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Martinsson, Johan

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PO Box 117
221 00 Lund
+46 46-222 00 00

Development and Evaluation of Methods in Source Apportionment of the Carbonaceous Aerosol

Johan Martinsson



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Faculty opponent

Assistant Professor Ulrike Dusek, Center for Isotope Research (CIO), Energy and
Sustainability Research Groningen (ESRIG), University of Groningen, Groningen,
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Development and Evaluation of Methods in Source Apportionment of the Carbonaceous Aerosol		
<p>Carbonaceous aerosols are known to affect human health negatively and to affect the climate of Earth. As specific types of aerosols originate from specific sources, it is important to know the amount of aerosols emitted from each source. Aerosol source apportionment is an important tool in mitigating air pollution and improving air quality. The subject of this thesis was the evaluation and development of methods that can be used to improve source apportionment of the carbonaceous aerosol.</p> <p>Wood-burning aerosol emissions have previously been assumed to absorb relatively more light in the ultraviolet region than in the infrared, as compared to traffic aerosol emissions. The research presented in this thesis shows that this assumption may not be valid for modern well-insulated wood stoves. Emissions from these appliances exhibit light absorption patterns similar to that for diesel combustion aerosols. Hence, light absorption source apportionment methods may not be reliable in areas with a high abundance of modern well-insulated wood stoves.</p> <p>A light absorption source apportionment method was compared to a source apportionment method based on radiocarbon and a chemical tracer. Good agreement was found for the apportioned wood-burning and biogenic aerosols, but a small discrepancy was observed in the apportionment of fossil fuel/traffic aerosol mass concentrations.</p> <p>The measurement of the heavier stable isotope of carbon, ^{13}C, is relatively cheap and easy, and was therefore evaluated as an alternative method of source apportionment. ^{13}C, chemical tracers and radiocarbon were measured in aerosol filter samples from a rural background station and source apportionment calculations were performed. These results were then compared to source apportionment results derived only from radiocarbon and chemical tracers. Measuring ^{13}C only led to minor insignificant changes in source allocation, and could not distinguish between biogenic and wood-burning carbon.</p> <p>Thermo-optical analysis is a common method in source apportionment of the carbonaceous aerosol. However, organic carbon can be falsely interpreted as combustion-related elemental carbon due to pyrolysis during the analysis. An attempt was made to remove the fraction of pyrolytic organic carbon using supercritical carbon dioxide. Adding a small amount of methanol during the extraction allowed a large proportion of the pyrolyzed carbon to be removed. The isolation of elemental carbon may improve source apportionment of combustion-derived aerosols.</p> <p>Finally, the impact of air mass exposure to different geographical surface categories on the observed chemical species of biogenic secondary organic aerosols was studied. Aerosol samples were collected on filters at a rural background station in southern Sweden. Chemical tracer compounds in biogenic secondary organic aerosols were measured. Air mass exposure to various geographical surface categories was calculated with the FLEXPART model. The results showed that air mass exposure to coniferous forests could explain many of the observed organic chemical species, while exposure to oceans did not contribute to the observed aerosol mass concentration. Mapping the effect of different geographical surface categories on the chemical composition of aerosols may provide an important tool in predicting how changes in land use may affect air quality.</p>		
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Development and Evaluation of Methods in Source Apportionment of the Carbonaceous Aerosol

Johan Martinsson



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Faculty of Science
Centre for Environmental and Climate Research (CEC)
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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. Den kolhaltiga aerosolen utgör en betydande del av atmosfärsaerosolens massa och är känd för att påverka människors och djurs hälsa negativt, framförallt påverkar den 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 aerosolerna. Eftersom specifika aerosoltyper släpps ut från särskilda källor är det viktigt att veta varifrån och hur mycket aerosoler som kommer från de olika källor som finns. De vanligaste källorna för utsläpp av kolhaltiga aerosoler är förbränning av biomassa, fossila bränslen samt utsläpp av biogena aerosoler, från t.ex. träd och växter.

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 utvecklat och utvärderat metoder som kan användas vid källkaraktärisering och källtilldelning av de kolhaltiga aerosolerna.

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 t.ex. 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, d.v.s. 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.

En komplett källtilldelningsstudie av den kolhaltiga aerosolen genomfördes för ett helt år (2014-2015) i syfte att jämföra mätmetoder sinsemellan. Vi använde oss av den skillnad i ljusabsorption som beskrivits ovan för att separera aerosoler genererade från trafik och ved-/biomassförbränning. Vi kunde se att under vintern absorberade aerosolen relativt mer ljus i UV än under andra årstider, detta kan indikera ökad förbränning av ved för uppvärmning under vinterhalvåret. När vi jämförde ljusabsorptionskälltilldelningsmetoden mot en källtilldelningsmetod som använder ^{14}C och levoglukosan fann vi att ljusabsorptionsmetoden tilldelade ungefär lika mycket kolmassa till vedeldnings- och biogen aerosol som ^{14}C - och levoglukosan-metoden. ^{14}C är en radioaktiv isotop av grundämnet kol och ett kraftfullt verktyg för att avgöra hur stor andel av aerosolerna som kommer från förbränning av fossila bränslen och levoglukosan är en molekyl som endast bildas vid förbränning av cellulosa, den fungerar således som en spår molekyl för ved-/biomassförbränning. Vi fann även att ljusabsorptionsmetoden överskattade trafikbidraget jämfört med ^{14}C - och levoglukosan-metoden med ca 30%. Vi konstaterade således att ljusabsorptionsmetoden var lämpad att uppskatta masskoncentrationen av kolhaltig aerosol från vedeldning och biogena källor men fungerade något sämre för trafik- och fossil aerosol, detta gällde åtminstone för vår mätstation som är placerad i skogen, långt från tungt trafikerade vägar.

Grundämnet kol har två stabila isotoper, ^{12}C och ^{13}C (utläses som ”kol-12 och kol-13”), 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. Vi kunde därefter jämföra två källtilldelningsmodeller (med och utan ^{13}C) i syfte att redogöra för hur mycket ^{13}C bidrog till källtilldelningen. Vi fann att ^{13}C endast bidrog med små, icke signifikanta, förändringar i källtilldelningen jämfört med modellen som endast använde ^{14}C - och levoglukosan-data.

En grundbult i källtilldelning av den kolhaltiga aerosolen är att mäta hur mycket kol det finns, på t.ex. ett filterprov. Ofta använder man då termo-optiska mätmetoder. Dessa metoder innebär att man förbränner provet och mäter hur

mycket restprodukter som bildas vid förbränningen, i form av koldioxid eller metan. Generellt brukar man dela in massan kol i två fraktioner; organiskt kol och elementärt kol. Det organiska kolet anses härstamma från en mängd olika källor som t.ex. biogena utsläpp från växter, förbränning av fossila bränslen eller biomassa. Elementärt kol anses däremot endast härstamma från förbränning av olika slag. Till det organiska kolet räknas den koldioxid eller metan som bildas vid förbränning i relativt låga temperaturer (200-500°C) i syrefri miljö vid termo-optisk analys. Det elementära kolet är den koldioxid eller metan som bildas vid höga temperaturer (500-800°C) i en syreförekommande miljö. Dock är separationen av det organiska från det elementära kolet ej problemfri. Det organiska kolet kan pyrolyseras, d.v.s. förkolnas och får därmed egenskaper som liknar det elementära kolet. Vi kan kalla detta kol för falskt elementärt kol. Detta kan korrigeras genom att optiskt mäta hur mycket ljus, från en IR-laser, som passerar filtret. Elementärt kol släpper igenom mindre ljus än organiskt kol. Dock finns stora osäkerheter med denna korrektion och forskarvärlden har försökt isolera det elementära kolet på allehanda tillvägagångssätt i decennier. Vi tog oss an en någorlunda oprövad teknik i dessa sammanhang; superkritisk koldioxidextraktion. Superkritisk koldioxid fås genom att utsätta koldioxid för en temperatur över 31°C och ett högt tryck på 73 bar. Koldioxiden antar då egenskaper som ligger mellan gas och vätska, det får därmed särskilda lösnings- och extraktionsegenskaper vi kan använda för att ta bort det organiska kol som orsakar pyrolys och därmed falskt elementärt kol. Koldioxid är dock ett opolärt lösningsmedel, således för att kunna lösa ut alla tusentals polära vattenlösliga ämnen i de organiska aerosolerna behöver vi tillsätta ett polärt lösningsmedel till koldioxiden, i detta fall metanol. Vi utförde extraktionen och kunde då se att vi kunnat reducera, och i många fall helt ta bort det pyrolytiska kolet. Resultatet öppnar för fortsatta studier av isolerat elementärt kol och en således en förbättrad källtilldelning.

Slutligen ville vi försöka koppla uppmätta masskoncentrationer i luft av biogen sekundär aerosol till olika landskapstyper. Biogen sekundär aerosol bildas av gaser som släppts ut från bl.a. växter. Genom oxidation i atmosfären och med hjälp av solljus kan sedan ångtrycket för dessa gaser sänkas och gaserna kan således kondensera på en befintlig partikel eller bilda partiklar själva genom att gaserna klumpar ihop sig, detta kallas även för nukleering. Vi samlade in atmosfäriska partiklar på filter under sommaren 2012, från dessa filter kunde vi sedan mäta karboxylsyror, organosulfater och nitroxy-organosulfater. Masskoncentrationerna av dessa ämnen kunde sedan kopplas till olika typer av landskap, t.ex. skog, jordbruksmark, berg etc., m.h.a. en modell som kallas FLEXPART. Våra resultat visade att luftmassans exponering för barrskog kunde förklara en stor andel av den totala variationen i masskoncentrationerna av flertalet uppmätta ämnen. Vi kunde även se att luftmassans exponering för hav och oceaner inte bidrog till signifikanta

masskoncentrationer av biogen sekundär aerosol. Kartläggning av olika landskapstypers inverkan på den biogena sekundära aerosolen kan vara viktig för att förutse hur förändrad landanvändning påverkar luftkvalitet.

Papers included in this thesis

- I. Martinsson, J., Eriksson, A. C., Elbæk Nielsen, I., Berg, Malmborg, V., Ahlberg, E., Andersen, C., Lindgren, R., Nyström, R., Nordin, E. Z., Brune, W. H., Svenningsson, B., Swietlicki, E., Boman, C., Pagels, J. H. (2015). Impacts of Combustion Conditions and Photochemical Processing on the Light Absorption of Biomass Combustion Aerosol. *Environmental Science and Technology*, 49, 14663-14671.
- II. Martinsson, J., Abdul, Azeem, H., Sporre, M. K., Bergström, R., Ahlberg, E., Öström, E., Kristensson, A., Swietlicki, E., Eriksson, Stenström, K. (2017). Carbonaceous aerosol source apportionment using the Aethalometer model - evaluation by radiocarbon and levoglucosan analysis at a rural background site in southern Sweden. *Atmospheric Chemistry and Physics*, 17, 4265-4281.
- III. Martinsson, J., Andersson, A., Sporre, M. K., Friberg, J., Kristensson, A., Swietlicki, E., Olsson, P. A., Eriksson, Stenström, K. Evaluation of $\delta^{13}\text{C}$ in carbonaceous aerosol source apportionment at a rural measurement site. In revision, *Aerosol and Air Quality Research*.
- IV. Abdul, Azeem, H., Martinsson, J., Eriksson, Stenström, K., Swietlicki, E., Sandahl, M. Towards the isolation and estimation of elemental carbon in atmospheric aerosols using supercritical fluid extraction and thermo-optical analysis. Accepted for publication, *Analytical and Bioanalytical Chemistry*.
- V. Martinsson, J., Monteil, G., Sporre, M. K., Kristensson, A., Eriksson, Stenström, K., Swietlicki, E., Kaldal Hansen, A. M., Glasius, M. Exploring sources of biogenic secondary organic aerosol compounds using chemical analysis and the FLEXPART model. In revision, *Atmospheric Chemistry and Physics Discussions*.

Author's contributions to the papers

- I. I performed the analysis of aethalometer data and wrote most of the paper. The study was planned by Joakim Pagels and Christoffer Boman. Robert Lindgren and Robin Nyström operated the wood stove. Joakim Pagels, Axel Eriksson and Erik Nordin conducted the aerosol measurements. Erik Ahlberg, Christina Andersen, William Brune and Birgitta Svenningsson were responsible for the simulations of photochemical processing.
- II. I planned and designed the study. I performed aethalometer and thermo-optical measurements. I was partly involved in the analysis of radiocarbon and levoglucosan. I performed most of the data analysis and wrote most of the paper. Moa Sporre performed the HYSPLIT modelling.
- III. I planned the study together with Kristina Eriksson Stenström. I was partly involved in the $\delta^{13}\text{C}$ measurements. I performed most of the data analysis and wrote most of the paper. The Markov Chain Monte Carlo modelling was performed by August Andersson. Moa Sporre performed the HYSPLIT modelling.
- IV. I planned the study together with Hafiz Abdul Azeem, Erik Swietlicki, Kristina Eriksson Stenström and Margareta Sandahl. Hafiz Abdul Azeem performed all the extractions and screening experiments, and wrote most of the paper. I performed the aerosol sampling on filters, the thermo-optical analysis, and wrote parts of the paper.
- V. I defined the scope of the paper, compiled all the data, performed the data analysis and wrote most of the paper. Guillaume Monteil performed the FLEXPART modelling. Moa Sporre performed the HYSPLIT modelling. Anne-Maria Kaldal-Hansen and Marianne Glasius performed the analysis of the organic compounds.

Abbreviations and acronyms

AAE	Absorption Ångström Exponent
AMS	Aerosol Mass Spectrometry
BC	Black Carbon
BrC	Brown Carbon
BSOA	Biogenic Secondary Organic Aerosol
BVOC	Biogenic Volatile Organic Compound
EBA	Ensemble-Based Apportionment
EC	Elemental Carbon
ERF	Effective Radiative Forcing
F ¹⁴ C	Fraction modern carbon
FLEXPART	FLEXible PARTicle dispersion model
GC-MS	Gas Chromatography with Mass Spectroscopy
GHG	Greenhouse Gas
HB	High Burn rate
HYSPLIT	HYbrid Single-Particle Lagrangian Integrated Trajectory
IR	Infrared
IRMS	Isotope Ratio Mass Spectroscopy
MAC	Mass Absorption Coefficient
MCMC	Markov Chain Monte Carlo (model)
NB	Nominal Burn rate
NOS	Nitrooxy Organosulfate
OA	Organic Aerosol
OC	Organic Carbon

OS	Organosulfate
PAM	Potential Aerosol Mass
PAH	Polycyclic Aromatic Hydrocarbon
PM	Particulate Matter
rBC	Refractory Black Carbon
RF	Radiative Forcing
scCO ₂	Supercritical CO ₂
SOA	Secondary Organic Aerosol
SP-AMS	Soot Particle Aerosol Mass Spectrometry
TBA	Tracer-Based Apportionment
TC	Total Carbon
UV	Ultraviolet
VOC	Volatile Organic Compound

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Introduction

This chapter gives a brief overview of the concept of the carbonaceous aerosol and its effect on climate and human health. An introduction to source apportionment is given and, finally, the aims and objectives of the work presented in this thesis are stated.

The carbonaceous aerosol

An aerosol is a collection of solid or liquid particles suspended in a gas or a mixture of gases. Aerosols are present in the atmosphere surrounding the planet. The concentrations may vary considerably, from hundreds of particles per cubic centimeter at the poles, to several orders of magnitude higher in densely populated regions. Particulate matter (PM) includes all types of aerosol particles such as minerals, salts, organic matter and metals.

Atmospheric aerosols play a key role in global, regional and local climate and health issues. The carbon-containing fraction of these aerosols is called the carbonaceous aerosol, and has severe impacts on both climate and health [1-3]. 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 makes it difficult to characterize them in climate models. Due to their effects on climate and health, it is important to develop policies and regulations that can reduce the emission of the kinds of aerosols causing these adverse effects.

The organic aerosol (OA) is subordinated the carbonaceous aerosol. The OA may constitute a large fraction (20-90%) of the total aerosol mass [4,5], and refers to the mass of the entire carbonaceous material, including oxygen and hydrogen. The OA can be formed in different ways. If it is released directly from its source it is called a primary organic aerosol. Examples of this are pollen, fungal spores and bacteria [6]. However, if the OA is formed by the condensation or nucleation of the oxidation products of gas-phase volatile organic compounds (VOCs) it is referred to as a secondary organic aerosol (SOA). VOCs may originate from both plants and combustion. VOCs of biogenic origin are referred to as biogenic VOCs

(BVOCs) and the SOA formed is then called a BSOA. BVOCs are mainly emitted by living plants and function as communication media as well as a way of processing and expressing biotic and abiotic stress [7-10].

The amount of total carbon (TC) is often divided into organic carbon (OC) and elemental carbon (EC). These fractions are defined by their thermal and oxidative resistance, where OC is suggested to be more susceptible to thermal degradation and volatilization than EC. OC is composed of various organic molecules and polymers. Common groups of compounds of OC include polycyclic aromatic hydrocarbons (PAHs), organic acids, alkanes, humic-like substances and cellulose [11-13]. EC is very similar to black carbon (BC), although it is quantified differently (BC is soot, which is quantified with optical methods). EC is formed by incomplete combustion of fossil fuels or biofuels. EC is highly refractive, chemically inert and insoluble in most solvents, hence it is very stable and is highly resistant to chemical degradation and transformation. Typical classifications of the carbonaceous fractions in ambient aerosols are shown in Figure 1.

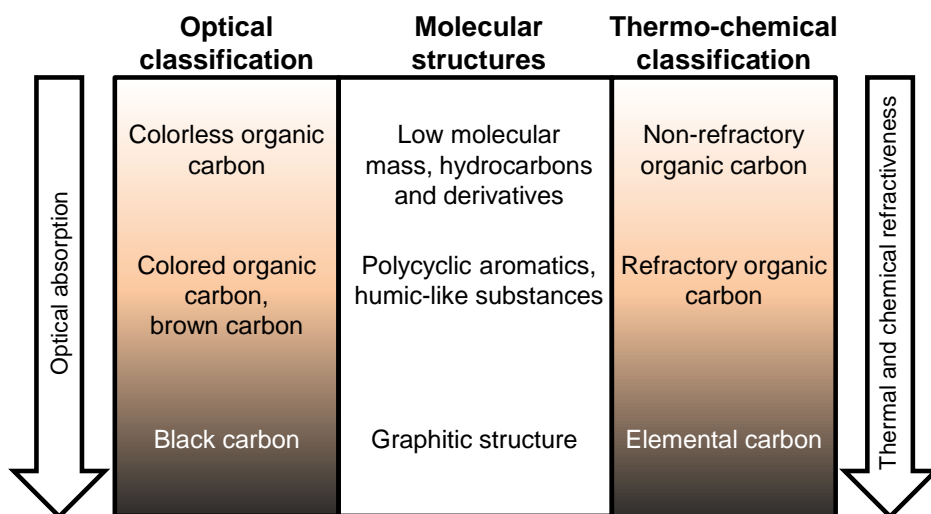


Figure 1. Illustration of the physicochemical properties and classification of different carbonaceous fractions often found in the ambient carbonaceous aerosol. Adopted and modified from Pöschl et al. [13].

The most common sources of the carbonaceous aerosol are the combustion of fossil fuels and biomass, and biogenic emissions. Biogenic carbonaceous aerosol can be divided into two main sub-groups: the biogenic primary organic aerosol and BSOA. The primary biogenic OA consists of pollen, fungal spores, bacteria and plant debris. BSOA are, as mentioned earlier, formed from BVOCs which go

into particle-phase. Common BVOCs are α -pinene, β -pinene, isoprene and limonene, all emitted from plants [7].

Climate change and aerosol-climate interaction

Since the industrial revolution in the 1800s, greenhouse gases (GHGs) such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) have been emitted to the atmosphere at an increasing rate. This has mainly been caused by the combustion of fossil fuels. This has led to the phenomenon known as global warming, and it has been estimated that the average temperature on the planet has increased by 0.9°C since the 1800s and is still increasing [1,14]. There is widespread agreement in the scientific community that this increase in temperature is caused by the emission of GHGs resulting from anthropogenic activities [1].

The anthropogenic emission of GHGs causes a perturbation in the radiative flux of the Earth's atmosphere. Radiative forcing (RF) is a measure of this perturbation, which indicates the changes in radiation due to a specific forcer [15]. Positive RF means that more radiation is entering than leaving the Earth's atmosphere, causing an increase in temperature. A negative RF means the opposite, i.e. more radiation is leaving the Earth than entering it, causing a decrease in temperature. The concept of effective radiative forcing (ERF) was introduced in the latest report from the Intergovernmental Panel on Climate Change (IPCC) [1]. ERF accounts for adjustments of atmospheric temperature, water vapor, clouds and the forcing agent, and is considered a better indicator of the global mean temperature response than RF, particularly for aerosols [1].

GHGs contribute to a positive RF. However, other atmospheric constituents also affect the climate. Aerosols are known to affect the climate in several, often complicated, ways. Aerosols differ from GHGs in many ways; GHGs are simple molecules with constant sizes, while aerosols vary greatly in size (from 1 nm to 10 μm), and are composed of a myriad of different chemical compounds. Many GHGs also have a long residence time in the atmosphere (years), while aerosols usually have residence times of several hours up to a few weeks. Figure 2 shows the values of RF and ERF for various emitted components.

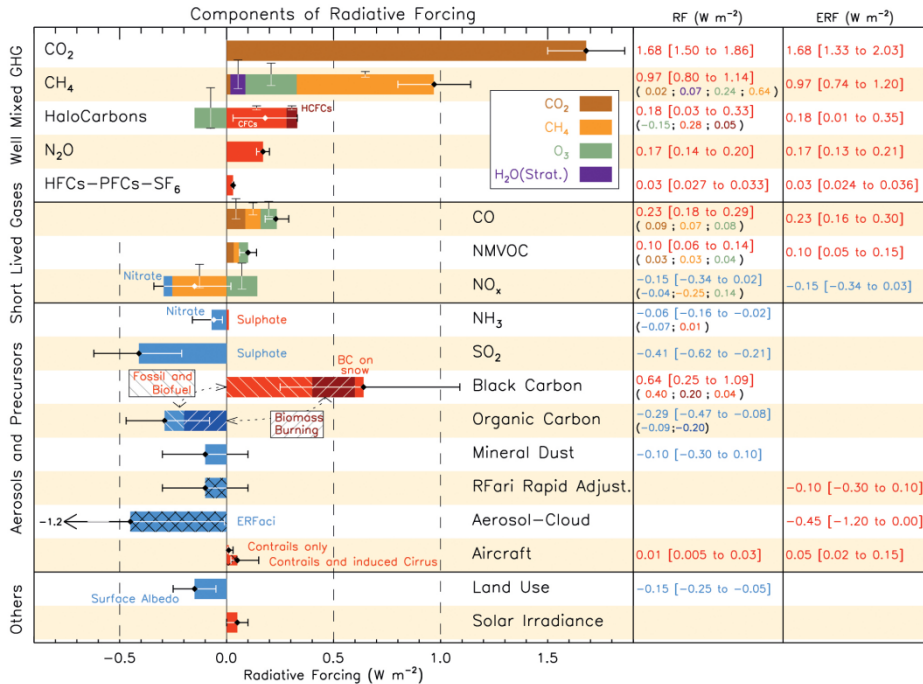


Figure 2.

Radiative forcing (RF) for several atmospheric components. From the Intergovernmental Panel on Climate Change (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 $\pm 50\%$ 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 W m^{-2}) is slightly different from the sum of the RF of the individual components (-0.33 W m^{-2}). 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 $-0.45 [-1.2 \text{ to } 0.0] \text{ W m}^{-2}$ and rapid adjustment of ari $-0.1 [-0.3 \text{ to } +0.1] \text{ W m}^{-2}$ results in an integrated component of adjustment due to aerosols of $-0.55 [-1.33 \text{ to } -0.06] \text{ W m}^{-2}$. CFCs = chlorofluorocarbons, HCFCs = hydrochlorofluorocarbons, HFCs = hydrofluorocarbons, PFCs = perfluorocarbons, NM VOC = Non-Methane Volatile Organic Compounds, BC = black carbon."

Due to the complexity of the effects of aerosols on climate it is convenient to make a general distinction between aerosol-radiation interactions and aerosol-cloud interactions. Aerosol-radiation interactions include 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, depending on the size and chemical composition of the aerosol particle.

When incoming sunlight is scattered off particles in the atmosphere, some of it will be scattered back into space, leading to cooling of the atmosphere [16]. Aerosols containing sulfates (SO_4), nitrates (NO_3) and mineral dust are known to

scatter light efficiently, and the total scattering has been estimated to correspond to a RF of $-0.5 \pm 0.4 \text{ W/m}^2$ [1].

During the absorption of light, the aerosol absorbs photons and releases the energy through the emission of long-wave radiation, which heats the atmosphere. It is well-known that BC from combustion processes absorbs light and heats the climate system [17]. Bond et al. [18] estimated the RF of BC to be $+ 1.1 \text{ W/m}^2$, thus suggesting that BC is the second largest climate forcer (see Figure 2), while other studies have proposed methane to be the second strongest, and BC the third [1]. Either way, the uncertainty in the RF of BC is very high.

The aerosol-cloud interaction is sometimes referred to as the “indirect effect”, and is caused by cloud formation. Cloud droplets are formed by the condensation of water on particles. The optical properties of the cloud will change as a result of changes in the chemical composition, size and number concentration of the aerosol particles [19]. For instance, a high aerosol number concentration will result in more, but smaller, cloud droplets, which will make the cloud brighter and thus reflect more of the incoming solar radiation back into space (increasing the albedo, or reflectivity, of the Earth). This will have a net cooling effect on the climate. This effect is often referred to as “the first indirect effect” [20]. Small cloud droplets may also increase the lifetime of clouds by delaying precipitation, also leading to an increase in the Earth’s albedo. This effect is called the “second indirect effect” [21].

The term brown carbon (BrC) was recently introduced with the intention of providing a more general nomenclature for organic aerosols with significantly higher absorption than BC in the ultraviolet (UV) region [22]. BrC has been shown to consist of conjugated molecular systems with functional groups such as nitro-phenols, PAHs and humic-like substances [12,23,24]. Extremely low-volatile organic compounds have also recently been suggested to exhibit enhanced UV absorption [25]. Due to its high absorption of UV light, BrC may have considerable effects on lower tropospheric photochemistry [23].

Thus, the effects of atmospheric carbonaceous aerosols on the climate are complex, and are today associated with considerably greater uncertainties than in the case of the GHGs. The greatest uncertainties are associated with BC and OC and, as can be seen from Figure 2, the combustion of fossil fuels and biofuels contributes to both cooling (through OC) and warming (through BC) of the climate.

Aerosols and health

It is estimated that around 7 million premature deaths are caused by air pollution globally each year [26]. In Europe, air pollution was recently estimated to cause 450 000 premature deaths per year [27], 5 000 of which in Sweden [28]. The term “air pollution” comprises both gases and PM. PM is responsible for several known negative health effects, such as cardiovascular disease and chronic obstructive pulmonary disease [29,30]. Dockery et al. [31] studied the relationship between the ambient concentration of PM and mortality in six large US cities, and found a clear correlation between elevated PM concentration and increased mortality.

Particle size is a very important parameter when discussing health effects [32,33]. Small particles ($<0.1\ \mu\text{m}$) have the ability to penetrate deep into the lungs, where they are deposited through diffusion. Larger particles ($>1\ \mu\text{m}$) can be trapped in the oral and nasal cavities by impaction on the mucous membranes, and be removed by coughing or sneezing. Particles in the interval $0.1\text{--}1\ \mu\text{m}$ are too small to be impacted on tissues and too large to be deposited through diffusion, and a large fraction of particles in this size interval is exhaled. Thus, smaller particles ($<0.1\ \mu\text{m}$) are generally regarded as being more hazardous than larger particles on a mass basis.

The organic aerosol contains complex and diverse chemical compounds. Many of these are toxic. PAHs are considered carcinogenic and have been shown to be detrimental to human health [34-37]. PAHs can be emitted from incomplete fossil fuel combustion [38], and are also formed during hot, air-starved, combustion of wood [39]. BC is also associated with negative health effects, and is considered to be more hazardous than PM in general [40,41]. Studies suggest that it is not the BC itself that is toxic, but that it may function as a vector, transporting toxic substances into the human respiratory tract [40]. Thus, combustion-generated particles can cause adverse health effects and their reduction should be prioritized in future regulatory policies.

Source apportionment of the carbonaceous aerosol

Since certain sources may emit specific types of aerosols, it is important to know the impact of a specific aerosol source on a geographical area. Here source apportionment plays a crucial role. An observed aerosol can be associated with a particular emission source by combining several measurement techniques with data analysis and statistics. Mass concentrations or fractions of mass are apportioned to possible sources, and source apportionment thus provides a

powerful tool for stakeholders and policymakers when determining how to regulate, and justifying the regulation of PM emissions.

Accurate source apportionment requires the measurement of several parameters. Fuzzi et al. [42] divided the source apportionment methods into “tracer-based apportionment” (TBA) and “ensemble-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 formed by the pyrolysis of cellulose and which thus provide a molecular tracer for biomass burning. EBA, on the other hand, relies on the properties associated to the total apportioned mass, although source specificity is reduced. EBA methods often include measurements of many different compounds with low source specificity, for instance, metals. The measured compound distribution can then be linked to a source that has a similar distribution of the measured compounds.

The parameters measured in both TBA and EBA are often directly affected by source usage. Thus a change in the use of the source will be reflected by changes in the measurements. Several source apportionment studies of the carbonaceous aerosol have already been performed [43-46]. However, there is a considerable need for further studies, and improvements. Research is needed to develop robust low-cost source apportionment techniques and to reduce the uncertainty. There is also need for further experimental data to improve and/or validate models that can be used by stakeholders and policymakers in drawing up regulations concerning emissions.

Aims and objectives of this work

The aim of this work was to evaluate and develop techniques and methods related to the source apportionment of the carbonaceous aerosol mass in the atmosphere. The specific aims and objectives are summarized below.

- To collect data from observations and measurements that can be used by modelers for more accurate estimation of source contribution.
- To develop a method for the separation of OC and EC in aerosol samples prior to ^{14}C analysis.
- To perform carbon isotope analysis on aerosol samples, and to evaluate its potential for source apportionment.
- To install a multi-wavelength soot photometer at a rural background measurement station, and evaluate the potential of the instrument for determining the contributions from fossil fuel/traffic soot and biomass-/wood combustion soot with high temporal resolution.

Environmental science

This is a doctoral thesis in environmental science, which is an interdisciplinary field, in contrast to classical disciplines such as physics, chemistry and biology. Interdisciplinarity is necessary in order to understand and study complex environmental systems, and environmental science is very well suited for the study of atmospheric sciences and air pollution, which are the subjects 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.

Various methods of source apportionment are used to determine the sources of different aerosols. Access to fast, cheap and reliable source apportionment methods would benefit society in many ways. Some of the methods that could be used to achieve this were evaluated in this work.

Materials and methods

Source apportionment may involve several different methods and techniques. This chapter gives a brief introduction to ways in which some measurement techniques and aerosol analysis methods can be applied for source apportionment purposes. Table 1 summarizes the techniques and methods used in this work.

Table 1.

Summary of aerosol sources, campaigns and methodologies employed in this work.

Paper	I	II	III	IV	V
Campaign					
Ambient		x	x	x	x
Laboratory	x				
Instrument/ Measured parameter					
Aethalometer/ Light absorption	x	x			
AMS/ Aerosol chemistry	x				
GC-MS/ Levoglucosan		x	x		
IRMS/ $\delta^{13}\text{C}$			x		
Single-stage accelerator mass spectroscopy/ ^{14}C		x	x		
Thermo-optical carbon analyzer/ OC, EC, TC		x	x	x	
UHPLC-q-TOF-MS*/ Biogenic SOA					x
Modelling					
FLEXPART					x
HYSPLIT		x	x		x
Ageing simulation					
PAM	x				

*Ultra-High Performance Liquid Chromatography coupled to a Quadrupole Time-Of-Flight Mass Spectrometer

Carbon mass measurements

Two important parameters in research on the carbonaceous aerosol are OC and EC. The most common method of separating organic and elemental carbon is to heat the sample gradually to volatilize the carbon, as illustrated in Figure 3. The filter containing the aerosol sample is placed in a sample oven, and then heated in several temperature intervals in an inert He atmosphere. This will volatilize the OC from the filter. In the second step, EC is volatilized in an oxidative He/O₂ atmosphere using several temperature intervals. All the compounds volatilized from the sample are fully oxidized to CO₂ in an oxidation oven and further converted to methane by passing hydrogen gas over a zinc catalyst in the methanator. In the final step, the methane is quantified using a flame ionization detector (FID). A schematic of the carbon analyzer is shown in Figure 3.

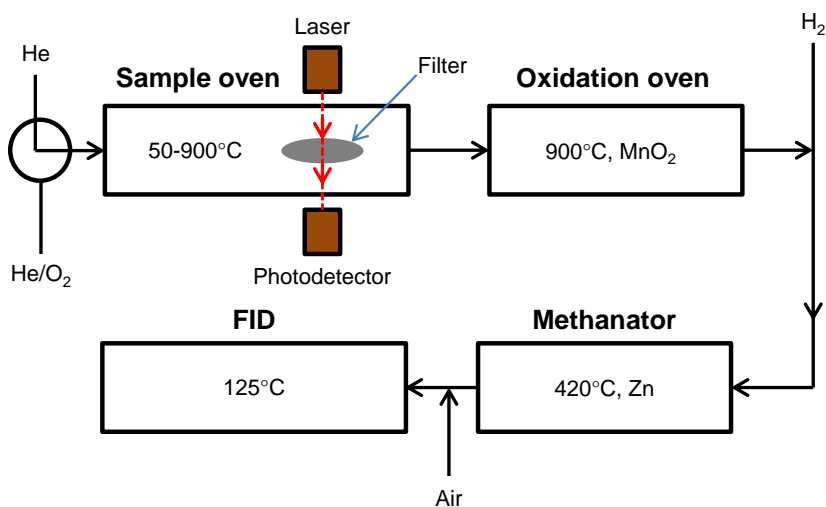


Figure 3.
Simplified schematic of the thermo-optical carbon analyzer.

The charring of OC is a well-known artefact in all OC/EC analyses. As the OC is heated, most of it is volatilized and leaves the filter. However, some of the OC may char when heated, especially when heated in the absence of an oxidizing agent, such as O₂. This charred OC can then be falsely interpreted as EC since it will leave the filter together with the EC in the next part of the process. This EC can be regarded as “artificial EC” in contrast to the “true EC” contained in the original sample. Optical methods have been introduced into thermal analysis to correct for this charring. A He/Ne 633 nm laser and a photodetector are used to

continuously measure the light transmission through the filter and sample during the whole thermal analysis (Figure 3). As OC starts to char in the inert He atmosphere the transmission decreases. The charred OC is finally oxidized in the He/O₂ atmosphere and the transmission signal increases again. The division between OC and EC is defined as the point at which the transmission signal returns to its initial value. The carbon evolved before this time is defined as OC and the carbon remaining on the filter is defined as EC. It is important to note that this separation relies on two assumptions. The first is that artificial EC has the same optical properties as true EC, and the second, is that artificial EC is easier to oxidize, and is thus removed earlier than true EC. However, it has been shown that one or both of these assumptions may not be valid [47], and there is, in fact, no infallible thermal protocol that can separate OC from EC. However, the protocol used in these analyses is a European standard protocol called EUSAAR_2, which was developed in order to harmonize OC/EC measurements performed in Europe [48]. The measurement uncertainty associated with the thermo-optical analysis of samples collected on filters at the Vavihill measurement station in southern Sweden, using the EUSAAR_2 protocol, has been estimated to be 17% [49].

Thermo-optical analyses of OC and EC were performed by the author and are reported in Papers II and IV. Some OC and EC results were also used in the study described in Paper III, however these results were obtained from an earlier study [44].

Optical measurements

Optical techniques have been used in source apportionment studies since the early 2000's [50-52]. Mainly light-absorption techniques have been utilized for this purpose. A common way to measure light absorption in aerosols is to use an aethalometer, which is a real-time, high-time-resolution light absorption instrument first described by Hansen et al. [53]. The seven-wavelength aethalometer used in the present work (model AE33, Magee Scientific) utilizes seven LEDs with wavelengths ranging from 370 to 950 nm (Table 2, Figure 4) [54]. An air flow is directed through a filter tape on which 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 (ATN_λ) is defined as:

$$ATN_\lambda = 100 \cdot \ln \left(\frac{I_{0\lambda}}{I_\lambda} \right) \quad (1)$$

where $I_{0\lambda}$ is the incoming light intensity and I_λ is the light intensity after passing through the filter in the wavelength λ . The aerosol attenuation coefficient, b_{ATN_λ} , can then be calculated by the change in attenuation, ΔATN_λ , as a function of the filter spot area A , sample air flow rate Q , and time Δt :

$$b_{ATN_\lambda} = \frac{A}{Q} \cdot \frac{\Delta ATN_\lambda}{\Delta t} \quad (2)$$

Table 2.
Wavelengths used in the aethalometer.

Wavelength (nm)	370	470	520	590	660	880	950
Color	UV	Blue	Green	Yellow	Red	IR	IR

Two main sampling artefacts must be taken into account in order to calculate the light absorption coefficient, $b_{abs\lambda}$. Scattering on and within the filter matrix can be wrongly interpreted as attenuation, even when the filter is not heavily loaded with particles. The second artefact is called “the shadowing effect”, and may occur when the filter is heavily loaded with particles. The optical path in the filter is decreased, leading to underestimation of the attenuation. This effect is more pronounced for freshly emitted soot, and almost negligible in aged ambient aerosols [55]. 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 is used to correct for scattering in the filter [54]. The measurement

uncertainty of the AE33 aethalometer used in this work has been estimated to be about 35% [56].

The aerosol light absorption can then be converted to aerosol mass concentrations of BC or BrC by using mass absorption coefficients (MACs):

$$BC_{\lambda} = \frac{b_{abs_{\lambda}}}{MAC_{\lambda}} \quad (3)$$

BC is, as mentioned in the introduction, one of the most efficient aerosol light absorbers, and has an estimated MAC value of $7.5 \text{ m}^2/\text{g}$ in 550 nm [57]. Hence, a large fraction of the ambient aerosol light absorption is associated to BC. BrC is nowadays regarded as the second most important component with regard to light absorption and the direct climate effect [58]. MAC values for BrC have been estimated to be in the range of $0.2\text{-}3 \text{ m}^2/\text{g}$ around 400 nm [22].

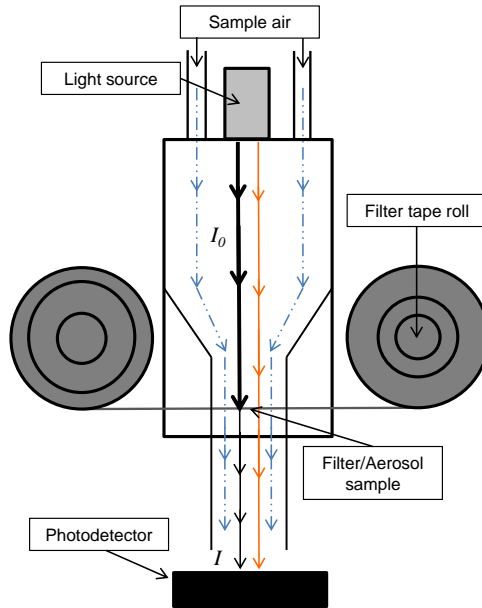


Figure 4.

Illustration of the aethalometer used in this work. Sample air is pumped into the instrument, and is then led through the filter containing the sample. A light source emits beams of light in seven wavelengths. Two light beams with an initial intensity of $I_{0\lambda}$ are passed through the filter carrying samples of the aerosol that were deposited at different rates (black and red lines). After the light beams have passed through the filter, the attenuated light intensity (I_{λ}) is measured by a photodetector. The filter is automatically switched to a new spot by rotation of the filter tape.

It has been discovered that there is a difference in the absorption of light between aerosols arising from biomass burning and fossil fuel combustion [50]. Wood smoke aerosols from biomass burning have a relatively higher light absorption in the UV ($100\text{-}400 \text{ nm}$) and blue ($450\text{-}500 \text{ nm}$) regions than in the IR ($>700 \text{ nm}$),

while the light absorption of fossil fuel combustion aerosols exhibit a less pronounced wavelength-dependence. An exception seems to be the combustion of coal, which is a fossil fuel, but has been shown to emit particles with high light absorption in the blue spectral region [59].

The relationship between the light absorption coefficients, $babs_{\lambda}$, and the wavelengths, λ , can be described by the absorption Ångström exponent:

$$AAE = - \frac{\log \frac{babs_{\lambda_1}}{babs_{\lambda_2}}}{\log \frac{\lambda_1}{\lambda_2}} \quad (4)$$

In Equation 4, $babs_{\lambda_1}$ and $babs_{\lambda_2}$ represent the light absorption coefficient for two wavelengths, λ_1 and λ_2 . These are usually widely separated (spanning from the UV to the IR, Table 3). If light absorption is measured at more than two wavelengths a function can be fitted to the data to calculate AAE.

Previous studies have found that fresh BC has an AAE around 1.0 and BrC a value greater than 2.0 [22,60]. BrC is thus assumed to have a stronger spectral dependence, with strong absorption in the UV and the blue spectral regions. Due to the difference in spectral dependence and assuming that BC and BrC are the only two light-absorbing components in ambient aerosols, it is possible to separate BC from BrC.

Table 3.

Representative AAE values found in the literature for traffic and biomass burning aerosols.

Type of aerosol	Spectral range (nm)	AAE	Reference
Biomass burning	467-660	2.1	Clarke et al. [61]
Biomass burning (cotton wood)	370-950	2.1	Day et al. [62]
Biomass burning (oak wood)	370-950	1.8	Day et al. [62]
Traffic emissions	300-1000	1.0	Kirchstetter et al. [50]
Biomass burning	300-1000	2.0	Kirchstetter et al. [50]
Diesel soot	450-700	1.1	Schnaiter et al. [63]

It is commonly assumed that wood smoke aerosol contains BrC and has an AAE of around 2, while fossil fuel combustion or traffic aerosols are dominated by BC, and an AAE around 1 [50,60]. Thus, by using a multi-wavelength light absorption instrument, like the aethalometer, it is possible to divide the total absorption in specific wavelengths, $babs_{\lambda}$, into biomass burning and fossil fuel combustion fractions. This method is often referred to as the aethalometer model [51]. Several studies have applied the difference in light absorption by BC and BrC to distinguish biomass burning aerosols from fossil fuel combustion aerosols

[24,51,52,64-66]. For accurate differentiation and apportionment it is crucial to use an AAE that is representative of the source. In most of the above-mentioned studies values of AAE were taken from the literature, some of these values are listed in Table 3.

AAE values for biomass burning may change drastically depending on the combustion conditions. It has been shown that low-temperature pyrolysis may generate aerosols with high organic content, with an AAE>2 [59], while hot, air-starved conditions may produce almost pure soot or BC [67], with a presumably lower AAE. Therefore, assuming an average value of AAE of 2.0 for all wood-burning conditions may be an oversimplification.

In addition to the uncertainty of variation of AAE values with combustion conditions, there is an additional uncertainty regarding whether the AAE may change as a result of photochemical processing in the atmosphere. Some studies have indicated that light absorption by BrC might decrease due to bleaching [68], while the opposite has been seen in others [69].

In the first study (Paper I), the AAE was derived from aethalometer measurements in order to study the impact of wood stove combustion conditions and burn cycles on AAE. Further, aethalometer absorption measurements made at the Vavahill measurement station in southern Sweden were used for source apportionment over a whole year (Paper II).

Aerosol analysis using tracers

Aerosols are comprised of a large variety of elements and chemical compounds. Some of these can be used to characterize the aerosol source. These kinds of compounds are sometimes referred to as tracers.

Radiocarbon

Three carbon isotopes are found on Earth. In atmospheric carbon dioxide, ^{12}C is the most abundant (99% by mass) followed by ^{13}C (1%) and ^{14}C (10^{-10} %). ^{12}C and ^{13}C are stable carbon isotopes, while ^{14}C is radioactive, and is often referred to as radiocarbon. Radiocarbon analysis is a powerful, but 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:



This radiocarbon is then oxidized into CO₂ and transported into the terrestrial system. A large fraction is also absorbed by the oceans. All living organisms contain some ¹⁴C, which is the basis for the commonly used ¹⁴C dating method [70]. ¹⁴C has a half-life of 5730 years, and decays to nitrogen (¹⁴N) through β-emission:



When a living organism dies, it is no longer in equilibrium with the environment, i.e., no new ¹⁴C enters the organism. The ¹⁴C present in the organism starts to decay and thus decreases in comparison to the stable carbon isotopes. Fossil fuels contain no ¹⁴C since it has decayed during the millions of years taken for organic matter to form these fuels. The natural atmospheric ¹⁴C concentration varies very little around the globe [71], however, the ¹⁴C concentration in atmospheric CO₂ has been altered by man in two important ways. The burning of fossil fuels leads to the emission of CO₂ that contains no ¹⁴C, thus reducing the fraction of ¹⁴CO₂. This is called the Suess effect [72]. Nuclear weapons tests carried out in the atmosphere during the 1950s and 1960s caused the release of neutrons, which reacted with nitrogen in the atmosphere (Equation 5), leading to an increase in the ¹⁴C concentration. This is called the bomb-pulse effect.

When measuring the ¹⁴C in environmental samples it is important to take both the Suess effect and the bomb-pulse effect into account. It is therefore common to report the results as the fraction modern carbon (F¹⁴C) [73], i.e. the ratio of ¹⁴C in a sample to that in a reference value predating 1950, before the nuclear weapons tests. Fossil fuels, for example, have an F¹⁴C of 0, as all the ¹⁴C has decayed. The F¹⁴C of biomass varies depending on the age of the plant. The value for trees, which can be quite old, may today reach 1.2 if the tree was growing during the bomb pulse [44].

Carbonaceous aerosol radiocarbon analysis was performed by first transforming all the carbon on aerosol-laden filters into graphite [74]. The graphitized samples, together with standards, were then pressed into aluminum capsules and mounted on a sample wheel. The ¹⁴C/¹²C ratio was then measured using accelerator mass spectrometry. The measurement uncertainty for the single-stage accelerator mass spectrometer at Lund University has been estimated to be 0.5-1% [75]. Radiocarbon analysis was performed in the study described in Paper II. Radiocarbon data were also used in Paper III, however, these data were obtained from an earlier study [44].

Stable carbon isotopes

The quantitative relation between different isotopes of an element may change as a result of physical or chemical transformation. Such transformations usually affect one of the isotopes more than the other; this is called isotope fractionation. Carbon isotope fractionation occurs during the relocation of carbon between different ecosystems and trophic levels in the food chain [76,77], and is driven by the small differences in mass between, for example, an abundant and a rare isotope.

The relative abundance of the stable carbon isotopes ^{12}C and ^{13}C , sometimes referred to as the ^{13}C signature has been widely used over the past three decades to characterize sources of ambient carbonaceous aerosols [78-85]. The technique relies on the fact that the ^{13}C signature differs between sources of carbonaceous aerosols. Figure 5 shows the carbon isotope composition of some common aerosol sources. However, it has been shown that the heavier isotope may be more depleted in compounds formed by oxidation processes. This effect is called the kinetic isotopic effect [86,87]. In general, aerosols from fossil fuel combustion are more enriched in ^{13}C than aerosols from biogenic and biomass combustion sources.

Plants can fractionate carbon isotopes differently depending on the metabolic pathway they use to transform CO_2 into carbohydrates [76]. C_3 plants, for instance, contain less ^{13}C than C_4 and plants using crassulacean acid metabolism. However, there may be differences between the ^{13}C signatures within the same metabolic group of plants. Conditions such as temperature, light and humidity may affect isotopic fractionation within a species [76,88]. Only C_3 plants are of relevance for the work presented in this thesis as they completely dominate the Swedish and Nordic flora [89].

The relative abundance of the stable carbon isotopes ^{12}C and ^{13}C is expressed as $\delta^{13}\text{C}$, and is defined in relation to an international standard, as in Equation 7.

$$\delta^{13}\text{C}_{\text{Sample}} (\text{‰}) = \left(\frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{Sample}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{Standard}}} - 1 \right) \cdot 1000 \quad (7)$$

A more positive $\delta^{13}\text{C}$ value indicates that the sample has a higher abundance of the heavier isotope, i.e. ^{13}C . $\delta^{13}\text{C}$ measurements in aerosol source apportionment studies have the benefits of being relatively cheap, and sample preparation is fast (compared to ^{14}C analysis). $\delta^{13}\text{C}$ was measured using isotope ratio mass spectrometry (IRMS) at the Department of Biology, Lund University. The measurement uncertainty was estimated to be $\pm 0.2\text{‰}$. Measurements of $\delta^{13}\text{C}$ were made in the source apportionment study described in Paper III.

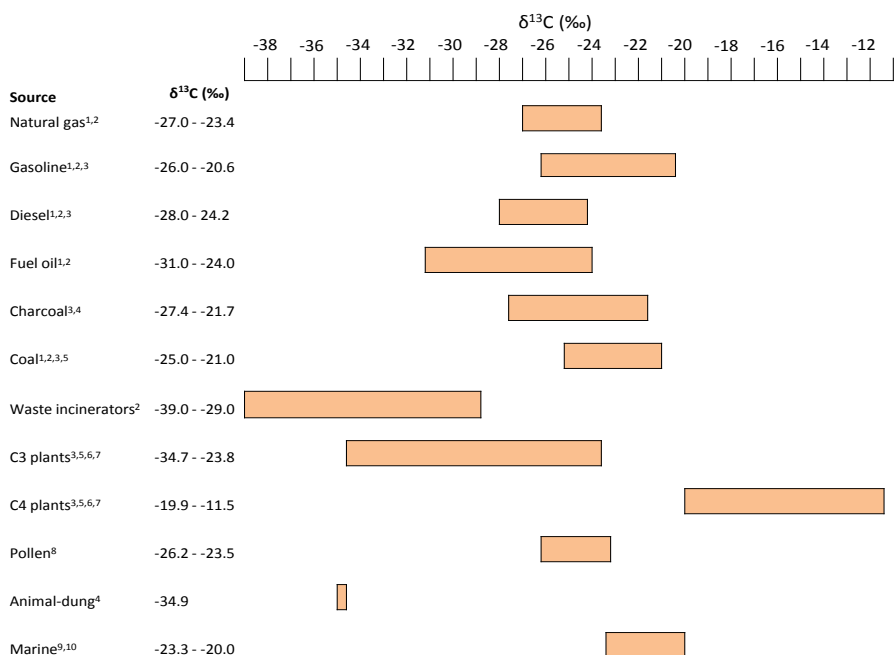


Figure 5. ^{13}C signatures in aerosols from various sources (¹[85], ²[84], ³[83], ⁴[78], ⁵[90], ⁶[81], ⁷[91], ⁸[82], ⁹[79], ¹⁰[92]).

Biomass burning tracers

The organic aerosol is comprised of 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 the pyrolysis of cellulose above 300°C [93]. It has been used in several source apportionment studies to quantify wood burning [43-46], however, its stability in the atmosphere is still being debated [94-96]. In the work described in this thesis, particles on filters were first extracted with dichloromethane and methanol during sonication. The extracts were then derivatized before being analyzed using gas chromatography with mass spectroscopy (GC-MS). Levoglucosan was then quantified by its mass-to-charge ratio (m/z) of 217. Levoglucosan was analyzed and used to quantify wood-burning in the study described in Paper II. The measurement uncertainty of the peak areas obtained from GC-MS was estimated to be $\pm 1\%$. Levoglucosan data were also used to quantify wood-burning in the study described in Paper III, although the data were taken from a previous study [44]. Levoglucosan analysis was performed at the Department of Chemistry, Lund University.

Tracers of biogenic secondary organic aerosol

Biogenic secondary organic aerosols (BSOA) are mainly formed by photo-oxidation of BVOCs. Hence, tracers of BSOA consist of the products of oxidation of these BVOCs; the precursor compounds usually being α -pinene or isoprene. The tracers may have been oxidized in several steps. Examples of BSOA tracers are dicarboxylic acids with 3 to 9 carbon atoms (C3-C9). Organosulfates (OSs) and nitroxy organosulfates (NOSs) can also be used as tracers of mixed air masses, i.e., air masses that have been exposed to biogenic as well as anthropogenic emissions [97-101]. Dicarboxylic acids, OSs and NOSs were measured with an ultra-high performance liquid chromatography with quadrupole time-of-flight mass spectrometry at the Department of Chemistry, Århus University, Denmark. The measurement uncertainty was estimated to be $< 20\%$ for carboxylic acids, and $< 25\%$ for OS and NOS. These data were used as BSOA tracers, as described in Paper V.

Separation and isolation of organic and elemental carbon using supercritical CO₂

Supercritical carbon dioxide (scCO₂) is a fluid state of CO₂, in which it is held above its critical temperature (304.24 K) and pressure (73.9 bar). In this state the CO₂ adopts properties that lie between those of a gas and a fluid, e.g., low viscosity and surface tension, but high diffusivity [102]. The high diffusivity and low surface tension reduce the extraction time compared to other solvents. scCO₂ has been shown to possess good properties as a solvent in chemical extraction processes. The low temperature allows extraction without thermal damage of the desired extracts, and the solubility can be varied by changing the pressure, allowing for selective extraction. scCO₂ also has the benefits of being inexpensive and having low toxicity and low environmental impact, in stark contrast to many other solvents. For this reason, the scCO₂ technique is gaining ground in research in the food industry [103]. One drawback of scCO₂ is that it is not very efficient for the extraction of high-molecular-mass compounds [104]. Furthermore, CO₂ is a non-polar molecule, which means that it cannot be used to extract polar compounds. However, aerosol samples contain a myriad of organic compounds and a large fraction of these are polar. In order to extract polar compounds CO₂ must be mixed with a polar solvent, such as methanol (CH₃OH). However, this increases the toxicity of the solvent.

In the work described in this thesis, the potential of using scCO₂ extraction to overcome the problem of charring of OC in thermo-optical analysis was

investigated (Paper IV). All scCO₂ extractions were performed at the Department of Chemistry, Lund University.

Auxiliary methods

The methods presented in this section are not in central focus of this thesis but deserves a description in order to interpret some of the results given below.

Aerosol mass spectrometry

Aerosol mass spectrometry (AMS) is a common and very useful method when studying the organic aerosol. It has a wide field of applications, from indoor local measurements to atmospheric global measurements. The instrument consists of an aerodynamic lens inlet where the aerosols are concentrated by reducing the amount of ambient gases. The aerosol particles then impact on a heated tungsten surface and become flash-vaporized. The vaporized aerosol compounds are ionized by electron impact and then analyzed by mass spectrometry. The high-resolution time-of-flight AMS used in the study described in Paper I is equipped with an additional intracavity laser vaporizer (1064 nm), and can be operated with the laser vaporizer alone, the tungsten surface alone, or both. This type of AMS is called soot particle AMS or SP-AMS. Laser vaporization allows the detection of refractory species such as soot and metals. More comprehensive descriptions of the instrument have been given by DeCarlo et al. [105], Canagaratna et al. [106] and Onasch et al. [107]. SP-AMS measurements of the OA and refractory black carbon (rBC) were performed on the aerosol generated by a conventional wood stove located at Umeå University. The measurement uncertainty has been estimated to be about 20% [108]. The derived data were used to determine the OA and rBC, as described in Paper I.

Simulation of atmospheric processing

An instrument called a potential aerosol mass (PAM) reactor is commonly used to simulate atmospheric processing or “ageing” of both ambient and experimental aerosols. The PAM reactor used in the present work consists of a 13.5 l flow tube reactor in which UV-light is used to produce ozone (O₃) and hydroxyl radicals (OH) that oxidize the incoming aerosol [109]. Two peak wavelengths, of 185 and 254 nm, are needed for the production of O₃ and OH, respectively. A few minutes residence time in the PAM reactor corresponds to several days in the atmosphere,

and the PAM reactor is therefore very useful in experiments where rapid processing is necessary. Atmospheric ageing using the PAM reactor was applied to wood stove emissions and evaluated in the study presented in Paper I. The uncertainty in OH exposure using the PAM reactor has been estimated to be 34% [110].

Aerosol modelling

The HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [111] uses meteorological data to calculate deterministic air mass trajectories in order to provide information on air mass origin and movement. HYSPLIT was used in the studies presented in Papers II, III and V.

The FLEXible PARTicle dispersion (FLEXPART) model [112] is similar to HYSPLIT. The main difference is that FLEXPART includes stochastic particle dispersion functions, which allows modelling of the dispersion of individual virtual particles (released from the receptor-site) from the bulk air mass trajectory. The FLEXPART model was used as described in Paper V.

Summary of papers

This chapter presents the most important results of the studies included in this thesis.

Optical properties of biomass burning aerosols-Paper I

The physicochemical properties of wood burning aerosols may vary considerably depending on combustion conditions and the stage in the burn cycle [39,59,67]. It is therefore difficult to describe these emissions in a way that is useful for the assessment of effects on climate and health. The optical properties of wood stove emissions have been poorly explored, which may influence the application of optically based source apportionment methods, such as the aethalometer model.

A modern conventional domestic wood stove [113] was used to generate aerosols from wood burning in order to study the optical properties of wood burning aerosols. Logs of birch (*Betula*) were placed on a bed of glowing embers, and the flue gases and aerosols generated were diluted and collected in a 15 m³ steel chamber. This chamber enabled sampling from different phases of the burn cycle. The burn cycle was divided into three phases, as in Eriksson et al. [39]. The first phase, *fuel addition*, started when the logs were added to the bed of embers. The *intermediate* phase started when the logs had caught fire and the oxygen concentration was below 14%. The intermediate phase ended when the oxygen concentration had increased above 14%, indicating the beginning of the *burn-out* phase. The stove was operated in two modes. The nominal burn rate (NB) was achieved by operating the stove as recommended by the manufacturer, and burning 2.5 kg fuel (~3 large wood logs) in each batch. A high burn rate (HB) was achieved by burning 3.5 kg fuel (~9 small wood logs) in each batch. A PAM reactor was connected to the sampling line in order to simulate atmospheric ageing.

The characteristics measured during a complete burn cycle are illustrated in Figure 6. Logs were added to the wood stove at $t=0$, and the AAE increased from 1.3 to 2.3. The concentrations of CO and OA also increased rapidly by factors of 3 and ~17, respectively. In the intermediate phase, flaming combustion took place, and

the AAE decreased to ~ 1.2 , and the emissions of OA and CO were in general low. The AAE remained around 1.0-1.3 during the final burn-out phase.

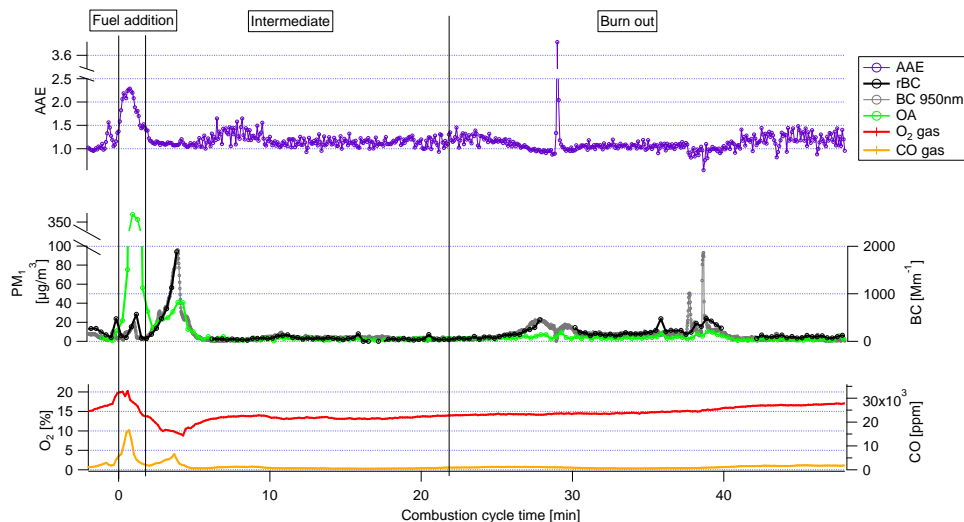


Figure 6.

Emissions and optical properties during a typical full cycle of wood burning in a modern domestic stove at nominal burn rate (three logs were added at $t=0$). Time-resolved AAE measured with the aethalometer (upper panel). Diluted (200 times) organic aerosol (OA, mass concentration), refractory black carbon (rBC, mass concentration) and total light absorption coefficient at 950 nm (BC) (middle panel). Concentrations of O_2 and CO in the flue-gas (lower panel). The main features of the cycle are reproducible.

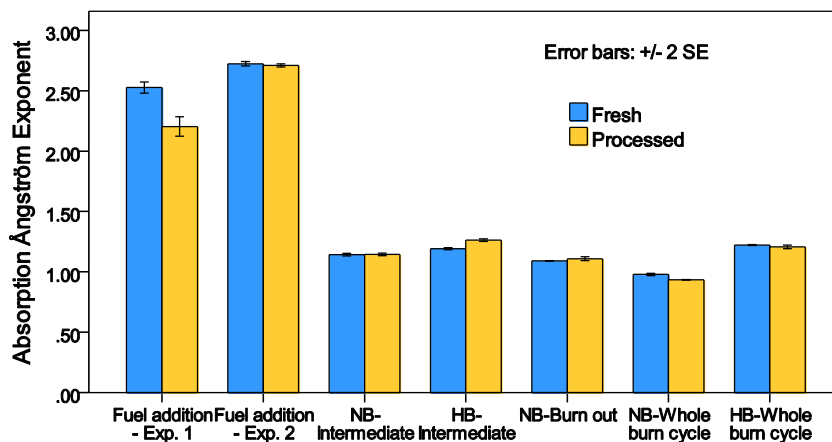


Figure 7.

Absorption Ångström Exponent (AAE, 370-950 nm) during the different phases of a complete burn cycle at nominal and high burn rates. The results for unprocessed aerosol are compared with the results from aerosol photochemically processed with the PAM reactor. The error bars represent ± 2 standard errors (SE) over time.

Figure 7 shows the AAE during the various phases of wood burning. Two experiments were performed to study the fuel addition phase (Exp. 1 and Exp. 2). The intermediate and burn-out phases were studied at nominal and high burning rates. It can be seen from Figure 7, that the AAE was somewhat higher at the HB than at the NB mode, during the same phase of combustion. These higher AAEs may be due to elevated concentrations of UV-absorbing PAHs, which are more abundant in hot, air-starved combustion, as can be expected at the HB [39]. A complete burning cycle using this type of wood stove emits aerosols with values of AAE in the range 1.0-1.2 (Figure 7).

In these experiments, the PAM reactor was set to simulate extreme atmospheric processing of the aerosol. The OH exposure was estimated to be $3 \cdot 10^8$ molecules/cm³·h, which corresponds to several days processing in the atmosphere. Despite the extreme processing, the AAE was in general unaffected (Figure 7). One reason for this could be that this extreme processing both creates and destroys light-absorbing chromophores [68], thus having no net effect on the absorption.

The most important result of these studies is that the aethalometer model, in which a value of AAE=2 is used for source apportionment of wood combustion aerosols, and AAE=1 for the source apportionment of traffic/fossil emissions, may incorrectly apportion aerosols from modern wood stoves as traffic/fossil-generated aerosols. Values of AAE above 2 may be reached in less efficient and poorly insulated wood stoves during the whole combustion cycle. However, as modern, well-insulated, wood stoves become more common, the predetermined AAEs in the aethalometer model may need to be revised.

Optically based source apportionment and method comparison-Paper II

Optically based source apportionment, for example, using the aethalometer model, is cheaper and faster than analyzing ¹⁴C and levoglucosan on filters. However, the accuracy of the aethalometer model is poorly explored. Furthermore, many source apportionments based on the aethalometer model have been conducted in densely populated areas, where the impact of wood burning and traffic emissions can both be expected to be high [51,52,114,115]. Few studies have been carried out on the performance of the aethalometer model in rural/background areas. The Vavihill measurement station is located in a rural area in southern Sweden. Atmospheric particles were sampled on quartz fiber filters (Ø=47 mm, N=123), over a 12-month period (June 2014-June 2015) with a time resolution of 72 hours. The particle light absorption was measured with an aethalometer at seven wavelengths,

over the same period, with 1-minute time resolution. Levoglucosan and radiocarbon (^{14}C) were measured in samples collected on filters. The aethalometer model was applied to the light absorption data, assuming an AAE of 1 for fossil fuel sources and 1.81 for wood burning.

It was found that the aethalometer model agreed well with the measured levoglucosan concentrations (Figure 8). Both methods indicate that wood burning emissions are higher during the winter months than during the summer. Elevated wood burning emissions during winter have been observed in previous studies conducted in this geographical area [44,45,116].

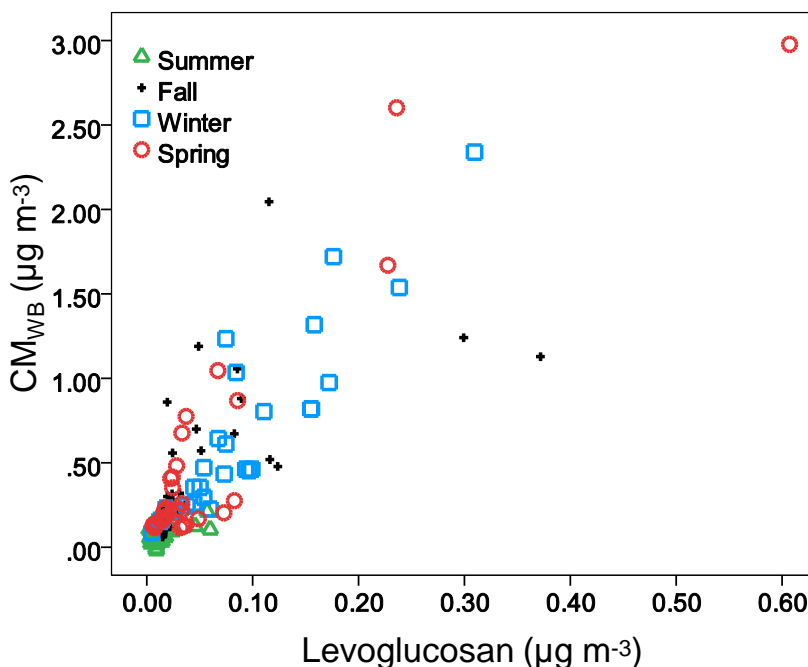


Figure 8. Comparison between carbonaceous matter derived from wood burning (CM_{WB}) using the aethalometer model and levoglucosan concentrations determined from filters.

The aethalometer model showed good agreement with the radiocarbon- and levoglucosan-based source apportionment. No significant differences were found between the two methods in apportioned wood burning ($p=0.8$) or biogenic aerosol ($p=0.3$) over the whole year (Figure 9). However, fossil fuel carbonaceous aerosol was significantly overestimated, by a factor 1.3, by the aethalometer model compared to source apportionment based on radiocarbon and levoglucosan measurements ($p=0.04$). A performed sensitivity analysis revealed that it is possible that this discrepancy originates from interference of non-light absorbing, presumably biogenic, carbon. It could also possibly be explained by the results

presented in Paper I, that biomass burning aerosols may have an AAE closer to unity, leading to biomass burning aerosols being falsely apportioned to fossil carbonaceous aerosols when using the aethalometer model. On the other hand, this explanation is contradicted by the good agreement between the two methods for wood burning (Figure 9).

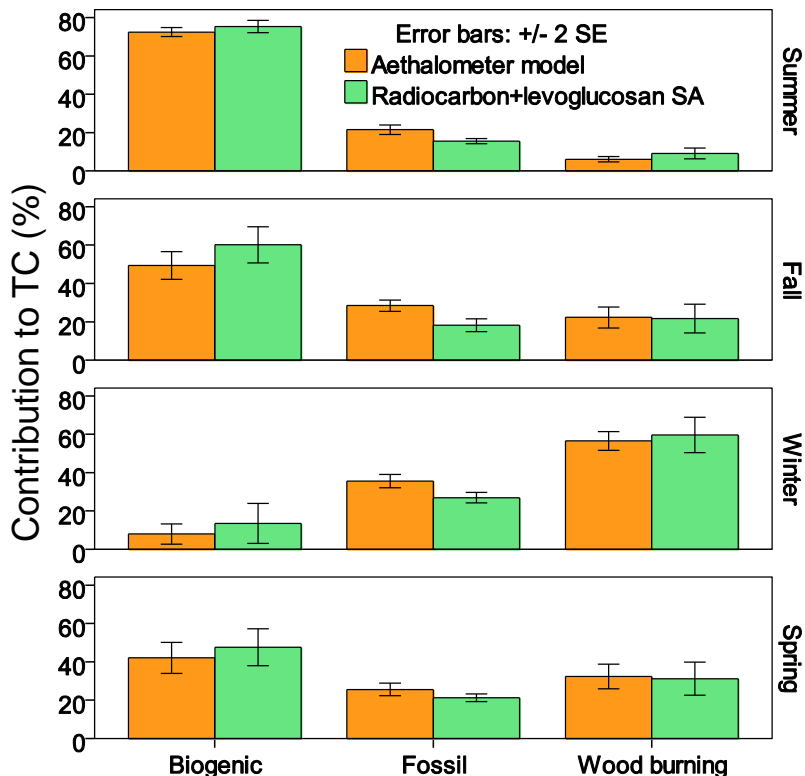


Figure 9. Seasonal comparison of the contribution to total carbon (TC) between the aethalometer model and radiocarbon + levoglucosan source apportionment (SA). Error bars show ± 2 SE.

Evaluating $\delta^{13}\text{C}$ as a source marker in source apportionment-Paper III

Paper III describes an investigation of the potential of using $\delta^{13}\text{C}$ as a tracer in source apportionment. Aerosols were collected on quartz fiber filters at the Vavihill measurement station during 2008-2009. $\delta^{13}\text{C}$ was measured on 25 filter samples, and the results were complemented with previous measurements of OC, EC, ^{14}C and levoglucosan which are presented in a study by Genberg et al. [44]. In addition, sawdust was collected from various C_3 tree species and $\delta^{13}\text{C}$ was

measured in order to establish reliable values of $\delta^{13}\text{C}$ in biogenic aerosols and aerosols arising from the burning of plants. However, it should be noted that isotope fractionation may occur between the raw biomass fuel and the aerosol produced by biomass combustion [91,117,118]. Samples of particles collected on filters and the sampled sawdust were treated similarly. An area of the filter corresponding to 10-50 μg carbon, and 100-300 μg sawdust was placed in separate tin capsules. Due to the limited amount of aerosol material, only single samples were analyzed, while triplicate sawdust samples were analyzed. The $\delta^{13}\text{C}$ of the samples was analyzed at the IRMS laboratory at the Department of Biology, Lund University. The measurement uncertainty was estimated to be $\pm 0.2\%$. Source-specific values of $\delta^{13}\text{C}$ were estimated based on the $\delta^{13}\text{C}$ measurements of the sawdust samples and a comprehensive literature study. These are known as endmembers.

The endmember values and the variations in $\delta^{13}\text{C}$, ^{14}C and levoglucosan-to-EC ratios were inserted into a Markov Chain Monte Carlo (MCMC) model [119,120]. The levoglucosan-to-EC ratio is used as it provides a measure of the amount of levoglucosan emitted per unit of EC. This ratio is available in the literature [121,122], and was used to establish the endmember distribution of this parameter. The values obtained from the analysis of the filter samples were then inserted into the model. Calculations were performed in Matlab, using 100 000 iterations for each sample, providing the best estimated median contribution of each source. Two model runs were compared: a three-component model including $\delta^{13}\text{C}$ data (MCMC3) and a two-component model excluding $\delta^{13}\text{C}$ data (MCMC2), in order to estimate the effect of $\delta^{13}\text{C}$ on source apportionment.

The $\delta^{13}\text{C}$ of the collected aerosols varied between -26.73‰ and -25.64‰, with a mean of -26.16‰ during the whole sampling period. Figure 10 shows the range of $\delta^{13}\text{C}$ during the different seasons. Aerosols were more enriched in $\delta^{13}\text{C}$ during the colder months (fall, winter and spring), than in the summer. The summer season also exhibits the greatest spread in $\delta^{13}\text{C}$ values, ranging from -26.73‰ to -25.85‰. This spread can be explained by the dominating emissions of the biogenic SOA, resulting from abundant C_3 plant species, which will probably have varying $\delta^{13}\text{C}$ values (Figure 5). However, it should be noted that the small seasonal differences in $\delta^{13}\text{C}$ are somewhat blurred due to the relatively large uncertainty of 0.2‰ in the IRMS measurements. The mean of the $\delta^{13}\text{C}$ values obtained from sawdust from C_3 tree species was -27.12‰, with a standard deviation of 1.2‰, and were in agreement with the $\delta^{13}\text{C}$ values of C_3 plants obtained from literature data.

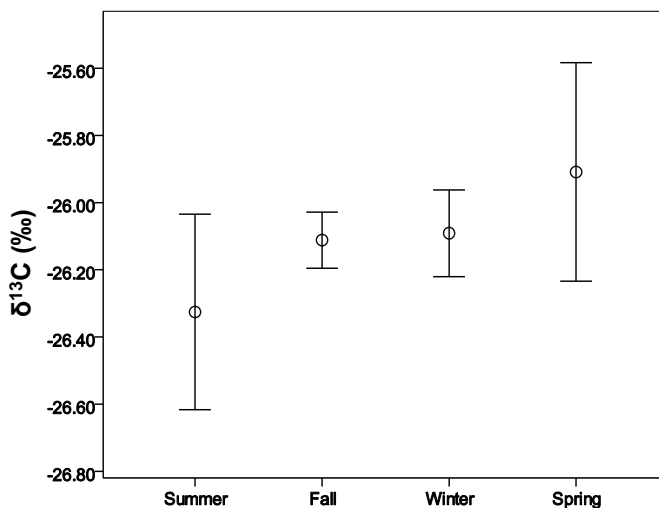


Figure 10.

Seasonal $\delta^{13}\text{C}$ values obtained from the analysis of aerosol samples collected at the Vavihill measurement station. Open circles display means, error bars display one standard deviation.

The $\delta^{13}\text{C}$ enrichment of aerosols during the colder months probably indicates the increased impact of fossil fuel combustion on ambient aerosols. In order to investigate the source contribution to the aerosols, a Markov Chain Monte Carlo model was used, as described above. During the summer, biogenic sources dominate (68%) the contribution of carbon to the carbonaceous aerosol, while fossil and biomass burning were minor contributors (11 and 21%, respectively). During the colder months, the biogenic emissions were significantly reduced (29-56%), while source contributions from fossil fuel and biomass burning increased (19-30% and 19-41, respectively). Air mass trajectory analysis showed that most of the sampled air masses (80%) originated from the north or west. Air masses from these directions had significantly higher emissions from biogenic sources than those from other directions.

Comparing the source contributions obtained using the two MCMC models, with $\delta^{13}\text{C}$ (MCMC3; $\delta^{13}\text{C}$, F^{14}C and levoglucosan) and without $\delta^{13}\text{C}$ (MCMC2; F^{14}C and levoglucosan), showed that including $\delta^{13}\text{C}$ led to minor insignificant changes to the apportionment, and it was concluded that the levoglucosan-to-EC ratio and F^{14}C are sufficient source indicators. The main issue of using $\delta^{13}\text{C}$ in rural areas, like the Vavihill measurement station, is that one of the dominating carbonaceous aerosol sources, the biogenic sources (i.e. C_3 plants), exhibits $\delta^{13}\text{C}$ source values totally overlapping those from burning of C_3 plants. Hence, as long as the biogenic aerosol and the biomass fuel are derived from plants with the same metabolic pathway, $\delta^{13}\text{C}$ cannot differentiate between biogenic and biomass burning.

Elemental carbon isolation using supercritical CO₂ extraction-Paper IV

Isolation of true EC followed by radiocarbon analysis for accurate source apportionment of the combustion aerosol is not feasible with current thermo-optical methods, due to the problem of charring of OC. Supercritical CO₂ extraction was evaluated in this work (Paper IV) with the aim of circumventing the problem of charring and isolating EC for further analysis.

Total suspended particles (all size classes of particles) were sampled on quartz fiber filters (Ø=102 mm, A=82 cm²) on the roof of the Physics Department at Lund University during September and October 2014. Areas measuring 2 cm² were punched out for scCO₂ extraction of OC. A screening experiment was conducted in order to evaluate which parameters in the extraction had the greatest impact on the removal of OC and pyrolytic OC, while maintaining a high recovery of EC. The amounts of OC, pyrolytic OC and EC were determined on 0.5 cm² sub-samples of the extracted filter punches by thermo-optical analysis, and then compared to untreated filter punches that had not been subjected to scCO₂ extraction. From these screening experiments it was discovered that scCO₂ with the addition of 10% methanol was the most efficient combination for the removal of OC and pyrolytic OC.

The temperature and pressure of the process were then optimized in order to extract the maximum amount of OC and pyrolytic OC. It was found that a temperature of 60°C and a pressure of 350 bar allowed complete removal of pyrolytic OC, 59% removal of total OC and an EC recovery of 78%. Hence, scCO₂+methanol extraction has the potential to circumvent the charring problem often encountered in the thermo-optical analysis of atmospheric aerosol filter samples. It should thus be possible to remove all the OC and pyrolytic OC from a filter sample by scCO₂+methanol extraction, followed by thermo-optical analysis. This would allow radiocarbon measurements to be made on a better-defined EC fraction, providing more accurate source apportionment of the combustion aerosol.

Connecting surface categories to aerosol chemical compounds-Paper V

During the summer months, carbonaceous background aerosols are dominated by biogenic sources. It has been estimated that 74-80% of the total carbon mass in samples collected at the Vavihill measurement station during the summer

originated from biogenic sources [44,45]. The apportionment was found to be similar in the present work (68-75%) (Papers II and III). Despite this large contribution during the summer, the biogenic sources that contribute most have not been extensively investigated. It is known that the emission of isoprene accounts for 70% of the total BVOC emissions globally, and is probably a key precursor in the formation of BSOAs [123]. Monoterpenes are probably equally important as isoprene, particularly in temperate zones, as in Scandinavia, where large boreal forests emit α -pinene and other monoterpenes [124,125].

BSOAs are made up of oxidation products of BVOCs and include several thousand different chemical compounds. Dicarboxylic acids are some of the more common compounds that can be found in BSOAs, and have been found to constitute up to 10% of the total carbon mass [126,127]. Organosulfates (OSs) and nitrooxy organosulfates (NOSs) have recently attracted increased attention due to their potential as tracers for atmospheric ageing in polluted air masses [97-101]. Like dicarboxylic acids, OSs and NOSs can constitute a considerable fraction of the carbonaceous aerosol mass concentration [128].

In order to investigate the effects of surface type on BSOA, nine carboxylic acids, eleven OSs and two NOSs were analyzed in aerosol filter samples obtained from the Vavihill measurement station during June-July 2012 by using a high-volume filter sampler with a PM₁-inlet. The time resolution of the sampled filters was 24 hours. The FLEXPART model was then used to calculate the dispersion of the aerosol 3, 5 and 7 days back in time. A footprint was determined by calculating the aggregated residence time of all simulated particles below the atmospheric boundary layer in a 0.2°x0.2° spatial box. The footprint was then superimposed on a high-resolution map containing 44 land surface categories defined by the European land monitoring service, Copernicus [129]. A category called “sea and ocean” was added to account for air masses exposed to marine environments.

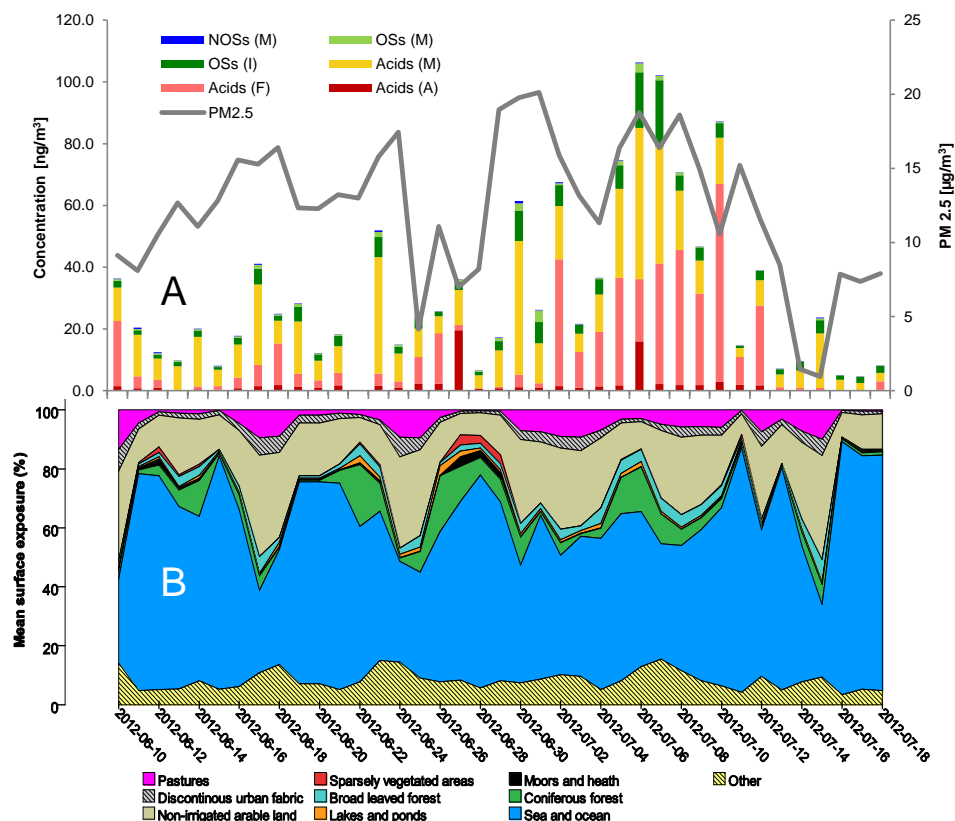


Figure 11.

Top panel (A) shows total concentrations of the measured carboxylic acids, organosulfates (OSs) and nitrooxy organosulfates (NOSs) in PM_{10} filter samples collected at the Vavihill measurement station. The thick gray line displays the $\text{PM}_{2.5}$ concentration. Capital letters in parentheses in the legend refer to the precursor class of the BSOA compounds: A=Anthropogenic, F=Fatty acid, I=Isoprene and M=Monoterpenes. Lower panel (B) shows FLEXPART generated 3-, 5-, and 7-day back-trajectories of the mean exposure of the arriving air masses to the nine surface categories considered with the greatest mean exposure. The category “other” represents the remaining 34 surface categories.

Figure 11A shows the 24-hour mass concentrations of the measured BSOA compounds, grouped into suggested precursor classes. Figure 11B shows the exposure of the aerosol to the nine surface categories with the largest average exposure. The category “other” represents the remaining 34 categories. The “sea and ocean” category dominated the exposure, averaging of 56% of the total exposure. The category “non-irrigated arable land” was also a major contributor to the exposure (average, 19%). Based on the results presented in Figure 11 it appears that exposure to “coniferous forest” is associated with a positive response in several of the observed BSOA compounds, mainly those derived from monoterpenes (denoted M in Figure 11A).

The relation between exposure to various surface categories and measured BSOA compounds was assessed through principal component analysis. A four-component solution with VARIMAX rotation was chosen, and explained 80% of the total variance. Principal component PC1 explained 49% of the variance in the data. Large contributors to this PC were several of the monoterpene-derived dicarboxylic acids and both monoterpene- and isoprene-derived OSs and NOSs. Coniferous forest was the surface category that contributed most to this PC. Hence, many of the measured BSOA compounds were probably associated with emissions from coniferous forest.

“Sea and ocean”, “non-irrigated arable land” and “pastures” were some of the surface categories that contributed to PC2. However, none of the measured BSOA compounds contributed to this PC, and it can thus be speculated that none of these surface categories contributes to the BSOA mass concentration. PC2 contributed 15% to the variance. The remaining two PCs contributed a total of 16% to the variance, but were more difficult to interpret.

Conclusions

The work described in this thesis was focused on evaluating and testing methods in modern carbonaceous aerosol source apportionment. In the first study (Paper I) it was shown that most of the particles produced by wood burning in a modern well-insulated wood stove had an AAE of 1.0-1.2, which is the same as that for traffic-generated diesel soot. Thus, the aethalometer model, in which it is assumed the wood burning have an AAE>2, may incorrectly apportion a large fraction of biomass burning aerosols as traffic emissions. However, it must be remembered that the use of modern, well-insulated wood stoves is a prerequisite for this false apportionment. It is possible that the use of modern well-insulated (AAE~1.2) and older, poorly insulated wood burning stoves (AAE>2) may lead to a biomass combustion aerosol with a mean AAE of 2. The measured wood stove emissions also serve as an emission inventory that can be used by modelers to estimate local, regional and global wood stove emissions.

The aethalometer model for source apportionment was applied to measurements conducted over a complete year at the Vavihill measurement station. When comparing the aethalometer model source apportionment to a ^{14}C and levoglucosan source apportionment method it was found that the aethalometer model performed well when estimating wood burning and the biogenic carbonaceous aerosol. However, it overestimated the fossil/traffic carbonaceous aerosol by a factor 1.3 throughout the whole year.

The potential of $\delta^{13}\text{C}$ to improve source apportionment of the whole carbonaceous aerosol (TC) was also investigated. The measured $\delta^{13}\text{C}$ overlapped with the $\delta^{13}\text{C}$ distributions from 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 had lower $\delta^{13}\text{C}$ than those in the colder period of the year. This is in accordance with the increased use of fossil fuels during the colder months, which have a higher $\delta^{13}\text{C}$ value.

A comparison of two Markov Chain Monte Carlo source apportionment models, with and without $\delta^{13}\text{C}$, showed that $\delta^{13}\text{C}$ had an insignificant impact on the results. $\delta^{13}\text{C}$ therefore appears to make a limited, if any, contribution to the source apportionment of the total carbon in rural areas. However, the contribution and

usefulness of $\delta^{13}\text{C}$ may be greater in urban areas, where fossil fuel combustion has a higher impact and biogenic emissions a lower impact. The analysis of $\delta^{13}\text{C}$ may provide a complement to, or a substitute for, the more expensive and time-consuming ^{14}C measurements when studying aerosols in urban areas.

The origin of the combustion aerosol can be determined by measuring the amount of ^{14}C in the combustion-derived carbonaceous fraction, (i.e. EC). However, the isolation of EC is not trivial since some OC is pyrolyzed leading to “artificial” EC in thermo-optical analysis. A method was developed using supercritical CO_2 with 10% methanol to extract OC, and more importantly, to extract the OC fraction susceptible to charring, pyrolytic OC. All the pyrolytic OC could be extracted, while maintaining an EC recovery of 78%. This technique has the potential to improve source apportionment of the combustion aerosol.

Land use and spatial vegetation patterns have an impact on the biogenic aerosol. An investigation was carried out to determine which surface types contributed most to the chemical compounds found in the BSOA. Several of the measured compounds were influenced by air mass exposure to coniferous forest, indicating that α -pinene is an important precursor in the BSOA. It was also concluded that air mass exposure to marine and agricultural environments did not influence the compounds found in the BSOA.

Outlook

Some new methods and techniques have been developed and evaluated for the more accurate source apportionment of the carbonaceous aerosol, however, this work must be continued.

Source apportionment based on radiocarbon and levoglucosan measurements is time-consuming, labor-intensive and expensive. Faster, inexpensive source apportionment methods, such as the aethalometer model, are therefore preferable. However, further investigations are required to assess how well such methods perform in the source apportionment of fossil/traffic-related carbonaceous aerosol in rural areas.

Pre-treatment with supercritical CO₂ with the addition of methanol may provide a means of removing pyrolytic OC. This would be very useful as a means of separating EC, and to allow further investigations of the sources of EC through ¹⁴C measurements.

The relation between land use and air quality can be investigated through measurements and modelling. Changes in the distribution of various kinds of vegetation can be expected as a result of the increase in global temperature. Future research questions should address how changes in land use due to climate change will affect aerosol composition and sources, and whether these changes will have further effects on the climate or human health.

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