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Methodological issues in GC-MS determination of particle-bound PAHs in time resolved wood burning emission samples

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Abstract

PAHs are products of incomplete combustion. One of their major sources are residential and commercial heating. When looking at BaP in PM10 the target value of 1ng/m³ was exceeded in Austria mainly in small cities. In Austria residential wood burning is with 57% the major source of BaP. To reduce emissions a detailed understanding of the formation of PAHs during the combustion process is necessary. In our study the emissions from small scale heating devices typical for the Austrian Market measured with a 5 min time resolution are looked at to investigate the influence of fuel, stove and combustion phase on the particulate PAH emission. Additionally, some methodological issues related to the measurement of particulate PAHs on quartz fibre filters using an ultrasonic extraction and GC-MS analysis are investigated before the combustion samples are analysed.

The investigation of the influence of the solvent on the extractability shows that the extractability of PAHs with different solvents depends on the matrix, whereby a matrix rich of carbon worsens the extraction, especially when using cyclohexane. Moreover, the suitability of teflon syringe filters with a hydrophilic PTFE membrane to replace centrifugation for the separation of undissolved material for the solution is checked. A syringe filter is usable, but a single compound, BghiP, shows a contradicting result. Furthermore, the question if the storage of the filters over longer time is possible, can be answered with yes, based on the reanalysis of filters after several years of storage in a deep freezer.

For the time resolved measurements two different stoves, a 6.5 kW, simple manually operated log wood device and a 10 kW manually loaded stove with an automatic primary and secondary air supply regulation, are used. Spruce logs, beech logs and commercial softwood briquettes are taken as fuels. The measurements last for two or three full-load cycles including the start-up phase. Particulate matter (PM10) is collected on quartz fibre filters with a time-resolution of 5 min. Additionally gas emission monitoring (O_2, CO_2, CO, NO_x, VOCs) is conducted continuously. Organic and elemental carbon values are available from earlier measurements.

The combustion process can be divided into different phases based upon temperature and when this was not possible on the CO_2-concentration. The combustion is divided into six phases: SUP (Start-up phase), SOP1 (Steady-operation phase 1), BOP1 (Burn-out phase 1), RLP (Reload-phase), SOP2 (Steady-operation phase 2) and BOP2 (Burn-out phase 2).

The most dominant feature for all combustions is the peak after reload of the fuel, which has its maximum either in RLP itself or in the beginning of SOP2 independent of fuel and stove. The peak is higher than in SUP, where also elevated emissions are seen. During stable combustion conditions like in SOP1 the lowest emissions can be found. After the reload in SOP2 and finally in BOP2 a difference between log wood and softwood briquettes as fuels is notable as for log wood the concentration generally constantly decreases but for softwood briquettes a small peak, consisting mainly of light PAHs, in the end is visible. In general, the change of emission during the combustion is mainly influenced by the combustion conditions and not by fuel or stove type. However, the stove type and the fuel have effects on the total emissions. Looking at beech as fuel, stove 2 with an automatic primary and secondary air supply regulation has lower emissions than stove 1. Also the fuel has an impact. When softwood briquettes are used the emissions are the lowest. The trend over time for PM10 and OC is similar, but differs from VOC and EC. Although only particle-bound PAHs are analysed 3-and 4-ring PAHs are most abundant.

Kurzfassung

PAKs entstehen bei der unvollständigen Verbrennung. Eine ihrer Hauptquellen ist die Beheizung von Wohnhäusern und Industrieanlagen. Wenn nur BaP im Feinstaub (PM10) betrachtet wir, wird der Zielwert von 1ng/m³ in Österreich hauptsächlich in Kleinstädten überschritten. In Österreich ist die Heizung von Wohnraum mit Holz mit 57% die Hauptquelle von BaP. Um die Emissionen zu reduzieren ist ein detailliertes Verständnis der Entstehung von PAKs während der Verbrennung notwendig. In unserer Studie werden die Emissionen von kleineren Heizgeräten, die typisch für den österreichischen Markt sind, mit einer Zeitauflösung von 5 min betrachtet um den Einfluss von Brennstoff, Ofen und Verbrennungsphase auf die Emission von partikulären PAKs zu untersuchen. Zusätzlich werden, vor der Messung der Verbrennungsproben, methodologische Fragestellungen bei der Messung von partikulären PAKs auf Quarzfaserfiltern mittels Ultraschallextraktion und GC-MS Analyse untersucht.

Die Untersuchung des Einflusses des Lösungsmittels auf die Extraktion zeigte, dass die Extrahierbarkeit von PAHS mit unterschiedlichen Lösungsmittels von der Matrix abhängt, wobei eine kohlenstoffreiche Matrix die Extraktion verschlechtert insbesondere wenn Cyclohexan verwendet wird. Außerdem wird die Eignung von Spritzenvorsatzfiltern mit einer hydrophilen PTFE Membran anstelle von Zentrifugieren für die Abtrennung von ungelösten Material von der Lösung kontrolliert. Der Spritzenvorsatzfilter ist einsetzbar nur die Ergebnisse für BghiP sind widersprüchlich. Zusätzlich kann die Frage, ob die Lagerung von Filtern über längere Zeit möglich ist, mit ja beantwortet werden, da die Analyse keine Hinweise für eine Zersetzung der Verbindungen liefert.

Für die zeitaufgelöste Messung werden zwei unterschiedliche Öfen, ein einfaches, manuell bedienbares 6.5 kW Gerät und ein manuell beladbarer Ofen mit automatischer Primär- und Sekundärluftzufuhr, verwendet. Fichtenholzscheite, Buchenholzscheite und kommerzielle Weichholzbrikettes werden als Brennstoff angewandt. Die Messungen umfassen zwei oder drei volle Ladungszyklen inklusive Startphase. Der Feinstaub wird auf Quarzfaserfiltern mit einer Zeitauflösung von 5 min gesammelt. Zusätzlich werden die Gasemissionen (O_2, CO_2, CO, NO_x, VOCs) kontinuierlich gemessen. Konzentrationswerte für Organischen und elementaren Kohlenstoff sind von früheren Messungen vorhanden.

Der Verbrennungsprozess kann basierend auf der Temperatur und wenn dies nicht möglich ist aufgrund der CO_2-Konzentration in verschiedene Phasen eingeteilt werden. Die Verbrennung wird in sechs Phasen eingeteilt: SUP (Startphase), SOP1 (konstante Verbrennungsphase 1), BOP1 (Ausbrennphase 1), RLP (Nachladephase), SOP2 (konstante Verbrennungsphase 2) und BOP2 (Ausbrennphase 2).

Das auffallendste Merkmal des Zeitverlaufs aller Verbrennungen ist die Zunahme der Emissionswerte nach dem Nachlegen des Brennstoffs, die ihr Maximum entweder in RLP oder am Beginn von SOP2 hat unabhängig von Ofen und Brennstoff. Die Spitze ist höher als in SUP, wo auch erhöhte Emissionen zu sehen sind. Während stabiler

Verbrennungsbedingungen wie in SOP1 werden die niedrigsten Emissionen gefunden. Nach dem Nachlegen in SOP2 und BOP2 ist ein Unterschied zwischen Holzscheiten und Weichholzbriketts sichtbar. Bei Holzscheiten sinken die Emissionen kontinuierlich, während bei den Weichholzbriketts die Konzentration am Ende nochmals ansteigt und eine Konzentrationsspitze zu sehen ist, die hauptsächlich aus leichteren PAHs besteht. Im Allgemeinen ist die Änderung der Emission während der Verbrennung hauptsächlich auf die Verbrennungsbedingungen und weniger auf Brennstoff oder Ofentyp zurückzuführen. Allerdings haben Ofenart und Brennstoff auch eine Auswirkung auf die Gesamtemission. Wenn Buchenholzscheite als Brennstoff verwendet werden hat Ofen 2 mit der automatischen Primär-und Sekundärluftzufuhr niedrigere Emissionen als Ofen 2. Auch der Brennstoff hat einen Einfluss. Wenn Weichholzbriketts verwendet werden sind die Emissionen am niedrigsten. Die Zeitverläufe von PM10 und OC sind ähnlich, aber unterscheiden sich von VOC und EC. Obwohl nur partikuläre PAHs analysiert werden, sind 3-und 4-Ring PAHs am häufigsten.

Contents

List of abbreviations

Ace	Acenaphthene
AcH	Acetone:Cyclohexane (1:1)
AcN	Acetonitrile
Acy	Acenaphthylene
ALS	Average of the lowest standard
Ant	Anthracene
b	intercept
BaA	Benz[a]anthracene
BaP	Benz[a]pyrene
BbF	Benzo[b]fluoranthene
BghiP	Benzo[g,h,i]perylene
BkF	Benzo[k]fluoranthene
BOP	Burn-out phase
c	Concentration
c_i	Concentration internal standard
cHex	Cyclohexane
Chr	Chrysene
d_{12}-Per	Deuterated-Perylene (d_{12})
DahA	Dibenz[a,h]anthracene
DcH1	Dichloromethane:Cyclohexane (3:2)
DcH2	Dichloromehtane:Cyclohexane (3:7)
DCM	Dichloromethane
EC	Elemental carbon
Fla	Fluoranthene
Flu	Fluorene
H-PTFE	Hydrophilized polytetrafluoroethylene
IcdP	Indeno[1,2,3-cd]pyrene
IST-P	Internal standard for spiking of samples
IST-S	Internal standard for spiking of standards
k	Slope
LOD	Limit of detection
LOQ	Limit of quantification
MC	Mean concentration
MT	Mean temperature
Naph	Naphthalene
OC	Organic carbon
PAH	Polycyclic aromatic hydrocarbons
Phe	Phenanthrene
PM10	Particulate matter ≤ 10µm
PP	Polypropylene
PUF	Polyurethane foam
Py	Pyrene
RLP	Re-loading phase
QFF	Quartz fibre filter
ROZ	Intermediate dilution for standard preparation
RST	Recovery standard
s	Standard deviation

SOP	Steady operation phase
SUP	Start-up phase
TocH	Toluene: Cyclohexane (3:3)
VOC	Volatile organic compounds

1. Introduction and Aims

1.1. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) are organic compounds that consist of two or more condensed aromatic rings. In their parent form hydrogen and carbon atoms are the only elements occurring in PAHs, but the compounds can also be substituted with e.g., nitrogen (nitro-PAHs), oxygen (oxo-PAHs) or sulphur (thio-PAHs) depending on their source and formation pathway [1]. PAHs are emitted during incomplete combustion or pyrolysis of carbonaceous matter [2]. In the ambient air PAHs can be found bound to particulate matter but also in the gas phase [3]. PAHs are also proven to be precursors of soot, which is also called elemental carbon (EC) [4] [5] . They are relevant for the environmental issues due to their toxicity and chemical stability once they were introduced into an ecosystem.

1.1.1. Sources of PAHs

PAHs are emitted by incomplete combustion. Major sources in indoor and outdoor air are residential and commercial heating. Main particulate emissions are related to combustion of solid fuels, e.g., coal or biomass. Other sources of PAHs are: cooking, tobacco smoke, motor vehicle exhaust particularly from diesel engines, industrial emissions (especially coking plants, gas works and refineries). The main natural source of PAHs are wild forest fires and volcanic activity [6].

PAHs are ubiquitous in the environment and can be found in the air, water and soil. Into the air PAHs are emitted directly. They exist either as gaseous compounds or constitute to particulate matter. The abundance of volatile PAHs is generally higher, which makes the condensation of PAHs from gas phase on particle surfaces an important issue [6]. Mainly through dry and wet deposition after local and long-range transport PAHs reach the surface water and soil [7]. PAHs in the gas phase have life times of less than a day, but particle-bound PAHs are stable for weeks and can undergo long-range atmospheric transport [6]. The majority of PAHs in soil are bound to soil particles [8]. Deposition of PAHs on water surfaces is the main way how they get into the water. Storm water, which is water flowing over land without being absorbed from rain and snowmelt event [9], and sanitary sewer effluents like roadway runoffs are further sources [8]. PAHs are only to some extend soluble in water, whereby the solubility of PAHs in water decreases with increasing molecular weight. Typically, PAHs are adsorbed to particles and sink to the ground and become part of the sediments [10]. As PAHs are hydrophobic they are accumulated in the soil, in the sediments of water bodies, in plants and over the food chain in animals [3]. Humans are exposed to PAHs through barbecued, grilled or smoke-cured meat or other roasted, baked or fried foods, but the main health related issue is the inhalation of PAHs from the ambient or indoor air [6].

1.1.2. Regulations and current situation of PAHs in the ambient air in Europe and Austria

Benzo(a)pyrene (BaP) is used as a marker substance to track and describe the PAHs in relation to the air quality. The target value for BaP in PM10 as marker substance for PAHs and their carcinogenicity in the EU is 1 ng/m³ in the annual mean. Since 2013 the target value is set as limit [11], [12]. However, the current limit for BaP is still associated with a quite high risk of $1x10^{-4}$, which means that the probability for being affected by cancer due to PAH exposure is one person in 10000 [13].

In Europe the limit value was in 2013 mainly exceeded in urban and suburban areas. Mostly countries in central and Eastern Europe exceed the limit. Among others Austria, Czech Republic, Slovenia and Poland cannot meet the limit. 25% of the population in urban areas in the EU-28 countries had to cope with BaP concentrations above the limit. Emissions from residential coal and biomass combustion have risen in the EU by 16% from 2004 to 2013 and now make it a major source for BaP (73% of total BaP emissions). Waste-burning, coke and steel production and road traffic contribute to BaP levels too. [14]

In Austria in addition to urban and suburban areas especially small cities have troubles to stay below the European limit. The limit of 1 ng/m³ annual mean BaP was exceeded at three stations in 2014. These stations were Ebenthal Zell in Carinthia (2.93 ng/m³), Wolfsberg in Carinthia) (1.69 ng/m³) and Weiz in Styria (1.58 ng/m³). Furthermore, Klagenfurt Völkermarkterstraße (Carinthia), Villach (Carinthia), Völkermarkt (Carinthia), Graz Süd (Styria) and Übelbach (Styria) had an annual mean over 1.0 ng/m³. The south of Austria is exposed to the highest BaP levels partly due to unfavourable metrological conditions. With the contribution of 57%, residential wood burning is the main source of BaP emissions in Austria. All limit exceedances occurred in small cities. The burning of biomass can be therefore seen as the major contributor to PAHs emission in Europe and also in Austria. [2]

1.1.3. Formation of PAHs and soot

At first small, instable organic molecules are formed by pyrolysis. In further steps these molecules react by for example condensations, ring closings and dehydrations to bigger, aromatic and therefore more stable structures. Which PAH is built depends on many factors. [15]

A crucial step is the formation of the first benzene ring, which can occur in different pathways. An example is the Acetylene way [16], where acetylene reacts with a vinyl radical (C_2H_3) and then an additional acetylene molecule is needed to close the ring [17]. The HACA (H-abstraction-C_2H_2-addition)-mechanism which includes H-elimination and C_2H_2-addition is a way to form bigger PAHs [18].

Heavy PAHs (≥5 rings) are expected to be molecular precursors of soot particles. In Figure 1 the formation of soot is shown in a simplified way. The formation process includes different steps [5]. Small molecules like benzene grow to larger PAH radicals by adding C2, C3 or other small molecules in reactions between aromatic species like

PAH-PAH radical recombination and addition. In a next step molecules are converted to particles for example heavy PAH molecules form nascent soot particles. After the formation of nascent soot, the size of the particles is increased by adding gas phase compounds like acetylene, PAH (including PAH radicals). Radical sites on the soot particles seem to be responsible for the addition in case of stable species. The sticking together of particles after collisions by Van-der Waals forces add to the size increase. Under pyrolytic conditions the formed particles undergo functional group elimination, cyclization, ring condensation and ring fusion. Further, a conversion from amorphous soot to more graphitic carbon material can occur. [17]

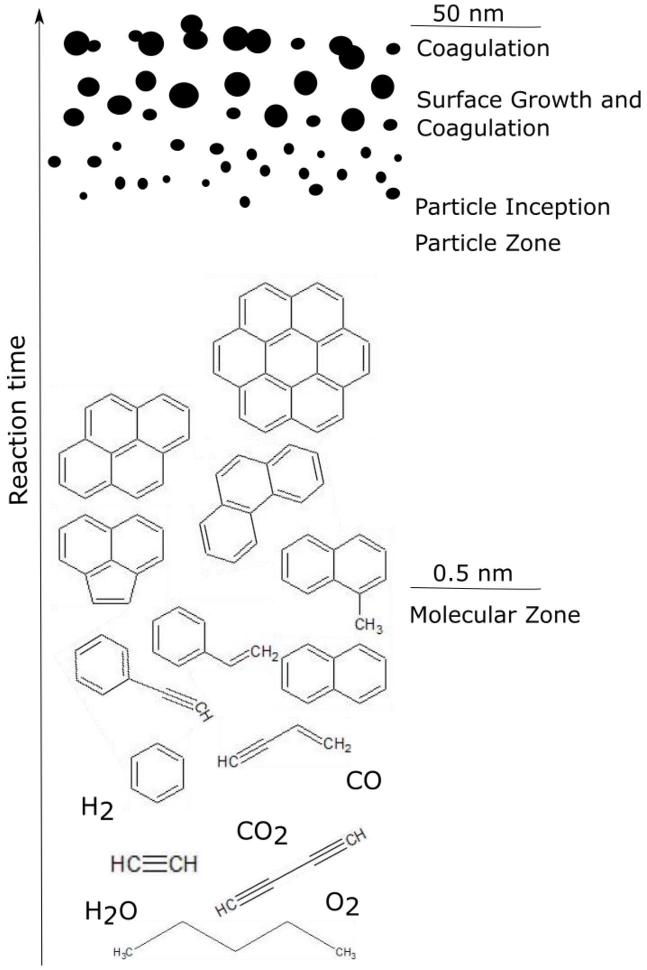

Figure 1: Scheme for the formation of soot [19]

1.1.4. EPA priority PAHs & gas-particle partitioning

Over 100 different chemicals belong to the group of PAHs [20]. The Environmental Protection Agency (USA) listed 16 priority PAHs particularly important for monitoring. Our analyses were focused on these compounds. In Figure 2 the structures of the EPA priority PAHs are listed [21]. The PAHs occurring mainly in the gas phase are shaded blue, whereas the compounds which occur mainly particle-bound are shaded in brown.

PAH with five rings and more are mainly bound to particles whereas PAHs with 2-3 rings predominately stay in gas phase. High temperatures shift the PAH partitioning into the gas phase. The gas/particle partitioning is changed by particle properties like size distribution, organic carbon content, particulate matter concentration, ambient air temperature and concentrations. [22], [23]

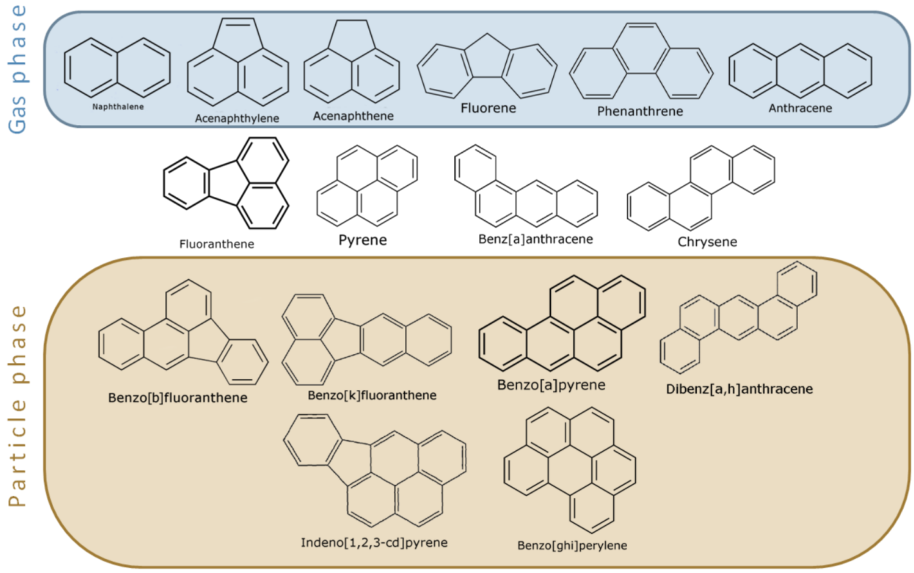

Figure 2: Structures of 16 priority PAHs (EPA). PAH occurring mainly in gas phase are marked in blue and compounds occurring mainly particle-bound are marked in brown

The EPA-priority PAHs are listed in Table 1. Their molecular weight and the number of rings, as well as vapour pressure and boiling point, which generally decrease and increase respectively with molecular weight, are noted.

Table 1: EPA-priority PAHs with their molecular weight, number of rings and their physical parameters

PAH	Molecular weight [g/mol]	Rings	Vapour Pressure at 25°C [Pa] [24]	Boiling Point [°C] [24]
Naphthalene (Naph)	128.17	2	-	-
Acenaphthylene (Acy)	152.19	3	9×10^{-1}	280
Acenaphthene (Ace)	154.21	3	3×10^{-1}	279
Fluorine (Flu)	166.22	3	9×10^{-2}	295
Phenanthrene (Phe)	178.23	3	2×10^{-2}	340
Anthracene (Ant)	178.23	3	1×10^{-3}	342
Fluoranthene (Fla)	202.25	4	1.2×10^{-3}	375
Pyrene (Py)	202.25	4	6.0×10^{-4}	393
Benz[a]anthracene (BaA)	228.29	4	2.8×10^{-5}	400
Chrysene (Chr)	228.29	4	5.7×10^{-7}	448
Benzo[b]fluoranthene (BbF)	252.31	5	6.7×10^{-5}	481
Benzo[k]fluoranthene (BkF)	252.31	5	5.2×10^{-8}	480
Benz[a]pyrene (BaP)	252.31	5	7.0×10^{-7}	496
Indeno[1,2,3-cd] pyrene (IcdP)	276.33	6	1.3×10^{-8}	536
Benzo[ghi]perylene (BghiP)	276.33	6	-	-
Dibenz[AcH]Anthracene (DahA)	278.35	5	3.7×10^{-8}	524

1.2. Aims

This work focuses on the measurement of particle-bound PAHs collected on quartz fiber filters (QFF) during small scale biomass combustion experiments with modern household devices. The aims can be divided into methodological issues and experimental, i.e. combustion related, issues.

In the methodological part following question are tried to be answered:

- How does the solvent choice influence the ultrasonic extraction of PAHs from quartz fibre filters?
- Does the carbon loading (organic and elemental carbon) influence the extraction procedure?
- Are syringe filters suitable for separation of undissolved material from the extract?
- Do the concentrations of PAHs change during storage of QFF over several years?

The questions are based upon the problems resulting from the very wide range of extraction methods and solvents which are allowed by the EN 15549 [25]. The inter-comparison study [26] shows that a wide choice of solvents, extraction and analytical methods cause significant variations in BaP measurement results among different laboratories. An uncertainty up to 30% is observed considering all 17 labs across Europe.

This work investigates the use of different solvents or solvent mixtures for ultrasonic extraction in order to describe the solvent influence. The best method resulting from this experiment would be used to measure the content of PAHs in emission samples from residential biomass combustion. The particle-bound PAHs would be considered in this case, as the samples were taken from diluted flue gas. Samples represent 5 minutes' intervals from seven combustion procedures and therefore allow to describe the PAH emissions for different combustion phases. In this part following questions will be answered:

- Which phases can be described in the combustion process?
- What are the PAHs emission factors?
- How do factors like biomass type, combustion phase and stove type influence the PAH emissions?
- How are the observed concentrations of PAHs related to other compounds?

2. Experimental

2.1. Analysis of PAHs

In this study PAHs are analysed using a GC-MS method. The quantification is based upon a combination of internal and external calibration.

2.1.1. Standard preparation

Deuterated benzo[a]pyrene (98 atom% D, Sigma Aldrich) and deuterated perylene (98 atom% D, Sigma Aldrich) are used as internal standards: surrogate and recovery. Both substances are weighed and diluted with cyclohexane in order to prepare solution A and solution B. In Table 2 the preparation of both solutions is summarised.

Table 2: Preparation of solution A and B

	Substance	Purity [%]	Weight [mg]	Volume [mL]	c_1 [µg/mL]	$c_{1corr.}$ [µg/mL]
Solution A	d_{12} -BaP	98	0.55	10	55	53.9
Solution B	d_{12} -Perylene	98	1.02	10	102	100.0

Further, a mixture of PAHs (PAK-Mix 18,100 µg/ml in cyclohexane, Neochema, Germany) containing 18 PAHs to identify and quantify the compounds is used. Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthene, acenaphthylene, phenanthrene, fluorene, anthracene, benz[a]anthracene, chrysene, pyrene, fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene and dibenz[a,h]anthracene are mixed in the standard solution, but only PAHs heavier than 1-methylnaphthalene (m/z=142.20) could be identified with the applied method. The purities of the compounds vary from 97- 99,8% (Table 44, Annex). Using the solutions A and B, as well as the mix-standard following solutions are prepared: recovery standard (RST), internal standard for spiking of samples (IST-P), internal standard for spiking of standards (IST-S) and an intermediate dilution for standard preparation (ROZ). Those are described in Table 3. For all dilutions the given amount is pipetted into glass volumetric flasks, which are then filled with cyclohexane to the volume given in the last column.

Table 3: Preparation of RST, IST-P, IST-S and ROZ50

	Amount A [mL]	Amount B [mL]	Amount mix standard [mL]	Volume [mL]
IST-P	1	-	-	10
IST-S	3	-	-	10
RST	-	2.5	-	10
ROZ	-	2.5	2.5	5

Finally, eleven calibration standards are prepared by mixing ROZ and IST-S (Table 4).

Table 4: Final preparation of standards

Standard	10a	10b	8	5	3	2	1	0.5	0.25a	0.25b	0.25c
Amount ROZ [mL]	1	1	0.8	0.5	0.3	0.2	0.1	0.05	0.025	0.025	0.025
Amount IST-S [mL]	0.25	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	1.5
Volume [mL]	5	5	5	5	5	5	5	5	5	5	5

The single calibrations are based on the ratio of the respective compounds to the internal (surrogate) standard (d-12 BaP, IST-S). For the preparation of standards, a constant amount of IST-S is used and only the concentration of ROZ is changed. To extend the range of the calibration a lower amount of IST-S is given to the highest standard and higher amounts of IST-S is mixed to the lowest standard. The ratio of the area of the analyte and the area of the internal standard is plotted against the ratio of the concentration of the analyte and the concentration of the internal standard for the calibration. The c/c_i values for all prepared standards are shown in Table 5.

Table 5: c/c_i ratios for the standards for all compounds

	c/c_i										
	10a	10b	8	5	3	2	1	0.5	0.25a	0.25b	0.25c
d_{12}-Per	12.36	6.18	4.95	3.09	1.85	1.24	0.62	0.31	0.15	0.08	0.05
Naph	12.34	6.17	4.94	3.09	1.85	1.23	0.62	0.31	0.15	0.08	0.05
Acy	12.24	6.12	4.90	3.06	1.84	1.22	0.61	0.31	0.15	0.08	0.05
Ace	12.24	6.12	4.90	3.06	1.84	1.22	0.61	0.31	0.15	0.08	0.05
Flu	12.12	6.06	4.85	3.03	1.82	1.21	0.61	0.30	0.15	0.08	0.05
Phe	12.12	6.06	4.85	3.03	1.82	1.21	0.61	0.30	0.15	0.08	0.05
Ant	12.24	6.12	4.90	3.06	1.84	1.22	0.61	0.31	0.15	0.08	0.05
Fla	12.34	6.17	4.94	3.09	1.85	1.23	0.62	0.31	0.15	0.08	0.05
Py	12.31	6.15	4.92	3.08	1.85	1.23	0.62	0.31	0.15	0.08	0.05
BaA	12.21	6.10	4.88	3.05	1.83	1.22	0.61	0.31	0.15	0.08	0.05
Chr	12.00	6.00	4.80	3.00	1.80	1.20	0.60	0.30	0.15	0.07	0.05
BaA+ Chr	12.10	6.05	4.84	3.03	1.82	1.21	0.61	0.30	0.15	0.08	0.05
BbF	12,24	6,12	4,90	3,06	1,84	1,22	0,61	0,31	0,15	0,08	0,05
BkF	12,36	6,18	4,94	3,09	1,85	1,24	0,62	0,31	0,15	0,08	0,05
BbF+BkF	12,30	6,15	4,92	3,08	1,85	1,23	0,62	0,31	0,15	0,08	0,05
BaP	12,12	6,06	4,85	3,03	1,82	1,21	0,61	0,30	0,15	0,08	0,05
IcdP	12,24	6,12	4,90	3,06	1,84	1,22	0,61	0,31	0,15	0,08	0,05
BghiP	12,24	6,12	4,90	3,06	1,84	1,22	0,61	0,31	0,15	0,08	0,05
DahA	12,21	6,10	4,88	3,05	1,83	1,22	0,61	0,31	0,15	0,08	0,05

The preparation procedure is schematically showed in Figure 3.

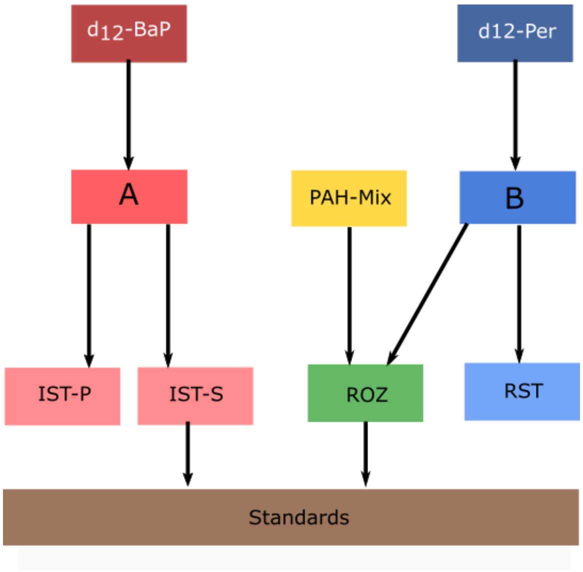

Figure 3: Scheme for the preparation of calibration standards

The calibration standards are filled in screw-cap amber vials and stored in the freezer. For the measurement they are taken out of the freezer and filled in GC vials equipped with 200 µL single use inserts. Vials which are not used for measurement immediately are put in the freezer again.

2.1.1.1. Sample preparation

All in this work analysed filters are quartz fibre filter. Particulate matter is sampled on those. To be more precise particles with a diameter ≤10 µm (PM10) are collected. Both, emission filters and ambient filters are used. The ambient filters are bigger with a diameter of 14 cm of the loaded area, whereas the emission filter only have a loaded area of 3.5 cm. For the whole work only particulate PAHs are considered.

Filter aliquots of quartz-fibre filters (both ambient and emission filters) are placed in glass Petri dishes. The samples are more precisely described in the following sections. For the determination of the extraction recovery, the samples are spiked with 50 µL of the recovery standard - a deuterated perylene (Per, d12 -Perylene), as described above. The concentration of the recovery standard is 25 µg/mL. Afterwards the filter segments or punches are transferred to a glass test tube with a screw cap. Next to the filters also reference material (PM10-like dust) is analysed. For analysis of the reference material (1649a, urban dust, U.S. department of commerce, National Institute of standards and technology, Gathersburg) approximately 150 mg of the material is directly weighed into the test tube and spiked there.

The “standard” solvent mixture is chosen according to the previously established method (AQUELLA quality manual, internal working group publication [27]) and contains a mixture of 2 mL cyclohexane and 3 mL dichloromethane. For experiments concerning the influence of solvents on the extraction efficiency different solvent combinations, based on the solvents listed in the EN 15549 are tested (see 2.5.1). Subsequently the samples are extracted in an ultrasonic bath at 30°C for 30 min. The procedure is repeated once and the combined extracts are divided from the solid filter residues using a glass capillary tube and transferred into new test tubes with screw caps. Then the extracts are spiked with 100 µL of a deuterated internal standard (surrogate standard, d_{12}-BaP) with a concentration of 5.4 µg/mL in order to correct the PAH concentration after applying the following steps. (The preparation of internal and recovery standard is described in 2.1.1.1). In the next step the extracts are evaporated to about 150-500 µL (depending on the PAH concentration, which was assessed in this step by visual judgement of the solution colour) in a nitrogen flow. The more intense yellow-orange the solutions are, the higher is the expected PAH concentration. Therefore, the samples are evaporated to lower volumes if their colour was pale yellow or even transparent. The extracts are then transferred to GC screw-cap amber vials equipped with 200 µl single use inserts. As sometimes solids, which are either insoluble particulate matter or fibres of the quartz filters, are present in the tubes, the extracts are centrifuged for 5 min at 2000 revolutions per minute (rpm) when necessary. Just the clear supernatant is used for analysis. In particular, the extracts of the reference material were murky and needed to be centrifuged. For experiments, where the influence of a syringe filter is examined, in addition to centrifugation syringe filters (Chromafil® Xtra H-PTFE-20/13) are used for particle removal (2.6).

2.1.2. GC-MS Analysis

The PAH determination is performed with a GC-MS method previously described by Kistler et al. [28]. The HP-5890 Gas Chromatograph is equipped with a HP-7683 auto sampler and a split/split-less injector operated in a pulsed split-less mode (0.2 min, 2.8 bar) at 300°C. A deactivated fused silica pre-column (1m x 0.25 mm) is applied in combination with an analytical capillary column (DB-5 MS- 95% dimethyl-. 5% phenyl siloxane, 30m x 0.25mm ID x 0.25µm film thickness) for the separation. Due to system maintenance the applied column is 1-2 meters shorter. The start of the temperature programme is equilibration at 50°C for 2 min. A rise of the temperature to 150°C with a rate of 20°C min^{-1} followed. Subsequently the temperature is increased to 300°C with a rate of 10°C min^{-1} and the last temperature is held for 20min. The GC to MS transfer line temperature was 300°C. As a carrier gas Helium 5.0 (Messer) with a column flow rate of 1 mL min^{-1} is used.

A quadruple mass spectrometer HP-5973 (70eV) is applied as a detector. MS temperatures are 230°C for the ion source and 150°C for the quadrupole. PAHs are recorded in the full scan mode and selected ion monitoring mode (SIM).

Sample and standard extracts are measured twice each time, which means that the results presented later on represent always the mean value of two subsequent measurements of the extract. Not all compounds could be separated sufficiently within the applied method. Therefore, two pairs of not fully separated compounds BaA and Chr, as well as BbF and BkF are quantified as sum in each case. A cleaning programme is carried out after each double determination to remove possible contaminations resulting from previous sample. The programme lasts for 50min and during the run the temperature is increased with a rate of 20°C per minute to 320°C.

2.2. Stability of calibration

Whole measurement period comprised two full months from mid-June to mid-August and standards prepared on March 1st 2016 are measured over the whole period to estimate their stability, and the stability of calibration during operation time of GC-MS system. The measurement of combustion samples (described in the second part of this work) takes place at the same time and the calibration measured at the closest time before the sample set is used to quantify the PAHs in the samples. The standards are grouped according to when they are measured and for each period of time an own calibration function is calculated to observe changes of the calibration with time. In Table 6 the time range and other details about the calibration functions are described.

Table 6: Description of the used calibration functions including abbreviations and time of measurement

Abbreviation	Time	Comment
K1	mid-June	At the beginning of measurement period, before the samples were measured
K2	beginning-July	After liner change (36 samples)
K3	mid-July	After measurement of 50-61 samples
K4	end-July	After further 10 samples
K5	mid-August	Two weeks after all samples were measured

For the comparison the slopes (k) and the intercept (b) of the functions are used. The change of the slope over time for each compound can be seen in Figure 4.

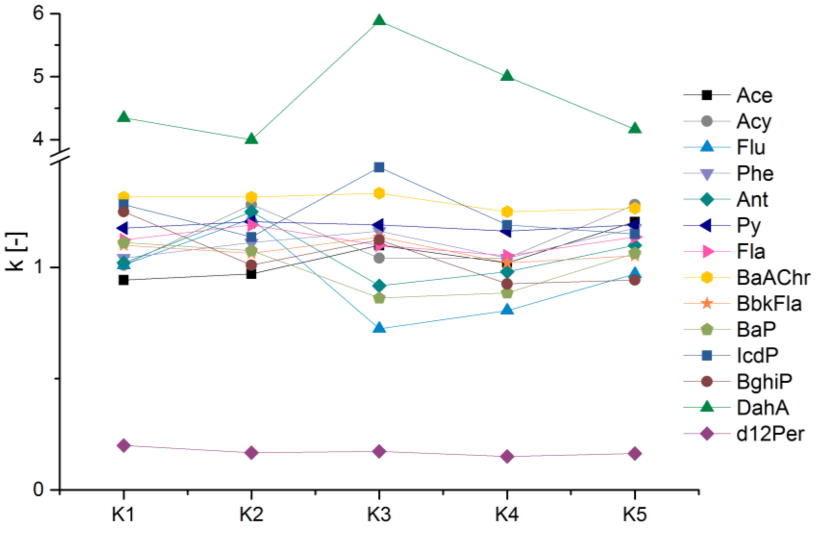

Figure 4: Change of slope (k) over time for the calibration functions of each compound

In Table 7 the slopes obtained for each calibrated compound are listed. The mean over all calibrations and the corresponding standard deviation (s) and relative standard deviation (s/x) are included too. Compounds lighter than 1-Methylnaphthalene (m/z=142.2) could not be seen in chromatograms acquired by this method. For the calibration a linear regression from standard 0.25c to 8 is used although not all standards are measured for each calibration. Each calibration contains at least four points.

Table 7: Slopes of calibrations including mean. standard deviation and relative standard deviation over all measurements

	Ace	Acy	Flu	Phe	Ant	Py	Fla	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA	d_{12}-Per
K1	0,94	1,01	1,01	1,04	1,02	1,18	1,12	1,32	1,10	1,11	1,28	1,25	4,35	0,20
K2	0,97	1,28	1,22	1,11	1,25	1,20	1,19	1,32	1,06	1,08	1,14	1,01	4,00	0,17
K3	1,10	1,04	0,72	1,16	0,92	1,19	1,10	1,33	1,14	0,86	1,45	1,12	5,88	0,17
K4	1,02	1,04	0,81	1,04	0,98	1,16	1,05	1,25	1,02	0,88	1,19	0,93	5,00	0,15
K5	1,20	1,28	0,97	1,18	1,10	1,19	1,14	1,27	1,05	1,06	1,15	0,94	4,17	0,16
mean	1,05	1,13	0,95	1,11	1,05	1,19	1,12	1,30	1,07	1,00	1,24	1,05	4,68	0,17
s	0,09	0,12	0,17	0,06	0,11	0,01	0,05	0,03	0,04	0,10	0,12	0,12	0,69	0,02
s/x	0,09	0,11	0,18	0,05	0,11	0,01	0,04	0,02	0,04	0,10	0,09	0,12	0,15	0,09

In general, it can be said that the slopes show neither a clear declining nor an increasing trend for all compounds which indicates that the standards were stable over the observed period of time of two months. Depending on the compound the relative standard deviation ranges from 1 (Py) to 18% (Flu), whereby it is under 10% for Phe, Py, Fla, BaA+Chr and BbF+BkF. The calibration of d_{12}-Per (recovery standard) was problematic as in the low concentrated area the separation of d_{12}-BaP (internal standard) and d_{12}-Per was insufficient. However, the calibration of d_{12}-Per used for the analysis of samples contained only standards higher than standard 2 ($c/c_i \approx 1.22$) as the ratio ($c_{d_{12}\text{-Per}}/c_i$) in the samples was not lower than that. For the comparison with the other compounds also only the higher concentrated standards were included. The relative standard deviation of d_{12}-Per is only 9%.

The slopes of most compounds are around 1.1, which shows that for those a use of common calibration based on the one of those compounds might be considered. Only the slope of DahA is clearly higher with 4.68 and thereby more sensitive. The slope of d_{12}-perylene is about six-times lower (0.17).

In Table 8 additionally to the slopes the intercepts of all calibrations are listed including the mean and standard deviation.

Table 8: Intercepts of calibrations including mean and standard deviation over all measurements

	Ace	Acy	Flu	Phe	Ant	Py	Fla	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA	d_{12}-Per
K1	0,11	0,31	0,12	-0,10	0,39	0,03	0,31	0,03	0,05	0,35	-0,14	-0,16	-0,88	0,21
K2	0,07	0,14	0,05	0,07	0,08	0,07	0,17	0,09	-0,01	0,10	-0,15	-0,02	-0,90	0,18
K3	-0,18	-0,04	0,03	-0,10	0,00	-0,06	-0,03	-0,04	0,04	0,00	-0,54	-0,34	-2,59	0,17
K4	-0,13	0,06	0,13	0,02	0,11	0,07	0,14	-0,02	0,04	0,16	-0,17	0,08	-1,35	0,29
K5	-0,08	0,15	0,19	0,03	0,21	0,12	0,22	-0,06	0,01	0,12	-0,26	-0,02	-1,28	0,34
mean	-0,04	0,12	0,10	-0,02	0,16	0,05	0,16	0,00	0,03	0,15	-0,25	-0,09	-1,40	0,26
s	0,12	0,13	0,07	0,08	0,15	0,07	0,13	0,06	0,03	0,13	0,17	0,16	0,70	0,08

In Figure 5 the change over time of the intercepts is shown. The intercept reflects the background signal of the instrument and sample respectively. As not only positive values were obtained no relative standard deviation was calculated. The mean intercept is positive for all compounds except Ace, IcdP, BghiP and DahA.

Table 9: Mean and standard deviation of intercepts over all measurements without K3

	Ace	Acy	Flu	Phe	Ant	Py	Fla	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA	d_{12}-Per
mean	-0,01	0,17	0,12	0,00	0,20	0,07	0,21	0,01	0,02	0,18	-0,18	-0,03	-1,10	0,29
s	0,11	0,10	0,06	0,08	0,14	0,04	0,08	0,06	0,03	0,11	0,05	0,10	0,25	0,06

For Ace and BghiP the intercept is more than -0.1 and is therefore likely to originate from variations of the background. K3 seems to be problematic as nearly all intercepts are negative. If K3 is excluded Ace and BghiP are just slightly negative which is explainable with variations of the measurement (Table 9).

Table 10: Intercepts of IcdP without standard 8 with mean and standard deviation

	K1	K2	K3	K4	K5	mean	s
IcdP	-0.01	-0.06	-0.1	-0.04	0.01	-0.04	0.04

IcdP has stronger negative intercepts which are not explainable with variations of the noise, but when the highest standard (standard 8) is excluded from the calibration the intercept increases to -0.04 in average. This indicated that for IcdP a separate calibration for the low and high concentration range is necessary (Table 10). For DahA the intercept is extremely negative which should not be the case. As the different PAHs were all in the same bought standard solution is it unlikely that concentration of only one compound is incorrect therefore the signal of the detector might be wrong for DahA. DahA peak shape resulting from the applied method was rather wide with insights for tailing. Moreover, the high temperature at the elution time is causing an additional phenomenon of column bleeding. Those factors might have been influencing for the integration quality of DahA. This compound is however not found in the combustion samples and therefore no further investigations are made. d_{12}-Per has a relatively high positive intercept (0.26) which might be related to the problems with separation in the low concentrated area.

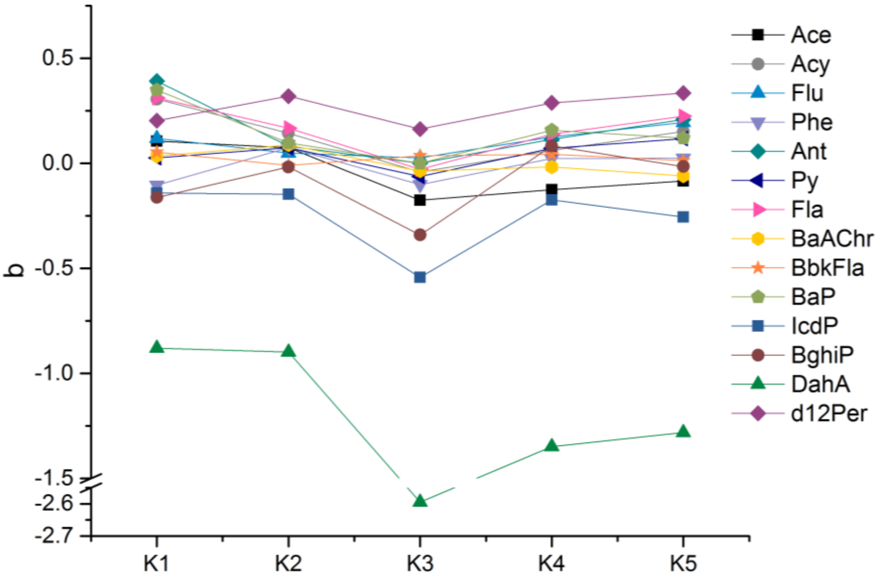

Figure 5: Change of intercept (b) over time for the calibration functions of each compound

The calibration is done using an internal surrogate standard. To check the influence of this standard on the calibration quality, the calibration procedure is repeated without considering it. For this only the area of calibrated compound is plotted against the concentration (Table 11). The relative standard deviations ranges from 32% (BbF+BkF) to 112% (BaP) and are thereby clearly higher than when an internal standard is used. This indicates that the use of an internal standard improves the quality of the quantification significantly.

Table 11: Slopes of calibrations including mean. standard deviation and relative standard deviation over all measurements without internal standard

	Ace	Acy	Flu	Phe	Ant	Py	Fla	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA	d_{12}-Per
K1	-71605	-33782	-54746	-90013	-24796	-81194	-42003	-147926	-308009	-18899	-114950	-72559	-78494	600196
K2	-27866	-5505	-25204	-25910	-30490	-24485	-11226	-9939	-238616	-8038	-55948	-38598	-41026	174809
K3	-145630	-46633	-17024	-92046	-29946	-68456	-45599	-98188	-298449	4750	-80437	-27177	-75155	216471
K4	-243300	-107129	-77754	-139994	-113180	-130680	-105857	-53069	-522628	-72850	-197171	-114067	-163131	179660
K5	-197850	-88494	-60582	-126034	-78053	-113675	-93278	-260280	-442574	-83415	-161408	-122440	-111641	121319
mean	**-137250**	**-56309**	**-47062**	**-94799**	**-55293**	**-83698**	**-59593**	**-113880**	**-362055**	**-35690**	**-121983**	**-74968**	**-93889**	**258491**
s	**88407**	**41233**	**25317**	**44143**	**38912**	**41384**	**39114**	**96618**	**116695**	**39814**	**57758**	**42997**	**46076**	**194011**
s/x	**-0,64**	**-0,73**	**-0,54**	**-0,47**	**-0,70**	**-0,49**	**-0,66**	**-0,85**	**-0,32**	**-1,12**	**-0,47**	**-0,57**	**-0,49**	**0,75**

A look at the intercept of the calibrations without the internal standard supports the necessity of an internal standard as there all intercepts except for d_{12}-Per are negative which indicates incorrect measurement, detection or integration (Table 12).

Table 12: Intercepts of calibrations including mean. standard deviation and relative standard deviation over all measurements without internal standard

	Ace	Acy	Flu	Phe	Ant	Py	Fla	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA	d_{12}-Per
K1	-71605	-33782	-54746	-90013	-24796	-81194	-42003	-147926	-308009	-18899	-114950	-72559	-78494	600196
K2	-27866	-5505	-25204	-25910	-30490	-24485	-11226	-9939	-238616	-8038	-55948	-38598	-41026	174809
K3	-145630	-46633	-17024	-92046	-29946	-68456	-45599	-98188	-298449	4750	-80437	-27177	-75155	216471
K4	-243300	-107129	-77754	-139994	-113180	-130680	-105857	-53069	-522628	-72850	-197171	-114067	-163131	179660
K5	-197850	-88494	-60582	-126034	-78053	-113675	-93278	-260280	-442574	-83415	-161408	-122440	-111641	121319
mean	**-137250**	**-56309**	**-47062**	**-94799**	**-55293**	**-83698**	**-59593**	**-113880**	**-362055**	**-35690**	**-121983**	**-74968**	**-93889**	**258491**
s	**88407**	**41233**	**25317**	**44143**	**38912**	**41384**	**39114**	**96618**	**116695**	**39814**	**57758**	**42997**	**46076**	**194011**

2.3. Accuracy and reproducibility

2.3.1. Reference material and reference filter

Before the measurements of samples are conducted, the reference material ERM®-CZ100 (Fine Dust (PM_{10}-Like)) is used to control the accuracy. The reference material is prepared two times and both extracts are measured at the same time. Additionally, a quartz fibre filter is used as a reference filter and is measured simultaneously with the reference material. The filter quantified first together with ERM®-CZ100 and later independently is used in order to check the accuracy throughout the determination of the samples and determine the reproducibility. As reference filter a high volume filter with a diameter of 14 cm collected in Leibnitz (Styria) on 20.01.2011 (sampled during the PMInter-project) is chosen. The filter is cut into 16 equal parts with 9.6 cm² area. For each measurement a sixteenth of the quartz-fibre filter is cut into smaller parts and eluted according to procedure described before. The first measurement of the filter, which took place in the same series as ERM®-CZ100, is treated as an accuracy check for the determination. In Table 13 the concentrations of PAHs given for the certified reference material (based on the measurement in 16 laboratories across Europe), including their uncertainty are listed. Benzo[b]fluoranthene and benzo[k]fluoranthene are listed separately in the certificate of analysis as a separation of these two compounds is not possible with our method. The sum of both is used for comparison.

Table 13: Certified values for ERM®-CZ100 including uncertainty

	concentration ± uncertainty [mg/kg]
BaP	0,72±0,05
BbF+ BkF	2,09±0,2
IcdP	1,07±0,1

The results of the analysis of ERM®-CZ100 (M1, M2) are shown in

Table 14. For the reference filter samples (F1-F6) the values are given in ng/m³ in Table 15. The bold marked measurement of the filter took place at the same time as the reference material was determined and as such is seen as the reference result.

Table 14: Results of measurements of reference material in mg/kg

	concentration [mg/kg]		
	BbF+BkF	BaP	IcdP
M1	1,92	0,68	1,07
M2	2,20	0,74	1,09

Table 15: Results of measurements reference filter in ng/m³

	concentration [ng/m³]		
	BbF+BkF	BaP	IcdP
F1	**0.24**	**0.15**	**0.21**
F2	0.24	0.11	0.20
F3	0.19	0.15	0.30
F4	0.28	0.13	0.23
F5	0.19	0.16	0.22
F6	0.18	0.17	0.25

For ERM®-CZ100 the results of both analyses of the material stay within the uncertainty given by the certificate of analysis. The standard deviation and relative standard deviation for the repeated analysis of the reference filter is determined. The results are listed in Table 16. The relative standard deviation ranges from 15% for BaP to 20% for BbF+BkF for six samples, each measured twice except F2 (n=3) and F3+F4 (n=5).

Table 16: Standard deviation (s) and relative standard deviation (rel. s) for BbF+BkF, BaP and IcdP for the reproducibility of the reference filter

	s [ng/m³]	**rel. s [%]**
BbF+BkF	0.04	20
BaP	0.02	15
IcdP	0.03	16

2.3.2. Multiple injection of standards and samples

Additionally, to the reference filter, also standards are used to estimate the reproducibility over the time, in this case two months. Three differently concentrated standards, which are analysed most frequently, are taken for an additional determination of the reproducibility. The standards are denoted with letters a (n=17), b (n=15) and c (n=12). The concentration increases from standard a to standard c. Standard 0.5, 2 and 8 are used. The data can be found in Table 5.

The reproducibility according to multiple injection (injection reproducibility) is estimated by injecting two samples five times in a row. The reference material (1649a) extracts prepared for solvent tests, as indicated in Table 20 (thus both including different solvents: DcH2-Sample 1 and the TocH-Sample 2 – detailed explanation given in further chapter), are used. In Table 17 the relative standard deviations of the samples and standards are shown.

Table 17: Relative standard deviation of multiple injection of samples (repeatability) and multiple standard measurements over 2 months' time (reproducibility).

	Relative standard deviation [%]							
	Py	Fla	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA
Sample 1	5	7	2	4	15	12	20	5
Sample 2	11	15	10	12	10	10	15	7
Standard a	9	17	13	6	6	16	8	22
Standard b	15	16	6	6	7	15	7	17
Standard c	10	6	6	5	9	10	11	13

The relative standard deviation ranges from 2- 20% for the measurement of the repeatability (injection reproducibility) and from 6-22 % for the determination of the reproducibility. The matrixes differ as for the repeatability samples were used whereas for the reproducibility standards were analysed. The results vary between the different samples respectively standards, whereas no clear difference between repeatability and reproducibility can be seen. The relative standard deviations for the multiple analysis of the reference filter (2.3.1) are similar to the values obtained for sample 1 and 2 and standard a-c respectively, only BbF+BkF, which has the lowest relative standard deviation here, has with 20% the highest relative standard deviation when the reference filters are considered.

From the uncertainty of measurements conducted within this work the highest relative standard deviation of all reproducibility and repeatability experiments are taken (Table 18). Among the highest observed values, the lowest relative standard deviation is observed for BaA+Chr with 13% and the highest for DahA with 22%.

Table 18: Highest relative standard deviation of all reproducibility and repeatability experiments

	Relative standard deviation [%]
Py	15
Fla	17
BaA + Chr	13
BbF + BkF	20
BaP	15
IcdP	16
BghiP	20
DahA	22

2.4. Limit of detection and limit of quantification

The limit of detection (LOD) is calculated as three-times the standard deviation of the multiple measurement (n=6) of the lowest standard (standard 0.25c). For the limit of quantification (LOQ) ten-times the standard deviation of the lowest standard is used. If the calibration did not cover values as low values as LOQ the average of the lowest standard (ALS) is taken instead. Values over the in bold marked one in Table 19 can be quantified. For the measurements values under either LOQ or ALS depending on which one is higher are not quantified. In the tables (Table 46-Table 52) they are denoted as <LOQ regardless of whether LOQ or ALS is higher.

Table 19: Limit of detection, limit of quantification and lowest point of calibration for all compounds

	Amount [ng]												
	Ace	Acy	Flu	Phe	Ant	Fla	Py	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA
LOD	1.18	14.9	9.79	5.07	7.75	7.25	3.30	5.86	7.14	12.2	10.6	16.5	32.5
LOQ	3.88	**47.8**	**32.6**	13.48	**26.5**	**24.1**	**11.0**	19.53	19.23	**38.0**	34.49	**55.1**	**108**
ALS	**30.0**	35.52	13.48	**32.9**	5.04	15.23	6.36	**21.4**	**31.1**	8.43	**49.5**	34.72	44.18

2.5. Influence of solvent

First experiments on this topic are presented in the bachelor thesis of B. Kirchsteiger [29]. In this case a combination of cyclohexane/toluene and cyclohexane/dichloromethane were applied. The results are not explicit. Based on the measurements of standards toluene seemed to be most adequate as solvent for high amounts of PAHs, but this result was not supported by the measurement of selected filter samples. Therefore, the issues are investigated again in this work. The results obtained within this part were presented at the Conference on Sustainable Energy and Environment Development (SEED) in Krakow, Poland in 2016 in form of a poster and scientific paper in the proceedings [30].

The influence of different solvent combination on the extraction efficiency of PAHs from reference material (1649a, Urban Dust) within ultrasonic extraction is investigated. The results are compared with experiments conducted with two different quartz fibre filter samples collected in Austria in winter 2010/11 using a high-volume sampler within the EU project PMInter in cooperation with the Air Quality Monitoring Networks from Styria and Carinthia. The diameter of the loaded filter area is 14 cm. The sampling time is 24 hours and the sampled air volume is approximately 720 m³. To account for different filter loadings one chosen sample was collected in an urban area (i.e. the city of Klagenfurt, Carinthia), representing a highly loaded filter (Filter 1). The second sample (Filter 2) was collected at a background site (Arnfels, Styria) and represents conditions with lower particulate matter concentrations (Figure 11). To obtain sample aliquots, the filters are cut into sixteen segments of equal area using a pre-cleaned cutting tool. For each analysis one of these segments is used. Additionally, carbon parameters, organic and elemental carbon (OC and EC), are measured using thermo-optical methods [31], [32].

2.5.1. Solvents combination

The respective solvents are combined to a total volume of 5 mL. Five different solvents in seven different combinations are investigated. The applied solvent combinations are listed in Table 20. The solvents are chosen based on the European Norm EN 15549 [33], but in addition to dichloromethane and toluene, which are recommended there for the ultrasonic extraction also other solvents are tested. For the accelerated solvent extraction additionally a dichloromethane/hexane mixture (1:1) and for the soxhlet extraction a hexane/acetone mixture (1:1) are recommended. Hexane/acetone mixture (1:1) is applied for the extraction of soil samples [34]. Acetonitrile is used as a solvent for the extraction of PAHs from vegetable oils and oilseeds [35] and is used for measurements of PAHs with HPLC systems.

Table 20: Solvents and solvent mixtures used for the sample extraction

Name	Solvent 1 [mL]	Solvent 2 [mL]	Ratio
DCM	Dichloromethane	-	-
DcH1	Dichloromethane	Cyclohexane	3:2
DcH2	Dichloromethane	Cyclohexane	3:7
cHex	Cyclohexane	-	-
AcH	Acetone	Cyclohexane	1:1
AcN	Acetonitrile	-	-
TocH	Toluene	Cyclohexane	3:3

Because acetonitrile is not suitable for the used GC-MS application, it must be noted that the samples extracted with acetonitrile are evaporated to dryness, then dissolved in 3 mL cyclohexane and put in an ultrasonic bath for 30 min before finally reducing the liquid volume to approximately 200 µl depending on the colour of the extract. The solvent use is based upon the EN 15549, but it is also designed to cover the different solvent features. In Table 21 the boiling point and polarity of the solvents are given. As parameter for the polarity the empirical solvent parameter $\mathrm{E_T^N}$, which is based on the solvatochromism of a pyridinium N-phenolate betaine, is shown [36]. The higher $\mathrm{E_T^N}$ the more polar is the solvent.

Table 21: Boiling points and polarity of used solvents

	Boiling point [°C] [36]	Polarity (E_T^N) [36]
Cyclohexane	80.8	0.006
Toluene	110.6	0.099
Dichloromethane	39.6	0.309
Acetone	56.1	0.355
Acetonitrile	81.6	0.460

The polarity of the solvents increases from cyclohexane (0.006) to acetonitrile (0.460). Their boiling point varies from 39.6°C for dichloromethane to 110.6°C for toluene. A low boiling point would be preferable as otherwise the evaporation of the solvent in the end can be very time-consuming. PAHs are non-polar substances with multiple conjugated double bonds thus non-polar solvents which are able to undergo π- π interactions should be ideal for the extraction. However, PAHs can be strongly adsorbed to organic matter. If the PAHs are strongly adsorbed a better desorbing aromatic solvent like toluene could be helpful [37]. For extraction of PAHs from soil using ultrasonic extraction the more polar solvents like methanol and acetonitrile are reported to be less efficient than less polar ones, like dichloromethane and acetone [38]. Another factor, which is reported in this study is the concentration of PAHs in the matrix, where more polar solvents are recommended for low polluted samples whereas highly polluted soil is better extractable with relatively nonpolar solvents like toluene or cyclohexane [39]. The matrix of particulate matter filter samples differs from soil samples, nevertheless also the ability of more polar solvents for increasing the extractability of PAHs is investigated. A combination of the nonpolar cyclohexane with more polar solvents could possibly combine the advantages of both and improve the extraction further.

2.5.2. Results

In Figure 6 exemplary extracts for the different solvent combinations applied to the reference material can be seen. The extracts for DCM, DcH1 and DcH2 have a yellow colour where DCM seems to have the most intense colour. The more cHex is used the paler is the colour. Sample extracted solely with cHex is clear without a shade of yellow. Also the one extracted with TocH is very pale too. AcH is standing out as the solution is black and murky resulting from soot particles, which were strongly hold in the suspension in this case. Considering only the colour, dichloromethane as single solvent, in combination with cyclohexane or cyclohexane in combination with toluene seem to be suitable for good extraction efficiency as PAHs in general have a yellow colour. AcH is difficult to assess due to black soot suspension but even if the extraction is good, the separation of suspended particles must be approached before the analysis. The usage of a syringe filter for this solvent combination is necessary.

Figure 6: Exemplary extracts for the different solvent combination (from left to right: DCM, DcH1, DcH2, cHex, AcH, TocH, AcN)

Table 22 lists the results including variation obtained for the reference material in ng per mg. For the assessment of the variation of the mean values from an intercomparison were taken [26]. In contrast to our study were only one method with different solvents in one laboratory was used, the intercomparison study compared results from eighteen laboratories across Europe, which applied various methods and solvents. Therefore, the overall uncertainty should only be seen as the maximal variation. Moreover, it has to be noted that the intercomparison only included BaP.

Table 22: Results of the determination of PAHs within the reference material with different solvents including standard deviations of the measurement (calculated as given in the text)

Analyte [ng/mg]	DCM	DcH1	DcH2	cHex	AcH	AcN	TocH	Mean
Py	6.6± 1.0	4.0±0.6	4.1±0.6	3.4±0.5	6.5±1.0	5.4±0.8	2.5±0.7	5.0±1.3
Fla	6.8±1.1	7.5±1.3	7.7±1.3	**3.8±0.6**	10.0±1.7	9.6±1.6	5.6±0.9	7.3±1.6
BaA+Chr	2.6±0.4	2.0±0.3	2.0±0.3	1.4±0.2	3.3±0.4	2.8±0.4	1.4±0.2	2.2±0.7
BbF+BkF	3.8±0.8	3.2±0.6	2.8±0.6	**1.0±0.2**	5.1±1.0	3.8±0.8	2.0±0.4	3.1±1.0
BaP	1.0±0.2	0.7±0.1	0.8±0.1	0.4±0.1	1.0±0.2	0.6±0.1	0.5±0.1	0.7±0.2
IcdP	2.1±0.3	2.3±0.4	1.7±0.3	**0.9±0.1**	2.4±0.4	1.7±0.3	1.3±0.2	1.8±0.7
BghiP	5.6±1.1	5.1±1.0	3.4±0.7	**0.9±0.2**	4.9±1.0	2.8±0.6	2.5±0.6	3.5±1.5
DahA	0.9±0.2	0.9±0.2	0.7±0.2	0.4±0.1	0.9±0.2	0.8±0.2	0.6±0.1	0.7±0.3
Mean	3.7	3.1	2.9	1.5	4.3	3.4	2.1	3.0

The results of the analysis of Filter 1 (highly loaded filter) and Filter 2 (light loaded filter) are summarized in Table 23 and Table 24, respectively. Loadings of the respective PAHs are given as ng per mm² of filter area to highlight differences in filter loadings.

Table 23: Results of the determination of PAHs on filter 1 with different solvents including standard deviations of the measurement (calculated as given in the text).

Analyte [ng/mm²]	DCM	DcH1	DcH2	cHex	AcH	AcN	TocH	Mean
Py	30.3±4.5	40.0±6.0	32.7±4.9	26.7±4.0	48.3±7.2	37.6±5.6	31.7±4.7	35.3±9.3
Fla	28.7±4.8	37.0±6.2	30.1±5.0	24.2±4.1	47.5±8.0	35.4±5.9	27.5±4.6	32.9±7.4
BaA+Chr	41.0±5.5	56.5±7.5	53.9±7.2	35.1±4.7	47.5±6.3	51.3±6.8	44.4±5.9	47.1±14.9
BbF+BkF	60.0±12.0	77.5±15.5	70.2±14.0	56.7±11.3	58.1±11.6	71.5±14.3	36.9±7.4	61.5±19.3
BaP	45.0±6.9	56.5±8.7	49.7±7.6	39.5±6.1	34.2±5.2	54.7±8.4	50.5±7.8	46.6±13.8
IcdP	48.4±7.8	55.0±8.9	53.8±8.7	39.5±6.4	56.3±9.1	53.0±8.6	77.2±12.5	54.7±20.3
BghiP	79.9±15.9	96.3±19.2	88.9±17.7	61.3±12.2	72.3±14.4	95.2±19.0	87.3±17.4	83.0±33.7
DahA	15.6±3.4	16.7±3.6	15.5±3.4	14.2±3.1	12.1±2.6	18.1±4.0	15.7±3.4	15.4±5.1

Table 24: Results of the determination of PAHs on filter 2 with different solvents including standard deviations of the measurement (calculated as given in the text)

Analyte [ng/mm²]	DCM	DcH1	DcH2	cHex	AcH	AcN	TocH	Mean
Py	5.8±0.9	7.3±1.1	7.3±1.1	7.1±1.1	12.1±1.8	6.7±1.0	5.8±0.9	7.4±2.7
Fla	5.8±1.0	6.4±1.1	7.1±1.2	6.0±1.0	11.5±1.9	6.2±1.0	5.2±0.9	6.9±2.8
BaA+Chr	2.8±0.4	3.6±0.5	3.5±0.5	3.3±0.4	4.1±0.5	3.5±0.5	2.9±0.4	3.4±1.5
BbF+BkF	4.1±1.0	5.7±1.1	5.8±1.2	4.5±0.9	6.4±1.3	5.5±1.2	6.2±1.2	5.9±1.8
BaP	4.3±0.7	4.3±0.7	4.5±0.7	4.2±0.6	4.7±0.7	4.5±0.7	4.7±0.7	4.4±2.2
IcdP	6.8±1.1	8.4±1.4	7.1±1.2	6.4±1.0	8.4±1.4	8.5±1.4	7.5±1.3	7.6±2.9
BghiP	5.7±1.1	6.5±1.3	6.1±1.2	4.7±0.9	7.3±1.5	8.3±1.7	6.5±1.3	6.4±2.8
DahA	4.1±0.9	5.5±1.2	4.5±1.0	4.2±0.9	5.5±1.2	5.0±1.1	4.5±1.0	4.8±2.7

The PM10, organic carbon (OC) and elemental carbon (EC) loadings for both filters are shown in Figure 7. Filter 1 has twice as high PM10 loading than Filter 2 and even three-times as much elemental carbon is found on Filter 1.

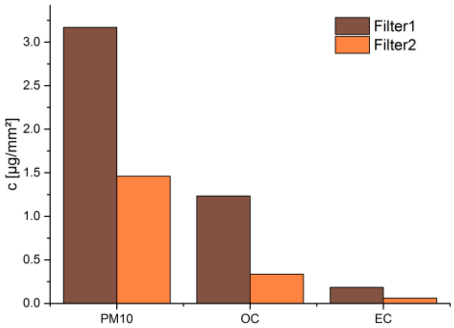

Figure 7: Values for PM10, organic carbon and elemental carbon on filter 1 and filter 2

Standard deviations given for the single compounds and measurement are based on the relative standard deviations given in Table 18. Part of research was shown at the SEED conference in Krakow in 2016. The values of the relative standard deviations can slightly vary from the values shown at the conference as at this point not all measurements are finished and considered.

The results obtained for different extractions are then combined to deliver the mean value for each component as listed in the last column of Table 22. Also the mean value for each extraction agent (combination of extraction agents) is assessed (last row of Table 22). To assign the overall uncertainty to that average the variations, more precisely the expanded uncertainties for the single PAHs and concentration levels, determined within an inter-laboratory intercomparison of PAH analyses on quartz filters are used [26]. The overall expanded uncertainty (OEU) is calculated using Equation 1.

$$OEU\% = \left[\left(\frac{U_{lab}}{\overline{C_{lab}}}\right) + \frac{\left(\left|\overline{C_{lab}} - C_{ref}\right|\right)}{\overline{C_{ref}}}\right] \cdot 100$$

U_{lab} … expanded uncertainties for the reported value
U_{ref} … expanded uncertainties for the reference value
$\overline{C_{lab}}$ … average concentration of the reported values by a laboratory
C_{ref} … reference concentration

Equation 1

The expanded uncertainties are reported in [26] on page 47- 50 1. For the reference value only laboratories with an overall ratio outlier/reported lower than 0.25 are included [26]. The decision whether a value is an outliner is based on a two tails statistical test of normal distribution of the random variable Z. When Z (Equation 2) is higher than 3 a measured value of a laboratory is considered as an outlier. Reported is the total amount of values reported by a laboratory.

$$Z = \frac{C_i - \bar{C}_i^*}{u_{bias}}$$

C_i … concentration measured by laboratory i
$\bar{C}_i^*$ … robust average calculated according to ISO-1328
u_{bias} … standard uncertainty (Equation 3)

Equation 2

$$u_{bias} = \sqrt{\frac{(1.25 \cdot s^*)^2}{p} + u_{e_i}^2}$$

s^* … standard deviation of input laboratories
p … amount input laboratories
$u_{e_i}^2$ … uncertainty of the reported value from laboratory i

Equation 3

Consequently, the variations given for the mean do not reflect standard variations of our measurements, but an estimate for an expanded uncertainty which can be expected for analysis using various methods for the determination of those compounds resulting from measurements conducted in seventeen national reference laboratories, which applied different extraction methods (Soxhlet extraction, accelerated solvent extraction, ultrasonic extraction, microwave extraction) [26].

In the cited study, differently loaded filters are analysed and the results show that filter loading effects are relevant (lower loadings lead to higher errors), therefore different overall expanded uncertainties are applied for measurements with Filter 1, Filter 2 and the Standard Reference Material (1649a) within this work. In case of Filter 1 and the Standard Reference Material (1649a) the overall expanded uncertainties determined for higher concentration levels (F30 – as given in [26]) for the respective compounds are applied, while the overall expanded uncertainty determined for lower concentrations (F10 – as given in [26]) is used for filter 2. Values of the single analyses falling out of the overall expanded uncertainty of the mean are marked in the above given tables in bold print.

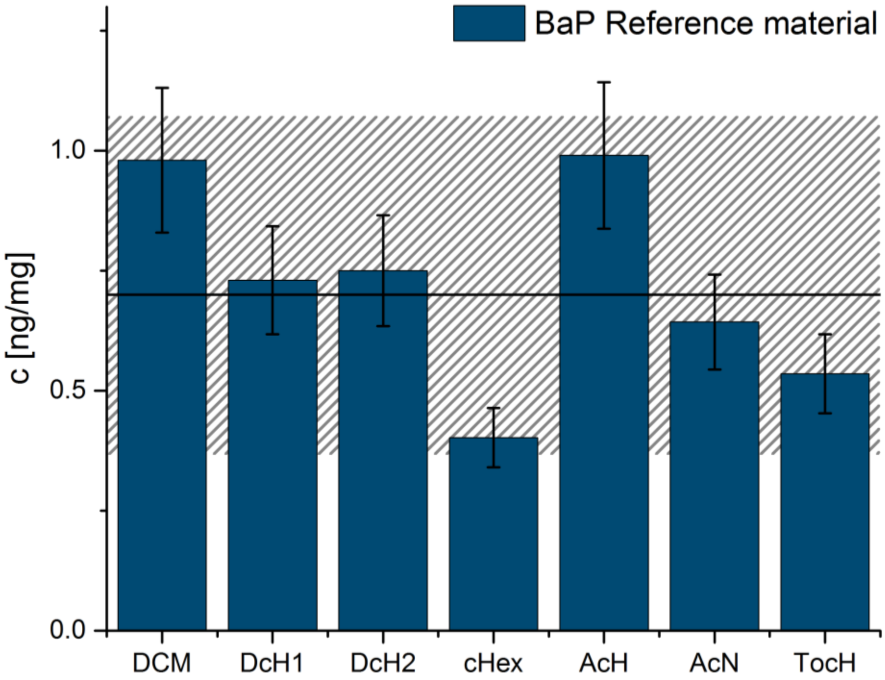

Figure 8: Concentration of BaP in the standard reference material (1649a). extracted with various solvents. Error bars reflect the standard deviation calculated by multiple injections of a single extract. The solid line represents the mean of all extractions, while the shaded area reflects the expanded uncertainty of the mean (calculated as given in the text).

Regarding the reference material (1649a) almost for all solvents the results do not exceed the overall expanded uncertainty as well. The only borderline case is when solely cHex is used as a solvent. For this solvent the underestimation of Fla, BbF+BkF, IcdP and BghiP in the reference material (1649a) cannot be explained with the overall expanded uncertainty. Analyses of the filter samples do not clearly reflect or disprove this trend, although cHex is for both filters always below the average for all compounds. For the higher loaded filter (Filter1) cHex reveals the lowest values for Py, Fla, BaA+Chr, IcdP and BghiP. Further investigations are, however, needed to answer this question with higher statistical significance. When acetone is used as solvent values for all compounds are above the mean and nearly for all PAHs (with exception of Py and BghiP) for the AcH mixture the maximal values are recorded. A look at the mean value for each combination of extraction agents, which ranges from 1.5 (cHex) to 4.3 (AcH), shows a similar picture.

Figure 9, Figure 10 and Figure 8 highlight the results exemplarily for BaP, as this compound is regarded as marker compound for the whole PAH group. The solid line represents the mean value calculated based on all extracts, while the shaded area describes the expanded uncertainty obtained within an independent inter-laboratory intercomparison [26] and is explained in detail above.

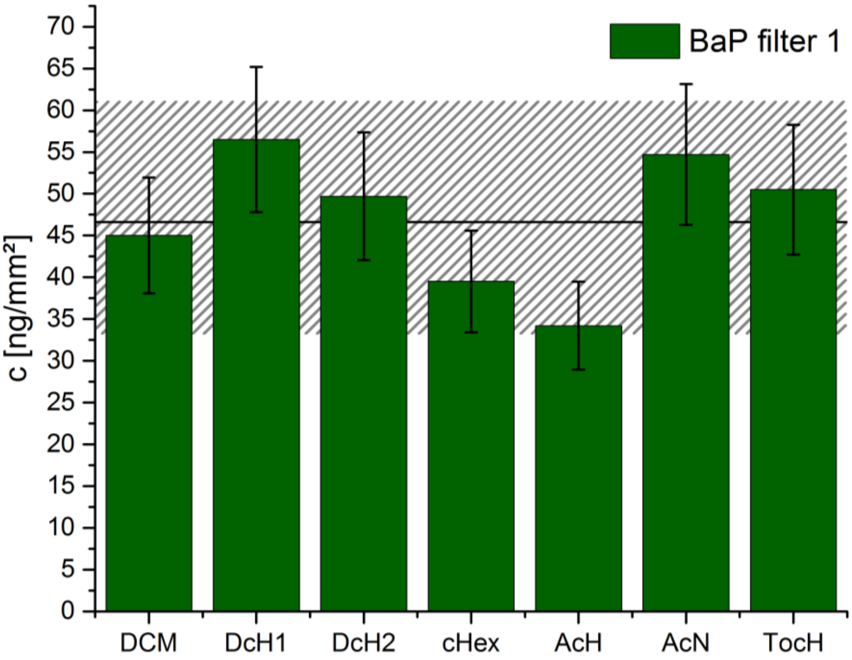

Figure 9: Filter loadings of BaP on filter 1, extracted with various solvents. Error bars reflect the standard deviation calculated by multiple injections of a single extract. The solid line represents the mean of all extractions. while the shaded area reflects the expanded uncertainty of the mean (calculated as given in the text).

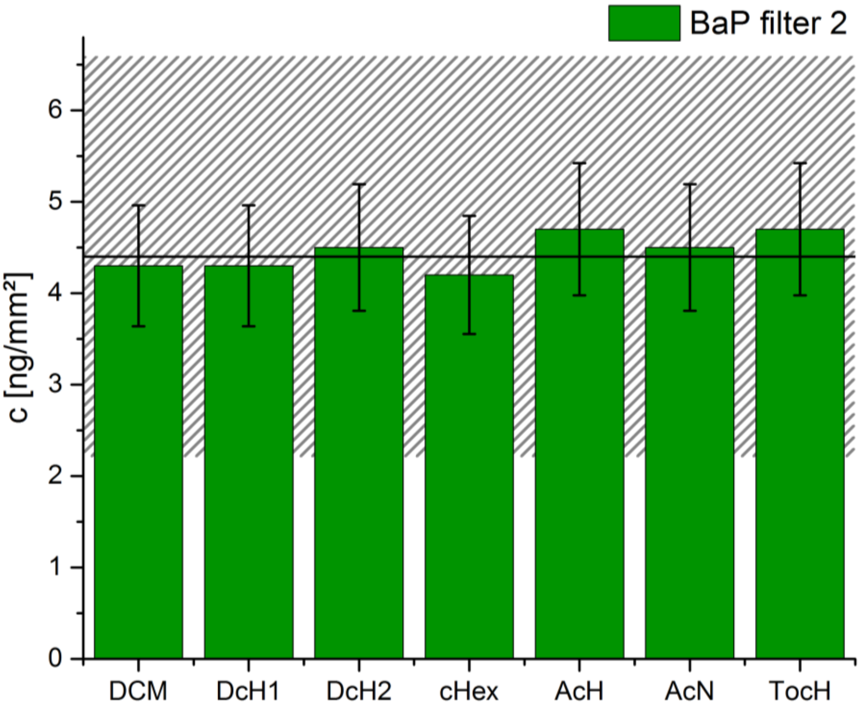

Figure 10: Concentration of BaP on filter 2. extracted with various solvents. Error bars reflect the standard deviation calculated by multiple injections of a single extract. The solid line represents the mean of all extractions. while the shaded area reflects the expanded uncertainty of the mean (calculated as given in the text).

Very good agreement of the results is obtained for filter 2 which has a lower loading. In this case the variations of the filter loadings are within 7.5%, which is even lower than the variations of multiple injections. The excellent agreement obtained for BaP loadings on filter 2 extracted with the respective solvents is seen for most of the other compounds too. The other PAHs excluding Py, Fla and BaA+Chr show also only variations within the standard deviation for filter 2. The values for Py, Fla and BaA+Chr differ within the standard deviation only if the value for AcH is excluded. AcH is a more polar solvent and therefore capable of desorbing compounds better even if they are adsorbed on particles. The smaller PAHs which are predominately in the gas phase are apparently especially good extractable with AcH, but not those which are expected to occur predominantly in the particulate phase.

Although some scatter of the BaP concentrations determined using different solvents is visible for the highly loaded filter and the reference material (1649a), all results remain within the overall expanded uncertainty of the mean. The results for all compounds for filter 1 stay within the overall expanded uncertainty, but vary more than the standard deviation (with one exception). For filter 1 only DahA varies within the standard deviation. The results for typical particle-phase PAHs are overall comparable to the findings shown for BaP and filter 1 (Figure 10).

Concluding, the results indicate that the used solvents do not influence the extraction efficiency if a filter with a simple matrix is analysed as the results vary less than the variation of the multiple injection. Looking at a more complex matrix the variation stays mostly within the overall expanded uncertainty but varies in almost all cases more than the variation through multiple injection. Especially cHex tends to have a lower efficiency when PAHs have to be extracted from a matrix with higher soot and particulate matter content.

2.6. Influence of syringe filter for particle removal from the extract

The use of syringe filters is a well-established method for removal of undissolved, suspended solids from extracts. The filters differ however in their features and are usually covered in a plastic shell, which can cause problems when organic solvents are used. The use if syringe filter and its potential influence on the analysis is compared to centrifugation in case of three different loaded biomass burning emission filters, characterized by variable soot content. Soot (EC) content and loading increases from Filter A to Filter C (Figure 11, Table 40 (Annex)). The colour of the filter reflects its soot content. The filters are sampled during the Aquellis FB project [40]. The diameter of the loaded area is 3.5 cm. The filters are divided in half. For one half a syringe filter and for the other one centrifugation is used to remove particles. A Teflon syringe filter (Chromafil ®Xtra H-PTFE-20/1, Macherey-Nagel) applicable for polar and nonpolar samples is used. The membrane is made of hydrophilic PTFE with a pore size of 0.20 µm. The filter diameter is 13 mm. Organic and elemental carbon measurements were done previously [40].

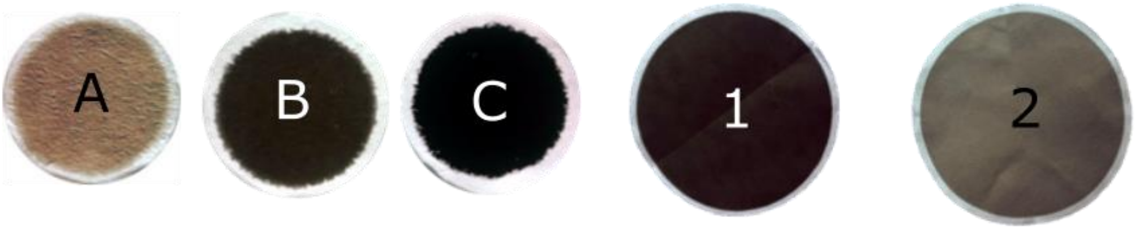

Figure 11: Filters for checking the influence of a syringe filter (A-B) with increasing soot content and differently loaded filters (high (1) and low (2)) for checking the influence of solvent

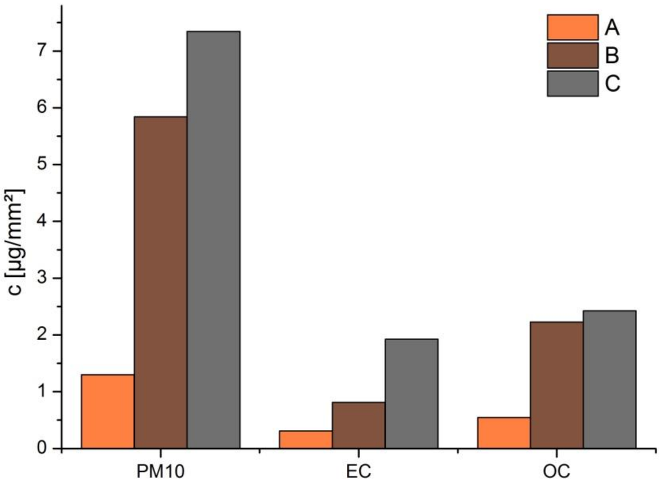

Figure 12: PM10, EC and OC concentration for filter A-C

Especially samples with a high soot concentration are interesting in the terms of GC-MS analysis. The undissolved soot particles in the extract can affect the GC inlet and column and significantly decrease their life time. Whereas filter parts (quartz fibres) can easily be separated by centrifugation, soot particles often are not easily removed on the tube bottom but remain dispersed in the solution. A syringe filter is an easy method to separate particles, but the influence of the syringe filter on the PAHs in the solution has to be checked first.

2.6.1. Results

The results obtained for filter A, filter B and filter C are shown in Table 41 (Annex). In Table 25 the ratios of the centrifuged and filter concentration are shown.

Table 25: Ratios of centrifuged to filtered value of measured PAH

	Ration centrifuged/filtered		
	A	B	C
Py	1.3	1.0	1.0
Fla	<LOQ	1.0	1.1
BaA+Chr	1.0	1.0	1.3
BbF+BkF	1.0	0.8	1.2
BaP	1.5	1.2	0.8
IcdP	1.0	0.9	1.1
BghiP	1.0	0.6	0.4
DahA	1.0	1.0	1.0

The ratios should be close to 1. In a range between 0.7 -1.3 the difference is in range of the uncertainty for multiple injection. Only for BghiP (B+C) and BaP (A) the ratio is outside the range. The value for BaP (A) is close to the quantification limit and therefore the absolute difference is only 0.002, which is a third of the standard deviation of most other compounds for filter A. Thus, the high ratio is most likely related to the low concentration and not the different preparation methods.

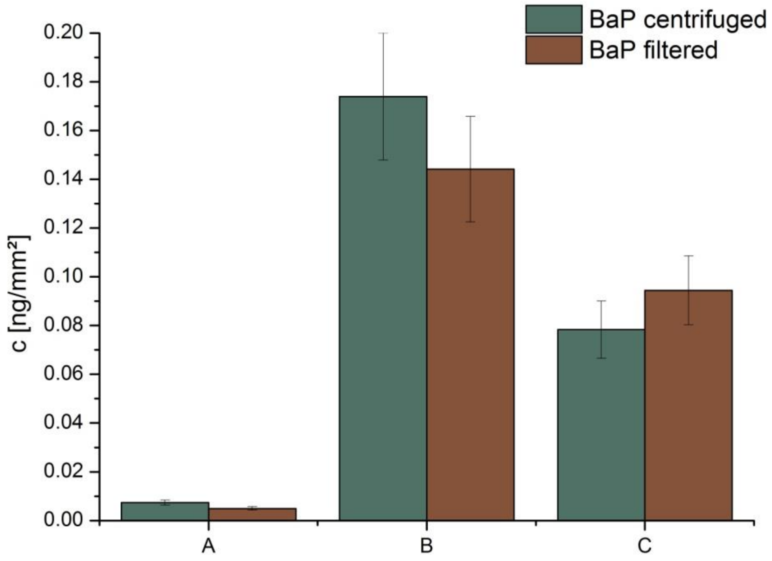

Figure 13: Concentration of BaP in ng/mm² on filter A, B and C after centrifugation and filtration respectively including standard deviation based on multiple injection

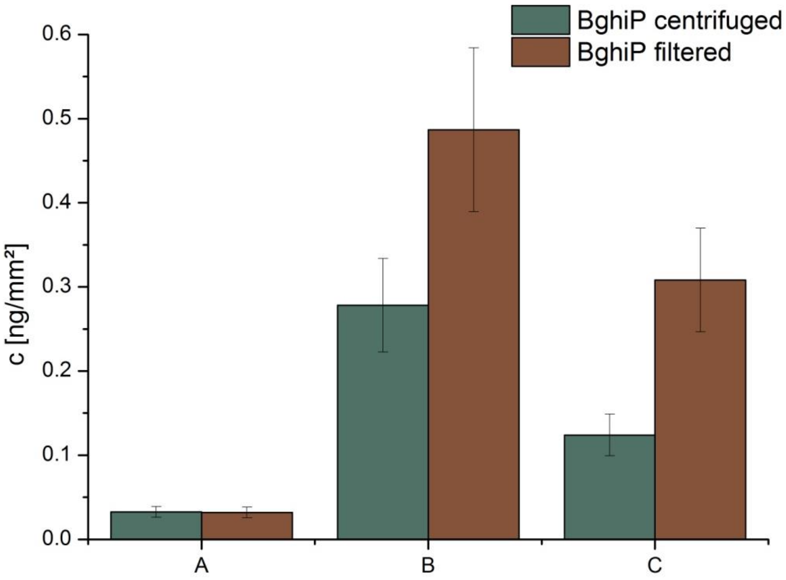

Figure 14: Concentration of BghiP in ng/mm² on filter A, B and C after centrifugation and filtration respectively including standard deviation based on multiple injection

If the differences in PM10, OC and EC are considered (Figure 12), it could be seen, that the filter with lowest loading showed again less variation than others. The values for PM10 and EC are increasing from filter A to filter C, only the organic carbon stays nearly the same for filter B and filter C. The PAH concentration is the highest for filter B and lowest for filter A for all compounds and for both centrifugation and filtration. As the PAH concentration is higher for B than for C, an increase in neither PM10 nor EC do necessarily lead to higher PAH concentrations. The organic carbon reflects PAHs slightly better as OC of filter B is at least similar to OC on filter C.

The results for BaP are shown in Figure 13. The differences between the centrifuged solution and the solution where particles are removed with a syringe filter are within the standard deviation of the measurement nearly for all compounds. As mentioned above only Benzo[ghi]perylene and BaP for the very low concentrated filter show a different behaviour. The BghiP concentration in filter A is similar among filtered and centrifuged extract, but filter B and filter C show significantly higher concentrations for the preparation using syringe filter (around 40% -70% difference for filter B and C respectively).

As the concentration has not increased for all three filters, but only for two of them it is unlikely that the additional amount roots from the syringe filter itself. A contamination of the solution is possible. A further possibility is the rising EC content. During combustion processes the formation of PAHs happens previously to the formation of EC. Thus, more EC is formed, more PAHs with higher masses are present, especially in internal or external mixtures with EC particles. However, a further investigation of this issue is needed. As also the uncertainties resulting from reproducibility tests for the heaviest measured PAHs are the highest, the results for those should be generally handled with caution. Nevertheless, for other measured PAHs both methods for particle removal from suspension are applicable.

2.7. Long-term stability of PAHs in particulate matter filter samples

The air quality monitoring networks are supposed to provide reports for BaP concentrations in yearly average. For this reason, the filters, which were sampled during one year are often stored to be analysed at the same time. Moreover, back-up filters are often used even after longer time period, either to check the previous results or to extend the result spectrum. Therefore, it is important to assure that the PAHs measured in samples stored over longer time remain the same. In case of this work, the combustion samples treated later were collected in 2007 within a different research question. Each filter was stored at -19°C in a freezer in a Polypropylene (PP) petri dish closed with parafilm. The stability of PAHs during such storage would be then checked based on back-up filters from other projects, of both ambient and directly emitted particles.

2.7.1. Ambient filter samples

Quartz fibre filters from two different ambient air samplings, which were previously analysed, are used to determine the long-term stability of in a freezer stored filters. The samples from Zederhaus were collected in 2009 [41] and the one from Knittelfeld in 2007 [42]. The diameter of the loaded area on each filter is 14 cm. For the analysis the filters are pooled and the same area of sample is taken from each filter in pool. Concentrations of selected PAHs are available from previous measurements and are taken for the comparison ([41], [42]). Details about the pools are given in Table 26.

Table 26: Period of time belonging to each pool, amount of days included in the pools and amount of punches, which were taken from each filter in the pool

	Period of time	Days	Punch (Ø 15mm) per filter
Zederhaus			
Z1	07.01- 13.01.2009	7	1
Z2	29.12.- 31.12.2009	3	2
Z3	01.01- 06.01.2009	6	1
Knittelfeld			
K1	29.11- 30.11.2007	2	1

2.7.2. Emission filters

Furthermore, emission samples (biomass burning) from BIOCOMB project (2007) [43] for which PAH concentrations are determined, are analysed. The diameter of the loaded area in case of those filters is 3.5 cm. For the analysis the whole back-up filter is used. In Table 27 information about combustion, PM10 loadings and remaining filter area are given.

Table 27: Details about emission filters (BIOCOMB) for testing of stability of filters

	Stove	Fuel	PM [mg/filter]	Area (rest)[cm²]	Comment
E1	Simplix 035 KW	Oak	1.980	6.409	not homogeneously loaded
E2	Simplix 035 KW	oak	1.875	5.100	homogeneously loaded
E3	WAMSLER Jupiter	briquettes	4.947	4.909	homogeneously loaded

2.7.3. Results

2.7.3.1. Ambient filters

The results of the analysis of samples from Knittelfeld and Zederhaus which was performed in 2016 and the results from previous measurements (2007 and 2009) are illustrated in Figure 15 and listed in Table 42 (Annex). Only five compounds are compared, as previous results are limited for those PAHs. The used relative standard deviation is based upon Table 18 (error through multiple injections). The variation between the bold marked pairs is larger than the assessed standard deviation. It must be noted that the quantification method is slightly changed between both measurements and thus the results may vary additionally.

For BaP the difference between both measurements varies only within the standard deviation. BbF+BkF and BghiP vary slightly more than the standard deviation in case of Z1 and Z2 (only BbF+BkF). IcdP has higher variations for all four samples. In most cases the concentration received from the more recent measurement is higher than from the older measurement. In particular, when just filters where the difference is higher than the standard deviation are looked at only once the old measurements give a higher concentration (BbF+BkF, Z2). In Table 28 the relative errors between the old and the new analysis related to the old concentration are summarised Equation 4.

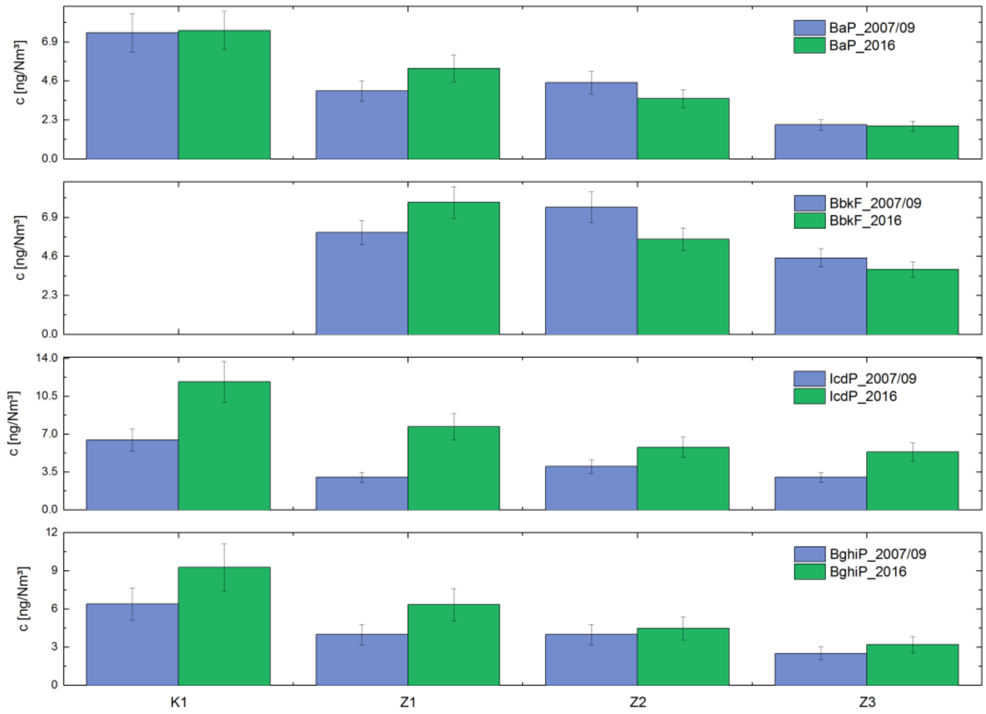

Figure 15: Comparison of filters (Knittelfeld and Zederhaus) from recently performed measurements (2016) and results from measurements from several years ago (2007/09) including standard deviation

The absolute relative error (Equation 4) between the measurements in 2016 (c_{2016}) and 2007/09 ($c_{2007/09}$) varies from 2 to 156%, where the highest deviation is found for IcdP and the lowest for BaP.

$$Relative\ error = \frac{c_{2016} - c_{2007/09}}{c_{2007/09}} * 100$$

Equation 4

The results are reasonably comparable and mainly even have a relative error under 35%. A decomposition of the analysed PAHs during storage could not be confirmed thus the analysis of filters which are properly stored in given condition is expected to provide reliable results. A contamination as reason for higher values for the later measurement cannot be excluded.

Table 28: Relative error of Knittelfeld and Zederhaus filters between measurements in 2016 and 2007/09

	Relative error [%]			
	K1	Z1	Z2	Z3
BaP	2	33	-21	-3
BbF+BkF	n.a..	30	-25	-15
IcdP	83	156	45	78
BghiP	45	59	12	27

2.7.3.2. Emission filters

The results of recent PAH analysis and values obtained in 2007 for biomass burning emissions are shown in Table 29. The standard deviation is based upon previous findings (Table 18).

The variation between the bold marked pairs is larger than the standard deviation. The differences for BghiP are always within the standard deviation and for BaP only for E3 the difference is larger. The other two analytes show higher differences for all filters. Only IcdP in Filter E1 is within the range. Similarly, to the ambient samples, more recent analysis provides mostly higher values. In Figure 16 the results of both measurements including standard deviation are depicted.

Table 29: Results of emission filters (E1-E3) from recently performed measurements (new) and results from measurements from several years ago (old) including standard deviation

	E1		E2		E3	
	2016	2007	2016	2007	2016	2007
	[ng/mg]		[ng/mg]		[ng/mg]	
BaP	559±84	675±101	816±122	675±101	**267±40**	**179±27**
BbF+BkF	**2677±535**	**1656±331**	**3391±678**	**1656±331**	**1125±225**	**381±76**
IcdP	968±155	667±107	**1207±193**	**667±107**	**552±88**	**182±29**
BghiP	528±106	690±138	691±138	690±138	341±68	237±47

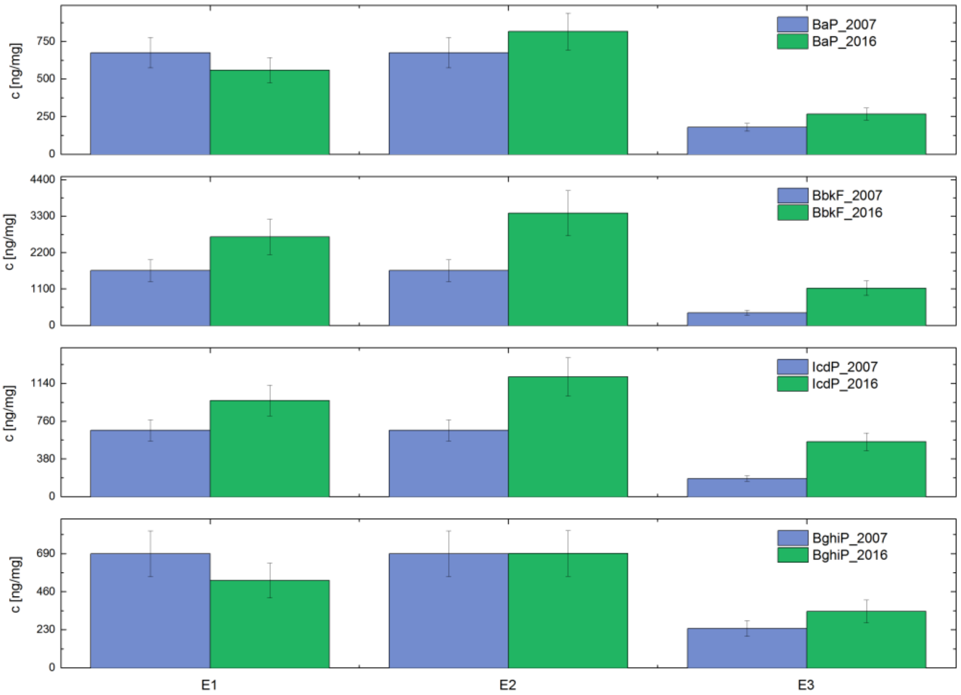

Figure 16: Comparison of emission filters (E1-E3) from recently performed measurements (new) and results from measurements from several years ago (old) including standard deviation

Table 30: Relative error of emission filters (E1-E3) between new and old measurements

	Relative error [%]		
	E1	E2	E3
BaP	-17	21	49
BbF+BkF	62	105	195
IcdP	45	81	190
BghiP	-24	0	44

The relative errors are listed in Table 30. The absolute relative error ranges from 17 to 195%.

In this case it must be however noted, that not only the quantification method between measurement in 2007 and 2016 has changed, but also a recent problem with calibration occurred. Recently analysed samples are quantified using a new set of calibration-, internal- and recovery standards, prepared in May 2016. When compared with standards prepared in March 2016, the calibration shows a ten-times higher slope, which is related to an error during standards preparation.

This error in standards is uncovered based on the comparison of multiple check of Standard 8 and of reference filter extracts prepared using an internal standard from March and May (old and new). Both are quantified using the old calibration based on solutions prepared in March. The comparison shows a relatively constant factor between the results. The factor is different for reference filter (RF) and for standard 8, as for both a different amount of internal standard is used. This suggests that a false concentration of the internal standard is the reason for the false results. The results obtained with the newer and wrongly prepared standard set are corrected by the average factor obtained over all four compounds (correction factor) of 6.8. Details can be found in Table 43 (Annex). For the presented results in Figure 16 and the corresponding Table 29 and Table 30 already the corrected values are shown.

3. PAH determination in combustion samples

The combustion samples were collected in 2007. The sampling is described in [44]. Two different small scale combustion stoves are used. One is a 6.5 kW, simple, manually operated log wood device (S1) and one a 10 kW manually loaded stove with an automatic primary and secondary air supply regulation (S2). Spruce logs, beech logs and commercial softwood briquettes are used as fuels. The measurements last for two or three full-load cycles including the start-up phase. The particulate matter (PM10) is collected on quartz fibre filters with a time-resolution of 5 min. Additionally gas emission monitoring (O_2, CO_2, CO, NO_x, VOCs) is conducted continuously. Table 31 provides basic parameters regarding sampling. The diameter of the loaded area of the filters is 3.5 cm. Organic and element carbon values are available from earlier measurements. Due to previous analyses only limited filter area, differing from filter to filter is available and the entire back-up sample is used for the PAH measurements. The used filter areas and the remaining particulate matter mass can be found in Table 45 (Annex).

Table 31: Sampling parameters for combustion samples and name of the different combustion tests

	Stove	Fuel type	Total Fuel [kg]	Loadings	Sampling time [min]	Filter (Number)
B1	S1	Beech	3.1	2	80	C5-C20 (n=16)
S1		Spruce	4.6	3	85	C21-C37 (n=17)
B2a	S2	Beech	3.9	2	90	C40-C57 (n=18)
B2b		Beech	4.0	2	80	C58-C73 (n=16)
R2a		Softwood Briquettes	4.1	2	90	C74-C91 (n=18)
R2b		Softwood Briquettes	4.0	2	95	C92-C110 (n=19)
R2c		Softwood Briquettes**	6.0	3	110	C111-C122, 56-65 (n=22)

** sampling during first and third stove loading

3.1. Qualitative evaluation of lighter PAHs and DahA signals in the matrices of combustion samples

Due to the complex matrix it is difficult to assign the PAHs Ace, Acy Flu and DahA in the combustion samples. To account for a possible shift of retention times due to matrix effects, or to point to other compounds also present within the sample a spiking experiment is conducted. Thus the sample C26 is spiked with 0,4 µL of a solution with about 49 µg/mL of PAH mixture. In Table 32 the retention times of standards are listed for the problematic compounds. In Figure 17 the chromatograms with and without spiking for the four compounds are shown. In the spiked samples a clear peak is visible in the areas where a compound peak (Ace, Acy Flu and DahA) should appear whereas in the unspiked samples almost no peak can be seen there. The peaks related to the substances are shaded in yellow. For clarification the chromatograms of unspiked samples are scaled higher, than those of the spiked sample.

Table 32: Retention times for Ace, Acy, Flu and DahA based on the standards

	Retention time
Ace	9.94
Acy	10.24
Flu	11.24
DahA	25.35

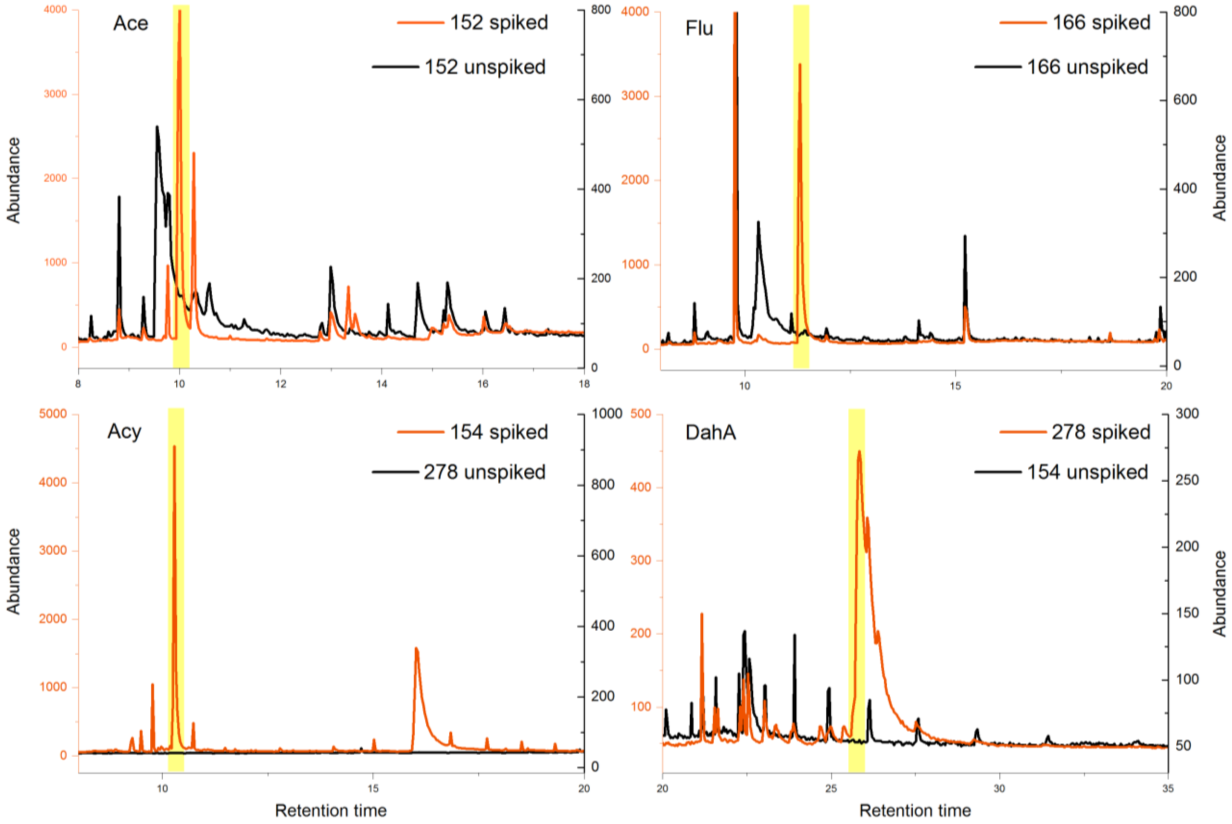

Figure 17: Chromatograms of spiked and unspiked C26 sample of Ace, Acy, Flu and DahA

The spiking experiment shows that no shift of retention times was observed, but other compounds are present. For their integration and evaluation an additional data base is required, but this is not done within this thesis.

3.2. Results

In the annex the values of all PAH measurements including other previous determined gas data, particulate matter and carbon concentrations [43] can be found (Table 46, Table 47, Table 48, Table 49, Table 50, Table 51, Table 52).

The whole B2a series was measured earlier [44]. The values are therefore marked in blue. Some samples in B2a and R2a are marked in red as the preparation of these samples took place already a year ago, and the samples were stored as extracts in the freezer in screw vials and were only analysed now.

3.2.1. Total PAH concentrations observed during different combustion series

In Table 23 the average total PAH (n=9 compounds detected) concentration for each series is shown (Table 33). For green beech logs, for yellow spruce logs and for brown softwood briquettes were used as fuel. Additionally, 1 stands for stove 1 and 2 for stove 2 (Table 31). The PAH analyses for series B2a were conducted a year before (shaded in green-grey). In case of series R2c (shade in brown-white) the stove is re-loaded two times (three full burning cycles), but sampling and analyses are conducted only during the first and third cycle. A direct comparison with other series is therefore not possible.

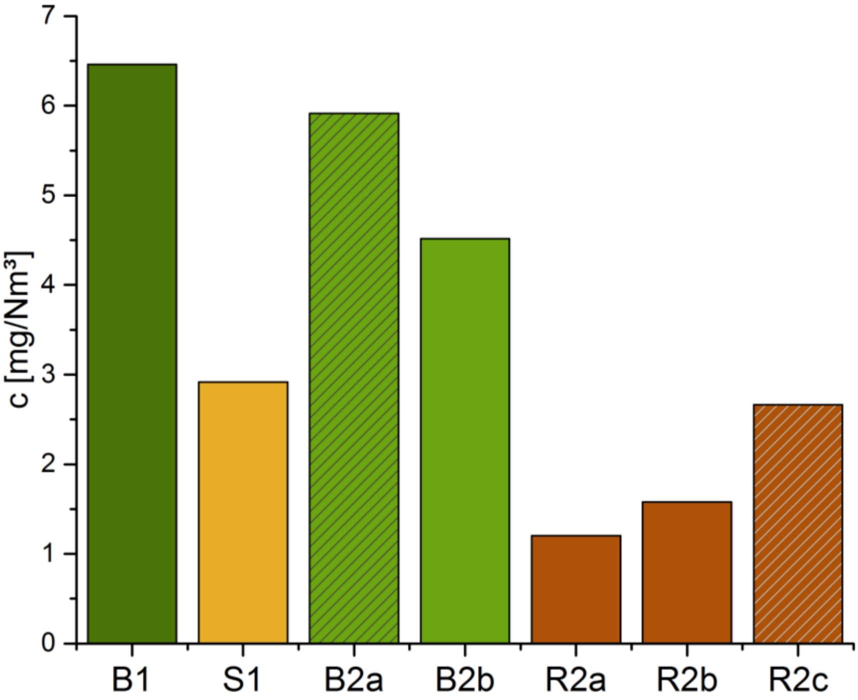

Figure 18: Total PAH concentration for each series where green is beech, yellow is spruce and brown are softwood briquettes. Additionally, 1 stands for stove 1 and 2 for stove 2

In general, beech logs show the highest emissions. A combustion with spruce logs results in more than 50% lower PAH concentrations, than for beech. Softwood briquettes show the lowest PAH concentrations, around one fourth of beech emissions are observed for the same stove. Comparing the first and the second heating system, the total PAH concentration for beech (the only fuel burned in both systems) is lower for stove 2. The difference is about 0.5 mg/Nm³ between B1 and B2a and about 2 mg/Nm³ between B1 and B2b.

3.2.2. Concentrations of single PAHs in the flue gas of different combustion experiments

The total concentration (average over all samples) of each PAH in particulate matter for each series are shown in Table 33 . The flue gas volumes are converted to norm cubic meters (Nm³) for 0°C and 1atm.

Table 33: Total PAH concentration of each series and total concentration of each PAH in each series

	mg/Nm³														
	Naph	Acy	Ace	Flu	Phe	Ant	Fla	Py	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA	Total
B1	n.a.	<LOQ	<LOQ	<LOQ	0.103	0.027	2.126	2.021	0.578	0.495	0.350	0.361	0.390	<LOQ	6.459
S1	n.a.	<LOQ	<LOQ	<LOQ	0.037	<LOQ	0.705	0.641	0.310	0.421	0.206	0.282	0.230	0.087	2.919
B2a	0.081	0.093	0.099	0.096	1.144	0.162	0.629	1.452	0.765	0.366	0.354	0.086	0.356	0.242	5.916
B2b	n.a.	<LOQ	<LOQ	<LOQ	0.605	0.050	1.236	1.060	0.443	0.425	0.243	0.260	0.200	<LOQ	4.518
R2a	n.a.	<LOQ	<LOQ	<LOQ	0.189	0.004	0.312	0.277	0.123	0.128	0.037	0.088	0.046	<LOQ	1.201
R2b	n.a.	<LOQ	<LOQ	<LOQ	0.282	0.067	0.499	0.438	0.085	0.082	0.037	0.035	0.056	<LOQ	1.580
R2c	n.a.	<LOQ	<LOQ	<LOQ	0.710	0.056	0.649	0.571	0.183	0.178	0.062	0.149	0.105	<LOQ	2.664

In Figure 19 the distribution of the total PAH concentration in particulate matter for each series between the single PAHs is shown.

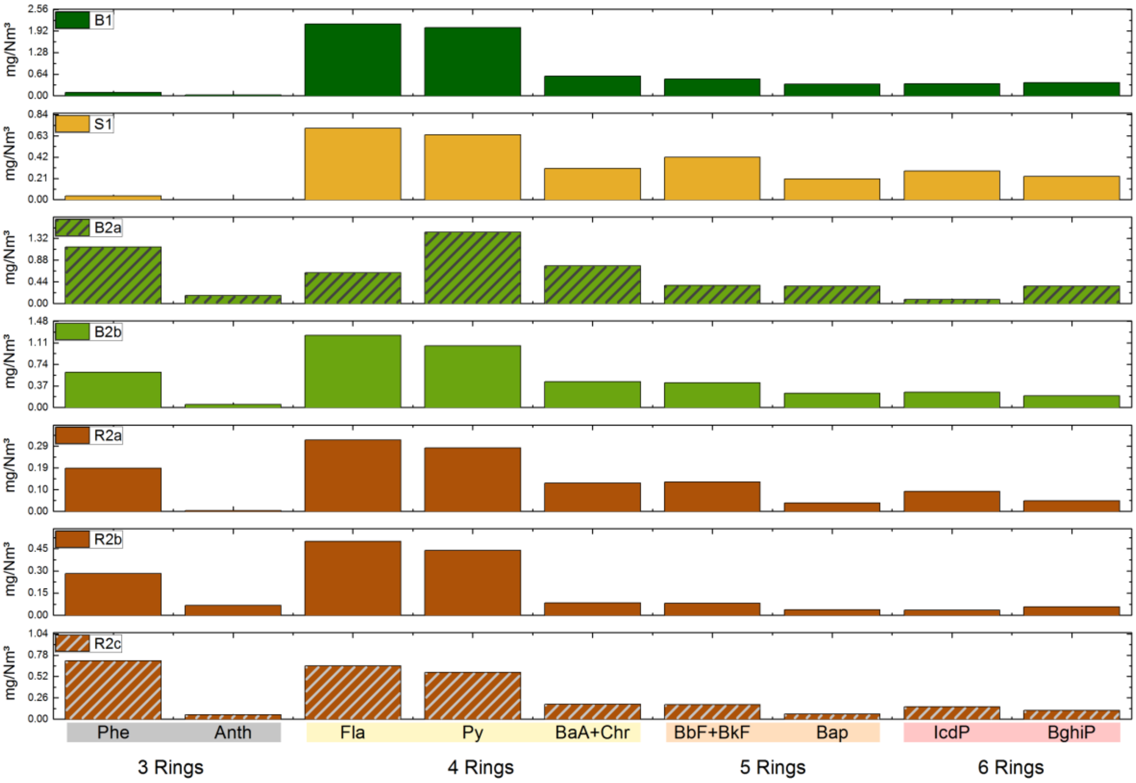

Figure 19: Concentration of each PAH for each series where green is beech, yellow is spruce and brown are softwood briquettes. Additionally, 1 stands for stove 1 and 2 for stove 2

For stove 1 Fla and Py shows generally the highest concentrations. These two PAHs are also the highest for most series of stove 2. Only in R2c Phe is higher, which however originates mainly from the emissions formed after the second stove loading. Interestingly, although Phe is the third highest PAHs for stove 2, it is parallel the lowest detected PAH for stove 1. The concentration of lighter PAHs (Phe, Fla, Py) in the analysed particulate matter is higher than the concentration of heavier PAHs, which suggests that a condensation of gaseous compounds occurs on particle surfaces. Based on another study characterising the emission of birch wood combustion on particles <2.5 µm 70% of the mass of PAH originated from Flu, Phe, Ant, Fla and Py. [45] Another study of the combustion of birch shows that they account for 59% of the total PAH emissions [46]. In both studies both particulate and semivolatile PAHs are sampled in the dilution tunnel. According to [46] most PAHs are volatile where on average 83% of all PAHs are found in PUF (Polyurethane foam), which is used for the sampling of semivolatile PAHs. In a correlated study [47] the distribution between gas and particulate phase for the same set-up is investigated. BghiP, IcdP, BaP, BbF, BkF, Chr and BaA are always found particulate bound and the distribution of Py, Fla, Ant, Phe and Flu is influenced by the sampling conditions especially the temperature. In our analysis, where only the particulate phase in the cold flue gas is sampled, these lighter PAHs (Flu, Phe, Ant, Fla and Py), which are less likely associated to particles, contribute from 47% (S1) to 81 % (R2b) of the total PAHs. In Figure 20 the percentage of each PAH of the total PAH concentration in mg/Nm³ for each series is shown to illustrate the distribution of the PAHs.

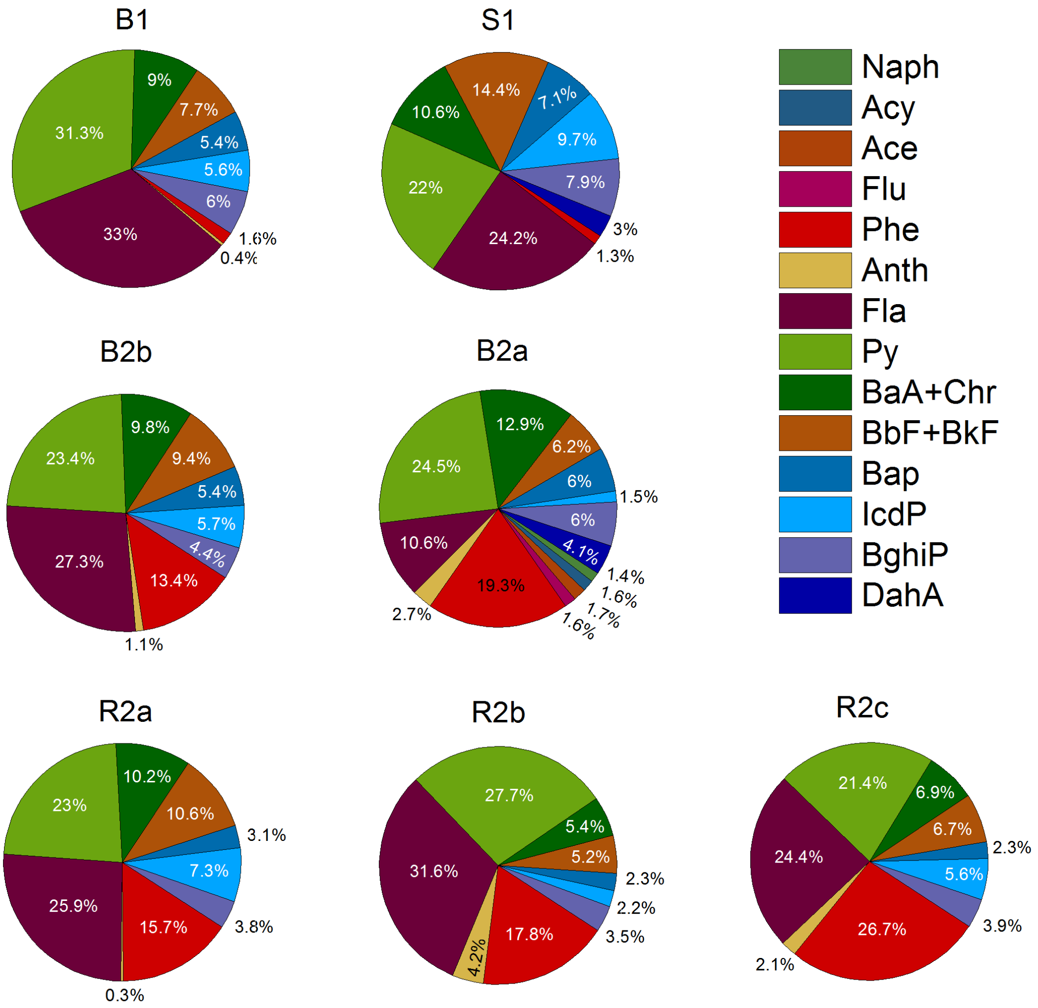

Figure 20: Percentage of each PAH of total PAH concentration for each series

3.2.3. Spearman's Correlations between different PAHs itself, their sum and other measured parameters

Spearman correlation matrices between different PAHs as well related to their sum are calculated. The Spearman correlation is used as a normality test (Kolmogorov-Smirnov) showed that normality of the data has to be rejected. All series are considered together. A two-tailed test of significance is performed and pairs where the correlation is significant at a 0.05 level are marked in purple in Table 34.

In Table 34 the correlation matrix of all PAHs with each other is shown. Naph, Acy, Ace and Flu are only measured for one series (C40-C57) thus the correlation coefficients are not representative for the whole data set. The correlations within one series are strong and significant, but especially Acy is not correlating with the sum of all PAHs in the series or other PAHs except Naph, Ace, Flu and Phe. The main possible reason for that is that those compounds are mostly related to gas phase and their presence in the particulate phase is related mostly with conditions favouring the condensation of semi-volatiles on particle surfaces.

Looking at the other PAHs a significant correlation between all compounds, but DahA and the sum of all PAHs can be found. A reason why DahA does not show correlation may be the low concentrations of this PAH in the samples and thus a limited number of values laying over the quantification limit. Nevertheless, a significant correlation between DahA and all PAHs related mostly to the particle phase is seen.

In general, all PAHs correlate with each other. Only Ant has no correlation with the majority of PAH. The low concentration and with that connected limited number of values could be an explanation for it. The available number of values for the specific compound or group can be found in the first column of Table 34, Table 35 and Table 36.

Table 34: Correlations matrix of PAHs combined for all series with each other (significantly correlated pairs are marked in purple)

	Naph	Acy	Ace	Flu	Phe	Ant	Fla	Py	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA	Sum
Naph (n=12)	1														
Acy (n=12)	0.664	1													
Ace (n=12)	0.972	0.755	1												
Flu (n=12)	0.993	0.720	0.986	1											
Phe (n=105)	0.692	0.210	0.566	0.657	1										
Ant (n=38)	0.860	0.489	0.832	0.839	0.417	1									
Fla (n=124)	0.699	0.252	0.580	0.678	0.642	0.147	1								
Py (n=121)	0.678	0.209	0.601	0.664	0.650	0.201	0.946	1							
BaA+Chr (n=116)	0.803	0.252	0.726	0.768	0.398	0.428	0.661	0.726	1						
BbF+BkF (n=107)	0.895	0.356	0.825	0.874	0.495	0.236	0.580	0.645	0.901	1					
BaP (n=60)	0.783	0.272	0.706	0.769	0.573	0.309	0.745	0.818	0.944	0.956	1				
IcdP (n=75)	0.944	0.517	0.867	0.909	0.573	0.139	0.818	0.759	0.699	0.819	0.645	1			
BghiP (n=63)	0.797	0.301	0.720	0.783	0.556	0.421	0.685	0.768	0.881	0.933	0.875	0.740	1		
DahA (n=16)	0.986	0.622	0.958	0.972	0.476	0.825	0.457	0.500	0.720	0.619	0.638	0.500	0.663	1	
Sum (n=124)	0.748	0.314	0.636	0.727	0.732	0.505	0.838	0.878	0.861	0.820	0.931	0.740	0.874	0.559	1

The picture is supported when looking at the correlation of PAHs grouped by number of rings. A significant correlation between all groups can be found (Table 35), although the correlation between 3-ring PAHs and 5-or 6-ring PAHs is weaker.

Table 35: Correlations matrix of PAHs grouped by number of rings combined for all series with each other (significantly correlated pairs are marked in purple)

	Sum Ring 3	Sum Ring 4	Sum Ring 5	Sum Ring 6
Sum Ring 3 (n=105)	1			
Sum Ring 4 (n=124)	0.597	1		
Sum Ring 5 (n=107)	0.383	0.731	1	
Sum Ring 6 (n=79)	0.414	0.721	0.894	1

The good agreement between BaP data and the sum of PAHs, as well as between ring-number sorted groups makes it possible to limit the further considerations to those subcategories.

In Table 36 the correlation of the PAHs with main combustion parameters: CO_2, O_2, CO, VOC, PM10, EC and OC is checked. The correlation between those parameters and PAHs groupd by number of rings and the sum of PAHs are analysed. All parameters except CO correlate significantly with the sum of PAHs. For O_2 all significant correlations are negative. 5-ring PAHs correlate significantly with all measured parameter. 3-ring PAHs are correlated with every parameter excluding CO. 6-ring-PAHs also show good correlation for nearly all parameter except CO_2 and O_2. 3-ring- PAHs are additionally not correlated to CO. For VOC, PM_{10}, EC and OC a correlation for all groups is existing. The significance level is 0.05 so there is a 5% possibility of getting a correlation by chance. Generally the correlation matrices and the evaluation of significantly correlated pairs need careful interpretation. In Tables 35 and 36 most of the calculations are based on a data set of more than 100 samples. Thus rather low correlation coefficients are already marked as significant. Correlation plots will help further evaluations.

Table 36: Correlations matrix of the sum of PAHs sorted by rings combined for all series with CO, VOC, PM10, EC and OC (significantly correlated pairs are marked in purple)

	Sum Ring 3	Sum Ring 4	Sum Ring 5	Sum Ring 6	Sum of all PAHs
O_2 (n=126)	-0.077	-0.221	-0.276	-0.174	-0.214
CO_2 (n=126)	0.068	0.216	0.294	0.176	0.215
CO (n=127)	0.137	0.108	0.217	0.293	0.119
VOC (n=127)	0.228	0.285	0.393	0.475	0.313
PM_{10} (n=129)	0.635	0.809	0.593	0.522	0.834
EC (n=110)	0.303	0.595	0.322	0.233	0.551
OC (n=110)	0.612	0.745	0.616	0.474	0.813

Further the time resolved concentrations will be considered.

3.2.4. Combustion phases

The combustion process can be divided into different phases. The discrimination can be based upon different factors, like CO_2, CO and T like reported in [48]. If general combination of temperature and several emissions is taken into consideration the combustion of log wood can basically be separated into three main phases: start-up, steady-operation and burn-out. Often it is difficult to clearly separate the different phases due to a fluent transition from one phase to another. Usually in the start-up phase the temperature is still quite low and the CO_2-concentration is rising due to the increasing rate of fuel conversion. The combustion in this phase is not yet stable and thus high CO and Volatile organic compounds (VOC) concentrations are prevailing. [48]

In the steady-operation phase the combustion is stabilized. A high CO_2-concentration as much wood is burned and low CO- and VOCs emissions are typical for this part of the combustion. Occasional a local lack of oxygen due to the position of the logs can disturb the combustion and lead to an increased emission of products of incomplete combustion like CO, VOCs and particles.

The combustion ends with the burn-out phase. The remaining fuel is burnt, and as its mass decreases the flames disappear and the temperature decreases, which forces the CO_2- decrease. Increasing CO and VOC-emissions can be observed.

If the combustion system is re-loaded, the opening of firing chamber and addition of cold wood logs during the combustion shortly cools down the oven and increases the amount of CO-and VOCs in the flue gas. [48]

In this work, re-loading of the stove happened once, when the CO_2 concentration decreased under 3%. In case of R2c two re-loadings took place, but samples were collected only during the combustion of the first and third loading.

Adjusted to the experiment set-up, combustion cycles investigated in this work are divided in six phases (one start phase (SUP), two main phases (SOP1, SOP2), two end phases (BOP1, BOP2) and a re-loading phase (RLP)). For R2c the re-loading phase is not recorded and also SOP2 and BOP2 are not measured but SOP3 and BOP3 (after second re-loading) are sampled. RLP is always determined according to the noted re-loading times and comprise one sample. The last sample collected before RLP is described as BOP1.

The definition of the combustion phases is based upon combination of temperature and CO_2-concentration, whereas the temperature is taken as the “first” (determining) parameter. SOP1 starts when temperature is >100% of the mean temperature for the first part. For the mean temperature of the first part the temperatures (MT1) from the beginning until the start of BOP1 are considered. SOP2 ends when the temperature is ≤ 100% of the mean temperature of the second part (MT2). For the mean temperature of the second part all values starting from SOP2 to the end of the combustion are taken.

If the phases cannot be determined by temperature, the CO_2-concentration is used as a second parameter. In such case SOP1 starts when the CO_2 concentration is > 95% of the mean CO_2-concentration of the first phase (MC1; beginning till end of SOP1) and SOP2 ends when the CO_2 concentration is ≤ 95% of the mean CO_2-concentration of the second phase (MC2; start of SOP2 until end). The parameters of the phase determination are summarised in Table 37.

Table 37: Parameters for division into combustion phases

	Start	End
SUP	Start of sampling	1.T>100% MT1 (2.CO_2>95% MC1)
SOP1	T>100% MT1 (2.CO_2>95% CT1)	When BOP1 starts
BOP1	Sample before RLP	
RLP	Loading of wood according to notes (CO_2 < 3% (online-monitoring))	
SOP2	Begins with sample after RLP	1.T≤100% MT2 (2.CO_2≤ 95% MC2)
BOP2	1.T≤100% MT2 (2.CO_2≤95% CT2)	End of sampling

For R2b samples are only taken after a second loading and not after the first loading of wood. SOP3 and BOP3 are therefore defined as SOP2 and BOP2 only that they take place after the second loading.

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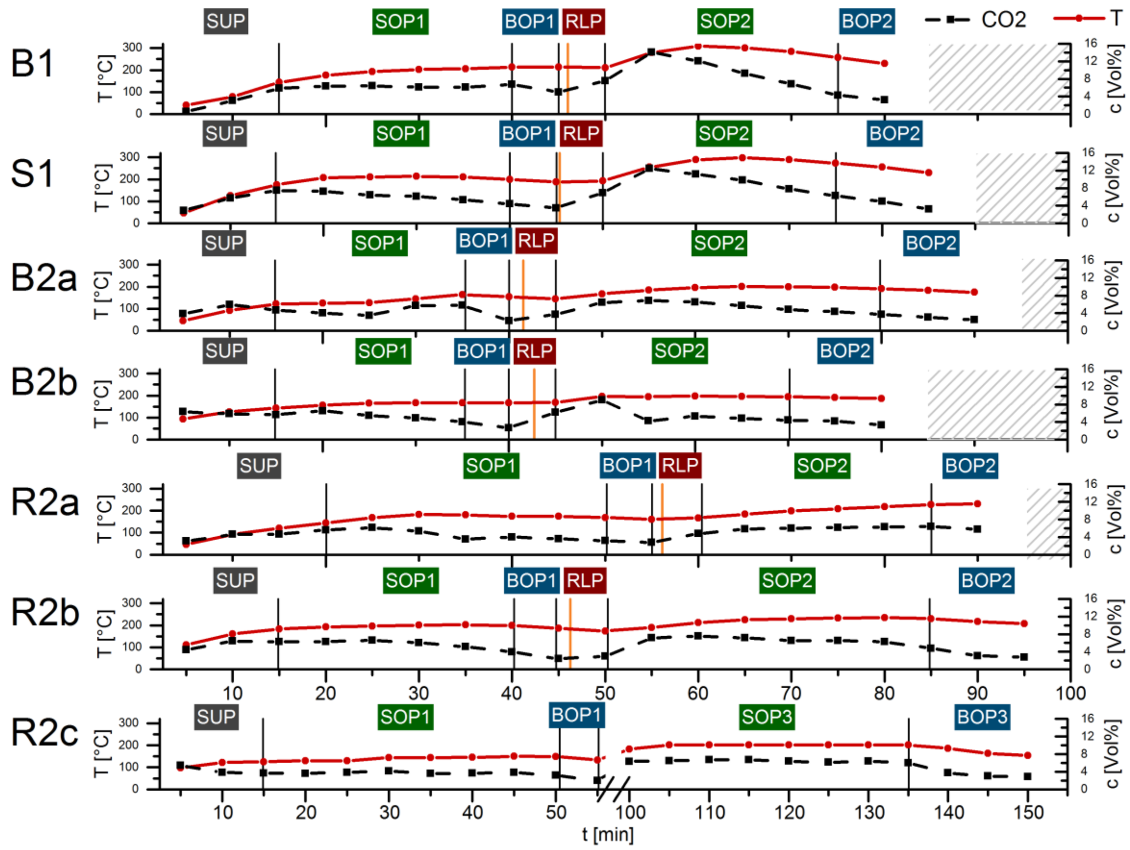

Figure 21: Temperature (red) and CO_2 concentration (black) over time for all series with classification in phases and exact time of reload (orange line)

In Figure 21 the time course of temperature and CO_2-concentration for the different series are shown. The classification in the combustion phases is marked in the graphs too. The time of reload is highlighted with an orange line.

3.2.5. Time resolved concentrations of PAHs in the flue-gas

For the analysis of the time trend of the combustion emissions for each series three figures were chosen. The first graph shows the change of the particulate matter concentration, where the share of OC and EC are shaded. Additional the course of the VOC concentration can be seen. If the scales of both were too different, an additional axis for VOCs was added on the right side (red). The second one shows the course of the total PAH concentration over time. The total concentration is divided in the groups according to the number of rings. In the last one the 5-ring PAHs are closer looked at. BaP, as a marker substance, is given as proportion of total 5-ring PAHS. The pink line represents the limit of quantification. If no data is available for one sample the area was shaded grey. In all graphs the combustion phases are marked and the exact time of reload is shown as a yellow line.

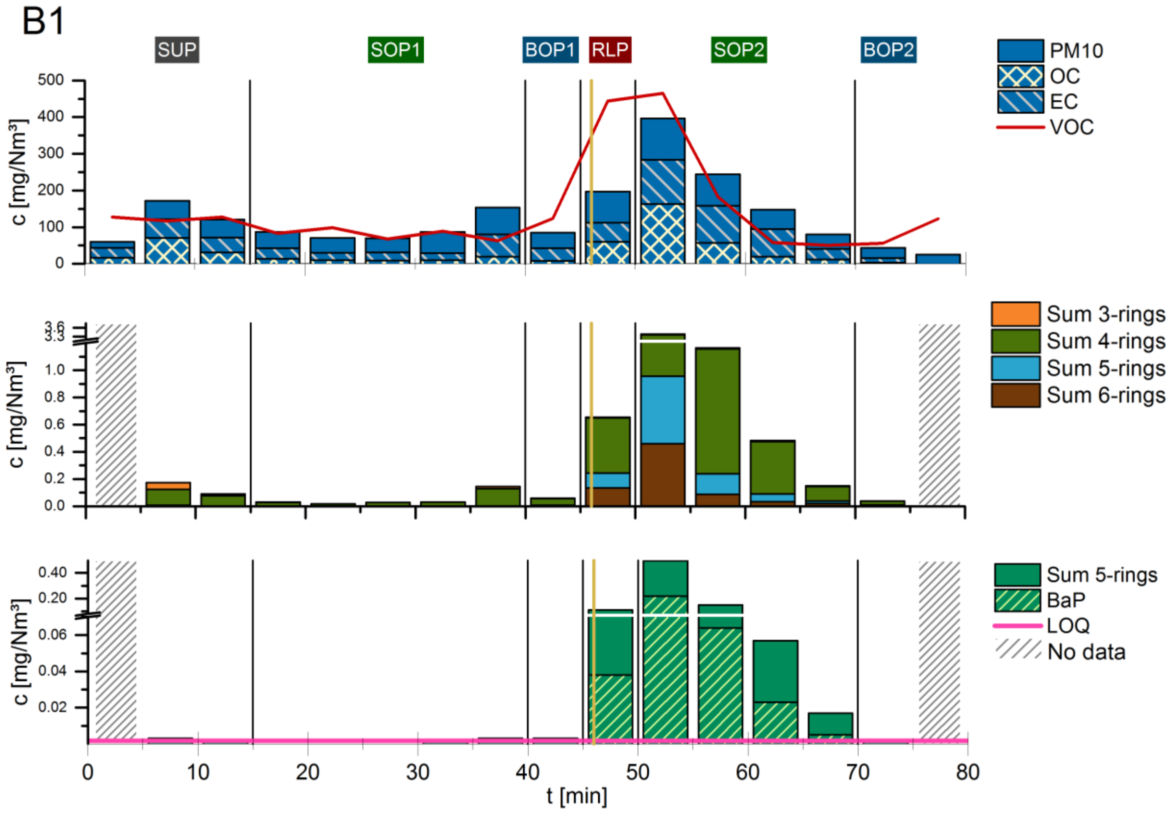

Figure 22: Detailed description of the emissions of B1 over time, where the phases (black) and the exact time of reload (yellow) is marked: Upper graph: VOC and PM10, where the proportions of OC and EC of it are shaded; Middle graph: Emissions of PAHs grouped according to their number of rings (stacked depiction); Lower graph: Sum of 5 ring PAHs where concentration of BaP is shaded including Limit of quantification

In Figure 22 the results for B1 are shown. As expected the emissions vary over time. In general, the course over time for the different PAH groups and other parameters like PM10, OC and EC are similar. In the SUP the emissions show a little peak at 0.17 mg/Nm³. When not differently stated the mentioned concentrations are referring to the sum of all PAHs for the following discussion. During SOP1 the emissions of all plotted components sink, when compared to SUP and then remain constant at about 0.03

mg/Nm³, until the end of the phase, where again an increase can be seen. In BOP1 the emission is at the same level as during SOP1. In the RLP the emissions increase stronger, especially the emission of VOC, which also does not have peaks in SUP and the end of SOP1 and rises again BOP2, increases instantly. For other compounds the emission peak occurs in the beginning of SOP2 with a maximum of 3.4 mg/Nm³ for the sum of PAHs. During SOP2 the emissions gradually decrease. The decline continues in BOP2.

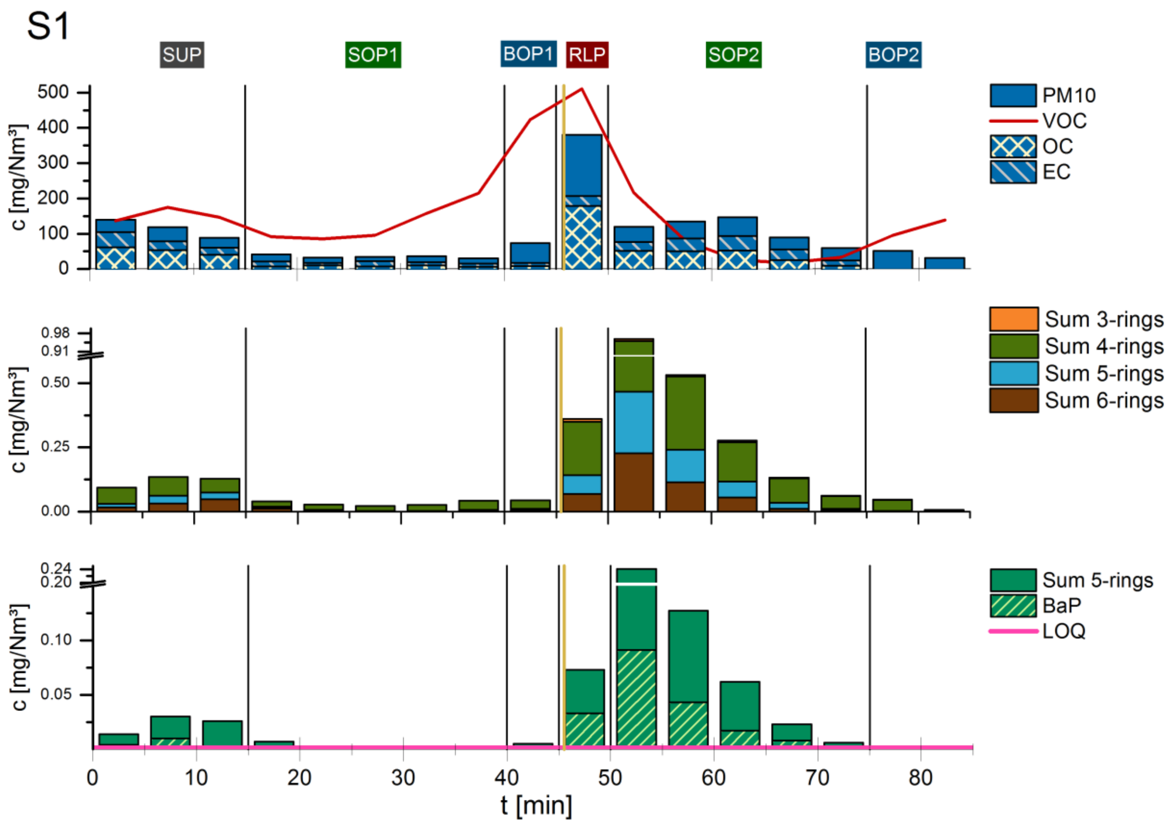

Figure 23: Detailed description of the emissions of S1 over time, where the phases (black) and the exact time of reload (yellow) is marked: Upper graph: VOC and PM10, where the proportions of OC and EC of it are shaded; Middle graph: Emissions of PAHs grouped according to their number of rings (stacked depiction); Lower graph: Sum of 5 ring PAHs where concentration of BaP is shaded including Limit of quantification

The series S1 can be seen in Figure 23. The course resembles B1 with a slightly increasing emission to 0.13 mg/Nm³ in the beginning (SUP) which decreases to a constant level (0.025 mg/Nm³) in SOP1 and then increases after reloading, to gradually decrease again towards the end. The maximal emission of all PAHs is 0.96 mg/Nm³ and thereby only about a third of the one from B1. The peak before BOP1 is missing compared to B1. In S1 the emissions just slightly increase in BOP1. The absolute value’s course is similar at the highest points, but lower in the decreasing phases. In contrast to B1 the course of PM10 and the other compounds varies around RLP as the maximum is for this series not only for VOC but also for the others reached one time interval earlier than the PAH emission does. VOC increases in BOP2 in contrast to the PAH emissions again.

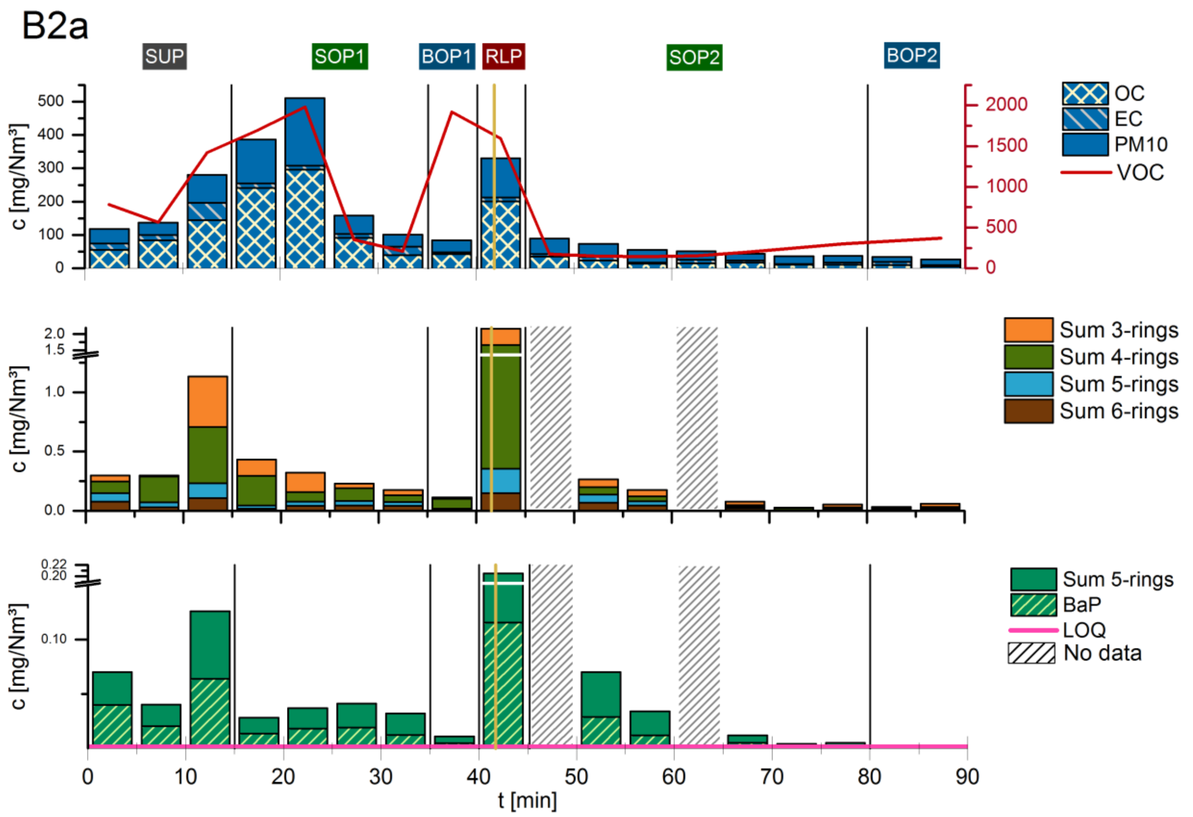

Figure 24: Detailed description of the emissions of B2a over time, where the phases (black) and the exact time of reload (yellow) is marked: Upper graph: VOC and PM10, where the proportions of OC and EC of it are shaded; Middle graph: Emissions of PAHs grouped according to their number of rings (stacked depiction); Lower graph: Sum of 5 ring PAHs where concentration of BaP is shaded including Limit of quantification

In Figure 24 details for series B2a are given. In the first half of the combustion the emissions show a completely different course than in other series. Other than before, the highest values for PM10, OC, EC and VOC are recorded during first stove loading in SOP1 with a maximum of nearly 500 mg/Nm³ for the PM10 emission and also PAHs show with a peak at 1.14 mg/Nm³ a high emission in this series on the border between SUP and SOP1. Although that is usually the case, the PM10 does not reveal the same trend as PAHs during the first loading cycle. While PM10 gradually increases from the beginning and then sinks mid-SOP1, the PAH emission remains constant for the first 10 min and then shows a peak in the end of SUP and decreases gradually during SOP1. After the first two phases both PM10 and PAHs change similarly. In BOP1 the emission remains at the same level as in the end of SOP1. In RLP the emissions of all monitored components increase in case of the sum of PAH to 2.17 mg/Nm³. In SOP2 the concentrations of all monitored parameters sinks and then stays the same towards the end of second combustion cycle. Only VOC increases again in the end.

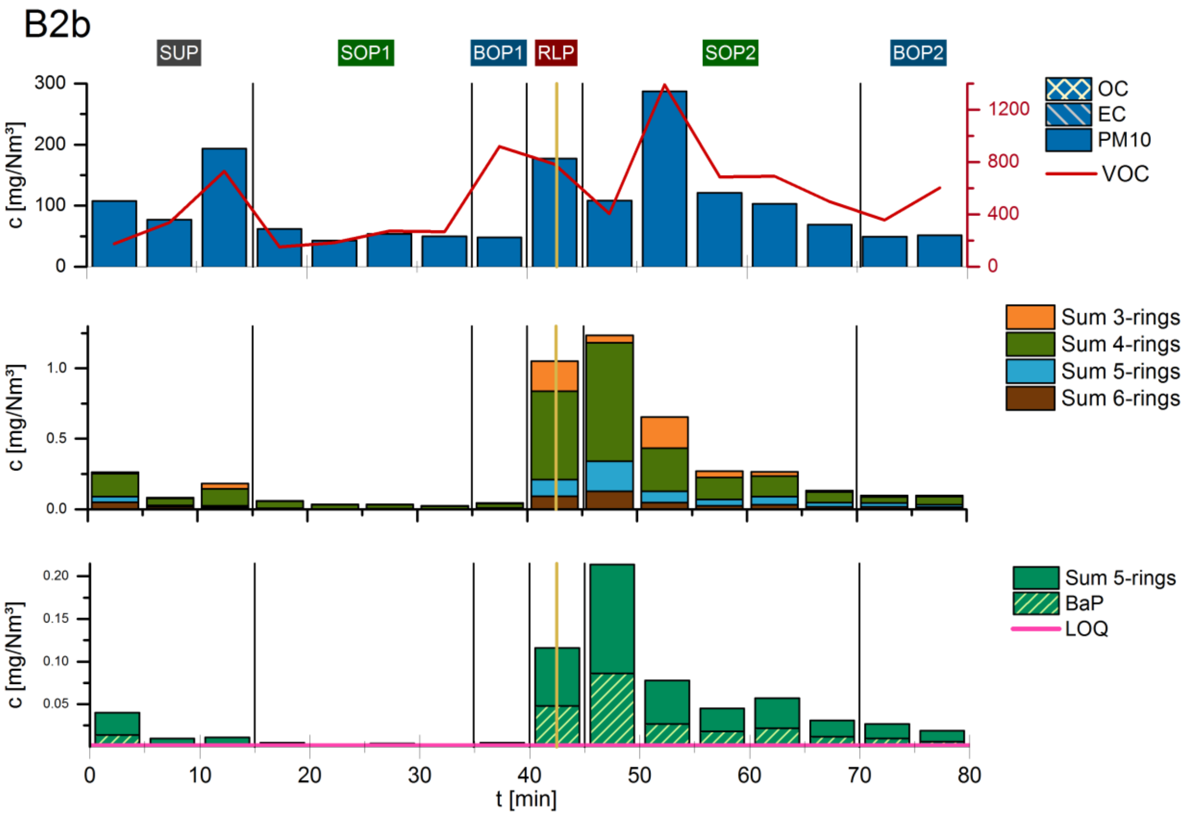

Figure 25: Detailed description of the emissions of B2b over time, where the phases (black) and the exact time of reload (yellow) is marked: Upper graph: VOC and PM10, where the proportions of OC and EC of it are shaded; Middle graph: Emissions of PAHs grouped according to their number of rings (stacked depiction); Lower graph: Sum of 5 ring PAHs where concentration of BaP is shaded including Limit of quantification

Figure 25 shows B2b in detail. For B2b no EC and OC data is available. The course is similar to B1 and S1. In the SUP the emissions are higher with 0.26 to 0.08 mg/Nm³ for the sum of PAHs but quickly sinks to about 0.03 mg/Nm³, with establishing high temperature. During SOP1 the emissions are constant and then increase when fuel is reloaded. The maximum for particulate PAH emissions is observed in the beginning of SOP2 with 1.23 mg/Nm³, followed by a stepwise decrease. The behaviour of PM10 around RLP is untypical as the maximum comes with 10min after RLP very late compared to the other series. VOC also changes differently as it has a local minimum just after RLP. However, for PAH the course over time is unremarkable. Compared to B1 the start-up phase emissions (0.09 -0.17mg/Nm³) are at similar level and the highest emission occurring in RLP (3.4 mg/Nm³) are about a third.

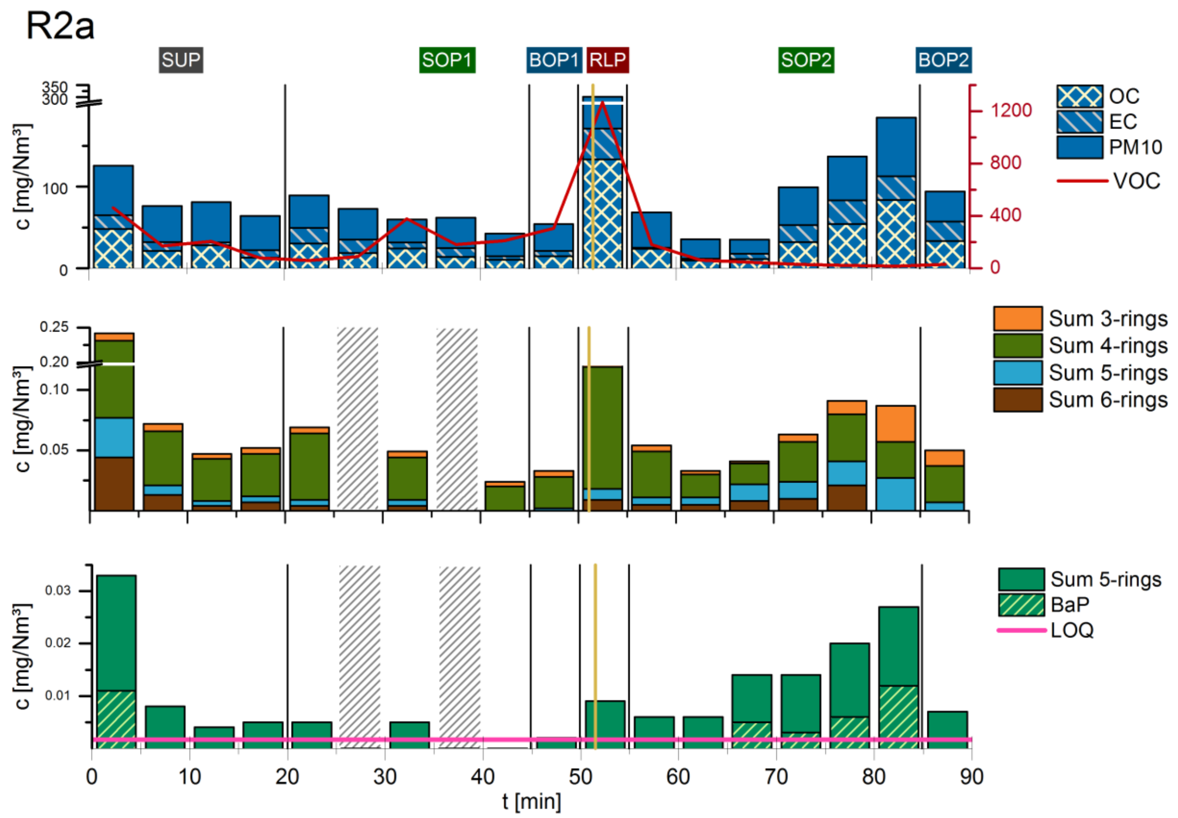

Figure 26: Detailed description of the emissions of R2a over time, where the phases (black) and the exact time of reload (yellow) is marked: Upper graph: VOC and PM10, where the proportions of OC and EC of it are shaded; Middle graph: Emissions of PAHs grouped according to their number of rings (stacked depiction); Lower graph: Sum of 5 ring PAHs where concentration of BaP is shaded including Limit of quantification

R2a is described in Figure 26. The emission in the first five minutes is especially for PAHs high (0.24 mg/Nm³) compared to the concentration in the rest of the course. The emission is even higher than in RLP (0.19 mg/Nm³). Afterward it decreases to a constant level at about 0.05 mg/Nm³ at the end of SUP. During SOP1 and also BOP1 the emission does not change much and stays around 0.05 mg/Nm³. In RLP the emission peaks to 0.19 mg/Nm³ and sinks during SOP2, but after about 65 min the emission increases again and get at around 85 min at the same level (about 0.09 mg/Nm³) as after reload. In BOP2 the concentration falls again. The PM10, OC and EC emissions are behaving in a similar way. For VOC the course over time is close to PAHs but after RLP it sinks and then stays the same until the end of the combustion. Compared to beech combustions the emission trend over time is different especially the broad peak in the end of SOP2 and the high emissions in the beginning are different in this series. However, it has to be noted that when using softwoods briquettes the emission is about a third lower than for beech and especially the emissions around the re-load are about a fifth lower which leads to a less distinctive peak.

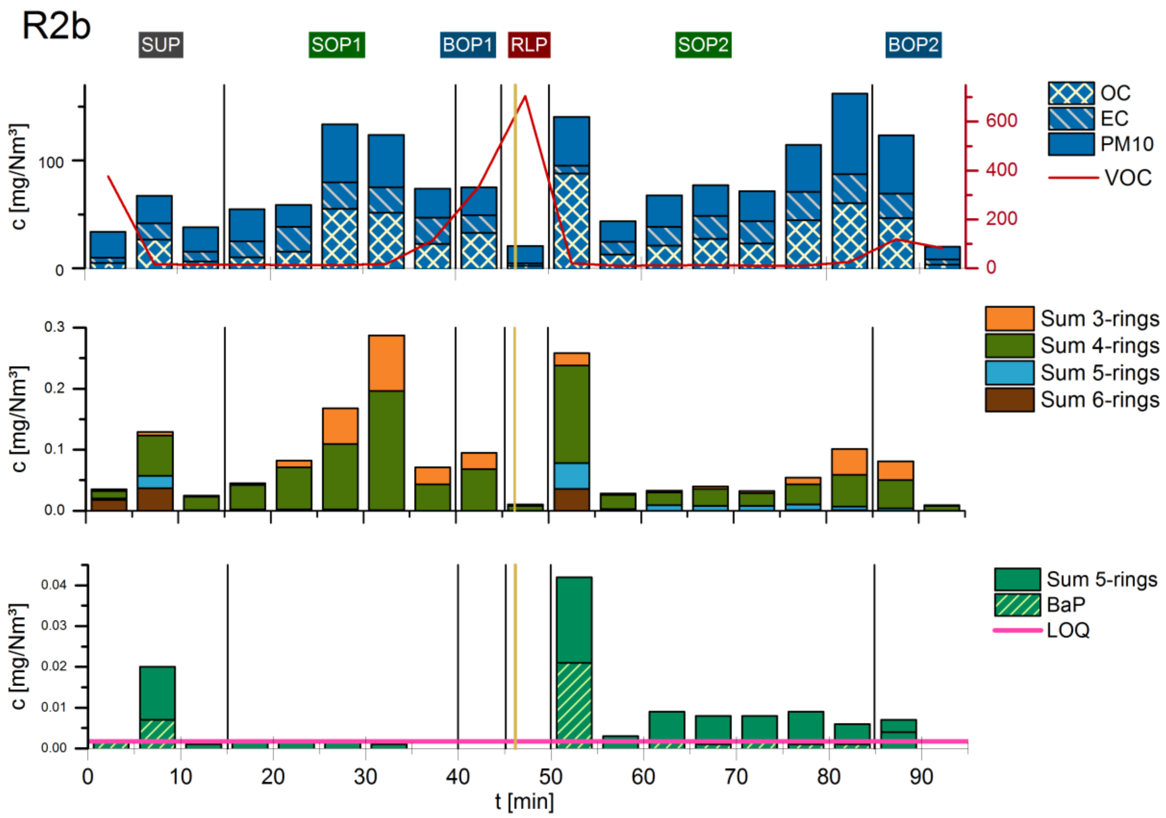

Figure 27: Detailed description of the emissions of R2b over time, where the phases (black) and the exact time of reload (yellow) is marked: Upper graph: VOC and PM10, where the proportions of OC and EC of it are shaded; Middle graph: Emissions of PAHs grouped according to their number of rings (stacked depiction); Lower graph: Sum of 5 ring PAHs where concentration of BaP is shaded including Limit of quantification

In Figure 27 the course of R2b is depicted. The emission during SUP are low and only a small peak (0.13 mg/Nm³) (in comparison to other series) occurs after 5 min. In SOP1 the emissions form a peak with exception of 5-ring and 6-ring PAHs. The sum of PAH is 0.29 mg/Nm³ on the top of the peak which is higher than the emission peak in the beginning of SOP2 with 0.26 mg/Nm³. The following BOP1 still has rather high emissions, while in the RLP the emissions are lower than during other tests. At the beginning of SOP2 the concentration is high, but then sinks. In the end of the phase another peak is visible for PAHs with a lower ring number and also VOC concentrations increases. Compared to R2a the trend of the combustion parameters before the reloading differs, but afterwards the course follows a similar pattern for total PAHs and PM10 emissions and also the absolute emission values are similar.

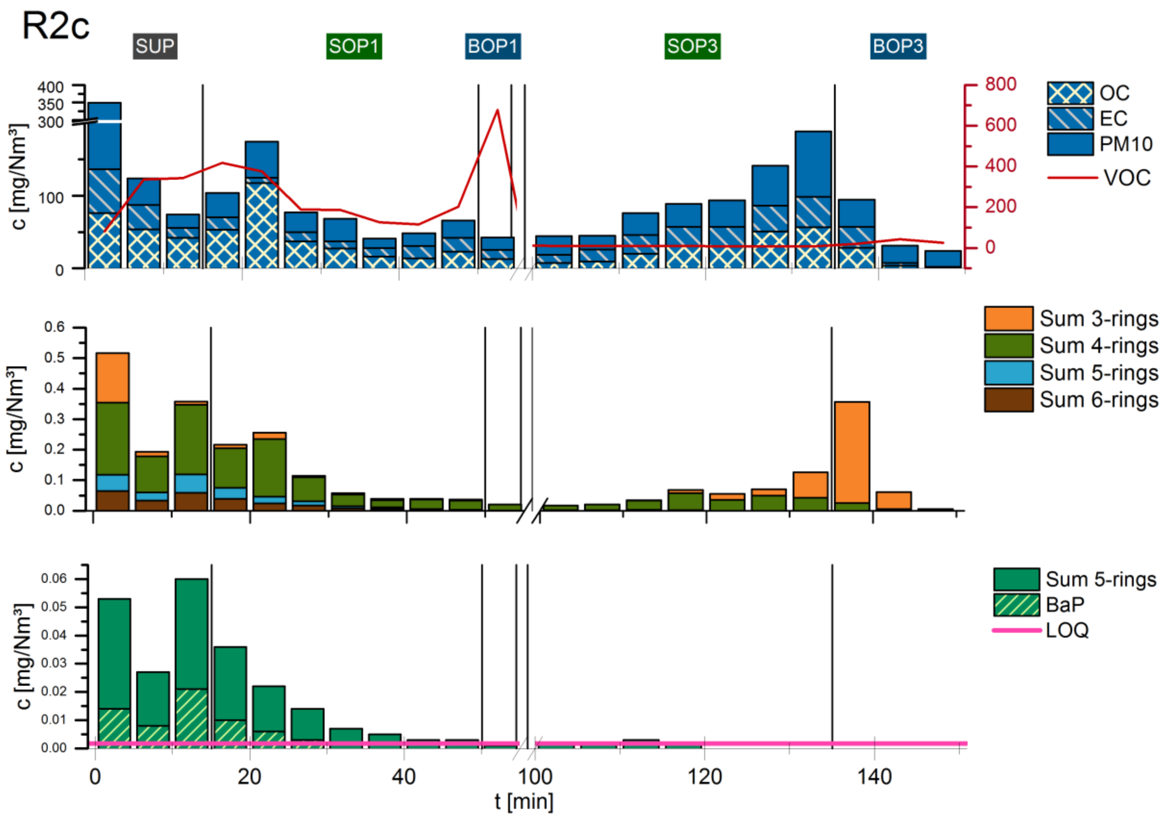

Figure 28: Detailed description of the emissions of R2c over time, where the phases (black) and the exact time of reload (yellow) is marked: Upper graph: VOC and PM10, where the proportions of OC and EC of it are shaded; Middle graph: Emissions of PAHs grouped according to their number of rings (stacked depiction); Lower graph: Sum of 5 ring PAHs where concentration of BaP is shaded including Limit of quantification

Figure 28 describes R2c. For this series second stove loading is not sampled. In SUP the emissions are high with up to 0.51 mg/Nm³ which is noticeably higher than for R2b and R2c in the beginning but with decreasing trend. In SOP1 the emission basically decreases and remains constant when reached 0.04 mg/Nm³ in the end. SOP3 after the second reload shows increasing emissions up to the end of the phase and then starts to sinks after reaching 0.38 mg/Nm³ as a maximum at the border to BOP3. For PAHs mainly lighter PAHs are found after the second re-loading. The SOP1 resembles R2a.

In Table 38 the sum of all PAHs for the different phases for all series are shown.

Table 38: Sum of all PAHs for the phase for all series

	Sum of all PAH [mg/Nm³]					
	SUP	SOP1	BOP1	RLP	SOP2	BOP2
B1	0,263	0,252	0,058	0,656	5,191	0,040
S1	0,354	0,154	0,043	0,361	1,960	0,053
B2a	1,744	1,176	0,111	2,170	0,620	0,096
B2b	0,525	0,152	0,045	1,050	2,553	0,193
R2a	0,413	0,142	0,033	0,196	0,367	0,050
R2b	0,188	0,653	0,095	0,010	0,544	0,090
R2c	1,067	0,760	0,020	-	-	-

In general, the highest emission peak can be seen around re-loading of the stove for all series independent of fuel and stove. The peak shows up either directly in the RLP or at the beginning of SOP2 depending on the exact time of reload as only every five minutes' samples are taken. The SUP either shows decreasing emissions or a small peak after the first sample. In the SOP1 the emissions tend to reach a constant level. Only R2b has a broad peak in the middle of the phase. After the with the reload associated peak the emissions start to sink again. When Briquettes are used as fuel the emissions have a peak at the end of SOP2 while for beech and spruce the emissions keep on decreasing. The course over time is for B1 and S1 similar. The concentration around re-load is yet higher for B1. For the series of stove 2 no uniform course over time can be seen. Looking at the different fuels B1 and B2b are similar but B2a differs. For using briquettes as a fuel no uniform course over time before the with the re-load associated peak. Nevertheless, the concentration of the emission is clearly lower for briquettes. The course over time of PAHs is comparable with PM10 and OC but differs from the course over time of VOC, a precursor of PAHs, and EC, a product of further combustion of PAHs. The choice of fuel and stove has only a minor influence on the change of PAH emission during the combustion. The influence of the combustion conditions is dominant.

4. Conclusion

4.1. Methodological part

The influence of the solvent on the extraction efficiency depends on the matrix. The extraction efficiency does not vary more than the variation of multiple injections for the lower loaded filter excluding Py, Fla and BaA+Chr. However, when AcH is excluded the variation is within the variation of multiple injections for these compounds again. Smaller PAHs mainly gaseous PAHs are seemingly especially efficiently extractable with AcH. The results for all compounds for filter 1 (higher loading) stay within the overall expanded uncertainty, but vary more than the standard deviation with exception of DahA.

The variation between the different solvent combinations is larger than the overall expanded uncertainty, which represents the variation of BaP measurements with various methods over eighteen laboratories across Europe, only for Fla, BbF+BkF, IcdP and BghiP using cHex to extract the reference filter. The choice of solvent influences the extraction efficiency when matrixes with higher soot and particulate matter are present especially cHex is apparently less efficient.

The differences between the application of centrifugation and the syringe filter for removal of particles are within the standard deviation of the measurement for nearly all compounds. Only BghiP for the two higher concentrated filters and BaP for the lowest concentrated filter vary more than the standard deviation. Nevertheless, the absolute difference between them is low probably because the sample's concentration is very close to the detection limit. For BghiP the usage of a syringe filter leads to higher concentrations for the higher concentrated filters (Filter A+ Filter B) of about 40-70%. The additional amount could originate from the syringe filter itself. A further investigation is needed. Except for BghiP a syringe filter can be used for the measurement of all other PAHs.

The long term stability of filters is checked with ambient and emission filters. For the ambient filters the variation is within or slightly above the standard deviation for BaP and for BbF+BkF (Z1+Z2) and BghiP (Z1) respectively. IcdP is always varying more than the standard deviation with the more recent measurement showing higher concentrations. Still, the reasonably comparable and the relative error is mostly smaller than 35%. No indications of a decomposition of the analytes collected on the ambient air filters during long term storage (several years) in a freezer could be found.

The emission filters stay within the standard deviation for BghiP and BaP (except E3). The other compounds vary more but again the more recently analysed filters give for the most part higher values. For the emission filter it is important to note that beside the change of the quantification method between 2007 and 2016 additionally a problem with the calibration occurred during the recent measurements and therefore a correction factor had to be applied. Considering this again a decomposition of the PAHs cannot be confirmed.

4.2. Combustion samples

The sum of PAH for each series is the highest for beech (about 5.5 mg/Nm^3) and the lowest for softwood briquettes (about 1.5 mg/Nm^3). For beech series with both heating systems are available and therefore it can be seen that stove 2 emits less PAHs than stove 1. The choice of fuel though has a crucial impact on the emission.

The most abundant PAHs for stove 1 and almost all series for stove 2 are Fla and Py. The exception is R2c where Phe is higher. A difference between the two stoves can be seen in the Phe emission which is the third most abundant PAH for stove 2 but is the lowest for stove 1. In general, lighter PAHs (Phe, Fla, Py) are higher concentrated in the particulate matter than the heavier ones. The lighter ones contribute from 47% (S1) to 81% (R2b) to the total PAHs.

The calculation of the Spearman correlation shows a significant correlation between the sum of all PAHs and the single compounds excluding Acy and DahA, which is connected to its low concentration and with that restricted number of usable values. Generally, all PAHs excluding Ant, which is low concentrated too, correlate significantly with each other. Additionally, when PAHs are grouped by ring number a correlation between all groups can be found. Furthermore, VOC, PM_{10}, EC and OC correlate with each group. The correlation of O_2, CO_2 and CO with the grouped PAHs is tested too but the correlation is not significant for all grouped PAHs.

The combustion of log wood can be divided into three main phases: start-up, steady-operation and burn out phase. In our experiments the combustion cycles can be separated in six phases including one start-up phase (SUP), two main phases SOP1, SOP2), two end phases (BOP1, BOP2) and a re-loading phase (RLP). RLP is defined by the time of re-load and BOP1 of the sample just before it. The remaining phases were separated based on temperature and CO_2-concentration, where temperature is considered first. SOP1 starts when temperature is >100% of MT1. SOP2 lasts until the temperature is ≤ 100% of MT2. If the temperature is not applicable to separate into phases the CO_2 concentration is considered, where SOP1 starts when MC1 > 95% and SOP2 ends when MC2 is ≤ 95%.

Looking at the course over time a dominant high peak starting in RLP over about 15 min with a maximum right after RLP is the most outstanding feature of all experiments or all fuels and both stoves. The reload of the stove is responsible for this peak. A second but way lower peak right after the start of the combustion in SUP can also be seen for all courses. If the combustion is stable and optimal like mostly in SOP1 the emissions are low and constant. After the reload in SOP2 and finally in BOP2 a difference between log wood and softwood briquettes as fuels is notable as for log wood the concentration generally constantly decreases but for softwood briquettes a small peak in the end is visible. Between stove 1 and stove 2 no difference in the course over time can be found. In general, the trend over time for PM10 and OC is similar, but differs from VOC and EC.

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6. Annex

Table 39: PM10, organic carbon and elemental carbon values for filter 1 and filter 2

	PM10 [µg/cm²]	OC [µg/cm²]	EC [µg/cm²]
Filter 1	317	123	18.4
Filter 2	146	33.7	6.01

Table 40: PM10, organic carbon and elemental carbon values for filter A, filter B and filter C

	PM10 [µg/mm²]	OC [µg/mm²]	EC[µg/mm²]
Filter A	1.30	0.54	0.30
Filter B	5.84	2.23	0.81
Filter C	7.34	2.43	1.93

Table 41: PAH concentrations on three differently loaded filters including standard deviation based multiple injections

	A [ng/mm²]	**B [ng/mm²]**	**C [ng/mm²]**
Py centrifuged	0.058±0,008	0.946±0.142	0.509±0.076
Py filtered	0.046±0.007	0.993±0.149	0.492±0.074
Fla centrifuged	<LOQ	0.859±0.146	0.460±0.078
Fla filtered	<LOQ	0.819±0.139	0.436±0.074
BaA+Chr centrifuged	0.044±0.006	0.905±0.118	0.439±0.057
BaA+Chr filtered	0.042±0.005	0.891±0.116	0.350±0.046
BbF+BkF centrifuged	0.049±0.010	0.627±0.125	0.344±0.069
BbF+BkF filtered	0.051±0.010	0.760±0.152	0.294±0.059
BaP centrifuged	0.007±0.001	0.174±0.026	0.078±0.012
BaP filtered	0.005±0.001	0.144±0.022	0.094±0.014
IcdP centrifuged	0.044±0.007	0.408±0.065	0.202±0.032
IcdP filtered	0.044±0.007	0.469±0.075	0.192±0.031
BghiP centrifuged	0.033±0.007	0.278±0.056	0.124±0.025
BghiP filtered	0.032±0.006	0.487±0.097	0.308±0.062
DahA centrifuged	0.033±0.007	0.106±0.023	0.069±0.015
DahA filtered	0.032±0.007	0.108±0.024	0.069±0.015

Table 42: Results of filters (Knittelfeld and Zederhaus) from recently performed measurements (2016) and results from measurements from several years ago (2007/09) including standard deviation

	K1		**Z1**		**Z2**		**Z3**	
	2007	2016	2009	2016	2009	2016	2009	2016
	[ng/m³]		[ng/m³]		[ng/m³]		[ng/m³]	
BaP	7,6±1.1	7,4±1.1	5,3±0.8	4,0±0.6	3,6±0.5	4,5±0.7	1,9±0.3	2,0±0.3
BbF+BkF	n.a..	n.a..	**7,8±1.6**	**6,0±1.2**	**5,6±1.1**	**7,5±1.5**	3,8±0.8	4,5±0.9
IcdP	**11,8±1.9**	**6,5±1.0**	**7,7±1.2**	**3,0±0.5**	**5,8±0.9**	**4,0±0.6**	**5,3±0.9**	**3,0±0.5**
BghiP	9,3±1.9	6,4±1.3	**6,3±1.3**	**4,0±0.8**	4,5±0.9	4,0±0.8	3,2±0.6	2,5±0.

Table 43: Ratios of the concentration of the reference filter and standard 8 using the old and new internal standard

	Ratio (o/n)				
	BbF+BkF	**BaP**	**IcdP**	**BghiP**	**Average**
RF	7.29	7.82	5.47	6.7	6.82
S8	3.72	3.49	3.2	3.6	3.50

Table 44: Purities and concentration of mix-standard (PAK-Mix 18)

	Purity [%]	c_1[µg/mL]	$c_{1corr.}$ [µg/mL]
Naph	99.8	100	99.8
Acy	99	100	99.0
Ace	99	100	99.0
Flu	98	100	98.0
Phe	98	100	98.0
Ant	99	100	99.0
Fla	99.8	100	99.8
Py	99.5	100	99.5
BaA	98.7	100	98.7
Chr	97	100	97.0
BbF	99	100	99.0
BkF	99.9	100	99.9
BaP	98	100	98.0
IcdP	99	100	99.0
BghiP	99	100	99.0
DahA	98.7	100	98.7

Table 45: Remaining loading and filter area of combustion filters

Filter	Used load [mg]	Used area [cm^2]	Filter	Used load [mg]	Used area [cm^2]	Filter	Used load [mg]	Used area [cm^2]
C1	5.23	5.28	**C47**	1.30	5.12	**C90**	2.65	5.32
C2	2.61	5.28	**C48**	4.57	4.34	**C91**	1.24	4.73
C3	1.97	5.28	**C49**	1.37	5.12	**C92**	0.57	6.10
C5	1.42	9.62	**C50**	1.10	5.12	**C93**	1.14	6.10
C6	1.59	4.30	**C51**	0.82	5.12	**C94**	0.65	6.10
C7	1.00	4.30	**C52**	0.78	5.12	**C95**	0.83	6.10
C8	0.75	4.30	**C53**	0.68	5.12	**C96**	0.81	6.10
C9	0.63	4.30	**C54**	0.57	5.12	**C97**	1.84	6.10
C10	0.61	4.30	**C55**	0.53	4.62	**C98**	1.86	6.10
C11	0.77	4.30	**C56**	0.56	5.12	**C99**	1.10	6.10
C12	1.25	4.30	**C57**	0.42	4.62	**C100**	1.47	6.10
C13	0.73	4.30	**C58**	1.84	7.61	**C101**	0.42	6.10
C14	1.71	4.30	**C59**	1.38	7.61	**C102**	2.52	6.10
C15	2.40	4.30	**C60**	3.52	7.61	**C103**	0.78	6.10
C16	1.54	4.30	**C61**	1.13	7.61	**C104**	1.18	6.10
C17	1.09	4.30	**C62**	0.82	7.61	**C105**	1.43	6.10
C18	0.65	4.30	**C63**	1.04	7.61	**C106**	1.27	6.10
C19	0.40	4.30	**C64**	1.09	7.61	**C107**	1.84	6.10
C20	0.23	4.08	**C65**	1.23	7.61	**C108**	2.91	6.10
C21	1.46	4.30	**C66**	4.11	7.61	**C109**	2.52	6.10
C22	1.25	4.30	**C67**	1.98	7.61	**C110**	0.52	6.10
C23	0.96	4.30	**C68**	6.24	7.61	**C111**	3.18	5.12
C24	0.48	4.30	**C69**	2.82	7.61	**C112**	1.33	5.12
C25	0.35	4.30	**C70**	2.45	7.61	**C113**	0.84	5.12
C26	0.39	4.30	**C71**	1.61	7.61	**C114**	1.17	5.12
C27	0.41	4.30	**C72**	1.15	7.61	**C115**	1.96	5.12
C28	0.34	4.30	**C73**	1.24	7.61	**C116**	0.87	5.12
C29	0.83	4.30	**C74**	1.21	4.14	**C117**	0.77	5.12
C30	3.82	3.79	**C75**	1.09	5.32	**C118**	0.63	5.12
C31	1.31	4.30	**C76**	1.18	5.32	**C119**	0.75	5.12
C32	1.39	4.30	**C77**	0.77	4.34	**C120**	1.00	5.12
C33	1.46	4.30	**C78**	1.02	4.14	**C121**	0.73	5.12
C34	0.95	4.30	**C79**	1.08	5.32	**C122**	0.42	5.10
C35	0.65	4.30	**C80**	0.98	5.32	**56**	0.63	5.10
C36	0.57	4.30	**C81**	1.01	5.32	**57**	0.68	6.10
C37	0.31	3.73	**C82**	0.54	4.14	**58**	1.11	6.10
C40	1.33	4.62	**C83**	0.90	5.32	**59**	1.09	5.10
C41	1.72	4.53	**C84**	3.95	4.14	**60**	1.12	5.10
C42	3.82	4.62	**C85**	1.07	5.32	**61**	1.87	6.10
C43	5.36	4.62	**C86**	0.56	5.32	**62**	2.73	6.10
C44	9.96	6.10	**C87**	0.98	4.73	**63**	1.60	6.10
C45	2.41	5.12	**C88**	1.49	5.32	**64**	0.47	5.10
C46	1.31	4.62	**C89**	1.98	5.32	**65**	0.47	5.10

Table 46: Gas data, temperature and PAH-concentrations for B1 over time

	[min]	[Vol%]		[mg/Nm^3]			[°C]	[mg/Nm^3]										
	Time	**O_2**	**CO_2**	**CO**	**VOC**	**PM10**	**T**	**EC**	**OC**	**Phe**	**Ant**	**Fla]**	**Py**	**BaA+Chr**	**BbF+BkF**	**BaP**	**IcdP**	**BghiP**
C5	5	20.1	0.548	605	127	60.1	40.7	27.5	16.4	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..
C6	10	17.3	3.03	747	117	172	78.7	51.5	70.2	0.037	0.011	0.057	0.053	0.009	0.003	<LOQ	0.003	<LOQ
C7	15	14.5	5.85	873	127	121	144	40.4	31.0	0.009	0.005	0.033	0.035	0.006	0.002	<LOQ	<LOQ	<LOQ
C8	20	14.2	6.39	724	83.3	86.7	177	28.8	13.8	0.002	<LOQ	0.014	0.011	0.003	<LOQ	<LOQ	<LOQ	<LOQ
C9	25	14.1	6.42	1097	98.4	70.8	193	19.8	9.94	<LOQ	<LOQ	0.009	0.006	0.003	<LOQ	<LOQ	<LOQ	<LOQ
C10	30	14.4	6.15	906	68.0	69.3	203	22.6	8.83	<LOQ	<LOQ	0.014	0.010	0.004	<LOQ	<LOQ	<LOQ	<LOQ
C11	35	14.4	6.09	1068	89.0	87.5	206	19.4	9.56	<LOQ	<LOQ	0.014	0.010	0.005	0.002	<LOQ	<LOQ	<LOQ
C12	40	13.7	6.79	877	63.3	154	213	60.8	19.7	0.006	0.011	0.059	0.057	0.009	0.003	<LOQ	<LOQ	<LOQ
C13	45	15.3	5.00	2725	123	84.7	214	34.6	8.12	0.002	<LOQ	0.024	0.019	0.007	0.003	<LOQ	<LOQ	0.003
C14	50	12.8	7.55	4424	444	197	211	52.2	60.1	0.006	<LOQ	0.160	0.178	0.068	0.072	0.038	0.070	0.064
C15	55	6.5	14.0	3583	465	397	279	120	163	0.019	<LOQ	1.042	1.095	0.275	0.275	0.220	0.239	0.221
C16	60	8.5	12.1	2382	182	244	309	102	57.1	0.010	<LOQ	0.449	0.353	0.114	0.087	0.064	0.026	0.062
C17	65	11.2	9.22	804	57.7	148	300	75.4	19.3	0.008	<LOQ	0.184	0.149	0.052	0.034	0.023	0.011	0.022
C18	70	13.4	6.86	1058	50.7	80.5	284	28.8	12.1	0.005	<LOQ	0.051	0.037	0.018	0.012	0.005	0.008	0.013
C19	75	15.9	4.28	3143	55.8	44.0	257	11.6	3.61	<LOQ	<LOQ	0.014	0.008	0.005	0.002	<LOQ	0.004	0.005
C20	80	16.9	3.25	8299	123	25.4	231	27.5	16.4	<LOQ	<LOQ	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.000

Table 47: Gas data, temperature and PAH-concentrations for S1 over time

	[min]	[Vol%]		[mg/Nm^3]			[°C]	[mg/Nm^3]											
	Time	O_2	CO_2	CO	VOC	PM10	T	EC	OC	Phe	Ant	Fla]	Py	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA
C21	5	17.4	2.92	1074	137	140	47.6	43.7	61.2	<LOQ	<LOQ	0.025	0.029	0.009	0.010	0.004	0.008	0.008	<LOQ
C22	10	14.5	5.75	1821	174	119	125	25.1	53.6	<LOQ	<LOQ	0.031	0.030	0.012	0.020	0.010	0.016	0.015	<LOQ
C23	15	13.0	7.47	1671	147	88.4	176	20.1	40.0	<LOQ	<LOQ	0.022	0.020	0.011	0.026	<LOQ	0.027	0.021	<LOQ
C24	20	13.2	7.26	1245	91.7	41.5	207	13.8	7.14	<LOQ	<LOQ	0.009	0.006	0.005	0.007	<LOQ	0.007	0.005	<LOQ
C25	25	14.0	6.40	1365	85.8	32.0	211	7.45	9.96	<LOQ	<LOQ	0.010	0.007	0.004	0.003	<LOQ	0.003	<LOQ	<LOQ
C26	30	14.3	6.12	1664	95.3	34.7	214	15.5	7.02	<LOQ	<LOQ	0.010	0.006	0.003	0.002	<LOQ	<LOQ	<LOQ	<LOQ
C27	35	15.0	5.34	2375	157	36.6	210	9.40	9.98	<LOQ	<LOQ	0.010	0.008	0.005	0.003	<LOQ	<LOQ	<LOQ	<LOQ
C28	40	16.0	4.41	3658	215	30.2	200	8.89	6.68	<LOQ	<LOQ	0.017	0.013	0.005	0.003	<LOQ	0.004	<LOQ	<LOQ
C29	45	16.9	3.47	6519	424	73.1	188	9.33	7.95	<LOQ	<LOQ	0.014	0.012	0.006	0.005	<LOQ	0.006	<LOQ	<LOQ
C30	50	13.5	6.94	3464	510	381	192	28.8	179	0.011	<LOQ	0.084	0.085	0.040	0.040	0.033	0.032	0.025	0.011
C31	55	8.1	12.4	1980	216	120	255	25.8	51.2	0.008	<LOQ	0.186	0.203	0.095	0.150	0.091	0.101	0.083	0.042
C32	60	9.3	11.2	1051	79.2	135	289	35.9	50.8	0.005	<LOQ	0.127	0.106	0.052	0.084	0.043	0.046	0.045	0.023
C33	65	10.6	9.83	589	25.5	147	297	40.8	52.7	0.007	<LOQ	0.071	0.052	0.029	0.045	0.017	0.023	0.021	0.011
C34	70	12.5	7.83	469	17.0	89.7	288	30.0	25.0	0.003	<LOQ	0.043	0.033	0.019	0.015	0.008	0.006	0.005	<LOQ
C35	75	14.0	6.24	779	33.6	59.2	273	15.4	9.42	0.002	<LOQ	0.024	0.016	0.009	0.006	<LOQ	0.003	0.002	<LOQ
C36	80	15.3	4.96	2232	95.4	51.1	255	<LOQ	<LOQ	0.001	<LOQ	0.022	0.015	0.006	0.002	<LOQ	<LOQ	<LOQ	<LOQ
C37	85	17.1	3.22	6510	138	31.2	230	<LOQ	<LOQ	<LOQ	<LOQ	0.004	<LOQ	0.003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table 48: Gas data, temperature and PAH-concentrations for B2a over time (red and blue marked values were analysed at different times)

	Time	O2	CO2	CO	VOC	PM10	T	EC	OC	Naph	Acy	Ace	Flu	Phe	Ant	Fla	Py	BaA+ Chr	BbF+ BkF	BaP	IcdP	BghiP	DahA
	[min]	[Vol%]		[mg/Nm³]			[°C]	[mg/Nm³]															
C40	5	16.6	3.83	2505	783	118	45.7	446	1304	0.008	0.011	0.011	0.0104	0.006	0.013	0.013	0.052	0.034	0.030	0.040	0.004	0.050	0.023
C41	10	14.8	5.92	3921	564	137	92.5	432	2230	<LOQ	<LOQ	<LOQ	<LOQ	0.008	0.002	0.112	0.077	0.028	0.020	0.020	0.016	0.014	<LOQ
C42	15	16.0	4.69	6278	1421	280	122	1458	4116	0.010	0.009	0.012	0.0120	0.383	0.011	0.078	0.327	0.069	0.062	0.064	0.007	0.067	0.033
C43	20	16.7	4.06	7399	1685	386	125	414	6968	<LOQ	<LOQ	<LOQ	<LOQ	0.108	0.029	0.122	0.098	0.030	0.015	0.013	0.010	0.007	<LOQ
C44	25	17.3	3.50	7310	1979	511	127	359	9116	0.006	0.010	0.005	0.006	0.140	0.005	0.016	0.033	0.029	0.019	0.018	0.003	0.020	0.018
C45	30	15.0	5.72	2494	351	158	145	318	2618	0.006	0.005	0.007	0.006	0.013	0.008	0.012	0.051	0.042	0.022	0.019	0.003	0.021	0.019
C46	35	14.9	5.76	1496	210	101	164	690	1067	0.007	0.010	0.010	0.010	0.006	0.012	0.008	0.010	0.037	0.020	0.012	0.005	0.014	0.023
C47	40	18.4	2.27	99316	1921	84.0	154	167	1248	<LOQ	<LOQ	<LOQ	<LOQ	0.009	0.002	0.034	0.036	0.014	0.006	0.005	0.004	0.003	<LOQ
C48	45	16.9	3.74	7405	1595	330	145	364	6180	0.008	0.003	0.010	0.010	0.445	0.028	0.193	0.732	0.388	0.090	0.115	0.014	0.111	0.023
C49	50	14.3	6.43	1496	175	89.0	168	223	1017	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..
C50	55	13.8	6.87	1502	149	73.0	185	298	669	0.011	0.014	0.014	0.013	0.007	0.017	0.010	0.009	0.042	0.041	0.029	0.008	0.027	0.032
C51	60	14.1	6.52	1452	145	55.0	195	82.0	395	0.009	0.012	0.012	0.011	0.006	0.014	0.008	0.007	0.028	0.022	0.012	0.005	0.013	0.027
C52	65	14.9	5.70	1693	151	51.0	201	309	431	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..
C53	70	15.8	4.80	2381	196	44.0	200	184	497	0.005	0.006	0.006	0.006	0.003	0.007	0.004	0.004	0.008	0.007	0.005	0.002	0.004	0.014
C54	75	16.3	4.35	2838	247	36.0	197	62.0	320	<LOQ	<LOQ	<LOQ	<LOQ	0.002	<LOQ	0.008	0.007	0.003	0.003	0.001	0.001	0.001	<LOQ
C55	80	17.0	3.67	3451	301	37.0	191	187	317	0.003	0.004	0.005	0.004	0.003	0.006	0.004	0.003	0.004	0.004	0.001	0.001	0.002	0.011
C56	85	17.6	3.09	4652	336	34.0	184	267	310	0.002	0.002	0.003	0.003	0.002	0.003	0.003	0.002	0.004	0.002	0.000	0.001	0.001	0.006
C57	90	18.2	2.47	6906	368	27.0	175	147	181	0.004	0.005	0.005	0.005	0.004	0.006	0.004	0.004	0.005	0.003	0.000	0.002	0.001	0.013

Table 49: Gas data, temperature and PAH-concentrations for B2b over time

	[min]	[Vol%]		[mg/Nm^3]			[°C]	[mg/Nm^3]											
	Time	**O$_2$**	**CO$_2$**	**CO**	**VOC**	**PM10**	**T**	**EC**	**OC**	**Phe**	**Ant**	**Fla]**	**Py**	**BaA+Chr**	**BbF+BkF**	**BaP**	**IcdP**	**BghiP**	**DahA**
C58	5	14.0	6.32	1.554	177	108	94.1	n.a..	n.a..	0.0103	<LOQ	0.072	0.067	0.023	0.026	0.014	0.025	0.025	<LOQ
C59	10	14.8	5.86	3163	338	76.9	126	n.a..	n.a..	0.006	<LOQ	0.021	0.022	0.007	0.010	<LOQ	0.009	0.007	<LOQ
C60	15	15.0	5.65	4636	729	193	143	n.a..	n.a..	0.033	0.003	0.055	0.054	0.012	0.011	<LOQ	0.008	0.006	<LOQ
C61	20	14.2	6.55	1663	151	61.8	157	n.a..	n.a..	0.003	<LOQ	0.021	0.019	0.008	0.005	<LOQ	0.003	<LOQ	<LOQ
C62	25	15.2	5.49	1999	185	43.0	165	n.a..	n.a..	0.002	<LOQ	0.012	0.012	0.005	0.003	<LOQ	<LOQ	<LOQ	<LOQ
C63	30	15.8	4.94	2807	274	53.8	168	n.a..	n.a..	0.003	<LOQ	0.012	0.010	0.005	0.004	<LOQ	<LOQ	<LOQ	<LOQ
C64	35	16.6	4.06	22679	268	50.1	168	n.a..	n.a..	0.002	<LOQ	0.008	0.007	0.004	0.003	<LOQ	<LOQ	<LOQ	<LOQ
C65	40	18.0	2.67	5985	918	48.0	167	n.a..	n.a..	0.005	<LOQ	0.012	0.012	0.007	0.005	<LOQ	0.004	<LOQ	<LOQ
C66	45	14.3	6.19	5301	784	177	168	n.a.	n.a.	0.196	0.017	0.297	0.250	0.082	0.068	0.048	0.047	0.046	<LOQ
C67	50	11.5	8.98	3969	406	108	196	n.a.	n.a.	0.0471	0.006	0.387	0.315	0.139	0.128	0.086	0.075	0.051	<LOQ
C68	55	16.3	4.27	7755	1392	287	195	n.a.	n.a.	0.204	0.018	0.137	0.125	0.046	0.051	0.027	0.027	0.021	<LOQ
C69	60	15.3	5.32	4936	686	121	198	n.a.	n.a.	0.0401	0.004	0.068	0.058	0.029	0.027	0.018	0.015	0.010	<LOQ
C70	65	15.8	4.82	4851	693	103	195	n.a.	n.a.	0.029	0.002	0.061	0.052	0.031	0.035	0.022	0.019	0.014	<LOQ
C71	70	16.2	4.42	3760	497	69.1	195	n.a.	n.a.	0.009	<LOQ	0.031	0.025	0.019	0.019	0.012	0.010	0.007	<LOQ
C72	75	16.5	4.22	2869	356	49.4	191	n.a.	n.a.	0.008	<LOQ	0.017	0.014	0.013	0.017	0.010	0.010	0.007	<LOQ
C73	80	17.3	3.32	5213	602	51.5	187	n.a.	n.a.	0.008	<LOQ	0.025	0.018	0.013	0.013	0.006	0.008	0.006	<LOQ

Table 50: Gas data, temperature and PAH-concentrations for R2a over time (red and blue marked values were analysed at different times)

	[min]	[Vol%]		[mg/Nm^3]			[°C]	[mg/Nm^3]											
	Time	O_2	CO_2	CO	VOC	PM10	T	EC	OC	Phe	Ant	Fla]	Py	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA
C74	5	17.2	3.10	1866	461	126	46.9	17.2	48.0	0.011	<LOQ	0.057	0.076	0.021	0.022	0.011	0.023	0.021	<LOQ
C75	10	16.1	4.63	1167	171	76.2	92.1	11.2	21.1	0.006	<LOQ	0.019	0.019	0.007	0.008	<LOQ	0.008	0.005	<LOQ
C76	15	16.1	4.66	1660	207	81.2	120	3.83	28.0	0.004	<LOQ	0.016	0.013	0.006	0.004	<LOQ	0.002	0.002	<LOQ
C77	20	15.2	5.63	889	79.5	64.0	144	9.02	13.1	0.005	<LOQ	0.016	0.013	0.006	0.005	<LOQ	0.007	<LOQ	<LOQ
C78	25	14.6	6.13	813	59.5	89.4	168	18.9	30.6	0.005	<LOQ	0.026	0.021	0.008	0.005	<LOQ	0.004	<LOQ	<LOQ
C79	30	15.4	5.31	971	88.8	72.9	183	16.4	18.7	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..	n.a..
C80	35	17.2	3.52	3207	378	59.8	180	7.18	24.4	0.005	<LOQ	0.016	0.012	0.007	0.005	<LOQ	0.004	<LOQ	<LOQ
C81	40	16.7	4.00	2591	181	62.0	174	11.0	13.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
C82	45	17.1	3.60	3691	212	42.5	174	4.35	10.3	0.004	<LOQ	0.010	0.007	0.003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
C83	50	17.5	3.17	4632	306	54.3	168	6.48	14.7	0.005	<LOQ	0.013	0.009	0.004	0.002	<LOQ	<LOQ	<LOQ	<LOQ
C84	55	17.9	2.79	7668	1267	301	161	37.6	134	0.078	<LOQ	0.047	0.041	0.013	0.009	<LOQ	0.009	<LOQ	<LOQ
C85	60	15.9	4.79	2573	182	68.6	167	1.45	24.0	0.005	<LOQ	0.017	0.014	0.007	0.006	<LOQ	0.005	<LOQ	<LOQ
C86	65	14.9	5.80	1156	63.1	35.6	184	2.33	9.64	0.003	<LOQ	0.008	0.006	0.005	0.006	<LOQ	0.005	<LOQ	<LOQ
C87	70	14.7	6.00	892	45.3	35.0	199	6.74	11.2	0.002	<LOQ	0.006	0.005	0.006	0.009	0.005	0.005	0.003	<LOQ
C88	75	14.5	6.14	661	31.1	99.4	209	20.5	32.2	0.006	<LOQ	0.013	0.010	0.010	0.011	0.003	0.006	0.004	<LOQ
C89	80	14.3	6.31	461	21.0	137	218	29.1	54.1	0.011	<LOQ	0.018	0.011	0.010	0.014	0.006	0.010	0.011	<LOQ
C90	85	14.2	6.40	371	17.6	184	227	28.9	83.7	0.026	0.004	0.015	0.010	0.005	0.015	0.012	<LOQ	<LOQ	<LOQ
C91	90	14.8	5.76	573	31.3	93.9	231	23.9	33.5	0.013	<LOQ	0.015	0.010	0.005	0.007	<LOQ	<LOQ	<LOQ	<LOQ

Table 51: Gas data, temperature and PAH-concentrations for R2b over time

	[min]	[Vol%]		[mg/Nm^3]			[°C]	[mg/Nm^3]											
	Time	O_2	CO_2	CO	VOC	PM10	T	EC	OC	Phe	Ant	Fla]	Py	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA
C92	5	16.0	4.40	1123	377	34.0	111	4.77	5.12	0.003	<LOQ	0.007	0.005	<LOQ	<LOQ	0.002	x	0.018	<LOQ
C93	10	14.2	6.40	291	16.6	67.2	161	15.1	26.7	0.006	<LOQ	0.025	0.032	0.009	0.013	0.007	0.016	0.021	<LOQ
C94	15	14.4	6.27	297	14.6	38.0	183	9.33	6.16	0.002	<LOQ	0.010	0.010	0.002	0.001	<LOQ	<LOQ	<LOQ	<LOQ
C95	20	14.5	6.29	346	14.5	54.8	193	14.8	10.2	0.003	<LOQ	0.022	0.015	0.003	0.002	<LOQ	<LOQ	<LOQ	<LOQ
C96	25	14.1	6.61	320	13.7	58.7	196	23.1	15.5	0.011	<LOQ	0.043	0.022	0.004	0.002	<LOQ	<LOQ	<LOQ	<LOQ
C97	30	14.6	6.04	291	13.0	134	201	24.6	55.2	0.050	0.009	0.061	0.042	0.004	0.002	<LOQ	<LOQ	<LOQ	<LOQ
C98	35	15.5	5.14	368	17.9	124	202	23.5	51.6	0.047	0.044	0.104	0.085	0.006	0.001	<LOQ	<LOQ	<LOQ	<LOQ
C99	40	16.6	3.99	1433	113	73.7	199	24.4	22.7	0.025	0.003	0.025	0.016	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
C100	45	18.1	2.42	7466	334	75.3	186	16.7	32.7	0.024	0.003	0.013	0.054	0.001	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
C101	50	17.7	2.96	7882	704	20.8	174	2.57	2.27	0.002	<LOQ	0.005	0.003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
C102	55	13.5	7.15	406	20.0	140	190	7.19	87.9	0.020	<LOQ	0.068	0.071	0.021	0.021	0.021	0.019	0.017	<LOQ
C103	60	13.1	7.53	275	10.3	43.6	212	12.0	12.7	0.002	<LOQ	0.010	0.009	0.004	0.003	0.000	<LOQ	<LOQ	<LOQ
C104	65	13.5	7.12	337	11.8	67.8	225	17.4	21.2	0.003	<LOQ	0.009	0.007	0.005	0.007	0.002	<LOQ	<LOQ	<LOQ
C105	70	14.1	6.50	398	13.7	77.1	230	21.5	27.2	0.004	<LOQ	0.013	0.010	0.005	0.007	0.001	<LOQ	<LOQ	<LOQ
C106	75	14.1	6.53	296	10.7	71.5	233	20.6	22.9	0.003	<LOQ	0.009	0.007	0.005	0.006	0.002	<LOQ	<LOQ	<LOQ
C107	80	14.2	6.27	291	10.4	115	235	26.4	44.6	0.011	<LOQ	0.016	0.011	0.006	0.008	0.001	<LOQ	<LOQ	<LOQ
C108	85	15.7	4.78	930	25.8	162	230	26.9	60.5	0.037	0.005	0.028	0.019	0.005	0.005	0.001	<LOQ	<LOQ	<LOQ
C109	90	17.4	3.08	4231	118	123	216	22.4	46.7	0.028	0.003	0.026	0.017	0.003	0.004	<LOQ	<LOQ	<LOQ	<LOQ
C110	95	17.8	2.77	5698	82.3	20.1	208	5.06	3.35	0.001	<LOQ	0.005	0.003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Table 52:: Gas data, temperature and PAH-concentrations for R2c over time

	[min]	[Vol%]		[mg/Nm³]			[°C]	[mg/Nm³]											
	Time	O_2	CO_2	CO	VOC	PM10	T	EC	OC	Phe	Ant	Fla]	Py	BaA+Chr	BbF+BkF	BaP	IcdP	BghiP	DahA
C111	5	14.8	5.42	874	81.3	349	97.8	60.5	76.3	0.149	0.013	0.111	0.096	0.029	0.039	0.014	0.035	0.030	<LOQ
C112	10	16.6	3.80	3251	336	124	122	34.0	53.5	0.015	<LOQ	0.049	0.050	0.019	0.019	0.008	0.018	0.015	<LOQ
C113	15	16.8	3.69	3073	342	74.3	125	13.7	42.1	0.011	<LOQ	0.093	0.098	0.037	0.039	0.021	0.033	0.026	<LOQ
C114	20	16.9	3.60	3324	417	104	130	17.1	53.1	0.012	<LOQ	0.053	0.053	0.023	0.026	0.010	0.022	0.017	<LOQ
C115	25	16.6	3.84	3201	375	175	130	6.96	118	0.021	<LOQ	0.087	0.082	0.020	0.016	0.006	0.014	0.010	<LOQ
C116	30	16.3	4.15	2012	188	77.2	144	12.6	37.1	0.004	<LOQ	0.033	0.034	0.012	0.011	0.003	0.010	0.007	<LOQ
C117	35	16.9	3.59	2181	186	68.6	144	9.58	27.4	0.005	<LOQ	0.017	0.014	0.007	0.007	<LOQ	0.008	<LOQ	<LOQ
C118	40	16.9	3.64	1586	127	40.8	145	11.6	16.1	0.004	<LOQ	0.012	0.008	0.004	0.005	<LOQ	0.006	<LOQ	<LOQ
C119	45	16.7	3.83	1201	115	48.6	150	17.0	13.7	0.002	<LOQ	0.015	0.011	0.005	0.003	<LOQ	0.003	<LOQ	<LOQ
C120	50	17.3	3.15	1811	202	65.9	149	18.9	23.1	0.004	<LOQ	0.015	0.011	0.004	0.003	<LOQ	<LOQ	<LOQ	<LOQ
C121	55	18.4	1.98	6102	678	42.6	133	13.0	12.6	<LOQ	<LOQ	0.006	0.009	0.004	0.001	<LOQ	<LOQ	<LOQ	<LOQ
C122	100	14.1	6.32	345	14.1	28.1	182	7.13	10.8	<LOQ	<LOQ	<LOQ	<LOQ	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
56	105	14.0	6.48	141	10.6	44.5	201	11.4	7.25	<LOQ	<LOQ	0.008	0.005	0.002	0.002	<LOQ	<LOQ	<LOQ	<LOQ
57	110	13.8	6.71	102	9.65	45.2	202	16.5	9.27	0.002	<LOQ	0.009	0.006	0.003	0.002	<LOQ	<LOQ	<LOQ	<LOQ
58	115	13.7	6.71	98.2	9.36	76.2	202	25.6	20.2	0.011	<LOQ	0.016	0.011	0.003	0.003	<LOQ	<LOQ	<LOQ	<LOQ
59	120	14.1	6.37	127	9.28	88.7	202	26.6	30.7	0.016	0.003	0.030	0.021	0.004	0.002	<LOQ	<LOQ	<LOQ	<LOQ
60	125	14.3	6.13	150	8.89	93.7	201	27.1	29.9	0.021	<LOQ	0.020	0.013	0.003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
61	130	13.9	6.43	122	7.87	142	201	35.3	50.9	0.072	0.012	0.028	0.019	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
62	135	14.2	5.99	146	7.54	189	201	41.8	56.9	0.312	0.020	0.025	0.017	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
63	140	16.4	3.71	1303	19.7	94.6	186	29.0	28.2	0.047	0.008	0.015	0.010	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
64	145	17.3	3.00	4085	43.2	31.1	164	4.07	3.44	0.002	<LOQ	0.004	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
65	150	17.4	2.85	4934	25.8	24.1	153	0.420	1.81	<LOQ	<LOQ	0.003	0.001	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ