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POLYCYCLIC AROMATIC HYDROCARBON
EMISSIONS FROM RESIDENTIAL WOOD
COMBUSTION

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Academic Dissertation

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Syvänniemi, May 2016

Kati Nuutinen

Abstract

Keywords: polycyclic aromatic hydrocarbons (PAHs), residential wood combustion, gas-particle partitioning, fine particle emissions

Wood and biomass combustion is favoured due to its expected lower climate impact compared to fossil fuels. However, incomplete combustion may produce significant emissions of pollutants that are hazardous to human health, e.g., polycyclic aromatic hydrocarbons (PAHs). Residential wood and coal combustion is one of the major sources of fine particles and PAHs in ambient European air. However, the emission factors of wood-fired appliances, particularly for PAHs, remain relatively poorly known.

In this study, new information on PAH emissions from different types of appliances, several operational practices and various combustion conditions was produced. In addition, the effect of sampling and dilution conditions on the emissions of PAHs and fine particles were studied.

Overall, the variation in particulate PAH emissions were large. Continuous combustion appliances such as small-scale pellet boilers had considerably lower PAH emissions compared to batch combustion appliances. Sauna stoves had high PAH emissions. More sophisticated and modern batch combustion devices involving the staging of combustion air had lower PAH emissions compared to conventional appliances. Poor user operation was found to cause considerably higher PAH emissions.

Novel method utilizing denuders was used for determining the partitioning of PAHs between the gas and particle phases. Sampling conditions greatly affected the partitioning. Correspondingly, due to changes in the partitioning of semivolatiles, the PM₁ mass emissions measured from diluted exhaust were higher than the parallel total dust emissions from hot, undiluted exhaust.

With dilutive sampling, more atmospherically relevant sampling conditions are created, and results that better mirror exposure and combustion quality are obtained. A precise definition of acceptable sampling conditions is needed.

The results of this work show that PAH emissions from residential wood combustion can be substantially reduced by modern technologies.

Abbreviations

CB	Chip boiler
CBC	Conventional batch combustion
CMH	Conventional masonry heater
DGI	Dekati gravimetric impactor
DR	Dilution ratio
EC	Elemental carbon (soot)
ED	Ejector diluter
EFC	Efficient combustion
FID	Flame ionization detector
FTIR	Fourier transmission infrared spectrometer
GC-MS	Gas chromatography-mass spectrometry
IBC	Improved batch combustion
IEBC	Inefficient batch combustion
LB	Log boiler
LS	Log stove
MCE	Modified combustion efficiency
MMH	Modern masonry heater
MW	Molecular weight
NAS	National application standard
NC	Normal combustion
NMVOC	Non-methane volatile organic compound
NT	New technology
NTP	Normal temperature and pressure, 273.15 K, 101.325 kPa
OC	Organic carbon
OGC	Organic gaseous carbon
OM	Organic matter
OT	Old technology
PAH	Polycyclic aromatic hydrocarbon
PB	Pellet boiler
PM ₁ , PM _{2.5} , PM ₁₀	Particle fraction consisting of particles whose aerodynamic diameter is below 1 µm, 2.5 µm, 10 µm
POA	Primary organic aerosol
POM	Particulate organic matter
PRD	Porous tube diluter
PS	Pellet stove

PTFE	Polytetrafluoroethylene
PUF	Polyurethane foam
RWC	Residential wood combustion
S	Cooking stove
SC	Smouldering combustion
SIM	Selected-ion monitoring mode in mass spectrometry
SOA	Secondary organic aerosol
SS	Sauna stove
SVOC	Semi-volatile organic compound
TEF	Toxic equivalent factor
TEOM	Tapered element oscillating microbalance
TEQ	Toxicity equivalent value
TS	Tiled stove
TSP	Total suspended particles
VOC	Volatile organic compound

List of publications

This thesis is based on four publications referred to in the text by their Roman numerals (I-IV). The publications are reproduced with the kind permission of the journals concerned.

- I Tissari, J., Hytönen, K., Lyyränen, J., Jokiniemi, J. (2007) A novel field measurement method for determining fine particle and gas emissions from residential wood combustion. *Atmospheric Environment*, 41, 8330-8344.

- II Hytönen, K., Yli-Pirilä, P., Tissari, J., Gröhn, A., Riipinen, I., Lehtinen K.E.J., Jokiniemi, J. (2009) Gas-particle distribution of PAHs in wood combustion emission determined with annular denuders, filter, and polyurethane foam adsorbent. *Aerosol Science and Technology*, 43, 442-454.

- III Lamberg, H., Nuutinen, K., Tissari, J., Ruusunen, J., Yli-Pirilä, P., Sippula, O., Tapanainen, M., Jalava, P., Makkonen, U., Teinilä, K., Saarnio, K., Hillamo, R., Hirvonen, M-R., Jokiniemi, J. (2011) Physicochemical characterization of fine particles from small-scale wood combustion. *Atmospheric Environment*, 45, 7635-7643.

- IV Nuutinen, K., Jokiniemi, J., Sippula, O., Lamberg, H., Sutinen, J., Horttanainen, P., Tissari, J. (2014) Effect of air staging on fine particle, dust and gaseous emissions from masonry heaters. *Biomass and Bioenergy*, 67, 167-178.

Contents

1 INTRODUCTION	10
2 AIMS OF THIS STUDY.....	11
3 SCIENTIFIC BACKGROUND.....	12
3.1 Properties of PAHs	12
3.1.1 Structures and properties	12
3.1.2 Health-related properties and exposure	16
3.2 Formation of PAHs and their transformation in the atmosphere	21
3.2.1 Emission formation in combustion.....	21
3.2.2 Formation of PAHs.....	23
3.2.3 Atmospheric conversion of organic compounds	25
3.2.4 Aspects of mass transfer in gas-particle mixtures	28
3.3 Dilutive sampling.....	33
3.4 RWC and regulation.....	36
3.4.1 European legislation concerning residential wood combustion.....	36
3.4.2 Air quality legislation related to PAHs in Finland	44
3.5 Role of wood combustion in Finland as a PAH emission source.....	44
3.5.1 Emission inventories	44
3.5.2 Effects on air quality	45
4 METHODS.....	48
4.1 Overview of the experiments	48
4.2 Combustion appliances	52
4.3 Aerosol sampling.....	53
4.3.1 Dilutive sampling process.....	53
4.3.2 PAHs.....	54
4.3.3 Particle mass.....	56
4.4 On-line measurements of gaseous compounds.....	57
4.5 Off-line analysis of aerosol samples	58
4.5.1 PAHs.....	58
4.5.2 Organic and elemental carbon contents of particles.....	59
4.6 Conversion of emissions.....	60
4.7 Data analysis	60
5 RESULTS AND DISCUSSION.....	62
5.1 Effect of dilutive sampling on the partitioning of organic species.....	62
5.1.1 Phase distribution of PAHs.....	62
5.1.2 Effect of the sampling technique on particle mass emissions	65
5.2.1 Overview of the studied PAH emissions and limitations of the data	70
5.2.2 PAH emissions from different combustion appliances.....	72
5.2.3 PAH emissions from different combustion phases	75

5.2.4 Effect of appliance operation on PAH emissions	77
5.2.5 PAH profiles for different combustion cases.....	78
5.2.6 Relationship between PAH emissions and other emissions.....	80
5.2.7 PAH content of particles	83
5.2.8 TEQ values of PAH emissions.....	85
6 AUTHOR'S CONTRIBUTION.....	86
7 CONCLUSIONS	87
8 FUTURE PROSPECTS.....	89
REFERENCES.....	91

ANNEX

ANNEX I: Methods used in selected studies

ANNEX II: PAH, CO and OGC emission factors from a conventional masonry heater, modern masonry heater, sauna stove, cooking stove and pellet stove (**I-III** and selected studies)

ANNEX III: PAH, CO and OGC emission factors from a wood stove, pellet boiler, chip boiler, log wood boiler and tiled stove (**III** and selected studies)

1 INTRODUCTION

Wood is a local energy source. Biomass absorbs CO₂ during its growth which reduces net CO₂ emission from combustion. Wood fuels are combusted efficiently and with low emissions in large power plants. In residential use, on the other hand, very low emissions are achieved using modern continuous combustion appliances such as pellet boilers (e.g., Orasche et al. 2012). Additionally, relatively low emissions can be attained by combining sophisticated batch combustion appliances with proper operational practices and high-quality wood fuel. However, wood combustion in residential units is also capable of producing high emissions of gaseous and particulate pollutants, e.g., various organic compounds such as polycyclic aromatic hydrocarbons (PAHs), black carbon and CO (e.g., Tissari et al. 2009), that affect air quality and health.

Respirable particles are considered the most harmful air pollutants to human health in the EU (EEA 2015b). In Europe, the estimated life expectancy has been reduced by 9 months on average due to ambient particles (WHO 2013). The size and composition of particles vary depending on their origin and formation mechanism. The understanding of the connection between the toxicological properties and chemical constituents of fine particles remains incomplete (Uski 2014). Nevertheless, biomass combustion products have been found to negatively affect respiratory and, possibly, cardiovascular health (e.g., Sigsgaard et al. 2015).

Various particle mass measurement methods are used in wood combustion emissions research. Different types of methods are also involved in the upcoming Ecodesign regulation. Sampling technology has particularly large effects on the semivolatile organic compounds in wood combustion emissions. The partitioning of these compounds between the gas and particle phase is strongly affected by sampling conditions such as the temperature and dilution ratio. Moreover, the measurement technique consequently affects the gained particle mass results considerably.

In this study, PAH emission factors for Finnish wood combustion appliances were determined. It was also investigated how the sampling technique affects the partitioning of PAHs and particle mass emission results.

2 AIMS OF THIS STUDY

In this study, PAH emissions from different types of appliances and combustion conditions were investigated. In addition, the effect of sampling and dilution conditions on the emissions of PAHs and fine particles were studied with advanced methods.

The specific aims were the following:

- To determine the PAH emission factors for Finnish residential wood combustion appliances (**I, II, III**) which had not been thoroughly investigated in previous studies and assess the role of residential wood combustion as a PAH emission source
- To determine how the combustion conditions affect PAH emission quantity or quality (**II, III**)
- To obtain novel information on the gas-particle partitioning of PAHs in dilution process (**II**)
- To evaluate the applicability of some commonly used particle mass measurement methods for wood combustion emissions rich in semivolatile matter (**IV**) and to investigate the European legislation and standardization concerning residential wood combustion in terms of methodology

3 SCIENTIFIC BACKGROUND



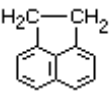
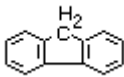

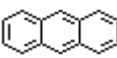
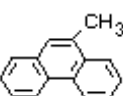
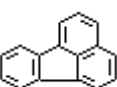

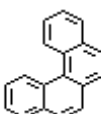
3.1 Properties of PAHs

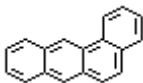
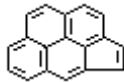
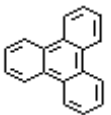
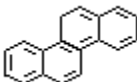
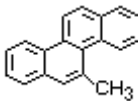
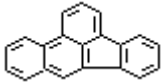
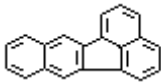
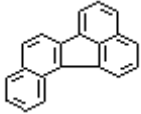
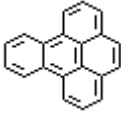
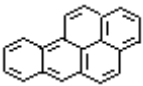
3.1.1 Structures and properties

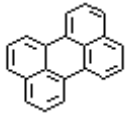
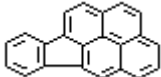
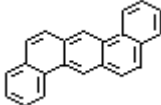
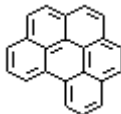
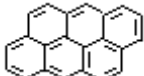
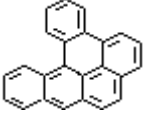
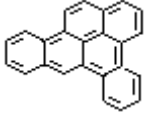

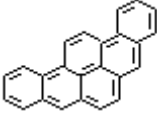
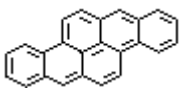
Polycyclic aromatic hydrocarbons (PAH) compose a large class of compounds consisting of hundreds of individual substances. These organic compounds contain two or more fused benzene rings. PAHs contain only carbon and hydrogen atoms (parent PAHs and their alkyl-substituted derivatives). The more general term 'polycyclic aromatic compounds' also covers the functional derivatives and heterocyclic analogues, such as nitro-, hydroxy- and oxy-PAHs or aza- and thia-arenes (WHO 1998).

The chemical and physical properties of PAHs vary greatly. The pure compounds are all solid at room temperature. In ambient air, PAHs are found in particulate material and in the gas phase, especially lower molecular weight PAHs. They have high melting points (up to 400 °C) and boiling points (up to 600 °C), low vapour pressures, very low water-solubilities and high n-octanol:water ($\log K_{ow}$) partitioning coefficients. The range of vapour pressures of PAHs covers more than 10 orders of magnitude. Vapour pressure mostly decreases with increasing molecular mass. PAHs dissolve in many organic solvents and are highly lipophilic. PAHs are rather chemically inert compounds and react either by electrophilic substitution or addition (WHO 1998). Table 1 describes the 30 PAH compounds analysed in this work.

Table 1. Selected polycyclic aromatic hydrocarbons (WHO 1998).

Compound	Abbr.	Molecular formula	Relative molecular mass	Structural formula
Naphthalene	Nap	C ₁₀ H ₈	128.8	
Acenaphthylene	Acy	C ₁₂ H ₈	152.2	
Acenaphthene	Ace	C ₁₂ H ₁₀	154.2	
Fluorene	Fle	C ₁₃ H ₁₀	166.2	
Phenanthrene	Phe	C ₁₄ H ₁₀	178.2	
Anthracene	Ant	C ₁₄ H ₁₀	178.2	
1-Methylphenanthrene	1MPhe	C ₁₅ H ₁₂	192.3	
Fluoranthene	Fla	C ₁₆ H ₁₀	202.3	
Pyrene	Pyr	C ₁₆ H ₁₀	202.3	
Benzo(c)phenanthrene	BcP	C ₁₈ H ₁₂	228.3	

Compound	Abbr.	Molecular formula	Relative molecular mass	Structural formula
Benz(a)anthracene	BaA	C ₁₈ H ₁₂	228.3	
Cyclopenta(c,d)pyrene	CcdP	C ₁₈ H ₁₀	226.3	
Triphenylene	Tri	C ₁₈ H ₁₂	228.3	
Chrysene	Chr	C ₁₈ H ₁₂	228.3	
5-Methylchrysene	5MChr	C ₁₉ H ₁₄	242.3	
Benzo(b)fluoranthene	BbF	C ₂₀ H ₁₂	252.3	
Benzo(k)fluoranthene	BkF	C ₂₀ H ₁₂	252.3	
Benzo(j)fluoranthene	BjF	C ₂₀ H ₁₂	252.3	
Benzo(e)pyrene	BeP	C ₂₀ H ₁₂	252.3	
Benzo(a)pyrene	BaP	C ₂₀ H ₁₂	252.3	

Compound	Abbr.	Molecular formula	Relative molecular mass	Structural formula
Perylene	Per	C ₂₀ H ₁₂	252.3	
Indeno(1,2,3-cd)pyrene	I123cdP	C ₂₂ H ₁₂	276.3	
Dibenz(a,h)anthracene	DahA	C ₂₂ H ₁₄	278.4	
Benzo(g,h,i)perylene	BghiP	C ₂₂ H ₁₂	276.3	
Anthanthrene	Antha	C ₂₂ H ₁₂	276.3	
Dibenzo(a,l)pyrene	DalP	C ₂₄ H ₁₄	302.4	
Dibenzo(a,e)pyrene	DaeP	C ₂₄ H ₁₄	302.4	
Coronene	Cor	C ₂₄ H ₁₂	300.4	
Dibenzo(a,i)pyrene	DaiP	C ₂₄ H ₁₄	302.4	
Dibenzo(a,h)pyrene	DahP	C ₂₄ H ₁₄	302.4	

3.1.2 Health-related properties and exposure

Benzo(a)pyrene is classified as carcinogenic, and many other PAHs are probably or possibly carcinogenic to humans (Table 2). PAHs may also exert immunologic and reproductive effects (Boström et al. 2002). Short-term health effects include eye and skin irritation, nausea, vomiting and inflammation. Long-term health effects include cancer (lung, skin, bladder, gastrointestinal), DNA damage, cataracts, kidney and liver damage, gene mutation cell damage and cardiopulmonary mortality (Kim et al. 2013).

The general public is exposed to PAHs through tobacco smoke; polluted air, water and soil; food and pharmaceutical products. In the non-smoking, non-occupationally exposed population, diet is often a major source of PAHs. For example, barbequed and smoke-cured meat, any high-temperature heat-processed food and vegetables grown in contaminated soil or exposed to atmospheric fall-out contain PAHs (IARC 2010).

Major sources of PAHs in ambient air consist of the processing of coal, crude oil and natural gas including coal coking, coal conversion, petroleum refining, creosote and coal-tar production; aluminium, iron and steel production; heating in power plants and households; cooking; combustion of waste; motor vehicle traffic; and tobacco smoking. Small amounts are released in the production and processing of PAHs. PAHs are used in the production of PVC, pigments and pesticides (WHO 1998).

Occupational exposure often relates to the use of coal and its further processing to coke and coal tar. Important sources of exposure are the use of coal tar and coal tar-derived products in industry. Exposure occurs, for example, in aluminium production, coke-ovens, the carbon electrode industry, paving and roofing involving coal-tar pitch, wood preservation with creosotes, chimney sweeping and thermoelectric power plants using coal and coal liquefaction (IARC 2010).

PAHs are absorbed into the circulation through the airways, skin and digestive tract. PAHs with two or three rings are absorbed more rapidly and extensively than larger compounds. PAHs are widely distributed throughout the body and rapidly metabolized to more soluble metabolites (epoxides, phenols, dihydrodiols, quinones, etc.). Reactive PAH metabolites can form DNA adducts. PAHs are eliminated from the body in the faeces, via biliary excretion, and in the urine (IARC 2010).

Table 2. Carcinogenicity, genotoxicity ((IARC 2010) and WHO 1998), and carcinogenic potencies (Larsen and Larsen 1998) of 30 PAHs.

Compound	Group (IARC 2010)	Genotoxicity (WHO 1998)	Carcinogenicity (WHO 1998)	Relative potency (Larsen and Larsen 1998)
Nap		-	(?)	
Acy		(?)	No studies	
Ace	3: Not classifiable as to their carcinogenicity to humans	(?)	(?)	
Fle	3: Not classifiable as to their carcinogenicity to humans	-	-	0.0005
Phe	3: Not classifiable as to their carcinogenicity to humans	(?)	(?)	0.0005
Ant	3: Not classifiable as to their carcinogenicity to humans	-	-	0.0005
1MPhe	3: Not classifiable as to their carcinogenicity to humans	+	(-)	
Fla	3: Not classifiable as to their carcinogenicity to humans	+	(+)	0.05
Pyr	3: Not classifiable as to their carcinogenicity to humans	(?)	(?)	0.001
BcP	2B: Possibly carcinogenic to humans	(+)	+	

+ positive, - negative, ? questionable, () results derived from a small database (WHO 1998)

Compound	Group (IARC 2010)	Genotoxicity (WHO 1998)	Carcinogenicity (WHO 1998)	Relative potency (Larsen and Larsen 1998)
BaA	2B: Possibly carcinogenic to humans	+	+	0.005
CcdP	2A: Probably carcinogenic to humans	+	+	0.02
Tri	3: Not classifiable as to their carcinogenicity to humans	+	(-)	
Chr	2B: Possibly carcinogenic to humans	+	+	0.03
5MChr	2B: Possibly carcinogenic to humans	+	+	
BbF	2B: Possibly carcinogenic to humans	+	+	0.1
BkF	2B: Possibly carcinogenic to humans	+	+	0.05
BjF	2B: Possibly carcinogenic to humans	+	+	0.05
BeP	3: Not classifiable as to their carcinogenicity to humans	+	?	0.002
BaP	1: Carcinogenic to humans	+	+	1

+ positive, - negative, ? questionable, () results derived from a small database (WHO 1998)

Compound	Group (IARC 2010)	Genotoxicity (WHO 1998)	Carcinogenicity (WHO 1998)	Relative potency (Larsen and Larsen 1998)
Per	3: Not classifiable as to their carcinogenicity to humans	+	(-)	
I123cdP	2B: Possibly carcinogenic to humans	+	+	0.1
DahA	2A: Probably carcinogenic to humans	+	+	1.1
BghiP	3: Not classifiable as to their carcinogenicity to humans	+	-	0.02
Anthra	3: Not classifiable as to their carcinogenicity to humans	(+)	+	0.3
DalP	2A: Probably carcinogenic to humans	(+)	+	1
DaeP	3: Not classifiable as to their carcinogenicity to humans	+	+	0.2
Cor	3: Not classifiable as to their carcinogenicity to humans	(+)	(?)	0.01
DaiP	2B: Possibly carcinogenic to humans	+	+	0.1
DahP	2B: Possibly carcinogenic to humans	(+)	+	1

+ positive, - negative, ? questionable, () results derived from a small database (WHO 1998)

Most PAHs with potential biological activity have from two to six aromatic rings in their structure. The metabolic activation of PAHs depends on their vapour pressure, adsorption to carrier particles, absorption to liquid carriers, lipid/aqueous partition coefficient and limit of solubility in

the lipid and aqueous phases of tissues. These properties are different for individual PAHs. Whether PAHs are in the vapour phase or particle bound affects the rate and extent of absorption of inhaled PAHs. The rate and extent of absorption of particle-bound PAHs by the respiratory tract depends on the particle size and the rate of release of PAHs from the particles (IARC 2010).

In general, carcinogenesis consists of numerous steps and processes involving genotoxic events (mutations), altered gene expression (epigenetic events) and altered cell survival (proliferation and apoptosis). PAHs may act at different stages of the carcinogenic process, exerting both mutagenic (genotoxic) and epigenetic (non-genotoxic) actions.

Several characteristics of PAHs affect their potent biological activity. One important property is the metabolic conversion of PAHs to reactive intermediates that can covalently bind to DNA, RNA and proteins. These DNA adducts may induce mutations and eventually the formation of tumours (tumour initiation). In addition, metabolites may react with other cellular targets and interfere with transcription, DNA replication, and protein synthesis. Certain PAHs may induce inflammatory processes. Specific PAHs also have a high affinity for the Ah receptor, which leads to interference of the biotransformation, growth and differentiation of cells. Stimulated cell growth promotes chemical carcinogenesis. PAHs have an inhibitory effect on gap junctional communication. Gap junctions are intercellular connections that connect the cytoplasm of two cells, allowing molecules, ions, etc. to pass through (Boström et al. 2002).

Certain structural requirements for PAHs to be mutagenic or carcinogenic have been revealed. Of the PAHs composed solely of fused aromatic rings, the compounds that have at least four rings and a so-called bay or fjord region in the molecular structure appear to be more active. Additionally, substitutions at certain positions may increase or decrease the biological activity. Certain structures contribute to the reactions of metabolites, for example, a bay region enables Ah-receptor binding (Boström et al. 2002).

For a practical comparison of PAH emissions, the emission of each individual PAH can be weighted with a relative potency factor or toxic equivalent factor (TEF) (e.g., Orasche et al. 2013, Orasche et al. 2012). In this approach, the potency factor of BaP is valued at 1, and other PAHs are

classified in relation to BaP based on their carcinogenic properties. The emissions of individual PAHs are multiplied by their potency factors and summed in order to obtain their toxicity equivalent (TEQ) values. These types of factors have been proposed by many authors and institutes; the relative potencies proposed by Larsen and Larsen (1998) are presented in Table 2. However, it should be noted that this concept does not consider the dose; in animal studies, high doses and short exposure times are used compared to the real-life low concentrations that humans are exposed to for long periods of time. Additionally, the metabolic interactions of PAHs are neglected in TEQs (Boström et al. 2002).

3.2 Formation of PAHs and their transformation in the atmosphere

3.2.1 Emission formation in combustion

Emission formation has been previously summarized in more detail, e.g., in Tissari 2008 and Sippula 2010. PAH formation is a complicated process and is affected by the combustion conditions and fuel properties. Some key aspects of the wood combustion process are briefly listed.

- Wood consists of carbohydrates (cellulose, hemicelluloses), lignin, organic extractives (fats, waxes, alkaloids, proteins, phenolics, resins, etc.), inorganic material (ash) and water (Pettersen 1984).
- When wood is heated, the constituents start to hydrolyze, oxidize, dehydrate and pyrolyze, and combustible volatiles, tarry substances and carbonaceous char are formed. An exothermic reaction, flaming combustion, starts when the ignition temperature of the volatiles and tarry substances is reached. Wood is gasified, and water, extractives, and decomposition products of cellulose, hemicellulose and lignin are vaporized. These substances are combusted either partially or completely in the flaming zone. During flaming combustion, char is formed. Flaming combustion ends when the flux of combustible volatile

substances drops below the critical level required for the propagation of a flame. As the process evolves, residual solid char gradually oxidizes (Rogge et al. 1998). The combustion stages appear simultaneously in a batch of logs, as well as in a large piece of fuel.

- The pyrolysis products of wood ingredients vary. For example, the pyrolysis of lignin forms phenolic compounds, such as methoxyphenols, as well as many other aromatic compounds (e.g., Rogge et al. 1998). In the thermal degradation of cellulose and hemicellulose, anhydrosugars, e.g., levoglucosan, galactosan and mannosan as well as furan derivatives, are formed (Simoneit 2002). Pyrolysis and combustion products either react further, e.g., degrade; oxidize or reduce; or react with each other.
- In the complete combustion of C and H, CO₂ and H₂O are formed. Wood contains N and S, which form NO, NO₂ and sulphuric compounds such as SO₂. Incombustible constituents such as ash remain on the grate as bottom ash or suspend in the flue gas (e.g., Flagan and Seinfeld 1998).
- The complete combustion of C and H requires sufficient mixing of the fuel and combustion air, ample temperature and residence time in the combustion zone. The formation of incomplete combustion products, e.g., CO, organic compounds such as PAHs and soot (elemental carbon), means that these requirements were not locally fulfilled (Flagan and Seinfeld 1998).
- In the combustion zone and in the cooling exhaust, chemical and physical interactions between the intermediates take place. Roughly, compounds grow, form new particles (nucleation) and move into the particle phase via condensation and adsorption. Additionally, particles interact via diffusion and coagulation, for example, which result in particle size growth.

A typical feature of residential wood combustion in small units is large variation of the combustion conditions and emissions (e.g., Tissari 2008). In general, the temporal variation of emission and flue gas temperatures during the batch combustion process is large; particle emissions from incomplete combustion conditions include a wide variety of compounds. The contributions of ash, organic matter (OM) and elemental carbon (EC) in

particles vary depending on the combustion phase (e.g., Elsasser et al. 2013, Eriksson et al. 2014, Leskinen et al. 2014) and combustion conditions (e.g., Tissari et al. 2008, Orasche et al. 2013). The organic fraction of wood combustion emission particles consists of thousands of compounds, of which a large fraction is unidentified (e.g., Rogge et al. 1998; McDonald et al. 2000; Schauer et al. 2001). Uniquely, wood combustion emissions contain large amounts of semivolatile compounds, and whether they are present in the gaseous or particle phase is largely dependent on the temperature. These features make RWC emissions challenging to measure and predict.

3.2.2 Formation of PAHs

In the incomplete combustion of organic materials, PAH formation involves two distinct reaction steps, pyrolysis and pyrosynthesis. During combustion at high temperatures and low oxygen concentrations, organic matter is cracked to small molecular fragments. As the temperature drops, the fragments recombine to form PAHs by pyrosynthesis (Simoneit 2002). Concerning wood combustion, two PAH formation mechanisms have specifically been discussed: breakdown reactions of lignin followed by further condensation reactions forming polycyclic aromatic material and ring formation reactions of molecules from acetylene and butadiene (Orasche et al. 2013). Low molecular weight PAHs and other molecules such as cyclopentadiene are suggested to serve as precursors for higher molecular weight PAHs; in the absence of oxygen, higher temperatures result in the formation of larger PAH molecules (Orasche et al. 2013).

The quality of organic combustion products is largely affected by temperature. According to Eriksson et al. (2014), monosaccharide anhydrides, such as levoglucosan, and methoxyphenols, which are formed in the pyrolysis of cellulose and lignin, are broken down to phenols at 600-700 °C and to methylated aromatics at >700 °C. As the temperature further increases, the yields of PAHs increase, because PAHs are more persistent at high temperatures than many other classes of organic compounds. As the temperature further increases above the optimal temperatures for PAH formation, EC formation increases (Eriksson et al. 2014).

PAHs are involved in soot formation in flames. Heavy PAH molecules form nascent soot particles, which gain mass via the addition of gas-phase

species such as acetylene and PAH radicals. These nascent soot particles coagulate, which increases their size significantly. Depending on the circumstances, the particles undergo functional group elimination, cyclization, ring condensation and ring fusion, accompanied by dehydrogenation and the growth and alignment of polyaromatic layers. As a result, more graphitic structures are formed (Richter and Howard 2000).

The oxidation of PAH and soot particles compete with the formation process. In the oxidation process, the mass of PAH and soot material is decreased by the formation of CO and CO₂. The main oxidation reactants are OH, O and O₂ (Richter and Howard 2000).

In wood combustion emissions, both gaseous and particle-bound PAHs exist. Concerning PAHs in particulate matter, Hays et al. (2003) found PAHs to be unimodally distributed over the accumulation and ultrafine particle size modes in PM_{2.5} emissions from residential wood combustion, with the geometric mean diameter of the log-normal PAH-particle size distribution ranging between 200 and 400 nm. PAHs with larger molecular weights (MWs) are preferentially segregated into finer particles and vice versa due to the following possible reasons: PAH diffusivity inversely correlates with MW, affecting partitioning; the Kelvin effect (the curved surfaces of smaller particles exert higher partial pressures, inducing the evaporation of lighter compounds); and larger compounds adsorb more easily onto larger surface areas (Hays et al. 2003 and references therein).

3.2.3 Atmospheric conversion of organic compounds

3.2.3.1 Fate of atmospheric organic compounds

In general, primary emissions are cooled, mixed, diluted, transported and chemically transformed in the atmosphere. The organic particulate and gaseous materials undergo processes that strongly affect their concentration and composition; on the contrary, black carbon, for example, has very low chemical reactivity in the atmosphere (Bond et al. 2013). The formation of atmospheric organic aerosols involves the direct emission of organic carbon from sources and the formation of secondary organic aerosols, SOA (Table 3, adapted from Seinfeld and Pandis 2006). The aging of primary organic emissions from, e.g., fuel combustion processes involves reaction with atmospheric oxidants (OH radicals, O_3 , NO_3 , etc.). The aging of organic compounds reduces their volatility and shifts the partitioning into the condensed phase, forming significant amounts of oxidized organic aerosols (Donahue et al. 2006).

Secondary organic aerosols are traditionally considered particle-phase organics, which are produced from VOCs, for example, terpenes. Nevertheless, an important proportion of secondary organic aerosols originate from semivolatile components with mainly anthropogenic sources (Donahue et al. 2006). Due to their low volatility, semivolatiles can produce SOA more effectively than high-volatility SOA precursors (Robinson et al. 2007).

In the atmosphere, organic compounds can undergo functionalization (addition of polar functional groups), fragmentation (cleavage of C-C bonds) and oligomerization (covalent association of two organic species). Kroll et al. (2011) described the atmospheric reactions of organic compounds as the movement through two-dimensional space with a number of carbon atoms n_C and an average carbon oxidation state \overline{OS}_C on the x- and y-axis. The combination of the reactions causes complex movement of the compounds through $\overline{OS}_C - n_C$ space, but over the course of time, the final product of the atmospheric oxidation of the organic species is CO_2 (Kroll et al. 2011) (Figure 1).

Table 3. Aspects affecting the formation of atmospheric organic aerosols (adapted from Seinfeld and Pandis 2006).

Process	Affecting factors
Organic carbon emission (gas+particle)	Sources: combustion (pyrogenic), chemical (commercial products,) geologic (fossil fuels), natural (biogenic)
Gas-phase chemical reactions producing SOA compounds from VOCs and SVOCs	Increasing temperature and sunlight intensity increase SOA Abundance of NO _x affects the reactions of parent VOCs with O ₃ , OH or NO ₃ Relative humidity Abundance of other VOCs
Partitioning of compounds between phases	Temperature (lower T increases the particle phase) Amount of other organics (larger amounts of OA may help a larger fraction of organic compounds to dissolve) Relative humidity increases the dissolution of water-soluble organic vapours due to a higher aerosol liquid water content
Particulate-phase reactions	SOA can increase by oligomerization or heterogeneous oxidation SOA can decrease by heterogeneous reactions breaking compounds to smaller ones, which are transferred to the gas phase

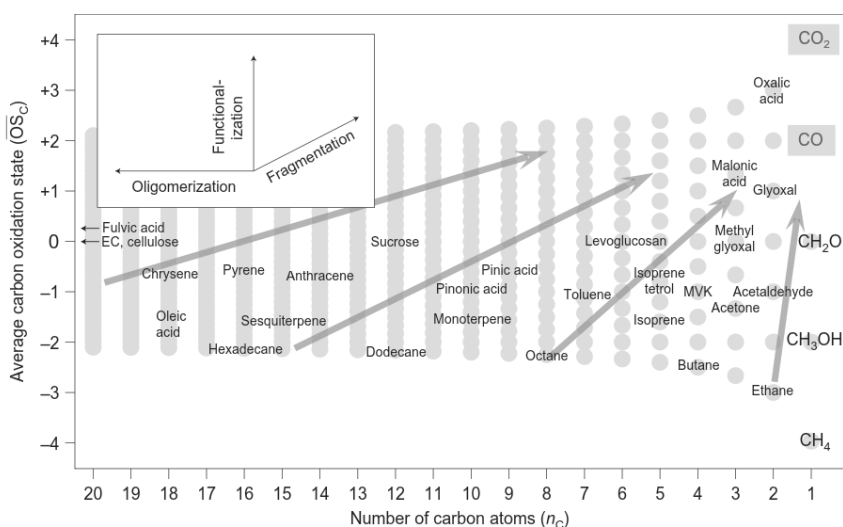


Figure 1. Possible combinations of the average carbon oxidation state and number of carbon atoms for stable organic molecules (Kroll et al. 2011).

3.2.3.2 PAHs in the atmosphere

In the atmosphere, PAHs are present in the form of gases (e.g., 2-ring PAHs) or solids adsorbed or absorbed to particle surfaces (e.g., 5-ring PAHs and larger); semi-volatile 3- and 4-ring PAHs are distributed between these two phases. The distribution between the phases depends on the vapour pressure of the compound and the surrounding temperature. Particle-bound PAHs are associated with fly ash or soot particles emitted during combustion (Finlayson-Pitts and Pitts 2000).

The ambient concentrations of PAHs vary from a few ng/m³ up to 100 ng/m³. The highest values have been reported close to the sources (Seinfeld and Pandis 2006). Concentrations are often higher in winter due to higher fuel consumption by small heating units, a lower height of the mixing layer and less intensive photo-oxidation and degradation of PAHs (Sippula et al. 2013). In the atmosphere, PAHs undergo reactions that lead to products that are more polar and water-soluble than the parent PAHs. For example, PAHs can react with NO₂, HNO₃, ozone and hydroxyl radicals; in these reactions, mono- and dinitro-PAHs, hydroxyl-substituted PAHs or carbonyl derivatives of PAHs can be formed (Boström et al. 2002, Seinfeld and Pandis 2006). With aging, gas-phase PAHs oxidize and form products of lower volatility that partition into the particle phase. These products may be more harmful to health compared to their parent analogues (Bruns et al. 2015). Thus, less toxic PAHs may eventually be important from a health perspective once they transform in the atmosphere.

PAHs are photodegraded either through direct photolysis by light with a wavelength <290 nm or indirect photolysis, i.e., photo-oxidation, by at least one oxidizing agent such as OH, O₃ or NO₃. Highly variable half-lives have been determined depending on the compound, oxidizing reactant, temperature and humidity, as well as the phase and material with which the PAHs are associated. Gaseous PAHs remain in ambient air for generally less than a day, whereas particle-bound PAHs may persist for weeks and be transported long distances. For particle-bound PAHs, the degradation rate can be considerably lower due to the stabilizing effect of carbonaceous particles. In the absence of sunlight and during cold winter conditions, degradation rates approach zero. As an example, the half-lives of several PAHs were determined to be one day or less when reacting with OH

radicals. For PAHs adsorbed onto soot, considerably longer half-lives (3.7-30 days) have been reported when reacting with NO_x (WHO 1998).

PAHs are removed from the atmosphere by dry or wet deposition of particles and vapours (Ravindra et al. 2008). The main sinks for PAHs are sediment and soil. PAHs are effectively adsorbed to the organic fraction of soil. The biodegradation of PAHs in the soil is slow but is a major route for PAHs to exit the soil. Heavier PAHs are especially persistent under environmental conditions in soil and groundwater (WHO 1998).

3.2.4 Aspects of mass transfer in gas-particle mixtures

In general, in a system involving vapours and particles, such as ambient air or a flue gas plume, mass can be transferred into the particle phase via various processes such as condensation, adsorption and nucleation (Seinfeld and Pandis 2006). Knowing the phase distribution is important in order to measure and understand the results of field studies, for example, the seasonal variation of results. Additionally, SOA formation is related to the gas-particle distribution of the oxidation products. Physical and chemical fates of compounds in the atmosphere and their subsequent transport through the air, water or soil environment are related to phase. Physical processes such as deposition as well as chemical reactivity, reaction products and lifetimes are phase-dependent. The phase distribution may even reflect the toxicological endpoints in the human body through, e.g., the bioavailability and deposition pattern in the respiratory system (Finlayson-Pitts and Pitts, 2000). In the following sections, some of the physical phenomena involved in mass transfer are described.

3.2.4.1 Vapour pressure

In a closed system over a solution consisting of a single compound *i*, there is no net transfer of molecules between the gas and liquid phases. Molecules are transferred in both directions, but the fluxes are equal. The equilibrium concentration of compound *i* in the gas phase (saturation vapour pressure $p_{s,i}$) is exponentially dependent on the temperature (Vesala 2004). Equations for p_s have been determined for compounds and compound classes, e.g., Sonnefeld et al. 1983 determined the saturation

vapour pressures for PAHs as a function of temperature at 10-50 °C (Eq. 1; values of A and B are given in Sonnefeld et al. 1983).

$$\log p_s = -\frac{A}{T} + B \quad (\text{Eq. 1}),$$

The vapour pressure reflects the ability of molecules to be transferred to the gas phase. In the real environment, liquids are mixtures of numerous compounds, such as the liquid organic phase on the surface of a soot particle. In the mixture, other compounds interact with the molecules of compound *i*. The lower the mole fraction of *i* in the solution, the more the vapour pressure of *i* over the solution drops (Raoult's law). In non-ideal solutions, if the forces between the molecules are stronger than the forces between the molecules of pure *i*, the saturation vapour pressure $p_{s,i}$ decreases.

$$p_{s,i} = \gamma_i X_i p_{s,i}^{pure} \dots (\text{Eq. 2}),$$

where X_i is the mole fraction of compound *i* in liquid and γ_i is the so-called activity coefficient (Vesala 2004, Seinfeld and Pandis 2006).

Moreover, the vapour pressure of a substance is always higher over a curved interface than over a flat surface (Kelvin equation) because, on a curved surface, as in a small droplet, there are fewer neighbouring molecules and thus less attractive forces keeping a molecule in the liquid phase, which means that it can escape to the gas phase more easily. The Kelvin effect can be significant for higher molecular weight organic compounds in particles with sizes of 200 nm and smaller (Seinfeld and Pandis 2006).

According to the ideal gas law, the mass concentration of compound *i* in a gas, c_i , is related to the partial vapour pressure p_i by Eq. 3:

$$c_i = \frac{p_i M_i}{RT} \quad (\text{Eq. 3}),$$

where M_i is the molar weight, R is the molar gas constant of 8,314 J mol⁻¹ K⁻¹ and T is the temperature (Seinfeld and Pandis 2006).

3.2.4.2 Gas-particle partitioning

If the compound has not established equilibrium between the phases, vapour either condenses on the particles or evaporates from the particles to the gas phase. Consequently, the particle diameter also changes. In condensation/evaporation, the mass transfer flux J of a compound will be proportional to the difference between the compound's gas phase concentration c_g and its equilibrium concentration in the gas phase at the particle surface c_{eq} .

$$J \sim c_g - c_{eq} \quad (\text{Eq. 4})$$

If $c_g = c_{eq}$, the compound is in equilibrium, and no net transfer between the phases exists. If $c_g > c_{eq}$, the gas phase is saturated with the compound, and some of it will condense on the available particle surface. The equilibrium concentration c_{eq} also depends on its ability to form solutions with other compounds present in the aerosol phase. If the compound does not form a solution with other aerosol-phase compounds (e.g., particles of solid inorganic salts), c_{eq} will be equal to the pure compound's saturation concentration c_s , and the aerosol phase will start to form once c_g exceeds c_{eq} . In the real environment, when organic compounds are already present in particles, organic vapours tend to dissolve in the particle-phase organics. In this case, the partitioning depends on the molecular properties of the compound as well as on the molecular properties and amount of the organic particulate phase that the compounds are dissolving into. The dissolution exhibits no threshold concentration, but the aerosol phase starts to form right away (Seinfeld and Pandis 2006).

In the absence of an organic particulate phase, adsorption can initiate gas-particle partitioning. Adsorption involves complex interactions between the adsorbed molecules and the particle surface. Adsorption can be based on physical forces (physisorption) or chemical forces (chemisorption). In the adsorption process, the particle surface is first partially covered with vapour molecules. Then, a monolayer is formed, which is occasionally followed by the formation of additional layers. In the adsorption of additional layers, vapour molecules interact with the already adsorbed molecules instead of the particle surface. According to theory, adsorption

can lead to a transfer of a fraction of the vapour phase to the aerosol phase, even if saturation in the gas phase has not yet been reached; nevertheless, the adsorbed mass is very small (Seinfeld and Pandis 2006). Absorption into an organic solution (dissolution) is considered the dominant partitioning mechanism over adsorption for both ambient aerosols and emissions dominated by organic material (Liang et al. 1997; Roth et al. 2005a; Shrivastava et al. 2006; Roth et al. 2005b).

Despite the mechanism leading to the partitioning between the gas and particle phases of a species, whether it is absorption, adsorption or their combination, the partitioning can be described by the partitioning coefficient defined as

$$K_p = \frac{F}{PM \times A} \quad (\text{Eq. 5})$$

where K_p is a temperature-dependent partitioning coefficient ($\text{m}^3/\mu\text{g}$), PM is the total ambient aerosol mass concentration ($\mu\text{g}/\text{m}^3$), and F and A are the aerosol (particle) and gas phase concentrations of the species ($\mu\text{g}/\text{m}^3$). Expressed as $F/A = K_p PM$, partitioning is a product of the partitioning coefficient and total particulate mass concentration. If PM increases, the amount of the species in the particle phase will increase because of the greater available surface area and volume of the particulate matter (Seinfeld and Pandis 2006).

Equilibrium between the gas and particle phases is not always attained. If the aerosol is not in equilibrium, dynamic models are needed for the interpretation of gas-particle partitioning data (May et al. 2013). The major factors determining the time needed for equilibrium to form in aerosols are the particle size, temperature and accommodation coefficient for the uptake of the gas into the particle (Finlayson-Pitts and Pitts, 2000). For polluted conditions in the atmosphere, the timescale is a few minutes or less, but if the number concentration is low, it can be several hours (Seinfeld and Pandis 2006).

A simplified theoretical relationship between the dilution and saturation ratio is described in Figure 2. Particles are considered solid particles (no dissolution of BaA into the organic layer). The temperature of the undiluted flue gas is assumed to be 250 °C. Four different concentrations of BaA in undiluted exhaust are included; using 200 $\mu\text{g}/\text{m}^3$ as an example, the point at

the extreme right corresponds to the undiluted concentration c_i (left y-axis). The concentration in the diluted exhaust decreases as the dilution ratio increases. At a dilution ratio of approximately 20, the total concentration of BaA in the diluted exhaust exceeds the saturation concentration (thick black line), and BaA is transferred from the gas phase to the particle phase through condensation. As the dilution ratio further increases, the BaA concentration in the diluted exhaust reaches a value below the saturation vapour pressure, and BaA starts to evaporate from the particles in order to reach equilibrium. The cooling caused by dilution with air at 20 °C reduces the saturation pressures of the semivolatile compounds in the exhaust until a temperature of ~20 °C is reached.

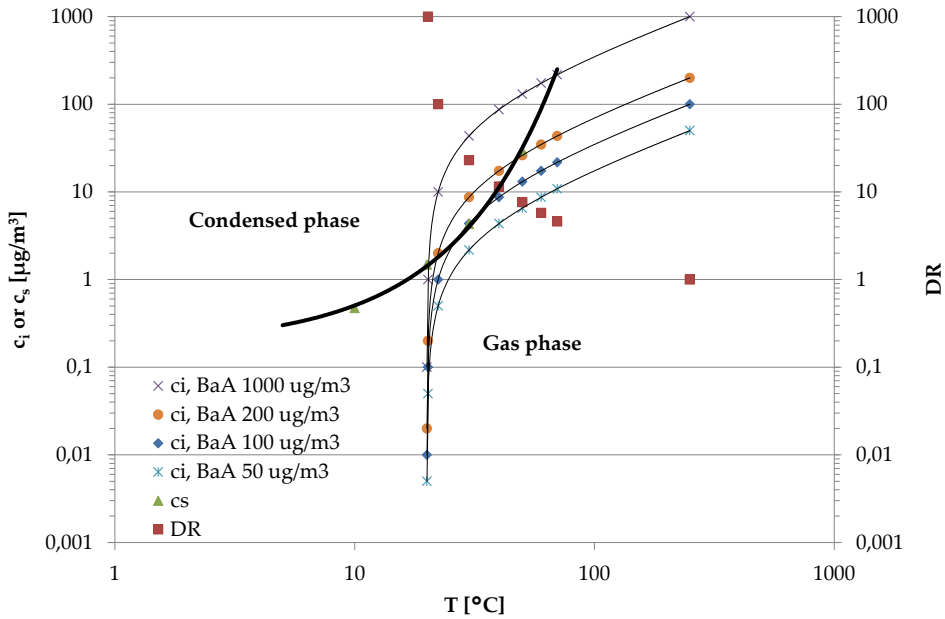


Figure 2. Concentration of BaA (c_i) in diluted exhaust (initial BaA concentration of 50, 100, 200, 1000 $\mu\text{g}/\text{m}^3$) as a function of the temperature of the diluted sample (T), DR as a function of the sample temperature (T) and the saturation concentration c_s of BaA at equilibrium as a function of T (c_s calculated according to Sonnefeld et al. 1983) ($T_{\text{hot exhaust}}=250$ °C and $T_{\text{dilution air}}=20$ °C).

3.3 Dilutive sampling

Dilution in aerosol measurements is often needed for practical reasons, such as to reach a level of concentration or temperature applicable for the measurement instruments. Dilution may be needed to reach the atmospheric level on a particle load, for example, in exposure studies. With dilution, coagulation can be arrested (Brockmann 2005), and water condensation due to cooling of the exhaust can be avoided (Biswas 2001). With dilutive samplers, atmospheric cooling and diluting processes are simulated (Hildemann et al. 1989). Nevertheless, dilution samplers are usually used in such a manner that the particle mass concentration in the diluted sample greatly exceeds the ambient level. There is concern that this leads to an overestimation of the emission relative to much more diluted atmospheric conditions (Lipsky and Robinson 2006, Shrivastava et al. 2006, Robinson et al. 2007, Donahue et al. 2009).

Dilution leads to fundamental changes in the gas-particle partitioning of organic species and sulphuric acid due to condensation. In the dilution process, nanoparticles can also be formed by nucleation (Kittelson 1998). Partitioning depends on the volatility distribution of organic compounds; dilution especially affects aerosols bearing a significant amount of semivolatile organics or sulphuric compounds, such as wood combustion and diesel engine emissions. For these emissions, the particle measurements of diluted exhaust can give significantly higher concentrations of total PM, as well as particulate organics and sulphate, compared to the measurements of hot exhaust (e.g., Ristimäki et al. 2010, Ozgen et al. 2014, Hildemann et al. 1989).

Increasing dilution causes further changes in gas-particle partitioning. As the dilution is increased after the ambient temperature level is reached (or the temperature of the dilution air), the concentration (partial vapour pressure) decreases. Because the saturation vapour pressure is constant in isothermal conditions, the saturation ratio (partial vapour pressure per saturation vapour pressure) decreases. In isothermal dilution, large decreases in fine particle mass emissions with increased dilution were found for wood combustion and a diesel engine operating at a low load (Lipsky and Robinson 2006). Increasing the dilution ratio from 20:1 to 120:1 decreased the PM_{2.5} mass emissions from a wood stove by over 60% and the

OC by 75%, whereas the EC showed no variation. The decrease in mass was due to changes in the phase partitioning of the semivolatile organic material, which tended to shift to the gas phase at high dilution in order to maintain the phase equilibrium (Lipsky and Robinson 2006). Similar strong mass decreases due to the evaporation of organics were observed by May et al. (2013) in laboratory combustion tests of various biomasses. These authors observed an evaporation of 50 to 80% of the organic aerosol mass during isothermal dilution from plume- ($\sim 1000 \mu\text{g}/\text{m}^3$) to ambient-like ($\sim 10 \mu\text{g}/\text{m}^3$) concentrations.

The dependence of particle mass emissions on the (sampling) conditions is approximated in Figure 3; the same type of approach is presented in Nussbaumer et al. 2008. Hot undiluted exhaust in the example consists of mainly elemental carbon, ash and some organic matter (1st bar). Diluted moderately with cool air, the sample is at atmospheric temperature, and semivolatile organic compounds condense and shift to the particle phase, causing a considerable increase in the (dilution-corrected) particle mass concentration (2nd bar). Higher dilution leads to evaporation of semivolatile organic compounds and decreases in the (dilution-corrected) particle mass concentration (3rd bar). Due to photo-oxidation, organic compounds may evaporate, transform to more polar and less volatile compounds, and return to the particle phase. Originally, gaseous compounds may shift to the particle phase as well (4th bar). The change in particle mass caused by oxidation and SOA formation varies greatly; the average organic aerosol enhancement ratio of 1.7 ± 0.7 for open biomass burning emissions was determined by Hennigan et al. (2011). Further information on the behaviour of semivolatile compounds, like PAHs, in different stages of the process is needed.

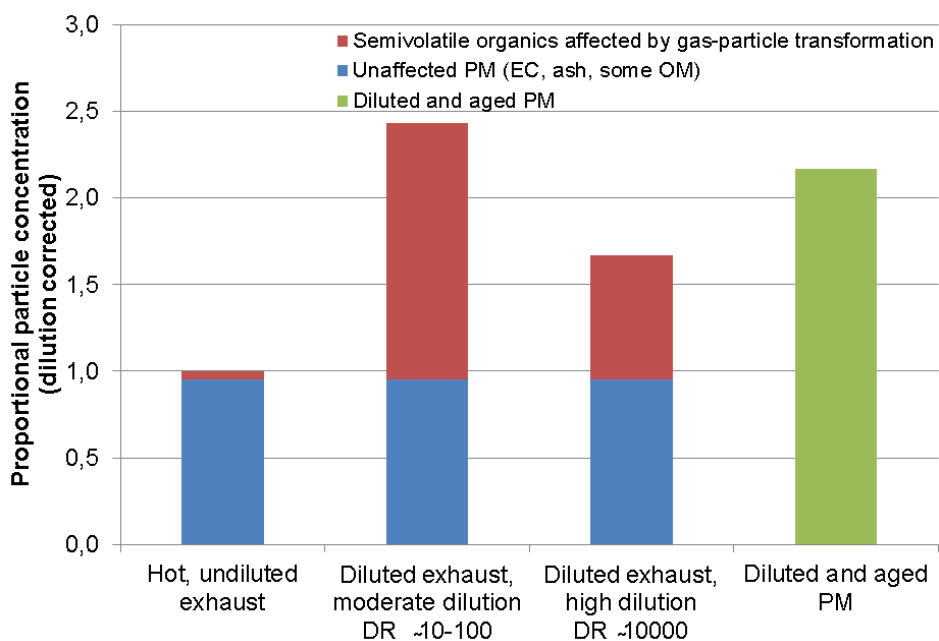


Figure 3. Schematic stages of wood combustion particle emissions: hot undiluted exhaust, exhaust diluted using low and high dilution ratios and aged exhaust.

3.4 RWC and regulation

3.4.1 European legislation concerning residential wood combustion

Regulation of particle emissions from residential wood combustion currently varies greatly between EU member states. In Finland, particle emissions are currently not regulated at all. In some countries, there exist national limit values for particle emissions. The upcoming Ecodesign Directive provides emission limits for particles; several parallel measurement methods are allowed. PAH emissions from RWC are not regulated.

3.4.1.1 Construction product regulation and harmonized product standards

The products used in construction need to have a CE-mark ((EU) 305/2011). For the CE-mark, the products need to fulfil the requirements set, for example, in the harmonized product standard. EN standards contain requirements concerning, e.g., an appliance's fire safety, efficiency and CO emissions. The renewal of the standards is on-going. New standard series EN 16510 by the Technical Committee CEN/TC 295 "Residential solid fuel burning appliances" include Part 1 on general requirements (and several sections of Part 2 for different appliance types). In the new series, methods for dust, OGC and NO_x measurements are described. Some product standards and CO emission limit values are listed in Table 4.

Table 4. CO emission limit values in selected EN standards.

Appliance type	EN standard	CO limit value (% at 13% O ₂)
Room heaters fired by solid fuel	EN 13240	1.0
Residential cookers fired by solid fuel	EN 12815	1.0
Slow heat release appliances fired by solid fuel	EN 15250	0.3
Multi-firing sauna stoves fired by natural wood logs	EN 15821	1.0

3.4.1.2 National regulations

Some European countries, such as Austria and Germany, provide national limit values for emissions from small combustion appliances (Tables 5 and 6). In Austria, the minimum efficiency is, for example, 80% for room heaters other than cooking stoves using solid fuel. In Austrian regulations, the particle emissions must be determined based on three particle samples for duration of 30 minutes each. CO, OGC and NO_x emissions must be determined as an average of two subsequent batches. In German regulations, CO and NO_x concentrations must be determined as an average of the whole combustion test, and the particle sample duration is 30 minutes.

In Finland, there are no particle concentration limit values for residential wood combustion appliances. National application standards (NAS) complement the harmonized product standards.

Table 5. Austrian emission limit values for small-scale combustion appliances using hand-fed solid fuel (Vereinbarung gemäß Art 15a B-VG über das Inverkehrbringen von Kleinf Feuerungen und die Überprüfung von Feuerungsanlagen und Blockheizkraftwerken).

Parameter	Emission limit value (mg/MJ)					
	Wood fuel		Other standardized biofuels		Fossil fuels	
	Room heaters	Central heating appliances	Nominal heat output <50 kW	Nominal heat output ≥50 kW	Nominal heat output <50 kW	Nominal heat output ≥50 kW
CO	1100	500	1100	500	1100	500
NO _x	150	150/100*	300	300	100	100
OGC	80/50*	50/30*	50	30	80	30
Dust	60/35*	50/30*	60/35*	60/35*	50/35*	50/35*

*From 1.1.2015 on

Table 6. German emission limits for room heaters and stoves (Erste Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes (Verordnung über kleine und mittlere Feuerungsanlagen – 1. BImSchV; internet: http://www.gesetze-im-internet.de/bimschv_1_2010/index.html; Hartmann et al., 2008)

Appliance type	Technical document	Step 2: Erected after 31.12.2014		
		CO (g/m ³)*	Dust (g/m ³)*	Minimum efficiency (%)
Room heater with flat furnace	DIN EN 13240	1.25	0.04	73
Room heater with filling furnace	DIN EN 13240	1.25	0.04	70
Slow heat release appliances	DIN EN 15250	1.25	0.04	75
Closed fireplaces	DIN EN 13229	1.25	0.04	75
Tiled stoves (flat furnace)	DIN EN 13229	1.25	0.04	80
Tiled stoves (filling furnace)	DIN EN 13229	1.25	0.04	80
Cooking stoves	DIN EN 12815	1.50	0.04	70
Central heating and cooking stoves	DIN EN 12815	1.50	0.04	75
Pellet stoves without water jacket	DIN EN 14785	0.25	0.03	85
Pellet stoves with water jacket	DIN EN 14785	0.25	0.02	90

*At 13% O₂

3.4.1.3 Ecodesign regulation

The EU legislation on Ecodesign and energy labelling is a tool for improving the energy efficiency of products. The Ecodesign Directive 2009/125/EC provides EU-wide rules for improving the environmental performance of products. The Energy Labelling Directive 2010/30/EU includes mandatory labelling requirements. The Ecodesign Directive is implemented through product-specific regulations (European Commission 2016). Ecodesign requirements are summarized in Tables 7 and 8.

Table 7. Ecodesign requirements for solid-fuel local space heaters ((EU) 2015/1185).

Appliance type: Solid-fuel local space heaters ((EU) 2015/1185)						
Appliances within the scope		Appliances outside the scope				Timetable
Solid-fuel local space heaters, nominal heat output ≤50 kW	Appliances for non-woody biomass only					From
	Appliances for outdoor use only					1.1.2022
	Appliances of which the direct heat output is less than 6% of the combined direct and indirect heat output at a nominal heat output					on
	Appliances not factory assembled or not provided as prefabricated components or parts by a single manufacturer to be assembled on site					
	Air heating products					
Sauna stoves						
Requirements						
Type of solid-fuel local space heater	Seasonal space heating energy efficiency*	PM at 13% O ₂	OGC at 13% O ₂	CO at 13% O ₂	NO _x at 13% O ₂	Other
Open fronted	≥30%	≤50 mg/m ³ [Method 1] or ≤6 g/kg (dry matter) [Method 2]	≤120 mg C/m ³	≤2000 mg/m ³	Biomass: ≤200 mg/m ³ , solid fossil fuel: ≤300 mg/m ³	Requirements for product information
Closed fronted, solid fuel other than wood pellets	≥65%	≤40 mg/m ³ [Method 1] or ≤5 g/kg (dry matter) [Method 2] or ≤2.4 g/kg (dry matter) for biomass or ≤5.0 g/kg (dry matter) for solid fossil fuel [Method 3]	≤120 mg C/m ³	≤1500 mg/m ³	Biomass: ≤200 mg/m ³ , solid fossil fuel: ≤300 mg/m ³	
Closed fronted, wood pellets	≥79%	≤20 mg/m ³ [Method 1] or ≤2.5 g/kg [Method 2] or ≤1.2 g/kg [Method 3]	≤60 mg C/m ³	≤300 mg/m ³	Biomass: ≤200 mg/m ³ , solid fossil fuel: ≤300 mg/m ³	
Cookers	≥65%	≤40 mg/m ³ [Method 1] or ≤5 g/kg (dry matter) [Method 2] or ≤2.4 g/kg (dry matter) for biomass or ≤5.0 g/kg (dry matter) for solid fossil fuel [Method 3]	≤120 mg C/m ³	≤1500 mg/m ³	Biomass: ≤200 mg/m ³ , solid fossil fuel: ≤300 mg/m ³	

Particle measurement methods 1-3 are described in (EU) 2015/1185 Annex III 4.a.i.1-3

*Calculation described in (EU) 2015/1185

Table 8. Ecodesign requirements for solid-fuel local boilers (EU) 2015/1189.

Appliance type: Solid-fuel local boilers (EU) 2015/1189						
Appliances within the scope		Appliances outside the scope				Timetable
Solid-fuel boilers with a rated heat output of 500 kW or less		Boilers generating heat exclusively for providing hot drinking water or sanitary water				From 1.1.2020 on
		Boilers for heating and distributing gaseous heat transfer media such as vapour or air				
		Solid-fuel cogeneration boilers with a maximum electrical capacity of 50 kW or more				
		Non-woody biomass boilers				
Requirements						
Type of solid-fuel local boiler	Seasonal space heating energy efficiency*	Seasonal space heating emissions** of				
		PM at 10% O ₂	OGC at 10% O ₂	CO at 10% O ₂	NO _x at 10% O ₂	Other
Boilers with a rated heat output of ≤20 kW	≥75%					
Boilers with a rated heat output of >20 kW	≥77%					
Automatically stoked boilers		≤40 mg/m ³	≤20 mg/m ³	≤500 mg/m ³		Requirements for product information
Manually stoked boilers		≤60 mg/m ³	≤30 mg/m ³	≤700 mg/m ³		
Biomass boilers					≤200 mg/m ³ (NO ₂)	
Fossil fuel boilers					≤350 mg/m ³ (NO ₂)	

Particle measurement methods 1-3 are described in (EU) 2015/1185 Annex III 4.a.i.1-3

*Calculation described in (EU) 2015/1189

**For manually stoked solid-fuel boilers that can be operated at 50% of the rated heat output in continuous mode and for automatically stoked solid-fuel boilers, the emission is expressed as a weighted average of the emission at the rated heat output and the emission at 50% of the rated heat output, calculation in (EU) 2015/1189

3.4.1.4 Particle mass emission measurement methods in regulations

In the final draft FprEN 16510-1 (January 2016), two particle measurement methods are described: measurement by sampling a partial flue gas sample over a heated filter from hot undiluted exhaust and measurement by sampling a partial flue gas sample from a full flow dilution tunnel using a filter at ambient temperature (Table 9). The first method gives the particle concentration in the solid fraction of the total particulate

matter concentration in mg/m^3 , and the latter gives the emission of particulate matter and condensables at room temperature in g/kg . In the hot exhaust method, the conditioning temperature of the filter is dependent on the temperature at which the filter holder and sampling line are maintained during sampling. The filter holder temperature may vary from 70 to 160 °C (condensation of water must be avoided). The filter conditioning temperature must be 35 K above the filter holder temperature but not more than 180 °C. The flue gas is diluted with a tunnel DR of 10-20 (FprEN 16510-1, January 2016).

In the Ecodesign requirements for solid-fuel local space heaters, several particle measurement methods are listed (Table 10). In (EU) 2015/1185, sampling with an electrostatic precipitator is one of the particle measurement methods that appears to be quite different from the methods described in FprEN 16510-1. Some inconsistencies with FprEN 16510-1 exist in the sampling durations, as well as in draught and appliance loads. According to the Ecodesign regulation (EU) 2015/1185, measurements and calculations shall be made using harmonized standards or other reliable, accurate and reproducible methods.

Table 9. Particle measurement methods in FprEN 16510-1 (January 2016).

Document	Measurement method	Sampling period	Unit
FprEN 16510-1, January 2016	<p>Partial flue gas sample over a heated filter: solid fraction of the total particulate matter is sampled (T(filter) 70-160 °C, no water condensation allowed). Constant sample flow.</p> <p>Pre-procedure of filter conditioning: temperature 35 K above the filter holder temperature but not more than 180 °C; at least 1 h with cooling in desiccator for at least 4 h.</p> <p>Post-procedure: filter conditioning at the same temperature as in the pre-procedure for at least 1 h, with cooling in a desiccator for at least 4 h.</p> <p>Draught 12 Pa</p>	<p>30-minute period, starting 3 min after reload.</p> <p>Determined for each cycle (batch) (more detailed description may be given in Part 2 concerning the appliance type in question)</p>	<p>mg/Nm³ (PM) at 13% O₂, (dry, 273.15 K, 1013 hPa)</p>
FprEN 16510-1, January 2016	<p>Partial flue gas sample from a full flow dilution tunnel using a filter at ambient temperature (not less than 20 °C): particulate matter and condensables are sampled. Isokinetic sample flow. Dilution ratio of 10-20. Dilution tunnel temperature of 25-50 °C.</p> <p>Pre-procedure of filter conditioning: drying in a desiccator for 24 h</p> <p>Post-procedure: drying in a desiccator for at least 8 h</p> <p>Draught 12 Pa</p>	<p>Determined for each cycle. Sampling starts directly after reload.</p> <p>More detailed description in the corresponding section of Part 2 concerning the appliance type in question.</p>	<p>g/kg_{dry fuel} (PME)</p>

Table 10. Particle measurement methods presented in (EU) 2015/1185.

Document	Measurement method	Sampling period
(EU) 2015/1185 Annex III 4.(a)(i)(1)	Partial dry flue gas sample over a heated filter	No description of draught or sample duration
(EU) 2015/1185 Annex III 4.(a)(i)(2)	Partial flue gas sample from a diluted flue gas using a full flow dilution tunnel and a filter at ambient temperature	Natural draught Over the full burn cycle
(EU) 2015/1185 Annex III 4.(a)(i)(3)	Partial flue gas sample using a fixed flue draught, from a diluted flue gas using a full flow dilution tunnel and a filter at ambient temperature or electrostatic precipitator.	Draught 12 Pa 30-minute period

3.4.1.5 Recommendations from projects concerning methodology

Rather recently, measurement methods in residential wood combustion have been a topic of two ERA-NET Bioenergy programme consortium studies. BIOMASS-PM focused on the need to interlink the physico-chemical characteristics of particles with health end-points. Condensable species particle measurement using dilution was recommended. A dilution ratio of 20 was recommended in order to measure the full potential of particle formation/growth due to the condensation of organic vapours. For example, human exposure studies in which higher dilution is used, the characteristics of the particles to be coupled with the exposure study results should be measured in corresponding conditions (Hytönen et al. 2008).

In EN-PME-TEST, the objective was to develop and validate a common European test method to determine particulate matter emissions from residential heating appliances and boilers burning solid fuels (Fraboulet 2015). In this project, short-term and long-term measurement methods were proposed. The short-term method was designed to meet the actual EN standards for combustion appliances. The long-term method was designed to better reflect the combustion quality and potential effect on health and the environment. The proposed short-term method measured particles with a heated filter from undiluted exhaust and organic gaseous carbon with an FID analyser, both sampled at 180 °C. A constant and homogenous temperature in the probe and filter holder improved the repeatability of the method. The proposed long-term methods included total carbon measurements using a micro-smog chamber and particle mass measurements using dilution. The oxidation of flue gas in a micro smog chamber promotes the formation of secondary organic aerosols. In dilution, the semivolatiles are condensed, but this method also enables the use of online aerosol instruments such as a TEOM (tapered element oscillating microbalance: particle mass concentration) and a more reliable use of impactors (Fraboulet 2015).

Related to methodology, an on-going European consortium project BeReal seeks to improve the test standards so that they better reflect the operating conditions of real-life installation (project web page: www.bereal-project.eu).

3.4.2 Air quality legislation related to PAHs in Finland

The BaP concentration has a target value of 1 ng/m³ established in the *Directive 2004/107/EC of the European Parliament and of the Council relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air*. Finland has implemented this directive through act 164/2007. BaP is considered a marker for carcinogenic risk due to PAHs. The target value is for the total content in the PM₁₀ fraction, averaged over a calendar year. In addition, the upper and lower assessment thresholds of 0.6 ng/m³ and 0.4 ng/m³ are given and are used in determining the number of sampling points in the zone. For monitoring of the BaP concentration, Finland is divided in two zones: the Helsinki metropolitan area and the rest of the country.

As a part of the Clean Air Policy Package of EC adopted in December 2013, EC published the *Proposal for a Directive of the European Parliament and of the Council on the reduction of national emissions of certain atmospheric pollutants and amending Directive 2003/35/EC*. In addition to the new national emission reduction commitments applicable from 2020 to 2030 for SO₂, NO_x, NMVOC, NH₃, PM_{2.5} and methane, annual emission reporting requirements are also given, which include the total national emissions of total PAHs (PAH-4) and the individual compounds BaP, BbF, BkF and I123cdP.

3.5 Role of wood combustion in Finland as a PAH emission source

3.5.1 Emission inventories

In EU-28, residential stationary combustion was a main source of PAHs, contributing 61% of the total PAH emissions. The source category of residential stationary combustion (1A4bi) presented in Figure 4 also includes the combustion of fuels other than wood, for example, coal (EEA 2015a). In Finland, the annual PAH emissions ranged between 13 and 18 t/a in 1990-2012. Residential wood combustion is the largest national emission source of PAHs and is estimated to have composed 80% of the PAH

emissions in Finland in 2012 (traffic, 7%). Thus, PAHs in the ambient air of communities mostly originates from residential wood combustion and traffic, whereas that in industrial environments also originate from foundries and coke ovens (Komppula et al. 2014).

Residential wood combustion is also a significant source of fine particles, causing approximately half of the total PM_{2.5} emissions in Finland; nevertheless, the upcoming update of the emission calculation will decrease the emissions from residential combustion by approximately 50% (Suoheimo et al. 2015), which would result in a contribution of approximately 25% of the total emissions. As a comparison, traffic, including both exhaust gases and road dust, caused approximately 20% of PM_{2.5} emissions in 2011. Of the national NMVOC emissions, residential combustion caused approximately 30% in 2011 (Komppula et al. 2014).

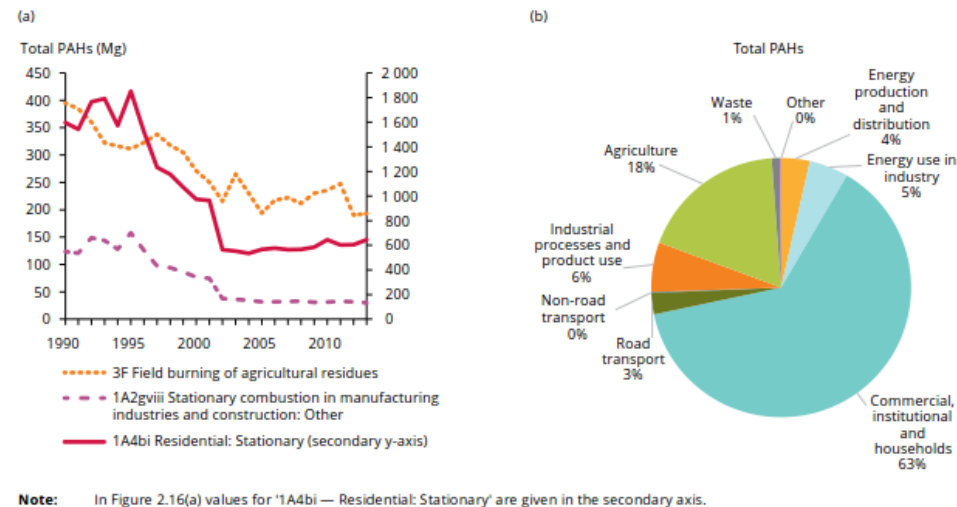
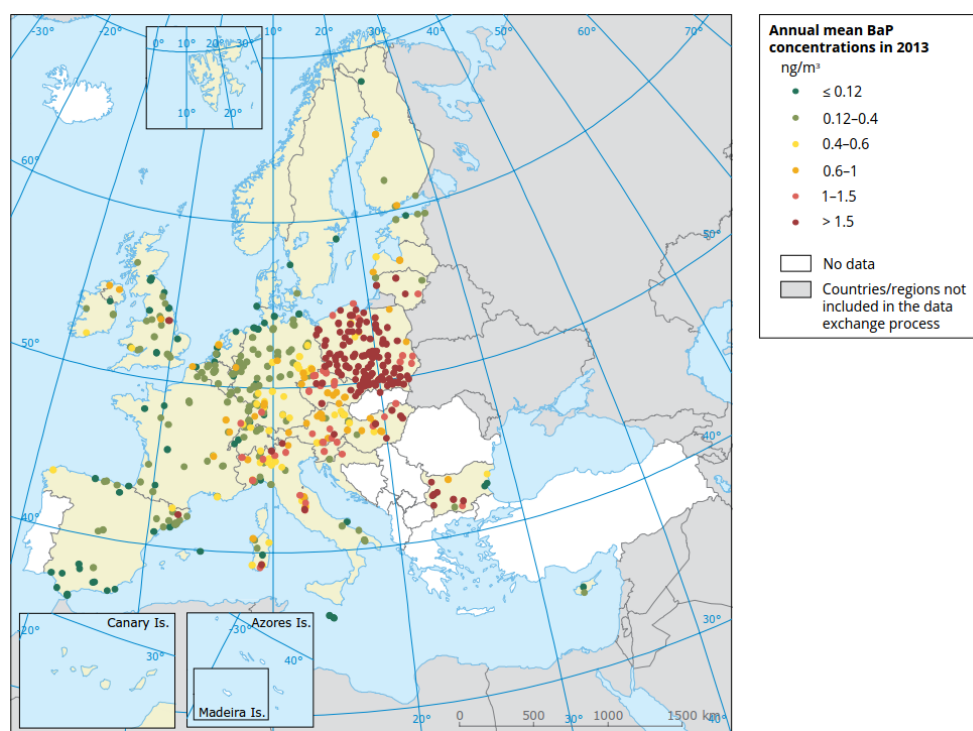


Figure 4. Total PAH emissions in the EU-28: (a) trend in total PAH emissions from the most important key categories, 1990-2013; (b) share of emissions by sector group, 2013 (EEA 2015a).

3.5.2 Effects on air quality

A recent European air quality report revealed that the BaP limit value of 1 ng/m³ is exceeded in large parts of Europe (Figure 5) (EEA 2015b). In

Finland, BaP concentrations are relatively low. The concentrations of particle-bound BaP were measured at 12 air quality stations in Finland in 2008-2012. The highest annual average concentration exceeding the limit value was measured at a station close to a steel manufacturing plant. High concentrations exceeding the limit value or the upper threshold value of 0.6 ng/m^3 were also measured in residential areas where wood was combusted in the households (Komppula et al. 2014).



Notes: Dark-green dots correspond to concentrations under the estimated reference level (0.12 ng/m^3). Dark-red dots correspond to concentrations exceeding the 2004 AQ Directive target value of 1 ng/m^3 .

Only stations reporting more than 14% of valid data, as daily, weekly or monthly measurements have been included in the map.

Source: Based on Air Quality e-reporting database (EEA, 2015a).

Figure 5. Ambient benzo(a)pyrene concentrations in Europe in 2013 (EEA 2015b).

In the Helsinki metropolitan area in 2014, the air quality was measured at two estates of detached houses where wood combustion was an important emission source. The measured annual average concentrations of

BaP were 0.6 ng/m³ (Vartiokylä) and 1.0 ng/m³ (Ruskeasanta). At Ruskeasanta, the concentration was at the level of the limit value. The seasonal variation was large at these sites; the concentration was clearly higher in winter (HSY 2015). Additionally, elevated PM_{2.5} concentrations were measured at these sites, and the highest daily concentrations were associated with small-scale wood combustion emissions (HSY 2015).

The effect of wood combustion was studied in seasonal measurement campaigns as well. In the Finnish suburb of Kurkimäki, Kuopio, wood combustion appeared to increase the PAH concentration; the average daily total PAH concentration was 1.6 times higher than the background concentration during the heating season. The background station was located 1.5 km outside Kurkimäki. The daily BaP concentrations varied from <0.5 ng/m³ to 3.5 ng/m³ (Hellén et al. 2008).

Studies of the contribution of wood combustion to outdoor particle concentrations have been performed around the world (some studies are listed in Sigsgaard et al. 2015 and WHO 2015). For example, in the Finnish suburb of Jynkkä, Kuopio, residential wood combustion composed 16% of the measured PM_{2.5} during the heating season when the average PM_{2.5} concentration was 6 µg/m³ (Yli-Tuomi et al. 2015). In the previously mentioned suburb of Kurkimäki, Kuopio, wood combustion did not appear to increase the daily average particle concentrations. Instead, high short-term peaks were detected in the PM_{2.5} concentration caused by local wood combustion (Hellén et al. 2008). In Helsinki, the contribution of residential wood combustion to the PM_{2.5} concentration in the cold season was 18-29% at urban sites and 31-66% at suburban sites (Saarnio et al. 2012).

4 METHODS

4.1 Overview of the experiments

The experimental procedures and aims of the four campaigns are summarized in Table 11.

Table 11. Overview of the campaigns in Papers I-IV.

Paper	Year of experiments	Location	Aim
I	2006	At field, Kuopio, Finland	To determine PAH emission factors for residential wood combustion appliances
II	2006	Laboratory, UEF	To determine PAH emission factors for residential wood combustion appliances To determine how the combustion conditions affect PAH emission quantity or quality To study the gas-particle partitioning of PAHs in dilution
III	2008- 2009	Laboratory, UEF	To determine PAH emission factors for residential wood combustion appliances To determine how the combustion conditions affect PAH emission quantity or quality
IV	2008	Laboratory, Tulikivi Ltd	To evaluate the applicability of some commonly used particle mass measurement methods for wood combustion emissions rich in semivolatile matter

The experimental procedures of **I** were performed at field which means that instead of measuring the emission from combustion appliances at the laboratory, it was done in the households in a residential area (Figure 6). The combustion appliances were operated by the residents with their own fuel wood. In **II**, the gas-particle distribution of PAHs from the diluted and raw, undiluted exhaust from a conventional masonry heater (Figure 6) was studied. Two operational practices, normal combustion (NC) and smouldering combustion (SC) were used, producing two clearly different combustion conditions for sampling. In normal combustion (NC), the batch and log sizes and other user-dependent variants in the operation were optimized. In the smouldering combustion (SC), the air intake was restricted, the log size was smaller, the batch size was larger and the piling

of the logs was loose. Taken together, these factors resulted in poor combustion conditions. In **III**, the PAHs contained in particles emitted from six various combustion conditions were studied. Six different combustion appliances were used, and a certain period of the combustion cycle or test was selected for particle sampling (Table 14). Beyond this study, the aim of the campaign was to produce particles with different characteristics in order to couple the toxicological properties with the physicochemical characteristics of the particles (Tapanainen et al. 2011, Tapanainen et al. 2012). In **IV**, two particle mass measurement methods were compared. The effect of air staging on the combustion emissions was also studied. Schematics of the measurement systems are presented in Figures 7-9 and 11. The measurement methods are briefly presented in Tables 12-15.

Table 12. Measurement methods in I.

Combustion appliance and code	PAH sampling period	Dilution for PAH sampling	PAH sampling method
MMH: Modern masonry heater	Whole combustion period of 6 batches (131 min)	Porous tube	A teflon membrane filter (Teflo, Gelman Scientific) and
CMH-b1: Conventional masonry heater (brick)	Whole combustion period of 2 batches (77 min)	diluter (dilution air heated to 180 °C) and an ejector	Amberlite XAD-4 (Supelco)
CMH-t: Conventional masonry heater (tiled)	Whole combustion period of 2 batches (89 min)	diluter (dilution air not heated),	adsorbent (particle fraction PM ₁₀)
S: Cooking stove	Whole combustion period of 5 batches (65 min)	DR 28-72, T 10-23 °C	
SS: Sauna stove	Whole combustion period of 3 batches (68 min)		

Table 13. Measurement methods in II.

Combustion appliance and code	PAH sampling period	Dilution for PAH sampling	PAH sampling method
Normal combustion (NC): Conventional masonry heater, normal combustion	Whole combustion period, 1+3 batches (80-85 minutes)	1) Dilution with a porous tube diluter (dilution air at ambient temperature), DR 82-119, T ~25 °C 2) None: PAH sampling from hot, undiluted exhaust, T 250-260 °C	Gas-phase PAHs: collected with annular denuders (URG Corp.) on the Amberlite XAD-4 resin (Supelco); particle-phase PAHs: collected on teflon filters (Pall) and a back-up PUF-plug (URG Corp.). No particle pre-cut. ISO 11338:2003, Heated filter/condenser /adsorber method. Particle-phase PAHs: quartz filters (Munktel Filter); gas-phase PAHs: XAD-2 resin (Supelco). No particle pre-cut.
Smouldering combustion (SC): Conventional masonry heater, smouldering combustion	The first half of the combustion period, 1+1 batches (35 min)	Dilution with a porous tube diluter (dilution air at ambient temperature), DR 69-176, T ~25 °C	As described in NC, diluted sample. No particle pre-cut.

Table 14. Measurement methods in III.

Combustion appliance and code	PAH sampling period	Dilution for PAH sampling	PAH sampling method
EFC: Pellet boiler, 25 kW nominal output, integrated fixed-grate burner, λ - sensor.	Steady-state operating conditions at a nominal load (2-3 h).	Porous tube diluter (dilution air at ambient temperature), DR 13, T 24 °C. PM ₁₀ pre-cut.	
IBC/34: Modern masonry heater	3rd and 4th batch (50 min). Represents relatively steady combustion at conditions in which the firebox walls are hot and a layer of glowing embers exists.	As for EFC, DR 26, T 26 °C	
CBC1: Conventional masonry heater 1	Whole combustion period of 1+2 batches (55 min)	As for EFC, DR 16, T 19 °C	PM ₁ sampling on PTFE filters (Millipore) with a Dekati gravimetric impactor (Dekati).
CBC2/F: Conventional masonry heater 2	The beginning of the second batch (15 min). Represents the firing phase.	As for EFC, DR 17, T 19 °C	
CBC3/23: Conventional masonry heater 3	2nd and 3rd batch (40 min). Represents relatively steady combustion at conditions in which the firebox walls are hot and a layer of glowing embers exists.	As for EFC, DR 20, T 23 °C	
IEBC/S: Sauna stove, no secondary air available.	1st and 2nd batches (20-35 min). Includes the firing phase and some of the combustion phase.	As for EFC, DR 24, T 19 °C	



Figure 6. Left: field measurements in Kuopio in February, 2006 (I); right: conventional masonry heater used in II and III.

Table 15. Measurement methods in IV.

Combustion appliance and code	PM sampling period	Dilution for PM sampling	PM sampling method
1 tnCMH: Conventional masonry heater			
2.7 tnCMH: Conventional masonry heater	1) During the second batch, starting from the addition of fuel to the moment when CO ₂ reached a value of 6%	1) Porous tube diluter (dilution air heated to 180 °C) and an ejector diluter (dilution air not heated), DR 46-180, T 22-30 °C	1) PM ₁ sampling on PTFE filters (Gelman Scientific, Teflon)
1 tnMMH: Modern masonry heater			
2.7 tnMMH: Modern masonry heater	2) From the second batch, starting 3 min after adding the fuel (30 min)	2) None: sampling from hot, undiluted exhaust, T 120-230 °C	2) Total dust measurement on cup-shaped quartz filters (Munktel)
1.2 tnMMH: Modern masonry heater			
1.85 tnMMH: Modern masonry heater			
1 tnMMH2: Modern masonry heater (duplicate test)			

4.2 Combustion appliances

The batch combustion appliances are briefly described below and in more detail in **I-IV**. A pellet boiler is described in Table 14 and in **IV** and was the only continuous combustion appliance in the experiments of this study. The pellet boiler is used for hot water production for central heating, whereas the batch combustion appliances used in the study were intended for space heating or cooking.

Sauna stove: a combustion appliance used for heating a sauna room to a temperature of approximately 70-80 °C. It is typically made of steel and filled with heat reserving stones of several tens of kilograms. In the sauna stoves used in the study, the structure was simple with primary air entering the firebox through the grate via an ash compartment under the grate (see also Tissari et al. 2009).

Conventional masonry heater: a slow heat release appliance that is intended to heat the space in which it is assembled even several days after fire has died. The appliance slowly releases the heat reserved in its massive

structure. They are typically made of bricks, soapstone, vermiculite, etc. and weigh ~1000-3000 kg. The word *conventional* refers to the traditional combustion technique with primary air entering the firebox through the bottom grate. No secondary air is introduced into the firebox. Some airflow may be introduced, for example, for flushing the firebox door glass.

Modern masonry heater: a slow heat release appliance with more advanced air staging. Secondary air is introduced in the firebox or the (secondary) combustion chamber. The construction parts such as stones, elements or bricks are fabricated by the manufacturer, and the appliances are assembled by the personnel educated and authorized by the manufacturer.

Cooking stove: cooking stoves have a hot plate where food can be cooked. They may also have a baking space. The cooking stove used in the study was made of soapstone.

4.3 Aerosol sampling

4.3.1 Dilutive sampling process

Dilutive sampling was used in **I-IV** (Tables 12-15). Sometimes, several dilution systems were used simultaneously for different samplers. For PAH sampling, in **I** the flue gas was diluted with the combination of an in-house built porous tube diluter (PRD) and an ejector diluter (ED) by Dekati Ltd. Schematics of these types of diluters are presented in Lyyräinen et al. 2004. Only the PRD was used in **II** and **III**. For mass measurements, the combination PRD+ED was used in **IV**.

The dilution ratios for PAH sampling ranged from 10 to 180. The temperature of the diluted sample was mostly below or equal to 25 °C. The dilution ratio *DR* was calculated based on the CO₂ concentrations (**I**):

$$DR = \frac{CO_{2,FG} - CO_{2,BG}}{CO_{2,D} - CO_{2,BG}} \quad (\text{Eq. 6}),$$

where $CO_{2,D}$ is the CO_2 concentration in the diluted gas, $CO_{2,FG}$ in the raw flue gas and $CO_{2,BG}$ in the dilution air. All concentrations are in dry gas, and the unit is %_{vol}.

4.3.2 PAHs

Four different types of equipment were used for PAH sample collection: a filter followed by an adsorbent (**I**, Figure 7); a heated filter/condenser/adsorbent according to ISO 11338:2003 (**II**, raw exhaust); a denuder method consisting of two annular denuders, a filter and a PUF adsorbent in series (**II**, dilute exhaust) (Figure 8); and a gravimetric impactor (**III**, Figure 9; Ruusunen et al. 2011). For the field measurement campaign of **I**, a compact method was selected. In **II**, the denuder method was selected for more accurate determination of the phase distribution of PAHs whereas in **III**, the impactor was used for the collection of relative large masses of size-segregated particles to be used in further toxicological studies.

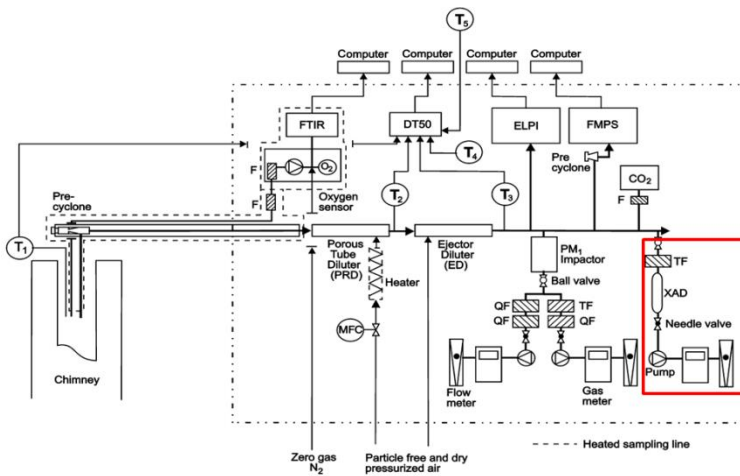


Figure 7. Schematics of the emission measurement system: the PAH sampling system is in the red frame (**I**).

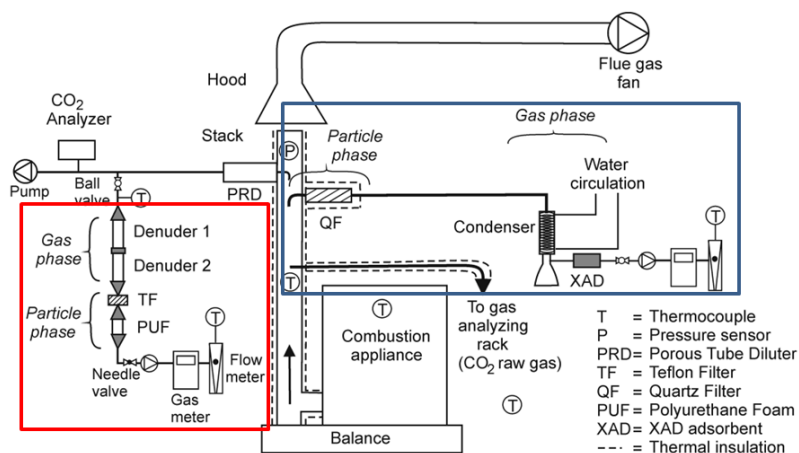


Figure 8. Schematics of the emission measurement system: the PAH sampling systems are in red and blue frames (II).

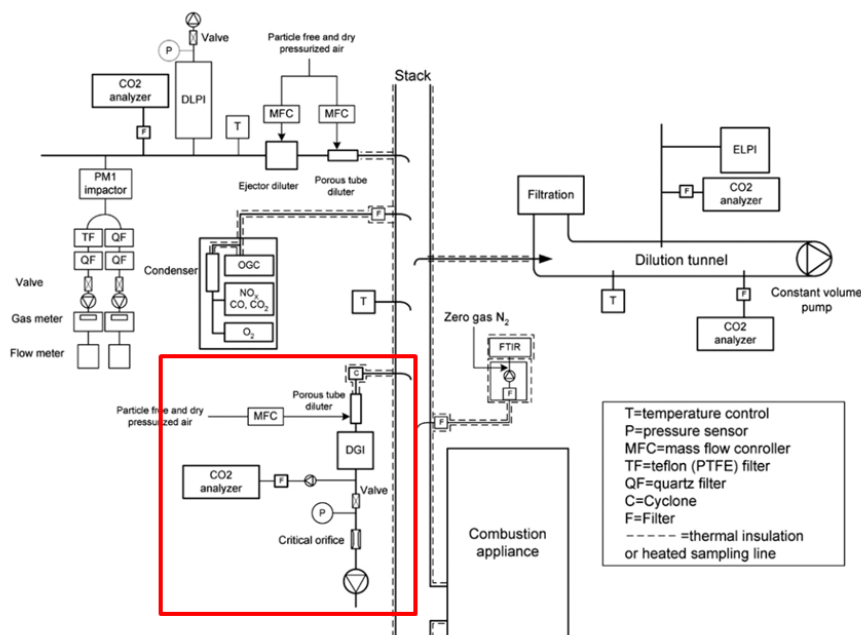


Figure 9. Schematics of the emission measurement system: the PAH sampling system is in the red frame (III).

For a more accurate gas-particle distribution measurement in **II**, the denuder method was used. In the methods consisting of a filter followed by an adsorbent, the gas-phase compounds (e.g., PAHs) may be adsorbed on the filter material or on the particles collected on the filter, causing an overestimation of the particle phase (positive particle-phase artefact). The particle-phase compounds can desorb in the sample stream during the sample collection and be collected on the adsorbent. This causes an underestimation of the particle-phase concentration (negative artefact) (e.g., Gundel et al. 1995). In the denuder method, these artefacts are avoided by collecting the gas phase prior to the particle phase and by using a back-up adsorbent after the filter. In **II**, 8-channel denuders made of glass (URG Corp.) were used (Figure 10).

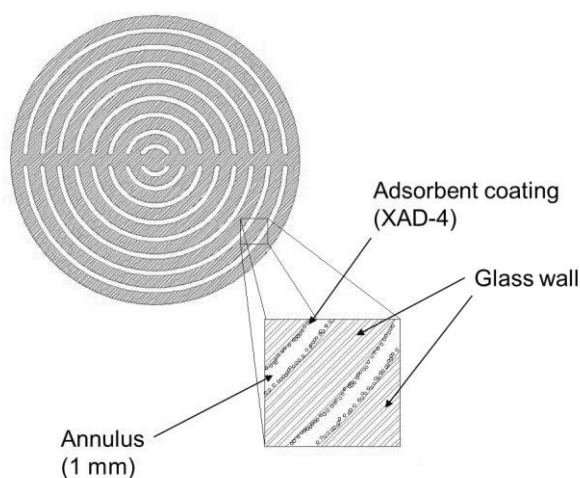


Figure 10. Cross-section of an 8-channel annular denuder.

4.3.3 Particle mass

The particle mass of the PM₁ fraction was measured from the diluted exhaust. The particle mass was collected on a plain Teflon filter (Tissari et al. 2008) usually with a filter holder system having two parallel lines, as in Figure 9 and described in **I**. Quartz filters were used in the system of four filter holders for the thermal-optical analysis of OC, EC and carbonate carbon. For the mass determination from the diluted exhaust, 47 mm PTFE-

filters (Gelman Scientific, Teflo or Pall Corporation) were used. The filter samples collected from the diluted exhaust were kept for 24 h at a constant temperature of 20 °C and a relative humidity of 40% before weighing with a microbalance Mettler Toledo MT1, sensitivity of 1 µg (I-IV).

In IV, the particle mass was collected from undiluted exhaust (total dust) by isokinetic sampling (Figure 11). The method resembles particle sampling method *partial flue gas sample over a heated filter* in EN 16510-1 (presented in 3.4.1.4). The quartz filters (Munktell ET/MK 360, 25 x 100 mm) were dried at 160 °C before and after sample collection, stabilized in desiccator for 4 h and weighed using a Precisa XT balance, sensitivity of 1 mg.

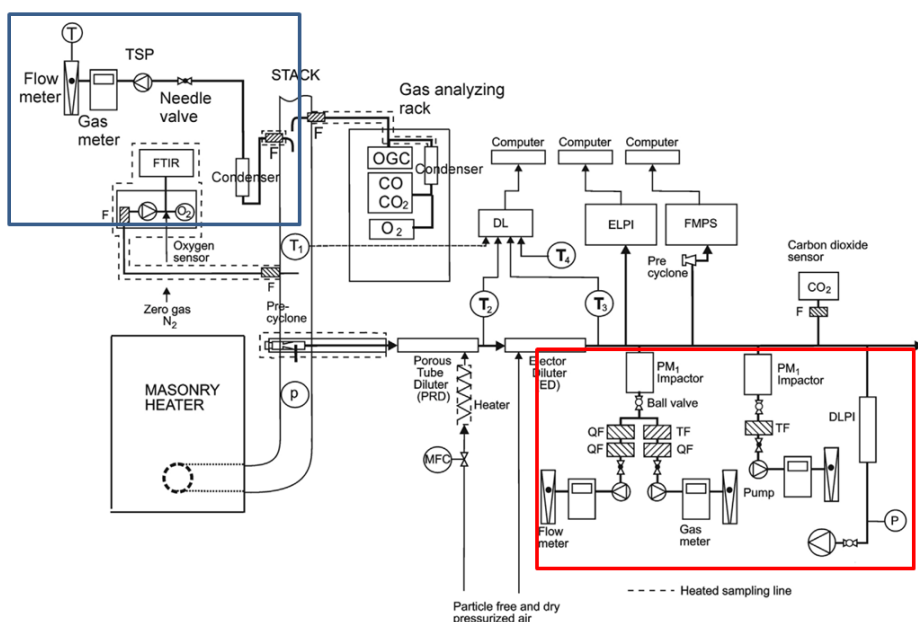


Figure 11. Schematics of the emission measurement system: PM₁ (diluted exhaust) sampling system in the red frame, total dust (undiluted exhaust) sampling system in the blue frame (IV).

4.4 On-line measurements of gaseous compounds

Gaseous components O₂, CO, CO₂ and NO_x were continuously measured using an ABB Hartman & Braun gas analyser system (ABB Cemas Gas Analyzing Rack, ABB Automation GmbH, Germany) (campaigns in II-IV).

The analyser system included also a flame ionization detector (FID) for measuring organic gaseous carbon (OGC). The FID was calibrated with propane. For analysing various VOCs as well as CH₄, H₂O, CO₂, CO and nitrogen oxides etc., a Fourier Transmission Infra Red (FTIR) spectrometer (Gaset DX-4000, Gaset Technologies Ltd., Helsinki, Finland) was used (campaigns in **I-IV**). The analyzer is equipped with a separate O₂-sensor (CrO). CO₂ concentrations were also continuously measured in the diluted exhaust for the determination of the dilution ratio (DR).

4.5 Off-line analysis of aerosol samples

4.5.1 PAHs

Either 15 (**I, II**) or 30 (**IV**) parent and alkyl-substituted PAHs that are either relatively abundant in emissions, are commonly measured or are identified as (probable) carcinogens and/or mutagens were analyzed. The sample preparation, extraction, clean-up steps and analysis are described in **I-III** and the involved references as well as in Table 16. Collected samples were spiked with an internal standard mixture of deuterated PAHs prior to extraction. PAHs were identified and quantified by comparing against an external standard mixture. GC-MS was used for the sample analysis.

In **III**, PAHs were analysed from a pooled sample; PM₁ samples from several replicates obtained with the same combustion appliance were combined. The samples were pooled in order to have enough uniform particle material for the toxicological and chemical analyses.

Table 16. Extraction and analysis of PAH samples.

Paper	Sample preparation	PAH extraction	PAH analysis
I		Filters: sonication with methanol:toluene (6:1) for 1 h; adsorbents: Soxhlet with dichloromethane for 16 h	15 PAHs*, GC/MS (Agilent (6890N GC/5973 inert MSD), SIM mode, GC column 5%-phenyl-methylpolysiloxane (HP-5-MS).
II		Dilute exhaust samples Denuders: toluene:dichloromethane (1:1); filters: sonication with methanol:toluene (6:1) for 1 h; PUF: Soxhlet with toluene:hexane (1:1) for 16 h Raw exhaust samples Filter: Soxhlet with methanol:toluene (6:1) for 16 h; adsorbent: Soxhlet with dichloromethane for 16 h	15 PAHs*, GC/MS (Agilent (6890N GC/5973 inert MSD), SIM mode, GC column 5%-phenyl-methylpolysiloxane (HP-5-MS).
III	The collected particle mass was removed from the substrate by extracting with methanol in an ultrasonic bath. The extracts were pooled to form a PM ₁ sample for each combustion case. After evaporation, the suspension was dispensed into glass tubes on a mass basis, dried under a nitrogen flow and stored at -20 °C (Tapanainen et al., 2011).	The dried samples were extracted with dichloromethane in an ultrasonic bath for 15 min.	30 PAHs**, GC/MS (Agilent (6890N GC/5973 inert MSD), SIM mode, GC column 50% phenyl methylpolysiloxane (DB-17ms, J&W Scientific)

*Acy, Ace, Fle, Phe, Ant, Fla, Pyr, BaA, Chr, BbF, BkF, BaP, I123cdP, DahA, BghiP

**Nap, Acy, Ace, Fle, Phe, Ant, 1MPhe, Fla, Pyr, BcP, BaA, CcdP, Tri, Chr, 5MChr, BbF, BkF, BjF, BeP, BaP, Per, I123cdP, DahA, BghiP, Antha, DalP, DaeP, Cor, DaiP, DahP

4.5.2 Organic and elemental carbon contents of particles

Organic carbon (OC), elemental carbon (EC) and carbonate carbon (CO₃) were analysed using a thermal-optical method on an OCEC Carbon Aerosol Analyzer (model 4 L) by Sunset Laboratory Inc. (OR, USA) and a NIOSH 5040 procedure (NIOSH 1999). The analysis and sample preparation are described in more detail in Sippula et al. 2007 and 2009.

4.6 Conversion of emissions

Emission q_e (mg/MJ_{fuel}) was calculated according to Eq. 7 (SFS 5624):

$$q_e = c_m \times n \times k \times Q_s \quad (\text{Eq. 7}),$$

where c_m is the concentration in dry gas in NTP (mg/m³), k is a factor depending on the fuel moisture and Q_s is the dry volume of flue gas formed in the combustion of dry fuel per energy unit (fuel) in NTP (m³/MJ); $Q_s=0.25$ m³/MJ for wood, and n is calculated as

$$n \approx \frac{D_t}{D_m} \approx \frac{20.9}{20.9 - E_m} \quad (\text{Eq. 8}),$$

where D_t is the CO₂ concentration formed in the stoichiometric combustion (%), D_m is the measured CO₂ concentration (%), 20.9 is the O₂ concentration in air (%) and E_m is the O₂ concentration in the flue gas (%).

The emission per fuel mass, q_m (mg/kg_{dry fuel}) was calculated as

$$q_m = q_e \times H_u \quad (\text{Eq. 9}),$$

where H_u is the lower heating value of dry fuel (MJ/kg).

The efficiency of the combustion appliances was not considered in **I-IV**. In some references, such as Orasche et al. 2012, the emission per produced energy unit q_{ep} (mg/MJ_{produced}) is given. For the comparison of emission values, q_{ep} was converted to q_e by following equation:

$$q_e = q_{ep} \times \frac{\eta}{100\%} \quad (\text{Eq. 10}),$$

where η is the efficiency of the appliance (%).

4.7 Data analysis

Simple linear regression was used for studying the relationships of emission components. Trendlines were determined with Microsoft Excel. R² value,

coefficient of determination, shows the reliability of the trend that is how closely the estimated values on the trendline correspond to actual data. Trendlines and R^2 values were used for evaluating how strongly the concentrations of the studied emission components were related to each other.

5 RESULTS AND DISCUSSION

5.1 Effect of dilutive sampling on the partitioning of organic species

5.1.1 Phase distribution of PAHs

Dilution of the exhaust with cool air (~20 °C) increased the proportion of particle-bound PAHs compared to hot exhaust (II). In hot exhaust, the majority of each PAH existed in the gas phase, whereas partitioning to the particle phase occurred in the diluted exhaust at 25 °C (Figure 12). These results agree with the theoretical saturation vapour pressures at least semi-quantitatively. In hot exhaust, the partial pressures of the studied PAHs (gaseous+particle phase) were clearly below the saturation vapour pressures of the pure compounds taken from literature (Yaws 2003; ISO 11338-2 2003) or estimated by a UNIFAC-based group contribution method (Figure 13). In the diluted exhaust, the vapour pressures (gas+particle) of lighter compounds from Acy to Ant were below the saturation vapour pressure (Figure 14). These compounds were mainly found in the gas phase; relatively small amounts were found in the particle phase. From Fla to heavier PAHs, the saturation pressure was approached or exceeded, and consequently, the proportions in the particle phase grew; condensation is suspected to govern the transfer to the particle phase. From BbF to heavier PAHs, the vapour pressure (gas +particle) was several orders of magnitude higher than the saturation vapour pressure in both combustion cases. These compounds existed mostly in the particle phase. The gas-phase concentrations well over the saturation vapour pressures indicate that the system is not in equilibrium. The mass transfer of PAHs of larger molecular mass is limited by low diffusivity.

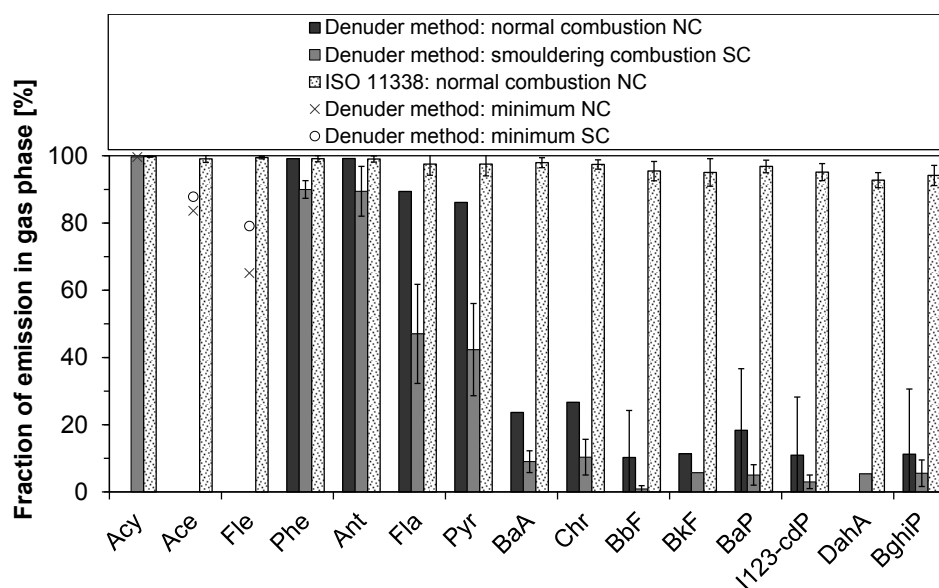


Figure 12. Gas-particle distribution of PAHs determined from the diluted exhaust with the denuder method and from hot, undiluted exhaust with method ISO 11338: normal combustion (NC) and smouldering combustion (SC) (II).

Measured from the diluted exhaust, the gas-phase emissions were 88% of the total (gas+particle) PAH emissions in normal combustion and 77% in smouldering combustion (Figure 12). In smouldering combustion, the total PAH concentrations were also higher than in normal combustion. The greater amount of organic mass on the particles (Frey et al. 2009) probably promotes the partitioning of PAHs in the particle phase by dissolution in the organic layer. The increased condensation of organic matter on agglomerate particles was also reflected in the higher effective density, larger particle size and more closed structure of the particles in smouldering combustion (Tissari et al. 2008).

In the determination of the phase distribution, some limitations exist. The determination of low sample masses may have caused uncertainty in the results. This uncertainty particularly affects the results from particle-bound fractions of the most volatile PAH compounds, especially when relatively high dilution ratios are applied. Furthermore, there is also considerable uncertainty in the theoretical values because, according to

literature, the saturation vapour pressures of certain PAHs vary greatly. In addition, the real-life saturation pressure of a compound is affected by the mole fraction (Raoult’s law) and activity of that compound. The sample also averages the result: the actual concentration and thus the saturation ratio varied during the sampling period.

In II, the particle mass concentration in the dilute exhaust under the prevailing conditions ranged from 0.4 to 2.2 mg/m³ in NC and from 2.1 to 20 mg/m³ in SC, which is 10 to 500 times higher than the ambient concentration of e.g. 0.04 mg/m³.

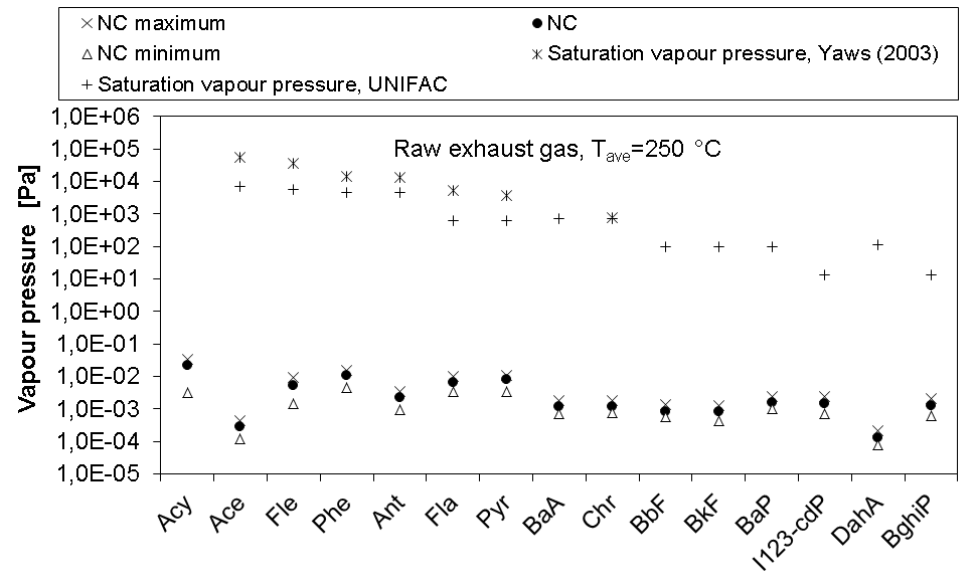


Figure 13. Partial vapour pressures (gas+particle concentration) in undiluted exhaust (250 °C) in normal combustion (NC) (II).

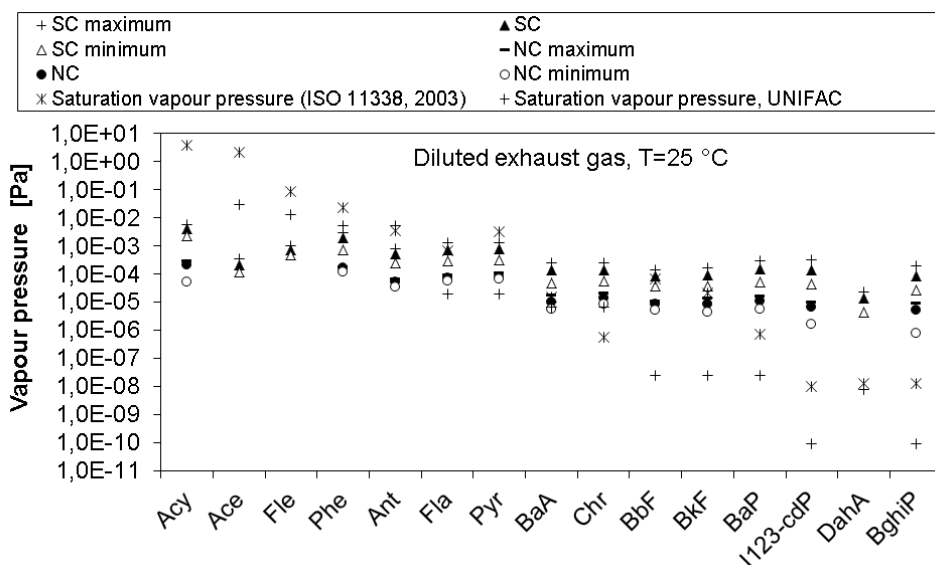


Figure 14. Partial vapour pressures (gas+particle concentration) in diluted exhaust gas (25 °C) in normal combustion (NC) and smouldering combustion (SC) (II).

5.1.2 Effect of the sampling technique on particle mass emissions

The impact of dilution on the measured particle mass concentration was studied in IV. Altogether, six conventional and modern masonry heaters were studied. The total dust mass emission was measured from the hot exhaust and PM₁ mass emissions from the diluted exhaust at ambient temperature. The particulate emissions measured from the diluted exhaust (PM₁) were a factor of 1.1 to 4.4 higher than the emissions measured from the hot exhaust (Figure 15), despite the fact that the hot exhaust sample also contained supermicron particles. This result is suspected to be due to condensing organic compounds that are included in the particle sample when dilution is applied, whereas a major part of these compounds remain in gas phase and pass through the filter in the hot exhaust measurement.

In parallel measurements in hot and diluted flue gas from a stove, Ozgen et al. (2014) found the particle emissions to be 4 times higher on average when measured from the diluted exhaust. The dilution ratio was approximately 10, and the sample temperature was 30-35 °C.

Correspondingly, in a comparison of hot exhaust sampling and sampling from a full flow dilution tunnel, Seljeskog et al. determined particle emissions measured from diluted exhaust that were approximately 4-fold and 8-fold for birch and spruce fuels, respectively, compared to results from hot exhaust. The combustion appliance was a stove; the dilution ratio was not reported (Seljeskog et al. 2016). The results of the effect of the condensable species are shown in Ellner-Schubert et al. (2010), who also found the diluted emissions to be higher in parallel measurements. Moreover, the dilution method produced relatively higher emissions at higher OGC concentrations. The mean dilution ratio was 5.7, and the temperature of the diluted exhaust was 56 °C. In general, for appliances with more complete combustion conditions, the effect of the sampling method is smaller (Nussbaumer et al. 2008).

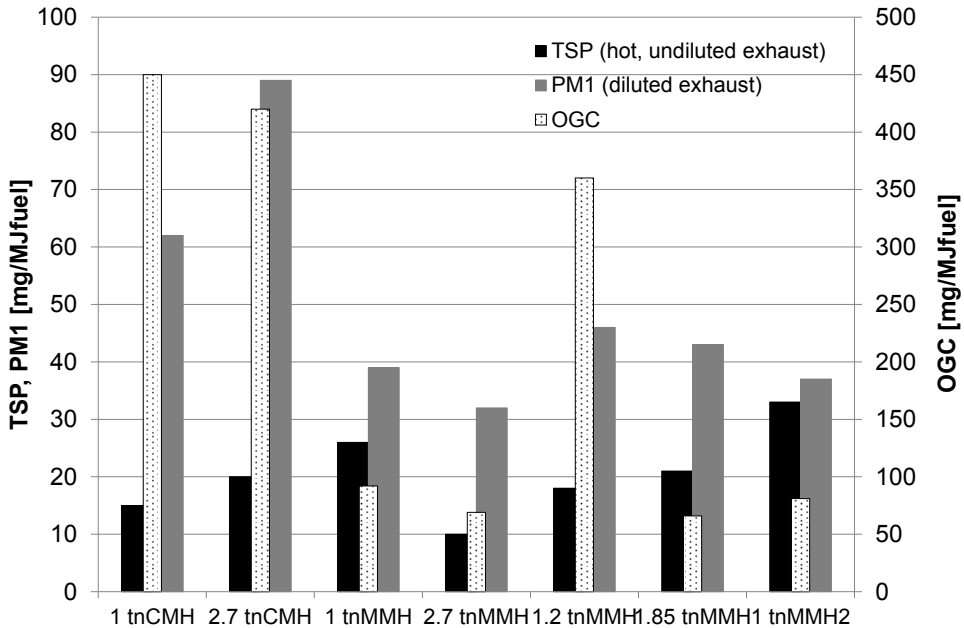


Figure 15. Total dust mass emission TSP (hot exhaust), PM₁ mass emissions (diluted exhaust at ambient temperature) and organic gaseous carbon emissions OGC from conventional masonry heaters (CMH) and modern masonry heaters (MMH), sampled during the second batch (IV).

The connection between the difference in PM₁ and the total dust results and other measured parameters was investigated in IV. Linear regression

trendlines are presented in Figure 16. The high OGC emissions and the high OC content in PM_{10} were associated with low values of the related total dust/ PM_{10} . These findings support the role of condensable organic compounds in the difference between the results from the two methods. Nevertheless, R^2 value, coefficient of determination, was low. In addition to condensable species, also several other phenomena give rise to differences between the particle masses measured from hot or diluted exhaust. Large particles consisting of unburned fuel or coarse bottom ash are included in total dust samples but are cut off from PM_{10} samples. Large particles occur rather randomly in the exhaust, and their existence may depend more on the combustion appliance's dimensions and flow rates in the firebox than on the combustion conditions, which could have caused the lack of connection of OC and OGC with TSP/ PM_{10} .

The TSP/ PM_{10} relation had strong connection with the flue gas temperature (Figure 16). Further, the TSP emissions had some connection with T (flue gas) ($R^2=0.62$) unlike with PM_{10} ($R^2=0.21$). The higher total dust emissions at higher temperatures could be associated with the technical details of the particle sampling: the post-sampling treatment at 160 °C probably causes a relatively greater loss of mass in the TSP samples, which are collected at flue gas temperatures below 160 °C compared to the filter samples collected from flue gas at higher temperatures (>160 °C).

In summary, sampling from hot exhaust on heated filters can be used successfully in the particle mass emission measurements from, e.g., large power production units. In residential wood combustion with emissions rich in semivolatile species, however, this type of method is not necessarily applicable. In comparing the small wood combustion appliances or technical solutions, the decrease in the amount of organic compounds caused by the improved combustion conditions may be unnoticeable in hot exhaust particle measurements because a large part of the organic material is in the gas phase. Organic gaseous carbon, on the other hand, can be measured with an FID, but it is unclear whether the sensitivity of this method is sufficient to detect the change in semivolatile material, the amount of which, compared to major gaseous hydrocarbons, is relatively small. In addition, hot exhaust sampling of total dust may give "random" results due to the incidentally existing very coarse particles that originate from unburned fuel. These coarse particles may be less important from a

health perspective but have major influence on the particle mass collected on the filters.

In dilutive sampling, the improvements in combustion technology that mostly affect the organic particle fraction can be better observed in the particle mass because the less important coarse particles are cut off during the dilution process. Importantly, however, the results are sensitive to the sampling conditions in dilutive sampling. To attain comparable results, a precise definition of acceptable sampling conditions is needed.

Dilutive sampling with moderate dilution may lead to an overestimation of the particle emissions compared to the greater dilution present in the atmosphere (Figure 3; e.g., Lipsky and Robinson 2006, Donahue et al. 2009). On the other hand, in the atmosphere, secondary organic aerosols are formed from the evaporated constituents, which may considerably increase the contribution of the emission source to the ambient particle burden (e.g., Robinson et al. 2007).

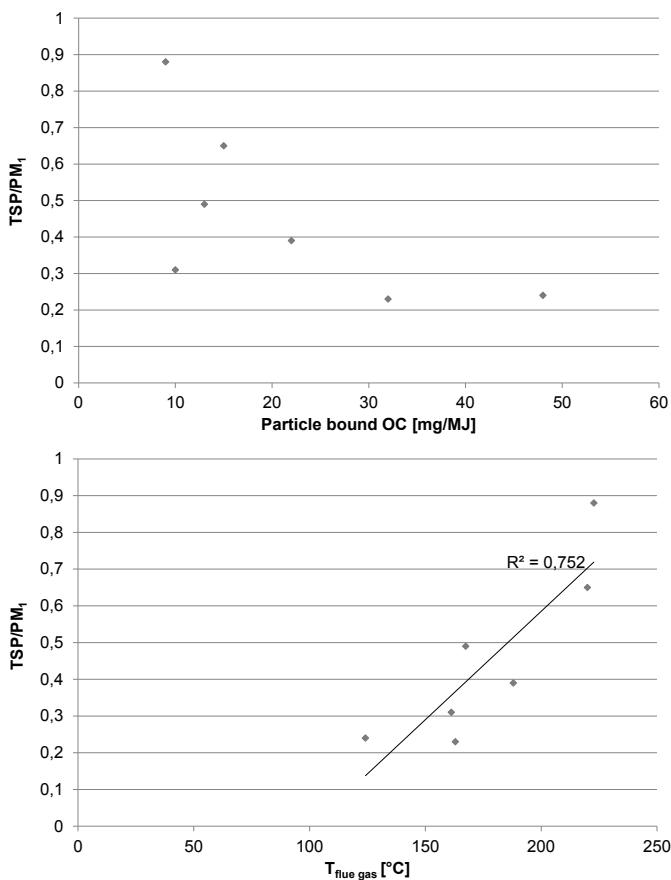


Figure 16. The TSP/PM_1 relation as a function of the 1) particle-bound organic carbon (OC) and 2) flue gas temperature (IV). Total dust (TSP) was determined from the hot exhaust, and PM_1 was determined from the diluted exhaust.

5.2 PAH emission factors of residential wood combustion

5.2.1 Overview of the studied PAH emissions and limitations of the data

The PAH, CO and OGC emission factors were determined in **I-III**. The results were compared to the results of selected European studies (Annex 1). The emission factors are presented in Annex 2. In **I** and **II**, PAHs were sampled both from the gaseous and particle phases, however in **III** only from the particle phase. The focus of this discussion is on the particle-phase PAHs. It is important to realize that some differences between the particle-bound PAH emissions from the studied cases may be due to altered partitioning, which depends strongly on the sampling conditions (e.g., Boman et al. 2005). Various sets of PAHs, either 15 (**I** and **II**) or 30 (**III**) were analyzed. In all the papers including the reviewed studies, the PAH sample was collected from the diluted exhaust. The dilution ratio varied from 1.5 to 176, except in the highly time-resolved PAH measurements in Eriksson et al. (2014), for which it varied from 300 to 3000.

Due to relatively small amount of appliances investigated, calculating the average emission for a certain appliance type was in author's opinion not reasonable. However, some comparison of appliance types is presented. Concerning batch combustion devices, the results that represent the whole combustion period were considered. For continuous combustion appliances, the results representing either steady-state combustion or a typical operation cycle with various loads were considered.

The particle-bound emissions of 15 PAHs measured in the various combustion situations varied substantially (Figure 17). In the following chapters, the PAH emissions are explored based on the combustion appliance type, the combustion phase and an operational point of view.

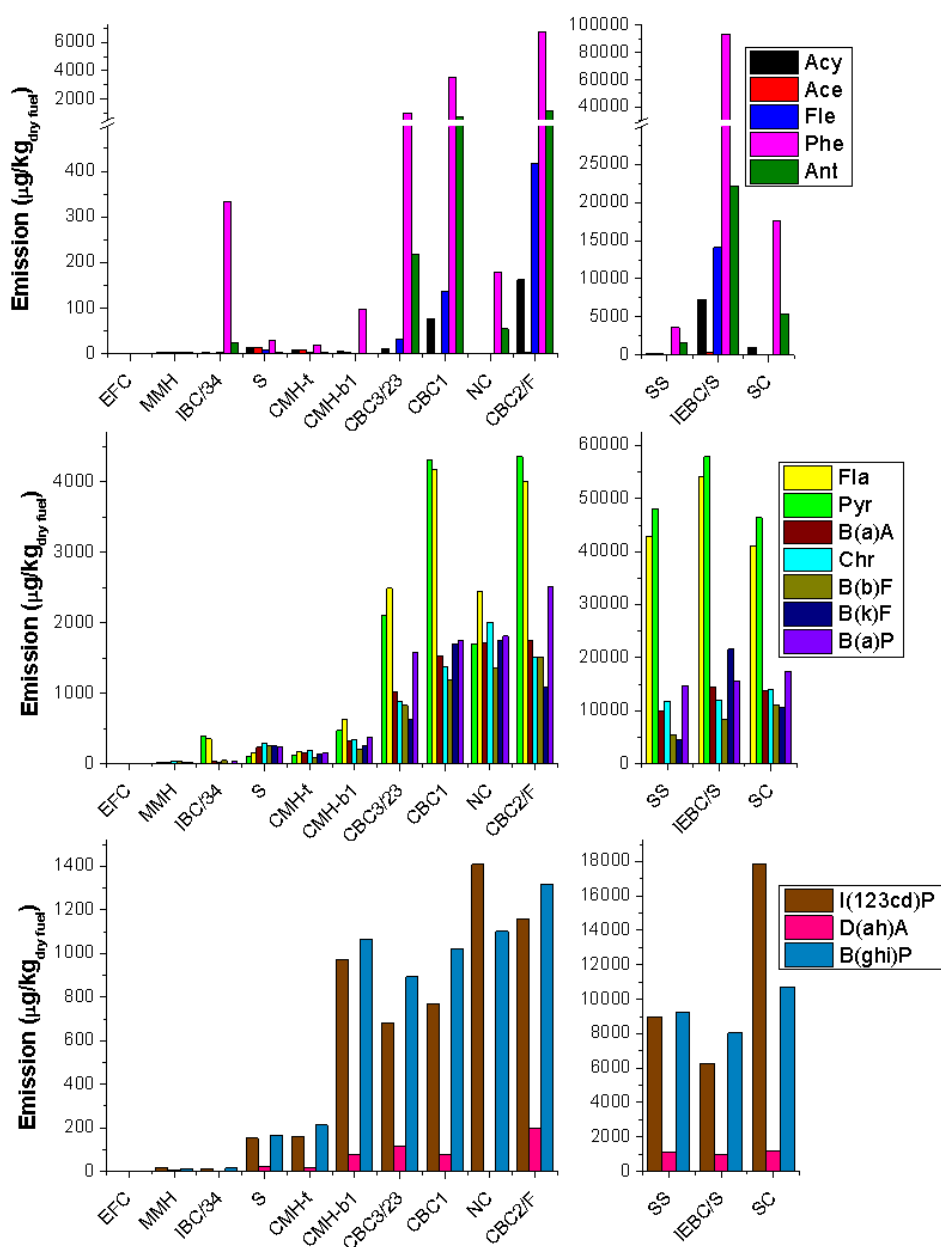


Figure 17. Particle-bound emissions of 15 PAHs (combustion case abbreviations explained in Tables 12-14). Space has been left blank if no data were available. **Note the various scales of the y-axes.**

5.2.2 PAH emissions from different combustion appliances

In this study, the variation in the emission factors of an individual PAH from different appliances is vast at over six orders of magnitude from ~0.01 µg/kg to 10000 µg/kg. The lowest emission factors were measured from a pellet boiler and the highest from a sauna stove. The modern masonry heater had lower emission factors compared to the conventional masonry heater and cooking stove. However, the emission factors within the appliance type vary greatly, e.g., by two orders of magnitude for the conventional masonry heater.

When the selected 15 single PAH emission factors from this work were compared to the applicable literature values, it can be observed that the highest emissions are released from the sauna stove (**I**), followed by the batch burning devices with old technology: a small, under-fire log boiler, a log stove (Jalava et al. 2012) and the conventional masonry heaters in **II** and **III**. In the case of the lighter compounds Acy, Ace, Fle, Phe, and Ant, the log stove and log boiler with old technology (Jalava et al. 2012) had higher emission factors than the sauna stove. A reason for this observation could be different sampling conditions and consequently different partitioning; the dilution ratio is not mentioned.

Modern batch burning devices, modern masonry heaters (**I**), a tiled stove, a down-draught log boiler and a modern log stove (Jalava et al. 2012) had lower emission factors than the old-technology appliances, but the conventional masonry heaters and cooking stove (**I**) also approached the level of modern appliance emissions of lighter compounds.

The lowest emission factors were determined from continuous combustion devices, pellet boilers and pellet stoves (**III**, Orasche et al. 2012; Jalava et al. 2012; Vicente et al. 2015); wood chip boilers (Orasche et al. 2012; Jalava et al. 2012); and a batch combustion appliance and down-draught log wood boiler at a nominal load (Orasche et al. 2012). Substantial differences related to appliance operation exist within the pellet boilers emissions. For example, the results from the pellet boilers in **III** and Orasche et al. 2012 are nominal load results, whereas, various loads and operational modes were included in the results from Jalava et al. 2012. The effect of combustion technology is demonstrated with the BaP emission factors (Figure 18).

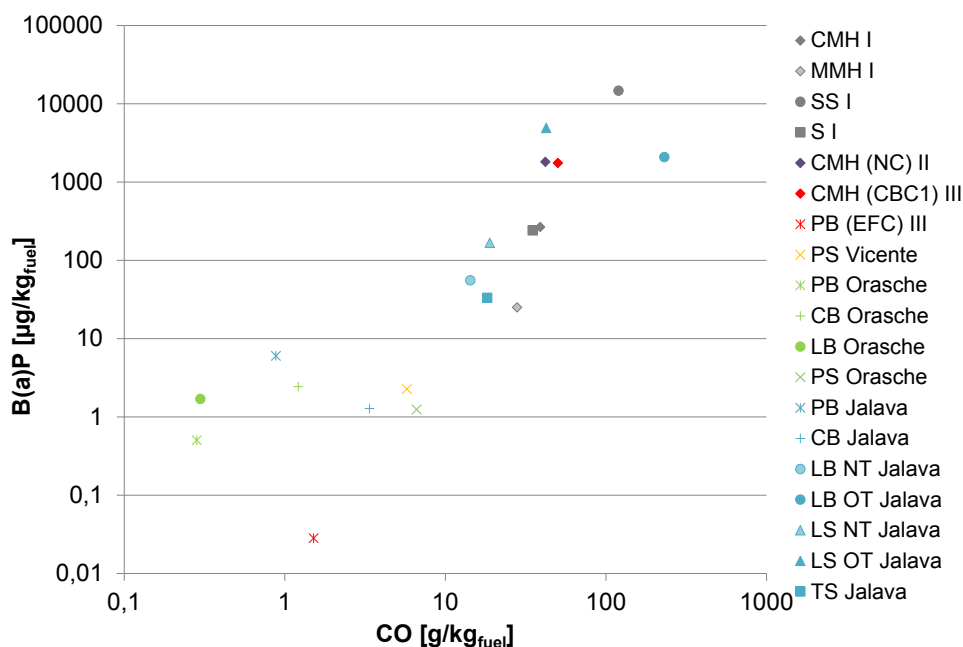


Figure 18. Particle-bound B(a)P emissions ($\mu\text{g}/\text{kg}_{\text{fuel}}$) as a function of the CO emissions ($\text{g}/\text{kg}_{\text{fuel}}$) of various combustion appliances (CMH conventional masonry heater, MMH modern masonry heater, SS sauna stove, S cooking stove (I), CMH (NC) conventional masonry heater (II), CMH (CBC1) conventional masonry heater, PB (EFC) pellet boiler (III); PS pellet stove (Vicente et al., 2015); PB pellet boiler, CB chip boiler, LB log boiler, PS pellet stove (Orasche et al. 2012); PB pellet boiler, CB chip boiler, LB NT log boiler new technology, LB OT log boiler old technology, LS NT log stove new technology, LS OT log stove old technology, TS tiled stove (Jalava et al. 2012)). **Note the logarithmic scale of the y-axis.**

Summed emissions of 11 PAHs ($\Sigma 11\text{PAHs} = \text{Phe, Ant, Fla, Pyr, BaA, Chr}$ (w or w/o Tri), BbF, BkF, (or sum of BF), BaP, I123cdP, BghiP) were compared. The differences between the appliance types in the emission of $\Sigma 11\text{PAHs}$ were qualitatively rather similar, as in the case of BaP with the exception that the modern masonry heater was in the range of continuous combustion appliances (Figure 19). For $\Sigma 30\text{PAHs}$ in III and Jalava et al. 2012, the comparison between the appliances is rather similar, with the continuous combustion devices expressing the lowest emissions. $\Sigma 30\text{PAHs}$ consists of compounds listed in Table 2.

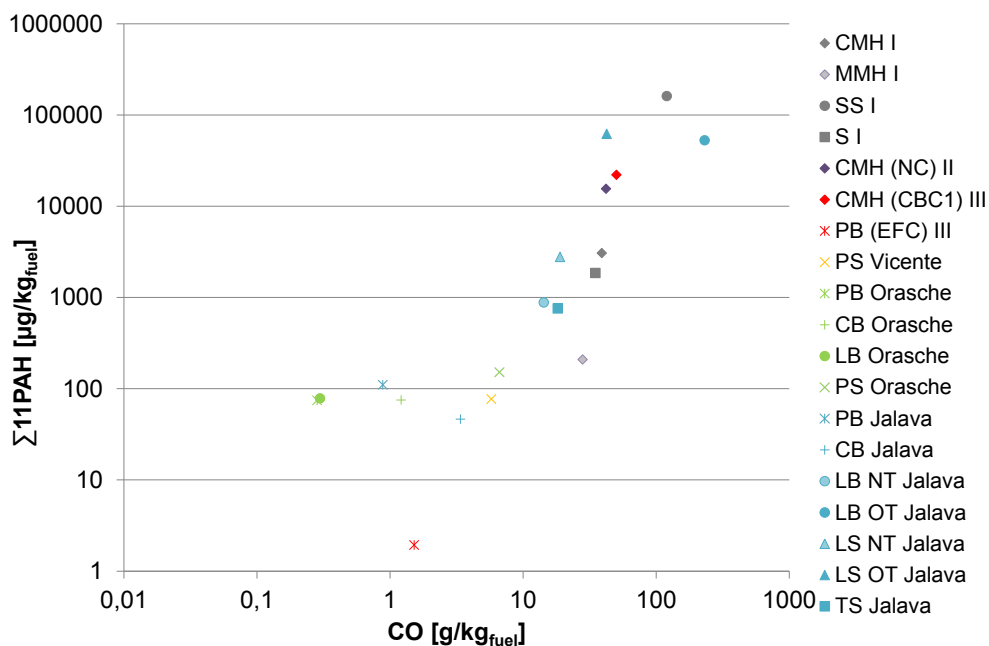


Figure 19. Particle-bound $\Sigma 11\text{PAHs}$ emissions ($\mu\text{g}/\text{kg}_{\text{fuel}}$) as a function of the CO emissions ($\text{g}/\text{kg}_{\text{fuel}}$) of various combustion appliances ($\Sigma 11\text{PAHs}=\text{Phe, Ant, Fla, Pyr, B(a)a, Chr (w or w/o Tri), B(b)f, B(k)f, (or sum of Bfs), B(a)p, I(123cd)p, B(ghi)p}$), (CMH conventional masonry heater, MMH modern masonry heater, SS sauna stove, S cooking stove (I), CMH (NC) conventional masonry heater (II), CMH (CBC1) conventional masonry heater, PB (EFC) pellet boiler (III); PS pellet stove (Vicente et al., 2015); PB pellet boiler, CB chip boiler, LB log boiler, PS pellet stove (Orasche et al. 2012); PB pellet boiler, CB chip boiler, LB NT log boiler new technology, LB OT log boiler old technology, LS NT log stove new technology, LS OT log stove old technology, TS tiled stove (Jalava et al. 2012)). **Note the logarithmic scale of the y-axis.**

The effect of the combustion technology on PAH emissions was studied in the distinct period of the combustion cycle in which relatively steady combustion conditions occurred in the already hot firebox of modern and conventional masonry heaters (cases CBC3/23 and IBC/34, III) (Figure 20). In this distinct period, the $\Sigma 30\text{PAH}$ emission factor was $1400 \mu\text{g}/\text{kg}_{\text{fuel}}$ for the modern masonry heater and $17000 \mu\text{g}/\text{kg}_{\text{fuel}}$ for the conventional masonry heater. The proportion of PAHs consisting of five or six fused benzene rings is much higher, almost 30% for the conventional appliance.

More efficient combustion caused by better mixing of the air and fuel in the firebox resulted in considerably lower PAH emissions.

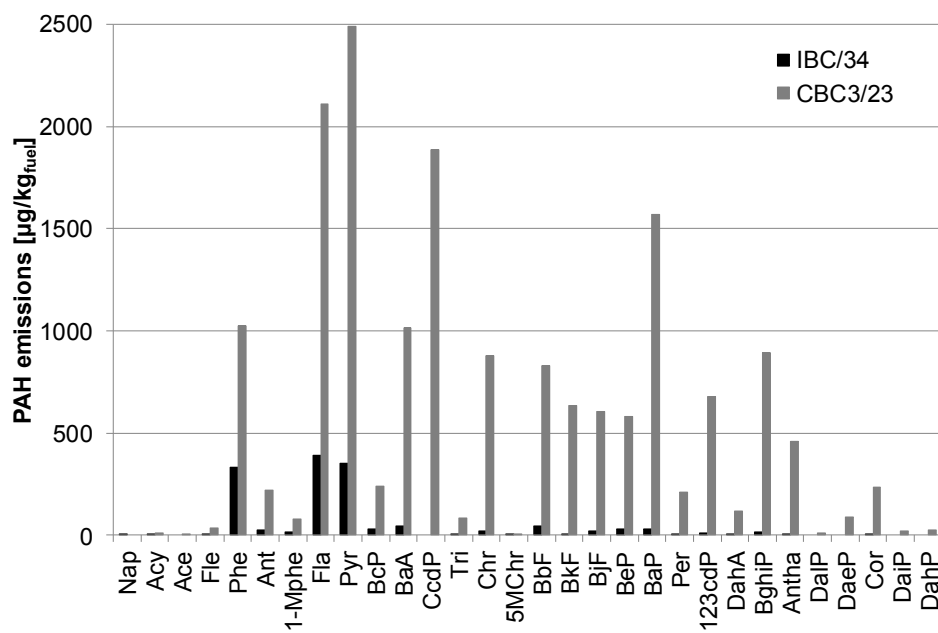


Figure 20. PAH emissions from the conventional masonry heater (CBC3/23: conventional batch combustion during the 2nd and 3rd batches) and modern masonry heater (IBC/34: improved batch combustion during the 3rd and 4th batches) at relatively steady combustion conditions (III).

5.2.3 PAH emissions from different combustion phases

The PAH emissions from three different conventional masonry heaters were studied during various combustion phases: 1) the whole combustion cycle (CBC1), 2) the firing phase of the second batch (CBC2/F) and 3) the relatively steady batch combustion in the 2nd and 3rd batches (CBC3/23) in III. Of the three cases, the PAH emission factors from the firing phase were mostly the highest (Figure 21).

Higher PAH emissions during the firing phase have been observed in other studies as well. The emission of each individual PAH from the wood stove was found to be higher during the devolatilisation phase (initial heating and wood drying without a visible flame) of the fuel compared to

the emission during the rest of the combustion cycle phase (Vicente et al. 2015). In Orasche et al. 2012, the cold-start emission of individual PAHs from boilers and pellet stoves were higher compared to the nominal load results, whereas lower emissions from the cold start compared to nominal load combustion were measured for wood stoves. For the wood stove, the whole batch was sampled, which likely smoothed the cold-start results. Leskinen et al. (2014) found the submicron particles emitted during the firing phase of the second batch from a modern masonry heater to consist mostly of organic matter (84% organic aerosols, 14% black carbon). This result was explained by the high burn rate, which led to insufficient mixing of the air and combustion gases. In addition, the firebox temperature was not high enough for instantaneous combustion of the gases. Instead, in the ignition of the first batch, the particles consisted mostly of black carbon and also of organic material (67% and 26%) (Leskinen et al. 2014). Concerning the emissions from wood stoves, Eriksson et al. (2014) found that the PAH emissions increased in the ignition phase after the addition of a new batch on the glowing embers. Large PAH emissions are also formed in the combustion phase during the fast burning associated with low residual O₂ and high CO emissions. In the burn-out phase, the PAH concentration was low.

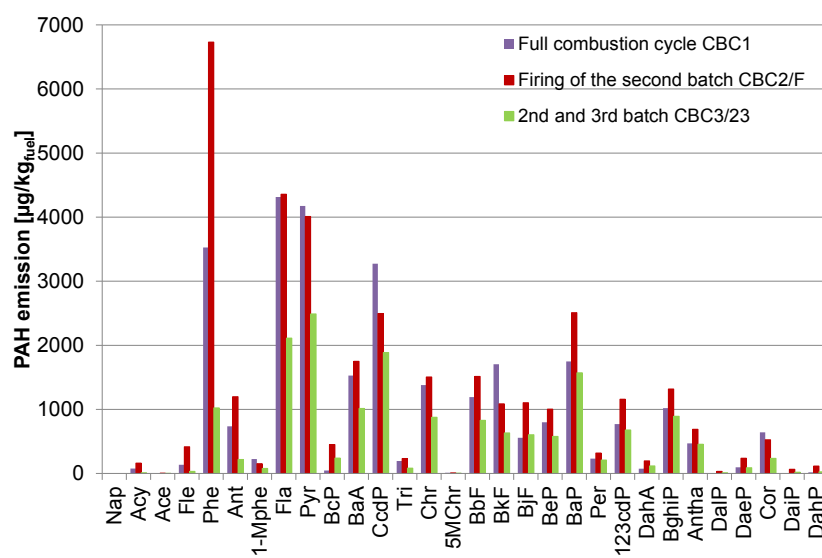


Figure 21. Particle-bound PAH emission factors from different periods of the combustion cycle of a conventional masonry heater (III).

5.2.4 Effect of appliance operation on PAH emissions

In II, the emissions from normal combustion (NC) and smouldering combustion (SC) in a conventional masonry heater were compared. The particle-bound $\Sigma 11\text{PAH}$ emission was $15500 \mu\text{g}/\text{kg}_{\text{fuel}}$ from normal combustion and $313800 \mu\text{g}/\text{kg}_{\text{fuel}}$ from smouldering combustion. The emission factors of individual PAHs were 6 to 100 times higher from smouldering combustion, and Phe and Ant increased the most (Figure 22). The emission of BaP increased by a factor of 10.

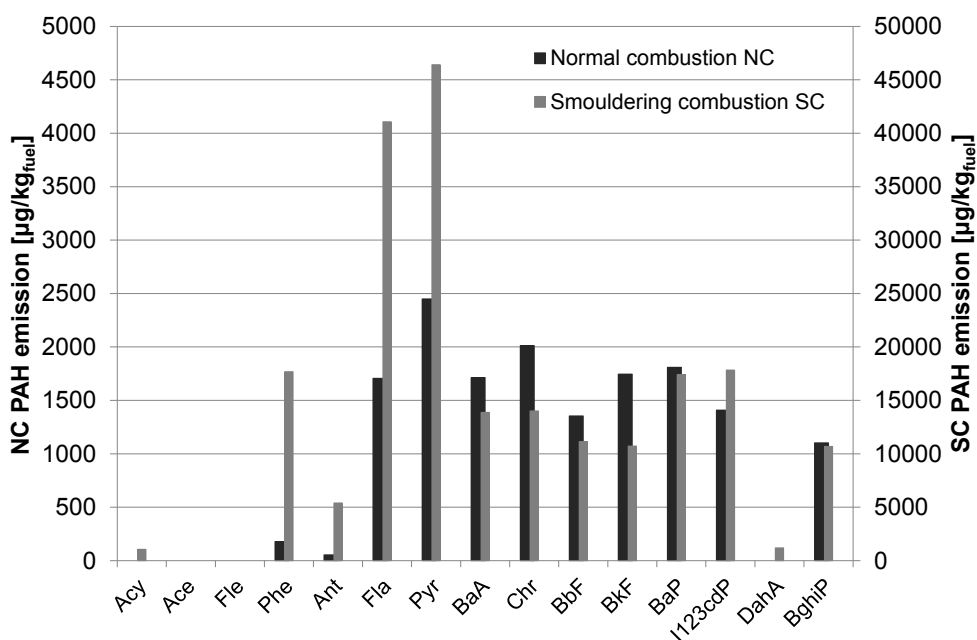


Figure 22. Particle-bound emission of 15 PAHs in normal combustion and smouldering combustion in a conventional masonry heater (II). Space has been left blank if no data were available. **Note the different scaling of the two y-axes.**

Operational practices have also been found to affect PAH emissions in the literature. Orasche et al. (2013) found that changes, even small, in log wood quality as well as the primary and secondary air supply had a rather strong influence on the combustion conditions and PAH emissions in batch combustion appliances. Overloading resulted in mostly the highest PAH emission factors. Pettersson et al. 2011 measured both semivolatile and

particle-bound PAHs and found that the total PAH emissions from a wood stove increased considerably under conditions of a high burn rate due to the lack of oxygen.

In continuous combustion, the influence of the user is typically smaller due to the automatic operation of appliances. Nevertheless, a start-up phase (e.g., Orasche et al. 2012) and partial-load operation (e.g., Johansson et al. 2004; Lamberg et al. 2011) may cause higher CO, PM and PAH emissions compared to steady combustion at a high load. Boman et al. (2011) found that a low load (1.7 kW_{fuel}) on a pellet stove resulted in total PAH emissions that were 16 times higher than at high load (5 kW_{fuel}). The emission of individual PAHs were 2 to over 400 times higher. The total PAH emissions were 140 times higher for intermittent operation (6 kW) than for operation at a nominal load for a 22 kW pellet burner with electrical ignition. For a pellet burner with a pilot flame, however, operation at a low load did not produce higher PAH emissions than at a nominal load (Johansson et al. 2004).

5.2.5 PAH profiles for different combustion cases

In the particle phase, various PAHs were among the most abundant compounds: Fla, Pyr, Chr, Phe, BaA, BbF, BkF, BghiP, I123cdP and BaP (**I-III**). In the total emissions (gas+particle phase), Acy, Pyr, Fla and Phe were among the most abundant compounds (**I** and **II**). Correspondingly, Phe, Fla and Pyr were the major PAHs in the nominal-load-combustion emissions from various combustion appliances in Boman et al., 2011 and Pettersson et al., 2011; Acy was not analysed.

In the highest PAH emission cases of the sauna stove (**I**) and smouldering combustion (**II**), Fla and Pyr (C16) dominated the particle-phase PAH emissions. Thus, in these cases, the proportion of lighter PAHs was emphasized. In this study, nevertheless, it is rather difficult to associate specific combustion conditions with a certain type of PAH profile because very different combustion conditions may have occurred during the sampling period, for example, producing first lighter and later heavier PAHs.

In the literature, the combustion temperature has been shown to affect the size of the formed PAH molecules: Orasche et al. (2013) concluded that

“The higher the temperature in the absence of oxygen, the larger the formed PAH molecules”. According to Eriksson et al. (2014), the distribution of PAHs was shifted toward larger molecules with roughly equal proportions of C16, C18 and C20 under hot, air-starved combustion conditions, whereas the proportion of lighter PAHs increased in the fuel-addition phase, in which the combustion temperature was lower. These authors explained that either lighter PAHs are formed in the fuel addition or the partitioning of lighter PAHs into the particle phase increased at lower temperatures and increased the concentration of organic emissions. In Leskinen et al. (2014) the same type of changes in the profiles can be found; the proportion of the 5- and 6-ring PAHs in the $\Sigma 30$ PAH particle-bound emissions was the highest, over 30% in smouldering combustion (in efficient and intermediate combustion cases <10%). In smouldering combustion in Leskinen et al. (2014), the primary air of a combustion reactor was restricted and the wood chip feed rate increased to create a lack of oxygen. Heavier PAHs beginning from BcP are presented in Figure 23. Leskinen et al. 2014 used a biomass combustion reactor to produce continuous emissions similar to that formed in real-life residential wood combustion. The efficient combustion mimicked low-emission continuous combustion conditions. The intermediate combustion conditions simulated the poor mixing of air and gasified fuel present, for example, in the partial load mode of a continuous combustion appliance. The smouldering combustion conditions produced emissions corresponding to that produced from batch combustion.

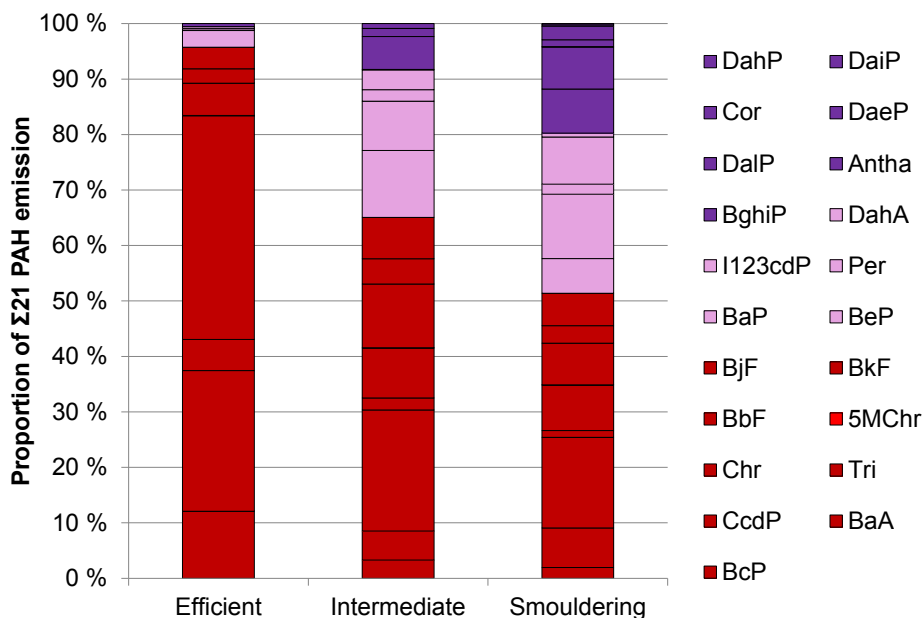


Figure 23. The proportions of heavier PAHs, beginning with BcP, in particle-bound $\Sigma 21$ PAHs in emissions from three combustion conditions created with a biomass combustion reactor. The PAHs are grouped based on the fused benzene rings in their structure, from 4 rings (red) to 6 rings (violet) (Leskinen et al. 2014). Values < limit of detection were neglected.

5.2.6 Relationship between PAH emissions and other emissions

Relationship between PAH and other emissions were investigated using the data of III. However, the inefficient batch combustion (IEBC) case was left out because of its clearly higher PAH emissions compared to other cases. In addition, in the improved batch combustion (IBC) case, no data on methane (CH_4) or benzene (C_6H_6) were available.

The results give an indication that PAHs are emitted in combustion conditions in which other organics (gaseous or particle phase) are also formed. The total PAH emission ($\Sigma 30$ PAHs) had a strong relationship with benzene, methane, organic gaseous carbon and particle-bound organic carbon emissions, whereas the connection with particle mass (PM_{10}) was weaker. EC explained the variation in $\Sigma 30$ PAHs rather poorly, which is

somewhat surprising considering that PAHs are EC precursors. Additionally, the relationship of the $\Sigma 30\text{PAHs}$ and CO was weak (Table 17). Instead, CO was strongly related to PM_{10} emissions in this data set. However, it should be noted that a substantial amount of CO is formed during the firing and combustion phase, as well as in glowing embers when PM, OGC and PAH emissions are typically low. Heavier PAHs appeared to associate with the gas-phase organics C_6H_6 and CH_4 than with OC. However, OC had strong relationship with lighter PAHs (Table 18).

The particle mass consists of an organic fraction, elemental carbon, and asheous species. Numerous processes are responsible for the formation and burn off of the variety of these constituents. In poor combustion conditions, the PAH content of the particles increases (e.g., II, Orasche et al. 2013, Leskinen et al. 2011). EC, on the other hand, forms at higher temperatures than PAHs form (Eriksson et al. 2014). The components are formed in somewhat different conditions, which may explain why PAHs and EC as well as PAHs and PM_{10} mass did not have strong connection.

Table 17. Coefficients of determination, R^2 (linear regression). Data from III excluding IEBC (five data pairs, except those marked with *, four data pairs).

	C_6H_6^*	CH_4^*	OGC	OC	MCE	PM_{10}	EC	CO	$\Sigma 30\text{PAHs}$
$\Sigma 30\text{PAHs}$	0.76	0.84	0.76	0.83	0.57	0.67	0.61	0.57	1
CO	0.08	0.19	0.6	0.33	1	0.78	0.13	1	
EC	0.94	0.99	0.42	0.69	0.13	0.51	1		
PM_{10}	0.38	0.56	0.63	0.6	0.78	1			
MCE	0.08	0.19	0.6	0.33	1				
OC	0.85	0.68	0.37	1					
OGC	0.34	0.68	1						
CH_4^*	0.87	1							
C_6H_6^*	1								

* IBC excluded, no FTIR data available

Table 18. Coefficients of determination, R^2 (linear regression). Data from III excluding IEBC (five data pairs, except those marked with *, four data pairs).

	C₆H₆*	CH₄*	OGC	OC
Nap	0.01	0	0.04	0.13
Acy	0.86	0.64	0.32	0.98
Ace	0.92	0.82	0.54	0.94
Fle	0.92	0.65	0.26	0.93
Phe	0.89	0.70	0.39	0.99
Ant	0.85	0.71	0.46	0.98
1MPhe	0.30	0.41	0.70	0.89
Fla	0.61	0.71	0.76	0.79
Pyr	0.56	0.74	0.85	0.70
BcP	0.85	0.78	0.34	0.53
BaA	0.71	0.85	0.83	0.75
CcdP	0.37	0.58	0.88	0.55
Tri	0.74	0.74	0.66	0.89
Chr	0.67	0.82	0.84	0.74
5MChr	0.43	0.53	0.72	0.70
BbF	0.78	0.89	0.80	0.79
BkF	0.26	0.40	0.73	0.54
BjF	0.94	0.99	0.68	0.76
BeP	0.77	0.90	0.82	0.77
BaP	0.82	0.97	0.82	0.73
Per	0.79	0.96	0.84	0.70
I123cdP	0.86	0.97	0.79	0.76
DahA	0.92	0.96	0.62	0.66
BghiP	0.75	0.94	0.87	0.69
AnthA	0.82	0.98	0.83	0.69
DalP	0.96	0.80	0.35	0.73
DaeP	1.00	0.90	0.52	0.84
Cor	0.43	0.53	0.72	0.70
DaiP	0.87	0.66	0.21	0.60
DahP	0.95	0.72	0.26	0.78

5.2.7 PAH content of particles

The results of this work and from the literature indicate that the PAH content of wood combustion-derived particles can vary remarkably (Table 19). In poor combustion conditions, the proportion of PAHs in the particle mass can be up to 10% and is typically <2% in conventional appliances and <0.5% in modern appliances. The data show that a higher PAH content is associated with appliances or combustion conditions in which a lack of oxygen, poor mixing or conditions otherwise favouring incomplete combustion are present. The increased PAH content of particles in poor combustion conditions is partly associated with increased condensation.

Table 19. PAH content of particle mass emissions from wood combustion (**III**: EFC efficient combustion, IBC/34 improved batch combustion during the 3rd and 4th batches, CBC1 conventional batch combustion 1 during a full cycle, CBC2/F conventional batch combustion 2 during the firing phase, CBC3/23 conventional batch combustion 3 during the 2nd and 3rd batches, IEBC/S inefficient batch combustion during the 1st and 2nd batches).

Σ PAH/PM mass [%]	PM [g/kg _{fuel}]	PM composition	Description	Particle fraction	Ref.
0.03	0.7	OC 19%, EC 41%	Modern masonry heater MMH	PM ₁₀ for PAHs, Particle mass PM ₁	I
6.0	2.7	OC 48%, EC 64%	Sauna stove SS		
0.6	0.8	OC 51%, EC 39%	Conventional masonry heater CMH-b1		
0.2	0.6	OC 70%, EC 25%	Conventional masonry heater CMH-t		
0.2	0.9	OC 28%, EC 68%	Cooking stove S		
0.7	2.1	OC ~20%, EC 32%	Conv. masonry heater, normal combustion	PAHs: no pre-cut, Particle mass PM ₁ , comp. PM _{2.5}	II , Frey et al. 2009
2.1	9.8	OC ~40%, EC 25%	Conv. masonry heater, smould. combustion		
0.0006	0.37	OC 5%, EC 1%	EFC	PM ₁	III
0.15	0.9	OC 7%, EC 49%	IBC/34		
1.9	1.5	OC 14%, EC 30%	CBC1		
1.8	1.3	OC 28%, EC 74%	CBC2/F		
2.8	1.0	OC 7%, EC 54%	CBC3/23		
8.3	4.8	OC 64%, EC 51%	IEBC/S		
3.1	1.9	OC ~30%, EC 35%	Log wood boiler, old	PM ₁	Jalava et al. 2012, Happonen et al. 2012, Kelz et al. 2012
0.3	0.3	OC <5%, EC 0%	Log wood boiler, new		
6.5	1.3	OC ~10%, EC 70%	Stove, old technology		
0.4	0.8	OC ~15%, EC 65%	Stove, new technology		
0.2	0.5	OC ~10%, EC 40%	Tiled stove		
0.02	0.3	OC <5%, EC 10%	Wood chip boiler		
0.1	0.1	OC 0%, EC 0%	Pellet boiler		
0.04	0.2	OC 2%, EC 1%	Biomass reactor, efficient combustion	PM ₁	Leskinen et al. 2014
0.2	1.1	OC 69%, EC 83%	Intermediate comb.		
3	3.0	OC 31%, EC 75%	Smouldering comb.		
~10	1.5		Log wood stove: Overloading	PM _{tot}	Orasche et al. 2013
~2	1.0-5.1		Log wood stove: spruce logs and briquettes, moist and dry logs, combustion in oxygen deficiency		
~0,5	1.0		Log wood stove: beech logs		

5.2.8 TEQ values of PAH emissions

For the combustion cases in **III**, the TEQ values, toxicity equivalents (22 PAHs included), are presented in Figure 24. The relative potency factors by Larsen and Larsen (1998) were used (see Table 2). The TEQ value for EFC is clearly the lowest, and the other combustion cases have TEQ values that are higher by factors of 430 to 382000 than that of EFC.

Based on the available TEQ values, the PAH emissions from batch-wise operated appliances exhibited clearly higher toxicity than from the modern pellet boiler. In addition, the PAH emissions from modern batch combustion appliances equipped with combustion air staging had a clearly lower toxicological potential than conventional technologies. However, due to the relatively similar PAH profiles in the emissions from different appliances, the TEQ values generally followed the same trend as the total PAH emissions. It should be noted that the TEQ values have their limitations; only the toxicity of PAHs is considered. Therefore, this toxicity assessment is insufficient for emission particles consisting of complicated mixtures of various chemicals.

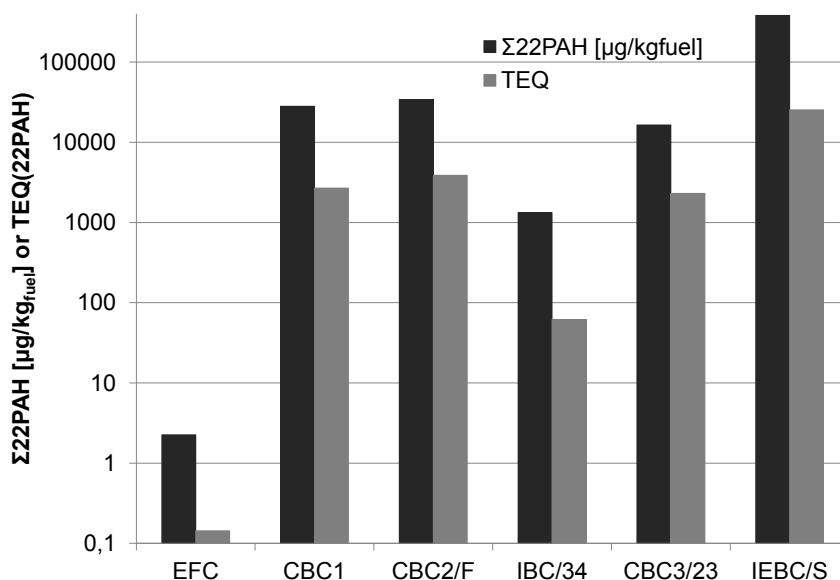


Figure 24. TEQ-values and Σ PAH emission factors for the combustion cases in **III** (22 PAHs). Note the logarithmic scale of the y-axis.

6 AUTHOR'S CONTRIBUTION

I: The author participated in the field measurements; carried out the sampling, the PAH analysis in the laboratory and the data analysis; and wrote the text concerning PAHs.

II: The author was responsible for the PAH sampling and the sample analysis, analyzed the data and wrote the paper.

III: The author participated in the planning of the measurements, managed the execution of the experiments at the test site and participated in the writing of the paper.

IV: The author wrote the part of the paper concerning the measurement method comparison and participated in the writing of the other parts.

7 CONCLUSIONS

Residential wood combustion as a PAH emission source in Finland.

Residential wood combustion is the greatest PAH emission source in Finland. In general, the PAH concentrations in ambient air are low in Finland compared to, e.g., Central or Eastern Europe (Fig. 5). In the countryside, wood is used more often as a primary heating source, but air quality problems may occur at the relative densely populated residential areas where wood combustion is a secondary source of heat in the households. In these areas, a target value of 1 ng/m³ for the annual average BaP concentration can be exceeded.

PAH emissions from residential wood combustion appliances. Particle and gaseous emissions from residential wood combustion vary to a great extent, depending on appliance type, operational practices and fuel properties. In this study, it was found that the emission factors of single PAHs varied by far more than other commonly measured emission components. The variation was even six orders of magnitude, from the 10⁻² range to the 10⁴ range in µg/kg_{fuel}. PAH emissions appeared to be much more sensitive to the combustion conditions compared to, e.g., particle mass emissions. The continuous combustion appliances such as the pellet boiler had considerably lower PAH emissions compared to the batch combustion appliances. The sauna stove had high PAH emissions. Concerning batch combustion devices for local space heating, more sophisticated and modern technologies involving the staging of combustion air had lower PAH emissions compared to conventional appliances equipped, in practice, with only a primary air supply. The results of this work show that with modern technologies, PAH emissions from residential wood combustion can be substantially reduced. Poor user operation was found to cause considerably higher PAH emissions, for example, Phe and Ant emissions were one hundred times greater compared to those from normal operational practices. PAH emissions appeared to be connected with organic gaseous carbon and particle-bound organic carbon emissions. Conversely, the connection with particle mass (PM₁), EC and CO were weak.

Gas-particle partitioning of PAHs in dilution. The sampling conditions greatly affected the partitioning of PAHs between the gas and particle

phases. In hot exhaust (~250 °C), PAHs were almost completely in the gas phase, whereas PAHs were found in the particle phase as well in the diluted exhaust at ambient temperature. Correspondingly, PM₁ mass emissions were higher when measured from the diluted exhaust than in the parallel total dust measurements from the hot, undiluted exhaust.

Evaluation of the particle sampling methods used for mass emission measurements. Wood combustion emissions consist largely of semivolatile organic species, which is why the measurement technique considerably affects the sampling conditions, partitioning of the sample analytes, and, consequently, the obtained particle mass results. Compared to hot exhaust sampling on heated filters, dilutive sampling creates more atmospherically relevant sampling conditions and yields results that better mirror the exposure and combustion quality. A precise definition of acceptable sampling conditions is needed.

8 FUTURE PROSPECTS

Based on the results of this study, several improvements for the particle mass measurement methods used for residential wood combustion emission can be proposed.

- The use of pre-cut (e.g., PM₁₀) would reduce the biasing impact of randomly existing coarse particles on particle mass. The health impacts of coarse particles are less important compared to respirable particles.
- The use of dilution gives more relevant information on aerosols. The sampling conditions should be described accurately (the range of dilution ratios or the target concentration in the dilute exhaust). The sampling temperature should be atmospheric.
- The range of methods proposed in regulations should be harmonized. In addition, the emissions should be measured from ignition to the end of the test for each appliance type to improve the representativeness and comparability. Limit values for emissions (mg/MJ) instead of concentrations (mg/m³) should be preferred.

In the author's opinion, the key knowledge gaps related to residential wood combustion emissions are as follows:

- The PAH emissions from appliances possessing sophisticated technical solutions, such as modern slow heat release appliances and sauna stoves, should be studied. Emissions data could encourage the consumers to choose lower-emitting appliances. Additionally, the effect of user operation, such as using wet fuel wood, on PAH emissions should be studied further.
- Systematic data on the repeatability, representativeness and applicability of hot exhaust sampling, dilutive sampling, and other proposed methods should be produced to find an appropriate and functional method for the particle emissions measurement.
- The volatility and behaviour of wood combustion aerosols in different dilution conditions should be determined. The emissions measured in certain conditions could be approximately

converted to the emissions in other reference conditions for comparison.

- Further work in coupling the emission characteristics with wood combustion health effects is needed. Based on this information, it could be possible to focus emission limits on the most essential particle properties from the perspective of health protection.
- The actual impact of restricting the emissions limits on air quality should be studied in order to improve the effectiveness of legislation.
- Atmospheric aging and SOA formation needs to be studied in order to understand the big picture of the impact of RWC on the ambient air particle load.

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ANNEX I: METHODS USED IN SELECTED STUDIES

Combustion appliance	Fuels	PAH sampling period	PAH sampling method
<i>Vicente et al., 2015</i>			
Pellet stove, 9,5 kW nominal output, top-feed.	Commercial wood pellets, pellets made of lignocellulosic residues, dust from furniture manufacturing, waste wood chips.	Steady-state operating conditions.	PM ₁₀ sampling from the diluted exhaust on teflon membrane filters.
Log wood stove, 9,6-18,2 kW output, manually fed, batch-operated, manual air control.	Log wood, maritime pine and eucalypt.	Two samples: 1) devolatilisation (10 min, started when new fuel batch was added and ended when the O ₂ started to drop) and 2) flaming+smouldering. (rest of the batch, new batch was added at 4% CO ₂ and a combustion chamber temperature of ~100 °C).	Dilution with full flow dilution tunnel (hood), DR for log wood stove ~25:1.
<i>Orasche et al., 2012</i>			
Pellet boiler, 25 kW nominal output, fuel supply with underfeed stoker, combustion plate, λ sensor.	Pellets.		
Multi-fuel boiler, 30 kW nominal output, fuel supply with underfeed stoker, step grate, λ sensor.	Spruce chips.	"Cold start", started from cold conditions (20 min), nominal load sampling (60 or 120 min).	Sampling of total dust from the diluted exhaust on quartz fibre filters. Dilution with full-flow dilution tunnel, DR 2:1-10:1.
Log wood boiler, 30 kW nominal output, down draught combustion principle, semiautomatic: refill by hand after approximately 6 hours, λ sensor.	Spruce logs, beech logs.		

Combustion appliance	Fuels	PAH sampling period	PAH sampling method
<i>Orasche et al., 2012</i>			
Pellet stove, 13 kW nominal output, top-feed, heat is provided for the service water of central heating. Pellets are dropped down to the combustion bin. A fan provides air through the grate. No λ sensor.	Spruce pellets.	"Cold start", started from cold conditions (20 min), nominal load sampling (60 or 120 min).	Sampling of total dust from the diluted exhaust on quartz fibre filters. Dilution with full-flow dilution tunnel, DR 2:1-10:1.
Log wood stove, 8 kW nominal load, manually fed, batch-operated.	Spruce logs, beech logs. Batches of 1,5 kg.	The sampling, both "cold-start" and nominal load, was performed over the whole batch (45 min).	
<i>Boman et al., 2011</i>			
Scandinavian pellet stove, 2-6 kW _{fuel} , continuous operation and fuel feeding also in low loads.	Softwood pellets.	Continuous combustion, loads 1,7 and 5 kW _{fuel} were applied.	Total PM sampling from the diluted exhaust on glass fibre filters, gaseous phase on PUF-plugs. Dilution with a full flow dilution tunnel setup (DR 1,5:1-4,3:1, T 45-75 °C).
<i>Pettersson et al., 2011</i>			
Wood stove, 9 kW nominal heat output, manually fed, batch-operated.	Log wood: birch, pine, spruce. Kindling batch of 3,5 kg, two main batches of 3 kg each.	Sampling during the second main batch. Various operation modes: normal, low-intensity combustion and high-intensity combustion (variation in draught, log size, massiveness of the wall structure, air inlet opening rate).	Total PM sampling from the diluted exhaust on glass fibre filters, gaseous phase on PUF-plugs. Dilution with a full flow dilution tunnel setup (DR 1,6:1-3,6:1, T 45-75 °C).
<i>Jalava et al., 2012</i>			
Pellet boiler, 21 kW nominal capacity, an automatic fuel feed. Overfed burner and a water-cooled combustion chamber. Combustion control is based on the furnace temperature. Staged combustion.		Duration of 10 h, included stable full and partial load operation and also a number of startup, load-change and shut-down procedures.	PM ₁ sampling from the diluted exhaust on PTFE filters with a DGI-sampler. Dilution with a porous tube diluter.

Combustion appliance	Fuels	PAH sampling period	PAH sampling method
<i>Jalava et al., 2012</i>			
Wood chip boiler, 30 kW nominal capacity, automatic fuel feed. Underfeed stoker, water-cooled combustion chamber. λ - and T(flue gas)-based control.		Duration of 10 h, included stable full and partial load operation and also a number of startup, load-change and shut-down procedures.	
Log wood boiler, 30 kW nominal capacity, manually fed. Down-draught combustion technology. Combustion control based on λ measurement. Modern technology.		Normal full day operation cycle including all burning phases.	
Log wood boiler, 15 kW nominal capacity, manually fed. An under-fire boiler. Combustion control based on a thermo-mechanical combustion air control. Considered old technology.		Normal full day operation cycle including all burning phases.	
Stove, 6 kW nominal heat output. Primary and secondary combustion zone. Combustion air supply: primary and window purge combustion air, primary air used only in the ignition. Manual air supply control. Modern technology.		Normal full day operation cycle including all burning phases.	PM ₁ sampling from the diluted exhaust on PTFE filters with a DGI-sampler. Dilution with a porous tube diluter.
Stove, 6.5 kW nominal heat output. Combustion air supply: primary air through the grate, window purge air, secondary air drawn in through nozzles located at the back of the combustion chamber. Manual air distribution adjustment by a damper. Old technology.		Normal full day operation cycle including all burning phases.	
Tiled stove, 4.2 kW nominal heat output. Combustion air entered through a vertical grate positioned in the stove door.		Normal full day operation cycle including all burning phases.	

ANNEX II: PAH, CO AND OGC EMISSION FACTORS FROM A CONVENTIONAL MASONRY HEATER, MODERN MASONRY HEATER, SAUNA STOVE, COOKING STOVE AND PELLET STOVE (I-III AND SELECTED STUDIES)

I: Paper I, II: Paper II, III: Paper III, V: Vicente et al. 2015, O: Orasche et al. 2012, B: Boman et al. 2011, P: Pettersson et al. 2011, J: Jalava et al. 2012

I: All values are averages of the whole combustion cycle, normal combustion. Conventional masonry heater: average of two values.
II: #1) Normal combustion, whole combustion cycle, #2) Poor combustion, the first half of the combustion cycle.
III: Conventional masonry heater: #1) whole combustion cycle, #2) firing phase, #3) combustion at relatively steady conditions. Modern masonry heater: the 3rd and 4th batches. Sauna stove: 1st and 2nd batches. Pellet boiler: steady-state combustion at a nominal load.
V: Pellet stove: average of four results when figures available; range is presented when bdl values present; nd is considered as 0. Wood stove: #1) devolatilization and #2) flaming and smouldering phase; average of two results when figures available; when bdl values present, range is presented; nd is considered as 0.
O: #1) Cold start; #2) nominal load. Log wood stove and log wood boiler figures: averages of two values.
B: #1) High load; #2) low load. P: Range of values, includes "normal", low-intensity and high-intensity combustion.
J: Wood stove and wood log boiler: #1) new technology results; #2) old technology results.

µg/kg _{dry fuel}		Conventional masonry heater						Modern masonry heater		Sauna stove		Cooking stove	Pellet stove			
		G		P			T	P	T	P	T	T	P		T	
Source		#1	#2	#1	#2	#3	#1						#1	#2	#1	#2
Nap	III			1,7	<0,125	<0,097		0,9		27,4						
	V												bdl - 1,0			
Acy	I						26450		250			45090	13900			
	II	23463	339702		1054											
	III			77,7	162	11,5		4,2		7297						
	V													nd		

µg/kg _{dry fuel}		Conventional masonry heater						Modern mason. heater		Sauna stove		Cooking stove	Pellet stove			
		G		P			T	P	T	P	T	T	P		T	
		#1	#2	#1	#2	#3	#1	P	T	P	T	T	#1	#2	#1	#2
Ace	I						260				1120	380				
	II	521	17068													
	III			2,5	4,4	1,3		<0,095		310						
	V												nd			
Fle	I						975				3210	800				
	II	4242	63127													
	III			137	418	33,4		4,7		14081						
	V												0,2			
															0,3	129
	B															
Phe	I						3670				26160					
	II	20489	154307	179	17677											
	III			3527	6731	1024		334		93185						
	V												15			
	O												51,1	10,6		
	B														59,7	1040
Ant	I						600				8730	170				
	II	6597	42836	55	5390											
	III			736	1198	219		24,3		22173						
	V												3,3			
	O												6,6	<0,418		
	B														6,4	171

µg/kg _{dry fuel}		Conventional masonry heater					Modern masonry heater			Sauna stove		Cooking stove	Pellet stove			
		G			P		T	P	T	P	T	T	P		T	
		#1	#2	#1	#2	#3	#1						#1	#2	#1	#2
1MPhe	III			225	154	79,0		14,9		3791						
	B														2,1	67,4
Fla	I						670				46700					
	II	10917	34028	1707	41070											
	III			4315	4337	2112		391		54162						
	V												bdl	- 15		
	O												81,7	49,8		
	B														27,0	424
Pyr	I						1205				51510	750				
	II	11165	31848	2449	46410											
	III			4174	4011	2489		352		57916						
	V												19,0			
	O												86,8	54,6		
	B														27,0	385
BcP	III			45,6	453	240		30,3		4211						
	O												4,1	3,4		
	B														1,2	16,6

µg/kg _{dry fuel}		Conventional masonry heater					Modern masonry heater			Sauna stove		Cooking stove	Pellet stove			
		G			P		T	P	T	P	T	T	P		T	
		#1	#2	#1	#2	#3	#1						#1	#2	#1	#2
BaA	I						330				10160	250				
	II	526	1272	1714	13875											
	III			1529	1751	1016		43,8		14451						
	V												6,3			
	O												12,3	7,1		
	B														4,0	50,1
CcdP	III			3273	2496	1887		<0,095		31618						
	O												16,8	<0,113		
	B														25,0	104
Tri	III			194	235	82,7		5,1		1760						
Chr	I						360				11960	na				
	II	712	1502	2012	14020											
	III			1381	1507	877		18,1		11986						
Chr+Tri	V												4,8			
Chr/Tri	O												15,3	13,3		
	B														6,4	67,4

µg/kg _{dry fuel}		Conventional masonry heater						Modern masonry heater			Sauna stove		Cooking stove	Pellet stove				
		G			P			T	P	T	P	T	T	P		T		
		#1	#2		#1	#2	#3	#1							#1	#2	#1	#2
5MChr	III				11,3	9,2	4,3		0,7		88,7							
BbF	I				1355	11139		155		50		5570	260					
	II	168	96		1192	1515	830		45,3		8405							
	III																	
B(b+k+j)F	V													4,1				
ΣBFs	O													20,4	8,0			
B(b+k)F	B															11,0	270	
BkF	I							205		40		4490	260					
	II	185	581		1745	10721												
	III				1706	1088	634		4,8		21622							
BjF	III				557	1105	605		18,3		4460							
BeP	III				799	1005	580		29,6		5934							
	V													3,5				
	O													5,0	1,8			
	B															4,6	75,1	

µg/kg _{dry fuel}		Conventional masonry heater						Modern masonry heater		Sauna stove		Cooking stove	Pellet stove			
		G		P			T	P	T	P	T	T	P		T	
#1	#2	#1	#2	#3	#1	P	T	P	T	T	#1	#2	#1	#2		
BaP	I					270				14880						
	II	225	783	1809	17413	2034										
	III			1749	2510	1572	30,9		15602							
	V										2,3					
	O										6,6	1,2				
	B													6,0	129	
Per	III			233	320	209		4,0		2110						
	V											nd				
	O											1,1	0,338			
	B													0,4	16,7	
I123cdP	I					590		20		9130	150					
	II	44	404	1409	17835											
	III			771	1158	679	10,9		6277							
	V										2,8					
	O										10,7	2,4				
	B													16,0	142	

µg/kg _{dry fuel}		Conventional masonry heater					Modern mason.heater		Sauna stove		Cooking stove	Pellet stove				
		G		P			T	P	T	P	T	P	T			
		#1	#2	#1	#2	#3	#1	P	T	P	T	T	#1	#2	#1	#2
DahA	I						50				1180	<20				
	II	na	55	na	1194											
	III			75,4	196	118		1,6		1011						
	V											nd				
	O											0,7	<0,225			
	B														1,2	2,5
BghiP	I						660		<30	9410	170					
	II	16	478	1102	10690											
	III			1019	1318	893		15,2		8043						
	V											bdl - 4,4				
	O											11,7	3,5			
	B														21	135
Antha	III			469	689	457		2,2		4841						
	O											1,5	1,1			
DalP	III			6,1	32,6	11,5		<0,095		62,6						
DaeP	III			96,4	239	90,2		<0,095		1004						
Cor	III			642	526	237		1,4		4669						
	V											nd				
	O											2,2	<0,225			
	B														11	270

µg/kg _{dry fuel}		Conventional masonry heater						Modern mason.heater		Sauna stove		Cooking stove	Pellet stove			
		G		P			T	P	T	P	T	T	P		T	
		#1	#2	#1	#2	#3	#1	P	T	P	T	T	#1	#2	#1	#2
DaiP	III			<0,152	66,5	20,4		<0,095		<0,481						
DahP	III			18,6	116	25,9		<0,095		94,7						
CO	I	39						28		120		35				
g/kg _{dry fuel}	II, T	42	148													
	III			50,3	21,7	17,3		7,2		82						
	V												5,77			
	O												7,1	6,6		
	B														2,50	10,6
OGC	I	3,3								13		2,3				
gC/kg _{dry fuel}	II, T	2,2	31,0													
	III			1,8	1,5	1,8		0,26		15,5						
	V												na			
	O												0,46	0,16		
	B														0,05	0,65

ANNEX III: PAH, CO AND OGC EMISSION FACTORS FROM A WOOD STOVE, PELLET BOILER, CHIP BOILER, LOG WOOD BOILER AND TILED STOVE (III AND SELECTED STUDIES)

III: Paper III, V; Vicente et al. 2015, O: Orasche et al. 2012, P: Pettersson et al. 2011, J: Jalava et al. 2012

III: Conventional masonry heater: #1) whole combustion cycle, #2) firing phase, #3) combustion at relatively steady conditions. Modern masonry heater: the 3rd and 4th batches. Sauna stove: 1st and 2nd batches. Pellet boiler: steady-state combustion at a nominal load.

V: Pellet stove: average of four results when figures available; range presented when bdl values present; nd is considered as 0. Wood stove: #1) devolatilisation and #2) flaming and smouldering phase; average of two results when figures available; when bdl values present, range presented; nd is considered as 0.

O: #1) Cold start; #2) nominal load. Log wood stove and log wood boiler figures: averages of two values.

J: Wood stove and wood log boiler: #1) new technology results; #2) old technology results.

µg/kg _{dry fuel}		Wood stove			Pellet boiler		Chip boiler		Log wood boiler		Tiled stove
		P		T	P		P		P		P
		#1	#2		#1	#2	#1	#2	#1	#2	
Nap	III				0,09						
	V	bdl	bdl				0,05		0,5 756		1,3
	J	0,4	74,5		0,000						
	III				<0,037						
	V	nd	nd								
Ace	J	4,1	3085		0,01		<0,026		19,0 3109		6,3
	III				<0,037						
	V	6,0	nd								
	J	<0,084	68,5		<0,011		<0,026		0,9 258		0,4

µg/kg _{dry fuel}		Wood stove			Pellet boiler		Chip boiler		Log wood boiler		Tiled stove
		P		T	P		P		P		P
		#1	#2		#1	#2	#1	#2	#1	#2	
Fle	III				<0,037						
	V	nd - bdl	nd								
	P			38 - 7030							
	J	5,0	4381		0,02		<0,026		39,9 3097		6,9
Phe	III				0,2						
	V	735	bdl - 65,1				5,1 1,8		103 1,3		
	O	1331	156,3		8,3 3,3						
	P			2280 - 9,7E+05							
Ant	J	355	16068		4,9		2,7		227 22558		162
	III				<0,037						
	V	128	7,2								
	O	264	35,6		<0,674 <0,317		<0,480 <0,275		23,3 0,29		
1MPhe	P			437 - 304000							
	J	48,6	3731		1,2		0,5		44 3546		23,9
	III				0,04						
1MPhe	P			144,4 - 142500							
	J	16,6	664		0,6		1,90		17,2 1101		12,4

$\mu\text{g/kg}_{\text{dry fuel}}$		Wood stove			Pellet boiler		Chip boiler		Log wood boiler		Tiled stove
		P		T	P		P		P		P
		#1	#2		#1	#2	#1	#2	#1	#2	
Fla	III				0,6						
	V	1099	91								
	O	1435	786		62,5	23,3	14,6	8,9	469	19,1	
	P			4560 - 836000							
	J	798	10857		32,0		13,7		181 8899		207
Pyr	III				0,8						
	V	2813	231								
	O	1364	792		69,4	25,0	17,4	10,7	473	22,6	
	P			3990 - 741000							
	J	751	9848		33,1		16,1		192 6383		178
BcP	III				0,02						
	O	54,2	50,7		4,2	3,3	2,9	3,4	21,4	2,8	
	P			68,4 - 11780							
	J	78,5	1258		3,31		1,7		15,8 960		17,4
BaA	III				0,03						
	V	1098	183								
	O	226	201		9,8	7,7	14,6	12,1	90,1	7,4	
	P			177 - 30400							
	J	189	4435		11,0		4,0		59,1 2843		44,4

$\mu\text{g/kg}_{\text{dry fuel}}$		Wood stove			Pellet boiler		Chip boiler		Log wood boiler		Tiled stove
		P		T	P		P		P		P
		#1	#2		#1	#2	#1	#2	#1	#2	
CcdP	III				0,09						
	O	139	91		4,7	1,0	7,6	0,3	102	0,6	
	P			47,5 - 62700							
	J	100	3532		5,8		3,9		68,1 2073		27,4
Tri	III				0,02						
	J	38,7	409		1,0		0,99		5,7 391,7		7,4
Chr	III				0,04						
	V	472	104								
	O	356	306		15,6	12,3	26,4	22,6	118,8	14,5	
	P			190 - 26600							
	J	191	2977		9,2		4,2		43 2081		40,0
5MChr	III				<0,037						
	J	0,4	8,3		0,01		<0,026		0,10 8,5		0,1
BbF	III				0,04						
	V	668	136								
	O	406	358		9,6	2,0	18,1	14,1	169	9,0	
	P			570 - 47500							
	J	158	3195		5,1		2,5		36 2034		31,4
BkF	III				<0,037						
	P			176,7 - 19000							
	J	<0,084	741		<0,011		<0,026		3,2 197		4,1

µg/kg _{dry fuel}		Wood stove			Pellet boiler		Chip boiler		Log wood boiler		Tiled stove
		P		T	P		P		P		P
		#1	#2		#1	#2	#1	#2	#1	#2	
BjF	III				0,02						
	J	124	2384		3,8		1,5		25,0 1199		21,7
BeP	III				0,07						
	V	430	89						64,4 1,6		
	O	102	88,6		2,5 0,5		8,3 2,6				
	P			209 - 18430							
	J	128	1969		4,1		1,8		23 995		21
BaP	III				0,03						
	V	589	78								
	O	179	150		4,2 0,5		13,2 2,4		62,3 1,7		
	P			304 - 45600							
	J	167	4905		6,0		1,3		55 2071		33
Per	III				<0,037						
	V	140	21								
	O	26,3	20,8		<0,264 <0,117		1,9 <0,113		12,9 0,2		
	P			45,6 - 6650							
	J	23	695		0,9		0,2		7,8 256		4,5

µg/kg _{dry fuel}		Wood stove			Pellet boiler		Chip boiler		Log wood boiler		Tiled stove
		P		T	P		P		P		P
		#1	#2		#1	#2	#1	#2	#1	#2	
I123cdP	III				<0,037						
	V	547	55								
	O	140	135		3,5 <0,217		16,0 1,4		76,0 1,3		
	P			247 - 28500							
	J	17,2	1532		1,4		0,4		14,7 634		13,2
DahA	III				<0,037						
	V	90,9	2,0								
	O	17,1	15,6		<0,371 <0,167		1,8 <0,145		6,6 0,3		
	P			26,6 - 5700							
	J	0,3	149		0,01		<0,026		1,0 58,7		0,3
BghiP	III				0,09						
	V	582	59								
	O	116	122		5,6 <0,117		12,5 1,0		67,7 1,0		
	P			162 - 18810							
	J	103	3812		6,3		0,8		26 1449		20,4
Antha	III				<0,037						
	O	53,2	45,0		1,4 <0,217		7,0 0,3		21,7 0,5		
	J	21,5	1119		0,7		<0,026		13,1 319		5,8
DalP	III				<0,037						
	O								7,2		
	J	1,2	30,1		0,03		<0,026		0,3 <0,194		<0,051

µg/kg _{dry fuel}		Wood stove			Pellet boiler		Chip boiler		Log wood boiler		Tiled stove
		P		T	P		P		P		P
		#1	#2		#1	#2	#1	#2	#1	#2	
DaeP	III				<0,037						
	O								6,3		
	J	<0,084	141		<0,011		<0,026		1,2 12,2		<0,051
Cor	III				<0,037						
	V	415	28								
	O	30,6	28,0		<0,362 <0,167		6,9 <0,145		24,5 <0,058		
	P			58,9 - 13300							
	J	20,8	278		2,2		<0,026		3,3 147		7,2
DaiP	III				<0,037						
	J	<0,084	<0,134		<0,011		<0,026		<0,032 <0,194		<0,051
DahP	III				<0,037						
	J	<0,084	<0,134		<0,011		<0,026		<0,032 <0,194		<0,051

µg/kg _{dry fuel}		Wood stove			Pellet boiler		Chip boiler		Log wood boiler		Tiled stove
		P		T	P		P		P		P
		#1	#2		#1	#2	#1	#2	#1	#2	
CO g/kg _{dry fuel}	III				1,52						
	V		53,95								
	O	37,99	24,6		1,09	0,28	7,16	1,21	10,51	0,3	
	P			20,9 - 136,8							
	J	18,9	42,5		0,9		3,4		14,3 232		18,2
OGC gC/kg _{dry fuel}	III				0,02						
	V	na	na								
	O	10,69	2,06		0,09	0,03	0,24	0,02	1,12	0,02	
	P			4,0 - 62,7							
	J	1,8	4,0		0,1		0,1		1,1 21,0		1,2