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BIOMASS COMBUSTION IN RESIDENTIAL HEATING: PARTICULATE MEASUREMENTS, SAMPLING, AND PHYSICOCHEMICAL AND TOXICOLOGICAL CHARACTERISATION

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BIOMASS COMBUSTION IN RESIDENTIAL HEATING: PARTICULATE MEASUREMENTS, SAMPLING, AND PHYSICOCHEMICAL AND TOXICOLOGICAL CHARACTERISATION

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Tiivistelmä
Kymmenen eurooppalaista tutkimusryhmää muodosti tutkimuskonsortion, joka koostui biomassan käytön, hiukkastutkimuksen ja terveystutkimuksen asiantuntijoista. Projektissa tarkasteltiin biomassan palamisessa syntyviä hiukkaspäästöjä sekä niiden mittaamista monitieteiseltä pohjalta.

Tutkimuksessa koottiin maakohtaiset tiedot Suomessa, Itävallassa, Saksassa ja Ruotsissa tehdystä viimeaikaisesta tutkimuksesta, joka koskee biomassan pienpolton pienhiukkaspäästöjä, ja niistä aiheutuvia terveysvaikutuksia.

Tutkimuksessa annettiin suosituksia biomassan pienpolton päästöjen mittaamisesta sekä niihin liittyvästä terveysvaikutustutkimuksesta.

Avainsanat
Biomassan pienpoltto, pienhiukkaset, päästöjen mittaus, toksikologia

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CLEAN BIOMASS COMBUSTION IN RESIDENTIAL HEATING: PARTICULATE MEASUREMENTS, SAMPLING, AND PHYSICOCHEMICAL AND TOXICOLOGICAL CHARACTERISATION

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Title
Biomass combustion in residential heating: particulate measurements, sampling, and physicochemical and toxicological characterisation.

Abstract
Ten European research teams in the field of biomass energy use, particle research and particle health effects formed a research consortium to evaluate the particle emissions formed in biomass combustion as well as the emission measurement techniques on a multidisciplinary basis.

Results from recent Finnish, Austrian, German and Swedish studies concerning particle emissions from biomass combustion and their health effects were summarized in the form of country reports. Recommendations and best practice procedures were given on the particle emission measurement from biomass combustion and investigation of the health effects of particulate emissions.

Keywords
Residential biomass combustion, fine particles, emission measurement, toxicology

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FOREWORD

This work is the final report of the research project "Clean biomass combustion in residential heating: particulate measurements, sampling, and physicochemical and toxicological characterisation (BIOMASS-PM)".

The BIOMASS-PM-project belonged to the ERA-NET Bioenergy Programme. The research partners in the project and the representatives of the organizations in the management committee were from **(a)** Finland: University of Kuopio (Prof. Jorma Jokiniemi, MSc Kati Hytönen), National Public Health Institute (Doc. Raimo O. Salonen) and Finnish Meteorological Institute (Prof. Risto Hillamo); **(b)** Austria: Graz University of Technology (Prof. Ingwald Obernberger); **(c)** Germany: Technology and Support Centre of Renewable Raw Materials (PhD Hans Hartmann) and Fraunhofer Institute of Toxicology and Experimental Medicine (PhD Bernd Bellmann), and from **(d)** Sweden: University of Umeå (PhD Christoffer Boman and Assoc. Prof. Bertil Forsberg), Umeå University Hospital (Prof. Thomas Sandström) and Energy Technology Centre in Piteå (Civ. Eng, Lic. Esbjörn Pettersson). The coordinator of the project was Professor Jorma Jokiniemi and the general secretary MSc Kati Hytönen, both from the University of Kuopio. The funding organizations were The Finnish Funding Agency for Technology and Innovation (Tekes), The Austrian Research Promotion Agency (FFG), The Agency for Renewable Resources (FNR) (Germany) and Swedish Energy Agency (Energimyndigheten).

In addition to the management committee members, several other scientists contributed to the project: **(a)** Finland: MSc Jarkko Tissari from the University of Kuopio; Prof. Maija-Riitta Hirvonen, MSc Pasi Jalava, PhD Arto Pennanen, MSc Mikko Happo, PhD Marko Vallius and MSc Piia Markkanen from the National Public Health Institute; and MSc Karri Saarnio, MSc Anna Frey, MSc Sanna Saarikoski, PhD Kimmo Teinilä, MSc Hilkka Timonen, MSc Minna Aurela and PhD Markus Sillanpää from the Finnish Meteorological Institute; **(b)** Austria: PhD Thomas Brunner, Dr. Georg Bärnthaler and Dipl.-Ing. (FH) Joachim Friesenbichler from Graz University of Technology; **(c)** Germany: Dipl.-Ing agr. Peter Turowski, Dipl. Phys Paul Roßmann, Dipl-Ing (FH) Frank Ellner-Schubert from Technology and Support Centre of Renewable Raw Materials; and **(d)** Sweden: MSc Maria Sehlstedt from the Umeå University Hospital and PhD Henrik Wiinikka from the Energy Technology Centre in Piteå.

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CONTENTS

1 EXECUTIVE SUMMARY

Background

Residential biomass combustion has a substantial contribution to the total fine particulate ($PM_{2.5}$; particle diameter < 2.5 µm) emissions in most European countries. This is mainly due to a widespread use of old, un-optimised small-scale biomass combustion systems for woody biomass in residential heating. Because of extensive adverse health effects associated with current ambient air $PM_{2.5}$ concentrations, there is pressure in the EU and many European countries to start or strengthen the regulation of combustion emissions in this sector. It has been recently estimated by the Clean Air for Europe (CAFE) Programme of the European Commission that in the year 2000, mainly due to long-term health effects of $PM_{2.5}$, there were nearly 350,000 premature deaths annually due to cardiovascular and respiratory diseases and cancer in the 450-million populations of the 25 EU member states. Moreover, tens of millions of elderly subjects with chronic lung and heart disease, asthmatic subjects of all ages and young children were estimated to frequently have an increased need for rescue medication and restricted daily activity due to health impairment provoked by $PM_{2.5}$. The total economical losses due to the health damage in 2000 were estimated at 268-781 billion euros (European Commission, 2005).

The present multidisciplinary project consortium consisted of ten internationally well-established research teams from four countries. The purpose of the BIOMASS-PM project was to strengthen the interdisciplinary scientific evidence on the advantages of new combustion technologies and emission after-treatment in small-scale biomass heating systems. Due to intensive research and development work carried out during the last decade, small-scale biomass combustion units have already reached a high technological standard in terms of thermal efficiency and low emissions. However, concerning the reduction of particulate emissions, still further work has to be done (Obernberger, 2004).

Summing up the results and conclusions from the country reports (Austria, Finland, Germany, Sweden), it can be outlined, that in all four countries small-scale biomass combustion technologies play a relevant role by providing 10% - 30% of the total energy demand for residential heating and hot water supply. Moreover, small-scale biomass combustion technologies are the dominating renewable energy source for residential heating. It is also similar for all four countries, that logwood is the most common biomass fuel used in stoves and boilers. However, wood pellets have gained rising interest as fuel for residential heating systems since their market introduction, and this trend is expected to continue.

In all four countries, old biomass combustion technologies (stoves and boilers) dominate the current stock of applications. Since these systems show significantly higher particulate emissions than modern small-scale combustion systems, residential biomass heating has often a relatively high contribution to the total national thoracic particle (PM_{10}; particle diameter <10 µm) and $PM_{2.5}$ emissions and is, therefore, facing increasing criticism. Comprehensive R&D work on the optimisation of small-scale biomass combustion devices has been performed during the last decade and, as a result of this, advanced residential biomass combustion technologies, operating at significantly lower particulate emissions than the old technologies, are already available. The lower particulate emissions have been achieved by improving the combustion conditions in ways that reduce the formation of organic aerosols and soot. However, the changeover from old to new residential biomass combustion systems

has, so far, not taken place. Also the development of secondary measures for particulate emission reduction is in all four countries just in the initial phase. Therefore, the same measures for the reduction of particulate emissions from small-scale biomass combustion can be proposed for Austria, Finland, Germany and Sweden:

- Financial support for the substitution of old combustion devices by modern systems.
- Provision of appropriate "user training" for non-automatically fed systems.
- Support of the R&D of low-particulate-emission combustion technologies.
- Support of the R&D and application of appropriate secondary particulate emission reduction technologies for residential biomass combustion systems.

There were significant differences between the four countries with regard to the existence of particulate emission limits for small-scale biomass combustion appliances. In Finland, no emission limits exist so far, and in Sweden particulate emission limits are fulfilled on a voluntary basis. In Austria, there are particulate emission limits, and it is expected that they will become more stringent within the coming years. The most ambitious emission limits in Europe with regard to particulate matter are soon expected to get into force in Germany (2015 target: 20 mg/Nm³, dry flue gas, 13 vol% O_2). A major problem is that different units and different O_2 reference levels are applied in different countries. Therefore, a harmonisation on a European level is recommended.

One of the main objectives of the project was a determination of feasible methods for particulate emission measurements, sampling and physicochemical characterisation. An appropriate best practise procedure was worked out. One of the most relevant aspects of this best practice procedure should be that it covers the evaluation of the whole process chain, starting from the combustion process (combustion quality, performance of the furnace) followed by particulate sampling, the physicochemical characterisation of particulate emissions, and the evaluation of emission-related health risks. A future aim should be to link the information gained from the physicochemical characterisation of particulate emissions with the results of toxicological studies in order to estimate the health risk potential of the emissions in relation to technologically and economically feasible small-scale biomass combustion systems. Consequently, the approach taken in the BIOMASS-PM project deviates from the commonly applied particulate sampling and measurement techniques, since in these procedures the interface with the toxicological evaluation of particulate emissions has not been taken into account.

Measurement of particulate emissions

The present best practise recommendations must apply to bad burnout conditions as they represent the most important challenge for future R&D of technologies as well as for health protection. As the first step of the procedure, due to presence of the condensable organic species at stove/boiler outlet, a dilution of the flue gas with clean air is recommended. Only clean air (filtered air) should be used for dilution. The dilution ratio has to be monitored continuously by parallel CO_2 or NO_x measurements in the diluted and undiluted flue gas.

The dilution ratio should be high enough to keep the temperature of the diluted flue gas <52°C in order to ensure a full yield of condensable species in particulate phase. The dilution ratio should be in a range of 20 for the full potential of particle formation by condensation of

organic vapours. However, higher dilution ratios can be applied, e.g. in connection to toxicological health studies.

A second important step of the best practise procedure is the determination of the gas phase composition (O_2, CO, CO_2, NO_x, OGC) with conventional flue gas analysers. These gas phase measurements should be performed in the undiluted flue gas at boiler/stove outlet, since conventional flue gas analysers are usually not designed for measurements in diluted flue gas flows.

The total emission of particulate matter should also be determined in undiluted gas due to two reasons. First, this procedure enables a comparison of the results from small-scale biomass combustion installations with those obtained from boiler tests that are usually performed without dilution. Second, losses of coarse fly ash particles occur during dilution, which means that a measurement in diluted flue gas would lead to an underestimation of the total particulate matter emission. The measurements should always be performed according to the respective test standards.

A stepwise chemical analysis procedure is recommended, so that the level of characterisation can be adjusted to different purposes. A basic fractionation into soot, organic and inorganic matter is currently highly relevant. There can be also fractionation of the carbonaceous matter into elemental (EC) and organic (OC) carbon. Further fractionation and speciation of the organic and inorganic matter can be performed, especially in scientific studies. The concentrations of known genotoxic PAHs in particulate phase emissions are of great interest.

Concerning all analysis methods mentioned above, it is important to adjust the pre-treatment, conditioning, handling and storage of the sampling substrates to the demands of the respective analysis method. As the dilution ratio applied during sampling may influence the chemical composition of particulate emissions, it should always be reported in connection to the results of chemical characterisation.

For automated furnaces in continuous operation, it is recommended to perform the measurements and particulate sampling at stable full-load and minimum load operations. For automated furnaces in on/off operation (especially relevant for Sweden), the tests should be done according to the Swedish P-marking regulations. Concerning batch combustion systems, also the first full batch or kindling wood ignition should be included in the test. Sampling during this first batch should start as soon as the CO_2 concentration exceeds 1 vol%. For all subsequent batches sampling should start at the beginning of the batch and should end as soon as the CO_2 concentrations decrease below 4 vol%.

When applying the present best practise procedure, the chemical and physical characterisation of particulate emissions from biomass combustion can be adjusted to the level of information needs for different purposes.

Investigation of health effects of particulate emissions

Aerosol exposure systems with on-line diluted flue gas from combustion installation are used in experimental human and animal studies. Also re-aerosolization of combustion emission particles collected in advance with, e.g. electrostatic precipitator, has been used in animal studies. Alternatively, one may collect size-segregated emission particles from diluted exhaust

and instill them in aqueous medium directly to cell culture or under visual control to the lower airways of experimental animals e.g. mice or rats.

Common requirements for both the aerosol exposure and the particulate collection method are:

- Evaluate the characteristics of the exposure system in advance using standard aerosol monitoring and sampling methods as reference.

- Avoid carefully any external contamination of the combustion emission particles and use methodologically similar sham exposure to filtered air or blank samples that control all stages of particulate sample handling.

- Report always the combustion technology, fuel and condition as well as the dilution ratio, temperature and the results from gaseous and particulate monitoring and chemical speciation as background information in the toxicological study report.

- The most important size range to be investigated in toxicological studies is PM_1. However, investigation of the coarse (> 1 μm) particles, mostly fly ash, or separation of the ultrafine particles (< 0.1/0.2 μm) from other submicron fine particles may be motivated in connection to some technologies or biofuels, or special health issues of interest.

- The non-toxicity of particulate sampling substrate needs to be confirmed in cell tests made in advance. The substrates should be pre-cleaned before sampling using the same solvent and cleaning protocol as in the actual particulate extraction. Blank substrates are processed similarly to the ones used in particulate sampling.

- Particulate collection needs to be done with dilution and cooling the flue gas <52 °C to include condensable material in particulate phase emission.

- After particulate sampling, collection substrates must be protected from sunlight and removed as quickly as possible for storage at -20 °C. For subsequent weighing and extraction, the frozen substrates and particulate material need be conditioned at room temperature for 4 hours in closed containers, followed by 16–18 hours in open containers before weighing.

Toxicological cell and animal studies need at least tens of milligrams of biomass combustion particles per size range and test condition, so that the same particulate material can be used for testing several different end-points as well as making chemical analyses of interest (e.g. ions, total and water-soluble elements, PAHs). Tens to hundreds of milligrams of size-segregated particulate mass have been recently collected from wood combustion experiments using a high-volume cascade impactor (HVCI). It collects particles at high volume (850 litres/min) in four size ranges ($PM_{0.2}$, $PM_{1\text{-}0.2}$, $PM_{2.5\text{-}1}$, $PM_{10\text{-}2.5}$), and the collected particulate mass can also be extracted from the sampling substrate, i.e. porous polyurethane foam, with a high 80-90% efficiency.

One of the main motivations for toxicological studies is to provide scientific evidence on the biological plausibility of adverse health effects reported in epidemiological studies. Experimental human and animal studies can be conducted on a limited number of research questions on biomass combustion aerosol due to ethical reasons and elaborate study setups, but toxicological cell studies can be utilized more flexibly to reveal the toxicity profiles of multiple combustion conditions. It can be stated that the traditional test of mutagenic activity in bacterial cell cultures (Ames′ test) should be mostly replaced by modern test batteries in cultured mammalian cells like macrophages and respiratory epithelial cells. In all toxicological setups, the dose-dependency and time-dependency of the different kind of response endpoints to biomass combustion particulate samples need to be known to avoid false negative findings.

The inflammatory activity of air particles has been linked for a long time to exacerbation of pulmonary diseases like asthma and chronic bronchitis, but more recently it has been suggested to contribute to atherosclerosis and acute vascular events such as cardiac infarction and stroke. Tissue damage induced in the lungs and other organs by combustion-derived particles can be also mediated, at least partly, by direct cytotoxicity, i.e. via increased apoptotic, i.e. programmed, cell death or un-programmed necrotic cell death, or via inhibition of DNA synthesis in the cells.

Genotoxicity is primarily regarded as the mechanism leading to increased carcinogenic risk. In connection to research on biomass combustion-derived particles, Comet assay can be used as a relatively easy and quick screening test of DNA damage. Its information can be complemented, e.g. by the more elaborate micronucleus test and PAH-DNA adduct test.

Future directions

It is obvious that the field of residential biomass combustion would much benefit from a European-wide harmonization of the emission test methods and procedures. Interdisciplinary research involving both the combustion and aerosol scientists as well as toxicologists on several topics is needed:

- More detailed comparison of different sampling and dilution methods is needed to define a standard method for the measurement of fine particle emission from residential biomass combustion installations.

- Further technological R&D is needed to improve both the primary measures (combustion and control systems) and the secondary measures (emission after-treatment) to reduce particulate emissions from small-scale biomass combustion systems.

- More information on the impact of real-life user practices on particulate emissions is needed as well as on the overall impact of small-scale biomass combustion emissions on local and regional air quality.

- More information is needed about the association between different kinds of particulate matter emissions from biomass combustion installations and their adverse health effect potential as assessed by experimental human and animal studies. Cardiovascular endpoints should be investigated in addition to respiratory endpoints. This would increase information about the biological plausibility of adverse health effects reported in epidemiological studies.

- Cell studies should provide a generic concept on the association of inorganic and organic chemical constituents with the inflammatory, cytotoxic and genotoxic activities of particulate emissions from a series of combustion technologies and biofuels. The representativeness of the results should be confirmed in selected experimental animal and human studies. This information would help the regulator to give emission limits to some potentially highly toxic constituents (e.g. PAHs), the industry to direct its product development towards health-wise cleaner and safer combustion installations, and the consumer to adapt for good operational practice.

It would be advantageous also to promote interdisciplinary research between the aerosol scientists and epidemiologists:

- New short-term panel studies with personal exposure monitoring and source-specific exposure modelling are needed. Contributions of biomass combustion source-specific outdoor $PM_{2.5}$ to indoor $PM_{2.5}$ should be assessed as well as lung dosimetry in relation to the physico-chemical properties of the particles (e.g. fresh emission nearby vs. aged regional emissions).

- GIS-based cohort studies on chronic respiratory and cardiovascular diseases and cancer are needed. Data on household heating appliances and relevant particulate emission factors need to be up-to-date, because they are in constant change due to altered appliance types and improvement of technologies.

The topics suggested for future research collaboration between the present research partners of the BIOMASS-PM project should be considered for funding in the 7th Framework Programme of the European Commission or ERANET-type collaboration of national funders.

2 PROJECT DESCRIPTION

2.1 INTRODUCTION

Residential biomass combustion has a substantial contribution to the total fine particulate ($PM_{2.5}$; aerodynamic particle diameter < 2.5 µm) emissions in most European countries. This is mainly due to a widespread use of old, un-optimised small-scale biomass combustion systems for woody biomass in residential heating. Because of extensive adverse health effects (e.g. about 350,000 excess deaths annually) associated with current ambient air fine particulate ($PM_{2.5}$) concentrations, there are pressures in the EU and many European countries to start regulation of combustion emissions in this sector. However, it is very difficult, because currently there are no common European test standards or EU regulatory limits for particulate emissions from small-scale biomass heating systems. Moreover, there is little scientific evidence on the source-specific harmful characteristics of the particulate matter including small-scale biomass combustion. For instance, it is not known how harmful the inorganic constituents of fly ash are to human health in comparison to the organic particles derived from poor combustion.

2.2 OBJECTIVES

Within this project a multidisciplinary consortium of ten internationally well-established research teams from four countries was formed. The purpose of the BIOMASS-PM project was to strengthen the interdisciplinary scientific evidence on the advantages of new combustion technologies and emission after-treatment in small-scale biomass heating systems.

The project covered the impact pathway from particulate emission source (biomass furnace) to the effects of particulate emissions on human health. The project partners focused their multilateral efforts on data and methodologies that can be applied for future development and documentation of clean combustion and emission control technologies in residential biomass heating systems.

The project had three more detailed objectives to reach its overall aim:

1. Evaluation of the present scientific data on particulate emissions from different small-scale biomass heating systems as well as on their causative physicochemical characteristics and harmful biological endpoints to human health.
2. Evaluation of the feasibility of methods currently used in the multidisciplinary particulate research on small-scale biomass heating systems.
3. Preparation of a best practise procedure for the overall interdisciplinary evaluation of the particulate emissions in future.

More detailed objectives are presented in subchapter 2.6.

2.3 PROJECT BACKGROUND

The project focused on particulate emissions from residential biomass heating systems within a capacity range of <200 kW_{th} (nominal boiler load). Since in this capacity range, mainly woody biomass is used as fuel, the project mainly dealt with woody biomass but also other fuel types (e.g. straw) were considered as possible future options for such heating systems. The project dealt with the whole impact pathway from particulate emission source (small-scale biomass plant) to the effects of particulate emissions on human health with special emphasis on characterisation of the role of new combustion technologies and emission after-treatment in prevention of harmful impacts on air quality and human health (Fig. 1).

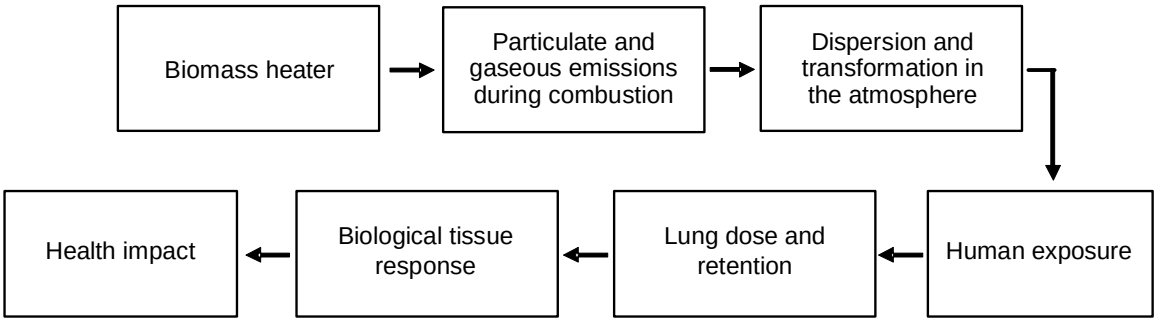


Figure 1: Chain of events from a residential biomass heating system to the effects of its particulate emissions on human health.

2.3.1 Technological development and emission measurements for clean combustion and emission control in residential biomass heating systems

Due to intensive research and development work carried out during the last decade, small-scale biomass combustion units have already reached a high technological standard in terms of thermal efficiency and low emissions. However, concerning the reduction of particulate emissions still further work has to be done (Obernberger, 2004).

Due to the fact that presently the total dust emissions from state-of-the-art small-scale combustion units do not exceed the respective emission limits, also no considerable efforts have been put on the development of particulate emission control devices for these plants. In principle, the application of baghouse filters or electrostatic precipitators (ESP) would be feasible options but these devices are currently applied only to large-scale systems. Therefore, they are generally not economically affordable for small-scale systems. Presently, R&D projects dealing with the development of aerosol precipitation devices for small-scale biomass combustion plants are ongoing but presently only one system is available on the market (ESP Zumik®on, Ruegg Cheminée AG, Switzerland).

All actual European and national regulations concerning particulate emissions from combustion processes regulate the total dust emissions. Consequently, simple gravimetric methods are usually applied to determine the total dust concentration in the flue gas. The disadvantage of these methods is that they are firstly discontinuously operating and secondly do not provide any information about the particle size distribution of the particulate emissions. Due to the increasing interest in the PM_{10} and $PM_{2.5}$ emissions, special impactors such as the Johnas II impactor have been developed in order to determine the emissions of these fractions.

However, also these impactors are discontinuously operating and do not provide any information about fluctuations of the emission over time. For a continuous monitoring of particulate emissions from biomass combustion units, mainly three technologies are commonly applied, namely electrical impactors, FMPS (Fast Mobility Particle Sizer) and SMPS (Scanning Mobility Particle Sizer) systems. However, these systems are very expensive compared to conventional gravimetric systems and, additionally, well educated and experienced personnel is needed to operate the equipment and to interpret the measurement results. Other current on-line technologies for particle concentration measurements (e.g. based on light scattering) are not precise enough and can only be applied as indicators for filter performance.

Particulate sampling for subsequent physicochemical analyses requires careful consideration of the sampling conditions (dilution, temperature) as well as the substrate material of the impactor. One problem with the conventional low volume samplers (especially with $PM_{2.5}$ and finer size ranges) is that the particle mass sampled may be limited for extensive chemical analyses.

2.3.2 Health impacts of fine particulate pollution from residential biomass combustion

The current ambient air $PM_{2.5}$ concentrations pose the greatest disease burden of all environmental exposures to the European populations. It has been recently estimated by the Clean Air for Europe (CAFE) Programme of the European Commission that in the year 2000, mainly due to long-term health effects of $PM_{2.5}$, there were nearly 350,000 premature deaths annually due to cardiovascular and respiratory diseases and cancer in the 450-million populations of the 25 EU member states. Moreover, tens of millions of elderly subjects with chronic lung and heart disease, asthmatic subjects of all ages and young children were estimated to frequently have increased medications and restricted daily activity due to health impairment provoked by $PM_{2.5}$. The total annual, direct and indirect, economical losses due to the health damage in 2000 were estimated at 268-781 billion euros (European Commission, 2005).

The current $PM_{2.5}$ emissions from residential biomass combustion have been estimated to contribute by about 20% to the total $PM_{2.5}$ emissions in the EU. The contributions in different countries can vary - for instance, in the Nordic countries a range from 12% to 67% has been estimated some years ago, with Finland and Sweden at around 40% (Sternhufvud et al., 2004). Moreover, a large part of the total polycyclic aromatic hydrocarbon (PAH) emissions have been attributed to residential biomass combustion.

It has been estimated in European and US residential communities with prevalent residential heating with old, un-optimized small-scale biomass combustion systems that the contribution of particulate pollution from these sources to the local ambient air $PM_{2.5}$ concentration can be 20-90% (Boman et al., 2003). Recently, it has been estimated from combined ambient air and chimney top measurements that just two households with the poorest combustion technologies and wood use were responsible for a large part of the highly increased ambient air PM_{10} and PAH concentrations in a residential area in Copenhagen (Glasius et al., 2006). Similarly, in a residential area with prevalent old small-scale wood combustion plants in Espoo, Finland (near Helsinki), the hourly and daily PM_{10} concentrations during weak winds in October 2005 exceeded the corresponding concentrations in busy traffic environments of Helsinki

(Myllynen et al., 2006). Thus, the close-to-the-ground particulate emissions from residential biomass heating systems have a potential for stronger than average local air quality impacts. This includes also penetration from outdoors to indoors (without effective air filtration) and leads to stronger than average personal exposures.

The scientific literature of impacts on ambient air quality and human health of particulate matter in areas with prevalent residential biomass combustion have been reviewed by Boman, Forsberg and Järvholm (Boman et al., 2003) and Naeher et al. (2007). There are only few epidemiological studies on mortality associations but more studies on hospital admissions and symptoms in asthmatic subjects, in whom there have been often stronger than average exposure-response relationships when compared to general urban environments.

The scientific literature on toxicity of particulate matter from wood combustion has been reviewed by Zelikoff et al. (2002). In experimental exposures of animals, wood combustion particles have induced inflammatory reactions and structural damage in the lungs as well as impaired immunological defence systems against bacterial infections. Wood combustion particles have also been genotoxic in several cell studies. More recently, mild pulmonary and systemic inflammation and an increased tendency towards blood coagulation have also been found in recent experimental human exposures to emissions from wood combustion (Barregård et al., 2006).

So far, the findings of toxicity in published studies have not been connected to the particulate characteristics (e.g., size, chemical composition) or source characteristics (good control vs. bad control of emissions). However, the research partners of the present project have on-going research projects on these important aspects.

2.4 METHODS

The research consortium summarised relevant standards, data and experiences concerning particulate emissions from residential biomass heating systems as well as of methods for measurement, sampling, and physicochemical and toxicological characterisation of particulate emissions from biomass combustion in the countries represented by the project partners and compared the results with the published literature from other countries. The present multidisciplinary methodologies were evaluated and feasible methods that can be recommended for use in future research and development were determined. On the basis of the current limited data, the critical physicochemical parameters of particulate emissions from residential biomass combustion with regard to particulate-induced health effects were identified. Finally, a best practise procedure for the overall interdisciplinary evaluation of particulate emissions from residential biomass combustion considering all relevant interfaces between measurements and sampling as well as physicochemical and toxicological characterisation was prepared.

Due to time and budget limitations the project could not conduct new experimental work but rather focused on an in-depth evaluation of methodological issues including refined analysis and interpretation of the newly achieved results of the partner teams in recently conducted and on-going national research projects.

2.5 INNOVATIVE CONTRIBUTION OF THE PROJECT

All over Europe different national or local standards concerning the measurements of particulate emissions from residential biomass heating systems are currently applied. Consequently, a great diversity of methods and procedures is used in particulate measurements, sampling and physicochemical characterisation of the particulate emissions. No systematic evaluation of these methodologies has been made, and there is rarely any toxicological characterisation of the particulate emissions. This situation makes it difficult for the European Union and national authorities to compare the emission test results from different countries and to be sure that a compliance with various emission standards based on particulate mass really reduces health risks among susceptible population groups. One of the main future research needs in the EU Thematic Strategy of Air Pollution (European Commission, 2005) up to 2020 is the identification of the responsible emission sources and causative physicochemical factors for particulate air pollution-induced health effects among susceptible population groups like cardio-respiratory patients and small children.

The project produced a multidisciplinary scientific basis for a European-wide harmonisation of the emission test methods and procedures for residential biomass heating systems. This will enable, on a common basis, a future research collaboration between the participating research partners for instance in the 7th Framework Programme of the European Commission. The project can also have inputs to the development of a European standard for measurement of particulate emissions from solid fuel burning appliances (CEN/TC 295/WG5 N55/2006). Professor Jorma Jokiniemi from UKU is a member of the CEN expert panel. Currently the standard development concerns only total particulate mass, but the results from the project can promote a development of future standards for relevant sampling and physicochemical characterisation of particulate emissions.

2.6 CONSORTIUM DESCRIPTION

2.6.1 Partners

The following partners formed the multidisciplinary consortium:

- University of Kuopio, Department of Environmental Science, Fine Particle and Aerosol Technology Laboratory (UKU), Finland
- National Public Health Institute, Department of Environmental Health (KTL), Kuopio, Finland
- Finnish Meteorological Institute, Air Quality Research (FMI), Helsinki, Finland
- Graz University of Technology, Institute for Process Engineering (TUG), Austria
- Technology and Support Centre of Renewable Raw Materials (TFZ), Straubing, Germany
- Fraunhofer Institute of Toxicology and Experimental Medicine (FHG), Hannover, Germany
- Umeå University, Energy Technology and Thermal Process Chemistry (UUE), Sweden
- Energy Technology Centre in Piteå (ETC), Sweden
- Umeå University Hospital, Department of Respiratory Medicine and Allergy (UUH), Sweden
- Umeå University, Department of Public Health and Clinical Medicine (UUP), Sweden

2.6.2 Project management

The project was coordinated by professor Jorma Jokiniemi (UKU). The coordinator and work package leaders formed the steering group of the project. The principal decision-making organization of the project was the management committee, which consisted of the leaders of ten partner teams.

The project was structured into two work packages (WP): (**1**) Biomass combustion technology and particulate emissions, and (**2**) Health effects of biomass combustion-derived particles. The work performed in each work package was arranged in four periods, of which each was finalised with a project workshop, where all partners participated (Tab. 1).

Table 1. Tasks, workshops, milestones and deliverables by workperiods.

Date:	**Jan-Jun 2007**	**Jul-Oct 2007**	**Nov 2007-Jan 2008**	**Feb-March 2008**
Workpackage	**Period 1-6 months**	**Period 7-10 months**	**Period 11-13 month**	**Period 14-15 months**
WP1: Biomass combustion technology and particulate emissions	Definition and division of tasks. Country reviews on current methods, protocols and data available on measurement, sampling and physicochemical analysis of particulate emissions.	Evaluation of the current methods and protocols used for measurement, sampling and physico-chemical analysis of particulate emissions. Assessment of interfaces with ambient air quality impacts.	Definition of feasible methods and protocols to be used in future measurement, sampling and physico-chemical analysis of particulate emissions. Assessment of interfaces between the methods and with WP2.	Definition of the best practise guideline for the methods and protocols in measurement, sampling and physico-chemical analysis of particulate emissions. Setting targets for future research collaboration.
WP2: Health effects of biomass combustion-derived particles	Definition and division of tasks. Country reviews on ambient air quality and human exposure and health impacts as well as on current methods, protocols and data used in toxicological characterisation of particulate emissions.	Evaluation of the current methods and protocols used in toxicological characterisation of particulate emissions. Assessment of inter-faces with ambient air quality and human exposure and health impacts.	Definition of feasible methods and protocols to be used in future toxicological characterisation of particulate emissions. Assessment of interfaces between the methods and with WP1.	Definition of the best practise guideline for the methods and protocols in future toxicological characterisation of particulate emissions. Setting targets for future research collaboration.
Management: - progress and cost reports to national funders as requested	Kick-off Workshop in Month 2 and 2nd Workshop in Month 6; Consortium agreement on IPR. Presentation of a mid-term progress report in ERA-NET Workshop in May 2007.	3rd Workshop in Month 10.	4th Workshop in Month 13.	5th Workshop in Month 15. Draft of a common Final Report in English.
Milestones:	Country reviews completed.	Methodological evaluation completed.	Definition of feasible methods and protocols.	Best practise guidelines for studies on biomass combustion technology, particulate emission and toxicology
Deliverables:	Establishment of public website, PowerPoint presentations to stakeholders.	Update of website information according to project progress.	Project mid-term report on the website and as PowerPoint presentations to stakeholders.	Common Final Report in English (public) and its wide communication.

2.6.3 Work packages

2.6.3.1 WP1. Biomass combustion technology and particulate emissions

WP-leader: Prof. Ingwald Obernberger, TUG
Partners: TUG, UKU, FMI, TFZ, UUE, ETC

Objectives

- Summary of all relevant standards, data and experiences concerning particulate emissions from residential biomass heating systems.

- Summary of all relevant standards, data and experiences concerning methods for particulate measurement, sampling and characterization.

- Determination of feasible methods for particulate measurements, sampling and physicochemical characterisation.

- Preparation of the combustion technology and particulate characterisation related part of the best practice procedure for the overall interdisciplinary evaluation of particulate emissions.

Work contents

First period: Country reviews on the current state-of-the-art of small-scale biomass combustion technologies with special respect to particulate emissions were worked out. Moreover, country reviews on current methods and data available concerning particulate emission measurement, sampling and characterization were prepared.

Second period: Methods for particulate emission measurement, sampling and characterisation were evaluated as well as interfaces with the work performed within WP2 were defined.

Third period: Future feasible methods and protocols for particle measurement, sampling and characterization in small-scale biomass combustion units were defined. Information was exchanged with WP2 in order to harmonize and adjust the methods applied for particle measurement, sampling and characterization with the needs of an evaluation of the health impact of particulate emissions.

Fourth period: Best practice guidelines for methods and protocols concerning measurement, sampling and characterization of PM emissions were worked out in close collaboration with WP2.

2.6.3.2 WP2. Health effects of biomass combustion-derived particles

WP-leader: Doc. Raimo O. Salonen, KTL
Partners: KTL, FHG, UUH, UUP

Objectives

- Evaluation of the epidemiological and toxicological data for health risk characterization of particulate emissions from biomass combustion on the basis of original scientific data provided by the project partners.

- Determination of the most feasible endpoints and reliable methods for epidemiological and toxicological characterization of the human health risks.

- Identification of the potentially critical physicochemical parameters of particulate emissions from residential biomass combustion with regard to particulate-induced health effects.

- Preparation of the health-related part of the best practice procedure for the overall interdisciplinary investigation of particulate emissions.

- Identification of areas of strategically important health research for future promotion of the use of clean combustion and emission control technologies in residential biomass heating systems.

Work contents

First period: The country-based epidemiological and toxicological data and current methods on ambient air and emission particulate research related to small-scale biomass combustion were reviewed and targets were set for their more detailed evaluation.

Second period: These data and methods of ambient air and emission health research were evaluated with the help of published literature from other countries and on other organic-rich emission particles (e.g. diesel soot).

Third period: Feasible methods and protocols for toxicological and epidemiological characterisation of particles from biomass combustion were defined. During this period there was an intensive discussion on the evaluation results with the WP1 participants in order to enable an adjustment of the toxicological characterization methods such that they best benefit the future biomass combustion technology and emission research.

Fourth period: Best practice guidelines for the methods and protocols concerning the toxicological characterisation of particulate emissions were worked out in close collaboration with WP1. In addition, strategically important areas of health research on ambient air and emission particles were identified from the point of view of future promotion of the development and use of clean combustion and emission control technologies in residential biomass heating systems.

2.7 WORKSHOPS

The project started with a **kick-off meeting** at Kuopio, Finland (08/02 – 09/02/2007), where 9 partner organizations were represented (21 participants). The most relevant topics of this meeting where:

- Introduction of all partners and presentation concerning their working fields
- Detailed definition of the work contents for the first working period.
- Contents of the project website (www.biomasspm.fi)
- Definition of the locations for the future project meetings

The **second project workshop** was held in Straubing, Germany (12/06 – 13/06/2007) where again 9 partner organizations were represented (19 participants). The most relevant contents of this workshop were:

- Presentation and discussion of the work performed during the first working period in both work packages (country reports)
- Detailed definition of the work contents for the second working period.
- First exchange of information and experience between WP1 and WP2 partners

The **third workshop** was held in Umeå, Sweden (08/10 – 09/10/2007) where all 10 partner organizations were represented (23 participants).The most relevant contents of this workshop were:

- Critical evaluation of the methods used by different disciplines in small-scale biomass combustion research (WP1 and WP2)
- The first draft of the best practice procedure
- Specification of issues which had to be considered carefully during the next working period

The **fourth workshop** was held in Graz, Austria (18/01 – 19/01/2008) where again all 10 partner organizations were represented (17 participants). This workshop was connected to the 2nd Central European Biomass Conference, which was at the same time Graz. TUG organised an Expert workshop in this Conference on "Fine particulate emissions from small-scale biomass combustion systems – emissions, measurement, sampling, characterisation and evaluation of health risks", in which the first results of the project were presented to a broad public audience. In addition to public presentation of the results, also an internal project meeting took place. The most relevant contents of this workshop were:

- Presentation of the project to a broad public audience
- Critical evaluation of the draft of best practise procedure
- Change of information between the workpackages concerning the methods, data needed etc.

The **final project workshop** was held in Helsinki, Finland, (27/03 – 28/03/2008) where all 10 partner organization were represented (22 participants). The first day was for internal meeting, and the second day was open for invited stakeholders. On this second day, 24 stakeholders

from 18 institutes or companies of 6 countries participated. The most relevant contents of this workshop were:

- Country reports concerning fine particle emissions and measurements from residential biomass combustion and air quality and health impacts of fine particles
- Best practise recommendations and conclusions of WP1- Biomass combustion technology and particulate emissions
- Best practise recommendations and conclusions from WP2- Health effects of biomass combustion-derived particles

3 COUNTRY REPORTS BY PARTICIPANTS

3.1 FINE PARTICLE EMISSIONS AND MEASUREMENTS FROM RESIDENTIAL BIOMASS COMBUSTION

3.1.1 Finland

In Finland, about 235,000 TJ of energy was used for space heating in 2004; this was 21% of energy consumption of the year. Of the energy used for heating, 12% was produced with small-scale wood combustion (Fig. 2) (Finland Statistics, 2004). Approximately 6.1 million m^3 of fuel wood was used in Finnish detached houses during the heating period in 2000-2001 (Sevola et al., 2003).

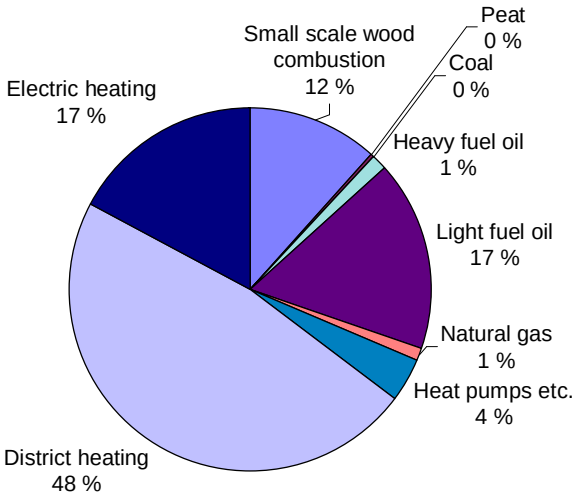


Figure 2. Energy sources for heating residential, commercial and public buildings in Finland (Finland Statistics, 2004)

Typically, in Finnish batch burning appliances, for example in masonry heaters and baking ovens, split logs of wood are burned with high burn rate. The appliances store heat in their massive structure and release it slowly during a long period of time. Also log boilers as well as burners and boilers for wood fuels like pellets and chips are used. National speciality is sauna stove which is used for a heating of a sauna room. On the amount of wood burning appliances, there is little exact information available; it has been estimated in Finland to exist 2.2 million fireplaces and 1.5 million sauna stoves and cauldrons.

There exist no emission limits for particles from small-scale wood combustion appliances in Finland yet. In the near future, the emission limits for CO and OGC will come into force. Most likely there will also become emission limits for particles in Finland like in many European countries in the future. In order to export their products, manufacturers of Finnish combustion appliances have developed their products to meet the emission legislation abroad.

Small-scale wood burning caused $PM_{2.5}$ emission of 7,600 t in Finland in 2000; this was 25% of total $PM_{2.5}$ emissions. From vehicular traffic including non-exhaust emission, the $PM_{2.5}$ emission was 5,800 t (19% of national total emission). Batch burning had a large contribution to the emissions from residential wood combustion (Karvosenoja et al., 2008).

Emissions from Finnish heat storing batch burning appliances range mostly between 30-100 mg/MJ for PM_1, 1200-3500 mg/MJ for CO and 100-310 mg/MJ for OGC, whereas the corresponding emissions from sauna stoves have been 130-160 mg/MJ, 3100-7900 mg/MJ and 590-720 mg/MJ, respectively (Tissari et al., 2005; Tissari et al., 2007b). PM_1 emissions from new masonry heaters equipped with secondary air introduction are significantly lower than the emission from conventional appliances.

Fine particles are composed of organic matter, elemental carbon and ash. The lower the PM_1 emission is, the lower is the emission of organic and elemental carbon. Higher burning temperature can increase the volatilisation of ash, and thus increase the ash emission although the PM_1 emission would decrease. E.g. the mixing of air and fuel in a firebox, the combustion temperature, the design of burning appliance, and the ash content and the composition of the fuel affect the chemistry of emitted particles. Usually, ash represents 5-90%, elemental carbon 1-40% and organic matter 7-60% of the PM_1 emission (e.g. Tissari et al., 2007a) (Fig. 3).

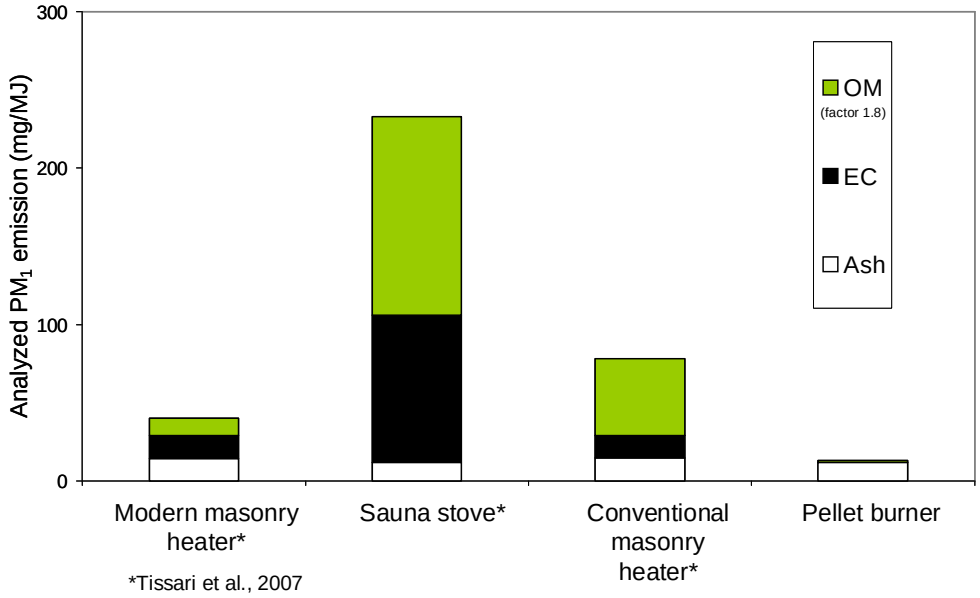


Figure 3. The composition of PM_1 emission from various combustion appliances.

In recent years, the knowledge on emissions from residential wood combustion has increased a lot. Yet more information for example on the effect of source-specific emissions on air quality and human health is needed. In order to decrease the emissions from small-scale wood combustion, a shift to more sophisticated burning appliances is recommended. Also the education on good operational practise, and fuel quality and storage would be advantageous.

3.1.2 Austria

In Austria, more than 580,000 main heating systems based on biomass combustion have been in operation in 2004, which amounts to about 17.2% of the total number of main heating systems. Considering also secondary heating systems, more than 1.08 million small-scale biomass appliances are in operation (Statistik Austria, 2007). The most common fuel used is logwood, which is used in tiled stoves, stoves as well as boilers. Old systems are still dominating the current stock of applications, however, during the last years about 15,000 to 20,000 newly installed modern biomass combustion systems per year could be observed. Among these newly installed systems pellet boilers have gained a dominating role.

Under consideration of the state-of-the-art of Austrian residential wood burning systems, a great variety of different technologies for logwood, wood chips and pellet combustion exists. This includes fully automated as well as manually fed boilers and stoves (Statistik Austria, 2007). Permanently performed R&D has lead to a steady technological improvement of these heating systems in terms of user friendliness, efficiencies and application of primary measures for emission reduction. However, the combustion technologies of modern biomass based residential heating systems are optimised with respect to specific standardised biomass fuels. Consequently, an optimised operation in terms of low emissions can only be achieved if the fuels, for which the boilers and stoves have been designed, are applied. In Austria biomass fuel quality criteria for logwood, wood chips and pellets are standardised according to ÖNORM M 7132, M 7133 and M7135.

In Austria, emission limits concerning small-scale biomass combustion are regulated according to the “Vereinbarung gemäß Art. 15 a B-VG über Schutzmaßnahmen betreffend Kleinfeuerungen (1998)” (~Agreement about article 15 a B-VG (federal constitution law) concerning protective measures for small-scale combustion plants (1998)). Presently the law is revised and new emission limits are expected to get into force soon. The total dust emission limit, which is presently 60 mg/MJ, will in a first step either remain the same or be reduced to 50 mg/MJ (depending on the fuel used and the combustion technology applied). In a second step (01/01/2015) the total dust emission limits are expected to be reduced to 20 to 35 mg/MJ (depending on the fuel used and the combustion technology applied).

Regarding particulate matter (PM_{10}) emissions in Austria, residential heating contributes with a share of 15.4%. More than 88% of these PM_{10} emissions from residential heating are caused by biomass combustion. As already mentioned, old combustion systems still dominate the stock of wood burning appliances in operation. One major disadvantage of these old systems is their high PM emissions. PM emission factors currently applied for older boilers and stoves account to 90 respectively 148 mg/MJ (Spitzer et al., 1998). This results in the fact that, as recently performed studies show, more than 90% of the PM_{10} emissions caused by wood combustion are related to these old appliances.

As actual studies have revealed, modern automated pellet, wood chip and logwood boilers show average PM_{10} emission factors of 20 mg/MJ (pellets and logwood boilers) as well as 20-30 mg/MJ (wood chip boilers) which underlines the technological improvements achieved (Statistik Austria, 2007; Obernberger and Thek, 2006). For tiled stoves average PM_1 emissions over a whole batch of 55 mg/MJ have been determined. Compared with the currently applied emission factors for older boilers and stoves mentioned above, these latest results show a significant PM emission reduction. Therefore, it is strongly recommended to

support the substitution of old biomass stoves and boilers by modern, preferably automated, small-scale biomass combustion systems, in order to achieve a considerable reduction of the PM-emissions in a CO_2-neutral and sustainable way. By this measure a reduction potential for PM emissions from small-scale biomass combustion of up to 75% could be obtained.

The shift from old to new biomass combustion systems would not only affect the overall PM emissions but also their chemical composition. While the PM_1 emissions of for instance old logwood boilers have been found to consist in average of 73 wt% organic aerosols and soot and 27 wt% inorganic salts (mainly alkaline sulphates, chlorides and carbonates), the content of organic carbon and soot in PM_1 emissions of modern wood chip, pellets and log wood boilers could be reduced to below 10 wt%. Therefore, also the health risks associated with the PM emissions from modern applications are assumed to be significantly lower. In order to investigate this issue in detail, a research project based on a cooperation between Austrian and Finnish research institutions, focusing on the health effects caused by particulate emissions from old and new small-scale biomass combustion plants, has just been started.

Future technological developments aim at the realisation of “zero emissions systems” (<5 mg/MJ PM_{10}) by applying appropriate primary and secondary measures. This target can be achieved by innovative CFD-aided furnace design, highly sophisticated process control systems as well as the application of efficient small-scale dust precipitators.

3.1.3 Germany

More than 14 million wood heating appliances are existing in Germany. Their number has been rapidly growing through the last years, although there was a market break in 2007. Highest growth numbers are recorded for wood stoves which have been increasing by 40000 to 60000 per year. But also pellet boilers were increasing by 20000 to 40000 units annually. While chances for improving the combustion quality are rather limited for log wood based room heaters (stoves) many new technical features have been introduced to improve the combustion quality of central heating boilers. These new systems are now mostly equipped with ventilators and power control systems which are guided by flue gas characteristics. Other features, such as mechanical heat exchanger cleanings, automatic de-ashing systems and load variability, have improved both operational comfort and the flue gas emission status.

However, such residential wood furnaces have been identified as a major source of fine particle emissions among all heating processes in Germany and they are increasingly moving into the focus of discussion concerning future measures for dust avoidance. Such furnaces contribute about 17% of all fine particle emissions in Germany and among all emission sources from residential heating their share is in the order of 85% with a tendency of further increase.

Concepts for stricter national emission regulations are currently being elaborated. The now foreseen two-step plan of the German emission directive (1.BImSchV) aims at introducing emission limits for stoves and room heaters, too. For central heating appliances a stepwise introduction of low particle emission furnaces shall be enforced. The now discussed emission targets for wood boilers are at a very low range of only 20 mg/Nm³ (at 13% O_2) and represent an ambitious goal for the year 2015. In view of the currently given emission levels of existing furnaces such targets can not safely be achieved without further technical measures.

Therefore, the development and use of secondary flue gas treatment systems seems to be crucial for the future development in small scale wood combustion. Several concepts and solutions for particle separation are currently being developed and tested (e.g. electrostatic precipitators). Recent tests show that a dust separation between 50 and 90% seems to be achievable at relatively low investment costs of around 1500 € per installation. Therefore, a generally optimistic outlook can be given for their market introduction.

During the last two decades significant improvements were recorded in the area of particle and gaseous emissions. For wood log furnaces, for example, the estimated total dust emission factors have declined from about 100 to 34 mg/MJ. In type testings the results are reported in mg/Nm³ (at 13% O_2); such tests show average dust emissions of 18 (pellet boilers), 22 (wood log boilers) and 25 mg/Nm³ (wood chip boilers). In practice, the emissions from type testing results can not always be achieved. Therefore, practice related test stand measurements using typical fuels and representative wood furnaces (room heaters and boilers) were recently conducted at TFZ. The results show, that for boilers there are only relatively small deviations from the type testings (mean dust increases by 2 to 10 mg/Nm³). Dust emissions from stoves are generally largely higher than for boilers, in average they ranged between 60 and more than 70 mg/Nm³.

Large deviations from such average values are given when the operation is not performed normally. Dust emissions usually react when too high or too low wood mass is loaded at each fuel charging cycle. Also the size of the applied logs proved to be important for room heating stoves. Here deviations from the optimum value reached an order of around 200%.

In all measurements it was found that the fine dust fraction (PM_{10}) comprised 88 to 98% of the total particle mass. The particles were even predominantly smaller than the aerodynamic diameter of 1 µm which is underlined by the $PM_{1,0}$-fraction representing 70 to 90% of the total particle mass.

Dust emission measurements can also significantly depend on the sampling method. This was observed in a series of 95 parallel measurements on wood stoves where sampling was done either before or after a flue gas dilution step (dilution with filtered ambient air at a ratio of around 6 and at 60 °C diluted flue gas temperature). It was found, that around 25% higher total dust emissions are usually measured after the dilution step, when the hydrocarbon concentration remains below 100 mg/Nm³ (at 13% O_2). But at very high hydrocarbon concentrations above 1000 mg/Nm³ even 3- or 4-times higher total dust concentrations can be measured by the usual gravimetric determination method.

Research on the composition of particles from wood combustion is still ongoing. For the time being results are only available for pellets and wood chip combustion (25 and 50 kW) having low total dust emissions (20 and 25 mg/Nm³). Such particles contain only little total carbon (5 to 12%) while the EC/OC-ratio was between 2 to 3.5. PCB, PCP, phenols and cresols were not detected and sulphate was the predominant component (30 to 40%) followed by potassium (around 30%). In the samples which were collected from those furnaces which had a more incomplete combustion (stoves) a different picture is expected.

The conclusions can be compiled as follows:

- In the technical development of furnaces a stronger focus should be made on room heaters (stoves).

- For stoves excessive particle emissions can be avoided by proper charging operation.

- Secondary flue gas treatment for particle removal becomes crucial in order to meet the upcoming stricter emission regulations for residential wood combustion appliances

- The determination of total dust emissions from wood stoves should be made at uniform flue gas temperatures. If the particles shall be analysed after sampling a flue gas dilution is useful to achieve representative particle mass and composition.

3.1.4 Sweden

The residential biomass sector and technology

In Sweden, energy from biomass (including peat) constituted 19% of the total national supply of 624 TWh in 2006. Approximately 0.99 million residential biomass burning units are in regular use today, distributed as 62% light wood stoves, 23% wood log boilers, 8% heavy wood stoves and 7% pellets units. The total annual use of biomass in these residential units corresponds to ~12 TWh, and a significant potential for a further increase exists, not at least as replacement of the still relatively extensive use of oil (~5.5 TWh) and electricity (~15 TWh) for household heating. The water-based systems (boilers) are used as primary heating sources while the stoves and open fireplaces mainly are used as secondary (comfort) heating sources.

During the last 20-30 years, there has been a continuous technological development of wood boilers including the use of down-draft combustion, sucking fan, primary and secondary air, isolated combustion chamber and heat accumulation water tanks. However, the majority of the 230 000 wood log boilers are still rather old, "not environmentally certified" and not connected to a water accumulator tank. Presently, only ~30% of the households with wood boilers have accumulation tanks in Sweden and the influence of the size of the fuel batch charge during combustion is of vital importance for the emission performance. Accordingly, rather large fuel charges often lead to too high burn rates which necessarily implies reduced air supply that subsequently may lead to drastically increased emissions of products of incomplete combustion (e. g. CO, hydrocarbons and soot).

Further, approximately 700 000 wood stoves of all kinds (e.g. chimney stoves, tiled stoves and open fireplaces) are in use in Sweden today. A trend is seen with installation of light (heating) wood stoves both in new and older houses, often as a complement to electricity heating and also because of the high cost factor. These stoves tend to be designed for lower heat outputs than previously and also to be more robust concerning the influence of handling, i.e. “Clean Burning“ stoves. Still, considerable uncertainties exist concerning annual wood consumption as well as emission performance for different kinds of stoves and fireplaces.

The potential for modern residential biomass technology, mainly by using pelletized fuels in specially designed appliances (boilers, burners and stoves) is significant. The use of wood pellets has increased significantly during the last 15 years and of the present total use of almost 1.7 million tonnes annually, approximately 25% (~2 TWh) are used in small residential appliances. In addition, wood chips are presently used for heating in 30 000-40 000 houses (estimated from 821 000 m^3 overturned wood chips), and may certainly be a suitable use of biomass also in small-scale systems.

Particle emission data and emission performance

The total PM_{10} emissions from residential biomass burning were 2005 estimated to be 4 500 tonnes which corresponds to ~7% of the national total PM_{10} emissions (Paulrud, 2007). It is, however, important to emphasize the fact that residential biomass heating constitutes a significantly larger fraction of the total emissions of fine particles (<1 µm) since traffic and other sources generates considerable emissions of coarse particles included in the size range of 1-10 µm.

Recently compiled estimates of PM emission factors for different systems illustrate the vast variation depending on appliance type and operating procedure (Todorović et al., 2007). It has for example been shown that the influence of firing procedure (e.g. fuel charge size) is of vital importance when using a wood boiler without an accumulator tank. Burning large wood charges in old boilers without water tank can generate PM emission factors of over 1300 mg/MJ_{fuel} which are in average 30 folds higher than for modern wood log systems operated in a proper way, and 50-100 fold higher than the emissions from modern well operated pellet systems. During optimized combustion of sawdust softwood pellets, is has been shown that the fine particle emissions are in the range of 10-15 mg/MJ_{fuel} which is the lower level obtained without using any flue gas cleaning device or other measure for PM reduction, like additives (Johansson et al., 2003; Boman, 2005; Wiinikka, 2005). These considerable differences in emission factors lead to the conclusion that around 75% of the total national particle emissions from residential biomass heating (4 500 tonnes/year) originate from old wood log boilers without accumulator tanks, 7% from modern wood log boilers with accumulator tanks, 14% from wood stoves (all kinds, light and heavy) and 4% from residential pellet appliances.

Particle size and composition

It has consistently been shown that fine (<1 µm) particles totally dominate (>90%) the PM emissions in all kinds of present residential wood log and pellet combustion systems (Johansson et al., 2004; Boman, 2005). Fine particle concentration, size distribution and composition are, however, clearly influenced by combustion conditions. In older and/or poorly operated appliances, over 90% of the PM mass typically consists of non-carbonate carbonaceous matter (i.e. soot particles and condensed organics) and only some percent of inorganic ash matter. This explains the higher PM emissions in the majority of the presently used residential wood log appliances compared to pellet combustion systems. Rather scarce information concerning fractionation of the carbonaceous matter in PM from wood combustion into elemental (soot) and organic carbon are presently available in Sweden. Concerning PM from residential wood combustion in general, polycyclic aromatic hydrocarbons (PAH) is only a minor group of organic constituents, although with potential health impact relevance, comprising typically <1% (maximum some few percent) by weight.

During low temperature smouldering combustion of wood the PM has instead been found to consist of a large number of other more oxygenated organic compounds related to pyrolysis products of the wood, e.g. levoglucosan and other sugar derivates as well as methoxyphenols (Schauer et al., 2001; Kjällstrand and Olsson, 2004). However, during incomplete combustion of wood at higher temperatures (>700 °C) the PM emissions are more dominated by carbon aggregates (soot) with mobility equivalent aggregate diameters typically in the range of 0.1-0.3 µm (Pagels et al., 2006). Consistent data also showed that the PM during efficient and nearly complete combustion of wood logs and softwood pellets consist more or less completely of fine alkali salt particles, like KCl, K_2SO_4, $K_3Na(SO_4)_2$ and K_2CO_3, with mobility equivalent diameters in the range of 0.05-0.09 µm (Johansson et al., 2003; Boman et al., 2004; Wierzbicka et al., 2005; Wiinikka et al., 2007).

Concluding remarks

A considerable potential for PM emission reduction within the residential biomass sector by a shift from old and poorly operating units to modern and properly working systems, therefore exists. Such a conversion and introduction of modern technology will not only drastically decrease the total PM mass emissions but also completely change the chemical composition of the PM. A significant potential is considered to be on the introduction of new small-scale pellet technology and possibilities for further technical development and emission reduction also exist for such systems, especially during intermittent and low-load operation. The influence on combustion behaviour and emission performance of other raw materials for pellets than pure stem-wood assortments is also important for future R&D work. In Sweden, rather extensive research programs have focused on technical and environmental issues of small scale bioenergy but the environmental regulation as well as technical development of small combustion appliances and flue gas cleaning systems have not been as strong as in central Europe so far. However, integrated markets, harmonised regulations and a growing concern about PM pollution presently puts a focus on these aspects related to PM emissions from small-scale biomass combustion. Beside the ongoing development and implementation of new residential biomass combustion technology and fuels, it is important to put efforts to determine the detailed physical and chemical aerosol properties during different combustion conditions, e.g. mixing status, soot-organics-ash interactions and trace metal behaviour. Such information is important for elucidating the links between aerosol particle emission characteristics and different adverse health effects during exposure to air pollution related to residential biomass combustion.

3.1.5 Summary

Within WP1 of the BIOMASS-PM project firstly the actual status concerning small-scale biomass combustion technologies, particulate emissions from small-scale biomass combustion and other sources, emission limits, standards applied for particle measurements and sampling as well as scientific methods applied for particle measurement, sampling and physicochemical characterisation of particulate emissions from small-scale biomass combustion have been summarised for the different partner countries (Austria, Finland, Germany, Sweden) and presented in country reports.

Summing up the results and conclusions from the country reports, it can be outlined, that in all 4 countries small-scale biomass combustion technologies play a relevant role by providing 10% - 30% of the total energy demand for residential heating and hot water supply. Moreover, small-scale biomass combustion technologies are the dominating renewable energy source for residential heating. It is also similar for all 4 countries, that logwood is the most common biomass fuel applied in stoves and boilers. However, wood pellets have been gaining rising relevance as fuel for residential heating systems since their market introduction and this trend is expected to continue.

In all 4 countries old biomass combustion technologies (stoves and boilers) dominate the current stock of applications and since these systems show significantly higher PM emissions than modern small-scale biomass combustion systems, residential biomass significantly contributes to the national PM_{10} emissions and is therefore also sometimes criticised. It has to be stated that comprehensive R&D work on the optimisation of small-scale biomass combustion devices has been performed during the last decade respectively is on-going and due to these R&D efforts, state-of-the-art residential biomass combustion technologies, which operate at significantly lower PM emissions than old technologies, are already available. These lower PM emissions are caused by improved combustion conditions which reduce the formation of organic aerosols and soot. However, the changeover from old to new residential biomass combustion systems has so far not taken place. Moreover, it has to be mentioned that the development of secondary measures for PM emission reduction (e.g. ceramic filters and electrostatic precipitators) is in all 4 countries just in the initial phase. Therefore, the same measures for the reduction of PM emissions from small-scale biomass combustion can be proposed for Austria, Finland, Germany and Sweden:

- Financial support of the substitution of old combustion devices by modern systems.
- Provision of appropriate “user training” for non-automatically fed systems.
- Support of the development of low PM combustion technologies.
- Support the development and application of appropriate secondary PM emission reduction technologies for residential biomass combustion systems

Moreover it has turned out that concerning PM emission limits for small-scale biomass combustion appliances significant differences between the 4 countries exist. While in Finland no PM emission limits exist so far, in Sweden PM emission limits have only to be fulfilled on a voluntary basis. In Austria PM emission limits exist and it is expected that they will be significantly reduced within the coming years. In Germany presently the European wide most ambitious emission limits regarding PM are soon expected to get into force (2015 target: 20 mg/Nm^3, dry flue gas, 13vol% O_2). Furthermore, different units and different O_2 reference levels are applied. A harmonisation on a European level would be of advantage.

Slide presentations on country reports are in the Annex.

3.2 AIR QUALITY AND HEALTH IMPACTS OF FINE PARTICLES

3.2.1 Finland

3.2.1.1 Contribution of biomass combustion to fine particle concentrations in Helsinki

Introduction

Urban air particulate matter is a complex mixture of primary particulate emissions (from industry, transportation, power generation and natural sources) and secondary material formed via gas-to-particle conversion of anthropogenic and biogenic emissions. Urban aerosol contains a substantial amount of carbonaceous material (Legrand and Puxbaum, 2007) that is composed of elemental carbon (EC) and organic carbon (OC). EC is a primary pollutant formed in combustion processes whereas OC is a complex mixture of different groups of compounds originating from a large variety of sources. The sources of OC were investigated in Helsinki using the data from the year-round measurements with a special emphasis on fine particles from biomass burning in wildfires and from wood combustion in residential heating.

Methods

The measurements were conducted in Helsinki (Finland) at an urban background station (SMEAR III, 60°20'N, 24°97'E, 26 m above sea level). The measurement site is located in the university campus area, 4 km northeast from the Helsinki city center. It was anticipated that the most important local source of fine particulate matter is vehicular traffic since there is a densely trafficked major road (60 000 cars/day) at a distance of less than 200 m from the station. However, the contribution of biomass combustion may be substantial, especially in winter. OC, EC, BC (black carbon) and water-soluble ions as well as the $PM_{2.5}$ mass concentration were measured continuously at SMEAR III. In addition to the continuous measurements the daily PM_1 filter samples were collected for the analysis of OC, EC, water-soluble organic carbon (WSOC), levoglucosan and major ions. All the measurements are summarized in Table 2.

Table 2. Instruments, aerosol components analyzed and the time-resolution of each measurement.

Instrument	Component	Time-resolution	Size range
Semicontinuous OC/EC	OC, EC	3 h	<1 µm
PILS-IC	Ions	15 min	<1 µm
Aethalometer	BC	5 min	<2.5 µm
FDMS-TEOM	$PM_{2.5}$	30 min	<2.5 µm
Filter cassette	OC, EC, WSOC, ions, levoglucosan	24(–72) h	<1 µm
MOUDI	WSOC, ions, mass	72 h	0.056–10 µm

Results

The positive matrix factorization analysis (PMF) was used to estimate contributions of various sources or source groups. During winter months (Dec. to Feb.) biomass combustion (Fig. 4, Factor 2) contributed 41% and during fall (Sep. to Nov.) 20% to fine particle organic carbon. Small-scale wood combustion is a significant source of fine particles in Helsinki. The fine particle concentrations from wood combustion are at their highest levels during winter due to the highest emissions and frequently appearing stable atmospheric conditions.

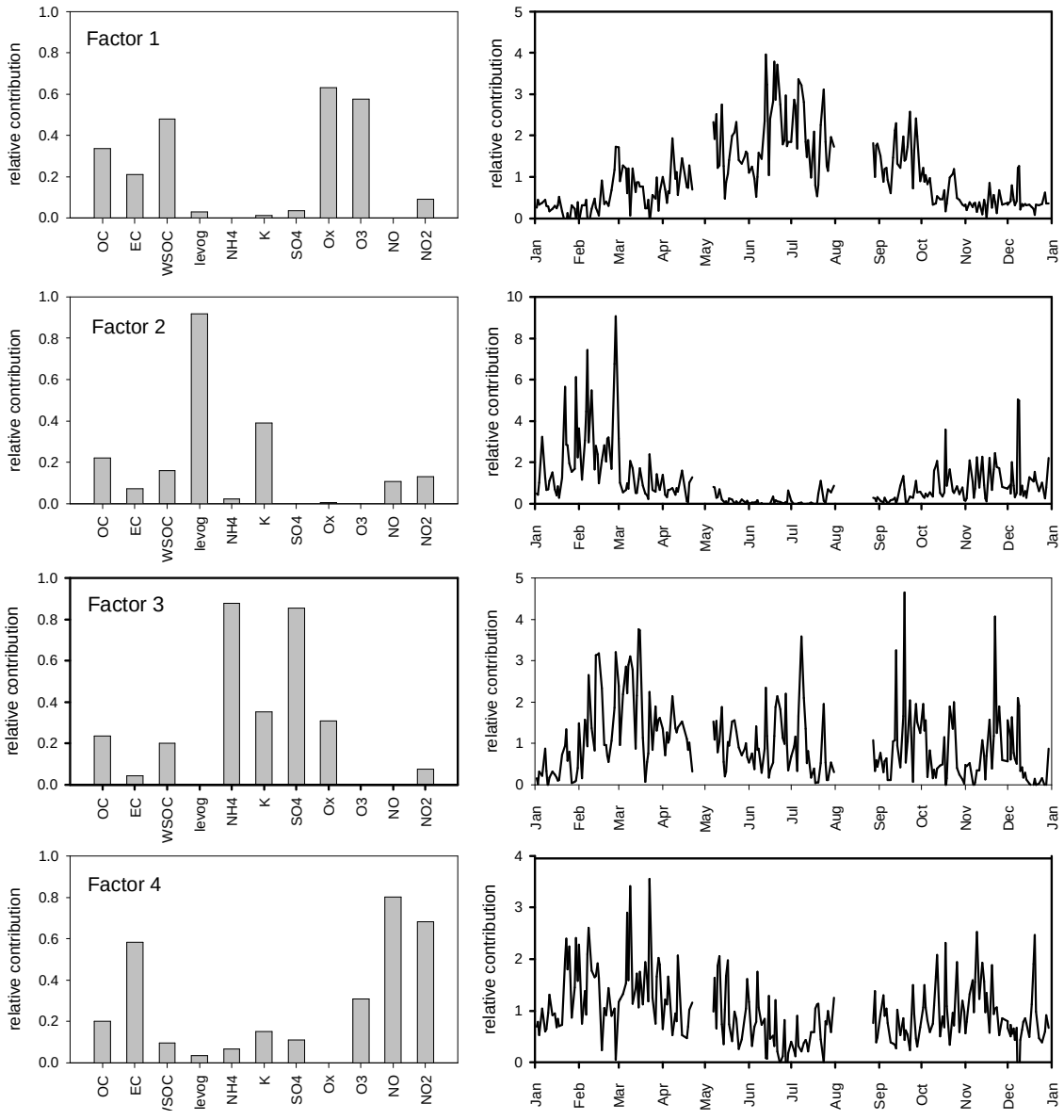


Figure 4. One-year data of fine particle composition was used to assess contributions of various sources on particulate matter organic carbon (Saarikoski et al., 2008). Factor 2 in the positive matrix factorization (PMF) analysis corresponds to biomass combustion (wildfire periods excluded). Other factors are secondary organic aerosol (Factor 1), long-range transport (Factor 3) and traffic (Factor 4).

3.2.1.2 Toxicological studies on PM emissions from biomass combustion

Biomass combustion causes a large share of the total $PM_{2.5}$ emissions throughout Europe. Urban air fine particles are thought to have a close association with the health impacts of particulate emissions originating from most combustion sources. Thus there are pressures in many countries to start, or to make more stringent, regulation of the emissions from small-scale biomass combustion. Due to different chemical composition compared to those from fossil fuel combustion, the biomass combustion-derived particles may pose different kind and level of toxicity and subsequent health risk than other ambient air particles of similar size. On the other hand, the European Union is likely to greatly increase the use of biomass energy in the coming decades in order to combat against global warming of the atmosphere. Overall, there are concerns how the increase in the use of biomass energy could be done without increasing the harmful effects of the combustion emissions on human health.

The question, how different chemical compositions of biomass combustion particles contribute to the toxic outcomes, is unanswered. Proposed toxicity mechanisms behind particulate-induced adverse health effects are cytotoxicity, inflammation associated injury (Dick et al., 2003), oxidative stress (Tao et al., 2003) and genotoxicity (Binkova et al., 2003; Farmer et al., 2003; Knaapen et al., 2004). The inflammatory activity of air particles is regarded as being linked to worsening of chronic cardio-respiratory diseases, whereas genotoxicity is primarily linked to the carcinogenic risk. These mechanisms can be activated in response to particulate exposure in alveolar macrophages (Jalava et al., 2005; Becker et al., 2005) that are the type of specialized white blood cells mainly responsible for the clearance of inhaled particles from the lung periphery.

Hirvonen et al. evaluated the toxic properties of particulate emissions from ordinary and poor combustion of log wood in one small masonry heater (average CO, OGC, and PM emissions were 2300 mg/MJ, 120 mgC/MJ and 100 mg/MJ for ordinary combustion, and 8100 mg/MJ, 1700 mgC/MJ and 600 mg/MJ for poor combustion). Ultrafine ($PM_{0.2}$), fine ($PM_{1\text{-}0.2}$ and $PM_{2.5\text{-}1}$) and coarse ($PM_{10\text{-}2.5}$) particulate samples were collected from diluted and cooled flue gas with a high volume cascade impactor (HVCI) (Sillanpää et al., 2003). The inflammatory, genotoxic and cytotoxic activities of the collected particulate samples were studied in a macrophage cell line (RAW264.7). The dose-related production of proinflammatory cytokine (TNFα), chemokine (MIP-2), and cytotoxicity (MTT-test, apoptosis, cell cycle) were measured.

In all size ranges, particles collected from both ordinary and poor combustion activated a dose-dependent production of cytokines in the macrophages. However, the ordinary combustion particles had a slightly higher proinflammatory potential as assessed by TNFα production, whereas the poor combustion particles were more potent inducers of chemokine (MIP-2) production. Ultrafine particles were the least potent. These comparisons were made at equal mass doses in cell cultures.

Significantly increased apoptotic cell death was detected by the poor combustion particles in all size ranges, whereas the particles from ordinary combustion caused only minor or no response. Moreover, in the cell cycle analysis, a significant inhibition of DNA synthesis was seen only by the poor combustion particles.

In conclusion, when adjusted to the emitted particulate mass or produced energy, the poor combustion particles in all size ranges increased acute cytotoxicity up to 3- to 10-fold compared to particulate samples from ordinary combustion. In addition, cell cycle analysis from experiments with the poor combustion particles showed increased apoptosis (programmed cell death) and a decrease in DNA synthesis in the cells, while those effects were not detected in exposure to particles from ordinary combustion. Also a 2-to 8-fold increase in the production of inflammatory mediators was measured in the macrophages after exposure to poor combustion particles.

3.2.2 Germany

At Fraunhofer ITEM the health effects of six different fly ash samples from large biomass combustion plants (bark, wood chips, waste wood, and straw), and co-firing plants (coal, co-firing of coal and sawdust) were investigated in a 28-day nose-only inhalation study with Wistar WU rats. Respirable fractions of carbon black (Printex 90) and of titanium dioxide (Bayertitan T) were used as reference materials for positive and negative controls. The exposure was done 6 hrs per day, 5 days per week at an aerosol concentration of 16 mg/m^3. The MMAD of all fly ash samples and reference materials in the inhalation unit were in a range between 1.5 and 3 µm. The investigations focused predominantly on the analysis of inflammatory effects in the lungs of rats by bronchoalveolar lavage (BAL) and histopathology.

For different parameters (percentage of polymorphonuclear neutrophils (PMN), interleucin-8 and interstitial inflammatory cell infiltration in the lung tissue) indicating inflammatory effects in the lung, a significant increase was observed for groups exposed to carbon black (positive control), C1 (coal) and C1+BM4 (co-firing of coal and sawdust) fly ashes. Additionally, for the same groups a significant increase of cell proliferation in the lung epithelium was detected. No significant effects were detected in the animal groups exposed to BM1 (bark), BM2 (wood chips), BM3 (waste wood), BM6 (straw) or titanium dioxide.

The common characteristic of carbon black, C1 and C1+BM4 is the high content of insoluble particles whereas the other biomass fly ash samples BM1, BM2, BM3 and BM6 mainly consist of soluble salts. After inhalation exposure, these salts are dissolved very fast and cleared from the lung by the blood stream. Therefore, the concentration of soluble fly ash particles is very low in the lung after long-term inhalation whereas insoluble particles accumulate in the lung. For the insoluble particle samples C1 and C1+BM4, the effects on inflammation and cell proliferation in the lung were similar or slightly lower than for the carcinogenic carbon black or diesel exhaust particles. For the soluble fly ash samples, no adverse health effects were detected in the present study.

Within the in-vitro study the same test and reference items were investigated by exposure to human alveolar epithelial cells (cell line A549) to see, if effects on human lung cells were comparable to rat lung cells. In this in-vitro study, inflammatory effects were induced by the biomass fly ash samples BM3 (waste wood), BM1 (bark) and C1+BM4 (co-firing coal and sawdust). The highest effect was observed for the BM3 sample which contained the highest percentage of heavy metals (Zn and Pb). In contrast to the 4 week inhalation exposure, in the short term in-vitro test the soluble salts of the biomass fly ash samples BM3, BM1, BM2 and BM6 could not be cleared from the exposure system. It was estimated that the concentration

of the soluble material per area of exposed cells was approximately 4 orders of magnitude higher in the in-vitro test compared to the in-vivo study.

The health relevance of particles from wood combustion in comparison to diesel soot was investigated in an in-vitro study in Switzerland by Klippel and Nussbaumer (2007). The lung fibroblast cell line V79 from Chinese hamster was exposed to particles from quasi complete wood combustion (C-BM, automatic wood boiler) and incomplete wood combustion (I-BM, badly operated wood stove) and of diesel soot from a modern type diesel engine (no soot filter) as control. Cytotoxic effects (viabilty test using tetrazoliumsalt XTT) and genotoxic effects (chromosome breakage by micro nucleus test) were analysed. The results showed that diesel soot had a medium level of toxicity and chromosome defects, while mainly inorganic particles from the automatic wood combustion exhibited app. 5 times lower toxicity. In contrast, soot from the badly operated wood stove exhibited app. 10 times higher toxicity and chromosome defects than diesel soot. The highest toxicities were found for condensable matter from the wood stove.

Fritsch, Diabeté and Krug (2006) at the FZK in Karlsruhe investigated fly ash particles (MAF-02) collected by electrostatic precipitation in a commercial municipial waste incinerator facility. The murine macrophage cell line RAW264.7 was exposed for 0.5-24 hrs to 10-300 µg/ml MAF-02 in culture medium. Cytotoxic effects (viability by tetrazolium salt), ROS induction, GSH /GSSG and haem oxigenase-1 (HO-1) content, Liberation of arachidonic acid (AA) and expression of Cyclooxygenase-2 (COX-2) were analysed. Main effects by MAF-02 exposure were increased mobilisation of AA and increase of COX-2, GSH, HO-1 and ROS.

Schauman et al. (2004) at the Fraunhofer ITEM, GSF and IUF investigated the health effect of ambient $PM_{2.5}$ particles from Zerbst (rural area) and Hettstedt (smelter area) in 12 healthy volunteers (non-smoker). By bronchoscopy a baseline bronchoalveolar lavage was performed (left upper lobe) and in the same lung saline as control (right lower lobe), 100µg PM of Zerbst (middle lobe) and 100µg PM of Hettstedt (lingula) were introduced by instillation. After 24 hrs by a second bronchoscopy a BAL was performed at the same locations. Investigate parameters were cell count (PMN, Lymphocytes, Macrophages), Cytokines (IL-1, IL-6, IL-8, TNF-α), oxidant radical generation after zymosan stimulation of BAL cells, surface marker on Monocytes and macrophages. The main results were an increase of IL-6 and TNF-α and influx of monocytes induced by Hettstedt PM.

3.2.3 Sweden

3.2.3.1 Air quality and exposure related to wood combustion

Measurements and modelling of air quality within the Swedish program BHM, “Biomass combustion, Health and Environment”, http://www.itm.su.se/bhm/, was concentrated to two pilot towns. In one of these, Lycksele, with about 9000 inhabitants situated in the inland of northern Sweden the yearly PM emissions from combustion were estimated to 66 ton, of which wood stoves/boilers contributed 36 tons and road traffic 1 ton.

A model, “Dispersion”, http://155.207.20.121/mds/bin/show_long?DISPERSION21, was used for evaluations of air quality. The most important findings were that the 98-percentile

levels of PM_{10} often exceed 50 µg/m^3 close to the old wood stoves. The influence areas were found small with a horizontal extension of less then a few hundred meters.

Sponsored by the Swedish Energy Agency a new internet tool for evaluation of air quality in residential areas with small scale wood-combustion called VEDAIR has been developed by SMHI, http://simair.smhi.se/luftkvalitet/documents/VEDAIR_forstudie.pdf.

The VEDAIR system is based on a combination of pre-calculated concentrations from models of larger (regional and urban) scales and direct model calculations from local scale. It is based on similar methods as the traffic pollution model SIMAIR. Comparison of measured and calculated concentrations of PM_{10} are done in Lycksele, a small town with about 9000 inhabitants in northern Sweden; http://simair.smhi.se/luftkvalitet/documents/m123.pdf. Measurements have been done during two winter periods, the first during December 2001 to Mars 2002 and the other during January 2006 to Mars 2006. Both periods shows strong variations of PM_{10} concentrations due to temperature. During cold conditions (temperatures below -10 ºC) the local contributions were large and during warmer conditions the local contributions were small. VEDAIR describes these variations rather well.

In the Swedish EMFO funded project TESS exposure calculations were done for the Stockholm area. The annual mean concentrations were calculated using the Airviro Air Quality Management System (SMHI, Norrköping, Sweden; http://airviro.smhi.se).

In the Greater Stockholm area about 70% of the PM_{10} residential heating emissions come from residential wood burning. Emission factors for wood burning were obtained from the Swedish National Testing and Research Institute's report 2003:08 "BHM – småskalig biobränsleeldning", http://www.itm.su.se/bhm. There are large uncertainties in the emission data for biomass burning. The estimated emissions of combustion particles (tons/year) in the Greater Stockholm (35x35 km^2) area during 2003 were 490 tons for residential heating and 122 tons for all motor vehicles, and the population weighted concentration was estimated approximately four times higher for residential heating (annual mean 0.59 µg/m^3). Other emission assumptions could significantly change the conclusions.

In a study from a residential area in West Sweden, where wood burning for domestic space heating is common, Molnár et al. (2005) reports on personal exposures as well as indoor and outdoor levels of $PM_{2.5}$. Wood combustion derived particles made statistically significant contributions to K, Ca, and Zn for both personal exposure and indoor concentration, the median levels of these elements being 66–80% higher for the wood-burning group. However, the mass concentration of $PM_{2.5}$ was not significantly elevated in wood burners. In addition, for the same population Gustafson et al. (2007) report that subjects using wood as a fuel had significantly higher median personal exposure to 1,3-butadiene (0.18 µg/m^3) compared with the referents (0.12 µg/m^3). Significantly higher indoor levels of benzene were found in the homes of wood burners (3.0 µg/m^3) compared with the reference homes (1.5 µg/m^3).

Epidemiological studies of biomass PM in Sweden are until now studies of short-term associations between ambient particle levels in areas with residential wood heating. These studies are of two kinds, panel studies with repeated measurements in a specific group of panellists and register studies of health care utilization and diagnoses in a population. Most of the studies were funded by the Swedish program BHM, "Biomass combustion, Health and Environment", http://www.itm.su.se/bhm/. These studies showed that particle levels below

PM_{10} limit values caused acute respiratory effects in asthmatics. However, biomass combustion derived particles are a potential health problem mainly in smaller municipalities where each population is too small to study effects on low frequent events such as deaths. Long-term studies of exposure to PM from wood burning have this far not been conducted in Sweden. Now initial funding has been provided by STEM to design a new study of long-term exposure. The plan is to first validate national property and taxation register data on heating systems using locally collected data. The planned study will build on a cohort with prospective data on smoking and other risk factors.

3.2.3.2 Experiences from Swedish studies with wood combustion aerosol exposure in healthy subjects

Particulate matter (PM) air pollution has been associated with adverse health effects in humans and both the respiratory and cardiovascular system has been shown to be affected. Several epidemiological studies have indicated that exposure to particle emission from wood combustion has the capacity to induce similar effects (Boman et al., 2006; Boman et al., 2003) but only a couple of experimental studies have investigated the impact of wood combustion aerosol exposure on human health.

Barregård and colleagues pioneered by using a controlled experimental exposure setup where 13 healthy human subjects were exposed for four hours to wood combustion aerosol and filtered air, at two different occasions. A small cast iron stove was used to generate the combustion aerosol and a partial flow was diluted with filtered air to reach a $PM_{2.5}$ target concentration 250 µg/m^3. Online measurements of PM properties and gases were conducted to monitor the exposures. Assessment of health impact was conducted by evaluation of symptoms, exhaled NO, breath condensate, blood and urine samples. The results from that study (Barregard et al., 2006; Barregard et al., 2008; Sällsten et al., 2006) indicate an inflammatory response to wood combustion aerosol as measured by an increase of exhaled NO and elevated levels of serum amyloid A. Increased levels of Factor VIII and Factor VIII/von Willebrand factor ratio in plasma may indicate an imbalance in coagulation factors. Moreover, an increased urinary excretion of free 8-iso-prostaglandin$_{2\alpha}$ and elevated concentration of malondealdehyde in exhaled breath condensate, both signs of an increased lipid peroxidation. A change in CC16 concentration in serum also indicates an increased permeability in the airway epithelium. Thus, the results show that exposure to wood combustion aerosol has the potential to affect inflammation, coagulation and possibly lipid peroxidation, all being factors which may be involved in the mechanisms causing negative health effects from PM exposure.

Sandström et al. have more recently also studied health effects of wood combustion aerosol by controlled human exposure. Nineteen healthy human subjects were exposed for three hours at two different occasions, once to combustion aerosol and once to filtered air. A residential wood pellet burner was used and adjusted for the generation of emissions that simulated low-temperature incomplete wood combustion. A partial flow from the pellet burner was mixed with filtered air to reach a target PM_1 concentration of 300 µg/m^3. Continuous measurements were carried out both in the flue gas and the chamber to monitor the combustion and the exposure conditions. Impact on health was assessed by sampling and evaluation of symptoms, lung function, exhaled NO, exhaled breath condensate and blood samples. In addition, bronchoscopies were performed 24 hours post exposure with collection endobronchial mucosal biopsies and lavages, which may be used for analyses of a range of biomedical

endpoints. The samples from this study is not completely analysed but the preliminary data indicate a moderate response. Increased levels of glutathione could be measured in bronchoalveolar lavage after the exposure to wood combustion aerosol. Glutathione is an antioxidant present in the airways which protects the airways from oxidative agents/free radicals that may be present in for example PM air pollution. This increase in glutathione may therefore indicate that the antioxidant defence has been turned on and that there might be a state of oxidative stress in the lung tissue. This might in turn result in tissue damage. In addition, preliminary data indicates a change in gene expression in alveolar macrophages. The analyses of which genes that are affected are not yet completed.

Furthermore, Löndahl and coworkers (2008) conducted experimental measurements of respiratory tract deposition of fine particles in healthy subjects during the same exposure campaign as described above. In this case, particles from two different combustion conditions, i.e. low-temperature incomplete combustion and efficient complete wood combustion, together with a reference particle, were compared. The results showed a relatively low deposition, and thereby exposure dose, in the respiratory tract, compared to traffic exhaust particles. This might help explain the relatively mild response determined in this exposure study, but further evaluation is needed.

In summary, exposure to wood combustion aerosol has been shown to affect the antioxidant defence, blood coagulation system and may cause an inflammatory response. However, these results are only based on two reported/performed investigations with human exposure of different kinds of wood combustion aerosol. It is therefore difficult to draw any general conclusions from that, but clearly there are some negative effects. To clarify the severity of the exposure to wood combustion aerosol on human health regarding e.g. magnitude of the effects compared to other combustion related aerosols, specific health endpoints and influence of combustion condition, more research is needed.

3.2.4 Summary

There are presently only few new studies utilizing a source-specific assessment of the contribution of biomass combustion-derived particulate matter to the outdoor air $PM_{2.5}$ concentration or its organic composition. These methodologies show large relative contributions even in cities with wide-spread district heating system, suggesting a role for not only local residential biomass combustion but also for regional and long-range transport of this type aerosol. So far, the new source-specific methods have not been applied to the assessment of the contribution of biomass combustion particles to the personal exposure or health of the residents.

The new experimental human exposure studies suggest that, in addition to chronic respiratory diseases like asthma, the aerosol from incomplete biomass combustion has a potential to do harm to the blood circulation and the heart. The animal and cell studies support the clinical findings that these aerosol particles may have relatively low direct inflammatory potency, but their high oxidative stress potential, direct cellular toxicity and impairment of cell cycle shown in the cell studies may add to their overall harmfulness. Understanding the chemical composition vs. toxicity relationships of biomass combustion-emitted particles is still at its early stages.

Slide presentations on country report are in the Annex.

4 METHOD EVALUATION AND DEFINITION OF FEASIBLE METHODS

4.1 SAMPLING AND DILUTION

4.1.1 Sampling and possible losses

Here sampling means an action where a sample is withdrawn from the exhaust and possibly conditioned, like for example diluted, and transported through a sample line to a measurement device, whether it is a filter, a collection plate or a continuous measurement device.

Whenever particles are lead through a line to a collecting device, particles are lost. This is because of the deposition of the particles which can occur due to e.g. electric forces, gravitational settling, thermophoresis, diffusion and impaction, as described by Brockmann, 2005. The effect of these phenomena on aerosol sample should be minimized by using as short sampling lines as possible, by using smooth curves, choosing conductive material for lines and by taking care of thermal insulation, optimizing flow rate and duct diameter and so on (see Brockmann, 2005). In any case, the losses in the sampling lines need to be estimated.

An important aspect to be considered is the size of the particles which will be sampled. In order to sample also large particles as it is done in the sampling of total dust or TSP (total suspended particles), isokinetic sampling is in general needed: The principles of isokinetic sampling have been described detailed elsewhere (for example Brockman, 2005). Briefly, the sample flow gas velocity in the probe has to be equal to the gas velocity in chimney, and the sample flow and gas flow directions have to be parallel. If sampling velocity is higher than the gas velocity in the chimney, sampling is super-isokinetic and for large particles, aspiration efficiency is below 100%. If sampling velocity is too low, sampling is sub-isokinetic and for large particles, aspiration efficiency is over 100% (Brockmann, 2005).

Conducting the isokinetic sampling has, however, some problems in batch burning where flue gas flow changes as a function of time during the combustion cycle (see Fig.5). Maintaining the isokinetic sampling from undiluted flue gas needs continuous tuning of the sample flow rate, which can be performed manually or automatically. Isokinetic sampling is less important for smaller particles which are less influenced by inertia and are capable to follow steeper streamlines. In general, particles smaller than approximately 1 µm behave like gas, i.e. they follow the gas flow even in sharp bends. Larger particles, however, can be removed from a gas flow by inertial forces, which accordingly is the case at non-isokinetic sampling conditions.

If the flue gas flow velocity is low (Fig. 5) the changes in the flue gas velocity do not affect the representativity of sampling since the settling velocity of particles affect the aspiration efficiency mostly rather than particle deposition on the walls (Brockmann, 2005; Grinshpun et al., 1993). In the example (Fig. 6), aspiration efficiency is lowered by more than 10% for particles of 60 µm in diameter when gas velocity is 0.7 m/s. In higher velocities, poorly adjusted sample flow can cause losses of large particles.

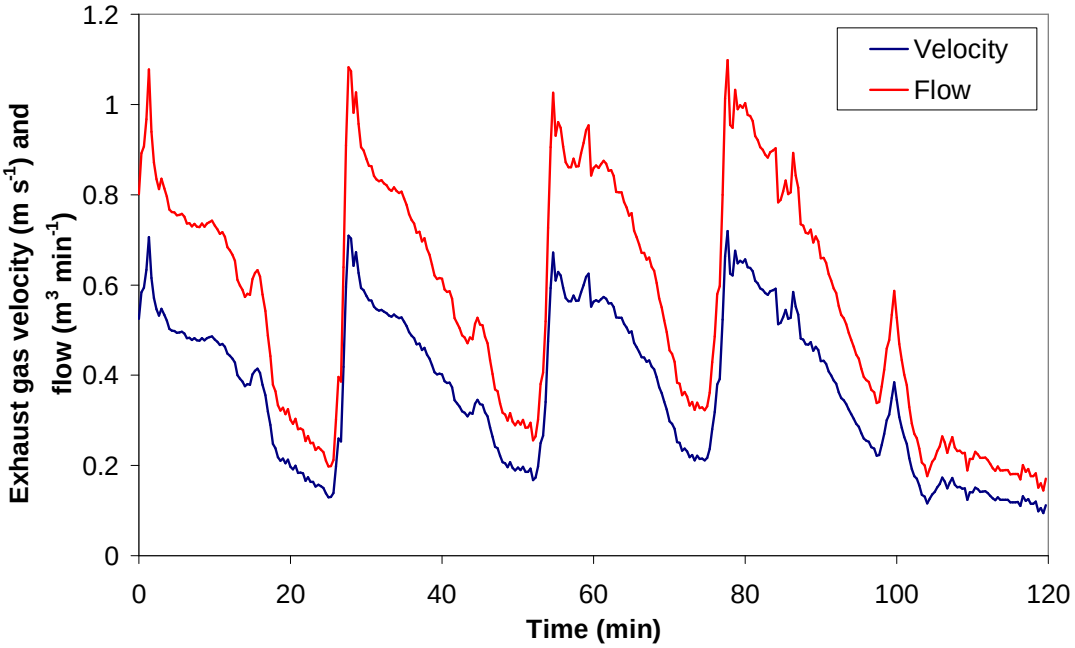


Figure 5. Variation of velocity and flow of exhaust gas in stack from batch burning (combustion appliance is masonry heater, d_i of chimney 180 mm).

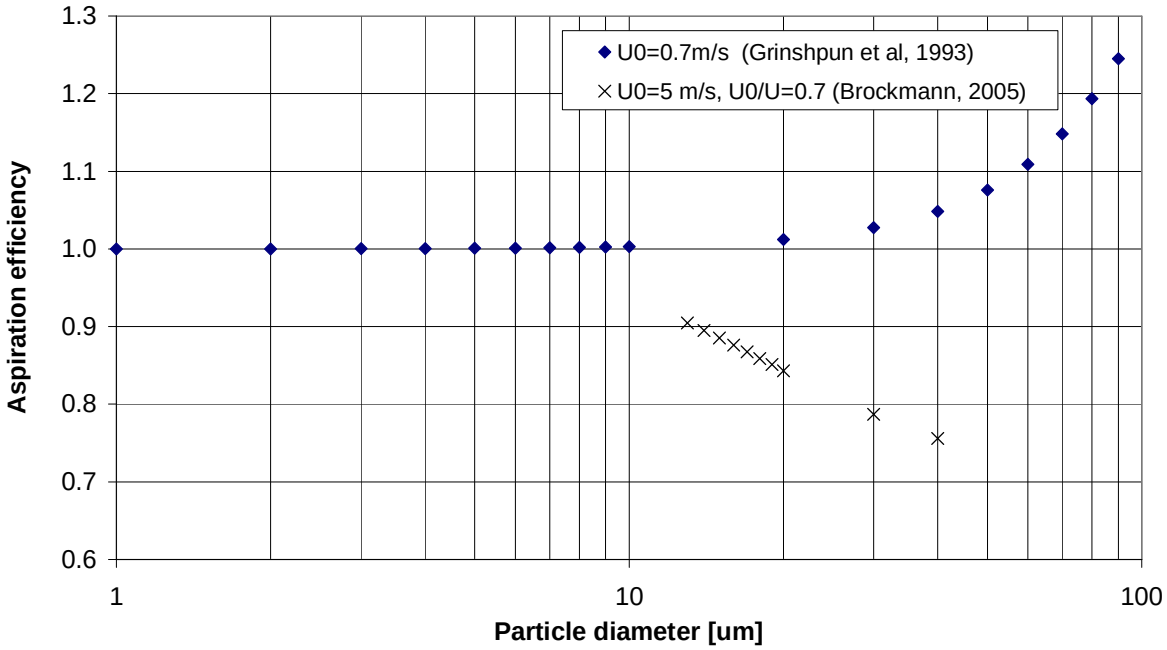


Figure 6. Two examples of aspiration efficiency in a sample inlet in isoaxial sampling: 1) gas velocity in chimney (U_0) is 0.7 m/s; the factor affecting the aspiration efficiency is the settling velocity of the particles (Grinshpun et al., 1993), 2) gas velocity in pipe is 5 m/s, and relation of the velocity in chimney and in inlet (U_0/U) is 0.7 (equations 8-20 and 8-21 in Baron and Willeke, 2005). Following initial values were used in calculation: inlet diameter 0.008 m, exhaust gas temperature 200 °C, pressure 101.3 kPa, density of spherical particles 1000 kg/m^3.

4.1.2 Sampling of certain size fractions of particles

The emission of particles which are smaller than 10 µm and smaller than 1 µm (PM_{10} and PM_1) in aerodynamic diameter should be measured. Dividing of the sample in other fractions below 10 µm, like $PM_{2.5}$, can also be done. Large particles have tendency to impact or settle on the sampling lines. If dilution is used, the collection of total particle samples is in practice impossible, because in any diluter the bends and constrictions exist into which the largest particles will impact. On the other hand, due to the random nature of the large particles (in batch burning), the collecting of the representative total particle sample is anyhow not straight-forward.

For present residential biomass combustion systems it has, however, been shown that the PM emissions are totally dominated by fine (<1 µm) particles, since the coarse fraction most often comprise <10% by weight (Boman, 2005; Brunner, 2006; Johansson et al., 2004). In large and medium scale (>1 MW) biomass boilers, however, a more pronounced coarse fraction of entrained char residues and/or mineral grains is typically seen which is clearly influenced by the load, i.e. gas velocities in the boiler (Brunner, 2006; Pagels et al., 2003).

Accordingly, isokinetic sampling is basically not needed for sampling of PM mass concentrations in small-scale (residential) biomass combustion systems and measurements will be relevant also when different kinds of dilution systems are used, as recommended in this report.

4.1.3 Dilution

When sampling in flue gases and exhaust emissions is to be performed, dilution is often needed for several reasons, e.g. simulation of ambient conditions (potential transformation), instrumental restrictions (e.g. temperature, concentration) and exposure condition requirements (e.g. human exposures). For on-line measurements of particle number and/or chemical composition, the dilution is certainly needed for the sensitive measurement instruments which can not survive with hot, humid, and possibly heavily particle-loaded flue gases. With the dilution, reactions between particles like coagulation can also be arrested in order to enable measurement on representative conditions (Brockmann, 2005).

In the dilution of flue gases, both partial pressure of gaseous species and aerosol temperature decrease. Many semivolatile species, i.e. compounds which can exist either in gas or particle phase during "normal" variations in ambient air depending on circumstances like their partial pressure and temperature, condense on particle surface during dilution. The condensation happens also in real life as the flue gas cools down after leaving the firebox, and eventually mixes with the ambient air. The condensation of the organic semivolatile species has a growing importance the more incomplete the combustion is, since the emission of unburned organic and elemental carbonaceous species increase. In addition, semivolatiles also evaporate from the surface of particles in the atmosphere during excess dilution (Robinson et al., 2007).

The reason why sampling from the diluted exhaust, and thus having also condensable organic matter in the particulate phase, is preferred is to improve the representativity of the sample in relation to aerosol which we are exposed to in the ambient air. As a result of condensation, the mass concentration, size distribution and composition of the particles may change. As the

chemical and physical properties of the particles change, also their capability to have adverse health effects may be altered.

The processes during ageing of primary flue gases, direct after the combustion appliance (furnace), of relevance for the flue gas aerosol emissions can be defined as

I) direct condensation of organic matter during cooling in the chimney (un-diluted emissions) or in the ambient air after emitted to the atmosphere (more or less diluted)

II) chemical transformation of particles in the atmosphere as a result of oxidation (e.g. by ozone) and/or other photochemical processes that includes both new particle formation and chemical transformation of primary particles as well as re-evaporation of previously condensed matter (organics)

In this project, the first aspect (I) is the main focus regarding emission sampling and procedures for determining emission factors and representative particulate mass, that may be used in further toxicological evaluation. The second aspect (II) is also of relevance for the overall assessment of different emission sources, although only briefly within the scope of the present project. The influence on the health related/toxicological capacity of the potential chemical and physical transformation that aerosol particles in the emissions from residential biomass heating may undertake is presently not known. Therefore, the further discussion in this report is based on the assumption that the most relevant sampling comprises “maximum” condensation of organic matter to the particulate phase to be sampled.

4.1.4 Dilution methods

Important issues to consider when choosing the dilution method are dilution ratio, flow rates, stability, mixing of the sample and dilution air, and particle losses in the diluter.

The validation of losses in the dilution method is important and they should be determined. Losses have to be low in order to be acceptable. When a new dilution method is introduced, the particle losses should be defined. Besides in the diluter, losses can occur in the transfer line from chimney to the diluter. It is therefore important to take care of the heating or insulation of the transfer line in order to avoid the condensation of the organics and deposition of the particles on cold transfer line walls.

Another important feature in the dilution is the background level of the measured quantity. For particle measurements, high quality (e.g. HEPA) filtered dilution air should therefore be used.

In the studies concerning emission measurement from residential wood/biomass combustion, different dilution methods have been used and generally found to be applicable e.g. whole flow dilution tunnels, mini dilution tunnels, dilution hoods and porous tube diluters in combination with ejector diluters. In Table 3, advantages and disadvantages of several such dilution methods, compiled within the present work, are accounted for. In Figures 7-9, the structures of some diluters have been presented. More pictures of diluters are available in manufacturers' homepages, for example www.dekati.fi.

Table 3. Advantages and disadvantages of certain dilution methods. (DR = Dilution Ratio)

Dilution method	Advantages	Disadvantages	Pay attention to
Ejector diluter (ED)	Stable Good mixing Can be used in the field	Losses (mainly of coarse particles) occur; they can be decreased with larger nozzle (stability decreases). DR cannot be adjusted.	Dilution ratio depends on temperature Small nozzles may clog up Losses have to be determined
Porous tube diluter (PRD)	Losses in diluter are minimized Wide range of DR can be applied Small size; can be used in the field	Sensitive to changes in sample flow	For proper mixing, after diluter there has to be some tubing before sampling equipment Losses have to be determined
PRD+ED	Stable Good mixing Losses have been minimized Wide range of DR can be applied Small size, can be used in the field	Tuning of the flows needs to be done carefully	Losses have to be determined
Dilution tunnel (whole/partial flow)	Stable	Dilution is usually high (except for whole flow tunnels) Large size; not suitable for field measurement	Losses have to be determined.
Mini-dilution tunnel	Simple and flexible	Not “standardized” Needs dedicated evaluation	Mixing has to be assured Losses have to be determined
Hood (total flow dilution tunnel)	Low DR can be achieved. “Natural draught” can be simulated	For number measurements, secondary dilution may be needed Large size	Mixing has to be assured The effect of background air on results has to be considered Losses have to be determined
CEN/TS 295 WG 5 "improved hood"	Suitable DR (10-20) for mass measurement. “Natural draught” can be simulated	Designed for TSP measurement, but losses are not defined For number measurements, secondary dilution may be needed Large size	Little experience of the method

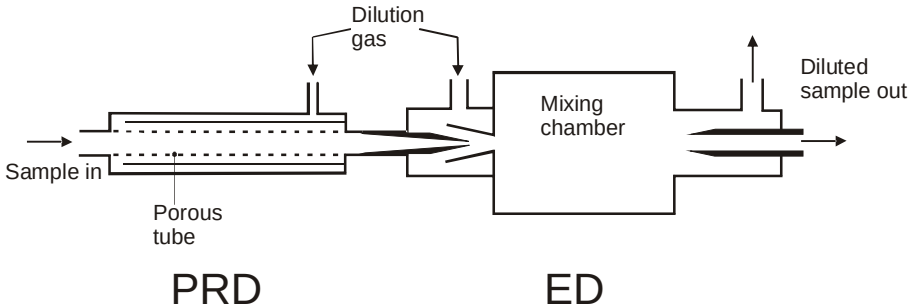


Figure 7. Porous tube diluter (PRD) and ejector diluter (ED) used in combination. Both diluters can also be used separately.

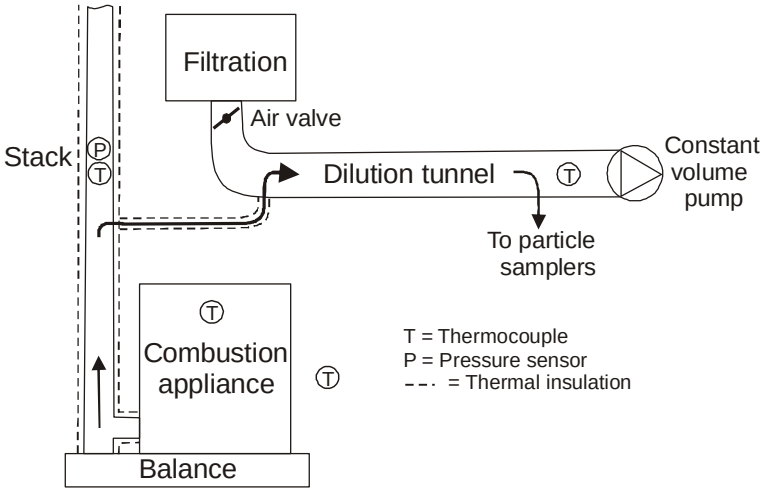


Figure 8. Dilution tunnel, where partial exhaust gas flow from chimney is sucked into the diluter. Also whole flow dilution tunnels can be used.

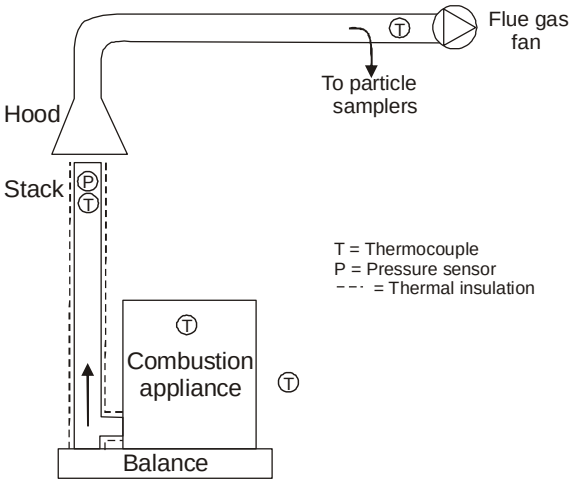


Figure 9. Dilution hood, where all the exhaust gas and dilution air are sucked into the hood by flue gas fan.

4.1.5 Dilution ratio

The suitable dilution ratio (DR) depends on the measurement device and on the emission of a combustion appliance which will be measured. Although it is difficult to define one "correct" DR, it is important to understand how the dilution affects the aerosol.

If maximum particle mass of the primary emission needs to be achieved, it has been shown that DR should be below 20:1. When DR is higher, not all the condensable organic matter will condense on the surface of existing particles, but the evaporation from the particles occurs. This causes a decrease of the particle mass emission related to the amount of organic carbon in particles (Lipsky & Robinson, 2006). It has to be noted, as discussed previously in 4.1.3, that the aerosol which has been diluted at such low DR does not necessarily correspond to the aerosol in real-life atmospheric conditions. Also the toxicological properties of the combustion aerosol in the atmosphere may change compared to the primary emissions, which has to be considered in the particle sampling for health effect studies (see also 4.5).

It has been estimated that using DR less than 100:1 likely overestimates the emitted primary fine particulate mass relative to the dilution occurring in the atmosphere, where DR can be around 10000:1 (Lipsky & Robinson, 2006). On the other hand, it has been observed that the evaporated organics to a large extent can form secondary organic aerosol (SOA) in the atmosphere. This means that although some of the particle mass (i.e. condensed organics) in the emission is lost during the high dilution, at least part of this evaporated material forms new particles in the atmosphere. However, presently the knowledge concerning chemical transformation of different groups of organic compounds in emissions from different sources are very scarce.

In order to have the most of the semivolatile organics in the particle phase, the temperature of the diluted exhaust gas should be lowered considerably compared to the flue gas temperature, and according to the engine standard ISO 8178 the temperature in the sampling point should be <52 °C.

Nevertheless, for particle number measurement from biomass combustion emissions, DR higher than 20:1 is many times needed for e.g. ELPI (electric low pressure impactor), SMPS (scanning mobility particle sizer) and FMPS (fast mobility particle sizer) to work properly. If all the possible condensable matter is needed to collect in particle phase of primary emission, and at the same time number measurement has to be conducted, for many combustion appliances either all the measurements have to be conducted from the more dilute exhaust, or two different stages of dilution are needed. If the latter is used, the dilution ratio has to be measured for both dilution stages.

To our knowledge, there are no scientific data that suggest a maximum DR which can be used. But the sensitivity of the measuring device, as well as the sensitivity of devices which are used for monitoring the DR set the maximum limits for the dilution.

4.1.6 Determination of dilution ratio

The dilution ratio (DR) should be monitored preferably continuously by measuring concentrations of CO_2, O_2 or NO_x from both undiluted and diluted exhaust gas. From these data, the dilution ratio can be calculated. The background concentration in the dilution air has to be taken into consideration in calculation; it should be measured before and after the test period, if continuous measurement is not possible. Determining the DR from flow rates can be challenging due to changing temperature and particle loading of the exhaust gas. The feasibility of using different flue gas components for determining DR has to be defined with respect to specific considerations in each case. Overall, the determination of DR is very important and that is why the measurement devices used for DR monitoring have to be accurate and have a measurement range wide enough.

4.2 PARTICLE MASS

4.2.1 Introduction

Depending on the particle size fraction of interest the determination of the particle mass concentration in the flue gas can be related to TSP (total suspended particulate matter), PM_{10}, PM_1 or other size fractions $<PM_1$. Thereby, TSP represents the basic parameter for the evaluation of PM emissions from combustion devices. All regulations and emission limits presently applied are based on this parameter. However, especially concerning the evaluation of health risks of PM emissions knowledge about the PM_{10} and PM_1 concentrations is of relevance, and therefore, also their determination is an important issue in the overall procedure proposed. Additionally, especially for scientific studies, the determination of the particle size distributions in the submicron size range is recommended.

Unfortunately, presently no reliable standard methods for the on-line determination of the mass concentration of particles emitted from a combustion process are available. Only TEOM (Tapered Element Oscillating Microbalance), as it is applied for air quality control, could be applied for PM_{10} or PM_1 measurements, however, it only works in highly diluted gas flows. Therefore, discontinuous methods are commonly used.

4.2.2 Sampling point

PM mass concentration measurements can generally be performed in the undiluted as well as in the diluted flue gas. Two important aspects have to be considered.

- If the determination takes place in the undiluted flue gas, condensable organic compounds, which later during the cooling of the flue gas form particles, pass the dust sampling device (this has been discussed previously in subchapter 4.1 Sampling and Dilution). Consequently, the mass concentration of PM in the undiluted flue gas is lower than the one in the diluted flue gas from the same combustion process due to the condensation of different organic compounds during the dilution step. This however, only is of relevance for measurements at poor burnout conditions since at almost complete burnout the flue gas in the stack contains in principle no condensable matter.

- Secondly, it has to be considered, that during the dilution step losses of coarse fly ash particles may occur, which leads to an underestimation of their emissions. As discussed previously also, this is of minor importance for residential biomass heating devices since only small fractions of coarse particles exist/are emitted in such systems.

4.2.3 Isokinetic sampling

All methods applied for the determination of the particle mass concentration in the flue gas are based on the extraction of a partial flow of the flue gas from the main stream. To achieve reliable results for coarse fly ash particles, isokinetic sampling must be applied (see subchapter 4.1 Sampling and Dilution). Especially during batch burning this requisition may lead to increased efforts since the flue gas volume flow permanently changes over one batch.

Isokinetic sampling is, however, not needed for PM_1 measurements since particles in this size range always follow the streamlines of the flue gas flow, and therefore no influence of the sampling velocity on the particle trajectories occurs.

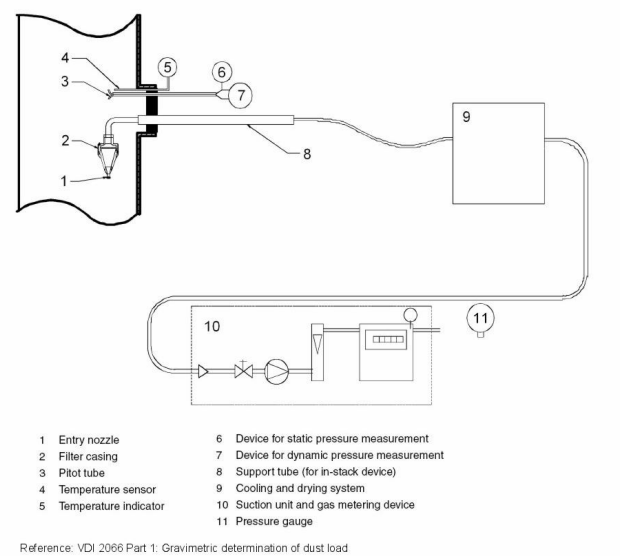
4.2.4 Methods applied

TSP, PM_{10}, PM_1 and the particle size distribution in the submicron range can be determined. Therefore, different methods and devices are usually applied.

Determination of the TSP mass concentration in the flue gas

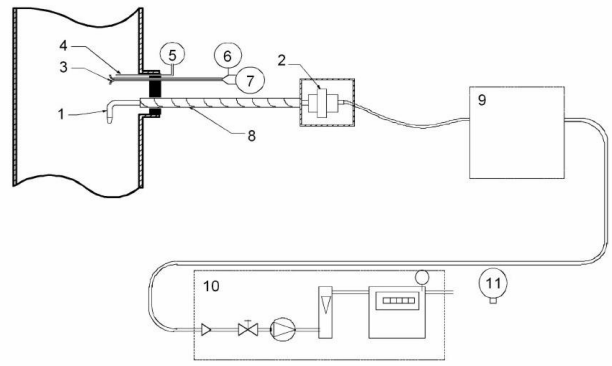
PM emission limits for biomass combustion processes all over Europe are related to the concentration of TSP (=total dust) and therefore, for this parameter appropriate standards already exist. The measurement procedure is described in EN 13284-1, *Stationary Source Emissions - Determination of Low Range Mass Concentration of Dust - Part 1: Manual Gravimetric Method*. In Austria and Germany the total dust determination equipment according to VDI 2066-1 is usually applied, which is based on the EN 13284-1. For the overall procedure on particle measurement, sampling and characterisation described, the application of this equipment or a comparable one is recommended.

The set-up allows for in-stack and out-stack measurements. Schemes of the measurement equipment for both types of measurements are shown in Figure 10. As can be seen from Figure 10, the flue gas is sucked through a filter placed in a filter casing (2). The filter casing can be placed in the stack or outside. If it is placed outside the stack, the sampling line upstream the filter and the filter casing have to be heated. Downstream the filter the flue gas is led over a suction and gas metering device (10). Isokinetic sampling is realised by using a standardised set of entry nozzles as well as by controlling the suction device. The filter is weighed before and after the measurement and by dividing the mass difference determined with the flue gas flow extracted, the mass concentration in mg/Nm^3 can be calculated.



1 Entry nozzle
2 Filter casing
3 Pitot tube
4 Temperature sensor
5 Temperature indicator
6 Device for static pressure measurement
7 Device for dynamic pressure measurement
8 Support tube (for in-stack device)
9 Cooling and drying system
10 Suction unit and gas metering device
11 Pressure gauge

Reference: VDI 2066 Part 1: Gravimetric determination of dust load



1 Entry nozzle
2 Filter casing
3 Pitot tube
4 Temperature sensor
5 Temperature indicator
6 Device for static pressure measurement
7 Device for dynamic pressure measurement
8 Suction tube (out-stack device)
9 Cooling and drying system
10 Suction unit and gas metering device
11 Pressure gauge

Reference: VDI 2066 Part 1: Gravimetric determination of dust load

Figure 10. In-stack and out-stack total dust sampling system according to VDI 2006-1

The method described in principle is quite simple. However, some issues have to be considered:

- As filter medium plan filters or quartz wool stuffed filter cartridges with or without plane filter can in principle be applied. Especially when low PM concentrations and mainly PM_1 emissions are expected, plan filters should be applied instead of quartz wool stuffed filter cartridges.

- The filter has to be treated at 180 °C before the measurement and then subsequent equilibration of the filter in a desiccator has to take place. According to VDI 2066 also after the measurement the filter has to be dried at 160 °C. This regulation is not useful if the PM sampled on the filter is forwarded to chemical characterisation since during the 160 °C thermal treatment, re-evaporation of easily volatile compounds may take place. Therefore, it is recommended only to place the filters in a desiccator if subsequent chemical analyses are foreseen.

PM_{10} and PM_1 determination

For the determination of PM_{10}, impactors or cyclones can be used while for the PM_1 measurements, only impactors are applicable. If cyclones are applied it has to be taken care that the cyclone has a steep precipitation curve at 10 µm to achieve reliable results.

Concerning impactors the German VDI guideline 2066 Part 5 and Part 10 describes the impaction method. Impactors are usually divided into subsequent stages in which particles with a particle size down to a certain cut diameter are precipitated. An impactor stage always consists of a nozzle plate, a spacer ring and a stagnation plate (see Fig. 11). Between the nozzle plate and the stagnation plate the flue gas is forced to change its flow direction. Particles which are too big (heavy) to follow this change of flow direction are precipitated and are colleted on a collection substrate placed on the stagnation plate. The flow velocity and the geometry of an impactor stage determine its cut diameter.

The mass of particles collected in an impactor stage is determined by weighing the collection substrate before and after the measurement. The particle concentration is then calculated by dividing the mass of particles collected by the flue gas volume flow through the impactor.

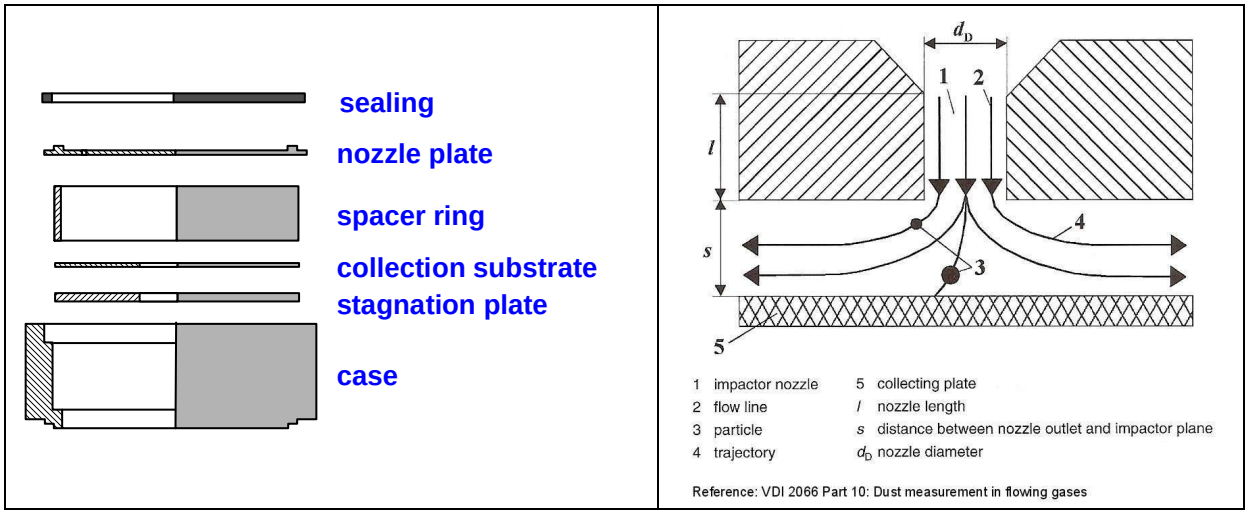


Figure 11. Scheme of an impactor stage as well as the principle of particle precipitation in an impactor

Impactors which are designed for PM_{10} and/or PM_1 measurements are available on the market. In Figure 12, two examples for such impactors are presented.

Johnas II impactor

Kalman KS 220 impactor

Figure 12. Impactors for PM_{10} and PM_1 determination available on the market

Explanations: Johnas II: size classes: >10 µm, 2.5 (or 4) – 10 µm; < 2.5 (or 4) µm
Kalman KS 220 size classes: 10 µm, 2.5 – 10 µm, 1 – 2.5 µm, < 1 µm

If low-pressure impactors are applied, cut sizes in the size range of down to some 10 nm can be achieved. Low-pressure impactors such as for example Dekati Low-Pressure Impactors (DLPI) or Berner-type Low Pressure Impactor (BLPI) typically have 4-8 precipitation stages in the submicron size range (Fig. 13). They are based on the same principle as shown in Figure 11, with the additional feature of reduced pressure in the submicron range that enables size specific separation also of fine particles. Consequently, with these devices information about the particle mass concentration of different size fractions of submicron particles can be obtained.

11-stage BPLI

13-stage DLPI

Figure 13. A 11-stage Berner-type low-pressure impactor (BLPI) and a 13-stage Dekati low-pressure impactor (DLPI).

Explanations: BLPI, Hauke Type LPI 25/0.018; cut diameters: 0.018 to 16 µm; Dekati DLPI: cut diameters: 0.03 to 10 µm.

Particles sampled with impactors can generally be forwarded to chemical characterisation but it has to be considered, that the sampling substrates applied, their pre-treatment, handling and storage most be adjusted to the needs of the chemical analyses method applied.

4.3 PARTICLE NUMBER

4.3.1 Introduction

As mentioned earlier, all air quality regulations, emission limits and health risk estimations are presently based on particle mass concentrations often expressed as TSP, PM_{10} or $PM_{2.5}$. In aerosol science particle number concentration and size distribution are, however, key parameters when discussing e.g. particle formation and transformation as well as the fate and effects in the atmosphere and in human health during exposure. Measurement of particle number has been applied during the greater part of the 20^{th} century and the development and insights in basic aerosol physics of fine particles as well as more adequate sampling methods relevant for determination of submicron particle number concentration and size distribution started during the 1960s (Spurny, 2001). During the last decades such methods have been used more routinely in emission studies from combustion processes as well as in ambient air quality monitoring and health related research. Particle number has also been suggested to be an even more relevant PM parameter than mass concentration regarding the documented health effects related to PM exposure, especially for the fine fraction (PM_1). In air pollution epidemiology, particle number has only been included as a parameter in a few numbers of studies and more scarce, and somewhat contradictionally information is available. In many aspects, a more detailed aerosol particle characteristics than total PM mass, like particle number, size, shape and chemical composition, is needed both in technical, health and atmospheric applications. Since measures of PM mass concentration are influenced by particle number, size, shape and composition all these properties needs to be considered if detailed aerosol characteristics is to be evaluated.

Aerosol systems in general and high-temperature (e.g. combustion) aerosols specifically are very dynamic and a number of physicochemical processes are in progress, e.g. nucleation (new particle formation), condensation, coagulation, deposition and chemical transformation. Since such processes may influence the number concentration and size distribution, it is rather complicated to measure and determine particle number correctly since one must avoid that the sampling procedure alters the number concentration and other properties of the aerosol (Biswas, 2001). In combustion processes specifically, the particle number concentrations are often extremely high with a considerable temperature gradient from the flame to the chimney outlet or exhaust pipe.

Measurement of particle number concentration and size distribution is today mainly performed by on-line (in-situ) methods with instruments that count the particles based on electrical and/or optical principles. The size classification is most often made either by inertial, electrical mobility or optical properties of the particles depending on e.g. size interval, specific particle characteristics and application. In the following, sampling aspects, measurement methods and instrumentations most commonly used today for determination of particle number concentration and size distribution in combustion processes are briefly summarized and some important aspects of the sampling and measurements procedure is given.

4.3.2 Sampling and dilution

Online measurement of particle number in combustion aerosols most often requires cooling and dilution of the hot and humid flue gases to reduce the particle number concentration to the operational range of the instrument used. Dilution is also needed to lower the temperature and to avoid condensation of water vapour during cooling (Biswas, 2001). When considering the measures of particle mass and number in an aerosol system it is important to consider the relation between these two parameters and the dynamics that may influence the characteristics of the particles. The aerosol may contain several modes of particles that range from nucleated primary particles (~0.001-0.05 µm), via accumulated particles (~0.05-0.5 µm) and up to coarse particles of several tens of micrometers (~1-50 µm). As an example it is given that if spherical particles with the same density are assumed, one single particle with a diameter of 10 µm has the same mass as 10^9 particles with diameters of 0.01 µm. If present, larger (coarse) particles will therefore dominate in mass while fine particles will dominate in number. However, as mentioned earlier in subchapter 4.1.2, the PM is dominated by fine (<1 µm) particles by weight, and therefore also even more by particle number, which therefore is the focus when performing particle number measurements in residential biomass combustion systems.

One important issue to consider directly related to number concentration and size distribution is the influence of coagulation processes. The coagulation rate is strongly dependent on number concentration and can be very significant initially in the flame or directly after the combustion zone where the concentrations of very small particles are extremely high. In Figure 14, a simple example is given by Wiinikka (2005), based on the theory of coagulation presented by Friedlander (1977), that illustrates the effect of coagulation on the particle concentration and the average particle diameter.

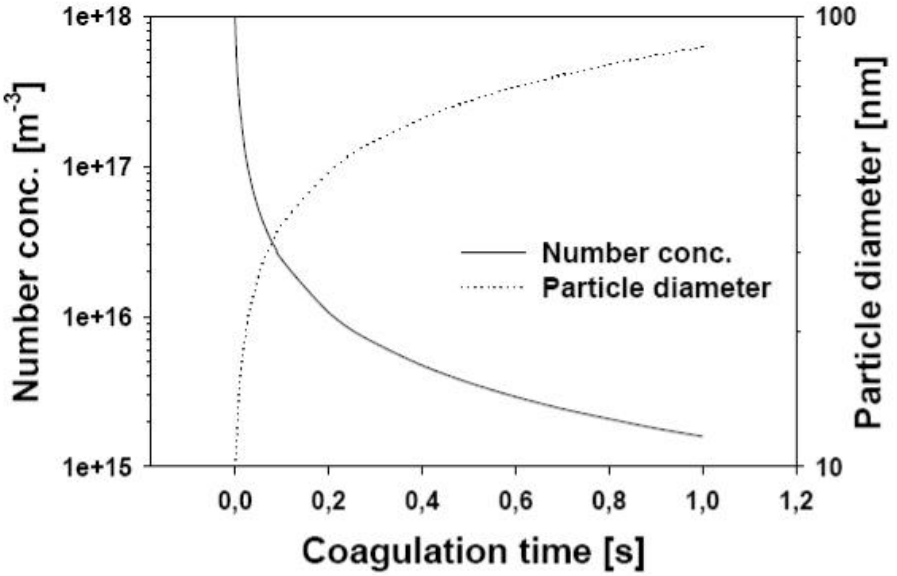


Figure 14. Effect of coagulation time on the particle number concentration and average particle diameter at a temperature of 1000°C in air (Wiinikka, 2005).

Typically particle number concentrations in the emissions from residential biomass combustion, sampled in flue gases (<200°C) with subsequent dilution, have shown to be 1-30*10^7 particles/cm^3 (Boman, 2005; Johansson et al., 2003; Tissari et al., 2007a) At these conditions the coagulation rate has decreased significantly and are of minor importance to consider. However, if sampling is performed close to the flame at higher temperatures, which may be the case in specific research applications, the influence of coagulation on number concentration and size distribution has to be considered.

Another important issue concerning particle number measurements in combustion systems is the potential formation of particles by homogeneous nucleation, i.e. new particle formation from gas species (organic and/or inorganic) without the presence of condensation nucleus. This phenomenon may occur under supersaturated conditions in flue gases when the temperature is decreased after the combustion zone and heat exchanger device as well as during dilution (and cooling) of hot flue gases or engine exhausts. In residential biomass combustion, however, when flue gases are extracted at <200°C and diluted before subsequent number concentration measurement, such nucleation mode particles have typically not/very seldom been determined. This can probably be explained by two circumstances; *I)* the dominating inorganic vapours (i.e. alkali species) condense at much higher temperatures (>500°C) and *II)* the semi-volatile organics usually have enough "seed" particles (soot and inorganic particles) to condense onto instead of forming new particles.

Since the aerosols from residential biomass combustion are totally dominated by fine particles, at least regarding particle number concentrations, requirements of isokinetic sampling conditions is most often of minor importance, as discussed in more detail previously in 4.1.2.

4.3.3 Particle classification and size determination methods and instruments

Measurements of aerosol particles properties like number, mass and chemical composition, can be divided in *integral measurements* over a given size range and *size-resolved measurements*. Applied on biomass combustion testing and research, size-resolved measurements are preferred since they give combined information of particle number concentration and size distribution. The size range for such measurements differs depending on methodological and instrumental considerations. For coarse particles (>1 µm), size classification is most often based on either inertial or optical properties, while for fine submicron particles, the size classification usually is based on inertial or electrical mobility properties. For inertial separation of fine particles, special conditions have to be used, i.e. low pressure and/or high velocities, to separate the particles from the gas phase. This is also discussed previously in subchapter 4.2. A brief description of the most commonly used (and recommended) state-of-the-art techniques applied on emission measurements of particle number concentration and size distribution is given here. For further and more detailed information on these and other techniques as well as sampling, dilution and analysis of aerosols in general and combustion aerosols in special, see also McMurry (2000) and Burtscher (2005).

Electrical low pressure impactor (ELPI)

The classification of an ELPI, as well as in all types of impactors, is based on inertial separation, as previously illustrated in subchapter 4.2.4 (Fig. 15). The particles are first charged before deposited on the different stages in series. The impaction stages are connected to a current amplifier and the charged over the stage is correlated to number of particles for each size class. In the ELPI from Dekati Ltd, which are the only commercially available system, the particles are separated in 12 stages between 0.030 (0.007 as an option) and 10 µm. The time resolution is very good with a response time <5 s. The wide size range covered by the same instrument is rather unique, but the size resolution in the submicron range is less good and a potential nucleation mode can hardly be measured by ELPI (Burtscher, 2005). Another consideration is the potential artefact caused by evaporation of particulate material in sub micrometer range where the pressure is decreased. By combining the ELPI (i.e. aerodynamic diameter) with e.g. SMPS systems (i.e. mobility diameter) one can gain information of particle density and structure.

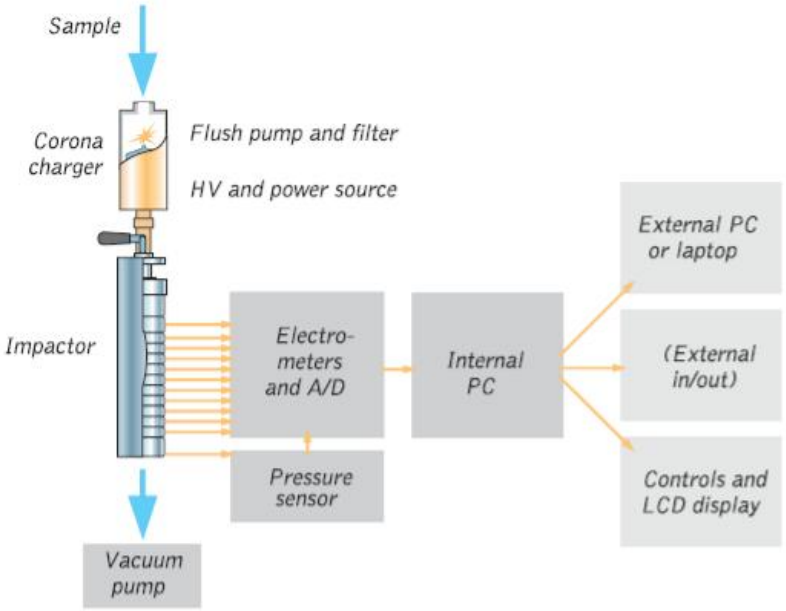


Figure 15. Illustration of the ELPI system manufactured by Dekati Ltd.

Scanning mobility particle sizer (spectrometer) (SMPS) systems

SMPS systems are integrated systems measurements of fine particle mobility size distribution (size classification) and concentration (particle counting). The size classification is made by a differential mobility analyzer (DMA) that works as an electrical spectrometer which classifies particles according to their electrical mobility equivalent diameter (see Fig. 16). Before the DMA, a bipolar diffusion charger establishes an equilibrium charge distribution of the aerosol and by scanning the voltage in the aerosol flow field in the DMA, together with adjusting the flow rate conditions, size distributions within the range typically of 0.005-500 µm can be covered for SMPS systems in general. The size range can, however, be extended, both downwards (~0.002 µm, "nano-DMA") and upwards (~1 µm, "long-DMA"). In the CPC, single particles are detected (counted) optically by light scattering. Before detection, the

aerosol passes a saturated n-Butanol (or water) vapor which after cooling makes the particles grow by condensation to approximately 10 µm. One drawback with SMPS systems when used in combustion applications is that the typical time resolution (i.e. total scan time) is in the order of minutes. In transient conditions, typically existing in residential wood combustion or varying load engine cycles, higher time resolution is preferable. Standard SMPS system can be somewhat tuned towards shorter scan times, but there are also special types of fast scanning electrical spectrometers and particle counters with time resolutions <1 second (as discussed below) (Fig. 17).

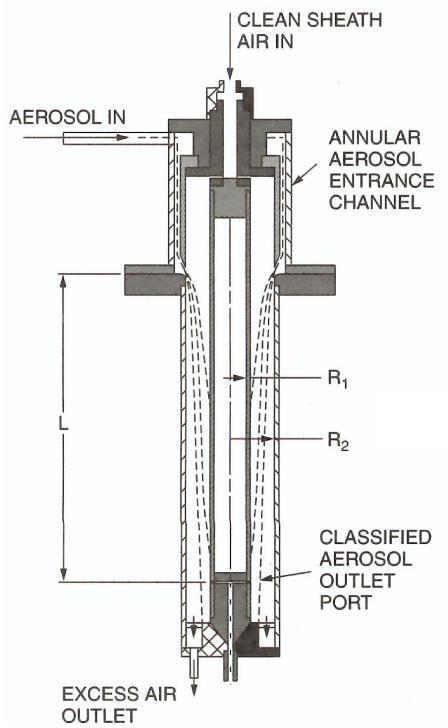


Figure 16. Illustration of a typical cylindrical DMA (from Flagan, 2001).

Figure 17. Examples of typical SMPS sytems manufactured by TSI Inc (left) and Grimm Aerosoltechnik GmbH (right).

Fast particulate sizer (spectrometer) systems

The need for particle size and number information with high time resolution, e.g. in some combustion applications, has lead to the development of different commercial instruments available. In principal, instead of using a scanning mode size classification these instruments work with parallel measurement of a number of size classes in the sub-micrometer range. The Fast Aerosol Particle Emission Spectrometer (FAPES) system by Grimm Aerosoltechnik GmbH (model TR-DMPS), comprise 10 parallel DMA´s with 21 size channels (0.006-0.5 µm) and aerosol electrometer detectors. The solution is very fast (time resolution of 0.1 s) and flexible but expensive and voluminous (Burtscher, 2005). Another, more compact approach is to use a segmented collection electrode of a mobility analyzer (DMA) which allows a parallel measurement in one analyzer (Burtcher, 2005). Examples of such instruments are the Fast mobility particle sizer^{TM} (spectrometer) (FMPS) manufactured by TSI Inc that size classifies particles in 32 channels of resolution (0.006-0.56 µm) with a time resolution of 1 s and the Fast Particulate Spectrometer (model DMS500) manufactured by Cambustion with a size spectrum of 0.005-2.5 µm and a time resolution of 0.1 s. These systems operate at ambient pressure, like SMPS systems, to prevent evaporation of volatile particles.

Aerodynamic Particle Sizer (APS)

For measurements of coarse mode particle number size and concentration APS is a commonly used type of instruments. The APS size classify the particles by aerodynamic properties via a particle acceleration nozzle and time-of-flight (TOF) measurement between two laser beams. The time resolution is high, i.e. real-time measurement, and the size range typically between 0.5 and 20 µm. A number of different APS models are available by TSI Inc and the instruments are very compact, portable and easy to operate.

4.3.4 Summary of particle number measurements

- Particle number concentrations and size distributions are highly relevant parameters in many aspects concerning health and climate related issues of air pollution and are recommended to be included in biomass combustion research activities. The question concerning the specific importance of PM number in relation to mass, size, chemistry etc. is, however, still to be elucidated and clarified.

- Aerosols in biomass combustion are very dynamic systems and a number of physicochemical processes have to be considered, e.g. nucleation, condensation, coagulation, deposition and chemical transformation, if adequate number and size measurements are to be performed.

- Dilution (and cooling) is in principal always needed, since the particle number concentrations are very high, i.e. too high for the instruments used.

- Size-resolved on-line (in-situ) measurements are preferred since they give “real-time” combined information of particle number concentration and size distribution.

- The focus for particle number measurements in residential biomass combustion systems are on the fine sub-micrometer sized mode since it totally dominates the PM emissions. The need for isokinetic sampling conditions are therefore of less importance.

- Several suitable measurement systems are presently available, that size classify particles by inertial or electrical mobility properties with subsequent detection (counting) by electrical or optical principals, and therefore recommended to be used for biomass combustion applications.

4.4 CHEMICAL CHARACTERISATION OF PARTICLES

4.4.1 Chemical composition of particles

The emissions from combustion of biomass contain increased concentrations of gaseous and particulate compounds that are known to be hazardous to human health. The chemical composition of particles can be divided into carbonaceous matter and into inorganic fraction, which includes e.g. alkali salts, crustal material and metals. Particulate organic matter (POM) can be separated further based on different properties, e.g. water-solubility and further into individual organic compounds or classes of compounds.

Carbonaceous matter, i.e. elemental carbon (EC) and organic carbon (OC), often constitute a major fraction of particulate matter. Soot, often referred to as EC or black carbon (BC) is a primary pollutant formed in combustion processes. Soot is the principal light-absorbing species in the atmosphere, playing an important role in the aerosol climatic forcing. Due to its specific surface properties, soot provides a good adsorption site for many semi-volatile compounds such as polycyclic aromatic hydrocarbons (PAHs). OC is an effective light scatterer and may contribute significantly to both visibility degradation and the direct aerosol climatic forcing. A significant fraction of the particulate OC is water-soluble (WSOC), making it important to various aerosol-cloud interactions.

The carbonaceous fraction of particulate matter consists of thousands of different compounds, e.g. n-alkanes, n-alcanoic acids, dicarboxylic acids, amino acids, nitrophenols and PAHs. The presence of semi-volatile, condensable, multiphase and polar organic compounds complicates the sampling and analysis of organic particulate matter. Only a small part of the particulate carbonaceous fraction has been able to be identified.

PAHs are products of incomplete combustion formed during burning of organic matter. PAHs occur in the form of gases, solids adsorbed to fine aerosol particles, and as semi-volatile compounds that are distributed between the gas- and the particle-phases. Several PAHs are considered carcinogenic and genotoxic. U.S. Environmental Protection Agency has proposed a list of 16 individual PAHs that should be determinated (U.S. EPA, 2004) as a minimum. Recently the interest to determinate the concentrations of even more PAHs has increased, with focus of more heavier compounds (i.e. 5-6 aromatic rings).

The inorganic fraction of particles from chemically not treated (“natural”) biomass combustion is composed mainly of different alkali salts (e.g. chlorides and sulphates of potassium) as well as minor amounts of certain trace metals, e.g. zinc. In the atmosphere, e.g. sulphate, nitrate

and ammonium in the particulate phase are known as secondary inorganic ions, since they are mainly formed from their precursor gases through gas-particle conversion.

With regard to combustion processes, metals are emitted either as vapour or solids. Along with carbonaceous matter, metals appear to play a significant role in determinating particulate health effects. The focus of metals in air pollution in general is put on the following metals, according to the EU directive on waste incineration (Directive 2000/76/EC): Sb, As, Cd, Co, Cr, Cu, Pb, Mn, Ni, Tl, V and Hg. For biomass combustion also Zn is of great relevance since in many cases it is the most dominant trace metal in particles from biomass combustion. Such metals may act as catalysts in the formation of reactive oxygen species (ROS) and are associated with the activation of many biological processes. In addition from the toxicological point of view, it is important to know if metals are in a soluble form (e.g. salts) or as insoluble form (e.g. oxides) (Limbach et al., 2007).

Water is an important component of atmospheric aerosols. Since the absorption of water increases particle size, it has an impact on the light scattering by, and the residence time of, atmospheric aerosols. In addition, water may change the chemical composition of particles by providing a medium for heterogeneous chemical reactions and by influencing the partitioning of semi-volatile compounds between the gaseous and particulate phases. The water content in aerosols depends on the chemical composition of the particles, as well as on ambient temperature and relative humidity.

Potassium, oxalate and levoglucosan are regarded as good signatures of biomass combustion in the atmosphere, although potassium can also be derived from soil and oxalate can be formed in the atmosphere from hydrocarbons of other primary sources than biomass combustion. Burning or pyrolysis of cellulose and hemicelluloses forms the stable monosaccharide anhydrides, levoglucosan and to a small extent its two isomers, mannosan and galactosan. They are an important class of compounds in the organic aerosol subfraction denoted water-soluble organic compounds.

The chemical characterisation is considered here to include the steps from sampling substrates to chemical analysis as follows: sampling substrate materials, preparation of sampling substrates, sample storage, weighing, sample pre-treatment and analysis methods.

4.4.2 Sampling substrates, preparation prior to sampling, and sample storage

The sampling substrate material and the preparation procedure have to be tailored to the sampling and analyses methods applied. Therefore, different possibilities exist.

Quartz filter

Quartz filter is mainly used for determination of OC and EC. Therefore, baking of a quartz filter is required (in 800-900 °C for 3-6 hours). After baking, the filters need to be stored protected from contamination, e.g. in petrislides. Quartz filter is not considered reliably weighable. After sampling, quartz filters are recommended to be stored protected from light and contamination in petrislides or wrapped in aluminium foil and preferably in freezer.

Quartz wool

Quartz wool is used for dust sampling (TSP) (quartz wool stuffed filter cartridges). Quartz wool is dried in oven (105-120 °C) and stored protected e.g. in desiccator with silica gel prior to analysis. Quartz wool can be weighed. After sampling, quartz wool is suggested to be stored in dry circumstances.

Glass fibre filter

Glass fibre filter is usually used for dust sampling (TSP). Glass fibre filters should be stored protected e.g. in desiccator with silica gel prior to analysis. Glass fibre filter can be weighed at least roughly. After sampling, glass fibre filters are recommended to be stored protected from light and contamination in petrislides or wrapped in aluminium foil and preferably in freezer.

Polytetrafluoroethylene (PTFE/Teflon) filter

PTFE-filters are commonly used for many analyses. Usually PTFE-filters do not need any pre-treatment prior to analysis and they are weighable. After sampling, PTFE-filters are recommended to be stored protected from light and contamination in petrislides and in freezer or in desiccator.

Polycarbonate film

Polycarbonate film is usually used as a sampling substrate in impactor sampling. Normally film is coated with vacuum grease. Polycarbonate film is weighable. The use of aluminium foil under the polycarbonate film can be used in order to stabilize the weighing. After sampling, polycarbonate film is recommended to be stored protected from light and contamination e.g. in petrislides and preferably in freezer or in desiccator.

Aluminium foil

Aluminium foil is usually used in impactor sampling. Usually aluminium foil is dried in >110 °C. If aluminium foil is coated with vacuum grease and the exhaust gas is hotter, higher baking temperature has to be used due to possible evaporation of grease during sampling. Aluminium foil can be weighed. After sampling, aluminium foil is recommended to be stored protected from light and contamination e.g. in petrislides and preferably in freezer or in desiccator.

4.4.3 Weighing

All the filter materials are considered weighable, except for quartz filter. The weighing of sampling substrates should be conducted in controlled conditions where the temperature and the relative humidity can be adjusted. The scale used for mass determination should have the partition of one microgram. The use of ionisator/ionizing unit is recommended, in order to avoid the interference of static charges during the mass determination.

4.4.4 Sample pre-treatment and analysis techniques

The best available analysis methods are recommended to be used as long as they are accurate and precise. Suitability of different sampling substrate materials is given in Table 4. Preferred sample pre-treatment and analysis methods for the determination of different subfractions or compounds are given as follows:

Elemental carbon (EC) and organic carbon (OC)

For determination of EC and OC, the analysis by using a thermal-optical method is recommended (e.g. Birch & Cary, 1996). Suitable temperature programmes include NIOSH 5040, Improve, Improve_A and corresponding programmes. The use of a quartz filter as a sample substrate is required for the analysis. Not any sample treatment is required prior to analysis. Moreover, the concentration of OC and EC together (NCC – non carbonate carbon) can be determined using a carbon analyser. For this analysis, also Al foils can be applied as sampling media.

Water-soluble organic carbon (WSOC)

The use of TOC-V_{CPH} organic carbon analyzer is suggested for the analysis of WSOC (e.g. Timonen et al., 2008). As long as a sampling substrate can be submerged into water, the method does not set any other limitations for the sampling substrate. Extraction is made with deionised water for 15 minutes and the sample solution is filtered prior to analysis, if needed.

Polycyclic aromatic hydrocarbons (PAH)

The use of gas chromatography – mass spectrometry (GC-MS) or high pressure liquid chromatography (HPLC) is recommended for the analysis of PAHs. Gas-phase PAHs can be analyzed for example from denuders coated with XAD and from XAD-adsorbents and particle-phase PAHs from PTFE-, quartz- and glass fibre filters and from polyurethane foams (PUF). Several quantitative extraction methods exist, e.g. extraction with ultrasonification or with Soxhlet apparatus.

Monosaccharide anhydrides (MAs)

The extraction with deionised water/tetrahydrofurane and the use of liquid chromatography – mass spectrometry (LC-MS) is suggested for analysis of levoglucosan and its isomer compounds, mannosan and galactosan (e.g. Dye and Yttri, 2005). The only requirement that method sets for sampling substrate is that it can be submerged into water/tetrahydrofurane solution. The sample solution is filtered prior to analysis, if needed.

Ions and dicarboxylic acids

For analysis of ions (e.g. sulphate, nitrate, chloride, sodium, ammonium, potassium, magnesium, calcium) and dicarboxylic acids (such as oxalate), the use of ion chromatography (IC) is recommended (e.g. Teinilä et al., 2000). For IC analysis, the sample is extracted with deionised water. Due to high blank values for some ions (e.g. Na^+), the use of some quartz filters may limit its suitability in the analysis. Filtering prior to analysis is used, if needed.

Elements

For determination of water-soluble elements, extraction with dilute HNO_3 and analysis with inductively coupled plasma – mass spectrometry (ICP-MS) are recommended (e.g. Pakkanen et al., 2001).

For total elemental analysis, several suitable methods exist: The sample is digested with mixture of HF and HNO_3 and analysed by i) ICP-MS (e.g. Jalkanen & Häsänen, 1996) or ii) inductively coupled plasma – optical emission spectrometry (ICP-OES). The use of internal standard is recommended. Another choice is to analyse elemental composition directly from the sample filter iii) by scanning electron microscopy (SEM) or transmission electron microscopy (TEM) combined with energy dispersive X-ray spectrometry (EDS) or electron energy loss spectroscopy (EELS), iv) by particle induced X-ray emission (PIXE) or v) X-ray fluorescence (XRF). The three latter methods are basically non-destructive, and hence the same sample can be used for other analyses. However, in this respect it has to be considered that easily volatile compounds (e.g.: chlorides) can be partly evaporated during SEM/EDS analyses. Several sampling substrate materials can be used in the analyses with ICP-MS and ICP-OES. Aluminium foil and polycarbonate film are the most suitable sampling substrates for the SEM/EDS analysis. In PIXE analysis, polycarbonate or other organic sampling substrate material can be used, except for PTFE. For XRF analysis, thin Teflon or polycarbonate filters are preferable, but there are also options to use also other sampling media in certain XRF applications.

Inorganic phase composition

The analysis of inorganic phase composition of the crystalline part of the PM can be performed by Powder X-Ray Diffraction (P-XRD). The analysis may be performed directly on samples on un-greased aluminum foils, but preferably by scratching the sample off the aluminum foils eventually followed by light grinding and/or analysis in a capillary. Besides a direct identification of phases qualitatively, also semi-quantitative information is gained. There are also other methods to determine inorganic speciation like XPS (X-ray photoelectron spectroscopy) and XSAFS (X-ray absorption fine structure spectroscopy).

Table 4. Suitability of sampling substrate materials for analysis methods.

Analysis method \ Substrate material	Quartz filter	Quartz wool	Glass fibre filter	PTFE filter	Polycarbonate film	Aluminium foil
Thermal-optical analyzer (EC & OC)	++	-	-	-	-	-
Carbon analyzer (NCC)	+	+	+	-	-	+
TOC-V_{CPH} organic carbon analyzer (WSOC)	+		+	+	+	+
GC-MS (PAHs)	+		+	+		
LC-MS (MAs)	+		+	+	+	+
IC (ions)	+/-		+	+	+	+
ICP-MS (elements)	+			+	+	+
ICP-OES (elements)	+			+	+	+
SEM/EDS (elements)					+	+
PIXE (elements)				-	+	
XRF (elements)				+	+	
P-XRD (inorganic phase composition)						+

++ required, + suitable, - not applicable.

4.4.5 Recommended determination

To be able to assess the behaviour, fate and potential effects of particles in the atmosphere and biosphere, several different PM properties (chemical and physical) are needed to be determined. Depending on the purposes of the measurement and the level of scientific research of the measurement, the following stepwise procedure for chemical analysis is recommended for biomass combustion PM emissions:

Step 1 – Basic fractionation

- Fractionation of the PM samples into; *soot*, *organic matter* and *inorganic matter*. Depending on analysis method the carbon content may be defined as “elemental”, “organic” and “carbonate” carbon.

Step 2 – Further fractionation and detailed speciation

- Fractionation and speciation of the organic matter into; *pyrolysis products* (e.g. levoglucosan and methoxyphenols), *PAHs* (minimum EPA’s 16 species but preferably a larger number) and potential *other organic compounds/classes of compounds* (e.g. kinones and other oxygenated PAHs)

- Fractionation and speciation of the inorganic matter into; *major species* (i.e. alkali salts) and *trace elements* (i.e. “heavy” metals)

Step 3 – Additional specific chemical and physical analysis

- Several optional (less standardized) chemical and physical analyses are available and useful for dedicated research issues including e.g. *hygroscopicity/water vapour up-take* (by hygroscopic tandem DMA) and *morphological and chemical information* by high resolution electron microscopy (SEM or TEM in combination with EDS or EELS).

4.5 TOXICOLOGICAL CHARACTERISATION OF PARTICLES

4.5.1 Experimental exposure studies

The first experimental exposures of healthy human subjects to aerosol emission from wood combustion have been conducted in Europe (Barregård et al. 2006 and 2008; Löndahl et al. 2008). They show mild inflammatory responses both in the respiratory tract and the systemic circulation, and a tendency towards increased coagulation of blood. In experimental animal and cell studies, intratracheal instillation and re-aerosolization of particles collected from biomass combustion experiments have been used together with direct exposure to diluted flue gas from biomass combustion. Like in humans, these studies have also shown increased inflammatory activity in the lungs and cells, and, in addition, cytotoxicity and signs immunosuppression and impaired clearance of the particles from the lungs of the animals (Zelikoff et al. 2002; Naeher et al. 2007).

4.5.2 Requirements for exposure method, particulate sample collection and storage for toxicological studies

Basic requirements for exposure method

Aerosol exposure systems with on-line diluted flue gas from combustion system are used in experimental human and animal studies. Also re-aerosolization of combustion emission particles collected in advance with, e.g. electrostatic precipitator, has been used in animal studies (see subchapter 3.2.2). However, a new versatile methodology is to make a high-volume, size-segregated collection of the emission particles (Fig. 18) and instill them in aqueous medium directly to cell culture or under visual control to the lower airways of test animals (see e.g. Jalava et al., 2005 and 2007; Happo et al., 2007).

Figure 18. Size-segregated particulate collection using a high-volume (850 litres/min) cascade impactor (HVCI) connected to a dilution tunnel, in which there was a 200-fold dilution of the flue gas from a log wood batch burning device.

Common requirements for both the aerosol exposure and particulate collection methods are:

- Evaluate the characteristics of your exposure system in advance (e.g. particulate size distribution, sampling / extraction efficiency or on-line exposure efficiency by mass and chemical composition) using standard aerosol monitoring and sampling methods as reference.

- Avoid carefully any external contamination of the combustion emission particles and use methodologically similar sham exposure to filtered air or blank samples that control for all phases of particulate sample handling (e.g. insertion to sampler, enclosure to container, transportation, particle extraction).

- Report always the combustion technology, fuel and condition as well as the dilution ratio and the results from gaseous and particulate monitoring and chemical speciation as background information in the toxicological study report.

Particulate sample collection and storage

The most important size range to be investigated in toxicological studies is PM_1. However, investigation of the coarse (> 1 μm) particles, mostly fly ash, or separation of the ultrafine particles (< 0.1/0.2 μm) from other submicron fine particles may be motivated in connection to some technologies or biofuels, or special health issues of interest. Particulate collection needs to be done with dilution and cooling the flue gas <52 °C to include condensable material.

The non-toxicity of particulate sampling substrate needs to be confirmed in cell tests made in advance. The substrates should be pre-cleaned before sampling using the same solvent and protocol as in the actual particulate extraction. Blank substrates are processed similarly to the ones used in particulate sampling.

Toxicological cell and animal studies need at least tens of milligrams of particles so that the same particulate mass can be used for testing several different end-points as well as making chemical analyses (e.g. ions, total and water-soluble elements, PAHs). The chemical characterization of differences between selected combustion conditions should be supplemented by parallel low-volume sampling of particles for analysis of important species (e.g. EC and OC) that cannot be measured from the HVCI samples due to technical reasons (e.g., unsuitability of sampling substrate).

Tens to hundreds of milligrams of size-segregated particles have been recently collected from wood combustion experiments using the HVCI (Fig. 18). A major advantage of this impactor is that it collects particles at high efficiency (850 litres/min) in four size ranges ($PM_{0.2}$, $PM_{1\text{-}0.2}$, $PM_{2.5\text{-}1}$, $PM_{10\text{-}2.5}$), and the collected particulate mass can also be extracted from the sampling substrate, i.e. porous polyurethane foam, with a high 80-90% efficiency (Sillanpää et al., 2003; Pennanen et al. 2007). The use of methanol and sonication seems to extract a fairly representative sample from the porous substrate with regard to water- and lipid-soluble species as well as poorly soluble solid particles (Jalava et al., 2005; Pennanen et al., 2007). So far, there is only limited experience from using a Teflon filter at the backup stage for $PM_{0.2}$. For more details see Figure 19.

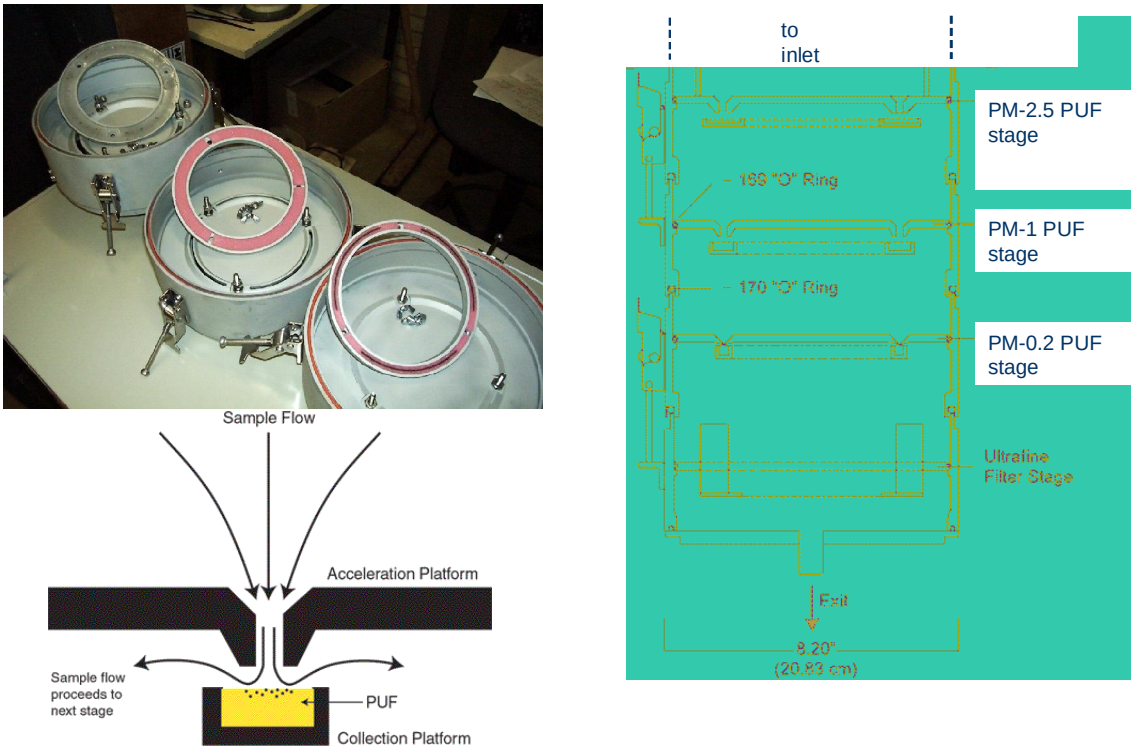


Figure 19. Schematic diagramme of the high-volume (850 litres/min) cascade impactor (HVCI) on the right. On the left, the operational principle of the three upper stages of the HVCI using polyurethane foam (PUF) strips as high-capacity sampling substrate for particles (Demokritou et al. 2002; Sillanpää et al. 2003).

The substrates containing collected particulate matter need to be carefully removed from the impactor stages to avoid contamination and mechanical loss of particles. These substrates must be protected from sunlight and removed as quickly as possible for storage at -20 °C. The frozen substrates need be conditioned at room temperature for 4 h in closed containers and for 16–18 h in open containers before weighing. During extraction particulate material, collected from several similar combustion conditions, can be pooled together per size-range to form a large single-sample mass to be divided into a large number of tubes used in chemical analyses and several toxicity studies with different end-points (Jalava et al., 2007; see also subchapter 3.2.1.2). The particulate samples need to be carefully protected from sunlight and kept frozen also during shipping from one laboratory to the other. The purpose of this is to reduce evaporation and chemical transformation of especially the organics.

The re-aerosolization experiments in animals needs several or tens of grams of particles, the collection of which needs to be arranged in a controlled manner, e.g. with an electrostatic precipitator. The same basic requirements for methodological evaluation, avoidance of contamination at every stage, and for storage of the collected particulate samples apply similarly to this technique as to the HVCI.

4.5.3 Special features in toxic responses

One of the main motivations for toxicological studies is to provide scientific evidence on the biological plausibility of adverse health effects found in epidemiological studies. Experimental human and animal studies can be conducted on a limited number of research questions on biomass combustion aerosol due to ethical reasons, but toxicological cell studies can be utilized more flexibly to reveal the toxicity profiles of multiple combustion conditions. With different chemical compositions, the inflammatory, cytotoxic and/or genotoxic activities of emitted particles may show differences that have important practical implications.

Experimental human studies

Toxicological studies in humans investigate causal relationship between selected, well-defined exposure conditions and usually rather immediate health responses in acute experiments. So far, most studies have been conducted in healthy subjects.

Highly relevant endpoints from the point of view of susceptible population groups have been investigated, e.g. pulmonary and cardiac function and inflammatory changes in bronchoalveolar lavage fluid (BALF) and blood after inhalation or instillation exposure to particles from wood combustion. More recently, also some investigations on blood coagulation factors and autonomic regulation of the blood circulation have been conducted. Time-courses of the different responses should be carefully evaluated, e.g. with positive control exposure to diesel exhaust, so that one does not miss data on positive responses due to too few or wrongly timed points of measurements.

Lung dosimetry of particles in association with well-characterised exposure condition gives useful additional information about the causal relationships and mechanisms. As shown in Figure 20, the deposition of particles at various levels of the respiratory track strongly depends on particle size. In addition to particle size, the hygroscopic properties of the particles (i.e. potential growth by water vapour up-take) are of great importance to consider regarding deposition pattern in the respiratory tract, as recently shown by Löndahl et al. (2008), for biomass combustion particles. Particles with diameter larger than 10 μm are mostly not inhalable to the lower airways and, thus, need not to be measured.

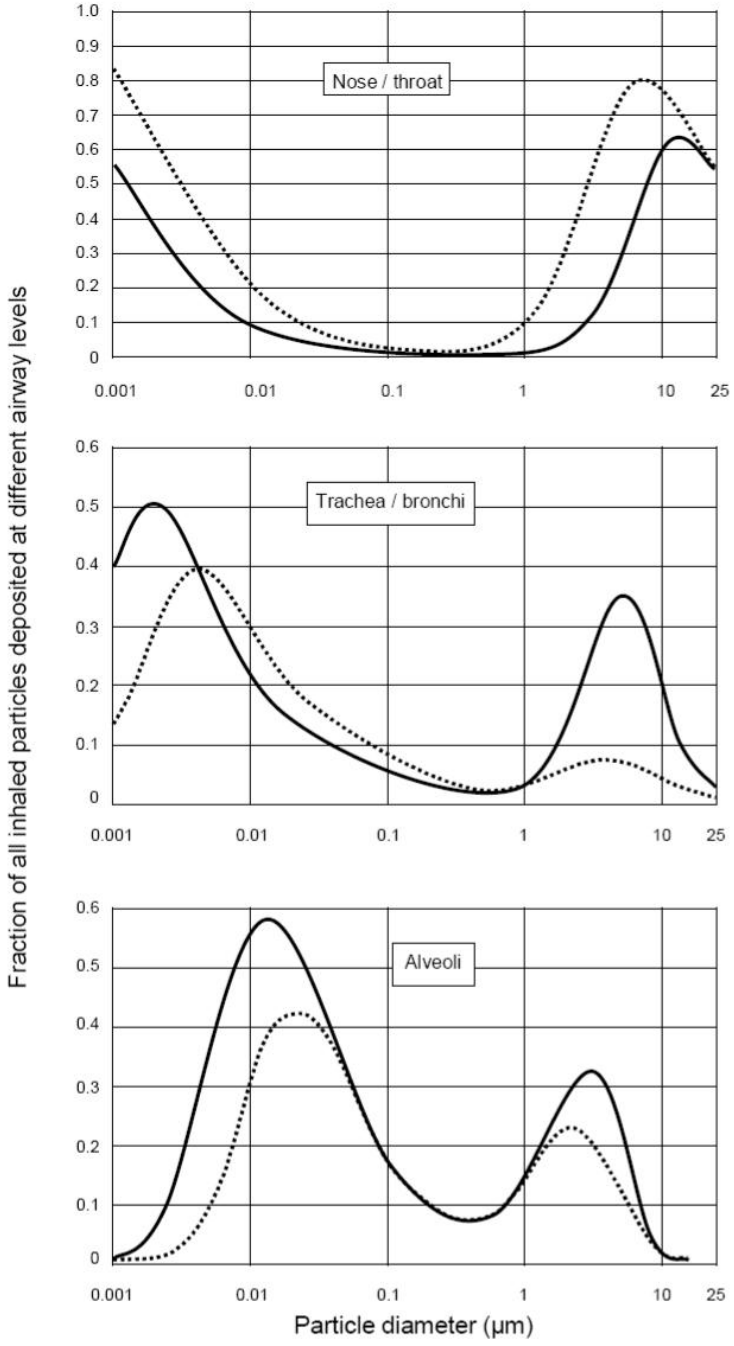


Figure 20. Deposition fraction of inhaled particles at three levels of the human respiratory tract as a function of particle size. Breathing at rest through the nose is marked by a dotted line, and breathing through the mouth during exercise by a solid line (USEPA, 2004).

One limitation to the experimental human studies on small-scale wood combustion is that double-blind experiments cannot be conducted due a characteristic bad smell arising from emissions of poor combustion conditions. However, well-characterized negative (filtered air / blank sample instillation) and positive (diesel exhaust) exposure conditions will add reliance to the future health data on different biomass combustion conditions.

Experimental animal studies

The main animal species for inhalation or instillation studies are mice and rats. Animal studies can be designed to investigate the causal relationship of selected, well-defined exposure conditions with both immediate and delayed health effects. Also the exposures need not to be only acute (1 day), but they can be subacute (1-28 days), and in search for carcinogenicity, subchronic (≤6 months) or chronic (>6 months). In addition, experimental animal models mimicking chronic human diseases (e.g. SO_2-induced chronic bronchitis, ovalbumin or ragweed-induced allergic asthma, pulmonary hypertension and heart failure) can be used in the experiments in addition to natively sensitive strains of healthy animals. However, it should be remembered that an experimentally induced disease brings an additional source of variability to the combustion emission-induced responses, and sometimes this variability can be large.

Highly relevant endpoints similar to those used in experimental human studies (e.g. pulmonary and cardiac function, inflammatory changes in BALF and blood, coagulation factors and autonomic control of the heart) can also be measured in the animal experiments. Again, time-courses of the different responses (e.g. cytokine concentration vs. influx of inflammatory cells or protein in BALF) should be carefully evaluated in advance, so that one does not miss data on positive responses due to too few or wrongly timed points of measurements (Happo et al., 2007). Lung dosimetry in connection to inhalation studies as well as negative (filtered air / blank sample instillation) and positive (diesel exhaust) exposure controls are recommended like in connection to experimental human studies.

Experimental cell studies

When thinking about the representativeness of *in-vitro* studies on the suggested biological mechanisms of cardio-respiratory health effects and, to a lesser extent, of lung cancer associated with chronic exposure to urban air particles, it can be stated that the traditional test of mutagenic activity in bacterial cell cultures (Ames′ test) should be mostly replaced by modern test batteries in cultured mammalian cells.

Macrophages are the main cell type taking up (phagocytosis) and clearing particles from the lungs. They have also a key role in orchestrating the inflammatory tissue response to the particulate exposure. Respiratory epithelial cells can also take up (pinocytosis) ultrafine but not larger particles. They can have a secondary role in chronic inflammation, and bronchial epithelial cells give most often rise to respiratory cancers caused by combustion-derived air pollutants (e.g. tobacco smoke, diesel exhaust). For these reasons, macrophages and respiratory epithelial cells should be the most frequently used mammalian cell types also in studies on biomass combustion-derived particles. The use of commercial human or mouse cell lines is favored due to their stability over time, when compared to primary cells freshly obtained for culturing from different individuals each time. Moreover, primary cells easily lose their viability, especially in prolonged experiments. In addition, the previous exposure history of the donor may affect the particle-induced responses in experimental settings.

The inflammatory activity of airborne particles has been linked for a long time to exacerbation of pulmonary diseases like asthma and chronic bronchitis, but more recently it has been suggested to contribute to atherosclerosis and acute vascular events such as cardiac infarction and stroke. Key parameters to be followed in this respect are the production of chemotactic

(e.g. MIP-2, IL-8) as well as proinflammatory (e.g. TNF-α, IL-6) cytokines. The tissue damage in the lungs and other organs potentially induced by combustion-derived particles can be amplified by direct cytotoxicity via increased apoptotic, i.e. programmed, cell death or un-programmed necrotic cell death, or via inhibition of DNA synthesis in the cells.

Genotoxicity is primarily regarded as the mechanism leading to increased carcinogenic risk. In connection to research on biomass combustion-derived particles, Comet assay can be used as a relatively easy and quick screening test. When motivated, its information can be complemented e.g. by the more elaborate micronucleus test or PAH-DNA adduct test.

The dose-dependency and time-dependency of the different kinds of responses to biomass combustion particulate samples need to be known, again to avoid false negative findings (Jalava et al., 2005 and 2007).

Reporting and implications of toxicological studies

Comparison of the toxic activities of particulate samples from different combustion conditions should not be made using only one mass dose for all, but the dose-relationship at 3-5 dose levels should be known. The responses to particulate instillations in cell cultures and animal lungs can be then compared at one representative dose-level for all, and the response ratios should also be reported as weighted by the particulate mass per emitted cubic metre or produced energy unit. This information tells an air quality or health expert about the relative harmfulness of inhaled air in vicinity to the source as well as a heater developer about the relative harmfulness of particulate emissions per produced heat energy. When this kind of information is connected to the chemical composition of particulate samples, it may help the regulator to give emission limits to certain harmful compositions (e.g. PAHs) and the industry to direct its product development towards solutions that pose a lower health risk to humans.

A third advantage may be objective evidence on harmful user practises that can then be better corrected via information campaigns as well as instructions and regulations given by the local authorities. One future issue to investigate in integrated emission-toxicology study setups is the harmfulness of fly ash originating from well-controlled biomass combustion installations. The answers to that question will contribute to the assessment on the need for emission after-treatment technologies in small-scale installations.

4.6 AIR QUALITY, EXPOSURE AND EPIDEMIOLOGY

Air quality and exposure

In areas of our countries where wood is available, wood burning for household heating is common as in almost every part of the developed world where wood is fairly cheap in comparison with oil, gas or electricity. Wood fires are also popular for recreational use in many places. The wood fuelled boilers, stoves and fireplaces in use, most of traditional type, have a serious impact on local air quality in many residential areas.

Residential heating with biomass has a great potential to cause health effects in cities and smaller communities because of several reasons: (1) release of the flue gas is near the ground level in immediate vicinity to neighbouring residents, (2) the highest heating season is during

cold weather conditions that associate with poor atmospheric mixing and dilution of the pollutants, (3) combustion technology presently used is often old and poorly optimized as well as highly influenced by operating practices, and (4) emission after-treatment technology, that may be an option also for residential use, is rarely used in small-scale installations.

Source apportionment studies indicate that wood combustion is a major source of ambient PM, PAHs and other hydrocarbons especially during winter. In areas with dense wood burning and unfavourable dispersion conditions, 40-80% of $PM_{2.5}$ and PAHs could be attributed to wood burning. For cities and regions (countries), more than half of the anthropogenic $PM_{2.5}$ emissions could come from wood burning.

Lycksele, a small town with about 9000 inhabitants situated in the inland of northern Sweden, was the major study area for measurements and modelling of air quality within the Swedish program BHM, "Biomass combustion, Health and Environment", http://www.itm.su.se/bhm/. The yearly PM emissions from combustion in Lycksele were estimated to be 66 ton. The main source was old wood stoves/boilers estimated to emit 35 tons per year. Dispersion modelling showed that in residential areas the 90-percentile levels often exceeds 50 $\mu g/m^3$ fine PM close to the old wood boilers, and that the annual contribution could be up to 9 $\mu g/m^3$ of fine PM close to sources. In Christchurch, New Zealand, it is estimated that more than 90% of wintertime ambient PM comes from heating stoves and open fires burning wood, and that many more deaths are attributed to wood combustion derived particles than to traffic pollution. Also in areas as Greater Stockholm the population exposure to combustion particles is estimated to be higher from residential wood burning than from traffic.

Fine particles are known to penetrate easily indoors. However, in homes using wood for heating there may be additional exposure. In a small study from a residential area in West Sweden, wood combustion derived particles made statistically significant contributions of K, Ca, and Zn for both personal exposure and indoor concentration, the median levels of these elements being 66–80% higher for a wood-burning group. Mass concentrations of $PM_{2.5}$ were however not found to be significantly elevated in wood burners, likely due to influence from other sources.

Epidemiology

In the developed world there is a group of studies from North America, many from Seattle, showing associations between wood combustion emission dominated $PM_{2.5}$ and lung function decrements in children, visits to emergency departments for asthma, hospitalizations for asthma, increases in asthma symptoms in children and increases in exhaled nitric oxide.

In Sweden, epidemiological studies have, until now, focused on short-term associations between ambient particle levels in areas with residential wood heating. These studies are of two kinds, panel studies with repeated measurements in a specific group of panellists, and register studies of health care utilization and diagnoses in a population. The objectives for such studies have been to investigate whether common levels below PM_{10} limit values cause any effects and whether wood combustion related PM results in similar relative risks or different than PM in general.

In Lycksele, Sweden, a strong association was found between black smoke ("soot"), mainly originating from wood burning and asthma emergency visits in winter. Relative risks were very high in relation to European results for black smoke and hospitalizations. Also symptoms in an asthma diary were associated with black smoke and $PM_{2.5}$.

Future needs to improve risk assessment

Long-term effects of exposure to PM from wood burning have so far not been conducted in Europe. Studies using GIS are now planned in Finland and Sweden. Long-term exposure will be estimated from register data. In Sweden, the plan is to first validate national property and taxation register data on heating systems using locally collected data. To have acceptable confounding control, studies will probably have to build on cohorts with prospective data on smoking and other major risk factors. Especially studies of long-term exposure should include the aspect of risk of additional indoor exposure among persons using wood stoves and boilers.

A general aspect is that epidemiological studies deal with real existing or past exposures, not the effects of a potential new scenario that may follow new technologies. It would be very useful to measure exposure to wood combustion products ($PM_{2.5}$, soot, PAHs etc) and study if any short-term effects occur in villages of single-family houses with the modern wood burning technologies. There may for example be newly built "ecological villages" to study.

It is important to undertake exposure monitoring and epidemiological studies among populations that, at least during the heating season, are exposed primarily to combustion particles from biomass burning. Such studies should thus be made in areas with a low regional background and limited emissions from traffic and industry.

Other groups than persons with respiratory disease may be as susceptible for short-term peaks in wood combustion particle emission levels, for example persons with heart disease are affected by particles from diesel engines and PM in general. Future panel studies may thus involve new types of panels.

The potential for health risk assessments would improve with better approaches to use source apportionment assessments in epidemiologic studies. Like this the proportion of particle associated health effects attributable to wood combustion could be estimated. New epidemiological studies should include up-to-date data on household heating appliances and relevant PM emission factors, because these are in constant change due to altered appliance types and improvement of technologies.

There is also a need for more of intervention research to assess both real exposure reductions achieved through the introduction of new technology and the estimated reduction in health risks.

4.7 ADVANCED METHODS

4.7.1 Introduction to on-line aerosol measurement methods

To understand and assess the potential health effects caused by biomass combustion one needs to know the whole chain "primary emissions"-"transport and transformation in the atmosphere"-"concentrations in the environment where the people are exposed by the pollutants". In principle the chemical emission data can be used in models to estimate how they contribute to the ambient particulate matter concentrations. Still today there is often a major discrepancy between modelled ambient concentrations and observations (Robinson et al., 2007; Rudich et al., 2007; Donahue et al., 2006). Concerning biomass combustion in the domestic heating, discrepancies are partly due to insufficient chemical data on emissions. There are a high number of different appliances, and only a few are tested. In addition, the testing methods may have limitations affecting the emission rate data (Lipsky and Robinson, 2006).

When the sample aerosol is diluted enough after combustion, technically the sampling and measurement of particulate matter in emissions approaches the ambient conditions (effect of dilution is discussed previously) enabling the use of advanced measurement methods. Advanced methods are measuring online the chemical composition or other properties in emissions. They have several advantages compared with the sampling and the subsequent chemical analysis in the laboratory. Main advantage is that due to sufficient time resolution, the online methods usually can follow different stages of the combustion process (for example batch combustion in a fireplace). In addition, the online measurement typically minimizes the effect of undesired artifacts on the results. A typical way of the artifact formation in offline sampling is the reaction of gas phase emissions with the sampling substrate or collected particulate matter. The limitation of online method is that in some cases requirements of the instruments are too high for the field use or the instrument setup is too heavy or space-consuming. Another restriction may be that the number of chemical components available for online analysis is limited, and sampling and laboratory analysis is needed to complete this deficiency. Here some online methods which can be used in biomass combustion experiments or emission rate tests will be presented briefly.

4.7.2 Instruments for carbonaceous material in PM

Soot or black carbon (BC)

Soot is the most light absorbing constituent of the atmospheric particulate matter. Therefore it is important for the climate change issue. Soot formation is also accompanied by PAH formation, and is therefore important also for health effects point of view. In wood combustion, existence of soot always indicates incomplete combustion conditions. Because soot is much better in absorbing light than any other compound in particulate matter emissions, the absorption can be interpreted to be only because of soot. Therefore soot is often called black carbon (BC), and the measurement is based on light absorption. Although BC can be measured directly from air sample, most common way is the sampling of particles on a filter or filter tape, and subsequent measurement of absorption. The absorption measurement

can be automatic and almost real-time (Particle soot absorption photometer (PSAP), Aethalometer).

Elemental carbon (EC) and organic carbon (OC)

The measurement of carbonaceous material in particulate matter can be based on thermal evolvement. In heating the sample incrementally, different carbonaceous materials evolve at different temperatures and different times. Briefly, organic carbon evaporates at lower temperatures (100-500 °C) and soot at higher temperatures (500-900 °C). The carbon content in the gas phase are detected either as CO_2 with a non-dispersive infrared analyzer (NDIR) or, when using special catalytic converters, as methane by flame ionization detection (FID). To complement the burning of soot, the latter temperature range is usually measured in a helium-oxygen mixture. The difference between BC and EC is instrumental. The method is already widely used in measuring ambient air EC and OC. In particulate matter emission measurements it is not yet used for on-line measurements, although it could work well especially for stable processes which do not need high time resolution.

4.7.3 Particle-into-Liquid Sampler (PILS)

One common way to collect particulate matter samples for the online analysis is to mix the sample aerosol with water vapour (steam). After cooling water condenses on particles and droplets can be collected using an impactor or cyclone. In the Particle-into-Liquid Sampler (PILS; Metrohm Peak Inc; Orsini et al., 2003) the droplets are collected using impaction on the quartz glass plate. The liquid collected by the PILS can be fed into instruments capable to analyze water-soluble constituents. Interfering gases should be removed before the PILS collection. This can be made with annular denuders. Inorganic ions can be measured with a PILS coupled with an ion chromatography (PILS-IC, Saarikoski et al., 2008) and water-soluble organic carbon with the PILS coupled with a total organic carbon analyzer (Timonen et al., 2008). Time resolutions are 15 min and 5 min, respectively.

4.7.4 Aerosol mass spectrometers (AMS)

Online measurement methods have been available for various physical particle properties including particle number size distribution and mass concentration. More recently new instruments have been developed to measure the particle size and composition simultaneously. The detection method in those instruments is based on mass spectrometry which is a sensitive technique to analyse atomic and molecular species in particulate matter. Concerning the vaporization, ionization and type of mass spectrometer there are many combinations, most of them custom-made by research groups. There are two commercialized versions in the international market (manufacturers: TSI Inc and Aerodyne Research Inc).

In Figure 21, one typical aerosol mass spectrometer is presented schematically. Briefly, the aerosol sample is fed to the instrument through the aerodynamic lens which is focusing the particle beam. Particle size is measured using the particle time-of-flight measurement (aerodynamic sizing), and after that the particles are impacted on a heated surface. After thermal vaporization and electron impact ionization, the composition of non-refractive particle material is analyzed using a mass spectrometer. In Figure 21, the mass spectrometer

type in quadrupole, but in the more advanced instruments mass detection is based on the time-of-flight measurement. The aerosol mass spectrometers have been used widely in atmospheric research, but it is excellent also in measurements of combustion aerosols from diluted and conditioned sample air (Robinson et al., 2007). A review of the method itself is presented in Canagaratna et al. (2006).

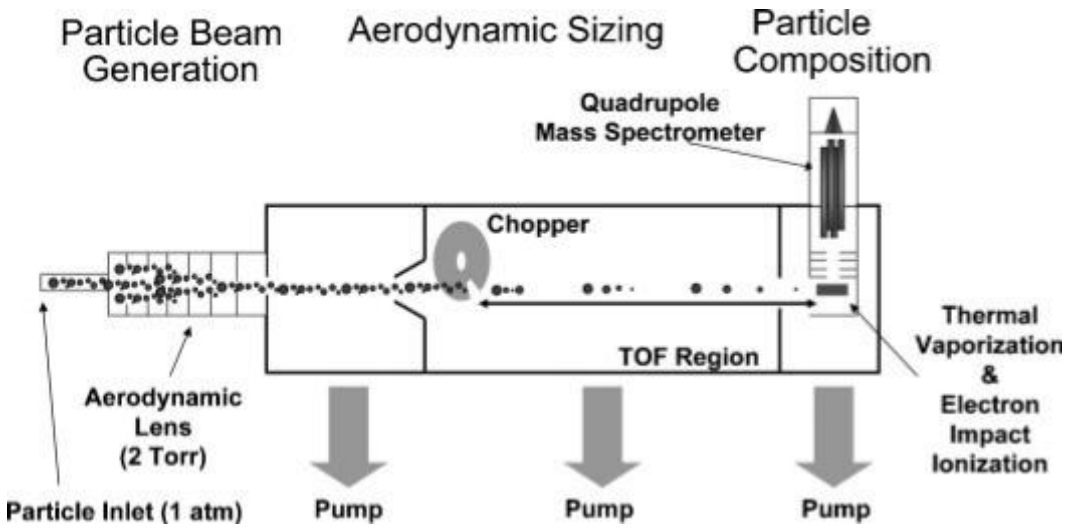


Figure 21. The Aerodyne Research AMS schematically.

5 SUMMARY OF RECOMMENDATIONS AND BEST PRACTICES

5.1 MEASUREMENT OF PARTICULATE EMISSIONS

One main focus of the project was put on the determination of feasible methods for PM emission measurements, sampling and physicochemical characterisation. An appropriate best practise procedure should be worked out. One of the most relevant aspects of this best practice procedure should be that it covers the evaluation of the whole process chain, starting at the combustion process (combustion quality, performance of the furnace) leading over the particle sampling and the physicochemical characterisation of PM emissions to the evaluation of health risks. A future aim should be to interlink the information gained from the physicochemical characterisation of PM emissions with the results of toxicological studies in order to estimate the potential of PM emissions for health risks. Consequently, the approach chosen deviates in some aspects from commonly applied particle sampling and measurement techniques, since in these procedures the interface with toxicological evaluation is not foreseen.

In the previous chapters different methods concerning PM sampling, measurement and characterisation have been described in detail. Based on these steps, the best practice guidelines for PM emission measurements, sampling and physicochemical characterisation, presented in the following, have been worked out.

Firstly it has to be mentioned that PM emissions from biomass combustion have to be divided into coarse particles (>1 µm) and fine particulate emissions (particles <1 µm). Recent research works have revealed that in residential biomass combustion devices the fine particulate emissions contribute with more than 90% in mass to the total PM emissions. Moreover, it has to be considered that fine particulate emissions consist of inorganic aerosols as well as carbonaceous species (organic aerosols and soot). Especially at poor burnout conditions (high CO and OGC emission levels), as they can be found in batch burning devices, organic aerosols and soot particles represent the dominating aerosol fraction. It has to be considered, that at typical flue gas temperatures of these devices at the boiler/stove outlet (up to 400°C), condensable organic compounds are still in the gas phase and condense during the further cooling of the flue gas in the ducts and the chimney as well as after mixing with ambient air at chimney outlet. It has to be pointed out, that this effect is only relevant for systems operating at poor burnout conditions. In modern pellet and wood chip furnaces for example, where with the exception of some minutes during the start-up phase, almost total burnout prevails, no relevant emissions of condensable organic species are measured at boiler outlet, and consequently, there is also no potential for subsequent additional particle formation. However, for the method presented bad burnout conditions represent the worst case scenario and therefore, the method is designed based on this case.

As a first step of the procedure, due to presence of these condensable semi-volatile organic compounds at stove/boiler outlet, the dilution of the flue gas with air is recommended. The aim of this step is to allow the condensation of all such semi-volatile matter in order not to underestimate PM emissions. Therefore, dilution tunnels (with full or partial flow dilution), dilution hoods, mini dilution tunnels and porous tube diluters in combination with ejector dilutors can be applied. It has to be taken care that in case of a partial flow dilution the sampling line between the flue gas duct and the dilution system has to be heated and/or isolated in order to avoid particle losses by condensation. Only clean air (filtered air) should be used for

dilution. The dilution ratio has to be monitored continuously by parallel CO_2 or NO_x measurements in the diluted and the undiluted flue gas.

An important aspect of the dilution step is the dilution ratio applied (dilution ratio = dilution air mass flow / flue gas mass flow). The dilution ratio influences the mass of particles measured as well as their chemical composition and therefore, can also have an influence on the toxicological evaluations of PM samples. The following aspects concerning the dilution ratio have to be considered:

- In any case the dilution ratio should be high enough to keep the temperature of the diluted flue gas <52°C in order to secure a full condensation of condensable compounds.

- If the full potential of particle formation/growth by condensation of organic vapours should be exhausted, the dilution ratio should be in a range of 20.

- However, for some particle measurement devices (e.g. SMPS, FMPS and ELPI) higher dilution ratios are needed due to the high number concentrations of particles in the flue gas from biomass combustion appliances. These higher dilution ratios bear the risk of re-evaporation of condensed semi-volatile compounds and therefore, the mass of particles measured, can be lower than at a dilution ratio of 20.

- On the other side it has to be considered, that in the atmosphere significantly higher dilutions of the flue gas with air take place. The same is true for controlled human exposure studies with biomass combustion emissions. In this respect, if results of such studies should be compared with the characteristics of PM sampled with the method proposed, the potential influence of different sampling conditions on aerosol has to be considered and higher dilution ratios than 20 matching the conditions prevailing during the exposure studies may be needed. The dilution ratio achieved in this case strongly depends on the particle sampling equipment applied (sampling from strongly diluted flows implies the utilisation of high volume samplers or the application of long sampling times) and on the sensitivity of the analysers which are used to monitor and control the dilution ratio.

A second important step of the procedure proposed is the determination of the gas phase composition (O_2, CO, CO_2, NO_x, OGC) with conventional flue gas analysers. These gas phase measurements should be performed in the undiluted flue gas at boiler/stove outlet since conventional flue gas analyses equipment is usually not designed for measurements in diluted flue gas flows.

Particle measurement and particle sampling should be performed in the diluted flue gas. In any case PM_{10} and PM_1 should be determined. Therefore conventional equipment such as impactors or cyclones can be applied. Further investigations of the particle size distribution in the range <1µm are also of interest, especially for scientific studies. Low-pressure impactors as well as systems based on differential mobility analysers (DMA) can be used. While conventional low-pressure impactors provide off-line data about the mass related concentrations and particle size distributions of PM emissions, electrical low-pressure impactors as well as DMA-based systems provide on-line data on number concentrations and number related particle size distributions. Moreover, samples taken with cyclones and impactors can be forwarded to chemical analyses for further characterisation. However, the

on-line systems provide the major advantage, that the influence of changing combustion process conditions on the PM emissions can be monitored.

TSP (total suspended particulate matter) should be determined in the undiluted gas due to two reasons. Firstly, the determination of TSP in the undiluted flue gas enables the comparison of the results with results gained from boiler testing and certification (which is usually performed without dilution). Secondly, losses of coarse fly ash particles will occur during the dilution step and therefore, an underestimation of TSP could result from a measurement in the diluted flue gas. TSP measurements should always be performed according to the respective testing standards.

Besides the characterisation of PM emissions by their particle size distribution and concentration in the flue gas, also their chemical characterisation is essential for an overall evaluation. Depending on the sampling technology applied (filters, cyclones, impactors) particle size selective analyses are possible. Concerning chemical characterisation a stepwise analysis procedure is recommended that comprise an increasing degree of detailed chemical information gained. The level of characterisation needed can therefore be related to different purposes, presently of relevance in research but potentially also in future evaluation and testing of different small-scale biomass combustion appliances. Primarily, a basic fractionation into soot, organic and inorganic matter is of relevance. Such fractionation can include fractionation of the carbonaceous matter into elemental (EC), organic (OC) and inorganic carbon. For such determination of carbonaceous species OC/EC-analysers and C-analysers can be used. Further fractionation and speciation of the organic and inorganic matter can be performed, especially in scientific research studies. In order to determine the concentrations of inorganic species wet chemical analyses, XRF, PIXE or SEM/EDX can be applied. Moreover, the concentrations of PAHs (16 PAHs according to US EPA) are also of interest for a chemical characterisation of PM emissions. In addition, especially for scientific studies, the determination of levoglucosan (as a tracer for emissions from wood combustion), ion speciation, water soluble elements, hygroscopicity as well as pyrolysis products is recommended. For a more detailed physicochemical characterisation, the latter could act as one basis for the toxicological evaluation of PM emissions. Finally, several optional and less standardized chemical and physical analyses are available and useful for dedicated research issues including e.g. hygroscopicity/water vapour up-take (by hygroscopic tandem DMA) and morphological information by high resolution electron microscopy (SEM or TEM).

Concerning all analyses methods mentioned above it is important to adjust the pre-treatment, conditioning, handling and storage of the sampling substrates to the demands of the respective analyses method. It has to be pointed out once again, that the dilution ratio applied during sampling may influence the chemical composition of the particles concerning their contents of organic species. Therefore, the dilution ratio applied during sampling should always be reported together with the results of the chemical characterisation.

Finally, the duration of sampling has an important impact on the results achieved. For automated furnaces in continuous operation it is recommended to perform measurements and sampling at stable full load operation and at stable operation at the minimum load possible. For automated furnaces in on/off operation (especially relevant for Sweden) the testing should be done according to the Swedish P-marking regulations. Concerning batch combustion systems also the first batch should be included (full batch or kindling wood ignition). Sampling during the first batch should be started as soon as CO_2 exceeds 1 vol%. For

subsequent batches sampling should start at the beginning and should end as soon as CO_2 decreases below 4 vol%.

When applying the procedure presented, the chemical and physical characterisation of PM emissions from biomass combustion can be adjusted regarding of the degree of detailed information needed for different purposes. In many aspects a basic fractionation (step 1) of the PM will presumably, to a significant degree, reflect potential differences in toxicological properties, but this has yet not been elucidated. In many cases, a more detailed chemical information will most certainly be needed. The data gained should in all cases be evaluated under consideration of the process conditions prevailing during the measurements and sampling (gaseous emissions, load conditions, furnace temperatures etc.) to derive correlations between particle characteristics and the mode of plant operation.

If also toxicological tests should be performed with particle samples gained from a test run, the particle sampling has to be tailored to the demands of this subsequent testing. This concerns the substrate preparation, pre-treatment, handling and storage as well as the size fractions of particles sampled. Moreover, most methods for toxicological tests demand for higher particle masses than collected with the commonly applied sampling equipment (some 10 mg of PM). Since particle sampling should again take place in the diluted flue gas, the application of high volume samplers is recommended in order to be able to collect sufficient particle mass within an acceptable sampling time.

Concluding, a scheme of the test set-up proposed is presented in Figure 22. In this example dilution is realised by applying a partial flow dilution tunnel.

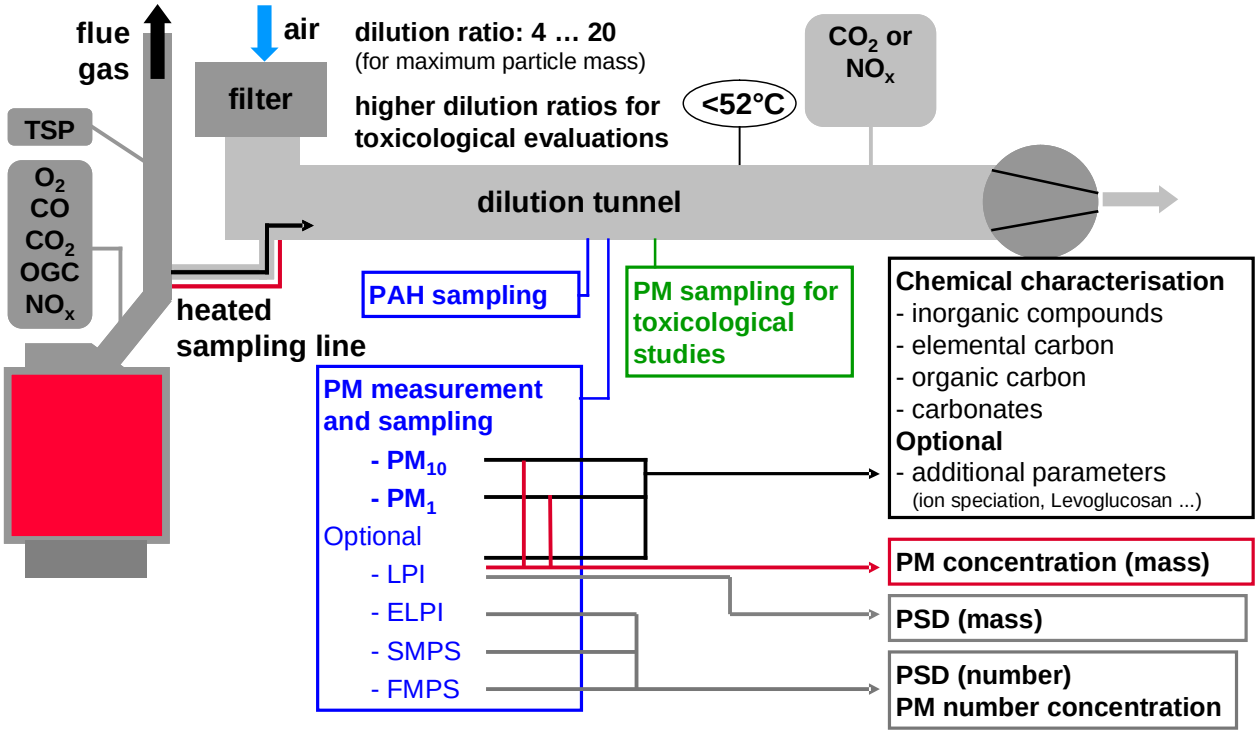


Figure 22. Test set-up proposed for the measurement, sampling and characterisation of PM emissions from small-scale biomass combustion plants (Explanations: set up based on flue gas dilution with a partial flow dilution tunnel; PSD particle size distribution)

5.2 INVESTIGATION OF HEALTH EFFECTS OF PARTICULATE EMISSIONS

Aerosol exposure systems with on-line diluted flue gas from combustion installation are used in experimental human and animal studies. Also re-aerosolization of combustion emission particles collected in advance with, e.g. electrostatic precipitator, has been used in animal studies. Alternatively, a new versatile methodology is to make a size-segregated collection of diluted emission particles and instill them in aqueous medium directly to cell culture or under visual control to the lower airways of mice or rats.

Common requirements for both the aerosol exposure and the particulate collection method are:

- Evaluate the characteristics of the exposure system in advance using standard aerosol monitoring and sampling methods as reference.

- Avoid carefully any external contamination of the combustion emission particles and use methodologically similar sham exposure to filtered air or blank samples that control for all stages of particulate sample handling.

- Report always the combustion technology, fuel and condition as well as the dilution ratio, temperature and the results from gaseous and particulate monitoring and chemical speciation as background information in the toxicological study report.

- The most important size range to be investigated in toxicological studies is PM_1. However, investigation of the coarse (> 1 μm) particles, mostly fly ash, or separation of the ultrafine particles (< 0.1/0.2 μm) from other submicron fine particles may be motivated in connection to some technologies or biofuels, or special health issues of interest.

- The non-toxicity of the particulate sampling substrate needs to be confirmed in cell tests made in advance. The substrates should be pre-cleaned before sampling using the same solvent and cleaning protocol as in the actual particulate extraction. Blank substrates are processed similarly to the ones used in particulate sampling.

- Particulate collection needs to be done with dilution and cooling the flue gas <52 °C to include condensable material in particulate phase emission.

- After particulate sampling, the collection substrates must be protected from sunlight and removed as quickly as possible for storage at -20 °C. For subsequent weighing and extraction, the frozen substrates and particulate material need be conditioned at room temperature for 4 hours in closed containers, followed by 16–18 hours in open containers before weighing.

Toxicological cell and animal studies need at least tens of milligrams of biomass combustion particles per size range and test condition, so that the same particulate material can be used for testing several different end-points as well as making chemical analyses of interest (e.g. ions, total and water-soluble elements, PAHs). Tens to hundreds of milligrams of size-segregated particulate mass have been recently collected from wood combustion experiments using a

high-volume cascade impactor (HVCI). It collects particles at high volume (850 litres/min) in four size ranges ($PM_{0.2}$, $PM_{1-0.2}$, $PM_{2.5-1}$, $PM_{10-2.5}$), and the collected particulate mass can also be extracted from the sampling substrate, i.e. porous polyurethane foam, with a high 80-90% efficiency.

During extraction particulate material, collected from several similar test conditions, can be pooled together per size-range to form a large single-sample mass to be divided into a large number of tubes used in chemical analyses and toxicological studies with different end-points. Also these particulate samples need to be carefully protected from sunlight and kept frozen during shipping from one laboratory to the other.

The re-aerosolization experiments in animals need several or tens of grams of biomass combustion derived particles, the collection of which needs to be arranged in a controlled manner, e.g. by using an electrostatic precipitator. The same basic requirements for methodological evaluation, avoidance of contamination at every stage, and for storage of the collected particulate samples apply also to this technique like to the HVCI.

One of the main motivations for toxicological studies is to provide scientific evidence on the biological plausibility of adverse health effects reported in epidemiological studies. Experimental human and animal studies can be conducted on a limited number of research questions on biomass combustion aerosol due to ethical reasons and elaborate study setups, but toxicological cell studies can be utilized more flexibly to reveal the toxicity profiles of multiple combustion conditions.

Highly relevant endpoints from the point of view of susceptible population groups can be investigated in both experimental human and animal studies, e.g. pulmonary and cardiac function and inflammatory changes in bronchoalveolar lavage fluid (BALF) and blood after inhalation or instillation of biomass combustion particles. More recently, also some investigations on blood coagulation factors and autonomic regulation of the blood circulation have been conducted. Time-courses of the different response endpoints should be carefully evaluated in advance, e.g. using diesel exhaust particles as positive control, so that one does not miss data on positive responses due to too few or wrongly timed points of measurements. Lung dosimetry of particles in association with good physico-chemical characterization of the exposure gives useful additional information about the causal relationships and mechanisms. The most commonly used animal species for particulate inhalation or instillation studies are mice and rats.

It can be stated that the traditional test of mutagenic activity in bacterial cell cultures (Ames′ test) should be mostly replaced by modern test batteries in cultured mammalian cells. Macrophages are the main cell type taking up (phagocytosis) and clearing particles from the lungs. They have also a key role in orchestrating the inflammatory tissue response to the particles deposited in the lung periphery. Respiratory epithelial cells can also take up (pinocytosis) ultrafine but not larger particles. They can have a secondary role in chronic inflammation, and bronchial epithelial cells give most often rise to respiratory cancers caused by combustion-derived air pollutants (e.g. tobacco smoke, diesel exhaust). The use of commercial human or mouse cell lines is often favoured due to their stability over time, when compared to primary cells freshly obtained for culturing, every time from different individuals.

The inflammatory activity of air particles has been linked for a long time to exacerbation of pulmonary diseases like asthma and chronic bronchitis, but more recently it has been suggested to contribute to atherosclerosis and acute vascular events such as cardiac infarction and stroke. Tissue damage induced in the lungs and other organs by combustion-derived particles can be also mediated, at least partly, by direct cytotoxicity, i.e. via increased apoptotic, i.e. programmed, cell death or un-programmed necrotic cell death, or via inhibition of DNA synthesis in the cells.

Genotoxicity is primarily regarded as the mechanism leading to increased carcinogenic risk. In connection to research on biomass combustion-derived particles, Comet assay can be used as a relatively easy and quick screening of DNA damage. Its information can be complemented, e.g. by the more elaborate micronucleus test or PAH-DNA adduct test.

In all toxicological setups, the dose-dependency and time-dependency of the different kind of response endpoints to biomass combustion particulate samples need to be known to avoid false negative findings.

5.3 FUTURE DIRECTIONS

It is obvious that the field of residential biomass combustion would much benefit from a European-wide harmonisation of the emission test methods and procedures as well as interdisciplinary research involving both the emission scientists and toxicologists on several topics:

- More detailed comparison of different sampling and dilution methods is needed to define a standard method for the measurement of fine particle emission from residential biomass combustion installations.

- Further technological R&D is needed to improve both the primary measures (combustion and control systems) and the secondary measures (emission after-treatment) to reduce particulate emissions from small-scale biomass combustion systems.

- More information on the impact of real-life user practices on particulate emissions is needed as well as on the overall impact of small-scale biomass combustion emissions on local and regional air quality.

- More information is needed about the association between different kind of particulate matter emissions from biomass combustion installations and their adverse health effect potential as assessed by experimental human and animal studies. Cardiovascular endpoints should be investigated in addition to respiratory endpoints. This would increase information about the biological plausibility of adverse health effects reported in epidemiological studies.

- Cell studies should provide a generic concept on the association of inorganic and organic chemical constituents with the inflammatory, cytotoxic and genotoxic activities of particulate emissions from a series combustion technologies and biofuels. The representativeness of the results should be confirmed in selected experimental animal and human studies. This information would help the regulator to give emission limits to some potentially highly toxic constituents (e.g. PAHs), the industry to direct its product development towards health-wise cleaner and safer combustion installations, and the consumer to adapt for good operational practice.

It would be advantageous also to promote interdisciplinary research between the aerosol scientists and epidemiologists:

- New short-term panel studies with personal exposure monitoring and source-specific exposure modelling are needed. Contributions of biomass combustion source-specific outdoor $PM_{2.5}$ to indoor $PM_{2.5}$ should be assessed as well as lung dosimetry in relation to the physico-chemical properties of the particles (e.g. new emission nearby vs. aged regional emissions).

- GIS-based cohort studies on chronic respiratory and cardiovascular diseases and cancer are needed. Data on household heating appliances and relevant particulate emission factors need to be up-to-date, because they are in constant change due to altered appliance types and improvement of technologies.

The topics suggested for future research collaboration between the present research partners of the BIOMASS-PM project should be considered for funding in the 7th Framework Programme of the European Commission or ERANET-type collaboration of national funders.

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