

Impact of residential wood combustion on urban air quality

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Doctoral thesis



Stockholm University

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Doctoral thesis
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“If mankind is to survive, we shall require
a substantially new manner of thinking.”

Albert Einstein (1879-1955)

Abstract

Biomass combustion has become a global concern due to its large impact on climate, air quality and human health. Among all possible types of biomass burning, wood burning is mainly used in cold regions as a primary or supplemental space heating source in residential areas. In several industrialized countries, there is a renewed interest in residential wood combustion (RWC) as an alternative to fossil fuel and nuclear power consumption. The main objective of this thesis was to investigate the impact of RWC on the air quality in urban areas. To this end, a field campaign was conducted in Northern Sweden during the winter season to provide a physico-chemical characterization of atmospheric aerosol particles and polycyclic aromatic hydrocarbons (PAH) and to determine their source apportionment.

A large day-to-day and hour-to-hour variability in aerosol concentrations was observed during the intensive field campaign. On average, total carbon contributed a substantial fraction of PM_{10} mass concentrations (EC 11%, and OC 35%) and a majority of the aerosol particles were found in the fine mode (PM_1 accounted for 76% of PM_{10}). Evening aerosol concentrations were significantly higher during weekends than on weekdays, probably caused by the use of wood burning for recreational purposes and/or higher space heat demand when inhabitants spend longer time at home. In the present work, continuous aerosol particle number size distribution measurements successfully provided source apportionment of atmospheric aerosol with high temporal resolution. The first compound-specific radiocarbon analysis (CSRA) of atmospheric PAHs demonstrated its potential to provide quantitative information on the RWC contribution to individual PAHs. Residential wood combustion accounted for a large fraction of particle number concentrations in the size range 25-606 nm (44-57%), PM_{10} (36-82%), PM_1 (31-83%), light-absorbing carbon (40-76%) and individual PAHs (71-87%) mass concentrations. These studies have demonstrated that the impact of RWC on air quality in an urban location can be very important and largely exceed the contribution of vehicle emissions during wintertime, particularly under very stable atmospheric conditions.

KEYWORDS: residential wood combustion, air quality, aerosols, black carbon, polycyclic aromatic hydrocarbons, particulate matter, particle size distributions, source apportionment, positive matrix factorization, compound-specific radiocarbon analysis.

List of papers

This doctoral thesis is based on the following papers, which are referred to in the summary by their Roman numerals. Published and accepted papers were reprinted with permission from the copyright holders.

I. Carbon content of atmospheric aerosols in a residential area during the wood combustion season in Sweden.

P. Krecl, J. Ström, and C. Johansson.

Atmos. Environ., 41, 6974-6985, 2007.

II. Diurnal variation of atmospheric aerosol during the wood combustion season in Northern Sweden.

P. Krecl, J. Ström, and C. Johansson.

Atmos. Environ., in press, doi:10.1016/j.atmosenv.2008.01.026

III. Contribution of residential wood combustion to wintertime atmospheric aerosol in Northern Sweden.

P. Krecl, E. Hedberg Larsson, J. Ström, and C. Johansson.

Atmos. Chem. Phys. Discuss., 8, 5725-5760, 2008.

Atmos. Chem. Phys., under review, 2008.

IV. Source apportionment of elevated wintertime PAH in a Northern Swedish town by compound specific radiocarbon analysis.

R. J. Sheesley, M. Kruså, P. Krecl, C. Johansson, and Ö. Gustafsson.

Manuscript intended for Environ. Sci. Technol.

Contribution of the author

The contribution of the author of this thesis to the papers is the following:

Paper I

The author was responsible for all measurements and instrumental maintenance. She also performed the laboratory analysis of EC/OC by thermo-optical transmittance, processed all data sets, and wrote the paper. The evaluation and interpretation of the results were performed in close cooperation with the co-authors.

Paper II

The author was responsible for all measurements in the field and instrumental maintenance. She processed and analyzed all data sets and wrote the paper. The evaluation and interpretation of the results were performed in close cooperation with the co-authors.

Paper III

The author performed the multivariate analysis of the data set presented in Paper II and also wrote the manuscript. The evaluation of the results was mainly performed by the author and the interpretation of the results was carried out in cooperation with the co-authors.

Paper IV

The author carried out the field measurements and was involved in the evaluation of the results, performed ^{14}C on TOC calculations, and contributed in the final edition of the paper.

Abbreviations

σ_a	LAC mass absorption cross section
^{14}C	Radiocarbon
AMS	Accelerator mass spectrometry
b_{ap}	Aerosol light absorption coefficient
CCSRA	Compound class-specific radiocarbon analysis
CH_4	Methane
CIS	Cooled injection system
CO	Carbon monoxide
CO_2	Carbon dioxide
CPC	Condensation particle counter
CSRA	Compound-specific radiocarbon analysis
DMA	Differential mobility analyzer
DMPS	Differential mobility particle sizer
EC	Elemental carbon
EEA	European Environmental Agency
EU	European Union
FDMS	Filter dynamics measurement system
FID	Flame ionization detector
F_M	Fraction of modern carbon
GC-MS	Gas chromatography - mass spectrometry
GFF	Glass fiber filter
H_2O	Water
HCl	Chloridric acid
He	Helium
IEA	International Energy Agency
LAC	Light absorbing carbon
LRT	Long-range transport
LT	Local time
M_{LAC}	LAC mass concentration
N	Nitrogen
N_2	Molecular nitrogen

N ₂₅₋₆₀₆	Particle number concentration, diameter range 25-606 nm
N ₂ O	Nitrous oxide
NIOSH	National Institute of Occupational Safety and Health
NO	Nitric oxide
NOSAMS	National Ocean Sciences Accelerator Mass Spectrometry
O	Oxygen
O ₂	Molecular oxygen
OC	Organic carbon
PAH	Polycyclic aromatic hydrocarbons
PC	Pyrolyzed organic carbon
PCGC	Preparative capillary gas chromatography
PM	Particulate matter
PM ₁	PM with diameter < 1 μm
PM ₁₀	PM with diameter < 10 μm
PMF	Positive matrix factorization
PSAP	Particle soot absorption photometer
PSAP-ITM	Custom-built PSAP developed at ITM
PUF	Polyurethane foam
R	Correlation coefficient
R ²	Coefficient of determination
RWC	Residential wood combustion
STD	Standard deviation
TC	Total carbon
TEOM	Tapered element oscillating microbalance
TOC	Total organic carbon
TOR	Thermo-optical reflectance
TOT	Thermo-optical transmittance
TSP	Total suspended particles
VOC	Volatile organic compounds
WHO	World Health Organization
WS	Wind speed

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1. Introduction

Our daily life would probably look very different if we did not use as much energy as we do today. Much of that energy comes from the combustion of different types of fuel and is used for machining goods and providing services. Transportation to and from work, cooking food, heating or cooling houses are a few of these simple things we take for granted.

Combustion of fossil fuels is the major source of energy for today's global economy and the main cause for the increased carbon dioxide (CO₂) concentrations in the atmosphere, which have led to a warming of the Earth's lower atmosphere. There has been a global tendency to move from fossil fuels to biofuels in recent years since the latter is a renewable and neutral CO₂ energy source. However, biomass combustion can as well as fossil fuels emit large amounts of particles and gases with adverse effects on the environment and health.

This doctoral thesis is focused on aerosol particles and polycyclic aromatic hydrocarbons (PAH) sampled in a wood-smoke impacted atmosphere, and deals with their physico-chemical characterization and source apportionment. This thesis summary is structured as follows: background knowledge and scientific goals of the investigations are presented in Chapter 1, methods are described in Chapter 2 while main results are summarized in Chapter 3. Finally, Chapter 4 presents concluding remarks and outlook.

1.1 Background

Biomass combustion has become a global concern due to its large impact on climate, air quality and human health. The combustion of biomass is defined as the burning of organic matter, and is the oldest and most widespread energy source used for a variety of applications. The use of biomass as an energy source covers a great number of biofuels (e.g., wood from felled trees or bushes, agricultural waste, animal waste, charcoal, peat, small branches from living trees, sawdust, and construction wood debris) and several end-use sectors (e.g., electricity production, heating, and transport). Burning can

be due to natural or anthropogenic fires and occurs in urban, rural, and remote areas. Natural wildfires, mainly grass and forest fires induced by lightning, take place in rural and remote areas. In residential areas biomass is burned for heating, cooking, waste disposal, celebrations, rituals, and recreational reasons (e.g., fireplaces, tobacco smoking). There is also a range of non-household uses like brick kilns, restaurant cooking, food drying, distilleries and tire retreading (Bond et al., 2004). In rural areas, domestic fires are mainly related to cooking and heating and open burning of grass/savanna and forest is used for clearing field waste in farming and ranching, slash-and-burn moving agriculture, and forest clearing to extend settlements. Due to atmospheric transport, the anthropogenic inputs described above can also affect remote areas.

Combustion is a complex sequence of exothermic chemical reactions between a fuel and an oxidant where the energy, chemically stored in the fuel, is converted to heat and radiation. In the large majority of combustion uses, the oxidant is oxygen obtained from the ambient air and a large number of gaseous and particulate by-products are produced. Emissions from biomass burning are known to be an important source of greenhouse gases (e.g., CO₂, methane (CH₄), and nitrous oxide (N₂O)) and chemically active gases such as carbon monoxide (CO), nitric oxide (NO), volatile organic compounds (VOC), and polycyclic aromatic compounds (e.g., PAH). Biomass combustion is also a significant global source of particulate matter (inorganic ash material, condensed organic compounds, and elemental carbon-containing particles).

Atmospheric aerosol particles affect the climate by modifying the global radiative balance directly and indirectly. The direct effect is caused by scattering and absorption of solar and infrared radiation in the atmosphere whereas the indirect effect is related to the change in optical and physical properties of the clouds since aerosols act as cloud condensation nuclei. The injection of anthropogenic aerosols into the atmosphere causes an increase in the aerosol load and, thus, has the potential to modify the Earth's energy balance. Even though the net effect of anthropogenic aerosols for the entire troposphere may still be cooling (Forster et al., 2007), recent experiments conducted over the Indian Ocean during the dry season have shown the ability of high concentrations of light-absorbing carbonaceous aerosols to enhance the solar heating of the lower atmosphere by ~50% (Ramanathan et al., 2007). Biofuel burning and fossil fuel combustion were identified as the main emission sources of carbon-containing particles observed over the Indian Ocean and are, hence, responsible for the atmospheric warming found between the heights 0.5 and 3 km (Stone et al., 2007). Besides the influence on the atmospheric radiative budget, carbonaceous aerosols are suspected to

have several other effects such as changes in the hydrological cycle (Ramanathan et al., 2001), cloudiness reduction (Ackerman et al., 2000), circulation and rainfall shifts (Menon et al., 2002), and reduction of surface irradiance (Satheesh and Ramanathan, 2000).

According to Andreae (1991), 66% of the world's biomass is burned in savanna and agricultural fires and the contribution of boreal forest is low compared to tropical areas. In industrialized regions with harsh winters, residential wood combustion (RWC) is frequently used as a primary or supplemental space heating source and for pleasure purposes. As an example, one-third of Swedish homes are completely or partially heated by wood combustion (Statistics Sweden, 2005). On a local perspective, these small-scale emissions can deteriorate the air quality even in small towns during winter-time, when stable atmospheric conditions frequently occur and therefore prevent the vertical dispersion of pollutants. This environmental problem has been reported in several developed countries such as Sweden (Hedberg et al., 2006), Norway (Kocbach et al., 2005), Denmark (Glasius et al., 2006), Switzerland (Szidat et al., 2007), USA (Gorin et al., 2006), New Zealand (Wang and Shooter, 2002) and Australia (Keywood et al., 2000).

An increase in the ambient aerosol burden may also give rise to other adverse side effects, such as visibility reduction (Gras et al., 2001) and could also be a risk factor for human health (WHO, 2003). Most particles emitted from wood combustion are in the fine fraction (diameters < 2.5 μm), resulting in large deposition in the lower respiratory tract (Boman et al., 2003). Particles containing carbon could also act as carriers for some harmful volatile and semi-volatile organic compounds (Lighty et al., 2000). Forsberg et al. (2005) calculated a life-span reduction of up to 7 months for the Swedish population due to the exposure to long-range transported atmospheric particles. Hotspot exposure to locally high concentrations of particulate matter (PM) due to nearby sources (e.g., wood smoke and heavily trafficked streets) was suggested to produce a much larger reduction in life expectancy (Forsberg et al., 2005). Wood smoke has also caused severe concerns about health effects due to the high PAH content. The great interest in studying PAHs is due to the mutagenic and carcinogenic effects on humans and animals caused by some of these compounds (Boström et al., 2002). Animal experiments suggest that PAHs might also give rise to immunological and reproductive effects (WHO, 1998). An important route of human exposure to PAHs in ambient air is via inhalation and this exposure increases the risk of cancer of the respiratory system (Boström et al., 2002).

Despite of the negative effects on air quality, human health and climate, biofuel combustion has received much less attention than fossil fuel emis-

sions (industrial and vehicles) and open biomass fires. On a global scale, biofuels and renewable waste comprised a relatively small fraction (10.6%, Fig. 1) of primary energy supply in 2004 (IEA, 2006) but the bioenergy potential is estimated to increase and reach 15% of the global primary energy by the year 2050 in a scenario of high economic growth and low greenhouse gas emissions (Fischer and Schratzenholzer, 2001). In the European Union, around 4% of the total primary energy consumption was supplied by biomass combustion in 2003 (EEA, 2006). In order to meet its obligation to reduce greenhouse gases emissions under the Kyoto Protocol and reduce energy dependency, the European Union has recently set 20% share of renewable energy in total energy consumption by 2020. Also by 2020, biofuels will account for 10% of total fuel consumption (EU, 2007).

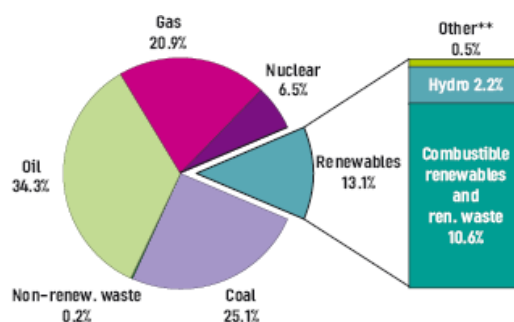


Figure 1. Fuel shares of world total primary energy supply in 2004. ** It includes geothermal, solar, wind, tide/wave/ocean energies. (From IEA, 2006).

There is currently limited information about the contribution of domestic wood fires to global biomass-burning emissions because of their scattered and small-scale sources. To understand the effects of RWC on the atmosphere and climate, it is necessary to implement sampling strategies tailored to address dedicated process questions. Such measurement strategies may provide consistent parameterizations for use in model simulations. Modelling climate effects of aerosol particles requires knowledge of aerosol optical, physical (e.g., particle number, size distribution, shape) and chemical properties. Laboratory studies have shown there is a large variability in gaseous and particulate emissions from wood burning depending on a number of factors (e.g., appliance type, burn rate, type and amount of fuel, and fuel moisture content) (Johansson et al., 2004a; Boman, 2005). It is difficult to relate the results of laboratory studies, where combustion takes place in a controlled environment, to measurements of ambient aerosol properties

where other emission sources are present and pollutants can undergo physical and chemical transformations as well as dispersion, well before reaching the measurement site. One way to overcome this difficulty is to combine field measurements with modelling results in order to estimate the average emission factors for RWC.

Domestic biomass combustion is especially important when considering population exposure to combustion particles and strong evidence suggests that other aerosol variables other than mass concentration should be considered in health studies, such as particle number, particle size and morphology, and chemical speciation (Lighty et al., 2000). The ability of numerical models to provide insights into the relationship between emission sources and human exposure requires a detailed characterization of emission sources and knowledge about processes affecting these species. Time-resolved measurements are important to help understanding how emission sources evolve during the day and how aerosol concentrations affect an exposed population. A better characterization of aerosol properties is also required for an accurate source apportionment of atmospheric pollutants. Source apportionment studies are needed to implement effective strategies and air quality regulations to control particulate matter and gaseous emissions, which is a prerequisite for the abatement of adverse health effects of these pollutants.

1.2 Scientific goals

The thesis is dedicated to evaluate the impact of wood combustion on urban air quality during wintertime in Sweden. This evaluation includes the physico-chemical characterization of aerosol particles and PAHs in ambient air and their source identification and apportionment. This work is based on the results of an intensive field campaign conducted in the town of Lycksele (Fig. 2, latitude: 64.55 °N, longitude: 18.72 °E) in Northern Sweden during winter 2005/2006. The measurement site was located in a residential area (Forsdala) where the majority of the houses are heated primarily or supplementally by wood combustion. Previous studies in this area reported high concentrations of PM and PAH in the winter season (Johansson et al., 2004b; Hedberg et al., 2006).

The main scientific questions of this thesis can be summarized as follows:

1. What is the carbonaceous fraction of atmospheric aerosol in a urban area affected by wood combustion emissions?
2. How do aerosol physico-chemical properties change during the day? Is there any difference between weekday and weekend aerosol properties?

3. What is the relative hourly contribution of emission sources to atmospheric aerosol? Is it possible to use particle number size distributions to identify the emission sources and apportion their contribution to atmospheric aerosol?
4. How important is wood burning for the concentration of individual PAHs in an area where RWC is a common practice during wintertime?

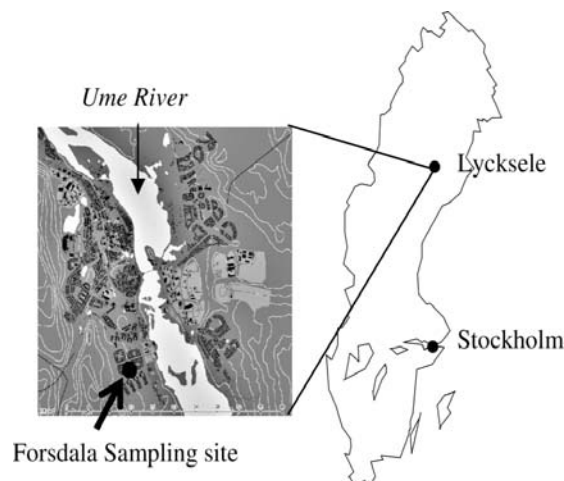


Figure 2. Location of the sampling site in a residential area in Lycksele, Forsdala, where many household use wood combustion for space heating. (From Hedberg et al., 2006).

This thesis is based on four papers; **Papers I-III** focus on the atmospheric aerosols and **Paper IV** deals with the PAH compounds in gas and particulate phases. **Paper I** quantifies the carbonaceous fraction of atmospheric aerosol by using a thermo-optical transmittance method (TOT), an Aethalometer and a custom-built particle soot absorption photometer (PSAP). Technical aspects on the conversion of aerosol light-absorption coefficients to light-absorbing carbon mass concentrations (M_{LAC}) are also discussed. In **Paper II**, the diurnal variations of PM_{10} , PM_1 , and M_{LAC} and particle number concentrations as well as the particle size distributions are analyzed. **Paper III** presents the results of the source identification and apportionment performed with a positive matrix factorization (PMF) model on the hourly particle number size distributions analyzed in **Paper II**. Finally, **Paper IV** investigates the concentration of several PAHs in the gas and particulate phases. A compound-specific radiocarbon analysis (CSRA) is performed to estimate the contribution of wood combustion to individual ambient PAHs.

2. Methods

2.1 Particle sampling and measurements

2.1.1 Carbonaceous aerosols

Aerosol light absorption characteristics play an important role in the Earth's climate system and visibility reduction while chemical composition, including attached organic and inorganic compounds, is relevant for human health. A number of instruments and techniques have been developed to perform carbonaceous aerosol measurements in air. Some instruments rely on the light-absorptive properties of the carbon-containing particles, thus providing aerosol light absorption coefficient measurements (Bond and Bergstrom, 2006). Other techniques determine elemental carbon (EC) and organic carbon (OC) fractions by thermal and thermo-optical carbon analysis, in which a portion of the sample is heated with subsequent detection of the volatilized or oxidized carbon that leaves the sample (Schmid et al., 2001). Unlike thermal methods, thermo-optical methods of EC/OC analysis add an optical correction for the OC pyrolysis. This correction can be done by continuously monitoring the filter reflectance (thermo-optical reflectance TOR; Chow et al., 1993) or filter transmittance (TOT; Birch and Cary, 1996).

In this thesis, EC/OC mass concentrations were obtained by using the TOT method and two optical filter-based instruments (an Aethalometer and a custom-built PSAP) provided the light-absorbing carbon (LAC) concentrations. Total organic carbon (i.e. EC+OC) was also measured by C/H/N elemental analysis.

Thermo-optical transmittance

In short, the thermal-optical transmittance method quantifies OC and EC by releasing carbon collected on a filter through heating/oxidation and convert it to CO₂, which in then reduced to CH₄ and quantified by flame ionization detection (FID). First, the sample is heated in steps in a pure helium (He) atmosphere for the determination of OC and carbonate carbon CC (if present). Then, the sample is combusted in a mixture of He and oxygen (O₂) for EC determination. In an oxygen-free environment, some OC constituents pyrolyze and produce non-volatile light-absorbing char that would be erro-

neously attributed to EC. This bias is corrected by measuring the light transmittance through the filter during the analysis. Since the pyrolyzed carbon (PC) reduces the filter transmittance, EC is defined as the carbon fraction that evolves after the filter transmittance returns to its initial value. Total carbon (TC) is calculated as the sum of EC and OC concentrations. If the thermogram shows a pronounced 4th peak the content of CC in the sample might be suspected (Fig. 3). Its presence can be verified by analyzing a second filter portion after its exposure to chloridric acid (HCl) fumes.

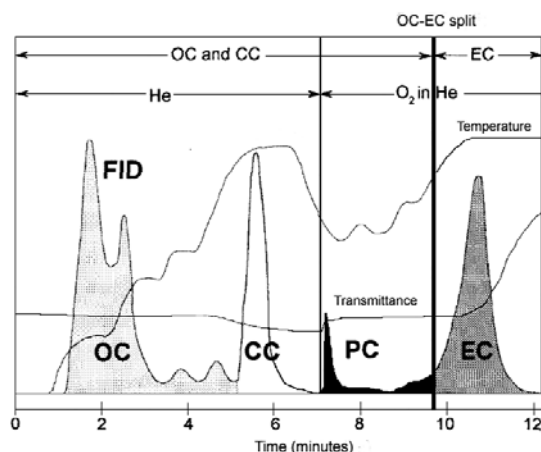


Figure 3. Example of a thermo-optical transmittance carbon analyzer thermogram for EC/OC analysis using the NIOSH protocol. (Adapted from Birch & Cary, 1996).

In this thesis (**Paper I**), aerosol samples for analysis of EC/OC were collected on quartz fiber filters using a sequential sampler SEQ 47/50 (Leckel GmbH, Germany) equipped with an impactor inlet of 10 μm cut-off size. The EC/OC analysis was carried out with a Thermal/Optical Carbon Aerosol Analyzer (Sunset Laboratory Inc., Forest Grove, USA) operating on the NIOSH method 5040.

Light-absorbing carbon measurements

The Aethalometer (Hansen et al., 1984) and PSAP (Bond et al., 1999) are the most frequently operated optical filter-based instruments to determine the aerosol light-absorbing coefficient with high temporal resolution. The measurement principle of these instruments is the same and relies on the strong light absorption of carbon particles in the visible and infrared part of the electromagnetic spectrum. The method is based on the integrating plate technique (Lin et al., 1973) that measures the attenuation of light transmitted through particles that are continuously collected on a filter. Filter-based ab-

sorption measurements need to be corrected to obtain the light-absorption coefficient of the airborne particles b_{ap} because light transmission is affected by scattering from collected particles and multiple scattering from the filter substrate (Bond and Bergstrom, 2006). Two important assumptions are made when using the light-absorption coefficient as a proxy for LAC mass concentrations. First, the aerosol absorption coefficient is linearly correlated to the mass of LAC on the filter, and second this relationship - represented by the LAC mass absorption cross section (σ_a) - is constant over time at the sampling site. σ_a is usually calculated by dividing the light-absorption coefficient by the EC mass concentration determined by an independent method (e.g., thermo-optical measurements).

In this study, two filter-based instruments were used: an Aethalometer (series 8100, Magee Scientific, USA) operated at a 880 nm wavelength with a PM_{10} sample inlet, and a custom-built PSAP operated at a wavelength of 525 nm without specific selective inlet. Measurements of LAC mass concentrations are presented in **Papers I-III**.

C/H/N elemental analysis

The sample is placed in the C/H/N elemental analyzer and combusted at high temperatures (~ 990 °C) in a stream of oxygen. Complete oxidation is reached and the resulting mixture consists of the main products of combustion for carbon (i.e., CO_2), hydrogen (i.e., H_2O) and nitrogen (i.e., N_2). Finally, this mixture is passed to a gas chromatography system for quantification of C, H, and N. In this work (**Paper IV**), samples were treated with HCl to eliminate possible inorganic carbonates fraction and then the total organic carbon (TOC) content was determined by a high-temperature catalytic C/H/N elemental analyzer (Carlo Erba Fisons, Italy).

2.1.2 PM mass concentrations

One of the instruments most widely used for direct-reading of PM mass concentrations is the Tapered Element Oscillating Microbalance (TEOM; Patashnick and Rupprecht, 1991). In TEOM devices, aerosol mass is collected on a filter placed at the end of a tapered vibrating tube and the amount of mass collected on the filter is related to the decrease in the vibrational frequency of the tube. To reduce the relative humidity in the sample, the sample is heated vaporizing also some volatile aerosol material such as ammonium nitrate and certain organic compounds. To overcome this problem, a Filter Dynamics Measurement System (FDMS; Grover et al., 2004) has been recently developed to account for both nonvolatile and volatile PM compounds. This new system incorporates a TEOM, a diffusion drying sys-

tem to minimize the effects of moisture on PM measurements, and a conditioned purge filter that assesses the volatile component of ambient PM.

In this work, mass concentrations were determined for PM with particle diameters below 1 μm (PM_1) and smaller than 10 μm (PM_{10}). Total PM_1 mass concentrations were measured with a TEOM (model 1400a, Rupprecht & Patashnick Inc., USA) operated at a temperature of 50°C to dry the aerosol whereas a FDMS (series 8500, Rupprecht & Patashnick, USA) provided total PM_{10} mass concentration measurements including the volatile PM fraction. PM_{10} measurements are reported in **Papers I, II and III**, and PM_1 measurements are shown in **Papers II and III**.

2.1.3 Particle size distributions

The differential mobility particle sizer (DMPS) is a powerful tool to carry out on-line measurements of submicron particle number size distributions. A DMPS system consists of a particle charger, a differential mobility analyzer (DMA) followed by a condensation particle counter (CPC). First, the sampled air passes through a particle charger in order to charge the particles with a known charge probability distribution. Then, the DMA classifies these charged particles according to their electrical mobility, which depends on the particle size and number of charges. During a measurement scan of the size distribution, the electric field in the DMA is varied in order to sequentially separate particles with different sizes. In the CPC, the aerosol-laden air is saturated with the vapor of a condensable fluid (e.g., butanol) causing the particles to grow by condensation to $\sim 10 \mu\text{m}$ and then are detected (counted) optically by a light-scattering system. Finally, the particle number size distributions are extracted by data inversion considering the charging efficiency as a function of particle diameter and corrections for multiple charges and ideal transfer function.

In this work, the DMA system consisted of a 370 MBq Ni-63 bipolar diffusion charger (AEA Technology QSA, Germany), a custom-built DMA (Vienna type; Winklmayr et al., 1991), and a conductive cooling-type CPC (model TSI 3760, TSI Inc., USA), covering particle diameters in the 25-606 nm range. Particle number concentrations are calculated from particle number size distributions and denoted with N_{25-606} , where the subindices indicate the smallest and largest particle diameters covered by the instrument. The results of DMPS measurements are presented in **Papers II and III**.

2.2 PAH sampling and quantification

PAH monitoring can be performed on samples collected using high-or low-volume samplers. First, the suspended particle matter is collected on a filter and then the gaseous phase fraction is trapped on a solid adsorbent (e.g. polyurethane foam PUF) located downstream of the filter. After a procedure of filter and plug preparation (including analytical extraction with a selected solvent and cleanup procedures), the PAH fractions are obtained and analyzed. Gas chromatography-mass spectrometry (GC-MS) is one of the most common techniques used for quantification of PAH mixtures present in atmospheric samples due to the high separation efficiency and low detection limits (Skoog et al., 1996). Gas chromatography separates the components of a mixture based on the rates at which they are carried through a liquid stationary phase by a gaseous inert mobile phase (e.g., He, N₂). The sample is vaporized and injected into the GC and carried by the inert gas through the column of the instrument (Fig. 4). Compounds are identified by their characteristic retention time (time to travel through the column) and quantified by spiking the sample with internal standards. Since two different molecules could have the same retention time, MS helps identifying the molecules by their characteristic mass to charge ratio. Once the chemicals are separated by GC, the mass spectrometer converts the individual molecules to ions and the ions are sorted and separated according to their mass and charge by using a strong electromagnetic field. By varying the strength of the electromagnetic field, ions of different mass can be focussed progressively and detected.

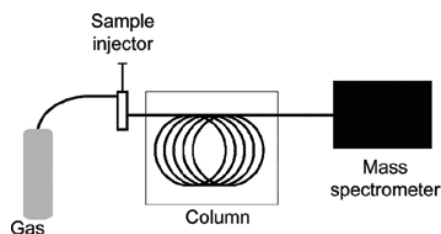


Figure 4. Scheme of a GC-MS.

In this work (**Paper IV**), two active high-volume air samplers were operated with borosilicate glass fiber filters (GFF) and PUF plugs to collect total suspended particle (TSP) matter and gas phase, respectively. After solvent extraction and clean-up of PAHs, individual PAHs were quantified by GC-MS employing a Fisons 8060 GC coupled to a Fisons MD 800

quadrupole mass spectrometer with the MS operated in selective ion monitoring mode.

2.3 Source apportionment of atmospheric aerosol

Different techniques, such as unique emission source tracers, air quality dispersion modeling or source-receptor modeling, can be employed to estimate the contribution of the emission sources to atmospheric aerosol. A number of elemental and molecular tracers (e.g., potassium and chlorine, methyl chloride (Khalil and Rasmussen, 2003), and levoglucosan (Hedberg et al., 2006)) has been used to identify and quantify wood smoke. However, the reliability of some of these tracers often suffers from high emission variability and lack of uniqueness. In contrast to these markers, radiocarbon (^{14}C) measurements provide an unambiguous source apportionment of contemporary and fossil fuel derived carbonaceous aerosol since it retains its identity without any atmospheric chemical change (Reddy et al., 2002). In the atmosphere, high temporal resolution measurements of many of these tracers are not possible due to the necessity of large sampling volumes to detect the concentrations accurately. On the other hand, atmospheric dispersion models can provide spatially and temporally resolved source contributions and are based on knowledge of the processes between source emissions and ambient concentrations of pollutants. They require large iterative processes and quantitative information of emissions and meteorology and, in some cases, it is also necessary to consider aerosol chemical transformation and removal processes. In contrast, source-receptor models infer source contributions at a certain site (the receptor) by determining the best-fit linear combination of emission source profiles needed to reconstruct the measured ambient concentrations. Emission sources are identified by comparing the modeled source profiles to reviewed identified source patterns. Among source-receptor models, positive matrix factorization has been extensively used for source apportionment of particle composition data, where the goal is to determine the sources that contribute to PM samples (e.g., Hedberg et al., 2005; Hedberg et al., 2006). PMF is a powerful multivariate least-squares technique that constrains the solution to be non-negative and takes into account the uncertainty of the observed data (Paatero and Taaper, 1994).

In this thesis, hourly mean particle number size distributions are analyzed using the PMF method to obtain the factor profiles and identify the emission sources (**Paper III**). **Paper IV** presents the source apportionment of TOC carried out using radiocarbon analysis (see Sect. 2.4) at the National Ocean

Sciences Accelerator Mass Spectrometry (NOSAMS) facility of the Woods Hole Oceanographic Institution (USA).

2.4 Source apportionment of PAHs

Several methods have been used to identify the emission sources of atmospheric PAHs such as specific source markers, PAH diagnostic ratios and source-receptor models (Ravindra et al., 2007). All these approaches are based on traditional emission inventories which are challenged by highly variable PAH emission factors, especially for biomass combustion (Zencak et al., 2007b). It is often difficult to discriminate between some sources because their PAH emissions do not have unique chemical composition (Ravindra et al., 2006) and PAHs undergo physical and chemical transformations between the emission source and the measurement site. Alternatively, radiocarbon analysis on PAHs provides an independent method for their source apportionment.

Carbon-14 is formed in the atmosphere and taken up by green plants during photosynthesis and experiences a continuous radioactive decay (half-life of 5730 years). Because ^{14}C has decayed in fossil materials, radiocarbon analysis enables a direct apportionment between fossil (such as petroleum or coal) and biogenic (recently synthesized organic material) contribution to carbonaceous species. Radiocarbon measurements are traditionally performed by counting the relative decay of individual carbon atoms by gas proportional counting or by liquid scintillation counting. But these methods present large uncertainties for small concentrations. In contrast, accelerator mass spectrometry (AMS), which accelerates ions to extraordinarily high kinetic energies before performing mass analysis, provides exceptional sensitivity to measure low abundances of isotopic substances. Nowadays, radiocarbon AMS allows measuring the ^{14}C content of samples containing less than 20 μg of carbon (Zencak et al., 2007a).

AMS coupled with improved carbon fraction collection techniques, such as preparatory capillary gas chromatography (PCCG), have allowed compound class-specific radiocarbon analysis (CCSRA) on atmospheric PAHs (Mandalakis et al., 2005; Kumata et al., 2006; Zencak et al., 2007b) and compound-specific radiocarbon analysis of PAHs in surface sediments (Mandalakis et al., 2004). The PCGC method allows an efficient harvesting of individual compounds with low natural abundance and the main components of the system are depicted in Fig. 5. Briefly, in PCGC the organic extract containing the compounds under investigation is repeatedly injected into the GC equipped with a cooled injection system (CIS) and a

capillary column. The end of the column is attached to an effluent splitter that diverts a portion of the effluent to the detector (e.g., a MS) while the majority is transferred to and trapped in a preparative fraction collector (Mandalakis and Gustafsson, 2003).

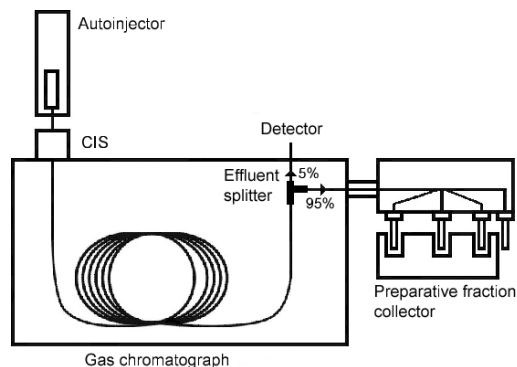


Figure 5. Scheme of an automated PCGC system.

To the best of our knowledge, **Paper IV** presents the first CSRA-based source apportionment on atmospheric PAHs. After extraction and cleanup of PAHs, their isolation for radiocarbon analysis was performed by PCGC using a gas chromatograph (HP 5890, Hewlett-Packard, USA) equipped with a mass spectrometer (MSD 5971A, Hewlett-Packard, USA), a HP 7673 Autoinjector, integrated with a Gerstel CIS, a zero-dead volume effluent splitter, and a Gerstel preparative fraction collector. The isolated PAH compounds were sent to NOSAMS for radiocarbon analysis by AMS. Radiocarbon results were reported as fraction of modern carbon (F_M), which is the $^{14}\text{C}/^{12}\text{C}$ ratio of the sample related to the $^{14}\text{C}/^{12}\text{C}$ ratio of a reference material corrected for possible contamination of the sample (filter blank correction) and natural isotopic fractionation (Zencak et al., 2007a). The F_M values were also converted to $\Delta^{14}\text{C}$ values, as described by Stuiver and Polach (1977), to compensate for the radioactive decay of ^{14}C after the sample collection.

3. Summary of results

3.1 Carbon content of atmospheric aerosol (Paper I)

The main objective of **Paper I** is to characterize the carbon fraction of atmospheric aerosol in a residential area in Lycksele during the wood combustion season. To that end, three methods are employed: a TOT method, an Aethalometer, and a custom-built PSAP (herein after referred to as PSAP-ITM). Additionally, we evaluate the performance of the PSAP-ITM in the field by comparing its results with Aethalometer measurements, which is a commercial instrument widely used for more than two decades. Finally we determine the site-specific σ_a for the PSAP-ITM by correlating PSAP-ITM light absorption coefficients with EC mass concentrations from TOT method. In this study, the Aethalometer is operated from the viewpoint of the user who acquires this instrument and runs it in an operational fashion to monitor carbon mass concentrations in urban areas. Thus, the standard output protocol of the Aethalometer's manufacturer, which provides direct readings of LAC mass concentrations, is employed. Total PM_{10} mass concentrations and meteorological variables are also measured.

Large variations in aerosol mass concentrations (i.e., EC, OC, PM_{10}) were observed during the intensive field campaign in Lycksele (Fig. 6).

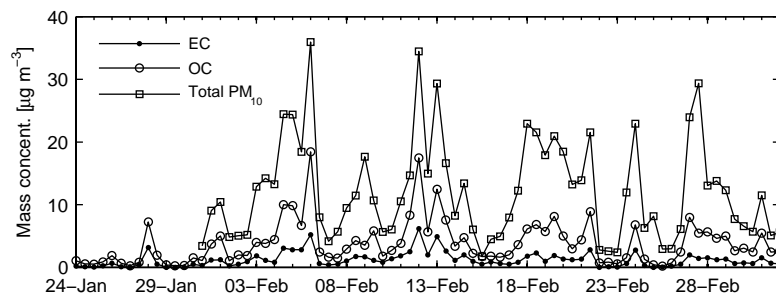


Figure 6. Time series of 12-hour integrated values of EC, OC, and total PM_{10} mass concentrations in Lycksele.

The mean and one standard deviation mass concentrations were $4.4 \pm 3.6 \mu\text{g m}^{-3}$ for OC, and $1.4 \pm 1.2 \mu\text{g m}^{-3}$ for EC. On average, the contribution of EC and OC to the total PM_{10} mass concentration was 10.7% and 35.4%, respectively. The OC/EC ratio ranged from 1.9 to 64.0 with a median value of 3.6. Aethalometer and PSAP-ITM measurements were found to be highly correlated ($R^2 = 0.92$, Fig. 7) for this site and time period. A site-specific σ_a of $20.09 \text{ m}^2 \text{ g}^{-1}$ was found for the PSAP-ITM for the winter 2005/2006, assuming a constant relationship between PSAP-ITM aerosol light absorption coefficients and EC mass concentrations. This value was applied to convert the PSAP-ITM aerosol absorption coefficients into LAC mass concentrations. In the period of simultaneous optical filter-based measurements, the mean value of LAC mass concentration was $1.29 \mu\text{g m}^{-3}$ (median $0.88 \mu\text{g m}^{-3}$) for the Aethalometer and $1.25 \mu\text{g m}^{-3}$ (median $0.84 \mu\text{g m}^{-3}$) for the custom-built PSAP. These results show that the custom-built PSAP is a reliable alternative for the commercial Aethalometer with the advantage of being a low-cost portable instrument.

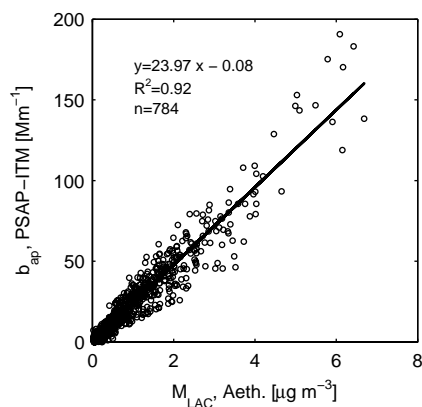


Figure 7. Linear correlation between hourly mean PSAP-ITM absorption coefficient and Aethalometer LAC mass concentrations (Lycksele, 30 Jan. - 9 Mar. 2006).

3.2 Diurnal variation of atmospheric aerosol (Paper II)

Paper II describes the temporal and diurnal variation of some aerosol physical properties (i.e. PM_{10} , PM_1 , M_{LAC} , particle number, and number size distributions) observed in Lycksele during winter 2005/2006, and their relationships with meteorological variables (air temperature and wind speed (WS)). Relatively high correlations ($R>0.75$) were found among aerosol mass and

number concentrations (PM_{10} , PM_1 , M_{LAC} , and N_{25-606}) together with a large day-to-day and hour-to-hour variability in aerosol concentrations. Evening aerosol concentrations were statistically significantly higher during weekends than on weekdays (Fig. 8). This large difference cannot only be explained by the lower air temperature and wind speed registered on weekends. A possible explanation could be that wood is combusted for recreational purposes and/or that the space heat demand is higher when inhabitants spend longer time at home during weekends.

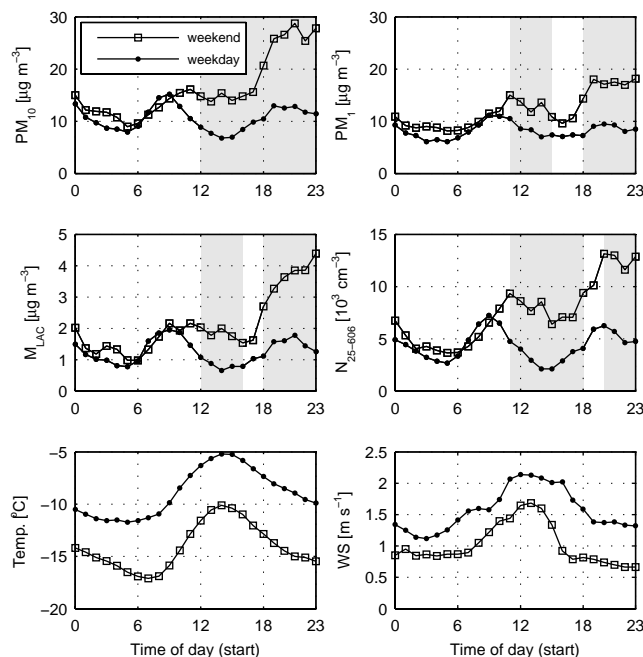


Figure 8. Mean diurnal variations of PM_{10} , PM_1 , M_{LAC} , N_{25-606} , air temperature and WS on weekends and weekdays in Lycksele, 31 Jan. - 9 Mar. 2006. Gray area indicates time of day when weekend aerosol concentrations are significantly higher than weekday concentrations at 95% confidence level.

On weekdays, particle number size distributions and concentrations varied diurnally with small particles (diameter < 30 nm) associated mainly with emissions from motor vehicles in the morning. The results suggest that a combination of emissions from residential wood combustion and traffic sources might explain the high evening concentrations of PM_{10} , PM_1 , particle number and light-absorbing carbon as well as large geometric mean diameters observed during weekdays and weekends. Strong correlations of

PM₁₀ and PM₁ with particle number size distributions are found for the diameter range 130-500 nm and are remarkably high on weekend evenings when larger particles were sampled. The correlation between light-absorbing carbon mass concentration and particle size distribution is high regarding both particle number and mass for particle diameters > 95 nm, and especially on weekends. High aerosol concentrations were associated with low air temperatures and very stable atmospheric conditions close to the ground.

3.3 RWC contribution to hourly atmospheric aerosol (Paper III)

In **Paper III**, the PMF method was applied to hourly mean particle number size distributions measurements to estimate the contribution of RWC to the total atmospheric aerosol loading in Lycksele. The sources were identified based on the particle number size distribution profiles of the PMF factors, the diurnal contributions patterns estimated by PMF for both weekends and weekdays, and correlation of the modeled particle number concentration per factor with measured aerosol mass concentrations (PM₁₀, PM₁, and M_{LAC}). Through these analyses, the factors were identified as local traffic (factor 1), local RWC (factor 2), and local RWC plus long-range transport (LRT) of aerosols (factor 3). In some occasions, it was difficult to detach the contributions of local RWC from background concentrations since the particle number size distribution profiles of RWC and LRT partially overlapped and the model was not able to separate these two sources. As a consequence, the contribution of RWC is reported as a range of values, being the minimum determined by factor 2 and the possible maximum as the contributions of both factors 2 and 3. A multiple linear regression of observed PM₁₀, PM₁, total particle number, and M_{LAC} concentrations is carried out to determine the source contribution to these aerosol variables. The results reveal that RWC is an important source of atmospheric particles in the size range 25-606 nm (44-57%) and for PM₁₀ (36-82%), PM₁ (31-83%), and M_{LAC} (40-76%) mass concentrations in the winter season. The contribution from RWC is especially large on weekends between 18:00 LT and midnight whereas local traffic emissions show similar contributions every day (Fig. 9).

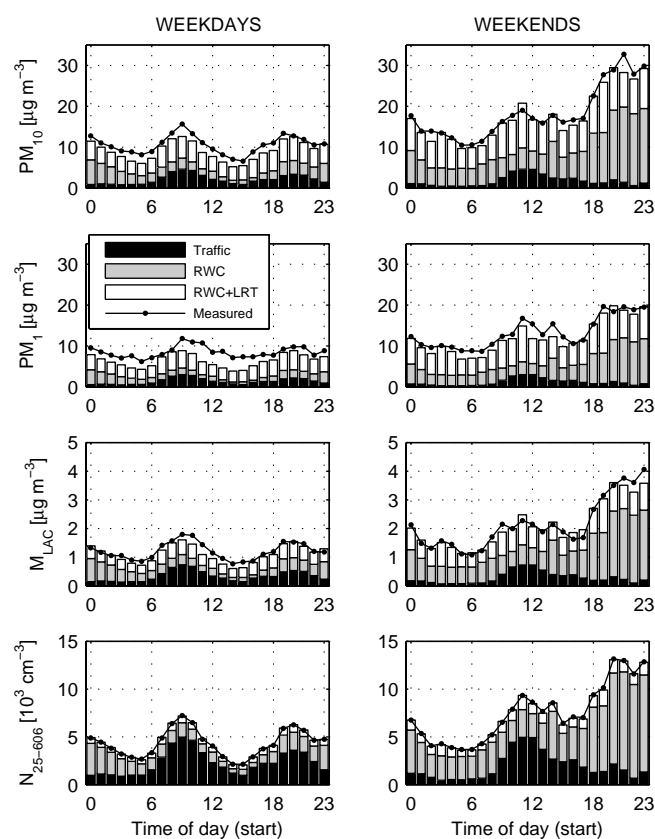


Figure 9. Mean diurnal contributions per factor to PM_{10} , PM_1 , M_{LAC} and N_{25-606} for weekdays (left panels) and weekends (right panels) in Lycksele. The daily mean measured concentrations are also shown with black lines.

3.4 Source apportionment of compound-specific PAHs (Paper IV)

In this study, compound-specific radiocarbon analysis was applied for the first time to a set of atmospheric samples collected in a residential area in Lycksele during winter 2005/2006. More than 25 PAH species were identified and quantified by GC-MS and most of them were present only in the particle phase due to the cold winter temperatures. Only compounds with high mass concentrations were selected for the CRSA analysis to meet the detection limit requirements of AMS. Five individual/paired PAH isolates from three pooled fortnight-long filter collections were analyzed by CSRA: phenanthrene, fluoranthene, pyrene, benzo[b+k]fluoranthene and indeno[cd]pyrene+benzo[ghi]perylene; phenanthrene was the only compound

also analyzed in the gas phase. A simple isotopic mass balance model was used to estimate the fraction biomass contribution from the measured $\Delta^{14}\text{C}$ results. Local biogenic emissions are not likely during winter in Lycksele due to the very low air temperatures that reduce biological activity and volatile organic carbon emissions. Snow-covered ground during the entire sampling period prevented the occurrence of grass fires in the region and incineration of household vegetable waste is not a common practice in the area. Thus, the contemporary radiocarbon content measured in Lycksele is attributed to wood burning.

The measured $\Delta^{14}\text{C}$ for PAHs ranged from -138.3‰ to 58.0‰ and this converted to a contribution from wood fuel combustion (f_{biomass}) of 71% for indeno[cd]pyrene+benzo[ghi]perylene to 87% for the PUF phenanthrene and particulate pyrene, respectively (Fig. 10). On average, 77% of the total organic carbon (TOC, defined as carbon remaining after removal of inorganic carbon by acid treatment) originated from wood combustion. This contribution value falls within the RWC contribution range for the measured PAHs.

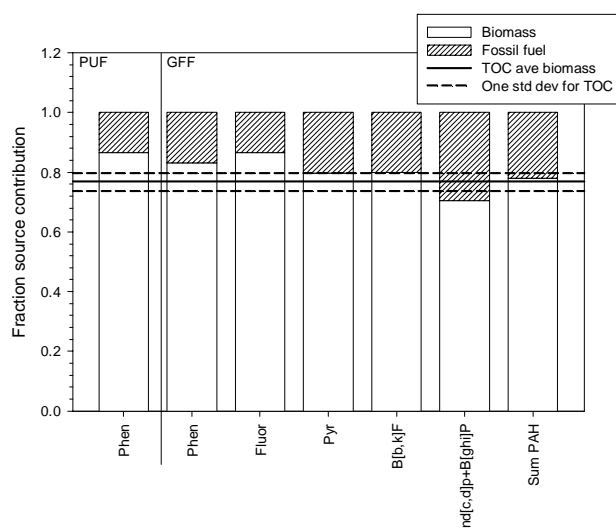


Figure 10. Fraction source contribution of biomass and fossil fuel combustion for individual PAHs (Phen: phenanthrene, Fluor: fluoranthene, Pyr: pyrene, B[b,k]F: benzo[b+k]fluoranthene, Ind[c,d]p+B[ghi]P: indeno[cd]pyrene+benzo[ghi]perylene) and sum of PAHs in Lycksele. Mean \pm 1STD of TOC are also shown.

4. Concluding remarks & outlook

The influence of residential wood combustion on the occurrence of atmospheric pollutants in an urban environment was investigated through the analysis of atmospheric concentrations of aerosol particles and PAH as well as source apportionment techniques.

During the intensive field campaign carried out in Lycksele in winter 2005/2006, a large day-to-day and hour-to-hour variability in aerosol particle mass and number concentrations (PM_{10} , PM_1 , M_{LAC} , and N_{25-606}) was observed. On average, total carbon contributed a substantial fraction of PM_{10} mass concentrations (EC 11%, and OC 35%) and most aerosol particles were in the fine mode (PM_1/PM_{10} ratio of 0.76). Evening aerosol concentrations were significantly higher on weekends than on weekdays, probably caused by the use of wood burning for recreational purposes and/or higher space heat demand when inhabitants spend longer time at home. In the present work, continuous aerosol particle number size distribution measurements successfully provided source apportionment of atmospheric aerosol with high temporal resolution. For the first time, compound-specific radiocarbon analysis of atmospheric PAHs was performed to determine the contribution of RWC to individual PAHs. Residential wood combustion accounted for a large fraction of particle number concentrations in the size range 25-606 nm (44-57%), and for PM_{10} (36-82%), PM_1 (31-83%), light-absorbing carbon (40-76%) and individual PAHs (71-87%) mass concentrations. These studies have demonstrated that the impact of RWC on air quality in an urban location can be very important and largely exceed the contribution of vehicle emissions during wintertime, particularly under very stable atmospheric conditions close to the ground.

Some scientific challenges still remain in relation to this research topic. As previously described in Sections 2.3 and 2.4, several source apportionment techniques have been developed to estimate the contribution of wood combustion to ambient pollutants. A new field campaign could be designed to learn more about the advantages and disadvantages of different source apportionment methods (e.g., PMF on particle size distribution, PMF on inorganic species, radiocarbon analysis of EC and OC, and specific source markers like levoglucosan) in areas with RWC and intercompare the

results. Simultaneous DMPS measurements at background sites should also be included when performing PMF analysis on aerosol particle number size distributions. This strategy would help to better differentiate the contribution of RWC and long-range transport to the atmospheric aerosol in areas where LRT could be a relevant particle source. Another interesting aspect is to study the spatial variability of aerosol mass and number concentrations during high pollution episodes to help identifying the areas in the city that are most affected by RWC. This information is especially relevant to implement effective strategies and air quality regulations to control PM and gaseous emissions.

Other challenges are connected to political and economical decisions which are crucial in an attempt to reduce these small-scale emissions. For example, emissions from RWC can be substantially decreased by substituting old technology appliances by modern biofuel technology which is already commercially available in several countries and environmentally approved (e.g., residential pellet burners). At the same time, targeted education should assist householders on how to lower the emissions from wood burning appliances already installed. Wood smoke can be largely reduced with a proper installation and operation of the burning device, regular maintenance, and only burning seasoned firewood instead of wet wood or household waste. A complementary measure would be to reduce the space heating requirement during the cold season by installing adequate insulation in windows, roofs and walls in present and future houses. Finally, increase public awareness of the considerable effects that RWC causes in the urban air quality to encourage householders to reduce their emissions and, thus, decrease the climate and health impacts.

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