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PM EMISSIONS FROM OLD AND MODERN BIOMASS COMBUSTION SYSTEMS AND THEIR HEALTH EFFECTS

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ABSTRACT: In this paper the results of a project focusing on the determination as well as chemical and toxicological characterisation of PM emissions from the most relevant biomass based residential heating systems performed at the BIOENERGY 2020+ GmbH are presented. Seven modern state-of-the-art as well as old technology boilers and stoves have been investigated within test stand measurement campaigns. Whole day operation cycles simulating real life operation conditions were therefore simulated. Gaseous as well as particulate emissions were determined and representative particulate emission samples were taken for subsequent chemical analyses and toxicological tests. The results clearly indicate that modern automated biomass combustion systems emit fewer particles than uncontrolled natural draught systems. However, the by far highest emissions were measured for an old technology logwood boiler. It has been shown that clear correlations between CO and OGC emissions originating from incomplete combustion and the particulate emissions exist. Moreover, not only the PM emission factors increase with decreasing burnout quality but also the organic carbon and soot concentrations in the particles. The evaluation of the toxicological tests has revealed that also the cell responses seem to correlate with the burnout quality. While PM samples taken under good burnout conditions showed only minor responses which were clearly below those of diesel exhaust PM, the responses of particles emitted by the old technology logwood boiler exceeded even the response levels of diesel exhaust PM.
Keywords: aerosol, biomass, combustion, small scale application, chemical composition.

1 INTRODUCTION

Due to increased efforts for CO_2 emission mitigation, the energetic utilisation of biomass has gained rising relevance all over Europe within the last decade. One important sector thereby is the utilisation of biomass in small-scale (residential) heating systems for room heating and warm water supply. In this capacity range a great variety of different modern biomass combustion systems such as pellet, wood chips and logwood boilers as well as different types of stoves (logwood and pellet stoves, tiled stoves, etc.) are presently available. However, it is well known that in many European regions the current stock of small-scale biomass heating systems operated is dominated by old logwood stoves and logwood boilers while modern technologies, which are just penetrating the market, only provide a minor contribution to the number of applications [1]. These old combustion systems show, due to their low technological level, significantly higher PM (particulate matter), CO, OGC (organic gaseous compounds) as well as PAH (polycyclic aromatic hydrocarbons) emissions than modern systems which leads to the situation that residential biomass combustion in many European regions is the main source for PM_1 (particles with a diameter <1 µm) emissions of the residential heating sector. It has additionally to be mentioned that PM_1 emissions from old biomass combustion technologies are dominated by carbonaceous particles (organic compounds and soot) which are generally suspected to be responsible for adverse health effects caused by ambient PM.

This situation is counterproductive regarding the further increase of biomass utilisation in the residential heating sector since it saps the public confidence in residential biomass combustion as an environmentally compatible, sustainable and CO_2-neutral heating technology. Since public opinion does, due a lack of information, in many cases not distinguish between old and modern combustion systems, the whole area of residential biomass combustion is concerned.

On the other side, scientific studies [1, 2, 3] have already shown that there are significant differences regarding the emissions, especially PM_1 emissions, of old and modern as well as automatically and not automatically controlled biomass-based residential heating systems. This not only concerns their magnitude but also their chemical compositions, since PM_1 emissions from modern biomass combustion systems have been found to contain significantly less carbonaceous compounds and mainly consist of inorganic salts (alkaline metal salts). As scientific investigations indicate these inorganic salts are much less harmful for human health than organic particles and soot, however, systematic studies regarding this issue are still missing.

Therefore, a research project dedicated to the investigation of health risks caused by fine PM emissions from different old and modern small-scale (residential) biomass combustion technologies has been performed at the BIOENERGY 2020+ GmbH, Graz, Austria, in cooperation with the Institute for Process and Particle Engineering, Graz University of Technology, Austria, the Department of Environmental Health, National Institute for Health and Welfare, Kuopio, Finland, as well as the Department of Environmental Sciences, University of Eastern Finland, Kuopio, Finland. The overall aim of the project was to investigate the whole chain starting at the definition of the performance of the combustion systems in terms of burnout and leading over an extensive chemical characterisation of the fine PM emissions to the investigation of the health risks caused by these emissions by toxicological in-vitro studies. By considering all these aspects of particle formation, particle characterisation and toxicity, the project aimed at working out correlations between the performance of the

combustion systems, the characteristics of their particulate emissions as well as the related health risks. Moreover, the results from the toxicological studies should be compared with results from tests based on the same methodology performed with urban aerosols as well as aerosols from diesel exhaust gases.

The project was based on test stand measurements, during which besides relevant operation parameters (gaseous emissions, boiler load, flue gas temperature, combustion chamber temperature etc.) PM emissions have been measured and PM samples have been taken and forwarded to chemical analyses as well as toxicological (in-vitro) tests. The specific aims of the toxicological in-vitro tests were to investigate cell death and to study the inflammatory responses caused by PM as well as to assess the PM induced genotoxicity and the oxidative stress as measures for possible health effects caused by these emissions. A broad variety of residential biomass combustion systems has thereby been tested covering automatically fed and automatically controlled boilers (pellet and wood chip boiler), manually fed and automatically controlled boilers (logwood boilers) as well as manually fed stoves (logwood fired chimney stoves and a tiled stove). With this selection of combustion technologies the major share of applications which are usually operated in Europe could be covered. It is important to mention that the test runs performed were based on whole day operation cycles and therefore, in contrast to other studies on PM emissions from residential biomass combustion, not only stable continuous operation phases but also transient operation phases have been investigated.

In this paper first results from the project are published which mainly focus on the presentation of the emission factors determined for the different residential biomass combustion systems, the chemical compositions of the PM emissions as well as first evaluations of the results gained from the toxicological tests performed.

2 THEORETICAL BACKGROUND

2.1 Definitions

In this paper all particle sizes mentioned are related to the aerodynamic diameter (ae. d.) which is defined as the diameter of a spherical particle with a density of 1 g/cm³ showing the same sedimentation behaviour in air as the particle of interest.

Ambient PM is generally classified in coarse mode (> 1 µm) and fine mode (< 1 µm) particles. Other classifications applied are total suspended particulate matter (TSP) which represents all particles present as well as PM_{10}, $PM_{2.5}$ and PM_1, which involve the particle fractions with a diameter <10, 2.5 and 1 µm respectively. Concerning particulate emissions from biomass combustion it can also be distinguished between a coarse mode (coarse fly ashes) and a fine mode (aerosols) which together form the TSP.

2.2 Sources of ambient PM

Coarse mode particles mainly originate from mechanical processes such as abrasion and particle dispersion by traffic, industrial and agricultural processes, handling of bulk material, as well as volcanic eruption and desert storms. Fine mode particles on the other side mainly originate from traffic, industry, agriculture as well as residential heating.

2.3 Particle formation during biomass combustion

PM emissions (TSP) from biomass combustion are categorised into coarse fly ashes and aerosols (see Figure 1). While a major share of ashes formed during biomass combustion is found as so called bottom or grate ash, a minor portion of ash particles is entrained from the fuel bed with the flue gas and forms the coarse fly ashes. Depending on the flow conditions in the furnace and the boiler, coarse fly ash particles are partly precipitated in these plant sections while the remaining part forms the coarse fly ash emissions. These coarse fly ash emissions are usually in a particle size range between some µm up to about 200 µm [4]. The particles mainly consist of refractory species such as Ca, Si, Mg as well as smaller amounts of K, Na and Mn bound as oxides, sulphates or phosphates. In residential biomass combustion systems coarse fly ashes usually only provide minor contributions of up to 10 wt% to the total particulate emissions. Moreover, due to their comparably large particle size, they are not respirable and therefore of almost neglectable relevance regarding health effects. Therefore, coarse fly ash emissions have not been considered in this paper.

The formation of aerosols (fine particles with a diameter <1 µm) is much more complex. Aerosols can be categorised into inorganic as well as carbonaceous particles [3, 5], whereas carbonaceous aerosols are divided into soot particles (elemental carbon) and particles consisting of organic compounds. Inorganic aerosols represent a fraction which is mainly influenced by the chemical composition of the fuel used. Volatile ash forming elements such as K, Na, S, Cl as well as easily volatile heavy metals (e.g. Zn, Pb) contained in the fuel are released into the gas phase during combustion. By gas phase reactions different compounds (alkaline metal sulphates, chlorides and carbonates, heavy metal oxides, etc.) are formed. As soon as one of these compounds becomes supersaturated, which could happen either due to the excessive formation of the respective compound or due to the cooling of the flue gas in the boiler, gas to particle conversion by nucleation and condensation processes takes place. Carbonaceous aerosols on the other side are formed by the condensation of organic vapours which are a result of an incomplete gas phase burnout as well as by an incomplete oxidisation of soot particles.

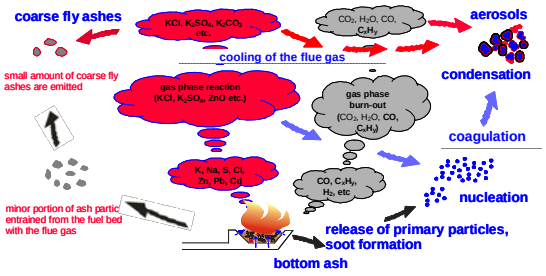


Figure 1: Particle formation during residential biomass combustion

Consequently, the formation of inorganic aerosols can mainly be influenced by the choice of the fuel applied (respectively its contents of inorganic aerosol forming species) while the formation of carbonaceous aerosols can be minimised by an optimisation of the combustion process (i.e. burnout optimisation).

2.4 Residential biomass combustion systems – overview

A broad variety of different residential biomass combustion technologies exists. Generally, these systems are operated nowadays with wood fuels such as logwood, wood chips and wood pellets of which logwood is the most widely applied fuel.

The technologies can generally be divided into natural draught systems as well as enforced draught systems. Typical representatives of natural draught systems are logwood stoves (chimney stoves, tiled stoves, fireplace inserts etc.). Since the transport of combustion air and flue gases in these systems is exclusively driven by natural draught, only limited possibilities regarding the optimisation of the mixing of combustion air and flue gases, which is an important requisite for achieving a good burnout, exist. Moreover, these systems are usually only manually controlled and operated in batch mode. Besides stoves also old logwood boilers are sometimes based on natural draught.

Pellets, wood chips and logwood boilers represent typical systems based on enforced draught. In this case flue gas fans are applied in order to control the combustion air supply and the transport of the flue gases from the combustion chamber to the chimney. Modern boiler technologies are fully automatically controlled and for pellet and wood chip boilers also fully automated fuel feeding systems represent the state-of-the-art. Due to these constraints the emissions of automatically controlled boiler systems are significantly lower than those of stoves.

Even if during the last years a significant increase of the yearly installed number of modern pellet, wood chip and logwood boilers has been recognised, the stock of applications presently in operation is generally dominated by old logwood boilers as well as old and modern stoves.

3 METHODOLOGY

3.1 Overview

The overall methodology of the work presented was based on test runs with different residential biomass combustion systems at a test stand at BIOENERGY 2020+ GmbH. During the test runs the plant operation was monitored, gaseous and PM emissions were determined and PM_1 emissions were sampled and forwarded to subsequent chemical analyses and toxicological tests. It is important to mention that the PM emission sampling took place over simulated whole day operation cycles (see section 3.3) which facilitates an evaluation of the emissions as they also occur during field operation. From the test runs performed with each combustion system, PM_1 samples from 2 representative tests were forwarded to chemical analyses and toxicological tests.

3.2 Small-scale biomass combustion systems investigated

The combustion systems investigated represent a representative cross section of residential heating technologies presently applied in Europe. Since the stock of applications in most countries is dominated by old combustion systems (sometimes older than 20 years) not only state-of-the-art technologies but also old technologies have been investigated. The following systems have been tested:

- pellet boiler (modern technology)
- wood chip boiler (modern technology)
- logwood boiler (modern technology)
- logwood boiler (old technology)
- logwood stove (modern “high quality” technology)
- logwood stove (old “low-price” technology)
- tiled stove (modern technology)

The pellet boiler as well as the wood chip boiler were equipped with automatic ignition systems, staged combustion, automated boiler cleaning systems as well as automated de-ashing systems. Their nominal boiler capacities were 21 kW respectively 30 kW. The pellet boiler was characterised by an overfed burner, a water cooled combustion chamber as well as a combustion control based on the measurement of the furnace temperature. The wood chip boiler consisted of an underfeed stoker combustion system and a water cooled combustion chamber. For combustion control flue gas temperature control and λ-control are applied.

The modern logwood boiler was based on a down-draught combustion technology and had a nominal boiler capacity of 30 kW. It was equipped with an automated boiler cleaning system. The fully automated combustion control concept is based on a λ-control. The old logwood boiler (nominal boiler capacity: 15 kW) on the other side was a typical under-fire boiler. For this system combustion control is based on a thermo-mechanic combustion air control by a primary air flap. In contrast to the pellet and the wood chip boiler both logwood boilers are manually fed and also the ash removal has to be done manually.

The modern stove (nominal heat output: 6 kW) consisted of a primary and a secondary combustion zone. Air supply was realised via primary and window purge air during ignition and only by window purge air during main combustion and burnout phases. The air supply control had to be manually adjusted. The old technology stove (nominal heat output: 6.5 kW) on the other side only consisted of one burning chamber. Combustion air was divided into primary air through the grate, window purge air as well as secondary air injected through nozzles from the backside of the combustion chamber. The air distribution had to be adjusted manually by a damper.

The tiled stove (nominal heat output: 4.2 kW) was designed according to the current guidelines of the Austrian tiled stove association. Air supply was realised through a vertical grate positioned in the stove door.

While the boiler systems investigated were equipped with flue gas fans the stoves represent typical natural draught systems.

3.3 Plant operation during the test runs, measurement and sampling periods

In former studies regarding the PM emissions of small-scale biomass combustion systems emission measurements and particle sampling usually took place during stable full and partial load operation conditions. However, these conditions are not representative for the real life operation of the systems. Therefore, it has been decided to operate the systems under typical real life conditions including also transient operation phases and to perform the measurements and PM sampling over the whole test run period.

For the pellet and the wood chip boiler typical whole day load cycles have been evaluated from field measurement data in order to define a representative operation cycle. The finally applied operation cycle had a

duration of 10 hours and included besides stable full and partial load operation also a considerable number of start-up, load change and shut down procedures.

Concerning the logwood boilers the fuel storage room was charged at the beginning of the test. For the modern logwood boiler it was once recharged and for the old technology logwood boiler 2 times recharging took place (due to the smaller volume of the fuel storage room). The overall heat produced from these subsequent batches was about the same as for the pellet and wood chip boiler over their whole operation cycle.

The manually fed stoves were operated at nominal load. Therefore, the firebox was filled with the recommended amount of logwood (1.6 kg). One ignition batch and 5 subsequent burning batches have been performed. This is of course a longer operation than it usually is applied in real life (usually about 3 to 4 batches), however, an increased number of subsequent batches was needed in order to gain the mass of PM_1 samples needed for the subsequent toxicological analyses (more than 50 mg).

In tiled stoves on the other side usually one fuel batch is burned (which takes about 1 to 1½ hours) and the heat is stored in the stove. After the fire has extinguished the heat stored is slowly released to the surrounding during the next 10 to 12 hours. Consequently, one test run with the tiled stove consisted of only one burning batch and particle samples gained from different, in terms of tiled stove operation comparable test runs were pooled to gain enough particle mass for the toxicological tests.

All measurements as well as the particle sampling for the toxicological tests started at the beginning of the test run (first ignition of the fuel) and ended after the shut down of the heating system. Consequently, all operation phases as they also occur during real life operation, have been covered by the sampling and measurements.

3.4 Test stand setup and measurements performed

A scheme of the test stand setup is presented in Figure 2. The setup is based on recommendations for particle sampling for toxicological tests, worked out within the ERA-NET Bioenergy project BIOMASS-PM [1] and generally follows the setup described in EN 13240. However, in contrast to EN 13240 flue gas dilution was applied for particle sampling for the following reason. Especially when operating old combustion systems and batch combustion systems based on natural draught, phases with increased emissions of condensable hydrocarbons occur. In the real life situation these gaseous emissions condense later on in the atmosphere and form secondary aerosols which provide a substantial contribution to the ambient air PM concentrations. Therefore, the flue gases were diluted before the particle sampling in order to convert condensable organic species into particles. The dilution was performed with pre-cleaned particle free pressurised air and the dilution ratio was adjusted in a way that the diluted flue gas had a temperature of below 40°C. The following measurements were performed:

- Continuous measurements:
  - Operation parameters: flue gas temperature, combustion chamber temperature, boiler load (for boiler systems), chimney draught.
  - Flue gas composition in the undiluted flue gas by using standard flue gas analysers for O_2 (paramagnetic sensor), CO (ND-IR), NO_x (CLD) and OGC (FID).
  - Determination of the particle size distribution (PSD) and the concentration of aerosols in the diluted flue gas with an electrical low-pressure impactor (ELPI 10 lpm).
  - All relevant data (temperatures, mass flows) of the dilution air.
- Discontinuous measurements and sampling:
  - Fuel and bottom ash sampling.
  - Manually fed systems (stove, tiled stove, log-wood boilers): weighing of the fuel and of the bottom ash.
  - Determination of the total fly ash (TSP) concentration in the undiluted flue gas according to VDI 2066.
  - Determination of the PSD and the concentration of aerosols in the diluted flue gas with 9-stage Berner-type low-pressure impactors (BLPI).
  - Determination of the PSD and the concentration of aerosols in the diluted flue gas and collection of sufficient PM sample mass (at least 50 mg) for toxicological studies with a 5-stage Dekati-gravimetric impactor (DGI).

In the following the test stand setup is described in detail (see also Figure 2).

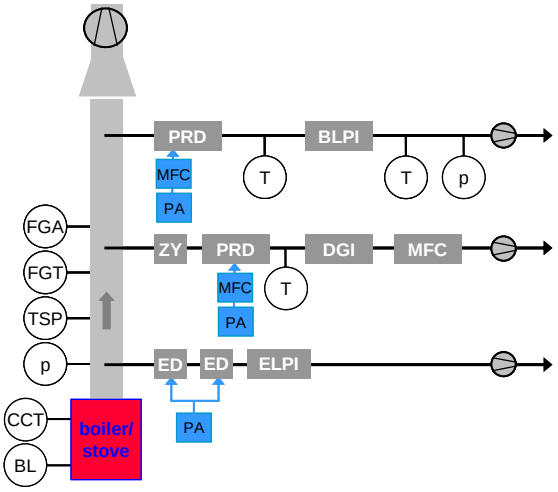


Figure 2: Scheme of the measurement and sampling system
Explanations: abbreviations: see text below

Combustion chamber temperature (CCT) as well as boiler load (BL) of the small-scale biomass combustion system (boiler/stove) are determined and recorded. In the undiluted flue gas the flue gas temperature (FGT), the concentration of total suspended particulate matter (TSP) and the gaseous emissions (CO, OGC, O_2, NO_x) are determined using standard flue gas analysers (FGA) and the chimney draught (p) is measured. For fine particulate emission measurements and particle sampling three different systems (ELPI – electric low-pressure impactor, BLPI – Berner-type low-pressure impactor, DGI – Dekati gravimetric impactor) are applied. With all these systems the emissions were measured in diluted flue gas. The DGI system was used for sampling PM for the further toxicological studies. This system consists of a heated cyclone (ZY, cut diameter: 10 µm), a porous tube diluter (PRD), the gravimetric impactor (DGI) and a pump. Mass flow controllers (MFC) are used to control the flow rates of the pre-cleaned particle free dilution air (PA) and

the diluted flue gas. The temperature (T) of the diluted flue gas is measured with Pt100 temperature sensors. The DGI itself consists of four precipitation stages with cut diameters of 2.5, 1, 0.5 and 0.2 µm (ae. d.) as well as a backup filter. A comparable dilution system was applied for the BLPI sampling line while flue gas dilution for the ELPI measurements was realised with two serial ejector diluters (ED). During BLPI measurement the flow rate of the diluted flue gas was controlled by a critical orifice accompanied by a pressure (p) and temperature (T) measurement.

3.5 Chemical analyses applied

The following methods were applied for chemical analyses of fuel, ash and aerosol samples:

- Characterisation of the fuel applied by wet chemical analyses regarding the moisture content (drying at 105°C), ash content (prCEN/TS 14775) as well as the concentrations of C, H, N (element analyser), Si, Ca, Mg, Mn, K, Na, Zn, S (pressurised multi-step digestion with HNO_3/HF/H_3BO_3; element detection with ICP-OES) and Cl (bomb combustion in oxygen, absorption in NaOH and detection by IC).
- Determination of the chemical composition of selected aerosol (BLPI and DGI) samples by pressurised multi-step digestion of the samples (HNO_3/HF/H_3BO_3) and element detection with ICP-OES or ICP-MS [6, 7].
- Determination of the contents of organic carbon (OC), elemental carbon (EC) and inorganic carbon (IC) in aerosol samples with a carbon/ hydrogen analyser (LECO RC-612). The sample is inserted into a quartz tube and heated to defined temperatures. Carbon containing compounds released from the sample are oxidized to CO_2, which is selectively detected by infrared cells. By choosing appropriate temperatures and carrier gases in the quartz tube total carbon (TC) as well as the fractions OC, EC and IC can be distinguished. Carbon released in a temperature window from 200 to 600°C under inert atmosphere is assigned to OC, carbon released between 600 and 900°C is assigned to IC, carbon detected after switching to oxidizing conditions to EC.
- Quantification of polycyclic aromatic hydrocarbons (PAH) in aerosol samples. A total of 30 PAHs was analysed using a gas chromatograph and a mass selective detector (6890N GC-5973 INERT MSD, Agilent Technologies) after extraction of the particulate samples with dichloromethane (see also section 3.6) [8].

3.6 Filter pre-treatment and sample preparation for toxicological tests

Prior to sampling the DGI filters (Fluoropore PTFE filters, Millipore) were washed twice with methanol, dried and weighed. After sample collections, the filter sets were packed in tin foil and double plastic bags and deep frozen for storage. Three stages (backup filter, 0.2 and 1 µm stage) of each DGI set were weighed and pooled to form one PM_1 sample. The size-segregated particulate samples were prepared for the toxicological studies using previously validated procedures [9, 10]. The PM_1 samples were extracted with methanol from the filters and then DGI filter sets taken during one test run were pooled in order to gain a representative sample for a whole day operation cycle. In case of test runs with the tiled stove, DGI samples from test runs at 3 successive days were pooled to gain sufficient sample mass of at least 50 mg. The excess methanol was evaporated and finally aliquots of the concentrated suspension, calculated on a mass basis, were dried in glass tubes under nitrogen (99.5%) flow and stored at -20 °C until their use within the toxicological tests.

3.7 Toxicological tests – general information and tests performed

Proposed toxic mechanisms behind PM-induced adverse health effects are cytotoxicity, inflammation associated injury [11], oxidative stress [12] and genotoxicity [13, 14, 15]. These mechanisms can be activated in response to PM exposure in alveolar macrophages [9, 16] that are the primary defence cell type against inhaled particles in the lung periphery. In Figure 3 the main mechanisms that are suggested as being involved in exposure to and health effects of particulate air pollution are shown [17].

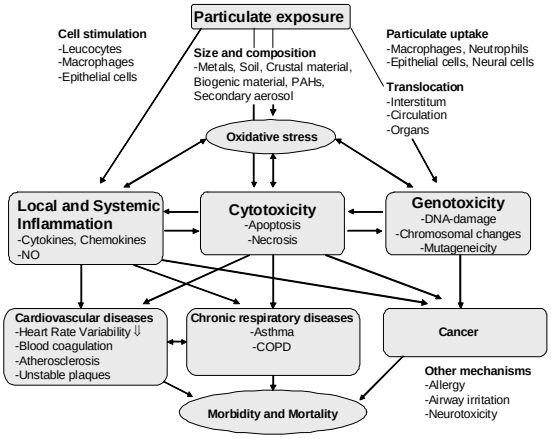


Figure 3: Main mechanisms that are suggested as being involved in exposure to and health effects of particulate air pollution

Inflammation has been regarded as the main mechanism behind the enhanced symptoms of the cardio-respiratory diseases, associated with ambient particulate levels. Inflammation causes worsening of e.g. asthma and COPD (chronic obstructive pulmonary disease) symptoms and often leads to the hospital admission in these subjects. Moreover, inflammation causes disturbance of heart functions, unstable plaques in the blood circulation and thus may lead to myocardial infarction.

Cytotoxicity, depending on its mechanism, may cause various symptoms in humans. These may vary from irritation to lesions in the lungs with heavy exposure, e.g. in occupational conditions. Cytotoxicity may also lead to many secondary mechanisms, such as inflammation and genotoxicity.

Genotoxic responses caused by the PM samples are behind cancer development. There is still not much data available, how the ambient levels of particulate matter affect the cancer development, but obviously they have some relevance. Recently, the indoor emissions from household combustion of biomass fuels (primarily wood) were classified as probably carcinogenic to humans (Group 2A) by IARC (International Agency for Research on Cancer). Also the diesel engine exhausts are

determined as carcinogenic (Group 2A) [18]. Therefore, also outdoor emissions from biomass combustion systems may have carcinogenic effects.

The overall aim of the toxicological tests was to evaluate the association between the toxic properties and the physicochemical characteristics of PM emissions from the different small-scale biomass combustion systems investigated. Therefore, the following tests have been performed.

- Detection of necrosis in order to investigate cell death caused by PM samples in macrophages and PI-staining using flow cytometry to investigate apoptosis and changes in the cell cycle.
- The measurement of the production of inflammatory mediators (cytokines) to study inflammatory responses caused by PM samples in macrophages.
- Detection of DNA single strand breaks with single cell gel electrophoresis (Comet) assay to assess the PM induced genotoxicity in the macrophages.

3.8 Fuels utilised during the test runs

For the test runs wood pellets according to ÖNORM M 7135, wood chips according to ÖNROM M 7133 as well as logwood according to ÖNORM M 7132 and ÖNORM CEN/TS 14961 were used as fuels. The results of the fuel analyses are presented in Table I. As comparisons with database values show, the fuels applied during the test runs are representative for the respective fuel category.

Table I: Chemical characterisation of the fuels applied
Explanations: PE-m … modern pellet boiler; WC-m … modern wood chip boiler; LW-m … modern logwood boiler; LW-o … old logwood boiler; ST-m … modern logwood stove; ST-o … old logwood stove; TST-m … modern tiled stove; mc … moisture content, ac … ash content; w.b. … wet basis; d.b. … dry basis

		PE-m	WC-m	LW-m	LW-o
mc	wt% w.b.	7.4	12.7	8.7	12.0
ac	wt% d.b.	0.4	0.3	0.6	1.0
C	wt% d.b.	49.9	49.0	48.3	48.6
H	wt% d.b.	6.1	6.3	6.1	6.2
N	wt% d.b.	0.1	0.1	0.1	0.2
S	mg/kg d.b.	61.1	56.5	103.0	131.0
Cl	mg/kg d.b.	12.0	12.0	11.1	18.0
Ca	mg/kg d.b.	888.0	861.0	1,140.0	2,530.0
Si	mg/kg d.b.	270.0	100.0	200.0	200.0
Mg	mg/kg d.b.	107.0	182.0	506.5	527.0
K	mg/kg d.b.	418.0	401.0	1,375.0	1,440.0
Na	mg/kg d.b.	14.8	2.7	1.9	2.0
Zn	mg/kg d.b.	11.4	6.2	3.5	3.0

		ST-m	ST-o	TST-m
mc	wt% w.b.	8.5	9.4	9.1
ac	wt% d.b.	0.7	0.6	1.9
C	wt% d.b.	48.3	48.3	48.4
H	wt% d.b.	6.3	6.1	6.0
N	wt% d.b.	0.2	0.1	0.2
S	mg/kg d.b.	89.3	89.5	137.5
Cl	mg/kg d.b.	14.2	10.6	12.8
Ca	mg/kg d.b.	1,090.0	1,100.0	5,955.0
Si	mg/kg d.b.	200.0	200.0	275.0
Mg	mg/kg d.b.	221.0	518.0	280.5
K	mg/kg d.b.	1,790.0	1,460.0	1,580.0
Na	mg/kg d.b.	2.0	2.0	3.7
Zn	mg/kg d.b.	2.1	2.3	2.6

The moisture contents of the fuels were generally on a comparably low level (below 13 wt% w.b.). The ash contents increase from pellets and wood chips (0.4 respectively 0.3 wt% d.b.) to the logwood fuels applied (0.6 to 1.9 wt% d.b.) whereas the most relevant ash forming elements are Ca, Si, Mg and K. The concentration levels of the most relevant inorganic aerosol forming element, K, increase from wood chips and pellets (401 respectively 418 mg/kg d.b.) to the logwood fuels (1,375 to 1,790 mg/kg d.b.).

4 RESULTS AND DISCUSSION

4.1 Particulate and gaseous emissions trends determined

In Figure 4 process data and emission trends recorded during test runs with the modern pellet boiler, the modern logwood boiler as well as the modern stove are presented. Regarding the PM emissions, the continuously recorded data gained from the ELPI are displayed and moreover, the TSP emission levels as well as the PM_1 emission levels determined with the BLPI are indicated over their sampling time (the start and the end of the horizontal lines indicate the start and the endpoint of the sampling). It has to be pointed out that the ELPI measurement provides particle number related data. Therefore, the mass related data have to be calculated by applying a correction factor considering the density and the particle size of the different particle fractions. Due to the heterogeneity of the particle collective it is not possible to calculate a reliable correction factor based on theoretical considerations and therefore, the number related ELPI results have been correlated with the in parallel performed gravimetric BLPI measurements in order to gain an average correction factor over a test run. In the diagrams these corrected mass related ELPI data are presented.

The top diagram for the pellet boiler presents the trends for the boiler load as well as the feed water temperature. From this trend the load programme of the daily operation cycle including start-up, load changes, stable load conditions as well as shut downs can be followed. With the exception of some very short periods (some seconds) acceptable burnout conditions prevailed. Only during the initial start-up phase as well as the shut downs and restarts of the boiler (around 12.00, 13.30 and 16.30) major CO, OGC and PM emission peaks occurred reaching about 30,000 mg/Nm³ for CO, 1,600 mg/Nm³ for OGC and 2,000 mg/Nm³ for PM_1 emissions. Especially partial load operation resulted in slightly increased PM_1 emissions which are mainly due to the, compared with full load operation, lower combustion chamber temperatures during these phases which lead to the formation of organic aerosols and soot emissions. However, also during partial load operation PM_1 emissions did not significantly exceed 20 mg/Nm³.

The wood chip boiler (not presented in Figure 4) was operated under the same load programme and showed a comparable behaviour regarding emissions, however, the emission levels were slightly higher.

Also during the most time of the operation of the modern logwood boiler good burnout conditions and consequently comparably low CO, OGC and PM_1 emissions prevailed. Compared with the pellet boiler, the emission peak during the start-up phase occurs over a significantly longer period (about 30 min. compared to about 10 min.) which is typical for logwood boilers [3]. This period is followed by stable operation characterised by very low emissions. During the burnout phase of the

first batch (starting at about 12.30) an increase of CO and PM_1 emissions can be recognised. As chemical analyses of PM samples taken with the BLPI during this burnout phase have revealed, these increased PM emissions are not due to decreasing burnout quality and higher formation ratios of organic aerosols but due to an increased K-release from the fuel to the gas phase followed by inorganic aerosol formation. The increased K-release is most probably due to higher temperatures in the fuel bed during charcoal burnout. As already mentioned, the operation cycle of the modern logwood boiler consisted of two batches. In Figure 4 the fuel recharging can be identified by the significant, but short emission peak at about 13.20. After some minutes stable combustion conditions are reached again and also the CO, OGC and PM_1 emissions are reduced to the same low level as during the first batch. At the end of the second batch again the increase of CO and PM emissions as reported for batch 1 can be recognised.

During the operation of the old technology logwood boiler (not shown in Figure 4) significantly higher emissions have been measured due to higher excess air ratios and consequently lower combustion temperatures.

As the diagrams regarding the stove operation clearly show, the operation behaviour of a natural draught system clearly differs from the one of enforced draught systems such as pellet and logwood boilers. The combustion process is characterised by three combustion phases, the ignition phase, the main combustion phase and the burnout phase. At the beginning of a combustion cycle, during the ignition phase, the O_2-content of the flue gas decreases while the furnace temperatures increase. As long as the O_2-concentrations are too high and the furnace temperatures are too low to achieve appropriate burnout conditions, high CO, OGC and PM_1 emissions are detected. As soon as stable combustion conditions have been reached the main combustion phase begins which is characterised by quite stable O_2-concentrations in the flue gas and sufficiently high temperatures in the furnace to provide acceptable burnout conditions. During this phase the gaseous and particulate emissions are significantly lower than during the ignition phase. At the end of the combustion cycle charcoal burnout takes place, the burnout quality decreases and the CO emissions increase. The OGC and the PM_1 emissions however stay on a rather low level which is due to the fact, that the main amount of volatiles has been released from the fuel during the ignition and the main combustion phase. The major part of the emissions generated during one combustion cycle is related to the ignition phase. Only during the first combustion batch this behaviour is not very pronounced since the stove is still heating up to operation temperature and therefore, generally higher emissions are measured due to the too low combustion temperatures.

The same behaviour has been determined for the old technology stove (not shown in Figure 4), however, the emissions were in general about doubled. The combustion process in tiled stoves (not shown in Figure 4) is comparable with the one in stoves, but, as already mentioned, it consists of only one batch.

Particle sampling with the DGI for the toxicological tests always started at the beginning of the test run and covered almost the whole test duration. Since the particle sampling capacity of the DGI is limited, the sampling foils had to be replaced during the test run. However, this could be done within some minutes and therefore more than 98% of the test run period could be covered by the DGI sampling. Therefore, particle samples representative for the whole operation period could be gained for the subsequent toxicological tests.

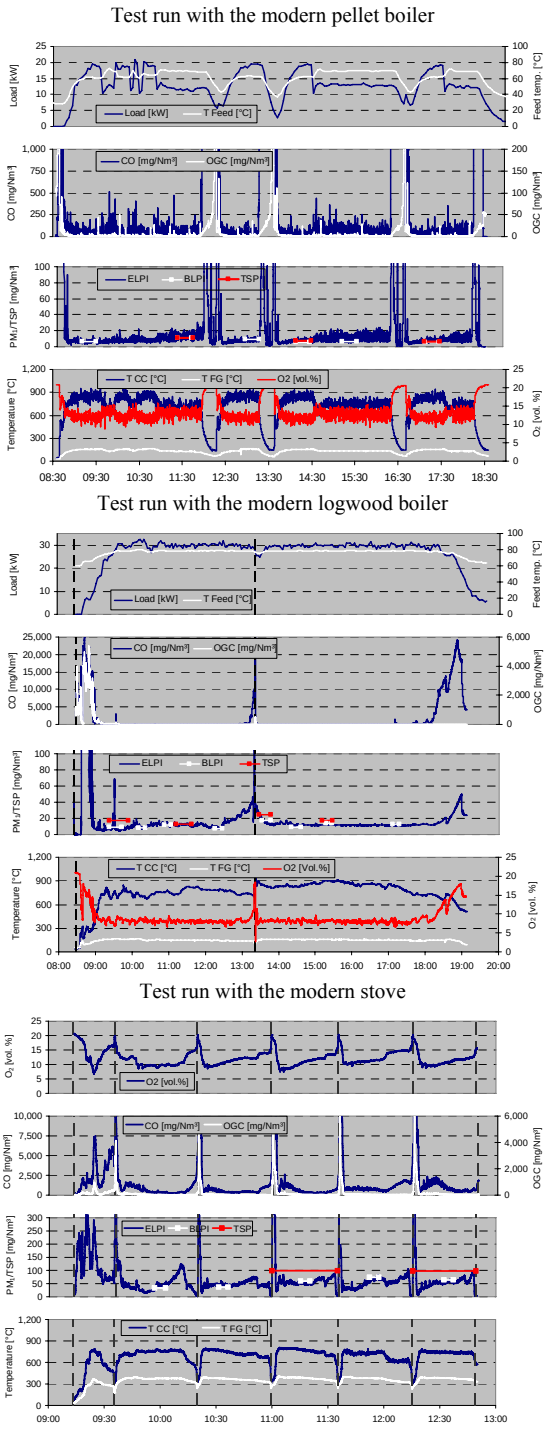


Figure 4: Operation parameters as well as gaseous and particulate emissions during test runs with different small-scale biomass combustion systems
Explanations: concentrations related to dry flue gas; TSP, PM_1, CO, OGC emissions related to 13 vol% O_2; TCC … combustion chamber temperature; TFG … flue gas temperature; TFeed … feed temperature; BLPI and TSP lines indicate the measured PM concentration over the respective sampling period

4.2 Average emissions over full testing cycles

With the exception of the tiled stove, where 6 test runs were needed to gain sufficient sample mass for two sets of toxicological tests, for all technologies 2 test runs have been performed. A summary of the mean values of the gaseous and PM_1 emissions determined during the test runs is presented in Table II. The PM_1 emission data have thereby been derived from the continuous ELPI measurements.

Table II: Mean values for gaseous and PM_1 emissions over the whole test runs for the different biomass combustion systems investigated

Explanations: PE-m … modern pellet boiler; WC-m … modern wood chip boiler; LW-m … modern logwood boiler; LW-o … old logwood boiler; ST-m … modern logwood stove; ST-o … old logwood stove; TST-m … modern tiled stove

Combustion system	Test run	O_2 vol% d.b.	CO mg/MJ	OGC mg/MJ	PM_1 mg/MJ
PE-m	1	12.6	47.1	2.5	6.2
	2	12.5	45.4	1.7	6.0
WC-m	1	12.2	168.1	3.0	15.3
	2	12.1	182.2	5.4	13.6
LW-m	1	8.6	700.4	78.7	14.2
	2	8.6	793.1	62.4	17.6
LW-o	1	11.3	12,632.3	1,143.8	106.1
	2	11.0	8,969.4	650.8	98.6
ST-m	1	12.5	1,048.2	94.2	47.2
	2	12.1	1,035.6	95.5	46.1
ST-o	1	10.8	2,355.4	223.9	74.2
	2	11.1	2,084.6	185.7	55.5
TST-m	1	15.4	1,207.3	52.4	31.3
	2	15.3	1,007.5	69.2	28.0

When analysing the data provided in Table II the combustion systems can be categorised in 3 groups. The first group are modern automated boiler systems namely the pellet boiler, the wood chip boiler and the modern logwood boiler. These systems represent the present state-of-the-art boiler technologies and distinguish themselves by the lowest CO, OGC and PM_1 emissions of all systems tested. Within this category the average PM_1 emissions increase from the pellet boiler (6.0 resp. 6.2 mg/MJ) over the wood chip boiler (13.6 resp. 15.3 mg/MJ) to the logwood boiler (14.2 resp. 17.6 mg/MJ). The leading role of the pellet boiler with respect to emissions can be explained by the fact that wood pellets are an extremely homogeneous fuel and therefore, no influences of the varying fuel quality can lead to disturbances of the combustion process. The logwood boiler on the other side can be operated at extremely low PM_1 emissions during stable operation phases (see Figure 4), however, due to the much more pronounced emission peak during start-up and during recharging the average PM_1 emissions are higher than those of the pellet boiler.

The second category involves modern natural draught systems (stove and tiled stove). With both systems about the same emission ranges for CO could be achieved, while for OGC and PM_1 emissions the tiled stove performed slightly better than the stove. However, the PM_1 emissions of these systems are about 5 to 8 times higher compared to the emissions of the pellet boiler and 2 to 3 times higher than the emissions of the modern logwood boiler.

The old technology logwood stove as well as the old technology logwood boiler represent the third category. Comparing the old logwood stove with the modern one, an increase of the CO and OGC emissions by more than 100% and of the PM_1 emissions by 20 to 60% must be mentioned. The worst results regarding emissions were gained from the test runs with the old logwood boiler. 10 to 15 times higher CO and OGC emissions than with the modern technology were determined. The PM_1 emissions were 5 to 8 times higher.

The mean values of the emissions over the test runs also clearly show the interdependencies between burnout quality and formation of gaseous and particulate emissions. As Figure 5 shows, a clear correlation between the CO and OGC emissions exists (R^2=0.9809, $p<0.05$). Moreover, Figure 6 underlines that with decreasing burnout quality (increasing CO emissions) also the PM_1 emissions significantly increase. Again, a direct correlation prevails (R^2=0.7538, $p<0.05$).

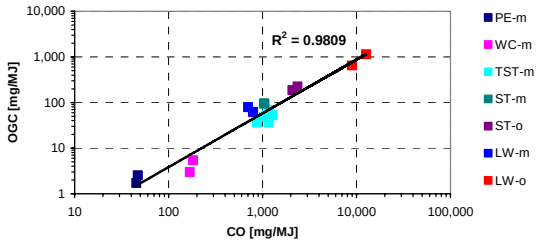


Figure 5: CO vs. OGC emissions

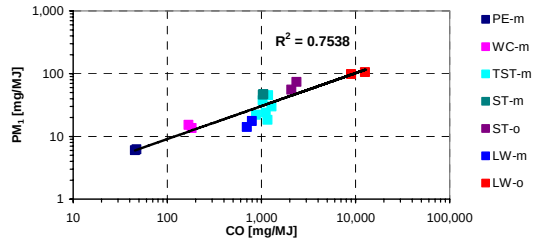


Figure 6: CO vs. PM_1 emissions

4.3 Chemical composition of the PM samples

PM emission samples taken with the BLPI have been analysed according to the methods mentioned in section 3.5. Based on the elemental composition of the samples their composition with respect to different chemical compounds has been estimated. Therefore, the following approach was applied. Since it is known that alkaline metals (K and Na) in aerosols are usually bound as sulphates, chlorides and carbonates firstly the alkaline sulphate concentration was calculated based on the assumption that all sulphur is bound by the alkaline metals. The same assumption was made for chlorine. The remaining alkaline metals, left over after the formation of chlorides and sulphates, where estimated to be bound as carbonates. All other elements detected (mainly Ca, Mg, Si and Zn) are assumed to be bound as oxides.

In Figure 7 the chemical compositions of BLPI samples taken during the test runs are summarised. The upper diagram shows the compositions of the inorganic fraction of the aerosols while the other diagram displays the overall composition of the samples (inorganic and carbonaceous part). The inorganic fraction of the PM_1 emissions mainly consists of alkaline metal compounds. With the exception of the old logwood boiler and the modern stove, where higher shares of alkaline carbonates respectively other oxides are found, alkali metal sulphates clearly dominate the aerosol composition. For

all samples with exception of the one from the modern stove alkaline metal compounds account to more than 80% of the total inorganic particles mass.

Regarding the analyses of the overall compositions of the particle samples, element recovery rates of more than 90% could be achieved (see Figure 7, lower diagram). With increasing aerosol emissions the concentrations of carbonaceous compounds clearly increase. While for the aerosols from the pellet boiler the concentrations of elemental and organic carbon were below the detection limit, they slightly increased for the wood chip boiler and the modern logwood boiler. Higher concentrations were determined for the stoves and the highest ones for the old logwood boiler. While for the stoves the elemental carbon emissions dominate the carbonaceous aerosol fraction, organic carbon is higher concentrated in the particles from the old logwood boiler. These results confirm that a basic PM_1 emission level is provided by the formation of inorganic aerosols (which is comparable for all the systems tested) and that the further increase of the emissions is caused by the formation of organic aerosols as well as soot emissions due to decreasing burnout quality.

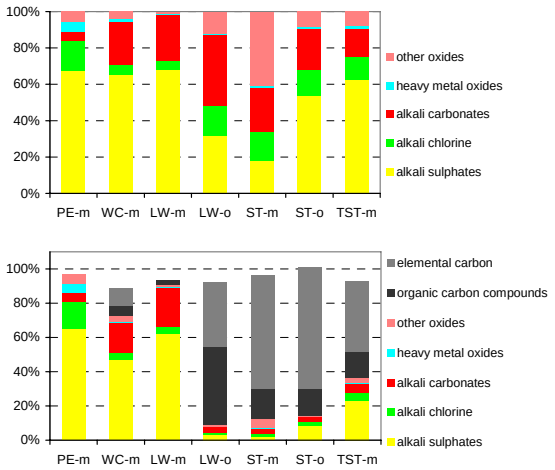


Figure 7: Chemical composition of PM_1 samples
Explanations: samples taken with the BLPI; organic carbon compounds = organic carbon determined * 1.4

Special attention was paid to the determination of the PAH concentrations in the particle samples since PAHs are known to be of significant health relevance. A fraction of the pooled, extracted DGI samples which have also been used for the toxicological tests has been analysed regarding in total 30 different PAHs. In Table III the results of these analyses are summarised related to three different categories of PAHs, namely the total of all PAHs analysed, the total of genotoxic PAHs defined by the WHO-ICPS (13 PAHs) and the genotoxic PAHs defined by the EU directive 2004/107/EC (6 PAHs). The results are given in µg/Nm³ and were calculated from the PAH concentrations in the PM sample analysed and the average PM emission measured for the respective test run.

As Figure 8 shows a clear but not significant correlation between the total PAH emissions and the total of the 13 genotoxic PAHs defined by the WHO exists (R^2=0.9813, p>0.05). About the same correlation was found for the total emissions of the 30 PAHs and of the 6 genotoxic PAHs according to the directive 2004/107/EC.

Table III: Particle bound PAH emissions determined for the different test runs
Explanations: data in µg/Nm³ related to dry flue gas and 13 vol% O_2 [a] … total PAHs determined (30 PAHs); [b] … genotoxic PAHs defined by WHO-IPCS criteria [19]; [c] … total of the 6 genotoxic PAH criteria compounds listed in the EU Directive 2004/107/EC [20]

Combustion system	Test run	Total PAH[a]	Geno-toxic[b]	Geno-toxic[c]
PE - m	1	14.6	8.8	2.6
	2	6.0	3.8	1.2
WC - m	1	8.4	4.7	1.2
	2	7.3	4.0	1.0
LW - m	1	103.9	36.9	12.2
	2	104.9	44.5	15.8
LW - o	1	18,853.8	6,474.3	2,191.7
	2	3,385.1	1,413.7	472.5
ST - m	1	465.9	262.7	78.6
	2	263.0	145.7	41.8
ST - o	1	8,786.3	3,725.9	1,522.0
	2	4,561.1	2,402.3	961.1
TST - m	1	98.9	56.1	19.7
	2	80.8	40.2	11.4

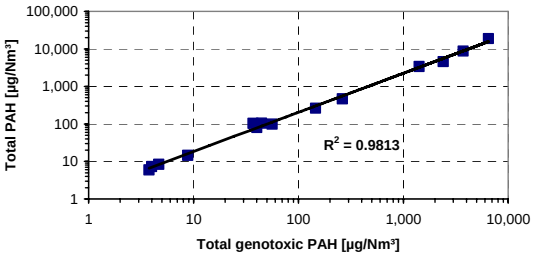


Figure 8: Total PAHs vs. total genotoxic PAHs according to WHO-IPCS [19]
Explanations: data in µg/Nm³ related to dry flue gas and 13 vol% O_2

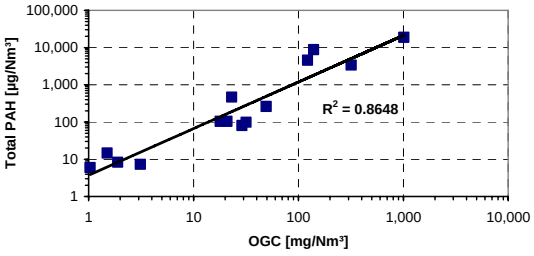


Figure 9: OGC vs. condensed PAH emissions
Explanations: data in µg/Nm³ related to dry flue gas and 13 vol% O_2

In Figure 9 a correlation between the average OGC emissions determined during the test runs and the particle bound PAH emissions (30 PAHs) are presented. As expected, these parameters show a good correlation (R^2=0.8648, p>0.05) which is mainly due to the fact that both are a result of incomplete combustion.

4.4 Toxicological in-vitro tests of PM samples

Mouse RAW264.7 macrophages were separately exposed to four doses (15, 50, 150 and 300 µg/ml) of each PM_1 sample for 24 hours. To rule out possible contaminations of PM samples and methodological

artefacts, each plate on which the macrophages had been placed also contained one untreated well as a cell control (CTRL) and a blank sample (Blank) in a volume corresponding to the dose of 150 µg/ml. The results for these two samples are additionally mentioned in the following diagrams. For a better estimation of the health risks caused by PM_1 emissions from the different biomass combustion systems investigated also results from in-vitro tests with diesel PM_1 (EURO II non-road engine) and urban ambient air $PM_{0.2-1}$ samples from Helsinki are included in the discussion of the results.

Figure 10 shows the results regarding the tumour necrosis factor alpha (TNFα) responses to the PM_1 samples, the cell membrane permeability measured with PI-exclusion test after the exposure to the PM_1 samples as well as the genotoxicity (olive tail moment) of the samples, measured with Comet assay after exposure to the PM_1 samples.

Generally, there is a good agreement concerning the results for the 2 samples of each combustion system tested. Moreover, it has to be pointed out that for all parameters investigated dose dependent responses were gained, which means that with increasing dosage of the PM_1 the reactions of the cells increase.

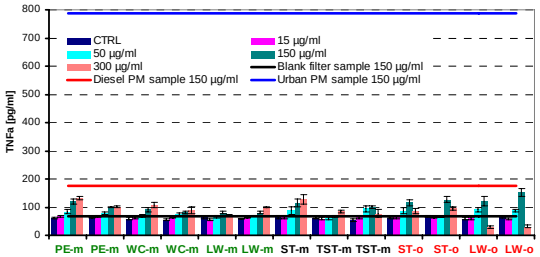
Overall, the TNFα response levels, which indicate inflammatory responses, are low. The response for the old technology logwood boiler derived samples decreases for the largest dose which is due to extensive cytotoxicity detected for these samples. Thus, at a dosage of 300 µg/ml only a reduced number of cells was alive that could produce inflammatory mediators. However, the response levels are quite low compared to the results for urban air PM_1 samples or diesel emission PM_1. The response to the blank sample is almost equal to the unexposed control.

The response levels for chemokine MIP-2 (not shown in Figure 10), which is also an indicator for inflammation, are higher than those for proinflammatory cytokine TNFα. Particles from the old technology logwood boiler are the most potent samples to cause the production of MIP-2 even exceeding the response for diesel PM at the same dose. The responses to the blank sample and the unexposed control did not significantly differ from each other.

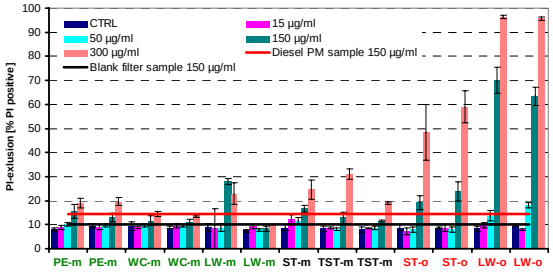
For the PI-exclusion method, which provides a measure for cytotoxicity, the magnitude of the responses varied strongly between the samples. Most of the samples caused statistically significant responses with at least the 150 µg/ml and the 300 µg/ml doses. The PI-exclusion method reveals the permeability of the cell membranes and thus, the fate of the cells. PM_1 derived from the old technology logwood boiler showed the largest response among the samples, causing almost all the cells to be PI-positive (to be dead) with the largest dose. Also the PM_1 samples from the old technology stove caused significantly larger responses than the remaining samples which showed rather modest response levels. The responses gained from the tests with the second sample from the modern logwood boiler, the second sample from the pellet boiler as well as the samples from the wood chip boiler and the tiled stove were on the same level as the response to the blank filter. Diesel PM_1 samples only caused small responses with this method, however, the responses were higher than those caused at the same dose by PM samples from the modern boiler systems as well as the tiled stove.

Almost all the samples caused a dose dependent decrease in cell viability/mitochondrial function when assessed with MTT-test (not presented in Figure 10), which is another indicator for cytotoxicity. In all cases, both samples from the same technology showed similar responses. The modern technology stove was the least and the old technology logwood boiler the most cytotoxic. The modern technology stove and logwood boiler had less cytotoxic particle emissions than the corresponding old technology systems. Cytotoxicity of most of the samples was at a comparable level with the diesel PM_1 and the urban $PM_{0.2-1}$ sample at the same dose whereas no significant trend regarding the responses to samples of automated boilers and batch combustion systems could be derived. However, the mechanism of cytotoxicity may be different.

Tumour necrosis factor alpha (TNFα) responses



Cell membrane permeability measured with PI-exclusion



Genotoxicity (Olive tail moment) of the samples, measured with Comet assay

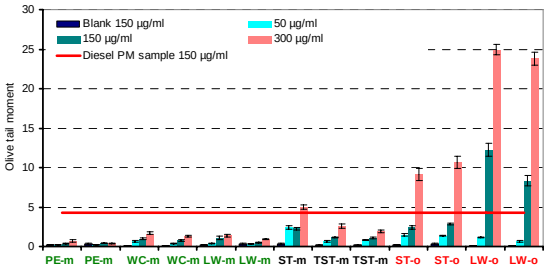


Figure 10: Results of in-vitro studies with PM_1 emission samples from the test runs performed and comparison with results of tests with urban aerosols and diesel engine PM emissions

Explanations: parameters after exposure to PM_1 samples from the different combustion systems investigated; control levels of blank filter sample (Blank), control (CTRL) and four doses (15, 50, 150 and 300 µg/ml) are presented as bars; results for diesel PM_1 sample (EURO II non-road engine) as well as urban (Helsinki) $PM_{1-0.2}$ sample are presented by horizontal lines

All samples investigated caused a dose dependent increase in genotoxicity (risk for cancer development). However, there were five samples (modern and old technology stoves and old technology logwood boiler) that can be considered to cause significant responses in

this method. The by far highest responses were caused by the PM_1 samples from the old technology logwood boiler. Both old and modern stoves caused increased genotoxicity, whereas the increase was more pronounced for the old technology samples. Significantly smaller responses were detected for the modern boiler systems as well as the tiled stove. With the exception of the old technology logwood boiler the responses for all other samples are (in most cases significantly) below the responses gained from the tests with diesel exhaust PM_1 at the same dose.

In Table IV a ranking of the results gained from the tests with the same particle mass dose (150 µg/ml) regarding the parameters presented in Figure 10 is summarised. The value 1 is thereby given to the lowest response detected while the other values are calculated from dividing the response by the lowest response detected.

Table IV: Ranking of selected results of the in-vitro tests
Explanations: s.o … the sample was omitted from the analysis due to high possibility of contamination; Diesel PM sample … diesel PM sample (EURO II non-road diesel, EN590 fuel); Urban PM … urban PM samples from Helsinki, n.a. … not applicable for comparison; bold number: lowest response detected

Combustion system	Test run	TNFα	PI-ex	Comet
PE - m	1	1.8	1.9	**1.0**
	2	1.5	1.6	1.2
WC - m	1	1.3	1.4	2.7
	2	1.2	1.3	2.1
LW - m	1	1.2	3.3	3.0
	2	1.2	**1.0**	1.4
LW - o	1	1.8	8.4	33.4
	2	2.3	7.6	22.7
ST - m	1	s.o	s.o	s.o
	2	1.7	2.0	6.3
ST - o	1	1.7	2.3	6.5
	2	1.9	2.8	7.8
TST - m	1	**1.0**	1.5	3.2
	2	1.5	1.4	2.9
Comparison to diesel and urban PM samples				
Diesel PM		2.6	1.7	11.7
Urban PM		11.7	n.a	n.a

5 SUMMARY AND CONCLUSION

Combustion tests with 7 different old and modern residential biomass combustion systems have been conducted simulating real life whole day operation cycles. During these test runs the gaseous and particulate emissions have been measured and PM_1 samples have been forwarded to chemical and toxicological tests. Therefore, for the first time, comprehensive data concerning gaseous and PM emissions of different old and modern residential biomass combustion systems, the chemical characterisation of their PM_1 emissions as well as the potential of these PM_1 emissions for causing health risks are available.

From the emission data it could be derived that the burnout quality significantly decreases from modern automated residential biomass combustion systems (pellet, wood chips and logwood boilers) over modern natural draught stoves and tiled stoves to old technology stoves and logwood boilers. As an example the average CO emissions over the whole operation cycle increased from the pellet boiler (45.4 to 47.1 mg/MJ) over the modern logwood stove and the tiled stove (1,000 to 1,200 mg/MJ) and the old technology logwood stove (2,100 to 2,350 mg/MJ) to the old technology logwood boiler, which showed exceptionally high emissions of up to 12,600 mg/MJ. A pronounced correlation between the average CO and OGC emissions could be detected. Moreover, also the average PM_1 emissions ranging from around 6 mg/MJ for the pellet boiler to about 106 mg/MJ for the old technology logwood boiler correlated well with the OGC and CO emissions. As chemical analyses of PM_1 samples taken during the test runs have shown, the concentrations of organic carbon and soot increase with decreasing burnout quality and consequently, the higher PM_1 emissions at low burnout quality are attributed to the formation of carbonaceous aerosols. Moreover, it has been shown, that the particle bound PAH emissions also correlate with the OGC emissions and consequently with the burnout quality.

As the toxicological studies performed with the particle samples gained from the test runs have shown, the combustion technology, respectively the burnout quality that is achieved, have a large role in the in-vitro responses caused by the particulate emission samples. The old technology logwood boiler was in its own class to cause both inflammatory and cytotoxic responses in the macrophages and also caused markedly increased genotoxicity. By these results, it is obvious that incomplete combustion is associated with larger toxic potential when compared to more complete combustion. This effect was also seen, but less dramatically, by comparing the old and modern technology stoves. On the other hand, PM_1 emission samples from wood chip and pellet boilers caused consistently the lowest response levels among the samples, except for cytotoxicity detected with MTT-test. Also the modern logwood boiler and the tiled stove samples had low response levels.

The lower response levels were also mostly associated with the combustion systems that showed lower PM_1 emission levels. This further widens the gap between the modern and the old technologies in terms of health risks. Most likely the cytotoxic responses of the PM_1 emissions from the pellet boiler and the wood chip boiler are associated with the inorganic compounds which dominate the composition of the samples. Moreover, the activated cellular pathway leading to cytotoxicity associated with these systems is probably of different type compared to those of the e.g. old technology logwood boiler or diesel PM_1 samples. This interpretation is also supported by the present finding that the particulate samples from old technology devices caused generally larger genotoxic responses than those from modern combustion systems.

In general these results suggest that the burnout quality that can be achieved in a combustion system mainly affects the relative harmfulness of the particulate emissions. This has implications in the mechanisms behind the adverse health effects. The responses induced by the present state-of-the-art combustion system derived particulate samples (modern pellet, wood chip and logwood boiler, stoves) were lower than those caused by the diesel PM_1 sample indicating that these PM emissions are less harmful. On the other side, the PM emissions of the old technology logwood boiler and old technology stove showed consistently more pronounced responses in most of the parameters than diesel PM. When compared to the urban air $PM_{0.2\text{-}1}$ samples in the same size range,

none of the emission particles from the biomass combustion systems investigated were even close to levels gained for inflammatory parameters. However, mineral composition in urban air is the major determinant of inflammatory responses. Concerning cytotoxicity urban air particulate samples and the PM_1 emissions of the combustion systems investigated were at the similar level.

Based on the data presented in this paper it can be concluded that the most efficient way to reduce health risks caused by residential biomass combustion is to optimise burnout. This leads (i) to decreased emission factors for PM_1, (ii) lower concentrations of carbonaceous compounds in the PM emissions and consequently (iii) less hazardous particles. The test runs performed have shown that modern residential biomass combustion systems show a significant improvement regarding this issue compared with old systems. Therefore, comprehensive efforts should be made in order to substitute old residential biomass heating systems, which distinguish themselves by incomplete combustion by modern state-of-the-art technologies. Moreover, additional efforts should be made to further develop modern residential biomass combustion systems in order to optimise burnout and minimise PM emissions, especially during partial load operation and under transient combustion conditions.

Further investigations and evaluations based on the data gained from the project are presently ongoing and are dedicated to a more comprehensive evaluation of other parameters which could have a potential influence on the toxicity such as for instance the heavy metal contents of the PM emissions.

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