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LICENTIATE THESIS IN ENVIRONMENTAL SCIENCE

EVALUATING METHODS IN SOURCE APPORTIONMENT OF THE CARBONACEOUS AEROSOL

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Evaluating methods in source apportionment of the carbonaceous aerosol

Licentiate thesis in Environmental Science

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Papers included in thesis

Paper I.

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Paper II.

   Martinsson, J., Andersson, A., Sporre, M. K., Friberg, J., Kristensson, A., Swietlicki, E., Olsson, P. A., Eriksson, Stenström, K. Source apportionment of the carbonaceous aerosol using $\delta^{13}C$ - A study in southern Sweden. Submitted to Plos ONE.

Author's contribution to paper

Paper I.   I performed analysis of aethalometer data and wrote most of the paper.

Paper II. I planned the study together with KS, performed data analysis and wrote the paper.

Related publications not included in this thesis

Articles and reports

Kecorius, S., Kivekäs, N., Kristensson, A., Tuch, T., Covert, D. S., Birmili, W., Lihavainen, H., Hyvärinen, A.-P., **Martinsson, J**., Sporre, M. K., Swietlicki, E., Wiedensohler, A., Ulevicius, V. 2015. Significant increase of aerosol number concentrations in air masses crossing a densely trafficked sea area. Oceanologia, In press.

Conference abstracts

Eriksson, A., Nordin, E., Nyström, R., Lindgren, R., Elbaek Nielsen, I., **Martinsson, J**., Ahlberg, E., Svenningsson, B., Swietlicki, E., Boman, C., Pagels, J. 2014. Time-Resolved Biomass Combustion Emissions-Impacts of Burn Rate and Atmospheric Processing. International Aerosol Conference (IAC), Busan, South Korea, 2014.

Eriksson, A., Pagels, J., **Martinsson, J**., Rissler, J., Nordin, E., Swietlicki, E. 2014. Chemical and microphysical characterization of black carbon containing urban, rural and laboratory aerosols. International Aerosol Conference (IAC), Busan, South Korea, 2014.

Martinsson, J., Eriksson, A., Elbæk Nielsen, I., Berg Malmborg, V., Nordin, E., Lindgren, R., Nyström, R., Swietlicki, E., Boman, C., Pagels, J. 2015. Relationship between light absorbing carbonaceous particulate emissions and biomass combustion conditions. Nordic Society for Aerosol Research (NOSA) Symposium, Kuopio, Finland, 2015.

Martinsson, J., Eriksson, A., Elbaek Nielsen, I., Berg Malmborg, V., Nordin, E., Svenningsson, B., Ahlberg, E., Lindgren, R., Nyström, R., Swietlicki, E., Boman, C., Pagels, J. 2015. Light absorbing carbonaceous particulates from biomass burning: dependence on cumbustion conditions and photochemical processing. European Aerosol Conference (EAC), Milan, Italy, 2015.

Berg Malmborg, V., Shen, M., Eriksson, A., Waldheim, B., Gallo, Y., **Martinsson, J**., Nilsson, P., Andersson, Ö., Johansson, B., Pagels, J. 2015. Absorption and chemical properties of combustion cycle resolved in-cylinder diesel soot. Nordic Society for Aerosol Research (NOSA) Symposium, Kuopio, Finland, 2015.

Reports and abstracts in reports

Martinsson, J., Swietlicki, E., Stenström, K. 2014. Seasonal Variations of Light-Absorbing properties in Atmospheric Aerosols in Southern Sweden. LUCCI Annual Report 2013/2014.

Martinsson, J. Using the Aethalometer for Source Apportionment of Carbonaceous Aerosols. 2014. Internal Report, LUNFD6(NFFR-3114)/1-17/(2013).

Martinsson, J., Stenström, K., Swietlicki, E., Olsson, P. A. 2015. δ^{13}C-A useful tool of source characterization of the carbonaceous aerosol at rural measurement sites? LUCCI Annual Report 2014/2015.

Populärvetenskaplig sammanfattning

Atmosfäriska partiklar (aerosoler) finns överallt i jordens atmosfär. Masskoncentrationen av dessa varierar kraftigt beroende på i vilken miljö man mäter. I stadsluft kan man uppmäta tiotals mikrogram per kubikmeter medan man i arktiska områden uppmäter nanogram per kubikmeter. De kolhaltiga aerosolerna är kända för att påverka människors och djurs hälsa negativt, framförallt påverkar dessa kroppens andningsvägar och kan ge upphov till olika hjärt- och lungsjukdomar. Aerosolerna har även effekter på jordens klimat. Genom att absorbera och sprida ljus värmer respektive kyler aerosolerna klimatet. De har även effekt på molnbildning och nederbörd.

Beroende på dessa kolhaltiga aerosolers fysikaliska och kemiska egenskaper påverkar de hälsa och klimat olika. Det är därför oerhört viktigt att karaktärisera dessa aerosoler. Eftersom en viss aerosoltyp släpps ut från en viss källa är det viktigt att veta varifrån och hur mycket aerosoler som kommer från de olika källor som finns. För de kolhaltiga aerosolerna är förbränning av biomassa, fossila bränslen samt utsläpp av biogena aerosoler, från t.ex. träd och växter, de vanligaste källorna.

Källkaraktärisering av den kolhaltiga aerosolen är ett mycket viktigt verktyg och kan i många fall ligga till grund för beslutsfattande t.ex. angående utsläppsminskningar eller andra åtgärder som avser att förbättra luftkvalitén. I denna avhandling har vi utvärderat två metoder som används ofta vid källkaraktärisering av de kolhaltiga aerosolerna; multivåglängds-ljusabsorptionsmätning och användning av stabila kolisotoper.

Aerosoler från förbränning av biomassa eller ved har förut generellt antagits absorbera relativt mer ultraviolett (UV) än infrarött (IR) ljus. Detta antagande har sedan använts i källkaraktäriseringsmodeller för att kunna räkna ut bidraget av aerosoler från biomassa-/vedförbränning. Vår forskning visar att detta antagande kan vara felaktigt ifall man förbränner biomassa i moderna kaminer eller anläggningar med god isolering. Utsläppen från moderna kaminer och anläggningar visar ljusabsorptions-mönster som är mer likt emissioner från dieselmotorer, där aerosolerna absorberar ungefär lika mycket UV- som IR-ljus. Detta betyder att den traditionella metoden, med antagandet om relativt mer UV- än IR-absorption, felaktigt kan karaktärisera partiklarna i områden där omfattningen och användningen av moderna välisolerade kaminer och anläggningar är stor.

Grundämnet kol har två stabila isotoper, ^{12}C och ^{13}C, där ^{13}C har en neutron mer än ^{12}C. ^{12}C är den vanligast förekommande kolisotopen på jorden (ca 98,9 %) medan ^{13}C endast utgör en liten andel (ca 1,1 %). Förhållandet mellan dessa två isotoper kan utnyttjas för att studera flöden i geokemiska kretslopp samt för att spåra födokällor och dieter i olika biologiska sammanhang. Detta är möjligt eftersom ^{13}C är något tyngre än ^{12}C och uppför sig därmed något annorlunda exempelvis i olika fysikaliska fasövergångar och flöden. Vi kan utnyttja detta inom aerosolforskningen. Tidigare studier har t.ex. visat att partiklar från förbränning av fossila bränslen innehåller mer ^{13}C än t.ex. partiklar från biomassa-/vedförbränning och biogena utsläpp. Vi mätte den relativa mängden ^{13}C på aerosoler från en mätstation i södra Sverige. Dessa data kompletterades med data från tidigare uppmätt ^{14}C och levoglukosan. ^{14}C är ett kraftfullt verktyg för att avgöra hur stor andel av aerosolerna som kommer från förbränning av fossila bränslen, medan levoglukosan är en molekyl som endast bildas vid förbränning av cellulosa (biomassa). Vi kunde därefter jämföra två källtilldelningsmodeller (med och utan ^{13}C) i syfte med att redogöra för hur mycket ^{13}C bidrog till källtilldelningen. Vi fann att ^{13}C endast bidrog med marginella förändringar i källtilldelningen jämfört med modellen som endast använde ^{14}C- och levoglukosan-data.

List of abbreviations

$\delta^{13}C$	Delta ^{13}C
λ	Wavelength
AAE	Absorption Ångström Exponent
ACI	Aerosol Cloud Interaction
AMS	Aerosol Mass Spectrometer
ARI	Aerosol-Radiation Interaction
BC	Black Carbon
BrC	Brown Carbon
BPOA	Biogenic Primary Organic Aerosol
BSOA	Biogenic Secondary Organic Aerosol
EBA	Ensemble-Based Apportionment
EC	Elemental Carbon
$F^{14}C$	Fraction modern carbon
GHG	Green House Gas
HB	High Burn rate
IR	Infrared
LAC	Light Absorbing Carbon
NB	Nominal Burn rate
OA	Organic Aerosol
PAM	Potential Aerosol Mass reactor
PAH	Polycyclic Aromatic Hydrocarbon
POA	Primary Organic Aerosol
PM	Particulate Matter
rBC	Refractory Black Carbon
RF	Radiative Forcing
SA	Source Apportionment
SOA	Secondary Organic Aerosol

SP-AMS   Soot Particle Aerosol Mass Spectrometer

SSAMS   Singe Stage Accelerator Mass Spectrometer

TBA   Tracer-Based Apportionment

TC   Total Carbon

UV   Ultraviolet

Content

1 Introduction

Atmospheric particles, i.e. atmospheric aerosols, are key players in global, regional and local climate and health issues. The carbon-containing fraction of these aerosols, the carbonaceous aerosol, has severe environmental impact on both climate and health [1,2]. The carbonaceous aerosol impact on climate is large, but the numbers are highly uncertain [1]. Carbonaceous aerosols originate from a diversity of sources and environments, which make them difficult to characterize in climate models. With respect to the above mentioned climate and health effects, it crucial to develop policies and regulations that can constrain emissions of the kinds of aerosols causing these adverse effects.

Since certain sources may emit specific types of aerosols it is important to know the influence and impact of an aerosol source for a geographical area. Here source apportionment (SA) plays a crucial role. By utilizing numerous measurements techniques together with data analysis and statistics with the common aim to reduce complexity into a limited number of source categories, SA studies associate observed aerosol with emission sources. Mass concentrations or fractions of mass are apportioned into possible sources, thus SA function as a powerful tool for stakeholders when determining and justifying how to regulate particulate matter (PM) emissions.

Commonly it is necessary to measure several parameters for an accurate SA. Fuzzi et al. [3] divided the receptor-based models[1] into "tracer-based apportionment" (TBA) and "ensamble-based apportionment" (EBA). TBA relies on molecular or atomic markers that have very high source specificity but constitute only a small fraction of the total apportioned mass. An example of these is levoglucosan, which is a molecular tracer for biomass burning. EBA on the other hand relies on properties corresponding to the total apportioned mass, although source specificity is reduced. EBA methods often include measurements of many different compounds with low source specificity, different metals for instance. Each measurement then contains a certain contribution of a specific compound. The measured compound contribution can then be linked to a source which has a similar distribution of the measured compounds.

For both TBA and EBA the measured parameters are often directly affected by the source usage, thus if the usage of the source is changed there is a response in the parameter. Several SA studies of the carbonaceous aerosol have already been performed, e.g. [4-7]. However, there is still large potential and need of improvements. Uncertainty needs to be minimized and research is needed to find techniques that can decrease costs of performing robust SA. There is also need for further experimental data to improve and/or validate models supporting stakeholders with relevant data for decisions.

To determine the sources of the aerosol mass, various methods of SA are used. The society would benefit by having access to fast, cheap and well-functioning SA methods. In this thesis some of these methods are evaluated.

1.1 Aim and objectives

The aim of this thesis work was to evaluate and improve techniques and methods that are related to the SA of the carbonaceous aerosol mass in the atmosphere. The objective was to produce data that can be used by modelers for more accurate estimation of source contribution. We have conducted a bottom-

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[1]Receptor based models uses measured pollutant mass concentrations at the receptor site. Usually this information is complemented with information regarding source profiles and meteorological data (i.e. wind direction and/or backward air mass trajectories).

up measurement campaign on biomass combustion from a conventional wood stove in order to study how stove operation is affecting the optical characteristics of particles in the effluents (Paper I). Furthermore, we have evaluated ^{13}C as a complementary parameter in source apportionment for the carbonaceous aerosol at a rural measurement station in southern Sweden (Paper II).

1.2 Environmental science

This is a thesis in environmental science. Environmental science differs from the classical disciplines such as physics, chemistry and biology since its pillars states that we need interdisciplinarity in order to understand and study complex environmental systems. Environmental science is very well suited for handling atmospheric sciences and air pollution, which is the discussion of this thesis. Air quality is affected by the physics of the atmosphere, the chemical interactions that take place between the myriad of compounds in the air, the biology of the plants that emit volatile organic compounds, and by human behavior and human politics.

2 Background

Aerosols are by definition particles suspended in a gas. Aerosols are present in the atmosphere all over the planet. The concentrations may vary drastically, from in artic regions with hundreds of particles per cubic centimeter to several orders of magnitudes more in cities. Particulate matter (PM) includes all types of aerosols like minerals, salts, organic matter, metals and so on. This chapter focus on describing the different types of aerosols and discusses climate and health effects from these.

2.1 Carbonaceous aerosols

The carbonaceous aerosol is the fraction of the aerosol that is built up by molecules containing carbon. Other common elements besides carbon include hydrogen, oxygen and nitrogen. Common components of the carbonaceous aerosol are soot, which is often referred to as black carbon (BC), and organic matter (OM). These two components are often referred to as the organic aerosol (OA). The OA may constitute a large fraction (20-90 %) of the total aerosol mass [8]. OA can be formed in different ways. If it is released directly from its source it is called primary organic aerosol (POA). POA might be pollen, fungal spores, bacteria and BC [9]. However, if the OA is formed by condensation or nucleation of volatile organic compounds (VOC) in gas-phase it is referred to as secondary organic aerosol (SOA). VOCs may originate from plants but also from combustion sources. If the VOCs have biogenic origin they are referred to as biogenic VOCs (BVOC) and the formed SOA is then called BSOA.

The amount of total carbon (TC) is often divided into organic carbon (OC) and elemental carbon (EC). These fractions are operationally defined by thermal and oxidative resistance, where OC is suggested to be more susceptible for thermal degradation and volatilization than EC. OC is composed of various organic molecules and polymers. Common groups of compounds include polycyclic aromatic hydrocarbons (PAH), organic acids, alkanes, humic-like substances and cellulose [10-12]. EC is more or less equal to BC, although quantified differently (BC is soot that is quantified with optical methods). EC is formed by incomplete combustion of fossil and/or biomass fuels. It is highly refractive, inert and is insoluble in most solvents, hence it is very stable and has a high resistance against chemical degradation and transformation.

The most common sources of the carbonaceous aerosol are combustion of fossil fuels, combustion of biomass and biogenic emissions. Biogenic sources are a large group containing two main sub-groups; biogenic primary organic aerosol (BPOA) and BSOA. BPOA consists of pollen, fungal spores, bacteria and plant debris. BSOA are as mentioned earlier formed from BVOC which go into particle-phase. Common BVOCs are α-pinene, β-pinene, isoprene and limonene, all emitted from plants.

2.2 Climate effects

CO_2, CH_4 and N_2O are greenhouse gases that are emitted to the atmosphere of Earth with an increasing rate since the industrial revolution in the mid 1800's. This has mainly been caused by combustion of fossil fuels. The mean temperature of Earth has increased with 0.75 °C ever since and is still increasing [1]. There is a widespread agreement in the scientific community that this increase in temperature is caused by the emissions of greenhouse gases (GHGs) and thus anthropogenic activities [1].

The anthropogenic emission of GHGs causes a perturbation of the radiative flux in the atmosphere of Earth. Radiative forcing (RF) is a measure of this perturbation which shows the changes in radiation [13]. A positive RF means that more radiation is entering than leaving Earth, causing an increase in

temperature. A negative RF means the opposite, i.e. more radiation is leaving Earth than entering, causing a decrease in temperature. The GHGs are all believed to contribute to a positive RF. However, there are other atmospheric constituents that have climatic effects. Aerosols are known to affect the climate in several and often complicated ways. Aerosols differ from GHGs in many ways, while GHGs are simple molecules with constant sizes aerosols vary greatly in size (1 nm − 10 μm) and are composed of a myriad of different chemical compounds. GHGs also have long residence time in the atmosphere (years) while aerosols usually have residence times of several hours up to a couple of weeks. Figure 1 shows RF for various emitted components.

Due to the complexity of the effects of aerosols on climate it is convenient to make a general distinction between aerosol radiation interactions (ARI) and aerosol-cloud interactions (ACI). The ARI includes what is sometimes called the "direct effect" which means that aerosols interact directly with incoming radiation. Here the aerosol may either scatter or absorb the incoming sunlight, which case often depends on size and chemical composition of the aerosol.

Scattering of the incoming sunlight means that the light is sent away in different directions, which also means that a fraction of the incoming light is sent back to space, thus cooling the atmosphere [14]. Aerosols containing sulfate (SO_4), nitrate (NO_3) and mineral dust are known to scatter light and the total scattering is estimated to a corresponding RF of -0.5 ± 0.4 W/m^2 [1].

During absorption, the aerosol absorbs photons and releases the energy through emission of long-wave radiation which heats the atmosphere. Black carbon (BC) from combustion processes is well-known for absorbing light and heating the climate system [15]. Bond et al. [16] estimated the RF of BC to + 1.1 W/m^2, thus suggesting BC to be the second largest climate forcer. However, other studies have proposed methane to be the second strongest and BC the third [1]. Nevertheless, the uncertainty of the RF of BC is still very high.

The ACI are sometimes referred to as the "indirect effect" and are caused by cloud formation. All clouds are formed by condensation of water on particles. By changing chemical composition, size and number concentration of aerosols the optical properties of the cloud will change [17]. For instance, a high aerosol number concentration will result in more but smaller cloud droplets, which will make the cloud brighter and thus reflecting more of the incoming solar radiation back to space (increasing the albedo of Earth). Thus, this effect will have a net cooling effect on the climate. This effect is often referred to as "the first indirect effect" [18]. The small could droplets may also increase the lifetime of clouds by delaying precipitation, hence also leading to an increased albedo of Earth. This effect is called the "second indirect effect" [19].

Recently, the term brown carbon (BrC) was introduced with the purpose of being a more general nomenclature for organic aerosols with a significantly higher light-absorption in ultraviolet (UV) [20]. BrC has been shown to be structured by functional groups such as nitro-phenols, PAH and humic-like substances [11,21,22]. Extremely low-volatile organic compounds have recently also been suggested for enhanced ultraviolet absorption [23]. Due to the high absorptivity of UV, BrC might have considerable effects on lower tropospheric photochemistry [21].

Thus, the climate effects of atmospheric carbonaceous aerosol is complex and are today associated with large uncertainties. In fact, the climate effect uncertainty of aerosols is much larger than the uncertainty of GHGs (Figure 1). Among the aerosols, BC and OC have significant uncertainty. And, as shown in Figure 1, combustion of fossil fuels and biomass burning contributes to both cooling (OC) and warming (BC) of the climate.
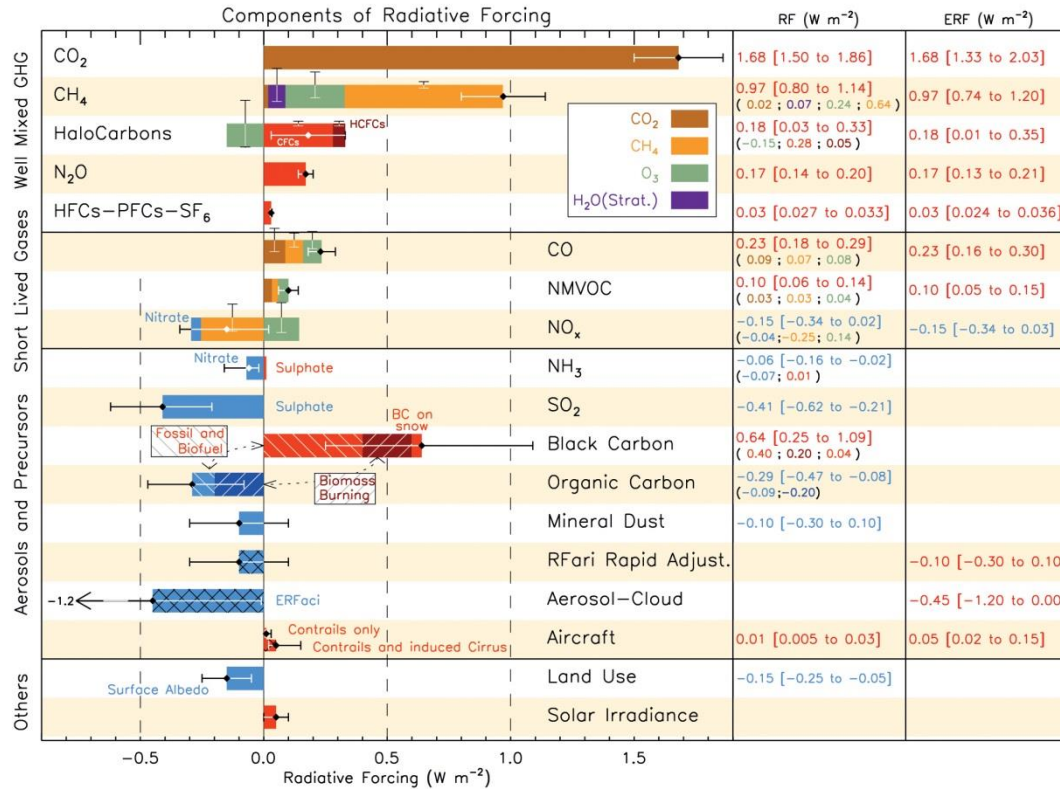
Figure 1. Radiative forcing (RF) for several emitted atmospheric components. From IPCC fifth assessment report [1]: *Figure TS.7 | Radiative forcing (RF) of climate change during the Industrial Era shown by emitted components from 1750 to 2011. The horizontal bars indicate the overall uncertainty, while the vertical bars are for the individual components (vertical bar lengths proportional to the relative uncertainty, with a total length equal to the bar width for a ±50% uncertainty). Best estimates for the totals and individual components (from left to right) of the response are given in the right column. Values are RF except for the effective radiative forcing (ERF) due to aerosol–cloud interactions (ERFaci) and rapid adjustment associated with the RF due to aerosol-radiation interaction (RFari Rapid Adjust.). Note that the total RF due to aerosol-radiation interaction (–0.35 Wm^{-2}) is slightly different from the sum of the RF of the individual components (–0.33 Wm^{-2}). The total RF due to aerosol-radiation interaction is the basis for Figure SPM.5. Secondary organic aerosol has not been included since the formation depends on a variety of factors not currently sufficiently quantified. The ERF of contrails includes contrail induced cirrus. Combining ERFaci –0.45 [–1.2 to 0.0] Wm^{-2} and rapid adjustment of ari –0.1 [–0.3 to +0.1] Wm^{-2} results in an integrated component of adjustment due to aerosols of –0.55 [–1.33 to –0.06] Wm^{-2}. CFCs = chlorofluorocarbons, HCFCs = hydrochlorofluorocarbons, HFCs = hydrofluorocarbons, PFCs = perfluorocarbons, NMVOC = Non-Methane Volatile Organic Compounds, BC = black carbon. Further detail regarding the related Figure SPM.5 is given in the TS Supplementary Material.*

2.3 Health effects

It is estimated that around 7 million premature deaths are caused by air pollution globally each year [24]. In Europe air pollution was recently estimated to cause 450 000 premature deaths [25]. The term "air pollution" comprises both gases and PM. PM is responsible for several known negative health effects such as cardiovascular diseases and chronic obstructive pulmonary disease [26,27]. Dockery et al. [28] studied the relationship between ambient concentration of PM and mortality in six large US cities, and found a clear correlation showing that elevated PM concentration was related to increased mortality.

Particle size is a very important parameter when discussing health effects. Small particles (<0.1 µm) have the possibility to penetrate deep into the lungs where they are deposited through diffusion, it is

5

thus hard to remove these particles. Larger particle sizes (>0.1 μm) can hit the oral and nasal cavities by impaction and be removed by coughing or sneezing. Thus, smaller particles are in general regarded as more hazardous than larger particles on a mass basis.

The organic aerosol is, as mentioned above, containing complex and faceted chemical compounds. Many of these are toxic. PAHs are considered carcinogenic and have shown to have negative impacts on human health [29-32]. PAHs can be emitted from incomplete fossil fuel combustion [33], and are also formed during hot air-starved combustion of wood [34]. BC is also associated with negative health effects, it is also considered as more hazardous than PM in general [35,36]. Studies suggest that it is not the BC itself that is toxic, instead it may function as a vector, transporting toxic substances into the human respiratory tract [35]. Thus, combustion-generated particles can cause adverse health effects and may be a priority in future regulations policies.

3 Methods and techniques used in source apportionment

This chapter gives a brief introduction to how different techniques and methods can be used for source apportionment purposes. The presented methods have been used in paper I and II. It should be noted that many of these below mentioned techniques can be used in both a bottom-up and a top-down approach, however they are here categorized as one or the other depending on how they were used in the appended papers.

3.1 Bottom-up emission inventories

Paper I focuses on characterizing the aerosol directly at its source, in this case a conventional wood stove. Studies of emissions at the source can be defined as "bottom-up inventories", since these form the basis for recognizing and characterizing the source emissions helping to identify specific source signatures and tracers for source/receptor modelling. These experiments and the generated data can then be used in the top-down approach discussed in 3.2 for the source apportionment. Measurement techniques used for the emission inventory in paper I are briefly discussed below.

3.1.1 Optical methods

Optical techniques have been used in SA studies since the mid 2000's [37-39]. It is mainly light-absorption techniques that have been utilized for this purpose. It has been discovered that there is a difference in spectral light absorbing dependence between aerosols from biomass burning and fossil fuel combustion [37]. Wood smoke aerosols from biomass burning have a relatively higher light absorption in the UV (100-400 nm) and blue (450-500 nm) regions compared to IR (>700 nm), while fossil fuel combustion aerosols have relatively constant light absorption from UV to IR.

The relationship between light absorbing carbon (LAC_λ), measured as the light absorption coefficient, and wavelength (λ) is described with a power law function:

$$LAC_\lambda = k \times \lambda^{-AAE} \qquad (1)$$

$$AAE = -\frac{log\frac{LAC_{\lambda_1}}{LAC_{\lambda_2}}}{log\frac{\lambda_1}{\lambda_2}} \qquad (2)$$

In Equation 1, k is a constant and AAE is the absorption Ångström exponent. In equation 2, LAC_{λ_1} and LAC_{λ_2} represent the light absorbing carbon for two wavelengths, λ_1 and λ_2. These are usually widely separated (from UV to IR, Table 1). If light absorption is measured at more than two wavelengths it is common to fit a function to the data in order to calculate AAE.

Aerosols measured by light absorption techniques are often referred to as BC. However, more recently BrC has gained more ground in the scientific community and is nowadays regarded as a second important component with regards to light absorption and the direct climate effect. It is commonly assumed that BC has an AAE of 1.0 and BrC above 1.0 [20,40]. BC is thus assumed to have constant absorption in all wavelengths, BrC is however assumed to have increased light absorption in the blue and UV. Due to the difference in spectral dependence and with the assumption that BC and BrC are the only two light absorbing components of the light absorbing carbon (LAC) it is possible to separate BC from BrC.

It is commonly assumed that wood smoke aerosol has an AAE of around 2.0 and fossil fuel combustion aerosol an AAE around 1.0 [37,40]. Thus, by using a multi-wavelength (two or more

wavelengths) light absorption instrument it is possible to divide the overall absorption in specific wavelengths, here called LAC_λ, into biomass burning and fossil fuel combustion fractions. Several studies have relied on this difference in spectral dependence and the division of light absorption in biomass burning and fossil fuel combustion aerosol [22,38,39,41-44]. For an accurate division and apportionment it is then crucial to use an AAE that is representative of the source. Most of the abovementioned studies have used AAE from the literature, some of this literature and corresponding AAE values are found in Table 1.

Table 1. Representative AAE values found in the literature and used in other studies.

Type of aerosol	Spectral range (nm)	AAE	Reference
Biomass burning	467-660	2.1	Clarke et al. [45]
Biomass burning (Cotton wood)	370-950	2.1	Day et al. [46]
Biomass burning (Oak wood)	370-950	1.8	Day et al. [46]
Traffic emissions	300-1000	1.0	Kirchstetter et al. [37]
Biomass burning	300-1000	2.0	Kirchstetter et al. [37]
Diesel soot	450-700	1.1	Schnaiter et al. [47]

AAE values for biomass burning may change drastically depending on burning conditions. It has been shown that low temperature pyrolysis may generate aerosols with high organic content with an AAE>2 [48], while hot air-starved conditions may produce almost pure soot or BC with a significantly lower AAE. Thus, just assuming an average AAE of 2.0 for all wood burning conditions might be an oversimplification.

In addition to this uncertainty, there is also an additional uncertainty in whether the AAE might change due to photochemical processing in the atmosphere. Some studies have indicated that the BrC light absorption might decrease due to bleaching [49], while other have seen the opposite, the BrC absorption is enhanced [50].

3.1.2 AMS-Aerosol mass spectrometer

The aerosol mass spectrometer (AMS) is today a common instrument and very comprehensive when studying the organic aerosol. It has a wide field of applications, from indoor local measurements to atmospheric global measurements. The AMS consists of an aerodynamic lens inlet where the aerosols are concentrated and the amount of ambient gas are reduced. The aerosols then impact on a heated surface and gets flash vaporized. Vaporized aerosols compounds are ionized by electron impact (EI) and then analyzed by mass spectrometry. Size distributions (vacuum aerodynamic diameter, d_{va} range: 50-1000 nm) are measured with particle time-of-flight from a mechanical chopper to the heated vaporizer. The high-resolution time of flight AMS (HR-ToF-AMS) used in paper I is equipped with an additional intracavity laser vaporizer (1064 nm) (SP-AMS) and can be operated with the laser vaporizer alone, the tungsten and laser, or the tungsten alone. The laser includes detection of refractory species such as soot and metals. For a more detailed and comprehensive description of the instrument see DeCarlo et al [51], Canagaratna et al. [52] and Onasch et al. [53].

3.1.3 PAM chamber

The potential aerosol mass reactor (PAM) is a 13.5 l flow tube reactor that use UV-light to produce ozone (O_3) and hydroxyl radicals (OH) that oxidize the incoming aerosol [54]. The PAM have two peak wavelengths of 185 and 254 nm that are both needed for the production of O_3 and OH. The PAM

is commonly used to simulate "ageing" or atmospheric processing and oxidation of both ambient and experimental aerosols. However, the cumulative OH exposure is often orders of magnitudes higher than ambient OH exposure, this means that an aerosol with a residence time of minutes in the PAM chamber corresponds to days in the atmosphere with regards to atmospheric processing. The PAM is therefore highly useful in experiments where rapid processing is necessary.

3.2 Top-down approach: Experimental methods used in source/receptor modelling

Common SA methods, here used in paper II, are discussed below. These methods were used in a top-down approach which means that aerosols were collected at a receptor site in the absence of distinct and well-pronounced aerosol sources. Instead there are several sources that all have an unknown contribution to the total carbonaceous aerosol mass. By utilizing below mentioned techniques together with data generated from bottom-up inventories it is possible to estimate source contribution to the aerosol.

3.2.1 Stable carbon isotopes

The quantitative relation between different isotopes of an element may change during physical and chemical transformation. Usually these transformations affect one of the isotopes more than the other, this is called isotope fractionation. Carbon isotope fractionation occurs during relocation of carbon between different ecosystems and trophic levels in the food chain [55,56]. The fractionation is driven by differences in mass between the abundant and rare isotope. Thus, lower atomic mass of the element leads to large mass difference [57].

The relative abundance of stable carbon isotopes (expressed as $\delta^{13}C$, see Equation 3) has been widely used during a long period of time to characterize sources of ambient carbonaceous aerosol [58-65]. The technique relies on that sources of carbonaceous aerosol differentiate in ^{13}C signature. Figure 2 shows the carbon isotopic composition of some common aerosol sources. However, it has been shown that compounds formed from oxidation processes may be more depleted in the heavier isotope, this effect is called the kinetic isotopic effect (KIE) [66,67]. In general, aerosol from fossil fuel combustion sources are more enriched in ^{13}C than aerosols from biogenic and biomass combustion sources.

Plants can fractionate carbon isotopes differently depending on with metabolic pathway they use in order to transform CO_2 into carbohydrates [55]. C_3 plants are for instance considerably more depleted in ^{13}C than C_4 and crassulacean-acid-metabolism (CAM) plants. However, there can be differences in $\delta^{13}C$ values within the same metabolic group of plants. Conditions such as temperature, light and humidity may affect the isotopic fractionation to differentiate within a species [55,68]. For the study in this thesis, C_3 plants are of the only relevance since these are completely dominating the Swedish and Nordic flora.

$\delta^{13}C$ is usually measured with isotope ratio mass spectrometry (IRMS), and the isotopic composition is expressed relative to an international standard as:

$$\delta^{13}C_{Sample}\ (‰) = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{Sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{Standard}} - 1 \right) \cdot 1000 \qquad (3)$$

A more positive $\delta^{13}C$ value means that the sample has a higher abundance of the heavier isotope, i.e. ^{13}C. $\delta^{13}C$ measurements in aerosol SA studies have the benefits that the analysis is relatively cheap and sample preparation is fast (compared to ^{14}C analysis).
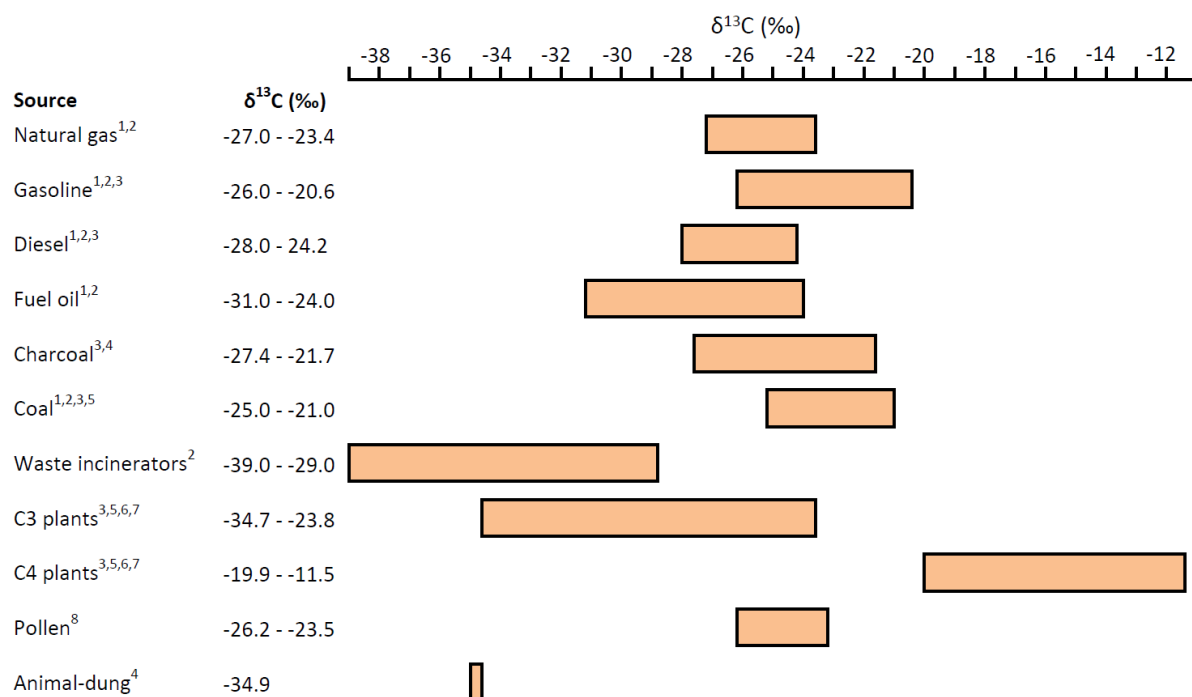
δ¹³C (‰) axis: -38 -36 -34 -32 -30 -28 -26 -24 -22 -20 -18 -16 -14 -12

Source	$\delta^{13}C$ (‰)
Natural gas[1,2]	-27.0 - -23.4
Gasoline[1,2,3]	-26.0 - -20.6
Diesel[1,2,3]	-28.0 - 24.2
Fuel oil[1,2]	-31.0 - -24.0
Charcoal[3,4]	-27.4 - -21.7
Coal[1,2,3,5]	-25.0 - -21.0
Waste incinerators[2]	-39.0 - -29.0
C3 plants[3,5,6,7]	-34.7 - -23.8
C4 plants[3,5,6,7]	-19.9 - -11.5
Pollen[8]	-26.2 - -23.5
Animal-dung[4]	-34.9

Figure 2. Aerosol isotopic composition of carbon from various sources ([1][65]; [2][64]; [3][63]; [4][60]; [5][69]; [6][61]; [7][70]; [8][62])

3.3 OC/EC separation and analysis

Two important parameters in research on the carbonaceous aerosol are the organic carbon (OC) and elemental carbon (EC). The most common way for separation of these two fractions is to use a thermal protocol where the sample is heated gradually in inert or oxidative atmospheres. An aerosol containing filter punch is placed in a sample oven, the sample is then heated in four temperature intervals in an inert He atmosphere, this part volatilize OC from the filter. In the second step there are another four temperature intervals where EC is volatilized in an oxidative He/O_2 atmosphere. All volatilized compounds from the filter are fully oxidized to CO_2 in the oxidation oven and further converted to methane by hydrogen gas over a zinc catalyst in the methanator. In the final step the methane is quantified by a flame ionization detector (FID).

A well know artefact in all OC/EC analyses are the charring of OC. As the OC is heated some of it is volatilized and thus leaves the filter. However, some of the OC may char when heated, especially when heated in the absence of an oxidizing agent, such as O_2. This char can the falsely being interpreted as EC since it will leave the filter during the EC part of the thermal protocol. This EC can be regarded as "artificial EC" in contrast to "true EC" which was sampled as EC from the start. Optical methods have been introduced to the thermal analysis in order to correct for this charring. A setup of a He/Ne 633 nm laser and a photodetector is continuously measuring the light transmission through the filter throughout the whole thermal analysis. As OC starts to char the transmission decreases, the charred OC is finally oxidized in the He/O_2 atmosphere and the transmission signal increases again. The split point between OC and EC are defined as when the transmission signal reaches its initial value, all carbon evolved before this time is defined as OC and all carbon that is left on the filter to evolve is defined as EC. It is important to note that this separation relies on two assumptions: First, that artificial EC has the same optical properties as true EC. Second, artificial EC is easier to oxidize and thus removed earlier than true EC. However, it has been shown that both of these assumptions are invalid [71]. Thus, there is no infallible thermal protocol that can separate OC from EC, however the protocol used in these analysis is a European standard protocol called

EUSAAR-2 which was developed in order to harmonize all OC/EC measurements made in Europe [72].

3.4 ^{14}C measurements

Analysis of radiocarbon (^{14}C) is a powerful, however expensive, tool to identify the contribution from fossil sources to aerosols. ^{14}C is produced naturally in the upper atmosphere when nitrogen is bombarded with neutrons produced by cosmic rays:

$$^{14}_{7}N + n \rightarrow \ ^{14}_{6}C + p \tag{4}$$

The radiocarbon is then oxidized into carbon dioxide (CO_2) and later transported into the terrestrial system. A large fraction is also absorbed into the surface of the oceans. All living organisms contain some ^{14}C which is the basis for the commonly used ^{14}C-dating method [73]. ^{14}C is an unstable isotope of carbon, it has a half-life of 5730 years and decays to nitrogen (^{14}N) through β-emission:

$$^{14}_{6}C \rightarrow \ ^{14}_{7}N + e^{-} + \tilde{\upsilon}_e \tag{5}$$

When the living organism dies the organism is no longer in equilibrium with the environment, i.e. no new ^{14}C is entering the organism, and the ^{14}C starts to decay and thus decrease in comparison to stable carbon isotopes. Thus, fossil fuels contain no ^{14}C since all have decayed after millions of years in the ground. The atmospheric ^{14}C concentration is approximately the same around the globe [74], however humans have altered the ^{14}C strongly in two ways. By burning fossil fuels and emitting the ^{14}C-free CO_2 to the atmosphere the overall fraction of $^{14}CO_2$ has decreased, this is called the Suess effect [75]. Humans have also altered the atmospheric ^{14}C by the tests of nuclear weapons in the atmosphere during the 1950's and 1960's. When the nuclear weapons were detonated, neutrons scattered from the detonation position then reacted with nitrogen as in Equation 4. This increase of the ^{14}C concentration is called the bomb-pulse effect.

When measuring ^{14}C in environmental samples it is crucial to take both the Suess and bomb pulse effect into account. It is therefore common to report the results as fraction modern carbon (F^{14}C) [76], i.e. the ratio of ^{14}C from a sample and a reference value dating 1950. Fossil fuels have a F^{14}C of 0, i.e. all ^{14}C has decayed. The F^{14}C of biomass vary depending on the age of the plant, for trees (which usually become quite old) the F^{14}C may reach 1.2 if the tree grew during the bomb-pulse [5].

3.5 Organic tracer molecules

The organic aerosol is comprised by a large variety of chemical compounds. Some of these compounds can be used to characterize the aerosol source. These kinds of molecules are sometimes referred to as organic tracers. Levoglucosan is an anhydride sugar that is formed during pyrolysis of cellulose above 300 °C [77]. It has been used in several source apportionment studies to quantify wood burning [4-7], however its stability in the atmosphere is still debated [78,79]. Particles on filters are first extracted with dichloromethane and methanol during sonication. The extracts are then derivatised before being analyzed in a gas chromatograph with mass spectroscopy (GS-MS). Levoglucosan is then quantified by the mass-to-charge ratio (m/z) of 217 and 246.

4 Summary of papers

Due to the complex nature of carbonaceous aerosol several different techniques and parameters need to be used and measured in order to extract relevant information regarding the sources. This chapter summarizes the main methods that generated original data and the results in the appended papers. Apart from the original ^{13}C data, Paper II uses data of OC, EC, ^{14}C and levoglucosan which were presented in Genberg et al. [5].

4.1 Light absorption measurements of combustion aerosols generated from a conventional wood stove

A modern conventional wood stove [80] was used to generate aerosols from biomass combustion. Logs of birch (*Betula*) were added on a bed of glowing embers, generated flue gases and aerosols were then diluted and sampled into a 15 m^3 steel chamber. This chamber enabled sampling from selected phases in the burn cycle. One burn cycle was divided into three phases as in Eriksson et al. [34]. Fuel addition started when logs of wood were added to a bed of embers. When the logs had caught fire and the oxygen concentration was below 14% the intermediate phase started. The intermediate phase ended when the oxygen concentration had increased above 14%, at that time the burn out phase started. The stove was operated in two modes; nominal (NB) and high (HB) burn rate. The NB mode was achieved by operating the stove as recommended by the manufacturer, that means combustion of 2.5 kg fuel (3 wood logs) at each batch. HB mode was generated by combustion of 3.5 kg fuel (9 wood logs) at each batch. A PAM reactor was connected in the sampling line in order to simulate atmospheric ageing.

4.1.1 Light absorption measurements

The seven wavelength aethalometer (model AE33) utilizes seven LEDs with ranging from 370-950 nm (Table 2, Figure 3) [81]. The aethalometer is a real-time, high time resolved light absorption measurement first described by Hansen et al. [82]. An air flow is directed through a filter where the aerosols are deposited on a spot, the seven LEDs irradiate the spot and the attenuation is continuously monitored. The aerosol deposition rate is proportional to the aerosol concentration and thus the optical attenuation rate. The optical attenuation through the filter is defined as

$$ATN = 100 \ln\left(\frac{I_0}{I}\right) \qquad (6)$$

where I_0 is the incoming light intensity and I is the remaining light intensity after passing through the filter. The aerosol attenuation coefficient b_{ATN} can then be calculated by the change in attenuation, ΔATN, as a function of the filter spot area A, flow rate Q and time Δt:

$$b_{ATN} \equiv \frac{A}{Q}\frac{\Delta ATN}{\Delta t} \qquad (7)$$

There are two main sampling artefacts that need to be accounted for in order to calculate the light absorption coefficient b_{abs}, in this thesis called LAC. When the filter is relatively unloaded with particles scattering on and within the filter matrix can be wrongly interpreted as attenuation and thus absorption enhancement. The second artefact is called "the shadowing effect" and may occur as the filter gets heavily loaded with particles, the optical path in the filter is decreased leading to an underestimation of the attenuation. This effect is more pronounced for freshly emitted soot and almost negligible in aged ambient aerosols [83]. The AE33 aethalometer uses dual filter loading spots with different aerosol deposition rates to correct for the shadowing effect and a correction factor of 1.57 to correct for filter scattering [81].

In paper I, the AAE was derived from the aethalometer measurements in order to study the impact of combustion conditions and burn cycles on AAE.

Table 2. Wavelengths and corresponding colors used in the aethalometer.

Wavelength (nm)	370	470	520	590	660	880	950
Color	Ultraviolet	Blue	Green	Yellow	Red	Infrared 1	Infrared 2
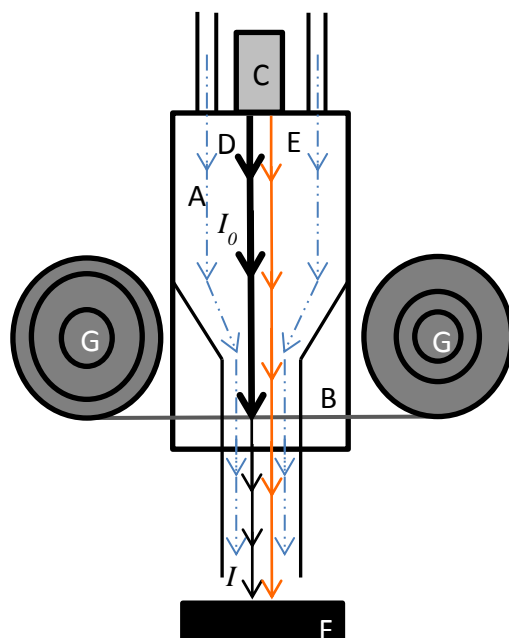
Figure 3. Schematic picture of the aethalometer. Ambient air is pumped into the instrument (A) and is then led through the filter (B). A light source (C) emits a beam of light with one or several wavelengths (depending on model). The initial light beam (D) has the intensity I_0 and I after passing through the filter (B). A reference beam (E) is irradiating a filter-spot where particles have been deposited at a different deposition rate as compared to the filter-spot of D. After the light beams have passed through the filter, remaining light intensity is measured by a photo-detector (F). The filter is automatically switched to a new spot by rotation of the filter tape (G).

4.1.2 Results

A complete burn cycle in the wood stove is illustrated in Figure 4. At time t=0 logs of wood were added to the wood stove. Immediately concentrations of CO and OA increased with factors of 3 and ~17, respectively. The AAE also increased from 1.3 to 2.3. In the succeeding intermediate phase, there is flaming combustion and the AAE has dropped to ~1.2. Here, the emissions of OA and CO are in general low. The AAE remain around 1.0-1.3 for the remaining burn out phase. Thus, a complete whole burn cycle from this type of wood stove emits aerosols with AAE 1.0-1.2 (Figure 5).
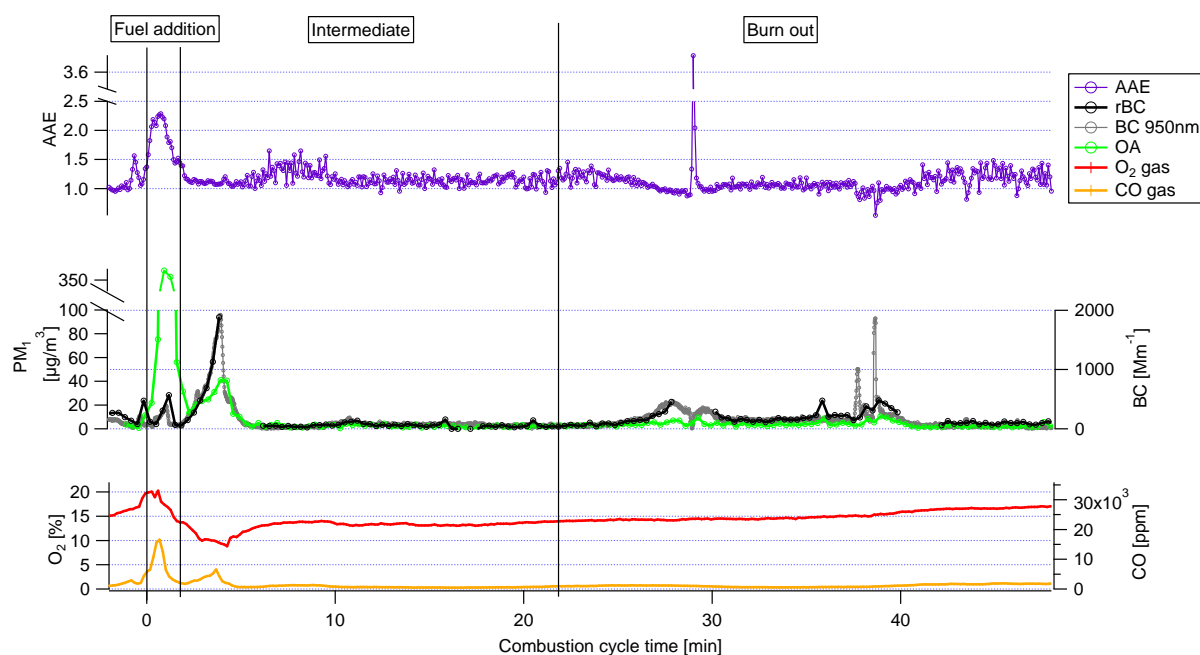
Figure 4. Transient emissions and optical properties during a typical full cycle (three wood logs were added at t=0). Time-resolved AAE as measured with the aethalometer (upper panel). Diluted (200 times) organic aerosol (OA), rBC and total light absorption coefficient at 950 nm (BC) (middle panel). O_2 (red) and CO (orange) concentration in the flue-gas (lower panel). The main features of the cycle are reproducible.

As seen in Figure 5, the HB mode during same combustion phases had somewhat higher AAE compared to NB. These higher AAEs might be explained by elevated concentrations of UV-absorbing PAHs which are more abundant in hot air-starved combustion as can be expected during HB [34].

In these experiments, the PAM was set to simulate extreme atmospheric processing of the aerosol. The OH-exposure was estimated to be $3 \cdot 10^8$ molecules/cm³·h, this OH-exposure corresponds to processing of several days in the atmosphere. Although the extreme processing, the AAE was in general unaffected (Figure 5). One possible explanation may be that this extreme processing both creates and destroys light absorbing chromophores, thus the net effect of these processes may end up with an unaffected absorption.

With regard to SA studies, the main result from this study is that the well-used aethalometer-model [38,39] that commonly uses AAE=2 for apportion wood combustion and AAE=1 for apportion traffic emissions may incorrectly apportion aerosols from modern wood stoves as traffic generated aerosol. Less efficient and insulated wood stoves may very well reach an AAE>2 during the whole combustion cycle. However, in a future scenario when modern, well-insulated, wood stoves may become even more common, the aethalometer-model may need to be revised.
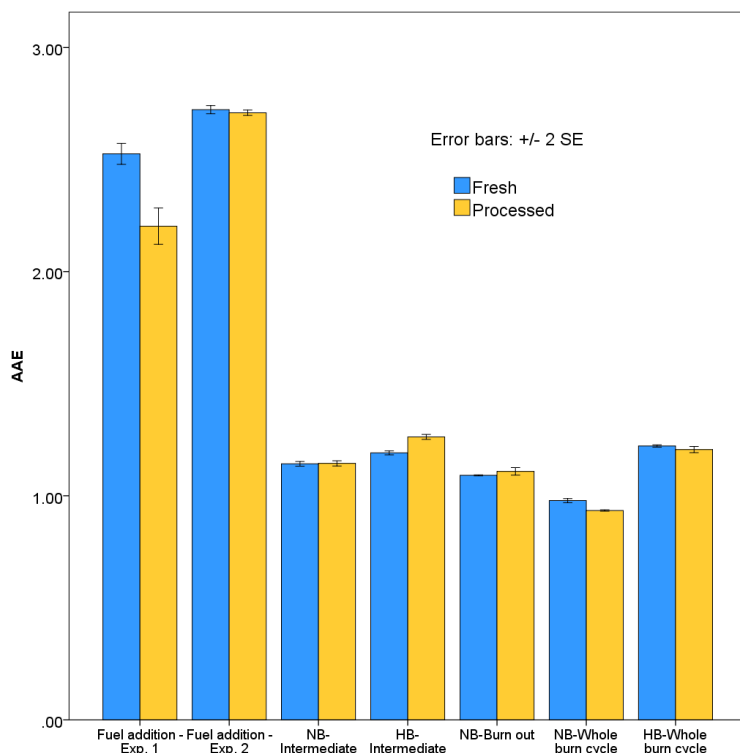
Figure 5. Absorption Ångström Exponent (AAE, 370-950 nm) for different phases during a burn cycle. Blue bars represent the fresh unprocessed aerosol while orange bars represents photochemically processed aerosol with the PAM flow tube. The error bars represent ±2 standard errors (SE) over time.

4.2 ^{13}C measurements and source apportionment

In paper II we investigated the potential of using δ^{13}C as a parameter in SA. Aerosols were collected on quartz fiber filters during 2008-2009. The sampling was conducted at Vavhill measurement station, a rural background site in southern Sweden. We measured δ^{13}C on 25 of these filter samples. This data was complemented with already measured parameters of OC, EC, ^{14}C and levoglucosan [5]. In addition, we collected and measured δ^{13}C on sawdust from various C_3 tree species in order to establish a justified δ^{13}C distribution of biogenic and biomass burning plants. Samples of particles collected on filters and sawdust were treated in similar way; filter area corresponding to 10-50 µg carbon and 100-300 µg of sawdust were placed in tin capsules, respectively. Due to the limited amount of filter material, particle samples were measured as single while sawdust was measured in triplicates. Tin capsules were then sent to the IRMS-laboratory at the Department of Biology at Lund University for analyses of δ^{13}C. Measurement uncertainty was estimated to be ± 0.2‰. Based on the δ^{13}C measurement of sawdust and a comprehensive literature study, source specific values of δ^{13}C could be estimated, these are known as endmembers.

Endmember values and variabilities of δ^{13}C, ^{14}C and levoglucosan-to-EC ratio were inserted in a Markov Chain Monte Carlo (MCMC) model [84,85]. The reason for using levoglucosan-to-EC ratio is that this ratio relates the amount of levoglucosan that is emitted per unit of EC. Fortunately this ratio is very accessible in the literature [86,87], which was needed in order to establish endmember distribution of this parameter. Measured parameters from filter samples were then also inserted to the model. Calculations were performed in Matlab, using 100 000 iterations for each sample. The best estimated median of each source contribution is presented from the calculations. Two different model runs were compared against each other, i.e. with and without inclusion of δ^{13}C in the model, with the purpose of estimate the effect of δ^{13}C in SA.

16

4.2.1 Results

For the collected aerosols, $\delta^{13}C$ varied between -26.73‰ and -25.64‰ with a mean of -26.16‰ during the whole sampling period. Figure 6 shows the range of $\delta^{13}C$ during the different seasons throughout the year. Aerosols were more enriched in $\delta^{13}C$ during the cold period (fall, winter and spring), compared to the warm season during summer. The summer season also has the largest spread of $\delta^{13}C$ values, ranging from -26.73‰ to -25.85‰. This spread can be explained by the expected dominating emissions of biogenic SOA, there are a large number of C_3-plant species abundant which most likely will represent different $\delta^{13}C$ values. The measured $\delta^{13}C$ on C_3-tree species sawdust were in line with literature data with a mean of -27.12‰ and a standard deviation of 1.2‰.
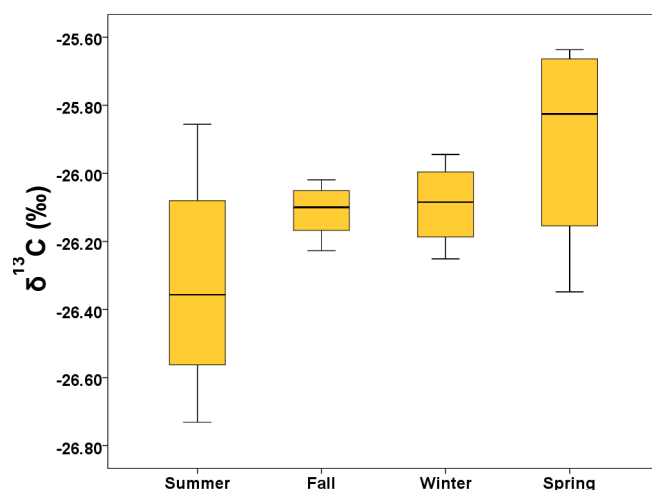
Figure 6. $\delta^{13}C$-values for sampled aerosols during measurement period at Vavihill measurement station. Seasonal boxplot (line within the box is the median, edges of the box are upper and lower quartile and outer edges are minimum and maximum).

$\delta^{13}C$ enriched aerosols during the cold months may be representative for increased impact of fossil fuel combustion on ambient aerosols. In order to investigate source contribution to the aerosols, a Markov Chain Monte Carlo model was used, as described in section 4.2. The results are displayed in Figure 7. During summer the biogenic sources dominates (68%) the contribution of carbon to the carbonaceous aerosol, fossil and biomass burning sources are minor contributors (21 and 11%, respectively). During the colder periods, the biogenic emissions are significantly decreased (29-56%) at the expense of increases in fossil fuel (19-30%) and biomass burning (19-41%) source contributions. Air mass trajectory analysis showed that a majority (88%) of the sample air masses were originating from north or west. Air masses from these directions had significantly higher emissions of biogenic sources compared to other directions.

Finally, comparing the source contribution between two MCMC models, with $\delta^{13}C$ (MCMC3) and without $\delta^{13}C$ (MCMC2), showed that $\delta^{13}C$ only contributes to minor changes in apportionment which derives the conclusion that levoglucosan/EC and $F^{14}C$ are two powerful source indicators (Figure 8). MCMC3 increase the overall source contribution of biomass burning with around 4%, while it is the decreasing the source contribution from biogenic sources with approximately 8%.
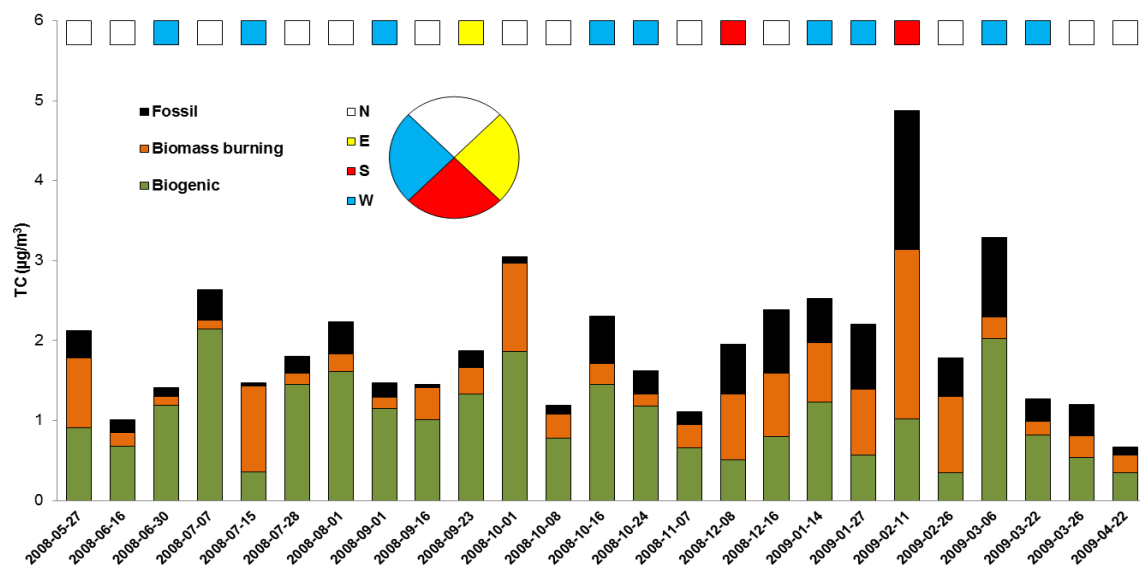
Figure 7. Apportionment of TC for all samples at Vavihill measurement station using the MCMC3 model with $\delta^{13}C$, Lev/EC and $F^{14}C$. Wind direction from trajectory analysis is showed by the top colored squares.
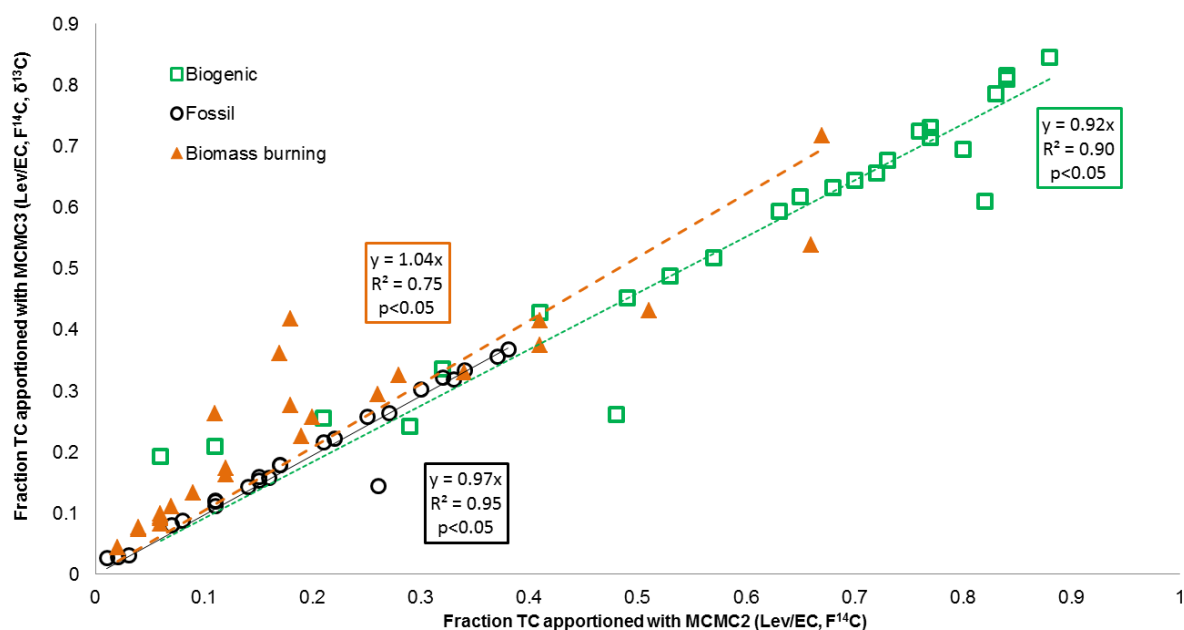

Figure 8. Comparison in fraction TC apportioned between MCMC2 and MCMC3. Fitted lines are forced through origo.

5 Summary and Conclusion

The work in this thesis has focused on evaluating and testing already existing methods in modern aerosol source apportionment. In paper I, we showed that a majority of the particles produced from a modern well-insulated wood stove showed an AAE of 1.0-1.2 which is the same as traffic generated diesel soot. Thus, the well-used aethalometer model, that assume wood burning particles having AAE>2, may incorrectly apportion a large fraction of biomass burning aerosols into traffic emissions. However, it is worth mentioning again that usage of modern well-insulated wood stove is a prerequisite for this falsely apportionment. It is possible that a comparable usage of modern well-insulated (AAE~1.2) and old poor-insulated (AAE>2) will end up with a biomass combustion aerosol with a mean AAE of 2.

In paper II, the potential of $\delta^{13}C$ as an improvement for source apportionment studies of the whole carbonaceous aerosol (TC) has been investigated. The measured $\delta^{13}C$ overlapped with the possible sources identified; biomass burning of C_3-plants, biogenic primary/secondary organic aerosol from C_3-plants, and fossil fuel combustion. Since both biogenic emissions and biomass combustion are derived from C_3-plants, this overlap is particularly pronounced for these two sources. It was found that summer aerosols were more depleted in $\delta^{13}C$ compared to the cold period of the year. This is in accordance with assumed increased use of fossil fuels, which have a higher $\delta^{13}C$, during cold months. A Markov Chain Monte Carlo based source apportionment of the TC gave results that were in line with hypotheses; biogenic emissions were dominating during summer and biomass- and fossil fuel combustion were dominating during winter. A comparison of two Markov Chain Monte Carlo models, with and without $\delta^{13}C$, showed that $\delta^{13}C$ only had minor impact on the results. Biogenic emission did in general decrease at the expense of increases in biomass combustion with the inclusion of $\delta^{13}C$ in the model. $\delta^{13}C$ may have a limited contribution to the SA of TC in rural areas. However, the contribution may be larger in urban areas with higher impact of fossil fuel combustion and lower impact of biogenic emissions. In urban areas $\delta^{13}C$ may act as a complement or a substitute for the more expensive and time consuming ^{14}C-measurements.

6 Outlook

Numerous methods and techniques are developed for a more accurate source apportionment of the carbonaceous aerosol. And this development needs to continue.

There is still a need for further investigation of the separation of OC and EC. It is well established that charring of OC during thermo-optical analysis hinders accurate apportionment of OC and EC. Pre-treatment with super-critical CO_2 with addition of methanol may have great potential in removing the part of OC that is responsible for charring. If this part can be completely removed, it is possible to oxidize the residual OC through TOA, and further have a sample with pure EC. This would be very valuable in order to investigate sources of EC through ^{14}C measurements.

Also, it is important that validation of the finding in paper I begin. Here, it is of importance to search for correlations between AAE and other well-used biomass burning tracers, such as levoglucosan.

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