

# Projektrapporter

## ***Emissions from small-scale combustion of biomass fuels – extensive quantification and characterization***

*C Boman  
A Nordin  
M Öhman  
D Boström  
R Westerholm*



Statens energimyndighet  
Box 310, 631 04 Eskilstuna

Rapporterna kan beställas från  
Studsvikbiblioteket, 611 82 Nyköping.  
Tel 0155-22 10 84. Fax 0155-26 30 44  
e-post [stubib@lib.kth.se](mailto:stubib@lib.kth.se)

---

**Titel:** Emissions from small-scale combustion of biomass fuels  
- extensive quantification and characterization

**Författare:** Christoffer Boman Energy technology and Thermal  
Process Chemistry,  
Umeå University  
Anders Nordin ”-  
Marcus Öhman ”-  
Dan Boström ”-  
Roger Westerholm Analytical Chemistry,  
Arrhenius Laboratory,  
Stockholm University

## **RAPPORT INOM OMRÅDET BIOENERGI/KLIMAT**

**Rapportnummer:** BIODK 05/10

**Projektledare:** Anders Nordin

**Projektnummer:** P21906-1

**Projekthandläggare  
på Statens Energimyndighet:** Irene Wrände

# **Emissions from small-scale combustion of biomass fuels - extensive quantification and characterization**

Christoffer Boman<sup>1</sup>, Anders Nordin<sup>1</sup>, Roger Westerholm<sup>2</sup>, Marcus Öhman<sup>1</sup>, Dan Boström<sup>1</sup>

<sup>1</sup>Energy Technology and Thermal Process Chemistry, Umeå University,  
SE-901 87 Umeå, Sweden

<sup>2</sup>Analytical Chemistry, Arrhenius Laboratory, Stockholm University,  
SE-106 91 Stockholm, Sweden

STEM-BHM (P12648-1 and P21906-1)

Umeå, February 2005

## SUMMARY

This work was a part of the Swedish national research program concerning emissions and air quality ("Utsläpp och Luftkvalitet") with the sub-programme concerning biomass, health and environment ("Biobränslen, Hälsa, Miljö" - BHM). The main objective of the work was to systematically determine the quantities and characteristics of gaseous and particulate emissions from combustion in residential wood log and biomass fuel pellet appliances and report emission factors for the most important emission components. The specific focus was on present commercial wood and pellet stoves as well as to illustrate the potentials for future technology development. The work was divided in different sub-projects; 1) a literature review of health effects of ambient wood smoke, 2) design and evaluation of an emission dilution sampling set-up, 3) a study of the effects of combustion conditions on the emission formation and characteristics and illustrate the potential for emission minimization during pellets combustion, 4) a study of the inorganic characteristics of particulate matter during combustion of different pelletized woody raw materials and finally 5) an extensive experimental characterization and quantification of gaseous and particulate emissions from residential wood log and pellet stoves.

From the initial literature search, nine relevant health studies were identified, all focused on effects of short-term exposure. Substantial quantitative information was only found for acute asthma in relation to PM<sub>10</sub>. In comparison with the general estimations for ambient PM and adverse health effects, the relative risks were even stronger in the studies where residential wood combustion was considered as a major PM source. However, the importance of other particle properties than mass concentration, like chemical composition, particle size and number concentration remain to be elucidated.

A whole flow dilution sampling set-up for residential biomass fired appliances was designed, constructed and evaluated concerning the effects of sampling conditions on the emission characteristics. Robust and applicable sampling conditions were identified and the system was then used in the following emission studies within the project.

Emission factors for a large number of gaseous and particulate components were determined for different residential wood log and pellet fired stoves as functions of variations in fuel, appliance and operational properties. Considerable variability of emission performance for wood log stoves was determined, with potentially high emissions of products of incomplete combustion (PIC) like CO, methane, NMVOC, PAH and soot during specific combustion conditions. However, by proper technical and/or operational measures the emission performance can be rather well controlled, and a significant potential for further technical development and improvement of the emission performance exists. The emissions of PIC as well as PM from the wood log stove were generally considerably higher compared to those from the pellet stoves. The use of up-graded biomass fuels, combusted under controlled conditions therefore gives advantageous conditions for optimization of the combustion process. Accordingly, present fuel pellets technology is well suited for the residential market but also provides possibilities for further improvements of the combustion technology and further minimization of the emissions of PIC, especially at low load operation.

The extensive characterization of hydrocarbons included 34 specific VOC's and 48 specific PAH's. Beside methane, ethene, acetylene benzene were the most dominant VOC's and the dominating PAH's were in all cases phenanthrene, fluoranthene and pyrene. Typical emission factors during "normal" conditions in the wood log stove of 100 mg/MJ<sub>fuel</sub> for NMVOC and 3600 µg/MJ<sub>fuel</sub> for PAH<sub>tot</sub> can be compared with typical

variations in the pellet stoves of 2-20 mg/MJ<sub>fuel</sub> for NMVOC and 10-200 µg/MJ<sub>fuel</sub> of PAH<sub>tot</sub>, respectively.

The PM was in all cases (wood log and pellet appliances) dominated by fine (<1µm) particles with mass median and count diameters in the range of 100-300 nm and 50-250 nm respectively as well as number concentrations in the range of  $4.6 \cdot 10^{12}$ - $1.1 \cdot 10^{14}$ /MJ<sub>fuel</sub>, with a trend of increase particle sizes at poorer combustion performance. The minor coarse fraction (1-25% of PM mass) consisted of carbonaceous unburned fuels residues with inclusions of calcium containing grains (1-10 µm). Total PM emissions for the wood log stove varied in the range of 37-160 mg/MJ<sub>fuel</sub> and for the pellet stove in the range of 15-46 mg/MJ<sub>fuel</sub>. During optimized combustion of biomass pellets, the fine PM totally consists of fine inorganic particles with mass median diameters between 100 and 120 nm and emission factors at 15-20 mg/MJ<sub>fuel</sub>. When burning different woody raw materials the inorganic fine particles is dominated by alkali salts like KCl,  $K_3Na(SO_4)_2$  and  $K_2SO_4$ . Beside the alkali compounds, zinc is found in a more complex form than e.g ZnO, ZnCl<sub>2</sub> and ZnSO<sub>4</sub>. However, the formation mechanism and exact phase composition remain to be determined.

## SAMMANFATTNING

Detta projekt ingick som en del i det omfattande svenska forskningsprogrammet "Utsläpp och Luftkvalitet" med underprogrammet "Biobränsle, Hälsa, Miljö" (BHM) som finansierats av Energimyndigheten. Huvudsyftet med det föreliggande projekt var att systematiskt kvantifiera och karakterisera utsläppen av gas- och partikelformiga föroreningar till luften vid förbränning i småskaliga ved- och pelletseldade anläggningar och rapportera emissionsfaktorer för de dominerande emissionskomponenterna. Fokuset i arbetet med emissionsfaktorer var på dagens kommersiella teknik vad gäller ved- och pelletskaminer men även att visa på potentialen för framtida teknik. Arbetet, som pågått under åren 2001-2004, delades in i olika delprojekt; 1) litteraturgenomgång kring hälsoeffekter av exponering för vedrelaterade luftföroreningar, 2) design, konstruktion och utvärdering av en provtagningsuppställning som bygger på utspädning av rökgaserna, 3) experimentell systematisk studie av hur emissionskarakteristiken påverkas av förbränningsförhållanden vid pelletseldning och samtidigt visa på potentialen för framtida pelletsteknik, 4) studie av den oorganiska karaktäristiken på partikelutsläppen vid förbränning av pellets med olika råvaror (stamved, hyggesavfall och bark) och slutligen 5) en omfattande experimentell studie med kvantifiering och karakterisering av gas- och partikelformiga utsläpp från dagens ved- och pelletseldade kaminer.

I den inledande litteraturgenomgången kring hälsoeffekter kunde endast 9 relevanta epidemiologiska studier identifieras i vilka alla fokuserade på effekter av korttidsexponering. Substansiell kvantitativ information återfanns endast för relationen mellan akuta astmabesvär och ökning av  $PM_{10}$ -halten i omgivningsluften. Sammantaget var dock skattningarna av de relativa riskerna för olika korttidseffekter i samband med exponering för vedrelaterade partikelföroreningar högre i de funna studierna jämfört med de allmänna riskbedömningar som gäller för partiklar i omgivningsluft. Betydelsen av andra partikelmått än masskoncentration, t ex kemisk sammansättning, partikelstorlek och partikelantal är dessutom inte klarlagda i dagsläget.

För att genomföra det omfattande arbetet med emissionsstudier konstruerades en provtagningsuppställning för småskaliga anläggningar som bygger på utspädning och kylning av rökgaserna. I ett inledande projekt studerades hur olika förhållanden i denna utspädningstunnel påverkade emissionskarakteristiken. Robusta och applicerbara provtagningsförhållanden bestämdes och uppställningen användes sedan i samtliga efterföljande mätkampanjer inom projektet.

Emissionsfaktorer för ett stort antal gas- och partikelformiga utsläppskomponenter bestämdes för olika småskaliga ved- och pelletseldade kaminer som funktion av olika bränsle-, anläggnings- och handhavandevariabler. En betydande variation i emissionsprestanda kunde konstateras vid eldning i vedkaminer med potentiellt mycket höga emissioner av oförbrända produkter som CO, metan, NMVOC, PAH och sot under specifika omständigheter. Med rätt anpassning av vedbränsle, teknik och handhavande kan dock sådana situationer sannolikt undvikas och utsläppen relativt väl kontrolleras på rimliga nivåer. Utsläppen av oförbrända produkter var generellt betydligt lägre vid eldning i pelletskaminer jämfört med vedkaminer. Studien visar således på de stora förutsättningar som användandet av förädlade biobränslen (t ex pellets) som eldas i väl anpassande anläggningar ger att optimera förbränningen och minska utsläppen av t ex CO, kolväten och sot. Även fast dagens pelletsutrustning är relativt väl fungerande med låga utsläpp generellt, finns dock ytterligare potential att reducera utsläppen av oförbrända produkter, speciellt vid låglast förhållanden.

Den omfattande karakteriseringen av kolväten i utsläppen innefattade 34 st VOC's och 48 st PAH's. Förutom metan var eten, acetylen och bensen de dominerande VOC komponenterna och de dominerande PAH komponenterna var generellt phenantrene, fluoranthene och pyrene. Typiska emissionsfaktorer för "normal" eldning i vedkaminer på 100 mg/MJ<sub>bränsle</sub> för NMVOC (non-methane VOC) och 3600 µg/MJ<sub>fuel</sub> för PAH<sub>tot</sub> kan jämföras med motsvarande typiska emissioner i pelletskaminer på 2-20 mg/MJ<sub>fuel</sub> för NMVOC och 10-200 µg/MJ<sub>br</sub> för PAH<sub>tot</sub>.

Partikelutsläppen dominerades i samtliga lägen (ved- och pelletseldning) av submikrona (<1 µm) partiklar med massmedian- och antalsmediandiametrar kring 100-300 nm och 50-250 nm respektive samt i antalskoncentrationer mellan  $4.6 \cdot 10^{12}$ - $1.1 \cdot 10^{14}$ /MJ<sub>bränsle</sub>. Under sämre (mer ofullständiga) förbränningsförhållanden tenderade partikelstorleksfördelningen att förskjutas uppåt. Den mindre fraktionen (1-25 vikts-%) av grövre partiklar (>1 µm) bestod av oförbrända kolhaltiga bränslerester med en mindre andel kalciuminnehållande korn (1-10 µm). De totala partikelemissionerna från ved- och pelletkaminerna varierade mellan 37-160 mg/MJ<sub>bränsle</sub> och 15-46 mg/MJ<sub>bränsle</sub>, respektive. Vid optimerad förbränning av träpellets ligger partikelemissionerna på 15-20 mg/MJ<sub>bränsle</sub> som då består enbart av submikrona oorganiska partiklar med massmediandiametrar på 100-120 nm. Det oorganiska partikulära materialet i utsläppen vid förbränning av pellets från skogsbaserade råvaror består till största delen av alkalialter, t ex KCl,  $K_3Na(SO_4)_2$  och  $K_2SO_4$ . Förutom dessa alkalialter återfinns zink som det dominerande spårämnet i partiklarna sannolikt i en mer komplex form än ren zinkoxid, zinkklorid eller zinksulfat, men bildningsmekanismer och kemisk (fas)sammansättning återstår att bestämma.

## **ACKNOWLEDGEMENTS**

The authors would like to acknowledge a number of persons and institutions for valuable contribution in different parts of the project, although not specified here but in the enclosed separate papers or manuscripts.

This work was a part of the Swedish national research program "Utsläpp och Luftkvalitet" with the specific sub-program concerning biomass, health and environment, called "Biobränslen, Hälsa, Miljö" (BHM), financed by the Swedish Energy Agency.

The work was also initially supported by the Center for Environmental Research in Umeå (CMF).



## CONTENTS

1	Introduction	1
1.1	Background	1
1.2	Objectives	1
2	Summary of designs, experimental procedures and results	3
2.1	Health effects review ( <i>Appendix 1</i> )	3
2.2	Dilution sampling set-up ( <i>Appendix 2</i> )	4
2.3	Emission minimization - "future technology" ( <i>Appendix 3</i> )	6
2.4	Inorganic PM from combustion of different woody raw materials ( <i>Appendix 4</i> )	8
2.5	Wood log and pellet stoves - emission characterization and quantification ( <i>Appendix 5</i> )	10
2.6	Emission factors - Summary	13
3	Conclusions	16
	References	18
	Publications	19
	Appendices (1-5)	



# 1 INTRODUCTION

## 1.1 Background

Biomass is a sustainable energy source with significant potentials for replacing fossil fuels and electricity for heating purposes, not at least in the residential sector. Present residential wood combustion can, however, be a significant source of ambient urban air pollution and the potential environmental health effects of e.g. volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH) and particulate matter (PM) are of special concern. Ambient exposure to these pollutants in general has been associated with different health effects such as cardiopulmonary disease/mortality and cancer risks [1]. It has further been shown that the PM from combustion sources is dominated by fine (<1 µm) particles and there is an increasing interest in their formation mechanisms, characteristics and specific implications to human health [2, 3]. Compared to modern technology, the majority of the presently used wood fired appliances often suffer from poorly optimized conditions, resulting in considerable emissions of products of incomplete combustion (PIC), e.g. CO, hydrocarbons and soot particles. New and upgraded biomass fuels provide possibilities of more controlled and optimized combustion with less emission of PIC. Wood pellets are generally a clean, dry and easily fed fuel to be used in special boilers, burners and stoves on the residential market. For future health impact assessments, regulatory standards and evaluations concerning present and future residential biomass combustion, a solid qualitative and quantitative knowledge of the emissions from different sources is of vital importance. Although, some limited work has been performed previously, there is still a strong need for detailed characterization and quantification of the emissions from residential biomass appliances when using different fuels and combustion techniques.

During the years of 2001-2004, an extensive national research program concerning emissions and air quality ("Utsläpp och Luftkvalitet") with a sub-program concerning biomass, health and environment ("Biobränslen, Hälsa, Miljö" - BHM) has been in progress financed by the Swedish Energy Agency. The overall objective with the BHM-program was to describe the influence of the use of biofuels for heat production in small and medium-sized combustion appliances regarding the emission distribution, air quality and potential health effects. Additionally, the program should aim to describe the situation in a possible future with increased use of biomass and also concern the potential for technology development. Within the residential sector, both water based heating systems (i.e. boilers) and air based heating systems (i.e. stoves and other fireplaces) were included for emission quantification and characterization, and the work was therefore divided between different national research groups. Further information concerning the BHM-research program and the included projects can be found elsewhere [4].

## 1.2 Objectives

The present work, which was a part of the BHM-program, had the main objective to systematically determine the quantities and characteristics of gaseous and particulate emissions from biomass combustion in residential appliances, as well as to report emission factors for the most important emission components. The focus was on present commercial wood log and fuel pellet stoves as well as to illustrate the potentials for future technology regarding emission minimization.

In addition to the work with emission studies, a literature review of adverse health effects related to ambient wood smoke exposure, were initially accomplished. The literature review contributed to the evaluation of the present knowledge concerning air pollution from biomass combustion and related adverse health effects, and was used as background material in the health effects cluster within the BHM-program.

The work included in this report was divided in five separate sub-projects which reports are enclosed in appendix 1-5. Appendix 5 is a manuscript including an extensive amount of emission data for the studied wood and pellet stoves. The sixth appendix is a summarizing proceeding presented at the international bioenergy conference in Rome, Italy 2004.

The separate sub-projects in appendix 1-5 had the following specific objectives:

- i) To review the scientific literature concerning adverse health effects from ambient air pollution in relation to residential wood combustion in modern society and if possible extract quantifications for the associations.
- ii) To design a dilution sampling system for emission measurements in residential biomass fired appliances and determine the influence of dilution sampling conditions on the characteristics and distributions of PM and PAH.
- iii) To determine the effects of temperature and residence time on the formation/ destruction and characteristics of products of incomplete combustion, especially PAH, and particulate matter during combustion of conifer stem-wood pellets in a laboratory fixed-bed reactor (<5 kW).
- iv) To determine the mass size, elemental and inorganic phase distributions of particulate matter from residential combustion appliances using different pelletized woody biomass fuels.
- v) To determine the characteristics and quantities of gaseous and particulate emissions from combustion in residential wood log and pellet stoves, and report emission factors for the most important emission components.

## 2 SUMMARY OF DESIGNS, EXPERIMENTAL PROCEDURES AND RESULTS

### 2.1 Health effects review (Appendix 1)

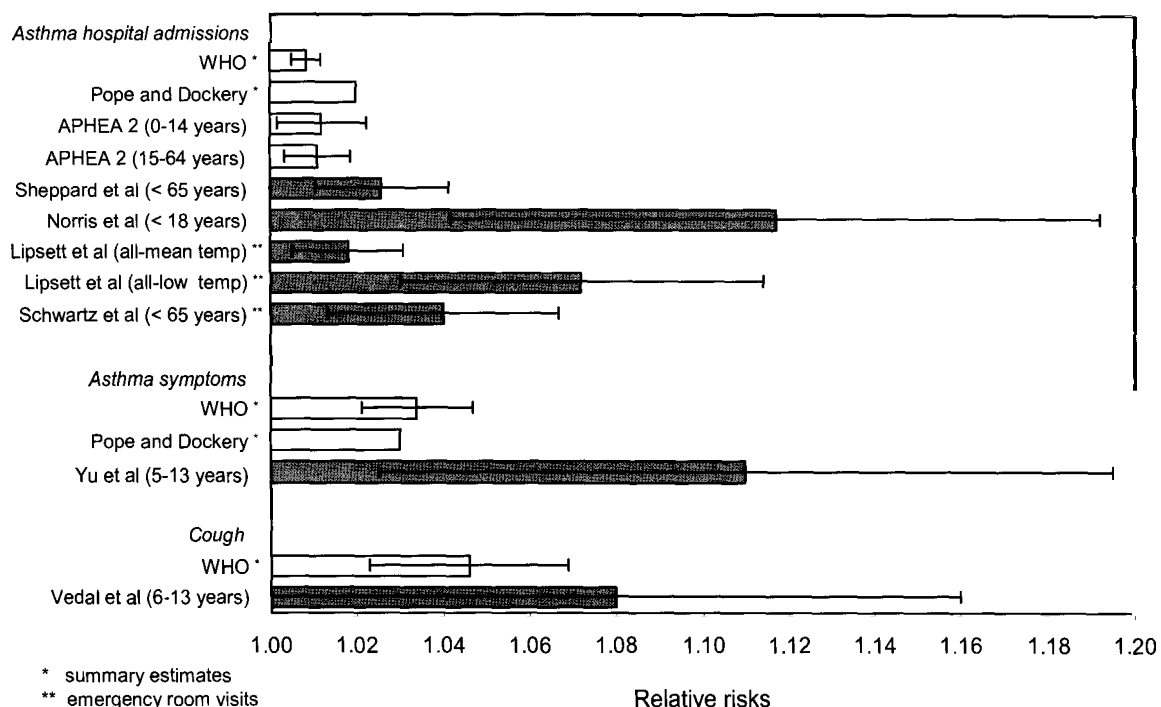
Initially, a literature review of reported adverse health effects from ambient air pollution in relation to residential wood combustion (RWC) in modern society was performed. The work focused on epidemiological studies from settings where RWC was mentioned as an important air pollution source. Beside epidemiological studies, also animal toxicology and controlled human studies contribute to the knowledge of the toxicity of different compounds or pollution mixtures. However, no controlled human exposure study has been reported dealing with wood smoke. On the other hand, a significant number of animal toxicology studies with wood smoke have been reviewed [5] as well as some epidemiological studies [6]. These and other relevant aspects of RWC, air quality and human health were also briefly summarized.

From the literature search, nine relevant studies were identified, all focused on effects of short-term exposure such as asthma admissions, respiratory symptoms, daily mortality and lung function. In Table 1, information of these nine studies and their results are briefly summarized.

**Table 1.** Summary of addressed health effects and brief results from the reviewed papers. The reference numbers in the table refers to the references in the full article (Appendix 1).

Effect	Reference	Subjects age	Pollution indicators	Significant positive associations with
Daily mortality	38	all ages	PM <sub>10</sub> , SO <sub>2</sub> , CO, NO <sub>x</sub>	PM <sub>10</sub>
Asthma symptoms	39	5-13 years	PM <sub>10</sub> , PM <sub>1</sub> , SO <sub>2</sub> , CO	PM <sub>10</sub> , PM <sub>1</sub> , CO
Asthma hospital admissions	40	< 65 years	PM <sub>10</sub> , PM <sub>2.5</sub> , CO, SO <sub>2</sub> , O <sub>3</sub>	PM <sub>10</sub> , PM <sub>2.5</sub> , CO, O <sub>3</sub>
	41	< 18 years	PM <sub>10</sub> , PM <sub>2.5</sub> , CO, NO <sub>2</sub>	PM <sub>10</sub> , PM <sub>2.5</sub> , CO
Asthma emergency room visits	36	all ages	PM <sub>10</sub> , NO <sub>2</sub> , O <sub>3</sub> , CoH	PM <sub>10</sub>
	43	all ages	PM <sub>10</sub> , SO <sub>2</sub> , O <sub>3</sub>	PM <sub>10</sub>
Peak expiratory flow and respiratory symptoms	35	children	PM <sub>10</sub>	PM <sub>10</sub> (in asthmatics)
	42	> 55 (COPD)	PM <sub>10</sub> , SO <sub>2</sub> , CO, NO <sub>2</sub>	PM <sub>10</sub> , NO <sub>2</sub>
Forced expiratory volume in 1 sec and forced vital capacity	37	children (grade 3 to 6)	Fine particulate, PM <sub>2.5</sub>	PM <sub>2.5</sub> (in asthmatics)

Substantial quantitative information was only found for acute asthma in relation to particulate matter with an aerodynamic diameter of <10 µm (PM<sub>10</sub>). In comparison with the present general estimations for ambient PM and adverse health effects (Figure 1), the relative risks are even stronger in the studies where residential wood combustion is considered as a major PM source. Thus, there seem to be at least no reason to assume that the PM effects in wood smoke polluted areas are weaker than elsewhere. Ambient exposure to combustion related fine particles in general have also been associated with cardiopulmonary disease and mortality as well as cancer risks, but the importance of other particulate properties than mass concentration, like chemical composition, particle size and number concentration remain to be elucidated.



**Figure 1.** Relative risks for different morbidity outcomes associated with a  $10 \mu\text{g}/\text{m}^3$  increase in  $\text{PM}_{10}$  (particulate matter with an aerodynamic diameter  $<10 \mu\text{m}$ ) with 95% confidence intervals as error bars. Studies where wood smoke is considered as a major air pollution source are shown by closed columns, and comparison estimates are represented by open columns. Detailed reference information is given in the full article (Appendix 1).

## 2.2 Dilution sampling set-up (Appendix 2)

Traditionally, emission measurements have been performed in undiluted hot (e.g. 120-180°C) flue gases. However, in some aspects traditional sampling in raw flue gases suffers from severe drawbacks for example related to; transient conditions with varying flue gas flows, and the condensable nature of many of the semi-volatile organic compounds. This may lead to different characteristics and distributions between the raw hot gases and the ambient air, as well as erroneous results and incorrect conclusions. Sampling at lower temperatures and under constant flow conditions is therefore desirable. The most extensively used and general applicable method is based on whole flow dilution in a dilution tunnel where a constant flow of diluted flue gases enables constant volume sampling (CVS). The methodology of using a CVS system was first designed and used for gasoline fuelled vehicles in the beginning of the 1970's [7] and has then been used and evaluated extensively. While the use of this kind of dilution sampling has become the standard reference method for internal engine emission measurements, the experiences and use of such methods for stationary sources and solid fuel combustion are presently more limited although some work have been performed. One example is the dilution sampling system defined by U.S. Environmental Protection Agency (US EPA) [8], which has been used for characterization of fine particulate matter and organic compounds from residential wood stoves. In Norway, there is also a standardized method with a dilution tunnel for determination of particulate emissions from residential wood stoves and furnaces [9], which in many aspects resembles the US EPA method.



(particulate + semi-volatile PAH) were not influenced by the variations in sampling temperature. The dominating PAH compounds were in all cases phenanthrene, fluoranthene and pyrene, which constituted approximately 70% of the total amount of PAH. The concentrations of those compounds were positively correlated with dilution ratio but no effects of variations in temperature were found.

The conditions and variations in the presently studied CVS system with a lower dilution ratio and somewhat longer residence time are also probably rather appropriate to closely simulate the conditions for residential combustion emissions. To minimize potential recovery losses and maximize the detection possibilities, the results from the present study suggests sampling at  $50\pm 5^\circ\text{C}$  with a dilution ratio of 3-4 times as robust and applicable sampling conditions.

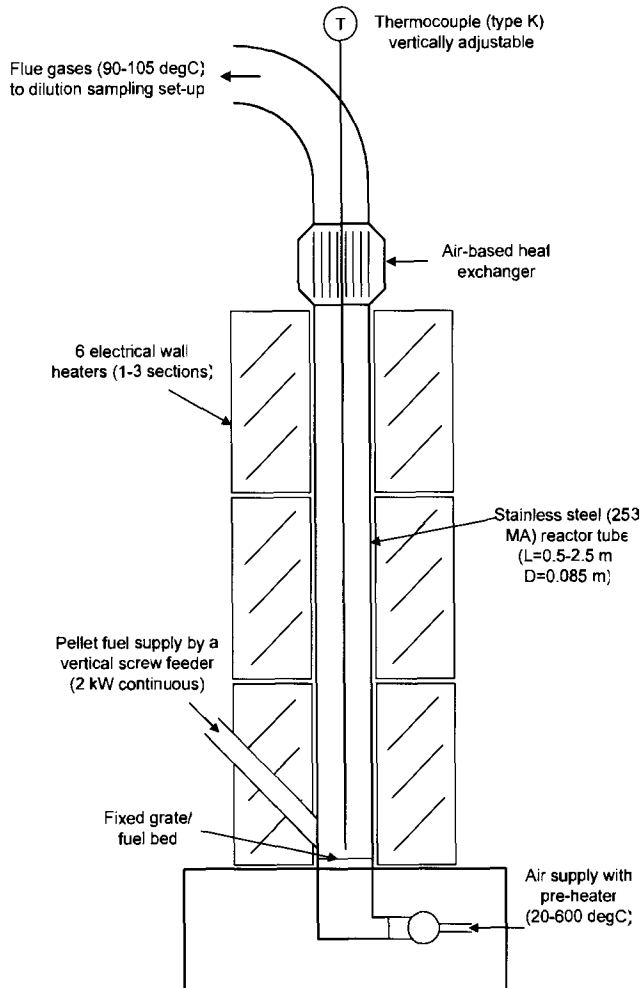
### **2.3 Emission minimization - "future technology" (Appendix 3)**

Present wood log appliances often suffer from extensive temperature in-homogeneities and short residence times at sufficiently high temperatures, resulting in excessive amounts of PIC. Recent preliminary results have shown that the waste amounts of simple gaseous PIC (e.g. CO and gaseous hydrocarbons) relatively easily can be avoided by isothermal, high temperature combustion of biomass pellets. However, no similar data is available for PAH and PM and many PAH components are generally considered to be relatively thermally stable.

In the present project the effects of temperature and residence time in a laboratory fixed-bed pellets reactor (Figure 3) on the emission formation/destruction and characteristics and of PIC, especially PAH, and PM was studied. Temperature and residence after the bed section in the reactor time was varied according to statistical experimental designs covering the ranges  $650\text{-}970^\circ\text{C}$  and  $0.5\text{-}3.5$  s, respectively. Also in this study, typical softwood pellets were used and combusted at  $2 \text{ kW}_{\text{fuel}}$ , corresponding to a typical situation for small houses during wintertime. The previously designed and evaluated dilution sampling setup was used and the emission responses were; CO, organic gaseous carbon (OGC), NO, VOC including 20 specific compounds, PAH (particulate + semi-volatile PAH) including 43 specific compounds,  $\text{PM}_{\text{tot}}$ , particle mass and count median diameter (MMD and CMD) and particle number concentration.

Temperature was negatively correlated with the emissions of all studied PIC, i.e. higher temperature resulted in lower PIC emissions with no significant effect of residence time. For NO a reversed correlation with temperature was determined, i.e. increasing emissions with increasing temperature. The  $\text{PM}_{\text{tot}}$  emissions were in the range of  $15\text{-}20 \text{ mg/MJ}_{\text{fuel}}$  with no effect of variations in temperature or time determined. The PM was totally dominated by fine ( $<1 \mu\text{m}$ ) particles consisting of potassium, oxygen, sulfur, carbon, chlorine, sodium and zinc. Fine particle mass and count median diameters as well as number concentration were significantly influenced of residence time, i.e. increased time resulted in increased particle sizes and decreased number concentrations. The mass and count median diameters varied in the range of  $100\text{-}180 \text{ nm}$  and  $80\text{-}105 \text{ nm}$  respectively, with number concentrations in the range of  $3\text{-}7 \cdot 10^{13} / \text{MJ}_{\text{fuel}}$ .

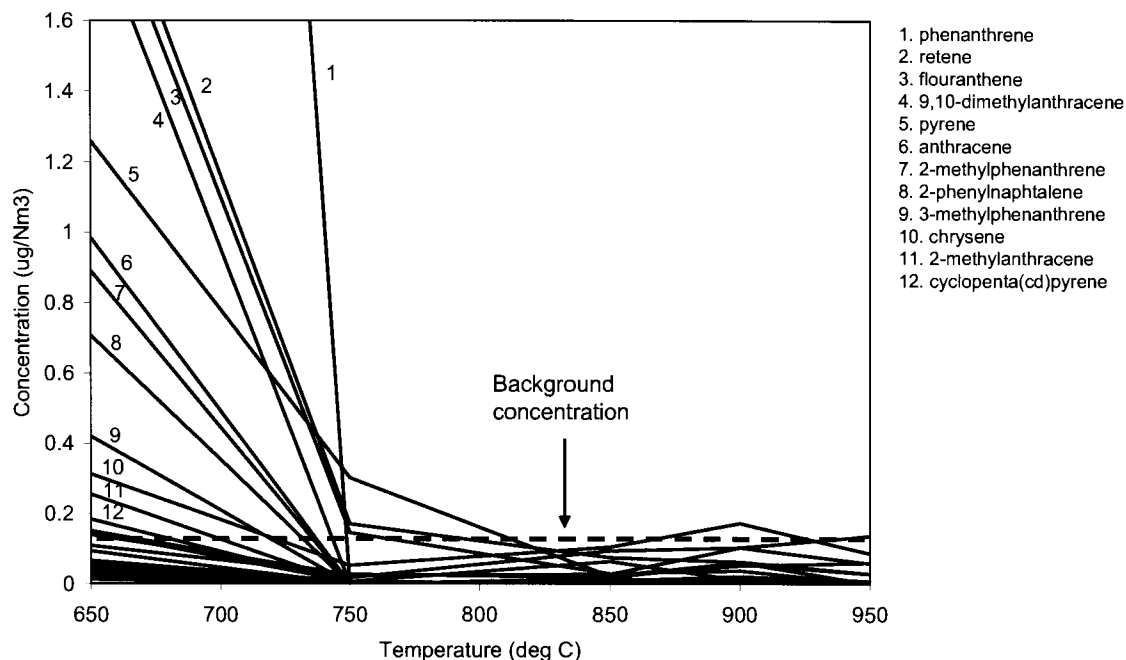




**Figure 3.** Schematic illustration of the experimental fixed-bed pellets reactor (<5 kW<sub>fuel</sub>).

The results in the present study have shown that it exist a significant potential to obtain optimized combustion conditions in residential pellet appliances with in principal a total depletion of PIC's by high temperature, intensive, air rich and well mixed conditions in the bed section. During such conditions the importance of residence time at high temperature was shown to be limited, although isothermal conditions during 0.5-1.0 s would be preferable for optimized results in practical situations. Such high temperature conditions in the fuel bed, which resembles the conditions in present commercial pellet appliances, may, however, increase the risk for potential ash related problems like slagging, especially during combustion of some qualities of more ash rich pellet fuels [10]. If such fuels are to be used and potential ash related problems should be prevented, air staging with lower fuel bed temperatures is preferable and the importance of sufficiently long residence time in the post-combustion zone for minimizing the emissions of PIC will therefore increase.

The extremely low emissions of PAH and other PIC can probably be explained by a prevention of the formation or instant oxidation rather than thermal destruction in the post-combustion zone. Although these results and conclusions are exciting and encouraging they may be consequences of both the excess surface temperatures of the burning fuel pellets and more reactor specific conditions, emphasizing the need for further verification studies and technology development work.



**Figure 4.** Concentrations of separate PAH compounds in the flue gases during combustion of softwood pellets as a function of temperature in the post-combustion zone after the fuel bed.

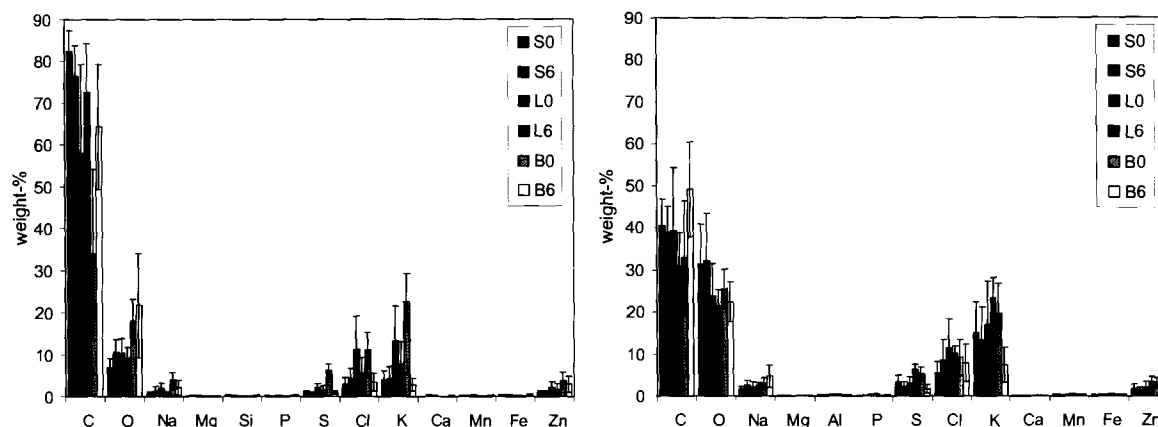
#### 2.4 Inorganic PM from combustion of different woody raw materials (Appendix 4)

The presently used raw materials for production of fuel pellets are generally stem-wood assortments ( $\approx 95\%$ ) such as sawdust, planer shavings or dried chips from sawmills and the wood working industry while bark, agricultural residues and other forest fuels only occasionally occurs [11]. However, in a future with an increasing utilization of the forest resources, also other types of wood forest based materials (e.g. bark and logging residues) might be used for pellet production.

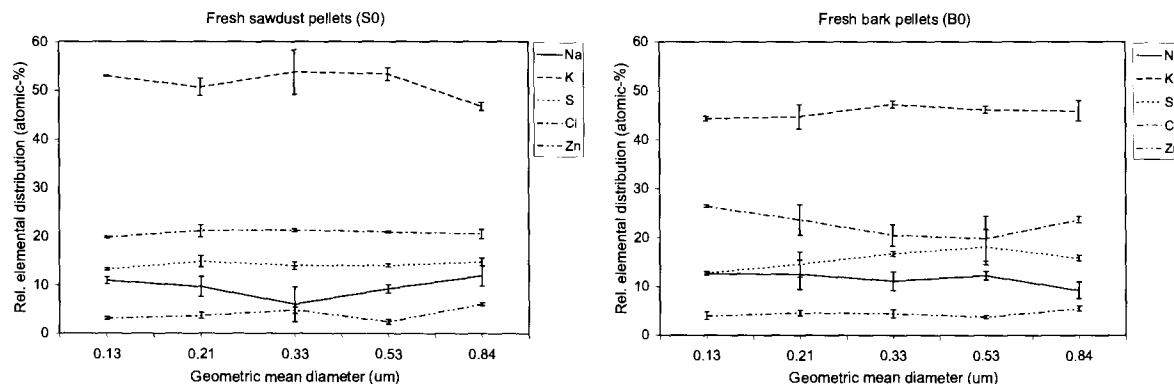
Therefore, the mass size, elemental and inorganic phase distributions of PM from different residential combustion appliances using different pelletized biomass fuels was determined. In addition, chemical equilibrium model calculations of the combustion process were used to interpret the experimental findings. Six different typical pellet fuels of softwood sawdust, logging residues and bark were combusted in three commercial pellet burners (10-15 kW). Total PM mass concentrations as well as particle mass size distributions were determined using a 13-stage low-pressure impactor with a pre-cyclone. The PM was analyzed for morphology (using ESEM), elemental composition (using EDS) and crystalline phases (using XRD). Selected impactor samples were also analyzed by time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) spectroscopy. These analyses methods provide chemical structural information and were used as complementary tools to ESEM/EDS and XRD for possible further detailed chemical characterization.

The emitted particles were mainly found in the fine sub-micron mode with mass median aerodynamic diameters between 0.20 and 0.39  $\mu\text{m}$ , and an average  $\text{PM}_{10}$  of  $92.3 \pm 6.2\%$ . Minor coarse mode fractions ( $>1 \mu\text{m}$ ) were present primarily in the experiments with bark and logging residues. Relatively large and varying fractions (28-92%) of PM were

determined to be products of incomplete combustion. The inorganic elemental compositions of the fine particle samples were dominated by K, Cl and S with minor amounts of Na and Zn (Figure 5). The relative distribution of these five elements within the fine mode in the different cases was rather homogeneous, only with a small trend of increased sulfur content with increased particle sizes in some cases (Figure 6). The dominating alkali phase detected was KCl with minor but varying amounts of  $K_3Na(SO_4)_2$  and in some cases also  $K_2SO_4$ .



**Figure 5.** Elemental composition of the fine PM from burner B (left) and burner C (right). Standard deviations within the fine mode (i.e. different impactor substrates) are shown as error bars. For burner B (using Al-foils) Al was excluded from the analysis, and for burner C (using quartz fiber filters) Si was excluded.



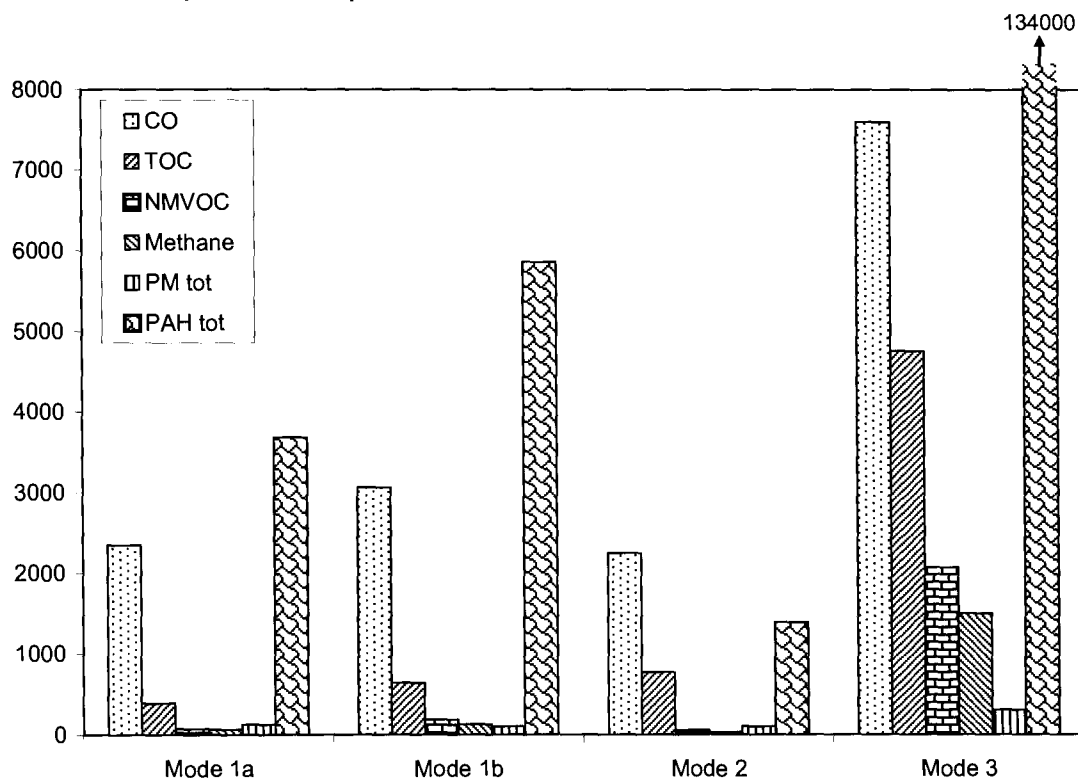
**Figure 6.** Typical relative elemental distributions of the five elements present within the fine mode on a carbon and oxygen free basis, illustrated by the results during combustion of pelletized softwood sawdust (left) and bark (right) in a residential burner. The average distribution (in atomic-%) is shown for each impactor substrate number 3-7 (0.13-0.84  $\mu\text{m}$ ) with standard deviations as error bars.

The results further indicated zinc to be almost fully volatilized in the reducing atmospheres of burning fuel particles and presumably forming a more complex solid phase than pure zinc oxide or some zinc salt. However, the formation mechanism and exact phase composition remain to be elucidated. With some constraints, the results also showed that the amounts and speciation of the inorganic PM seemed to be quite similar to what was predicted by chemical equilibrium calculations.

## 2.5 Wood log and pellet stoves - emission characterization and quantification (Appendix 5)

Present residential wood combustion can be a major air pollution source mainly of hydrocarbons and PM in urban environments. The potential for increased use of biomass and reduction of emissions by using new technologies is, however, significant. Despite the previously well documented extent and importance of these pollution sources and components, relatively limited information is available concerning detailed emission characteristics and quantification for different appliances and fuels. The characteristics and quantities of gaseous and particulate emissions from combustion in residential wood log and pellet stoves were therefore determined and emission factors for the most important emission components reported in an extensive experimental study. A large number of gaseous and particulate components were studied for wood log and pellet stoves with systematic variations in fuel, appliance and operational properties. Birch wood logs were combusted in a wood stove under different simulated operation conditions (modes) and conifer logs of pine and spruce were also included for comparison. Two conifer sawdust pellets (6 and 8 mm in diameter) were combusted with variations in chimney draught and fuel load.

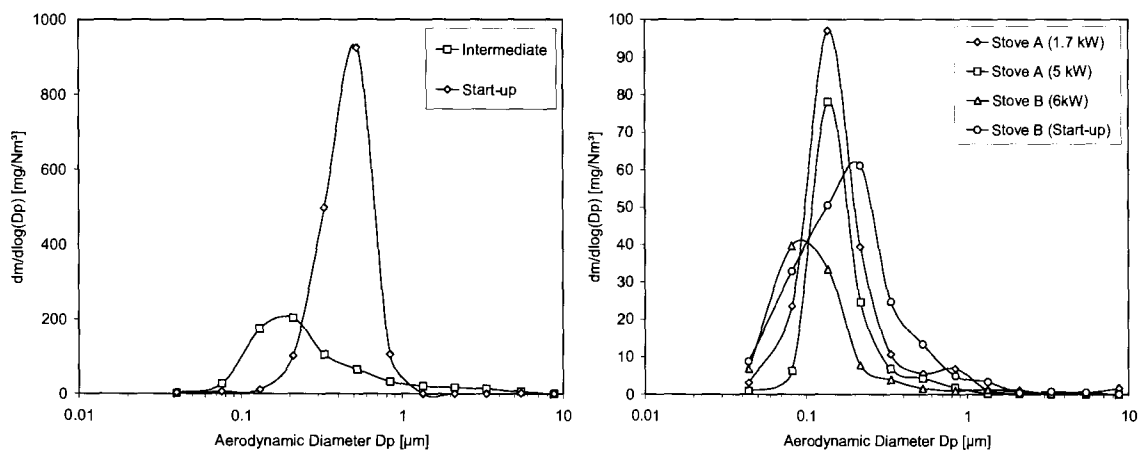
Considerable variability of emission performance in the wood log stove was determined, with potentially very high emissions of products of incomplete combustion (PIC) during specific conditions (Figure 7). However, by proper technical and/or operational measures the emission performance can be rather well controlled, and a significant potential for further development and optimization therefore exists.



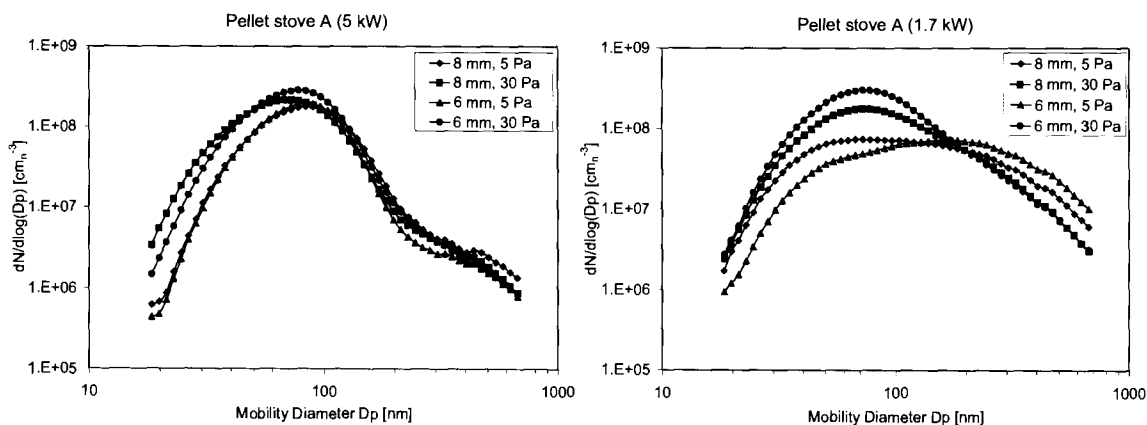
**Figure 7.** Comparison between the average emissions of the main components from the wood stove during different operation modes, given as mg/MJ<sub>fuel</sub> (PAH given as µg/MJ<sub>fuel</sub>). TOC given as CH<sub>4</sub>-equivalents. The conditions in the different modes aimed to simulate; Mode 1 (a) = "Normal" stove and fuel conditions (2 experiments with birch wood), Mode 1 (b) = "Normal" stove and fuel conditions (2 experiments with conifer wood), Mode 2 = "Cold and air starved" combustion with moist and large logs (2 experiments with birch wood), Mode 3 = "Intensive" combustion with high draught and extra dry and cleaved logs (2 experiments with birch wood).

The emissions of PIC as well as PM from the wood log stove were generally considerably higher than from the pellet stoves. Accordingly, the use of up-graded biomass fuels with controlled combustion conditions gives advantageous conditions for optimization of the combustion process compared to traditional batch wise firing of wood logs. There is, however, still a potential for further minimization of PIC emissions in residential pellets applications, especially at low loads.

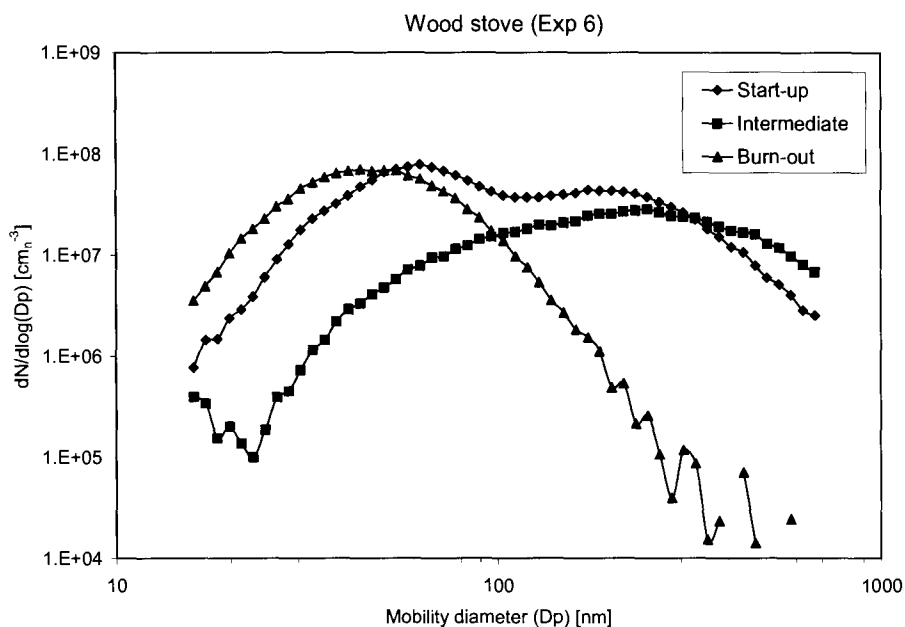
The extensive characterization of hydrocarbons included 34 specific VOC's and 48 specific PAH's. Beside methane, ethene, acetylene and benzene were the most dominant VOC's and the dominating PAH's were in all cases phenantrene, fluoranthene and pyrene. Fine sub-micron particles dominated in all cases the PM with 80-95% as PM<sub>1</sub>. The minor coarse fraction consisted of carbonaceous unburned fuels residues with inclusions of calcium containing grains (1-10 μm). Fine particle mass median and count diameters were in the range of 100-300 nm and 50-250 nm respectively with number concentrations at  $4.6 \cdot 10^{12}$ - $1.1 \cdot 10^{14}$ /MJ<sub>fuel</sub> (Figure 11-13).



**Figure 11.** Typical particle mass size distribution for the wood log stove (left) and pellet stoves (right), measured by the LPI. Upper impactor stage and pre-cyclone not included. (concentrations are normalized to 10% O<sub>2</sub>)

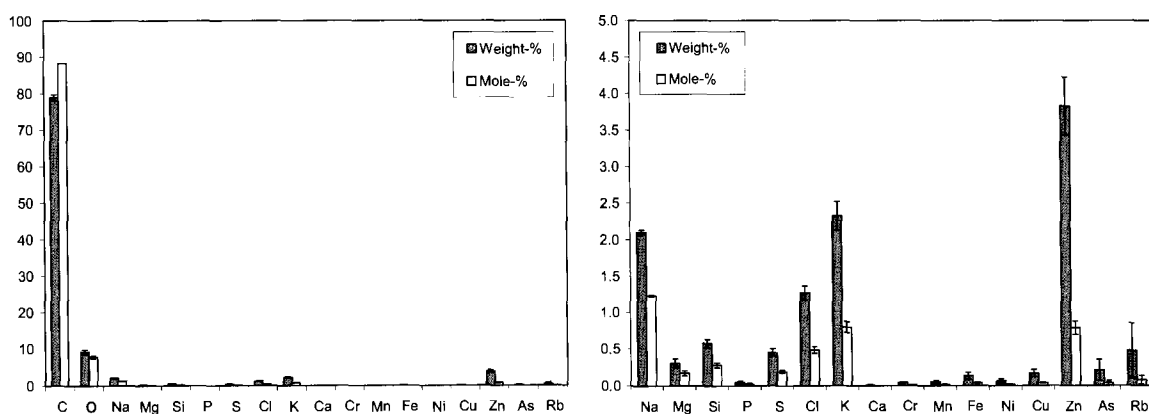


**Figure 12.** Average fine particle number size distributions for one of the pellet stoves measured by the SMPS. For each case, the size distributions during experiments with variations in pellet fuels (6 and 8 mm) and chimney draught (5 and 30 Pa) are included.



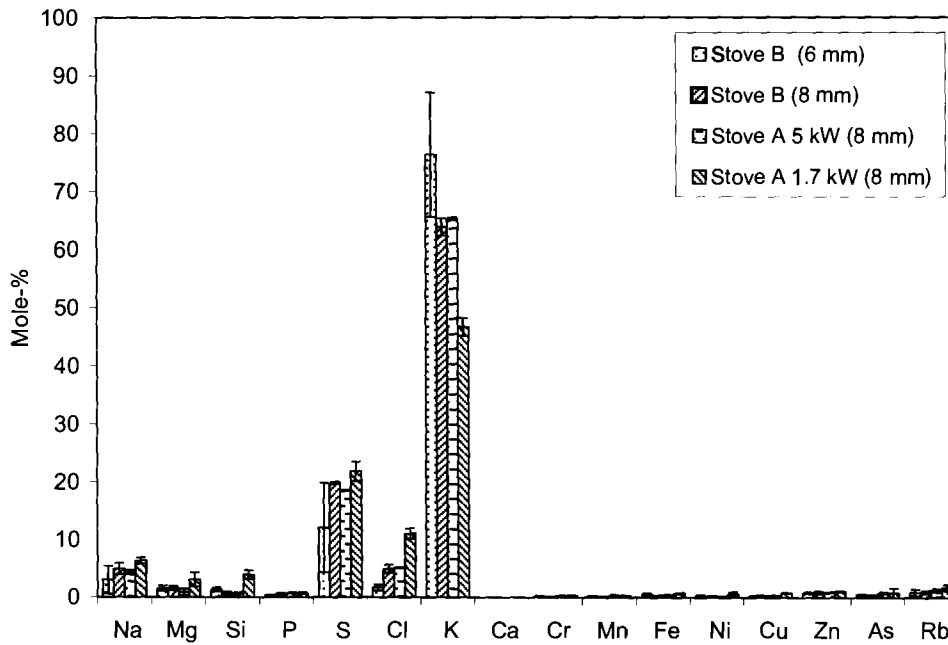
**Figure 13.** Typical average fine particle number size distributions for the wood stove during different phases of a combustion cycle, measured by the SMPS. The tail of the intermediate distribution below 25 nm is most probably an artefact of the operation (ventilation) of the CPC. (concentrations are normalized to 10% O<sub>2</sub>)

The emissions of PM<sub>tot</sub> varied in the range of 37-160 mg/MJ<sub>fuel</sub> for the wood log stove and 15-46 mg/MJ<sub>fuel</sub> for the pellet stoves. Previous studies of "optimized" combustion of softwood pellets with almost a total depletion of PIC have shown that the emissions of inorganic PM are in the range of 15-20 mg/MJ<sub>fuel</sub> (see Appendix 3 and [12]). Assuming similar ash composition and volatilization conditions therefore confirms that the PM from the wood stove experiments were dominated by PIC (i.e. carbonaceous material) which also was illustrated by the high content of carbon detected by SEM/EDS in the fine PM. The elemental composition of the fine PM from the birch wood combustion is shown in Figure 14.



**Figure 14.** Elemental composition of fine mode particles in the emissions from birch wood combustion in the wood stove (mode 1, exp 2, intermediate phase). Results presented as average values of 3 area analyses (100\*100 μm) on impactor stage 3 (Dg=130 nm) with standard deviation shown as error bars. In the left diagram all analyzed elements are shown, and in the right diagram a different scaling is used to get a better resolution of the less abundant elements (C and O not shown). Aluminum was excluded from the analysis since Al-foils were used as sampling substrates.

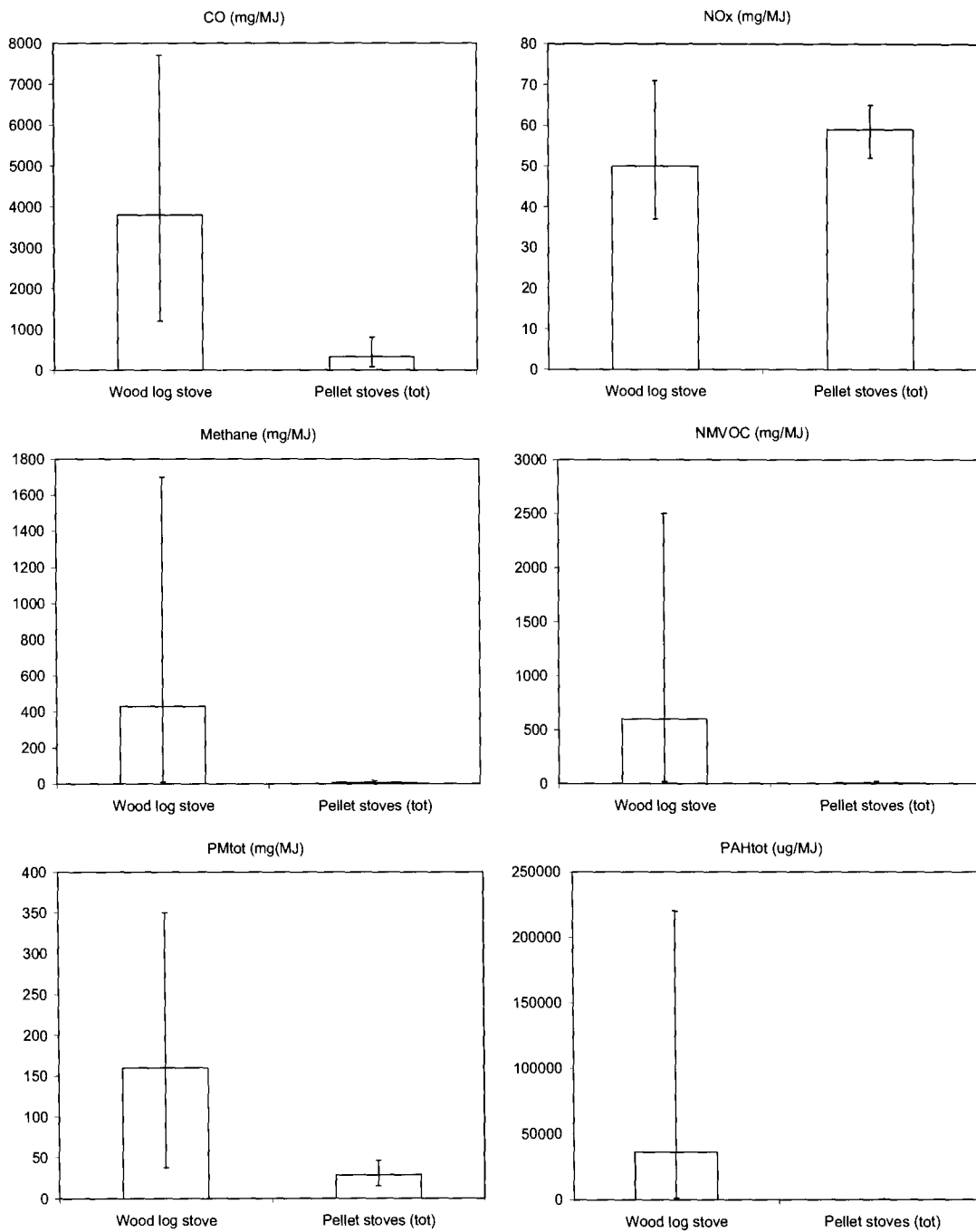
The amount of carbonaceous material was relatively low in the pellet stove PM and in Figure 15, the relative elemental composition of inorganic elements in the fine particles from the pellet stoves are shown on a carbon and oxygen free basis. In accordance with previous data from residential pellet burners, the fine inorganic PM was dominated by potassium, sulfur and chlorine in the form of  $K_2SO_4$ ,  $K_3Na(SO_4)_2$  and  $KCl$ . Sodium and in some cases also zinc were also found as important elements in the fine PM. Alkali carbonates were not detected in the analysis but could not be excluded as additional alkali phases in some cases. The degree of volatilization, subsequent gas-to-particle conversion and final phase composition may, however, differ significantly and is influenced by combustion temperature, local air to fuel ratio and fuel properties/composition.



**Figure 15.** Relative elemental composition (on a C, O and Al free basis) for the fine mode particles in the emission from combustion of softwood pellets in two pellet stoves. Results presented as average values of 3 area analyses ( $100 \times 100 \mu\text{m}$ ) on impactor stage 3 ( $D_g=130 \text{ nm}$ ) with standard deviation shown as error bars.

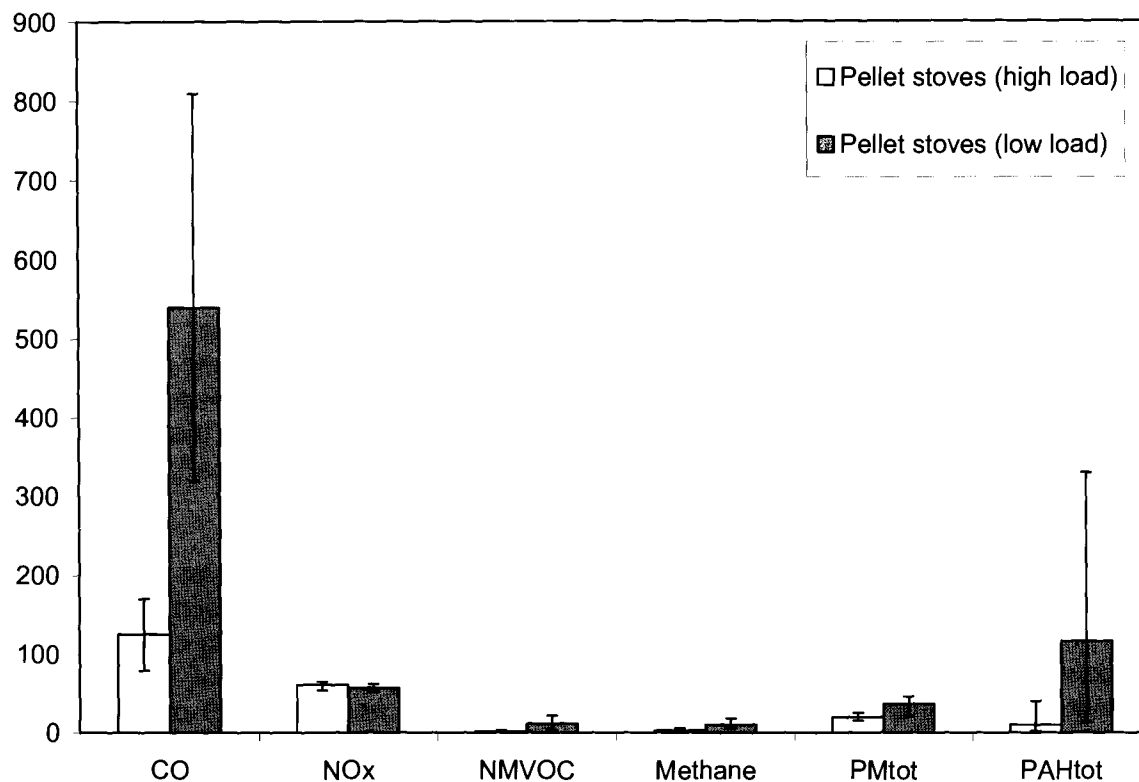
## 2.6 Emission factors - Summary

Based on the extensive characterization and quantification work within the project with residential wood log and pellet stoves, as discussed above, emission factors and their variability can be extracted. As discussed previously, significant higher emissions, mainly of PIC, were generally determined during wood log combustion than pellets combustion. However, significant variations in emission factors were also determined for specific appliances as a function of variations in combustion conditions, fuel properties and operation. In Figure 16, the average emissions of the main components determined during the different campaigns are presented. To better illustrate the emission levels and their variations for the pellet stoves, the emissions factors determined at different fuel loads are presented in Figure 17.



**Figure 16.** Summary of average emission factors of the main components determined for the wood log and pellet stoves, with the interval shown for highest and lowest average values determined during different experiments in the present campaigns.





**Figure 17.** Summary of average emission factors for the pellet stoves during high (5-6 kW<sub>fuel</sub>) and low (~2 kW<sub>fuel</sub>) load operation, with the interval shown for highest and lowest average values determined during different experiments in the present campaigns.

### 3 CONCLUSIONS

Based on the results in the separate sub-projects included in this report, the following general conclusions with significant implications for future environmental health impact assessments, legislations and technical development can be draw:

- Emissions from residential biomass combustion include a number of air pollutants with potential adverse health effects, and an increasing interest concerning their potential implications to human health can be seen. A limited number of dedicated epidemiological studies have been performed but substantial quantitative information is found for acute asthma in relation to PM<sub>10</sub>. Ambient exposure to combustion related fine particles in general have also been associated with cardiopulmonary disease and mortality as well as cancer risks, but the importance of other particulate properties than mass concentration, like chemical composition, particle size and number concentration remain to be elucidated.
- Emission factor ranges for different residential biomass fired stoves have been determined as functions of variations in fuel, appliance and operational properties. There was a considerably variability of emission performance during different fuel, combustion and operation conditions. Considerably emissions of products of incomplete combustion (PIC), e.g. CO, hydrocarbons and soot, can obtain during specific situations during batch wise firing of wood logs. However, the emissions of PIC can be rather well controlled by proper technical and/or operational measures, and a significant potential for further development and optimization therefore exists.
- The emissions of PIC as well as PM from the wood stove were in all cases shown to be considerably higher compared to those from the pellet stoves. Accordingly, the use of up-graded pellets biomass fuels, combusted under continuous and controlled conditions give advantageous combustion conditions compared to traditional batch wise firing of wood logs. There is, however, still a significant potential for further minimization of PIC emissions in future pellets technology, especially at low load operation.
- The importance of high temperature (>850°C) in the bed zone with intensive, air rich and well mixed conditions with isothermal conditions for 0.5-1.0 s in the post combustion zone was illustrated for small-scale softwood pellets combustion to obtain complete combustion conditions with almost a total depletion of PIC.
- Extensive VOC and PAH characteristics were determined for a wide range of residential biomass combustion appliances during different fuel and operational conditions. Beside methane, ethene, acetylene and benzene were the dominating VOC's and phenantrene, fluoranthene and pyrene were in the dominating PAH's.
- The PM from residential pellet appliances combusted is totally dominated by fine (<1 µm) particles in the range of 100-300 nm (aerodynamic diameter) depending on combustion conditions. The minor and varying fraction of coarse (>1 µm) particles, consisting of carbonaceous unburned fuel residues and mineral grains (e.g CaO and/or CaCO<sub>3</sub>) which is more pronounced when burning e.g. bark and logging residues.
- During optimized and complete combustion of biomass fuels, the emissions of inorganic particulate matter still remain. This inorganic PM is dominated by fine (<1

$\mu\text{m}$ ) particles deriving from volatilized ash forming elements, with mass concentrations below in the range of 15-20 mg/MJ<sub>fuel</sub>.

- The fine inorganic PM is dominated by potassium, sodium, sulfur and chlorine in varying amounts strongly depending on fuel composition, mainly found in the form of KCl,  $\text{K}_3\text{Na}(\text{SO}_4)_2$  and  $\text{K}_2\text{SO}_4$ . Besides the alkali material, zinc is found in considerable amounts presumably in a more complex form than ZnO,  $\text{ZnCl}_2$  and  $\text{ZnSO}_4$ . During combustion, zinc is to large degree volatilized within the reducing atmospheres of the burning fuel particles, subsequently forming fine particles. However, the formation mechanism and exact phase composition remain to be determined.
- The present problems with potentially high emissions of PIC (e.g. CO, hydrocarbons and soot) from residential biomass (i.e. wood log) combustion can be avoided by relatively simple technical and/or operational measures and future small-scale biomass technology shows significant potentials.
- Considering the use of modern and "low-emitting" residential biomass combustion technologies using different biomass fuels and their potential implications for air quality and human health, some of the most urgent questions at issue seem to be to determine the formation mechanisms, detailed chemical characteristics and potential environmental health effects for the alkali and trace element (e.g. zinc) containing fine particles.

## REFERENCES

1. Holgate ST, Samet JM, Koren HS, Maynard R, editors. Air pollution and health. London: Academic Press; 1999.
2. Lighty JS, Veranth JM, Sarofim AF. Combustion aerosols: factors governing their size and composition and implications to human health. *Journal of Air and Waste Management Association* 2000;50(9):1565-1618.
3. Avakian MD, Dellinger B, Fiedler H, Gullet B, Koshland C, Marklund S, Oberdorster G, Safe S, Sarofim A, Smith KR, Schwartz D, Suk WA. The origin, fate and health effects of combustion by-products: a research framework. *Environmental Health Perspectives* 2002;110(11):1155-1162.
4. Swedish Energy Agency. National research programme "Biobränslen, Hälsa och Miljö" (BHM). Preliminary Report 2003. Available at <http://www.itm.su.se/bhm>. (In Swedish)
5. Zelikoff JT, Chen LC, Cohen MD, Schlesinger RB. The toxicology of inhaled woodsmoke. *Journal of Toxicology and Environmental Health, Part B* 2002;5:269-82.
6. Larson TV, Koenig JQ. Wood smoke: emissions and noncancer respiratory effects. *Annual Review of Public Health* 1994;15:133-56.
7. Habbi K. Characterization of particulate lead and vehicle exhausts-experimental techniques. *Environmental Science and Technology* 1970;4:239-59.
8. U.S. Environmental Protection Agency. Method 5 G - Determination of particulate matter emissions from wood heaters (dilution tunnel sampling location). *Federal Register* 2000;65(201):61867-76.
9. Enclosed wood heaters - Smoke emission - Part 2: Determination of particulate emission. Norwegian Standard NS 3058-2, 1994. p. 1-12.
10. Öhman M, Boman C, Hedman H, Nordin A, Boström D. Slagging tendencies of wood pellet ash during combustion in residential pellet burners. *Biomass and Bioenergy* 2004;27:585-596.
11. Hillring B, Vinterbäck J. Wood pellets in the Swedish residential market. *Forest Products Journal* 1998;48(5):67-72.
12. Wiinikka H. Particle emissions from wood pellet combustion. Licentiate thesis. Luleå University of Technology, Luleå, Sweden, 2003.

## PUBLICATIONS

(Appendix 1-5)

1. Boman BC, Forsberg AB, Järvholm BG. **Adverse health effects from ambient air pollution in relation to residential wood combustion in modern society.**

*Scandinavian Journal of Work, Environment and Health 2003;29(4):251-260.*

2. Boman C, Nordin A, Westerholm R, Pettersson E. **Evaluation of a constant volume sampling set-up for residential biomass fired appliances - influence of dilution conditions on particulate and PAH emissions.**

*Submitted to Biomass and Bioenergy*

3. Boman C, Pettersson E, Lindmark F, Öhman M, Nordin A, Westerholm R. **Effects of temperature and residence time on emission characteristics during fixed-bed combustion of conifer stem-wood pellets.**

*Manuscript*

4. Boman C, Nordin A, Boström D, Öhman M. **Characterization of inorganic particulate matter from residential combustion of pelletized biomass fuels.**

*Energy and Fuels 2004;18:338-348.*

5. Boman C, Pettersson E, Nordin A, Westerholm R, Boström D. **Gaseous and particulate emissions from combustion in residential wood log and pellet stoves - experimental characterization and quantification.**

*Manuscript*

### Licentiate thesis:

**Particulate matter and products of incomplete combustion from residential biomass pellet appliances - emissions and potential for future technology**

Christoffer Boman, Umeå University, June 2003

## **APPENDICES**

**Not included in the report due to copyright law**