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DISSERTATION

Particulate matter and odor emission factors from small scale biomass combustion units

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unter der Leitung von

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“There's so much pollution in the air now that if it weren't for our lungs there'd be no place to put it all”.

Robert Orben

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Kurzfassung

Emissionen aus Biomasseverbrennung bestehen aus hunderten gasförmigen und partikulären Verbindungen. Die Emissionen hängen dabei stark von den existierenden Verbrennungstechnologien ab, die zu umweltfreundlichen Lösungen weiter entwickelt werden müssen.

Ebenso werden für die Immisionsinventuren verlässliche Datensätze benötigt um realistische Szenarien für Emissionsreduktionen zu entwickeln.

Aufgrund der Bedeutung von heimischen Holzarten im Hausbrandsektor befasst sich diese Studie mit einer umfangreichen Erfassung der Emissionen aus der Verbrennung von 12 mitteleuropäischen Holzarten, sowie von Holz-Briketts in einem modernen Kaminofen. Die Brennstoffauswahl wurde noch durch Pellets ergänzt, die in einem automatischen Pelletofen verbrannt wurden.

Für jede Brennstoffart wurden Partikel- und Gasemissionsfaktoren bestimmt. Von den mit einer speziellen Verdünnungsapparatur gesammelten $PM_{2.5}$ und PM_{10} Proben wurden umfangreiche „chemische Profile" ermittelt. Zusätzlich wurden Geruchsmessungen in Abgas vorgenommen. Der Geruch von Holzrauch wurde bis jetzt nur selten als Problem betrachtet, obwohl dieser auf die Anwesenheit von anderen, potentiell toxischen Schadstoffen im Holzrauch hindeutet.

Aus dem Verhältnis von Geruchseinheiten und PM_{10} der Emissionsmessung wurde abgeleitet, dass bei einem Auftreten von 30 µg m^{-3} PM_{10} von Holzrauch in der Außenluft mit einer Geruchswahrnehmung zu rechnen ist. Diese Bedingungen werden insbesondere in besiedelten alpinen Tallagen in der Heizperiode oft erreicht. Die gasförmigen Emissionen mit Ausnahme von NO_x lagen beim Pelletofen am niedrigsten. Geruch war beim Betrieb der Pelletsverbrennung Betrieb nicht nachweisbar. Die PM_{10} Emissionen waren gering, jedoch vergleichbar mit den niedrig emittierenden Holzarten aus den Kaminofen-Experimenten. Die Mehrzahl der Holzarten weisen aber etwa die 10-fache PM_{10} Emission im Vergleich zu den Pellets auf.

Die Emissionen der als Marker für die Holzrauchverbrennung angewendeten Verbindungen wiesen deutlich unterschiedliche Muster auf, im Vergleich zu Emissionen von „traditionellen Öfen". Trotz der hohen Variabilität des „diagnostischen Verhältnisses" von PM_{10} und Levoglucosan, konnte ein charakteristisches Verhältnis für den Kaminofen abgeleitet werden. Ebenso unterschied sich das Levoglucosan/Mannosan Verhältnis für Hartholz von jenem der „traditionellen Öfen", während das Verhältnis für Weichholz robust, vergleichbar für sehr unterschiedliche Ofentypen war.

Die im Experiment verwendeten modernen Öfen, emittierten mehr polycyklische aromatische Kohlenwasserstoffe (PAKs) als es erwartet. Mit Hilfe eines multilinearen Regressionsmodells konnte gezeigt werden, dass die BaP Emissionen durch die Input-Variablen „Abbrandgeschwindigkeit" und „EC Emissionen" abgeleitet werden können. Rasche Abbrände mit hohen Verbrennungstemperaturen bewirken relativ höhere EC-Emissionen, gekoppelt mit einer höheren PAK Bildung. Dieses Ergebnis ist erheblicher Bedeutung, da Holzrauch einen großen Anteil and der Emission von PAKs in vielen europäischen Ländern hat. Um am Sektor der Emissionen der Biomasseverbrennung insbesondere den Feinstaub zu verringern werden Ofentauschprogramme durchgeführt. Diese Studie zeigt nun, dass die Emissionsreduktion bei Umstieg von „alter“ auf „neue“ Technologien für PAH und Ruß in deutlich geringerem Ausmaß ausfällt, als bei Feinstaub.

Die bedeutet, dass der EU - Grenzwert für BaP von 1 ng m^{-3} als Jahresmittelwert in der Außenluft in jenen Regionen, in welchen bereits hohe Werte auftreten, nicht einfach durch Ofentauschprogramme reduziert werden kann, bzw. in Regionen, in welchen ein Umstieg von fossilen Brennstoffen (Gas, Heizöl-EL) auf Biomasse-Feuerungen mit Zunahmen der BaP Belastung gerechnet werden muss.

Schlüsselwörter

Biomasseverbrennung, Feinstaub, Holzrauchgeruch, Levoglucosan, Benzo(a)pyren, Mitteleuropäischen Holzarten

Abstract

Wood burning is a significant source of particulate matter (PM) in Europe, especially in the cold season.

Comprehensive knowledge of wood burning emissions may help to evaluate the existing technologies and to develop environmentally friendlier solutions, applicable for local societies. On the other hand it is important from emission inventories' point of view to work with updated emission profiles in order to obtain reliable scenarios and plan adequate strategies for reducing the pollution levels.

Therefore this work offers an exhaustive study on emissions from burning of 12 Central European wood types, wood pellets, briquettes and garden waste in two popular, modern stoves. Additionally a measurement of odor emissions was conducted to assess the possible impact of wood smoke odor nuisance in Mid European countries.

Concerning the findings of this study it was derived that already for an ambient wood smoke concentration of 30 µg m^{-3}, the odor could be recognized. It was also predicted that the short-term odor nuisance may be significant, especially in mountain valleys, where wood smoke could be trapped by the temperature inversion for longer time and short term local concentrations might occur several times higher than the average.

Lowest gas emissions were observed for the automatically fired pellet heater. Also no odor was detected in exhaust samples from pellets burning. PM levels for the pellet stove were similar to those obtained for lowest emitting wood types. The "high emitters" among wood logs reached levels an order of magnitude higher than pellets. The substances recognized as unique wood burning tracers and applied for source apportionment studies were found in significant concentrations. The levoglucosan/mannosan ratios were stable and higher for hardwood fuels than observed from a tiled stove. The levoglucosan/PM ratio showed a much larger variation. It was observed, that the emission of tracer compounds from wood types considered here, are influenced by batch-to-batch variations (e.g. wood types from a wood species exhibiting widely different combustion properties within a test series and between studies under comparison.

The modern stoves used in the experiment, emitted considerable amounts of toxic Polycyclic Aromatic Hydrocarbons (PAHs).The BaP/PM ratios were variable and were shown to depend strongly on the burn rate. Applying a multiple linear regression model it was possible to explain the BaP/PM_{10} emission ratio with high quality of fit including the burn rate and elemental carbon (EC) as input parameters.

Wood burning emissions are an extremely prominent source of BaP in the ambient air and the use of small stoves increases significantly the threat of exceeding the threshold limit of BaP (in the European Union 1 ng m^{-3} annual average). The study shows that flue gas from modern small scale heating systems could contain elevated BaP concentrations (with emissions higher by a factor of 10 for high burn rate combustion). Thus, a stove change program might reduce the PM emission but will not be not be likewise effective reducing the PAH emissions.

Key words

Biomass, Central Europen wood types combustion, particulate matter, odor, levoglucosan, benzo(a)pyren

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List of Abbreviations

General Abbr.

FWF/O   Abbreviation for this study

TUV   Vienna University of Technology

ABC-W   Austrian Bioenergy Center, Branch Wieselburg, Austria

“3 studies”   data from 3 studies performed fully or in part at TU Vienna, for pellet stove and chimney stoves using the test stand at the Institute of Chemical Engineering. The “3 studies are: FWF/O, this study; BIOCOMB (Luisser et al., 2008); AQUELLIS FB (Schmidl et al., 2008a).

Emissions related Abbr.

PM_{10} Particulate Matter with aerodynamic diameter

$PM_{2.5}$ Particulate Matter with aerodynamic diameter

PM_{tot} Total Particulate Mater

C_xH_y Volatile hydrocarbons

NO_x Nitrogen oxides

EC   Elemental Carbon

OC   Organic Carbon

CC   Carbonate-bounded Carbon

TC   Total Carbon

PAHs   Polycyclic Aromatic Hydrocarbons

BaP   Benzo(a)pyrene

BaPE   Benzo(a)pyrene Equivalent

HULIS   Humic Like Substances

Analytic related Abbr.

GC-MS Gas Chromatography – Mass Spectrometry

HPLC   High Performance Liquid Chromatography

IC   Ion Chromatography

ICP-OES   Inductively Coupled Plasma – Optical Emission Spectroscopy

GF-AAS   Graphite Furnace Atomic Absorption Spectroscopy

XRF   X-Ray Fluorescence Spectroscopy

NDIR   Not-Dispersive Infra-Red

OU Odor Unit (also European Odor Unit)

SD   Standard Deviation

RSD   Relative Standard Deviation
SEM   Standard Error of Mean

Fuels related Abbr.

Hardwood   here: all broadleaf species
Softwood   here: all conifer species incl. larch
WP   Wood pellets
WP (FL)   Wood pellets – full load operation
WP (PL)   Wood pellets-part load operation
BR (SW)   Wood briquettes made of softwood
BR (HW)   Wood briquettes made of hardwood
EH   European hornbeam
EB   European beech
BPop   Black poplar
TO   Turkey oak
SO   Sessile oak
PO   Pedunculate oak (also known as common oak)
BL   Black locust
SF   Silver fir
EL   European larch
NS   Norway spruce
BP   European black pine
SP   Scots pine
N   Pine needles
C   Pine cones
L   Old leaves
GW   Garden waste, including old leaves and needles

Stove related Abbr.

RF1   6kW manually fired chimney stove
RF2   8kW manually fired chimney stove
RM   6kW automated pellet stove
REP   10kW manually fired chimney stove with controlled air supply
WJ   6.5 kW simple manually fired chimney stove
GU   50 kW automated pellet and chip boiler
SI   35kW old technology logwood boiler

Land Codes:

A Austria

CZ Czech Republic

HU Hungary

N-IT Northern Italy (South Tyrol)

PT Portugal

SI Slovenia

SK Slovak Republic

S-DE Southern Germany (Bavaria and Baden Würtemmberg)

CH Switzerland

1. General Introduction

1.1. Background

An increasing interest of biomass utilization for energy production worldwide is observed. Large potential of biomass, both native and wastes are still available and are an attractive alternative to shrinking fossil fuel resources. Biomass stocks are renewable and their utilization is seen as climate friendly due to CO_2 neutral nature of biomass.

Austria is placed, with 30.8% renewable fuel use (data reported for year 2010 by Federal Ministry of Agriculture, Forestry Environment and Water Management, 2012) at the fourth position in Europe (behind Sweden, Latvia and Finland). Next to waterpower and hydropower, biomass s is the third prominent energy carrier in land and its use increases constantly.

The most often applied biomass utilization method is combustion. This, like any other combustion of carbonaceous material, may lead to emissions of gases and particles into the atmosphere. Moreover, the combustion of biomass, especially in a small scale (residential) was found to cause much higher particulate matter (PM) emissions than popularly used light fossil fuels (light oil and natural gas; Austrian Energy Report, 2003). The expected PM emissions may rise strongly, due to inappropriate combustion technology and maloperation (Houck and Tiegs, 1998).

Inefficient biomass combustion results in emissions of very small particles (with aerodynamic diameters of 2.5 microns or lower [$PM_{2.5}$]), composed mainly of carbonaceous compounds. Such small particles are known to cause a range of undesired effects on climate (e.g., black carbon scattering effects) and human health (Innes, et al., 2000; Naeher et al., 2007).

Moreover particles generated during combustion of bio-materials contain a large mixture of partially not identified chemicals with considerable share of toxic compounds (e.g., polycyclic aromatic hydrocarbons [PAHs] and phenols; Kocbach Bølling et al., 2009). Various epidemiological studies have proved that wood burning particles, due to their micron-near-size and chemical properties may result in pulmonary and cardiovascular diseases or have a carcinogenic impact (Boman et al., 2003).

Regardless of all threats related to biomass burning, it is still widely propagated method of heating in numerous European countries (Bari et al., 2011; Goncalves, et al., 2012; Meyer, 2012). Also in Austria, the wood-biomass heating systems are highly spread. Over 16 % of principal residences uses wood based heating as a main energy source, while for secondary residences the number rises to over 20% (Statistik Austria, 2007).

This statistical data, however, covers only data for main heating methods, but does not concern a common practice of installing a secondary heater (mostly representing a small scale technology), which supports the energy supply in the fall and spring periods, but are also appreciated for aesthetic value.

Due to lack of statistical numbers experts have estimated the number of small stoves, which are currently in use in Austria to around one million, including traditional and modern heating devices (Biermayr et al., 2010). 20% of Austrian households use a biomass-based heating device, with a prevailing wood as a fuel (Statistik Austria, 2007).

Taking this into consideration, it could be predicted that biomass may have a significant influence on particulate matter emissions in Austria and other European countries of similar geo-economic situation. Moreover, it is highly probable that small scale combustion systems may contribute in the same or even higher degree to the overall particulate matter emissions, than biomass boilers. According to statistical data, about 50% of all single stoves in Austria are fired with logwood. Among all “only-wood-heated” households included in the statistical report (principal residences, Statistik Austria, 2007), 53% are equipped with wood boilers and 39% with a single wood stove. It may be assumed that for leisure residences, cottages and mountain huts this ratio differs to single stoves advantage. Therefore, concerning that small scale furnaces cause typically about 40% more PM emissions than boilers (e.g., Spitzer et al., 1998; Schmidl et al., 2011) a high contribution of small stoves to overall pollution is to be expected.

Data obtained in this study comprise the PM emission factors obtained for a small modern chimney stove for different wood-biomass types used in the Central Europe. The presented PM data contains a characterization of over 60 compounds or compound classes. The reported emission factors are supplemented by gas emission rates and completely new information considering wood odor thresholds. A detailed definition of goals achieved in the frames of this study is presented in **Chapter 2**.

1.2. Motivation

As previously mentioned, biomass is an important fuel on the global scale. Nevertheless, the particulate emissions remains still a major problem. Launching of this study was inspired on the following:

- Wood smoke is known to be a significant contributor to winter ambient particulate matter in Austria and other European countries (Puxbaum et al. 2007; Szidat et al., 2007; Caseiro et al., 2009; Bari et al., 2010; Piazzalunga et al., 2011), but scientific examination of emissions from wood fuels burnt locally in small scale appliances is still limited. Most of the studies were done in last few years and concern only selected regions (e.g., Hedberg et al., 2002 – Scandinavia; Schmidl et al., 2008a,b - Austria; Bari et al., 2009- Germany; Goncalves et al., 2010 - Portugal).
- The existing emission studies concentrate mostly on operational factors and concentrate less on different wood species examination.
- Only a few authors report a rich chemical characterization of particulate matter from small scale biomass combustion systems for mid-European wood species (Hedberg et al., 2002; Schmidl et al., 2008a,b).
- The emission factors for particulate matter and polycyclic aromatic hydrocarbons emissions proposed in the emission inventories require a continuous actualization regarding new combustion technologies.

- To the best of my knowledge, by the beginning of this project no experiments examining odor nuisance from small scale biomass combustion were reported, although this phenomenon is noticeable (Bari et al.,2010), especially in small "wood burning communities" (abundant in Alpine region) and may be a reason of lower life-comfort in wood smoke affected areas. Until the launch of this study only a general examination of relation of odor to PM and carbon monoxide (CO) for burning in a 40 kW boiler (Ebbinghaus, 1993) was published.
- Finally, a personal motivation is connected with adverse health effects of combustion-related particulate matter. With the quantification of emissions and qualitative chemical analysis of collected particulate matter I would like indirectly contribute to assessment of the health risks related with present technologies.

1.3. Combustion systems

Biomass burning is the oldest technique applied by mankind to excite heat. The routine domestic use of fire began around 50 000 to 100 000 years ago (Bowman et al., 2009), however the control over the fire is reported already before appearance of *Homo sapiens* (Karkanas et al., 2007). Ever since, humans were searching for efficient combustion methods, resulting in maximal energetic efficiency. This trend has evolved together with civilization and reached the current, technologically advanced level. Nevertheless, even if high technologies are available, the actual status of combustion systems differs considerably in the regional scale. Above all, the economic factor is crucial for determining the technological advancement. Furthermore, it is also affected by the lifestyle and tradition, as well as by the level of education in the society. Last, but not least, the natural resources limiting the fuel availability, are important. As a result, the combustion devices used around the world vary strongly.

The simplest systems (e.g., open fire, "bucket stoves", or primitive clay stoves) are described for the third world countries in Africa (Ezzati et al., 2000), Asia (Bhattacharya et al., 2002) and South America (McCracken and Smith, 1998). This type of burning is extremely inefficient and cause vast emissions (adequately to amount of gained energy), which contribute significantly to overall regional emission (Brocard et al., 1998, Smith, 2006). This is a considerable environmental problem, as biomass is the cheapest available energy source in these regions, and due to that fact is used in much wider scale than, for example in Europe (mostly for cooking).

The developed regions e.g., USA, Australia, West and Central Europe, dispose of entirely different combustion technology (examples listed by Houck and Tiegs, 1998; Musil-Schläffer et al., 2010). The technology development, due to sufficient funds can set priorities (e.g., to cope with a problem of sustainability of resources, reduction of air pollution, reduction of negative health effects) differing from those achievable in developing countries.

In Austria, the combustion of biomass is performed in a wide variety of fireplaces, stoves and boiler types (Wörgetter and Moser, 2005), which are characterized by different engineering features and therefore ensure more or less efficient combustion. The combustion efficiency is more exactly defined by the term of energy conversion efficiency, simplified to the ratio between the energetic input and output of energy conversion process. In case of combustion the efficiency could be, moreover, described through the emissions of non-burnt carbon resulting from burning process. The combustion efficiency may be therefore expressed as ratio of carbon dioxide (CO_2 – fully burned carbon) to the sum of all carbon species resulting from combustion (CO_2, CO, hydrocarbons [C_xH_y], and particulate-bounded C). Nevertheless, researchers use more often a modified version of the efficiency factor (MCE – modified combustion efficiency), which neglects the C_xH_y and particulate-C in the overall scale, as most of unburnt carbon occurs in form of CO, and is therefore expressed as molar ratio: $CO_2/(CO_2+CO)$ (e.g., Gupta et al., 2001; McRae et al., 2006; Shen et al., 2011). MCE gives a description if the burning was dominated by flaming or smoldering (Ward and Hardy, 1991). Throughout the combustion efficiency information on gaseous and particulate emissions and odor levels are expressed. The more efficient is the burning process, the higher amount of carbon is totally burnt (emitted as CO_2) and lower are the emissions other pollutants.

There are several systems of classification of furnaces used nowadays for residential heating in developed countries. Among classification parameters the size of furnace, type of fuel, purpose of burning (heating or cooking), geo-meteorological and economic conditions of the region, burning habits and tradition can be listed. According to this division some furnaces may be ascribed to certain regions. For example, simple small cast iron cookestoves are used in Asia, but could rather not be found in European households. Open fireplaces are popular in the United States and Commonwealth Countries, masonry- and sauna stoves are typical for Scandinavia and tiled stoves are gladly used in Alpine lands (e.g., according to data reported by Schmidl et al. [2008b] 450 000 tiled stoves exist in Austrian households and each year 10 000 are installed) .

According to size criterion, EEA/EMEP (EEA, 2012; and previous versions) have divided the combustion appliances into residential (up to 50 kW power output) and non-residential with much higher energy output (up to few MW). In fact only the residential sources are in the interest of particulate matter studies, as the observed tendency show that the bigger and more automated is the combustion plant, the lower emission rates are expected (Nussbaumer, 2003). The heating devices used in households are boilers (with ~30-50kW energy output) and small stoves. The first class is more often automated and could be fired with logwood, briquettes, wood chips or different types of pellets (wood or crop), causing low to intermediate emissions. Small stoves, although they represent a wide variety of technological solutions, are in most cases operated manually and fired with logwood and sawdust briquettes, being reported to contribute significantly to emissions (e.g., Schmidl et al., 2011).

Currently, small (2-10kW) chimney, log wood stoves (typically cast-iron, sometimes equipped with a natural stone or ceramic shell) are coming into prominence at the markets of Europe (Biermayr et al., 2010). The same source indicates also a rise of sales-figures for small scale furnaces for pellets, which are more frequently automated (automation of firing and air supply), and could be equipped with many useful functions as for example operation through a mobile phone. These two types were therefore chosen for the investigation conducted in this study.

1.4. PM Emissions from biomass burning

The discussion concerning technological advancement of biomass burning furnaces should include above all, the description of their PM emission factors. The further important aspect is the composition of emitted particulate matter. On this basis the stoves and technologies may be classified upon efficiecy and economy.

A large number of studies concerning PM emission factors for different small scale wood burning devices were launched. The majority of studies have been done in Scandinavia and USA. In the last years a trend to characterize emissions from locally used combustion appliances appeared also in Europe, resulting in first comprehensive emission profiles for stoves in Austria (Schmidl et al., 2008b), Germany (Bari et al., 2009) and Portugal (Alves et al., 2011, Goncalves et al., 2011).

Comparison of emission factors of those and other experiments is shown below.

Formation of particulate emissions is supported by numerous factors, classified into three main groups:

- appliance reliant factors (i.e. stove size, air supply regulation, burning chamber interior);
- fuel reliant factors (i.e. fuel type, ash content, moisture) and
- operational factors (i.e. kindling method, amount of fuel used).

These criteria work nearly always together and should be regarded, by comparison of reported emissions. Figure 1 comprises an example of emission factors obtained during six different studies for seven different small scale wood (pellet) combustion technologies.

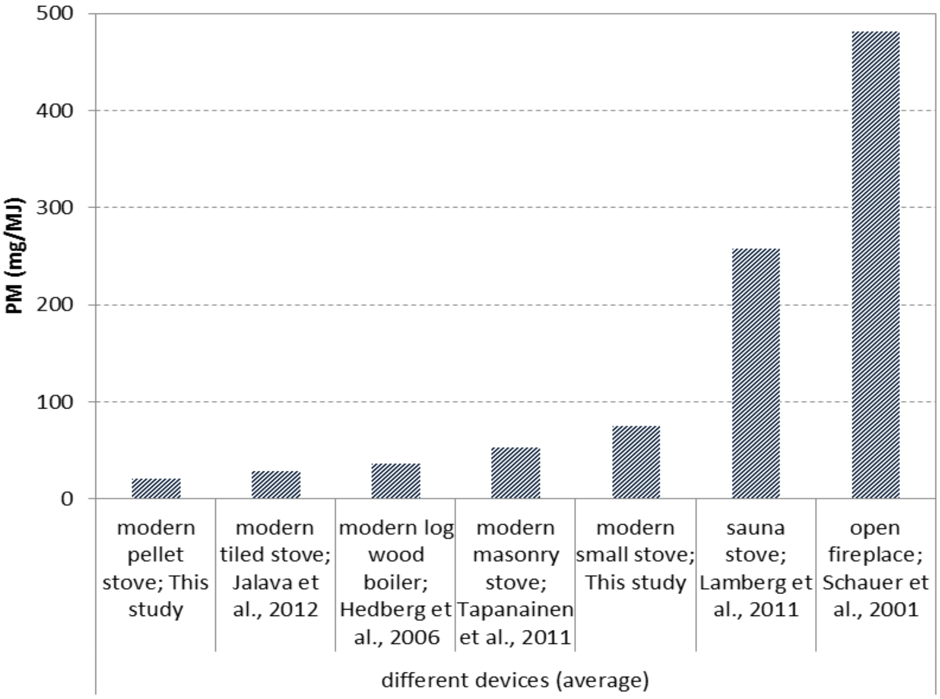


Figure 1. Particulate emissions from different types of small scale combustion appliances.

Open fireplaces and sauna stoves lead to highest emission factors, and are generally characterized by inefficient combustion. In case of fireplaces a large loss of heat due to the open burning chamber is observed. This results in lower temperatures in the burning chamber, leading to smoldering combustion. Sauna stoves, contrary to fireplaces are used for very fast warm up of the rooms (saunas) and represent a very hot and quick combustion. This results in very high oxygen demand, which could not, in most cases, be alleviated due to simple construction of stoves. Moreover in many cases water is poured upon very hot stoves, what lead to quick cool down and possible smoldering at the end of burning.

As mentioned, the factors influencing particulate matter formation during combustion need to be considered together. Figure 2 depicts how much the emissions from burning the same wood type in a very similar stove (under standardized conditions, obtained at the same test stand) can differ. Else than supposed, particle emission factors from the same wood types, burnt in modern devices of the same type (with only difference concerning power output) not always were comparable and varied (strongly in case of oak [PO] and less intensive in case of spruce [NS]).

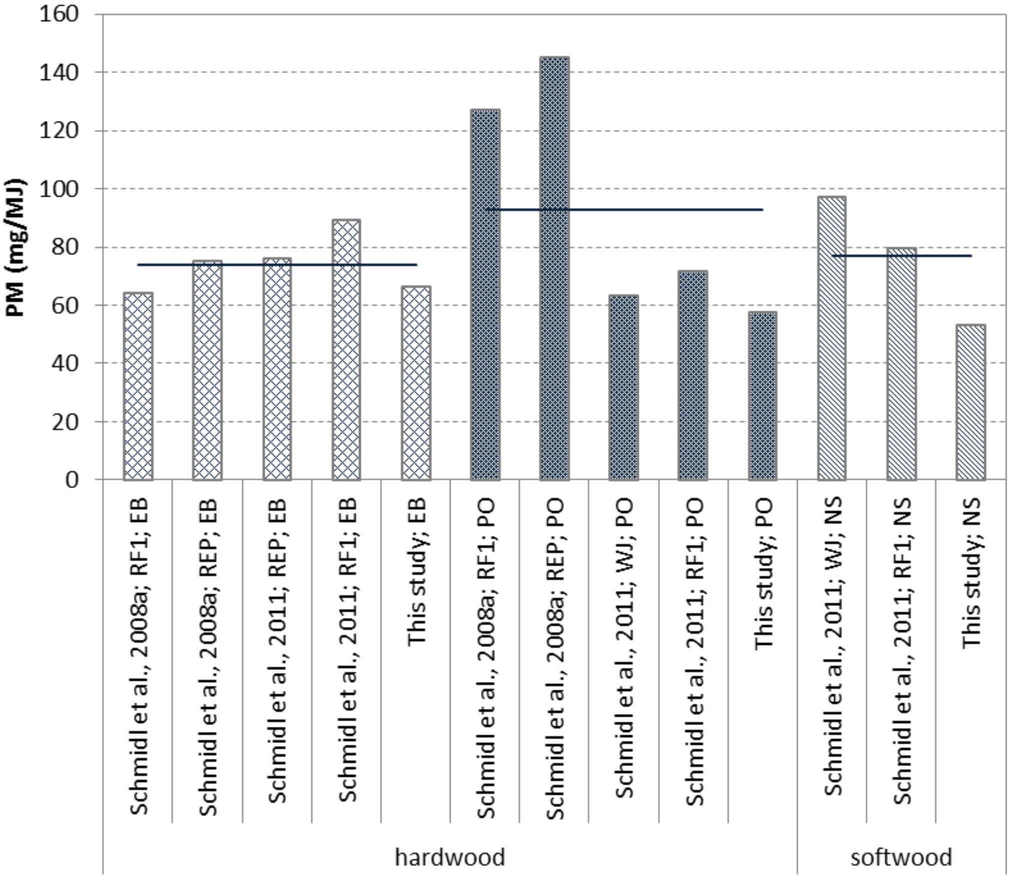


Figure 2. Particulate emissions from typical Austrian wood fuel burnt in modern small scale appliances (6kW-10kW). EB-European beech; PO-pedunculate (common) oak; NS-Norway spruce.

Already a tiny operational difference or a difference resulting from fuel characteristic (morphology and physical parameters) could result in significantly variable emissions. Several studies have reported the influence of parameters as fuel volume, fuel moisture, air supply (e.g., Burnet et al., 1990; Hays et al., 2003; Jordan and Seen, 2005; Pettersson et al., 2011; Shen et al., 2011; Schmidl et al., 2011) on the emissions. Significant differences have been recognized, however none of the parameters was declared as most influential (Figure 3).

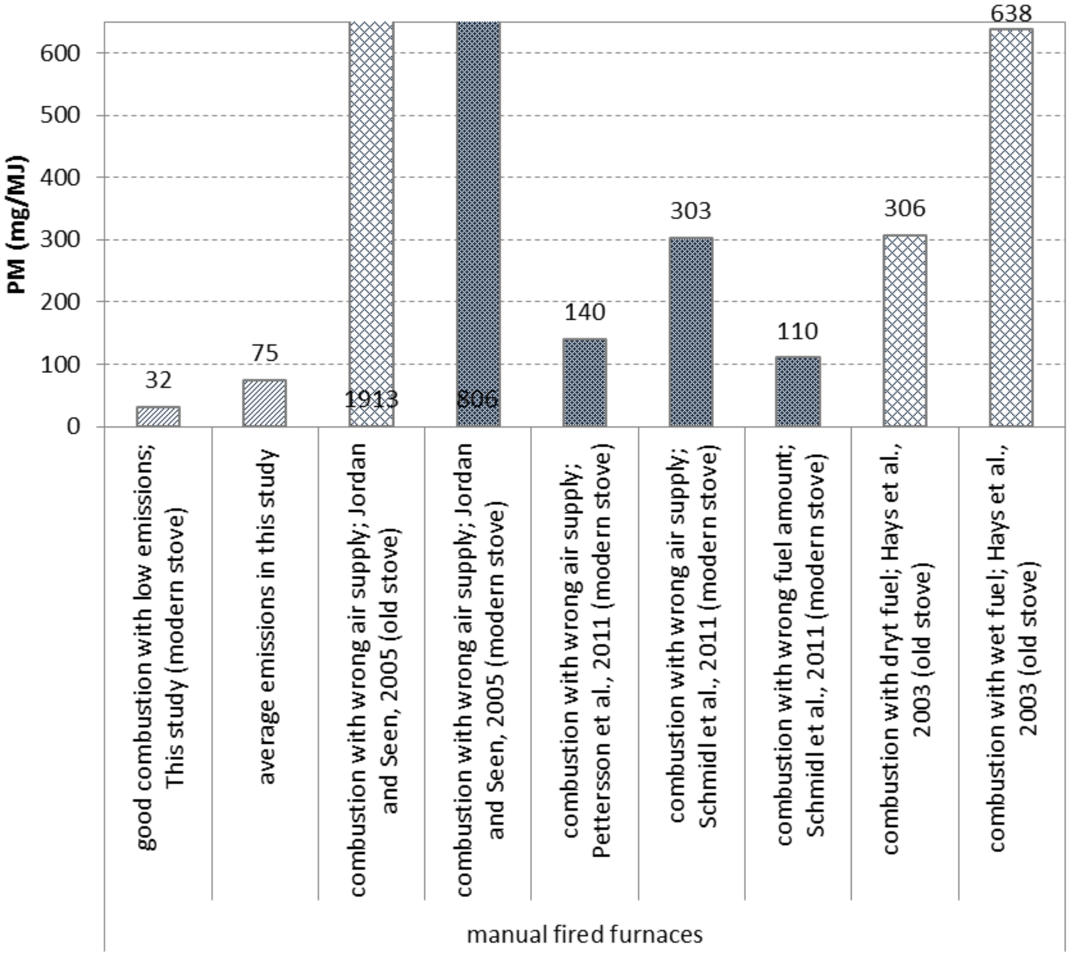


Figure 3. Particulate matter emissions from small stoves according to operational conditions. The value reported by Pettersson et al. (2011) is an average of three combustion modes, run with varying air supply and fuels of different moisture.

Also automatically fired pellet stoves are not free from variation. Their emissions are significantly lower than from log wood stoves, and burning conditions, due to high level of automation, remain more stable, however may also differ, e.g., between full- and part-load operations (Boman et al., 2011; Schmidl et al., 2011; this study). Surprisingly comparing the findings of this study and other values reported for modern pellet heaters no trend is noticeable. Boman et al. (2011) has found emissions for part-load burning significantly higher than for full-load operation, Schmidl et al. (2011) has reported inverse situation, while in the study of Obernberger et al. (2007) and in this project the difference is barely remarkable.

A comparison of recent finding enables supposing, that one of the most prominent factors influencing formation of particulate matter during combustion is the air supply. Study of Jordan and Seen (2005) and Schmidl et al. (2011) resulted in very high emission factors for all runs with inadequate air supply regulation, while results of this study (primary and secondary air supply regulated according to operational manuals of stove manufacturer) stay relatively stable. Another significant parameter is the age of the furnace. Old technologies result generally in higher emissions (Bergauff, 2010) and are reported to be much more sensitive to condition changes (Jordan and Seen et al., 2005). A modern technology is able to reduce particular emissions of a factor 4-5 in comparison with old devices (Table 1). This is combined with efficiency rise of about 50%, what means that burning of the same amount of wood in an advanced stove doubled the amount of gained thermal energy (Aasestad, 2006). Inadequate supply of fuel and bad fuel quality (too high moisture or high content of bark) might also significantly influence the particulate emissions as depicted in Figure 3.

Table1. Particulate matter emission factors from advanced- and old-technology furnaces.

Reference	Furnace	Technology	PM ($mg\ MJ^{-1}$)
Fine et al., 2004a	wood stove	with catalytic function	106
Fine et al., 2004a	wood stove	non-catalytic function	110
Jordan and Seen, 2005	wood stove	modern	1072
Hedberg et al., 2006	log wood boilers	modern	36
Schmidl et al., 2008a	chimney stoves	modern, certified in Austria	77
Bari et al., 2009	residential stove	modern	40
Bergauff, 2010	wood stove	modern; US-EPA certified	50
Gonçalves et al., 2010	chimney stove	modern, certified in Austria	114
Bari et al., 2011	log wood boiler	modern	24
Pettersson et al., 2011	wood stove	Modern, natural draft	140
Schmidl et al., 2011	chimney stoves	modern, certified in Austria	88
This study, 2012	chimney stove	modern, certified in Austria	75
Average			**161**
McDonald et al., 2000	wood stove	old	272
Hedberg et al., 2002	soap stone stove	old	81
Gullet et al., 2003	wood stove	old	599
Hays et al., 2003	chimney stove	old	406
Jordan and Seen, 2005	wood stove	old	1619
Hedberg et al., 2006	log wood boiler	old	797
Bergauff, 2010	wood stove	old; US-EPA not certified	55
Gonçalves et al., 2012	wood stove	old	516
Average			**543**

*…Single results from studies averaged, [1]… for values given in $mg\ m^{-3}$, emission factors "$mg\ MJ^{-1}$" calculated using a factor of 0.6 (averaged from Schmidl et al., 2011), [2]… for values reported as $g\ kg^{-1}$ wood, emission factors "$mg\ MJ^{-1}$" calculated regarding a heating value of 16 $MJ\ kg^{-1}$.

Kocbach Bølling et al. (2009) and Nussbaumer (2010) distinguish the constituents of biomass combustion particulate matter into:

- soot particles (reported as EC in this study);
- inorganic ash particles (in this study presented as the sum of ions and non-soluble species);
- condensable organic compounds.

Both studies indicate that formation of compounds representing each group is favored by varying combustion parameters. Considerable differences are to be noticed between pellets and log wood appliances. Efficient combustion (characterized by high temperatures and sufficient oxygen supply) results in formation of higher amounts of fly ash (inorganic particles) and elemental carbon. Particles from manually operated small appliances are generally dominated by organic matter (Kocbach Bølling et al., 2009 and references cited therein), with higher values reported for older appliances (e.g., Fine et al., 2004a,b) and slightly lower observed for new technologies (e.g., this study).

The emission ratios (particulate matter related emission factors, here reported as µg mg^{-1} PM) of different organic compounds might distinct between the combustion technologies.

A comparison of two competitive organic compounds emitted during biomass combustion, which are of high significance for ambient air studies is shown below (Figure 4a,b,c). First of them is levoglucosan (Lev), described widely as a macro-tracer suitable for modeling of wood smoke impact on ambient aerosol concentration (Simoneit et al., 1999). Levoglucosan is a dehydrated saccharide, a product of thermal decomposition of cellulose chains. Its formation is ascribed to rapid temperature increase (Shafizadeh et al., 1968), which is observable in the ignition phase of burning. The second compound of interest is benzo(a)pyrene (BaP), representing a group of polycyclic aromatic hydrocarbons (PAHs). BaP is a minor tracer (occurring in biomass smoke in concentrations more than ten times lower than levoglucosan), but is of high importance because of its undesired health effects (Pierson et al., 1989). BaP is formed on the way of pyrolysis and further pyrosynthesis, and depend strongly on temperature and oxygen concentration in the burning chamber.

A compilation of data, illustrating the emission ratios for two described compounds has been done regarding results from different studies. Figure 4a shows the comparison of levoglucosan and BaP emission ratios (to PM) for modern and old wood stoves and therefore is of highest importance for the further discussion presented in this study.

Figure 4b and c present a compilation dedicated to other technologies and is interesting in terms of general comparison, especially for estimation of pollution levels in regions, where other devices may play an important role.

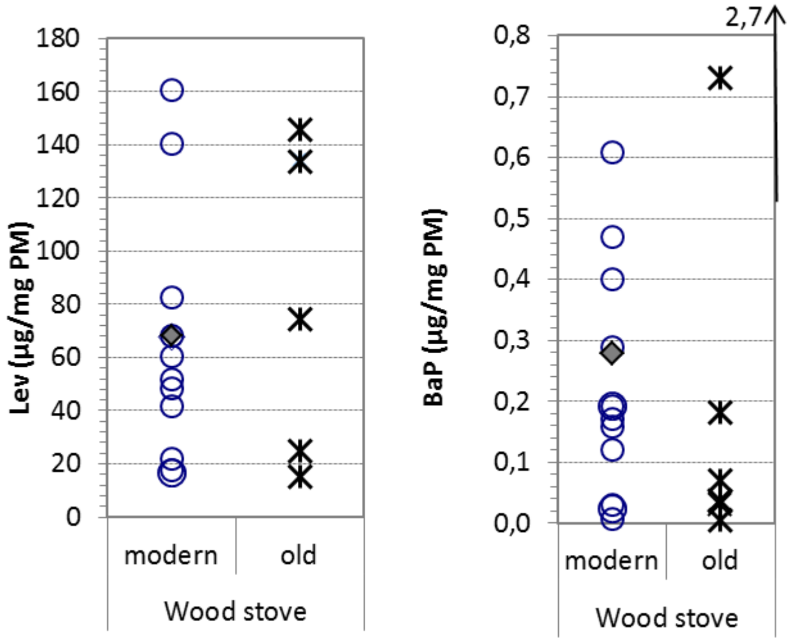


Figure 4a. Levoglucosan and Benzo(a)pyrene emission ratios (µg Lev [respectively BaP]) for modern and old technology wood stoves (legend and reference list below). In case of BaP (old stoves) one of the values extends strongly out of the typical range (2.7).

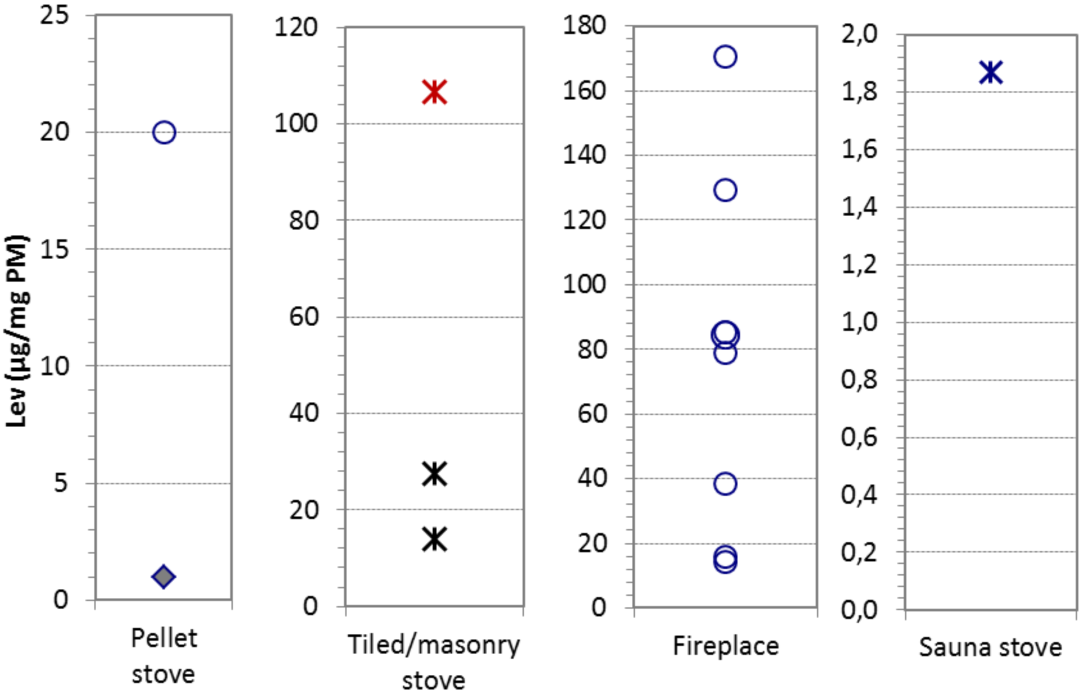


Figure 4b. Levoglucosan emission ratios (µg Lev per mg PM) for different technologies (reference list below).

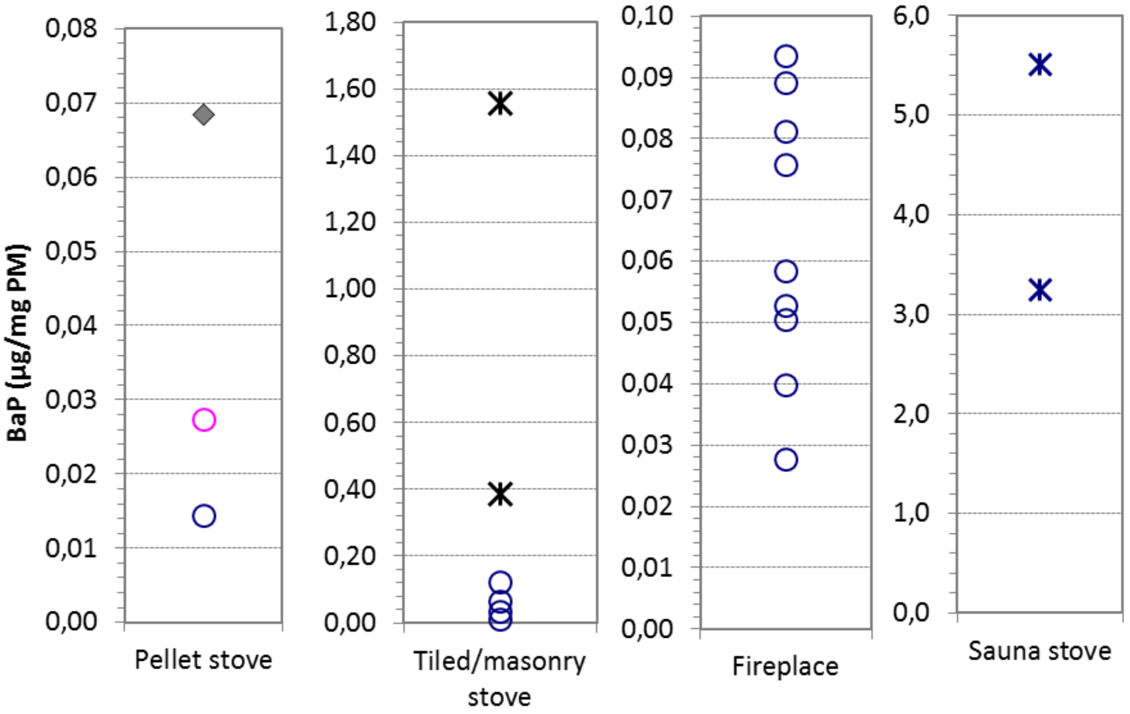
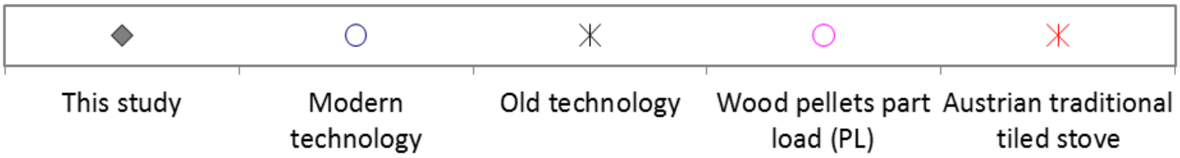


Figure 4c. Benzo(a)pyrene emission ratios (µg Lev per mg PM) for different technologies (reference list below).

Legend:



Data compiled from:

Rogge et al., 1998; McDonald et al., 2000; Fine et al., 2001; Schauer et al., 2001; Fine et al., 2002; Hedberg et al., 2002; Gullet et al., 2003; Hays et al., 2003; Fine et al., 2004a; Fine et al., 2004b; Jordan and Seen, 2005; Hedberg et al., 2006; Kocbach et al., 2006; Mazzoleni et al., 2007; Tissari et al., 2007; Schmidl et al., 2008a; Schmidl et al., 2008b; Bari et al., 2009; Frey et al., 2009; Bergauff, 2010; Gonçalves et al., 2010; Saarnio et al., 2010; Bari et al., 2011; Boman et al., 2011; Lamberg et al., 2011; Pettersson et al., 2012; Schmidl et al., 2011; Tapanainen et al., 2011; Gonçalves et al., 2012; Jalava et al., 2012, this study.

As already mentioned, levoglucosan is generally emitted in much higher concentrations than benzo(a)pyrene. This is related mainly to the fact, that wood is composed in 30-60% of cellulose, which is an initial product for levoglucosan formation. The lowest emissions of levoglucosan are assigned to pellet stoves, however also in this case values are variable (between pellet stove and boiler). Surprisingly low levoglucosan levels were reported for a traditional sauna stove (Saarnio et al., 2010), although the overall PM emission was very high. Similar levels of levoglucosan were observed for experiments with open fireplaces and wood stoves, for both old and modern technologies, what led to the conclusion that levoglucosan formation is less sensitive to burning conditions and relates to not-technology-limited factors (e.g., fuel type).

BaP emissions are definitely less variable among the similar furnace type. This points that PAH formation is more related to the technology, than the formation of anhydrosaccharides and therefore might be seen as potential parameter to distinguish between emissions of “old” and “new” furnaces.

The lowest BaP levels are reported for pellet stoves (all devices complied here are equipped with automatic combustion air supply; Bari et al., 2010; Boman et al., 2011; this study), the highest for sauna stoves (Tissari, et al., 2007; Lamberg et al., 2011). Open fireplaces depict lower BaP, due to easy access of air to the combustion chamber and low combustion temperatures. Chimney stoves with closed chamber are characterized by variable BaP emissions. The higher BaP share is noticeable for modern appliances, characterized by higher burning rates (Pettersson et al., 2011; Schmidl et al., 2011; this study).

Inorganic compounds have only a small contribution to emissions from small scale manually operated combustion furnaces. Different studies report values in the range 1-15% according to combustion conditions, fuel and furnace (Alves et al., 2011; Schmidl et al., 2011).

The highest concentration of inorganic fraction in emissions is reported to appear for “high burning” operations (Ancelet et al., 2011). The most abundant non-organic constituent of particulate emissions is elemental carbon (EC, also called soot), built on the way of very hot and quick combustion with insufficient amount of oxygen for oxidizing it to CO_2. Generally elemental carbon is much more “advanced” form of emission in comparison to organic carbon (OC), and higher EC emissions are characteristic for better combustions. Therefore pellet stoves and modern log wood appliances emissions drift in this direction. Other inorganic compounds occur in particulate matter as water soluble salts or non-soluble oxides. Dominating are potassium compounds (K_2SO_4, KCl, K_2CO_3, possibly also K_2O or silicates; Obernberger et al.,2007; Alves et al, 2011; Schmidl et al, 2011), what enables introducing K^+ ion as an inorganic tracer for wood combustion (Khalil and Rasmussen, 2003; Caseiro et al., 2009).

The formation of other inorganic constituents is strongly dependent on the temperature and the composition of raw fuel (van Lith et al., 2004*)*. Inorganic particles are often bigger than 10 µm in diameter and therefore do not contribute to fine aerosol in the atmosphere.

Concluding, the properties of combustion (related strongly to applied technology) determine the characteristic of particulate matter emissions. However, the technological parameters cooperate strongly with features of the fuel and therefore it is not only a technology related-, but also user limited question, which compounds would be formed in excess during the burning process.

1.5. Impact of biomass burning on ambient air.

Natural and anthropogenic biomass burning has been reported to be a major contributor to carbonaceous aerosols in South Asia, Europe and both Americas (e.g., Mayol-Bracero et al., 2002; Venkataraman et al., 2005).

A precise source apportionment study requires detailed characterization of emissions. The review of recent data have shown that in case of wood burning particles the source must be seen as a composition of various emission points with different origin and characteristics. Many of the apportionment studies are based on levoglucosan as a tracer for wood smoke in ambient air. However, as deducted from the latest data levoglucosan emissions may vary during different burning conditions, leading to wrong assessment, if made on the base of inappropriate emission profiles. An improvement of results for source apportionment could be achieved by applying of combined source apportionment methods (Sheesley et al., 2007; Sandradewi et al., 2008; Gilardoni et al., 2011).

Many residential areas of Europe suffer because of elevated winter atmospheric particulate matter (PM) levels (e.g., Bauer et al., 2006, 2007a,b, 2009 - Aquella Group of Studies, TUV; Putaud et al., 2010), and therefore a proper assessment of wood smoke impact is of high importance. Past research has shown that a significant part of winter aerosol could be ascribed to residential biomass combustion (e.g., Pashynska et al., 2002; Glasius et al., 2006; Szidat et al., 2006; Puxbaum et al., 2009; Caseiro et al., 2009; Yttri et al., 2009; Bari et al., 2009,2010). According to the European Emission Inventory (Schaap et al., 2004) biomass burning aerosol contributes to 45% primary $PM_{2.5}$. Kupiainen and Klimont (2007) report 50-65% of organic carbon (OC) from biomass combustion (times a factor of 1.3-1.7 [Turpin et al., 2000] results in organic matter [OM]) in Western and Eastern Europe respectively. Puxbaum et al. (2007) have found, using levoglucosan as an atmospheric tracer for wood smoke contribution, 20-50% of the organic matter (OM) for the cold seson from biomass burning at European background sites.

Schmidl et al. (2008b) and Caseiro et al. (2009) studied the influence of wood combustion on ambient air in Austria. Using emission data for local fuels and stove type characteristic for alpine sites, a contribution of wood smoke OC to observed atmospheric OC up to 70% was found for the city of Graz in the heating season.

Similarly to Austria, residential wood burning is reported to have a significant influence on air quality in Northern Italy (Piazzalunga et al. 2011), South Germany (Bari et al., 2011) or Switzerland (Szidat et al., 2007). The wood smoke contribution to PM_{10}-organic matter in those studies (reported for winter measurement campaigns) was 20-50% (depending on the site, lowest for a large city and highest for a town located in Alpine valley), 49% (small community), and 88% (closed Alpine valley), respectively for the cited studies.

Mainly residential areas are highly affected by wood smoke. Glasius et al. (2006), Piazzalunga et al. (2011) and Harrison et al. (2012) report low levels of biomass-burning particulate matter for urban stes in large cities (Copenhagen, Milan and London respectively). Contrary, much higher wood burning particles concentrations were reported for residential communities (e.g., Ward et al., 2006 - for Libby, a small town in Montana, USA; Larsen et al., 2012 - for Cantù in French Alps). Lowlands are exposed to meteorological factors (e.g., wind) and pollution transport has a significant influence (Gilardoni et al., 2011). Closed mountain valleys are more prone to temperature inversion, what favors trapping the pollution in the low altitude for longer periods (Ward et al., 2006; Szidat et al., 2007). Geographical properties of a region are one of the crucial factors discriminating the ambient aerosol concentration. Moreover, the altitude influences also the number and quality of local emission sources. Due to economic reasons most industry is located in wide plains; therefore the relative impact of local residential emissions (primary emissions) might have much higher share to overall in the mountain sites.

The influence of wood combustion on ambient particulate matter was confirmed by use of various apportionment methods, including chemical mass balance modeling (CMB), positive matrix factorization (PMF), ^{14}C (radioactive carbon based) measurements, aethalometer measurements or macro tracer methods (e.g., Sandradewi et al., 2008; Caseiro et al., 2009; Pastorello et al., 2011). Many recent studies deal with defining the most exact method providing the estimation of wood smoke impact on the atmospheric aerosols. New findings let the conclusion, that it is highly possible that tracer methods applying literature emission factors, may lead to significant underestimations of wood burning impact. Piazzalunga et al. (2011) suggest that the underestimation is possible due to secondary aerosol formation from wood burning emissions, as well as from inappropriate PM/Lev conversion factors. The wood smoke impact estimated with the combined methods was around 60% higher than for the estimate from PM/Lev ratio.

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2. Synthesis

2.1. Goals of the thesis

2.1.1. Overall objectives

The overall objectives of this thesis were:

- obtaining "reality-near" emission factors for modern small scale wood combustion;
- characterizing the chemical composition of particulate biomass burning emissions;
- use of the results for interpreting of ambient air data.

2.1.2. Specific goals

Specific aims of this study were:

- optimizing a dilution-sampling system used in previous studies (Luisser et al., 2008; Schmidl et al., 2008a) for collecting different fractions of particulate matter (PM) on quartz-fiber- and cellulose ester filters;
- developing a method for measurement of odor in wood stove flue gas;
- obtaining emission factors of gases (CO, NO_x, C_xH_y), PM, and polycyclic aromatic hydrocarbons (PAHs) for a modern, small biomass burning device, emphasizing the impact of the fuel on examined emissions;
- assessing the odor thresholds for combustion of investigated fuels and finding their relations with measured emissions;
- characterizing the PM from small scale biomass burning by analysis of the major classes of compounds: carbon sum parameters (EC, OC, CC), anhydrosugars, non-polar tracers, humic like substances (HULIS), inorganic ions and other inorganic ash particles;
- linking of the emission study results with ambient air data, by constructing of region-specific profiles of wood smoke emissions.

2.2. Choice of the fuels and combustion appliances

One of the crucial questions for launching the study was the choice of appropriate fuels and furnaces. The intention was to run tests with fuels and stoves representative for Central European countries. Only small scale devices were taken into consideration, as previous studies showed that this kind of combustion can release much more PM than wood boilers (e.g., Schmidl et al., 2011).

However, practically no homogenous data on share of fuelwood in the domestic sector is available.

The fuel use could be assessed in different ways:

- on the basis of felling statistics;
- on the basis of growing stocks;
- on the basis of market research;
- according to surveys delved on wood stove users.

For instance Fine et al., (2004 and previous papers cited therein), as well as Goncalves et al. (2010) have reported emissions for burning of wood types growing respectively: in the USA and Portugal.

The choice of fuel for this study is based likewise, on the growing stocks and considered the species with abundance of more than 5% of the forests area either in Austria or in its neighboring countries (Czech Republic, Hungary, North Italy [province South Tyrol], Slovak Republic, Slovenia, South Germany [Bavaria and Baden-Württemberg] and Switzerland) .

The example of Austria shows, that the crop of fuelwood import and export plays a minor role (e.g., according to Schilcher and Schmidl (2010) the net import represent only 4% of the Austrian demand of fuelwood). It was assumed that most probably the whole Central Europe would represent more or less the same pattern (due to congenial forest areas) and therefore the local grown wood would play a significant role. Moreover, many small scale appliances users obtain fuel from own sources (private forests or gardens), and therefore the market derived data could not always be directly applied, especially regarding log wood.

As a result, 12 wood species were chosen: black locust, black pine, black poplar, European beech, European hornbeam, European larch, Norway spruce, pedunculate oak, Scots pine, sessile oak, silver fir and Turkey oak. Additionally hardwood sawdust briquettes (obtained from local store, but produced in Slovenia) and wood pellets were tested, because of their considerable share, as derived from the market studies. The “Austrian firewood profile” obtained by this method is more sophisticated than the one reported for by Schmidl et al. (2008b), who proposed ratio of 70%/20%/10% for spruce, beech and briquettes respectively, based upon felling data for fuelwood.

A relevant information is provided by Bari et al. (2011) and Meyer (2012), who report that share of hardwood in the wood fuel used in the domestic sector of Germany and Switzerland amounts to >90% and 57% respectively. Those studies forebode that users of small stoves prefer hardwood fuels due to their higher calorific value and more enjoyable burning behavior.

On the other hand, the PM ambient studies provide an inverse data, extracted from ratios of anhydrosugars: levoglucosan (Lev) to mannosan (Man), measured in the ambient air. Schmidl et al. (2008b) have reported significantly higher Lev/Man ratios in emissions of hardwood burning, what was confirmed also in other studies (e.g., Bari et al., 2009). Measuring of Lev/Man ratios in the ambient air pointed on softwood to be dominating fuel in Styria and Carinthia (Bauer et al., 2007a,b).

Some sources indicate that woodfuel use is strongly dependent on the regional supply. In Switzerland, Sandradewi et al. (2008) have found, for three biomass-burning-affected sites (Roverdo, Zürich, Rieden), the predominance of hardwood burning in Roverdo, and explicit softwood burning impact at the both other sites. The findings were proved by the statistical data for fuel use in Roverdo (95% of hardwood used for residential burning). In further statements authors assumed that the local availability of fuel should be concerned, as the softwood burning impact in Zürich correlates with the forest composition in the region (60% softwood species). Piazzalunga et al., (2011) reported recently, also from ambient data, that the softwood burning impact is characteristic for an alpine site in Lombardy (city of Sondrio), while hardwood burning emissions dominate in the sites located at plain (Mantova, Lodi). Therefore, the forest growth statistics based choice of fuels done before launching this thesis is assumed to reflect the real situation in the selected region.

Wood burning as the single heating source is most relevant for detached houses and houses with few apartments in suburban and rural areas. Nevertheless the distribution of small stoves may be more scattered also in the city, as many users install this kind of burners as an additionally heating method, e.g., in spring and autumn, or just for aesthetic reasons. The Central European market provides a wide range of small burning devices, representing a wide range of technological status.

According to the budget limitations only two stoves were tested. A middle-priced manually operated chimney stove and an automatically fired pellet stove, required for tests with wood pellets, both from the local manufacturer and approved for sale at Austrian market, were chosen.

2.3. Sampling setup

Choice of the right method of sampling is a topic requiring a wide discussion, especially in case of sampling of the combustion emissions. There are numerous factors, which must be taken into consideration by designing a sampling apparatus. Therefore, a precise description of the sampling conditions is very important, because the differences in protocols may result in misunderstanding of emission formation and distort the emission factors.

The initial point of this study was a system used already for two foregoing projects (Luisser et al., 2008 and Schmidl et al., 2008a). The sampling equipment is described in Schmidl et al. (2011). The probe, the dilution line and the dilution tunnel, where the sample is mixed with clean dilution air were adopted directly. The changes, done in order to fulfill the intensions of the project, followed upon the size separation step. The 2.3 $m^3 h^{-1}$ PM_{10} separator was replaced with two same type anodized aluminum single-stage impactors (with separation efficiencies of 50% for particles with 10 µm and 2.5 µm for obtaining PM_{10} and $PM_{2.5}$ samples respectively) of lower flow (each of 1 $m^3 h^{-1}$). An additional sampling line not equipped with PM separation device was installed in parallel. A fourth outlet was intended for sampling of diluted gas for odor measurement. Each separator was followed by three filter holders - one made of aluminum with a 7 cm long cone assuring a homogenous distribution of the particles on the filter, and two of polycarbonate. The flow to the filter holder containing a cellulose acetate filter was reduced with a needle valve, in order to prevent a premature overload resulting with a fall of pressure drop across the filter.

Flow was regulated by automatic mass flow controllers and additionally checked by readings of a gas meter located at the end of each line.

The total PM sampling was done only on one quartz fiber filter, placed in an aluminum filter holder, frontally to a pump working with a flow of 5 L min^{-1} (0.3 $m^3 h^{-1}$). After passing this filter, the exhaust was directed to the NDIR CO_2 detector, to assess the stability of the dilution ratio, comparing concentrations of CO_2 in the diluted and undiluted exhaust.

The temperatures of the flue gas before and after dilution, were constantly controlled with a magnetic thermocouple (type K). The temperature of sampling points was assigned to 20-40 °C (adequately to the combustion temperature and ambient conditions) according to data collected by Schmidl et al. (2011).

The odor sampling line is described in detail in **Part 5** of **this chapter**. The schematic drawing (Figure 1) presents the whole measurement set-up.

The updates of the sampling apparatus resulted in the loss of isokinetic flow from the dilution tunnel into PM separators. Due to the change of the duct diameter (34 cm in the cooling pipe and 10 cm for each separator), a significant change of the gas flow velocity from the cooling pipe to the separator inlets ($U_0/U = 0.3$) was induced, what lead to “super-isokinetic”. A review of Kulkarni et al. (2011) report for horizontal, isoaxial super-isokinetic sampling losses in aspiration efficiency and internal remarkable deposition effects depending on the nozzle parameters. The problem of anisokinetic sampling concerns mostly particles with large diameters (which due to their high masses are not able to follow the sampling stream). Most of researchers recommend therefore isokinetic methods of sampling (e.g., Ledbetter, 1972; review of Kocbach Bølling et al., 2009), to reduce uncertainties in mass estimation due to uncontrolled loss of particles in the sampling duct. On the other hand, as mentioned in the same sources, wood smoke PM is mostly represented by particles with diameters lower than 2.5 µm and therefore the threat of mass loss is considered low for this project.

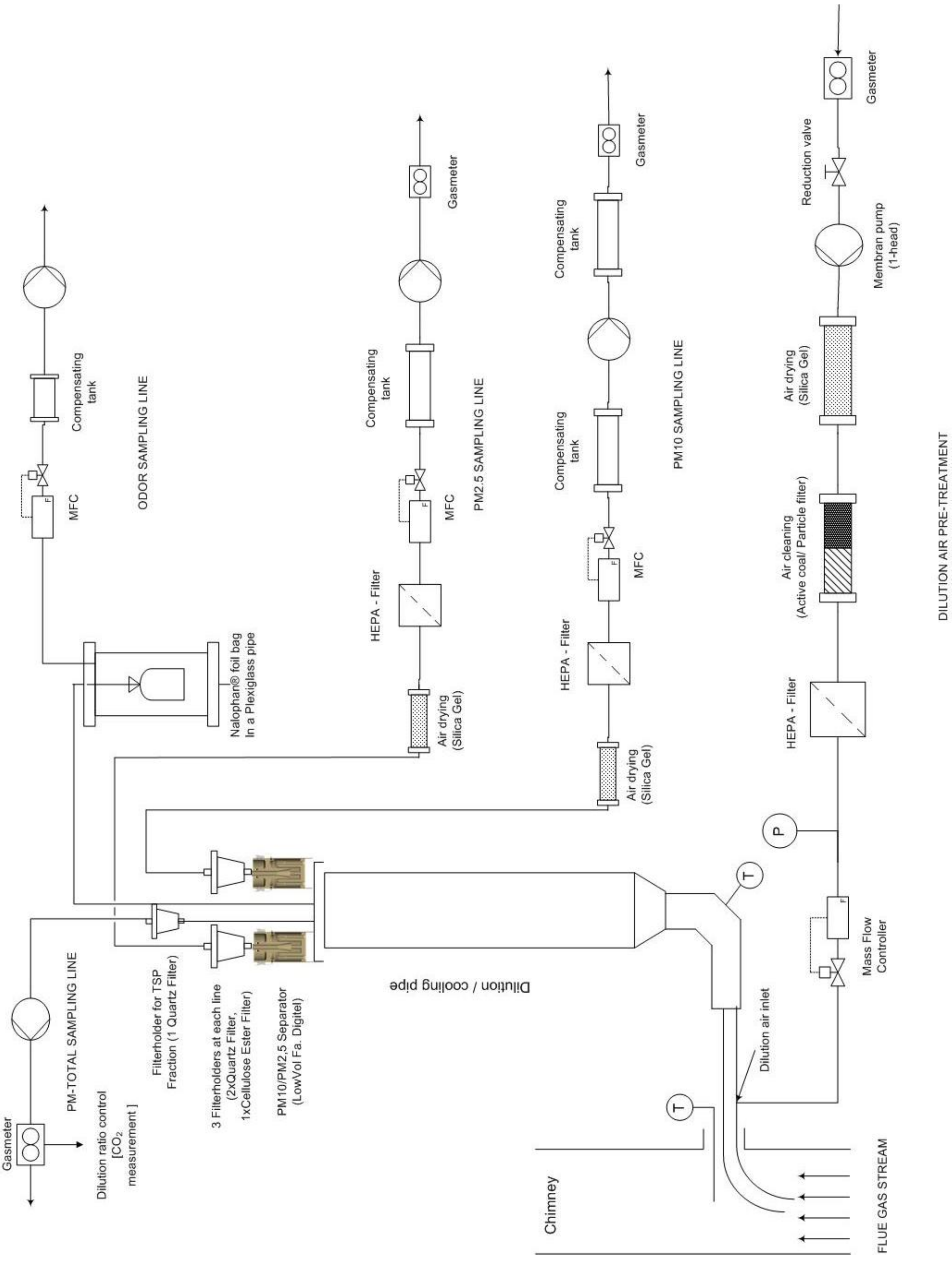

Figure 1. Sampling apparatus used in the experiment.

Dilution of exhaust is nowadays a recommended technology for the wood smoke sampling (e.g., Boman et al., 2011). The US EPA has proposed a method of dilution tunnel measurement already in the late eighties (e.g., Hartman et al., 1989). However, many studies in Europe were applying “hot” PM sampling as a representative technique for obtaining of emission factors for national inventories, as it is based on a German standard method (e.g., Spitzer et al., 1998). The recent experience (e.g., Nussbaumer et al., 2008) show that “hot” exhaust sampling does not include condensable organic fraction particulate matter and therefore results in a high underestimation of actual PM mass (a factor of 3-9, as reviewed in Pettersson et al. [2011], in particular for logwood stoves, for which OC emissions are of high importance). Both mentioned studies indicate that also the dilution ratio is not without denotation. It is believed that the dilutions under a factor of 10 may cause an overestimation of emissions. Contrary, Lipsky and Robinson (2006) showed that for dilution ratios considerably higher than 20 times a decrease of PM mass due to vaporization is possible (also reported by Nussbaumer et al., 2008).

The dilution factors in this study were between 10 and 20 (with an exception for pellet combustion where three to four times diluted exhaust was sampled, nevertheless it was considered to have less effect on the result due to the fact that pellet emissions are dominated by inorganic emissions).

The flue gas residence time in the dilution tunnel was about 60 seconds. This time is enough for cooling the diluted exhaust down to the ambient temperature and assures a condensation of semi-volatile organics (Schmidl et al., 2011).

Another sampling threat relates to the situation when flue gas stays too long in the dilution tract, what increases considerably the risk of condensation of organic compounds on the walls of sampling adjustment.

This is one of so-called “sampling artifacts”, which can be an important source of significant errors.

Due to varying behavior of sampled compounds inside the system, following effects are possible:

- condensation of semi-volatile organic compounds in the dilution duct, resulting in underestimation of mass (negative effect);
- desorption of semi-volatile organic compounds from the particulate mass, what likewise lead to underestimation of the particle-phase organics (negative effect);
- adsorption of volatile organic compounds on filter material or particles loaded on filter material, leading to overestimation of the particulate mass and organic carbon load (positive effect).

Positive and negative artifacts could cooperate, and therefore their effect is difficult to predict. The dimension of artifact depends on the sample type, sampling medium and conditions of sampling (e.g., temperature and pressure). Lipsky and Robinson (2006) found that OC artifact for wood smoke may contribute between 25 and 50% to bare filter OC, however with high uncertainty. As Chow et al., (2010) reports, the negative artifact is believed to be lower for quartz fiber filter, than for Teflon.

The problem of volatilization of semi volatile compounds during sampling should be concerned in case polycyclic aromatic hydrocarbons. It is generally suggested to use different filters types accompanied with a second medium (second filter or PUF-tube), and to collects blanks (Watson et al., 2008 [EPA]; Hytönen et al., 2009) in order to estimate the undesirable effects.

In this study no solution for assessing of artifacts was used. This enlarges the possibility of errors due to sampling artifacts. However, for example in the case of toxic PAHs, the volatilization should be neglectable as BaP and other heavier PAHs are known to be found practically only in particulate phase on the filter (about 80-99%, e.g., Peltonen and Kuljukka, 1995; Riva et al., 2011).

The sampling of diluted exhaust has started immediately after kindling and the tests were conducted for "cold stove"($T_{stove} \leq T_{ambient}$ at the beginning of sampling) or with "cooled-down stove" - in case of a second experiment on the same day the stove was cooled down to 30-40°C. This condition was not fulfilled for tests with pine needles, pine cones and old leaves, as well as for a single test with European hornbeam, where the start temperatures were respectively 45,59,60 and 90°C and for those cases an influence on emissions may be expected (Goncalves et al., 2011).

2.4. Sample management

To assure the unity of experimental data, all samples were treated in the same way, according to a scheme presented in the flow diagram below (Figure2). The organized system of sample treatment aimed reducing the possibility of undesirable random errors due to different conditions of transport, storage or preparation of samples. Prior to combustion experiments quartz-fiber filters were pre-baked in 550°C for minimum 5 hours. This is an approved procedure reported also for other studies (e.g., Schmidl et al., 2008b, Goncalves et al., 2010, Vecchi et al., 2009) and guarantees an oxidation of the organic carbon present on the filter matrix. After baking filters were cooled down in the desiccator, over ultra-pure distilled water (MILLI-Q, MILIPORE, resistance of 18.2 MΩ), then placed carefully in disposable Petri-dishes and put for 48 hours in a particle-free air conditioned room (temperature 20°C±1, relative humidity 50%±5). During conditioning the cover plates of Petri-dishes remained half open. After conditioning, filters were weighed with a microbalance (Sartorius MP) twice (or three times in case of mass differences bigger than 10%). The filter mass is therefore an arithmetic mean of two balancing runs.

An empty reference filter was balanced every hour, to assure the stability of room and balance conditions.

Filters prepared for sampling were stored in tightly closed Petri-dishes in the "clean-room". Shortly before sampling a set of filters were taken out and placed in the filter holders. The cellulose ester filters did not undergo any pre-treatment before balancing. After weighing they were stored similarly to quartz filters.

Immediately after sampling, the filter holders were transported to the analytic laboratory, where filters were removed from the filter holders and placed in clean disposable Petri-dishes. All samples, also the cellulose filters, were conditioned before balancing (again for 48 hours), to avoid the mass differences ascribed to hygroscopic properties of quartz fiber filter matrices and collected particulate load (Weingartner et al., 1997; Swietlicki et al., 2008; Dusek et al., 2011). Each loaded sample, similarly to the procedure for empty filters, was balanced twice or, if the difference between readouts was higher than 10 percent, three times. Particulate mass was calculated as a difference of mass averages noticed for loaded and unloaded filter.

If not immediately processed, the quartz filter samples were stored in tightly closed Petri-dishes in the freezer (-18°C) to avoid the volatilization of semi-volatile organics covered in the particulate phase during sampling. All preparations for chemical analyses were done in the particle-free room (weighing, cutting and punching) or in the analytic laboratory (extraction and measurements). It was minded that the samples do not come in contact with any other source of fine particles.

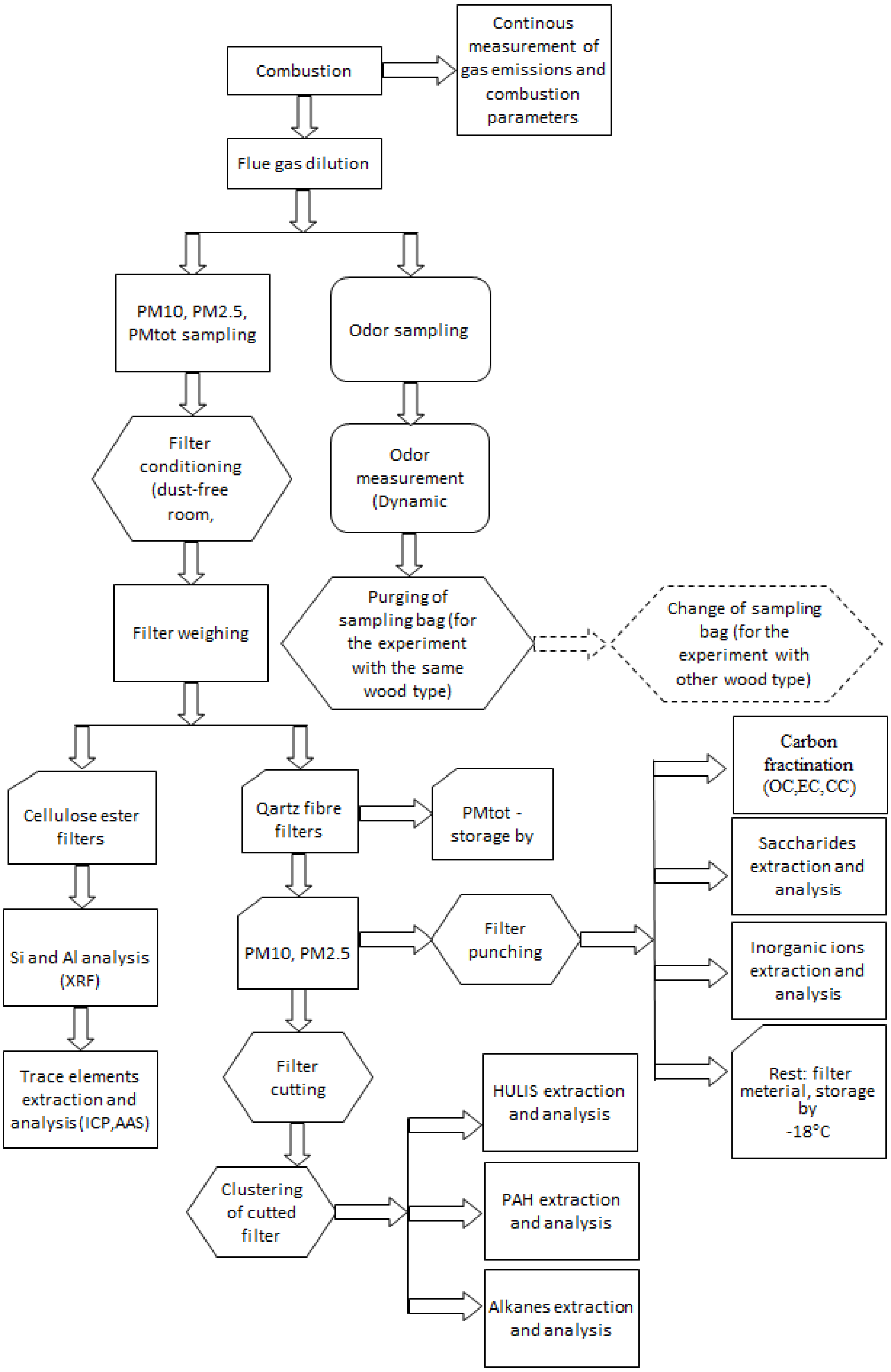

Figure 2. Flow diagram of sample management.

2.5. Evaluation of the wood smoke odour detection method

Unpleasant smell is ascribed to liquid, solid and gaseous sources, but in fact it is defined as a sensual response to a complex mixture of volatile and semi-volatile chemicals. Monitoring of odors can be accomplished in several ways: chemical analyses, electronic methods and dynamic dilution olfactometry, which takes advantage of the human sensory response.

The odor issue in the environment is treated with much consideration in USA and Canada, where appropriate ambient air limits for odorous emission sources (mostly wastewater, animal treatment and industry), (as reviewed by Mahin, 2001) exist. Also Europe has deployed limitations for industrial or agricultural odors in ambient air, but wood smoke is still not regarded as a considerable nuisance. The German GIRL directive (UWS Umweltmanagement, 2008) exemplifies one of the first trials for controlling of odor, including household combustion as a potential source.

Smoky smell is generally considered pleasant. Nevertheless some regions are massively aggrieved with this phenomenon (reported by Bari et al., 2010 for a small “wood burning” community) and due to “overdoses” a pleasant smell becomes there a reason of complaints for the inhabitants. Moreover, odor perception is a signal of elevated concentration of emissions, which may affect human health. The mountain valleys are especially exposed to the negative effects of wood smoke, due to often occurring temperature inversion and limited possibilities for air masses exchange (Lehner and Gohm, 2010).

A first attempt of characterizing wood smoke odor is described in the diploma thesis of Ebbinghaus (1993), who reports odor levels measured in smoke from burning of mixed Mid European wood types (varying moisture and log size), in a 40 kW boiler based on 5-minutes sampling intervals. Within the duration of the recent study also other odor concerning reports appeared (Baumbach et al., 2010; Schleicher et al., 2011). Baumbach et al. (2010) have measured odorous emissions from typical German wood boilers. Schleicher et al. (2011) is a Danish report considering modern logwood stoves, but only a short description therein is dedicated to odor topic. Both mentioned studies apply the dynamic dilution olfactometry to assess the odor thresholds.

This thesis concentrates on small stoves, which are known to cause generally higher emissions than boilers and therefore also higher odor levels were expected.

Likewise, the dynamic dilution olfactometry has been chosen as a measurement method. This method was elaborated in the seventies in Germany and has become the most applicable solution for detection of environmental odor (as reviewed by van Harreveld et al., 1999). It is based on the answers of a trained panel of persons, who fulfill certain requirements. The measurement is very sensitive to variable parameters and a standardization of odor detection conditions is reported to be a very important issue (e.g., DEP, 2002; vanDoorn et al., 2002). Van Doorn et al. (2002) indicate that the results obtained before the standardization of olfactometry methods may not be comparable with those obtained nowadays. The normed measurements are more objective, sensitive and reproducible.

According to this knowledge, the design of the measurement system for this study was based on the European standard for dynamic dilution olfactometry (European Norm, DIN EN13725, 2003).

The exhaust samples were collected after the pre-dilution (using the same dilution apparatus as for particulate matter samples). This is important due to high expected odor levels, high temperature and high humidity of sampled gas, which might result in the condensation of water vapor and organics in the sampling bag. The sample was transferred to the Nalophan sampling bag directly from the dilution tract, using a so-called “sampling lung” (the sample bag is placed within a rigid, leak-proof container; the air inside the container is evacuated with the pump, which cause the bag to fill with sample with the similar flow as evacuation is conducted; the flow is regulated by mass flow controller), a method recommended in the standard. The particulate matter samples were taken over the whole burning period and therefore also odor estimation was conducted during the same time, in order to obtain a conformable ratio between wood smoke odor and PM emissions. The flow of the sample was fitted to the sampling bag volume and expected burning velocity. The sampling over the whole burning cycle, as done in this study differs from that reported by Ebbinghaus (1993), who obtained the results for five minute intervals. Those values show extremely high variation (odor during the ignition phase is up to a factor of 10 higher than during the inherent burning). Averaged concentrations are significantly lower than peaks of highest possible odor, what points out that actual emission of odorants occurs only during a short time of burning cycle. Results of this study are more stable than previously reported and therefore it is possible to compare them with other emission data.

Once collected, the sample was stored maximally for 30 minutes at ambient temperature, but protected from direct sunlight impact, to avoid condensation, transformations of chemicals and eventual diffusion of sample.

A detailed description and schematic drawing of measurement system and sampling line is shown in **Chapter 3**. The olfactometer itself is a self-built device (Figure 3) consisting of four suspended body flow meters, a membrane pump, valves system and air cleaning duct (active carbon, particle filter and silica gel). The sniffing port is made of funnel shaped glass, while the cable assembly is made of Teflon and equipped with plastic- or polished stainless steel fittings. The air flow rate at the sniffing port was at least 15 L min^{-1} (in case of blind tests), and therefore accounted for the variability of individual breathing (sniffing) volumes during odor evaluation.

All materials used for the sampling and measurement systems were declared as odorless.

Prior to the experiments, the panel members were trained in order to familiarize them with test procedures and check their ability to recognize the standard odorant (n-butanol). The assessing of odor threshold was based on the binary answers (detected/not detected) collected for ten to twenty different dilutions, presented to each of four deployed panelists.

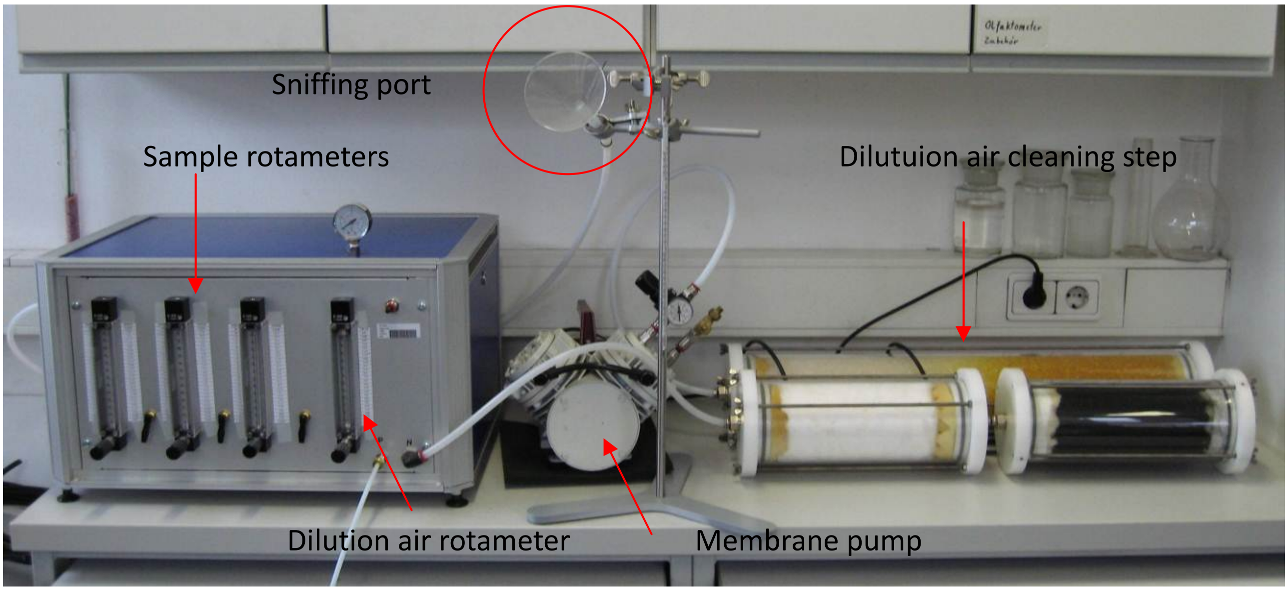

Figure 3. TUV-Olfactometer.

The threshold determination method has been optimized. Instead of deriving of the geometric mean of the dilution level, at which the consistently correct series of positive answers appear, the binary results were introduced to a probit model. This type of regression could be applied in case of normal distribution of data points and is a mathematical solution for interpretation of binary data, especially to estimate dose-response curves (e.g., Dale et al., 1998). It was decided to use a probit function instead extracting the mean of detection point concentration mostly because of high uncertainties of the answers in the threshold range (the discrimination between “guess” and “recognition” was very often ambiguous).

2.6. Chemical analyses and uncertainties of results

Samples collected in the series of combustion test included:

- five burnings with wood pellets in an automatic stove (three tests with full load [FL] and two test with part load [PL] operation);
- three tests with most wood logs and briquettes in a manually fired stove (BR, EH, EB, BPop, TO, SO, BL, SF, NS, SP, BP);
- two tests with PO;
- one test with EL and each of “garden waste” sort (L, N, C).

All combustion test were conducted under carefully controlled conditions, at the laboratory test stand (Institute of Chemical Engineering, TUV).

Over 60 components of wood smoke particulate matter were determined. Analytical methods, their detection limits and the uncertainties of obtained results are listed in the Table 1. In the first step the carbon amount was defined, and differenced into organic-, elemental- and carbonate-bounded-C (OC, EC, and CC respectively). For the characterization of the inorganic part the results of elemental analysis (AAS, ICP, and XRF) were compared with those obtained from liquid chromatography (isocratic HPLC), in order to distinguish the amount of soluble potassium, calcium, magnesium and sodium, from the overall content of those elements in the sample.

From eleven analyzed saccharides (gradient HPLC), seven compounds were found in a detectable range: levoglucosan, mannosan and galactosan (in all samples, with a quantified contribution to the PM concentration) as well as mannitol, xylitol, glucose and sucrose (in some samples, at significantly lower concentrations).

A detailed description follows in the **Chapter 4** of the thesis.

Table 1. Methods, detection limits related to samples analyzed in this study and uncertainties of obtained results.

Compound/ compound class	Method	Filter medium	Detection limit [1]	Unit	Uncertainties of results	Uncertainty Dimension [2]
Particulate matter (PM_{10},$PM_{2.5}$)	Gravimetry	Quartz and cellulose filters	0.5	mg	20	SEM%
Carbon OC/EC/CC/TC	Thermal -optical Method with FID detection (Sunset Lab)	quartz filter punches	32.4 [3]	$\mu g\ MJ^{-1}$	16/16/17/5	SEM%
Anhydro- saccharides	HPLC	quartz filter punches	3.5 (Man)-15.8 (Lev)	$\mu g\ MJ^{-1}$	27	SEM%
Ionorganic ions[4]	HPLC	quartz filter punches	0.5 (Cl^-)-159(NH_4^+)	$\mu g\ MJ^{-1}$	22 (K^+)	SEM%
HULIS	CO_2-NDIR	quartz filter pools	66 HULIS-C [5]	$\mu g\ MJ^{-1}$	30	SEM%
PAHs	GC-MS	quartz filter pools	0.11 (RET)-1.09 (BaP);	$\mu g\ MJ^{-1}$	20	SEM%
Alkanes	GC-MS	quartz filter pools	0.16 (C20)-2.43 (C26)	$\mu g\ MJ^{-1}$	25	SEM%
Trace Elements	XRF, ICP, AAS	cellulose filters	0.3 (Cd)-61 (Na)	$\mu g\ MJ^{-1}$	30	SEM%

[1]… Detection limits calculated, if no additional information given, as three times the standard deviation of the lowest standard and given for compound with lowest and highest detection limit among all compounds analyzed with the method. [2]…SEM…standard error of mean, relative; [3]…detection limit according to Subramanian et al. (2006) for the same method; [4]…carbonate ion concentrations derived from Carbonate-C measured with thermal-optical method and calculated from stoichiometric ratio; [5]…as defined for the same method during AQUELLA Studies (e.g. Bauer et al., 2009).

Only a small number of test were done for each wood type the variation of results is sometimes high thus uncertainties are for those cases considerable. For these reasons mainly ranges of obtained results are presented in the following chapters (**Chapter 3** and **Chapter 4**). Schmidl et al. (2011) have found that the uncertainty of results for highly constant burning conditions (pellet boilers) comes mostly from analyses, and accounts to 1-5% relative range. The uncertainties observed in this project were much higher, what points the considerable contribution of burning related parameters. With SEM of 5%, the TC was the best defined fraction of PM_{10}. Other analyzed compound classes represented SEM between 10 and 30% with highest, observed for mineral ash components.

The PM masses collected with both PM_{10} and $PM_{2.5}$ lines were characterized by homogenous variances (F-test) and no statistically significant difference between both data sets was found.

The standard deviations (RSD) found for CO and NO_x compounds were slightly higher than those reported by Schmidl et al. (2011) for the same test stand (16 and 11% respectively), while 43% for C_xH_y was comparable.

The absolute PM concentrations among all tests with one stove type were burdened with an uncertainty of SEM = 13% for pellet stove and 25% for wood logs and briquettes. No statistical significant difference was found for the averaged PM emissions from hardwood- and softwood combustion (two-sided t-test, with result 0.57, compared with theoretical t value of 1.96, for 31 degrees of freedom and P=95%).

Concerning the pellet combustion, the differences between operation modes (full- and part load) were noticeable. The results obtained for part-load burnings were more stable, than those for full load mode and showed the lowest uncertainty for Zn (SEM = 0.1%) and the highest for Al (33%), (on average SEM amounted to 13%). It must be however noticed, that only two samples were measured. The uncertainties of full-load operation runs were in range 8-38% (for EC and trace elements respectively), with average of 22%, which is equal also the average of relative standard errors for all tests with pellets.

Also the result of odor measurement was found to be highly variable. A SEM of 15% was found for all tested wood types. The statistical significance of probit model applied as a calculation method for odor testing, was proven for each wood type at P = 95% for most of the cases (not satisfactory confidence level was observed for several experiments, but P was never lower than 70%).

A t-test applied to hardwood- and softwood logs odor values showed a statistically significant difference between means (t = 2.02, compared with theoretical value of t = 1.96, for 31 degrees of freedom, P=95%). The significant differences between hardwood and softwood were found also for mannosan, retene and NO_x (confidence level of 95%).

Due to large variety of wood types chosen for the experiment only a few tests with each fuel were possible, what have significantly influenced the uncertainties originating from batch-to-batch variation. Moreover, the additional factor of personal perception ability was observed for olfactometry. Therefore further tests, including more repeated runs for the same fuel and conditions, and employing more panelists are highly recommended to improve the reliability of results.

2.7. Account of research progress due to scientific work, linking papers presented in following chapters

Results of the experiment are compiled in a collection of scientific papers being published or being prepared for publication in refereed journals. Following chapters include a discussion on topics presented above.

The first paper (presented in the **Chapter 3**) reports about the emission factors for gaseous compounds and PM_{10} as well as about the odor levels for wood smoke from small scale combustion units (wood log chimney stove and pellet burner). The relation between the quality of the burning process, given in terms of modified combustion efficiency (MCE; a factor considering the ratio of emitted CO_2 to all carbonaceous species; see also in **General Introduction**) was examined. Emission factors reported for PM_{10} and gaseous components (CO and C_xH_y) were compared with the calculated “concentrations of odor”. It has been found, that emissions from the same stove could be highly variable also for the same fuel, especially for particulate matter. Odor levels in diluted wood smoke were assessed with a help of dynamic dilution olfactometry. Hardwood smoke was characterized by slightly lower odor levels than softwood smoke (difference statistically significant at P = 95%), but among both groups there were species emitting either high or low (e.g., SO and EL). No odor was detected in emissions from wood pellet stoves, for both part- and full load operations. Nevertheless, particulate emissions of wood pellets were comparable with low emitting wood logs (BPop and EL). The PM_{10} emissions of log woods were highly variable (20 to 220 mg MJ^{-1}). Less variable were concentrations of gaseous compounds in emissions. Only nitrogen oxides (NO_x) were fuel dependent and showed a dispersion according to the content of nitrogen in raw fuel.

There was a noticeable relation (inversely proportional) between the MCE factor and odor, C_xH_y and PM_{10} (R^2= 0.67; 0.76 and 0.52 respectively). That relation pointed out, that all mentioned emissions are favored by the similar burning conditions (smoldering) and their ratios may be expected to be stable. Due to that fact, a factor for estimation of odor from particulate matter has been directed and applied to ambient air data obtained in Austrian apportionment studies. According to high variations of results this approach needs to be proved with a larger number of tests and devices.

The paper has been published in Atmospheric Environment in April, 2012.

The second paper (presented in **Chapter 4**) copes with chemical characterization of particulate matter emissions. This is a general work providing emission profiles obtained for hardwood and softwood during experiments with small scale furnaces of modern technology. Profiles are based on the emission factors for wood types characteristic for Pannonian Lowlands and the Alpine region.

The presented profiles include characterization of carbonaceous particles (EC, OC); anhydrosugars, HULIS, organic trace components (alkanes and particulate PAHs) and inorganic ash particles.

The work shows likewise the balances of component groups in biomass burning PM. The profiles and balances are averaged for all tested fuel groups: pellets, briquettes, softwood, hardwood and garden waste. The automated pellet stove PM emissions are characterized by different content than emissions from burning of wood logs and briquettes, even for cases when an absolute PM emission was the similar (e.g., for larch, poplar and briquettes). Burning of pellets generates mostly fly ash (inorganic particles consistinmg prevalently of potassium and calcium salts (or oxides). For chimney stove was observed that emissions of hardwood logs demonstrated higher inorganic emission content (about 10-12%), however also one softwood (fir) was found to show this tendency. Most particulate matter from chimney stove could be however assigned to carbonaceous material.

Nevertheless, in comparison with studies on emissions from traditional stoves, the modern chimney stove has lower total carbon emissions. The observed carbonaceous fractions contain likewise more elemental carbon (EC) and the values for OC are lower. The differences between tradional stoves were found also for emissions in the organic phase – levoglucosan is generated in lower rates, while alkanes and PAHs are represented in higher concentration.

Levoglucosan and related anhydrosugars (mannosan and galactosan) were investigated more exactly, mostly because of their high importance for the source apportionment studies. The observed relative concentrations varied strongly in PM from combustion of different wood types, but were rather stable for the tests with the same wood type, what points out that the emissions are strongly wood type related. The ratios between levoglucosan and mannosan were higher than previously reported (for hardwood) and comparable for softwood, and the tendancy observed in previous studies that hardwood species result in higher Lev/Man ratios was likewise noticed. The diagnostic ratios of levoglucosan to PM used for assessing of biomass combustion impact on the ambient air were found to differ for ratios reported for an “old” stove.

This may point out the necessity of combining of emission profiles for different technologies and fuels, according to available statistical data.

The paper has been prepared for submission to Atmospheric Environment, as a continuation of the study presented in **Chapter 3**.

The last paper presented in this work (**Chapter 5**) is dedicated to an exact description of particulate-bound polycyclic aromatic hydrocarbons (PAHs) derived from biomass combustion. The work emphasizes benzo(a)pyrene (BaP) emission factors. This compound has been reported to demonstrate carcinogenic and mutagenic activity on cells (Kocbach Bølling et al., 2009) and is monitored in ambient air, e.g. in Europe (EN, 2004). An ambient annual target value for BaP was set to 1 ng m^{-3}. The result of this study shows that this target value may be reached only by emissions from wood combustion. The average BaP emission factor for tested fuels was 27.1±6.7 µg MJ^{-1}.In relation to PM_{10} it accounts to 312±60 ng per mg PM. Assuming about 10 to 20 µg m^{-3} wood-smoke contribution to ambient air aerosol (e.g., in winter months in Austria, as reported by Caseiro et al., 2009), the exposure to BaP would lay between 3.12 and 6.24 ng m^{-3}.

BaP emission rates were alike to other PM related emissions highly variable and do not show any significant trend according to the fuel. It was, however observed that burning conditions may have a crucial effect on PAHs formation. Surprisingly, the wood types with moderate overall particle emission factors were found to be responsible for high BaP levels (e.g., EB, TO). This could be explained with low relative moisture of those fuels and quick burning, which resulted in very hot flame and short, local drop of oxygen concentration during the combustion. The influence of different parameters on BaP emissions were proven with multiple linear regression and a good fitting of burn rate and EC concentration was found in order to model the BaP concentrations. This is in line with findings, regarding formation pathways of PAHs, which are reported to be generated at the same way, as elemental carbon and permits a suggestion to model the concentration of wood smoke originated BaP in the ambient air using an easier obtainable and wider provided value of EC.

The paper is going to be submitted as a completion to both others of this series, most probably in Atmospheric Environment.

2.8. Differences between PM_{10} and $PM_{2.5}$ composition from small scale residential heating

Chapters 3, 4 and 5 concentrate on PM_{10} from wood combustion, nevertheless also $PM_{2.5}$ and total particulate matter (PM_{tot}) was sampled and analyzed during experiments. Many previous studies examining the size distribution of particles showed that most of wood combustion particles (80-95%) are in the fine range ($PM_{2.5}$), (e.g., Rau, 1989; Hedberg et al., 2002; Pettersson et al., 2011). In this study only the mass distribution (no particle number distribution) between both fractions was measured. The data obtained from gravimetric measurements showed, however, the same trend as previously reported resulting in 85% of mass assigned to particles with aerodynamic diameter lower than 2.5 microns (burdened with higher uncertainty for pellet stove, due to low number of tests) (Figures 4a,b).

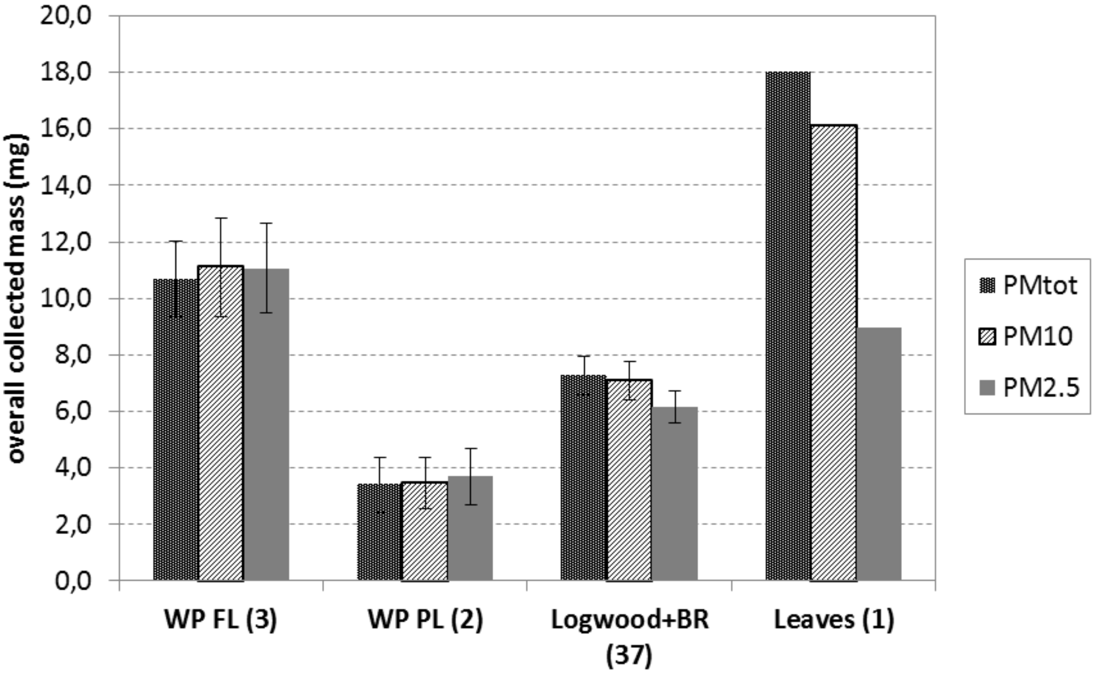

Figure 4a. The average mass distribution in wood smoke samples: overall mass of PM fractions collected on filters (during one combustion run, summed up for three filters, except PM_{tot} - collected only on one filter, and multiplied acurately to compare with PM_{10} and $PM_{2.5}$). Uncertainty showed in terms of standard error of mean (SEM), the number of samplings given in brackets.

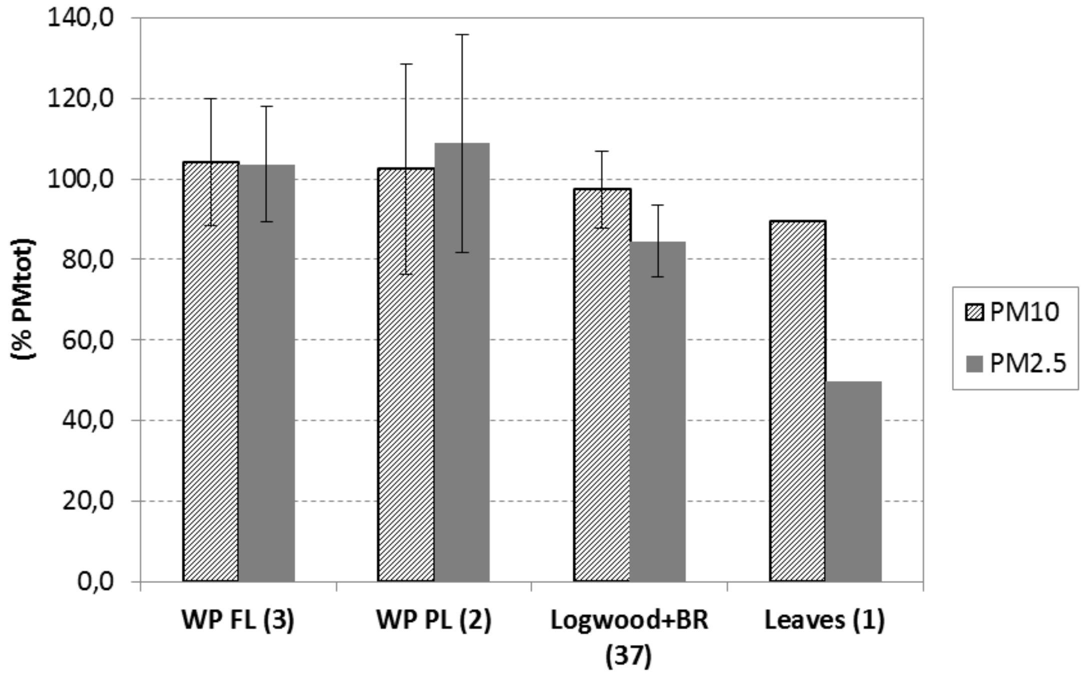

Figure 4b. The average mass distribution in wood smoke samples: PM_{10} and $PM_{2.5}$ masses related to PM_{tot}.Uncertainties showd as relative SEM.

In general, the differences between masses observed either for PM_{10} or $PM_{2.5}$ are nor considerable, especially when the high variations of the obtained results are concerned. A behavior different than pellets and logwood was observed in case of burning of old leaves. The difference between both fractions account in this sample to 50%, but resulted only from one burning test.

In average $PM_{2.5}$ accounted to 85% and PM_{10} to 98% of total particle mass. It has been noticed that pellets and briquettes smoke show the smallest differences between $PM_{tot}/PM_{10}/PM_{2.5}$ mass emissions (negative values could be assigned to sampling and measurement errors). Likewise, for most hardwood types (excluding temperate oak species: PO and SO) the differences were lower than 10% and therefore within the measurement uncertainty. Contrary, a significant difference between PM_{10} and $PM_{2.5}$ emission factors was found for softwood types (25%) and garden waste (40%). The highest mass difference was noticed for leaves, needles and sessile oak emissions, which represent generally the highest emitting fuels in the experiment.

The size range of single PM constituents analyzed during this study followed the mass relation among both fractions. Recent studies have shown, especially for highly efficient heating systems (boilers and pellet stoves), that most of inorganic particles are of larger diameter and organic emissions could be assigned to the PM_1 fraction (Kocbach Bølling et al., 2009; Nussbaumer, 2010). There was no significant difference in chemical composition of both examined size fractions. Variations observed by comparing of masses were not strong enough to affirm a legitimate dissimilarity. Fluctuations observed for a few analyzed components may be assigned to both differences between particle size, and to uncertainty of measurement related to very low concentrations found in the samples.

Most studies dealing with the PM distribution are based on particle number measurements which are used to support the gravimetric data. This was not the case in this study and therefore the difference observations between PM_{10} and $PM_{2.5}$ for small stoves are less sensitive.

Inorganic ash particles are represented mostly by water soluble salts (e.g., K_2SO_4, K_2CO_3, KCl). The electroneutrality requires that cations and anions stay in a balance considering their charge. Typically the samples of PM_{10} and $PM_{2.5}$ represented similar concentrations of ionic species, resulting in comparable ion balance. Pellets burning in automatically operated stove resulted in a much higher inorganic ion content than burning of wood and garden biomass (Figure 5 and **Chapter 4**). In case of pellets emissions the concentrations of ions in $PM_{2.5}$ were slightly lower than PM_{10}. The slope of the ion balance plot was 0.89 for pellets burning generated PM_{10} and 0.54 for $PM_{2.5}$ (Figure 5a). For the logwood stove, the ion balance was nearly the same for the two size fractions (with slopes of A=0.73 and 0.79 for PM_{10} and $PM_{2.5}$ respectively), (Figure 5b), indicating that around 70% of anions present in wood smoke are those, which were analyzed (Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}). For all cases the ion balance show a quality of fit with R^2=0.90-0.996. The lower fit of cations to anions ratio found for $PM_{2.5}$ from pellets burning may be ascribed to the same sampling, which has been treated as an outlier in case of PM_{10}, indicating possibly a random sampling problem. Therefore the trend excluding this data point also for $PM_{2.5}$ was shown (A=0.75; R^2=0.89).

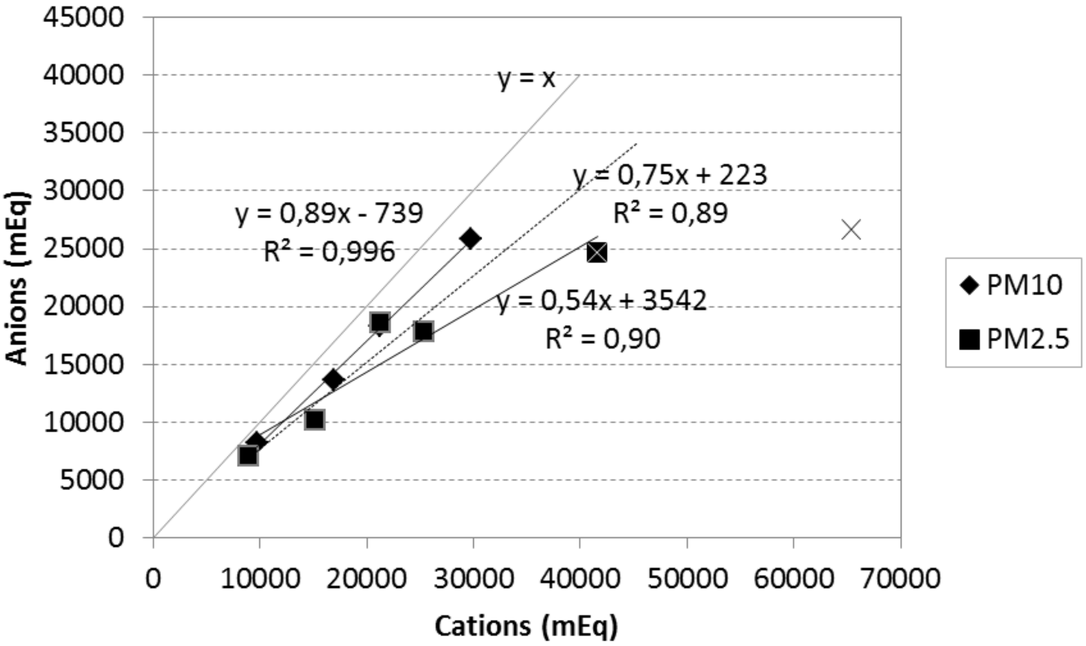

Figure 5a. Ion balance: wood pellets (FL+PL). Sample marked with “x” (PM_{10}-no background, $PM_{2.5}$-with black background) relates to FL test, which seems to be not in line with the tendence and: is not included in PM_{10} trend; is included in the $PM_{2.5}$ trend (solid line) or not included in the $PM_{2.5}$ trend (dotted line).

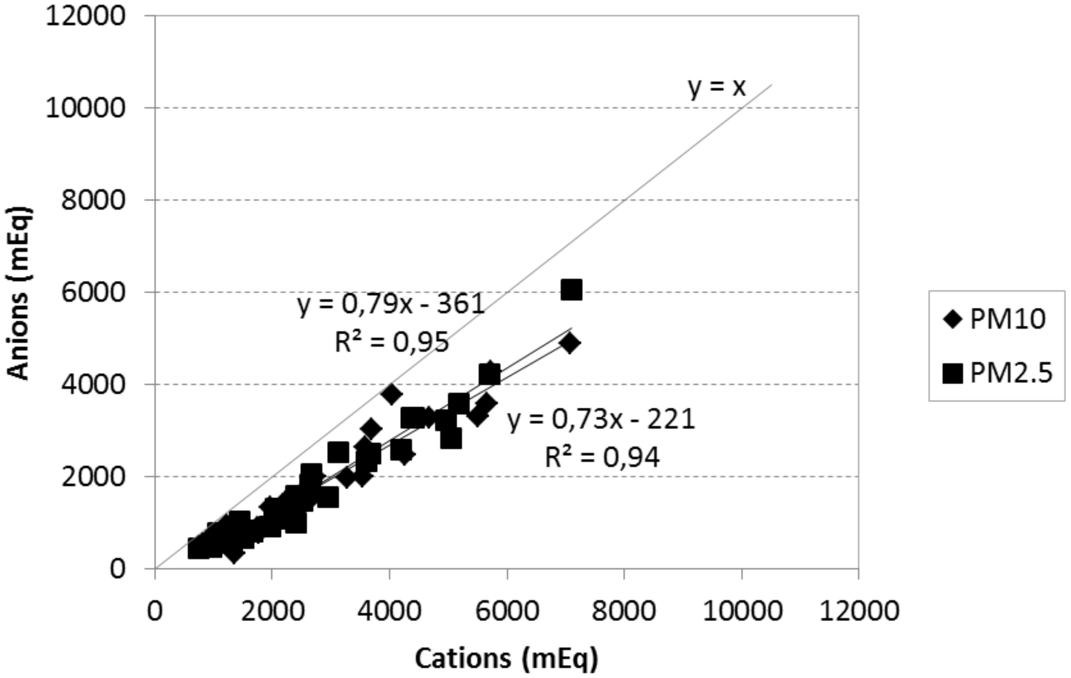

Figure 5b. Ion balance: logwood and briquettes, for both size fractions.

The most abundant inorganic ash constituents found in wood (wood pellets) smoke particles extract are potassium (K^+) and sulfate (SO_4^{2-}) ions. Both represent concentrations lying nonambiguous over the limit of detection for the applied method (for the details see paragraph 6) and show a good agreement in emissions across both fractions (slope A=0.98 [PM_{10}] and 0.95 [$PM_{2.5}$]) of wood burning PM. Other situation was observed for pellets burning, where higher amounts of K^+ was noticed for PM_{10}.

The measurements of the non-soluble inorganic fraction (nominated in this work as “other inorganic ash components, consisting of over twenty elements – mostly metals) show much higher variability and less agreement between size fractions, being observed in higher concentrations in PM_{10}. This measurement is, however, burdened with threat of particle loss due to filter handling before the extraction. Prior to ICP extraction the XRF measurement is conducted and during this experiment it was observed that parts of particle loading released from cellulose acetate filter matrices. The samples with visible damage were removed from the experiment; however it is possible that filters with less intensive and therefore not observable damage of particle load were analyzed and constitute to obtained result.

The relations between selected inorganic components are shown in Figures 6a and 6b.

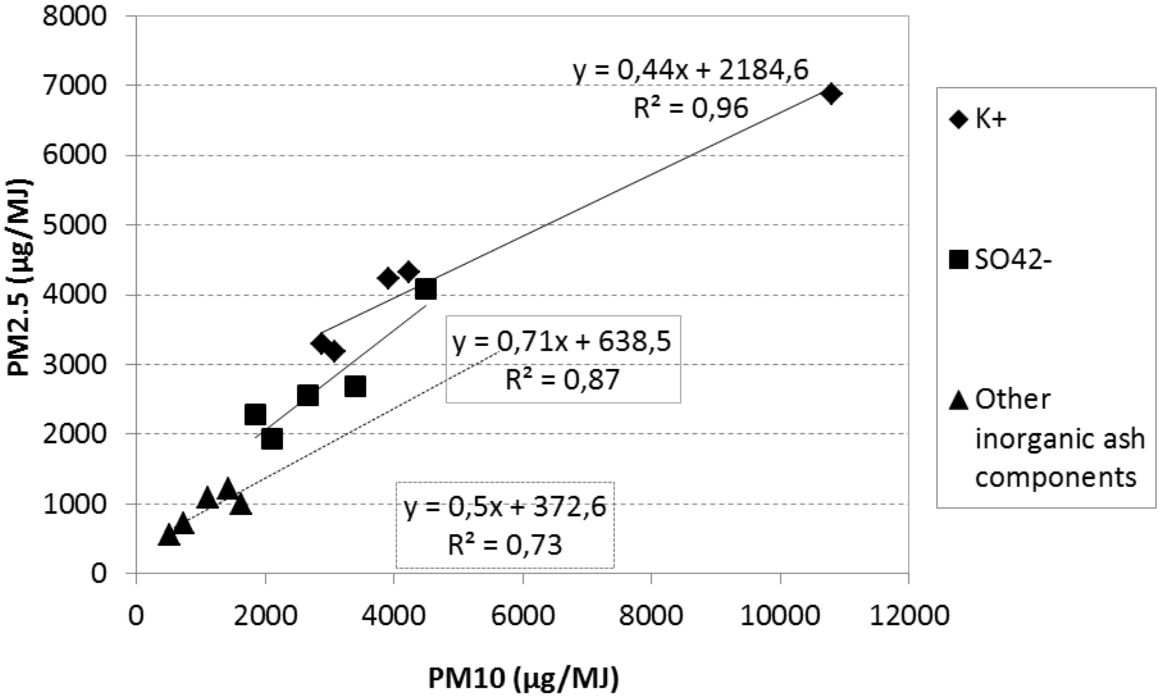

Figure 6a. Mass agreement of selected inorganic emissions from wood pellets burning (FL+PL), between PM_{10} and $PM_{2.5}$. The equation in solid-lined square relates to agreement between SO_4^{2-}concentrations in both size fractions, the one in dashed- line square relates to weak agreement observed for insoluble inorganic ash particles (triangles) and one without line representents weak across-fraction agreement for K^+ ions.

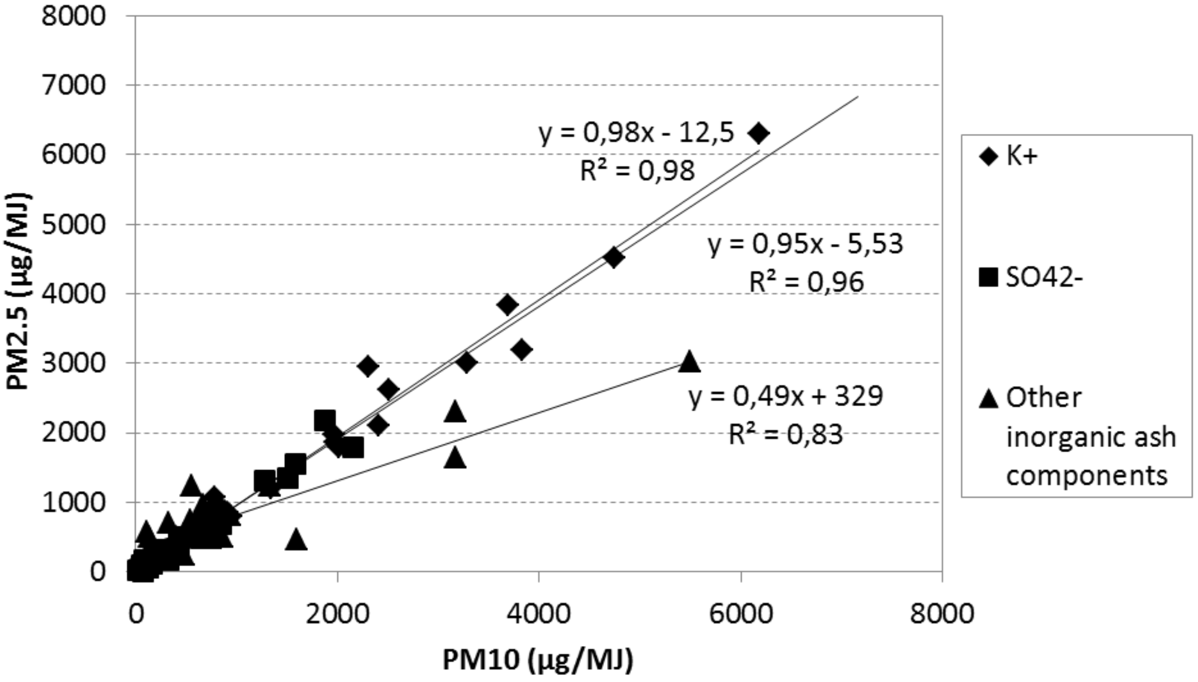

Figure 6b. Mass agreement of selected inorganic emissions from wood logs and briquettes burning, between PM_{10} and $PM_{2.5}$.

Congenial mass agreement was observed for carbonaceous fractions of the pellets experiments. For both, elemental- (EC) and organic carbon (OC) emission factors observed for pellets show a good correlation between size fractions (R^2 = 0.89 and 0.94 with slopes of 1.03 and 0.74 for EC and OC respectively).

No perfect fit was found for logwood and briquettes measurements (Figure 7). However, a linear relation with slope around 1, between most of samples could be noticed. In fact, if the detached points (marked with circles and representing EB and BP combustions) are removed, the relations become significant with a slope of 0.96 and R^2 of 0.93 (EC).

The OC fit represents the lower slope (0.9) and is less stable (R^2 of 0.86) pointing out that more measurements show a difference between both fractions.

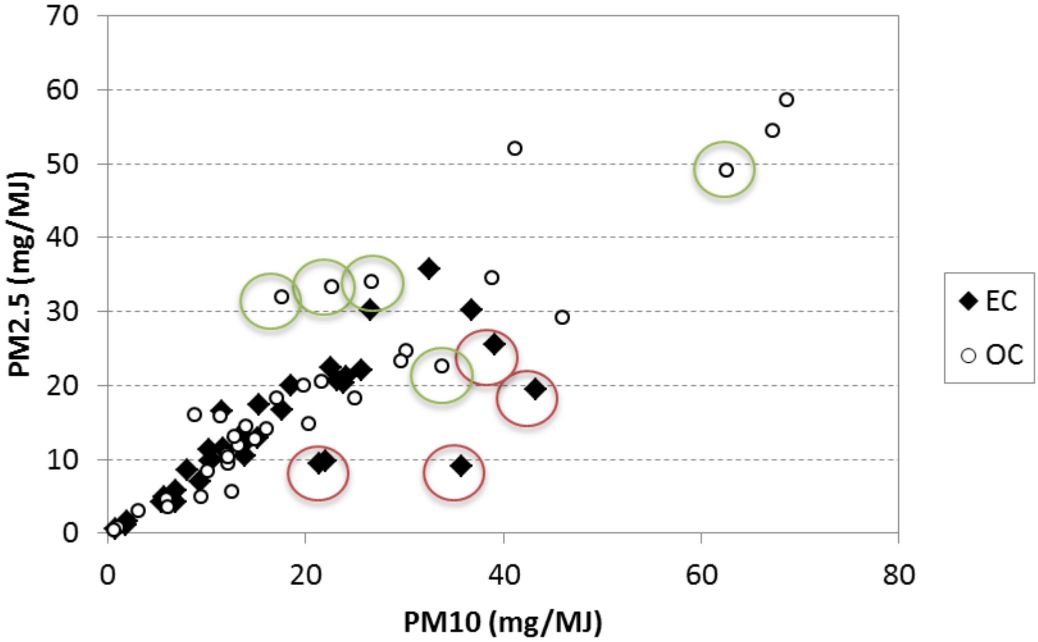

Figure 7. Size fraction agreement for carbonaceous emissions for wood log and briquettes combustion. The "susspected" data poits were marked with red circles in case of EC and green circles in case of OC emissions.

Further consideration of the points outside the regression range shows that the scattered points may be ascribed to a misleaded estimation of carbon fractions. This problem of wrong assessment of the split between OC and EC results very likely from the thick and dark particle loading on the filters (what was observed for both cases – EB and BP samples observed in this study). For $PM_{2.5}$ the measured EC levels were lower. It is assumed, from visual analysis of the EC/OC analysis results that the PM_{10} data with higher EC assessment may fit better in cases of both EB and BP samples (Figure 8).

Moreover it could be noticed that the PM_{10} OC content is in cases of softwoods (SF, NS, BP, SP) somewhat higher, than for $PM_{2.5}$, what could explain, at least partially the observed difference between the masses of both size fractions for these samples.

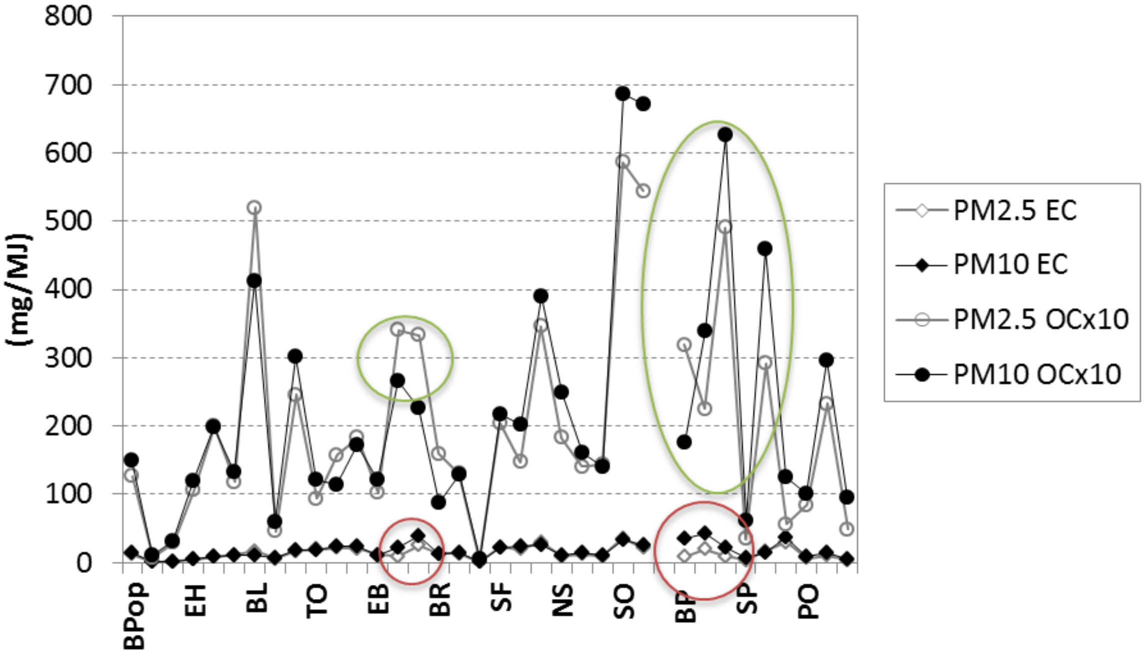

Figure 8. Comparison of carbonaceous emissions for all wood logs and briquettes burning samples (OC values multiplied by a factor of 10 for better dimention). Green and red circles are adequate to samples marked in the Figure 7. For both EB samples and the first sample of BP the elemental carbon in the $PM_{2.5}$ fraction is much lower than in PM_{10}, while organic carbon is higher, what may describe an analytical problem with assesing the OC/EC split for highly loaden samples.

Similarly to PM constituents presented above also organic tracers: levoglucosan, mannosan, galactosan, retene and benzo(a)pyrene represented a good agreement between PM_{10} and $PM_{2.5}$ masses. Small differences favoring PM_{10} were observable in case of PAHs (ideno(c,d)fluoranthene, ideno(cd)pyrene, benzo(ghi)perylene , anthranthrene and dibenzo(ah)anthracene). The alkanes (C22-C34) were found in very low, but similar concentrations in both fractions, except two samples with highest organic fraction (sessile oak and old leaves). The most abundant n-alkanes found in wood smoke samples were C26-C30, predominantly in the $PM_{2.5}$ fraction.

Summing up, none of the analyzed components (or compound class) resulted in significant and clear difference of mass emissions between PM_{10} and $PM_{2.5}$. Only OC results, evidenced a gentle distinction, in case of softwood samples. This result may lead to conclusion that the difference in overall mass between PM_{10} and $PM_{2.5}$ observed for softwood combustion tests might to some extend be attributed to compounds which were not analyzed not analyzed in this study, but are known to occur in softwood burning emissions (due to characteristic of raw softwood fuels, e.g., Rogge et al., 1998; McDonald et al., 2000; Oros and Simoneit, 2001) e.g., dicarboxylic acids or resin derivates.

A part of the observed mass difference might be also assigned to humidity associated with the sampled particles, therefore the mass differences reported here should be treated rather as a tendency than as significant values.

Concerning the information presented above and no significant differences in the chemical characteristics for PM_{10} and $PM_{2.5}$, the following discussion focused on the PM_{10}, samples, which represent the most often measured and modeled particulate matter size fraction in Central European countries.

2.9. Regional specific emission profiles

The data from this study do not suffice for comprehensive emission profiles for Central European countries.

However, with the obtained emission information it is possible to investigate potential differences of wood smoke emissions between countries due to differencies of forest coverage and wood grown in these countries.

Here, region-oriented emission profiles have been tailored and comprise just compounds of highest significance for wood burning emissions. The profiles consist of emission factors for particulate matter, OC, EC, levoglucosan, mannosan, sum of inorganic ions and sum of other inorganic ash particles. Similar profiles were presented also for BaP emissions in **Chapter 5**, where PAHs are being discussed. It should be noticed that in the case of BaP “hardwood scenario” concerns a share of 90%/10% for hardwood and briquettes and does not include any softwood fuel.

Below two country specific scenarios of wood shares are presented.

In the first one it is assumed that the users of small scale heating systems choose more often hardwood fuels, for instance due to their higher calorific value and burning effects. For this reason a hardwood/softwood/briquettes ratio is assessed to 70/20/10% (HWSC).

The second scenario, argued in **Chapter 3**, is based on the assumption that fuel share in the domestic sector equals, more or less, the share of wood species in regional forests and therefore based on the national forest inventories information (FISC). Tables 2a,b and c presents: (a) the share of trees growing in the Central European forests; (b) share of fuelwood calculated according to Scenario 1; (c) share of fuelwood calculated according to Scenario 2.

Table 2a. Tree species, in percent of forest area in Austria and neighboring countries (as given in **Chapter 3**) presented as % of specie per wood area. The national codes are explained in the list of abbreviations at the beginning of the thesis.

	AT	S-DE	CZ	HU	SK	SI	N-IT	CH
EH			1	5	6		3	
EB	10	16	7	6	31	31	1	18
BPop				11				
TO	2	7	7	11	3	7		2
SO				21	11		1	
PO								
BL				24	2			
Other HW	12	13	9	11	7	14	2	13
Σ Hardwood	24	36	24	89	60	52	7	33
SF	2	4	1		4	8	1	13
EL	5	2	4		2		28	6
NS	54	42	53		23	32	53	42
BP	1	15	17		7	6		4
SP	5						11	
Other SW	1	1		12	1	2		1
Σ Softwood	68	64	75	12	37	48	93	66

Table 2b. Scenario 1: HWSC. Use of wood for household heating assessed to ratio 70/20/10% (hardwood/softwood/briquettes) and adapted to area of regional grown species (presented in % of species share).

Scenario 1: HWSC	AT	S-DE	CZ	HU	SK	SI	N-IT	CH
EH			3	4	7		30	
EB	29	31	20	5	36	42	10	38
BPop				9				
TO	6	14	20	9	4	9		4
SO				17	13		10	
PO								
BL				19	2			
Other HW	35	25	26	9	8	19	20	28
Σ Hardwood	70	70	70	70	70	70	70	70
SF	1	1	<1		2	3	<1	4
EL	1	1	1		1		6	2
NS	16	13	14		12	13	11	13
BP	<1	5	5		4	3		1
SP	1						2	
Other SW	<1	<1		20	1	1		<1
Σ Softwood	20	20	20	20	20	20	20	20

Table 2c. Scenario 2: FISC. Briquettes use account to around 10%; wood types, distributed as grown in the local forsts account to 90%; exception: AT: use of wood = share of growth areas, remaining part (accounting in the forest to blanks, gaps and shrubs) is related to use of wood briquettes.

Scenario 2: FISC	AT	S-DE	CZ	HU	SK	SI	N-IT	CH
EH			1	5	5		3	
EB	10	14	6	5	28	28	1	16
Bpop				10				
TO	2	6	6	10	3	6		2
SO				19	10		1	
PO								
BL				22	2			
Other HW	12	12	8	10	6	13	2	12
Σ Hardwood	24	32	22	80	54	47	6	30
SF	2	4	1		4	7	1	12
EL	5	2	4		2		25	5
NS	54	38	48		21	29	48	38
BP	1	14	15		6	5		4
SP	5						10	
Other SW	1	1		11	1	2		1
Σ Softwood	68	58	68	11	33	43	84	59

Tables 3a,b show emission profiles calculated for Mid European countries for the hardwood and forest inventory scenarios. It is evident from table 3a,b that the PM emission factors proposed for both fuel share patterns are similar for whole concerned region. It demonstrates that for assessing of regional emission profiles the influence of the different burning technologies has to be considered.

Table 3a. Regional specific wood smoke emission factors for PM_{10} the chemical balance and combustion tracer compounds for Scenario 1 (HWSC).

	mg MJ^{-1}	% PM_{10}							
Scenario 1	PM_{10}	EC	OC	Inorg. ions	Other inorg. ash particles		Levoglucosan	Mannosan	Lev/Man
AT	64.7	27.0	30.7	4.78	1.39		5.33	0.48	11.2
S-DE	66.4	27.8	31.3	4.87	1.52		6.00	0.47	12.7
CZ	66.1	26.1	31.2	4.98	1.69		7.33	0.52	14.1
HU	63.4	26.4	31.8	5.97	1.54		7.50	0.51	14.7
SK	63.0	28.4	31.4	4.86	1.41		5.11	0.44	11.6
SI	65.8	28.8	31.1	4.72	1.37		4.61	0.42	10.9
N-IT	54.6	24.2	32.9	4.69	1.50		6.51	0.55	11.8
CH	65.1	28.3	31.0	4.81	1.30		4.46	0.45	9.9

Table 3b. Regional specific wood smoke emission factors for PM_{10} the chemical balance and combustion tracer compounds for Scenario 2 (FISC).

	mg MJ^{-1}	% PM_{10}							
Scenario 2	PM_{10}	EC	OC	Inorg. ions	Other inorg. ash particles		Levoglucosan	Mannosan	Lev/Man
AT	55.8	25.8	33.0	3.39	1.55		5.61	1.16	4.9
S-DE	60.4	27.6	32.7	3.77	1.58		5.33	0.91	5.9
CZ	55.1	26.2	32.7	3.24	1.60		5.77	1.08	5.3
HU	63.3	25.8	31.4	6.24	1.56		7.91	0.42	18.7
SK	60.2	27.4	31.1	4.41	1.43		4.99	0.61	8.1
SI	63.6	27.6	31.3	4.25	1.48		4.66	0.70	6.6
N-IT	44.5	26.1	36.1	3.17	1.42		6.53	1.55	4.2
CH	60.9	26.4	31.8	4.13	1.51		4.86	0.98	5.0

The regional PM_{10} emission factors calculated for Scenario 1 (assessing 70% of hardwood) are slightly higher and more stable among selected countries than those calculated with Scenario 2. Alike, most PM components represent similar rates in the both cases. Nevertheless, a few exceptions, showing a higher relation to wood type were found. The crucial difference of a “country specific compound” is observed for mannosan. This anhydrosugar, which is formed during pyrolisis of hemicelluloses, appears to be a deciding factor influencing the Lev/Man ratios, used for discrimination between hardwood and softwood combustion.

Next to the Lev/Man ratio also the PAH retene has been reported to be emitted in different amounts from softwood and hardwood combustion (e.g., Fine et al., 2002). Therefore a difference in regional emissions has been also predicted. However, in this study higher retene emission rates were found also for temperate oaks (PO,SO), which contribute 1-19% to the overall share of fuelwoods in examined countries, therefore the differences in retene emissions do not always show the same behavior as the Lev/Man ratios. The inversely proportional relation between Lev/Man ratios and retene is better noticeable for Scenario 2 of fuel share, as seen in Figure 9.

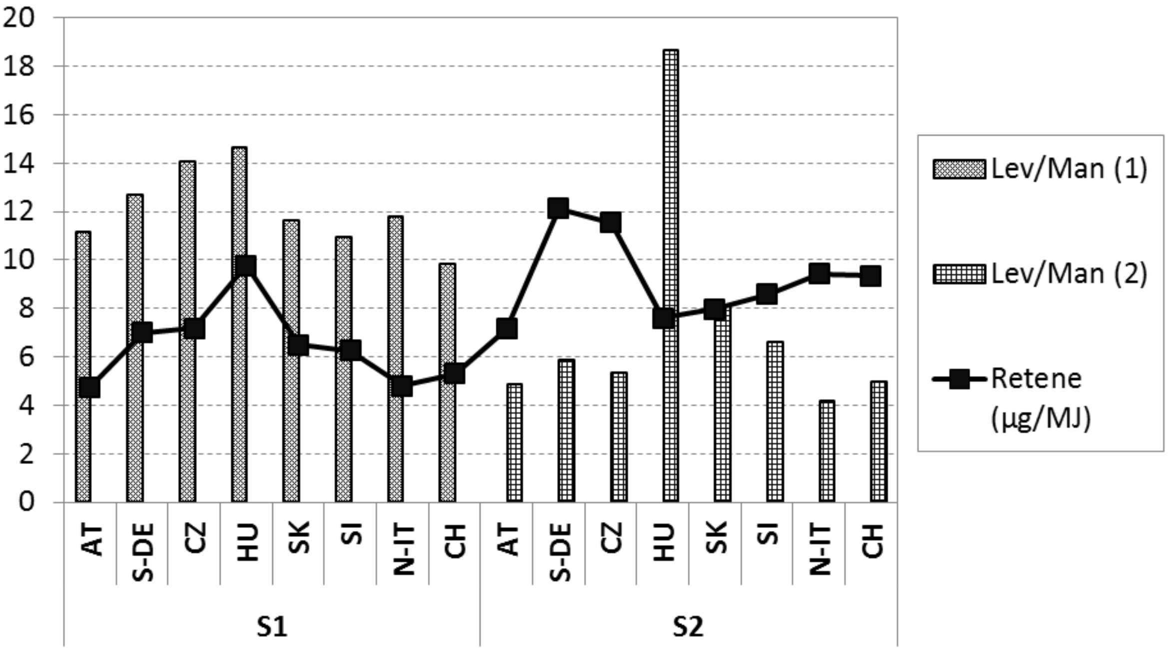

Figure 9. Lev/Man ratios and retene emission factors estimated for both considered fuelwood share scenarios: (S1) and (S2).

2.10. Estimation of ambient odor in Austria

A group of detailed source apportionment studies was done within a project AQUELLA (e.g., Bauer et al.,2009) at the TUV in the bygone years. Particulate matter sources were assessed, using a macro tracer approach for Burgenland, Lower Austria, Carinthia, Salzburg, Styria, Vienna and Upper Austria. The chemical profile for residential wood combustion emissions from burning of “Austrian” bio-fuel types (spruce, beech, softwood briquettes, oak and larch) obtained within experiments conducted with a residential tiled stove, typical for Alpine region (Schmidl et al., 2008b, data from “Kachelofenverband” cited therein). The study of Schmidl et al. (2008b) and further reports for the project AQUELLA estimate the PM/Lev ratio to 10.7, 11.2 and 14.2 adequately to region and locally used wood.

The result of this study shows that it might be possible to predict the wood smoke odor nuisance using wood smoke particulate matter data. The prediction of odor nuisance might be conducted using different scenarios of firewood share. As an example, four possible portioning scenarios for Austrian sites were checked:

- the “Austrian mix” reported by Schmidl et al. [2008a];
- the hardwood/softwood scenario obtained from the levoglucosan to mannosan ratios (Schmidl, 2008b);
- the “hardwood scenario” as described in the previous paragraph (HWSC);
- the “share according to grown species” scenario, as described in the previous paragraph (FISC).

Each scenario includes about 10% share of wood briquettes. The result comprised in the Table 4 points out, that not much difference in odor perception threshold is expected while applying those assumptions. The result obtained from Lev/Man based calculation is surprisingly similar with the hardwood scenario.

Table 4. Discrimation of odor perception thresholds, for three fuelwood scenarios, for Austria.

	Scenario	Biomass	Share (%)	Single odor perception thresholds (µg m^{-3})	Odor perception threshold (µg m^{-3} PM_{10})
1	Austrian Mix	Beech	20	60.9	30
		Briquettes	10	27.5	
		Spruce	70	20.8	
2	Lev/Man ratios for AQUELLA Sites*	Briquettes	10	27.5	43
		Hardwood	17	61.2	
		Softwood	73	40.2	
3	“Hardwood” scenario (70% of hardwood and 20% of softwood used according to species grown in forests)	Beech	29	60.9	50
		Temperate oaks	6	61.5	
		Fir	1	28.7	
		Larch	1	14.2	
		Spruce	16	20.8	
		Black pine	<1	98.6	
		Scots pine	1	38.6	
		Other conifers	<1	ND	
		Other decedious	35	61.0	
		Area not covered with forest	9		
		Undefined = Briquettes	10	27.5	
4	According to grown species (%forest area)	Beech	10	60.9	33
		Temperate oaks	2	61.5	
		Fir	2	28.7	
		Larch	5	14.2	
		Spruce	54	20.8	
		Black pine	1	98.6	
		Scots pine	5	38.6	
		Other conifers	1	ND	
		Other deciduous	12	61.0	
		Area not covered with forest	8		
		Undefined = Briquettes	9	27.5	

* Average value, calculated from data extracted for AQUELLA sites listed in Table 4; % of softwood derived from equation proposed by Schmidl et al. (2008b), based on spruce and beech; ND... no data

Table 5 comprises wood smoke PM concentrations, reported within the Project AQUELLA for selected Austrian sites, measured during the cold season (October-April). Reported data relate to days or periods, which do not necessarily exceed the daily ambient PM_{10} limit of 50 µg m^{-3}, but represent the highest wood smoke contribution (calculated according to levoglucosan concentrations, using the factors [F_{ws}] reported above) to ambient PM_{10} (PM_{WS}). The compilation points out the regions in Austria, where wood smoke odor nuisance may cause a significant annoyance (recognizable for averaged data). In all considered cases the PM_{WS} was lower than perception threshold calculated for wood smoke odor. Nevertheless, concerning a 15% error (as calculated for odor threshold estimations, **Paragraph 6**) a possible odor nuisance was predicted for four stations. The prognosis is related to different scenarios of fuelwood use and shows that in both cases establishing use of spruce and beech as main fuelwoods the odor perception would occur already at lower ambient wood smoke PM concentrations. As noticed in the Table 4, the wood smoke odor may be attributed mostly to background, rural stations.

Table 5. Estimation of ambient odor nuisance caused by wood smoke measured in Austrian background monitoring stations. PM concentrations for periods (days) with the highest wood smoke contribution extracted from data obtained within personal communication with Dr. Heidi Bauer and Barbara Klatzer, data based on compilation from 16.06.2009.

Province	Measurement station	Type of station	PM µg m^{-3}	PM$_{WS}$ µg m^{-3}	Lev/ Man	F$_{ws}$	Odor perception			
							Scenario1	Scenario 2	Scenario 3	Scenario 4
							T_p = 30	T_p = 43	T_p= 50	T_p = 33
Burgenland	HEILIGEN-KREUZ	BCG/RU	62.9	27	7.4	14.2	possible	-	-	possible
	KITTSEE	IN/SU	44.4	8.9	5.3	11.2	-	-	-	-
Carinthia	GURTSCHI-TSCHACH	BCG/RU	33.9	17	3.4	10.7	-	-	-	-
	KLAGENFURT KOSCHATSTR.	BCG/UB	49.0	21	7.6	14.2	-	-	-	-
	KLAGENFURT VÖLKER-MARKTERSTR.	TR/UB	70.1	16	4.7	10.7	-	-	-	-
	LAVAMÜND	BCG/RU	62.4	25	6.7	11.2	possible	-	-	possible
Lower Austria	MISTELBACH	BCG/RU	42.4	12	8.2	14.2	-	-	-	-
	ST. PÖLTEN	ND	54.8	13	5.2	11.2	-	-	-	-
	SCHWECHAT	IN/SU	52.6	9.9	5.4	11.2	-	-	-	-
	STIXNEUSIDL	BCG/RU	125.8	27	9.1	14.2	possible	-	-	possible
Salzburg	SALZBURG ANTHERING	BCG	32.3	8.7	5.5	11.2	-	-	-	-
	SALZBURG LEHEN	BCG/UB	45.5	14	6.0	11.2	-	-	-	-
	SALZBURG RUDOLFSPLATZ	TR/UB	74.2	12	5.7	11.2	-	-	-	-
Styria	GRAZ BOCKBERG	BCG	36.3	14	6.2	11.2	-	-	-	-
	GRAZ DON BOSCO	TR/UB	93.7	21	4.7	10.7	-	-	-	-
	GRAZ SÜD	BCG/UB	99.2	24	4.6	10.7	possible	-	-	possible
	HARTBERG	BCG/UB	101.1	12	4.3	10.7	-	-	-	-
	KNITTELFED	BCG/UB	50.8	19	2.9	10.7	-	-	-	-
	KÖFLACH	BCG/UB	55.8	13	4.6	10.7	-	-	-	-
	PEGGAU	IN/RU: regional area	69.5	17	5.9	11.2	-	-	-	-
Upper Austria	ENZENKIRCHEN	BCG/RU regionalarea	46.9	13	5.3	11.2	-	-	-	-
	LINZ NEUE WELT	IN/UB	57.0	11	4.5	10.7	-	-	-	-
	LINZ RÖMERBERG	TR/UB	109.6	14	4.2	10.7	-	-	-	-
	STEYREGG	IN/SU	45.8	1	4.4	10.7	-	-	-	-
Vienna	KENDLERSTR.	BCG/UB	106.1	13	5.3	10.7	-	-	-	-
	LOBAU	BCG/UB	79.3	9.2	7.1	14.2	-	-	-	-
	RINNBÖCKSTR.	TR/UB	69.8	8.9	4.7	10.7	-	-	-	-
	SCHAFBERG	BCG/SU	76.5	7.3	5.2	11.2	-	-	-	-

T_p… perception threshold;BCG…background; UB…urban; SU…suburban; RU…rural; TR…traffic; IN…industrial ND…no data

Combined data derived by Ebbinghaus (1993) and from this study show, that the strongest wood smoke odor nuisance can be expected during the ignition phase of burning (when most of the emissions are generated).

For ambient air it is expected that the strongest peak for odor perception occurs during the cold season, mostly in the morning and evening hours, when people are in their homes and a lot of burnings is being launched. Most probably the odor nuisance would looses its intensity within relatively short time. Due to this short-time character of wood smoke odor occurrence and big discrepancies in concentration within a short time it is hardly possible to observe the intensity of odor effect for averaged data, as presented in Table 5. Glasius et al. (2006) and Poulain et al. (2011) report a diurnal variation of wood smoke PM with a factor of 2-4. If this would be applied to concentrations listed in Table 5, it could be concluded, that wood smoke smell can be recognized at all Austrian sites characterized by occurrence of a “wood burning community”.

An important further step would be the investigation of the short term maxima of wood smoke odor as well as the influence of different stove types.

2.11. Conclusions

To summarize, since domestic biomass burning is becoming a popular alternative, favored from economic and environmental point of view, the emissions connected with this source can not be neglected.

The most discussed topic connected to small scale combustion is emission of fine particles, which, due to their physico-chemical features, establish a high potential risk for climate and human health.

Wood smoke particulate matter is known to be a massive problem in residential areas, which could be denominated as “wood burning societies”. Emission factors for such locations are burdened with very large dispersion. Already during laboratory tests within this project (2 stoves, 16 fuel types) highly variable results were found for replicate experiments (typically 30-40% for most of compounds). A large variation is expected in the real world conditions where stove types , fuel use and operational parameters are not as controlled as in the laboratory. However, the ambient concentrations are an integration over a large number of emitters, thus the scientific skill to derive regionally valid emission factors is to estimate or assess the types of appliances in a region including their wood use and operational habits.

Gaseous emissions were found to be much higher (one order of magnitude) for the manually fired log wood stove, compared with pellet burner. Only NO_x does not show this trend and correlates rather with nitrogen content in the fuel, than with combustion parameters.

Pellet burner emissions are not generating odor nuisance, while a wide range of odor thresholds was found for burning of different types of wood. Although a significant difference was found between hardwood and softwood odor thresholds, there were high- and low emitting species among both groups.

The PM_{10} absolute emissions were comparable with $PM_{2.5}$ emissions for hardwood (except temperate oak species), briquettes and pellets tests. Contrary, differences of PM_{10} and $PM_{2.5}$ emissions were found for softwood species and garden waste.

Both PM_{10} and $PM_{2.5}$ consist mostly of carbonaceous particles, for logwood with TC levels of about 55%, with highest value for a combustion test with BP (79%). Contrary wood pellets were characterized only by about 20% of carbonaceous particles in the emission. Relatively high elemental carbon (EC) concentrations were found for the chimney stovein comparison to data derived for other stoves (e.g., a traditional tiled stove).

The most prominent compound class in pellets burning PM emissions was inorganic ash, while for logwood burning - carbonaceous organic tracers. Highest values found for single constituents of PM of tested biomass smoke for both systems were elemental carbon, levoglucosan and potassium.

Polycyclic aromatic hydrocarbons (PAHs) measured in the particulate phase were found in notable concentrations and showed a large variation between combustion tests. The highest emitted toxic particulate phase PAHs were fluoranthenes (BbF, BjF, BkF), and the fuel with highest toxic PAHs emissions were old leaves followed by TO. Benzo(a)pyrene (BaP) was found in all measured samples. The lowest emitting wood species generated around twice to three times higher BaP concentrations than pellets. The highest BaP emissions were nearly 20 times higher than those from pellet combustion. BaP emissions were mostly in line with EC concentration what points out the same formation pathway of both classes. BaP emissions in rage, as found during the experiment, may contribute significantly to the ambient particulate matter, and result in violation of ambient BaP limitations. In the worst case scenario, during a strong wood burning event in the atmosphere the ambient BaP concentrations as derived from this study may reach even 3-6 ng m^{-3}.

It was observed that very fast burning (with high burn rate) cause higher BaP emissions, than slow smoldering. The most possible factor influencing BaP emissions was the proper and sufficient access of combustion air to the burning chamber. Oxygen supply is supported by other factors like fuel features, combustion chamber construction, etc. BaP concentrations for the same wood types measured within three different campaigns in the emissions from three different stoves showed for beech, oak and spruce distinguishable trends in BaP/PM_{10} ratios. Concluding, the emissions are dependent on a whole system of parameters, which could be combined accidentally and therefore are hardly predictable.

These findings differ from those reported for previous TUV studies, where CO and particulate matter emissions were reported to be influenced mainly by wood type, within a group of similar stoves. According to knowledge gained here the variation of emissions for the same wood type from burning in the same stove under comparable conditions may be significant.

The most wood type dependent vale measured was odor. It was found that odor relates mostly to C_xH_y emissions, could be however also modeled with particulate matter. According to a relation between odor and PM concentration in measured emission it was assessed that the wood smoke odor is recognizable when ambient wood smoke PM concentration exceed 30 µg m^{-3} (if derived for the “Austrian mix”: spruce, beech and briquettes).

A wood stove change out from “old” to “new” technologies is expected to result in the reduction of overall PM emissions. According to different sources a reduction between a factor of 8 and 10 for the particulate matter mass may be expected. However, this study showed that modern technology stoves can bring only a limited improvement in case of PAHs (e.g., BaP) emissions; about three times lower than what is expected for PM.

The work confirmed the findings of a previous study done at TUV, that two separate profiles should be used for source apportionment for chimney logwood stoves and pellet stoves.

Emission factors and odor thresholds obtained for furnaces and fuels tested here could be applied for emission inventorying and source apportionment studies, should be, however, combined with source profiles obtained for other stoves.

Assuming that biomass burned in small scale appliances is obtained mostly from local markets or collected in the garden (forest), the biogeographically differences become significant for emissions, which relay on fuel type. The most prominent difference in the Central Europe could be observed between Alpine lands and Pannonian Plains. Results of this project show the difference in emissions only for two stoves, but even in this case it was verifiable.

It is hoped that this study will stimulate further investigations in this field.

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3. Odor, gaseous and PM_{10} emissions from small scale combustion of wood types indigenous to Central Europe[1]

Abstract

In this study, we investigated the emissions, including odor, from log wood stoves, burning wood types indigenous to mid-European countries such as Austria, Czech Republic, Hungary, Slovak Republic, Slovenia, Switzerland, as well as Baden-Württemberg and Bavaria (Germany) and South Tyrol (Italy). The investigations were performed with a modern, certified, 8 kW, manually fired, log wood stove, and the results were compared to emissions from a modern 9 kW pellet stove. The investigated wood types were deciduous species: black locust, black poplar, European hornbeam, European beech, pedunculate oak (also known as " common oak"), sessile oak, turkey oak; and conifers: Austrian black pine, European larch, Norway spruce, Scots pine, silver fir, as well as hardwood briquettes. In addition, "garden biomass" such as pine cones, pine needles and dry leaves were burnt in the log wood stove. The pellet stove was fired with softwood pellets.

The composite average emission rates for log wood and briquettes were 2030 mg MJ^{-1} for CO; 89 mg MJ^{-1} for NO_x, 311 mg MJ^{-1} for C_xH_y, 67 mg MJ^{-1} for particulate matter PM_{10} and average odor concentration was at 2430 OU m^{-3}. CO, C_xH_y and PM_{10} emissions from pellets combustion were lower by factors of 10, 13 and 3, while considering NO_x - comparable to the log wood emissions. Odor from pellets combustion was not detectable. C_xH_y and PM_{10} emissions from garden biomass (needles and leaves) burning were 10 times higher than for log wood, while CO and NO_x rise only slightly. Odor levels ranged from not detectable (pellets) to around 19000 OU m^{-3} (dry leaves). The odor concentration correlated with CO, C_xH_y and PM_{10}. For log wood combustion average odor ranged from 536 OU m^{-3} for hornbeam to 5217 OU m^{-3} for fir, indicating a considerable influence of the wood type on odor concentration.

Keywords: wood smoke, odor, biomass combustion, particulate emissions, pellet stove, log wood stove

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[1] …Magdalena Kistler, Christoph Schmidl, Emmanuel Padouvas, Heinrich Giebl, Johann Lohninger, Reinhard Ellinger, Heidi Bauer, Hans Puxbaum, 2012. Atmospheric Environment 51, 86-93.

Research highlights:

- Study reports emissions from burning of 12 wood types and pellets in modern stoves.
- We examine CO, hydrocarbons (C_xH_y), PM_{10} and odor.
- Emissions show high inter-species variability.
- Odor from wood burning is PM_{10} and C_xH_y related and is formed mostly during smoldering.
- Pellets burning in an automatically operated stove does not cause odor.

1. Introduction

In the current climate issue, biomass combustion is one of the recommended technologies for reducing fossil fuel consumption. Biomass combustion, however, is a source of fine particles (PM), carbon monoxide (CO), nitrogen oxides (NO_x) and volatile organic compounds (VOC), including toxic and carcinogenic constituents, such as polycyclic aromatic hydrocarbons (PAH). The emissions depend crucially on fuel type, combustion technology, combustor type and individual parameters, such as lighting the fuel and operation habits.

As far as the combustion technology is concerned, highest emitters are manually operated small units (fireplaces, stoves) when fired with wood logs or “primitive fuel” (e.g. leaves, twigs). Fireplaces and stoves emissions have been reported for US wood types (e.g., Fine et al., 2004 and other references cited therein); Northern European wood (e.g., Johansson et al., 2003; Sippula et al., 2007; Boman et al., 2011; Pettersson et al., 2011), Western Mediterranean wood types (Gonçalves at al., 2010), wood from European Alpine regions (e.g. Schmidl et al., 2008, 2011, Bari et al., 2009), and for fuels used in Asia for cooking and heating (e.g. Sheesley et al., 2003).

Little attention has been directed to an additional problem encountered with biomass combustion, the odor. In literature pertaining to odor prevention, biomass combustion is considered as a source, but quantitative data are practically absent. For the improvement of working and living conditions, many countries apply regulations to limit odorous emissions from various sources (Henshaw et al., 2006). Nicell (2009) describes facilities, activities and chemicals identified as source of potentially offensive odors. This study does not explicitly mention wood smoke as a potential odorant, however, phenols, which are important constituents of wood smoke (Kjällstrand et al., 2000, Kjällstrand and Petersson, 2001), are considered. Bari et al. (2010), report about wood smoke smell, however not in a quantitative manner. The first source with quantitative odor data from biomass combustion so far appears to be a master thesis (Ebbinghaus, 1993) reporting data from combustion of mixed mid-European wood types with different moisture content in a 40 kW boiler. It reports five-minute averages maximum peaks for dry log wood of 30000 -105000 OU m^{-3} in wood smoke, with accompanying very high CO emissions of around 4% v/v., indicating prevalence of smoldering combustion conditions.

Around 26% domestic applied thermal energy in EU households comes from renewable sources, among which biomass combustion is predominant (98%) (European Biomass Association, 2007). Being aware of the potential increase in emissions of major and minor pollutants, including odorous substances, we launched a series of investigations including olfactometric measurements, focused on burning wood types from Central Europe, of which several have not been tested until now. Logwood combustion tests were performed on a test stand with a manually operated, typical modern stove used for space heating of homes in the region. The results were compared with an automated, small pellet combustor of newest technology.

This paper reports the results of odor-, gas- and PM_{10} mass emissions and the dependence of odor levels on gas or particulate matter concentrations. The detailed chemical analyses of particulate emissions including wood smoke tracers and PAHs are to be presented in further communications.

2. Experimental

2.1. Stove and fuel choice

Tests with wood logs and "garden biomass" were performed with a modern, 8kW "chimney type" iron, log wood stove with fireclay lining ("A"). This manually loaded stove is certified to fulfill the current Austrian emission standards defined in state laws, e.g. for Vienna in LGBl. (2005). Combustion air is provided through a grate in the bottom (primary air) and a slit in the back wall (secondary air). Exhaust gases are redirected two times prior to entering the chimney. Airflow is controlled manually via rotary knob connected to a valve system that adjusts both primary and secondary combustion airflow. Our test procedure for log wood and briquettes included two fuel loads starting from the cold stove and adding the second load after burn down of the previous load (when CO_2 concentration in exhaust falls below 3%). Each load consisted of around 1.3kg of wood (2 or 3 wood logs sized on the average 3x5x25 cm, assuring a full power output), totaling around 2.6 kg fuel per test (Table 2). Ignition was performed with commercial lighter cubes (2-3 cubes, trade name ''ECOMA''). The test ended when the CO_2 concentration in exhaust dropped below 3%. The total duration of a test procedure was 50-80 min. The tests with garden biomass were performed with around 1.2 kg of fuel and the test duration was 20-30 min (Table 2). The stove was filled for the first load, then ignited and several times refueled.

Due to sampling over whole burning (inclusive start up phase) the test procedure is close to "reality" since the products of incomplete combustion of the ignition are included in our measurement cycle.

The second test stove ("B") is a modern automatically fired pellet burner with internal pellet storage. The fuel is supplied to the combustion chamber via an "auger screw". Combustion air supply is adjusted adequately for the selected thermal output by a fan situated in the flue gas stream. Air enters through holes under the fuel bed. Both fuel load and fan speed are controlled automatically, only the percentage of power output (30 – 100%) is set by the user. Our test consisted of part load runs of about 75 min and full load runs of around 80-370. Ignition took place with an electrical resistance heater and air supply from a blower. The ignition phase was not included in tests with pellets.

Wood fuels were selected among tree species indigenous for Austria (AT), and neighboring countries (or regions): Czech Republic (CZ), Hungary (HU), Slovak Republic (SK), Slovenia (SI), Switzerland (CH), Baden-Württemberg and Bavaria (South Germany, DE) and South Tyrol (Northern Italy, IT). Tree species with abundance of more than 5% of the forest area in each country have been chosen for the test burns (data obtained from national forest inventories: Austrian Forest Inventory, 2010; Forest Inventory, Germany, 2010; Italian National Forest Inventory, 2010; Swiss Forest Inventory, 2010; as well as from national forest reports: Forest Report Hungary, 2009; Forest Report Czech Republic, 2008; Cop, 2007; Moravcik, 2007). Cylindrical hardwood briquettes ("Forest briketi" 28 cm, 8 cm diameter) were obtained from "Istrabenz Energetski Sistemi", Slovenia.

Table 1. Share of tree species in forests of selected Central European countries. (Sources: see text).

Wood		**Austria**	**Baden-Württemberg and Bavaria (Germany)**	**Czech Republic**	**Hungary**	**Slovak Republic**	**Slovenia**	**South Tyrol (Italy)**	**Switzerland**
Total forest cover [% of land area]		47	37	36	20	41	60	45	30
Botanic name	**Common name**	**(% of woodland area)**							
Carpinus betulus	European hornbeam			1	**5**	**6**		3	
Fagus sylvatica	European beech	**10**	**16**	**7**	**6**	**31**	**31**	1	**18**
Populus nigra	Black poplar				4(**11**)*		0		
Quercus cerris	Turkey oak	2[a]	**7**[a]	**7**[a]	**11**	3	**7**[a]	0	2[a]
Quercus petraea	Sessile oak				**21**[b]	**11**[b]		1[b]	
Quercus robur	Pedunculate oak								
Robinia pseudoacacia	Black locust				**24**	2			
Other deciduous		12	13	9	11	7	14	2	13
Total deciduous		24[d]	36	24	88	59	52	7	34
Abies alba	Silver fir	2	4	1		4	**8**	1	**13**
Larix decidua	European larch	**5**	2	4		2		**28**	**6**
Picea abies	Norway spruce	**54**	**42**	**53**		**23**	**32**	**53**	**42**
Pinus nigra	Austrian black pine	1	**15**[c]	**17**[c]		**7**[c]	**6**[c]	0	4[c]
Pinus sylvestris	Scots pine	**5**						**11**	
Other coniferous		1	1	0	12	1	2	0	1
Total coniferous		67[d]	64	75	12	41	48	93	66

*…4% correspond to Black poplar, while 11% is a contingent of all poplar types (including Hybrid poplar), [a]…sum of all oak species, [b]…sum of temperate oak species (*Q.petraea, Q.robur*), [c]…sum of all pine species, [d]… remaining 9% is dedicated to blanks, gaps and shrubs, for abbreviations see text.

In the series of 44 measurements seven types of hardwood, five types of softwood, briquettes (beech) and wood pellets were burned. In addition combustions of pine cones, dry pine needles and dry leaves (orchard leaves and maple) were performed, to obtain emissions from non conventional material, sometimes used for starting the firing of wood logs. The fuels were obtained from local markets or from private forest owners in Austria and Hungary; “garden biomass” (cones, needles and leaves) from a private garden. Logs were stored in a dry place to achieve relatively stable water content recommended for fuel wood. Sampling and calculation details are presented in Table 2. Elemental composition, ash and water content of tested fuels are listed in Table 3.

2.2. Gas emission measurement

Gas emission measurements started with the ignition of the fuel and were performed at a test stand (Notified Testing Laboratory for Combustion Systems, Institute of Chemical Engineering Vienna University of Technology). The gaseous emissions were determined continuously over the test period with a time resolution of 10 seconds. The test stand maintains a static pressure of 12 Pa in the chimney during the test by means of a blower. Measurements of exhaust gases followed in general the standards for automatically fired stoves (DIN EN 14785, 2006) and for manually fired systems (DIN EN 13240, 2001). Carbon monoxide (CO), nitrogen oxides (NO_x) and total gaseous organic compounds (C_xH_y) were assessed, as these emissions are regulated by legislation in Austria. The amount of oxygen (O_2) and carbon dioxide (CO_2) in the exhaust gas were determined in order to assess the combustion conditions.

The results of CO, NO_x, C_xH_y were calculated for standard conditions for temperature and pressure (STP, 273 K, 1013 hPa), and normalized to a volumetric oxygen content (O_{2ref}) of 13% in the exhaust gas, according to Equation 1. This procedure accounts for varying dilution factors due to differences in process control of the systems:

$c_S= \rho_S \cdot v_S(21\text{-}O_{2ref})/(21\text{-}O_{2meas})$ (Equation 1),

where s is one of the parameters CO, NO_x or C_xH_y; c_S is the concentration of the compound in mg m^{-3}; ρ_S are the densities of the gaseous components: 1.25 kg m^{-3} (CO), 2.05 kg m^{-3} (NO_2) and 1.64 kg m^{-3} (C_xH_y; propane equivalent), respectively; v_S is the volume mixing ratio of compound s in ppm determined in dry (CO, NO_x), or in wet exhaust (C_xH_y); O_{2ref} is the reference oxygen concentration of 13% and O_{2meas} is the average oxygen concentration during the measurement. All results were converted to mg MJ^{-1} using a conversion factor f_J resulting from Equation 2as (respectively Equation 2bs, for C_xH_y), where $E_{D(W)}$ is the quantity of dry (wet) exhaust in m^3 kg^{-1} and LHV is the lower heating value (MJ kg^{-1}). Results converted into different units are presented in Table 3s.

$f_J= 21E_D/((21\text{-}O_{2\ ref}) \cdot \text{LHV})$ (Equation 2a)

$f_J = 21E_W/((21\text{-}O_{2\ ref}) \cdot \text{LHV})$ (Equation 2b)

Conversion for PM_{10} is performed in analogy for dry gas from the measured mg m^{-3} STP at O_{2meas}, to the reference oxygen concentration (13% v/v).

2.3. Particulate matter sampling

Particulate matter ($PM_{2.5}$, PM_{10} and total particulate fraction) was collected on filters, after pre-dilution of the exhaust, over the whole combustion time (two continuous full-load runs). The dilution apparatus was constructed for previous studies and consists of two sampling lines, which were modified, for the current project purposes. The detailed characterization of the original particle sampling system is given in Schmidl et al. (2011). Our modifications included two separate lines for PM_{10} and $PM_{2.5}$ and a line without a pre-separation stage. The internal volume of dilution tunnel is 0.04 m^3, resulting in a residence time in the tunnel of 60 seconds. The sampling flow velocity into the $PM_{10}/PM_{2.5}$ sampling heads was higher than the flow in the dilution tunnel with $U_0/U = 0.3$, leading to super-isokinetic conditions. Sampling occurs at near ambient temperatures.

Most of the European studies so far used quartz, glass fiber or organic based front-filters for sampling without a back-filter for sampling artifact corrections (e.g., Kocbach et al., 2006, Boman et al., 2011). Jordan and Seen (2005) used a quartz front – quartz back up filter combination and observed 4% of the mass of the front filter at the back up filter.

Thus we notice that we have not used a back up filter to infer positive artifacts for the deposit on the front filter. This type of sampling however is until now quite common in Europe and thus our results are comparable to the results from earlier European studies.

Exhaust from the chimney was collected about two meters above the burning chamber. In the first step, the exhaust was diluted and entered a 0.2 m wide and one meter long aluminum dilution tunnel. As a consequence, the temperature of the exhaust decreases to near ambient level. Dilution air was pre-treated with activated carbon, silica gel and a particle filter. The flow was regulated with a mass flow controller (MFC, Vögtlin, Red-y Smart Series), thereby the dilution ratio could be easily adjusted over a wide range. After the dilution tunnel the size separation step was achieved with two parallel commercial low volume sampling heads (PM_{10}, $PM_{2.5}$ Digitel, Ag, Switzerland, flow rate 1.0 m^3 h^{-1} each), each sampling head was followed by three filter holders, two equipped with quartz fiber (Tissuquartz, Pall Life Science) and one with mixed cellulose ester filters (GN-4 Metricel, Pall Life Science). The flows were regulated with MFCs (Bronkhorst). One additional filter holder was attached without any separation step in order to check whether the particulate emissions from biomass combustion are predominately in the size range of PM_{10}.

In the super-isokinetic condition employed it is likely, that a certain fraction of the “coarse” fraction of PM_{10} is lost. At an estimated upper bound the loss of the PM_{1-10} size fraction is 30-50% and assuming a contribution of this fraction of around 10% (Pettersson et al., 2011) the total error in the PM_{10} mass determination is 3-5%, which is within the range of the estimated error of the PM determination.

The collection of smoke from smoldering flames bears a range of problems, which are not fully resolved. Details of sampling problems are discussed in the review paper of Kocbach Bølling et al. (2009). They refer to problems due to diffusion losses, sampling artifacts, and dependence of the emission factor of PM on the dilution ratio. Sampling artifacts are widely discussed for ambient air sampling (e.g. Turpin et al., 2000). For emission sampling far higher loadings of the filters for PM samplings are achieved. Thus it was assumed that the relative error from adsorption of vapors on quartz fibers would diminish. However, Lipsky and Robinson (2006) report for tests with small wood stoves, that for wood smoke sampling with quartz and Teflon – quartz backup filter combinations a positive sampling artifact due to OC condensation on the quartz filter of around 23% in relation to the result of a single quartz front filter was derived. Lipsky and Robinson (2006) however cite also other papers, where lower artifact formation was observed.

Table 2. Sampling and calculation details.

Fuel name	Index	Stove	Burning type	Number of tests	Dilution factor	Wet fuel mass (kg)	Burn rate (kg h^{-1})	LHV (kJ kg^{-1})	Average T [°C] in flue gas	MCE Factor	O_2	CO_2
										(%)	(% v/v)	
Wood pellets	WP	B	FL1	2	3	2.3	1.4	17706	132	99.8	14.2	6.2
	WP	B	FL2	1	3	12.6	1.9	17706	130	99.7	13.9	6.4
	WP	B	PL	2	3(4)*	1.00	0.7	17706	92	99.6	17.5	3.1
Wood briquetts	BR	A	FL	3	10	2.65	2.0	17177	183	97.5	15.6	4.8
European hornbeam	EH	A	FL	3	10	2.63	2.5	16117	184	98.0	14.4	6.0
European beech	EB	A	FL	3	10	2.63	2.8	15857	195	97.8	13.2	7.1
Black poplar	BPop	A	FL	3	10	2.59	2.2	16778	109	96.8	15.4	5.0
Turkey oak	TO	A	FL	3	10	2.61	2.7	16709	196	96.9	13.8	6.5
Sessile oak	SO	A	FL	3	10	2.64	2.1	16164	145	93.9	16.9	3.5
Pedunculate oak	PO	A	FL	2	10	2.63	2.2	15750	154	94.8	16.7	3.7
Black locust	BL	A	FL	3	10	2.66	1.9	16676	149	96.5	16.3	4.2
Silver fir	SF	A	FL	3	10	2.61	2.0	16686	175	94.3	15.6	4.6
European larch	EL	A	FL	1	10	2.63	2.5	17162	176	97.7	13.8	6.5
Norway spruce	NS	A	FL	3	10	2.61	2.1	16481	174	96.9	15.3	5.0
Black pine	BP	A	FL	3	10	2.61	2.3	17610	179	97.1	14.7	5.4
Scots pine	SP	A	FL	3	10	2.63	2.1	-	170	97.9	14.4	5.8
Dry leaves	L	A	ST	1	15	1.25	5.3	17364	196	95.5	13.6	6.3
Pine cones	C	A	ST	1	15	1.14	3.3	17265	175	95.4	11.7	8.3
Pine needles	N	A	ST	1	20	1.14	4.6	18761	192	95.7	11.7	8.0

FL…full-load operation, PL…part-load operation, ST…special test, LHV…lower heating value, MCE…modified combustion efficiency calculated as a ratio $c_{CO_2}/(c_{CO_2}+c_{CO})$ where c_{CO_2} *and* c_{CO} are the measured volume mixing ratios of CO_2 and CO , *…different dilution factors of both tests.

Table 3. Fuel chemical composition (% w/w of raw fuel).

Fuel	C	H	N	O	S	Ash	Water
	(% w/w)						
WP	47.47	5.79	0.08	40.16	0.01	0.31	6.28
BR	46.88	5.47	0.08	42.33	0.01	0.03	5.20
EH	44.51	4.85	0.21	38.39	0.01	1.14	10.89
EB	45.53	5.41	0.37	38.25	0.01	0.41	10.01
BPop	45.53	4.94	0.07	37.75	0.01	0.99	10.70
TO	45.29	5.22	0.13	39.99	0.01	1.16	8.20
SO	45.20	4.74	0.17	37.89	0.01	1.29	10.70
PO	45.53	4.71	0.07	36.67	0.01	0.24	12.76
BL	45.06	5.12	0.12	40.67	0.01	0.49	8.53
SF	46.06	5.36	0.08	37.41	0.01	0.66	10.42
EL	43.02	5.61	0.06	42.41	0.01	0.60	8.30
NS	46.68	4.85	0.08	37.06	0.01	0.41	10.92
BP	47.53	4.86	0.10	35.60	0.01	0.25	11.66
SP	NA	NA	NA	NA	N.A.	NA	NA
L	41.99	4.71	0.95	38.83	0.01	5.37	8.13
C	47.16	5.18	0.18	38.71	0.01	0.79	7.97
N	45.65	5.40	0.68	39.17	0.01	2.31	6.77

C…carbon, H…hydrogen, N…nitrogen, O…oxygen, S…sulfur (under detection limit of the method), NA…not analyzed, for the fuel in Table 2 .

2.4. Odor sampling

For the olfactometric analyses, about 20 liters of flue gas was collected continuously behind the dilution tunnel (same as for particulate matter sampling), during the entire burning process. Pre-dilution factors of 10-20 assured that no condensation of water vapor occurred before and during the measurements. According to the sampling standards for odor assessment given in European Union norm DIN EN 13725 (2003), a smell- and tasteless, liquid- and temperature resistant (-60-220°C) Nalophan (polyethylene terephthalate, Kalle) sampling bag was used. The inlet of the sampling bag was equipped with an odorless Teflon tube. The whole equipment was placed in a tight Plexiglas pipe. To achieve a stable flow of the sample into the sampling bag, air was pumped constantly out of the pipe. The flow rate, set and regulated with mass flow controllers (MFC, Bronkhorst), varied between 0.25 and 0.35 L min^{-1}, depending on combustion time. After a single measurement, the sampling bag was purged with purified air. Being used for one fuel type, it was replaced by a new one.

2.5. Analytical procedures

2.5.1. Filter weighing and sample preparation

Previous to sampling, quartz fiber filters were baked for 5 hours at 550°C, cooled in a desiccator with water vapor saturated atmosphere, equilibrated for 48 hours in an air conditioned room (20 ± 1°C, 50±5% relative humidity) and weighed with a microbalance (Sartorius M5P with range up to 1 g ±0.5 µg). The same procedure was repeated with loaded filters. Loaded filters were stored at -18°C.

2.5.2. Olfactometry

Olfactometry is a widely used method, which allows measuring of odor concentration (given as Odor Units "OU" per cubic meter) and deriving the odor thresholds (Hudson and Ayoko, 2008a, b).

The measurement of odor was performed by dynamic dilution olfactometry, involving a self-built diluting device (olfactometer, Figure 1) and a panel of four people, who determine the odor threshold, i.e. the dilution ratio, where no smell is experienced.

The pre-diluted odor sample was mixed with purified air (active carbon, particulate filter and silica gel), in ratios ranging between 1:10 and 1:10000. Usually 10-20 dilutions, in a random order, were presented to panelists during a single measurement. Binary answers (yes/no) were collected discretely.

The dilution was performed with four suspended-body flow meters. One of them controlled the neutral air flow, which was constant during the whole measurement (~15 L min^{-1}). The other three flow meters worked in different ranges and were adjusted manually to set a desired dilution. The dilutions achieved with the device are comparable to short-time dilutions in ambient air.

23 co-workers (14 women and 9 men) aged between 18 and 60 (average age 32) took part in the experiment. Eating, drinking, smoking and using cosmetics, shortly before and during the measurement was not allowed. Each test was performed with four panelists; the mean testing time of a single sample was between 10 and 20 seconds, according to the response of the testing person. Each test began with the presentation of neutral air and of a concentrated sample. As we designed a double-choice measurement, each panel member was supposed to give a binary answer (0 – no wood smoke odor or 1- wood smoke odor present).

The ability of the panelists to recognize the odor threshold was examined with standard tests with n-butanol in nitrogen (59.6 ppmMol n-butanol) – a certified reference material (CRM) suggested in the standard procedure DIN EN 13725 (2003). The range of an admissible threshold value during the standard test was 20-90 ppbMol n-butanol. The tests yielded a detection limit within our panelists of 73.1 ppbMol n-butanol, with all panelists passing.

The European Odor Unit (OU$_E$) refers to the dilution factor of an odorous compound that is necessary to reach the odor threshold. It elicits a physiological response from a panel (detection threshold) equivalent to that elicited by one European Reference Odor Mass (EROM), evaporated in one cubic meter of neutral gas at standard conditions. One EROM is an equivalent to 123mg n-butanol (CAS 71-36-3) evaporated in one cubic meter of neutral gas, resulting in a concentration of 0.04 µmol mol^{-1}.

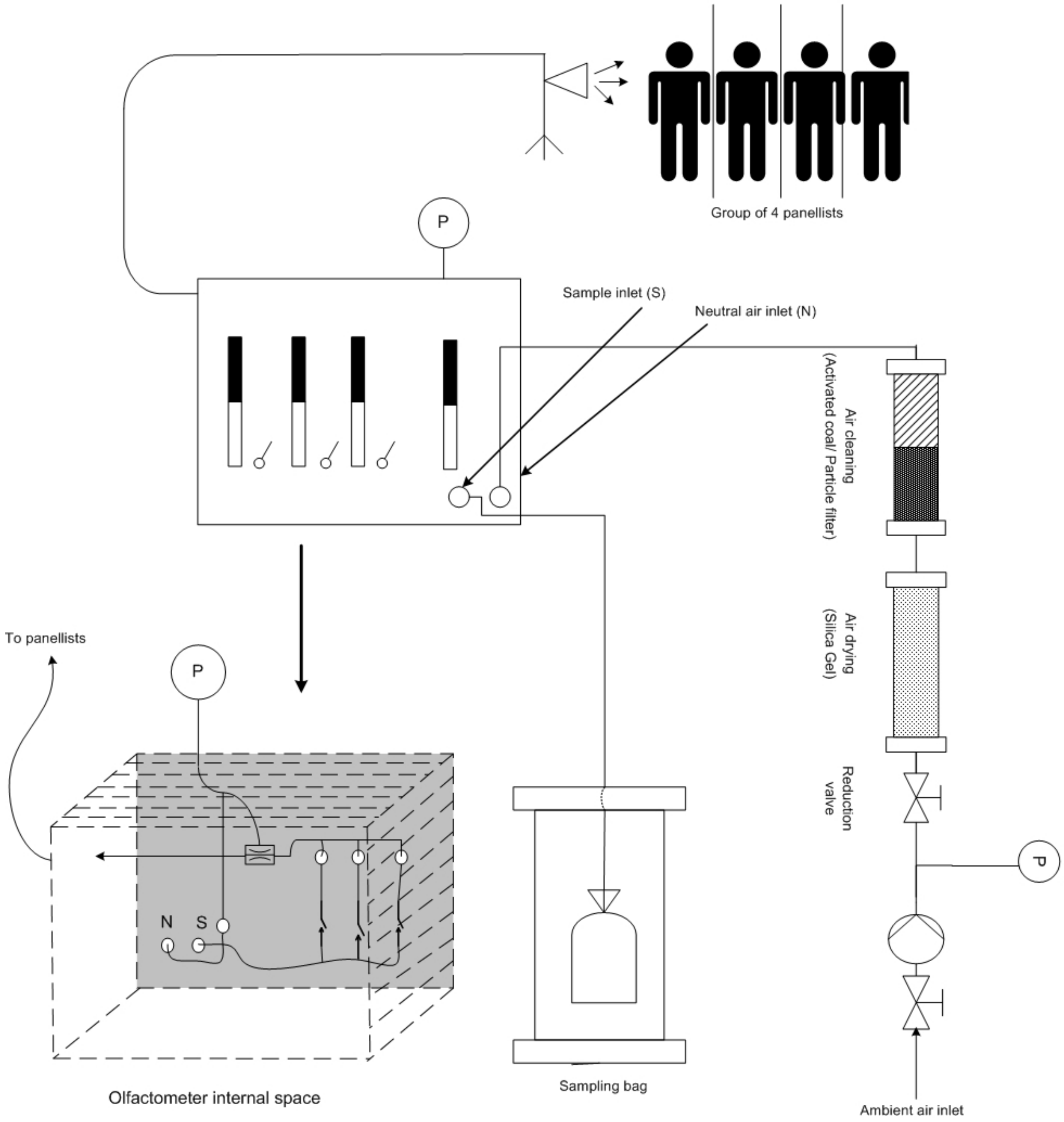

Figure 1. Odor measurement schema.

In order to estimate the odor thresholds the answers of the panel members were subjected to a probit analysis, which is a well established method for modeling probabilities of binary outcomes (Finney, 1971). We decided to use a probit instead of a logit model solely for convenience reasons, since probit models are easier to interpret. Our choice of the probit model is also supported by a work of Chambers and Cox (1967), who showed that extremely large samples, are necessary, in order to distinguish between probit and logit models.

3. Results and discussion

The study shows a wide diversity of emission factors according to fuel, appliance and combustion mode. Expectations were to investigate situations, which happen in real life and not only under laboratory conditions. For this reason no special treatment of fuels and stoves was performed. Emphasis was put on keeping the firing chamber clean and to assure the recommended wood volume and proper air supply. In consequence, quite high relative standard deviations between different tests of a single wood type under identical firing conditions were observed.

To obtain information about the combustion efficiency we derived the modified combustion efficiency factor (MCE) given in Table 3. MCE values >90% suggest that more than 50% of the emissions were produced by flaming combustion, whereas when MCE <90%, more than 50% of the emissions originated in the smoldering phase (Ward and Hardy, 1991). All tests in this study represent emissions predominantly from the flaming combustion, with an average MCE of 96.8%.

3.1. Gas phase and particle emissions

Emission factors obtained in the study are presented in Table 4. Observed ranges for the individual tests are given likewise in Table 4. In case of pine cones the PM_{10} emissions were, due to relatively fast (in comparison with wood) and clean (in comparison to other garden waste) combustion and resulted short sampling time, not detectable. They ranged from 16 to 625 mg MJ^{-1} with surprisingly low values for poplar and larch, similar to the emissions from the pellet stove, relatively high emissions for sessile oak (221 mg MJ^{-1}) and an extremely high value for unconventional fuel (dry leaves) combustion. Pine needles smoke PM_{10} was well in the range of log wood. CO and NO_x emissions of the garden biomass samples were within the range of the emissions from log wood, while C_xH_y emissions were higher for all types of garden biomass.

Table 4. Averages and ranges for observed emission factors .

Fuel	CO	CO range	NO$_x$	NO$_x$ range	C$_x$H$_y$	C$_x$H$_y$ range	PM$_{10}$	PM$_{10}$ range	Odor	Odor range
	(mg MJ^{-1})								(OU)	
WP FL1	118	103-134	94	86-102	58	52-64	21	18-23	ND	-
WPFL2	188	-	131	-	5	-	31	-	ND	-
WP PL	245	236-254	74	73-76	8	7-9	16	14-18	ND	-
BR	1482	1309-1632	63	57-72	163	108-204	32	7-51	1804	1594-2218
EH	1234	989-1545	110	107-116	462	159-982	41	31-46	536	292-720
EB	1410	1009-1989	95	77-111	234	110-443	66	36-95	1563	1468-1748
BPop	1856	1599-2035	65	60-74	216	119-285	20	5-46	2843	1798-3661
TO	1816	1437-2201	88	77-104	206	113-352	59	55-64	1781	1526-2079
SO	3681	3050-4123	131	126-137	657	544-767	222	194-250	4226	3456-5270
PO	3253	3249-3257	104	102-105	452	380-525	57	35-80	1973	1954-1992
BL	2000	1844-2262	118	104-131	239	113-320	67	24-98	1689	1039-2906
SF	3497	3070-3993	105	82-146	581	442-712	100	79-132	5217	3951-5985
EL*	1263	-	58	-	179	-	21	-	2422	-
NS	1901	1781-2019	69	60-74	267	222-332	53	48-60	3815	2069-5211
BP	1710	1310-2379	64	58-68	243	151-368	101	80-113	1589	1361-2039
SP	1189	1101-1263	70	69-70	109	73-161	53	17-79	2134	1576-2503
L*	2249	-	132	-	1543	-	626	-	18963	-
C*	2821	-	89	-	1106	-	<LOD	-	3524	-
N*	2204	-	111	-	1424	-	85	-	7346	-

*…single test, <LOD…under limit of detection, ND…not detected.

Automated regulation of fuel and combustion air supply in pellet stove assured efficient and relatively clean combustion with low particulate emissions. The tested device showed a burning rate dependent PM$_{10}$ emission – increasing PM$_{10}$ with increasing burning rates: 16 mg MJ^{-1} PM$_{10}$ at 0.7 kg h^{-1}; 20 mg MJ^{-1} at 1.4 kg h^{-1} and 30 mg MJ^{-1} at 1.9 kg h^{-1}. Previous study with the same appliance reported even lower PM$_{10}$ emissions from wood pellets of around 3 mg MJ^{-1} for full load and 10 mg MJ^{-1} for part-load (Schmidl et al., 2011). Scandinavian studies reported higher PM emissions from pellet stoves. Sippula et al., 2007 obtained a PM$_1$ emission rate of 58 mg MJ^{-1} for commercial pellets fired in an 8 kW automated German pellet stove ("Wodtke GmbH"). Boman et al. (2011) investigated PM$_{tot}$ emissions from a Scandinavian 6 kW and a North American 9.5 kW "exempt" pellet stove and reported 16 and 23 mg MJ^{-1} for full load respectively 34 and 40 mg MJ^{-1} for part load operation.

Interestingly, two wood types tested here (poplar and larch), as well as briquettes emitted equally low amounts of PM$_{10}$, as observed for pellets. This result is surprising, because pellets combustion was considered consistently "cleaner" than log wood. Log wood exhibited, depending on the wood type, a wide range of PM_{10} emissions (20-221 mg MJ^{-1}) what is depicted in Figure 1. The lowest emissions obtained are around two orders of magnitude higher if compared to the PM_{10} emission from combustion of extra light fuel oil in domestic boilers (Hübner et al., 1996; Austrian Energy Report, 2003).

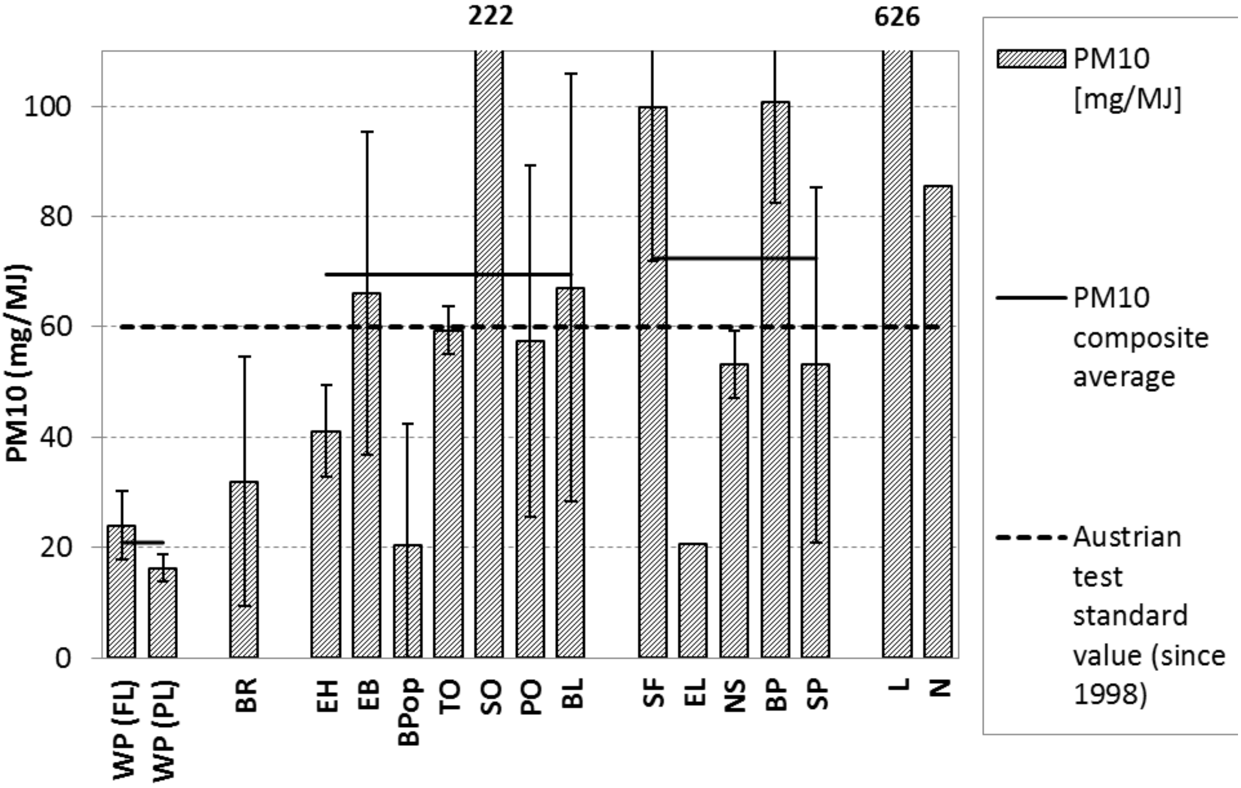

Figure 2. Average emission rates of PM_{10}. Error whiskers given in terms of standard deviation. Dashed line represents the Austrian emission limit for standardized test conditions.

Relatively low emissions in the pellets test during both burning modes (full- or part-load) were obtained for CO (142 and 245 mg MJ^{-1}) and C_xH_y, (40 and 8 mg MJ^{-1}). Contrary to pellets, wood logs burned in full-load mode in manually fired stove caused in many cases much higher emissions. Among 12 wood types and briquettes, the highest values for CO and C_xH_y were obtained for sessile oak (3681 mg MJ^{-1} CO and 657 mg MJ^{-1} C_xH_y), and the lowest values (1189 CO mg MJ^{-1} and 109 mg MJ^{-1} C_xH_y) for Scots pine. The most common fuelwoods in Austria, spruce and beech show likewise an emission of 1900 and 1400 mg MJ^{-1} CO, 267 and 234 mg MJ^{-1} C_xH_y, respectively of 53 and 66 mg MJ^{-1} PM_{10}.

The PM_{10} emission rates depend on the burning quality (expressed in terms of MCE factor) which is strongly influenced by the relation of smoldering and flaming combustion phase (Figure 3).

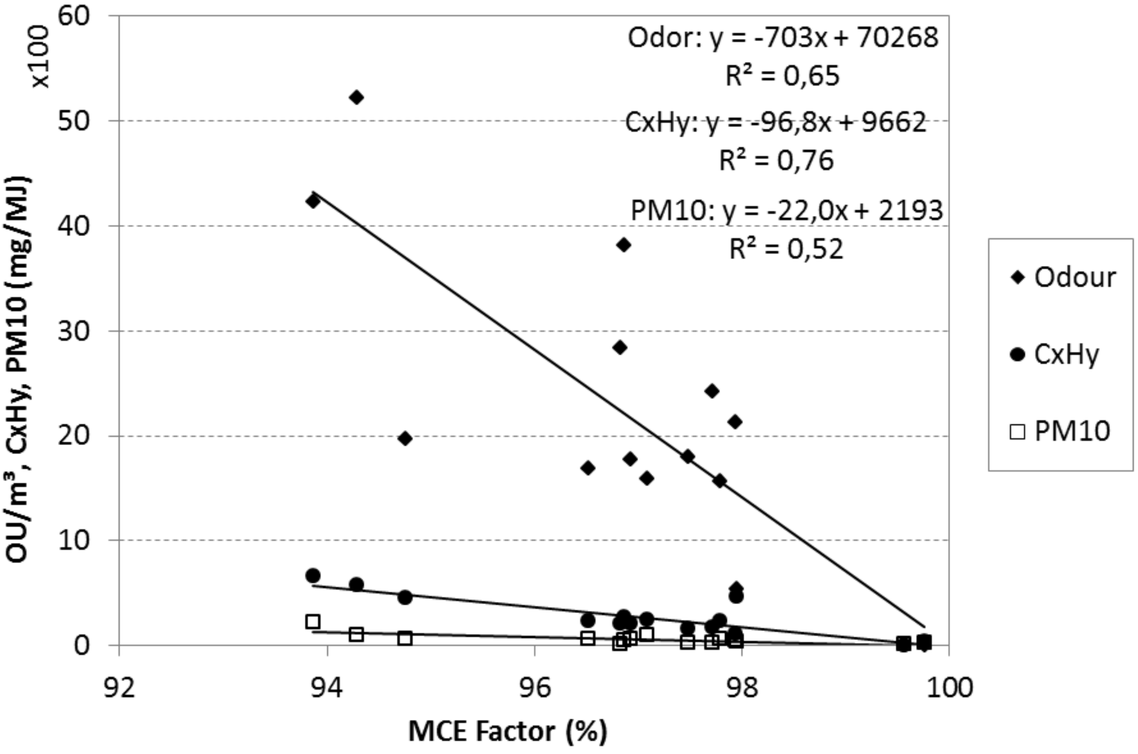

Figure 3. Correlation between PM_{10}, C_xH_x, and odor emissions and modified combustion efficiency (MCE).

Nitrogen oxides emissions show a different behavior than other determined components. Test averages range between 58 and 131 mg MJ^{-1}, with lowest values for larch (58 mg MJ^{-1}) and highest for sessile oak (131 mg MJ^{-1}) and dry leaves (132 mg MJ^{-1}) smoke. The NO_X emissions from pellets combustion were close to the median of the tested fuels. However, there is a statistically significant difference of 30% for the NO_x emissions from hard- and softwood combustion (102 and 75 mg MJ^{-1} NO_x). There is an obvious influence of the nitrogen content in the fuel with 0.16% N for hardwood, 0.08% N for softwood and 0.95% for dry leaves (averaged data from Table 3) , however also combustion conditions e.g. temperature seem to play a significant role (Figure4).

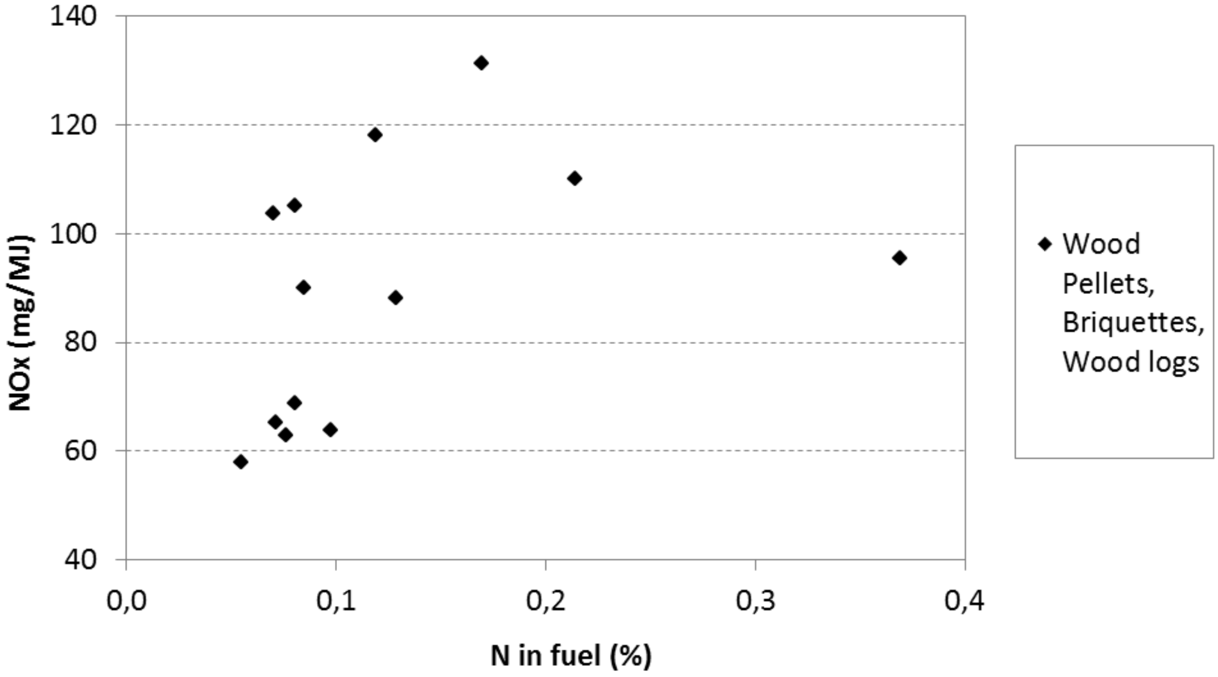

Figure 4. Correlation between nitrogen oxides (NO_x) emission rates and nitrogen contents of the fuel.

Summarized composite data for pellets, wood fuels with briquettes, hardwood and softwood, as well as “garden biomass” (excluding cones) in different units simplifies comparison with results from other studies, and are of interest for emission inventories and modeling purposes (Table 5). In the composite data for CO, the log wood groups (softwood, hardwood) as well as garden biomass (leaves and needles) exhibit comparable emission rates (around 1900-2200 mg MJ^{-1}), while the pellet stoves were one order of magnitude lower. C_xH_y emissions were quite variable in the tests. Wood logs emitted between around 280 mg MJ^{-1} C_xH_y (softwood) and 350 mg MJ^{-1} C_xH_y (hardwood); pellets - more than one order of magnitude less, leaves and needles around a factor of 5 more, than wood logs. For PM_{10} emissions soft- and hardwood log types were in a comparable range (around 70 mg MJ^{-1}), pellets emissions were a factor of 3.5 lower, leaves and needles a factor of 5 higher than wood logs.

Table 5. Composite averages for wood pellets, logs and garden biomass.

	Fuel	Wood pellets	Wood logs and briquettes	Hardwood logs	Softwood logs	Garden biomass (N+L)
	Number of tests	**n=5**	**n=36**	**n=20**	**n=13**	**n=2**
CO*	**mg MJ^{-1}**	183	2030	2125	2012	2226
	mg $m^{-3\ a}$	282	3117	3263	3078	3909
	g $kg^{-1\ b}$	3.2	34	35	34	40
	RSD (%)	35	43	43	45	-
NO_x*	**mg MJ^{-1}**	93	89	102	75	121
	mg $m^{-3\ a}$	144	137	156	116	214
	g $kg^{-1\ b}$	1.7	1.5	1.7	1.3	2.2
	RSD (%)	25	28	22	29	-
C_xH_y**	**mg MJ^{-1}**	27	311	347	291	1484
	mg $m^{-3\ a}$	36	409	456	380	2232
	g $kg^{-1\ b}$	0.5	5.1	5.6	4.9	26.8
	RSD (%)	105	68	70	64	-
PM_{10}*	**mg MJ^{-1}**	21	67	70	72	356
	mg $m^{-3\ a}$	32	103	107	111	634
	g $kg^{-1\ b}$	0.4	1.1	1.1	1.2	6.2
	RSD (%)	30	73	86	47	-
Odor**	**OU**	ND	2430	2087	3036	13155
	RSD (%)	-	53	56	48	-

ND…not detected; RSD…relative standard deviation; *… measured in dry exhaust; **…measured for wet exhaust; [a]… calculated for normalized volume of exhaust; [b]… in dry fuel basis

Comparing our findings with literature data, we notice analogue tendencies, as well considerable differences. Tissari et al. (2008) reports CO and NO_x emissions from birch wood combustion in masonry stove, which are in line with those obtained here: 42 g kg^{-1} wood CO and 1.4 g kg^{-1} wood NO_x. CO of 143 mg MJ^{-1} for pellets (average of part- and full-load modes) reported by Schmidl et al. (2011) were not much different, while 1457 mg MJ^{-1} for wood logs (beech, pedunculate oak, Norway spruce) and softwood briquettes were definitely lower than in the current work. Both Tissari et al. (2008) for birch, and Schmidl et al. (2011) for pellets, briquettes and tested logs report lower gaseous organic compounds emissions (C_xH_y), e.g. around 2.2 g kg^{-1} wood (birch), 5.8 mg MJ^{-1} (wood pellets) and 125 mg MJ^{-1} (wood logs and briquettes). Interestingly, PM_{10} emissions from birch wood combustion (2.1 g kg^{-1} wood) are a factor of two higher (Tissari et al., 2008), than the average for log wood in this study, while averaged PM_{10} emission factor from Schmidl et al. (2011) study is in good agreement with current results. Bari et al. (2009) report, for beech combustion in a “residential stove”, a PM_{10} emission of 21 mg m^{-3} what is about five times lower than our result for beech, while in the same study, the 113 mg m^{-3} PM_{10} for pine smoke was close to our result.

In 1997 and 1998, a comprehensive emission test of Austrian domestic combustion units was performed at 180 randomly chosen households, thus considering “real world” conditions in a large variety of boilers and stoves. This data is compiled in Austrian Energy Report (2003). The average emission rates for log wood stove survey are included in Table 4. The PM_{tot} results, however, were obtained by “hot” sampling, which underestimates the particle concentrations occurring in the ambient air. Pettersson et al. (2011) discussed two results from Scandinavian sources (Bäfver, 2008, Ortega, 2008) where diluted mass emissions from wood stoves were 3-9 and 5-12 times higher, than for undiluted “hot” sampling.

CO, C_xH_y and PM_{10} emissions from the modern, certified “chimney” stove chosen for this study are around a factor of two lower than the respective emissions from the “Austrian” stoves collective. We can conclude from this result, that modern, certified stoves tend to emit notably less CO, C_xH_y and PM_{10} compared to the typical Austrian “average” which included a wide variety and age range of devices under undefined operation conditions.

The emission limits of the Austrian certification procedure (beech wood, two combustion cycles, standardized conditions, hot start), mentioned above are presented in the Table6. Comparing our test results, we have to consider the differences to the standard test procedure (i.e. including most of the incensing phase and choosing other wood types). Average emissions of CO and C_xH_y, are exceeding the emission limit for 90% of tested fuels, PM_{10} – for 39 % of the tested fuels. In case of NO_X average results for individual wood types were within the limit. Averaged CO and C_xH_{yy} emission rates are considerably above the standard limits: CO around a factor of two, C_xH_y nearly a factor of four higher. Certain wood types exhibit the emission rates even higher than the average obtained in the current test, which allows the conclusion, that country specific emission rates have to be derived considering the different wood types available in different countries of Europe.

Table 6. Comparison of emission rates for small log wood stoves from an emission survey of Austrian log wood stoves from 1997/98, averaged results for modern log wood stove tests, and the emission limits for new log wood stoves in Austria

	CO	**NO_x**	**C_xH_y**	**PM**
	(mg MJ^{-1})			
Austrian test 1997/98 log wood stoves	4463	106	664	148 PM_{tot} “hot”
This test – 8kW stove, wood logs and BR	2030	89	311	67 PM_{10}
Schmidl et al. (2011), (EB, PO, SP, BR) average from 2 stoves (6 and 6.5 kW)	1454	91	125	81 PM_{10}
Pettersson et al. (2011) birch, NS, pine 9kW stove, average from 3 modes	3600	47	820	140 PM_{tot}
New Austrian Standard 1998 (beech,”hot start”)	1100	150	80	60 PM_{tot} “hot”

3.2. Odorous emissions from wood combustion

Our aim was to create a matrix of odorous substances emission data for different wood types to derive information about the occurrence of wood smoke odor dependent on other wood smoke parameters, which are currently used in dispersion models in order to derive information about the odor nuisance potential in wood burning communities. Due to this intention, our study concentrated on average odor thresholds for the complete burning processes and not on individual combustion phases. Odor phenomena are considerable for manually fired stoves, while no odor was detected for pellet combustion in the automatically fired stove. The odor thresholds for briquettes, wood logs and garden biomass combustion range between 536 and 18963 OU m^{-3} (Table 4b). A high variability among each measurement relates to the individual character of the test with panelists. This is plotted by Figure 5.

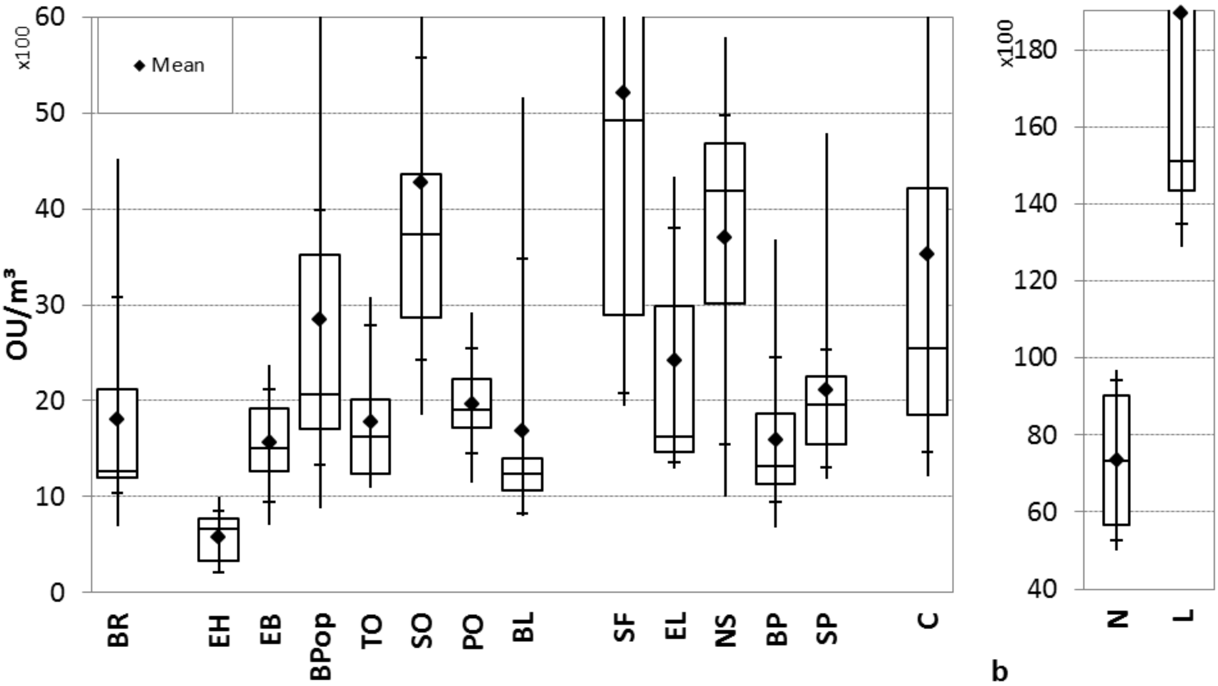

Figure 5. Odor thresholds (OU m^{-3}). Whiskers present 10 and 90 percentile as well as maximal and minimal values. Garden biomass – needles and dry leaves are presented with separate scaling.

Odor is a sensorial signal caused by compounds, which are volatile at room temperature (Rossiter, 1996), thus odor threshold is considered to correlate with the concentration of gaseous organic compounds in the exhaust.

The highest odor concentration was observed by burning dry leaves. The result differs strongly (one order of magnitude) from wood smoke. The highest wood smoke odor threshold (5217 OU m^{-3}) was observed for fir smoke, the lowest, 536 OU m^{-3} for hornbeam smoke. The average odor threshold of hardwood smoke

(2087 OU m^{-3}) is lower than that of softwood smoke (3036 OU m^{-3}), although among both fuel groups there are high- and low emitting species. This behavior of smoke from different wood types can be observed in the correlation with CO emissions depicted in Figure 3. The correlation is significant at the P=95 level. Contrary to odor, the average emissions of C_xH_y show the reversed order (Table 3). For CO and PM_{10} the emissions from hard- and softwood were similar.

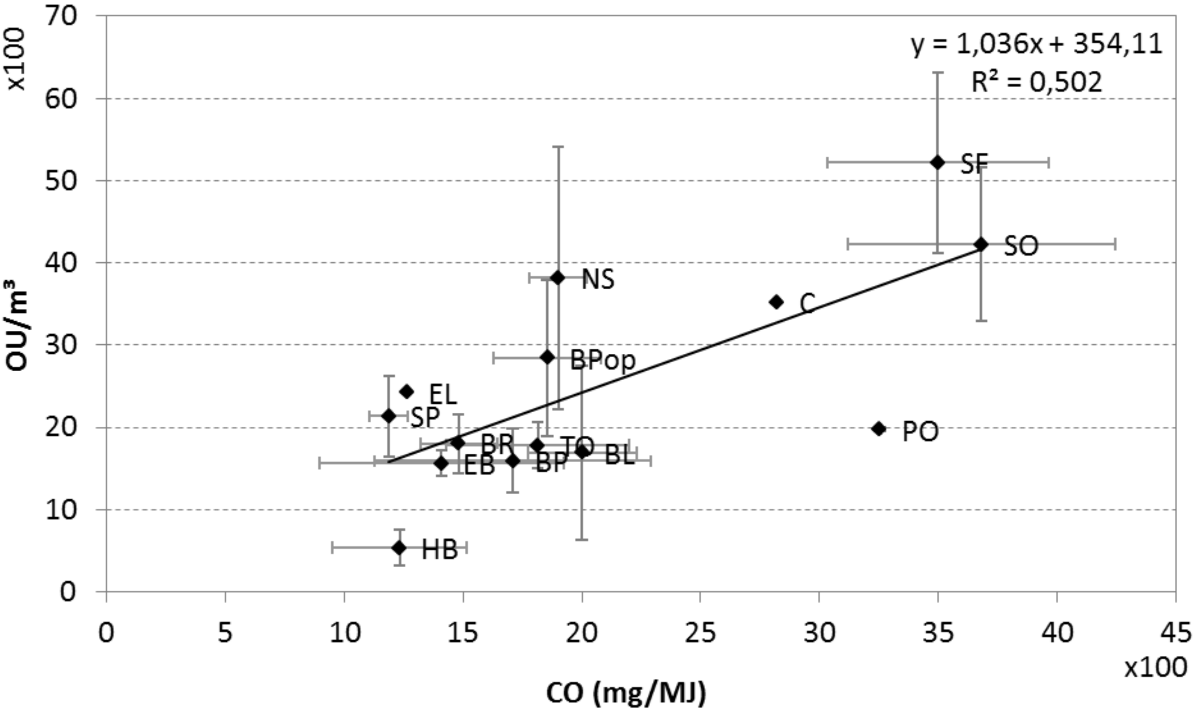

Figure 6. Correlation of odor and CO showing high and low emitters among fuels. Softwood types are marked with bold italics. Whiskers present standard deviations. The correlation is significant at the P95 level.

The emission rates of measured pollutants depend closely on combustion efficiency (in terms of MCE). Positive slopes are reported for emissions generated mainly by flaming combustion, while negative slopes originate from emissions by the smoldering processes (Sinha et al., 2003). Current sampling was conducted over a complete burning process thus negative slopes for the odor, PM_{10} and C_xH_y emissions in the plot against MCE (Figure 3), which were observed indicate that the emissions of a complete burning cycle are dominated by smoldering occurring during the start-up and end phases of burning, when no more flames are observable.

Relying on the fact that odor is mainly emitted during smoldering; we are able to explain the differences between odor concentrations in our experiment and the study of Ebbinghaus (1993). The highest reported values for log wood, from 30000-105000 OU m^{-3} were recorded in 5 min intervals during start- and end -

phase at extremely high CO levels, while we report averaged odor threshold over the whole combustion cycle.

Although odor thresholds among different wood types do not vary too much, for most softwood species the odor concentration was higher than for hardwood species. A potential explanation might give the guaiacol (2-methoxyphenol) content in emissions. Guaiacol is possibly the leading odorous substance in wood smoke, considered to be responsible for smoky smell (Czerny and Buettner, 2009) and it occurs generally in higher amounts in softwood than in hardwood smoke (Kjällstrand and Petersson, 2001). A combined study on methoxyphenols and wood smoke odor relationship is still required to prove this hypothesis.

An interesting diagnostic ratio in wood smoke is its relationship to particles. This ratio can be applied to derive the ambient PM concentration from wood smoke, which is accompanied by exceeding the odor threshold, i.e. the potential for an odor perception. It gives also a possibility to estimate the odor concentration if ambient wood smoke concentrations are known from tracer measurements. Table 7 compiles the averaged ratios PM_{10} (µg m^{-3})/Odor (OU m^{-3}) for tested fuels. The "Austrian mix" is based on estimated fuel data given in Schmidl et al. (2008) (70% spruce, 20% beech and 10% briquettes) and is derived according to Equation 3, where C_x is an ambient PM concentration for selected species, which allows odor perception.

$$C_{\text{Austrian mix}} = 0.7 \cdot C_{spruce} + 0.2 \cdot C_{beech} + 0.1 \cdot C_{briquettes} \quad \text{(Equation 3)}$$

Table 7. PM_{10} [µg m^{-3}]/Odor [OU m^{-3}] ratios for composite "hardwood", "softwood" and "Austrian mix".

	PM (µg m^{-3})/odor (OU m^{-3})	
	Average	Median
Wood pellets	-	-
Wood logs and briquettes	53.4	43.0
Hardwood logs	66.4	62.1
Softwood logs	40.4	28.8
Needles and leaves	39.6	27.7
Austrian mix*	29.8	-

*…70% spruce, 30% beech and 10% briquettes (Equation 3)

Applying the relationship of odor threshold and PM_{10} emission rates to PM ambient concentrations, we obtain that for the "Austrian mix" smoke odor could be perceived at the ambient wood smoke concentration of already about 30 µg m^{-3}.

High wood smoke concentrations reported for suburban and urban sites in pre-Alpine forested environments, e.g. in Styria and Salzburg on days exceeding the EU daily mean limit value of 50 µg m^{-3} (EC, 2008) were in the range of 20-30 µg m^{-3} as average over a period of 2-7 days (Caseiro et al., 2009). Due to the daily variation of domestic emissions occurring from chimneys at low elevation above ground, namely in stagnant periods, hourly maxima of wood smoke PM are expected to exceed considerably the daily averages. Thus, wood smoke odor levels above the threshold level are likely during winter days in wood burning communities situated in areas with reduced ventilation.

4. Conclusions

Among fuels chosen for combustion tests are both species dominant in lowland as in mountainous forests of Europe, thus the emission data are of relevance for many countries. Furthermore, emissions of the main tree types of the Pannonian lowlands have not been reported before.

Measured emissions showed large variation among fuel types, e.g. PM_{10} emissions from European larch and black poplar were a factor of ten lower than from sessile oak; likewise odor concentration in European hornbeam smoke were a factor of ten lower than in silver fir smoke. The variability of emission rates combined with the diversity in the tree species distribution in European countries appeals to the presumption of different averaged emission rates of wood smoke components for different countries of Europe.

The data of this, and comparable studies show, that modern wood combustion technologies for small scale appliances, are lowering the emission of particles for manually fired log wood stoves to around 70-140 mg MJ^{-1}. This is in the lower part of the range indicated in the review by Kocbach Bølling (2009). The observed PM emissions for small pellet stoves were quite in the range given in the review (10-50 mg MJ^{-1}). The emission of wood and pellet stoves is predominantly in the fine (<2.5 µm) size range, thus a similar emission of $PM_{2.5}$ can be anticipated. Considering a typical heat demand of 100 GJ per household, a pellet appliance equipped home would emit around 1-6 kg of fine particles per year. This is still 1-2 orders of magnitude higher than emissions from gas or oil (extra light, low sulfur) based heat supply. The planned large scale introduction of wood combustion based domestic heating systems in Austria (planned for up to 400.000 households) would increase the Austrian $PM_{2.5}$ emission by around 6% based on an average emission of 30 mg MJ^{-1}, if the old “high emitting” solid fuel based heating systems are not replaced. As most of the wood smoke emissions are occurring during the cold season, their impact during the cold period would range up to a 12% increase for ambient $PM_{2.5}$(PM_{10}) concentrations.

From the dependence of C_xH_y PM_{10}, odor and the MCE it could be derived, that the respective emissions during the complete burning cycle as sampled in our study, are dominated by the smoldering phases that are occurring during the start-up and end phases of burning when no more flames are observable. We have started the log wood combustion tests with relatively smokeless lighter cubes. In practice, wood combustion is often started with waste paper, kindle wood, twigs and other igniting material. This causes far higher fine particles emissions in the ignition phase, as can be anticipated from our tests with garden leaves and needles. Thus, the emission rates observed, though considered to be close to “real world” conditions are at the low end of the actual occurring emissions.

The relationship of PM_{10} and odor concentration was used to derive a “critical” ambient PM_{10} level from wood smoke where wood smoke odor becomes perceivable. The PM_{10} levels, where wood smoke odor exceeds the odor threshold was around 40 µg m^{-3} for softwood and 60 µg m^{-3} for hardwood. Peak emissions during the incensing phases are, however, a factor of 10-50 higher than the burning cycle averages, as derived from the results of the Ebbinghaus (1993) study. Thus frequent short term occurrences of wood smoke odor is likely for many communities with traditional and modern wood stove use.

The odor units can be used in dispersion models to estimate the impact of odor nuisance from wood combustion.

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4. Chemical characterization of particulate matter from combustion of Central European wood types in residential modern stoves[1]

Abstract

In this study we investigate the chemical composition of PM_{10} emissions from combustion of the major wood species grown in 8 Mid-European countries in standard test cycles. The logwood tests were performed with a modern 8kW chimney stove, additional pellets burning tests with a 9kW pellet stove. The PM_{10} emissions ranged from 20 mg MJ^{-1} for wood pellets (WP), 71 mg MJ^{-1} for hardwood and briquettes (HW+BR), 66 mg MJ^{-1} for conifer softwood (SW) to 356 mg MJ^{-1} for garden waste (GW). Emissions of elemental carbon (EC) ranged from around 3 mg MJ^{-1} for WP, 18 mg MJ^{-1} for HW+BR, 20 mg MJ^{-1} for SW to 50 mg MJ^{-1} for GW. The compositional balances yielded unidentified rests of 26% for WP, 38% for HW+BR, 30% for SW and 28% for GW. The unidentified rest is considered to consist mostly of humidity for WP, as inorganic ash material constitutes 51% of highly hygroscopic salts. For GW emissions a high organic carbon (OC) content of 56% limits the conversion factor "f" from organic matter (OM = f*OC) to 1.3-1.4. For the logwood tests, assuming 5-10% humidity of the PM_{10} samples, a back calculated OM/OC conversion factor ranged from 1.6-1.7 for SW and 2.0-2.2 for HW+BR. Levoglucosan contents in PM_{10} showed a wide range for the individual fuels, e.g. from 0.3% for beech (EB) to around 20% for common oak (PO); even WP levoglucosan emissions were observed with 0.1% for full and 0.3% for part load. Including results of three further studies performed at the same test site with comparable stoves types yielded a "grand average" PM_{10}/Lev ratio of 18, with a range of 15 – 24 for 6 test series, which is a factor of 1.6 higher than the average for the "Austrian mix" from a tiled stove of around 11 (Schmidl et al., 2008). The levoglucosan/mannosan ratio (Lev/Man) was consistent for all chimney stoves tests, with a grand average of 3.1 for SW, also observed for the softwood WP. For HW the chimney stove studies yielded a Lev/Man ratio of 19.5, which is a factor of 1.6 higher, than observed from the tiled stove tests. The emission profiles of the investigated species were for WP comparable to those of an earlier study with a similar pellet stove (BIOCOMB project, Luisser et al., 2008), although PM_{10} emissions were around a factor of 2 higher in this study. Major differences of the chimney stoves profiles compared to those reported for a tiled stove are occurring for EC (higher for chimney stoves), OC (lower for chimney stoves), alkanes (higher for chimney stoves), PAHs (higher for chimney stove) and for inorganic ions (higher for chimney stoves, except the case of NH_4^+). For trace elements including Al and Si relatively similar results were obtained for both stove types.

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[1] …Magdalena Kistler, Christoph Schmidl, Carlos Ramirez-Santa Cruz, Imran Shahid, Azam Mukhtar, Andreas Limbeck, Heidi Bauer, Hans Puxbaum, 2012. Prepared for submission to Atmospheric Environment.

The differences to the tiled stove results reflect the different combustion properties of the stoves, i.e. higher combustion temperatures in the modern logwood stoves which lead to higher EC, higher PAHs, lower OC and higher inorganic ash constituents emissions, in particular of K^+, Cl^- and SO_4^{2-}. The profiles for the pellet and the chimney stove are an important step for creating the data base of technology based emission inventories for wood smoke PM, EC/OC, levoglucosan, mannosan, galactosan, as well as BaP and the “EU” PAHs (EU directive 2004/107/EU).

Key words: Wood smoke, wood stove, biomass combustion, pellets, logwood, levoglucosan, mannosan, emission profiles

Research highlights:

- Log wood PM_{10} emissions from the chimney stove varied from 20-220 mg MJ^{-1}.
- The pellet stove PM_{10} emission of 20 mg MJ^{-1} over lapped with the chimney stove range.
- The PM/levoglucosan ratio of 18 is a factor of 1.6 higher than for a tiled stove.
- The levoglucosan/mannosan ratio of hardwood was 1.6 times higher than for a tiled stove.
- Emission profiles for the chimney stove differ from profiles of conventional stoves.

Abbreviations:

TUV	Technical University Vienna
ABC-W	Austrian Bioenergy Center, Branch Wieselburg
WS	Wood smoke
PM_{10WS}	PM_{10} from wood smoke
BaP_{WS}	BaP from wood smoke
HW	Hardwood (broadleaf trees)
SW	Softwood (conifers)

Tree/fuel types:

AL	Alder
AS	Ash tree
BI	Birch
BL	Black locust
BPop	Black poplar
CH	Chestnut
EH	European hornbeam
EB	European beech
PO	Pedunculate oak (common oak)
SO	Sessile oak
TO	Turkey oak
BP	Austrian black pine
EL	European larch
MA	Maple
NS	Norway spruce
SP	Scots pine
SF	Silver fir
BR	Briquettes
BR_{HW}	Hardwood briquettes
BR_{SW}	Softwood briquettes
C	Pine cones
N	Pine needles
L	Dry leaves
WP	Wood pellets

Garden trees: cherry tree, pear tree, peach tree, elder, mulberry

FL	Full load
PL	Part load

1. Introduction

Biomass smoke is an important constituent to air pollution in Europe, in particular at suburban and rural sites (Glasius et al., 2006; Puxbaum et al., 2007; Szidat et al., 2007; Caseiro et al., 2009; Brandt et al., 2011). Current efforts in the residential heating sector involve the use of advanced technologies for reducing environmental threats from gaseous and particulate emissions (e.g. Nussbaumer, 2003; Obernberger et al., 2007; Hrdička and Šulc, 2011). However particulate emissions are still a problem, especially for logwood combustion. Tendentiously, the emissions from modern biomass combustion units are inversely proportional to the size. Larger appliances (over 30 kW nominal output power) are often equipped with automatic control systems, regulating fuel and combustion air dosage, which reduce significantly the emission rates. On the contrary, small scale logwood fireplaces, stoves and other units (in the range from a few to 30 kW) are mostly hand-operated with respect to fuel load and regulation of combustion air supply), leading to unintended mal-operation and elevated emission rates. (Johannson et al., 2004; Nussbaumer et al.; 2008, Schmidl et al., 2011). Therefore, although small scale wood logwood combustion has not a leading role for space heating with respect to biomass fuel consumption, its contribution to ambient air particulate matter concentrations might dominate the particle emission from space heating in a region. In particular, emissions of “old” stoves and boilers have been identified predominant sources of fine particles emissions from biomass use in several European countries (Sternhufvud et al., 2004; Pastorello et al., 2011; Meyer, 2012).

Due to the high variability of fine particles emission rates from different types of wood combustion appliances analysis of the ambient occurrence of wood smoke is often performed by receptors models (e.g., Schauer et al., 1996; Holden et al., 2011; Piazzalunga et al., 2011). A detailed knowledge of particulate matter composition of “typical” wood smoke “profiles” is required for several of the receptor models, in particular for CMB (chemical mass balance). The incorporation of toxicologically relevant parameters is finally of importance to assess the wood smoke impact at ambient levels with respect of compliance with air quality standards, e.g. for European Union members of components regulated in the directives 2004/107/EC and 2008/50/EC (EC, 2004; EC, 2008).

There are several methods for estimating the impact of residential biomass combustion to ambient aerosols. Tracer models make use of levoglucosan (Lev), generated during the incomplete combustion of cellulose (e.g., Simoneit, 1999; Leithead et al., 2006; Puxbaum et al., 2007; Zhang et al., 2008; Caseiro et al., 2009), also in combination with the ^{14}C (radioactive carbon based) method for differentiating recent and fossil carbon (Jordan et al., 2006; Gelencser et al., 2007; Holden et al., 2011; Yttri et al., 2011). Restrictions are envisaged, if levoglucosan/PM emission ratios determined are not representative for the regional wood smoke emissions (e.g., Hedberg et al., 2006, Glasius et al., 2006). In addition, secondary formation of wood smoke derived PM are included in the ratio observed in ambient air, while it is not the case in the data from emission studies. Indications of secondary biomass combustion derived organic matter (OM) have been reported e.g., by Feczko et al. (2007), who observed significant correlations between “humic like substances” (HULIS) concentrations and biomass tracers at two low level background sites (Aveiro, Portugal; K-Puszta, Hungary). In the combination studies of tracers and the ^{14}C method, secondary biomass combustion PM are not separately assessed and included in the biomass burn OC (e.g., Gelencser et al., 2007; Yttri et al., 2011). Holden et al. (2011) discuss biomass secondary aerosol formation as a potential source for unaccounted contemporary carbon and point to studies of SOA (secondary organic aerosol) formation during ageing of biomass combustion smoke (Gao et al., 2003; Engling et al., 2006; Grieshop et al., 2009). Thus, higher ratios of PM/Lev observed in ambient air as compared to stove emission data are expected to result from ambient studies accounting for the total of PM from biomass combustion. E.g., Piazzalunga et al. (2011) recommend the use of PMF (positive matrix factorization) for deriving an appropriate levoglucosan/PM emission ratio for assessing the wood smoke contribution of ambient fine particles. Another interesting approach for assessing the biomass source contribution is the combined use of on-line aerosol mass spectrometry, aethalometer, and ^{14}C (Sandradewi et al., 2008; Lanz et al., 2008).

Wood smoke emission profiles have already emerged from wood combustion in US studies (Rogge et al., 1998; Fine et al., 2004) and from Northern Europe (e.g. reviewed by Kocbach Bølling et al, 2009; Pettersson et al., 2011; Lamberg et al., 2011), and Western Europe (Alves et al., 2011; Gonçalves et al., 2010, 2011), while less information is available for Mid European stove and wood types (e.g. Luisser et al., 2008; Schmidl et al., 2008a, b, 2011).

This study contains a detailed characterization of particulate matter constituents and the establishment of emission profiles for two modern small stove types. The study extends the profiles presented by Schmidl et al. (2008a,b, 2011) and Luisser et al. (2008) from typical “Alpine” wood species (spruce, beech and in less coverage oak and pine) onto wood species characteristic for the Pannonian Lowlands (black locust, hornbeam, ash, alder, turkey oak, sessile oak) and includes chemical characterization of combustion of garden waste.

Moreover the diagnostic ratios of Lev/PM, Lev/Mann and Lev/Gal are deduced from anhydrosugars emissions, to be compared with those reported for local ambient air studies. The emission profiles are reported for 12 wood types common in nine European countries (Austria, Czech Republic, Hungary, Slovak Republic, Slovenia, Switzerland, as well as Baden-Württemberg and Bavaria (Germany) and South Tyrol (Italy). The data are explored for the variability of emission profiles with respect to stove and fuel variation and serve as basis for developing technology based pollution reduction scenarios.

This paper is done in order to supplement the results presented in a previous work (Kistler et al., 2012) concerning odor, gaseous- and particulate emissions from small scale combustion. It would be followed by a third study regarding particulate phase PAHs emissions (Kistler et al., in preparation, here: **Chapter 5**). We present here only in short the technical information on stove types and sampling procedures, as the detailed description of the combustion experiments and wood chemical data, wood type distribution in Central European countries, emission of CO, NOx, CxHy, PM_{10}, and odor threshold is presented in the previous publication (Kistler et al., 2012, here: **Chapter 3**).

2. Experimental

2.1. Combustion experiments

The most growing tree species in Central Europe are: black locust, black pine, black poplar, European beech, European hornbeam, European larch, Norway spruce, pedunculate oak, Scots pine, sessile oak, silver fir, Turkey oak (reported Kistler et al., 2012, according to national forest inventories, data of forest area). The high abundance of listed wood types result in easy access to this wood, especially in a private scale, and therefore it was seen as reasonable to examine the wide range of emissions causing by their combustion. Additionally our study covered also tests with sawdust briquettes (hardwood, the most popular in locale store) and wood pellets, which are lower priced and provided widely on the market either in countryside or in the cities.

Combustion was conducted in an 8 kW manually operated log wood stove of the middle price class. For pellets burning a 9 kW automatically fired pellet stove, with internal pellet storage from the same producer. The pellet stove was operated in part- and full load modes (PL, FL), while the wood stove was run with nominal input, the combustion cycle based on two fuel loads including the ignition phase. The detailed description of stoves and sampling parameters is provided in previous publication (Kistler et al., 2012).

PM_{10} was collected on quartz- and cellulose ester filters (PALL, 45 mm diameter).The size segregation was assured by single impaction stage low-volume separator with efficiency of 50% for particles with aerodynamic diameter lower than 10 µm (Digitel, AG, $1m^3\ h^{-1}$).

Sampling was conducted at near ambient temperatures (20-30°C), under super-isokinetic conditions.

The ignition phase was not included in sampling of emissions from pellet combustion (which is a common testing practice, defined also in the testing norm), while the sampling of log wood burning started immediately after ignition. Emission tests were conducted generally with “cold stove”($T_{stove} \sim T_{ambient}$ at the beginning of sampling) or with “cooled-down stove” - in case of a second experiment on the same day the stove was cooled down to 30-40°C. This condition was not fulfilled for tests with garden waste, as well as for a single test with European hornbeam, where the start temperatures were respectively 45-60 and 90°C.

2.2. Analytical part

2.2.1. Filter preparation and weighing

The PM mass was determined gravimetrically as described in Kistler et al. (2012). Prior to weighing fall sampled filters were conditioned (20°C, ±1, 50%±5 relative humidity) for at least 48 hours to asses a stable, comparable water content in filter material and particle load.

Filter blanks were weighed parallel to samples and the readout was corrected accordingly to masses found on filter blanks.

Samples were stored in -18°C.

2.2.2. Carbon fractions

Organic carbon (OC), elemental carbon (EC) and carbonate carbon (CC) were determined with the "SUNSET OC-EC Lab Instrument" (Birch and Cary, 1996). A prolonged NIOSH (National Institute of Occupational Safety and Health) protocol, with the duration of 13 minutes was used. A temperature ramp rising up to 870°C allows the integration of CC. The detection of each carbonaceous fraction was performed using the different thermal stability of OC, EC and CC. Small filter disc of 10 mm diameter was punched out from the quartz filter shortly before the analysis and was shifted into the sampling oven of the instrument on the quartz spoon. The first phase of the measurement is carried out in the pure helium atmosphere and provides a measure of OC. During the second phase of the measurement EC is quantified. This requires oxidizing atmosphere (95% He, 5% O_2). The detection is assured with flame ionization detector (FID). Prior to detection the organic vapors from the first phase are oxidized to CO_2 and than converted to methane. CO_2 from oxidation of EC in the second phase is alike converted to CH_4. For the calibration reasons, after the analysis of each sample a constant volume of methane with known concentration is injected into the sample oven.

The transmittance of the laser beam through the filter during the heating procedure is recorded in order to identify the split point between elemental and organic carbon. After the transmission signal reached its initial value, the FID signal is attributed to EC. Carbonate carbon is integrated as the sharp peak occurring at the highest temperature phase (870°C).

The total carbon (TC) content is calculated as a sum of OC, EC and CC.

2.2.3. Saccharides

The determination of saccharides was performed with an improved high performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). This method is recommended for atmospherically relevant saccharides (e.g., from biomass burning or biogenic activity) and has been described by Iinuma et al. (2009).

Small discs of quartz filters were punched and aliquots from each filter (0.78 cm^2) were extracted in a separate eprouvettes with 3 mL ultra-pure water (Milli-Q, 18.2 MΩ resistance) under 30 min ultrasonic agitation. Extract was filtered through a syringe filters (0.45 µm, Chromafil, Macherey-Nagel) to remove ion-soluble material. Analysis was carried out using a Dionex ICS-3000 system consisting of a gradient pump, column compartment (with pre-column and analytical column Carbo-Pac MA1) and electrochemical detector with working gold electrode. A constant flow of sodium hydroxide (0.4 mL min^{-1}) with a concentration increase from 480 mM to 650 mM was set. The eluent was prepared at the beginning of each week of 50% low carbonate sodium hydroxide (Roth) and ultra-pure water (Milli-Q). The calibration curves for all sugars were measured daily. Standards were prepared from 1000 µl mL^{-1} stock solutions each week and were stored in -18°C.

Data acquisition and integration was performed with Chromeleon software (Dionex).

2.2.4. Humic Like Substances (HULIS)

Analysis of HULIS was performed according to procedure described in (Limbeck et al., 2005). Samples were clustered according to wood type- generally filters from two tests were combined for the analysis (in case of black poplar, black locust and European larch only one filter was taken). In each case 9.6 cm² of active filter area (two times ½ filter) were extracted (except larch, and garden biomass samples were only one filter was available, though the sample area was 4.8 cm²). The extraction of each sample was carried out twice: with ultra-pure water (Milli-Q) and diluted NaOH (Merck) respectively. Subsequently both extracts were combined and per-concentrated by solid phase extraction with size exclusion (ISOLUTE C18 cartridges, Biotage). This step was followed by a clean-up on an anion exchange column (ISOLUITE SAX, Biotage) placed in a flow injection system. The extract was instilled in the oven, oxidized and the resulting CO2 was quantified with not dispersive IR detector.

2.2.5. Non-polar organic compounds

Polycyclic aromatic hydrocarbons (PAHs) and n-alkanes C22-C38 were extracted together from combined samples (Kistler et al., in preparation for submission). The extraction efficiency was tracked by using deuterated internal standards (d-50 tetracosane and d12-benzo(a)pyrene; Sigma-Aldrich) at the onset of the extraction and 1-bromopentadecane (Fluka) at the end of the procedure prior to injection.

Determinations were made with a GC-MS system described by Kotianova et al. (2008). Analyzed compounds were identified using their electron ionization mass spectra and comparing them to the spectra from the NIST library. A series of standards for PAHs (benzo(de)anthracene-7-one, benzo(a)pyrene, benzo(e)pyrene, benzo(ghi)perylene and coronene [all: Fluka]), as well as for n-alkanes (C22, C24, C26, C28, C30 and C32 [all: Fluka]) was used for calibration. Those compounds, for which no calibration curve was done were quantified using a calibration curve of the nearest lower carbon number n-alkane (n-alkanes) or benzo(ghi)perylene (PAHs).

2.2.6. Inorganic ash particles:

Inorganic ions

The cations: sodium, ammonium, potassium, magnesium and calcium, as well as anions: chloride, nitrate and sulfate were determined by isocratic ion chromatography. Small discs of loaded filters (with diameter of 10 mm) were punched out, placed in eprouvettes and extracted in 12 mM methane sulphonic acid (cations) and ultra-pure Milli-Q water (anions). The determination was performed with a Dionex CS12A cation exchange column, respectively Dionex AS12A anion exchange column, auto-regenerated suppressor and Dionex QIC, respectively Dionex CD20, conductivity detectors.

Quantification was carried out with calibration curves of external standards. Standard solutions were prepared from stock solutions and stored by low temperatures. A set of standards were measured four times during each batch. For the integration of results the Dionex Chromeleon software was used.

Other inorganic trace components

The analysis of particulate trace inorganic constituents was carried out with XRF (Al, As, Si) and with ICP-OES, GF-AAS (B, Ba, Cd, Cr, Co, Cu, Fe, Mn, Ni, P, Pb, Sn, Sr, Ti, V and Zn) from the cellulose ester filters. XRF was performed with a Philips X-Unique II 1480, wavelength-dispersive X-ray fluorescence spectrometer, with a rhodium target X-Ray tube (50 kV, 40 mA, Kα = 0.616 Å). The flow proportional detector was operated with 10% v/v methane in argon PR-gas (Messer, Austria).

For calibration aerosol-generated filter standards were used. Measurement validation was done with NIST Certified Reference Material 2709.

After XRF analysis the filters were digested in *aqua regia* with addition of hydrofluoric acid. This step was carried out in closed Teflon vessels, under pressure in a microwave oven. In the further step the bulk of the acid was removed by boiling out from the open vessels and the final solution was prepared with dilute hydrochloric acid (2% v/v). The sample digests were analyzed. A detailed description of the method is given in Handler et al. (2008).

3. Results and discussion

3.1. Carbonaceous fractions and elemental balance

The EC/OC/CC values obtained from transmission thermo-optical measurement of were already determined by Shahid (2011). However, the results presented in this work were re-integrated, with attention of manually setting the split point between organic and elemental fraction. It has to be noted, that EC/OC determinations of wood smoke are relatively uncertain due to the fact, that organic material from smoldering combustion contains a “brown” carbon fraction, which is difficult to determine with conventional EC/OC instrumentation (see e.g. Wonaschuetz et al., 2009 and discussion therein). From brown carbon and related constituents charring artefacts during the heating procedure in the thermal optical are envisaged, increasing with the relative amount of OC present in the sample. The method used in this work is frequently used for wood smoke samples, thus results are comparable with data from other papers. But from the Wonaschuetz et al. (2009) study can be derived, that the method applied tend to over estimate the EC contributions in particular for samples with high OC.

For the elemental balances the data from the determination of EC/OC/CC; inorganic ions, the non-soluble fractions of the major inorganic elements and the trace elements have been used. Table 1 summarizes the data for fraction balance, based on carbonaceous fractions, inorganic ions and remaining inorganic fraction. The CC masses were recalculatet using C/CO_3^{2-} stoichiometric, and have been included in the inorganic ions group. Mineral constituents determined by XRF (Si, Al, As) and "elements" determined by ICP (respectively AAS) have been summarized into the group nominated as "trace elements", where also "non-soluble" parts of K and Ca have been included. The remaining unidentified part is denominated to "rest PM (OC)" and expresses a sum derived for a non-accounted contribution of H, O and hetero-atoms from the organic material. For the second case described in the study OM was derived from the relation OM = OC*1.5. This is a conversion derived from the mass balance of garden leaves combustion (Schmidl et al., 2008c).

Table 1. Summary results of non carbonate carbon fractions, inorganic ions, other inorganic ash constituents (expressed as oxides), rest (for sum formed with OC, and for sum formed for OM=1.5*OC). For details see text.

	WP (FL)	WP (PL)	BR	EH	EB	BPop	TO	SO	PO	BL	SF	EL	NS	BP	SP	L	N
PM_{10} (mg MJ^{-1})	24	16	32	41	66	20	59	222	57	67	100	21	53	101	53	626	85
	%PM_{10}																
Carbon fraction																	
OC	11	9	19	37	32	28	23	31	33	35	27	46	34	36	38	55	58
EC	15	13	30	20	34	22	37	14	22	21	25	26	22	34	39	10	19
TC	26	22	49	57	66	50	60	45	55	56	52	72	56	71	77	65	77
Inorganic Ash Components																	
Inorganic ions	46.2	51.0	4.4	4.4	4.3	7.4	10.2	3.2	8.6	5.3	8.3	4.3	2.0	1.2	2.3	0.7	0.9
Trace Elements	2.6	1.1	2.9	1.2	0.5	0.8	0.3	2.1	3.4	1.0	1.9	0.5	0.5	1.7	1.4	0.9	0.6
Unidentified																	
Rest PM (OC)	25	26	43	37	29	42	30	50	33	38	38	23	41	26	19	34	22
Rest PM (OC*1.5)	20	22	34	19	13	28	18	35	16	20	25	0	24	8	0	6	-7

The results of the balances are aggregated for pellets, HW+BR, SW and GW in Figure 1 and Table 2. For WP the dominant emission component are inorganic ions, which has been observed and reported in detail for Scandinavian studies (Kocbach Bølling et al., 2009), and for an Austrian study (Schmidl et al., 2011). GW exhibited high absolute emissions, in particular leaves. The carbonaceous fraction was dominated by OC. The undetermined rest of 28% disappears, when OM is calculated from OC with a factor of 1.5 for HW+BR and SW there is a tendency for SW to exhibit slightly higher TC contributions than for HW+BR (Figure 1 and Table 2). On the other hand, HW+BR show slightly higher contributions of the inorganic ions as well as of trace elements than SW. In total it results for a larger unexplained fraction for HW+BR than for SW. The unidentified rest is attributed to unaccounted amounts of humidity associated with the inorganic ions and the organic fraction. From growth curves of inorganic salts (Na^+, K^+, NH_4^+ salts) (Rissler et al., 2009) it can be derived, that the humidity of inorganic ash constituents of wood combustion residues may amount at 50%

rel. ambient humidity still up to 50% (m/m), which would explain at large the unidentified fraction of the WP tests. The unidentified fraction in the HW+BR and SW samples represents likely a water content of estimated 5-10%, and the H, O and hetero atoms of the OC. For an assumed humidity of 5-10% the back calculated conversion factor for OM from OC would be 1.6-1.7 for SW and 2.0-2.2 for HW+BR. It appears that HW+BR OM emissions are oxidized at a higher degree than SW. However, there is also the possibility, that HW+BR smoke particles are more hygroscopic than smoke particles from SW.

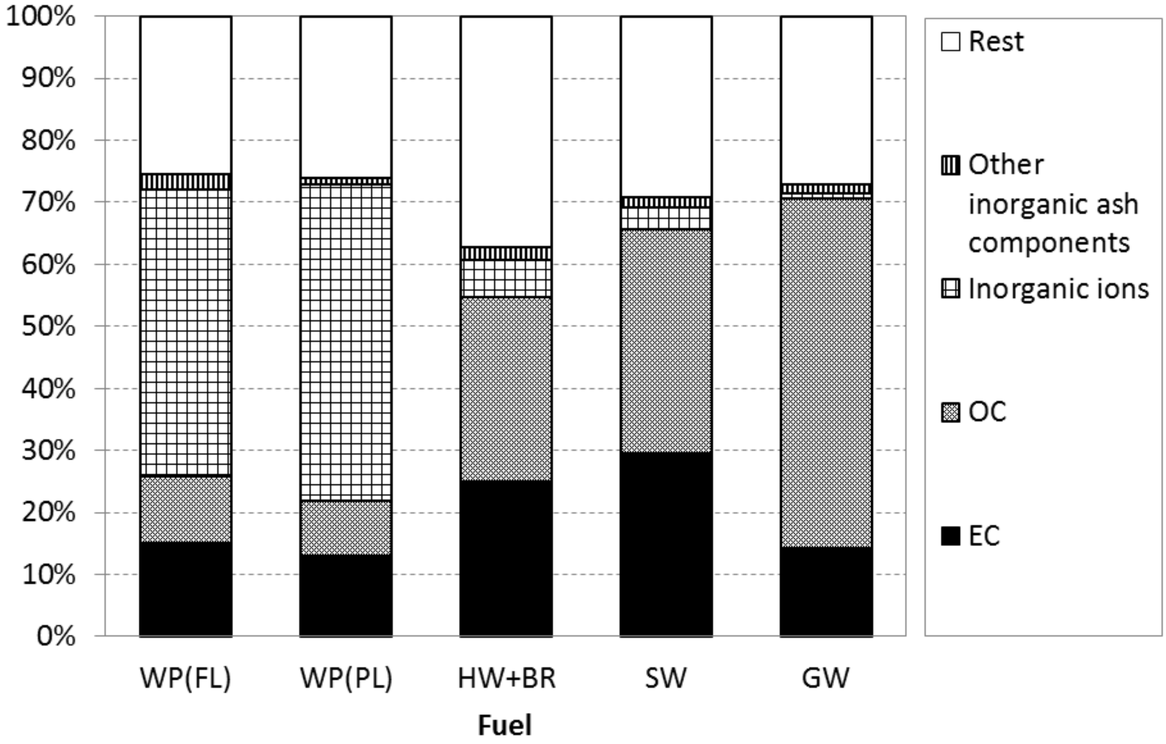

Figure 1. Balance results of non carbonate carbon fractions EC, OC, inorganic ions, other inorganic ash constituents, rest (for sum formed with OC). For details see text.

Table 2. Balance results of non carbonate carbon fractions EC, OC, inorganic ions, other inorganic ash constituents, rest (for sum formed with OC, and for sum formed for OM=1.5*OC). Details in the text.

	WP	HW+BR	SW	GW
PM_{10} (mg MJ^{-1})	20	71	66	356
	% PM_{10}			
Carbon fractions				
OC	10	30	36	56
EC	14	25	30	14
TC	24	55	66	71
Inorganic Ash components				
Inorganic ions	49	6	4	1
Trace Elements	2	2	1	1
Unidentified				
Rest PM (OC)	26	38	30	28
Rest PM (OCx1.5)	21	23	11	0

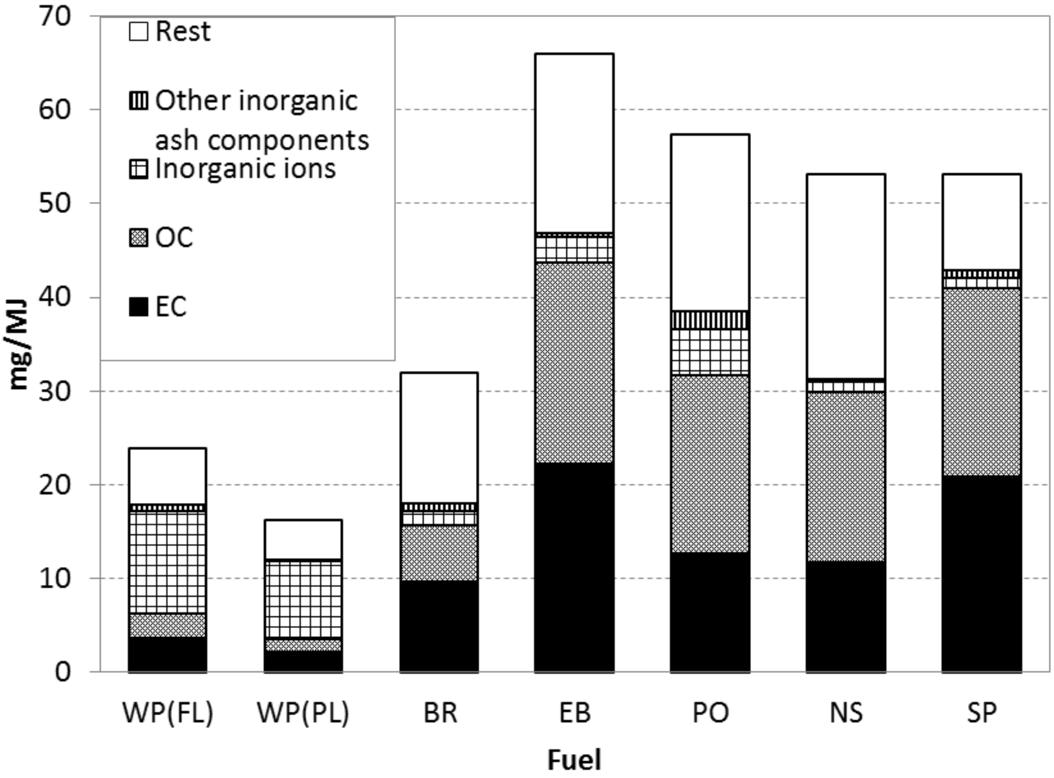

Figure 2. Balanced emission rates of non carbonate carbon fractions EC, OC, inorganic ions, other inorganic ash constituents, rest (for sum formed with OC) for individual wood species. Details in the text.

In the presentation of the balanced emission rates for selected individual wood species (Figure 2) representing pellets, briquettes and most popular HW and SW types for the Alpine district and surroundings, it becomes evident, that briquettes although characterized by relatively low emission rates, differ still considerably in the elemental emission profile from pellets. It is likewise observed that hardwood smoke particles contain a higher fraction of inorganic ash constituents than softwood. A conclusive explanation for the variability of the undetermined rest between the different wood species is not possible from the data accessed so far.

3.2. Organic speciation of smoke emissions

3.2.1. Anhydrosugars

Anhydrosugars are the largest contributors to OC, among analyzed compounds. The dominant anhydrosugar in wood smoke is levoglucosan. In lower concentrations mannosan and galactosan are regularly observed. Occasionally also mannitol, xylitol and glucose were observed in very low concentrations. The occurrence of sugar alcohols is ascribed to presence of fungal spores (Bauer et al., 2008), which may imply that smoke containing mannitol and xylitol originates from fuel with higher moisture, attacked, at least partially by mold. The suggestion is moreover supported by the fact that the highest amount of sugar alcohols was found in the garden waste (mostly leaves).

Table 3. Major anhydrosugars (levoglucosan, mannosan, galactosan) fractions in PM_{10} from wood types.

		Levoglucosan	Mannosan	Galactosan	Lev/Man*	Lev/Gal*	PM/Lev*
	Fuel	**%PM**	**%PM**	**%PM**			
	WP(FL)	0.10	0.02	0.01	6	7	1031
	WP(PL)	0.27	0.11	0.02	2	13	373
	BRI	5.0	0.41	0.09	12	57	20
	EH	4.6	0.16	0.08	28	58	22
	EB	0.3	0.02	0.01	19	23	288
	BPop	2.4	0.19	0.06	13	40	42
	TO	0.40	0.03	0.02	14	24	251
	SO	13.4	0.57	0.28	24	48	7
	PO	19.9	0.60	0.38	33	52	5
	BL	9.7	0.32	0.17	31	58	10
	SF	1.7	0.85	0.14	2	12	58
	EL	10.2	2.61	0.92	4	11	10
	NS	5.8	1.63	0.28	4	21	17
	BP	2.7	0.82	0.10	3	27	38
	SP	1.7	0.52	0.10	3	18	59
	N	0.8	0.16	0.06	5	12	126
	L	3.6	0.32	0.55	11	7	28
Average	**WP**	0.18	0.06	0.02	3	11	548
	HW+BR	7.0	0.29	0.14	**24**	51	**14**
	SW	4.4	1.3	0.31	**3**	14	**23**
	GW	2.2	0.24	0.31	9	7	45
Median	**WP**	0.18	0.06	0.02	3	11	548
	HW+BR	4.8	0.25	0.08	**19**	58	**21**
	SW	2.7	0.85	0.14	**3**	19	**38**
	GW	2.2	0.24	0.31	9	7	45

*…ratios are derived from averages.

In the combustion experiments with pellet stove levoglucosan and related anhydrosugar emissions were constantly very low, but detectable (Table 3). The same was noticed for anhydrosugars relative fractions in PM_{10}. For the chimney stove, a large variation of the emission rates of Lev (and its concentrations in PM_{10}) was observed (Figure 3). The variability of relative Lev concentration was observed between the different wood types, but not within the test triplicates. The concentrations of Lev in PM_{10} ranged from as low as 0.4% for TO, to around 20% in wood smoke from PO. The average for BR and HW was 7%, for SW 4.4 %.

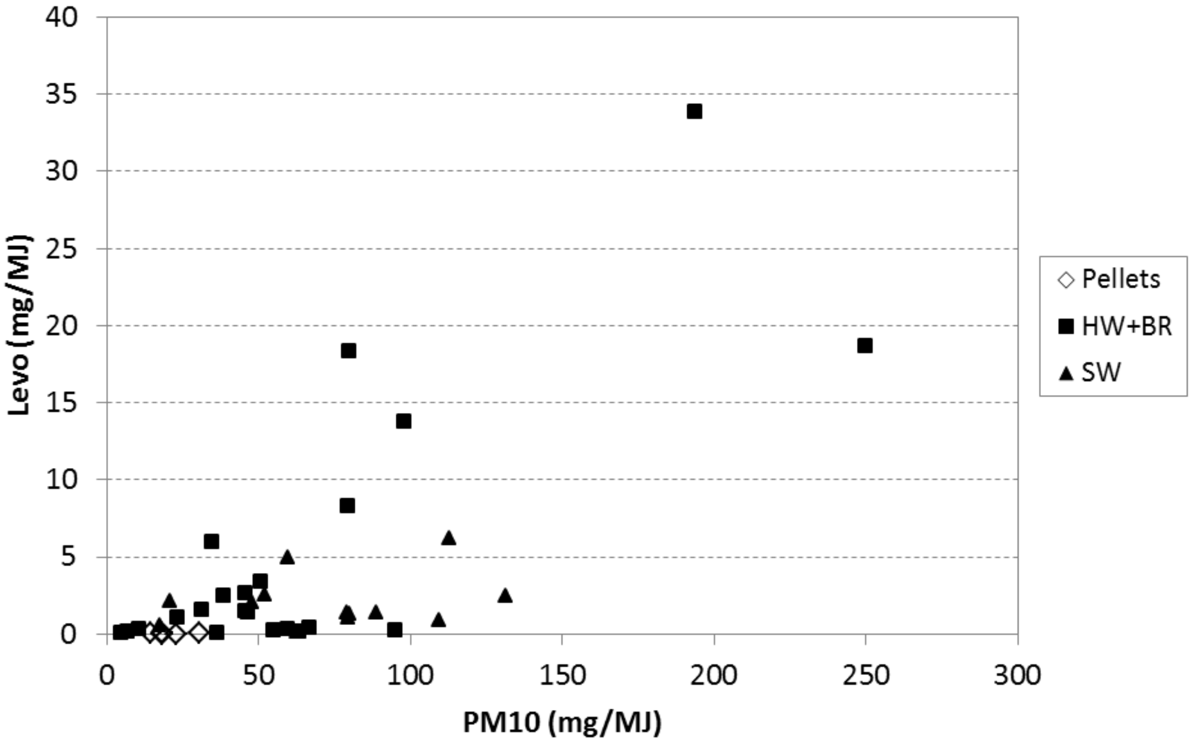

Figure 3. Levoglucosan vs. PM_{10} emission rate for individual tests.

The levoglucosan/mannosan (Lev/Man) ratio within the triplicates was relatively stable. The Lev/Man ratio for BR and HW ranged from 12-33 for BR and HW, and 2-4 for SW, with grand averages of 24 for HW+BR and 3 for SW. Also the Lev/Man ratio of 3 for WP was within the softwood range. The higher relative emissions of mannosan from softwood can be seen in Figure 4.

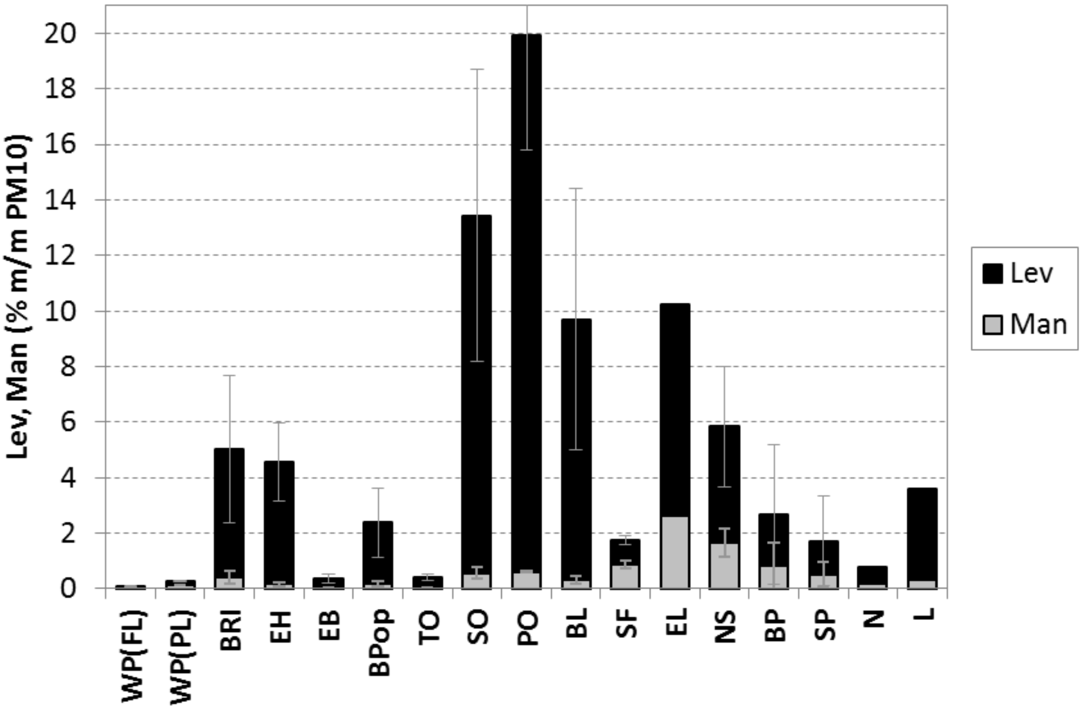

Figure 4. Levoglucosan and mannosan content in PM_{10} emissions from different bio-fuel types (WP, BR, logwood); error bars in terms of standard deviation.

The levoglucosan/galactosan (Lev/Gal) ratio has been reported to decrease for smoke from garden waste combustion when compared to logwood combustion (Schmidl et al., 2008c). In the garden leaves test in the Schmidl et al. (2008c) study, an average Lev/Gal ratio as high as 1.3 was observed, compared to a range of 3.4-31 for log wood combustion in a tiled stove (Schmidl et al., 2008b). In our experiment, averaged Lev/Gal ratios were around 50 for HW and 14 for SW. The garden waste exhibited a higher Lev/Gal ratio, of around 7. Similarly to the tiled stove combustion experiment, European larch emissions gave a Lev/Gal ratio of 11, not far from the leaves ratio. Also SF yielded a Lev/Gal ratio of 12, close to EL. Thus, although the Lev/Gal ratio might be indicative for garden waste combustion, it has to be considered, that the base-case of log wood combustion yields Lev/Gal ratios of around 50 for HW and 14 for SW. This means that for a qualitative assessment of wood combustion emissions to PM_{10} the type of wood mainly used in the area will be influential on the Lev/Gal ratio of concentrations of anhydrosugars observed in ambient air.

The PM/Lev ratio is used as a diagnostic ratio for assessing the contribution of wood smoke to ambient PM levels. From combustion experiments with a tiled stove Schmidl et al. (2008) derived a PM/Lev ratio of 10.7-11.2 for an “Austrian mix” of wood types. In a similar way including a larger set of emission data Piazzalunga et al. (2011) have obtained a PM/Lev ratio of 10.4 for the Italian province of Lombardy. From data for US wood types for Arizona and Washington a quite lower PM/Lev ratio of around 5 (estimated from the reported TC/Lev ratios of 6-7) was obtained (Holden et al., 2011). The PM/Lev ratios discussed above are centered around 10 and below, which is typical for older stove and fire place types. In the current study we obtained PM_{10}/Lev ratios for “new” stove types. As reviewed by Kocbach Bølling et al. (2009)

combustion in newer stove types leads to lower PM emissions but higher relative contents of EC in PM due to higher combustion temperatures. These conditions are also influential on the anhydrosugars emissions. In Table 4 the levoglucosan contents (Lev/PM in µg mg^{-1}) and PM/Lev ratios - „stove"averages - from combustion tests at TUV (Gonçalves et al., 2010 in cooperation with TUV) are compiled. The first study has been performed with a traditional tiled stove installed in a residence. The six tests series with the four different chimney stoves have been performed at the TUV test stand, one of them with Portuguese wood in cooperation with the University of Aveiro. The individual data of the chimney stoves showed a spread similar to the diagram in Figure 3. The averages of the test series, however, are relatively similar, in a range of 49-68 µg mg^{-1} Lev/PM_{10}. The "grand average" for the chimney stoves accounts to 55 µg mg^{-1} Lev/PM_{10}, yielding a PM_{10}/Lev ratio of 18. The median is very close to the average indicating a normal distribution of the data.

Table 4. Compilation of levoglucosan contents (Lev/PM in µg mg^{-1}) and PM/Lev ratios – "stove" averages - from combustion tests at TUV (Gonçalves et al., 2010 in cooperation with University of Aveiro). Average and median for chimney stove tests (CS).

Reference	Stove	wood	Levoglucosan	PM_{10}/Lev
			µg mg^{-1} PM_{10}	*factor*
Schmidl et al., 2008a	Tiled stove	"AT mix"	91	11
Schmidl et al., 2008b	CS RF1	HW	52	19
	CS REP	HW, SW, BR	60	17
Schmidl et al., 2011	CS WJ	HW, SW, BR	49	21
	CS RF1	HW, SW, BR	42	24
Gonçalves et al., 2010	CS RF1 Portugal wood	HW, SW	68	15
This study	CS RF2	HW, SW, BR	60	17
				from ave/med
Chimney stoves	CS Average	Average	55	18
	CS Median	Median	56	18

From Table 4 it can be derived, that PM_{10}/Lev ratio of chimney stoves is consistently higher than of the tiled stove.

The levoglucosan/mannosan (Lev/Man) ratio is indicative for SW and HW emissions (Schmidl et al., 2008a). In Table 5 Lev/Man ratios from combustion tests of four studies conducted at TUV (Schmidl et al., 2008a,b; Schmidl et al., 2011, this study), are aggregated for the four different studies, sorted for SW and HW. The SW ratio is very stable and comparable for tiled stove and the chimney stoves. The Lev/Man ratio for SW was also observed for the pellet stove emissions in the same range as for the other stoves. Lev/Man ratios for HW were consistently higher for the chimney stoves compared to the tiled stove.

Table 5. Lev/Man ratio from combustion test of four TUV studies (Schmidl et al., 2008a,b; Schmidl et al., 2011, this study), aggregated data for the four studies.

Reference	Stove	Lev/Man	Lev/Man
		SW	HW
Schmidl et al., 2008b	Tiled stove	3.3	12.5
Schmidl et al., 2008a	Chimney stove RF1, REP	3.6	21
Schmidl et al., 2011	Chimney stove RF1, WJ	2.9	16
	Pellet stove Pellets	2.8	
This study	Chimney stove RF2	3.2	21.6 (incl. BR)
	Pellet stove	3.1	
Chimney stoves	Average	**3.1**	**19.5**
	Median	3.1	20.3

Table 6. Lev/Man ratio from combustion test of chimney and pellet stoves (Schmidl et al., 2008b; Schmidl et al., 2011, this study), aggregated data for wood types.

Average (number of tests)	**Lev/Man**
HW	
Briquettes HW (1)	12.1
Oaks (8)	20.7
Beech (7)	18.2
Hornbeam (2)	25.7
Garden trees HW (6)	18.7
Other HW -AS,AL,BL,Bpop,BI,CH,MA (7)	20.3
SW	
Briquettes SW (5)	2.9
Spruce (4)	3.4
Pines (3)	3.5
Larch (2)	3.9
Silver fir (1)	2
WP	
Pellets (2)	2.9
Ave/Med	
Average HW logs+BR (29)	19.3
Median HW logs+BR (29)	19.5
Average SW logs+BR (29)	3.1
Median SW logs+BR+WP (29)	3.2

The Lev/Man ratio for different individual wood types showed some variation for HW and SW types. Only HW briquettes differed in the Lev/Man ratio yielding only about half of the typical ratio for HW. The reason for the difference might be either a not declared SW content or different combustion properties. The Lev/Man ratio for HW briquettes is similar to the Lev/Man ratio for HW obtained from combustion test with the tiled stove.

3.3. Discussion of ambient Lev/PM ratios

The diagnostic ratio of Lev/PM deduced from emission studies show large variations for different combustion experiments with “new” and “old” types of stoves, boilers and fire places. For this reason the use of the Lev/PM ratio for deriving ambient wood smoke PM levels has been questioned by some authors (e.g. Hedberg et al., 2006, Glasius et al., 2006). The early assessments based on the Lev/PM ratio, however, were based on a very small selection of wood combustion test results (e.g. Caseiro et al., 2009). Improvements of deriving a realistic Lev/PM ratio for ambient wood smoke studies have been put forward by using combined methods, e.g. on-line aerosol mass spectrometry, aethalometer, and ^{14}C (Sandradewi et al., 2008; Lanz et al., 2008) or PMF (Piazzalunga et al., 2011). Sandradewi et al. (2008) derived PM(bb)/Lev ratios of 8-17 for Roveredo, 20 for Reiden and 25 for Zurich, indicating a regional dependence of the PM(bb)/Lev ratio. A similar observation of regional differences is reported by Piazzalunga et al. (2011) who derived PM(bb)/Lev ratios of 9-23 for 6 sites during 3 campaigns in northern Italy. In this study, a PMF-derived averaged PM(bb)/Lev ratio of 16.9 was obtained, in contrast to a ratio of 10.4 derived from a large set of emission data. Further ambient observations of PM(bb)/Lev ratios are reported for Elverum (Norway) where for PM_{10}(bb)/Lev an estimated range of 14-23, and for PM2.5(bb)/Lev a range of 10-18 with an average of 15 is derived (Yttri et al., 2009).

The ambient PM/Lev ratios in European studies appear to be consistently higher (e.g. ~ 10-20) than the earlier emission derived factors (~ 7-11), which is to some part a result of secondary particle formation from emitted fumes. However, a range of biomass combustion devices is expected to exhibit higher PM/Lev ratios, than observed from “old” stoves and fireplaces. The current study shows that certain types of “new” stoves have the potential to increase the ambient PM/Lev ratios, which might be considered also for modern boilers and medium sized units based on chipped fuels. Creating a data base of technology based emission inventories for wood smoke PM, EC/OC, levoglucosan, mannosan, galactosan, as well as BaP and the “EU” PAHs (EU directive 2004/107/EU) would be helpful to assess in detail the wood smoke contribution to ambient PM levels.

3.4. Combined emission profiles for regionally used fuels

Emission profiles of wood smoke are required for use in advanced aerosol source receptor models (e.g. discussion in Schmidl et al., 2008b). The profiles for the individual biomass species tested in this study are available in the emission data base. Here, aggregated profiles for WP, HW+BR, SW and GW are listed in Table 7. Major differences of the chimney stoves profiles compared to those reported for a tiled stove (Schmidl et al., 2008b) are occurring for EC (higher for chimney stoves), OC (lower for chimney stoves), alkanes (higher for chimney stoves), PAHs (higher for chimney stoves) and for inorganic ions (with exception of NH_4^+ higher for chimney stoves). For trace elements including Al and Si relatively similar results were obtained for both stove types. The differences to the tiled stove results reflect the different combustion properties of the stoves, i.e. higher combustion temperatures achieved by chimney stoves, which lead to higher EC, higher PAHs, lower OC and higher inorganic ash constituents (in particular of K^+, Cl^- and SO_4^{2-}) in emissions, (Kocbach Bølling et al., 2009).

The WP profiles can be compared with those from a similar stove tested in the BIOCOMB project (Luisser et al., 2008; Schmidl et al., 2011). For the major components very similar relative contents of EC, OC and inorganic ions were observed, while PM_{10} emission rates were higher (24 mg MJ^{-1} for full load) in this, than in the BIOCOMB study (12 mg MJ^{-1} for full load, stove "A") (Schmidl et al., 2011).

The profiles for the pellet and the chimney stove (Table 7) are an important step for creating the data base of technology based emission inventories for wood smoke PM, EC/OC, levoglucosan, mannosan, galactosan, as well as BaP and the "EU" PAHs (EU directive 2004/107/EU).

Table 7. Aggregated emission profiles for pellet stove (WP), and chimney stove (HW+BR, SW, GW).

Compound	Method	WP(FL)	WP(PL)	HW+BR	SW	GW
PM_{10} (mg MJ^{-1})		24	16	71	66	356
Carbon fractions (%PM)						
OC	TO	11	9	30	36	56
EC	TO	15	13	25	30	14
TC	TO	26	22	55	66	71
Organic components						
Saccharides (%PM)						
Levoglucosan	HPLC	0.1	0.3	6.97	4.44	2.20
Mannosan	HPLC	0.02	0.11	0.29	1.29	0.24
Galactosan	HPLC	0.01	0.02	0.14	0.31	0.31
Other saccharides	HPLC	0.06	ND	0.10	0.06	0.12
Sum: saccharides		0.19	0.40	7.47	6.09	2.88
HULIS-C		<LOD	NA	0.73	0.24	0.90
Alkanes (%PM)						
C22	GCMS	0.004	NA	0.013	0.011	0.0085
C23	GCMS	0.003	NA	0.013	0.0081	0.015
C24	GCMS	<LOD	NA	0.035	0.023	0.069
C25	GCMS	<LOD	NA	0.025	0.019	0.039
C26	GCMS	<LOD	NA	0.031	0.037	0.044
C27	GCMS	<LOD	NA	0.031	0.036	0.076
C28	GCMS	<LOD	NA	0.043	0.044	0.046
C29	GCMS	<LOD	NA	0.051	0.043	0.14
C30	GCMS	<LOD	NA	0.031	0.036	0.034
C31	GCMS	<LOD	NA	0.034	0.030	0.089
C32	GCMS	<LOD	NA	0.031	0.023	0.041
C33	GCMS	<LOD	NA	0.026	0.038	0.049
C34	GCMS	<LOD	NA	0.013	0.022	0.015
C35	GCMS	<LOD	NA	<LOD	<LOD	<LOD
C36	GCMS	<LOD	NA	<LOD	<LOD	<LOD
C37	GCMS	<LOD	NA	<LOD	<LOD	<LOD
C38	GCMS	<LOD	NA	<LOD	<LOD	<LOD
Sum: alkanes		0.01		0.38	0.37	0.67

PAHs (%PM)						
7-on	GCMS	0.028	NA	0.11	0.08	0.16
RET	GCMS	0.011	NA	0.0065	0.030	0.018
BbF+BkF	GCMS	0.021	NA	0.089	0.056	0.14
BjF	GCMS	0.015	NA	0.043	0.033	0.071
BeP	GCMS	0.0081	NA	0.029	0.022	0.043
BaP	GCMS	0.0068	NA	0.030	0.023	0.061
Per	GCMS	<LOD	NA	0.021	0.011	0.039
IcdF	GCMS	<LOD	NA	0.030	0.017	0.041
IcdP	GCMS	<LOD	NA	0.046	0.028	0.073
BghiP	GCMS	0.0092	NA	0.050	0.029	0.073
Anth	GCMS	0.0094	NA	0.011	0.015	0.029
DBA	GCMS	<LOD	NA	0.022	0.0093	0.026
Cor	GCMS	<LOD	NA	0.027	0.014	0.032
Sum PAHs		0.11	-	0.51	0.37	0.80
Inorganic ash components						
Inorganic ions (%PM)						
Na$^+$	IC	2.1	2.0	0.07	0.03	0.0
NH$_4^+$	IC	0.2	0.4	0.4	0.19	0.1
K+	IC	23.2	21.4	2.4	1.5	0.1
Mg^{2+}	IC	0.1	0.1	0.02	0.02	0.0
Ca^{2+}	IC	0.7	0.9	0.3	0.3	0.2
Cl$^-$	IC	5.2	5.7	1.0	0.8	0.1
NO$_3^-$	IC	0.5	2.7	0.3	0.2	0.0
SO$_4^{2-}$	IC	12.2	16.7	1.1	0.3	0.1
CO$_3^{2-}$	TO (from CC)	2.02	1.05	0.38	0.29	0.18
Sum: Inorganic ions		46.16	51.02	5.97	3.62	0.88
Trace elements (%PM)						
Al	XRF	0.028	0.053	0.039	0.029	0.036
As	XRF	0.001	0.001	0.001	0.001	0.004
Si	XRF	1.31	0.19	0.12	0.090	0.063
B	ICP-OES	0.026	0.017	0.012	0.012	0.010
Ba	ICP-OES	0.009	0.005	0.002	0.002	<LOD
insol. Ca	ICP-OES	0.0	0.0	0.21	0.17	0.14
Cd	ICP-OES	0.003	0.002	0.001	0.004	0.001
Co	ICP-OES	<LOD	<LOD	<LOD	<LOD	<LOD
Cr	ICP-OES	0.053	0.087	0.11	0.11	0.20
Cu	ICP-OES	0.029	0.029	0.014	0.009	0.009
Fe	ICP-OES	0.071	0.14	0.084	0.063	<LOD
insol. K	ICP-OES	0.0	0.0	0.99	0.76	0.45
Li	ICP-OES	0.006	0.002	0.002	0.005	<LOD
insol. Mg	ICP-OES	0.0	0.0	0.011	0.010	0.013
Mn	ICP-OES	0.058	0.039	0.003	0.011	0.007
insol. Na	ICP-OES	0.0	0.0	0.20	0.050	<LOD
Ni	ICP-OES	0.008	0.018	0.014	0.011	0.007
P	ICP-OES	0.031	0.023	0.033	0.023	0.018
Pb	GF-AAS	0.027	0.029	0.009	0.006	0.035
insol. S	ICP-OES	0.28	0.0	0.22	0.26	0.21
Sr	ICP-OES	0.001	0.002	0.005	0.002	<LOD
Ti	ICP-OES	0.002	0.005	0.006	0.004	<LOD
Zn	ICP-OES	0.63	0.47	0.045	0.068	0.051
Sum: Other inorganic ash elements		2.57	1.11	2.13	1.70	1.26

4. Conclusions

The objective of the current work was to chemically characterize the composition of particulate matter from combustion of wood logs, briquettes and pellets.

The stove type and fuel type have the strongest influence on the relative emissions reported in this study. The emissions from the automated pellet stove were characterized by very high inorganic ash particles content, while the chimney stove emitted mostly carbonaceous particles of which organic and elemental carbon was predominant.

The most prominent group of compounds emitted from incomplete combustion in the chimney stove was levoglucosan (ranging from 0.3 to 20%), followed by mannosan and galactosan (with concentrations a factor of 3 to 10 lower). In the contrary to previous studies (Schmidl et al., 2011) levoglucosan and mannosan were observed in detectable quantity from pellets combustion under full and part load, conserving the Lev/Man ratio for softwood. Thus it has to be considered that organic wood smoke tracer compounds may be also emitted from pellet stoves, though in far lower quantities than from logwood combustion.

The absolute PM emissions reported for this study were variable, between tested wood types (e.g., 20 mg MJ^{-1} for poplar, 220 mg MJ^{-1} for sessile oak), but also within tests with the same fuel. This effect was also observed for the emissions of levoglucosan. However, the relative fractions of the anhydrosugars were similar for the same wood type.

The levoglucosan to mannosan ratios discriminated decidedly between hardwood and softwood combustion, and were higher among all modern stoves from tests at TUV for hardwood than those reported for an Austrian tiled stove.

The levoglucosan to galactosan ratio for burning of leaves in the chimney stove was considerably higher than reported for open burning (Schmidl et al., 2008c). It was in the range reported already for some wood types with higher galactosan emissions such as larch and fir. This has to be considered when using Lev/Gal ratios for identification of waste biomass burning in the ambient air.

It was noticed that the diagnostic ratios of PM/Lev for chimney stoves were around a factor of 1.6 higher than those reported for a traditional Austrian tiled stove. The PM_{10}/Lev ratio of around 11 established for combustion of regional wood types (“Austrian mix”) by Schmidl et al. (2008b) may under estimate the wood smoke contributions from ambient studies, since also other appliances for woody fuels may exhibit a higher PM_{10}/Lev than derived from the tiled stove.

The emission profiles for the chimney stove differ also for EC, OC, ions, and PAHs from the tiled stove profiles, indicating wood type related, a technology related influences on the emission characteristics of wood smoke emissions. Thus, the profiles for the pellet and the chimney stove are an important step for creating the data base of technology based emission inventories for wood smoke PM, EC/OC, levoglucosan, mannosan, galactosan, as well as BaP and the “EU” PAHs (EU directive 2004/107/EU; EC, 2004).

Concluding, the findings of the study indicate that wood type related, as well as technology related emission profiles for the different major types of appliances using woody biomass fuels are needed for establishing composite wood smoke profiles for regional modeling of the wood smoke impact on ambient air.

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5. Particulate phase PAHs emissions from combustion of Central European wood types in modern residential stoves[1]

Abstract

We report emission rates of PM_{10} and particulate PAHs from burning (standard test cycles) of the major wood species grown in eight Mid-European countries. The logwood tests were performed with a modern 8kW chimney stove, additional pellets tests with a 9kW pellet stove. The observed benzo(a)pyrene (BaP) emission rates for briquettes and logwood ranged from 3-37 µg MJ^{-1}, the BaP/PM_{10} (µg mg^{-1}) emission ratio from 0.09-0.63. The variation of the BaP/PM_{10} emission ratio is explained with a multiple linear regression model including EC and the burn rate as input variables with a quality of fit ($R^2 = 0.79$). This indicates that the increased BaP emission rates occur during high burn rates (under temporarily hot and air starved conditions), as discussed already in Pettersson et al. (2011), and may be expected under standardized combustion conditions due to e.g., wood related “batch-to-batch” variations. Including results of two further studies performed at the same test site with comparable stoves wood type specific emission rates are obtained for multiple data sets from beech, common oak, spruce and briquettes, as well as aggregated results for “other hardwood” and “other softwood” emissions. The averaged emission rate for all tested logwoods and briquettes is 18 µg MJ^{-1} for BaP and 87 mg MJ^{-1} for PM_{10} (standard combustion cycles). A comparison with literature data indicates that actual BaP/PM ratios from wood combustion are lower than inferred from *EEA/EMEP* (2009) emission data, and stove exchanges from old to modern stoves would not result in BaP reductions as predicted from inventory data.

Keywords: Wood smoke, wood stove, biomass combustion, benzo(a)pyrene, BaP emission rate, BaP emission ratio

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Research highlights:

- BaP emission from four chimney stoves (29 wood and briquette samples) varied from 3-45 µg MJ^{-1}.
- The BaP variation is modeled with “burn rate (kg h^{-1})” and EC (mg MJ^{-1}) as input variables.
- BaP/PM ratios from wood combustion are lower in real world than inferred from emission inventory data.
- Stove exchanges might not result in BaP reductions as predicted from inventory data.
- Ambient PM_{10}WS (wood smoke) levels of 5 µg m^{-3} are associated with 1±0.5ng m^{-3} BaPWS.

Definitions:

“Hardwood” is used here for all broadleaf species; “softwood” for all coniferous wood, including larch, which is a “deciduous” conifer.

“3 studies”: data from 3 studies performed fully or in part at TU Vienna, for pellet stove and chimney stoves using the test stand at the Institute of Chemical Engineering. The “3 studies are: FWF/O, this study; BIOCOMB (Luisser et al., 2008); AQUELLIS FB (Schmidl et al., 2008a).

<u>Stove types:</u>

RF1 6kW manually fired chimney stove
RF2 8kW manually fired chimney stove
RM 6kW automated pellet stove
REP 10kW manually fired chimney stove with controlled air supply
WJ 6.5 kW simple manually fired chimney stove
GU 50 kW automated pellet and chip boiler
SI 35kW old technology logwood boiler

Abbreviations:

TUV   Technical University Vienna, Austria
ABC-W   Austrian Bioenergy Center, Branch Wieselburg, Austria
FL   Full load
WS   Wood smoke
PM_{10WS} PM_{10} from wood smoke
BaP_{WS} BaP from wood smoke
HW   hardwood (broadleaf trees)
SW   softwood (conifers)

<u>Fuels (wood species):</u>

AL   Alder
AS   Ash tree
BL   Black locust
BPop   Black poplar
EH   European hornbeam
EB   European beech
PO   Pedunculate oak (common oak)
SO   Sessile oak
TO   Turkey oak
BP   Austrian black pine
EL   European larch

Chapter 5

NS	Norway spruce
SP	Scots pine
SF	Silver fir
BR	Briquettes
BR_{HW}	Hardwood briquettes
BR_{SW}	Softwood briquettes
C	Pine cones
N	Pine needles
L	Dry leaves
WP	Wood pellets

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely described as carcinogenic and mutagenic chemicals (e.g., Asita et al., 1991, Danielsen et al., 2009) and therefore worldwide their emissions are being controlled. The global emission of the 16 EPA PAHs was estimated for 2004 at 520 Gg y^{-1} with biofuels (56.7%) and wildfires (17.0%) as major sources, and among them firewood burning as predominant source (Zhang and Tao, 2009). Emission densities of the 16 EPA PAHs for the EU27 countries (8.8 kg $km^{-2}y^{-1}$) are comparable to the respective emission density of Asia (9.4 kg km^{-2} y^{-1}), quite higher than in Northern America (2.0 kg km^{-2} y^{-1}) due to higher population densities (data compiled from Zhang and Tao, 2009; supplemental material). From the European emission inventory (EMEP) can be derived, that high emission densities of PAHs in Western and Central Europe are due to a high share of domestic heating emissions in those countries (EEA/LRTRAP, 2012).

In the past century PAH emissions were mainly linked to industries and transportation (Working Group on PAH, 2001). Observations of BaP at seven European EMEP background sites indicated a relatively low background concentration of 0.01-0.24 ng m^{-3} for 2006 (Gusev et al., 2008). The modeled annual mean BaP values for the atmospheric surface layer in 2006 within the European region ranged from 0.01-1 ng m^{-3}, with an average level of 0.4 ng m^{-3} (Prevedouros et al., 2004Early reports identified residential wood combustion as a significant source of ambient air pollution from PAHs in rural communities in US, Scandinavia and Australia, as already discussed by Ramdahl (1983), Ramdahl et al. (1984), Sexton et al. (1985) and Freeman et al. (1990). The wide spread occurrence of wood smoke as a major winter source to fine atmospheric particles has been now manifested from studies at US, New Zealand and European rural and urban sites as reviewed in Kocbach Bølling et al.(2009). The association between biomass fuels and PAH emissions is also intensively studied at Asian sites, since in many countries biomass fuels are used for cooking and heating (e.g., Zhang et al., 2007; Wang et al., 2008).

Most of the ambient PAH measurements in non-urban environments have been performed in campaigns (e.g., Marchand et al., 2004; Ward et al., 2006; Hellén et al., 2008; Bari et al., 2011a,b) thus annual mean values of PAHs in wood smoke emission regions are still rare. The EU target value for benzo(a)pyrene (BaP, one of most toxic particulate matter PAHs, which was established as marker for overall PAH pollution in the ambient air) of 1 ng m^{-3}, however, is defined “for the total content in the PM_{10} fraction averaged over a calendar year” by the directive of European Union Parliament (EN, 2004). More recently investigations of BaP at some non-urban European sites reveal that there is a problem of BaP exceeding the target value which seems to a large extent connected to the use of fuelwood for domestic space heating. e.g., BaP annual mean values in Lungau (an Austrian inner alpine valley) were 1.4 – 2.8 ng m^{-3} in the years 2000-2007; and 17 of 19 urban and rural sites in Austria exhibited annual means above the EU “upper threshold value” of 0.6 ng m^{-3}, which means that a long term monitoring at those sites is required (Spangl et al., 2008). A Swiss study reports exceeding of the EU target value for BaP in a densely populated valley in southern Switzerland, and at further 4 rural sites exceeding of the EU “upper threshold value” (Gehrig, 2011).

Actually, there is no discrepancy between the rural background value of 0.4 ng m^{-3} BaP for Europe as derived from Prevedouros et al. (2004) and local observations of 1 ng m^{-3} BaP and higher for the patchy situated rural settlements. As the actual air quality situation in a rural settlement will be highly dependent on the energy use and the ventilation properties of the region, rather regional modeling programs than individual PAH measurements will be required to identify potential "hot spots" exceeding the EU ambient air quality limit.

For atmospheric dispersion models emission inventories of PAHs including source type characteristics and wood type consumption will be required. For receptor models emission profiles of the diverse biomass appliances and wood types are needed.

Emission data have already emerged for the estimation of PM and PAHs from wood combustion in US studies (compiled in EPA/AP42, 2009) and from Northern Europe (e.g., reviewed by Kocbach Bølling et al, 2009; Pettersson et al., 2011; Lamberg et al., 2011) while less data are available for Western (Alves et al., 2011; Gonçalves et al., 2010, 2011) and Mid European stove and wood types (e.g., Bari et al., 2011a; Schmidl et al., 2008b, 2011).

As already mentioned, PAHs are exerting a carcinogenic potential. Of high interest are the compounds of highest toxicity. The strength of their overall harmful effect can be expressed by a "benzo(a)pyrene – equivalent" (BaPE) (EPA, 1993). The main PAHs required to derive the BaPE are prevailing in the particulate phase (e.g., Hytönen et al., 2009). We focus on particulate PAH emissions from 12 wood species characteristic for the alpine and lowland regions of nine Central European countries. The investigations were performed with modern, certified stoves: manually fired, 8 kW, log wood stove, and 9 kW, automatic pellet stove. The investigated wood types were deciduous species: black locust (BL), black poplar (BPop), European hornbeam (EH), European beech (EB), pedunculate oak (PO), sessile oak (SO), turkey oak (TO); and conifers: Austrian black pine (BP), European larch (EL), Norway spruce (NS), Scots pine (SP), silver fir (SF), as well as hardwood briquettes (BR). In addition, "garden biomass" such as pine cones (C), pine needles (N) and dry leaves (L) were burnt in the log wood stove. The pellet stove was fired with softwood pellets (WP). We add a compilation of relevant data to give an overview about the BaP emission rates from residential wood combustion.

This is the second part reporting results of a project investigating the chemical composition of fine particulate matter PM_{10} from biomass combustion and a continuation of "Odor, gaseous and PM_{10} emissions from small scale combustion of wood types indigenous to Central Europe" (Kistler et al., 2012). We present here only in short the technical information on stove types and sampling procedures, as the detailed description of the combustion experiments and wood chemical data, wood type distribution in Central European countries, emission of CO, NO_x, C_xH_y, PM_{10} and odor threshold is presented in the previous publication (Kistler et al., 2012).

2. Experimental

2.1 Stoves and fuel

The tests have been performed with a modern, certified 8 kW “chimney type” iron log wood stove with fireclay lining (RF2) and an automatically loaded modern small 9 kW pellet burner (RM).

Our test procedure for log wood and briquettes included two fuel loads starting from the cold stove and adding the second load after burn down of the previous load. The test was ended when the CO_2 concentration in the exhaust fell below 3%. Each load consisted of around 1.3 kg of wood (2 or 3 wood logs) per test. Ignition was performed with commercial lighter cubes.

The tests with garden biomass were performed with around 1.2 kg of fuel. The stove was filled for the first load, then ignited and several times refueled.

Due to sampling over whole burning cycles (including the start-up phase) the test procedure is considered close to “reality” since the products of incomplete combustion of the ignition phase are included in our measurement cycle.

The pellet burner is equipped with internal pellet storage. The fuel is supplied to the combustion chamber via an “auger screw”. Combustion air supply is adjusted adequately for the selected thermal output by a fan situated in the flue gas stream. Both fuel load and fan speed are controlled automatically, only the percentage of power output (30 – 100%) is set by the user. Our test consisted of part load runs of about 75 min and full load runs of around 80-370 min. Ignition took place with an electrical resistance heater and air supply from a blower. The ignition phase was not included in tests with pellets.

Wood fuels were selected among tree species indigenous for Austria (AT), and neighboring

countries or regions: Czech Republic (CZ), Hungary (HU), Slovak Republic (SK), Slovenia (SI), Switzerland (CH), Baden-Württemberg and Bavaria (South Germany, S-DE) and South Tyrol (Northern Italy, N-IT). Tree species with abundance of more than 5% of the forest area in each country have been chosen for the test burns (The data obtained from national forest inventories are listed in detail in Kistler et al., 2012). In addition we study emissions from hardwood briquettes (“Forest briketi”, Slovenia) and softwood pellets.

Further details of stove and operational details, as well as the combustion test procedures are given in Kistler et al. (2012), (**Chapter 3**).

2.2. Emission sampling

Gaseous emissions (CO, NO_x, C_xH_y) were sampled and determined with continuous gas analyzers using European standard methods. Details of the set up and data evaluation are given in Kistler et al. (2012)

Particulate matter sampling was performed with a dilution manifold allowing the collection of “total PM” (PM_{tot}), PM_{10} and $PM_{2.5}$ (seven filters) in parallel operated 47 mm filter holders. The basic design of the manifold is shown in Schmidl et al. (2011), modifications as applied in the current report are given in Kistler et al. (2012). For this report we used filters from the PM_{10} line. The dilution manifold operates with dosing dry and particle free air directly after the chimney probe into the sampling line. The dilution ratios and filter volume sampling rates were adjusted in such a way, that PM emissions of “complete” test runs involving igniting and combustion of two loads were collected on one set of filters and no filter changes were required during the tests. Dilution ratios applied were 3-4 for the pellets combustion tests, 10 for the log wood combustion tests and 15-20 for the garden biomass tests. The dilution ratios were pre set by the mass flows applied to the manifold (for dilution and sampling air streams) and controlled with on-line CO_2 determination direct in the flue gas and in the sampling gas after dilution. The manifold was operated with a PM_{10} and a $PM_{2.5}$ pre separator, each connected to three filter holders, two of them equipped quartz filters (Pall Tissuequartz) and one with mixed cellulose ester filter (Pall GN-4 Metricel). One additional filter holder (with quartz fiber filter) was operated without the size separation.

Further details of manifold operation, involved fuel mass, burn rate, heating value, flue gas temperature, modified combustion efficiency, O_2 and CO_2 are reported in Kistler et al., 2012).

Particulate PAHs were determined from the quartz fiber filters. The list of determined PAHs (Table 1) includes the seven PAHs used in US source apportionment studies (Schauer et al., 1996) and six of the seven PAHs recommended by the EU for ambient monitoring (EN, 2004) which are required to derive the BaP toxicity equivalent. These PAHs are five- and six-ring PAHs and occur in the ambient air in wood smoke emissions as well as in ambient air nearly exclusively in the particulate phase (e.g., Pettersson et al., 2011 – supporting information; Kishida et al., 2011). The three-ring PAHs are only partially present in the particulate phase, but are included since they are recommended for the CMB data set for organic PM source attribution (Schauer et al., 1996). Two four-ring PAHs which have not been determined due to their semi volatile behavior but are of interest because of their not neglectable contribution to benzo(a)pyrene-equivalent (BaPE) are benzo(a)anthracene and chrysene. The missing emission factors have been estimated from emission ratios of those PAHs of interest in relation to BaP determined for other wood smoke PAH emission studies (Hays et al., 2003; Jordan and Seen, 2005; Gonçalves et al., 2010; Boman et al., 2011; Pettersson et al., 2011; Jalava et al., 2012; Table 2).

Table 1. PAHs analyzed in wood smoke, abbreviations, and factors used for estimates of BaA and Chr concentrations from BaP data, for estimating BbF and BkF concentrations from the sum, and for deriving the BaP-equivalent (BaPE). PAHs with carcinogenic potential shaded with bold font.

Compound	Index	Ring	BaPE$	f
benzanthrone	7-one	3		
retene	Ret	3		
benzo(b)fluoranthene+benzo(k)fluoranthene	**BbF+BkF** [a,b]	**5/5**	**0.1/0.01**	**BbF/BkF=2.0**
benzo(j)fluoranthene	BjF [b]	5		
benzo(e)pyrene	BeP	5		
benzo(a)pyrene	**BaP** [a,b]	**5**	**1**	
perylene	Per	6		
indeno(1,2,3-cd)fluoranthene	IcdF	6		
indeno(1,2,3-cd)pyrene	**IcdP** [a,b]	**6**	**0.1**	
benzo(ghi)perylene	BghiP [a,b]	6		
anthanthrene	Anth	6		
dibenz(ah)anthracene	**DBA** [a]	**5**	**1**	
coronene	Cor	7		
Not analyzed / derived				f_{BaP}
benz(a)anthracene	***BaA*** [a,b]	***4***	***0.1***	***BaA/BaP=0.8***
chrysene	***Chr*** [a]	***4***	***0.001***	***Chr/BaP=1.1***

[a]… included in EPA-16, [b] … included in EU Directive 2004/107/EC, f_{BaP}… factor relative to BaP, explained through data from Table 2, …$ from EPA (1993)

Likewise, BbF and BkF estimates have been inferred from the analyzed sum BbF+BkF applying a BbF/BkF ratio of 2.0 derived from the above mentioned studies). The limit value of 1 ng m^{-3} BaP was derived for a lifetime increased risk of 10^{-4} including contributions from other PAHs, as the risk was derived from workplace exposure data where also a mix of PAHs was present (Working group on PAH, 2001). The BaPE, however, allows a comparison, whether differences in the emission profiles of the carcinogenic PAH members occur for different fuel or appliance types.

Table 2. Emission ratios for BbF/BkF, BaA/BaP, Chr/BaP derived from literature studies

Reference	**Stove**	**Comments**	**Fuel**	**PM**	**unit PM**	**BbF**	**BkF**	**BaP**	**BaA**	**Chr**	**Unit PAH**	BbF/BkF	BaA/BaP	Chr/BaP
Hays et al., 2003	woodstove	fuel- high moisture	white oak	8,8	**g kg^{-1}**			0,56	0,18	0,17	**mg kg^{-1}**		0,32	0,30
	woodstove	fuel- high moisture	white oak	10,2	**g kg^{-1}**			0,58	0,1	0,12	**mg kg^{-1}**		0,17	0,21
	woodstove	fuel- low moisture	white oak	4,9	**g kg^{-1}**			0,11			**mg kg^{-1}**			
	woodstove	Fuel - low moisture	Douglas fir	2,3	**g kg^{-1}**			0,16	0,1	0,1	**mg kg^{-1}**		0,63	0,63
	woodstove	fuel- high moisture	Douglas fir	6,3	**g kg^{-1}**			0,87	0,65	0,5	**mg kg^{-1}**		0,75	0,57
Jordan and Seen, 2005	modern stove	airflow open	white gum	19	**g kg^{-1}**			0,55	0,67	0,83	**mg kg^{-1}**		1,22	1,51
	modern stove	a. 1/2 closed	white gum	28	**g kg^{-1}**			0,39	0,36	0,47	**mg kg^{-1}**		0,92	1,21
	modern stove	a. closed	white gum	54	**g kg^{-1}**			0,22	0,34	0,67	**mg kg^{-1}**		1,55	3,05
Bari et al., 2009	residential stove		beech	21	**mg m^{-3}**	0,61	0,66	0,91	0,85	0,86	**µg m^{-3}**	0,92	0,93	0,95
	residential stove		pine	113	**mg m^{-3}**	0,43	0,4	0,4	0,34	0,26	**µg m^{-3}**	1,08	0,85	0,65
Gonçalves et al., 2010	modern wood stove	6 kW	*eucalyptus globulus*	2,1	**g kg^{-1}**	0,23	0,29	0,34	0,42	0,66	**mg g^{-1}OC**	0,81	1,26	1,97
	modern wood stove	6 kW	*pinus pinaster*	1,2	**g kg^{-1}**	6,16	2,90	5,28	6,21	8,88	**mg g^{-1}OC**	2,12	1,18	1,68
	modern wood stove	6 kW	*quercus suber*	2,8	**g kg^{-1}**	0,09	0,35	0,09	0,18	0,26	**mg g^{-1}OC**	0,25	1,98	2,83
	modern wood stove	6 kW	*Acacia longifolia*	1,3	**g kg^{-1}**	0,62	0,79	0,43	0,63	1,00	**mg g^{-1}OC**	0,78	1,46	2,32
Boman et al., 2011	pellet stove 1	high load 5kW	pellets	16	**mg MJ^{-1}**			310	210	330	**ng MJ^{-1}**		0,68	1,06
	pellet stove 1	low load 1.7 kW	pellets	34	**mg MJ^{-1}**			6700	2600	3500	**ng MJ^{-1}**		0,39	0,52
	pellet stove 2	high load 6 kW	pellets	23	**mg MJ^{-1}**			35	72	130	**ng MJ^{-1}**		2,06	3,71
	pellet stove 2	low load 2 kW	pellets	40	**mg MJ^{-1}**			750	690	620	**ng MJ^{-1}**		0,92	0,83
Pettersson et al., 2011	small stove		birch spruce pine	140	**mg MJ^{-1}**	680	250	610	230	200	**µg MJ^{-1}**	2,72	0,38	0,33
	small stove		birch spruce pine	110	**mg MJ^{-1}**	150	51	88	21	26	**µg MJ^{-1}**	2,94	0,24	0,30
	small stove	mode 1	birch			59	20	30	18	22	**µg MJ^{-1}**	2,95	0,60	0,73
	small stove	mode 1	birch			200	66	100	34	44	**µg MJ^{-1}**	3,03	0,34	0,44
	small stove	mode 1	spruce			500	160	300	34	37	**µg MJ^{-1}**	3,13	0,11	0,12
	small stove	mode 1	spruce			81	25	38	11	13	**µg MJ^{-1}**	3,24	0,29	0,34
Jalava et al., 2012	modern wood stove		wood	46	**mg MJ^{-1}**	188		198	224	227	**ng mg^{-1} PM**		1,13	1,14
											Average	2,0	0,8	1,1

2.3 Analysis of particulate matter

Filter weighing and sample preparation

Previous to sampling, the quartz fiber filters were baked for 5 hours at 550°C, cooled in a desiccator with water vapor saturated atmosphere, equilibrated for 48 hours in an air conditioned room (20 ± 1°C, 50±5% relative humidity) and weighed with a microbalance (Sartorius M5P with range up to 1 g ±0.5 µg). Gravimetric analysis of particulate matter was performed after equilibration of the loaded filters at the same conditions. Between sampling and analyses, filters were stored at -18°C to minimize the degradation of the trace organics. For analysis of the carbon species (EC, OC, CC) the quartz fiber filters were punched with a steel punch of 10 mm diameter for the analysis. For organic substances filters from parallel samples were cut into halves (4.8 cm² active surface per half filter) and 1-3 halves depending on filter loads were used for analysis.

Carbon

Organic Carbon (OC), Elemental Carbon (EC) and Carbonate Carbon (CC) were determined with a "SUNSET OCEC Lab Instrument" using the NIOSH 5040 protocol (NIOSH, 1999; discussed in Watson et al., 2005) in the transmission mode.

PAHs determination

The particulate PAH determination was performed with composite filter samples combined usually from 3 burn cycles (except for PO and SO from two; BPop, BL, EL, N and L from one cycle) performed with the same wood types under experimentally comparable conditions. From the five pellets burning experiments, three from full-load operation (two from 1.4, one from 1.9 kg h^{-1} burn rate) were combined.

The samples were spiked with deuterated internal standards for PAHs and alkanes (d_{50}-tetracosane and d_{12}-benzo(a)pyrene; Aldrich) to estimate the recoveries. For extraction reasons each sample was treated twice with a mixture of 3 mL cyclohexane and 2 mL dichloromethane and placed in ultrasonic bath for 15 minutes. The combined extracts were evaporated to 200µL in nitrogen atmosphere. After the extraction process, a third internal standard (1-bromopentadecane) was added. PAHs determination was carried out with the GC-MS system described for alkanes in Kotianova et al. (2008).

The HP-5890 Gas Chromatograph is equipped with a HP-7683 auto sampler and a split/splitless injector (300°C) operated in a splitless mode (2min). For the separation an analytical capillary column (DB-5 MS - 95% dimethyl-, 5% phenylsiloxane, 30m x 0.25mm ID x 0.25µm film), preceded with a deactivated fused silica pre-column (1m x 0.32mm) was applied. Helium 5.0 (Messer) was used as a carrier gas. Detection was carried out with a quadruple mass spectrometer HP-5973 (70eV). PAHs were recorded in the full scan mode and selected ion monitoring (SIM) mode.

For identification and quantification standards of PAHs 7-one, Ret, BaP, BeP, BghiP and Cor (Fluka) were used. Other PAHs were identified according to their electron ionization spectra (compared with spectra from the NIST library) and quantified with the calibration curve of BghiP. Each sample as well as each standard was measured twice. A blank measurement was conducted at the beginning of the day.

The practical detection limit of the method determined from 3s of a standard sample at low concentration is 0.04-0.1 ng μL^{-1} for PAHs. For the determinations of 3 filter halves and converted to the dimensions of the emission data the detection limit ranges from 0.1-0.3 µg MJ^{-1}.

3. Results and discussion

All results presented in the study are standardized for volumetric oxygen concentration (13% in the exhaust) and are calculated for standard conditions of temperature and pressure (273 K, 1013 hPa).

3.1 PAH Emission rates

The PAH emission rates of the analyzed PAHs for pellets, briquettes, 11 wood types and “garden waste” are listed in Table 2. The profiles show a considerable similarity. Since BaP is the main PAH of interest due to the EU regulation and the relative contribution of BaP to total determined particulate PAHs quite constant (around 6 % of the determined PAHs), we concentrate the further discussion on BaP.

Table 3. PM_{10} and PAH emission data for pellets, briquettes, 11 wood types, and “garden waste” (GW)

	SWP	Hardwood-briquettes and hardwood logs								Softwood logs				GW	
	WP(FL)	BR	EH	EB	BPop	TO	SO	PO	BL	SF	EL	NS	BP	L	N
PM10 (mg MJ^{-1})	24	32	41	66	46	59	222	57	98	100	21	53	101	626	85
	PAH (µg MJ^{-1})														
7-one	6.7	24	74	128	37	116	62	41	40	71	21	22	104	403	223
Ret	2.5	2.5	1.6	2.0	1.4	2.0	16.1	8.0	9.0	31.9	6.4	3.8	52	53	23
BbF+BkF	5.1	17	53	113	29	104	50	33	37	53	16	14	71	358	185
BjF	3.5	8.0	27	56	14	49	24	14	18	25	12	6.1	38	192	96
BeP	1,9	5,1	18	40	9,7	35	15	9,6	11	17	5,8	11	22	116	58
BaP	1.6	3.0	17	36	11	37	22	12	16	22	6.3	6.3	29	199	77
Per	ND	ND	10	26	5.4	25	8.1	ND	5.6	10	ND	2.3	18	123	49
IcdF	ND	ND	19	42	8.9	36	13	4.0	8.4	17	ND	4.1	26	138	51
IcdP	ND	2.4	31	67	15	54	26	14	21	28	ND	8.2	40	221	94
BghiP	2.2	7.3	33	68	16	53	27	17	23	28	6.8	9.0	38	220	95
Anth	2.2	8.1	ND	9.3	2.9	10	5.1	ND	3.1	7.0	8.4	1.6	10	129	32
DBA	ND	nd	7.0	21	3.2	18	ND	ND	ND	5.4	ND	ND	13	116	28
Cor	ND	3.7	18	40	9.3	27	14	6.2	12	14	ND	4.9	19	29	51

nd…not determined, *… calculated with additional data

The BaPE’s have been derived with additional information accounting for the BbF/BkF split and for missing four-ring PAHs BaA and Chr and supplemented values of IcdP and DBA, obtained from averaged contribution of those PAHs to the sum of all measured PAHs (the relative contributions of measured PAHs to the sum of all PAHs measured were found to be stable for all wood types), (Table 4). On the average over all tests the BaPE = 1.9 times BaP.

Table 4. Emission rates of potentially carcinogenic PAHs from stove tests including estimated missing data for BaA and Chr and the estimate of BbF and BkF results from the recorded sum of BbF+BkF. Inferred data are in bold.

	WP(FL)	BR	EH	EB	BPop	TO	SO	PO	BL	SF	EL	NS	BP	L	N
	PAH (µg MJ^{-1})														
BaA	1.3	2.4	14	29	8.8	30	18	10	13	17	5.0	5.0	23	159	61
Chr	1.8	3.3	19	40	12	41	24	14	18	24	6.9	6.9	31	219	84
BbF	3.4	11	35	76	19	69	33	22	25	35	10	9.5	47	239	123
BkF	1.7	5.7	18	38	9.7	35	17	11	12	18	5.2	4.7	24	119	62
BaP	1.6	3.0	17	36	11	37	22	12	16	22	6.3	6.3	29	199	77
IcdP	2.4	2.4	31	67	15	54	26	14	21	28	7.6	8.2	40	221	94
DBA	0.8	2.4	7.0	21	3.2	18.0	8.1	4.6	5.9	5.4	2.4	2.5	13	116	28
BaPE	3.1	7.1	33	75	19	72	38	22	28	35	11	11	53	380	135
BaPE/BaP	1.9	2.4	1.9	2.1	1.7	1.9	1.7	1.8	1.7	1.6	1.8	1.8	1.9	1.9	1.8

The variation of the BaP emission rate is visualized in Figure 1. Wood pellets gave the lowest emission rates of the performed combustion tests. Low emission rates (≤12 µg MJ^{-1}) for briquettes and logwood were observed for BR, EL, NS and BPop, high (>25 µg mMJ^{-1}) for TO, EB and BP. Intermediate BaP emission rates (13-24 µg MJ^{-1}) were obtained for PO, EH, SO, BL and SF. Garden waste (L,N) generated the highest BaP emission rates, with needles around twice as high and leaves a factor of five higher than the “high” emitters from logwood (Figure 1).

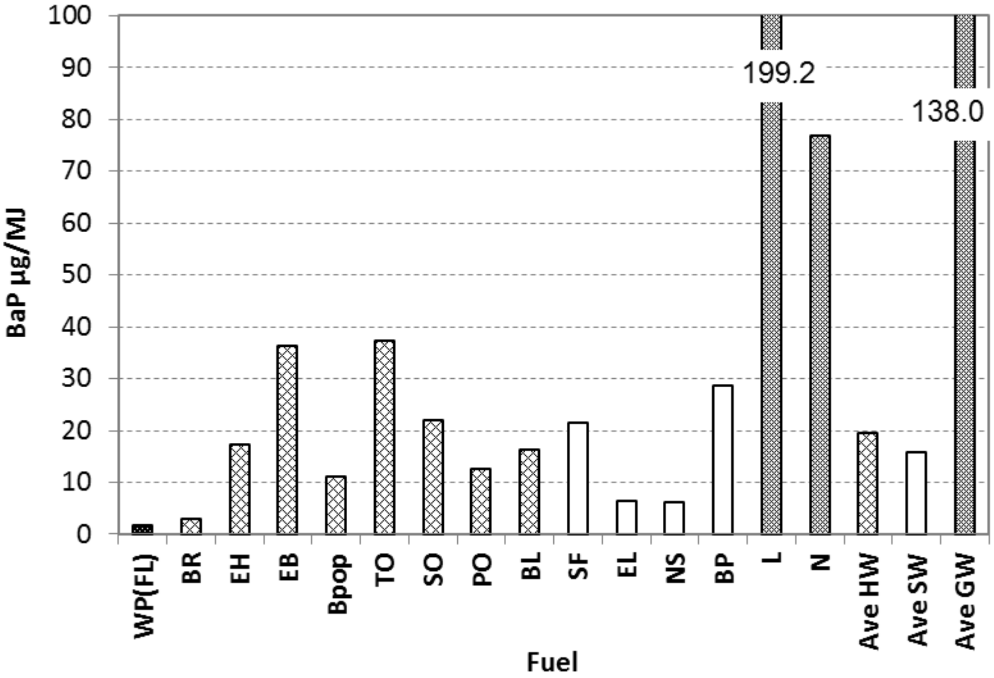


Figure 1. Emission rates of BaP for tested fuels (wood pellets full load; briquettes, hardwood and softwood species, garden waste)

Boman et al. (2011) observed very low emission rates e.g., for BaP for wood pellets (mainly pine wood) for high load (e.g., an average of 0.31 µg MJ^{-1} for an automated Scandinavian and 0.035 µg MJ^{-1} for an American stove with intermittent operation), however increased emissions for low load (6.7 and 0.75 µg MJ^{-1}). Schmidl et al. (2011) observed a BaP emission of 0.7 µg MJ^{-1} for a full load and 4.7 µg MJ^{-1} for the start-up phases (softwood pellets, GU). Our result of 1.6 µg MJ^{-1} BaP emission for wood pellets (softwood, full load) is on the higher end of the reported values.

The emission rates of BaP of briquettes and log wood were quite variable in a range of 3-37 µg MJ^{-1} (Table 2) with an average of 18.2 and a median of 16.9 µg MJ^{-1}. The averages for the 8 hardwood types including briquettes (19.5 µg MJ^{-1}) and for 4 conifer types (15.7 µg MJ^{-1}) were higher for hardwood due to two "high" emitters (TO, EB) in the hardwood group compared to one "high" emitter (BP) in the softwood group. Jenkins et al. (1996) have reported already, that PAH emissions (total as well as particulate phase) were more influenced by burning conditions than by fuel type. For instance Hays et al. (2003) observed fivefold higher BaP emissions for "humid" (24 - 29% moisture content) compared to "dry" (12 %) fuelwood conditions for burning log wood). In this experiment, however, all efforts were made to keep burning conditions as far as they can be influenced from technical settings constant. E.g., fuel loads. Ignition, chimney draft, air inlet opening were performed standardized or kept identical in the logwood experiments. Thus, inherent properties of the fuel (water content, fuel density, combustion temperatures and oxygen demand during the combustion tests) might be influencing parameters for the variability of the PAH emission rates. Our tests were performed with logs seasoned over two years with a moisture content of 8-13% (Table 3 in Kistler et al., 2012 – **Chapter 3**).

3.2 Relationship of BaP with CO, PM$_{10}$ and other combustion parameters

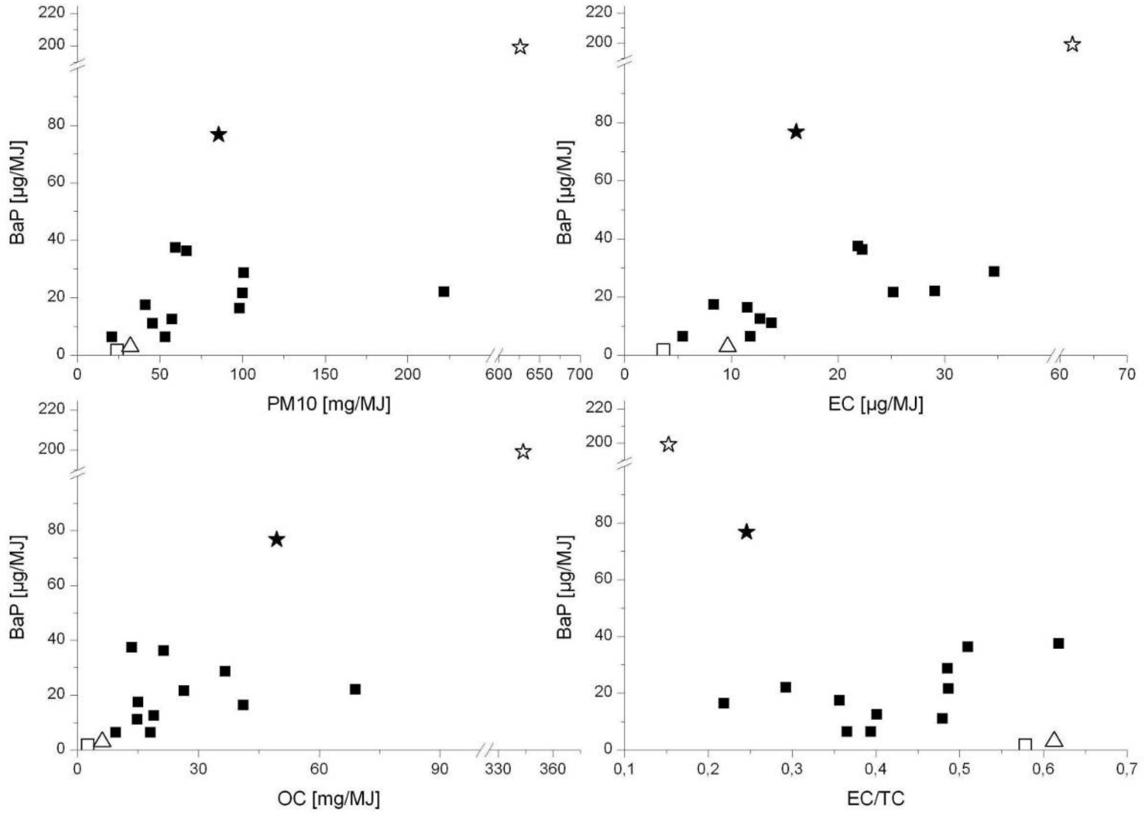
The relationship of the BaP emission rate with other combustion parameter has been examined graphically (Figures 2a,b and c) from the compiled combustion parameters in Table 5. The results for the correlation analysis are listed in Table 6. For "all" fuels including garden waste the emission rate of BaP was highly correlated with PM$_{10}$ ($R^2 = 0.83$), EC ($R^2 = 0.71$) and OC ($R^2 = 0.90$) emission rates and with the burn rate (Table 6).

Table 5. Emission rates of BaP, CO, PM_{10}, EC, OC in PM_{10}, and combustion parameters

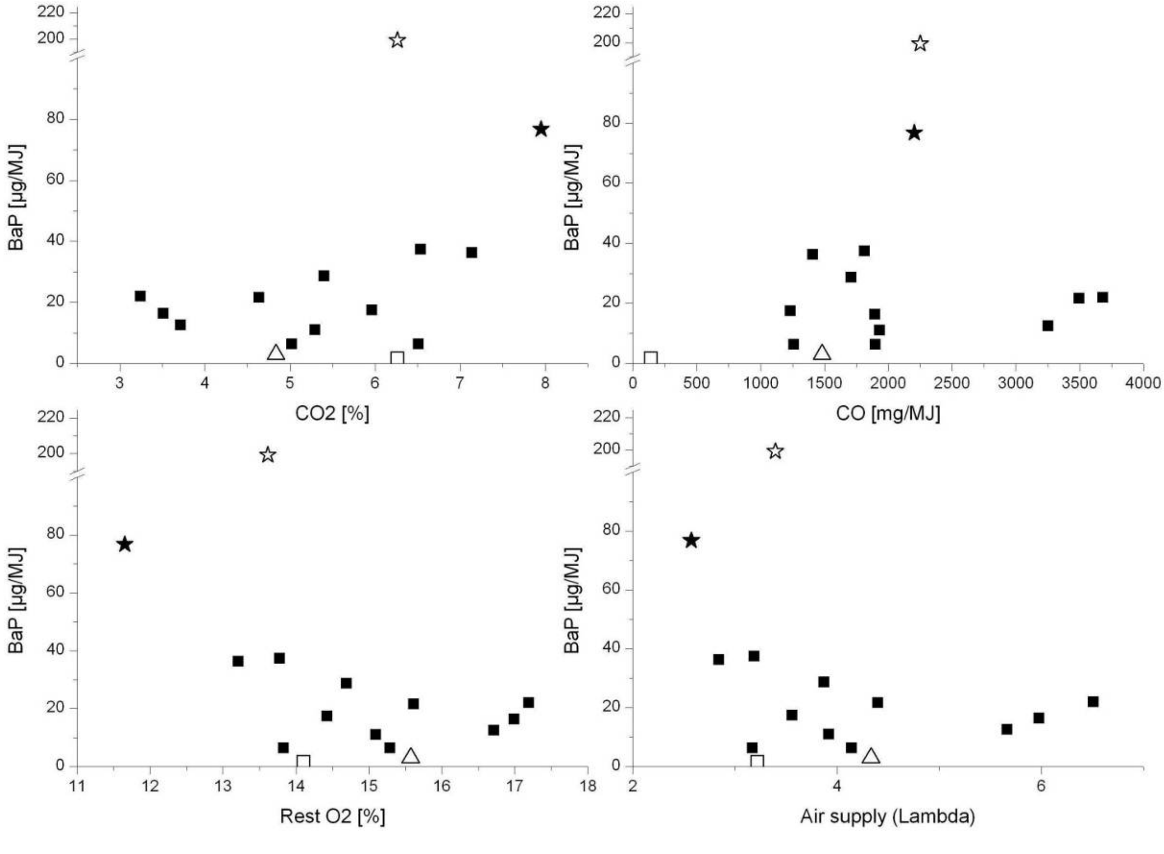
	BaP	CO	PM_{10}	EC	OC	FG Temp.	Air sup-ply	EC/TC	CO_2	Burn rate	Fuel density (12-15% HR)
Fuel	µg MJ^{-1}	mg MJ^{-1}	mg MJ^{-1}	mg MJ^{-1}	mg MJ^{-1}	°C	λ		%	kg h^{-1}	g cm^{-3}
WP(FL)	1.6	142	24.0	3.7	2.6	132	3.2	0.58	6.3	1,7	0.65
BR	3.0	1482	32.0	9.7	6.1	183	4.3	0.61	4.8	2,0	1.12
EH	17.4	1234	41.2	8.4	15.1	184	3.6	0.36	6.0	2,6	0.61
EB	36.2	1410	66.0	22.3	21.4	194	2.8	0.51	7.1	3,0	0.65
BPop	11.0	1933	45.6	13.8	14.9	125	3.9	0.48	5.3	2,3	0.40
TO	37.4	1816	59.4	21.9	13.5	195	3.2	0.62	6.5	3,0	0.84
SO	22.0	3681	221.9	29.1	69.0	145	6.5	0.29	3.2	2,4	0.68
PO	12.5	3253	57.4	12.7	18.9	154	5.7	0.40	3.7	2,3	0.71
BL	16.3	1896	98.2	11.5	41.2	105	6.0	0.22	3.5	1,8	0.74
SF	21.6	3497	99.9	25.2	26.5	175	4.4	0.49	4.6	2,0	0.60
EL	6.3	1263	20.7	5.5	9.5	176	3.2	0.37	6.5	2,7	0.35
NS*	6.3	1901	53.2	11.8	18.1	174	4.1	0.39	5.0	2,1	0.38
BP	28.6	1710	100.8	34.7	36.7	179	3.9	0.49	5.4	2,4	0.84
L	199.2	2249	626.1	61.9	343.7	196	3.4	0.15	6.3	5,0	ND
N	76.8	2204	85.5	16.1	49.4	192	2.6	0.25	8.0	3,8	ND
Ave HW	19.5	2088	77.7	16.2	25.0	161	4.5	0.44	5.0	2,4	0.7
Ave SW	15.7	2093	68.6	19.3	22.7	176	3.9	0.43	5.4	2,3	0.5
Ave GW	138.0	2226	355.8	39.0	196.6	194	3.0	0.20	7.1	4,4	-
Ave all	33.1	1978	108.8	19.2	45.8	167	4.1	0.41	5.5	2,6	0.7
Med all	17.4	1896	59.4	13.8	18.9	176	3.9	0.40	5.4	2,4	0.7
Med HW+BR	16.9	1856	58.4	13.2	17.0	169	4.1	0.44	5.1	2,3	0.7
Med SW	13.9	1805	76.5	18.5	22.3	176	4.0	0.44	5.2	2,3	0.5
Med GW	138.0	2226	355.8	39.0	196.6	194	3.0	0.20	7.1	4,4	-
Ave BR+logs	18.2	2090	74.7	17.2	24.2	166	4.3	0.44	5.2	2,4	0.7
Med BR+logs	16.9	1856	58.4	13.2	18.5	176	4.0	0.44	5.2	2,3	0.7
BaP/PM_{10} (from averages) = 0.30											
BaP/PM_{10} (from medians) = 0.29											

ND…no data; Ave…arithmetic mean; Med…median

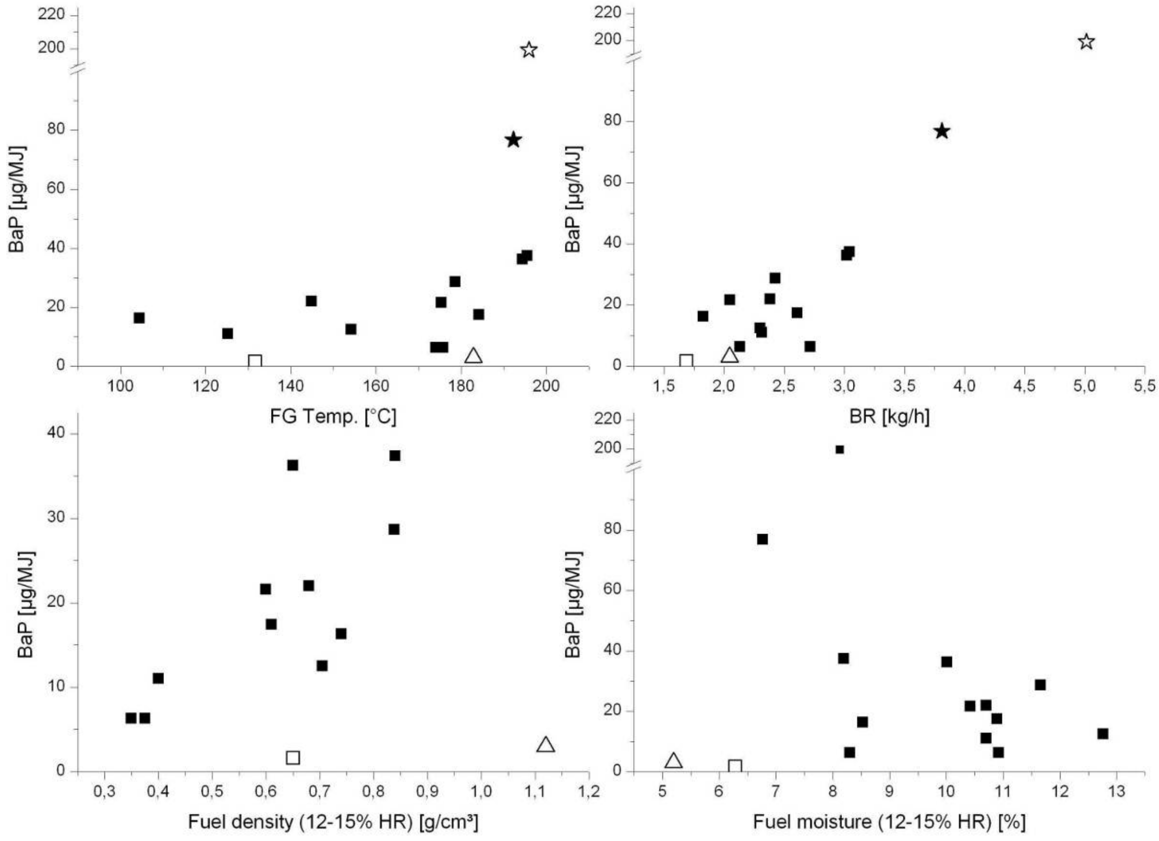
The graphical analysis is divided into three sections: co-emissions, combustion parameters and wood related parameters.



a) BaP relation vs. other emissions



b) BaP relation vs. combustion parameters



c) BaP relation vs. fuel related parameters

Figure 2a,b,c. Visualization of the interrelations of the BaP Emission rate with other combustion parameters (emission rates of PM_{10}, EC, OC, EC/TC, flue gas temperature, burn rate, fuel moisture and density, air supply [λ], CO,CO_2, and rest O_2). WP and BR marked with white square and triangle respectively, garden waste marked with white and black stars (L and N respectively).

Table 6. Correlation coefficients (r) for chemical and physical parameters (Table 5, Figures 2a,b,c) for all tested fuels including garden waste. Significant correlations (P=95%) are marked in bold numbers.

All fuels (n=15)	**BaP**	**CO**	**PM_{10}**	**EC**	**OC**	**FG Temp.**	**Air supply**	**EC/TC**	**CO_2**	**Fuel density (12-15% HR)**
BaP	*1,000*									
CO	0,153	*1,000*								
PM_{10}	**0,911**	0,304	*1,000*							
EC	**0,840**	0,390	**0,896**	*1,000*						
OC	**0,946**	0,210	**0,988**	**0,860**	*1,000*					
FG Temp.	0,421	-0,017	0,207	0,365	0,240	*1,000*				
Air supply	-0,280	**0,616**	0,051	-0,014	-0,051	**-0,607**	*1,000*			
EC/TC	**-0,559**	-0,341	**-0,599**	-0,379	-0,614	0,107	-0,245	*1,000*		
CO_2	0,347	**-0,547**	-0,004	0,038	0,091	**0,608**	**-0,966**	0,105	*1,000*	
Fuel density (12-15% HR)	0,225	0,002	0,130	0,255	0,072	0,183	0,179	0,397	-0,174	*1,000*
BR	**0,921**	0,095	**0,741**	**0,705**	**0,791**	**0,609**	-0,461	-0,497	**0,560**	-0,078

ρ...wood density for 12-15% water content; BR… Burn Rate in kg fuel h^{-1}; FG °C… flue gas temperature; λ …air supply

In the correlation plot of BaP and PM_{10} emission rates of the fuels (not including garden waste) the data points are limited by two lines with low (0.1) and high (~0.7) BaP/PM (µg mg^{-1}) emission ratio (Figure 3). SO, the wood type with high PM_{10} and moderate BaP emissions situated around the low grade was accompanied by higher concentrations of EC and OC, burn rate and flue gas temperature below average, but higher CO concentrations. Wood types with high BaP and moderate PM_{10} emissions are burning rapidly and "hot", with lower than average O_2 concentrations.

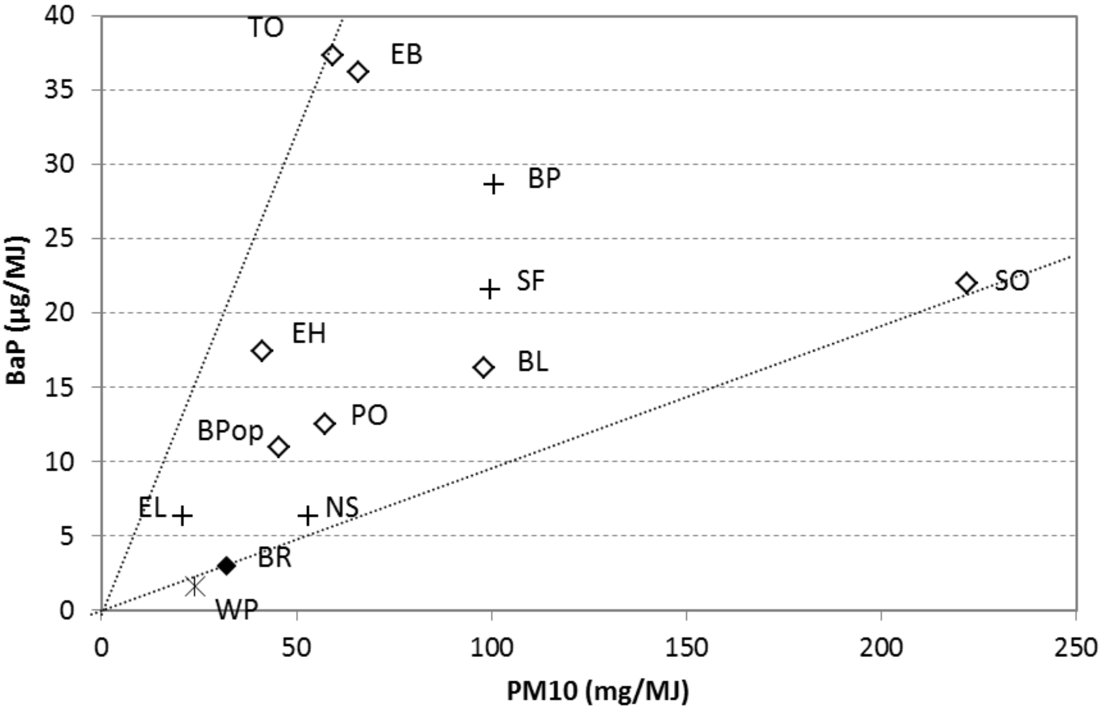


Figure 3. Emissions of BaP vs. PM_{10} from FWF/O combustion tests with two stoves (pellets, logwood and briquettes).

The lowest O_2 concentration during the combustion cycles of EB was around 6%, which is shown in the oxygen time trends from combustion tests in Figure 4. The oxygen minimum was lower for EB than for other fuels, but is not as low as in oxygen-starved experiments performed by Pettersson et al. (2011).However, the O_2 plot of EB shows a feature of a very rapid initial combustion after the fuel reload, which might have led to local oxygen deficiencies, accompanied by the BaP formation. Turkey Oak showed likewise a rapid initial burn after reloading, while this phenomenon was less developed for black pine exhibiting a fast combustion "pulse" followed by slower combustion.

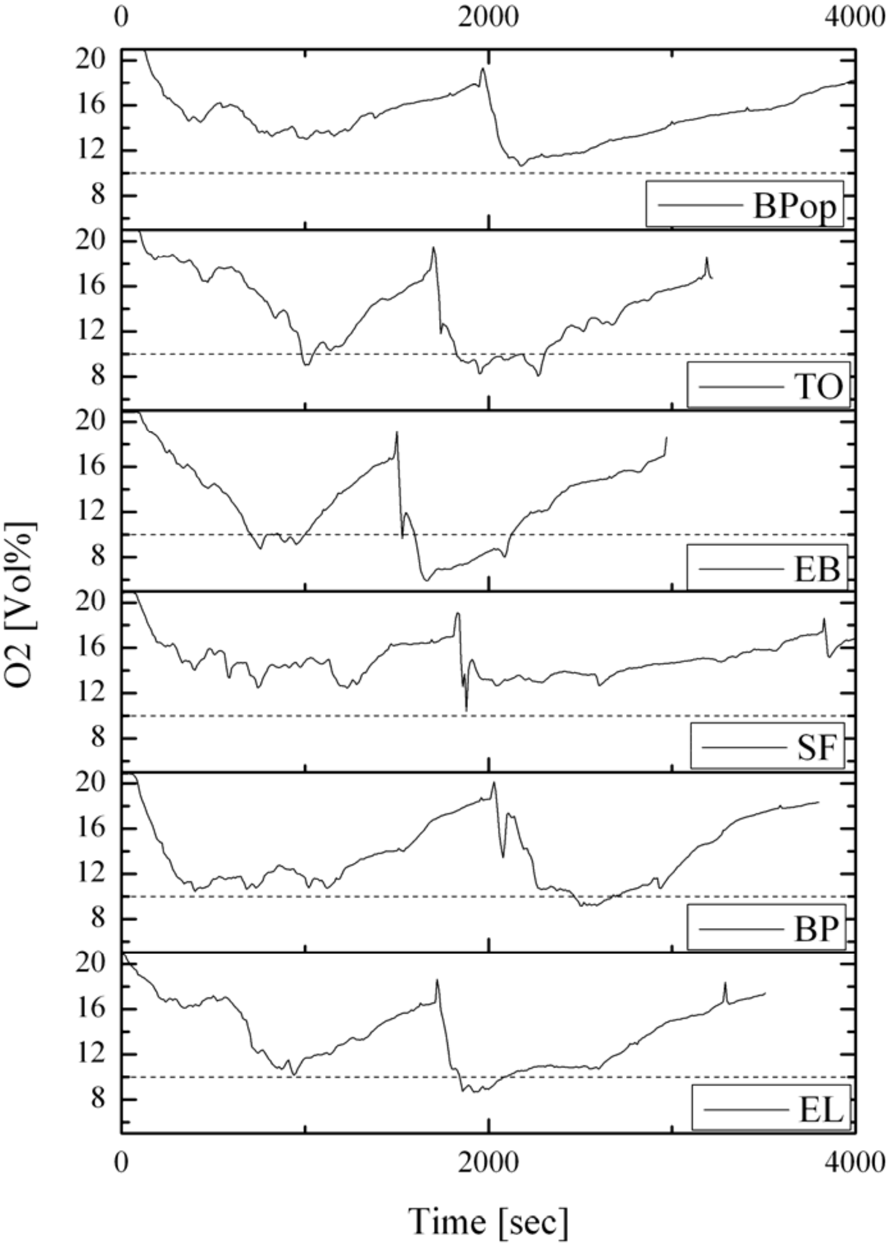


Figure 4. Time trend of the O_2 concentrations during the combustion cycles ofblack poplar (BPop), Turkey Oak (TO), European beech (EB), silver fir (SF), black pine (BP), European larch (EL) in the chimney stove RF2 (Project FWF/O).

A significant (P=95%) correlation of BaP was obtained with EC ($R^2 = 0.58$) for “all fuels” including logs, briquettes and pellets (Figure 5a). Interestingly, the four conifer samples resemble a perfect fit on the linear interrelation of BaP and EC with an R^2 of 0.97 and an increment of 0.85 (Figure 5b). A higher variation of the BaP/EC ratio is observed for hardwood logs and briquettes ($R^2 = 0.46$, Figure 5c), with “high BaP” emitters (TO and EB) on the steeper side of the slope; while the BaP/EC ratio for SO is similar to softwood.

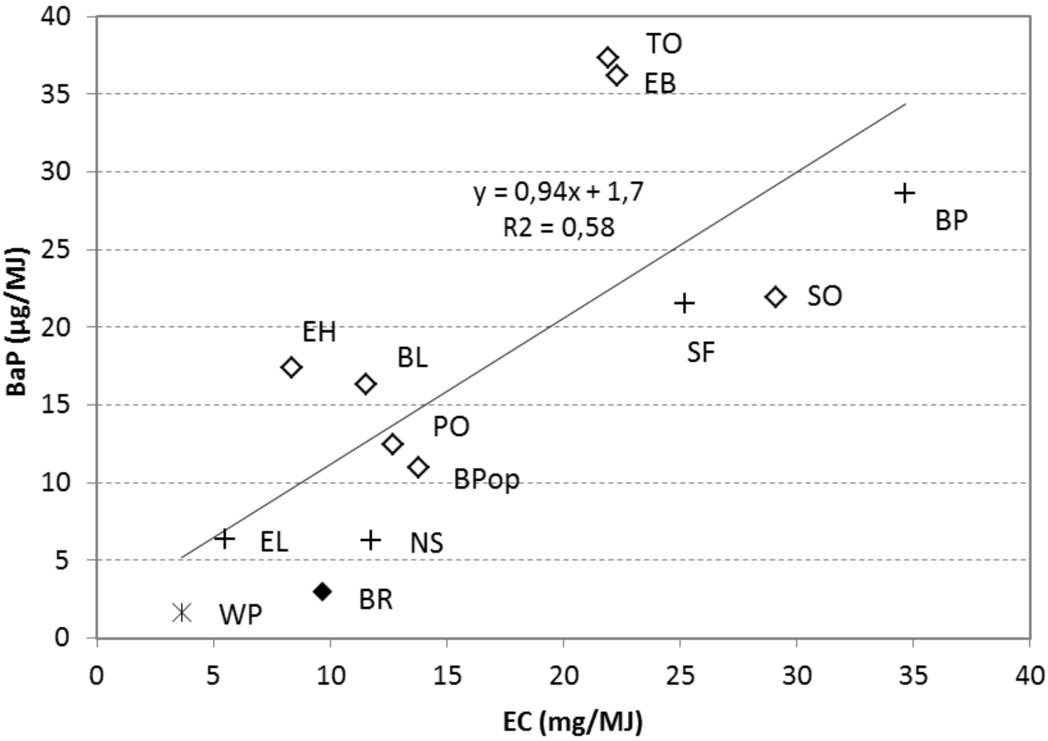


Figure 5a. Emission of benzo(a)pyrene (BaP) vs elemental carbon (EC) from FWF/O combustion tests (*two* stoves), hardwood logs and briquettes (top); b) softwood logs and pellets, bottom). Correlations are significant at P95%.

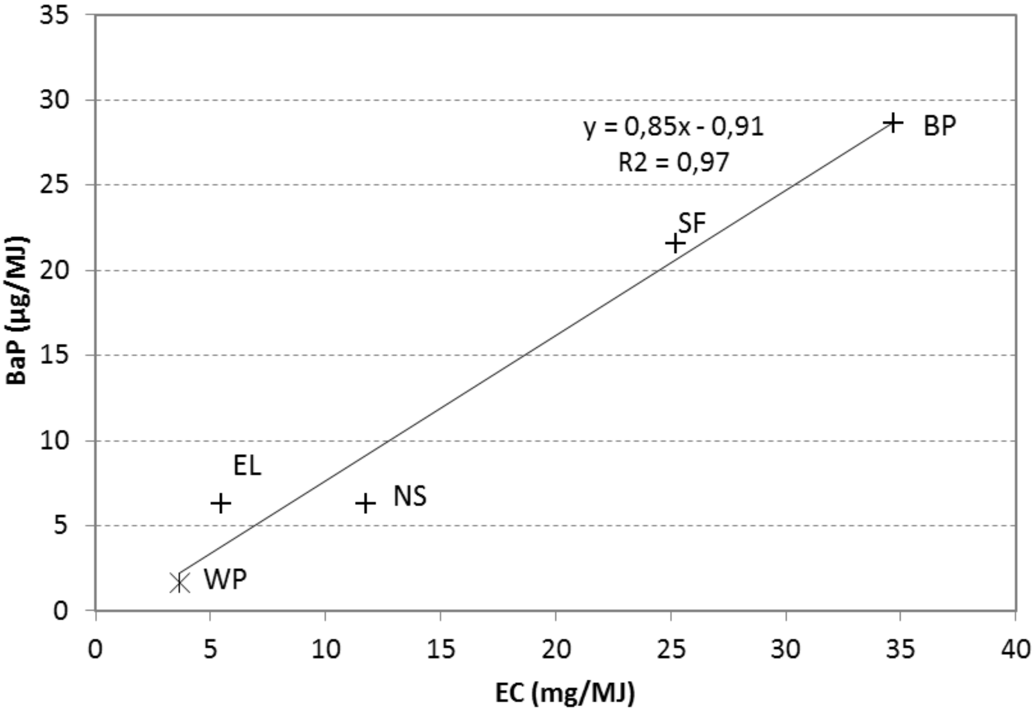


Figure 5b. Emission of benzo(a)pyrene (BaP) vs elemental carbon (EC) from FWF/O combustion tests (*two* stoves) (softwoods).

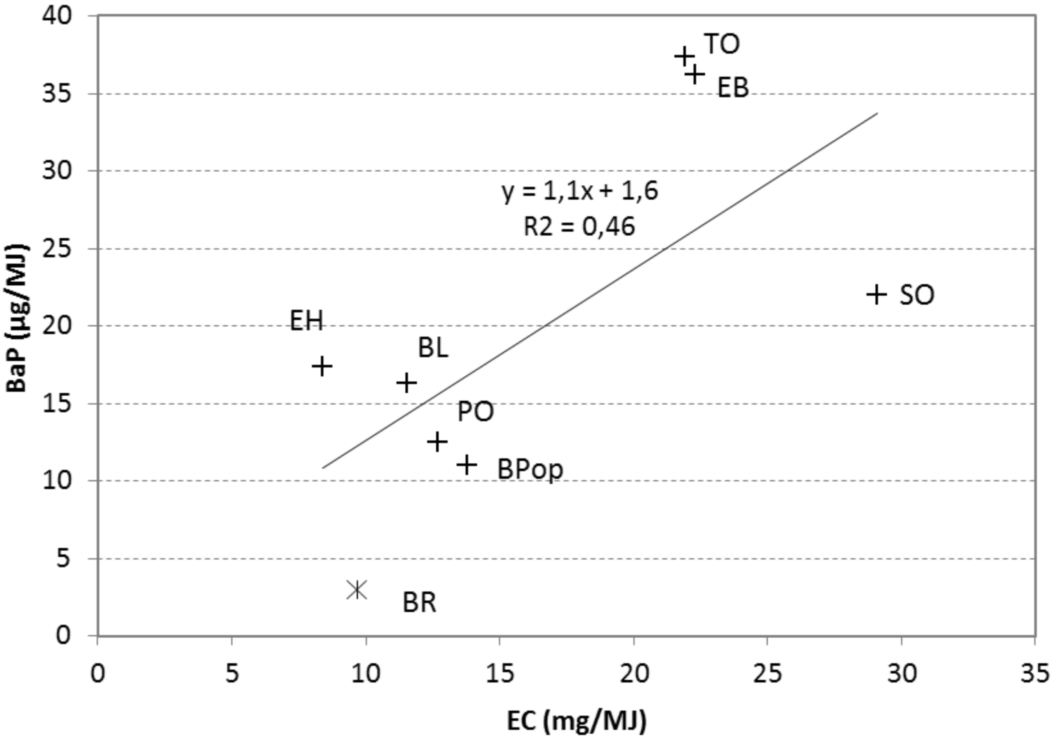


Figure 5c. Emission of benzo(a)pyrene (BaP) vs elemental carbon (EC) from FWF/O combustion tests (*two* stoves) (hardwood and briquettes).

The correlation observed between BaP and EC is consistent with the EC formation mechanisms discussed, involving PAHs as intermediates in the soot formation pathways important factors for the EC yield Fitzpatrick et al. (2008).

We examined the relationship of the BaP emission rate with other combustion parameters with a multiple linear model and obtained the best quality of fit (R^2 = 0.79) for the input variables “burn rate” and EC emission rate. In this analysis the influence of the burn rate explains about 75%, the EC emission rate about 25% of the BaP emission rate. For softwoods with higher BaP emission (SF, BP) as well as for SO, the contribution from EC was higher (40-45%). Their burn rate was close to the average and they burned with fewer tendencies of fast burns after the reloading (Figure 4), however their EC emission rates were the highest of the logwood data set (Figure 5a). The fit between estimated and real data is depicted by Figure 6.

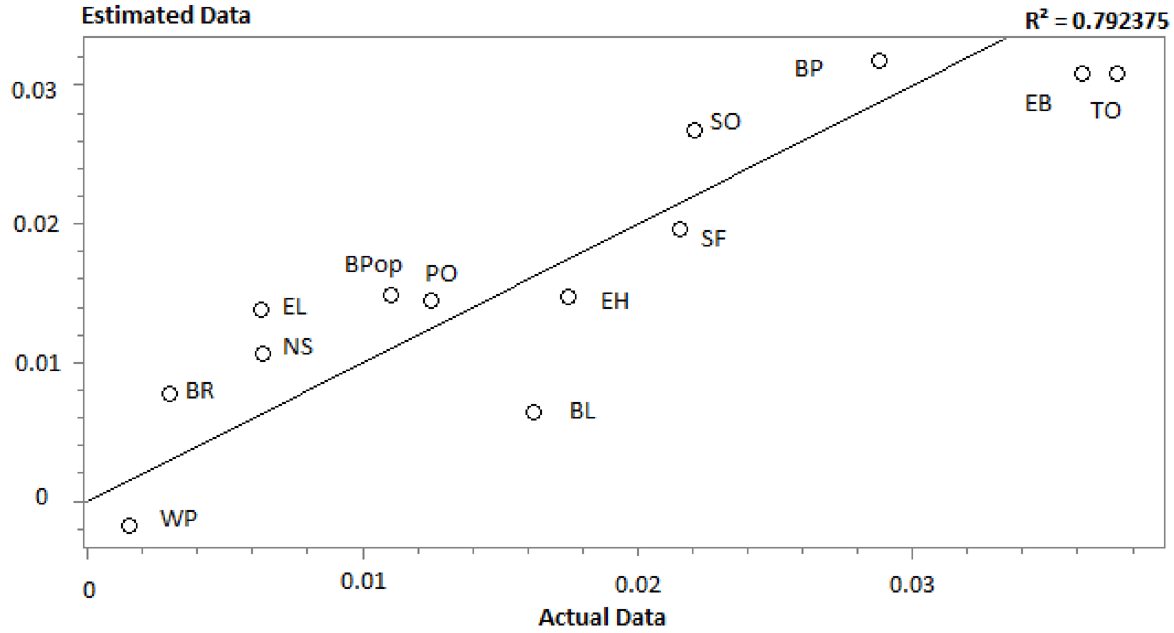


Figure 6. Result of the multiple linear model comparing estimated data with actual data for BaP (mg MJ^{-1}). Input variables were burn rate and EC emission rate. The details of the model (analysis of variance and statistical significance) are presented in Table 7.

The increased formation of EC and PAHs during fast hot burns in connection with oxygen starved conditions has been described recently (Pettersson et al., 2011; and discussion therein). In a Scandinavian stove during “normal operation” the oxygen decreased to about 5%, in the low moisture – high burn rate tests it dropped to 1-3% in the test runs. Pettersson et al. (2011) have observed, that dry (8% moisture) and finely cleaved logs yielded temporarily high heat output and local oxygen deficiencies resulting in dramatically higher emissions of PAHs as compared for the cases with logs of higher moisture (16 and 23% moisture) and lower burn rate. The observed effect – we denominate it here as “POIS”-effect (“Pettersson-oxygen-inefficient-supply” effect) is much weaker than in the Pettersson et al. (2011) experiments. The oxygen drop in our experiments was down to 6% (Figure 4), however, the drop was less in some cases with higher BaP formation (SF, BP, SO). It appears, that some wood types exhibit a tendency for the fast burns (e.g., TO and EB in our test), while others develop relatively high EC levels during a more equilibrated combustion (e.g., SF, BP and SO).

Table 7. Detailed results of the multiple linear modelling for the BaP emission and influencing parameters “burn rate (kg h^{-1}) and EC (mg MJ^{-1}). Model calculated with DataLab Software, the following data expressed the analysis of variance for the constructed model.

```
=============================================================
Multiple Linear Regression: D:\DataLab\data\magda_absolut_1.asc
=============================================================
Number of Objects .............: 13
Number of Input Variables .....: 2
Degrees of Freedom ............: 10
Target Variable ...............: BaP [mg MJ-1]

Mean of Target Values .........: 0.016935
Std.Dev. of Target Values .....: 0.011842
Mean of Calculated Values .....: 0.016935
Std.Dev. of Calc. Values ......: 0.010541

Standard Dev. of Residuals ....: 0.0059
Quality of Fit ................: 0.7924
Adjusted Quality of Fit .......: 0.7509
F-Statistic ...................: 19.082 (p=0.0004)
Durbin-Watson Statistic .......: 2.2021
 -----------------------------------------------------
 ANOVA       DF  sum of squares   mean square      F
 -----------------------------------------------------
 Regression    2    1.33347E-03    6.66735E-04   19.082
   Residual   10    3.49406E-04    3.49406E-05
      Total   12    1.68288E-03
 -----------------------------------------------------
Regression coefficients:
 Col-#   Var-Name      Coefficient      Std.Err.(coeff)   t-Test  alpha
 ---------------------------------------------------------------------
    -  INTERCEPT    -2.7909228E-02 +/- 9.7590391E-03    -2.860  0.0170
    3  Burn rate kg   1.3937014E-02 +/- 4.3161614E-03     3.229  0.0090
    6  EC µg/MJ      7.4817928E-04 +/- 1.8836918E-04     3.972  0.0026

Results of regression:
    Obj.   Target Value   Regr.Result     Difference
  -------------------------------------------------
    1 WP   1.64000E-03   -1.69038E-03     -0.003330
    2 BR   3.00300E-03    7.84195E-03      0.004839
    3 EH   1.74030E-02    1.47189E-02     -0.002684
    4 EB   3.62110E-02    3.08547E-02     -0.005356
    5 BPop 1.09890E-02    1.46747E-02      0.003686
    6 TO   3.73750E-02    3.08700E-02     -0.006505
    7 SO   2.19600E-02    2.70818E-02      0.005122
    8 PO   1.24800E-02    1.36852E-02      0.001205
    9 BL   1.63090E-02    6.17592E-03     -0.010133
   10 SF   2.15550E-02    1.94924E-02     -0.002063
   11 EL   6.31000E-03    1.40479E-02      0.007738
   12 NS   6.29000E-03    1.05882E-02      0.004298
   13 BP   2.86340E-02    3.18175E-02      0.003183
```

4. Intercomparison with other related studies

Combustion experiments with comparable stoves have been performed in the “AQUELLIS FB” (Schmidl et al., 2008a) and the “BIOCOMB” (Luisser et al., 2008) projects. Included in the BIOCOMB project were also tests with a “universal” boiler for pellets, wood chips and grains, and a wood log boiler.

In all cases the chimney stove tests were performed at the same TUV test stand as for the stoves reported in this study (here denoted as ”FWF/O” study), some tests (boilers) were performed at the ABC center, Branch Wieselburg. The same analytical procedures were applied except for EC/OC. The EC/OC method employed used a linear heating in oxygen in conjunction with a delta EC tracking in transmission mode (“TLT” method, Schmidl.et al., 2011). The comparability of the two methods was recently tested and a relationship of EC (Sunset) and EC (TLT) close to one was obtained (Imran Shahid, personal communication).

Data from the above mentioned studies (here now denominated as “3 studies”) are included in the comparison for those combustion tests, where BaP results were available. BaP and EC, OC were calculated in the studies in % m/m relative to PM_{10}, and are listed in Table 8.

Table 8. BaP and PM_{10} emission rates, OC, EC, TC concentrations, EC/TC ratio, for combustion tests from "3 studies" ("AQUELLIS FB", "BIOCOMB", "FWF/O").

			PM_{10}	OC	EC	TC	EC/TC	BaP	BaP
Project	Stove	Fuel	**mg MJ^{-1}**	**%PM_{10}**	**%PM_{10}**	**%PM_{10}**		**%PM_{10}**	**µg MJ^{-1}**
Aquellis FB	RF-1a	EH	64.1	22	41	62	0.65	0.0095	6.1
	RF-1a	EB	101.8	22	30	52	0.58	0.0254	25.8
	RF 1a	AS	82.8	19	49	68	0.72	0.0066	5.5
	RF-1a	AS	105.1	11	48	59	0.81	0.0067	7.0
	REP	PO	145.3	31	22	53	0.41	0.0116	16.9
	REP	BR(SW)	72.3	31	26	58	0.45	0.0055	4.0
	REP	EB	74.6	33	18	51	0.35	0.0107	8.0
	REP	AL	45.4	16	46	62	0.74	0.0397	18.0
	REP	SP	116.2	21	46	68	0.68	0.0112	13.0
Biocomb	WJ	EB	87.3	21	49	71	0.70	0.0489	42.7
	WJ	PO	55.5	21	30	51	0.60	0.0195	10.8
	WJ	NS	223.3	35	15	50	0.31	0.0202	45.2
	WJ	BR(SW)	96.9	27	47	74	0.64	0.0179	17.3
	RF-1b	PO	99.8	25	16	41	0.38	0.0131	13.1
	RF-1b	BR(SW)	74.5	21	48	69	0.69	0.0266	19.8
	RF-1b	NS	78.6	34	24	58	0.42	0.0198	15.6
	RF 1b	EB	98.8	36	34	70	0.48	0.0202	19.9
	SI	PO	84.2	35	35	70	0.49	0.0802	67.6
	SI	PO	40.8	19	23	42	0.55	0.0675	27.5
	GU	WP	33.8	38	25	63	0.39	0.0124	4.2
	GU	WP	11.0	2	0.2	2	0.07	0.0047	0.5
	GU	WC	27.9	21	23	44	0.53	0.0128	3.6
	GU	WC	13.2	4	0.5	5	0.10	0.0070	0.9
FWF/O	RM	WP(FL)	24.0	11	15	26	0.58	0.0068	1.6
	RF2	BR(HW)	32.0	19	30	49	0.61	0.0094	3.0
	RF2	EH	41.2	37	20	57	0.36	0.0423	17.4
	RF2	EB	66.0	32	34	66	0.51	0.0548	36.2
	RF2	BPop	45.6	33	30	63	0.48	0.0241	11.0
	RF2	TO	59.4	23	37	60	0.62	0.0630	37.4
	RF2	SO	221.9	31	13	45	0.29	0.0099	22.0
	RF2	PO	57.4	33	22	55	0.40	0.0217	12.5
	RF2	BL	98.2	42	12	54	0.22	0.0166	16.3
	RF2	SF	99.9	27	25	52	0.49	0.0216	21.6
	RF2	EL	20.7	46	26	72	0.37	0.0304	6.3
	RF2	NS	53.2	34	22	56	0.39	0.0118	6.3
	RF2	BP	100.8	36	34	71	0.49	0.0284	28.6
	RF2	L	626.1	55	10	65	0.15	0.0318	199
	RF2	N	85.5	58	19	77	0.25	0.0899	76.8

The PM_{10} and BaP emission rates of the studies under comparison are presented graphically in Figure 7(a,b,c). The data from the tests from stoves and boilers chosen for comparison are largely within the "two enveloping branches" indicating the lower BaP/PM_{10} (µg mg^{-1}) ratio of around 0.1 and an upper ratio of around one. Although the slope of the BaP/PM relationship shows quite a spread, the basic observation that the majority of results is within a range of 0.1-0.3 BaP/PM_{10} (µg mg^{-1}), (Figure 3) is also at large reproduced with the data set from the "3 studies": Data points above a 0.3 slope are exclusively from hardwood (AL, EH, EB [two runs], TO).

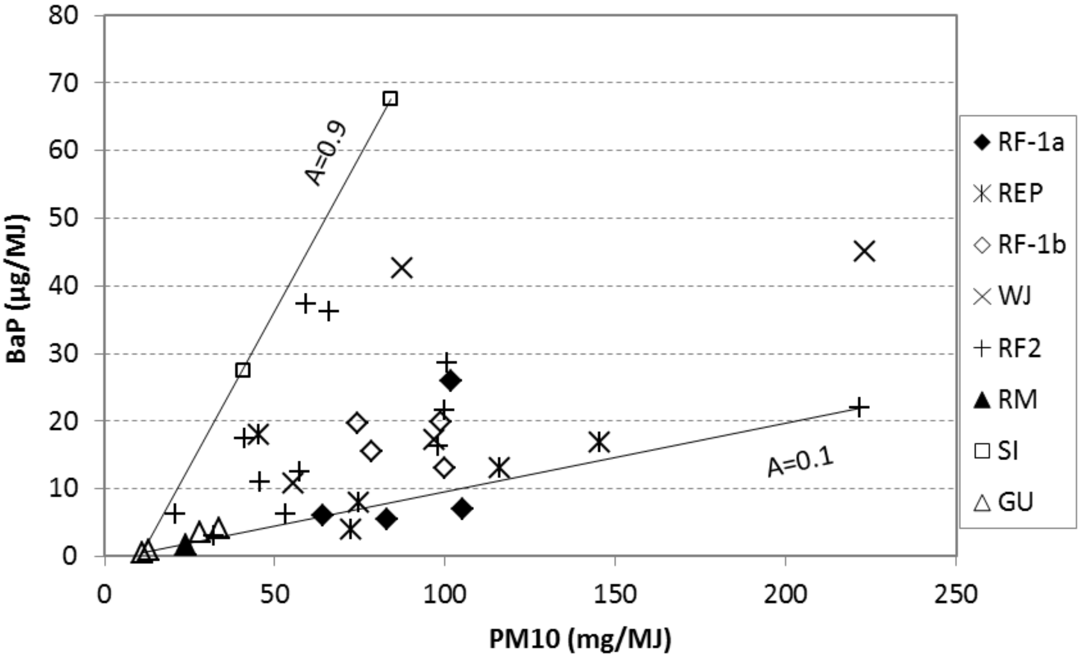


Figure 7a. BaP vs. PM_{10} emission rates for all tests with BaP data from the "3 studies", including pellet stove (RM), chimney stoves (REP, RF1, RF2, and WJ), pellet and chip boiler (GU), and logwood boiler (SI); A-increment.

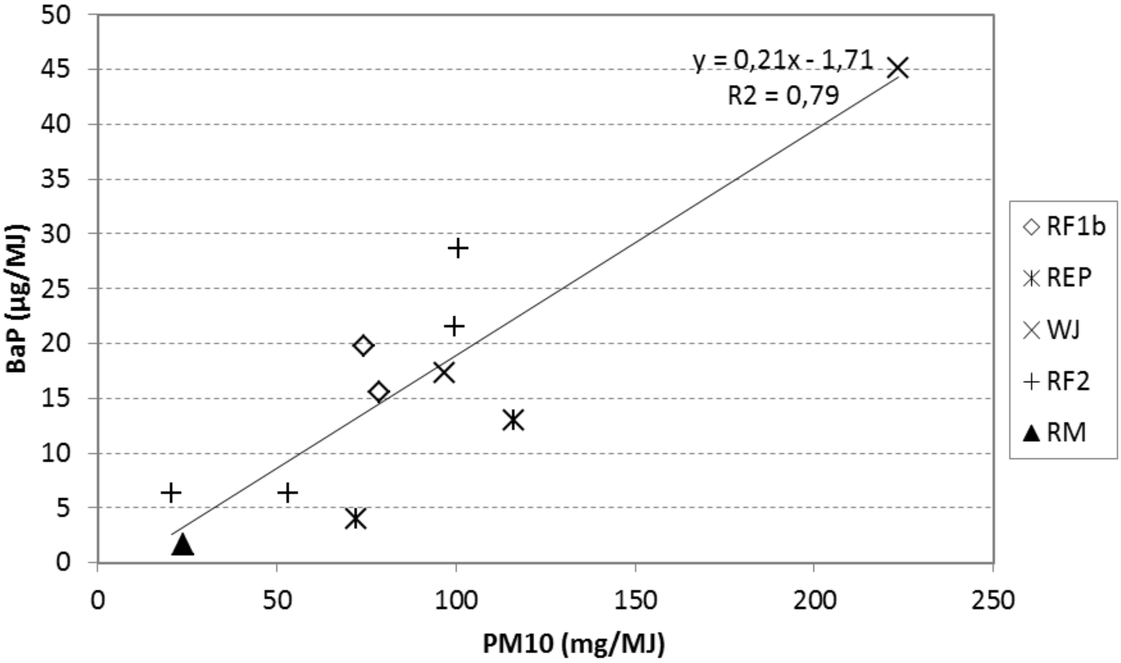


Figure 7b. Emission of BaP vs. EC from the "3 studies" for softwood logs and pellets, bottom). Correlation for is significant at P=95%.

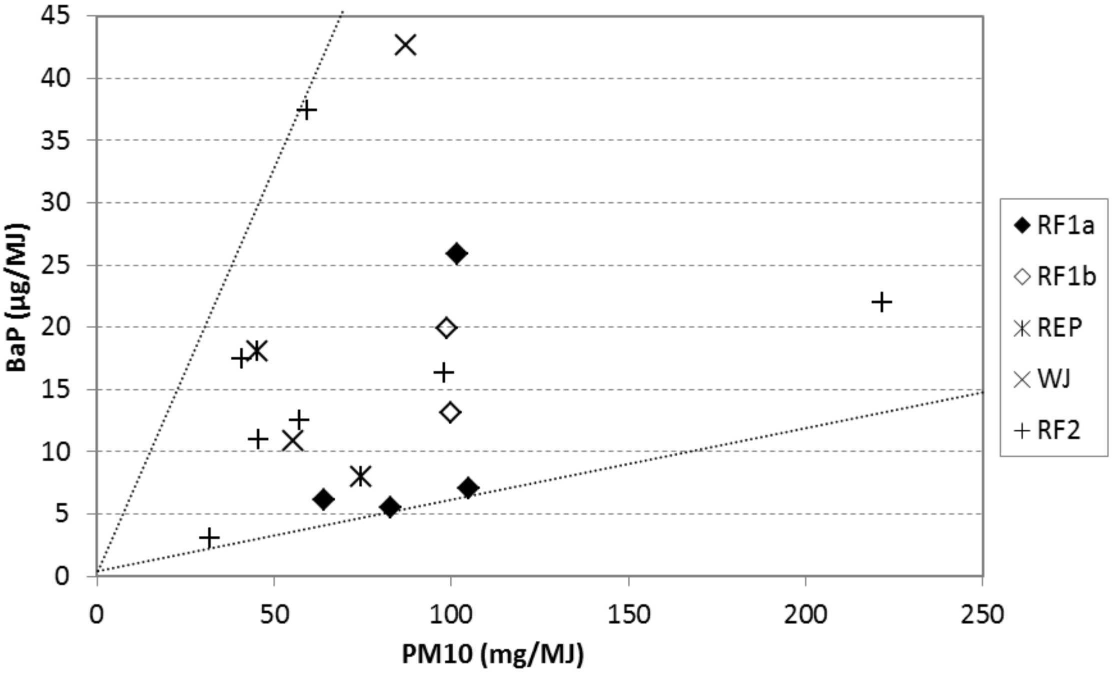


Figure 7c. Emission of BaP vs. EC from the “3 studies” combustion tests for hardwood logs and briquettes. No regression observed.

All stoves and the pellet boiler were of very recent production, only the SI logwood boiler is an “old” system.

5. Emissions of major mid European tree species from chimney stoves

A comparison of the emission ratio of BaP/PM_{10} of 3 major tree species and briquettes in different stoves is shown in Figure 8. For PO, NS and BR the BaP/PM_{10} ratio variations were in a comparable range for stoves RF1b, RF2 and WJ. Consistently lower BaP/PM_{10} ratios were obtained for the REP stove compared to the others, which is likely due to the sensor controlled air supply of the REP. For beech a high variation of the BaP/PM_{10} ratio was observed, with a low level of around 0.1 in the REP and up to 0.8 in the RF2 stove. The RF1a and RF1b series were performed in the same stove RF1, and RF2 is another stove but from the same series as RF1. Thus, the observed difference for the BaP/PM_{10} ratio in the RF stoves is considered a result of different burning characteristics of different beech wood batches which exerted a different combustion behavior and not a result of construction differences (see also the discussion in section “PAH emission rate” on the BaP formation due to hot oxygen deficient combustion). The observation of largely different combustion behavior from different wood batches though under standardized combustion conditions has been observed also for other wood types than beech, e.g., for EH and pines, thus is not limited to specific hard- or softwood types (Schmidl, personal communication). However, certain wood types, e.g., the oaks PO, SO and spruce showed a relative constancy of the BaP/PM_{10} ratio for tests with largely different PM_{10} emission rates, while EB exhibited a wide range of BaP/PM_{10} ratios, with similar PM_{10} emission rates. In particular, PO and NS were not susceptible of high burn rates leading to comparably high BaP emissions in the examined tests.

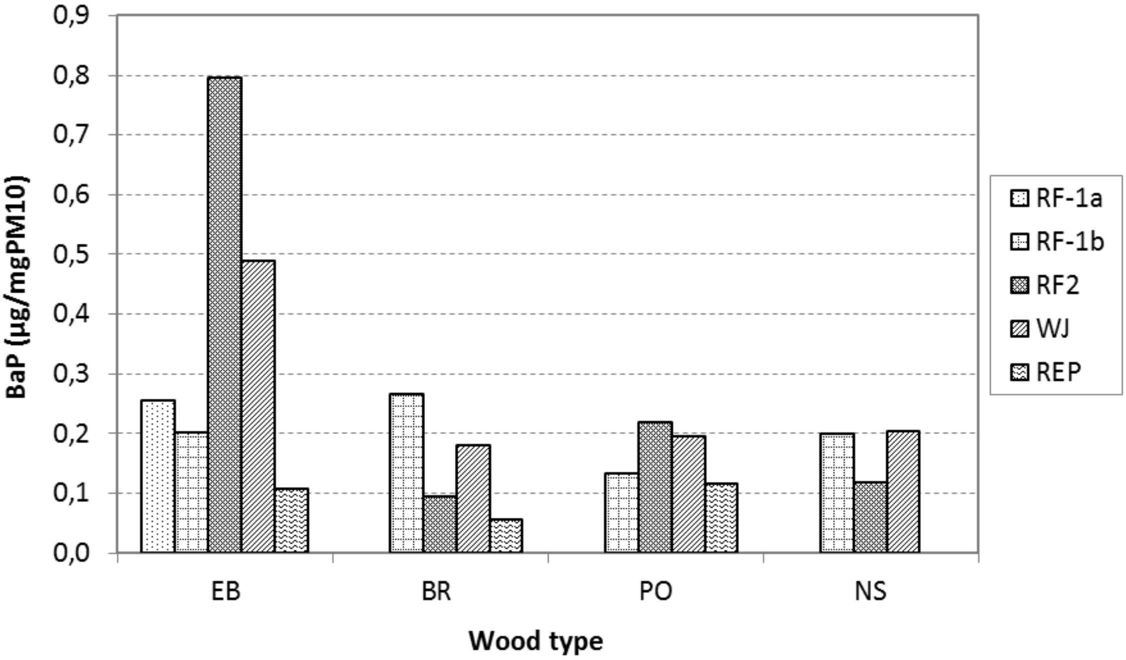


Figure 8. BaP/PM_{10} emission ratios for specific wood types (beech, briquettes, spruce and common oak) from different stoves.

The results for the major mid European wood species are summarized in Table 9. The data include the PM_{10} and BaP emissions and BaP/PM_{10} ratio from the three "chimney stove studies" for PO, EB, NS and BR, other hardwood (including AS, AL, HB, BL, SO, TO), other softwood (including SP, BP, SF, EL) and garden waste. The grand average is for "logs and briquettes".

Table 9. Summary results for PM_{10} and BaP emissions and BaP/PM_{10} ratio from the three "chimney stove studies" for common oak, beech, spruce, other hardwood (including A, AL, EH, BL, SO, TO) and other softwood (including SP, BP, SF, EL) and garden waste. The grand average is for "logs and briquettes". Averages originate from data comprised in Table 8.

Average (number of tests)	**PM_{10} mg MJ^{-1}**	**BaP µg MJ^{-1}**	**BaP/PM_{10} µg mg^{-1}**
Common oak (4)	90	13	0.16
Beech (5)	86	27	0.32
Spruce (3)	118	22	0.17
Briquettes SW+HW (4)	69	11	0.15
Other HW -AS,AL,EH,BL,SO,TO,BPop (11)	85	16	0.24
Other SW - SP,BP, SF,EL (4)	84	17	0.23
Garden waste (2)	356	138	0.61
Pellets (1)	24	1.6	0.07
Average logs+BR (29)	87	18	0.22
Median logs+BR (29)	79	16	0.20

While the BaP/PM_{10} emission ratios are relatively similar for PO, NS and BR, the emission ratio for EB is around a factor of two, due to the tendency of EB of fast burn rates and hot burns. From mechanistic studies (Pettersson et al., 2011; Lamberg et al., 2011) it was shown that increased burn rates accompanied by high temperatures and oxygen starved conditions are the major influencing parameter for elevated BaP emissions in modern stoves. In the cited studies "extreme" conditions were simulated to infer the effects on BaP emission rates. This study reveals that even under standardized combustion conditions batch to batch variations of the BaP emission rate may occur mainly as a result of the burn rate induced oxygen-inefficient-supply effect.

Combustion tests with Portuguese wood from the "BIOEMI" project, included test burns at TUV with one of the chimney stoves, RF1, with analytical work performed at University of Aveiro (Gonçalves et al., 2010). The mean of three hardwood types (*eucalyptus globulus. quercus suber. acacia longfolia*) yielded average emission rates of 114 mg MJ^{-1} $PM_{2.5}$ and 8 µg MJ^{-1} BaP and a BaP/$PM_{2.5}$ (µg mg^{-1}) ratio of 0.08, which is on the lower end of the slopes observed for mid European wood. In contrast, combustion of *pinus pinaster* with an emission rate of 62 mg MJ^{-1} $PM_{2.5}$ and 86 µg MJ^{-1} BaP resulted in a BaP/$PM_{2.5}$ (µg mg^{-1}) ratio of 1.4, higher than the ratios obtained for the mid European wood. It seems that the logwood burned with a low rate yielding lower burn temperatures while the pine exhibited a fast hot burn.

6. Emission rate comparison with other studies

Reports dealing with national emissions of wood combustion indicate that in the US as well as in Europe the predominant wood smoke emissions originate from the stock of "old" stoves and boilers. Sternhufvud et al. (2004) investigated the amounts of wooden fuel for use in fireplaces, stoves and boilers in four countries (Denmark, Finland, Norway, Sweden) and showed that there is a quite different distribution of wood consumption and appliance type in those countries. However, the sum of wood used in old types of stoves and boilers dominates the wood consumption in Scandinavia. Given the far lower emission rates of modern equipment it was derived, that the wood smoke emissions of old equipment dominates by far (93% in Finland, 99% in Denmark and Norway) the ambient fine particle levels originating from woody biomass combustion. This tendency is also known for Austria, as estimated e.g., in a report of Winiwarter et al. (2007).

An inventory of residential wood combustion emissions for Lombardy (Pastorello et al., 2011) indicates that residential fire wood is used by 56.4% of the households only for heating, 3.2% only for cooking and 38.4% both for cooking and heating. Traditional devices (open fireplaces, traditional stoves and closed fireplaces) are almost three-quarters of the total number of appliances at regional level, whereas the percentage penetration for pellet stoves and innovative stoves is around 5% each (Pastorello et al., 2011).

For Switzerland a similar mix of old and modern appliances for wood combustion was estimated to (70:30); firing with a hardwood to softwood ratio of 57:43 (Meyer, 2012). Highest wood smoke emissions originate from "fireplace ovens", masonry stoves and closed fire places, followed by cooking stoves.

In Portuguese households 35 PJ of wood is consumed per year, 83% used for heating and 17% for cooking (Gonçalves et al., 2012). The largest percentage of wood (51%) is burned in fireplaces, followed by conventional stoves (22%). From the inventory can be derived that BaP/$PM_{2.5}$ (µg mg^{-1}) emission ratios are ranging from **0.03 – 0.06** in the Portuguese districts.

In Austria in 2009, 45% of woody biomass used for heating was logwood, 7% pellets and 48% chips, bark and other sawmill side products (Statistik Austria 2011), 95.4 PJ (82%) of woody biomass energy was consumed for residential heating and further 20.6 PJ (18%) for district heating. Felling of fuelwood was reported for 2005 to be 41% deciduous, 59% conifer woods (discussed in Luisser et al., 2008). From the information on logwood use and hardwood felling we estimate a use of **70-90%** of hardwood and 10-30% of softwood in logwood stoves. Larger units e.g., for district heating, as well as pellet and chip boilers are preferentially fired with softwood.

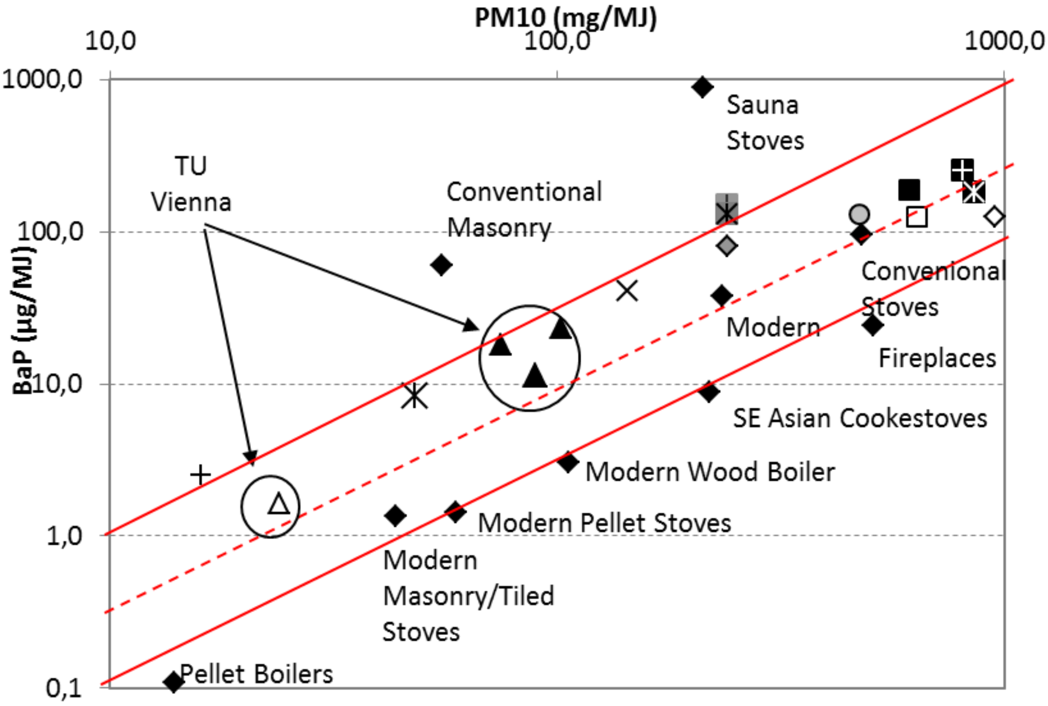
From this short overview follows, that in many European countries the majority of residential wood combustion emissions originate from "old" fireplaces, stoves and boilers.

The information about the about the PAHs emissions of “old stoves” is however relatively limited. Aggregated data are reported for US by EPA/AP42 (2009); for Europe in the EEA/EMEP data base (EEA. 2009). A compilation of data for deriving “typical” BaP/PM ratios for different appliance types is compiled in Table 10. BaP and PM emission rates from aggregated data sets (EPA, EEA), literature data from stove tests and data from the 3-studies (FWF/O: this work. BIOCOMB and AQUELLIS FB) are included in Figure 9 in double logarithmic scale.

Table 10. Compilation of data for deriving “typical” BaP/PM ratios for different appliance types from aggregated data (EPA, CORINAIR) and averages from relevant studies, for wood combustion(if not else given).

	Reference	**Stove**	**PM mg MJ^{-1}**	**BaP µg MJ^{-1}**	**BaP/PM**
Masonry/tiled stoves	Lamberg et al., 2011	Masonry heater new	51	1,7	0,033
	Tapanainen et al., 2012	Masonry heater new	52	0,60	0,012
	Jalava et al., 2012	Tiled stove new	28	1,8	0,065
	Tissari, et al., 2007	Masonry heater conventional	44	17	0,386
	Lamberg et al., 2011	Masonry heater convential	67	104	1,558
Sauna stoves	Tissari et al., 2007	Sauna stove raditional	169	930	5,511
	Lamberg et al., 2011	Sauna stove traditonal	257	834	3,245
Old wood stoves	McDonald et al., 2000	Catalytic wood stove	238	13	0,052
	Hedberg et al., 2002	Soapstone stove	81	225	2,778
	Gullet et al., 2003	Woodstove	504	35	0,069
	Jordan and Seen, 2005	Stove old	1472	20	0,014
	Jalava et al., 2012	Wood stove	74	272	3,672
	Gonçalves et al 2012	Woodstove old	516	14	0,027
Modern wood stoves	Hays et al., 2003	Woodstove	406	29	0,070
	Jordan and Sean 2005	Stove new	493	29	0,011
	Pettersson et al., 2011	Small modern stove	110	88	0,800
	Jalava et al., 2012	Wood stove	46	9	0,198
	Gonçalves et al., 2010	RF1	116	33	0,284
Open fireplaces	Rogge et al., 1998	Fireplace	650	26	0,040
	McDonald et al., 2000	Fireplace	397	16	0,041
	Schauer et al., 2001	Fireplace	495	30	0,060
	Hays et al., 2003	Fireplace	538	41	0,076
	Gullet et al., 2003	Fireplace artificial (sawdust logs)	315	27	0,084
	Fine et al., 2004	Fireplace	386	32	0,082
	Lee et al., 2005	Open fireplace simulation	494	0,04	0,0001
	Gonçalves et al 2012	Fireplace	818	22	0,027
Small moder pellet stoves	Boman et al., 2011	Pellet stove part load	37	3,7	0,108
	Boman et al., 2012	Pellet stove full load	20	0,17	0,010
	Riva et al., 2011	Pellet stove new 10,5 kW	122	0,40	0,400

South East Asian cookestoves	Oanh et al., 2005	Lao improved stove	238	17	0,070
	Oanh et al., 2005	Nepaleese metallic stove medium	275	3,6	0,013
	Oanh et al., 2005	Nepalese metallic stove small	238	16	0,067
	Oanh et al., 2005	Nepaleese ceramic - medium	181	11	0,062
	Oanh et al., 2005	Lao traditional	281	3,9	0,014
	Oanh et al., 2005	Vietnam traditional	294	0,29	0,001
	Oanh et al., 2005	Cambodian traditional	213	10	0,047
	Oanh et al., 2005	Nepalese clay stove small	175	26	0,147
	Oanh et al., 2005	Thai bucket stove	163	4,2	0,026
	Oanh et al., 2005	Chinese clay stove	150	6,0	0,040
	Oanh et al., 2005	Vietnam traditional (sawdust briquettes)	231	5,6	0,024
	Oanh et al., 2005	Thai traditional (wood)	200	3,2	0,016
Averages		Modern masonry stoves	44	1,4	0,036
		Conventional masonry stoves	55	60	0,972
		Sauna stoves	213	882	4,378
		Conventional wood stoves	481	96	1,102
		Modern wood stoves	234	38	0,273
		Open Fireplaces	512	24	0,051
		South East Asia Cookestoves	220	8,9	0,044
		Modern small pellet stoves	59,5	1,4	0,173
Inventory data	Corinair/EMEP 2006	Domestic stove	810	250	0,309
	Corinair/EMEP 2006	Advanced stove	240	150	0,625
	Corinair/EMEP 2006	Fireplace	860	180	0,209
	EEA/EMEP 2009	Advanced fireplace	240	130	0,542
	Corinair/EMEP 2006	Small boilers <50kW	475	130	0,274
	Corinair/EMEP 2006	Medium boilers 50kW-1MW	240	80	0,333
	EPA (1996)	Conventional stove	956	125	0,131
	EPA, (1996)	Non catalytic stove	613	187	0,305
	EPA, (1996)	Catalytic stove	638	125	0,196
	Baumbach,2010	Small stove worst case	144	41	0,285
	Baumbach, 2010	Small stove best case	16	2,5	0,156
	Baumbach, 2010	Small stove state of art	48	8,3	0,173
TUV studies	Kistler et al., 2012	RM	24	1,6	0,068
	Kistler et al., 2012	RF2	75	18	0,244
	Schmidl et al., 2011	RF1, WJ	102	23	0,233
	Schmidl et al., 2008a	RF1, REP	90	11	0,141



Legend:

◆ Averages [literature data]
⊞ Corinair Advanced Stove
⊠ Corinair Advanced Fireplace
◆ Corinair Medium Boilers (50kW-1MW)
■ EPA Non Catalytic Wood Stove
× Baumbach Stove-Worst-Case
+ Baumbach Stove-Best-Case
▲ FWF/O
▲ Aquellis FB
⊞ Corinair Domestic Stove
⊠ Corinair Fireplace
○ Corinair Small Boilers (<50kW)
◇ EPA Conventional Wood Stove
☐ EPA Catalytic Wood Stove
⋇ Baumbach Stove-State-of-Art
△ FWF/O Pellet Stove
▲ Biocomb

Figure 9. Compilation of BaP and PM emission rates from aggregated data sets (EPA, EEA), literature data from stove tests and data from the “3-studies” in logarithmic scale. Diagonal full lines indicate BaP/PM$_{10}$ (µg mg^{-1}) ratios of 0.1 and 1; dotted line 0.3.

Around 70% and more of firewood in Europe are used in “old” type stoves and boilers with around 5-10 times the PM emissions of “modern” stoves and boilers. From this follows, that 90-95% of wood smoke emissions originate from “old” appliances. This relationship is not valid for BaP emissions, which in many cases are in a similar order of magnitude as for “modern” stoves. Aggregated emission factors for BaP and PM - namely BaP/PM ratios in the EEA data, are consistently higher than observations (Figure 9), seemingly as a result of over estimated BaP emission rates for old as well as for new types of wood stoves.

Highest BaP/PM ratios are reported for sauna stoves and old masonry stoves, where high burn rates are used accompanied by high combustion temperatures. “Tiled” masonry stoves are in wide spread use in Austria as well as in Switzerland, Southern Germany and Northern Italy. For “old”, conventional stoves and fireplaces, the BaP/PM (µg mg^{-1}) ratios are low, as for example 0.03 derived for Portuguese residential wood combustion emissions (derived from data in Gonçalves et al., 2012). The “grand average” for “modern” chimney stoves from the “3 studies” from TU Vienna for the BaP/PM (µg mg^{-1}) ratio is 0.22 (Table 3).

7. Ambient BaP/PM ratio observations

For the Libby, Montana, study Ward et al. (2010) report ambient concentrations of 6.3 ng m^{-3} BaP and 28.3 µg m^{-3} PM$_{2.5}$ for the 2004/5 heating period. Considering a 70% wood smoke contribution to PM$_{2.5}$ estimated by Ward et al. (2006), an ambient BaP/PM$_{2.5}$ ratio of **0.32** (µg mg^{-1}) can be derived.

Bari et al., (2010, 2011a, b) investigated the occurrence of wood smoke tracers and PM$_{10}$ during cold season at two wood burning communities in Germany. For the 2005/6 study in Dettenhausen an average PM$_{10}$ of 35.2 µg m^{-3}, a biomass burn contribution to PM$_{10}$ of 59% (Bari et al., 2010) and a BaP average of 1.6 ng m^{-3} (Bari et al., 2011b) is reported. Following the assumption, that the main contributor to BaP is wood smoke a BaP/PM$_{10}$ ratio of 0.08 (µg mg^{-1}) is obtained. From graphical information in Bari et al. (2011a) and assuming a 59% contribution of wood combustion to PM$_{10}$ a Ba/PM$_{10}$ ratio of 0.12 (µg mg^{-1}) can be derived. Thus, the observed ambient BaP/PM$_{10}$ ratio in the cold season in Dettenhausen is around **0.1** (µg mg^{-1}). The main fuel in the area is beech and the emissions of wood smoke are estimated to originate by 90% from hardwood (Bari et al., 2011b).

For a rural site “Moitinhos” near Aveiro (Portugal) a one year average of 0.74 ng m^{-3} BaP, 23 µg m^{-3} PM$_{2.5}$ (Oliveira et al., 2007) and a levoglucosan level of 0.52 µg m^{-3} (Puxbaum et al., 2007) is reported. The PM$_{2.5}$/Levoglucosan emission ratio from Portuguese wood from a fireplace and a conventional stove yielded a median of 10.9 (calculated from data given in Gonçalves et al., 2012). From these data a PM$_{2.5}$ level from wood combustion of 5.7 µg m^{-3} (25% of PM$_{2.5}$) is obtained. Gelencsér et al. (2007) derived a contribution of biomass burn sources to total carbon for “winter” of 75%, for fossil combustion sources of 3% for the Moitinhos site (designated therein as “Aveiro”). As the average BaP concentration of 0.74 ng m^{-3} originates from emissions in the winter period (Oliveira et al., 2007) we assume an upper limit of fossil sources to the observed BaP average of 5%. From this a BaP/PM$_{2.5}$ ratio from wood smoke of **0.11** is derived, which can be compared with the respective ratio for the district of Aveiro of 0.03 from the emission inventory of Gonçalves et al. (2012). The discrepancy of this analysis (95% of BaP to originate from wood smoke) to the result of Oliveira et al. (2007) that PAHs observed at Moitinhos are predominantly from traffic sources is explained by Dvorska et al. (2012) which conclude from comparison of EPA16 emission profiles that PAH diagnostic ratios of the standard EPA set are not suited for discriminating source contributions from traffic and wood combustion.

A reevaluation of data from two AQUELLA reports (AQUELLA Niederösterreich, Bauer et al., 2008; AQUELLA Zederhaus, Bauer et al., 2010) gave BaP/PM_{10} ratios for wood smoke of **0.06** for a Lower Austrian site near the Hungarian border, **0.12-0.13** for 3 central lower Austrian sites, and **0.2** for the Zederhaus site in an inner Alpine valley. In the reevaluation the result of Belis et al. (2011) was considered, that the levoglucosan tracer with a PM_{10}/levoglucosan ratio of 10.4 (e.g., as derived by Schmidl et al., 2008b) underestimates the ambient PM_{WS} level by around 30%. A detailed discussion of the use of levoglucosan for assessing wood smoke derived PM levels is in another paper of this series.

The available results of ambient observations of a BaP/PM ratio from wood smoke combustion indicate that the integrated emissions from wood combustion in a wood combustion region may vary due to different stove and boiler types, wood types and operational procedures. The ratio, however, exhibits interesting properties. It can be used to check the quality of regional model results used for predicting the contribution of wood smoke to PM levels, and once determined, it would be possible to estimate the BaP contributions from wood smoke from estimated levels of PM from wood smoke, which might be more easily accessible than BaP measurements over long time periods.

Observed ambient BaP_{WS}/PM_{10WS} or $BaP_{WS}/PM_{2.5\,WS}$ (µg mg^{-1}) ratios so far were in an estimated range from about 0.1-0.3, which is also consistent with the range where the majority of emission ratios for many types of stoves are found (Figure 9). From this can be derived, that ambient levels of BaP_{WS} of 1 ng m^{-3} would occur for PM_{10WS} concentrations of 3-10 µg m^{-3}. E.g., for Dettenhausen (Gemany) an annual mean PM_{10} concentration of 10 µg m^{-3} from biomass combustion would result in an annual mean of BaP_{WS} of 1 ng m^{-3}. Likewise for Libby (Montana) for an annual mean level of $PM_{2.5}$ of 3.1 µg m^{-3} the 1 ng m^{-3} threshold of BaP would be achieved from domestic wood smoke sources.

8. Final considerations

The study comprises tests with softwood (4 types), hardwood (7 types) and hardwood briquettes (one type). Most of the samples are combined of 2-3 combustion cycles. The results showed a large variance of emission rates of BaP (RSD = 63%) and PM_{10} (RSD = 71%). The variance of the BaP emission rate could be explained with a help of a multiple linear regression model including the burn rate and EC as input variables. Although the tests were performed under standardized conditiones including two loads starting from the cold stove with the ignition phase, the “burn rate induced oxygen-inefficient-supply effect” as described by Pettersson et al. (2011) was a main contributor to increased BaP emission rates. The variation of the burning conditions of the tested wood types with respect to burn rate and EC formation were of dominating influence for the observed BaP emission rates. It appeared that certain wood types were less susceptible for exhibiting high burn rates, with fewer tendencies for air starved conditions. No clear discrimination for soft- or hardwood was derived from the model; highest emitters of BaP comprised both wood types, TO, EB and BP.

The very high emission rates of BaP from garden waste (L, N) combustion indicate the uncontrolled increase of emissions when using slash and other garden waste for igniting the stove.

A combined evaluation of 29 emission tests from four different chimney stoves, all performed at the same test stand at TUV involving identical analytical methods (except for EC) was possible, combining data from this study (FWF/O), the BIOCOMB (Luisser et al., 2008) and the AQUELLIS FB (Schmidl et al., 2008a) study. BR, EB, PO and NS emissions have been tested in 3-5 stoves, allowing an intra- and inter-stove comparison. One of the tested chimney stoves (REP) differed from the others as it was equipped with an automated control of the air supply. The BaP emission rates for REP were a factor of 3-4 lower than the averages from the other stoves for BR and EB. For PO no clear difference to the other stoves was observed. A check of the Figure 8 shows, that increases of the inter-stove BaP emission rate occur for BR and EB without notable increases of the PM_{10} emission rate. Thus, it appears that BaP emission rates for BR and EB are more or less independent of the respective PM_{10} emission rate. In contrast, for PO and NS a strong dependence of the BaP emission rate from the PM_{10} emission rate is evident from Figure 11, with $R^2 = 0.9$ for PO and $R^2 = 0.99$ for NS. There is no obvious reason for the different behavior of BR and EB vs. NS and PO, however, in the latter case the association of increasing BaP with increasing PM_{10} emissions point to different combustion properties which may imply the different BaP formation behavior.

The relatively large data sets for BaP and PM_{10} emission rates from the “3 studies” allows to establish an averaged emission rate for briquettes, logwood and hardwood from chimney stoves of 18 µg MJ^{-1} BaP and 87 mg MJ^{-1} PM_{10}. Grand averages for BR_{HW}+hardwood logs (17.3 µg MJ^{-1} BaP, 83 mg MJ^{-1} PM_{10}, n=19) were similar to those of BR_{SW}+softwood logs (17.8 µg MJ^{-1} BaP, 94 mg MJ^{-1} PM_{10}, n=10). For the individual wood types the BaP emission rate of BR and PO were around a factor of 2 lower, than for NS and EB (Table 9). The BaP emission rate of the tested pellet stove (WP) was around a factor of 10 lower than for BR and logwood; the averaged emission rate of garden waste around a factor of 8 higher.

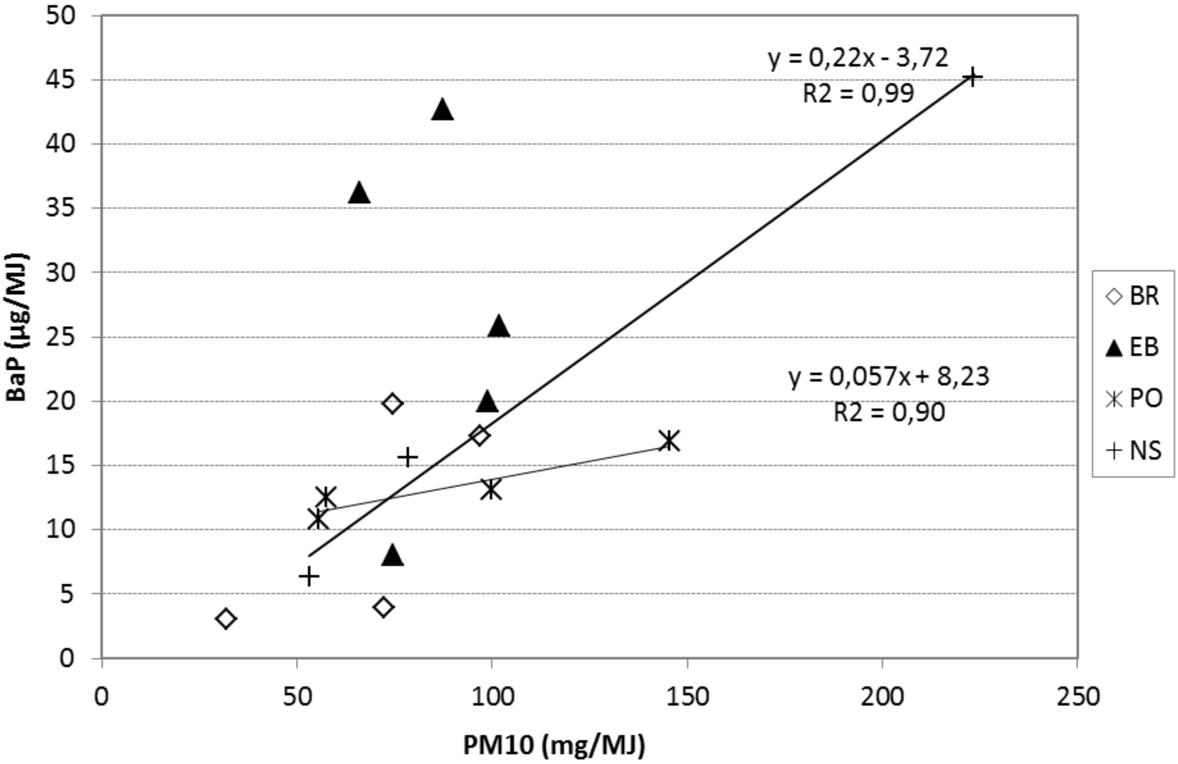


Figure 11. Inter-stove relations of BaP and PM_{10} emission rates for BR, EB, NS and PO. Data from "3 studies".

A recommended BaP and PM_{10} emission rate for chimney stoves for use in emission inventories would require an estimate including non-standard operations with respect of fuel quality, non-standard ignition techniques, fuel overloading, or "low air supply". Assuming that in 25-50% of the cases mal-operation leads to a doubling of the emission rates (e.g., Schmidl et al., 2011), the resulting numbers would be 104-130 mg MJ^{-1} PM_{10} and 22-27 µg MJ^{-1} BaP. These rates are comparable with the grand averages for modes 1-3 experiments performed with a modern Swedish wood stove (mainly birch, but also spruce, pine test burns with low, medium and high moisture, and three different air settings, isolated and not isolated operation) of 140 mg MJ^{-1} PM_{10} and 36 µg MJ^{-1} BaP (Pettersson et al., 2011).

Differences in BaP and PM_{10} emissions due to a different wood type distribution in the mid-European countries can be estimated: A) from the wood type distribution of the countries, including 10% briquettes use, B) assuming a hardwood-scenario with 10% briquettes and 90% hardwood logs, as logwood stoves are operated preferentially with hardwood. The evaluation of emissions in 8 different countries for the tested type of stoves show that the country to country differences in the emission rates for the forest wood type distribution, as well as for a hardwood scenario (Table 11), are minor considering the uncertainty of the influence of mal-operations. From the Pettersson et al. (2011) study can be derived, that logwood seasoned over one season (fuel moisture ~ 16%) burning with lower burn rate exhibit considerably lower BaP emission rates (around a factor of five lower than in this study, performed with logs of around 10%

moisture), while in fast burns with drier (8% moisture), finer cut logs BaP emission rates were around a factor of seven higher than in our experiment.

Table 11. Country specific evaluation of BaP and PM_{10} emission rates for chimney stoves for two emission scenarios: "A" (FD) – wood fuel use according to countries forest tree share; "B" (HW) - hardwood scenario (10% BR, 90% HW), HW scenario according to hardwood distribution in presented countries.

Country	**BaP (µg MJ^{-1})**		**PM_{10} (mg MJ^{-1})**		**BaP/PM (µg mg^{-1})**	
	A (FD)	B (HW)	A (FD)	B (HW)	A (FD)	B (HW)
AT	12	20	56	86	0.22	0.23
S-DE	16	22	60	100	0.27	0.22
CZ	13	18	55	90	0.23	0.20
HU	16	18	63	84	0.26	0.21
SK	20	22	60	84	0.32	0.26
SI	19	21	64	88	0.30	0.24
N-IT	9	17	45	71	0.21	0.24
CH	15	21	61	86	0.25	0.24

Comparison with BaP and PM_{10} ($PM_{2.5}$) emission rates from aggregated data and other studies indicates highly different behavior for old/new masonry stoves, old/new logwood stoves. A conclusive number for an averaged BaP/PM_{10} ($PM_{2.5}$) emission ratio cannot be derived due to the large spread of the emissions from different technologies (within and between the groups "old" and "new"). The median BaP/PM_{10} ($PM_{2.5}$) emission ratio of the literature data is 0.08 (µg mg^{-1}) with a 1st quartile of 0.04 and a 3rd quartile of 0.27. Ambient observations are sparse. The available data for the European sites show a range of 0.06-0.2, average 0.12 (µg mg^{-1}) and are close to the range of the 3rd quartile from the emission data. The BaP_{WS}/PM_{10WS} ($PM_{2.5WS}$) ratio as observed in ambient air integrates the emissions from a large number and variety of wood combustion appliances. Though ageing might increase secondary aerosol contributions from wood smoke emissions, loss processes might lower the ambient levels of PAHs, changing the original emission signature during air mass transport. For densely wood smoke emitting regions the actual BaP_{WS}/PM_{10WS} ratio derived from ambient observations is expected to reflect the integrated emissions in real world. The comparison with modeled emission rates might allow a quality check of the respective emission data. If suitable data sets for BaP/PM_{10} ($PM_{2.5}$) become available for ambient sites a comparison with emission inventories might help to check for correct emission ratio data, respectively a prediction of ambient BaP levels from wood smoke becomes possible from modeled wood smoke $PM_{2.5}$ or PM_{10} levels.

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Appendix

Table A1. Single experiment list, gas emissions measured during the experiment, particulate mass emissions (PM_{10}, $PM_{2.5}$) of each combustion.

Nr.	Filter set	Date	Fuel	stove	O_2	CO_2	Odor	CO	NO_x	C_xH_y	PM_{10}	$PM_{2.5}$
					(%)	(%)	(OU m^{-3})	(mg MJ^{-1})				
1	FWF 1	2009-03-13	WP (FL)	Pellet stove	14.2	6.2	ND	103	102	64	18	19
2	FWF 2	2009-03-17	WP (FL)		14.2	6.2	ND	134	86	52	23	22
3	FWF 3	2009-03-18	WP (PL)		17.6	3.0	ND	254	73	9	14	15
4	FWF 4	2009-03-18	WP (PL)		17.4	3.1	ND	236	76	7	18	19
5	FWF 5	2009-03-19	WP (FL)		13.9	6.4	ND	188	131	5	31	30
6	FWF 6	2009-04-29	Bpop	Chimney logwood stove	15.1	5.3	3661	1933	60	242	46	47
7	FWF 7	2009-04-29	Bpop		15.5	4.8	3070	1599	74	119	5	3
8	FWF 8	2009-04-30	Bpop		15.5	4.9	1798	2035	62	285	11	12
9	FWF 9	2009-04-30	EH		14.7	5.7	720	1545	107	246	31	26
10	FWF 11	2009-06-03	EH		13.5	6.8	292	989	107	982	46	43
11	FWF 12	2009-06-04	EH		15.1	5.3	595	1168	116	159	46	42
12	FWF 13	2009-06-08	BL		17.0	3.5	1039	1896	119	320	98	120
13	FWF 14	2009-06-08	BL		15.5	4.8	1123	1844	104	113	24	23
14	FWF 15	2009-06-09	BL		16.3	4.2	2906	2262	131	285	80	66
15	FWF 16	2009-06-09	TO		14.0	6.3	1526	1437	104	113	55	50
16	FWF 17	2009-06-15	TO		14.1	6.3	2079	1803	83	154	60	57
17	FWF 18	2009-06-15	TO		13.2	7.0	1738	2207	77	352	64	64
18	FWF 19	2009-06-16	EB		13.0	7.4	1472	1009	111	110	36	35
19	FWF 20	2009-06-16	EB		13.5	6.8	1468	1232	98	149	67	66
20	FWF 21	2009-06-17	EB		13.1	7.2	1748	1989	77	443	95	94
21	FWF 22	2009-06-17	BR		15.7	4.7	2218	1632	60	204	39	45
22	FWF 23	2009-06-18	BR		15.8	4.6	1600	1506	72	176	51	52
23	FWF 24	2009-06-18	BR		15.2	5.1	1594	1309	57	108	7	5
24	FWF 25	2009-06-22	SF		15.2	5.0	4164	3428	87	588	89	72
25	FWF 26	2009-06-22	SF		15.4	4.8	2069	3070	82	442	79	64
26	FWF 27	2009-06-23	SF		16.3	4.0	5211	3993	146	712	132	118
27	FWF 28	2009-06-23	NS		15.5	4.8	5985	2019	60	332	60	45
28	FWF 29	2009-06-24	NS		15.2	5.1	3951	1902	73	248	52	38
29	FWF 30	2009-06-24	NS		15.2	5.2	5714	1781	74	222	48	40
30	FWF 31	2009-06-25	SO		17.4	3.0	3456	3870	131	767	250	170
31	FWF 32	2009-06-26	N		17.0	3.5	5270	4123	126	659	194	150
32	FWF 33	2009-06-26	PN		16.4	4.0	3953	3050	137	544	ND	110
33	FWF 34	2009-07-01	BP		14.5	5.7	1361	1440	68	151	80	83
34	FWF 35	2009-07-01	BP		15.8	4.5	2039	2379	58	368	113	74
35	FWF 36	2009-07-02	BP		13.9	6.1	1368	1310	65	210	110	82
36	FWF 37	2009-07-21	SP		14.8	5.6	2503	1263	69	161	17	11
37	FWF 38	2009-07-22	SP		14.7	5.5	2324	1101	70	94	79	65
38	FWF 39	2009-07-22	SP		13.8	6.3	1576	1201	70	73	63	43
39	FWF 40	2009-07-23	PO		16.4	4.0	1992	3249	105	380	35	26
40	FWF 41	2009-07-23	PO		17.0	3.4	1954	3257	102	525	80	69
41	FWF 42	2009-07-28	EL		13.8	6.5	2422	1263	58	179	21	12
42	FWF 43	2009-07-28	N		11.7	8.0	7346	2204	111	1424	85	55
43	FWF 44	2009-07-28	C		11.7	8.3	3524	2821	89	1106	<LOQ	<LOQ
44	FWF 45	2009-07-28	L		13.6	6.3	18963	2249	132	1543	626	348

Table A2. Carbon fractions, anhydrosugars and inorganic ions in PM_{10} single tests (sample F44<LOQ).

Filter set	OC	EC	CC	Lev	Man	Gan	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
	(% PM_{10})													
FWF 1	11	15	0.38	0.12	0.02	0.02	1.9	0.2	15.8	0.1	0.7	6.5	0.4	10.2
FWF 2	15	18	0.50	0.08	0.01	0.01	2.0	0.3	18.3	0.1	0.5	6.7	0.4	11.6
FWF 3	9	10	0.20	0.24	0.11	0.02	0.8	0.4	21.2	0.1	0.8	5.8	3.0	14.6
FWF 4	9	16	0.22	0.30	0.11	0.02	3.3	0.4	21.6	0.1	1.1	5.7	2.4	18.8
FWF 5	6	13	0.33	0.09	0.02	0.01	2.5	0.2	35.4	0.1	0.8	2.3	0.5	14.7
FWF 6	33	30	0.12	3.18	0.28	0.04	0.2	0.3	2.0	0.0	0.2	0.6	0.4	1.2
FWF 7	21	16	0.12	0.96	0.08	NF	0.2	0.8	2.5	0.04	0.5	1.1	0.5	1.5
FWF 8	30	19	0.18	2.98	0.20	0.07	0.3	0.9	2.7	0.16	0.9	1.1	0.3	1.6
FWF 9	38	18	NF	4.84	0.16	0.08	0.03	0.7	0.9	0.01	0.2	0.8	0.2	0.5
FWF 11	43	17	NF	3.03	0.11	0.05	0.02	0.8	1.0	0.01	0.2	1.3	0.2	0.5
FWF 12	29	26	0.08	5.81	0.22	0.11	0.1	0.7	1.5	0.01	0.2	1.1	0.3	0.7
FWF 13	42	12	0.01	14.04	0.45	0.23	0.0	0.5	0.8	0.01	0.2	0.7	0.3	0.4
FWF 14	25	29	0.08	4.67	0.15	0.10	0.1	0.8	4.0	0.1	0.8	1.5	1.1	1.8
FWF 15	38	22	0.04	10.40	0.35	0.17	0.02	0.3	0.7	0.02	0.3	0.2	0.3	0.3
FWF 16	22	34	0.11	0.44	0.03	0.02	0.03	0.5	6.0	0.03	0.4	2.3	0.4	2.9
FWF 17	19	40	0.09	0.48	0.03	0.02	0.03	0.2	3.9	0.02	0.3	1.5	0.5	2.5
FWF 18	27	36	NF	0.27	0.02	0.01	0.02	0.2	4.0	0.02	0.3	1.0	0.4	2.0
FWF 19	33	28	0.06	0.29	0.01	0.02	0.02	0.2	1.5	0.02	0.3	0.8	0.2	0.5
FWF 20	40	32	0.05	0.54	0.03	NF	0.02	0.2	2.0	0.02	0.2	0.8	0.2	0.6
FWF 21	24	41	0.05	0.22	0.01	0.01	0.01	0.2	2.5	0.01	0.2	0.7	0.2	0.9
FWF 22	23	34	0.04	6.38	0.50	0.09	0.07	0.2	2.2	0.02	0.2	1.0	0.4	0.8
FWF 23	25	30	0.04	6.72	0.58	0.12	0.04	0.2	1.7	0.02	0.4	0.8	0.3	0.6
FWF 24	9	26	0.04	1.96	0.16	0.05	0.03	0.3	1.2	0.03	0.5	0.7	0.3	0.4
FWF 25	24	25	0.08	1.56	0.77	0.12	0.02	0.2	4.2	0.02	0.3	1.7	0.2	0.8
FWF 26	26	30	0.06	1.75	0.79	0.14	0.02	0.1	4.8	0.01	0.2	1.9	0.3	0.8
FWF 27	30	20	0.08	1.90	1.01	0.17	0.01	0.1	4.7	0.01	0.1	1.6	0.3	1.4
FWF 28	42	17	NF	8.32	2.22	0.32	0.02	0.2	0.8	0.02	0.2	0.2	0.1	0.1
FWF 29	31	27	0.03	4.95	1.38	0.26	0.02	0.2	0.8	0.02	0.2	0.3	0.2	0.2
FWF 30	29	22	0.03	4.28	1.30	0.26	0.02	0.2	0.8	0.02	0.2	0.4	0.1	0.2
FWF 31	27	13	0.03	7.48	0.36	0.20	0.01	0.1	0.8	0.01	0.1	0.1	0.1	0.3
FWF 32	35	13	0.07	17.48	0.73	0.35	0.01	0.1	2.5	0.01	0.1	0.5	0.3	1.1
FWF 33	30	16	0.04	15.35	0.62	0.30	0.04	0.2	1.2	0.01	0.2	0.6	0.1	0.5
FWF 34	22	45	0.07	1.67	0.43	0.05	0.03	0.1	0.5	0.02	0.2	0.3	0.1	0.1
FWF 35	30	38	0.04	5.51	1.79	0.20	0.02	0.2	0.4	0.02	0.2	0.2	0.0	0.1
FWF 36	57	20	0.03	0.78	0.25	0.04	0.02	0.1	0.2	0.01	0.1	0.1	0.0	0.0
FWF 37	35	40	0.10	3.48	1.00	0.20	0.08	0.2	1.4	0.04	0.4	1.0	0.3	0.4
FWF 38	58	19	0.05	1.35	0.47	0.08	0.05	0.0	0.4	0.02	0.2	0.2	0.1	0.1
FWF 39	20	59	0.06	0.29	0.07	0.01	0.02	0.0	0.3	0.02	0.3	0.1	0.1	0.1
FWF 40	29	27	0.14	17.0	0.59	0.28	0.09	0.2	5.7	0.02	0.3	1.8	0.5	2.3
FWF 41	37	17	0.08	22.9	0.62	0.48	0.07	0.2	2.5	0.01	0.2	1.1	0.3	0.8
FWF 42	46	26	0.07	10.2	2.61	0.92	0.04	0.4	1.3	0.04	0.5	1.1	0.3	0.2
FWF 43	58	19	NF	0.79	0.16	0.06	0.02	0.1	0.2	0.02	0.2	0.2	0.0	0.2
FWF 45	55	10	0.04	3.61	0.32	0.55	0.01	0.05	0.09	0.01	0.09	0.12	0.02	0.11

Teble A3. Carbon fractions, anhydrosugars and inorganic ions in $PM_{2.5}$ single tests (sample F44<LOQ).

Filter set	OC	EC	CC	Lev	Man	Gan	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
	% $PM_{2.5}$													
FWF 1	10	18	0.20	0.13	0.02	0.01	1.52	0.3	17.2	0.04	0.4	6.7	0.5	12.0
FWF 2	13	20	0.15	0.08	0.01	0.01	0.84	0.2	19.3	0.03	0.3	4.4	0.4	11.4
FWF 3	8	10	0.17	0.28	0.13	0.04	0.80	0.3	21.0	0.03	0.3	5.3	2.6	12.8
FWF 4	9	14	0.12	0.25	0.10	0.03	1.55	0.4	21.9	0.08	0.7	4.2	2.3	13.9
FWF 5	7	13	0.28	0.07	0.02	0.01	1.56	0.1	22.9	0.02	0.3	2.3	0.5	13.6
FWF 6	27	27	0.05	2.68	0.24	0.07	0.17	0.4	1.8	0.01	0.2	0.5	0.3	1.2
FWF 7	23	21	0.13	0.96	0.08	NF	0.24	1.4	2.8	0.05	0.7	1.2	0.7	1.8
FWF 8	25	14	0.15	2.04	0.17	0.06	0.20	0.5	2.0	0.03	0.5	0.7	0.8	1.4
FWF 9	40	19	0.06	4.96	0.21	0.11	0.05	1.2	1.0	0.02	0.3	0.8	0.3	0.4
FWF 11	46	20	0.05	3.26	0.13	0.07	0.03	0.9	1.1	0.01	0.2	1.5	0.2	0.6
FWF 12	28	27	0.08	6.08	0.24	0.13	0.12	0.8	1.6	0.01	0.3	1.2	0.4	0.7
FWF 13	43	14	0.02	13.44	0.50	0.31	0.02	0.5	0.9	0.01	0.1	0.8	0.3	0.4
FWF 14	20	25	0.08	3.89	0.13	0.08	0.05	0.8	3.4	0.03	0.5	1.2	0.9	1.5
FWF 15	37	25	0.04	10.35	0.37	0.21	0.05	0.4	0.9	0.01	0.2	0.3	0.3	0.4
FWF 16	19	40	0.08	0.44	0.03	NF	0.03	0.6	6.1	0.02	0.3	2.4	0.4	3.1
FWF 17	28	37	0.11	0.43	0.03	0.03	0.02	0.1	5.2	0.01	0.2	1.4	0.4	2.4
FWF 18	29	32	0.14	0.26	0.03	0.03	0.02	0.2	4.1	0.02	0.3	0.9	0.4	2.0
FWF 19	29	32	0.00	0.29	0.02	0.02	0.02	0.3	1.6	0.02	0.3	0.8	0.2	0.5
FWF 20	51	14	0.05	0.47	0.03	0.03	0.0	0.3	1.8	0.01	0.3	NA	NA	NA
FWF 21	35	27	0.15	0.19	0.01	NF	<LOD	0.1	2.2	0.01	0.2	0.5	0.3	0.7
FWF 22	35	28	0.10	6.94	0.54	0.12	0.0	0.3	2.1	0.02	0.3	0.7	0.3	0.7
FWF 23	25	25	0.05	6.07	0.53	0.13	<LOD	0.2	1.7	0.02	0.2	0.4	0.6	0.3
FWF 24	10	23	0.00	1.92	0.17	0.07	<LOD	0.5	1.2	0.05	0.6	0.5	1.1	0.6
FWF 25	28	31	0.10	2.00	1.02	0.17	<LOD	0.1	5.3	0.01	0.2	2.2	0.2	1.2
FWF 26	23	31	0.05	1.76	0.77	0.17	<LOD	0.1	4.9	0.02	0.2	2.2	0.2	1.0
FWF 27	29	26	0.12	2.45	1.32	0.26	<LOD	0.1	5.3	0.01	0.1	2.2	0.4	1.9
FWF 28	40	22	0.05	8.79	2.35	0.46	<LOD	0.3	1.0	0.02	0.3	0.3	0.2	0.4
FWF 29	37	33	0.07	5.78	1.62	0.40	<LOD	0.3	1.0	0.02	0.2	0.3	0.1	0.1
FWF 30	36	25	0.03	5.01	1.56	0.39	<LOD	0.4	0.9	0.02	0.2	0.4	0.2	0.3
FWF 31	34	21	0.05	11.48	0.54	0.34	<LOD	0.1	1.2	0.01	0.1	0.1	0.1	0.3
FWF 32	36	15	0.06	18.54	0.75	0.42	<LOD	0.2	3.0	0.01	0.1	0.5	0.2	1.2
FWF 33	32	20	0.03	16.94	0.60	0.31	0.03	0.4	1.7	0.01	0.2	0.7	0.2	0.5
FWF 34	38	11	0.03	1.06	0.30	0.06	0.002	0.2	0.4	0.01	0.1	0.2	0.1	0.1
FWF 35	30	26	0.05	5.16	1.62	0.24	0.01	0.1	0.3	0.01	0.2	0.2	0.0	0.1
FWF 36	60	12	0.05	0.76	0.23	0.04	0.001	0.1	0.3	0.01	0.2	0.1	0.1	0.0
FWF 37	31	36	0.07	3.35	0.93	0.22	0.01	0.6	1.5	0.04	0.5	0.9	0.5	0.4
FWF 38	45	27	0.04	1.25	0.43	0.09	0.03	0.1	0.4	0.02	0.2	0.2	0.1	0.0
FWF 39	13	70	0.05	0.40	0.10	0.06	<LOD	0.1	0.4	0.02	0.2	0.2	0.1	0.1
FWF 40	32	26	0.22	18.10	0.66	0.57	0.1	0.4	7.1	0.03	0.4	2.1	0.6	2.4
FWF 41	34	15	0.13	19.08	0.60	0.54	0.0	0.3	2.6	0.01	0.2	1.2	0.2	0.7
FWF 42	41	36	0.23	10.83	2.69	1.03	<LOD	0.6	1.6	0.06	0.8	1.2	0.4	0.5
FWF 43	33	31	0.07	0.64	0.13	0.06	NA	NA	NA	NA	NA	0.1	0.0	0.1
FWF 45	62	8	0.10	3.45	0.46	0.59	<LOD	0.1	0.1	0.01	0.1	0.0	0.0	0.0

Table A4a. Mineral components (measured with ICP,AAS and XRF) in PM_{10}(sample F44<LOQ).

Filter set	Al	As	Si	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
	% PM_{10}										
FWF 1	0.02	0.001	1.7	0.020	0.009	0	0.005	<LOD	0.060	0.028	0.094
FWF 2	0.04	0.002	1.8	0.022	0.011	0	0.002	<LOD	0.060	0.032	0.082
FWF 3	0.07	0.001	0.2	0.013	0.005	0	0.002	<LOD	0.102	0.028	0.205
FWF 4	0.04	0.001	0.1	0.020	0.005	0	0.003	<LOD	0.072	0.029	0.075
FWF 5	0.02	0.001	0.5	0.036	0.008	0	0.001	<LOD	0.038	0.026	0.037
FWF 6	0.06	0.001	0.4	0.011	<LOD	0	0.003	<LOD	0.045	0.009	0.024
FWF 7	0.05	0.003	0.2	0.009	<LOD	0.05	0.001	<LOD	<LOD	0.018	0.108
FWF 8	0.05	0.000	0.1	NA	NA	NA	NA	NA	NA	NA	NA
FWF 9	0.05	0.000	0.2	0.010	<LOD	0.17	0.001	<LOD	0.125	0.021	0.415
FWF 11	0.03	0.000	0.2	NA	NA	NA	NA	NA	NA	NA	NA
FWF 12	0.03	0.000	0.1	0.011	<LOD	0	<LOD	<LOD	0.104	0.018	0.139
FWF 13	0.03	0.000	0.1	0.010	<LOD	0.01	<LOD	<LOD	<LOD	0.016	0.037
FWF 14	0.03	0.002	0.1	NA	NA	NA	NA	NA	NA	NA	NA
FWF 15	0.02	0.000	0.0	0.009	<LOD	0	<LOD	<LOD	<LOD	0.006	0.019
FWF 16	0.03	0.001	0.1	NA	NA	NA	NA	NA	NA	NA	NA
FWF 17	0.02	0.000	0.1	NA	NA	NA	NA	NA	NA	NA	NA
FWF 18	0.01	0.000	0.1	0.005	<LOD	0	0.001	<LOD	0.074	0.005	0.026
FWF 19	0.05	0.001	0.2	NA	NA	NA	NA	NA	NA	NA	NA
FWF 20	0.04	0.000	0.2	0.009	<LOD	0	0.001	<LOD	<LOD	0.007	0.028
FWF 21	0.01	0.000	0.1	0.013	0.001	0.10	0.001	<LOD	<LOD	0.016	0.024
FWF 22	0.04	0.001	0.1	NA	NA	NA	NA	NA	NA	NA	NA
FWF 23	0.05	0.001	0.1	0.025	0.002	1.45	0.003	<LOD	0.158	<LOD	0.088
FWF 24	0.09	0.000	0.2	<LOD	<LOD	0.05	<LOD	<LOD	0.299	<LOD	0.136
FWF 25	0.01	0.000	0.1	0.007	0.001	0.01	0.003	<LOD	0.058	<LOD	0.040
FWF 26	0.03	0.000	0.1	0.009	0.001	0.07	0.003	<LOD	0.103	<LOD	0.058
FWF 27	0.01	0.000	0.0	0.007	<LOD	0.00	0.005	<LOD	0.039	0.004	0.046
FWF 28	0.02	0.001	0.1	0.007	0.001	0.07	0.005	<LOD	0.073	0.008	0.048
FWF 29	0.04	0.000	0.1	0.016	0.004	0.20	0.006	<LOD	0.098	<LOD	0.050
FWF 30	0.04	0.000	0.1	0.025	<LOD	0.26	0.008	<LOD	0.146	<LOD	0.061
FWF 31	0.01	0.000	0.0	0.005	0.001	0.05	0.001	<LOD	0.036	0.002	0.018
FWF 32	0.02	0.000	0.0	0.019	0.002	0.31	0.001	<LOD	0.053	0.004	0.034
FWF 33	0.02	0.001	0.0	0.015	0.002	0.16	0.002	<LOD	<LOD	0.012	0.071
FWF 34	0.02	0.000	0.1	0.007	<LOD	0.23	0.002	<LOD	0.053	<LOD	0.042
FWF 35	0.02	0.000	0.0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FWF 36	0.01	0.000	0.1	0.005	<LOD	0	0.001	<LOD	0.037	<LOD	0.017
FWF 37	0.08	0.005	0.3	0.025	0.003	0.14	0.010	<LOD	0.181	0.013	0.168
FWF 38	0.02	0.000	0.1	0.008	<LOD	0	0.003	<LOD	<LOD	<LOD	0.074
FWF 39	0.03	0.001	0.1	NA	NA	NA	NA	NA	NA	NA	NA
FWF 40	0.09	0.001	0.1	0.024	0.003	0	0.001	<LOD	0.232	0.031	0.142
FWF 41	0.04	0.000	0.1	0.009	<LOD	0	<LOD	<LOD	0.119	<LOD	0.058
FWF 42	0.04	0.001	0.1	0.017	0.002	0	0.003	<LOD	0.141	0.011	<LOD
FWF 43	0.06	0.004	0.1	0.012	<LOD	0.01	0.002	<LOD	0.201	0.014	<LOD
FWF 45	0.01	0.000	0.0	0.008	<LOD	0	0.001	<LOD	<LOD	0.004	<LOD

Table A4b. Mineral components (measured with ICP,AAS and XRF) in PM_{10}-continuation, (sample F44<LOQ).

Filter set	K	Li	Mg	Mn	Na	Ni	P	Pb	S	Sr	Ti	Zn
	% PM_{10}											
FWF 1	0	0.003	0	0.064	0	0.010	0.042	0.040	3.330	0.002	0.002	0.765
FWF 2	0	0.013	0	0.054	0	0.008	0.029	0.021	4.139	0.002	<LOD	0.762
FWF 3	0	<LOD	0	0.035	0	0.023	0.025	0.028	2.387	<LOD	0.005	0.468
FWF 4	0	0.002	0	0.043	0	0.014	0.021	0.030	3.090	0.002	<LOD	0.469
FWF 5	0	0.002	0	0.055	0	0.006	0.022	0.021	3.565	0.001	<LOD	0.367
FWF 6	0.01	<LOD	0	<LOD	0	0.007	0.022	0.024	0.558	<LOD	<LOD	0.067
FWF 7	0	<LOD	0.017	0.004	0	0.027	0.036	0.005	0.362	<LOD	0.005	0.079
FWF 8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 9	0	<LOD	0.019	0.003	0.22	0.021	0.026	0.015	0.271	<LOD	<LOD	<LOD
FWF 11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 12	0	0.002	0	<LOD	<LOD	0.014	0.021	0.002	0.308	<LOD	<LOD	<LOD
FWF 13	0	<LOD	0.001	<LOD	0.09	0.008	0.019	0.004	0.265	<LOD	<LOD	<LOD
FWF 14	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 15	0.53	<LOD	0	0.002	<LOD	0.004	0.034	0.002	0.314	<LOD	<LOD	<LOD
FWF 16	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 17	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 18	0	<LOD	0.001	0.002	<LOD	0.005	0.029	0.006	0.687	<LOD	0.002	0.012
FWF 19	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 20	0	<LOD	0	0.001	<LOD	0.006	0.055	0.002	0.310	<LOD	<LOD	0.074
FWF 21	0	<LOD	0.008	0.002	<LOD	0.005	0.020	0.004	0.406	0.003	<LOD	0.003
FWF 22	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 23	1.45	<LOD	0.032	<LOD	<LOD	0.016	0.063	0.032	0.610	0.011	0.016	0.097
FWF 24	0.36	<LOD	0.015	<LOD	<LOD	0.031	0.065	0.022	0.648	<LOD	<LOD	<LOD
FWF 25	0.16	<LOD	0	0.008	<LOD	0.007	0.025	0.007	0.440	0.001	<LOD	0.014
FWF 26	0.73	0.001	0.007	0.008	<LOD	0.007	0.034	0.008	0.510	<LOD	<LOD	0.025
FWF 27	2.95	<LOD	0.004	0.008	<LOD	0.004	0.021	0.013	0.959	<LOD	<LOD	0.071
FWF 28	0.41	<LOD	0.01	0.022	<LOD	0.017	0.027	0.009	0.336	0.001	<LOD	0.071
FWF 29	0.32	0.008	0.005	0.018	<LOD	0.026	0.049	0.016	0.543	0.002	<LOD	0.167
FWF 30	0.71	<LOD	0.02	0.020	<LOD	0.010	0.052	0.008	0.370	<LOD	<LOD	0.127
FWF 31	0.86	<LOD	0.0037	0.002	<LOD	0.002	0.027	0.001	0.224	0.001	<LOD	0.003
FWF 32	0.56	<LOD	0.02	0.003	<LOD	0.005	0.022	0.003	0.561	0.001	0.001	<LOD
FWF 33	2.74	<LOD	0.01	0.005	<LOD	0.009	0.021	0.006	0.817	0.002	0.001	<LOD
FWF 34	0.30	<LOD	0.01	0.003	<LOD	0.006	0.018	0.004	0.157	0.002	0.002	0.014
FWF 35	0	<LOD	<LOD	0.001	0.05	<LOD	0.003	0.001	<LOD	<LOD	<LOD	<LOD
FWF 36	0.13	<LOD	0.0021	0.002	<LOD	0.002	0.010	<LOD	0.068	<LOD	0.000	0.017
FWF 37	0.45	<LOD	0.01	0.020	<LOD	0.018	0.029	0.006	0.356	0.004	0.010	0.215
FWF 38	0.16	<LOD	0	0.006	<LOD	0.004	0.009	0.001	0.082	<LOD	0.001	0.038
FWF 39	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 40	2.10	<LOD	0.02	0.012	0.30	0.047	0.036	0.013	1.388	<LOD	<LOD	<LOD
FWF 41	0	<LOD	0.0047	0.002	<LOD	0.014	0.020	0.006	0.472	<LOD	<LOD	<LOD
FWF 42	0	<LOD	0	0.011	<LOD	0.015	0.016	0.003	0.217	<LOD	<LOD	0.038
FWF 43	0.92	<LOD	0.01	0.012	<LOD	0.011	0.028	0.049	0.338	<LOD	<LOD	0.082
FWF 45	0.18	<LOD	0.0048	0.002	<LOD	0.003	0.008	0.021	0.197	<LOD	<LOD	0.020

Table A5a. Mineral components (measured with ICP,AAS and XRF) in $PM_{2.5}$, (sample F44<LOQ).

Filter set	Al	As	Si	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
	%$PM_{2.5}$										
FWF 1	0.016	0.002	1.480	0.015	0.007	0	0.005	<LOD	0.054	0.037	0.044
FWF 2	0.013	0.000	0.051	0.018	0.008	0.14	0.002	<LOD	0.036	0.028	0.125
FWF 3	0.025	0.000	3.605	NA	NA	NA	NA	NA	NA	NA	NA
FWF 4	0.021	0.001	0.095	0.022	0.004	0	0.002	<LOD	<LOD	0.018	0.132
FWF 5	0.009	0.000	0.041	0.053	0.007	0.01	0.001	<LOD	<LOD	0.023	0.090
FWF 6	0.018	0.000	0.617	0.011	0.002	0.54	0.003	<LOD	<LOD	0.007	0.208
FWF 7	0.075	0.000	0.671	0.013	0.002	0.48	0.001	<LOD	<LOD	0.059	0.733
FWF 8	0.060	0.000	0.102	0.023	0.004	0.28	0.003	<LOD	<LOD	0.102	0.205
FWF 9	0.061	0.001	0.053	0.009	<LOD	0.08	0.001	<LOD	<LOD	0.017	0.195
FWF 11	0.021	0.000	0.206	NA	NA	NA	NA	NA	NA	NA	NA
FWF 12	0.032	0.000	0.087	0.039	0.002	0.34	<LOD	<LOD	<LOD	0.021	0.160
FWF 13	0.019	0.000	0.039	0.009	<LOD	0.02	<LOD	<LOD	<LOD	0.012	0.068
FWF 14	0.057	0.000	0.057	0.015	0.002	0	<LOD	<LOD	<LOD	0.027	0.138
FWF 15	0.026	0.000	0.069	0.009	<LOD	0	<LOD	<LOD	<LOD	0.005	0.030
FWF 16	0.019	0.001	0.104	NA	NA	NA	NA	NA	NA	NA	NA
FWF 17	0.015	0.000	0.119	0.020	<LOD	0.04	0.001	<LOD	<LOD	0.016	0.104
FWF 18	0.021	0.000	0.108	NA	NA	NA	NA	NA	NA	NA	NA
FWF 19	0.033	0.000	0.122	NA	NA	NA	NA	NA	NA	NA	NA
FWF 20	0.020	0.001	0.084	NA	NA	NA	NA	NA	NA	NA	NA
FWF 21	0.014	0.001	0.091	0.015	<LOD	0.17	0.001	<LOD	<LOD	0.006	0.035
FWF 22	0.032	0.002	0.080	NA	NA	NA	NA	NA	NA	NA	NA
FWF 23	0.058	0.003	0.154	NA	NA	NA	NA	NA	NA	NA	NA
FWF 24	0.286	0.000	0.571	<LOD	<LOD	1.40	<LOD	<LOD	0.793	0.079	0.470
FWF 25	0.032	0.001	0.067	0.007	<LOD	0	0.003	<LOD	<LOD	<LOD	0.028
FWF 26	0.032	0.000	0.060	0.013	0.001	0.06	0.003	<LOD	0.138	0.005	0.045
FWF 27	0.009	0.000	0.030	0.007	0.001	0.06	0.005	<LOD	<LOD	0.006	0.023
FWF 28	0.031	0.000	0.087	0.022	<LOD	0.19	0.004	<LOD	0.112	0.041	0.087
FWF 29	0.034	0.008	0.092	0.015	<LOD	0	0.006	<LOD	0.153	<LOD	<LOD
FWF 30	0.041	0.001	0.099	0.018	<LOD	0.55	0.007	<LOD	0.153	0.022	0.085
FWF 31	0.015	0.000	0.026	0.013	<LOD	0	0.001	<LOD	0.042	0.004	0.027
FWF 32	0.036	0.001	0.043	0.010	<LOD	0.08	0.001	<LOD	0.117	0.006	0.030
FWF 33	0.020	0.000	0.034	0.009	0.001	0.04	0.001	<LOD	0.070	0.006	<LOD
FWF 34	0.033	0.003	0.145	NA	NA	NA	NA	NA	NA	NA	NA
FWF 35	0.030	0.000	0.038	0.012	<LOD	0	0.001	<LOD	0.076	0.017	0.039
FWF 36	0.015	0.002	0.099	0.012	<LOD	0	0.001	<LOD	0.043	0.007	0.044
FWF 37	0.099	0.003	0.369	NA	NA	NA	NA	NA	NA	NA	NA
FWF 38	0.028	0.000	0.134	0.022	0.001	0.10	0.004	<LOD	<LOD	0.004	0.037
FWF 39	0.033	0.000	0.186	0.010	<LOD	0.16	0.005	<LOD	0.110	0.062	0.114
FWF 40	0.073	0.001	0.135	0.024	<LOD	0	<LOD	<LOD	0.219	0.017	0.087
FWF 41	0.044	0.000	0.050	0.013	<LOD	0.15	<LOD	<LOD	0.120	0.008	0.063
FWF 42	0.083	0.000	0.309	0.027	<LOD	0	0.005	<LOD	0.415	<LOD	<LOD
FWF 43	0.071	0.000	0.084	0.028	<LOD	0.40	0.002	<LOD	<LOD	0.343	0.203
FWF 45	0.022	0.001	0.028	0.008	0.001	0	0.001	<LOD	0.075	0.015	0.074

Table A5b. Mineral components (measured with ICP,AAS and XRF) in $PM_{2.5}$-continuation, (sample F44<LOQ).

Filter set	K	Li	Mg	Mn	Na	Ni	P	Pb	S	Sr	Ti	Zn
	%$PM_{2.5}$											
FWF 1	0	0.003	0.01	0.049	0	0.007	0.016	0.039	3.184	0.001	0.002	0.687
FWF 2	0	0.010	0.12	0.038	0	0.007	0.019	0.016	3.247	0.001	0.007	0.586
FWF 3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 4	0	0.001	0.18	0.022	0	0.005	0.017	0.024	2.770	0.001	0.014	0.407
FWF 5	0	0.007	0.06	0.041	0	0.005	0.013	0.021	3.358	0.001	0.011	0.296
FWF 6	0.33	0.001	0.27	0.002	0	0.003	0.033	0.002	0.552	0.001	0.033	0.024
FWF 7	0	<LOD	0.47	0.006	0	0.014	0.044	<LOD	0.326	<LOD	0.096	<LOD
FWF 8	0	0.004	0.19	0.007	0	0.008	0.028	<LOD	0.327	0.005	0.011	<LOD
FWF 9	0.05	<LOD	0.16	0.007	0	<LOD	0.029	0.012	0.229	<LOD	0.020	<LOD
FWF 11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 12	0.34	<LOD	0.14	0.003	0	0.016	0.026	0.003	0.412	0.004	0.021	<LOD
FWF 13	0.10	<LOD	0.04	0.003	0	0.005	0.014	0.002	0.273	<LOD	0.004	<LOD
FWF 14	0	<LOD	0.08	<LOD	0	0.016	0.063	<LOD	0.508	0.003	0.006	<LOD
FWF 15	0.30	<LOD	0.02	0.001	0	0.003	0.045	<LOD	0.297	<LOD	0.001	<LOD
FWF 16	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 17	0	<LOD	0.11	0.003	0	0.004	0.034	<LOD	0.908	<LOD	0.009	<LOD
FWF 18	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 19	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 20	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 21	0.24	0.001	0.03	0.002	<LOD	0.004	0.022	0.003	0.386	0.001	0.006	<LOD
FWF 22	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 23	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 24	4.20	<LOD	0.42	<LOD	<LOD	0.068	0.116	0.067	1.358	<LOD	0.012	<LOD
FWF 25	0	0.002	0.01	0.002	<LOD	0.004	0.025	0.006	0.488	<LOD	<LOD	<LOD
FWF 26	0.94	<LOD	0.04	0.003	<LOD	0.004	0.043	0.007	0.527	<LOD	0.002	<LOD
FWF 27	1.49	<LOD	0.01	0.003	<LOD	0.003	0.022	0.013	0.845	<LOD	0.001	0.037
FWF 28	0.12	<LOD	0.02	0.011	0.201	0.008	0.035	<LOD	0.266	<LOD	0.002	<LOD
FWF 29	0.23	<LOD	0.03	0.007	0.303	<LOD	0.082	0.006	0.338	<LOD	<LOD	<LOD
FWF 30	0.53	<LOD	0.06	0.009	<LOD	0.012	0.046	<LOD	0.387	0.005	0.003	<LOD
FWF 31	0.47	<LOD	0.00	0.002	<LOD	0.003	0.023	0.002	0.329	<LOD	0.000	<LOD
FWF 32	0.52	<LOD	0.02	0.004	<LOD	0.008	0.026	0.004	0.633	<LOD	<LOD	<LOD
FWF 33	2.31	0.001	0.01	<LOD	0	0.004	0.021	0.004	0.846	0.002	<LOD	<LOD
FWF 34	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 35	0.38	<LOD	0.01	0.002	0	0.004	0.013	<LOD	0.133	<LOD	0.002	<LOD
FWF 36	0.25	<LOD	0.02	<LOD	0	0.004	0.011	<LOD	0.103	<LOD	0.001	<LOD
FWF 37	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
FWF 38	0.22	0.001	0.02	0.004	0	<LOD	0.011	0.006	0.090	0.001	0.002	<LOD
FWF 39	0.48	<LOD	0.09	0.004	<LOD	0.007	0.019	<LOD	0.175	<LOD	0.010	<LOD
FWF 40	0	<LOD	0.04	<LOD	0	0.019	0.026	0.009	1.106	<LOD	<LOD	<LOD
FWF 41	0.08	<LOD	0.06	0.008	0.16	0.007	0.019	0.007	0.393	<LOD	0.003	<LOD
FWF 42	0.63	<LOD	0.10	<LOD	0	0.021	0.035	<LOD	0.439	<LOD	<LOD	<LOD
FWF 43	1.20	<LOD	0.09	0.008	0	0.027	0.032	0.052	0.352	<LOD	0.005	<LOD
FWF 45	0.36	<LOD	0.02	<LOD	0	0.013	0.013	0.023	0.227	<LOD	0.001	<LOD

NA…not analysed; NF…not found; <LOD…under limit of detection; <LOQ…under limit of quantification (in case of sample F44, due to extremely low mass).

Curriculum Vitae

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Russian – Basic

Publications in refereed journals:

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Awards:

First Place for the oral presentation at the
International Forum-Competition of Young Researchers "**Topical Issues of Subsoil usage**",
Ministry of education and Science of The Russian Federation, St. Petersburg Mining University, **04.2011**.

Stipendium for sporting achievements, University of Wrocław, Poland, **2006-2007**