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Particulate and gaseous emissions from manually and automatically fired small scale combustion systems

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ABSTRACT

In an extensive wood combustion source test series 2 automatically and 2 manually fired appliances, and 8 fuel types were investigated with respect to their particulate (PM10) and gaseous emissions. Softwood briquettes, beech, oak and spruce logs, wood pellets as well as further biogenic fuels: wood chips, *miscanthus* (elephant grass) pellets and *triticale* ("energy crop") pellets were tested. Gaseous emissions were measured continuously while PM10 was sampled with a dilution system and averaged over standard test cycles. Manually fired stoves exhibited highly variable emissions resulting in an uncertainty of 30% for most measured compounds, determined in a series of replicate experiments. Average PM10 emissions from manually fired appliances were around 130 mg m⁻³ (standard conditions for temperature and pressure (STP), 13%O₂, dry gas), equivalent to 90 mg MJ⁻¹. Wood pellets and chips combustion under full load operation with automatically fired appliances emit almost one order of magnitude less PM10, respectively: 12–21 mg m⁻³ (STP, 13%O₂, dry gas), or 8–14 mg MJ⁻¹.

Around 30% of total particle mass from manually fired systems account for elemental carbon and 30–40% for organic carbon, resulting in carbonaceous fraction content of around 90%. On average around 5% of PM10 emitted by manually fired stoves consisted of levoglucosan while this anhydrous sugar was below detection limit in full- and part load operation of automatically fired systems. Generally, emissions from automated systems were relatively constant for the same fuel type predominantly consisting of inorganic constituents. Emissions are mainly influenced by the mode of operation, start-up, full load or part load for a given fuel type.

Surprisingly high emissions were observed for *triticale* pellets: 184 mg m⁻³ (125 mg MJ⁻¹) PM10 and 466 mg m⁻³ (395 mg MJ⁻¹) NO_x, (under full load operation, STP, 13%O₂, dry gas), originating from high chlorine and nitrogen contents of the fuel.

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1. Introduction

Wood has long been used as a fuel for domestic heating mainly as logs and is now being increasingly used in the form of pellets and chips. It is locally available in most rural areas of mid-Europe, is a renewable source of energy, and is competitively priced relative to oil and gas. Furthermore the use of biomass for room heating is regarded " CO_2 neutral". The conversion of the chemical energy from wood into thermal energy, however, involves emissions in form of gases and particulate matter which can seriously affect public health (Chapman et al., 1997; Englert, 2004; Peden, 2005; Bari et al., 2010a). This led to legislative regulations concerning emissions from small scale combustion units (e.g. §15 agreement between Austrian government and federal states; Lasselsberger, 2003). Prior to selling all types of appliances have to be tested following European standards (EN 13240 and EN 303-5) in accredited laboratories. Emission factors of gaseous emissions, i.e. carbon monoxide (CO), nitrogen oxides (NO_x) and total hydrocarbons (C_xH_y), are limited as well as of dust emissions.

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Emissions of particulate matter such as the fraction smaller than 10 μ m aerodynamic diameter (PM10) have become a major environmental topic in the European Union in particular since the short time standard for PM10 in ambient air, of 50 μ g m⁻³ to be exceeded not more than 35 times in a year (Council Directive, 1999/30/EC) is frequently violated in most urban regions in Europe (Querol et al., 2004; Van Dingenen et al., 2004). Recent studies showed that during the winter half year wood burning is one of the major contributors of primary particles in the atmosphere over large parts of Europe (Glasius et al., 2006; Puxbaum et al., 2007; Lanz et al., 2008; Caseiro et al., 2009; Szidat et al., 2009; Yttri et al., 2009; Bari et al., 2010b). According to recent emission inventory studies small scale biomass combustion is the most important emission source of primary particulate organic material in the cold season in Europe (Schaap et al., 2004).

Source apportionment studies as well as emission inventories depend on reliable data about emission sources. There is, however, lack of information concerning the characterisation of particulate emissions from small scale biomass combustion systems in central Europe. Several studies were carried out in the United States (e.g. Rogge et al., 1998; McDonald et al., 2000; Fine et al., 2001; Schauer et al., 2001; Oros and Simoneit, 2001a and b), in Scandinavia, from where the largest number of studies were performed so far (reviewed until 2008/09 in Kocbach Bølling et al., 2009; Boman et al., 2011; Pettersson et al., 2011); in Southern Europe (Gonçalves et al., 2009). For the mid-European Alpine region results concerning chemical characterisation of fine particulate emissions (PM10) from burning typical wood types in a tiled stove were reported by Schmidl et al. (2008a).

The combustion technique as well as operational parameters like fuel load, airflow setting and fuel itself has an important influence on the amount and the composition of particle emissions (Kjällstrand and Olsson, 2004; Jordan and Seen, 2005; Johansson et al., 2004; Fine et al., 2002, 2004a and b). A systematic study of such influencing factors is hampered by the fact that burning conditions in small domestic stoves, in particular when manually fired, are highly variable. Hence the planning of the current combustion tests included a) a selection of the main types of wood combustion appliances including manually and automated fired types common in mid-Europe, b) main wood types common in mid-Europe and two "new" bio-fuel types, c) measurement cycles including the start-up phase, full load and part load conditions to give insight about potential emissions ranges under "near real life" situations, d) emissions during maloperation tests.

2. Experimental

2.1. Tested systems

Four different combustion facilities were tested: automatically fired systems A and B and manually fired systems C and D.

System A is a commercial automatically fed pellet stove with a nominal power output of 6 kW. The stove has internal pellet storage from where the fuel is supplied to the combustion chamber via an auger screw. The fuel bed is situated in a pot with holes which allow combustion air to enter. The air supply is controlled by a fan situated in the flue gas stream in order to adapt the airflow to the selected thermal output and the fuel load respectively. Both fuel load and fan speed are controlled automatically, only the percentage of power output (30-100%) is set by the user. System A was provided directly by the manufacturer.

System B is a biomass boiler with a power output of about 40 kW, and considerably larger than system A. System B can be

operated with any kind of wood, bark, *miscanthus* or *triticale*, either in form of pellets, chips or grain. In system B the fuel is supplied from the separate fuel tank to the combustion chamber via an auger screw. The fire bed is situated on a moving grate that slowly transfers the fuel ash to an ash tray. Combustion air enters through the grate and through holes in the wall of the chamber. Airflow is controlled automatically by a fan situated at the end of the flue gas stream behind the heat exchanger where the hot exhaust gases transfer their thermal energy to water. System B was also provided directly by the manufacturer.

System C is a relatively simple "chimney type" logwood stove for manual operation with a nominal power output of 6.5 kW. For reaching the nominal output 1.5 kg of wood (2–3 logs) are burnt in every fuel load. Combustion air enters through a grate in the bottom of the burning chamber. The volume of the burning chamber is approximately 24 L ($30 \times 28 \times 28$ cm). The exhaust gases are redirected once prior to entering the chimney. Airflow can be adjusted manually by a simple slide valve. System C was obtained from a local hardware store.

System D is a more sophisticated "chimney type" logwood stove for manual operation with a nominal power output of 6 kW. Combustion air enters the burning chamber (volume 17.5 L, $28 \times 25 \times 25$ cm) through a grate in the bottom (primary air) and a slit in the back wall (secondary air). For full load operation 2–3 wood logs with 1.3 kg in total are burnt per load. Exhaust gases are redirected 2 times prior to entering the chimney. Airflow is controlled manually via a rotary knob connected to a valve system that adjusts both primary and secondary combustion airflow. System D was provided by the manufacturing company. The chimney stoves are iron stoves with chamotte lining.

2.2. Tested fuel types

Table 1 presents elemental composition, water content and lower heating value of all tested fuels. Wood pellets used for automatically fired systems A and B were complying with Austrian ÖNORM M7135 (2000) and German DIN 51731 Plus (2007) standards. Wood pellets and wood chips are mostly made from softwood, e.g. spruce, which is indicated by the low ash values (Table 1). Beside the two main fuels (wood pellets and wood chips) for automatically fired biomass combustion systems also the relatively new bio-fuels "energy-corn" (triticale pellets) and "elephantgrass" (miscanthus pellets) were tested. Triticale plants are hybrids of wheat (Triticum) andrye (Secale) and originally used as forage crops in Europe. Miscanthus is an Asian giant reed with the botanic name Miscanthus giganteus, a natural hybrid from Miscanthus chinensis and Miscanthus sacchiflorus. The wood types chosen for logwood experiments represent most common wood types in Austria and other mid-European Alpine regions. Spruce (Picea abies) respectively briquettes (usually made of spruce) constitute 66% of timber (78% of total softwood) felled in Austria. Beech (Fagus sylvatica) is the most common hardwood with 6.7% (56.5% of total hardwood) in Austria and together with oak (Quercus robur, 2.0% of total, 16.5% of hardwood) the tested wood types cover around 75% of timber felled in Austria (Austrian Federal Forest Office, 2006). Beech is also standard fuel for test procedures for logwood (EN 13240, 2001/2003). The moisture contents of the raw fuels (Table 1) are relatively low and close to the "equilibrium moisture" (Simpson and TenWolde, 1999), which is typically around 9.2–9.5% (dry weight) for 50% r.h. and a temperature range of 0–20 °C. Logwood in mid-Europe is often seasoned over 2 seasons in a split mode ready for use. Thus, moisture contents of log wood used in our study is likely on the lower end of "typical" use in Europe, but seemingly a frequent case for mid-Europe.

	C	н	N	s	0	Δ	14/	THM	$f_{\rm J} ({\rm mg}~{\rm Nm}^{-3}{ m ->}{ m mg}~{\rm MJ}^{-1})$	
	<u> </u>	п	IN	3	0	Λ	vv			
	% w w ⁻¹ d.b.						% w w ⁻¹ w.b.	kJ kg ⁻¹ d.b.	dry	wet
Wood pellets	50	6.3	0.12	0.01	43	0.26	7.6	18,676	0.65	0.76
Beech logs	50	6.1	0.41	0.02	42	1.71	6.5	18,098	0.68	0.79
Briquettes	51	5.5	0.12	0.01	43	0.28	7.7	19,081	0.63	0.73
Oak logs	48	5.4	0.35	0.01	44	1.65	9.7	18,973	0.59	0.69
Spruce logs	51	5.6	0.12	0.01	43	0.28	8.5	19,239	0.62	0.73
Wood chips	47	6.2	NA	< 0.01	47	0.44	34	17,868	0.63	0.83
Miscanthus pellets	44	6.0	NA	< 0.01	46	3.64	8.4	16,856	0.61	0.73
Triticale pellets	42	6.6	NA	0.19	46	4.85	8.6	18,505	0.55	0.67

Table 1
Elemental composition (C, H, N, S, O) and ash (A) from dry fuels; water content (W) and lower heating value (LHW) of tested fuel types

List of abbreviations: C...carbon, H...hydrogen, N...nitrogen, S...sulphur, O...oxygen, A...ash, W...water content, LHV... lower heating value, f_1 ... conversion factor from mg Nm⁻³ (13%O₂) to mg MJ⁻¹ for dry (CO, NO_x, PM10) and wet (C_xH_y) measured emissions, % w w⁻¹...mass percent; d.b... dry basis, w.b. wet basis.

2.3. Testing procedure

The testing procedure for automatically fired systems was performed in general following the European standard (EN 303-5, 1999). However, in addition to the standard testing procedure we also conducted measurements during the system start-up phase. Fine particulate matter and gas measurements were conducted in parallel during all experiments. Each experiment was divided into start-up, part load and full load periods. The gas data were logged continually (time resolution: 10 s) whereas the collection system for fine particulate matter operated in intervals between 60 and 120 min during each of the three operation modes.

For manually fired systems testing procedure followed in far the European standard EN 13240 however with the difference that the start-up phase of the burn was included. While in the EN standard the test starts with loading the fuel on an existing fire bed, samples were taken starting from the ignition of the fuel in this test series. Furthermore in our measurements three fuel loads were included which is not the case in the standard where only one load is tested. The general handling of the stoves, mainly concerning the amount of fuel and the airflow settings, followed the instructions in the user manuals provided by the manufacturers. For the logwood stoves additional tests were performed where the influence of possible maloperations on the emissions was investigated. Main parameters that can be influenced by the user investigated in this study were the airflow setting and the amount of fuel burnt per load. Burn rates for full load were around 1.3 kg h^{-1} for system A, 8.5 kg h^{-1} for system B, 2 kg h^{-1} for system C and 1.8 kg h^{-1} for system D.

The changes of the standard testing protocols and additional measurements with maloperations were within the general aim of this work. The tests were aimed to get an overview about the possible ranges of emissions from small scale combustion units at near "real life" operation conditions. Possible maloperations for the logwood stoves included "low air" (lowest setting to maintain combustion) and "high fuel" (fuel loading three times the nominal load).

We want to note, that all tests were performed by skilled personnel and standardised chimney-conditions (with a static pressure of 12 Pa). Thus, in real world conditions rather higher emissions will take place from kindling with twigs and other garden waste material, from the actual fuel wood conditions, as well as from variable meteorological conditions and different "chimney-properties" acting in a different way on the airflow than at the test conditions.

2.3.1. Exhaust gas measurement

Gaseous components i.e. oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x) and gas phase organics (C_xH_y) were determined continuously during all tests. All measurements of exhaust gases were conducted at accredited

emission test laboratories. Automatically fired systems were tested at the Federal Institute of Agricultural Engineering, Wieselburg (Lower Austria, Austria). Tests with manually fired systems were performed at the Institute of Chemical Engineering, Vienna University of Technology (Vienna, Austria).

2.3.2. Particle sampling

The design of the sampling equipment used for collection of particles is based on dilution sampling systems similar to reported systems from previous studies (Hildemann et al., 1991; Schauer et al., 1999; Sippula et al., 2007).

Fig. 1 gives a detailed drawing of the sampling equipment used for all tests in this study. The sampling probe is equipped with a thermocouple to measure flue gas temperature. Part of the gas stream is extracted and diluted with pre-cleaned dilution air immediately after leaving the hot chimney. Dilution air is taken from outside the building to simulate ambient dilution conditions. Air volume is measured with a dry gas meter. Pre-treatment of dilution air includes drying with activated silica, cleaning with activated carbon and two particle separation steps: one with a homemade particle filter consisting of compressed glass wool and a second with a high efficiency particulate-free air (HEPA) capsule (Pall Life Sciences). The flow is controlled with a mass flow controller (MFC) from Vögtlin Instruments (Red-y Smart Series). Thus, the dilution ratio can be adjusted over a wide range to different exhaust gas particle concentrations and sampling times.

The diluted gas enters the dilution tunnel where the diameter increases and exhaust gas and dilution air are mixed effectively through turbulence. At the entrance of the dilution tunnel the temperature is measured again. With the dilution factors of 1:10 to 1:15 the temperature of the sampling gas at this stage was only a few degrees Celsius higher than ambient temperature. The dimensions of the dilution tunnel are 1 m in length and 0.2 m in width resulting in an average residence time of 50 s at a flow rate of 2.3 m³ h⁻¹. This allows the gas to cool down to ambient temperatures and organic compounds to condense. The aerosol particles are then sampled after a size separation step on filters at near ambient dilution conditions.

The size separation step is performed with a commercial low volume sampling head (Digitel AG, Switzerland) working on a onestage impactor principle with a separation efficiency of 50% for particles with 10 μ m aerodynamic diameter at a flow of 2.3 m³ h⁻¹. The following manifold allows 8 aluminium filter holders (Pall Life Sciences) to be connected. A further thermocouple determines the temperature inside the manifold, to ensure that the collection of particles is carried out at near ambient conditions.

The 8 filter holders are equipped with 6 quartz fibre filters (Tissuquartz, Pall Life Sciences) for organic and ion analysis and 2 mixed cellulose ester filters (GN-4 Metricel, Pall Life Sciences) for metal analysis. The sample flow through quartz fibre filters was

set to 0.33 m³ h⁻¹ (5.48 L min⁻¹) per filter and therefore was double as high as through cellulose filters with a flow of 0.165 m³ h⁻¹ (2.74 L min⁻¹) per filter. This was necessary because of the high pressure drop of cellulose filters and the resulting lower maximum loads. The flows through both sampling lines

were regulated with MFCs (Bronkhorst) after drying the sampling gas with activated silica to refer the sampled volume to dry conditions. HEPA capsules were used to protect MFCs from any contamination. Finally sampled gas volumes were measured with terminal dry gas meters.



Fig. 1. Scheme of sampling equipment.

2.4. Analytical methods

2.4.1. Weighing and sample preparation

Gravimetric analysis was performed with a microbalance (Sartorius M5P with range up to 1 g reading to \pm 0.5 μg) after 48 h equilibration in an air-conditioned room (20 \pm 1 °C, 50 \pm 5% relative humidity). For analysis of ions and carbon species, small discs with 8 or 10 mm diameter were punched out of the quartz tissue filters with steel punches. For the determination of metals and trace elements first by XRF and then by ICP, whole cellulose filters were used.

2.4.2. Anhydrous sugars

The determination of levoglucosan and other anhydrosugars including mannosan and galactosan was carried out by high performance liquid chromatography (HPLC) with electrochemical detection (ED40, Dionex). Compounds were separated on a Carbo-Pac PA10 column using gradient elution with 1 mL min⁻¹ dilute sodium hydroxide, starting at 30 mM sodium hydroxide (88% Milli-Q water and 12% of 250 mM NaOH by volume) increasing to 40 mM. For the amperometric detection a gold working electrode was used. The analytical system was cleaned by rinsing with 250 mM NaOH for 5 min after every sample (Caseiro et al., 2007).

2.4.3. Anions

Anions (Cl⁻, NO₃⁻, SO₄²⁻) were eluted from quartz tissue filters with high purity water (Millipore Milli-Q Plus 185). After sonication and centrifugation, the extract was analysed on an AS17A anion-exchange column, with an ASRS Ultra II auto-regenerating suppressor, and a model CD20 conductivity cell detector (all system parts from Dionex).

2.4.4. Cations

Cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) were eluted from the filters by extracting with the chromatography eluent, 0.1% v v⁻¹ methane sulphonic acid. After sonication and centrifugation, the extract was analysed on a Dionex QIC ion chromatograph with a CS12A cationexchange column, and a conductivity detector.

2.4.5. Carbon

TC – total carbon, was determined by combustion of all material on the filter, in oxygen, at 1000 °C and measurement of the resulting CO₂ by non-dispersive IR photometry (NDIR, Maihak). The method is described in Jankowski et al. (2008).

EC – *elemental carbon*, was determined in the same apparatus on material previously heated in oxygen at 340 °C to burn off the organic matter (Cachier et al., 1989). Additionally samples were analysed with a modified thermal-optical transmission, linear temperature program (TLT) method (Method no.9b in Schmid et al., 2001; apparatus described in Jankowski et al., 2008). Fig. 4 gives an example for results obtained from TLT analysis.

CC – *carbonate carbon*, was determined by the TLT—method as the last peak evolving from the decarboxylation of carbonates at temperatures higher than 550 °C.

OC – organic carbon, was calculated as the difference TC – (EC + CC).

2.4.6. Metals and trace elements

Cellulose acetate filters have been analysed by a Philips X'Unique II (model 1480) wavelength-dispersive X-ray fluorescence spectrometer for Al, P and Si. The system was equipped with a rhodium x-ray tube, operated at 50 kV and 40 mA. The XRF measurement method was optimised using aerosol-generated filter standards which were prepared in our laboratory. For quality control the certified reference material NIST 2709 has been used.



Fig. 2. On-line emission concentrations of CO₂, NO_x, CO and C_xH_y during a standard test with manually fired system D.

After XRF—analysis cellulose acetate filters were digested in *aqua regia* with addition of hydrofluoric acid, under pressure in sealed Teflon vessels in a microwave oven. The bulk of the acid was then removed by boiling off (from the open vessels), and the final solution was prepared in dilute hydrochloric acid ($2\% v v^{-1}$). The sample digests were analysed by atomic spectroscopy—inductively coupled plasma optical emission spectroscopy for Ba, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Sn, Sr, Ti, V and Zn and for As and Sb with electro-thermal atomic absorption, respectively (Handler et al., 2008).

3. Results and discussion

All results are calculated for standard conditions STP (273 K, 1013 hPa). Unless specified otherwise the emission values are normalised to volumetric oxygen content (O_2 ref) of 13% in the exhaust gas. This procedure is performed to account for varying dilution factors due to differences in process control of the systems. The conversion was calculated using Eq. (1), where c_s is the concentration of the compound in mg m⁻³ (normalised to STP and 13%O₂, dry gas); v_s is the determined volume mixing ratio of compound *s* in ppm (in dry gas) and ρ_s is the density of the measured gas at STP; O_{2 ref} is the reference oxygen concentration (here 13%), O_{2 meas} is the averaged actual oxygen concentration during the measurements.

$$c_{\rm s} = \rho_{\rm s} \cdot \nu_{\rm s} \left(21 - O_{2 \, \rm ref} \right) / (21 - O_{2 \, \rm meas}) \tag{1}$$



Fig. 3. On-line emission concentrations of CO_2 , NO_x and C_xH_y from system B running with wood pellets under full load operation.

Where s is one of the parameters CO, NO_x or C_xH_y and their respective densities are 1.25 kg m⁻³, 2.05 kg m⁻³ and 1.64 kg m⁻³ (defined in EN 303-5). Similar to gaseous compounds also particle emission values were corrected to 13% of oxygen in the exhaust gas and calculated for standard conditions. Concentrations of CO, NO_x and PM10 were calculated in this way and are given as concentrations in mg m⁻³ (STP, 13%O₂, dry gas), C_xH_y concentrations are given for wet gas (STP, 13%O₂). The results can be converted into mg MJ⁻¹ by the corresponding factor f_J (in Table 1) according to Eq. (2).

$$\left[\mathrm{mg}\,\mathrm{MJ}^{-1}\right] = \left[\mathrm{mg}\,\mathrm{m}^{-3}\mathrm{STP},\,13\%\mathrm{O}_{2}\right]^{*}f_{\mathrm{J}} \tag{2}$$

3.1. Gaseous emissions

Gaseous emission concentrations of 45 emission tests are summarised in Table 2. Results from repeated measurements with same system and same fuel type were averaged. The number of single tests used for averaging is also given in the Table 2. Generally, gaseous emissions from manually fired systems are highly variable as shown in Fig. 2, while automatically fired systems exhibit relatively constant emissions as shown in Fig. 3. Therefore, a higher number of tests with manually fired stoves were performed to reduce uncertainty of calculated averages.

The major difference, more than one order of magnitude, between automatically fired systems A and B and manually fired systems C and D was observed for CO. Especially under full load conditions automatically fired systems exhibit very low CO emissions, consistently less than 100 mg m⁻³, indicating almost ideal combustion conditions. Under part load and in particular in start-



Fig. 4. Results from TLT analysis from different operation modes of automatically fired system B.

up phases CO emissions increase substantially reaching up to 1000 mg m⁻³ for wood chips and *triticale* pellets. As operating conditions depend on different parameters like the existence and size of a hot water tank or heat demand of the household, estimates of regional emission factors require additional operational information to the statistical data such as stove/boiler type, power, load conditions, fuel, and for boilers the presence and capacity of the storage tank.

Manually fired systems generally emit higher amounts of CO, typically in the range of 1000–3000 mg m⁻³ on average during a standard test. Similar CO emissions were observed for the corresponding wood types tested in systems C and D indicating that wood type, i.e. structure, elemental composition, water and ash content, has a higher influence on CO emissions and combustion efficiency respectively than the stove model (within a group of similar stoves).

Similar results as for CO, though in a lower concentration range, were found for gas phase hydrocarbons (C_xH_y) . Automatically fired systems running in full load operation emitted hardly any detectable gas phase organics. Substantially higher emissions were found in part load and start-up phases. Manually fired systems exhibited much higher emissions of C_xH_y typically one to two orders of magnitude higher than automatically fired systems for wood respectively standard wood pellets.

Nitrogen oxides (NO_x) emissions showed a dependence of the nitrogen content in the fuel. Therefore highest values were found for *triticale* and *miscanthus* pellets which have typically higher nitrogen contents compared to wood biomass (Hartmann et al., 2000).

The comparison of emissions between manually fired systems and automatically fired systems bears an intrinsic difficulty. Tests with manually fired stoves include the start-up phase and two

Fable 2
Average gaseous and particulate emissions (concentrations normalised to STP, 13%O ₂); and chemical composition (%) of emitted particles PM10

System	Fuel	TID	п	02	η	CO	NO _x	C _x H _y	PM10	EC	OC	Ions	TE
				[%]		$[mg m^{-3, 13\%0}_2]$			[% of PM10]				
System A	WP	SU	1	12.0	94 ^a	178	125	17.1	13.0	15.8	22.0	29.3	2.01
		FL	1	10.4		51	128	4.1	12.1	13.7	5.3	50.5	3.27
		PL	1	15.3		751	121	24.3	4.6	13.8	4.7	50.1	1.86
System B	WC	SU	1	11.1	88 ^a	1046	93	28.3	44.2	23.2	20.7	22.9	1.67
		FL	1	8.4		52	145	1.5	20.9	0.5	4.3	61.4	4.01
		PL	1	11.2		325	124	5.9	28.1	32.8	2.1	32.5	2.17
	TP	SU	1	10.7	90 ^a	1020	345	11.0	205.1	17.5	10.6	63.2	0.55
		FL	1	9.3		78	466	0.6	183.8	0.5	9.8	77.5	1.96
		PL	1	11.2		388	454	3.3	236.5	16.6	10.3	57.3	0.86
	MP	SU	1	11.0	94 ^a	489	183	20.1	35.8	45.2	22.3	5.9	0.04
		FL	1	8.4		5	287	0.5	12.5	1.0	1.5	45.6	< 0.01
		PL	1	9.5		43	225	1.3	24.1	42.9	20.9	11.8	< 0.01
	WP	SU	1	11.2	84 ^a	491	118	17.9	52.0	24.6	38.2	8.2	0.67
		FL	1	8.9		7	115	0.4	16.9	0.2	2.0	68.9	2.38
		PL	1	10.7		72	97	1.3	32.0	54.8	7.4	19.5	1.47
System C	BR	Std	3	15.1	73	1331	176	177.3	150.9	36.7	34.9	1.21	0.21
	BE	Std	6	14.0	73	2779	155	304.5	111.4	31.6	38.8	4.30	0.12
	OA	Std	2	15.4	73	2948	166	223.5	107.3	24.2	26.8	5.30	0.17
	SP	Std	6	14.7	75	2240	96	209.3	156.6	28.7	35.7	1.34	0.25
	SP	LA	1	17.8	56	3971	70	1217	488.7	16.8	51.6	1.37	0.16
	SP	HF	1	15.5	63	2370	60	544	178.1	40.3	35.1	1.66	0.02
System D	BR	Std	2	14.8	70	1491	151	35.5	115.5	37.6	33.1	1.30	0.44
	BE	Std	3	12.9	74	2472	156	151.0	131.3	37.0	35.6	4.49	0.30
	OA	Std	2	14.8	76	3074	163	123.5	121.8	29.8	22.2	6.10	0.20
	SP	Std	6	14.6	68	2161	87	124.2	128.3	32.9	28.3	1.95	0.28
	SP	LA	1	14.8	73	2841	86	312	146.7	7.3	42.79	0.74	0.26
	SP	HF	1	12.6	75	1989	80	118	78.9	41.7	15.76	1.75	3.07

List of abbreviations: TID...test identification, η ...efficiency, TE...trace elements, WP...wood pellets, WC...wood chips, TP...*triticale* pellets, MP...*miscanthus* pellets, BR...briquettes, BE...beech, OA...oak, SP...spruce, SU...start-up phase, FL...full load, PL...part load, Std...standard test, LA...low air, HF...high fuel.

^a Average efficiencies for start-up phase, full load and part load operation.

additional fuel loadings, which is close to realistic conditions. Emissions from automatically fired systems are for different operation modes separately determined. For deriving the emissions in near "real life" situations assumptions about the typical proportions of start-up, part load and full load operation have to be made. These proportions, however, depend on different parameters like existence and dimensions of hot water tank or the heat consumption of the household in relation to the nominal power output of the system. If there is no statistical information on this topic, an estimation of typical emissions for automatically fired systems bears considerable uncertainties.

3.2. Particulate emissions

The chemical composition of particulate emissions (PM10) is summarized in groups of compounds expressed as fractions of total mass. The parameters elemental carbon (EC), organic carbon (OC), sum of ions and sum of trace elements are given in Table 2. Sum of ions includes the cations potassium (K⁺), calcium (Ca²⁺), magnesium (Mg²⁺) and ammonium (NH₄⁺) and the anions chloride (Cl⁻), nitrate (NO₃⁻) and sulphate (SO₄²⁻). Aluminium, antimony, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, phosphorus, silicon, strontium, tin, titanium, vanadium and zinc form the sum of metals and trace elements. In the further text the sum of these components is referred as trace elements. The difference to 100% (around 30%) is accounting for hetero atoms and moisture.

Generally, high inorganic fractions coming along with low total carbon (TC) levels refer to high grades of combustion and usually lower particulate emissions. The best correlation between a gas compound and PM10 was found for gas phase organics (C_xH_y). The Pearson correlation-coefficient for all standard measurements without *triticale* tests (n = 42) is 0.8. Tests with *triticale* were defined as outliers and are therefore not included in the correlation

analysis because of their absolutely different behaviour concerning particulate matter emissions.

Organic and elemental carbon are the most important parameters for characterising combustion aerosols. Fig. 4 shows results from the thermo-optical temperature gradient carbon analysis (TLT), so called thermograms, from wood pellet combustion PM10 samples of system B obtained for different combustion phases. Signals between 50 and 350 °C can be assigned to organic compounds, while the very pronounced peaks at 400-500 °C arise from oxidation of EC. Carbonates have higher thermal stability so that signals from this carbon fraction would occur above 550 °C. In the example thermograms no carbonate carbon signals were observed. Different combustion phases exhibit different carbon patterns (Fig. 4). In the start-up phase the EC signal is very pronounced, additionally a small peak from organic carbon fraction is found at 150 °C. During part load phase hardly any organic compounds are evolving, also the amount of EC is reduced. The small temperature - shift of the EC signal can be explained by the different thickness of particle layers, which influence the accessibility of oxygen and therefore oxidation temperatures. The thermogram of full load samples of system B does not show any carbon signals; hence emissions during this stage are almost completely inorganic.

Table 2 presents average results from carbon analysis with the TLT method. The trend of higher emissions of carbon fractions during start-up and part-load phase as shown in Fig. 4 for wood pellets was observed for all fuels in both automatically fired systems.

3.2.1. Manually fired systems

Both manually fired systems exhibited quite similar absolute particle emissions with a similar chemical composition of particulate matter for all four tested wood types. Around 30% of total PM10 was accounted for soot; 30–40% for organic carbon (respectively 50–60% of organic material if a conversion factor OM/

OC of 1.5 is applied according to Schmidl et al. (2008b)), and only a few percent (1.5–7.4) of PM10 consisted of ions. Trace elements in fact were found to be very low lying in the range of 0.13–0.51%. The small difference in the average particle emission concentrations, 134 mg m⁻³ for system C and 126 mg m⁻¹³ for system D, is not significant. Concerning the chemical composition of emitted particles the results indicate that not stove type, but wood type has a higher influence. As displayed in Fig. 5 relative compositions of emitted PM show more similarities between same wood types burned in different systems than between different wood types burned in the same system. Thus the inter-stove correlation for same wood types is higher than the intra-stove correlation for different wood types. These results are also confirmed by CO measurements (see chapter 3.1). This conclusion is likely only valid for stoves of the same type and similar design.

3.2.2. Automatically fired systems

Fig. 6 gives an overview of the chemical composition of particles emitted by systems A and B operating under different load conditions and with different fuels. All values are given as absolute emission concentrations in mg m⁻³. Due to their high emissions $(184-237 \text{ mg m}^{-3})$ the results for all three tests with system B firing *triticale* pellets (TP) are shown on a reduced scale (1:4). Chemical composition of particle emissions from automatically fired systems generally exhibit higher inorganic fractions (i.e. ions) due to higher grade of combustion. Under full load operation hardly any carbonaceous compounds, neither EC nor OC, are emitted. In part load operation and in the start-up phase EC and OC become more important forming at least half of total PM10 emissions (except for TP). Higher absolute amounts of ions, mainly potassium, sulphate and chloride, emitted during full load operation can be attributed to the higher temperatures in the combustion chamber



Fig. 5. Absolute and relative emission concentrations from manually fired systems C and D.



Fig. 6. Particulate emissions from automatically fired systems A and B for different load conditions: start-up (A), part load (B) and full load (C). List of abbreviations: WP...wood pellets, WC...wood chips, TP...*triticale* pellets, MP...*miscanthus* pellets.

and the resulting higher volatility of inorganic compounds. Boman et al. (2011) showed, that main compounds observed in the emissions from pellet combustion are K_2SO_4 , K_3NaSO_4 and KCl. The big difference in absolute amount and relative composition of emissions between *triticale* pellets and all other tested fuels can mainly be ascribed to its high ions emission values. The reason for this may be found in the elemental composition of this fuel. The ash content of 4.8% is much higher than that of the other fuels and the chlorine content, which is mainly responsible for the high KCl—emission concentrations, was found to be 0.23% of dry mass of the fuel. All other fuels had less than 0.02% of chlorine. High levels of chlorine for *triticale* pellets were also observed by Launhardt et al. (2000).

3.3. Anhydrous sugars

Anhydrous sugars, in particular levoglucosan, decomposition products from incomplete combustion of cellulose and hemicelluloses have been described previously as unique trace components for biomass combustion (e.g. Simoneit et al., 1999 and Jordan et al., 2006). Macro-tracer concepts use conversion factors to calculate the wood smoke contribution to PM10 from ambient levoglucosan concentrations (Schmidl et al., 2008a). We therefore analysed levoglucosan and mannosan in all wood combustion samples to investigate the influence of system and wood type on anhydrous sugars emissions. Results are summarised in Table 3.

Automatically fired systems A and B did not emit detectable amounts of anhydrous sugars in full- and part-load operation, however during start-up phase levoglucosan and mannosan were detected. Therefore levoglucosan is no suitable tracer for the automated fired wood combustion techniques. An inorganic compound like potassium could serve as tracer compound for particulate emissions from automatically fired appliances instead. In case of manually fired systems anhydrous sugars have been detected in all samples. Similar as for gaseous emissions and particulate matter composition, emissions of anhydrous sugars show a better agreement in the emissions for same wood types than for same stove types. Generally, levoglucosan levels were rather variable reaching from 1 to 9% (of PM10) or 0.03-0.37 expressed as levoglucosan fraction of organic carbon. The average fraction of levoglucosan in PM10 emissions from all standard tests with systems C and D was around 5% resulting in a conversion factor of 20 for conversion of levoglucosan to total PM10. Also the results of the sugar analysis suggest a differentiation of source profiles from automatically and manually fired systems for source apportionment.

The ratio of levoglucosan/mannosan has been recently described by Schmidl et al. (2008a) to be wood type specific, with low ratios of around 3 for softwoods and higher values of around 15 for Austrian hardwoods. As displayed in Table 3 results from this study confirm these findings. Levoglucosan/mannosan ratios for beech and oak wood combustion in systems C and D were around 14 for beech and 17 for oak compared to spruce with 3.5 and briquettes with 2.5 and therefore are in good agreement with ratios found for mid-European wood types burnt in a tiled stove by

Table 3

Levoglucosan and mannosan concentrations as well as levoglucosan/organic carbon and levoglucosan/mannosan ratios of wood combustion samples.

System	Fuel	TID	п	Levoglucosan	Mannosan	Lev/OC	Lev/Man
				[% of PM10]			
System A	WP	SU	1	3.95	1.39	0.18	2.85
		FL	1	<lod< td=""><td><lod< td=""><td>-</td><td>-</td></lod<></td></lod<>	<lod< td=""><td>-</td><td>-</td></lod<>	-	-
		PL	1	<lod< td=""><td><lod< td=""><td>-</td><td>_</td></lod<></td></lod<>	<lod< td=""><td>-</td><td>_</td></lod<>	-	_
System B	WC	SU	1	5.02	2.99	0.24	1.68
		FL	1	<lod< td=""><td><lod< td=""><td>-</td><td>-</td></lod<></td></lod<>	<lod< td=""><td>-</td><td>-</td></lod<>	-	-
		PL	1	<lod< td=""><td><lod< td=""><td>-</td><td>-</td></lod<></td></lod<>	<lod< td=""><td>-</td><td>-</td></lod<>	-	-
	TP	SU	1	0.24	0.01	0.02	18.24
		FL	1	<lod< td=""><td><lod< td=""><td>-</td><td>-</td></lod<></td></lod<>	<lod< td=""><td>-</td><td>-</td></lod<>	-	-
		PL	1	<lod< td=""><td><lod< td=""><td>-</td><td>-</td></lod<></td></lod<>	<lod< td=""><td>-</td><td>-</td></lod<>	-	-
	MP	SU	1	0.35	0.02	0.02	16.43
		FL	1	<lod< td=""><td><lod< td=""><td>-</td><td>-</td></lod<></td></lod<>	<lod< td=""><td>-</td><td>-</td></lod<>	-	-
		PL	1	<lod< td=""><td><lod< td=""><td>-</td><td>-</td></lod<></td></lod<>	<lod< td=""><td>-</td><td>-</td></lod<>	-	-
	WP	SU	1	0.83	0.37	0.02	2.25
		FL	1	<lod< td=""><td><lod< td=""><td>-</td><td>-</td></lod<></td></lod<>	<lod< td=""><td>-</td><td>-</td></lod<>	-	-
		PL	1	<lod< td=""><td><lod< td=""><td>-</td><td>_</td></lod<></td></lod<>	<lod< td=""><td>-</td><td>_</td></lod<>	-	_
System C	BR	Std	3	2.89	1.34	0.08	2.23
	BE	Std	6	2.61	0.19	0.07	13.6
	OA	Std	2	7.67	0.59	0.29	14.3
	SP	Std	6	6.29	2.14	0.18	3.11
System D	BR	Std	2	2.05	0.67	0.06	2.73
	BE	Std	3	1.08	0.08	0.03	14.1
	OA	Std	2	8.73	0.37	0.39	22.0
	SP	Std	6	4.86	1.42	0.17	3.75

List of abbreviations: TID...test identification, WP...wood pellets, WC...wood chips, TP...*triticale* pellets, MP...*miscanthus* pellets, BR...briquettes, BE...beech, OA...oak, SP...spruce, SU...start-up phase, FL...full load, PL...part load, Std...standard test.

Schmidl et al. (2008a) and also for Mediterranean wood types. Gonçalves et al. (2010) report levoglucosan/mannosan ratios of 3 for the maritime pine (softwood) and ratios of 11, 25 and 34 for the Mediterranean hardwood species golden wattle, cork oak and eucalyptus, respectively. In the start-up phases of automatically fired systems A and B the levoglucosan/mannosan ratios were consistent with the fuel types as well: Low values for wood pellets (2.3–2.9) and wood chips (1.7) of spruce wood and high values for *miscanthus* (16) and *triticale* (18) pellets which behave similar to typical Austrian hardwood types with respect to the levoglucosan/ mannosan ratios for conifer wood the result of Bari et al. (2009) for pine remains unexplained.

3.4. Maloperation tests

In addition to standard measurements a number of maloperation tests were performed, to investigate a further potential "user derived" influence on emissions. While operating errors are not really relevant for automatically fired systems—here the user influence on the system performance is indeed very small—manually fired systems offer some options of maloperation. Beside fuel type the main parameters which can be influenced by a user are the amount of fuel and the airflow setting. Hence these two parameters were varied during the series of maloperation tests. In the "low air" experiments the airflow was set to a minimum level, so that there was still flaming combustion and the fire did not extinguish. For the "high fuel" tests the combustion chamber was loaded with the total amount of fuel, which usually is burnt in three loads, at one time.

Results of the measurements showed that user habits have a major influence on emissions from manually fired systems. As displayed in Fig. 7 total particle emissions ranged from 79 to 489 mg m^{-3} , in other words the influence of the user on particulate emissions from small scale logwood stoves may influence PM10 emissions up to a factor of 6. Likewise composition of particle emissions differs considerably. By reduction of airflow, for instance, organic carbon levels in particulate emissions increase, induced by an undersupply with oxygen and resulting incomplete combustion. An interesting observation was made for the "high fuel" maloperation in system D: total PM10 emissions were lower than in the standard test. Generally, system D seems to be less sensitive to maloperation than system C. Nevertheless the importance of detailed, high quality user information and instruction about the optimum operation of the stove becomes clear from the results of the maloperation tests.



Fig. 7. Comparison of standard test and maloperation PM10 composition of manually fired systems C and D.

3.5. Uncertainties

For automatically fired systems uncertainties of results are relatively small, namely for samples that are taken during steady state conditions at full load and part load when emission concentrations are rather constant. For those cases we assume that main sources of uncertainties are in a similar number from the testing procedure and from analysis. The uncertainty for analysis is considered in a 2-5% relative range for mass determination as well as most analytical techniques for the main constituents. The variation of the CO₂ signal during a test burn gave a relative standard deviation (rsd) of around 7%. The uncertainty of the firing of different fuels of the same type is estimated to be around 10-15%. Thus, an overall uncertainty of around 10-20% can be estimated for results or automatically fired systems.

In case of manually fired systems emissions are influenced by many parameters—not all of them can be quantified or taken into account. Even under carefully controlled condition emissions are highly variable and therefore sampling uncertainties are typically much higher than analytical uncertainties (Schmidl et al., 2008a). To get a better understanding of the uncertainty connected to our measurement results, we performed three series of tests (each n = 6) keeping all considerable parameters, mainly stove type, wood type and amount of wood, constant. All other results for manually fired systems represent an average of at least 2 measurements (oak). Numbers of averaged tests are given in Table 1. The standard deviations found for gaseous compounds were around 10% rel. for CO and NO_x and significantly higher for C_xH_v with 50% rel. For absolute PM10 concentrations as well as for relative fractions EC, OC, ions and trace elements an average standard deviation of 30% rel. was found. Compared to common analytical uncertainties, usually lying in the range of 2–5% rel. the overall measurement uncertainties are a result of the high variability of emissions from manually fired combustion systems, where the observed uncertainties of 10-50% are not surprising.

3.6. Particle classification

Kocbach Bølling et al. (2009) have proposed to classify the particle emissions from wood stoves into the main types "inorganic", "soot" and "organic" particles, which is equivalent to our results for "ions", "EC" and "OC", as shown in Figs. 5, 6 and 7, as well as numbers in Table 2. We have not attempted to convert the OC into organic material (OM), but one can estimate OM from OM = 1.5 (OC) (Schmidl et al., 2008a).

In the Kocbach Bølling et al. (2009) classification the emissions from pellets combustion under "full load" are predominantly "inorganic". During "start-up" and under "part load" operation, additional amounts of "soot" and "organics" are enfaced, exceeding in the boiler (system B) the emissions of "inorganic" particles (Fig. 6). For "triticale" pellets high emissions of "inorganics" prevail during all experiments, with some "organics" in the "full operation" respectively with some "soot" and "organics" present in "start-up" and "part load" operation.

For the logwood under "nominal load" test conditions, "organics" are the dominant particle phase if accounted for "OM" with an approximate fraction of 2/3; "soot" of about 1/3 of the PM emissions (Fig. 5). The "inorganics" fraction forms around 1-2% of PM10 for softwood, 4-6% for hardwood (Table 2). During maloperation tests with "low air" the "organics" fraction becomes the dominant PM10 emission, while at "high fuel" system C emitted increased amounts of "soot" and "inorganics", while system D responded in lower emission than in the "nominal load" case however with a higher relative fraction of "soot" than in the "nominal load" case.

3.7. Comparison of PM emissions with literature data

A literature survey of existing fine PM emissions data from residential appliances fired with woody biomass is given in Kocbach Bølling et al. (2009). The pellet stove (System A) PM10 emissions during the three tested phases of around $3-9 \text{ mg MI}^{-1}$ fired with commercial pellets were slightly below the lower end of the range reported in the review for "pellet stoves and boilers" $(10-50 \text{ mg MJ}^{-1})$. The pellets boiler (System B) emissions of PM10 when fired with commercial pellets were 11–39 mg MJ⁻¹ and well within the range of the review. The PM10 emissions of the boiler when fired with wood chips or miscanthus pellets were within the range obtained from system B for the wood pellets. However, when fired with triticale pellets, the PM10 emissions of system B increased to a range of 119–154 mg MJ⁻¹, which is around 5 times higher than for the standard pellets fuel. This emission can be compared to emissions from oat combustion (Boström et al., 2009), where fine particle emission concentration of around 280 mg MJ⁻¹ occurred (number extracted from a graph and tentatively converted to mg MJ⁻¹). Launhardt and Thoma (2000) observed from combustion of triticale whole crops in a 50 kW "multi fuel furnace" PM emissions of 255 mg m⁻³ (STP, normalised to 13%O₂) "dust" determined with a "hot" sampling procedure. Using an estimated conversion factor of 0.65 this results in 170 mg MJ⁻¹, which cannot be directly compared to the previous results obtained by sampling after a dilution step.

The composite averaged emissions (averages of the 4 tested fuels) of PM10 for logwood combustion in system C is 86 mg MJ^{-1} , for system D is 81 mg MJ^{-1} (calculated from Table 2 with the conversion factor indicated in Table 1). This is in the lower quarter of the range of $34-330 \text{ mg } MJ^{-1}$ for "modern wood stoves" as noted in the review of Kocbach Bølling et al. (2009). Under "low air" operation a high PM10 emission of System C of around 500 mg MJ^{-1} exceed the mentioned range in the review.

4. Conclusions

Emissions from small scale manually fired wood combustion appliances, i.e. room stoves, in individual tests are highly variable. In a series of replicate experiments a variability of typically 30% relative was found for most main constituents. In contrast, the variation of the emission concentrations of major constituents in automated appliances was within a relative standard deviation of 7%. Furthermore carbon monoxide (CO) and gaseous hydrocarbon (C_xH_y) emissions are more than an order of magnitude lower for automatically fired systems. Generally, lowest values were found during full load operation in automated units. Nitrogen oxides (NO_x) emissions, however, are in a similar range for manually and automated fired units for standard fuels. Due to elevated nitrogen content of the biofuels: *miscanthus* and *triticale* pellets, their NO_xemissions were around double (*miscanthus*) and triple (*triticale*) the emissions of standard fuels.

Absolute PM10 emissions as well as the relative composition differed significantly between manually and automatically fired systems and between operation modes of automatically fired systems. The range of emissions concentrations reached from 12 to 21 mg m⁻³ (STP, 13%O₂, dry gas) for wood pellets, wood chips and *miscanthus* chips in automated units under full load operation, and from 111 to 151 mg m⁻³ (STP, 13%O₂, dry gas) for standard experiments with briquettes and logwood from spruce, beech and oak in manually fired wood stoves. The highest emissions of PM10 (184 mg m⁻³ STP, 13%O₂, dry gas, under full load) occurred by burning *triticale* pellets in an automated fired biomass boiler. The high particulate emissions from *triticale* combustion are mainly caused by a high potassium chloride content of the emissions due

to chlorine content of 0.23% of the fuel, two orders of magnitude higher than in standard woody biomass.

The chemical composition of PM10 emissions from manually fired systems differed significantly from automatically fired systems. Logwood stoves emitted high amounts of carbonaceous material with 70% TC of PM10 on average, while particulate emissions from automatically fired systems (pellet stove and boiler) consisted mainly of inorganic potassium salts. Hence the use of one wood smoke source profile with high OC and levoglucosan in source apportionment will miss to account for automated fired biomass devices. Findings from this work suggest the use of two separate profiles, one for manually fired systems (stoves, fireplaces) and one for automatically fired appliances (boilers, pellet stoves). Levoglucosan, an anhydrous sugar formed during incomplete combustion from cellulose-containing material was detected in all samples from manually fired systems. On average levoglucosan was around 5% of PM10, resulting in a factor of 20 for conversion of levoglucosan to PM10. Automatically fired appliances did not emit levoglucosan in full- and part load. During the start-up phase small amounts of anhydrous sugars were measured. Levoglucosan/mannosan ratios, which can be used to estimate the proportion of hardand softwood combustion ambient wood smoke, are in good agreement with recent results reported for combustion of Austrian wood types in a tiled stove (Schmidl et al., 2008a).

CO and particulate emissions—absolute as well as composition—from manually fired logwood stoves are mainly influenced by the wood type, i.e. structure, elemental composition, water or ash content. The influence of the appliance, within a group of similar stoves, is only minor.

Maloperation of manually fired stoves can lead to a substantial increase of particulate emissions. Highest values, around 4 times higher than average from standard tests, were found in an experiment with reduced airflow setting. This parameter seems critical for using emission data from tests under "optimal" conditions for estimating "real world" emission data from logwood stoves.

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