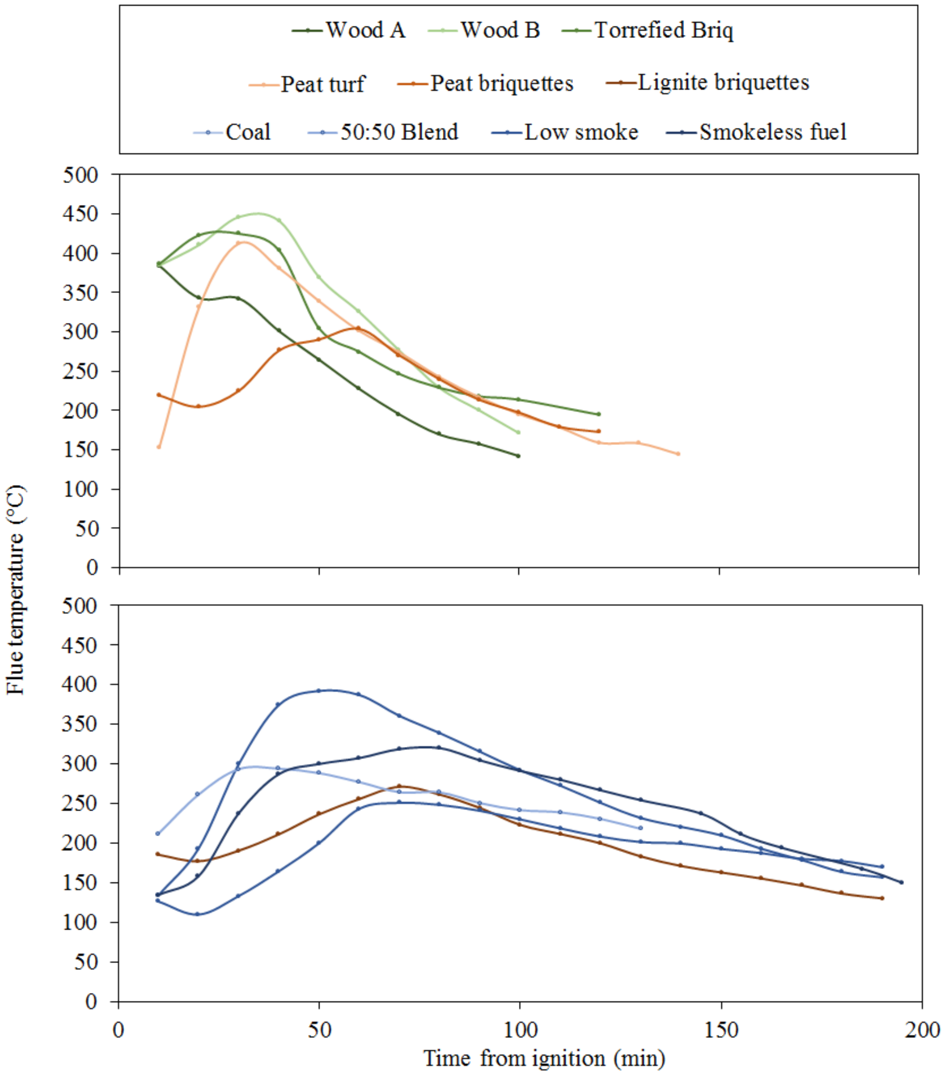


Figure 11-5. Flue gas temperature variation for wood fuels (green), peat & lignites (red/yellow) and coals (blue).

11.2.3. References

BELL, M. L., EBISU, K., PENG, R. D., SAMET, J. M. & DOMINICI, F. 2009. Hospital Admissions and Chemical Composition of Fine Particle Air Pollution. *American Journal of Respiratory and Critical Care Medicine*, 179**,** 1115-1120.

HARKER, J. H. & BACKHURST, J. R. 1981. *Fuel and Energy*, London, New York, Academic Press Inc.

11.3 Appendix III. Supplementary material for Chapter 5.

11.3.1. Observations of correlations between combustion conditions and PM

The impact of combustion conditions on burning rate, NO_x, CO and particulate is shown in Figure 11-6. Each data point on the PM trendline corresponds to one of the filters shown below. It is clear that NOx and dark soot are correlated with the flaming phase.

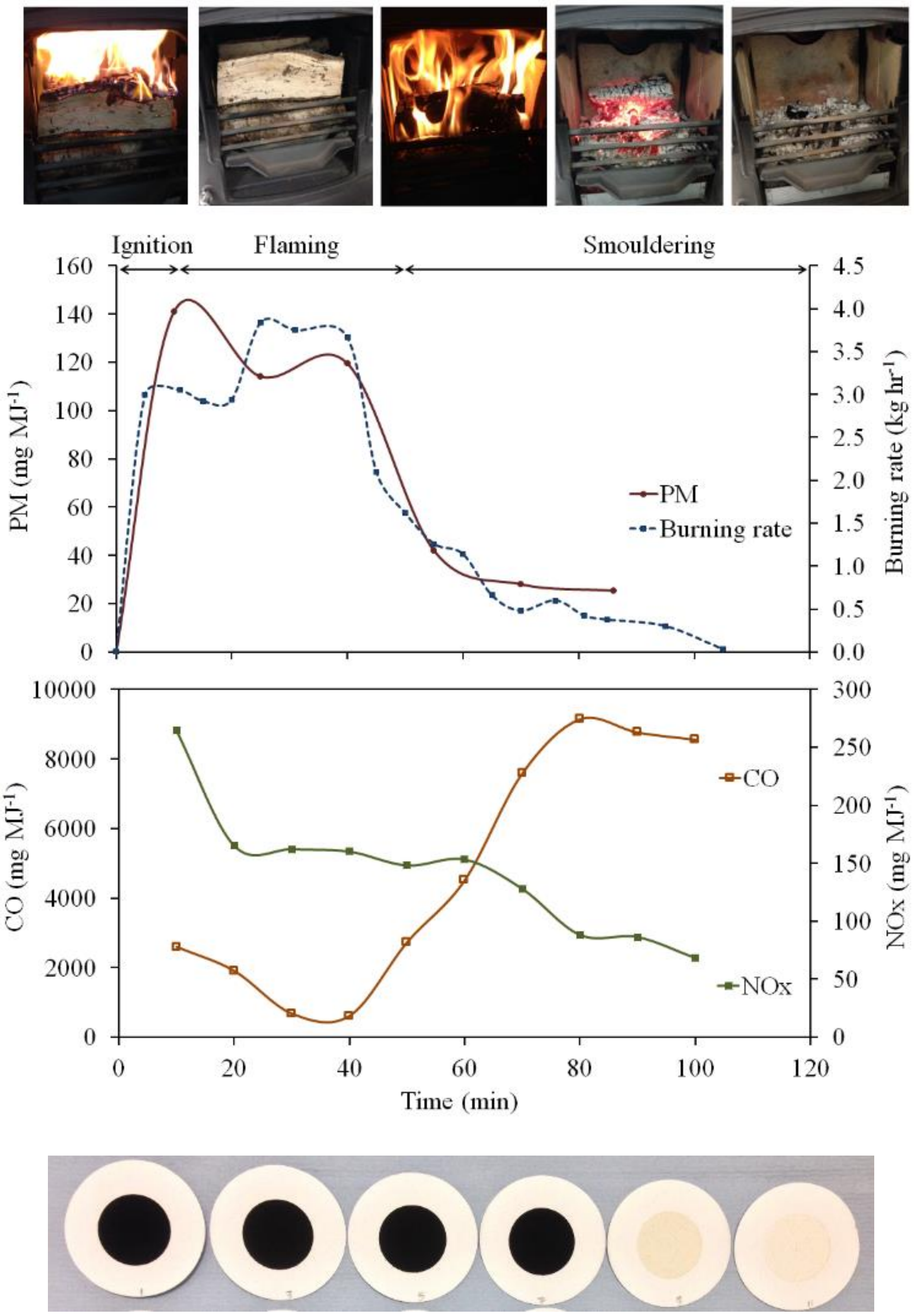


Figure 11-6. Emissions profile for Wood B (birch logs).

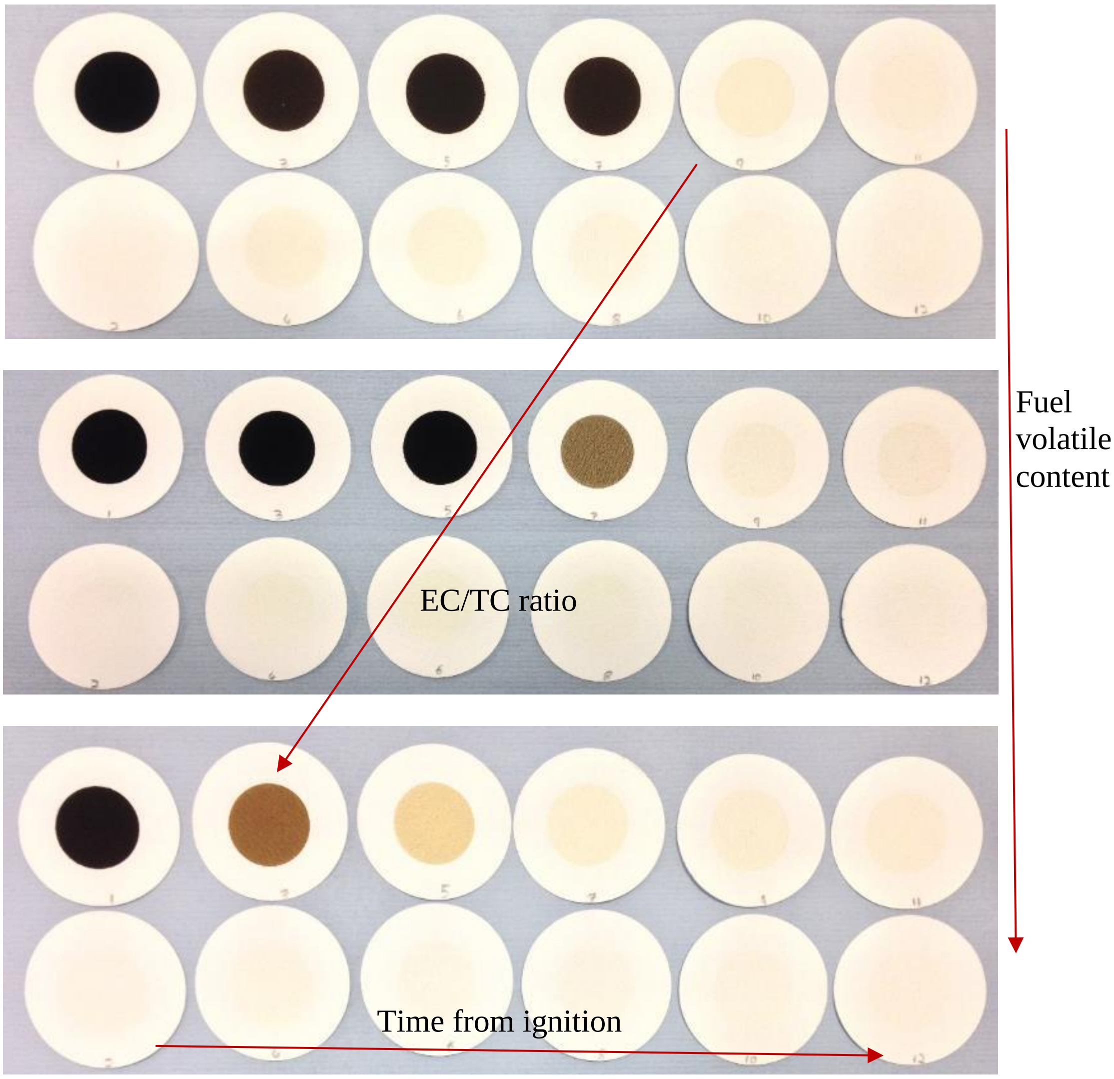


Figure 11-7. Photos of the front and backing filters for wood A (top), torrefied briquettes (centre) and smokeless fuel (bottom).

The high volatile wood fuels are dominated by black particles (high EC) due to combustion of volatiles and there is a relatively short smouldering phase due to the relatively low fixed carbon content. The filter photos show that torrefaction reduces the duration of the volatile combustion stage which is associated with the highest emissions of PM through soot formation. Very low volatile fuels such as charcoal and smokeless fuel (bottom) are dominated by fixed carbon burning which does not produce large quantities of EC. The initial black filter may be due to interference from the firelighter. The images also show a ‘transition’ phase whereby the PM is coloured brown due to the release of volatiles which are not converted to EC in the flame. For wood fuels, the transition phase last only a matter of minutes but can be tens of minutes for the smokeless fuel. As described in Chapter 2, it is understood that brown carbon is largely a product of low temperature smouldering burns. During one test using pine, the fuel did not properly ignite and entered into a smouldering phase throughout the entire combustion cycle.

This resulted in a prolonged low-temperature burn with high CO and high brown carbon, as shown in Figure 11-8.

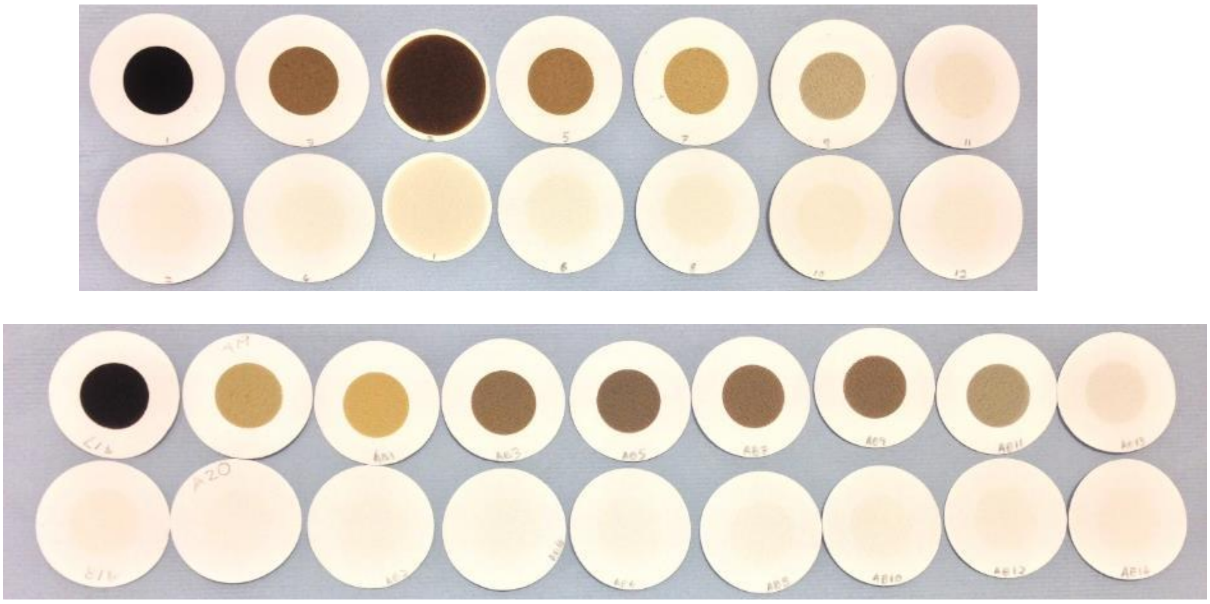


Figure 11-8. Photos of the front and backing filters for lignite (top) and smouldering pine (bottom)

There is also a stronger discolouration of the backing filters from smouldering burns, indicating that the particles or condensed organics are less than the pore size of the filter (0.3 µm). In addition to the brownness of the filters, there is an increase in the mass of condensate collected from the impingers as evidenced by a stronger discolouration of the water.

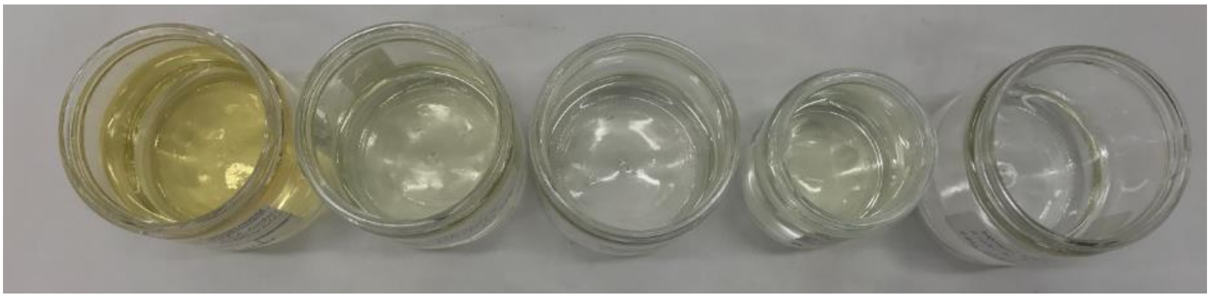
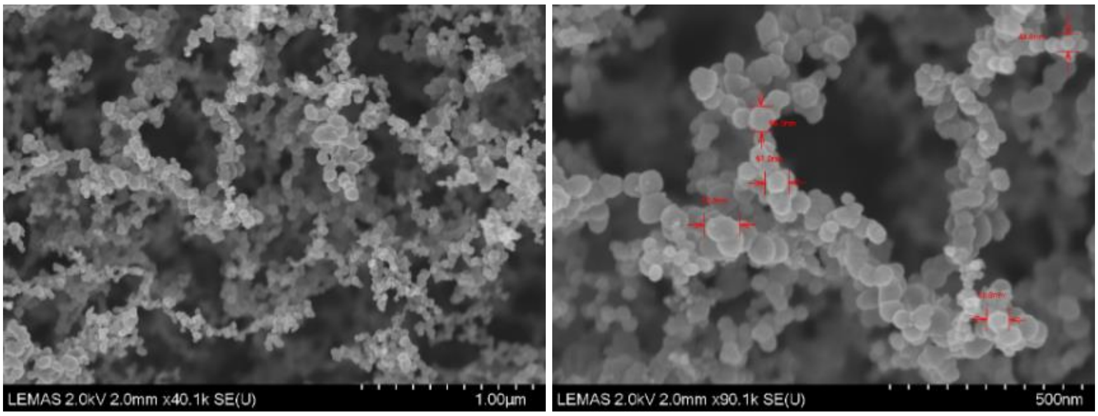


Figure 11-9. Photos of the impinger condensate for Wood A, pine, torrefied briquettes, peat briquettes and smokeless fuel (left to right).

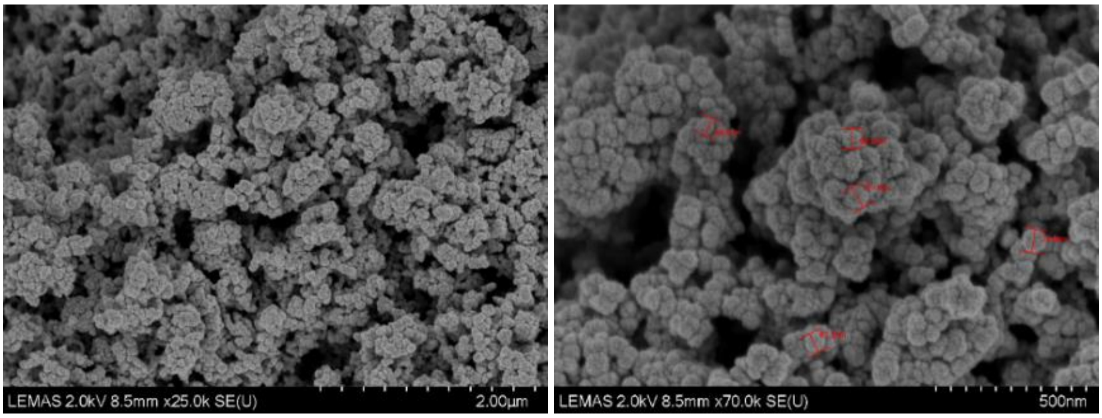
11.3.2. Electron microscopy

SEM images are presented in Chapter 5 for flaming phase wood PM, transition phase wood PM (brown carbon), and soot generated by model compounds. In addition to these images, more detailed investigation of particles was carried out on samples generated from difference fuels and combustion conditions.

(a) Pine (flaming phase, high EC)



(b) Wood A (flaming phase, high OC)



(c) Fuel 7 (coke-derived MSF)

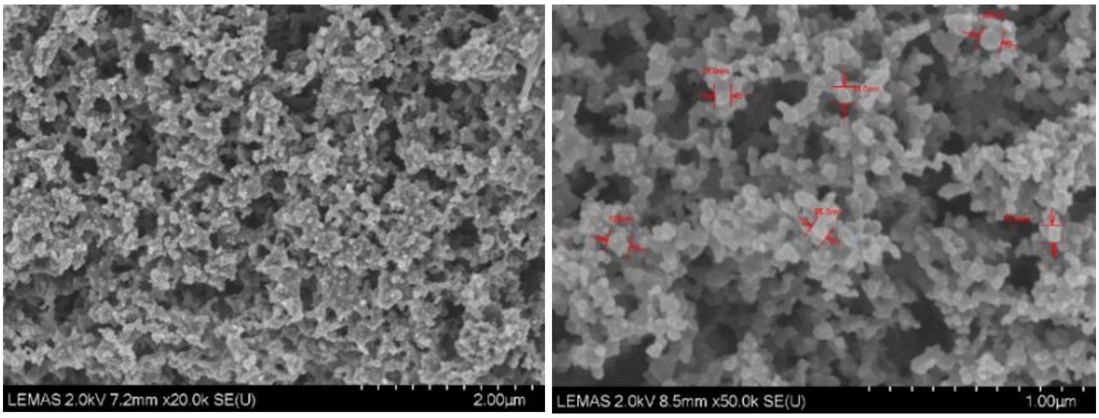
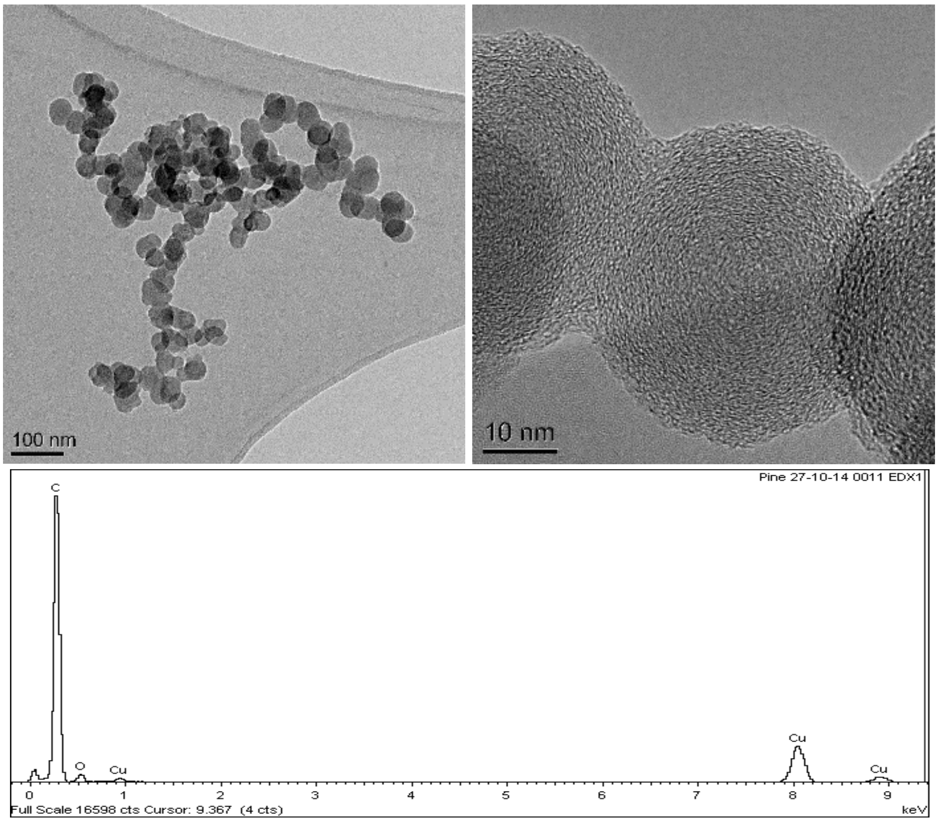


Figure 11-10. SEM images showing the morphology of selected fuel soot samples

(a) Pine soot particles



(b) Fuel 7 (coke-derived MSF)

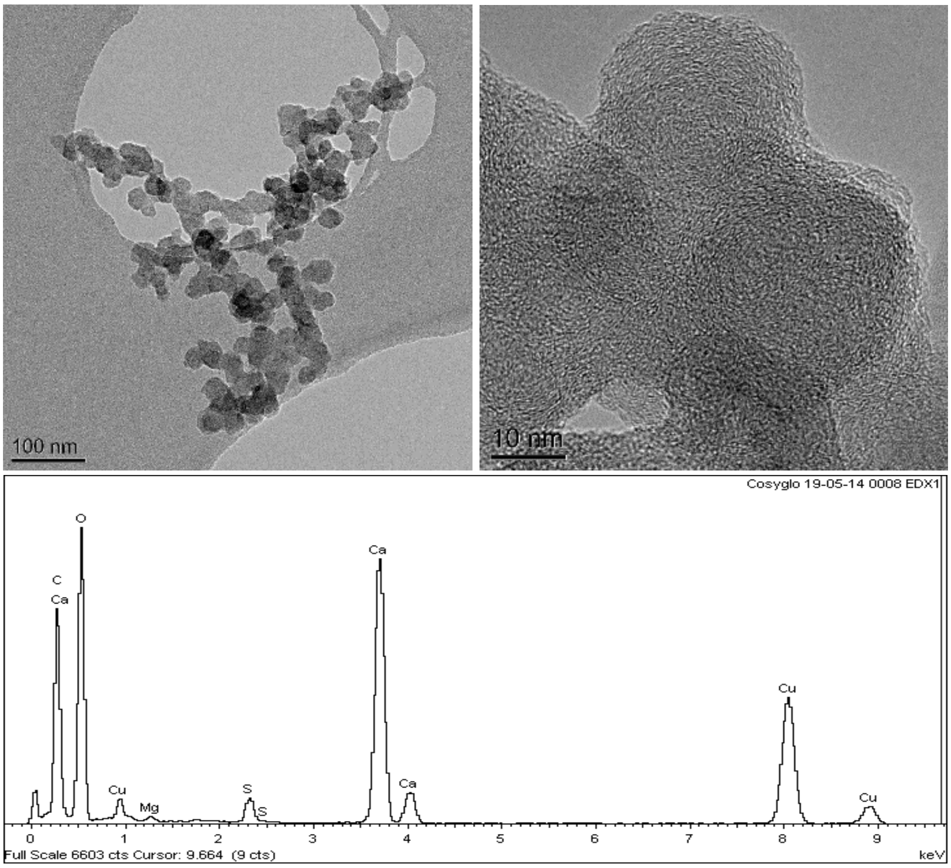


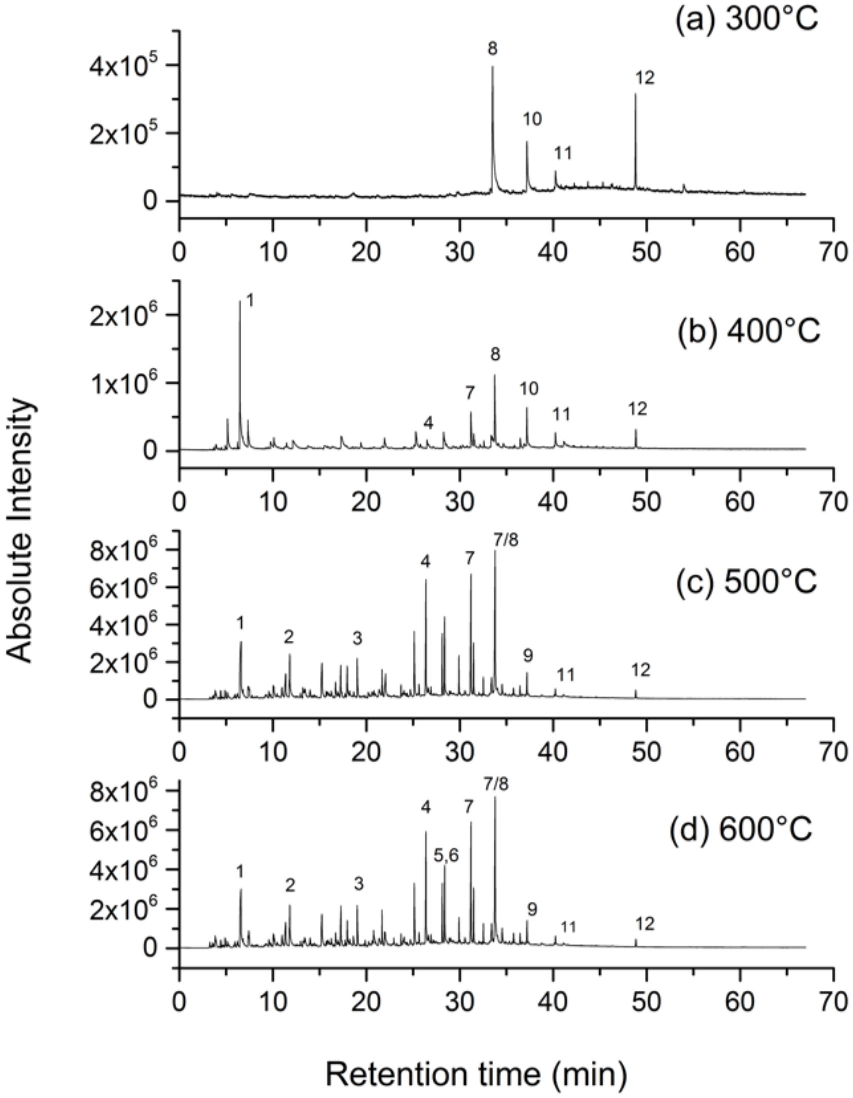
Figure 11-11. TEM/EDS results for recovered soot particles

As shown in Figure 11-10, fuel type and combustion conditions have a significant impact on particle size and morphology. The modified combustion efficiencies (MCE) during sampling for pine, wood A, wood B and fuel 7 were 0.96-0.98, 0.87-0.92, 0.95-0.99 and 0.93-0.95 respectively. The slightly lower MCE value for wood A is consistent with the higher OC emissions reported in Chapter 5. Interestingly, this seems to have an impact of the morphology of the emitted particles. The lower efficiency appears to cause the soot clusters to become more closed and sticky compared to the open branched chains of high MCE burns.

The fuel source also appears to impact on the morphology of emitted particles. The SEM images of the fuel 7 (coke-derived MSF) reveal particles with a more granular and less spherical structure than wood burning particles. This was confirmed by TEM as shown in Figure 11-11. EDS analysis also showed the wood burning particles to be highly carbonaceous, typical of EM particles. The EDS analysis of the fuel 7 particles, however, showed a presence of oxygen, calcium and sulphur. This suggests that not all of the sulphur in the fuel is bound in the ash, with a fraction being released to atmosphere. It should be noted here that the soot particles analysed were liberated from the filters using acetone which would likely have removed any organic coatings.

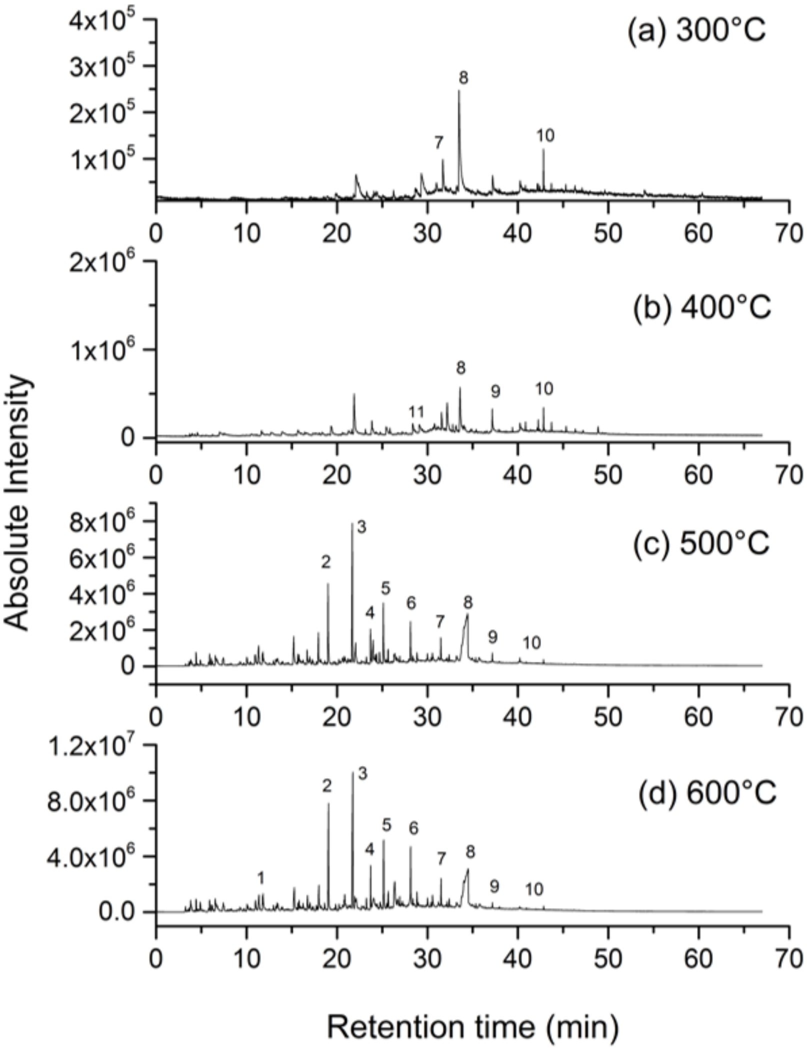
11.3.3. Py-GC/MS

The composition of the organic fraction of the fuels was also analysed by pyrolysis gas chromatography mass spectromety, as described in Chapter 3. Pyrolysing the samples in a helium atmosphere at different temperatures allows the identification of the thermal breakdown products of each fuel. The chromatograms produced from the pyrolysis of wood B (Birch, *Betula sp.*) and torrefied spruce briquettes (*Picea sp.*) at 4 temperatures are shown in Figure 11-12 and Figure 11-13 respectively, together with a table of peak assignments. For comparison, the chromatogram for Polish coal pyrolysied at 700°C is shown in Figure 11-14. In comparison to Wood B, the torrefied briquettes show lower abundances of volatile organic species such as acetic acid at 300°C and 400°C. Lower temperature pyrolysis mostly releases organic acids, including resin acid (dehydroabietic acid) for the torrefied spruce briquettes. As the temperature increases, higher abundances of methoxypenols and lignin derivatives are observed. These include guaiacyl-lignin components for the hardwood and guaiacyl- and syringyl- components for the softwood. Slightly lower abundances of 1,2-Cyclopentanedione were detected in the torrefied fuel, which are important intermediates in the formation of soot (see chapter 2). In comparison to the wood fuels, pyrolysis of the coal based fuels yielded tar compounds (toluene, xylene and xylenol) as a number of aliphatic compounds. This is to be expected given the composition of the parent fuel (see chapter 2).



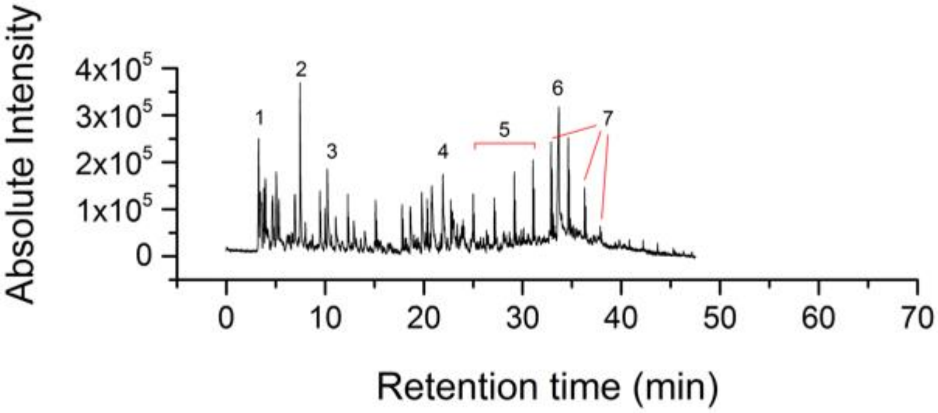
1	Acetic acid
2	3-furaldehyde
3	Guaiacol
4	Syringol
5	Acetyleugenol
6	1,2,4-trimethoxybenzene
7	Methoxyeugenol
8	Levoglucosan
9	Pentadecanoic acid
10	Hexadecanoic acid
11	Octadecanoic acid
12	Squalene

Figure 11-12. Py-GC/MS results of Wood B (Birch logs)



1	Furfural
2	Guaiacol
3	Creosol
4	Ethylguaiacol
5	4-vinylguaiacol
6	Eugenol acetate
7	Guaiacylacetone (smoke flavour)
8	Levoglucosan
9	Hexadecanoic acid
10	Dehydroabietic acid
11	Eugenol

Figure 11-13. Py-GC/MS results of torrefied spruce briquettes.



1	Maytansine
2	Toluene
3	o-xylene
4	2,6-Xylenol
5	Decane derivatives
6	Levoglucosan
7	Acyclic alkanes

Figure 11-14. Py-GC/MS results of Polish coal at 700°C.

11.4 Appendix IV. Supplementary material for Chapter 6.

Supplementary material for chapter 6 has been published alongside the journal article and is available online (http://dx.doi.org/10.1016/j.biortech.2016.04.057). The document consists of two figures showing the py-GC/MS chromatograms of the heartwood and bark samples. This analysis was performed by K. Parmar and hence is not included here (see section 1.3).

11.4.1. Ash analysis

Additional material is also presented from the analysis of undergrate ash residues. This analysis was performed by SEM/EDS in order to investigate the elemental composition of the ash, in the hope of understanding why slagging occurred with the reed briquettes. A comparison of SEM/EDS analysis for wood ash and reed is given in Figure 11-15 and Figure 11-16. The clinker formed in the stove bed during reed briquette combustion is shown in Figure 11-17. The low ash melting temperature of biomass compared to coal is well known from large scale high temperature industrial combustion, but this is believed to be the first time slagging has been observed in household scale stoves. It was hypothesised that the high Cl, Si, Na and Mg content of the reed caused the fuel to have a lower ash melting temperature. The impact of these elements on ash thermal behaviour can be expressed by the base to acid ratio $R_{b/a}$:

$$R_{b/a} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + TiO_2 + Al_2O_3 + P_2O_5}$$

Where the numerator represents base oxides and the denominator acid oxides. $R_{b/a} < 0.5$ represents a low risk of slagging whereas $R_{b/a} > 1$ represents a severe slagging risk (Gudka et al., 2012). The base to acid ratios for different fuels are shown in Figure 11-18. It should be noted, however, that this ratio is derived from coal testing and analysis and therefore may not be as fully representative of the slagging risk for biomass due to significant differences in K, Ti and Al (Teixeira et al., 2012). Cl and S are also omitted. Nevertheless, there is a clear linear relationship between base to acid ratios for different types of biomass (woody, torrefied and herbaceous). The calculated $R_{b/a}$ values range from 5.5 to 7.5 for oak sticks and 0.3-1.1 for bagasse, straw and reed. The high values for the wood fuels are a results of high Ca contents and do not necessarily indicate a higher slagging tendency than fuels such as reed because the relationship between percent basic and softening temperature is parabolic (Baxter et al., 2012).

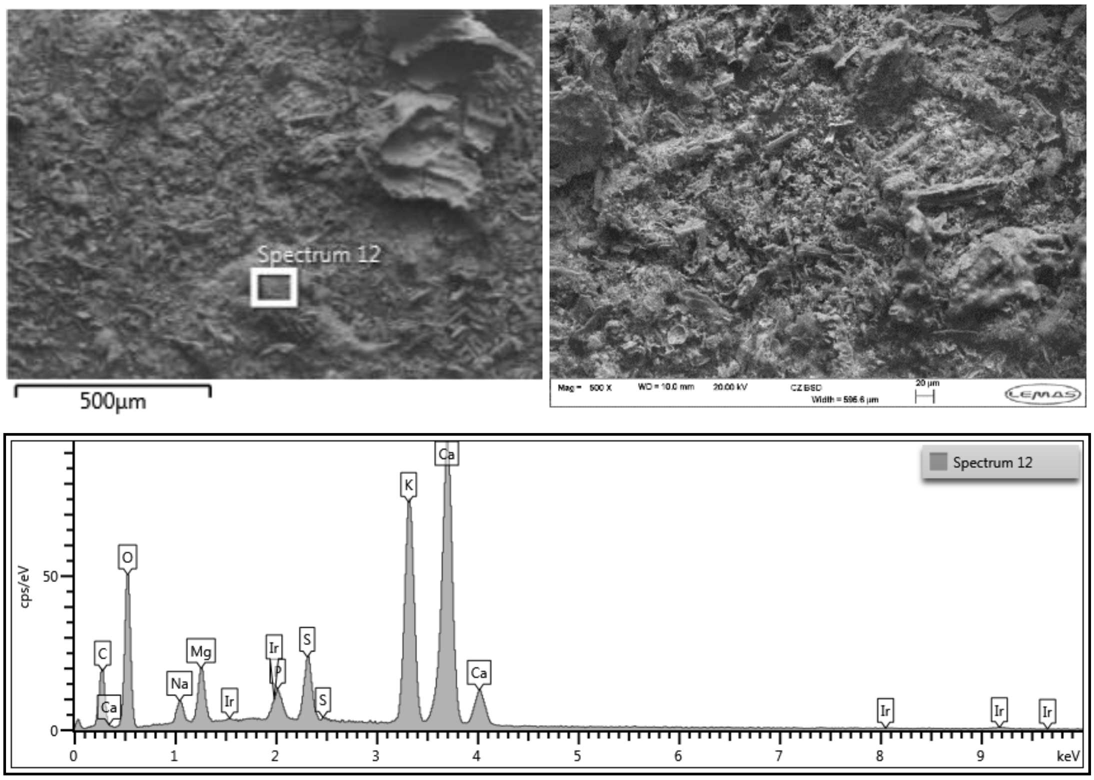


Figure 11-15. SEM/EDS analysis of Ash wood logs residue.

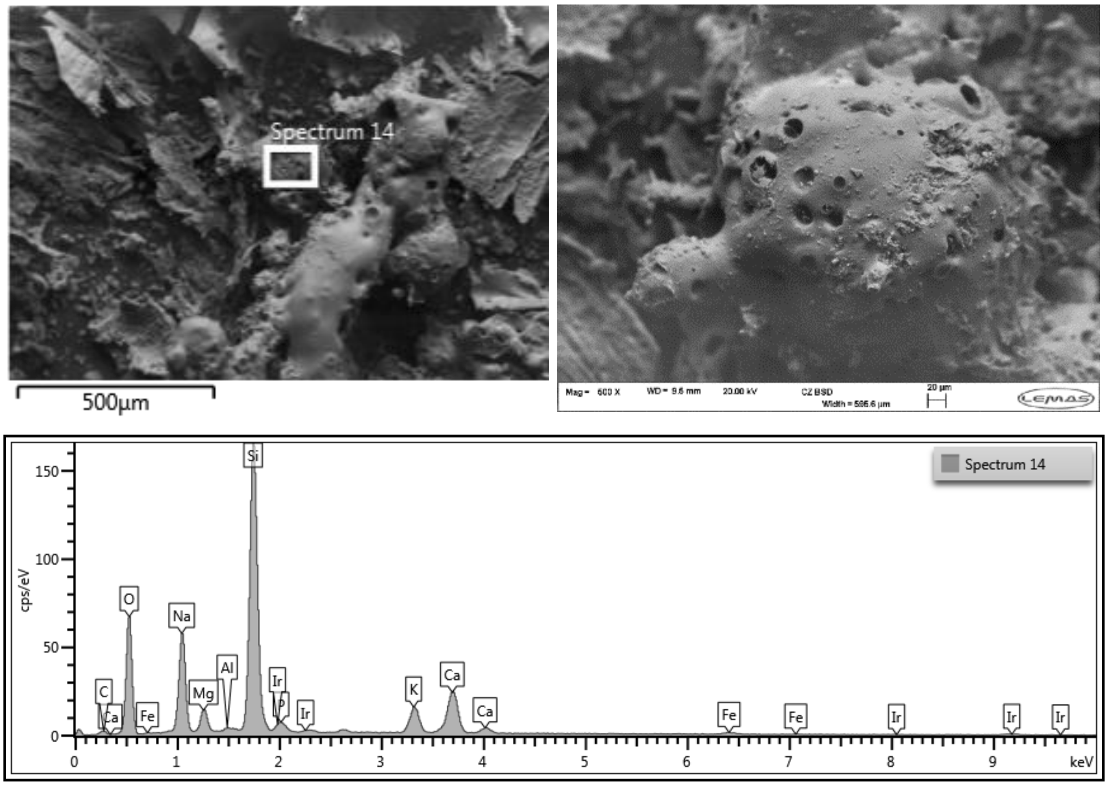


Figure 11-16. SEM/EDS analysis of reed briquette residue.

Figure 11-17. Photo showing clinker formed during the reed briquette combustion test.

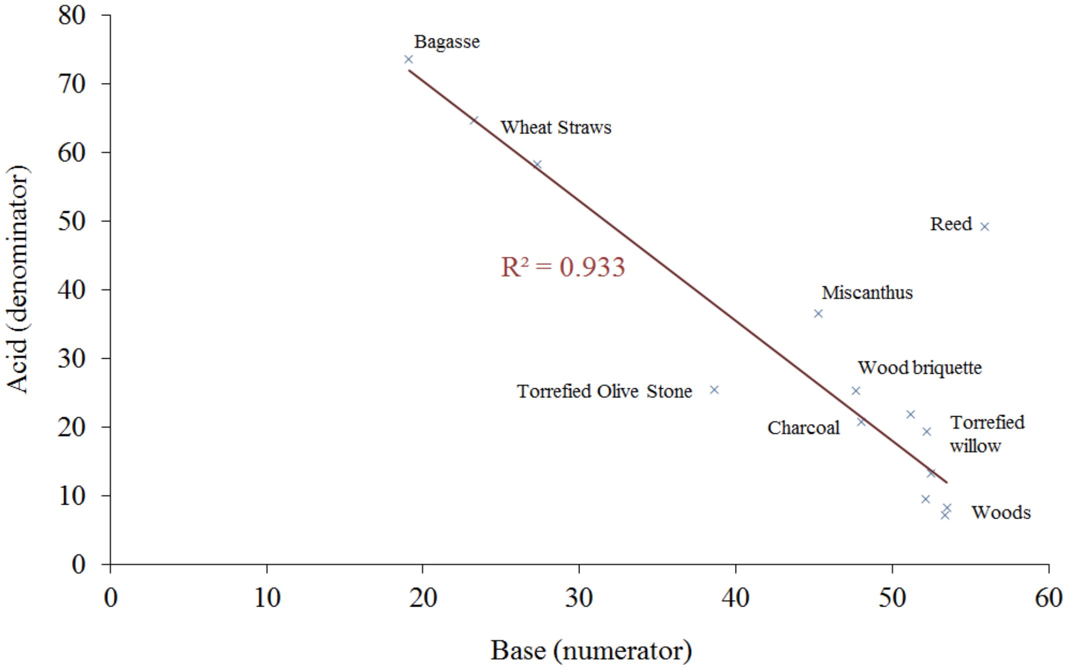


Figure 11-18. Base to acid ratios for a selection of fuels.

11.4.2. Additional Fuels

As described in Chapter 2, there is a growing affinity for non-traditional residential fuels in the UK and abroad (Roy and Corscadden, 2012). These consist of synthetic logs or briquettes made from fast growing energy crops or from agricultural residues. A journal article titled '*The Impact of Agronomy on the Potential of Agricultural Residues for Small Scale Domestic Heating*' is currently under development. This project has been set up in collaboration with Ian Shield and Carly Whittaker from Rothamsted Research on the characterisation and emissions testing of a variety of agricultural residues. The majority of the fuels are wheat and barley straws from different sites which have been subjected to different fertilisers and growing conditions, as shown in Table 11-10. In addition, sugarcane bagasse and miscanthus fuels were used for comparison, which are available in large quantities.

Fuel	Site	N (kg Ha^{-1})	K as K_2SO_4 (kg Ha^{-1})	Notes
Winter wheat straw	013			Low S, high Cl
Winter wheat straw	093	192	90	P. Predicted high S, low Cl fuel.
Winter wheat straw	123	240	180	N split dose, Na until 2000. Mg high. Predicted poor fuel.
Winter wheat straw	143			Low S, low Cl
Spring barley straw	424	144	90	High P, Mg
Spring barley straw	443	144	90	High Si, P, Mg
Spring barley straw	723	144		N, P & K from farmyard manure
Bagasse	-	-	-	Brazilian sugarcane bagasse
Miscanthus	-	-	-	Commercially made briquettes

Table 11-10. Agricultural residues used in the study

Fuel characterisation was carried out using the methods outlined in Chapter 3. For the emissions testing, the samples needed to be briquetted following milling (<4 mm) and drying. Initial briquetting trials used a hydraulic press with a 50 mm dia, 65 mm long die. The max pressure applied was 30 MPa and a heating jacket heated the die to 125°C. However, the briquettes were substantially smaller than the commercially made reed and sawdust briquettes which had been thermally extruded, as shown in Figure 11-19. There was also a significant rebound effect during straw briquetting. Consequently, briquetting was outsourced as described in Chapter 3. Characterisation results of the fuels are presented in Table 11-11.

The straw briquettes proved difficult to ignite using the standard firelighter method and batch testing. Hence a bed of charcoal was used to bring the bed up to temperature before straw briquettes were loaded. A batch of ~700 g of briquettes was added approximately every 40 minutes. It was found that the frequency of reloading has a substantial impact on emissions; the longer the fuel bed is left to burn out, the lower the temperature and poorer the combustion of the ensuing batch, leading to increase organic, CO and CH_4 emissions.

	% db				% db				CV	Cl
Sample	C	H	N	S	MC	VM	FC	Ash	MJ kg^{-1}	%
Straw 013	44.3	6.2	0.5	0.10	6.7	82.3	12	7.0	17.62	0.06
Straw 093	50.3	5.5	0.5	0.06	5.8	79.6	16.2	4.2	19.71	0.03
Straw 123	47.8	5.2	0.6	0.08	8.7	78.6	16.8	4.7	19.59	0.04
Straw 143	43.2	6.2	0.4	0.24	6.6	87.7	6.6	5.7		0.02
Straw 424	48.7	5.1	0.9	0.10	7.4	75.1	19.0	5.9	19.75	0.11
Straw 443	48.2	5.1	0.9	0.10	7.8	74.2	19.3	6.5	19.66	0.13
Straw 723	47.4	5.2	0.5	0.06	7.3	76.6	18.2	5.2	19.23	0.05
Bagasse	48.2	5.6	0.3	0.03	5.9			5.4		0.01
Miscanthus	47.3	5.7	0.8	0.10	9.1			4.6		0.25

Table 11-11. Characterisation of the agricultural residue samples.

Inorganic analysis was also carried out and substantial differences were found compared to the standard commercial fuels used in chapters 4 and 5. The SiO_2 content of the 60% SiO_2 in the ash of bagasse ash and wheat straw ash was over 60%. The bagasse also contained significantly higher levels of Al and Fe which will affect the ash softening properties. The briquette size and shape also varied by fuel type, as shown in Figure 11-19.

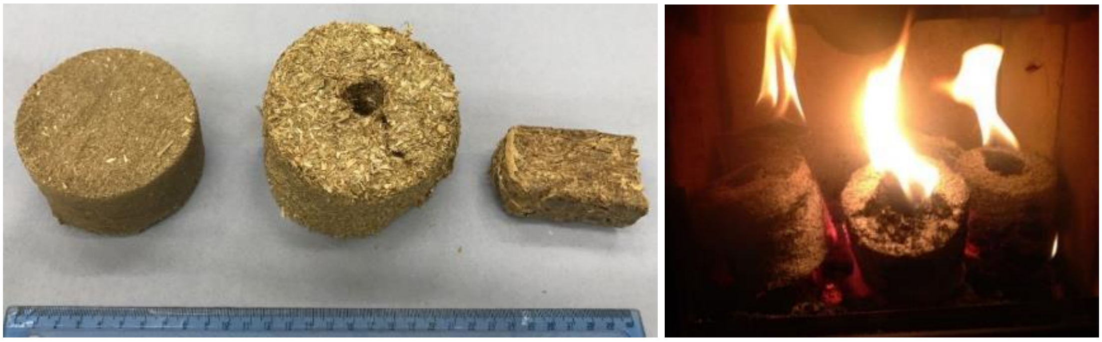


Figure 11-19. Photos showing the bagasse (left), straw (centre) and miscanthus (right) briquettes during emissions testing.

Emissions testing revealed large differences between the fuel types. An example emissions plot is shown in Figure 11-20 for barley straw briquettes (site 424). The flaming and smouldering phases identified in earlier chapters can be easily distinguished by the modified combustion efficiency (MCE). For these tests, MCE never dropped below 0.6 during the smouldering phases and was generally 0.9 or above during flaming. HCl, SO_2, formaldehyde and acetic acid peak in the flaming phase just after fuel addition, whereas CO and CH_4 peak in the smouldering phase. Interestingly, up to 50 ppm of N_2O is emitted alongside NO and NO_2, which has important implications for climate is it has a GWP of up 300. Temperature also plays a key role in emissions formation and is presented for barley straw 443 in Figure 11-21. The high bed temperature at the start is due to the charcoal used to ignite the fuel. The trihedron temperature, approx. 500 mm from the stove surface, peaks at 31°C. Filters generated in this study were analysed for EC and OC by Sunset Laboratories using the NIOSH thermal optical method. Results verified those of earlier work which used TGA to determine EC/OC.

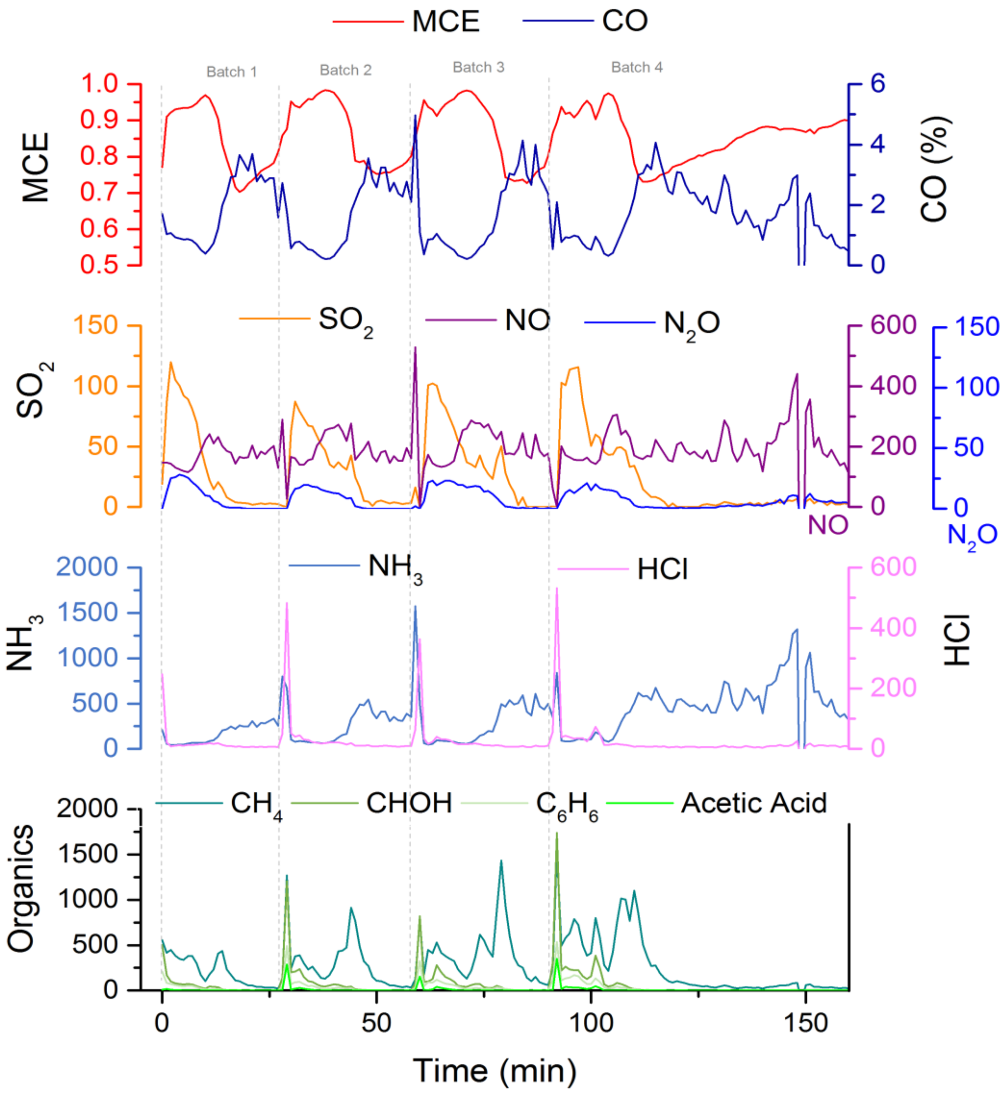


Figure 11-20. Emissions profile for barley straw 424 briquettes. Axes show concentrations in ppm at 13% O_2 and STP, unless otherwise stated.

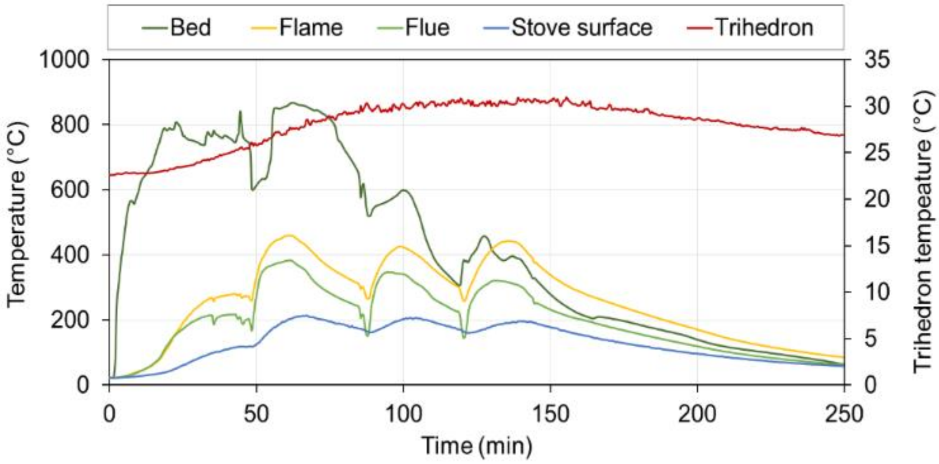


Figure 11-21. Temperature profiles for barley straw 443 briquettes.

References

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