DISSERTATION

CHARACTERIZATION OF REAL-LIFE BENZO(A)PYRENE EMISSIONS OF RESIDENTIAL WOOD COMBUSTION FURNACES

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Kurzfassung

Die Erwärmung des Klimasystems erfordert Lösungen zur Vermeidung von Treibhausgasemissionen. Biomasse ist eine klimafreundliche Alternative zu fossilen Brennstoffen, da ihr Einsatz nahezu CO_2 neutral ist. Allerdings stellt die Biomasseverbrennung eine bedeutende Emissionsquelle verschiedener Schadstoffe, die besonders bei unvollständiger Oxidation entstehen können, dar. Speziell bei kleineren Verbrennungsanlagen besteht ein erhöhtes Risiko für vermehrte Schadstoffemissionen. Aufgrund der besonders hohen Toxizität wird der Gruppe der polyzyklischen aromatischen Kohlenwasserstoffe (PAKs) besondere Bedeutung beigemessen. Ziel dieser Arbeit ist es, den Wissensstand zu Emissionen von PAKs aus Kleinfeuerungsanlagen zu erweitern. Neben der Einführung innovativer methodischer Ansätze bei der Probenahme, wurden anhand von zwei Messserien BaP Emissionen von realitätsnahe betriebenen Biomassekleinfeuerungen ermittelt und im Hinblick auf Referenzwerte diskutiert. In einer weiteren Messserie wurde der Einsatz von oxidativen Katalysatoren als Reduktionsmaßnahme untersucht.

Da der repräsentative Charakter von Benzo(a)pyren (BaP) für die Gruppe der PAKs anhand von Literaturstudien bestätigt werden konnte, war es möglich sich bei den Messungen auf nur diese Substanz zu konzentrieren. Es wurde daher untersucht, ob es möglich ist BaP mittels einer kompakteren und daher auch flexibleren Messmethode als jene für verschiedene PAKs, zu bestimmen. Messungen ergaben, dass nach zehnfacher Verdünnung eines Abgasstroms die Bestimmung von BaP in ausschließlich der partikulären Phase zulässig ist. So konnten deutlich mehr als 90% von BaP dargestellt werden, ungeachtet von unterschiedlichen Abgasqualitäten, sowie ungünstigen bis optimalen Verbrennungsbedingungen. Außerdem konnte gezeigt werden, dass Abdampfverluste von bereits gesammeltem Probenmaterial vom Filter aufgrund von schwankender Abgasqualität eine unbedeutende Rolle spielen. Die vereinfachte Messmethode konnte in den darauffolgenden Messserien angewendet werden.

In der ersten Messserie wurden BaP Emissionen von sechs automatischen Kesseln in unterschiedlichen Betriebszuständen bestimmt. Um eine exakte Abgrenzung phasenspezifischer Emissionen zu gewährleisten, wurden die Betriebszustände Start, Stopp, Teillast und Nennlast, die alle im realen Betrieb bei Endnutzern vorkommen, im Voraus genau definiert. Die Konzentrationswerte von Start- und Stopp-Betrieb waren im Durchschnitt um ein bis zwei Größenordnungen höher als jene, die während den stationären Betriebszuständen bestimmt wurden. Die Betriebssequenz hat daher auf die Höhe der gesamten BaP Emissionen entscheidenden Einfluss. Weiters konnte ein größeres Risiko für erhöhte Emissionen von Unterschubfeuerungen im Vergleich zu horizontal beschickten Feuerungen und Abwurffeuerungen gezeigt werden. Eine

Korrelationsanalyse ergab, dass elementarer Kohlenstoff (EC) im Vergleich zu allen anderen bestimmten Parametern der beste Indikator für BaP ist.

In der zweiten Messserie wurden Emissionen aus realitätsnahem Betrieb von 13 modernen Kleinfeuerungen, nämlich vier Pelletöfen, sechs Scheitholzöfen und drei Scheitholzherden, untersucht. Neben BaP wurden Kohlenmonoxid (CO), organische Kohlenwasserstoffe (OGC), Stickstoffoxide (NO_x) und, gemessen aus heißem (TSP) oder verdünntem Abgas (TSP_{dil}), Gesamtstaub, Gesamtkohlenstoff (TC), EC und organischer Kohlenstoff (OC) bestimmt. Die Geräte wurden entsprechend zweier Messzyklen, die einen realitätsnahen Betrieb abbilden und erst vor Kurzem in einem europäischen Projekt entwickelt wurden, betrieben. Die BaP Emissionswerte lagen zwischen 0.5 und 130 µg MJ^{-1}. Obwohl die niedrigsten Emissionswerte generell bei Pelletöfen gemessen wurden, wies einer der vier Pelletöfen den höchsten gemessenen BaP Wert auf, was zeigt, dass auch automatische Feuerungen zu erhöhten BaP Emissionen führen können. Im Zuge der Messungen konnte die Wiederholbarkeit der Messzyklen untersucht und bestätigt werden. Für die meisten Emissionsparameter zeigte der Vergleich mit Emissionsfaktoren der europäischen und österreichischen Emissionsinventur, dass der vermehrte Einsatz moderner Technologien, wie sie in dieser Arbeit untersucht wurden, zu verringerten Emissionen führen würde. Für BaP konnte gezeigt werden, dass es besonders schwierig ist charakteristische Emissionsfaktoren festzulegen, da die Werte wesentlich weiter streuen als jene anderer gemessener Parameter. Der Bedarf einer weiteren Datensammlung für die Charakterisierung von BaP Emissionen ist daher gegeben.

In der dritten Messserie wurde der Einfluss oxidativer Katalysatoren auf PAK-Emissionen im Abgas häuslicher Kleinfeuerungen untersucht. Hierfür wurden zwei Pt/Pd-Katalysatoren mit jeweils gleicher katalytischer Beschichtung aber unterschiedlichen Trägermaterialien eingesetzt. Ein spezieller Teststand, der synchrone Messungen von katalytisch behandeltem und unbehandeltem Abgas der gleichen Flamme ermöglicht, wurde dabei verwendet. Neben BaP wurden weitere 18 PAKs, CO, OGC, TSP_{dil}, TC, EC und OC bestimmt. Generell konnte ein deutlicherer Effekt des Katalysators mit dem metallischen Träger, der eine 3.5-fach größere Reaktionsfläche aufweist als jener mit keramischen Träger, beobachtet werden. Mit den getesteten Katalysatoren konnte das hohe Reduktionspotential auf die gasförmigen Abgasbestandteile CO (-88% und -69%) und OGC (-39% und -27%) gemäß früherer Studien bestätigt werden. Allerdings wurden die Emissionen von TSP_{dil} bei der Behandlung mit dem metallischen Katalysator um 17% erhöht, was den Bedarf weiterer Untersuchungen zeigt. Die Summe der gemessenen PAKs konnten im Versuch mit dem metallischen Katalysator um 63% und BaP im Speziellen um 84% vermindert werden, was das hohe Potenzial zur Reduktion von PAK-Emissionen aus Biomassekleinfeuerungsanlagen aufzeigt.

Abstract

Because of climate warming solutions against emissions of greenhouse gases are required. Biomass is widely recognized as a CO_2 neutral fuel and counts as climate friendly alternative to fossil fuels. However, biomass combustion is an important emissions source of numerous pollutants due to incomplete oxidation in the combustion process. Especially small scale combustion processes, occurring during residential wood combustion, have an increased risk for higher emissions. The group of polycyclic aromatic hydrocarbons (PAHs) causes special concern as they are particularly toxic. Hence the objective of this work is to contribute to the knowledge about PAH emissions from residential biomass combustion as it occurs at the end user. Beside the introduction of innovative methodical approaches, real-life BaP emissions of small scale wood combustion furnaces were determined and the impacts of two oxidizing catalysts were investigated.

The guiding role of the representative PAH compound benzo(a)pyrene (BaP) was confirmed by a literature study. Thus it was possible to focus the measurements on a single compound. This was the basis to investigate whether BaP can be measured with a more compact and flexible method than necessary for the determination of a larger number of different PAHs. Tests revealed that after ten-fold dilution of the flue gas BaP can be determined in particulate matter samples and the sampling of gaseous PAHs can be omitted. Clearly more than 90% of BaP could be determined by analyzing TSP_{dil} samples only, independently from the respective combustion conditions and flue gas composition. Moreover it could be shown that evaporation of BaP already sampled on the filter is negligible, also during fluctuating flue gas quality. The new measurement method was then applied to measure BaP emissions in three different test series.

In the first measurement series BaP emissions of six automatic boilers were determined during different operation conditions. The operation modes “start, stop, part load and nominal load”, all relevant at end-user operation, had been explicitly defined in advance. Thus specific emission values could be determined for the respective operation modes. Because BaP values from start and stop operation were one to two orders of magnitude higher than those from steady-state operation, it could be concluded that the operation sequence decisively impacts the total BaP emissions. Moreover, a higher risk for increased emissions from underfed systems compared to top-fed and horizontally fed systems was indicated. A correlation analysis exhibited that elemental carbon (EC) is the best indicator for BaP among all determined parameters.

In the second measurement series real-life oriented emissions of 13 state of the art small scale residential wood combustion furnaces, including four pellets stoves, six log wood stoves and three log wood cookers were investigated. BaP, carbon monoxide (CO), organic gaseous compounds (OGC), nitrogen oxides (NO_x), as well as, sampled either from hot flue gas (TSP) or from diluted and cooled flue gas (TSP_{dil}), total suspended particles, total carbon (TC), elemental carbon (EC) and organic carbon (OC) were measured. The furnaces were operated according to real-life oriented testing methods which had been recently developed in a European project. BaP emission values were between 0.5 and 130 µg MJ^{-1}. Although lowest emission values were generally determined from pellet stoves, one of four pellet stoves exhibited also the highest measured BaP value, indicating that even at automatic furnaces increased BaP emissions may occur. In course of the measurements the repeatability of he real-life test methods was analyzed and could be confirmed. For most emission parameters the comparison with emission factors used in the European and Austrian emission inventory indicates that the increased use of state of the art residential wood combustion furnaces, as those analyzed in this work, would lead to reduced emissions. For BaP it was shown that it is especially difficult to suggest characteristic emission factors, as they are more variable than other determined emissions. This indicates the need of a wider data collection for the characterization of BaP emissions.

In the third measurement series the effect of oxidative catalysts on PAH emissions from residential wood combustion furnaces was investigated. Therefore two Pt/Pd honeycomb catalysts, having the same coating but different carrier materials, were used. A special test stand which allows parallel measurements of catalytically treated and untreated flue gas from the same combustion flame was used. Beside BaP also 18 further PAH compounds, CO, OGC, TSP_{dil}, TC, EC and OC were determined. Generally, a more pronounced effect was observed for the measurements with the catalyst with the metallic carrier, having a 3.5 times bigger reaction surface than the catalyst with a ceramic carrier. By these catalysts a substantial reduction of the gaseous flue gas compounds CO (-88% and -69%) and OGC (-39% and -27%) could be shown, which is in line with the outcomes of previous studies. Unexpectedly TSP_{dil} emissions clearly increased by 17% due to the treatment with the metallic catalyst, which indicates the need of further investigations. Nevertheless in the test with the metallic catalyst PAHs were substantially reduced by 63% and in particular BaP by 84%. The high potential of PAH reduction thanks to catalytic treatment was clearly demonstrated.

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1 Introduction

1.1 The role of biomass combustion

The combustion of biomass is the most traditional way for supplying heat. Before the 19th century firewood was the dominant fuel for energetic use worldwide [1,2]. Today biomass accounts for 10% of worlds energy supply [3]. But still almost 40% of the world population relies on firewood for cooking or heating [2]. In 2017 75% of actually used biofuels (solid, liquid and gaseous) are used for residential purposes, 21% for industry, followed by transport accounting for 10% [4]. Biomass fuels are regionally available, support regional added value, do not require far transports and are independent from volatile prices of fossil fuels. From the environmental point of view the most substantial benefit is that biomass is an almost carbon neutral energy source because carbon dioxide emissions that are released during combustion had been previously adsorbed during the growth of the plant [5]. Except of the CO_2 which is emitted in the supply chain or for the processing, biomass combustion is CO_2 neutral and therefore it counts as climate friendly alternative to fossil fuels [6]. Especially in Austria, where 47.6% of the landscape is covered with forests [7], biomass combustion is the dominant renewable source for heating covering almost 30% of the Austrian heat supply [8].

1.2 Global warming and air quality

Global warming has been identified as the most serious environmental issue since time immemorial [9]. The increasing concentrations of greenhouse gases like CO_2, CH_4, N_2O or various fluorinated gases are reported to be responsible for climate change [10,11]. While CO_2 makes the major share of greenhouse gas emissions (e.g. 85% in Austria [11]) also the other pollutants are highly relevant as they have a much higher greenhouse effect than CO_2. In 2016 CO_2 concentration in air has exceeded the historical 400 ppm mark. Just recently in May 2019 it already reached 415 ppm indicating the rapid rise [12]. It is calculated that so far human activities have caused 1°C of global warming compared to pre-industrial levels which is ascribed to increasing concentration of greenhouse gases in the atmosphere. Global warming is likely to reach 1.5°C between 2030 and 2052 if it continues with the current rate. It is expected that a increase of 2°C will lead to severe effects like substantial rise in the sea level, more frequent hot extremes, heavy precipitation, probability of drought or climate related risks like food security or sufficient water supply [13]. According to the Paris Agreement of the United Nations framework Convention on Climate Change (UNFCC) 184 member countries have committed to take steps to limit temperature increase to 1.5°C above pre-industrial levels [14]. Policies are under enormous pressure to introduce measures in order to substantially reduce greenhouse gas emissions. The European goal is to become the first climate neutral continent by 2050 [15]. According to the latest government plans Austria should become climate neutral even by 2040 [16]. As calculated in an Austrian energy scenario renewable electricity and heat supply are fundamental factors for energy transition beside the environmental friendly traffic, thermal restoration, a change to long-lasting and recyclable products and a change in eating habits [17]. Already so far especially in Austria heat supply from biomass combustion constitutes a substantial share of renewable and climate friendly energy supply and is therefore a fundamental basis which contributes to reach climate goals [8].

Beside the increased emissions of greenhouse gases also other pollutants from anthropogenic activities lead to problems for environment and human health [18]. Important pollutants are particulate matter (PM), ammonia (NH_3), nitrogen oxides (NO_x), volatile organic compounds (VOC), carbon monoxide (CO) and various heavy metals [19,20]. Effects are for example acid rain, eutrophication, impacts on cloud formation and on radiation and various health impacts due to poor air quality like irritation of the airways, change in lung function, cardiovascular diseases or allergies. PM and VOC are bulk parameters which summarize a variety of different substances with various effects. PM comprises solid particles and liquid droplets [21] which provide surfaces for potential adsorption of compounds from the gas phase. It is commonly characterized by the aerodynamic diameters of the particles [22]. The smaller the particles are the deeper they can penetrate into the lung and the higher is the potential risk for the human health. PM is typically classified as PM10, PM2.5 and PM1. These abbreviations stand for Particulate Matter and the respective number gives the upper cut-off diameter. Thus PM10 samples contain particles up to an aerodynamic diameter of 10 µm, while PM2.5 and PM1 are subsets of particles smaller than 2.5 µm and 1 µm respectively. All of these cut-off diameters are defined for a collection efficiency of 50%. While rather coarse particles are retained predominantly in upper areas of the respiratory system fine particles are breathed more deeply into the lung to bronchis or even to the alveolis. VOC comprises the volatile share of organic substances. Both groups PM and VOC include huge varieties of different compounds with very diverse properties. Some of the compounds are distinctly harmful and they are particularly analyzed and reported as for example CH_4 which is a strong greenhouse gas [20,23]. Also the group of polycyclic aromatic hydrocarbons (PAHs) which is well known for its toxic effects is often separately investigated [20,23]. PAHs itself comprise several hundreds of different chemical species which occur either in the gas phase as VOC or in the particle phase as PM. They are described more in detail in chapter 1.5.

Only recently, it has been shown that the fate of air pollution had been underestimated so far. Due to new models it was calculated that 8.8 million premature deaths worldwide, of which 800000 in

Europe, are caused by PM2.5 in the ambient air. It is stated that the health impact of air pollution is even bigger than that of tobacco smoking which is estimated to cause 7.2 million premature deaths per year [24]. As reported by the World Health Organization PM2.5 cause oxidative stress, direct cellular toxicity, impaired renewal of damaged cells, lung damage with secondary inflammation and genotoxicity. It is suggested that PAHs inherent in particulate emissions are closely linked with these effects [25].

1.3 Biomass fuels and combustion devices

The term biomass includes a big variety of organic materials which base on photosynthetic fixation of carbon. These are dead or alive plant and animal residues, excrements and organic materials from technological transformation processes [26,27]. Biomass fuels vary widely as for example in chemical composition, in physical state or in energy content. Firewood as one type of biomass fuels has itself highly variable properties because it is produced from different tree species which were grown in different places at different growth conditions. Moreover processing and storage significantly influences quality and properties of wood fuels [27]. Wood is commonly used as log wood, chipped wood and compressed wood like pellets and briquettes for combustion purposes. Due to transformation to pourable wood fuels like wood chips and pellets it can be used for automatic and stationary combustion processes [26].

Biomass combustion systems can be divided into manually operated and automatically operated furnaces. Operation of automatic furnaces is characterized by the possibility to operate in steady state operation like continuous nominal load or part load operation. Thanks to automatic fuel and air supply and the use of small fragmented fuels like pellets or wood chips, automatic furnaces can be operated for hours at stationary combustion conditions without relevant changes in combustion performance. However, for each steady state operation also a start and a stop phase are implied. Both, steady state operation like nominal load and part load but also discontinuous operation phases like start and stop operation occur during typical operation, though to different extent depending on the operation behavior of the end-user. Automatically operated biomass combustion technologies can be divided into fixed bed furnaces, fluidized bed burners and entrained flow gasifiers whereas the latter two are only used for large scale purposes. Fixed bed furnaces are used for pellet stoves and automatic central heating systems. They can be differentiated according the combustion method which are top-fed, horizontally fed and underfed operation. Especially the top-fed and the horizontally fed systems are combined with manifold grates and burner systems, like dumping grates, moving grates, or tunnel burners. While automatic boilers which are used for central heating systems can be operated either with pellets or with wood chips automatic roomheaters are normally operated with pellets [26].

Operation of manually operated furnaces is characterized by batch wise combustion. Fuel like wood logs is provided and positioned by hand before each batch and air supply is adjusted manually. Combustion conditions during batches are not stationary but underlie variations in combustion rate, temperature and flue gas composition as a consequence of the predominance of respective combustion phases during the batch. Consequently a single batch represents already various combustion phases as it contains an ignition phase, full flaming and a burnout phase. Especially manually operated furnaces which are typically operated with wood logs or briquettes are manifold. They can be differentiated by three basic combustion principles which are through burning, top burning or under burning. Through burning and top burning are used predominantly for roomheaters like open fireplaces, closed fireplaces, chimney type wood stoves, masonry heaters, cookers or sauna stoves. They are usually operated with natural draught. Under-burning represents the latest development as it allows a most likely continuous combustion process. It is commonly used for log wood boilers and operated with fan assisted draught systems [26].

1.4 Emissions from biomass combustion

Basically the combustion process consists of four consecutive and to some extent parallel substeps of physical and chemical processes. In the first step the fuel is dried due to heating up to 150 °C. In the second step the pyrolysis takes place. Lignocellulose is decomposed at temperatures above 150 °C to light combustible gases like carbon monoxide (CO), methane (CH_4) and hydrocarbons. During gasification, which presents the third step, the solid fuel that remains after pyrolysis is gasified at temperatures up to 500 °C. In the last step, the oxidation, the combustible gases which were formed during pyrolysis and gasification are oxidized at temperatures between 700 and 1500 °C [26,27]. In order to achieve an optimum combustion process with a potentially complete oxidation of combustion gases, favorable conditions in the combustion chamber must be provided. These can be summarized with the “3-T-rule” (“temperature – time – turbulence”). An appropriate combustion temperature between 650 and 1300 °C, sufficient residence time of one to two seconds with the combustion gases and adequate mixing with combustion air are the decisive factors for the complete burn-out of the combustion gases [27]. In a complete combustion process mainly carbon dioxide (CO_2) and water vapour (H_2O) and, depending on the fuel composition, also smaller amounts of NO_x, sulfur dioxide (SO_2), hydrochloric acid (HCl) and ash particles are emitted [28,29]. In wood combustion processes there is a high risk of partially incomplete oxidation because of locally poor mixing of combustion air and fuel causing a lack of available oxygen, unfavorably low combustion temperatures or short residence times in the combustion chamber. Especially small combustion units which are typically used for residential applications are generally less carefully monitored and controlled than large combustion units. Therefore unfavorable combustion conditions may happen more often resulting in a higher risk of increased emissions of unwanted pollutants formed during poor oxidation [1]. Basically these are CO, organic compounds in the gas phase (volatile organic compounds; VOC) or in the solid phase (particulate organic matter) or soot [28].

In the European emission inventory, the sector group “commercial, institutional and household” is indicated as the primary sector group for the emissions of PM2.5, PAHs, CO and PM10. This sector group represents predominantly combustion pollutants from households and commercial and institutional buildings including also residential combustion sources. Emission sources are also assessed for subgroups from the sector groups. Residential combustion sources (“Residential: Stationary”) including residential wood combustion appliances account for 51% of PM2.5 and 42% of PAHs [30] indicating the high relevance of residential combustion appliances for the whole sector group. Similarly in Austria “commercial, institutional and households” is the primary sector group for PM2.5, PAHs and CO as exemplarily presented for PM2.5 and PAHs in Figure 1 [31].

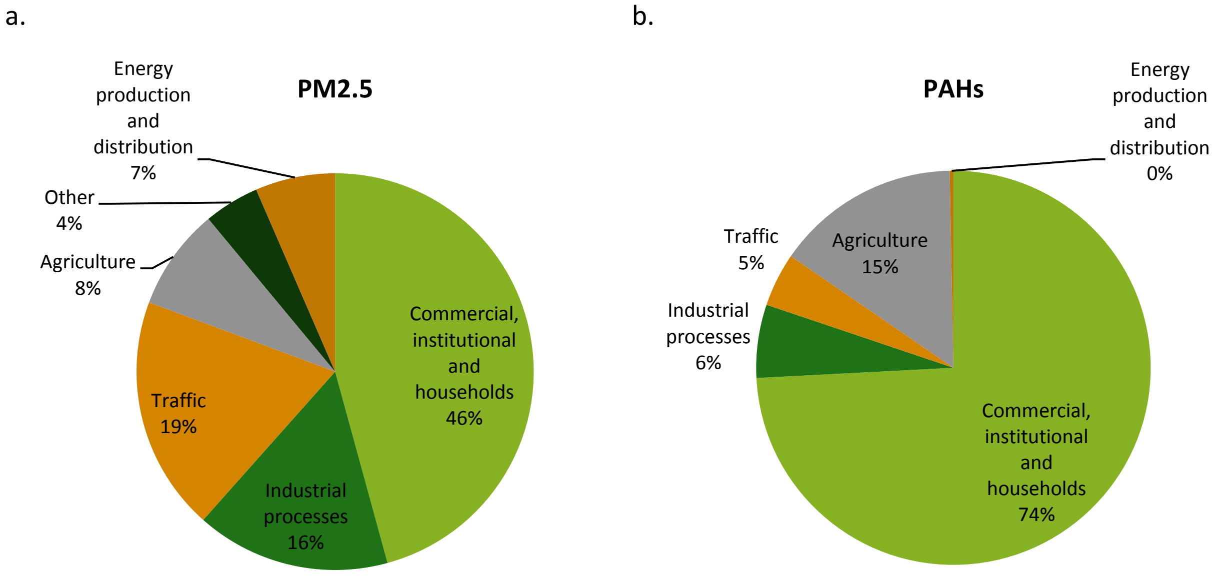
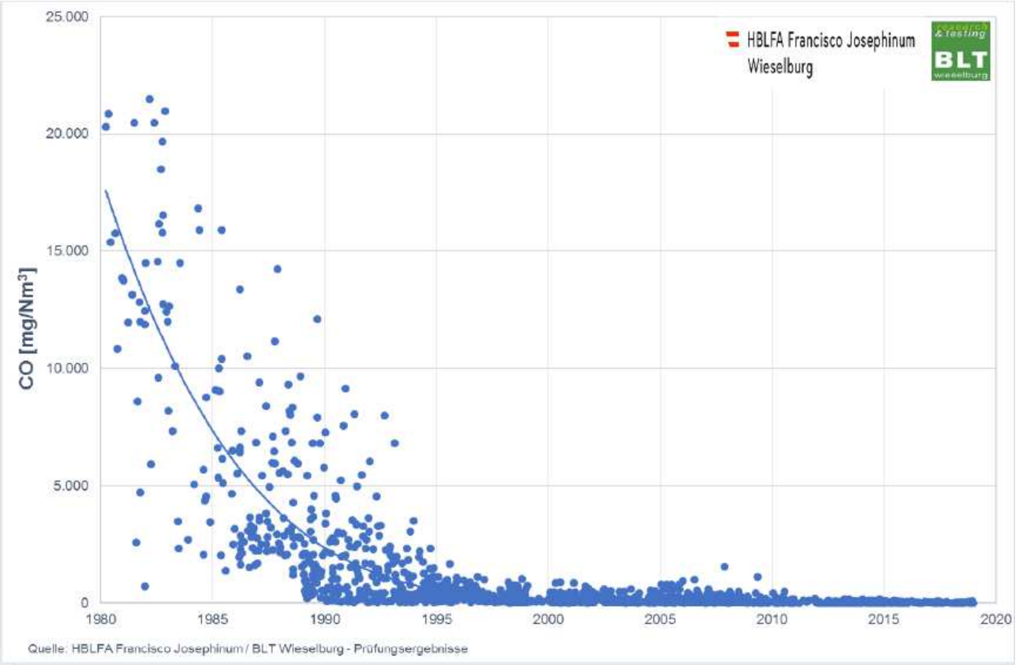


Figure 1: Share of emissions by sector groups in Austria in 2017 for PM2.5 (a.) and PAHs (b.). Data taken from Anderl *et al.* (2019) [31]

While emission inventories provide a good overview for whole countries or unions the more specific data on emissions sources can be obtained by source apportionment analysis of air quality measurements. For example measurements in two Alpine valleys showed that 88% and 65% respectively of the total carbonaceous matter originated from non fossil sources which are mainly attributed to wood combustion appliances [32]. In another study it could be shown that in a residential area in Germany 93% of PM10-bound PAHs originate mainly from combustion processes, whereas wood combustion makes clearly the largest share [33]. Studies like these indicate that wood combustion for heating can lead to regionally significantly increased emissions.

There is an urgent need to tackle emissions of atmospheric pollutants from biomass combustion and in particular from residential wood combustion. To drive the technical progress towards low emitting combustion technologies governments have been introducing thresholds for emissions from biomass combustion [34–36]. For example in 2015 the European Ecodesign directive was implemented which comes into force in 2022. There thresholds for CO, NO_x, OGC and TSP for residential wood combustion are defined for the whole European Union. The legislative pressure has already proven to be partly successful. As for example shown by standard type testing results of biomass boilers in Austria, emissions decreased drastically. While in the 1980s CO emission values of tested boilers varied between 1000 and above 22000 mg m^{-3} nowadays they are constantly below 100 mg m^{-3} (Figure 2) [37].



Quelle: HBLFA Francisco Josephinum / BLT Wieselburg - Prüfungsergebnisse

Figure 2: CO emissions of small scale biomass boilers measured in certification tests since 1980. Data presented by Sulzbacher (2020) [37].

These emission values were assessed by type test protocols which include favorable operation conditions like stationary full load and part load operation [38]. However, as for example shown in recent studies emission values reached in type tests can not be reached at real-life operation. PM emissions from practice related tests were mostly twice as much than from type tests [39,40]. In order to lower emissions from end-user operation, technological development has to be forced to also reduce emissions from operation phases like start, stop or load change operation. The introduction of real-life oriented test sequences and corresponding thresholds in the licensing process for combustion technologies would contribute to attain the whole potential towards low emission combustion technology.

1.5 Polycyclic aromatic hydrocarbons

1.5.1 Properties, sources and effects of PAHs

PAHs are a complex group of several hundreds of chemicals. They are organic compounds which contain only carbon and hydrogen and consist of two or more fused aromatic rings [41]. The distribution between the gas and particle phase varies according to the temperature conditions and the presence of particulate matter in the ambient air [42,43]. While some species with higher vapour pressures (e.g. naphthalene) occur primarily in the gas phase species with lower vapour pressure (e.g. dibenzo(a,h)anthracene) occur primarily sorbed on particles. Some species are semivolatile and occur in both in the gas and in the particle phase. Due to their chemical structure PAHs are the most stable form of hydrocarbons [44]. Therefore they tend to accumulate and are prone to long-range transboundary atmospheric transport and deposition. Consequently PAHs are listed as persistent organic pollutants (POPs) in the Aarhus protocol 1998 in order to contribute to a reduction of formation [45]. As investigated in many studies which are summarized in some reviews [46–48] there is no doubt about the toxic effects of PAHs. The main routes of exposure are inhalation, dermal contact and ingestion [46]. Beside short term health effects like eye and skin irritation, nausea, vomiting and inflammation, they cause a big variety of serious long term effects like skin, lung, bladder and gastrointestinal cancers, DNA, cataracts, kidney and liver damage, gene mutation, cell damaging and cardiopulmonary mortality [46]. They are formed from pyrogenic sources including all kinds of combustion processes, petrogenic sources like petroleum product spills or biological sources as products from plants and bacteria [47]. However, the single largest source is incomplete combustion either from anthropogenic or from natural processes [49]. These can be forest fires, vulcanoes, industrial processes, transportation, wood burning in stoves or cigarette smoking [44,47]. Thus they are present ubiquitously in the environment. Consequently methods were developed which allow for tracing back pollutants to their origin. For this purpose PAH fingerprints of tracer substances from the exhausts of major combustion sources like from coke ovens, from diesel and gasoline engines or from wood combustion were evaluated [50]. By means of source apportionment methods using diagnostic ratios of chemical tracers it was possible to show the impact of residential combustion sources on regionally increased PAH concentrations [33,51,52]. For example it was determined for two Italian regions, the Po plain and in the Valtelline valley, that more than 75% of BaP emissions in the winter are caused by biomass burning [52]. But also emission inventories indicate the substantial input of domestic heating to PAH pollution [30,53]. As presented in chapter 1.4 in the European Union in 2017 residential combustion sources accounted for 42% of PAH emissions. The importance of domestic heating and in particular of residential wood combustion regarding increased PAH concentration is clear.

1.5.2 Regulation and violations

At present there are no emission thresholds defined for PAHs. Although, European air quality policies set limit values for pollutants in the ambient air with harmful effects on human health. For Benzo(a)pyrene (BaP), which is used as marker for the carcinogenic risk of PAHs, a limit value of 1 ng m^{-3} as average of one year was set [54]. The European Air Quality Report of 2015 presented results of a measurement campaign which covered 22 countries all over Europe. 32% of the values measured by 657 stations exceeded the limit value for BaP. Residential combustion of coal and biofuels is stated as one of the main sources for BaP [18]. In Austria the number of exceedances decreased in the last years. While in 2010 in five out of 26 measurement stations the limit value was exceeded, in 2018 only one of 30 stations was above the limit value [55,56]. Although the situation in Austria improved in the last years, the topic is still relevant. Monthly or quarterly BaP values of air quality reports for Carinthia in Austria (Figure 3) and Switzerland illustrate that exceedances are caused by strongly increased values during the winter [57,58]. This is ascribed on the one hand to less atmospheric dispersion during the winter months and on the other hand to increased domestic heating activity [57,58]. A measurements report of Switzerland illustrates that in rural regions higher values were determined than in urban regions which are, however, more exposed to other emission sources like traffic or industry [57]. This confirms the important role of residential combustion as BaP emitter.

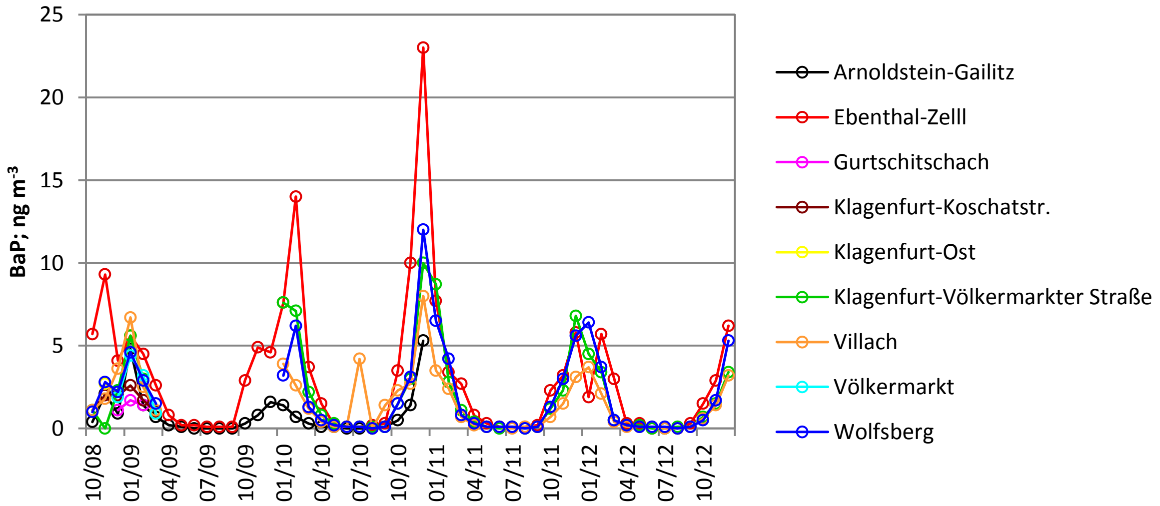


Figure 3: Monthly average values of BaP measurements from nine places in Carinthia from October 2008 to December 2012. Data taken from Spangl *et al.* (2013) [58].

1.5.3 BaP as guiding substance

A fundamental step towards PAH prevention is a thorough investigation of formation patterns. So far, many studies about PAH emission measurements from residential wood combustion furnaces were published. Different selections of PAH species were presented which hinders comparability of the outcomes [59–72]. Though, for further evaluations it is useful to have one value representing the relevance of the whole range of PAHs. As mentioned BaP counts as the guiding substance among PAHs as it is one of the most toxic compounds in this group [73–75]. Moreover it is the by far most studied PAH compound [76]. The role as guiding substance can be shown by measurements in previous publications about different residential wood combustion furnaces as presented in the following paragraph.

PAH species which contribute most to the total toxicity of PAHs were identified. Therefore randomly selected measurements of publications with high numbers of determined PAH species were used [59,63,67,68,77]. After multiplying the emission values with toxic equivalents (TEQ) published by Larsen and Larsen (2007) [78] it turned out that BaP, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene and dibenzo(a,h)anthracen accounted for at least 80% of the total toxicity. Four of them are the listed PAHs in the Aarhus protocol confirming the importance of the selected representatives. Consecutively, a total of 45 measurements of four publications [59,72,79,80] were used to examine the correlation of BaP with the toxicity of the six selected PAH coumpounds. As shown in Figure 4 BaP values indicate a strong correlation with the toxicity of the selected PAH group. According to a two-tailed *t*-test for paired samples this correlation is highly significant ($p<0.001$). BaP dominates the overall toxicity of the selected PAH compounds. This suggests that for investigations on PAH emissions the focus shall be set on BaP.

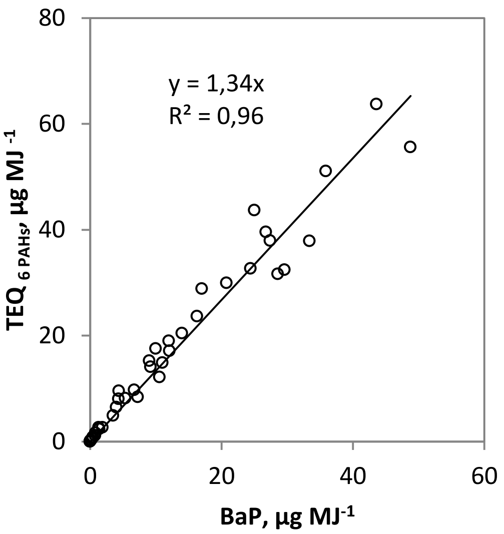


Figure 4: Correlation of BaP with summarized TEQs of BaP, Fluoranthene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene and Dibenzo(a,h)anthracene. For references see the text above.

1.5.4 Determination methods for PAHs

Several methods for the determination of PAHs from combustion processes were developed. Some of them are shortly described in Table 1. Basically determination methods consist of two separate steps which are sampling and analysis. As already mentioned some PAHs occur primarily in the gas phase, some are primarily sorbed on particles and some are semivolatile meaning that according to the flue gas conditions they are variably distributed between the gas and the particle phase. The different thermodynamic properties of PAHs make sampling rather complex. In order to be capable to retain a preferably high number of different PAHs various approaches are applied. For measurements the flue gas is for example cooled by a dilution tunnel, by a water cooled probe or by a condenser in order to increase the share of PAHs in the particle phase. Sampling is realized in at least two steps by for example a filter and an adsorber. In addition condensates and rinsing solutions have to be respected for the quantitative analysis. For analysis the samples are extracted and analysed by high performance liquid chromatography or by gas chromatography-mass-spectrometry.

As shown in chapter 1.5.3 BaP can be considered as a suitable representative for the toxicity of PAHs. Focussing in the measurements on a single substance like BaP which occurs primarily in the particle phase could allow for simplifying the measurement process.

Table 1: Overview of some methods for the determination of PAHs in the flue gas of stationary sources

Short name	Long name	Short description
VDI 3874 [81]	VDI 3874 Stationary source emissions; Determination of polycyclic aromatic hydrocarbons (PAH); GC/MS method	Sampling of a partial stream by a cooled suction tube. Most condensables are thereby removed. Other condensables are precipitated in a condensation recipient at a temperature of < 30 °C. Then the flue gas stream is passed through a solid adsorbent. The condensate, the solutions from rinsing of the suction tube and the extract of the solid adsorbent are combined and transferred into a toluene phase. Separation and analysis is carried out by gas chromatography-mass-spectrometry.
ISO 11338-1 Method A [82]	ISO 11338-1 Stationary Source emissions – Determination of gas and particle-phase polycyclic aromatic hydrcarbons Part 1: Sampling Method A – Dilution Method	Isokinetic sampling by a heated probe and rapid cooling to <40 °C by a dilution tunnel. Then the flue gas stream is conveyed through a glass fiber filter and a solid adsorbent. The filter and the adsorber are extracted and analysed.
ISO 11338-1 Method B [82]	ISO 11338-1 Stationary Source emissions – Determination of gas and particle-phase polycyclic aromatic hydrcarbons Part 1: Sampling Method B – (Heated) filter/condenser/adsorber method	Isokinetic sampling by a heated probe. Then the flue gas is conveyed through a heated particle filter and consecutively through a condenser which cools the sample gas below 20 °C. Gaseous PAHs are than retained by impingers or solid adsorbents.
ISO 11338-1 Method C [82]	ISO 11338-1 Stationary Source emissions – Determination of gas and particle-phase polycyclic aromatic hydrcarbons Part 1: Sampling Method C – Cooled probed/adsorber method	Isokinetic sampling into a water-cooled probe which is lined with a glass, quartz or titanium insert. Thereby the flue gas is cooled to below 40°C. The condensate is caught by a flask. Downstream a solid adsorber and a filter are installed.
ISO 11338-2 [83]	Stationary source emissions – Determination of gas and particle-phase polycyclic aromatic hydrocarbons – Part 2: Sample preparation, clean-up and determination	The samples are combined and extracted with a suitable organic solvent and concentrated with an evaporator. Analysis is carried out by high performance liquid chromatography or by gas chromatography mass spectrometry.

1.5.5 Literature overview about BaP emissions measurements

Different influences like fuel type, operating conditions or technology were investigated in various studies. To enable a concise and comparable overview of published data only BaP values are presented in Table 2. In the original publications they are calculated either on a volume-, mass- or energetic basis and presented in mg $m^{-3}_{d.b.}$ referred to 13% O_2 in the flue gas, in µg kg^{-1} wet fuel, in µg kg^{-1} dry fuel or in µg MJ^{-1}. In order to allow a comparison of the values from different studies the values are calculated all to µg MJ^{-1}. Because the required fuel data for the calculations were not always sufficiently available, conversion factors were calculated for the fuels which were used in this work. The harmonized values in µg MJ^{-1} which are presented in Table 2 can be recalculated using the conversion factors presented in the bottom of the table. The simplification leads to a deviation from the original data, and thus is an approximation only, but allows comparability of previously published data. In the following paragraphs outcomes of publications on BaP emissions from residential wood combustion furnaces are summarized and needs for further research are elucidated.

- Most of the studies focus on the emission characterization of various furnaces used for residential wood combustion either at different operation or operated with different wood types.
- Published values are assessed predominantly from manually operated systems, like log wood stoves, fireplaces, log wood boilers, masonry heaters or sauna stoves [59,61,63,66,67,72,77,84]. Measurements represent emissions that occur in whole batches, including ignition at the beginning, full flaming in the intermediate phase and burnout at the end of the batch.
- In some works the influence of fuel type was investigated [59,66,67]. A significant impact on BaP or PAH emissions due to the used type of logwood has not been reported. Though, it has been shown that clearly lowest emissions can be achieved with briquettes. The work of Kistler (2012) [67] indicates that garden wastes (pine needles and leaves) should be avoided as BaP emissions were clearly highest compared to various wood fuels.
- Orasche *et al.* (2012) [77] compared emissions from batches starting either with a cold system with no preceding warming up batch (cold start) or with a preheated system. BaP emissions were mostly significantly higher from the measurements with cold starts.
- The preconditioning of the systems but also other aspects of the test design differs from study to study. As shown by Orasche *et al.* (2012) [77] these aspects can have a significant impact on BaP emissions. For example the definition of the end of a batch and the resulting sampling period varies. Sampling is stopped either when the flame expires, when the wood mass is reduced to a defined share or after a defined time span. These and other differences in testing make it hard in order to draw conclusions by comparisons of the outcomes from different studies.
- Several studies present values from automatic systems like pellet stoves, pellet boilers and wood chip boilers [61,63,65–67,77]. The emissions from wood chip boilers were rather higher than those from pellet boilers [63,77].
- Boman *et al.* (2011) [79] compared emissions from operation at high load (near nominal load) and from low load of two small scale pellet furnaces. For both, BaP emissions were lower at operation near nominal load.
- In the work of Orasche *et al.* (2012) [77] the emissions of automatically operated furnaces were investigated. PAH and BaP emissions were considerably higher when cold starts were included than when only warm starts were investigated in the operation sequences. In this work start operation phases were always combined with nominal load operation, but the time span of nominal load after start differed which hinders to identify phase specific emission pattern.

- Jalava *et al.* (2012) [63] presented values from a modern pellet boiler and a modern wood chip boiler including various phases, imitating typical operation of automatic residential wood combustion furnaces at the end-user. Therefore the results of this and also of the previously mentioned work [63,77] represent rather values that may occur in rea-life. However, combined values disable to identify emissions that occur in specific operation phases and the real impact of specific operation as for example cold start operation on total emissions.
- Studies comparing manually operated furnaces like log wood stoves and automatic furnaces like pellet stoves indicate that the latter exhibit lower BaP emissions [66,67,85]. However, measured operation sequences especially of automatic furnaces do not or poorly represent realistic operation.
- The combination of all values in Table 2 are presented in boxplots in Figure 5a and b. Considering the different y-axis of the boxplots it is clearly indicated that BaP emissions from automatically operated furnaces are clearly lower than from manually operated furnaces. BaP emissions from sauna stoves were by far the highest. However, these comparisons must be considered with caution because test sequences, sampling periods, fuel type and sampling design differ. Moreover many values from automatic furnaces are conducted during steady-state operation excluding start and stop operation phases. Consequently, BaP emissions from pellet stoves, pellet boilers and wood chip boilers might be underestimated. But also the values of manually operated furnaces do not necessarily represent emissions that are relevant in real-life.
- Further data analysis is impeded due to differences in the test design, measurement practices and poor descriptions of test conditions.

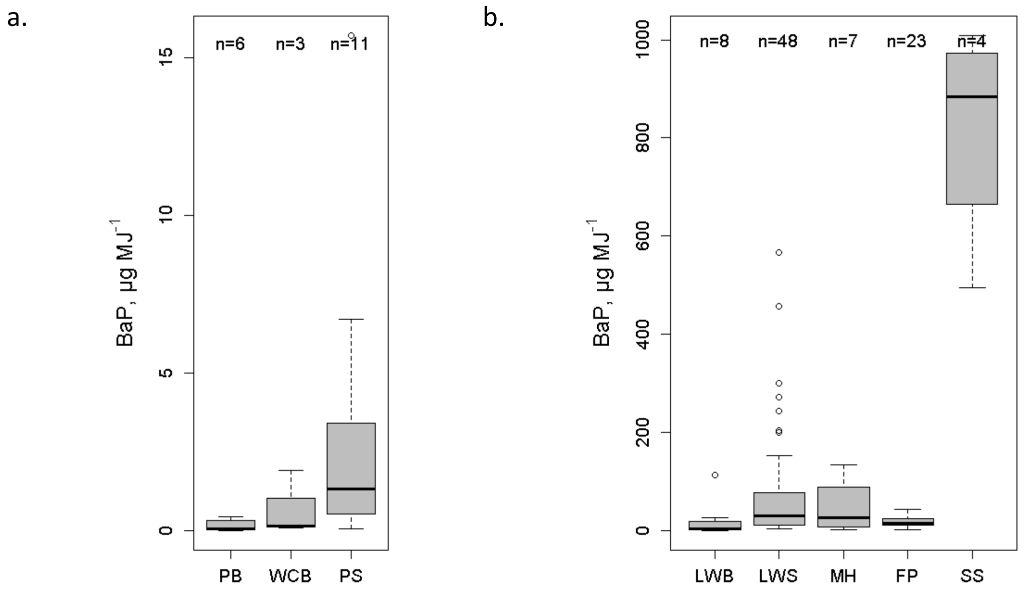


Figure 5: Comparison of BaP values presented in Table 2 from automatic (a.) and manually operated (b.) residential wood combustion furnaces. PB=pellet boiler, WCB=wood chip boiler, PS=pellet stove, LWB=log wood boiler, LWS=log wood stove, MH=masonry heater, FP=fireplace, SS=sauna stove. Used values were harmonized to the same unit (µg MJ^{-1}) using conversion factors presented in Table 2. Conversion presents approximation of emission values allowing for harmonization to the same unit.; The bold lines indicate the medians, the boxes comprise values from the 25%- to the 75%-quantiles, the whiskers comprise values from the minimum value to the maximum value, excluding outliers. Values which exceed 1.5 times the span of the 25%- or rather 75%-quantile from the outer barrier of the box are defined as outliers, indicated with small circles.

Table 2: BaP emission data from published literature possibly recalculated for the harmonization of values to µg MJ^{-1} (conversion factors listed at the end of the table); (LWB=log wood boiler, PS=pellet stove, FP=fireplace, LWS=log wood stove, PB=pellet boiler, WCB=wood chip boiler, MH=masonry heater, SS=sauna stove)

Ref.	**type of furnace**	**fuel**	**operation**	**BaP, µg MJ^{-1}**
Bari *et al.* (2011) [65]	LWB (30 kW)		"complete combustion conditions"	0.569[1]
	LWB (30 kW)		"incomplete combustion conditions"	4.79[1]
	PS (7.6 kW)		"complete combustion conditions"	4.89[1]
	PS (7.6 kW)		"incomplete combustion conditions"	15.7[1]
Boman *et al.* (2011) [79]	PS (5.5 kW)	pellets	continuous operation at high load (no start included)	0.04
	PS (5.5 kW)	pellets	continuous operation at low load (no start included)	0.75
	PS (5 kW)	pellets	continuous operation at high load (no start included)	0.31
	PS (5 kW)	pellets	continuous operation at low load (no start included)	6.70
Gonçalves *et al.* (2012) [59]	FP	Briquettes/ Pellets	whole batch	1.33[2]
	FP	Eucalyptus	whole batch	3.47[2]
	FP	Maritime Pine	whole batch	12.0[2]
	FP	cork oak	whole batch	13.9[2]
	FP	Golden wattle	whole batch	16.1[2]
	FP	Olive	whole batch	27.1[2]
	FP	Portugues oak	whole batch	35.5[2]
	FP	holm oak	whole batch	43.2[2]
	LWS	Briquettes/ Pellets	whole batch	3.83[2]
	LWS	Portugues oak	whole batch	4.29[2]
	LWS	cork oak	whole batch	4.35[2]
	LWS	Maritime pine	whole batch	5.28[2]
	LWS	Golden wattle	whole batch	9.31[2]
	LWS	Eucalyptus	whole batch	20.6[2]
	LWS	Olive	whole batch	23.5[2]
	LWS	holm oak	whole batch	24.2[2]
Hedberg *et al.* (2002) [84]	commercial LWS	birch logs		244[3,4]
Jalava *et al.* (2012) [63]	modern PB (21 kW)	soft wood pellets	ten hours operation including full load, part load, load change, start-up, shut down procedures	0.321[5]
	modern WCB (30 kW)	wood chips	ten hours operation including full load, part load, load change, start-up, shut down procedures	0.069[5]
	modern LWB (30 kW)	beech logs	two full load batches	3.07[5]
	old LWB (12 kW)	beech logs	three full load batches	113[5]
	modern LWS (6 kW)	beech logs	six full load batches	7.84[5]
	old LWS (6.5 kW)	beech logs	six full load batches	272[5]
	modern MH (4.2 kW)	beech logs	one full load batch	1.83[5]
Kaivosoja *et al.* (2012) [72]	SS (18 kW)	birch logs	average value of full load batches without catalytic treatment	936
	SS (18 kW)	birch logs	average value of full load batches with catalytic treatment	495
Kistler (2012) [67]	PS (9 kW)	soft wood pellets	full and part load operation (no start included)	1.6
	LWS (8 kW)	hardwood briquettes	two full load batches including cold start	3.0

Ref.	type of furnace	fuel	operation	BaP, µg MJ^{-1}
	LWS (8 kW)	European larch	two full load batches including cold start	6.3
	LWS (8 kW)	Norway spruce	two full load batches including cold start	6.3
	LWS (8 kW)	Black poplar	two full load batches including cold start	11
	LWS (8 kW)	pendunculate oak	two full load batches including cold start	12
	LWS (8 kW)	Black locust	two full load batches including cold start	16
	LWS (8 kW)	European hornbeam	two full load batches including cold start	17
	LWS (8 kW)	Sessile oak	two full load batches including cold start	22
	LWS (8 kW)	Silverfir	two full load batches including cold start	22
	LWS (8 kW)	Black pine	two full load batches including cold start	29
	LWS (8 kW)	European beech	two full load batches including cold start	36
	LWS (8 kW)	Turkey oak	two full load batches including cold start	37
	LWS (8 kW)	pine needles	two full load batches including cold start	77
	LWS (8 kW)	dry leaves	two full load batches including cold start	199
Orasche *et al.* (2012) [77]	PB (25 kW)	spruce pellets	cold start and nominal load operation, 20 min	0.43
	PB (25 kW)	spruce pellets	warm start and nominal load operation, 120 min	0.030
	PS (13 kW)	spruce pellets	cold start and nominal load operation, 20 min	1.3
	PS (13 kW)	spruce pellets	warm start and nominal load operation, 120 min	0.077
	LWB (30 kW)	spruce logs	cold start and nominal load operation, 20 min	10
	LWB (30 kW)	spruce logs	warm start and nominal load operation, 60 min	0.12
	LWB (30 kW)	beech logs	cold start and nominal load operation, 20 min	25
	LWB (30 kW)	beech logs	warm start and nominal load operation, 60 min	0.12
	WCB (30 kW)	spruce chips	cold start and nominal load operation, 20 min	1.9
	WCB (30 kW))	spruce chips	warm start and nominal load, 120 min	0.15
	LWS (8 kW)	beech logs	full load batch inclusive cold start	9
	LWS (8 kW)	beech logs	full load batch inclusive warm start	11
	LWS (8 kW)	spruce logs	full load batch inclusive cold start	17
	LWS (8 kW)	spruce logs	full load batch inclusive warm start	12
Ozgen *et al.* (2014) [66]	advanced LWS (8 kW)	spruce	ignition (20 min), full load batch (1h), overloaded batch with closed air valve (1h)	36
	advanced LWS (8 kW)	oak	ignition (20 min), full load batch (1h), full load batch (1h)	48
	advanced LWS (8 kW)	false acacia	ignition (20 min), full load batch (1h), full load batch (1h)	76
	advanced LWS (8 kW)	beech	ignition (20 min), full load batch (1h), overloaded batch with closed air valve (1h)	94
	advanced LWS (8 kW)	hornbeam	ignition (20 min), full load batch (1h), full load batch (1h)	153
	advanced LWS (8 kW)	beech	ignition (20 min), full load batch (1h), full load batch (1h)	204
	advanced LWS (8 kW)	spruce	ignition (20 min), full load batch (1h), full load batch (1h)	456
	closed FP (11 kW)	hornbeam	ignition (20 min), full load batch (1h), full load batch (1h)	4.7
	closed FP (11 kW)	beech	ignition (20 min), full load batch (1h), overloaded batch with closed air valve (1h)	8.3
	closed FP (11 kW)	hornbeam	ignition (20 min), full load batch (1h), overloaded batch with closed air valve (1h)	8.5
	closed FP (11 kW)	beech	ignition (20 min), full load batch (1h), full load batch (1h)	9.5
	closed FP (11 kW)	spruce	ignition (20 min), full load batch (1h), full load batch	12.0

Ref.	**type of furnace**	**fuel**	**operation**	**BaP, µg MJ^{-1}**
			(1h)	
	closed FP (11 kW)	oak	ignition (20 min), full load batch (1h), overloaded batch with closed air valve (1h)	12.2
	closed FP (11 kW)	spruce	ignition (20 min), full load batch (1h), overloaded batch with closed air valve (1h)	15.0
	closed FP (11 kW)	false acacia	ignition (20 min), full load batch (1h), overloaded batch with closed air valve (1h)	18.0
	closed FP (11 kW)	false acacia	ignition (20 min), full load batch (1h), full load batch (1h)	25.0
	closed FP (11 kW)	oak	ignition (20 min), full load batch (1h), full load batch (1h)	25.8
	open FP (8 kW)	hornbeam	ignition and further 8 refuellings (lower mass than defined by the manufacturer)	10.0
	open FP (8 kW)	oak	ignition and further 8 refuellings (lower mass than defined by the manufacturer)	17.0
	open FP (8 kW)	false acacia	ignition and further 8 refuellings (lower mass than defined by the manufacturer)	18.0
	open FP (8 kW)	beech	ignition and further 8 refuellings (lower mass than defined by the manufacturer)	22.0
	open FP (8 kW)	spruce	ignition and further 8 refuellings (lower mass than defined by the manufacturer)	32.0
	PB (25 kW)	low quality pellets	one hour full load operation (no start included)	0.04
	PB (25 kW)	high quality pellets	one hour full load operation (no start included)	0.08
	PS (8 kW)	low quality pellets	one hour full load operation (no start included)	1.10
	PS (8 kW)	high quality pellets	one hour full load operation (no start included)	1.90
	traditional LWS (6 kW)	false acacia	ignition (20 min), full load batch (1h), full load batch (1h)	25
	traditional LWS (6 kW)	hornbeam	ignition (20 min), full load batch (1h), overloaded batch with closed air valve (1h)	44
	traditional LWS (6 kW)	beech	ignition (20 min), full load batch (1h), overloaded batch with closed air valve (1h)	52
	traditional LWS (6 kW)	beech	ignition (20 min), full load batch (1h), full load batch (1h)	56
	traditional LWS (6 kW)	oak	ignition (20 min), full load batch (1h), full load batch (1h)	66
	traditional LWS (6 kW)	Spruce	ignition (20 min), full load batch (1h), full load batch (1h)	67
	traditional LWS (6 kW)	Oak	ignition (20 min), full load batch (1h), overloaded batch with closed air valve (1h)	100
	traditional LWS (6 kW)	hornbeam	ignition (20 min), full load batch (1h), full load batch (1h)	566
Pettersson *et al.* (2011) [61]	LWS (9 kW)	birch	full load batch inclusive warm start	30
	LWS (9 kW)	pine	full load batch inclusive warm start	38
	LWS (9 kW)	birch	full load batch inclusive warm start	100
	LWS (9 kW)	Spruce	full load batch inclusive warm start	300
Tissari *et al.* (2007) [60]	conventional MH	spruce	end-user operation	10.2[3]
	conventional MH	birch	end-user operation	26.4[3]
	SS	alder and aspen	end-user operation	1009[3]
Lamberg *et al.* (2011) [68]	modern PB		efficient combustion, continuous combustion , 2-3 h	0.002[5]
	modern MH	birch logs	improved batch combustion, 50 min collection in the 3rd and 4th batch	1.65[5]
	conventional MH	birch logs	conventional batch combustion, 55 min inclusive ignition (CBC1)	93.5[5]
	conventional MH	birch logs	conventiona lbatch combustion, 15 min from the beginning of the second batch (CBC2/F)	134[5]

Ref.	type of furnace	fuel	operation	BaP, µg MJ^{-1}
	modern MH	birch logs	conventional batch combustion, 40 min during second and thrid batch (CBC3/23)	84.0[5]
	SS	birch logs	inefficient batch combustion, ignition and second batch	834[5]

[1]… values presented in mg $m^{-3}_{d.b}$ at 13% O_2 and converted to µg MJ^{-1} with the factors 0.91 for pellet fuels and 0.81 for log wood fuels

[2]… values presented in µg $kg^{-1}_{d.b.}$ and converted to µg MJ^{-1} with the factor 0.055 for briquettes and 0.053 for log wood fuels.

[3]… values presented in µg $kg^{-1}_{w.b.}$ and converted to µg MJ^{-1} with the factor 0.068 for all log wood fuels.

[1, 2, 3]… conversion factors were calculated using fuel compositions presented in Publication II (see chapter 7.2 [86]). For all log wood fuels the composition of beech logs was used, for compressed fuels the composition of pellets was used. Conversion presents approximation of emission values allowing for harmonization to the same unit.

[4]… PAHs determined from PM2.5 samples

[5]… PAHs determined from PM1 samples

The summary of literature data of PAH emissions values illustrates that even though many PAH emission values of biomass combustion have been published there is a lack of systematic emission characterization of residential wood combustion furnaces. Only measurement values from operation sequences which occur at the end-users are informative about the real impact on ambient air. Otherwise, technology specific measurement data may lead to over- or rather underestimations of characteristic PAH emissions. The knowledge of typical emission levels for residential wood combustion furnaces is important in order to find technology specific reduction strategies. Moreover the quality of emission inventories relies on the availability of real-life oriented emission values.

Furthermore the published emission data do only scarcely allow for discovering phase specific emission patterns within combustion processes of residential wood combustion furnaces due to little measurement data or diffuse differentiation of operation phases. Especially for boilers which are automatically regulated according to the actual heat demand, the operation is highly variable. Phase specific values would allow for identifying the influence of the operation program and contribute to an adequate development of emission mitigation strategies.

1.5.6 Control mechanisms for PAH emissions

Studies about techniques for the removal of PAH emissions are rather limited so far [87]. For stationary combustion sources investigations were carried out primarily for large scale units like municipal or industrial waste incinerators or coal fired power plants. The use of activated carbon was shown as interesting option for PAH removal [88,89]. Higher removal efficiencies can be achieved when metal catalysts are supported on activated carbon filters. In a laboratory test it could be shown that from catalytic elements copper, palladium (Pd) and platinum (Pt) the most efficient removal of PAHs by more than 95% was achieved with the Pt-catalyst [90]. Hsu *et al.* (2016) [91] tested different arrangements for PAH emission reduction in large scale combustion units and came to the result that adsorption on activated carbon, indeed, effectively impacts emissions of PAHs but only by transferring gas-phase PAHs to solid phase. Consequently the PAH concentration in the dust is increased which causes secondary pollution. In comparison the integration of a catalytic filter is more effective because PAH concentration in the retained dust is significantly lower. In other studies it could be shown that the wet flue gas desulfurization has the co-benefit of effective PAH removal [92] and wet electrostatic precipitation represents a very efficient option for PAH removal [93]. All in all there are various options for the reduction of PAHs. However, they are rather complex which is reasonable for large scale combustion units but not applicable for small scale applications.

Also for vehicles, representing a type of smaller scale combustion units, PAH reduction from emissions was investigated in some studies. It could be shown that catalytic converters are effective for the reduction of PAH emissions. For both, gasoline and diesel engines, PAH emissions from the flue gas can be substantially reduced [94,95]. For gasoline engines a reduction of 94% was revealed [95].

In the work of Ravindra *et al.* (2008) it is stated that so far PAH emissions from domestic sources like residential wood combustion are largely unregulated, but the adoption of catalytic devices could offer an effective reduction measure [44]. However, for PAH removal from domestic combustion so far only little information is available. Kaivosoja *et al.* (2012) [72] presented values of a sauna stove from combustion tests either with or without the integration of a catalyst for flue gas treatment. PAH emissions (15 different PAHs) were reduced by a Pt/Pd catalyst by almost a third and in particular BaP emissions by a half indicating the high reduction potential. Similar tests were conducted by Fine *et al.* (2004) [71] who also used a Pt/Pd catalyst in a log wood stove. In tests with an integrated catalyst PAH emissions (12 different PAHs) were, however, higher than when omitting the catalyst. In both studies comparisons were drawn by outcomes of consecutive combustion tests. Because combustion performance of manually operated furnaces as tested in the two works often vary from batch to batch this could also influence the results of comparative tests from consecutive test runs.

Therefore differences which are ascribed to the impact of the catalysts could be a result of variable combustion conditions.

The effect of oxidative catalysts on PAH emissions was only scarcely investigated and the effect could not be clarified so far. However, it was already shown that it could provide an interesting option for PAH emission reduction. Further investigations would provide a valuable input to the clarification of the effect of catalytic treatment on the flue gas of biomass combustion

2 Objectives

The overall objective of the thesis is the investigation of BaP emissions from residential wood combustion furnaces by standardized real-life operation procedures in order to contribute to the development of effective mitigation strategies for PAH emissions from end-user operation. The results should provide comparable emission values representing end-user operation and demonstrate critical combustion phases for BaP emissions. Beside the generation of real-life emission data, also the development of a compact measurement set up for BaP, and the introduction of standardized real-life measurement procedures should provide valuable inputs for the development of PAH reduction measures.

The following research questions were formulated:

- Is it possible to obtain a simplified and more compact measurement set up, when only the guiding substance BaP is measured?
- In which range are real-life BaP emissions of automatic small scale biomass boilers and what are the most critical operation phases?
- In which range are real-life BaP emissions of different types of modern wood stoves?
- Which effect has the integration of commercially available catalysts on PAH emissions from residential wood combustion furnaces at real-life operation?

3 Methodology

3.1 Investigated combustion furnaces

In this work 20 state of the art furnaces are investigated. The majority are small scale furnaces with nominal heat capacities below 50 kW which are typically used for residential wood combustion (Table 3). Different types are chosen comprising nine automatic furnaces with automatic fuel and air supply including six boilers and three stoves, and nine manually operated furnaces including six log wood stoves and three cookers. The nominal capacities of the stoves and cookers are between 6 and 10 kW. The nominal capacities of the boilers range between 12 and 500 kW whereas four of them are between 12 and 15 kW, one has 70 kW and one has 500 kW. For investigations of the impact of catalysts on the flue gas another log wood stove with a nominal capacity of 10 kW is used.

Table 3: Investigated heating furnaces

type of furnace	Nominal capacity, kW	Combustion method
pellet boiler	12	underfed combustion
pellet boiler	15	underfed combustion
pellet boiler	15	top-fed combustion
pellet boiler	15	horizontally fed combustion
pellet boiler	70	horizontally fed combustion
multifuel boiler operated with pellets and wood chips	500	horizontally fed combustion
pellet stove	8	top-fed combustion
pellet stove	8	top-fed combustion
pellet stove	10	top-fed combustion
pellet stove	10	top-fed combustion
log wood stove	6	top burning
log wood stove	6	top burning
log wood stove	6	top burning
log wood stove	6	top burning
log wood stove	7	top burning
log wood stove	8	top burning
log wood stove	10	top burning
logwood cooker	7.5	top burining/through burning
logwood cooker	7.5	top burining/through burning
logwood cooker	8	top burining/through burning

3.2 Test operation

For the characterization of emissions of automatically operated furnaces stationary operation phases like nominal load operation or part load operation and also unsteady operation phases like start and stop operation have to be evaluated in order to represent typical emission behavior.

Measurements for automatic boilers are carried out for start, stop, full load and part load operation respectively. While for steady state operation the measurement period was defined only by a minimum time span of one hour at steady combustion conditions, the measurement periods for start and stop operation were defined more in detail. The start phase was defined to begin when the ignition system is started. It ends when both, the CO concentration and the flue gas temperature move towards conditions typical for steady state operation which has to be identified by pretests in advance. The start phase and consequently also the sampling period stops when both, a temperature- and a CO-criterion are fulfilled. This is accomplished when the flue gas temperature reaches 90% of the flue gas temperature during full load operation and when CO concentration falls below a CO concentration of 100 ppm above CO concentration at full load operation (Figure 6a). The stop phase was defined to begin when the fuel supply rate decreases, which is indicated by increasing CO concentration and stops when air supply stops (Figure 6b). The clear definitions of beginning and end of start and stop operation allows to distinguish sharply between emissions from different phases. Examples for start, stop and full load sampling phases are presented in Figure 6 by some combustion parameters.

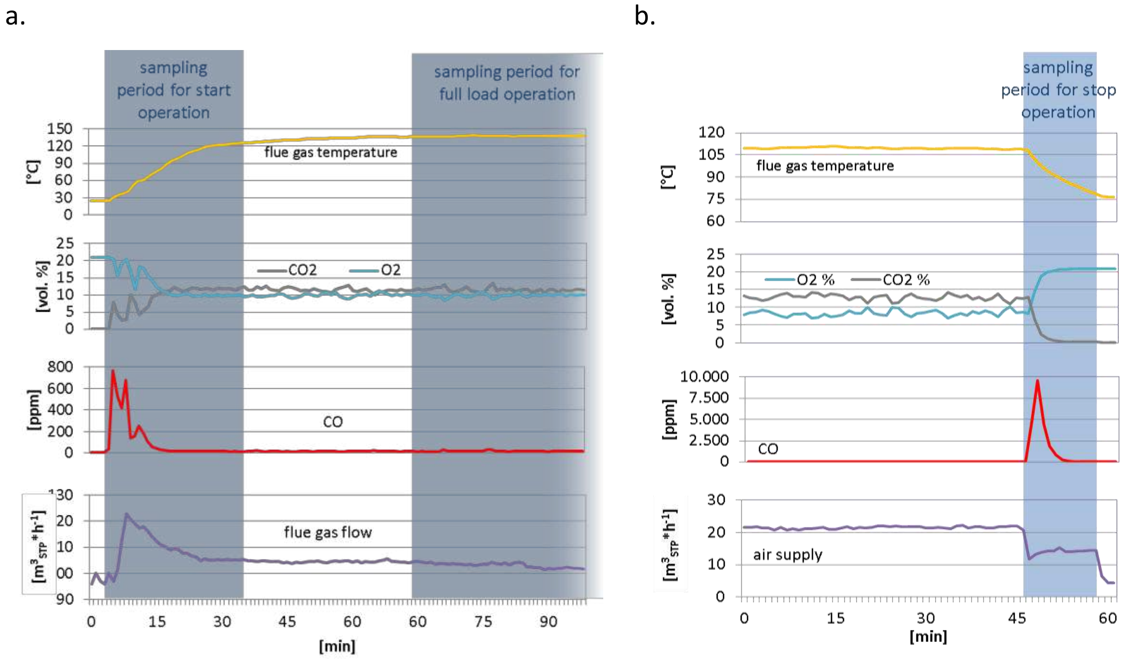


Figure 6: Examples of emissions measurement periods for start and full load operation phases (a.) and stop operation phase (b.) at automatic boilers presented by some combustion parameters.

For pellet stoves and also for log wood stoves, test protocols were recently defined in a European project called “beReal” (www.bereal-project.eu). Because these protocols aim to represent typical operation behavior of the end-user they are chosen for the characterizations in this work.

The protocol for pellet stoves includes more than the four typical operation phases, which are measured at the boilers. It includes for example beside a start from cold conditions also two restarts starting from preheated conditions, part load phases at two different load levels, a load change and two operation breaks and lasts almost eight hours (Figure 7a). Instead of having specific values for each operation phase, the test protocol enables to evaluate one combined value representing emissions at typical end-user operation. While gaseous flue gas compounds are measured continuously as highlighted by the blue indication in Figure 7a sampling of particulate emissions are carried out only during the combustion operation and not during standby phases as indicated by the darker blue indications.

At manually operated furnaces combustion performance can vary from batch to batch, as a result of for example variations in the fuel amount and quality, air supply or the temperature conditions in the combustion chamber. Consequently the characterization of manually operated combustion furnaces is carried out over several batches. Sampling of both gaseous flue gas compounds like CO and OGC (organic gaseous compounds) and particulate flue gas compounds (TSP, TSP_{dil}) are carried out over whole batches. The beginning of a batch is defined by the ignition of the fuel at first batches or by closing the door of the combustion chamber after refueling for consecutive batches. The end of the batch is defined by the decrease of the present CO_2 concentration to a limit value which is evaluated during the batch. This limit value is specified to be a quarter of the maximum CO_2 concentration that occurred during the batch (e. g. $\frac{15\%}{4} = 3.75\%$) but is by minimum 3% and by maximum 4%.

Equivalently to pellet stoves also for logwood stoves a beReal protocol is applied which, however, differs substantially from that of pellet stoves. The operation protocol comprises one ignition batch starting from cold conditions, four consecutive full load batches, three part load batches and a cooling down phase. Sampling of gaseous flue gas compounds is carried out continuously over the whole time span of combustion operation as indicated by light and darker blue indications (Figure 7b). Sampling of particulate flue gas compounds is carried out during the first, third, fifth and seventh batch as indicated by the darker blue indications allowing for intermediate sample preparation during batches two, four and six.

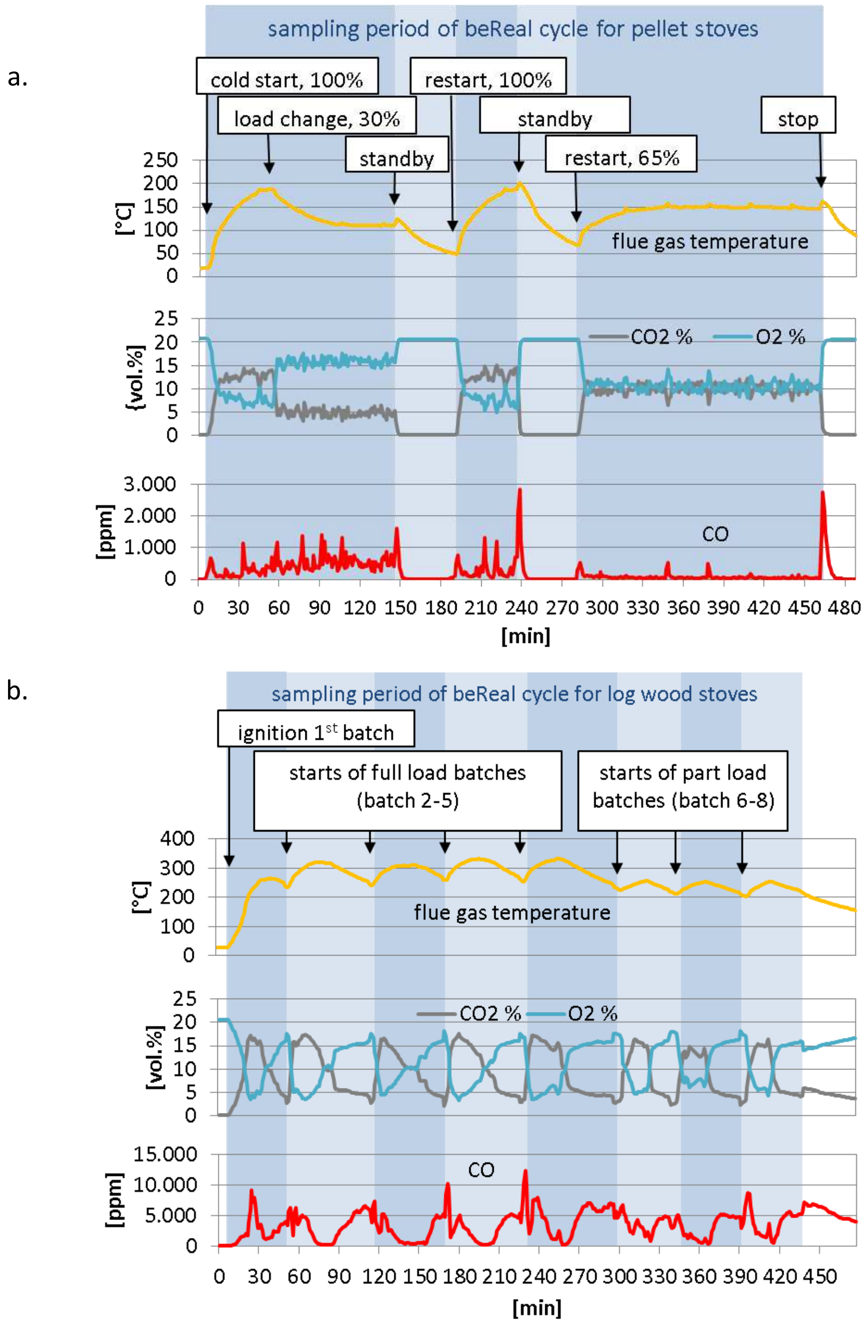


Figure 7: BeReal cycles for pellet stoves (a.) and log wood stoves (b.) presented by selected combustion parameters. The sampling periods of combustion parameters are indicated by the blue areas, whereas discontinuously measured parameters (TSP, $\mathrm{TSP_{dil}}$, BaP, EC, OC, TC) were determined in the periods indicated by darker blue areas.

For log wood cookers no beReal cycle has been developed so far. However, equal to log wood stoves cookers represent manually operated combustion furnaces with batch-wise combustion. In some surveys it was shown that there are many analogies in the real-life operation of stoves and cookers [96–98]. Consequently it was decided to apply the protocol for log wood stoves also for cookers.

3.3 Emission measurement

For emission characterization gaseous and particulate flue gas compounds are determined. For each part of the work described within this thesis measurement parameters are chosen according to the focus of the investigation. Because also synchronous measurements are carried out, for each parameter two measurement equipments are required. In the following sections all used measurement methods are presented. The names and suppliers of the used measurement equipments are indicated in the brackets.

The gaseous flue gas compounds O_2, CO_2, CO, OGC and NO_x are measured continuously, with state of the art techniques, providing data with high time resolution.

- O_2 is determined with paramagnetic cells operating in a range of 0 to 25% respectively (NGA 2000 - MLT4, Emerson Process Management, Fisher-Rosemount GmbH & Co.; PG-350 E, Horiba Ltd.).
- CO_2 is determined by non-dispersive infrared spectroscopy (NDIR) in ranges of 0 to 20% or 0 to 30% respectively (NGA 2000 - MLT4, Emerson Process Management, Fisher-Rosemount GmbH; PG-350 E, Horiba Ltd.)
- CO is also determined by non-dispersive infrared spectroscopy (NDIR). Because wide fluctuations of CO concentrations are possible two measurement devices are combined. This allows to determine lower concentrations with higher resolutions but also to tap higher concentrations above 5000 ppm as they can also occur in unfavorable combustion phases. Measurement ranges are between 0 and 5000 ppm and 0 to 10% respectively (low and high CO range: NGA 2000 - MLT4, Emerson Process Management, Fisher-Rosemount GmbH; low CO range: PG-350 E, Horiba Ltd.; high CO range: VA-3001, Horiba Ltd.).
- NO_x which includes the two individual substances NO and NO_2, is determined either by a chemiluminescence detector or by an absorption measurement. While the chemiluminescence detector is, after conversion of NO_2 and NO, suitable to measure both, NO and NO_2, there are two separate optical detectors in the second measurement set up. NO is determined by NDIR spectroscopy and NO_2 by UV spectroscopy. The values of separate measurements are then summarized to the combined parameter NO_x. Measurement equipment which is used in this work covers a range of 0 to 2500 ppm NO_x or 0 to 500 ppm NO and 0 to 2500 ppm NO_2 respectively. (PG-350 E, Horiba Ltd.; NGA 2000 - MLT4, Emerson Process Management, Fisher-Rosemount GmbH)

- OGC is measured by flame ionization detectors (FID) operating in a range of 2-100000 mg m^{-3} respectively (Thermo-FID ES, Mess- und Analysentechnik GmbH; Thermo-FID PT63LT Mess- und Analysentechnik GmbH)

Contrary to gaseous flue gas compounds particulate flue gas compounds are measured by discontinuous methods. Sampling and analysis happens in separate working steps. While sampling is done at the test stand analysis is carried out in a consecutive step in the laboratory. Total suspended particles are sampled either from the hot and undiluted flue gas (TSP) or from the diluted flue gas at temperature below 40°C (TSP_{dil}). TSP and TSP_{dil} samples are both used for quantitative analysis of the particle concentrations. TSP_{dil} samples are also used for further analysis of carbonaceous species which are total carbon (TC), elemental carbon (EC) and organic carbon (OC) and of BaP and other PAHs.

TSP is determined according to the "Austrian and German method" [99]. For sampling a partial flue gas stream is conveyed isokinetically through a sampling probe to a filter cartridge (Figure 8a). The filter cartridge contains a stuffed quartz wool cartridge (3.5 g per cartridge) and a glass fibre plane filter for particle separation. The filter unit is positioned outside the stack and heated to 160 °C during sampling in order to avoid water condensation within the filter cartridge. To collect also remaining particles on the inner surface of the equipment upstream the filter, the probe is rinsed with isopropanol after sampling and the rinsing fluid is collected in a ceramic vessel. For the gravimetric analysis of TSP the stuffed cartridge, the glass fiber filter and the ceramic vessels are weighed before and after sampling with a precision balance. Prior to weighing, the filters and the ceramic vessels are dried for 1 hour at 180 °C and cooled for at least 8 hours in a desiccator. TSP emission concentration is determined by referring the particle mass to the volume of the partial flow stream.

TSP_{dil} is sampled after dilution at temperatures below 40 °C with quartz fibre filters. The sampling method was adapted from the "Dilution Method" in ISO 11338-1:2003 [82] for the requirements of quantitative BaP sampling. Similarly to the sampling of TSP the flue gas is conveyed through a probe to a filter cartridge. Before the filter the flue gas is cooled to a temperature of 40 °C or below by dilution of approximately 1:10 with purified air by a porous tube (Figure 8b). The dilution ratio is monitored and regulated by the configuration of a mass flow controller and a mass flow meter. Because semivolatile substances condense at ambient temperatures they are efficiently collected due to cooling. Dilution ratio is regulated by the configuration of a mass flow meter and a mass flow controller. Sampling is performed with a quartz fiber plane filter only. The plane filter is then used for chemical analysis of TC, EC, OC and PAHs. Similar to TSP measurements quantitative analysis of TSP_{dil} is carried out by weighing the plane filter samples before and after sampling with a precision balance.

Instead of drying the samples at 180 °C they are dried in the desiccator for 48 hours avoiding evaporation of substances which would volatilize at higher temperatures.

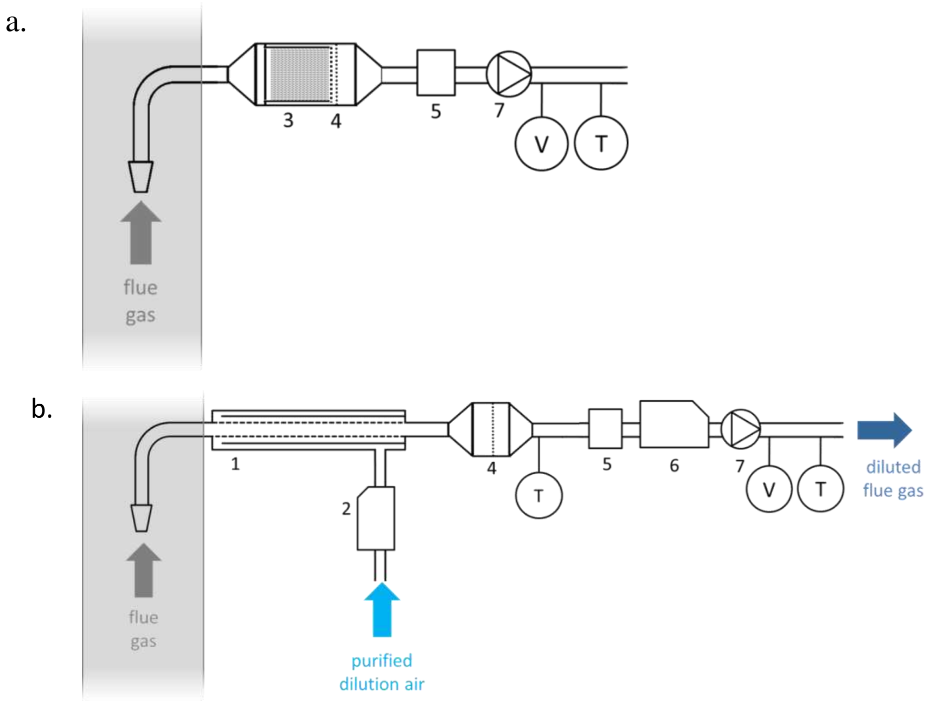


Figure 8: Schemes of (a.) TSP- and (b.) TSP_{dil}-sampling set-ups. 1. Porous Tube Diluter; 2. Mass flow controller; 3. Stuffed filter cartridge; 4. Quartz fiber filter; 5. Drying unit; 6. Mass flow meter; 7. Vacuum pump.

The carbonaceous species TC, EC and OC are determined by thermal-optical method. The measurements are conducted with a SUNSET Lab OC-EC Aerosol Analyzer which is operated according the EUSAAR2 protocol in the transmission mode [100]. Filter punches with 5 mm diameter from the TSP_{dil} samples are used. Due to a special sequence of temperature conditions and modulated oxygen availability (helium phase and oxygen phase) a staged combustion of carbonaceous material from the filter takes place. Carbonaceous material is volatilized of the filter and converted to CO_2 in a MnO_2 oxidizer. CO_2 is then reduced to CH_4 via a nickel catalyst which is quantified with a flame ionization detector. Simultaneous measurement of the transmittance of the filter punch allows to distinguish between OC and EC. TC represents the sum of these parameters.

For the determination of 19 PAHs a method, which bases on EN 15549:2008 [101], designed for the determination of PAHs from ambient aerosol samples is used. These 19 PAHs are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(e)pyrene, BaP, perylene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, dibenz(a,h)anthracene. In this work in most tests the focus is set on BaP only. For the determination of PAHs filter punches are extracted with 6 mL cyclohexane and dichlomethane (1:1). Extracts are then analyzed with a gas chromatograph operating with pulsed splitless injection and separation is conducted on DBMS5 capillary column with helium as carrier gas. A single-quadrupole mass spectrometer which operates in electron ionization mode at 70 eV is used for the detection.

3.4 Calculation of emission values

Emission values are presented either in mg m^{-3} at standard temperature and pressure (STP; 273.15 °C, 101,325 Pa), referred to a standardized oxygen content of 13% in dry flue gas or in mg MJ^{-1} based on fuel input. To shorten the description values are expressed as "mg $m^{-3}{}_{STP}$ at 13% O_2" or as "mg MJ^{-1}". Generally emissions are calculated first in mg $m^{-3}{}_{STP}$ at 13% O_2. Values in mg MJ^{-1} are calculated due to transformation of values in mg $m^{-3}{}_{STP}$ at 13% O_2 with fuel related parameters. For the concentration values of PAHs µg is used instead of mg which is, however, not extra indicated in the presentation of the calculations in the following descriptions.

In the first part the calculation of emissions of single phases for automatic furnaces or batches for manually operated furnaces are presented (equations 1, 2 and 3). The calculation of emission values for whole operation cycles is presented consecutively.

Emissions of continuously measured gaseous flue gas compounds are given as means over the time span of a combustion phase. They are measured on a volume basis in parts per million (ppm). Calculation of concentration values on a mass basis related to 13% O_2 (mg $m^{-3}{}_{STP}$ at 13% O_2) are conducted according the formulas of DIN EN 16510 [102]. For the concentration of CO and NO_x equation 1 is applied. G stands for the concentration of the gaseous flue gas compounds CO or NO_x given either in mg $m^{-3}{}_{STP}$ at 13% O_2 or in ppm, $d_x$is the density of the respective compound which is 1.25 for CO. For NO_x the density of NO_2 is used which is 2.05 (kg $m^{-3}{}_{STP}$). $O_{2\,average}$ is the mean O_2 concentration of the considered combustion phase (%).

$$G_{mgm^{-3}{}_{STP},13\%\,O_2} = G_{ppm}\, d_x \,\frac{21-13}{21-O_{2\,average}}$$

(Equation 1)

Also for OGC the calculation of concentration values is conducted according to DIN EN 16510 [102] as presented by equation 2. In contrast to CO and NO_x OGC is measured from the moist flue gas. Instead of d_x $\frac{12}{22{,}4}$ is inserted where 12 is molecular weight of C (g mol^{-1}) and 22.4 is the standard volume of an ideal gas (dm^3 mol^{-1}). OGC stands for OGC concentration either in mg $m^{-3}{}_{STP}$ at 13% O_2 or in ppm. $G_w$and G_d stand for the specific gas volume either in wet or in dry conditions meaning that the water vapor from the flue gas is either included or excluded.

$$OGC_{mgm^{-3}{}_{STP},13\%\,O_2} = OGC_{ppm}\frac{12}{22{,}4}\frac{21-13}{21-O_{2\,average}}\frac{G_w}{G_d}$$

(Equation 2)

Concentration values of discontinuously measured parameters in the particle fraction (TSP, TSP_{dil}, TC, EC, OC, BaP and other PAHs) are calculated by dividing the sample mass of the combustion phase by the extracted flue gas of the respective phase. The calculation for single combustion phases is presented in equation 3 where P is the concentration of the particulate flue gas compound (mg $m^{-3}{}_{STP}$ at 13% O_2), $m_{filter,end}$ is the mass of the filter after sampling (mg), $m_{filter,start}$ is the mass of the filter before sampling (mg) and $V_{gasmeter}$ is the extracted flue gas volume at STP measured by a gasmeter ($m^3{}_{STP}$).

$$P_{mgm^{-3}{}_{STP},13\%\,O_2} = \frac{\sum(m_{filter,end} - m_{filter,start})}{\sum V_{gasmeter}}\frac{21-13}{21-O_{2\,average}}$$

(Equation 3)

For combustion cycles as for example according to beReal protocols values from single combustion phases are combined to emission values representing the whole cycle. Different flue gas volumes of the single combustion phases are respected in the calculation. This is done due to phase-wise volume weighing of the flue gas volumes. Therefor equation 4 according to the definitions for data evaluation for beReal protocols [103] is applied before the former presented equations (equations 1, 2 and 3) are used. The preceding calculation step is equal for gaseous and particulate emissions. E stands for the emission concentration for whole test cycles (ppm), $\mathrm{E_i}$ for the average flue gas concentration of one parameter in the respective phase (ppm) and $\mathrm{V_{i,STP}}$ is the total flue gas volume at STP of the respective phase ($m^3{}_{STP}$).

$$E_{ppm} = \frac{\sum_i E_i V_{i,STP}}{\sum_i V_{i,STP}}$$

(Equation 4)

Emission values in mg MJ^{-1} are calculated by the conversion of emission values in mg $m^{-3}{}_{STP}$ at 13% O_2 with fuel related parameters as presented by equation 5. E stands for the emission concentration of the respective flue gas compound either in mg MJ^{-1} or in mg $m^{-3}{}_{STP}$ at 13% O_2, $V_{dry\ flue\ gas}$ for the volume of the dry flue gas at STP related to 13% O_2 from the combustion of one kg fuel ($m^3{}_{STP}$ kg^{-1}, 13% O_2) and H_u for the lower heating value of the respective fuel (MJ kg^{-1}).

$$E_{mg\,MJ^{-1}} = \frac{E_{mgm^{-3}{}_{STP},13\%\,O_2} V_{dry\ flue\ gas}}{H_u}$$

(Equation 5)

4 Summaries of the publications

Research presented within the publications was carried out as a cooperation between BEST Bioenergy and Sustainable Technologies GmbH and Vienna University of Technology. The presented results were evaluated by myself as I took the leading part in the organization and conduction of the experiments, the evaluation of the results and the dissemination work. Colleagues from BEST Bioenergy and Sustainable Technologies GmbH gave input to the experimental part, evaluation and interpretation of the results and to dissemination work. Colleagues from Vienna University of Technology conducted chemical analysis of the filters and gave input to the evaluation and interpretation of the results and to dissemination work. All co-authors commented on the results and on the contents of the manuscripts.

4.1 Publication I

In the first chapter a compact technique for BaP measurements in the flue gas from residential wood combustion furnaces and results of method validation are presented. Furthermore BaP emission behavior of automatic boilers was investigated. Because the focus was set on BaP as representative PAH the sampling could be specialized and consequently simplified according the properties of a single compound. The sampling method is derived from the dilution method presented in ISO 11338-1. For the sample collection only a quartz fiber filter for solid particles is used while an additional unit for the collection of gas phase PAHs is omitted. The validation of the method was carried out in order to identify whether more than 90% of BaP can be sampled with a quartz fiber filter only. Therefore the sampling loop was extended with a XAD adsorber unit downstream the quartz fiber filter capable to retain gas phase PAHs from the flue gas. In the first validation step six different flue gases from residential wood combustion furnaces from favorable to poor combustion conditions, as indicated by their CO concentrations (19 to 11300 mg m^{-3}) were conveyed through the sampling loop. In two further validation steps the tendency of BaP to reevaporate from the filters was tested. This was done by sampling at varying flue gas composition as it occurs at batch combustion of a log wood stove. In a further step an exaggerated scenario of flue gas variation was produced. Flue gas of particularly poor combustion conditions (CO concentrations up to 3%) was sampled until significant PM masses were collected. Then two of three samples were flushed with purified air for 15 and 30 minutes.

In the second part BaP emissions from the operation of six automatic boilers including five pellet boilers and one multifuel boiler, which was operated with both pellets and wood chips, were investigated. Measurements were carried out at start, stop, nominal load and part load operation for the assessment of phase specific emissions which are all relevant in real-life operation. For nominal load and part load operation measurements were carried out for at least one hour at steady-state conditions. Measurements for start and stop operation were conducted over the whole time span of start and stop phases. The start phase was defined to begin when the ignition system was started. It ended when CO concentration and combustion temperature move towards typical levels for nominal load operation. The stop phase was defined to begin when the fuel supply rate decreases, which is indicated by increasing CO concentration and stopped when air supply stopped. Beside BaP measurements also CO, OGC, TSP_{dil}, EC, OC and TC measurements were carried out. Results were used to characterize phase specific BaP emissions, for the identification of technology specific impacts on BaP emissions and for the identification of correlations with other emission parameters.

The method validation showed that BaP sampling with a quartz fiber filter even of various flue gas qualities is adequate as no BaP was detected in the gas phase. At typical flue gas fluctuation from a log wood stove, representing a batch-wise operated combustion furnaces, there was no evaporation of particle phase BaP to the gas phase identified. Even at the exaggerated scenarios only negligible amounts of BaP evaporated from the filter into the gas phase, which did by far not violate the validation criterion of 90% of BaP determined by the filter. Therefore the simplified method was shown to be adequate for BaP measurements in wood combustion furnaces.

As operation phases had been explicitly defined in advance, the BaP emissions from start, stop, nominal load and part load operation could be clearly differentiated. Measurements indicated that especially start and also stop phases are decisive for total BaP emissions because average emission values were one to two orders of magnitude higher than at nominal and part load operation. In average the values from start, stop, part load and nominal load operation were 10257, 3055, 104 and 81.2 ng m^{-3} at standard temperature and pressure (STP) referred to 13% O_2 respectively. Therefore, operation modes ranging from long term continuous operation at nominal load to operation with consecutive starts and stops highly impact the BaP emissions. The comparison of top-fed, horizontally fed and underfed systems indicated that there is a higher risk for increased emissions from underfed systems. The comparison of determined emission parameters revealed that EC is the best indicator for BaP among the measured emissions. According to the results of unsteady operation phases also CO and TSP_{dil} indicated good correlations.

4.2 Publication II

In the second chapter real-life oriented emissions of 13 state of the art small scale wood combustion furnaces were investigated with real-life oriented operation protocols which were defined in an European project. Beside BaP also CO, OGC, NO_x, particles sampled either from hot flue gas (TSP) or from diluted and cooled flue gas (TSP_{dil}), TC, EC and OC were measured. Four pellets stoves, six log wood stoves and three cookers, all available on the Austrian market, were operated with wood pellets or beech logs. In this work real-life oriented emission values were assessed by means of innovative real-life test protocols. As described before these operation protocols were developed and validated in a recent European project called “beReal” (www.bereal-project.eu [104]) which aim to represent the operating conditions at the end-user. They are applicable for measurements in laboratories and can be conducted within one day with the same measurement equipment as is the one used in standard type tests. The operation sequence for firewood roomheaters which was applied for log wood stoves and cookers comprises one full load batch for ignition, four additional full load batches, three part load batches and a cooling down phase. The sequence for pellet stoves lasts almost eight hours and includes a cold start, two warm starts, operation at nominal load, at part load, standby phases, load changes and burn-out phases. For three furnaces triple measurements were carried out confirming the repeatability of the beReal test method. Results contribute to the assessment of the reliability of the novel beReal methods. Results from beReal measurements were compared with type test results in order to identify the informative value of the latter about real-life emissions. This was done by the comparison with the results of CO, which is a common indicator for the overall combustion performance. Moreover beReal values for CO, OGC, NO_x, TSP, TSP_{dil} and BaP were compared with suggested emission factors for the European and Austrian emission inventory. Emission inventories aim to represent real-life emission by deriving emission factors from published data, and consequently depend on availability of real-life representing emission values. The data confrontation allows for analyzing reasonability of real-life emission factors from suggested factors in inventories.

BaP emission values which were evaluated with real-life oriented operation sequences were between 0.5 and 130 µg MJ^{-1} indicating a particularly wide range of four orders of magnitude. In comparison CO values were between 159 and 2237 mg MJ^{-1}. The trend from literature data of lower emissions from automatic furnaces was partly confirmed as for CO, OGC, TSP, TSP_{dil}, TC, EC and OC emission values from PS were significantly lower than for measured log wood furnaces. Three of four PS exhibited the lowest BaP values of below 1 µg MJ^{-1}. However, for one pellet stove exceptionally higher emissions including the highest value for BaP were determined. While the value for example of CO was within the range of determined values (CO: 832 mg MJ^{-1}), the BaP value was exceptionally higher than those from other furnaces (130 µg MJ^{-1}), indicating the risk of extremely high BaP emissions due to unfavorable combustion conditions. The repeatability analysis confirms the previously published results. It has been shown that beReal test methods are not less reliable than standard type tests, although they include operation phases that occur in real-life. The comparison of beReal results with type test results illustrates that type test results provide limited information on real-life emissions as well as on the relative air quality impact of single furnaces. Determined values for log wood furnaces (log wood stoves and cookers) and pellet stoves scatter around or are below the corresponding emission factors of the European emission inventory specified for residential wood combustion furnaces of highest technological standard (“Advanced and Ecolabelled stoves and boilers” and “Pellet stoves and boilers”). However, only for BaP measured values of log wood stoves and cookers are predominantly higher than the corresponding emission factor of 10 µg MJ^{-1} with the highest value at 86.4 µg MJ^{-1}. For pellet stoves three of four measured values are clearly below the suggested emission factor of 10 µg MJ^{-1} and below the values for log wood furnaces. Nevertheless, one value from a pellet stove (130 µg MJ^{-1}) exceeds this emission factor by far. The comparison with the emission factors indicates that even when emission values from this work were evaluated with real-life oriented test sequences, most values are still in the range or even below the suggested emission factors for residential wood combustion furnaces of higher standard in the European emission inventory. Concerning CO, OGC, TSP and TSP_{dil} this indicates that used emission factors in the European emission inventory do not necessarily underrate calculated emissions because of a scarce availability of real-life emission values. On the other hand it indicates that the increased use of state of the art combustion furances as used in this work would lead to reduced emissions. Because of the wider range of BaP values it is more difficult to suggest characteristic emission factors indicating the need of a wider data collection as for example done in this work.

4.3 Publication III

In the last chapter of the work the impact of two oxidative honeycomb Pt/Pd catalysts on emissions of residential wood combustion furnaces was examined. Catalysts represent a type of secondary emission abatement which had been proven to be effective against CO and OGC emissions. Though, the impact on PM or compounds in the PM like PAHs is not clarified so far. In this work the impact of two commercially available oxidizing Pt/Pd catalysts on the flue gas from a log wood stove at real-life operating conditions was assessed. The catalysts have equal noble metal coating but either metallic or ceramic honeycomb carriers resulting in 3.5 times higher reaction surface of the metallic catalyst. Emission measurements were carried out at a special test stand which consists of a log wood stove, a post combustion chamber and a flue gas line. The post combustion chamber and the flue gas line are separated into two symmetric compartments enabling synchronous measurements of differently treated flue gas from the same combustion process. The use of this setup allows to find out the effect of catalytic treatment excluding impacts of variable combustion conditions. Equal combustion conditions were validated in a preceding test where the flue gas was identically treated in both compartments while parallel measurements were carried out. Differences were used for the evaluation of measurement uncertainties. One test sequence consisted of seven consecutive batches. CO and OGC were measured continuously over the whole tests. TSP_{dil} was sampled in batches one, three, five and seven, and then used for further analysis of carbonaceous species (EC, OC and TC) and PAHs. Beside BaP, 18 further PAHs were analyzed in the TSP_{dil} samples in order to identify whether possible decreases of BaP are caused by transformations to other PAHs. Moreover the impact on CO, OGC, TSP_{dil}, TC, EC and OC was investigated.

The preceding validation test indicated widely according conditions as CO, OGC and TSP_{dil} differentiated in the batches by maximum, 6.8%, 6.0% and 4.4%. Generally, the more pronounced effect was observed at measurements with the metallic catalyst which led to a substantial reduction of PAHs by 63%. In particular highly toxic BaP was reduced by 84%. The reduction was exclusively related to higher-molecular-weight PAHs. Lower-molecular-weight PAHs, which exhibited generally low concentrations rather increased. Unexpectedly TSP_{dil} emissions clearly increased by 17% due to the treatment of the metallic catalyst. Because from carbonaceous species no clear trend could be observed, it is not possible to attribute this increase to a particular carbonaceous fraction. Also the test with the ceramic catalyst indicated a trend of PAH reduction, although the results for PAHs but also for TC, EC and OC were not significant. The high impact on gaseous flue gas compounds CO and OGC due to the used catalysts was confirmed according to previous studies as CO was reduced by 88% and 69% and OGC by 39% and 27%. The results demonstrate the high potential of catalytic reduction of PAHs and also of CO and OGC, which were achieved at measurements over whole batches. However, the increase of TSP_{dil} opens new questions and has to be further investigated.

5 Summary of scientific contributions

To summarize, in this study BaP emissions of 20 wood combustion furnaces were investigated. Beside the investigation of BaP emissions also some methodological aspects were researched. The main outputs are summarized according to the research questions in the objectives in chapter 2 and presented in the following sections.

- Is it possible to obtain a simplified and more compact measurement set up, when only the guiding substance BaP is measured?

After the marker-like character of BaP for the toxicity arising from PAH emissions had been confirmed by a literature survey a simplified measurement method focusing on BaP could be developed. It was shown that BaP is sampled quantitatively from the cooled flue gas (<40 °C) with a quartz fiber filter. Even at various flue gas compositions from poor to favorable combustion conditions clearly more than 90% of BaP was retained in the particulate matter samples. Due to the use of the more compact and transportable equipment, measurements can be carried out in variable testing environments, even with limited space offer.

- In which range are real-life BaP emissions of automatic small scale biomass boilers and what are the most critical operation phases?

It was shown that the operation program of automatic boilers is decisive for their BaP emissions as concentrations at start and stop operation were in average one to two orders of magnitude higher than at steady-state operation (start: 0.5 to 47 µg MJ^{-1}, stop: 0.2 to 14 µg MJ^{-1}, part load: 0.04 to 0.25 µg MJ^{-1}, nominal load: 0.01 to 0.52 µg MJ^{-1}; Figure 9). The phase specific characterization was enabled due to the precise definition of the start and stop operation phases. A higher risk for increased BaP emissions was indicated for underfed systems compared to top-fed and horizontally fed systems. The comparison with literature data including combined values of various operation phases illustrates the necessity of the evaluation of phase specific values, as the phase impact is otherwise not identifiable (Figure 9). Moreover a correlation analysis exhibited that EC is the most suitable indicator for BaP but also for CO and TSP_{dil} a correlation with BaP was observed.

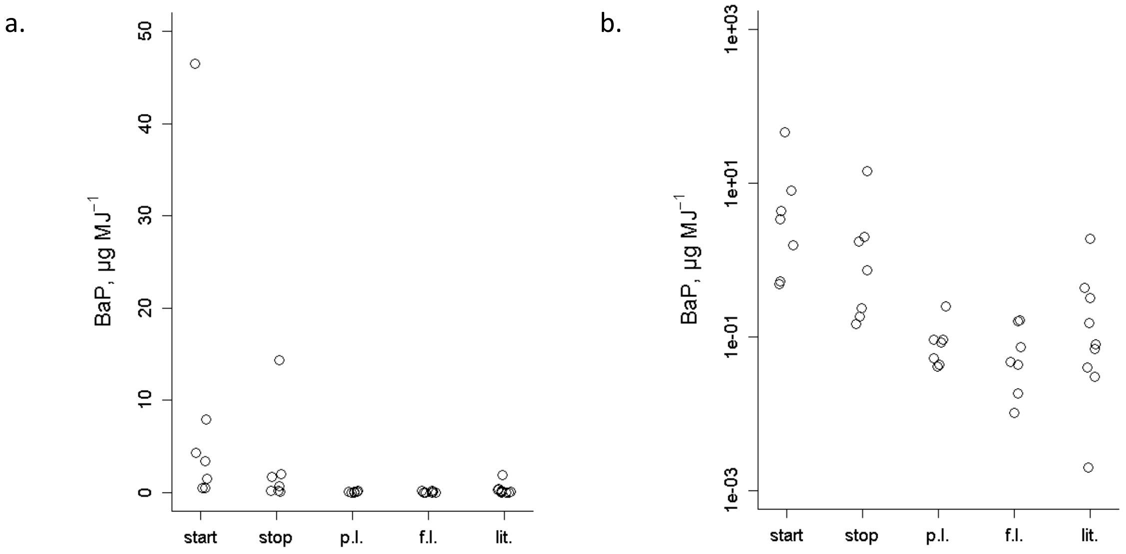


Figure 9: BaP values from automatic boilers (pellet boilers and wood chip boilers) measured at start, stop, part load ("p.l.") and full load ("f.l.") and suitable literature values (lit.) as given in Table 2. Plots are presented with linear scale (a.) and with logarithmic scale (b.). Those values which were published in µg m^{-3}$_{d.b.}$ at 13% O$_2$ were converted to mg MJ^{-1}. Conversion factors (0.91 for pellet fuels and 0.81 for wood chips) were calculated using fuel compositions presented in Publication II in chapter 7.2 [86]. Conversion presents approximation of emission values allowing for harmonization to the same unit.

- In which range are real-life BaP emissions of different types of modern wood stoves?

During these measurements a particularly wide range of BaP emission values from 0.5 µg MJ^{-1} to 130 µg MJ^{-1} was observed. The lowest values were achieved in measurements of three of four pellet stoves (0.5, 0.7 and 0.8 µg MJ^{-1}). Nevertheless also the highest BaP emission value (130 µg MJ^{-1}) was determined from this technology-group indicating that even at automatic systems unfavorable system configuration at start and stop can lead to particularly high BaP emissions. BaP values for log wood stoves were between 7.9 and 29.7 µg MJ^{-1} and for cookers between 27.4 and 86.4 µg MJ^{-1}. Except of one value the data for pellet stoves and log wood stoves of this work, determined at real-life oriented test sequences, are in the ranges of corresponding published values determined at various operational conditions (Figure 10). The wide ranges of literature values indicate the relevance of a systematic procedure for real-life emission characterization. For cookers for which no published BaP emission values could be found, BaP emission values were rather higher than those from log wood stoves of this work, though not on a significant level (Figure 10). Also for CO, OGC, NO$_x$, TSP, TSP$_{dil}$, TC, EC and OC real-life emission values were assessed. In course of the measurement series repeatability analysis for recently developed real-life test sequences was conducted which contributes to evidence the reliability of the novel sequences. The comparison of emission values of this work with corresponding type testing results revealed that the latter serve limited information about the real impact on air quality. Moreover the comparison of the real-life oriented emission factors with corresponding emission factors of Austrian and European emission inventory revealed that installations of furnaces of highest technological standards would lead to decreased emissions from residential wood combustion furnaces.

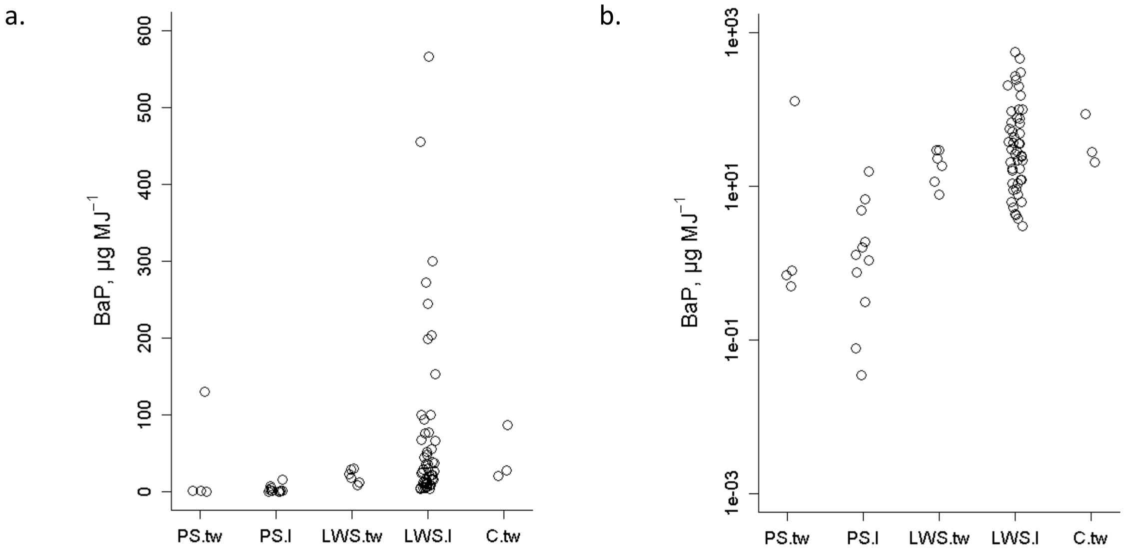


Figure 10: BaP emission values for pellet stoves ("PS"), log wood stoves ("LWS") and cookers ("C") in this work (".tw") and suitable literature values (".l") as given in Table 2. Plots are presented with linear scale (a.) and logarithmic scale (b.).

corresponding data PS and LWS published in literature presented with

- Which effect has the integration of two types of oxidative honeycomb catalysts on PAH emissions from residential wood combustion furnaces at real-life operation?

The impact of two oxidative Pt/Pd honeycomb catalysts was investigated with an innovative test stand allowing for synchronous measurements of differently treated flue gas streams. A preceding validation test confirmed according conditions in the parallel streams of the special test stand. While for one catalyst no significant impact on PAHs was observed, at the other catalyst, a metallic honeycomb catalyst, PAHs were clearly reduced by 63% and in particular BaP was reduced by 84% indicating the high potential for PAH reduction. This result was achieved at log wood combustion including ignition, full flaming and burnout phases as it occurs at real-life operation. An extensive reduction of gaseous flue gas compounds CO and OGC was confirmed. Although, a clear increase of TSP_{dil} was observed. This indicates that further investigation of the impact of these catalysts is required.

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7 Scientific Publications

7.1 Publication I

Klauser, F.; Schwabl, M.; Kistler, M.; Sedlmayer, I.; Kienzl, N.; Weissinger, A.; Schmidl, C.; Haslinger, W.; Kasper-Giebl, A. Development of a Compact Technique to Measure Benzo(a)Pyrene Emissions from Residential Wood Combustion, and Subsequent Testing in Six Modern Wood Boilers. *Biomass Bioenergy* **2018**, *111*, 288–300. https://doi.org/10.1016/j.biombioe.2017.05.004.

7.2 Publication II

Klauser, F.; Carlon, E.; Kistler, M.; Schmidl, C.; Schwabl, M.; Sturmlechner, R.; Haslinger, W.; Kasper-Giebl, A. Emission Characterization of Modern Wood Stoves under Real-Life Oriented Operating Conditions. *Atmos. Environ.* **2018**, *192*, 257–266. https://doi.org/10.1016/j.atmosenv.2018.08.024.

7.3 Publication III

Klauser, F.; Schmidl, C.; Reichert, G.; Carlon, E.; Kistler, M.; Schwabl, M.; Haslinger, W.; Kasper-Giebl, A. Effect of Oxidizing Honeycomb Catalysts Integrated in a Firewood Room Heater on Gaseous and Particulate Emissions, Including Polycyclic Aromatic Hydrocarbons (PAHs). *Energy Fuels* **2018**, *32* (11), 11876–11886. https://doi.org/10.1021/acs.energyfuels.8b02336.

8 Curriculum Vitae

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Employments:

At present:	Researcher at BEST – Bioenergy and Sustainable Technologies GmbH (formerly: "BIOENERGY 2020+ GmbH") Inffeldgasse 21b, 8010 Graz franziska.klauser@best-research.eu Area: Fixed Bed Conversion Systems Unit: Emission Technology and Research
08/2014 - 01/2018:	Junior Researcher at BIOENERGY 2020+ GmbH
03/2014 - 07/2014:	ERASMUS internship at SLU Sweden in Umeå, Department: Forest Technology and Biomaterials
03/2013 - 10/2013:	Project assistant at Bioenergy 2020+ GmbH
06/2012 - 07/2012:	Minor employment at TU Munich/TFZ Straubing
Before 2011	Various employments in different companies (food and feed processing, insurance, plant breeding, farming in Ireland)

Education:

Since 2016:	PhD at Vienna University of Technology Doctoral programme in Natural Sciences - Technical Chemistry Title of the doctoral thesis: Characterization of real-life benzo(a)pyrene emissions of residential wood combustion furnaces
2011- 2014:	University of Natural Resources and Life Sciences, Vienna and Technical University of Munich International Master programme: Material and Energetic Exploitation of Renewable Raw Materials (NAWARO)

	Title of Master thesis: Pellet off-gassing during storage Influence of raw material and O_2 availability
2008 – 2011	University of Natural Resources and Life Sciences, Vienna Bachelor: Agricultural Sciences
2002 - 2007	Secondary school qualification for Food Technology and Biotechnology (Francisco Josephinum) School leaving examination - with distinction
1994 - 2002	Elementary school and Grammar school

Language skills:

- German (native)
- English (fluent)
- Latin
- Spanish (basics)

International Experience:

- Farming in Ireland (06/2005 – 07/2005))
- Semester abroad at TU Munich, Germany (04/2012 – 08/2012)
- Internship at SLU Umea, Sweden (04/2014 – 07/2014)

Research Topics:

- Biomass Combustion
- Combustion derived emissions with focus on dust and polycyclic aromatic hydrocarbons
- Pellet off-gassing during storage

Scientific activities:

Publications

Meier, F.*, Sedlmayer, I., Emhofer, W., Wopienka, E., Schmidl, C., Haslinger, W., Hofbauer, H., 2016. Influence of Oxygen Availability on off-Gassing Rates of Emissions from Stored Wood Pellets. Energy Fuels 30, 1006-1012. https://doi.org/10.1021/acs.energyfuels.5b02130*

Klauser, F.*, Schwabl, M., Kistler, M., Sedlmayer, I., Kienzl, N., Weissinger, A., Schmidl, C., Haslinger, W., Kasper-Giebl, A., 2018c. Development of a compact technique to measure benzo(a)pyrene emissions from residential wood combustion, and subsequent testing in six modern wood boilers. Biomass Bioenergy 111, 288–300. https://doi.org/10.1016/j.biombioe.2017.05.004*

Klauser, F.*, Carlon, E., Kistler, M., Schmidl, C., Schwabl, M., Sturmlechner, R., Haslinger, W., Kasper-Giebl, A., 2018a. Emission characterization of modern wood stoves under real-life oriented operating conditions. Atmos. Environ. 192, 257–266. https://doi.org/10.1016/j.atmosenv.2018.08.024*

***Klauser, F.**, Schmidl, C., Reichert, G., Carlon, E., Kistler, M., Schwabl, M., Haslinger, W., Kasper-Giebl, A., 2018b. Effect of Oxidizing Honeycomb Catalysts Integrated in a Firewood Room Heater on Gaseous and Particulate Emissions, Including Polycyclic Aromatic Hydrocarbons (PAHs). Energy Fuels 32, 11876–11886.* https://doi.org/10.1021/acs.energyfuels.8b02336

Lectures

***Meier, F.**, Schwabl, M., Sedlmayer, I., Kistler, M., Schmidl, C., Weissinger, A., Haslinger, W., 2016. Benzo(a)pyrene emission in the flue gas from modern biomass boilers, in: 24th EUBCE Proceedings. Presented at the 24th European Biomass Conference, Amsterdam.*

*Schmidl, C., Kelz, J., **Klauser, F.**, Kumar-Verma, V., Schwabl, M., Schwarz, M., 2016. Real-life emission of automatically stoked biomass boilers. Presented at the 20th ETH Conference on Combustion Generated Nanoparticles, Zurich.*

***Klauser, F.**, Schwabl, M., Sedlmayer, I., Kistler, M., Schmidl, C., Weissinger, A., Haslinger, W., Kasper-Giebl, A., 2017. A compact BaP emission measurement method for residential wood combustion and preliminary results from modern biomass boiler testing. Presented at the 5th Central European Biomass Conference, Graz.*

*Sturmlechner, R., Schmidl, C., Carlon, E., Reichert, G., Stressler, H., **Klauser, F.**, Kelz, J., Schwabl, M., Kirchsteiger, B., Kasper-Giebl, A., Höftberger, E., Haslinger, W., 2019. Real-life emission factor assessment for biomass heating appliances at a field measurement campaign in Styria, Austria, Air Pollution in: Aveiro, Portugal, 2019: pp. 221–231.* https://doi.org/10.2495/AIR190221

Posters

***Meier, F.**, Schwabl, M., Sedlmayer, I., Kleinhappl, M., Schmidl, C., Haslinger, W., 2015. Benzo(a)pyrene Emission Measurements in Flue Gas from Residential Biomass Combustion Appliances, Presented at the 23rd European Biomass Conference and Exhibition, Vienna.*

***Klauser, F.**, Kelz, J., Schwabl, m., Stressler, H., Sturmlechner, R., Reichert, G., Schmidl, C., Weissinger, A., 2017. Clean Air by Biomass – Demonstration of clean and efficient combustion of biomass, Presented at the 5th Central European Biomass Conference, Graz.*

***Klauser, F.**, Schmidl, C., Schwabl, M., Haslinger, W., 2018. Effect of an oxidizing catalyst on PAH emissions at firewood combustion, Presented at the 22nd ETH-Conference on Combustion Generated Nanoparticles, Zurich.*

Master thesis

***Meier, F.**, 2014. Pellet off-gassing during storage: The impact of storage conditions and type of source material. University of Natural Resources and Life Sciences, Vienna.*