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Emissions of G~~g~~ases and V~~v~~olatile O~~o~~rganic C~~c~~ompounds ~~(VOCs)~~ from R~~r~~esidential H~~h~~eating: A~~a~~ C~~c~~omparison of B~~b~~rown C~~c~~oal B~~b~~riquettes and L~~l~~ogwood C~~c~~ombustion

Patrick Martens[†~~1~~],
Hendryk Czech[*,†~~1~~,‡~~2*~~],
Jarkko Tissari[§~~3~~],
Mika Ihalainen[§~~3~~]-,
Heikki Suhonen[§~~3~~],
Martin Sklorz[‡~~2~~],
Jorma Jokiniemi[§~~3~~],
Olli Sippula[§~~3~~,∥4], and
Ralf Zimmermann[†~~1~~,‡~~2~~]

[†]~~[1]~~University of Rostock, Dr.-Lorenz-Weg 2, D-18059~~,~~ Rostock, Germany

[‡]~~[2]~~Helmholtz Center Munich, Ingolstädter Landstraße 1, D-85764 Oberschleißheim, ~~/~~Germany

[§]~~[3]~~Department of Environmental and Biological Sciences, University of Eastern Finland, P.O.
Box 1627, FI-70211 Kuopio, Finland

[‖]~~[4]~~Department of Chemistry, University of Eastern Finland, P.O. Box 111, FI-80101 Joensuu,
Finland

[*]~~Corresponding author: Hendryk Czech,~~

[*]Email: hendryk.czech@uni-rostock.de.

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~~Graphical Abstract~~.

~~1.~~ Abstract

Coal continues to be a major source of energy for residential heating in some parts of the world due to its low price and good availability. However, only ~~few~~little information on emissions for coal combustion in small-scale appliances, in particular manually-operated stoves, is available.

This study investigates the emissions of gases and volatile organic compounds (VOCs) from brown coal briquettes (BCBs) burned in a typical Central European wood stove and compares them to emissions from spruce wood logs. Special emphasis was placed on the evolution of emissions over consecutive batches. In comparison to wood, BCBs made from Lusatian lignite showed higher emissions of compounds that were attributed to the decomposition of lignin, while emissions that were attributed to having originated from pyro~~-~~synthesis did not show significant differences between both fuels. Furthermore, a 20-fold higher emission factor for SO_2 was obtained from BCB combustion, which is known for its deleterious effect. ~~A~~In addition~~al~~ to a reduction in the carbon footprint, replacing BCBs with logwood as a fuel for residential heating might be beneficial for human health due to vast differences in SO_2 emissions, whereas a potential effect from the reduction of organic emissions is questionable due to the rather small differences in organic emissions.

1. Introduction

~~2. Introduction~~

Rising anthropogenic emissions from preindustrial to present day have significantly increased ambient air pollution worldwide,[1,2]~~,~~ and ambient air pollution has been shown to severely affect human health[3,4] and the climate.[5]~~.~~ Especially, the combustion of solid fuels in households has been identified as a major cause of mortality in low- and medium-income countries.[6,7] Aerosols from residential combustion of solid fuels are highly variable in their physical properties and the chemical composition, depending on the type of appliance, appliance design, combustion conditions, user practices, and type of fuel~~,~~[8–13] and have shown differences in toxicological responses in *in~~-~~ vitro*[14,15] and *in~~-~~ vivo* studies.[14]

Residential combustion of coal in stoves and boilers, although having been phased~~ing~~ out in many countries due to their carbon footprint, is still important for heating and cooking in some parts of the world, e.g., China, Poland, and the Czech Republic,[16] and hence is still a major contributor to air pollution in China[17–19] and Europe.[20–22]~~.~~ Previously, most of the research on coal combustion was focused on emissions of particulate matter (PM)[23–30] and VOCs[31–35] for Chinese appliance-coal combinations. However, some studies have pointed out that the type of coal and the type of appliance can affect overall quantities of emissions as well as their composition.[28,29] Chinese households that still rely on coal, predominantly rural ones, mostly consume medium-rank, bituminous coals, whereas in Europe, the type of coal being consumed depends on the local availability of coal in the respective country.[16] In Poland, which is the European country with the highest coal consumption in the residential sector, predominantly bituminous coals are being consumed, whereas coals of lower rank, i.e., peat and brown coal, are being consumed in other European countries, e.g., Ireland and the Czech Republic.[16] As for the appliances, although a Chinese program for replacement of coal and biomass cooking stoves with other appliances (heating systems fueled with natural gas or powered with electricity) was generally considered effective, households that still rely on coal for heating and cooking mainly use traditional, highly~~-~~-emitting stoves rather than "improved" stoves with moderate emissions.[31,36] In Europe, there are approximately 70 million solid fuel combustion appliances,[37] ~~;~~ and to the authors' knowledge, there is no robust information on the current state of technology (thermal efficiency and emitted emission levels) of stoves being installed in all of Europe. For Germany, a European country with a high standard of living, the German Association of Chimney Sweepers reports that 70% of single-room, biomass heaters have been erected after 1995[38] and are therefore considered rather modern by the authors. It is reasonable to assume that stoves being installed in other European countries are of comparable age due to a comparable standard of living. For a European coal burning region, that is the Moravian-Silesian region,[39] a program to exchange old, highly-emitting stoves was considered successful; however, no information is available on how many outdated appliances may still be in use. In Poland, coal is burned in 70% of single-family households in coal stoves and low efficiency-boilers with many of the later ones being considered old and manually-~~-~~operated.[40] Stoves, in particular old ones, can contribute disproportionately to the local air burden due to comparably high emissions as well as improper operation and inefficient use of energy.[12,37,41] Junninen et al.[20] estimated that coal combustion in stoves and low-efficiency boilers accounts for 50% of the concentration of PM below 10~~-~~ μm at a downtown site in Krakow, Poland in winter. Schnelle-Kreis et al.[42] analyzed semi~~-~~volatile organic compounds sampled at a downtown site in Augsburg, Germany, and estimated that coal combustion accounts for approximately 30% of winter PM below 2.5~~-~~ μm, although Germany had already replaced coal as a fuel for residential heating with boilers and stoves with other less-polluting fuels and heating appliances. This demonstrates the need to investigate emissions from European appliance–~~-~~coal combinations as well.

To the best of the authors' knowledge, only a few studies have investigated emissions from residential coal combustion in Europe, and these studies have mainly focused on effects of different boiler designs (old vs~~vs.~~ modern) and fuels (biofuels vs~~vs.~~ coal) on PM emissions.[43–46] It was found that old boilers emit up to two orders of magnitude more PM and polycyclic aromatic hydrocarbons (PAHs) than modern boilers.[43] Also, emissions factors of organic markers for coal combustion, such as hopanes, were found to vary by two orders of magnitude depending on the boiler design.[46] Stoves generally differ from boilers due to their discontinuous mode of operation, leading to temporarily changing emission concentration and chemical composition.[8,43,47] To our knowledge, only two studies have focused on European residential coal–~~-~~stove combinations. Mitchell et al.[48] investigated emissions from a range of different fuels, including coal, in a residential stove and attributed emissions in specific burning phases to major fuel properties and combustion parameters. Lin et al.[21] characterized PM signatures from coal emissions in a stove via aerosol mass spectrometry and used them to estimate the contribution of coal burning among other solid fuel combustion to local air pollution in Ireland.

This study aims to determine emission factors (EFs) of gases and VOC emissions from the combustion of brown coal briquettes made from Lusatian lignite in a non-heat-retaining, small-scale residential heating appliance. EFs from brown coal briquette combustion are then compared to EFs from the combustion of spruce logwood, which is widely ~~-~~used for residential heating in Central and Eastern Europe, in the same stove.

~~1.~~2. Materials and~~&~~ M~~m~~ethods

~~1.1.~~2.1. Experimental S~~s~~et~~-~~up

~~1.1.1.~~2.1.1. Stove

The combustion experiments were carried out with a modern, non-heat-retaining single-room heating appliance (*Aduro 9.3*, Aduro A/S, Denmark, energy efficiency class: A+), which is approved for installation in the European Union and Norway. According to the manufacturer, both wood logs and brown coal briquettes are suitable fuels. Generally, coal up to the rank of brown coal can be burned in common wood stoves without hesitation. Only for burning coal of higher rank, e.g., bituminous coals and anthracite, stoves have to be built from heat-resistant steel that is able to endure the higher temperatures present during combustion of these fuels. Thus, the wood stove used for testing is more representative for areas of the Czech Republic and Hungary where brown coal is mined and still being consumed.[16] To the authors' knowledge however, there is no robust information on how well stoves that are in use are maintained or how old they are. Therefore, this modern stove likely represents appliances being installed in the last decade up to today. The appliance is equipped with three dampers, which regulate the combustion air. The primary air supply is only opened for a few minutes upon ignition of the fuel, the secondary air supply is used to regulate the energy output, and the tertiary air supply is used to reduce flue gas emissions. The division of combustion air supply into multiple smaller air supplies is commonly referred to as air staging. The effects of air staging on emissions from small-scale combustion appliances are discussed elsewhere.[49] Flue gases were led from the firebox into the stack, which was placed below a hood. The draught from the hood was regulated to ~~(~~12.0 ± 0.5~~)~~ Pa below ambient pressure via dampers.

~~1.1.2.~~2.1.2. Fuel C~~c~~haracterization

Spruce logs (*P~~p~~icea abies*) and Lusatian brown coal briquettes (*Rekord*, Lausitz Energie Bergbau AG, Germany) were tested as fuels for residential heating. Both fuels were analyzed for their calorific properties, water content, and elemental composition by an external laboratory based upon international standards. The results of the analyses are provided in Table 1.

~~1.1.3.~~2.1.3. Combustion P~~p~~rocedure

In total, ~~ten~~ 10 combustion experiments consisting of six experiments with brown coal briquettes (BCBs) and four experiments with spruce logs (SLs) were carried out. Each experiment were designed to represent realistic use of both fuels during an evening session of ~~four~~ 4 h~~ours~~ and comprised three and five batches for BCBs and SLs, respectively. The number of batches and amount of fuel being burned (SL: 5 batches á<!--AQ1: The meaning of "á" here and throughout is unclear. Please provide alternate text. --> 2 kg; BCB 3 batches á 1.7 kg) differed due to inherent fuel properties, specifically the ease of ignition and the burn rate.[50]

For the SL experiments, the combustion procedure was conducted as described by Miersch et al.~~.~~[51] ~~.~~ Briefly, five consecutive batches of spruce logs were burned with a weight of approximately 2 kg each. The cold appliance was ignited top-down using, from bottom to top, three logs á 300~~-~~ g~~-~~, five wood sticks á 150~~-~~ g, and 150~~-~~ g of small wood sticks and lasted 35~~-~~ min, whereas following batches, having consisted of three logs with a total weight of ~~approx.~~ ~2~~-~~ kg, lasted 45~~-~~ min each. For refueling of the stove, glowing embers were stoked and the primary air supply was opened prior to adding new batches. After the fifth batch was consumed, the remaining embers were stoked, and the secondary air supply of the appliance was closed for the remaining 25~~-~~ min of the experiments according to the shut-down instructions of the manufacturer.

For the BCB experiments, two batches of SL were burned before adding the first batch according to the instructions of both the manufacturer of the stove and the manufacturer of the BCB. This is done due to the BCB's poor ease of ignition. After the second batch of spruce was consumed, three consecutive batches of BCBs were added, with each batch consisting of three briquettes with a weight of 0.58~~-~~ kg per briquette. Before adding a new batch, the remaining embers were stoked each time. The first batch of BCB lasted 1~~-~~ h, while the other two batches lasted 1~~-~~ h 20~~-~~ min each. Additionally, the latter two were stoked ~~one~~ 1 h~~our~~ after they were added to the appliance. After the third batch was consumed, the remaining ember was stoked and the secondary air supply of the appliance was closed for the remaining 20~~-~~ min of the experiments.

~~1.2.~~2.2. Instrumentation

All emissions were monitored for the entire combustion period, that is, from the ignition of the first batch until the end of the burn-off. For BCB experiments, this included both batches of SL that were burned prior to the briquettes. However, these two batches were not considered for the calculation of EFs for BCB experiments.

~~1.2.1.~~2.2.1. Gas A~~a~~nalysis

The bulk flue gas composition, including water (H_2O), carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x~~-~~ =~~-~~ $NO+NO_2$ as NO_2 equivalents), sulfur dioxide (SO_2), ammonia (NH_3), hydrogen cyanide (HCN), and methane (CH_4), was~~ere~~ continuously monitored by a Fourier ~~-~~transform infrared spectroscope (FTIR; *DX4000*, Gasmet Technologies Oy, Finland). Furthermore, organic compounds monitored by the FTIR were grouped into the compound classes: non-methane alkanes, unsaturated aliphatics, aromatics, carbonyls, and alcohols (for a list of compounds and their assignment, see Table S1). All emissions were measured directly from the stack through an insulated and externally heated (180~~-~~ °C) sampling line.

~~1.2.2.~~2.2.2. Untargeted A~~a~~nalysis of O~~o~~rganic F~~f~~lue G~~g~~as C~~c~~onstituents

For the untargeted analysis of organic compounds, flue gas was isokinetically sampled from the stack~~,~~ and transported via a heated sampling probe (180~~-~~ °C) to a combined porous-tube ejector diluter (*DAS*, Venaconra Oy, Finland). The target dilution ratio was 30 in SL experiments, whereas a dilution ratio~~n~~ of 60 was targeted for the initial 10~~-~~ min and 30 for the remaining 230~~-~~ min of BCB experiments. Exact dilutions were determined from the analysis of CO_2 in the stack and after dilution. Dilution with clean compressed air prevents condensation of water or sulfuric acid droplets, and the exhaust gas is cooled down to room temperature. Primarily, the dilution was applied to lower and adapt absolute emission levels to the linear range of the instrument. Subsequently, diluted flue gases passed an unheated 4~~-~~ m stainless steel tubing (ID: 1.175~~-~~ mm) to the heated sampling unit (220~~-~~ °C). Dilution of emissions can lead to both condensation of SVOCs on particles, in the case of a small dilution factor due to a reduction of the saturation vapor pressure, but also to evaporation of SVOCs, in case of great dilution factors that reduce emissions levels far below the saturation vapor pressure. Heating of the aerosol also shifts SVOCs condensed on particles to the gas phase due to increasing saturation vapor pressures. With the set~~-~~up of the sampling in the present study, the authors were aiming for overall EFs of VOC species. In the sampling unit, the internal standard (toluene methyl-D3, 98% purity; mass-to-charge ratio *m/z*~~-~~ =~~-~~ 95; Cambridge Isotope Laboratories, Inc.) was constantly added at levels of 300 to 600 ppb$_v$ to the diluted flue gas. After each experiment, exact concentrations of the internal standard were determined by replacing the sample aerosol with a calibration gas (benzene 0.96~~-~~ ppm, toluene 1.01~~-~~ ppm, *p*-xylene 0.72~~-~~ ppm, 1,2,4-trimethyl benzene 1.39~~-~~ ppm, in: N_2, Linde AG, Germany) and comparing the signal intensity of the internal standard $C_7H_5D_3$ to that of ~~the~~ regular toluene C_7H_8 (*m/z*~~-~~ =~~-~~ 92). A glass fiber filter (F-0,1GF, M&C Tech Group, Germany) heated to 220~~-~~ °C was used to remove particles and evaporate semi~~-~~volatile organic substances. All gaseous compounds were transported from the hot sampling unit to the ion source of the mass spectrometer via a 3~~-~~ m stainless steel capillary (ID 280~~-~~ µm, MXT Guard column) in heated stages of 235~~-~~ °C/240~~-~~ °C/245~~-~~ °C to prevent back-condensation. For this study, we define all organic compounds that were identifiable in the gas phase after the hot filtration to be VOCs (in the following as VOC$_{SPI}$).

Organic gaseous compounds were analyzed by a time-of-flight mass spectrometer (TOF-MS; *Compact Reflectron Time-of-Flight Spectrometer II*, Kaesdorf Geräte für Forschung and Industrie, Germany) using single-photon ionization (SPI) at 118~~-~~ nm (10.49~~-~~ eV), which is an ionization technique that predominantly yields molecular ions and only little fragmentation.[52] Generally, all compounds having an ionization energy below the photon energy of 10.49~~-~~ eV can be ionized, but there are considerable differences in ionization efficiencies between compound classes.[53] Vacuum~~-~~ ultra~~-~~violet radiation used for ionization was produced by frequency tripling of the third harmonic of a pulsed Nd:YAG laser (Spitlight 400, Innolas GmbH, Krailling, Germany; 40~~-~~ mJ at 355~~-~~ nm, pulse duration: 5–~~-~~7~~-~~ ns, 20~~-~~ Hz) in a gas cell filled with 4~~-~~ mbar of xenon. Ions were in turn extracted by a delayed electric field, transported to the mass analyzer, and detected at a micro channel plate (MCP, Chevron plate, Burle Electro-Optics Inc.).

~~1.3.~~2.3. Data P~~p~~reprocessing and A~~a~~nalysis

Prior to data evaluation, signals in the mass spectra obtained from the SPI-TOFMS were corrected with a blank measurement of nitrogen (purity of 99.5~~-~~%, total hydrocarbon <200~~-~~ ppb; Linde AG). Subsequently, intensities, which were merged to unit mass resolution, were processed with a Savitzky~~-~~–Golay filter with a polynomial order of five and a frame length of nine. All signals were individually converted from voltages to concentrations by normalizing them to the signal of the internal standard (D_3-toluene). Individual *m/z* values were corrected for their relative photo ionization cross sections to toluene, as described by Adam et al.[53]~~.~~ Subsequently, the signals were corrected for their dilution and flue gas moisture. EFs were calculated as described by Reda et al.[54]~~.~~

For statistical analysis, the Matlab~~®~~ Statistical Toolbox (R2019b, The MathWorks Inc., Massachusetts, USA) was used. When performing statistical tests, *p*~~-~~ values were considered significant at a level below 0.05, if not stated otherwise. In addition, tests on statistical difference of two means w~~as~~ere carried out with a two-sample *t*~~-~~ test for unequal variances. Results are reported as average EF~~-~~ ± ~~-~~ standard deviation.

~~2.~~3. Results

~~2.1.~~3.1. Evolution of G~~g~~ases and VOCs during the C~~c~~ombustion E~~e~~xperiments

Wood combustion in small-scale heating appliances has~~ve~~ been shown to pass through three distinct burning phases: (1) “~~‘~~ignition”~~’~~, (2) “~~‘~~stable combustion”~~’~~, and (3) “~~‘~~ember”~~’~~.[10,11] Previous research has derived the burning phases from emission~~s~~ profiles of bulk carbonaceous species, such as CO_2, CO, and organic gaseous carbon from a flame ionization detector (FID). Thus, these parameters are used to point out differences in the combustion behaviors of SL and BCBs (Figure 1). Instead of the FID, we used the sum of concentrations determined from the SPI-TOFMS measurements to describe the evolution of organic constituents. Due the steel tubing between the dilutor and the sampling unit being cold, only organic emission profiles from *m/z* 40 (propyne/allene; smallest organic compound monitored with SPI-TOFMS with 118~~-~~ nm VUV photons) to *m/z* 92 (toluene) were used to describe the combustion behavior and labeled $VOC_{SPI,40\text{-}92}$. Signals with higher *m/z* originate from higher molecular compounds, which showed a noticeable carry-over effect due to condensation in the steel tubing. Average intensities over 4~~-~~ h and individual batches were considered for the *m/z* range up to *m/z* 202.Generally, trends of gases and VOCs were very similar in both solid fuels. The “~~‘~~ignition”~~’~~ phase is characterized by rapidly increasing emissions of CO_2 and peaking emissions of incomplete combustion products, such as CO, CH_4, and $VOC_{SPI,40\text{-}92}$. Subsequently, the fuel transits to a “~~‘~~stable combustion”~~’~~ phase with lower emissions of incomplete combustion products compared to “~~‘~~ignition”~~’~~. In BCB experiments, CO_2 emissions often exhibited maxima during this phase, whereas in SL experiments, CO_2 emissions continuously decreased from the beginning until the end of a batch. One apparent difference between both fuels was a higher emission of incomplete combustion products in BCB than in SL experiments during this phase, which might be a result of the poorer ease of ignition of BCBs. In SL experiments, rapidly declining emissions of CO_2 and gradual increases of CO and CH_4 mark the transition from the “~~‘~~stable combustion”~~’~~ to the “~~‘~~ember”~~’~~ phase, which is known for char oxidation. In BCB experiments, CO_2 emissions fell evenly until the end of the batch, and higher emissions of CO and CH_4 throughout the “~~‘~~stable combustion”~~’~~ phase do~~es~~ not give a clear indication of the transition to the “~~‘~~ember”~~’~~ phase. For the final 30~~-~~ min of the combustion experiments, the secondary air supply was completely shut, and SL showed considerable increases of CO. In BCB experiments however, emissions increased more gradually and CO emission could possibly be higher after the experiment was terminated.

Similar to other inorganic gases (Figure 2), emissions of NO_x exhibited a concave emission profile with an increase~~ing~~ at the beginning and a decline~~ing~~ at the end of a batch. Interestingly, both fuels emitted NO_x at similar levels, although the fuel-N in BCB was approximately seven times higher. However, BCBs emitted significantly higher levels of NH_3, HCN, and SO_2. In SL experiments, emissions of NH_3 and SO_2 were barely noticeable, and HCN showed only small peaks upon adding of a batch. In BCB experiments, NH_3 showed an emission profile similar to CO with peaks at the beginning and gradual increases at the end, and HCN and NH_3 showed a profile similar to CO_2.

~~2.2.~~3.2. Effect of E~~e~~ase of I~~i~~gnition on O~~o~~rganic E~~e~~missions

As addressed in the previous section, organic emissions occur predominantly during the ignition of an individual batch. The poorer ease of ignition, likely due to less~~er~~ content of volatile matter in coal (55% for the Lusatian lignite[55]) than in wood (~~≈~~~80%[50]), was expected to lead to enhanced organic emission upon ignition. The ignition is usually associated with poorer combustion efficiency and hence high CO emissions. The modified combustion efficiency (MCE), which is an indicator for the efficiency of combustion, is calculated according to eq ~~(~~1~~)~~ and can be used to estimate the time a batch needs~~ed~~ to ignite properly. Here, $[CO_2]$ refers to the concentration of CO_2 in the exhaust gas and $[CO_2 + CO]$ refers to the sum of concentrations of CO_2 and CO. We defined the ignition time as the time between adding of a batch and the point when proper combustion ($MCE = 0.975$) conditions after the global MCE minimum was reached (Figure 3 top). Due to the small wood pieces used for ignition of the first SL batch, the MCE was generally at high levels and the estimation of the ignition time by the method the authors proposed failed. These batches are therefore being omitted in the following.

$$MCE = \frac{[CO_2]}{[CO_2 + CO]} \qquad (1)$$

Generally, positive correlation (Pearson's $r = 0.63$, $p = 1.9 \times 10$~~E~~$^{-5}$) between ignition times and VOC_{SPI} of individual batches for all experiments can be observed (Figure 3, bottom). Ignition times of BCBs are found to be four times longer ($p = 1.6 \times 10$~~E~~$^{-04}$) with an ignition time of ~~approx.~~ ~16 min ± 9 min, and organic emissions of BCBs were estimated to be on average two times higher ($p = 2.3 \times 10$~~E~~$^{-2}$). For SL batches, the positive correlation is stronger than for all of our experiments ($r = 0.89$, $p = 7.6$~~E-~~$\times 10^{-6}$) since the majority of organic compounds was emitted directly upon adding of a batch. In BCB experiments however, the correlation was weaker ($r = 0.46$) and not significant ($p = 0.13$), which could be a result of higher emissions of VOC_{SPI} throughout an individual batch of BCBs.

~~2.3.~~3.3. 4 ~~-~~h EF from L~~l~~ignite and S~~s~~pruce L~~l~~ogwood C~~c~~ombustion

Prior to calculating EF for individual VOCs, mass spectra were normalized to the intensity of the internal standard, corrected for their individual dilution and flue gas moisture, and afterward~~s~~ averaged over the entire 4~~-~~ h combustion cycle. Figure 4 shows two exemplary spectra from both types of experiments averaged over the entire 4~~-~~ h combustion cycle. In both spectra, intensities in the lower *m/z* range from 40 to 86 mostly appeared as groups of triplets or quartets with *m/z* intervals of 6 to 10 between each group. The amount of possible sum formulae for each signal shrinks down to a reasonable number when considering ~~the~~ an ionization threshold of 10.49~~-~~ eV, ionization cross sections,[53]~~;~~ and general abundanc~~i~~es of VOC in wood combustion emissions and assuming that the vast majority of the organic aerosol consists of carbon, oxygen, and hydrogen. Peaks with the lowest *m/z* within each multiplet cannot have chemically reasonable sum formulae with oxygen and therefore represent polyunsaturated aliphatic hydrocarbons, e.g., propadiene/propyne (*m/z* 40), vinyl acetylene (*m/z* 52), and cyclopentadiene (*m/z* 66). Signals with higher *m/z* within each triplet~~s~~ or quartet~~s~~ can be assigned to reasonable sum formulae containing oxygen, e.g,. acetaldehyde (*m/z* 44), acrolein/butene (*m/z* 56), or acetone/propanal (*m/z* 58). In the higher *m/z* range, signals that likely arise from mono- and polycyclic aromatic species, such as benzene (*m/z* 78), toluene (*m/z* 92), styrene (*m/z* 104), xylene (*m/z* 106), and naphthalene (*m/z* 128) as well as phenolic species, e.g., phenol (*m/z* 94) and methyl phenol (*m/z* 108), can be observed.

Spectra from SL experiments (Figure 4a) were characterized by large signals of parent aromatic and polycyclic aromatic hydrocarbons, i.e., benzene and naphthalene, while carbonyls, aliphatics, and other aromatic species are comparably low. As for the multiplets in the smaller *m/z* range, the signal intensities appear to decrease from groups with smaller to larger *m/z*. Within each of these multiplets, the signal with the smallest *m/z*, attributed to emissions of polyunsaturated aliphatic hydrocarbons with multiple double bonds or triple bonds, was~~ere~~ much more intense than the others.

In the BCB experiments (Figure 4b), mass spectra were more complex and not dominated by a few abundant compounds, such as benzene and naphthalene. Although both of these were still two of the most abundant species, they were clearly not as prominent as they were in SL experiments. Instead, smaller VOCs, e.g., with three and four carbon atoms, were distinctly more prominent reaching concentration levels similar to that of benzene in BCB experiments. Within these multiplets, signals with the smallest *m/z* were not dominating, but instead monounsaturated hydrocarbons and carbonyls, e.g., propene (*m/z* 42), acetaldehyde (*m/z* 44), acrolein/butene (*m/z* 56), and acetone/propanal (*m/z* 58), were the most abundant species. In the higher *m/z* range, substituted benzenes as well as unsubstituted and substituted phenolic species were more abundant than in SL experiments.

Eventually, EFs for the 5 bulk inorganic combustion gases (CO, NO_x, SO_2, NH_3, and HCN), CH_4, the ~~5~~five organic compound classes monitored with ~~the~~ FTIR (the reader is referred to Table S1 in the S~~s~~upplementary ~~material~~ Information for a list of targeted compounds and their assignment to the compound classes), and 10 selected VOCs monitored with ~~the~~ SPI-TOF-MS were calculated according to the Finnish Standard Association method SFS 5624 as described by Reda et al.[54] and are presented in Table 2. The VOCs monitored with ~~the~~ SPI-TOFMS were selected due to the availability of photoionization cross sections.[10]

~~3.~~4. Discussion

~~3.1.~~4.1. Conversion of F~~f~~uel-N and F~~f~~uel-S

~~3.1.1.~~4.1.1. Fuel-N

The conversion of fuel-N has~~ve~~ been intensively studied in the past for both the combustion of coal and biomass.[56,57] Generally, NO_x is formed by three major mechanisms: (1) thermal, (2) prompt, and (3) fuel-N conversion, with the former two being negligible due to relatively low temperatures for the combustion of wood and low-rank coals in small-scale appliances. Processes involved in fuel-N conversion are the primary devolatilization of the fuel into incondensable gases, tar, and char~~,~~ and the secondary devolatilization of tar and char into incondensable gases. Incondensable N-containing gases are intermediates, such as HCN and NH_i radicals ($i = 0$–3), as well as NO_x. If O_2 is available, intermediates can be oxidized to NO, whereas they can also interact and reduce NO to molecular N_2 if O_2 is lacking.[58] Because of the high correlation of NO_x emissions to fuel-N, NO_x EFs (Table 2) were converted to ~~a~~ mg kg^{-1} by division with the respective heating value (Table 1).

Comparing NO_x EFs from those in the literature, EFs from SL experiments in this study were almost identical to the EFs reported in an earlier study with the same stove but another lot of SL[51] as well as similar to other wood combustion experiments with comparable fuel-N.[59,60]

Generally, the experiments are on the lower side of NO_x emissions when also considering biomass combustion experiments with higher fuel-N.[8,10,61,62] To the authors' knowledge, EFs of intermediates, such as HCN and NH_3, were reported less frequently in recent studies for biomass combustion in small-scale combustion appliances. In previous work with the same appliance and SL,[51] EF for both HCN and NH_3 were ~~approx.~~ ~~~three~~3-times higher, although the fuel-N content was much lower than in this study.

For residential coal combustion, information on emissions from stoves relevant for European emission scenarios is scarce, since most of the research was focused on boilers,[43,45,46]~~,~~ which are generally larger and might have more efficient NO_x reduction due to operational/technological aspects.[56] To the authors' knowledge, NO_x EFs for coal combustion in stoves relevant for Europe were only reported for coal briquettes from various coals by Mitchell et al.[48] varying from 204~~ mg MJ^{-1}~~ to 438 mg MJ^{-1}, which are clearly higher than any of the other EFs found for biomass. This can mostly be explained by the fuel-N content in their fuels, which was 2.5 times as high as fuel-N in the BCB. The same appliance was tested later by Mitchell et al.[61] with biomass and resulted in NO_x EFs comparable to the literature cited before. As for NH_3 and HCN, no information was reported for European small-scale appliances to the authors' knowledge. For the combustion of coal in a traditional Chinese appliances, EFs of NH_3 were reported to be 36.5 mg MJ^{-1}, while an advanced heating stove emitted 4.8 mg MJ^{-1}, which is in line with the EFs found here.[63]

Surprisingly, NO_x EFs from BCBs were only ~~approx.~~ ~20% higher than EFs from SL, although BCBs have a seven times higher fuel-N content. To compare NO_x emissions from BCBs to emissions from other biomass with similar fuel-N, EFs as well as the release of fuel-N as N in NO_x were~~as~~ calculated according to eq ~~(~~2~~)~~ for EF from this study, which were previously converted to g kg^{-1}~~,~~ and for other work cited before. Here, RF_{NO_x} refers the fraction of N in the fuel released as NO_x in percent, $EF_{NO_x,\,N}$ is the EF for N in NO_x on a g kg^{-1} fuel basis, and fuel-N is on a g kg^{-1} basis. Furthermore, EFs of NO_x from the literature for biomass combustion were subjected to orthogonal regression and non-simultaneous, observational prediction bounds (95% interval; Figure 5) were calculated to give information about the predictability of observations made in this study from literature observations. Similar to EFs from the literature and observations in this study, the regression and prediction bounds were converted to RF_{NO_x} according to eq ~~(~~2~~)~~. Previous studies have already reported a linear correlation of fuel-N and

NO_x-N,[61,64] which was also found (Pearson's *r*~~-~~ =~~-~~ 0.92) within the range of biomasses and fuel-N used for this analysis

$$\mathrm{RF}_{\mathrm{NO_x}} = \frac{\mathrm{EF}_{\mathrm{NO_x\text{-}N}}}{\mathrm{fuel-N}} \times 100 \qquad (2)$$

According NO_x EFs and $\mathrm{RF}_{\mathrm{NO_x}}$ (Figure 5), observations for NO_x EFs and $\mathrm{RF}_{\mathrm{NO_x}}$ from SL experiments can be predicted with literature observations, whereas observations from BCB were outside of the 95~~-~~% non-simultaneous, observational prediction bounds of the model, which indicates that there might be a different fate for fuel-N than NO_x in BCBs. Differences in the chemical constitution of fuel-N in biomass and coal~~,~~ and the retention of N in char could play an important role. In both biomass and coal, fuel-N appears in different chemical moieties, and hence fuel-N is often reduced to its binding situation, i.e., whether N is bound as amino functions in proteins or ~~as N~~ is bound in heterocyclic structures (e.g., pyrrole or pyridine).[57,65] The difference between both fuels is that, in biomass, N is mainly found in proteins (85%) and free-amino acids, whereas, in coal, heterocyclic, nitrogen-containing five-membered ring and six-membered ring moieties, which might convert to more refractory structures and accumulate in char during combustion, are dominant. However, previous research has shown that fuel-N does not accumulate in the char during pyrolysis, and therefore the retention of fuel-N in the residual char is not a major sink for fuel-N in Lusatian lignites.[55] Also, fuel-N is not emitted in considerable amounts as oxidation intermediates. Emissions of HCN and NH_3 are usually one order of magnitude lower than NO_x and accounted for approximately 1.8~~%~~ and 0.8% of fuel-N for both BCB and SL, respectively. No statistical differences between both fuels were found for the release fractions for HCN and NH_3, respectively. Another plausible sink is the reduction of NO_x to N_2, which is known to occur in the primary combustion zone of solid fuel boilers[66,67] and likely plays a role in the stove as well although the conditions are not optimized for NO_x reduction due to the batch-wise combustion. Feldmeier et al.[67] reported that the influence of the appliance, in their case boilers, is greater for higher than for lower fuel-N, which could explain why the SLs with low fuel-N were predictable from literature observations, whereas NO_x EFs from BCBs cannot be predicted. Also, catalytic effects of mineral matter, e.g., by iron in coal, may contribute to conversion of NO_x to N_2.[68] Thus, we cannot fully attribute the relatively low NO_x emissions to the stove or the BCBs.

~~3.1.2.~~4.1.2. Fuel-S

S-containing emissions clearly originates~~s~~ from the S bound in the fuel in both coal and biomass.[69] EFs in the literature vary largely,[64,70,71]~~;~~ and EFs found in the present study agree with earlier findings. For coal combustion in European appliances, Czaplicka et al.[45] reported EFs of approximately 190 mg MJ^{-1}, being approximately twice as high as EFs found here with 100 ± 10 mg MJ^{-1}, although the fuel-S content was comparable. Křůmal et al.[46] reported EFs of 143~~ mg MJ^{-1}~~ to 658 mg MJ^{-1} for various coals and coal briquettes, with EFs of their brown coal briquettes being most comparable to EFs found in the present study. Lamberg et al.[64] also found almost identical SO_2 emissions for small-scale combustion of peat with a comparable fuel-S content of 8 and 12 mg kg^{-1}. The Chinese coal–stove combination, for which more information is available, has~~ve~~ generally lower EFs of SO_2 than the European ones, which is likely due to minerals added to their coal during briquetting.[72] Calculating the release of S as SO_2 with the same approach as for NO_x in eq ~~(~~2~~)~~, we find average release fractions of 31 ± 6~~%~~ and 14 ± 1% for SLs and BCBs, respectively. These findings indicate that the majority of S might be released into the gas phase as sulfates in PM or still be bound in the bottom ash. However, these two possible fates for S cannot be ruled out with the analysis conducted in this study.

~~3.2.~~4.2. Comparison of E~~e~~mission F~~f~~actors from 4 h of B~~b~~urning of S~~s~~pruce L~~l~~ogs and B~~b~~rown C~~c~~oal B~~b~~riquettes

~~3.2.1.~~4.2.1. Bulk F~~f~~lue G~~g~~ases

CO and CH_4 are important indicators for incomplete combustion conditions, and CO was already used to evaluate ignition times via the MCE. Comparing EFs from SL experiments with the literature, the average EF for CO of 1001 ± 168 mg MJ^{-1} was lower than in previous work using SL in the same stove (2040 ± 420 mg MJ^{-1})[51] and lower than EFs from other batchwise-operating, small-scale appliances.[8,43,49,51,59,73] EFs for CH_4 with 28.3 ± 6.7 mg MJ^{-1}, however, were comparable to previous work with the same stove (26.3 ± 3.7 mg MJ^{-1})[51] and by approximately a factor of 4 lower than those of conventional masonry heaters.[49,62] Furthermore, CO concentrations are well below the limit value of 3 g MJ^{-1} (converted from the limit value of 4 g m^{-3} at 13% O_2 using the conversion factor reported in Table 2) for single-room heating appliances documented in the German Federal Immision Control Act (1. BImSchV). The difference to previous experiment indicates that there might be a difference in fuel properties, e.g., fuel moisture, which was 2% lower in the present study than in the previous experiments, possibly leading to a fast ignition and hence low emissions. However due to emissions still being in line with mean CO EFs of 784 mg MJ^{-1} reported by the manufacturer for BCBs, we consider the tested stove representative for modern Central European appliances.

For coal combustion, information on combustion in European households is mostly limited to boilers,[43,45,46] which differ from stoves due to their continuous mode of operation. Stove emissions on the other hand are much more dynamic due to constantly changing fuel properties, temperature, and λ and are therefore harder to optimize. Nevertheless, CO EFs are three times lower than what was found previously for old boilers under nominal load in steady-state operation.[43] Modern boilers on the other hand usually emit by a factor of three up to one order of magnitude less CO under nominal load than the stove in the present study.[43,45] At a reduced load, which is more representative for operation in households, old boilers emit up to one order of magnitude more CO than the stove in the present study, whereas modern boilers still emit CO by a factor of three to seven less.[46] For coal combustion in manually operated small-scale appliances, the only information available is reported by Mitchel et al.[48] with EFs varying from 6.0 to 11.1 mg MJ^{-1} for coal briquettes made from various coals. Information on different Chinese coal–stove combinations, which might differ from European emission scenarios due to differences in the type of coal and the appliance design, is readily available.[23,32,72] CO and CH_4 EFs vary largely from 1 400 to 7 500 mg MJ^{-1} and 0.8 to 480 mg MJ^{-1} for different coal–stove combinations, respectively.[72] Therefore, results of the present study of 1 450 ± 180 mg MJ^{-1} for CO and 30 ± 6 mg MJ^{-1} for CH_4 are on the lower side of stove–coal combinations tested before. Furthermore, CO values are also well below the limit value of 3 g MJ^{-1} (converted from limit value of 4 g m^{-3} at 13% O_2 using the conversion factor reported in Table 2) of 1. BImSchV (German Federal Immision Control Act). In fact, the present experiments are very well in line with the procedure defined by DIN EN 13240:2001 + A2:2004 (D) requiring at least two batches with a combustion period of at least 1 h and a weight of 1.4 kg per batch.

Comparing emissions of BCB and SL obtained in this study, EFs of CO were significantly different between both fuels, whereas CH_4 EFs from both fuels were not significantly different. Interestingly, CO EFs from BCB are lower than most of the EFs reported in the literature for wood, which suggests that the efficiency of the combustion is comparable to wood combustion. However, one of the reasons why CO emissions are comparably low in BCB in comparison to

SL experiments are the relatively low emissions during burn-off when the secondary air supply was completely shut (Figure 1). Here, CO emissions increase tremendously in SL, whereas emissions of BCBs increase more slowly, which could be due to a lower burn rate and thus a lower rate of char oxidation. As the burn-off is an important phase for CO emissions,[10] CO emissions from BCBs might be underestimated due to premature termination of the combustion experiment. Differences in overall MCEs from both fuels are very small with an average of 0.976 and 0.966 for SL and BCB, respectively. Differences in MCEs when the burn-off phase was omitted in data integration were slightly higher but still comparable with 0.985 and 0.966 for SL and BCB, respectively. Regarding CH_4 emissions, it is surprising that EFs were comparable when considering the differences in fuel properties. The poorer ease of ignition due to less~~er~~ content of volatile matter in coal (55% for the Lusatian lignite[55]) than in wood (~~≈~~~80%[50]) was expected to lead to enhanced CH_4 emission upon ignition. Nevertheless, the difference between both fuels is not significant.

~~3.2.2.~~4.2.2. Individual VOCs

Combustion processes are a combination of different chemical and physical processes, e.g., distillation, pyrolysis, and oxidation.[74,75] Especially, pyrolysis as a major decomposition path for the macromolecular network in the fuel has been intensively studied in the past.[76,77] It was shown that the fuel composition, in the case of wood cellulose, hemicellulose and lignin, ~~are~~ is the major paramete~~r~~s for the composition of VOCs emitted upon combustion. Coal originates from biomass and is altered by physical and chemical processes over periods of up to several hundred million years. Due to heat and pressure during coalification, the coal loses moisture and volatile matter, i.e., sidechains in lignin monomers, and increases in aromaticity and fixed carbon.[78] Thus, coal properties depend on both the type of biomass it was formed from and the degree of coalification. The coal from the Lusatian mining area is thermally immature (lignite) and formed from a slight dominance of arborescent biomass<!--AQ2: Please check if the addition of “biomass” here is appropriate. --> over reed-mire vegetation in a predominantly terrestrial environment.[79] Currently exploited lignite deposits in Poland[80] and the Czech Republic[81] have formed under similar low-lying mire environments from predominantly arborescent biomass, and therefore we conclude that the coal from the Lusatian mining area is likely representative for other Central and Eastern European lignite deposits as well.

The comparison of EFs from both fuels is visualized in a volcano plot (Figure 6). Differences between fuels in gaseous emissions were already discussed, and therefore this section will focus on organic compound classes monitored by the FTIR spectroscope and on the individual VOCs detected with SPI-TOFMS. The analysis of organic flue gas constituents with the FTIR spectroscope did not reveal apparent differences between both fuels. BCBs emitted slightly more non-methane alkanes and aromatics than SLs, whereas the EFs of carbonyls, alcohols, and unsaturated aliphatics were not significantly different. Differences between both fuels were more apparent in mass spectra from SPI-TOFMS (Figure 4). As already described in a previous section, BCB emitted more~~,~~ smaller hydrocarbons and carbonyls as well as substituted benzenes and PAHs, which are known decomposition products of wood and lignite.[82] Interestingly, benzene, naphthalene, vinyl acetylene, and styrene did not show significant differences between both fuels. Previous work found that emissions of benzene emissions from residential wood combustion are less increased than early incomplete combustion products of wood polymers, like cellulose, hemicellulose, and lignin, when the ignition occurs slowly.[10] It seems likely that these compounds are less sensitive to the ease of ignition due to similar formation pathways, i.e., pyro synthesis in flames.[83] In a previous section, we already associated the slower ignition of BCBs with greater amounts of VOCs (Figure 3). Thus, this suggests that emissions from BCBs are mainly characterized by higher emissions of organic compounds with petrogenic origin, while VOCs with pyrogenic origins show no significant differences. Effects of other flue gas constituents like SO_2 in BCB experiments might play an important role for the formation of pyrolytic compounds as well, since SO_2 was shown to substantially reduce PAH emissions,[84] ~~;~~ which could be a result of an oxidizing effect of SO_2 on PAHs or their gaseous precursors.

Differences between emissions of different batches, which were observed for a heat-retaining stove with a massive-soapstone structure in previous research,[10] were negligible for both fuels, as indicated by Figure 3. A comparison of EFs from both fuels under hot-start conditions, i.e., EFs averaged from batch 3 to burn-off in SL experiments and batch 1 to burn-off, did not reveal apparent differences to the comparison of the entire combustion experiments and is therefore not shown.

~~4.~~5. Conclusions

This study demonstrates that BCBs made from low-rank, German coal have a similar emission behavior to SLs, which is a commonly~~-~~ used fuel in Central Europe. The differences between overall emissions of major combustion gases, CO and CH_4, were negligible in the present experiments. Surprisingly, NO_x was emitted only 20% higher from BCB experiments despite the seven times higher fuel-N content, and we believe that the stove design may be responsible for relatively low NO_x emissions from BCBs. The most striking differences between emissions from both fuels were 20-fold higher SO_2 emissions, which was not surprising due to the 50-fold higher fuel-S content in BCBs. Organic emissions monitored with an FTIR spectroscope and SPI-TOFMS were predominantly emitted upon adding of a new batch from both fuels. Slightly higher emissions of organic compounds from BCB were attributed to their poorer ease of ignition and thus longer times to reach combustion conditions with moderate emissions. Overall, organic emission of BCBs had a higher proportion of compounds with petrogenic emissions, whereas compounds that are likely formed in flames, i.e., highly unsaturated compounds, did not show significant differences. On average, the ignition of BCBs was estimated to take four times longer than the ignition of SLs, which was proposed to be the reason for higher emission of organic incomplete combustion products with petrogenic origin. Our results imply that a reduction in emissions can be achieved by choosing fuels that ignite faster, i.e., fuels with more volatile matter.

Future research should focus on the physical and chemical characterization of particles being emitted from coal combustion. Furthermore, emissions induced by maloperation of stoves is also of big interest because the authors believe that overall emission levels from coal burning are highly sensitive to bad user practices due to the poor ease of ignition. Since the stove tested in this study is a rather modern appliance with comparably low emissions, future research should also investigate emissions from older appliances that may still be installed in most parts of Europe.

~~Associated content~~.

Supporting Information

- ~~Supplement_Manuscript_Lig_vs_Spru_onlineChemV2.2.docx:~~ Summary of compounds monitored with FTIR and their assignment to compound classes (PDF)~~.~~

~~Notes~~.

The authors report no conflict of interest.

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~~9. References~~

(1) Lamarque, J.-F.; Bond, T. C.; Eyring, V.; Granier, C.; Heil, A.; Klimont, Z.; Lee, D.; Liousse, C.; Mieville, A.; Owen, B.; Schultz, M. G.; Shindell, D.; Smith, S. J.; Stehfest, E.; van Aardenne, J.; Cooper, O. R.; Kainuma, M.; Mahowald, N.; McConnell, J. R.; Naik, V.; Riahi, K.; van Vuuren, D. P. Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application. *Atmos. Chem. Phys.* 2010, *10* (15), 7017–7039~~. DOI:~~, 10.5194/acp-10-7017-2010.

(2) Naik, V.; Horowitz, L. W.; Fiore, A. M.; Ginoux, P.; Mao, J.; Aghedo, A. M.; Levy, H., II Impact of preindustrial to present-day changes in short-lived pollutant emissions on atmospheric composition and climate forcing. *J. Geophys. Res.: Atmos.*~~*J. Geophys. Res*~~ 2013, *118* (14), 8086–8110,~~. DOI:~~ 10.1002/jgrd.50608.

(3) Sram, R. J. Impact of Air Pollution on the Health of the Population in Parts of the Czech Republic. *Int. J. Environ. Res. Public Health*~~*Int. J. Environ. Res. Public Health*~~ 2020, 17, 6454~~. DOI:~~, Published Online: Sep. 4, 2020. 10.3390/ijerph17186454. ~~Published Online: Sep. 4, 2020.~~

(4) Pope, C. A., III; Dockery, D. W. Health effects of fine particulate air pollution: lines that connect. *J. Air Waste Manage. Assoc.*~~*J. Air & Waste Manage. Assoc.*~~ 2006, *56* (6), 709–742,~~. DOI:~~ 10.1080/10473289.2006.10464485.

(5) Andreae, M. O.; Ramanathan, V. Climate change. Climate's dark forcings. *Science* 2013, *340* (6130), 280–281,~~. DOI:~~ 10.1126/science.1235731.

(6) Cohen, A. J.; Brauer, M.; Burnett, R.; Anderson, H. R.; Frostad, J.; Estep, K.; Balakrishnan, K.; Brunekreef, B.; Dandona, L.; Dandona, R.; Feigin, V.; Freedman, G.; Hubbell, B.; Jobling, A.; Kan, H.; Knibbs, L.; Liu, Y.; Martin, R.; Morawska, L.; Pope, C. A., III; Shin, H.; Straif, K.; Shaddick, G.; Thomas, M.; van Dingenen, R.; van Donkelaar, A.; Vos, T.; Murray, C. J. L.; Forouzanfar, M. H. Estimates and 25-year trends of the global burden of disease attributable to ambient air pollution: an analysis of data from the Global Burden of Diseases Study 2015. *Lancet* 2017, *389* (10082), 1907–1918~~. DOI:~~, 10.1016/S0140-6736(17)30505-6.

(7) Silva, R. A.; Adelman, Z.; Fry, M. M.; West, J. J. The Impact of Individual Anthropogenic Emissions Sectors on the Global Burden of Human Mortality due to Ambient Air Pollution. *Environ. Health Perspect.* 2016, *124* (11), 1776–1784~~. DOI:~~, Published Online: May. 13, 2016. 10.1289/EHP177.~~Published Online: May. 13, 2016.~~

(8) Orasche, J.; Seidel, T.; Hartmann, H.; Schnelle-Kreis, J.; Chow, J. C.; Ruppert, H.; Zimmermann, R. Comparison of Emissions from Wood Combustion. Part 1:

Emission Factors and Characteristics from Different Small-Scale Residential Heating Appliances Considering Particulate Matter and Polycyclic Aromatic Hydrocarbon (PAH)-Related Toxicological Potential of Particle-Bound Organic Species. *Energy Fuels* 2012, *26* (11), 6695–6704~~. DOI:~~, 10.1021/ef301295k.

(9) Bhattu, D.; Zotter, P.; Zhou, J.; Stefenelli, G.; Klein, F.; Bertrand, A.; Temime-Roussel, B.; Marchand, N.; Slowik, J. G.; Baltensperger, U.; Prévôt, A. S. H.; Nussbaumer, T.; El Haddad, I.; Dommen, J. Effect of Stove Technology and Combustion Conditions on Gas and Particulate Emissions from Residential Biomass Combustion. *Environ. Sci. Technol.* 2019, *53* (4), 2209–2219~~. DOI:~~, 10.1021/acs.est.8b05020.

(10) Czech, H.; Sippula, O.; Kortelainen, M.; Tissari, J.; Radischat, C.; Passig, J.; Streibel, T.; Jokiniemi, J.; Zimmermann, R. On-line analysis of organic emissions from residential wood combustion with single-photon ionisation time-of-flight mass spectrometry (SPI-TOFMS). *Fuel* 2016, *177*, 334–342~~. DOI:~~, 10.1016/j.fuel.2016.03.036.

(11) Elsasser, M.; Busch, C.; Orasche, J.; Schön, C.; Hartmann, H.; Schnelle-Kreis, J.; Zimmermann, R. Dynamic Changes of the Aerosol Composition and Concentration during Different Burning Phases of Wood Combustion. *Energy Fuels* 2013, *27* (8), 4959–4968~~. DOI:~~, 10.1021/ef400684f.

(12) Kelz, J.; Brunner, T.; Obernberger, I.; Jalava, P.; Hirvonen, M.-R. PM emissions from old and Modern Biomass Combustion Systems and their Health effects. In *Proc. of the 18th European Biomass Conference and Exhibition*~~. DOI:~~, 10.5071/18thEUBCE2010-OA11.5.

(13) Kjällstrand, J.; Olsson, M. Chimney emissions from small-scale burning of pellets and fuelwood—examples referring to different combustion appliances. *Biomass Bioenergy* 2004, *27* (6), 557–561~~. DOI:~~, 10.1016/j.biombioe.2003.08.014.

(14) Ihantola, T.; Di Bucchianico, S.; Happo, M.; Ihalainen, M.; Uski, O.; Bauer, S.; Kuuspalo, K.; Sippula, O.; Tissari, J.; Oeder, S.; Hartikainen, A.; Rönkkö, T. J.; Martikainen, M.-V.; Huttunen, K.; Vartiainen, P.; Suhonen, H.; Kortelainen, M.; Lamberg, H.; Leskinen, A.; Sklorz, M.; Michalke, B.; Dilger, M.; Weiss, C.; Dittmar, G.; Beckers, J.; Irmler, M.; Buters, J.; Candeias, J.; Czech, H.; Yli-Pirilä, P.; Abbaszade, G.; Jakobi, G.; Orasche, J.; Schnelle-Kreis, J.; Kanashova, T.; Karg, E.; Streibel, T.; Passig, J.; Hakkarainen, H.; Jokiniemi, J.; Zimmermann, R.; Hirvonen, M.-R.; Jalava, P. I. Influence of wood species on toxicity of log-wood stove combustion aerosols: a parallel animal and air-liquid interface cell exposure study on spruce and pine smoke. *Part. Fibre Toxicol.* 2020, *17* (1), 27~~. DOI:~~, Published Online: Jun. 15, 2020. 10.1186/s12989-020-00355-1. ~~Published Online: Jun. 15, 2020.~~

(15) Kanashova, T.; Sippula, O.; Oeder, S.; Streibel, T.; Passig, J.;~~ohannes,~~ Czech, ~~Hendryk~~H.; Kaoma, T.; Sapcariu, S. C.; Dilger, M.; Paur, H.-R.; Schlager, C.; Mülhopt, S.; Weiss, ~~Carsten~~C.; Schmidt-Weber, C.; Traidl-Hofmann, C.; Michalke, B.; Krebs, T.; Karg, E.; Jakobi, G.; Scholtes, S.; Schnelle-Kreis, J.; Sklorz, M.; Orasche, J.; Müller, L.; Reda, A.; Rüger, C.; Neumann, A.; Abbaszade, G.; Radischat, C.; Hiller, K.; Grigonyte, J.; Kortelainen, M.; Kuuspalo, K.; Lamberg, H.; Leskinen, J.; Nuutinen, I.; Torvela, T.; Tissari, J.; Jalava, P.; Kasurinen, S.; Uski, O.; Hirvonen, M.-R.; Buters, J.;~~eroen,~~ Dittmar, G~~unnar~~.; Jokiniemi, J.; Zimmermann,

R. Emissions from a modern log wood masonry heater and wood pellet boiler: Composition and biological impact on air-liquid interface exposed human lung cancer cells. *J. Mol. Clin. Med.* 2018, *1* (1), 23-25~~. DOI:~~, 10.31083/j.jmcm.2018.01.004.

(16) Kerimray, A.; Rojas-Solórzano, L.; Torkmahalleh~~Amouei Torkmahalleh~~, M. A.; Hopke, P. K.;~~, Ó Gallachóir, B.P. K.; Ó ~~Gallachóir, B. P. Ó. Coal use for residential heating: Patterns, health implications and lessons learned. *Energy Sustainable Dev.*. 2017, *40*, 19–30~~. DOI:~~, 10.1016/j.esd.2017.05.005.

(17) Li, H.; Zhang, Q.; Zhang, Q.; Chen, C.; Wang, L.; Wei, Z.; Zhou, S.; Parworth, C.; Zheng, B.; Canonaco, F.; Prévôt, A. S. H.; Chen, P.; Zhang, H.; Wallington, T. J.; He, K. Wintertime aerosol chemistry and haze evolution in an extremely polluted city of the North China Plain: significant contribution from coal and biomass combustion. *Atmos. Chem. Phys.* 2017, *17* (7), 4751–4768~~. DOI:~~, 10.5194/acp-17-4751-2017.

(18) Huang, R.-J.; Zhang, Y.; Bozzetti, C.; Ho, K.-F.; Cao, J.-J.; Han, Y.; Daellenbach, K. R.; Slowik, J. G.; Platt, S. M.; Canonaco, F.; Zotter, P.; Wolf, R.; Pieber, S. M.; Bruns, E. A.; Crippa, M.; Ciarelli, G.; Piazzalunga, A.; Schwikowski, M.; Abbaszade, G.; Schnelle-Kreis, J.; Zimmermann, R.; An, Z.; Szidat, S.; Baltensperger, U.; El Haddad, I.; Prévôt, A. S. H. High secondary aerosol contribution to particulate pollution during haze events in China. *Nature* 2014, *514* (7521), 218–222~~. DOI:~~, 10.1038/nature13774.

(19) Lin, C.; Huang, R.-J.; Ceburnis, D.; Buckley, P.; Preissler, J.; Wenger, J.; Rinaldi, M.; Facchini, M. C.; O'Dowd, C.; Ovadnevaite, J. Extreme air pollution from residential solid fuel burning. *Nat. Sustainability~~Sustain~~* 2018, *1* (9), 512–517~~. DOI:~~, 10.1038/s41893-018-0125-x.

(20) Junninen, H.; Mønster, J.; Rey, M.; Cancelinha, J.; Douglas, K.; Duane, M.; Forcina, V.; Müller, A.; Lagler, F.; Marelli, L.; Borowiak, A.; Niedzialek, J.; Paradiz, B.; Mira-Salama, D.; Jimenez, J.; Hansen, U.; Astorga, C.; Stanczyk, K.; Viana, M.; Querol, X.; Duvall, R. M.; Norris, G. A.; Tsakovski, S.; Wåhlin, P.; Horák, J.; Larsen, B. R. Quantifying the impact of residential heating on the urban air quality in a typical European coal combustion region. *Environ. Sci. Technol.* 2009, *43* (20), 7964–7970~~. DOI:~~, 10.1021/es8032082.

(21) Lin, C.; Ceburnis, D.; Hellebust, S.; Buckley, P.; Wenger, J.; Canonaco, F.; Prévôt, A. S. H.; Huang, R.-J.; O'Dowd, C.; Ovadnevaite, J. Characterization of Primary Organic Aerosol from Domestic Wood, Peat, and Coal Burning in Ireland. *Environ. Sci. Technol.* 2017, *51* (18), 10624–10632~~. DOI:~~, 10.1021/acs.est.7b01926.

(22) Schladitz, A.; Leníček, J.; Beneš, I.; Kováč, M.; Skorkovský, J.; Soukup, A.; Jandlová, J.; Poulain, L.; Plachá, H.; Löschau, G.; Wiedensohler, A. Air quality in the German–Czech border region: A focus on harmful fractions of PM and ultrafine particles. *Atmos. Environ.* 2015, *122*, 236–249~~. DOI:~~, 10.1016/j.atmosenv.2015.09.044.

(23) Shen, G.; Chen, Y.; Xue, C.; Lin, N.; Huang, Y.; Shen, H.; Wang, Y.; Li, T.; Zhang, Y.; Su, S.; Huangfu, Y.; Zhang, W.; Chen, X.; Liu, G.; Liu, W.; Wang, X.; Wong, M.-H.; Tao, S. Pollutant emissions from improved coal- and wood-fuelled cookstoves in rural households. *Environ. Sci. Technol.* 2015, *49* (11), 6590–6598~~. DOI:~~, 10.1021/es506343z.

(24) Shen, G.; Yang, Y.; Wang, W.; Tao, S.; Zhu, C.; Min, Y.; Xue, M.; Ding, J.; Wang, B.; Wang, R.; Shen, H.; Li, W.; Wang, X.; Russell, A. G. Emission factors of particulate matter and elemental carbon for crop residues and coals burned in typical household stoves in China. *Environ. Sci. Technol.* 2010, *44* (18), 7157–7162~~. DOI:~~, 10.1021/es101313y.

(25) Chen, Y.; Tian, C.; Feng, Y.; Zhi, G.; Li, J.; Zhang, G. Measurements of emission factors of PM2.5, OC, EC, and BC for household stoves of coal combustion in China. *Atmos. Environ.* 2015, *109*, 190–196~~. DOI:~~, 10.1016/j.atmosenv.2015.03.023.

(26) Chen, Y.; Sheng, G.; Bi, X.; Feng, Y.; Mai, B.; Fu, J. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environ. Sci. Technol.* 2005, *39* (6), 1861–1867~~. DOI:~~, 10.1021/es0493650.

(27) Zhi, G.; Chen, Y.; Feng, Y.; Xiong, S.; Li, J.; Zhang, G.; Sheng, G.; Fu, J. Emission characteristics of carbonaceous particles from various residential coal-stoves in China. *Environ. Sci. Technol.* 2008, *42* (9), 3310–3315~~. DOI:~~, 10.1021/es702247q.

(28) Zhang, Y.; Schauer, J. J.; Zhang, Y.; Zeng, L.; Wei, Y.; Liu, Y.; Shao, M. Characteristics of particulate carbon emissions from real-world Chinese coal combustion. *Environ. Sci. Technol.* 2008, *42* (14), 5068–5073~~. DOI:~~, 10.1021/es7022576.

(29) Wang, Y.; Xu, Y.; Chen, Y.; Tian, C.; Feng, Y.; Chen, T.; Li, J.; Zhang, G. Influence of different types of coals and stoves on the emissions of parent and oxygenated PAHs from residential coal combustion in China. *Environ. Pollut.* 2016, *212*, 1–8~~.~~ ~~DOI:~~, Published Online: Feb. 1, 2016. 10.1016/j.envpol.2016.01.041. ~~Published Online: Feb. 1, 2016.~~

(30) Ge, S.; Xu, X.; Chow, J. C.; Watson, J.; Sheng, Q.; Liu, W.; Bai, Z.; Zhu, T.; Zhang, J. Emissions of air pollutants from household stoves: honeycomb coal versus coal cake. *Environ. Sci. Technol.* 2004, *38* (17), 4612–4618~~. DOI:~~, 10.1021/es049942k.

(31) Tsai, S. M.; Zhang, J.~~ J.~~; Smith, K. R.; Ma, Y.; Rasmussen, R. A.; Khalil, M. A. K. Characterization of non-methane hydrocarbons emitted from various cookstoves used in China. *Environ. Sci. Technol.* 2003, *37* (13), 2869–2877~~. DOI:~~, 10.1021/es026232a.

(32) Wang, Q.; Geng, C.; Lu, S.; Chen, W.; Shao, M. Emission factors of gaseous carbonaceous species from residential combustion of coal and crop residue briquettes. *Front. Environ. Sci. Eng.* 2013, *7* (1), 66–76~~. DOI:~~, 10.1007/s11783-012-0428-5.

(33) Liu, C.; Zhang, C.; Mu, Y.; Liu, J.; Zhang, Y. Emission of volatile organic compounds from domestic coal stove with the actual alternation of flaming and smoldering combustion processes. *Environ. Pollut.* 2017, *221*, 385–391~~. DOI:~~, 10.1016/j.envpol.2016.11.089.

(34) Klein, F.; Pieber, S. M.; Ni, H.; Stefenelli, G.; Bertrand, A.; Kilic, D.; Pospisilova, V.; Temime-Roussel, B.; Marchand, N.; El Haddad, I.; Slowik, J. G.; Baltensperger, U.; Cao, J.; Huang, R.-J.; Prévôt, A. S. H. Characterization of Gas-Phase Organics Using Proton Transfer Reaction Time-of-Flight Mass Spectrometry: Residential Coal Combustion. *Environ. Sci. Technol.* 2018 (*52*~~5~~), 2612–2617~~. DOI:~~, 10.1021/acs.est.7b03960.

(35) Zhang, J.; Smith, K. R. Emissions of Carbonyl Compounds from Various Cookstoves in China. *Environ. Sci. Technol.* 1999, *33* (14), 2311–2320~~. DOI~~,~~:~~ 10.1021/es9812406.

(36) Sinton, J. E.; Smith, K. R.; Peabody, J. W.; Yaping, L.; Xiliang, Z.; Edwards, R.; Quan, G. An assessment of programs to promote improved household stoves in China. *Energy Sustainable Dev.*~~*Energy for Sustainable Development*~~ 2004, *8* (3), 33–52~~.~~ ~~DOI:~~, 10.1016/S0973-0826(08)60465-2.

(37) DUH and DEC. *Residential wood burning*:*Environmental impact and sustainable solutions*. https://www.clean-heat.eu/ (accessed 2021-04-18).

(38) German Federal Association of Chimney Sweepers. *Erhebung des Schornsteinfegerhandwerks*. https://www.schornsteinfeger.de/sonderdruck-2019.pdfx?forced=true&forced=true (accessed 2021-07-10).

(39) Pechrová, M.; Kolářová, A. The efficiency of subsidies for air quality: A case study on the Moravian–Silesian region. *ER-CEREI* 2014, *17* (2), 67–74,~~. DOI:~~ 10.7327/cerei.2014.06.02.

(40) Institute of Environmental Economics. *Energy efficiency in Poland*:*2013 review*. https://europeanclimate.org/wp-content/uploads/2014/09/EnergyEfficiency-in-Poland-Review-2013.pdf (accessed 2021-07-11).

(41) Vicente, E. D.; Alves, C. A. An overview of particulate emissions from residential biomass combustion. *Atmos. Res.* 2018, *199*, 159–185~~. DOI:~~, 10.1016/j.atmosres.2017.08.027.

(42) Schnelle-Kreis, J.; Sklorz, M.; Orasche, J.; Stölzel, M.; Peters, A.; Zimmermann, R. Semi volatile organic compounds in ambient PM2.5. Seasonal trends and daily resolved source contributions. *Environ. Sci. Technol.* 2007, *41* (11), 3821–3828~~. DOI:~~, 10.1021/es060666e.

(43) Šyc, M.; Horák, J.; Hopan, F.; Krpec, K.; Tomšej, T.; Ocelka, T.; Pekárek, V. Effect of Fuels and Domestic Heating Appliance Types on Emission Factors of Selected Organic Pollutants. *Environ. Sci. Technol.* 2011, *45* (21), 9427–9434~~. DOI:~~, 10.1021/es2017945.

(44) Horak, J.; Kubonova, L.; Krpec, K.; Hopan, F.; Kubesa, P.; Motyka, O.; Laciok, V.; Dej, M.; Ochodek, T.; Placha, D. PAH emissions from old and new types of domestic hot water boilers. *Environ. Pollut.* 2017, *225*, 31–39~~. DOI:~~, 10.1016/j.envpol.2017.03.034.

(45) Czaplicka, M.; Cieślik, E.; Komosiński, B.; Rachwał, T. Emission Factors for Biofuels and Coal Combustion in a Domestic Boiler of 18 kW. *Atmosphere* 2019, *10* (12), 771~~.~~ ~~DOI:~~, 10.3390/atmos10120771.

(46) Křůmal, K.; Mikuška, P.; Horák, J.; Hopan, F.; Krpec, K. Comparison of emissions of gaseous and particulate pollutants from the combustion of biomass and coal in modern and old-type boilers used for residential heating in the Czech Republic, Central Europe. *Chemosphere* 2019, *229*, 51–59~~. DOI:~~, 10.1016/j.chemosphere.2019.04.137.

(47) Win, K. M.; Persson, T. Emissions from Residential Wood Pellet Boilers and Stove Characterized into Start-up, Steady Operation, and Stop Emissions. *Energy Fuels* 2014, *28* (4), 2496–2505~~. DOI:~~, 10.1021/ef4016894.

(48) Mitchell, E. J. S.; Lea-Langton, A. R.; Jones, J. M.; Williams, A.; Layden, P.; Johnson, R. The impact of fuel properties on the emissions from the combustion of biomass

and other solid fuels in a fixed bed domestic stove. *Fuel Process. Technol.* 2016, *142*, 115–123~~. DOI:~~, 10.1016/j.fuproc.2015.09.031.

(49) Nuutinen, K.; Jokiniemi, J.; Sippula, O.; Lamberg, H.; Sutinen, J.; Horttanainen, P.; Tissari, J. Effect of air staging on fine particle, dust and gaseous emissions from masonry heaters. *Biomass Bioenergy* 2014, *67*, 167–178~~. DOI:~~, 10.1016/j.biombioe.2014.04.033.

(50) Vassilev, S. V.; Vassileva, C. G.; Vassilev, V. S. Advantages and disadvantages of composition and properties of biomass in comparison with coal: An overview. *Fuel* 2015, *158*, 330–350~~. DOI:~~, 10.1016/j.fuel.2015.05.050.

(51) Miersch, T.; Czech, H.; Hartikainen, A.; Ihalainen, M.; Orasche, J.; Abbaszade, G.; Tissari, J.; Streibel, T.; Jokiniemi, J.; Sippula, O.; Zimmermann, R. Impact of photochemical ageing on Polycyclic Aromatic Hydrocarbons (PAH) and oxygenated PAH (Oxy-PAH/OH-PAH) in logwood stove emissions. *Sci. Total Environ.* 2019, *686*, 382–392~~. DOI:~~, 10.1016/j.scitotenv.2019.05.412.

(52) Hanley, L.; Zimmermann, R. Light and molecular ions: the emergence of vacuum UV single-photon ionization in MS. *Anal. Chem.* 2009, *81* (11), 4174–4182~~. DOI:~~, 10.1021/ac8013675.

(53) Adam, T.; Zimmermann, R. Determination of single photon ionization cross sections for quantitative analysis of complex organic mixtures. *Anal. Bioanal. Chem.* 2007, *389* (6), 1941–1951~~. DOI:~~, 10.1007/s00216-007-1571-x.

(54) Reda, A. A.; Czech, H.; Schnelle-Kreis, J.; Sippula, O.; Orasche, J.; Weggler, B.; Abbaszade, G.; Arteaga-Salas, J. M.; Kortelainen, M.; Tissari, J.; Jokiniemi, J.; Streibel, T.; Zimmermann, R. Analysis of Gas-Phase Carbonyl Compounds in Emissions from Modern Wood Combustion Appliances: Influence of Wood Type and Combustion Appliance. *Energy Fuels* 2015, *29* (6), 3897–3907~~. DOI:~~, 10.1021/ef502877c.

(55) Friebel, J.; Köpsel, R. F. W. The fate of nitrogen during pyrolysis of German low rank coals — a parameter study. *Fuel* 1999, *78* (8), 923–932~~. DOI:~~, 10.1016/S0016-2361(99)00008-3.

(56) Ozgen, S.; Cernuschi, S.; Caserini, S. An overview of nitrogen oxides emissions from biomass combustion for domestic heat production. *Renewable Sustainable Energy Rev.* 2021, *135*, 110113~~. DOI:~~, 10.1016/j.rser.2020.110113.

(57) Glarborg, P. Fuel nitrogen conversion in solid fuel fired systems. *Prog. Energy Combust. Sci.* 2003, *29* (2), 89–113~~. DOI:~~, 10.1016/S0360-1285(02)00031-X.

(58) Stubenberger, G.; Scharler, R.; Zahirović, S.; Obernberger, I. Experimental investigation of nitrogen species release from different solid biomass fuels as a basis for release models. *Fuel* 2008, *87* (6), 793–806~~. DOI:~~, 10.1016/j.fuel.2007.05.034.

(59) Kistler, M.; Schmidl, C.; Padouvas, E.; Giebl, H.; Lohninger, J.; Ellinger, R.; Bauer, H.; Puxbaum, H. Odor, gaseous and PM10 emissions from small scale combustion of wood types indigenous to Central Europe. *Atmos. Environ.* 2012, *51* (C), 86–93~~. DOI:~~, 10.1016/j.atmosenv.2012.01.044.

(60) Schmidl, C.; Luisser, M.; Padouvas, E.; Lasselsberger, L.; Rzaca, M.; Ramirez-Santa Cruz, C.; Handler, M.; Peng, G.; Bauer, H.; Puxbaum, H. Particulate and gaseous emissions from manually and automatically fired small scale combustion systems. *Atmos. Environ.* 2011, *45* (39), 7443–7454. DOI: 10.1016/j.atmosenv.2011.05.006.

(61) Mitchell, E. J. S.; Gudka, B.; Whittaker, C.; Shield, I.; Price-Allison, A.; Maxwell, D.; Jones, J. M.; Williams, A. The use of agricultural residues, wood briquettes and logs for small-scale domestic heating. *Fuel Process. Technol.* 2020, *210*, 106552~~.~~ ~~DOI~~,~~:~~ 10.1016/j.fuproc.2020.106552.

(62) Lamberg, H.; Nuutinen, K.; Tissari, J.; Ruusunen, J.; Yli-Pirilä, P.; Sippula, O.; Tapanainen, M.; Jalava, P.; Makkonen, U.; Teinilä, K.; Saarnio, K.; Hillamo, R.; Hirvonen, M.-R.; Jokiniemi, J. Physicochemical characterization of fine particles from small-scale wood combustion. *Atmos. Environ.* 2011, *45* (40), 7635–7643~~. DOI:~~, 10.1016/j.atmosenv.2011.02.072.

(63) Li, Q.; Jiang, J.; Cai, S.; Zhou, W.; Wang, S.; Duan, L.; Hao, J. Gaseous Ammonia Emissions from Coal and Biomass Combustion in Household Stoves with Different Combustion Efficiencies. *Environ. Sci. Technol. Lett.* 2016, *3* (3), 98–103~~. DOI:~~, 10.1021/acs.estlett.6b00013.

(64) Lamberg, H.; Tissari, J.; Jokiniemi, J.; Sippula, O. Fine Particle and Gaseous Emissions from a Small-Scale Boiler Fueled by Pellets of Various Raw Materials. *Energy Fuels* 2013, *27* (11), 7044–7053~~. DOI:~~, 10.1021/ef401267t.

(65) Ren, Q.; Zhao, C. Evolution of fuel-N in gas phase during biomass pyrolysis. *Renewable Sustainable Energy Rev.* 2015, *50*, 408–418~~. DOI:~~, 10.1016/j.rser.2015.05.043.

(66) Nussbaumer, T. Combustion and Co-combustion of Biomass: Fundamentals, Technologies, and Primary Measures for Emission Reduction. *Energy Fuels* 2003, *17* (6), 1510–1521~~. DOI:~~, 10.1021/ef030031q.

(67) Feldmeier, S.; Wopienka, E.; Schwarz, M.; Schön, C.; Pfeifer, C. Applicability of Fuel Indexes for Small-Scale Biomass Combustion Technologies, Part 2: TSP and NOx Emissions. *Energy Fuels* 2019, *33* (11), 11724–11730~~. DOI:~~, 10.1021/acs.energyfuels.9b02589.

(68) Ohtsuka, Y.; Mori, H.; Nonaka, K.; Watanabe, T.; Asami, K. Selective conversion of coal nitrogen to N2 with iron. *Energy Fuels* 1993, *7* (6), 1095–1096~~. DOI:~~, 10.1021/ef00042a056.

(69) Sommersacher, P.; Brunner, T.; Obernberger, I. Fuel Indexes: A Novel Method for the Evaluation of Relevant Combustion Properties of New Biomass Fuels. *Energy Fuels* 2012, *26* (1), 380–390~~. DOI~~,~~:~~ 10.1021/ef201282y.

(70) Sippula, O.; Lamberg, H.; Leskinen, J.; Tissari, J.; Jokiniemi, J. Emissions and ash behavior in a 500 kW pellet boiler operated with various blends of woody biomass and peat. *Fuel* 2017, *202*, 144–153~~. DOI:~~, 10.1016/j.fuel.2017.04.009.

(71) Bruns, E. A.; Krapf, M.; Orasche, J.; Huang, Y.; Zimmermann, R.; Drinovec, L.; Močnik, G.; El-Haddad, I.; Slowik, J. G.; Dommen, J.; Baltensperger, U.; Prévôt, A. S. H. Characterization of primary and secondary wood combustion products generated under different burner loads. *Atmos. Chem. Phys.* 2015, *15* (5), 2825–2841~~. DOI:~~, 10.5194/acp-15-2825-2015.

(72) Zhang, J.; Smith, K. R.; Ma, Y.; Ye, S.; Jiang, F.; Qi, W.; Liu, P.; Khalil, M. A. K.; Rasmussen, R. A.; Thorneloe, S. A. Greenhouse gases and other airborne pollutants from household stoves in China: a database for emission factors. *Atmos. Environ.* 2000, *34* (26), 4537–4549~~. DOI:~~, 10.1016/S1352-2310(99)00450-1.

(73) Evtyugina, M.; Alves, C.; Calvo, A.; Nunes, T.; Tarelho, L.; Duarte, M.; Prozil, S. O.; Evtuguin, D. V.; Pio, C. VOC emissions from residential combustion of Southern

and mid-European woods. *Atmos. Environ.* 2014, *83*, 90–98~~. DOI:~~, 10.1016/j.atmosenv.2013.10.050.

(74) Greenberg, J. P.; Friedli, H.; Guenther, A. B.; Hanson, D.; Harley, P.; Karl, T. Volatile organic emissions from the distillation and pyrolysis of vegetation. *Atmos. Chem. Phys.* 2006, *6* (1), 81–91~~. DOI:~~, 10.5194/acp-6-81-2006.

(75) Yokelson, R. J.; Griffith, D. W. T.; Ward, D. E. Open-path Fourier transform infrared studies of large-scale laboratory biomass fires. *J. Geophys. Res.: Atmos.*~~J. Geophys. Res~~ 1996, *101* (D15), 21067–21080~~. DOI:~~, 10.1029/96JD01800.

(76) Solomon, P. R.; Serio, M. A.; Suuberg, E. M. Coal pyrolysis: Experiments, kinetic rates and mechanisms. *Prog. Energy Combust. Sci.* 1992, *18* (2), 133–220~~. DOI:~~, 10.1016/0360-1285(92)90021-R.

(77) Collard, F.-X.; Blin, J. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. *Renewable Sustainable Energy Rev.* 2014, *38*, 594–608~~. DOI:~~, 10.1016/j.rser.2014.06.013.

(78) O'Keefe, J. M. K.; Bechtel, A.; Christanis, K.; Dai, S.; DiMichele, W. A.; Eble, C. F.; Esterle, J. S.; Mastalerz, M.; Raymond, A. L.; Valentim, B. V.; Wagner, N. J.; Ward, C. R.; Hower, J. C. On the fundamental difference between coal rank and coal type. *Int. J. Coal Geol.* 2013, *118*, 58–87~~. DOI:~~, 10.1016/j.coal.2013.08.007.

(79) Sýkorová, I.; Pickel, W.; Christanis, K.; Wolf, M.; Taylor, G. H.; Flores, D. Classification of huminite—ICCP System 1994. *Int. J. Coal Geol.* 2005, *62* (1–~~-~~2), 85–106~~. DOI:~~, 10.1016/j.coal.2004.06.006.

(80) Widera, M. Genetic classification of Polish lignite deposits: A review. *Int. J. Coal Geol.*~~International Journal of Coal Geology~~ 2016, *158*, 107–118~~. DOI:~~, 10.1016/j.coal.2016.03.004.

(81) Havelcová, M.; Sýkorová, I.; Mach, K.; Dvořák, Z. Organic Geochemistry of Fossil Resins from the Czech Republic. *Procedia Earth Planet. Sci.* 2014, *10*, 303–312~~. DOI:~~, 10.1016/j.proeps.2014.08.021.

(82) Song, Y.; Tahmasebi, A.; Yu, J. Co-pyrolysis of pine sawdust and lignite in a thermogravimetric analyzer and a fixed-bed reactor. *Bioresour. Technol.* 2014, *174*, 204–211~~. DOI:~~, Published Online: Oct. 12, 2014. 10.1016/j.biortech.2014.10.027. ~~Published Online: Oct. 12, 2014.~~

(83) Mansurov, Z. A. Soot Formation in Combustion Processes (Review). *Combust., Explos. Shock Waves* 2005, *41* (6), 727–744~~. DOI:~~, 10.1007/s10573-005-0083-2.

(84) Streibel, T.; Mühlberger, F.; Geißler, R.; Saraji-Bozorgzad, M.; Adam, T.; Zimmermann, R. Influence of sulphur addition on emissions of polycyclic aromatic hydrocarbons during biomass combustion. *Proc. Combust. Inst.* 2015, *35* (2), 1771–1777~~. DOI:~~, 10.1016/j.proci.2014.07.046.

Table 1. Fuel P~~p~~roperties and E~~e~~lemental C~~c~~omposition~~.~~

~~P~~parameter	~~U~~unit	m~~M~~ethods for ~~S~~spruce	~~S~~spruce logs	~~M~~methods for brown coal	b~~B~~rown coal briquettes

		logs		briquette	
moisture content	% (w/w)	DIN EN ISO 18134-2:2017-05	6.9	DIN 51718: 2002-06	14.4
lower heating value	MJ kg^{-1}[a]	DIN EN ISO 18125:2017-08	19.4	DIN 51900-1: 2004-02	24.0
ash content	g kg^{-1}[a]	DIN EN ISO 18122:2016-03	7	DIN 51719: 1997-07	68
carbon	g kg^{-1}[a]	DIN EN ISO 16948:2015-09	511	DIN 51732: 2014-07	635
hydrogen	g kg^{-1}[a]	DIN EN ISO 16948:2015-09	61	DIN 51732: 2014-07	48
oxygen	g kg^{-1}[a]	DIN EN ISO 16993:2016-11	420	DIN 51733: 2016-04	234
nitrogen	g kg^{-1}[a]	DIN EN ISO 16948:2015-09	1.0	DIN 51732: 2014-07	6.8
sulfur	g kg^{-1}[a]	DIN EN ISO 16994:2016-12	0.15	DIN 51724-3: 2012-07	7
chlorine	mg kg^{-1}[a]	DIN EN ISO 16994:2016-12	<50	DIN 51727: 2011-11	240
potassium	mg kg^{-1}[a]	DIN EN ISO 11885 (E22): 2009-09	0.73	DIN EN ISO 11885 (E22): 2009-09	0.34
sodium	mg kg^{-1}[a]	DIN EN ISO 11885 (E22): 2009-09	0.05	DIN EN ISO 11885 (E22): 2009-09	0.61
calcium	mg kg^{-1}[a]	DIN EN ISO 11885 (E22): 2009-09	2.73	DIN EN ISO 11885 (E22): 2009-09	13.9
silicon	mg kg^{-1}[a]	DIN EN ISO 11885 (E22): 2009-09	0.11	DIN EN ISO 11885 (E22): 2009-09	13.2

iron	mg~~-~~ kg$^{-1,a}$	DIN EN ISO 11885 (E22): 2009-09	0.028	DIN EN ISO 11885 (E22): 2009-09	13.9

[a] ~~d~~Dry basis

Table 2. EFs of I~~i~~norganic G~~g~~ases E~~e~~volving during C~~c~~ombustion (CO, NOx, SO2, NH3, HCN) A~~a~~s W~~w~~ell as T~~t~~en S~~s~~ingle VOC in M~~m~~g/MJ (D~~d~~ry B~~b~~asis)~~.~~ [a]~~EFs from both fuels were tested for statistical difference in their means by using the t-test for unequal variances (α = 0.05). Significant differences of means are indicated by a bold font style.~~

Exp.	SL1	SL2	SL3	SL4	BCB1	BCB2	BCB3	BCB4	BCB5	BCB6	$-\log_{10}(p)$
CO	1110	757	1109	1028	1236	1470	1776	1365	1354	1498	**2.3**
NO_x	40	34	32	33	41	37	44	38	45	40	**1.5**
SO_2	5	5	7	4	93	102	106	96	87	112	**5.9**
NH_3	1.16	0.60	1.11	0.70	3.04	2.78	3.92	2.60	2.93	3.18	**4.9**
HCN	1.00	0.43	0.35	0.55	4.10	1.69	2.20	1.86	3.46	1.85	**2.4**
CH_4	38	25	25	25	19	29	37	29	31	37	0.2
N-M Alk	9.5	5.5	7.1	6.7	10	12	25	18	33	35	**1.8**
Uns. Al.	29	22	19	17	28	29	43	20	31	47	1.3
Arom.	21	20	14	16	19	26	34	20	35	36	**1.8**
Alc.	2.7	2.2	2.3	1.6	2.4	1.7	2.7	0.8	1.3	3.6	0.1
Carb.	7.9	6.3	6.5	4.3	7.9	6.0	8.8	2.5	4.6	9.9	0.1
MCE	0.97	0.98	0.97	0.98	0.97	0.97	0.96	0.97	0.97	0.96	**2.1**
PRP	1.32	0.45	0.58	0.34	6.13	4.55	8.03	2.70	5.66	10.60	**2.4**
AA	2.57	0.82	0.60	0.63	4.46	3.91	5.61	2.33	2.93	9.75	**1.9**
VAC	0.23	0.16	0.17	0.12	0.19	0.08	0.20	0.03	0.06	0.23	0.4
BTD	0.45	0.16	0.17	0.11	1.35	0.78	1.45	0.34	0.91	1.94	**2.0**

BENZ	6.44	5.44	5.66	3.76	4.63	3.76	4.95	1.29	2.27	5.18	1.0
TOL	0.79	0.57	0.53	0.34	1.70	1.34	2.25	0.81	1.41	2.55	**2.2**
STYR	0.29	0.25	0.25	0.15	0.43	0.28	0.43	0.12	0.27	0.56	0.8
IND	0.06	b.d.l.	0.01	b.d.l.	0.19	0.13	0.27	0.08	0.13	0.42	**2.0**
NAP	2.27	1.81	1.92	1.34	1.54	1.15	1.76	0.53	0.77	2.18	0.8
MNAP	0.13	0.09	0.09	0.06	0.27	0.18	0.26	0.09	0.13	0.45	**1.3**

[a] EFs from both fuels were tested for statistical difference in their means by using the *t* test for unequal variances ($\alpha = 0.05$). Significant differences of means are indicated by a bold font style. Conversion factor: 1.33 MJ m^{-3} (13% O_2). Abbreviations: NO_x = NO + NO_2 as NO_2 equivalents; N-M Alk = non-methane alkanes; Uns. Aliph. = unsaturated aliphatics; Alc. = alcohols; carb. = carbonyls; PRP = propene; AA = acetaldehyde; VAC = vinyl acetylene; BTD = butadiene; BENZ = benzene; TOL = toluene; STYR = styrene; IND = indene; NAP = naphthalene; MNAP = methyl naphthalene; MCE = modified combustion efficiency; “b.d.l.” = below detection limit.

~~Conversion factor: 1.33 MJ m^{-3} (13% O_2).~~

Figure 1. Examples for emission profiles of CO_2~~2~~ (both black), CH_4~~4~~ and CO (red), and volatile organic compounds detected with ~~the~~ SPI-TOFMS ($VOC_{SPI,40-92}$,~~;~~ blue; refer to the sum of all compounds with even *m/z* from 40 to 92 as toluene equivalents) for a representative spruce log (a) and brown coal briquette experiment (b).

Figure 2. Examples of emission profiles of NO_x (black), HCN and NH_3 (red, dashed and solid lines), and SO_2 (blue) for a typical spruce experiment (a) and a typical brown coal experiment (b).

Figure 3. Determination of the time needed to ignite an individual batch of BCBs via the modified combustion efficiency (MCE) (top). Correlation of ignition times for individual batches both for spruce logs (SL) and brown coal briquettes (BCB) with overall quantities of organic emissions (as toluene equivalents) determined with the untargeted SPI-TOFMS for individual batches (bottom). The first batch of SL experiments was not taken into account.

Figure 4. 4~~-~~ h examples for average mass spectra of a spruce log experiment (a) and a brown coal briquette experiment (b). Please note that the spectra were standardized to the internal standard D3-toluene, and concentrations of individual VOCs may be obtained from their relative photoionization cross (PICS).

Figure 5. NO_x emission factors (a) and ~~the ~~release fraction of fuel-N as N in NO_x (b) as a function of the fuel-N content for this study (red) and the literature (black). The regression model was created by subjecting NO_x EFs and fuel-N from the literature to orthogonal regression.

Figure 6. Volcano plot for the comparison of EFs (energy basis) of inorganic bulk gases quantified by FTIR and ~~ten ~~10 individual VOCs quantified by SPI-TOFMS. *p*~~-~~ values were calculated with a *t*~~-~~ test for unequal variances. Different levels of significance are indicated by horizontal lines, and different fold-changes are indicated by vertical lines for better orientation. Abbreviations: N-M Alk~~-~~ =~~-~~ non-methane alkanes; UA~~-~~ =~~-~~ unsaturated aliphatics; Alc. = alcohols; carb. = carbonyls; PRP~~-~~ =~~-~~ propene; AA~~-~~ =~~-~~ acetaldehyde; VAC~~-~~ =~~-~~ vinyl acetylene; BTD~~-~~ =~~-~~ butadiene; BENZ~~-~~ =~~-~~ benzene; TOL~~-~~ =~~-~~ toluene; STYR~~-~~ =~~-~~ styrene; IND~~-~~ =~~-~~ indene; NAP~~-~~ =~~-~~ naphthalene; MNAP~~-~~ =~~-~~ methyl naphthalene.