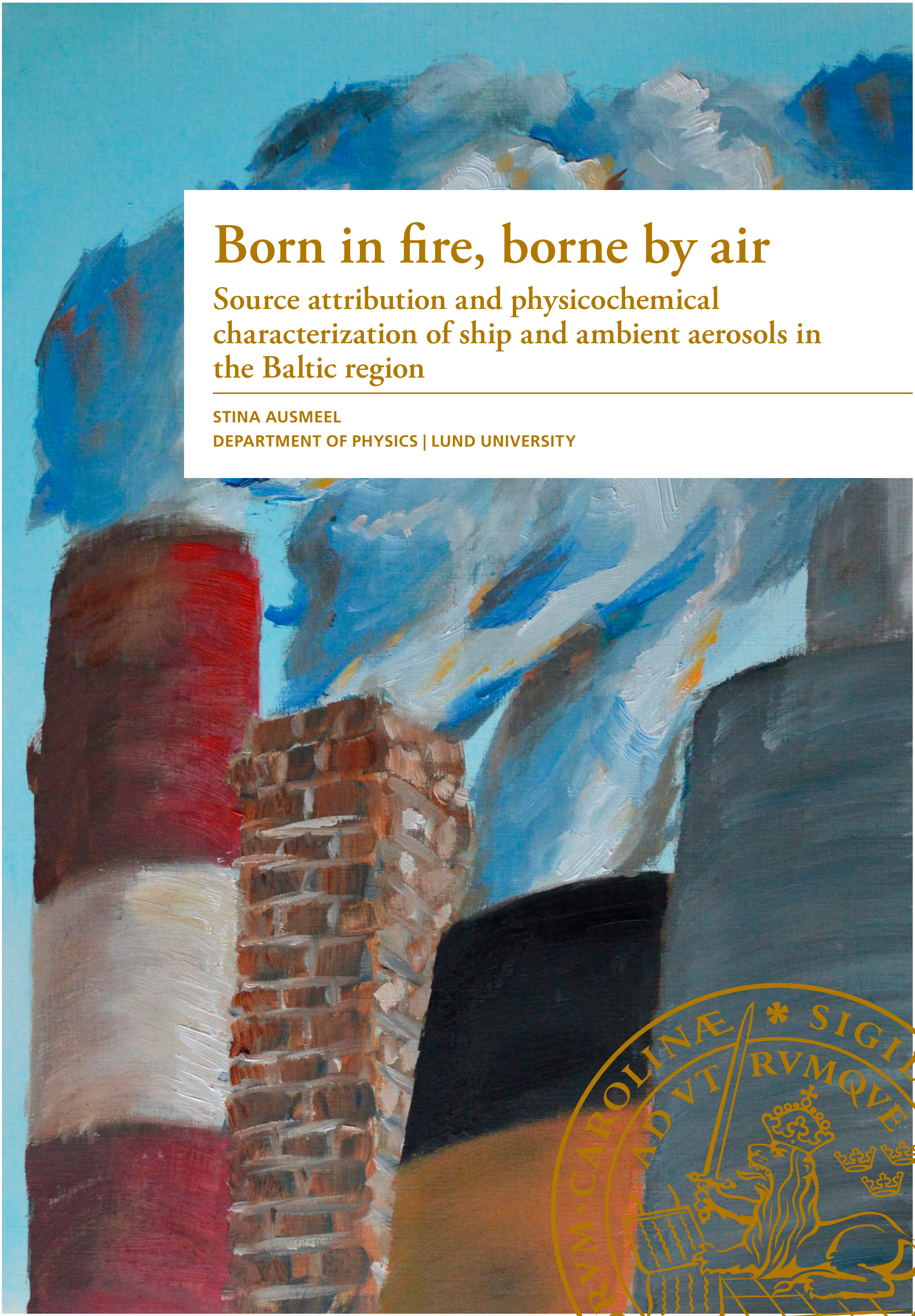
Born in fire, borne by air

Source attribution and physicochemical characterization of ship and ambient aerosols in the Baltic region

Ausmeel, Stina

2020

Citation for published version (APA):
Ausmeel, S. (2020). *Born in fire, borne by air: Source attribution and physicochemical characterization of ship and ambient aerosols in the Baltic region*. Division of nuclear physics, Department of Physics, Lund University.



Born in fire, borne by air

Source attribution and physicochemical characterization of ship and ambient aerosols in the Baltic region

---

STINA AUSMEEL

DEPARTMENT OF PHYSICS | LUND UNIVERSITY

Born in fire, borne by air

Source attribution and physicochemical characterization of ship and ambient aerosols in the Baltic region

Stina Ausmeel

LUND
UNIVERSITY

DOCTORAL DISSERTATION
by due permission of the Faculty of Engineering, Lund University, Sweden.
To be defended in the Rydberg Lecture Hall,
Department of Physics, Professorsgatan 1, Lund.
Friday, April 17th 2020, at 09:15 a.m.

Faculty opponent
Dr. Martin Gysel Beer, Laboratory of Atmospheric Chemistry,
Paul Scherrer Institute, Switzerland

Organization LUND UNIVERSITY Department of Physics Division of Nuclear Physics Author: Stina Ausmeel	**Document name** Doctoral dissertation **Date of issue** 2020-03-24 Sponsoring organization

Title and subtitle: Born in fire, borne by air: Source attribution and physicochemical characterization of ship and ambient aerosols in the Baltic region

Abstract

Aerosol emissions from anthropogenic activities cause detrimental health effects and affect the climate system. Combustion is a large source of airborne fine particulate matter (PM$_{2.5}$) and the uncertainties of the climate role of these emissions are still large. A good understanding of the microphysical properties of aerosols from various sources and their atmospheric aging is essential for accurate assessment of the health and climate impact. It is also important to follow up legislative actions aimed at reducing emissions, with ambient observations. The overall aim of this thesis is to present results from field observations of aerosols from combustion sources, and contribute to the general knowledge on the particle concentrations and physicochemical properties in the Baltic region.

Ship and traffic emissions were investigated in detail in several field campaigns in Sweden. Soot, or black carbon, was specifically measured with several different measurement techniques. Other aerosol components were also monitored, including gaseous species, organic matter, and sulfate, which is of specific interest in ship emission characterization. Additionally, source apportionment of the carbonaceous aerosol from a field campaign in northern Poland is presented, which adds to the knowledge about black carbon emissions in a polluted part of Europe.

The absorbing equivalent black carbon emission factor (EF$_{eBC}$) was measured for over 300 fresh ship plumes in a Port within a sulfur emission control area. EF$_{eBC}$ had decreased by 30 %, from 0.48±0.81 to 0.34±0.40 g(kg fuel)$^{-1}$ between 2014 and 2015 after a reduction of fuel sulfur content. If such a reduction is expected as marine fuel quality is improved, this can have important implications also outside emission control areas, as a global sulfur cap is implemented. A more complete physicochemical characterization and simulated aging of ship plumes of an age between about 20 and 30 minutes was performed at a coastline, and the contribution of one shipping lane to local aerosol concentration was quantified. Novel methods to tie plumes to individual ships and to estimate contribution to coastal exposure were developed. Ships contributed as much as 10-18 % of ultrafine particles at the coast, but only about 1 % or less (40 ng m^{-3}) to local PM. Non-refractory PM$_1$ was mainly organics and sulfate (56 and 36 %, respectively), and the average eBC contribution was 3.5±1.7 ng m^{-3}. The absorption Ångström exponent of the plume eBC was close to unity, indicating black (BC) rather than brown carbon (BrC). Oxidation flow reactor treatment of the aerosol was performed, resulting in occasionally strong increase in secondary aerosol mass.

The ambient aerosol and its BC fraction was characterized in an urban and rural environment in southern Sweden, and the transport of the aerosol between these nearby sites was investigated. The conclusion was that there was 2.2-2.5 times higher BC mass and up to four times higher BC number concentration at the urban site. Additionally, the soot particles in the city were slightly smaller and less coated. The influence of an urban plume at the rural site was possible to detect and quantify during specific meteorological conditions. The regional background dominated the total aerosol contribution, and was largely due to southeastern air masses.

A quantification of particle sources in Polish air is lacking. Winter field campaign data from northeastern Poland showed that domestic coal combustion, domestic wood combustion and traffic contributed 41, 21, and 38 % respectively to carbonaceous particulate matter. The three sources were separated using a combination of apportionment methods based on aerosol absorption properties and chemical markers.

Generally, the eBC concentrations were approximately twice as high in Poland as in Sweden, and twice as high in a Swedish city compared to a rural background site. Emissions from a large shipping lane were not a large source of eBC at the coastal sampling site. However, despite the relatively good air quality in Sweden, air pollution is still above the environmental quality objectives, and of importance to health locally, and climate in general.

Key words: anthropogenic air pollution, aerosol, black carbon, plumes, ship emissions, absorption, source apportionment, climate

Classification system and/or index terms (if any)

Supplementary bibliographical information		**Language: English**
ISSN and key title		**ISBN** 978-91-7895-470-4 (print) 978-91-7895-471-1 (pdf)
Recipient's notes	**Number of pages: 81**	Price
	Security classification	

I, the undersigned, being the copyright owner of the abstract of the above-mentioned dissertation, hereby grant to all reference sources permission to publish and disseminate the abstract of the above-mentioned dissertation.

Signature   Date 2020-03-09

Born in fire, borne by air

Source attribution and physicochemical characterization of ship and ambient aerosols in the Baltic region

Stina Ausmeel

LUND
UNIVERSITY

Cover by Michael Persson

Faculty of Engineering
Department of Physics
Lund University

ISBN 978-91-7895-470-4 (print)
ISBN 978-91-7895-471-1 (pdf)

Printed in Sweden by Media-Tryck, Lund University
Lund 2020

Media-Tryck is a Nordic Swan Ecolabel
certified provider of printed material.
Read more about our environmental
work at www.mediatryck.lu.se
MADE IN SWEDEN

All we have to decide
is what to do with the time that is given to us.

Gandalf

Table of Contents

Populärvetenskaplig sammanfattning

I Sverige så är antalet aerosolpartiklar i luften oftast runt 500-10 000 per kubikcentimeter. En kubikcentimeter är ungefär lika stort som en sockerbit, eller en speltärning. Det betyder att du i varje andetag andas in mer än en miljon partiklar. Detta kan nästan uppfattas som en overklig siffra. Vi märker ju ingenting? Om vi då istället befinner oss i en förorenad storstad så kan vi räkna med minst tio gånger så många partiklar i varje andetag! Partiklarna som håller sig 'svävande' i luften utan att falla ner till marken, så att vi kan andas in dem, är nämligen mycket små. Upp till tiotals mikrometer (miljondels meter) i diameter är de aerosolpartiklar som finns i atmosfären och i inomhusluften. Så mängden partiklar i en kubikmeter luft motsvarar alltså en massa på några få, upp till några hundra, mikrogram.

Trots att vi för det mesta inte märker partiklar i luften, så påverkar de oss och vår omgivning. I varje andetag fastnar en andel av partiklarna i luftvägarna och kan orsaka hälsoproblem. Runt 790 000 människor dör i förtid i Europa varje år till följd av sjukdomar orsakade av luftföroreningar. Två av tre personer i EU bor i städer som överskrider världshälsoorganisationen WHO:s riktlinjer för luftkvalitet. Partiklarna påverkar även jordens klimat genom att växelverka med solljuset och genom att bilda moln. Förenklat kan man säga att vissa partiklar bidrar till att sprida tillbaka solljuset ut från jorden, som en spegel, medan andra bidrar genom att absorbera ljuset och värma atmosfären. Partiklar kan alltså både ha en kylande och en värmande effekt på klimatet beroende på deras kemiska och fysiska egenskaper. Enligt FN:s klimatpanel, IPCC, så är klimateffekter från aerosoler och moln det som vi är mest osäkra kring, jämfört med till exempel effekter från växthusgasen koldioxid. Därför är det viktigt att förstå partiklars olika egenskaper, eftersom dessa i sin tur styr hur hälsa och klimat påverkas.

Av samma anledning som små partiklar är svåra för oss att upptäcka med blotta ögat, så krävs det också speciella metoder för att studera dem. Det blir inte enklare av att atmosfären består av partiklar från massvis av olika källor, som blandas och sedan transporteras med vädersystem runt jorden. På vägen så kommer partiklarnas egenskaper att ändras genom processer i atmosfären. För att förstå partiklarnas kemiska innehåll mäter man med flera olika instrument, deras diameter mäts med ytterligare andra instrument, och så vidare. Därför har vi använt flera olika mätmetoder i studier av atmosfärspartiklar, som kompletterar varandra för att ge en så omfattande bild som möjligt av vilka partiklar människan släpper ut, deras form, kemi, koncentration, och ursprung.

Partiklarna som främst studeras och beskrivs i denna avhandling kommer från olika typer av förbränning. Utsläppen har orsakats av mänsklig aktivitet, såsom uppvärmning, transport och energianvändning. Två studier har gjorts på utsläpp från skeppstrafik, en studie har gjorts på trafikutsläpp i Malmö och partiklar på landsbygden i Skåne, och en studie har gjorts på olika organiska partiklar och sotkällor som transporteras till landsbygden i Polen.

I den första artikeln (Paper I), så beskrivs hur vi mätte utsläpp av sot från skepp i inloppet till Göteborgs Hamn. Målet med studien var att mäta sot under två perioder, före respektive efter att svavelhalten i bränsle begränsades i januari 2015. Genom att mäta både sot och koldioxid i realtid med hög tidsupplösning, så kunde vi urskilja enskilda avgasplymer från skeppen. Från dessa plymer kunde vi räkna ut hur mycket sot per enhet bränsle som varje skepp släpper ut (skeppets sotemissionsfaktor). Det vi såg från observationer av 346 skeppsplymer var att medelemissionsfaktorn minskade med 29 %. Exakt varför sotet minskar när svavelhalten i bränslet minskar vet vi inte säkert, men det beror troligtvis på en generell övergång till andra typer av renare bränslen, med högre kvalitet än tidigare typiska skeppsbränslen. En annan slutsats var att de flesta skepp hade en relativt låg emissionsfaktor, medan några få hade markant större utsläpp. De 10 % av skeppen som hade högst emissionsfaktorer bidrog till runt 37 % av sotet.

I den andra och tredje artikeln (Paper II och III), beskrivs hur vi mätte aerosoler från skepp vid kusten, i Falsterbo i Skåne. Till skillnad från artikel I som handlade om skeppsutsläppens egenskaper, så ville vi med denna studie mäta hur skeppstrafiken påverkade de faktiska halterna som människor som bor nära kusten påverkas av. I detta fall var skeppen längre bort (mellan 7 och 20 km) från mätutrustningen än i Göteborgs Hamn (runt 500 m). Detta gjorde det svårare att urskilja enskilda plymer för vissa ämnen, t.ex. koldioxid. Partikelantalshalten var den variabel som tydligast visade på skeppsplymer, och korrelerade väl med förutspådda plympassager som fås fram med hjälp av skeppspositions- och vinddata. För att beräkna bidraget av ämnen som inte ökade synligt i koncentration vid passage av en skeppsplym, så togs en metod fram för att plocka ut tidsperioder med, respektive utan, skeppspåverkan. Skillnaden mellan dessa användes för att uppskatta individuella skepps bidrag till bland annat lokala sotnivåer. Under våra mätningar 2016, så bidrog skeppstråket utanför Falsterbo (där en stor del av skeppsflottan som åker genom Öresund in till Östersjön passerar) med en ökning på 10-18 % av antalet partiklar, samt ungefär 1 % av totala partikelmassan (partiklar mindre än 0,5 mikrometer) och 2 % av sotmassan. Skeppstråket utanför

Falsterbo bidrar alltså inte till en stor andel av partikelmassan i luften. Främst beror detta på att de uppmätta partiklarna är mycket små, dvs många till antalet men liten massa. Om dessa partiklar växer under transport längre inåt land så kan bidraget bli större. Samt, i denna studie undersöks ett enskilt skeppsstråk. Den totala luftföroreningen från skepp är större på grund av utsläpp från skepp på andra platser. I skeppsplymer med relativt höga koncentrationer, så bestod de till största del av svavelhaltiga och organiska ämnen. Resultaten som presenteras i denna avhandling bidrar till den större vetenskapliga förståelsen av skeppsutsläpp på olika sätt. Dels, så får vi från dessa observationer bättre mätdata på hur stora partikelutsläppen är i denna typ av miljö, vilket inte har varit känt innan men är relevant för både miljö och hälsoeffekter. Dels, kan mätresultaten användas för att jämföra med och bekräfta resultaten från modellberäkningar av skeppsutsläpp i Östersjöområdet.

Trafik är en stor källa till luftföroreningar, både globalt och med lokal påverkan för de människor som bor och befinner sig i städer .I den fjärde artikeln (Paper IV) så ges en detaljerad beskrivning av trafikutsläppens egenskaper i stad och på landsbygd. I detta fall, så gjordes mätningar på två platser, i Malmö och i en skog på Skånes landsbygd, med runt 60 km avstånd mellan. Under rätt meteorologiska förutsättningar gick det att studera partiklarna från Malmös kemiska och fysiska egenskaper då de nådde fram till landsbygdmätningarna. Massan av sot i luften var ungefär dubbelt så hög i staden som på landsbygden, och antalet sotpartiklar var upp till fyra gånger högre i stadsmiljön under rusningstrafik. En slutsats är att även om närliggande städer påverkar luftmiljön på den svenska landsbygden, så har transport av luftföroreningar från övriga Europa störst påverkan.

I den femte artikeln (Paper V) så mätte vi sot, och dess absorption av ljus vid olika våglängder. Våglängdsberoendet kan kopplas till olika sotegenskaper, vilket i sin tur kan kopplas till olika sotkällor och källor av organiska partiklar. Främst kan man skilja på sot från fossila trafikkällor (t.ex. diesel), och sot från förbränning av biomassa (t.ex. ved) och koleldning i hushåll. Från filterprover som samlades in under vintertid, och analyserades i Polen, så kunde markörer för förbränning av biomassa identifieras och kvantifieras. I kombination med ljusabsorption kunde därmed tre olika källor för sot och organiska partiklar separeras; trafik (38 %), biomassa (21 %) och kol (41 %). I denna del av Europa kommer alltså den största delen av dessa partiklar från hushållseldning av kol och biomassa, som används till matlagning och uppvärmning av bostäder.

Problem med luftföroreningar återstår. Och eftersom de kan transporteras mellan länder och från skepp långt ute på haven, så krävs internationella samarbeten för att minska utsläppen. Detta är en stor utmaning, men vi kan också se tillbaka på framgångsrika samarbeten kring att skydda människa och miljö. Ett exempel är förbudet av ozonnedbrytande freoner, som gjort att ozonhålet över Antarktis återhämtar sig, samt krafttag mot svavelutsläpp som gör att orden ’surt regn’ inte längre toppar rubriker om miljöproblem. I tider av oro, med politisk instabilitet, hot mot mänskliga rättigheter och dramatiska effekter av klimatförändringar såsom extremväder, översvämningar och skogsbränder, så är det inte så konstigt att mer osynliga och långsamt smygande faror, såsom miljöeffekter av luftburna partiklar, inte alltid prioriteras högt. Men likväl finns de där. Och trots att det finns många hål att laga i den läckande båten *SS Mänskligheten*, så har flera redan täppts igen. Och om vi, med olika expertis och resurser, hjälps åt med att täppa, ösa, och styra båten, så kommer vi nog kunna segla med full fart in i en ljusare framtid. Skepp-o-hoj!

Papers included in this thesis

I. **Ausmeel, S.**, Hallquist, Å., Thomson, E., Jalkanen, J.-P., Kristensson, A.: Observed Reduction in Equivalent Black Carbon Emission Factors from Ships Within a Sulfur Emission Control Area. Under revision, *Geophysical Research Letters*.

II. **Ausmeel, S.**, Eriksson, A., Ahlberg, E., Kristensson, A.: Methods for identifying aged ship plumes and estimating contribution to aerosol exposure downwind of shipping lanes. *Atmospheric Measurement Techniques* 2018, 12, 4479-4493, DOI: 10.5194/amt-12-4479-2019.

III. **Ausmeel, S.**, Eriksson, A., Ahlberg, E., Sporre, M. K., Spanne, M., Kristensson, A.: Ship plumes in the Baltic Sea Sulfur Emission Control Area: Chemical characterization and contribution to coastal aerosol concentrations. Under revision, *Atmospheric Chemistry and Physics Discussions*, DOI: 10.5194/acp-2019-1016.

IV. Ahlberg, E., **Ausmeel, S.**, Spanne, M., Roldin, P., Kristensson, A., Pauraite, J., Swietlicki, E., Eriksson, A.: Summertime Traffic and Long Range Soot Properties Observed at Urban and Rural Sites in Southern Sweden. Manuscript in preparation.

V. Kristensson A., **Ausmeel, S.**, Pauraite, J., Eriksson, A., Ahlberg, E., Byčenkienė, S., Degórska, A.: Source contribution to rural carbonaceous winter aerosol in north-eastern Poland. *Atmosphere* 2020, 11, 263, DOI:10.3390/atmos11030263.

Author's contribution to the papers

I. I was responsible for the MAAP-eBC measurements in 2015 together with A.K. I performed the analysis of the aerosol data (except for the AIS ship identification) and wrote the paper with minor contributions from the co-authors.

II. I participated in the planning and set-up of the measurements, and was the operational project manager of the summer campaign. I carried out the measurements together with the other authors. I performed the analysis of the aerosol data and developed the method to identify ship contribution without visible plume particle mass contribution (except for the development of the AIS/wind plume encounter method). I wrote most of the paper, with major contributions from co-authors to the section 3.1.

III. I participated in the planning and set-up of the measurements, and was the operational project manager of the summer campaign. I carried out the measurements together with the other authors. I performed the analysis of the aerosol data (except for oxidation flow reactor data). I wrote most of the paper, with major contributions from co-authors to the section 3.5.

IV. I assisted with the aerosol measurements, both during the intensive campaign at the urban site, and continuous instrument service at the rural site. I performed most of the APM measurements and data analysis. I performed most of the SP-AMS data analysis and performed the plume analysis of the particle size distribution and organic aerosol. I wrote the parts of the manuscript concerning APM and SP-AMS.

V. I prepared the aethalometer data from Poland for analysis and assisted in interpreting the results. I did most of the literature search and wrote the introduction section and the section on meteorological influence.

Other publications

Peer-reviewed papers not included in the thesis

Ahlberg, E., **Ausmeel, S.**, Eriksson, A., Holst, T., Karlsson, T., Brune, W. H., Frank, G., Roldin, P., Kristensson, A., Svenningsson, B.: No particle mass enhancement from induced atmospheric ageing at a rural site in northern Europe. *Atmosphere* 2019, 10(7), DOI: 10.3390/atmos10070408.

Ausmeel, S., Andersen, C., Nielsen, O. J., Østerstrøm, F. F., Johnson, M. S., Nilsson, E. J.K.: Reactions of Three Lactones with Cl, OD, and O_3: Atmospheric Impact and Trends in Furan Reactivity. *Journal of Physical Chemistry A* 2017, 121, 21, p. 4123-4131, DOI: 10.1021/acs.jpca.7b02325.

Andersen, C., Nielsen, O. J., Østerstrøm, F. F., **Ausmeel, S.**, Nilsson, E. J.K., Sulbaek Andersen, M. P.: Atmospheric Chemistry of Tetrahydrofuran, 2-Methyltetrahydrofuran, and 2,5-Dimethyltetrahydrofuran: Kinetics of Reactions with Chlorine Atoms, OD Radicals, and Ozone. *The Journal of Physical Chemistry A* 2016, 120, 37, p. 7320-7326, DOI: 10.1021/acs.jpca.6b06618.

Conference abstracts as lead author

Ausmeel, S., Kristensson, A., Eriksson, A, Ahlberg, E., and Degórska, A.: Invariable source contribution to wintertime rural aerosol in Warmia-Mazuria, Poland. European Aerosol Conference, 2019.

Ausmeel, S., Eriksson, A., Ahlberg, E., Roldin, P., Kristensson, A., Bjerring Kristensen, T., Elbæk Nielsen, I., Klenø Nøjgaard, J., Spanne, M., Swietlicki, E.: Simultaneous Soot Particle Aerosol Mass Spectrometer Measurements at Urban and Rural Sites for Investigation of the Physicochemical Properties of Traffic Emissions. European Aerosol Conference, 2019.

Ausmeel, S., Kristensson, A., Ahlberg, E., Kling, K., Eriksson, A., Spanne, M.: Ambient ship aerosol measurements around the Baltic Sea – An overview. Shipping and the environment, 2017.

Ausmeel, S., Kling, K., Ahlberg, E., Spanne, M., Eriksson, A., Kristensson, A.: Coastal measurements and characterization of one hour old ship plumes. European Aerosol Conference, 2017.

Ausmeel, S., Kristensson, A., Ahlberg, E., Eriksson, A., Hansson, A., Mattson, A., Spanne, M.: Ship emissions of particles and their health effects in Sweden – A pilot study in Falsterbo. 13th Informal Conference on Atmospheric and Molecular Science, 2016.

Ausmeel, S., Kristensson, A., Psichoudaki, M., Faxon, C., Kuuluvainen, H., Thomson, E., Eriksson, A., Mellqvist, J., Pettersson, J., Hallquist, Å., Svenningsson, B., Hallquist, M.: Black carbon emission factors from shipping. Nordic Society for Aerosol Research Symposium, 2016.

Symbols and abbreviations

λ	wavelength
σ_{abs}	light absorption coefficient
AAE	absorption Ångström exponent
AIS	automatic identification system
BC	black carbon
BrC	brown carbon
CM	carbonaceous matter
CO_2	carbon dioxide
eBC	equivalent black carbon
EC	elemental carbon
EEPS	engine exhaust particle sizer
EF	emission factor
HFO	heavy fuel oil
HYSPLIT	Hybrid Single Particle Lagrangian Integrated Trajectory Model
IMO	International Maritime Organization
LAC	light absorbing carbon
LNG	liquefied natural gas
MAAP	multi angle absorption photometer
MAC	mass-specific absorption cross section
MDO	marine diesel oil
MGO	marine gas oil
m/z	mass-to-charge ratio

NECA	NO_x emission control area
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
OA	organic aerosol
OC	organic carbon
OM	organic aerosol mass
PAH	polycyclic aromatic hydrocarbon
PAM-OFR	potential aerosol mass oxidation flow reactor
PM	particulate matter
PM_X	The total particulate matter with a diameter less than x µm
rBC	refractory black carbon
RF	radiative forcing
SECA	sulfur emission control areas
SO_2	sulfur dioxide
SO_4^{2-}	sulfate
SOA	secondary organic aerosol
SMPS/DMPS	scanning (or differential) mobility particle sizer spectrometer
SP2	single particle soot photometer
SP-AMS	soot particle aerosol mass spectrometer
UFP	ultra fine particles
VOC	volatile organic compound

Background and aim

During the past hundred years, there has been a dramatic increase in human population and change in lifestyle, due to industrialization and technological development. This has been accompanied by an increasing energy demand for production, transportation, and other activities thought to increase and maintain living standards. This has, among other things, resulted in air pollution problems, mainly due to emissions from industries and the transportation sector, which is well known today. The global warming effect and severe smog events are often on the news and a cause of concern worldwide. There are measures being taken to reduce greenhouse gas emissions, and improve air quality, both on international and local levels. To be able to point out important pollutants and sources and to predict future scenarios, a good understanding of the emissions is crucial. One type of air pollution which is relatively difficult to characterize in a simple way is airborne particles, aerosols. Particles in the atmosphere range over a large size span (a few nanometers, 10^{-9} m, up to tens of micrometers, 10^{-6} m). The particles can have various shapes and densities, contain a vast amount of chemical compounds, and after emission they can undergo transformation processes in the atmosphere which alter the original properties. These properties govern the potential impacts on health, climate, and the environment. Hence, the atmosphere, the climate system, and the human body make up complex systems and it is important to research both the whole system, its interactions, and its individual components. In this thesis, the research presented aims to contribute to the knowledge about anthropogenic aerosol emissions. Particularly, the focus has been to quantify particle concentrations and impact on air quality, and to characterize the physicochemical properties of different aerosol sources.

Transportation accounts for a substantial fraction of air pollution emissions. Today, more than 80 % of the global trade volume is transported by ships. In many places, there is an increase in shipping activities in parallel with decreasing emissions from other, land-based transportation sources as these are subject to stricter regulations. Therefore, the relative contribution of ship emissions to the total air pollution becomes higher. Hence, especially in coastal areas, there is a concern regarding the emissions from marine shipping and the impact on air quality. The focus of paper I-III in this thesis is combustion emissions from ships. The aim is to gain more detailed knowledge about the emissions and local aerosol burden from shipping along the coastline in the North and Baltic Seas.

The allowed ship fuel sulfur content has been reduced from 1 % to 0.1 % in the North Sea and Baltic Sea from January 1, 2015. This regulation will most probably result in a change in the aerosol pollution from shipping. An expected change is lower sulfur dioxide and consequently sulfate aerosol levels. But depending on the means to reach these limits, which could be achieved by e.g. switching to other fuels, desulfurizing existing fuels, or by exhaust after-treatment, other aerosol properties might also be affected as a consequence. Therefore, the emissions of black carbon (soot), which is an important component for health and climate effects, have been investigated in a harbor area, before and after the regulation. Many studies in the Baltic region have focused on gaseous pollutants. There is a need for more detailed characterization of ship emissions performed in real-world settings, including particle size distributions as the ship emissions reach coastal areas, particulate matter levels, and chemical composition. The ship emission studies presented in this thesis aim to present quantification and physicochemical characterization of the ambient coastal ship emission aerosol. The results will give an estimate of the contribution of shipping to the local air pollution, which can be used by local authorities to assess population exposure and health effects. The results could also be used in comparison with models, to make further conclusions about effects on air quality and climate on a larger geographical scale.

More and more people are living in urban areas, and are hence affected by the local air quality in cities. Despite many efforts to reduce emissions and improve air quality, transport is a large contributor of particulate emissions. Diesel and gasoline driven vehicles emit soot, or black carbon. In paper IV, the aim is to provide detailed characterization of black carbon emissions from traffic. Specialized instrumentation is used for characterization of properties of individual soot particles. With two nearby measurement sites, one in a city center and one in the countryside outside the city, the aim is to get a broader view of the traffic emissions in the region of interest. Not only is it relevant to characterize the fresh emissions, but since a large fraction of the population in Sweden is exposed to a substantial fraction of particles transported from distant particle sources, the aged particle physicochemical properties are also relevant.

For the same reason as described above, the long-range transport of particles distributes emissions from different sources over large areas. In regions affected by poor air quality, it is of high relevance to know which sources are the main contributors to elevated air pollution levels. If the sources are well known, legislation and action can be targeted more effectively. In Paper V, the aim is to identify and quantify different sources of combustion generated particles. The physicochemical properties of organic matter and black carbon are used to attribute a kind of fingerprint to certain sources. Specifically, since the measurements were performed in Poland during winter time, the sources related to domestic heating as well as traffic are the main focus.

In addition to an overall contribution to the research field described above, the main research questions which this thesis aims to cover are:

- What are the effects on soot particle emission factors due to policy enforcement on fuel quality in sulfur emission control areas?
- What are the aerosol physicochemical properties in ship plumes after short atmospheric aging in an emission control area, and how large is the total contribution from ships to total aerosol concentrations?
- What are the physicochemical properties of fresh and aged traffic emissions at an urban and rural location located close to each other, and how is the air quality affected by long-rage transport compared to local sources?
- What is the source contribution of traffic, biomass, and household coal burning to observed carbonaceous matter concentrations at a field site in northern Poland?

Introduction

An aerosol is a suspension of liquid or solid particles in a gas. Aerosols in the atmosphere have different origin and largely varying physical and chemical properties. Some natural sources of aerosol particles are sea salt from wave breaking over the oceans, volcanoes, and biogenic particles from vegetation. Some anthropogenic sources are traffic, wood burning, industries, and erosion of roads and tires. Energy related anthropogenic activities is the main contributor (85 %) to atmospheric fine particulate matter [1]. Legislative and technological efforts have been, and are still being, made to reduce these emissions, which have a negative impact on both environment and health. In this introductory section, some general effects of aerosols on humans and the environment are described, as well as the properties of some types of combustion emission aerosols and current regulations.

Climate, health, and the environment

Why do we care about the details of the atmospheric aerosols? Studying aerosols is of course very interesting from simply a physics and chemistry perspective, but there are immense effects connected to the anthropogenic emissions of aerosols into the atmosphere. Air pollution affects everyone breathing the air as well as the environment around us and the climate system.

Anthropogenic combustion results in emission of several air pollutants. One very important species is the long-lived greenhouse gas carbon dioxide (CO_2), which currently perturbs the natural atmospheric greenhouse effect causing global warming. In addition to CO_2, other co-emitted greenhouse gases and particulate matter will also affect the climate system. PM is a short-lived species, with an atmospheric lifetime of a days or weeks in the troposphere, compared to years or decades for many greenhouse gases. The climate effect of $PM_{2.5}$ from combustion is still associated with large uncertainties [2]. In short, PM can have both cooling or warming effects, depending on the physicochemical properties. PM can interact with solar radiation directly, by absorbing or scattering incoming light, called the direct aerosol effect. The IPCC 5th

Assessment Report estimates that BC from fossil fuel and biofuel emissions contribute to a direct radiative forcing of +0.4 (+0.05 to +0.8) W m^{-2} relative to pre-industrial conditions. Additionally, BC deposition on snow reduces the reflectance of the Earth's surface (albedo) and gives rise to an additional estimated forcing of +0.1±0.1 W m^{-2} [2]. With melting of the ice caps in the Arctic, an increase in shipping activities and consequently an increase in BC is expected in the sensitive Arctic region [3, 4]. Bond *et al.* (2013) estimated a total forcing of BC, including all mechanisms and feed-backs, to be +1.1 W m^{-2} (+0.17 to +1.48 W m^{-2}) [5], which can be compared to CO_2 in the industrial era, with a forcing of +1.82 (+1.63 to +2.01) W m^{-2}.

Despite the warming effect of BC, the total aerosol radiative forcing is estimated to be in the range from –2.3 to –0.1 W m^{-2} [2]. This is partly due to co-emission of other aerosol species from combustion processes, which act as cooling agents and counter balance the warming of the BC. For example, sulfate (SO_4^{2-}) and organic aerosols scatter solar radiation directly. The indirect aerosol effect, that is the effect of aerosols on clouds, is also cooling. Figure 1 shows an example of anthropogenic ship emissions resulting in lines of bright clouds over the Northern Pacific. Aerosol particles affect the cloud droplet size and number concentration, and consequently climate relevant cloud properties, such as reflectivity, lifetime, and precipitation. Primary emitted BC is mostly not hygroscopic and will not form cloud droplets, but upon atmospheric aging, transformation of the BC can increase the cloud formation potential [6]. Additionally, anthropogenic BC may also act as ice nucleating particles in mixed-phase clouds, which could be associated with significant climate warming [7].

For shipping specifically, the net radiative forcing is cooling, –0.026±0.004 W m^{-2} [8], mainly due to the large sulfate fraction of the aerosol mass. However, due to regulations of fuel sulfur content in the 21st century, this effect is expected to decrease in magnitude or even change to warming in the future [9]. This negative effect on climate as a result of legislation might seem counterintuitive, but the driving force behind the sulfur limitation is the public health benefits, which are described further below. Sofiev *et al.* (2018) estimate a reduction in premature mortality of more than 30 % due to this action, and simultaneously a reduced cooling effect from shipping of about 80 % [10].

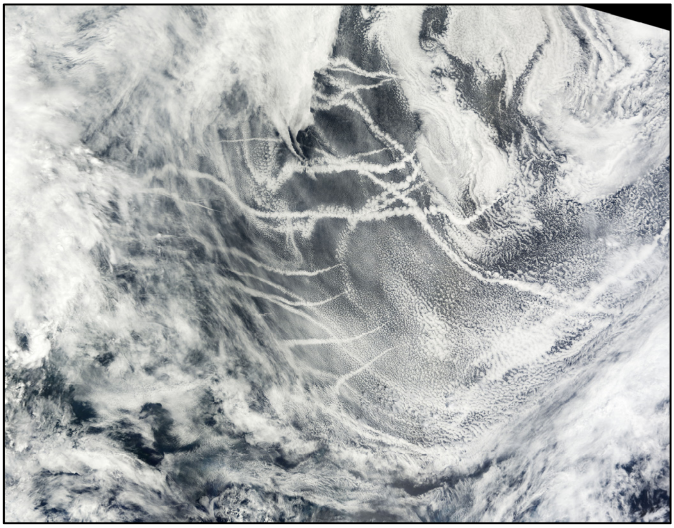


Figure 1.
Picture of ship tracks in the Northern Pacific. Bright clouds are formed along the exhaust plumes of ships. The image is captured by The Moderate Resolution Imaging Spectroradiometer (MODIS) on NASA's Terra satellite (July 13, 2008) [11].

In industrial countries during the mid-1900's, high levels of air pollutants together with unfavorable meteorological conditions, caused intense smog ('smoke-fog') and consequently poor visibility, eye irritation, troubles breathing, and death [12, 13]. The link between air pollution and human health has since been a topic of research. Fine particles with a diameter below 2.5 µm ($PM_{2.5}$) and ultrafine particles with a diameter below 0.1 µm (UFP) are small enough to be transported deep into the respiratory system, and have high probability of depositing in the lung alveoli [14]. Due to the small size, the particles can be translocated from the lung into the blood stream and affect other parts of the body. From epidemiological studies we know that PM causes respiratory and cardiovascular diseases, resulting in increased mortality due to long-term exposure as well as acute effects [15, 16]. Hoek *et al.* (2013) associated a mortality risk increase of 6 % per 10 µg m^{-3} increase in $PM_{2.5}$ and the same per 1 µg m^{-3} increase in black carbon [17]. $PM_{2.5}$ has also recently been defined as carcinogenic [18] and linked to increased risks of dementia [19]. Health effects of air pollution exposure can be expressed in many ways, commonly as 'premature deaths'. While severe pollution events can lead to acute health effects and deaths related to those events, the effects of long-term air pollution exposure are not always noticeable to individuals directly. It can therefore also be useful to use other terms than 'death' to describe the health effects of PM, for example morbidity, years of life lost (YLL), or disability adjusted life years (DALY). The excess mortality rate in Europe due to ambient air pollution has been estimated to 790 000 per year [20].

Clear relations between $PM_{2.5}$ exposure and health effects have been documented, but not all $PM_{2.5}$ is equally harmful. As more advanced monitoring of air pollution is put in place, a more detailed approach to link aerosol properties to effects on humans will be possible. For example, black carbon is specifically harmful compared to the total $PM_{2.5}$ [21, 22] and diesel and gasoline engine exhaust is highlighted as a carcinogenic air pollution source [23]. Relatively small and fractal like particles, like soot, have a large surface to bulk ratio and the large surface area can hence act as a carrier of toxic compounds such as metals, polycyclic aromatic hydrocarbons (PAHs), and other organic compounds. This thesis includes studies of traffic exhaust, as well as other combustion sources, in particular shipping exhaust. PM from shipping is in the ultra-fine range [24-26], and can hence reach deep into the lung with a high deposition efficiency. The annual premature deaths in Europe due to ship emissions have been estimated in model studies, and range from about 7000 up to 50 000 [27, 28].

In addition to the effects of PM described above, there are many other consequences related to combustion emissions. An example is the emission of gaseous species, nitrogen oxides (NO_x) and volatile organic compounds (VOCs). Long-term exposure of NO_x and VOCs can have negative health effects, but these compounds are also precursors of ground level ozone (O_3) which causes adverse effects on the respiratory system, and harms agriculture through crop damage. Emissions of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) oxidize in the atmosphere, and potentially form sulfuric acid (H_2SO_4) and nitric acid (HNO_3). Hence, in addition to the impacts on health and climate, ship emissions, and other sulfur rich sources, also cause acidification [29-31]. Changing cloud properties can affect regional and global precipitation patterns with implications for e.g. agriculture and consequently for society in large. Since air pollutants can be transported large distances, the source region is not the only one exposed to the effects of high emissions. The environment and its changes can be described in scientific terms, but will inevitably also be connected to economy and politics. Conflict might arise when different environmental concerns are put against each other, or against completely other issues which are also highly relevant to society. The next section will give a brief overview of the current legislation on particle emissions and specifically on the shipping sector.

Policy and regulations

Air pollution has been established as a large and multifaceted problem to humanity. And, for the reasons mentioned earlier, efforts have been made to mitigate and reduce multiple air pollutants, including greenhouse gases, PM, and other harmful substances. Major air pollution issues around the 1970's, which were recognized by the scientific community and the public and which led to action and policymaking, were severe smog events and acid rain in Europe and the United states [32, 33].

Since the 1970's, there have been substantial emission reduction in parts of the world, but also increase in other parts. The Convention on Long-Range Transboundary Air Pollution (CLTRAP) which was established in 1979 was an important milestone for tackling air pollution emissions. Later, several specific emission protocols and have been added, e.g. on sulfur, nitrogen oxides, volatile organic compounds, and heavy metals [34], and national air quality protocols have been established in many countries. Figure 2 shows the $PM_{2.5}$ emissions from fossil sources for all continents, as well as for international shipping and aviation (based on data from the Emissions Database for Global Atmospheric Research - EDGAR v. 4.2 [35]). A majority of the PM emission reduction can be attributed to decreasing SO_2 emissions worldwide. The rapid economical and industrial development in China accounts for the largest $PM_{2.5}$ emissions related to fossil fuel use today.

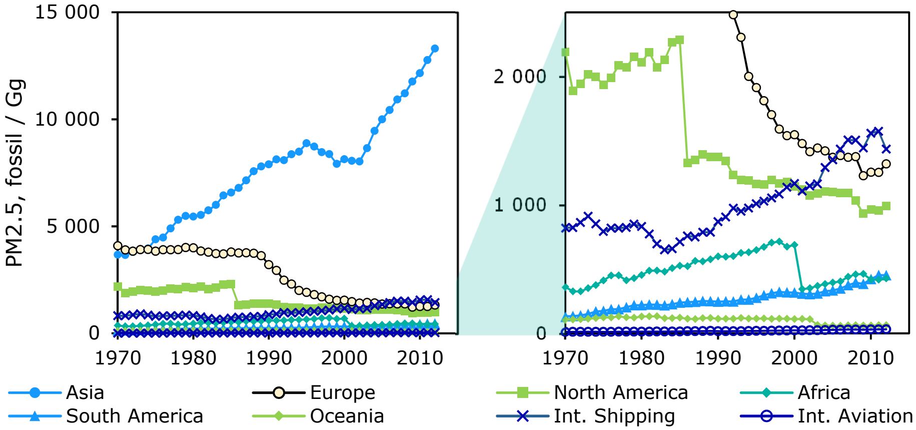


Figure 2.
Sum of $PM_{2.5}$ emissions from fossil sources per continent and from international shipping and aviation. [35, 36]. The right panel shows the same data as left, but zoomed in.

Despite the progress of international collaboration towards cleaner air, there are remaining issues and risks. As can be seen in Figure 2, the $PM_{2.5}$ from fossil fuel use was increasing in the 2000's in Asia, Africa, and South America, as well as from international shipping and aviation. There is also a global tendency towards urbanization. Hence, even in countries with relatively low national pollution levels, the pollution and the population is concentrated in larger cities, where severe pollution events can occur and where the long term exposure can be above the guideline levels. According to the European Environmental Agency (EEA), more than two thirds of the European Union's urban population was exposed to concentrations exceeding the air quality guidelines of the World Health Organization (WHO) for $PM_{2.5}$ in 2017 (see Table 1) [1]. On a global scale, only 2 % of the urban population is living in areas where the PM_{10} concentrations are below the WHO guidelines [37]. There is no scientifically established safe level of PM. Therefore, people are still exposed to harmful levels of PM to a large extent, and especially vulnerable groups such as elderly, children, and ill are at a higher risk. Despite general improvements of $PM_{2.5}$ levels in Europe and North America (see Figure 2), there are many recent examples of severe pollution events in large cities all over the world. For example in Paris, March 2014 [38], in the United Kingdom, April 2014 [39], in Beijing, December 2016 [40], in Delhi, November 2016 [41], in Salt Lake City, January 2017 [42], and in Santiago de Chile, May 2018 [43].

At present, there are different levels of legislation and recommendations which concern the PM levels in northern Europe and Sweden. These are summarized in Table 1 below. Currently, PM pollution regulations and guidelines concern two measures, PM_{10} and $PM_{2.5}$. These are measured as daily average values and annual average values. The daily average is also associated with a maximum number of allowed exceedance days per year. For $PM_{2.5}$, there are non-binding guidelines from the World Health Organization (WHO) and only an annual limit in the European Union. In Sweden, only the annual limit is binding, while the daily limit is a goal [44].

Table 1. Comparison between different levels of guidelines and objectives for $PM_{2.5}$ and PM_{10}.

Air pollutant	Time average	WHO guideline	EU limit	Swedish environmental quality standards[a]	Swedish environmental quality objectives[b]
$PM_{2.5}$ ($\mu g\ m^{-3}$)	24 h	25	-	-	25 (AE: 3)[c]
	year	10	25	25	10
PM_{10} ($\mu g\ m^{-3}$)	24 h	50	50 (AE: 35)	50 (AE: 35)	30 (AE: 35)
	year	20	40	40	15

Adapted from Naturvårdsverket [45].

[a] In Swedish 'Miljökvalitetsnormer'

[b] In Swedish 'Miljömål'

[c] AE = "allowed exceedances", i.e. the number of days per year that the limit may be exceeded.

In Figure 2, it can be seen that international shipping has become an important source of PM emissions on a global scale, with higher $PM_{2.5}$ and BC contribution than both Europe and North America in 2012. International waters have not been covered by as strict regulations as land based sources until more recently, in the 2010's. Today, more than 80 % of the global trade volume is transported by ships. The shipping trade volume also has a predicted annual growth of 3.4 % for 2019-2024 [46]. Shipping is an energy efficient mean of transport and in the period 2007-2012 it contributed to about 3.1 % of global anthropogenic carbon dioxide emissions [47]. In the International Convention for the Prevention of Marine Pollution from Ships (MARPOL) Annex VI [48], the main exhaust gas emissions of sulfur oxides (SO_x) and nitrogen oxides (NO_x) are limited. In revised versions of MARPOL Annex VI, reduction of particulate matter emissions is also considered within the SO_x emission controls. The International Maritime Organization (IMO) have regulated the fuel sulfur content in several steps, which is summarized in Figure 3. The maximum mass fraction of sulfur in marine fuels has in total decreased from 1.5% to 0.1% between the years 2010 and 2015 in designated Sulfur Emission Control Areas (SECAs). In 2016 it was decided that a global reduction of the fuel sulfur limit was going to be implemented, with a cap of 0.50 % sulfur in fuel oil on board all ships from January 1st 2020. The new requirements on marine fuels will likely affect the fuel price, and monitoring will be needed to assure compliance [49]. According to Mellqvist *et al.* (2017), the compliance rate in the Baltic region has been high, 92-94 % during 2015-2016 [50].

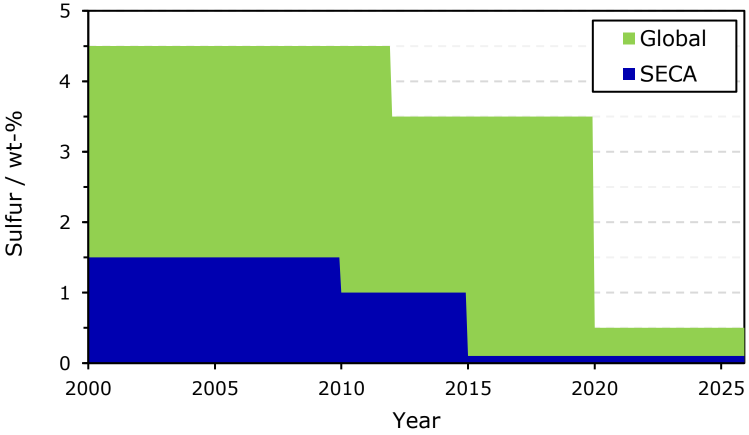


Figure 3.
MARPOL Annex VI regulation of fuel sulfur limits over time, globally and in sulfur emission control areas (SECA).

Adaption to the sulfur regulations can be achieved through either desulfurization of existing marine fuels, switching to other fuel types, or by exhaust after-treatment by scrubbers to remove SO_2 [51]. However, if scrubber systems which release the scrubber water into the ocean are used, this will not improve the issue of ocean acidification. Rather, if all ships would use scrubbers the acidification level of the Baltic Sea would reach the levels of the 1970-1990s [52]. The most common techniques to reduce sulfur emissions are however related to fuel change. Heavy fuel oil (HFO) is a low-grade fuel with high viscosity, common in marine transport. HFO has a relatively high content of sulfur, ash, carbon residue (high molecular weight hydrocarbons), PAHs, and metals [53] compared to cleaner marine fuels. Cleaner fuels are e.g. marine diesel oil (MDO) and marine gas oil (MGO) which are composed of various blends of distillates. Other alternative fuels are liquefied natural gas (LNG) and various biofuels [54, 55]. The modelled fuel distributions of the Baltic Sea fleet for the years 2006-2018 can be seen in Figure 4. Between 2014 and 2015, the use of HFO decreased from 77 % to 12 %, while the use of distillate fuels (MDO and MGO) increased from 22 % to 88 %, due to the SECA regulation.

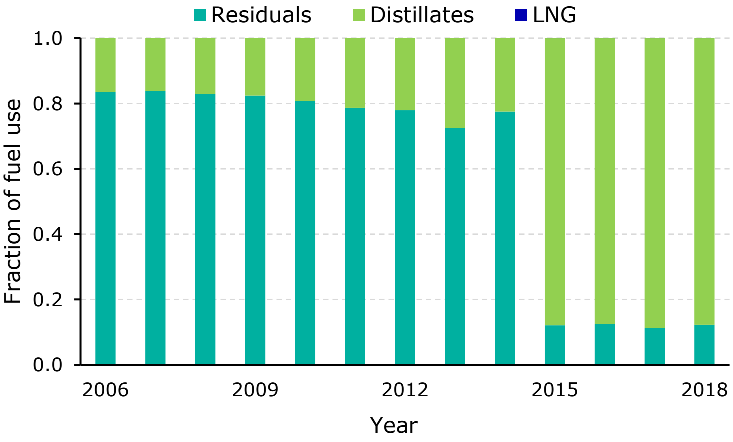


Figure 4.
Modelled marine fuel use in the Baltic Sea 2006-2018, distributed between residual fuels (HFO), distillates (MDO and MGO), and liquefied natural gas (LNG). The figure is based on data from the Finnish Meteorological Institute, courtesy of Jukka-Pekka Jalkanen.

NO_x emission limits depend on engine speed, and are different for ships built in different years, with Tier II applying to ship engines constructed after 2010 and Tier III after 2015 for ships operating in NO_x Emission Control Areas (NECA). In 2021, there is a planned introduction of a NECA in the Baltic Sea and the North Sea, which will affect the Baltic Region [56, 57]. In addition to the fuel sulfur and NO_x regulations, future limits on black carbon (BC) are expected [58] and IMO has a strategy with the aim to reduce greenhouse gas emissions by at least 50 % by 2050 [59]. Finally, a comment on shipping regulation which is not related to air pollution, but is still of relevance for the work presented in this thesis. Through IMO's International Convention for the Safety of Life at Sea (SOLAS), an Automatic identification system (AIS) must be carried by all passenger ships, and on other ships depending on size [60]. AIS transceivers broadcast information for tracking ships, including the ship identity number, position, speed, and course, among other things.

This thesis presents results from different field observations in the Baltic region. The three first papers have specifically focused on ship emissions, hence the regulation applying to shipping in this region is of importance for interpreting data and when comparing these to observations in other geographical regions. In the last two papers, observations from inland urban and rural field sites are presented. These are affected by EU and local regulations (Table 1).

Combustion aerosols

Figure 5 a-b shows the energy consumption in the European Union based on sectors, and the global contribution to primary air pollutants from energy related sources. From the pie chart, it is seen that transport and households stands for more than half of the energy consumption in the EU. Globally, combustion sources contribute to a majority of the anthropogenic emissions of $PM_{2.5}$, as well as nitrogen oxides, and sulfur dioxide.

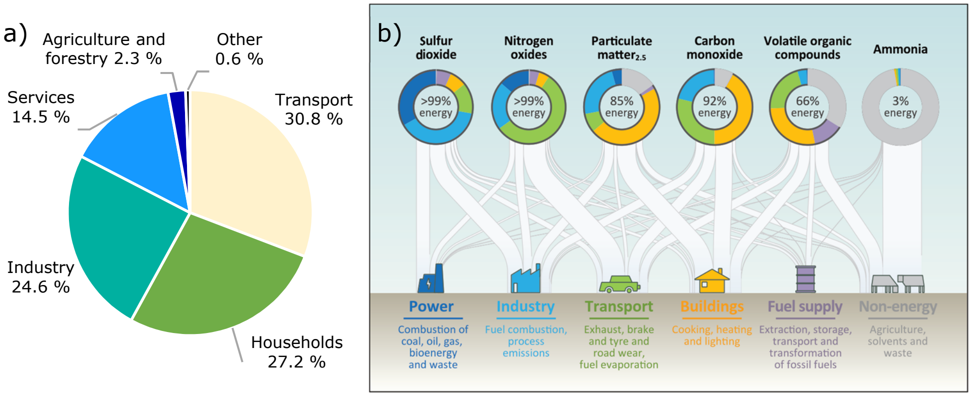


Figure 5.
a) Energy consumption for EU-28 by sector, based on data from 2017. Data on international aviation are included in the category "other" [61]. b) Estimated energy-related contribution to global emissions of primary air pollutants by human-related activities [62] (IEA energy report, all rights reserved.).

In this thesis, the aim has been to study ambient aerosols from specific combustion sources; marine, and land based traffic, and domestic wood and coal combustion. Combustion is a complex process, including physicochemical reactions and transformation, both inside the engine or flame, and after emission. Fuel, temperature and engine technology etc. govern the combustion process, and consequently the formation of particulate matter and gaseous species. Dilution, condensation of vapors, and coagulation and restructuring of particles affect the PM after emission.

PM from combustion of diesel and marine fuel contains soot, sulfur, organic material, ash, and metals [63-65]. Gaseous species emitted are nitrogen oxides (NO_x) and volatile organic compounds (VOC), which can contribute to secondary organic aerosol (SOA) formation with atmospheric aging. PM emitted directly from the source is referred to as primary emissions. The organic fraction of PM from diesel engines includes PAHs [66] which are harmful to human health [67]. Metals and PAHs are also found in ship emissions [68, 69]. Lubrication oil in engines is a source of organic aerosol (OA) from combustion sources [70, 71]. Sulfur emissions are significant for crude marine oil and coal combustion [72]. Sulfur emitted as SO_2 transitions into particulate sulfate via atmospheric aging, which can be measured with aerosol mass spectrometry. The soot and organic carbon fraction of the combustion aerosols are complex. In this thesis, several types of soot and OA have been investigated, with different measurement techniques and at different geographical locations. When carbonaceous aerosols are discussed, there is a myriad of terms which can be used. The meaning of the common terms has sometimes changed over time, and can also vary between scientific fields. In the context of atmospheric aerosols, the appropriate terms for describing the carbonaceous aerosol is typically determined by the measurement technique used.

The term *carbonaceous aerosol* simply means the fraction of the aerosol which contains carbon. It is a wide concept, including elemental carbon as well as organic molecules containing carbon, oxygen, hydrogen, and other atoms, organic salts, and so on. The terminology presented below is based on the proposed definitions by Petzold *et al.* (2013) [73] and Pöschl (2005) [74]. These definitions are mainly based on the atmospheric relevance of the particles, i.e. the properties that govern climate, atmospheric chemistry, and air quality.

In atmospheric aerosol science, the commonly used *black carbon* (BC) is a qualitative term, which generally refers to particulate matter which 1) contains a high fraction of graphite-like, sp^2-bonded carbon atoms, 2) consists of aggregated carbon spherules, 3) absorbs visible light strongly, 4) is refractory with a volatilization temperature near 4000 K, and 5) is insoluble in liquids present in the atmosphere. In order to be quantitative, additional information about the BC is required. *Equivalent black carbon* (eBC) is used when BC concentrations are derived from optical absorption measurement techniques.

eBC is converted from a light absorption coefficient, using the mass-specific absorption cross section (MAC). *Refractory black carbon* (rBC) is used for BC, which is derived from incandescence measurement techniques, and is defined as having a volatilization temperature near 4000 K and being insoluble. Similarly, *elemental carbon* (EC) is defined based on the particle thermochemical properties. EC is the carbonaceous material which is stable in inert atmosphere up to 4000 K, and in the presence of oxygen, up to 340 °C. In this thesis, EC is obtained from off-line analysis of filter samples, while rBC has been measured with on-line techniques. From filter analysis, the fraction of *organic carbon* (OC) is also obtained. In contrast to EC, OC has lower volatilization and degradation temperatures, as well as weak absorption of visible light. OC is a collective term for particulate matter consisting of a large variety of organic molecules. A term which is used more and more in addition to BC is *brown carbon* (BrC), which is the organic aerosol matter which is also light absorbing, but with a brown rather than black color due to stronger light absorption at shorter wavelengths in the visible range. BrC can originate from combustion, but can also be SOA. Finally, in addition to the concepts above, there are some collective terms which groups different carbonaceous aerosol types together depending on context. *Total carbon* (TC) can be used for the total mass of all carbonaceous aerosol particle matter (OC+EC). *Light absorbing carbon* (LAC) can be used for the sum of eBC and BrC, i.e. the total carbon fraction of the aerosol which absorbs visible light strongly. Finally, perhaps the most common popular scientific term *soot*. Soot is a collective qualitative term for the carbonaceous particulate matter emitted from incomplete combustion, and a well-known concept also for non-scientists. Mixed particles are called "BC-containing" or "soot-containing" rather than just BC or soot. Figure 6 a-b shows transmission electron microscopy (TEM) images of a soot particle with and without coating. The complex morphology of the soot aggregate makes definitions of soot particle size and shape complicated, and the large surface to bulk ratio seen in this figure illustrates the potential for a large amount of surface adhesives.

The carbonaceous aerosol from shipping, has been shown to include other light absorbing species in addition to BC and BrC, defined by Corbin *et al.* (2019) as *tarBC* and *charBC* [75]. These BC types are connected to the use of HFO, while for MGO, BC was the dominating LAC [76].

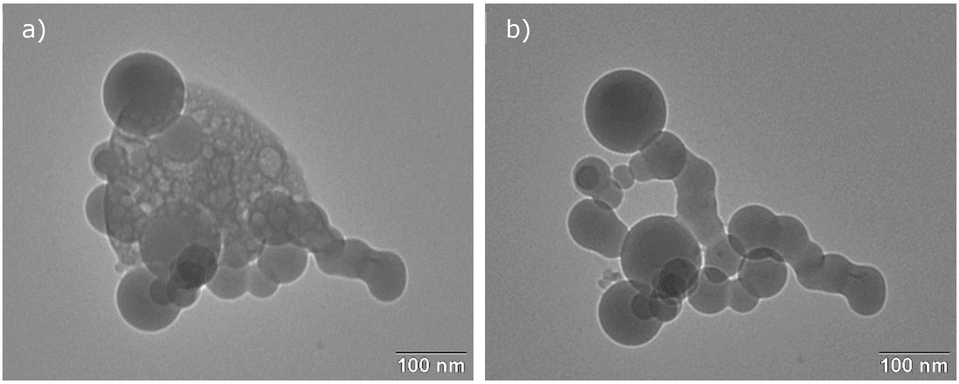


Figure 6.
Transmission electron microscopy (TEM) image of a soot aggregate collected at the east coast of Barbados in June 2013. The soot is most likely from shipping due to lack of other sources. a) Soot particle covered in coating (sulfates), and b) the same particle after exposure of the electron beam, resulting in evaporation of the coating. The images are previously unpublished but used in the analysis presented by Kristensen *et al*. (2016) [77].

As soon as a soot particle leaves a car tailpipe or ship smoke stack, it will undergo physical and chemical transformation, called atmospheric aging. Atmospheric aging can result in condensation of material onto the soot aggregate, as seen in Figure 6 a, which alters the hygroscopic properties of the particle and consequently affects the cloud formation properties and lung deposition. Uptake of coating materials and potentially water will also change the morphology of the soot particle through restructuring into a more compact shape [78, 79]. Condensation of organics can also change the absorbing properties of the BC, transforming it into BrC [80]. Enhanced light absorption due to a coating of organic material scattering more light towards the BC core, is known as lensing [81] and affects the climate effects of atmospheric BC.

It has become rather clear that the work of characterizing combustion emissions in the ambient environment is far from a straightforward task. Figure 7 shows the main concepts and processes which affect the formation, transformation, sampling, and hence characterization and source apportionment of combustion aerosols. This thesis does not aim to cover all parts in any detail, but the complex nature of the aerosol is relevant to keep in mind when studying and communicating information on combustion emissions.

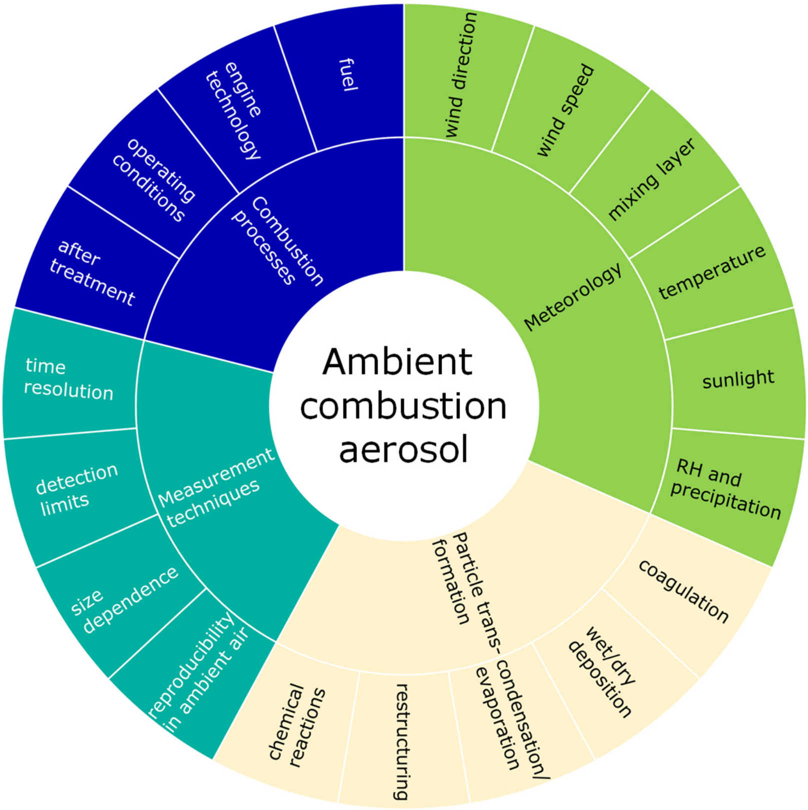


Figure 7.
Schematic chart of some of the processes which affects combustion aerosols before emission in the combustion process, and during atmospheric aging, and some measurement limitations during aerosol sampling.

Methods

Sampling sites

The studies presented in this thesis are all based on ambient data, from intensive measurement campaigns. A map of the sampling sites is shown in Figure 8, and the choices of locations are described here.

The exhaust emissions from shipping can be measured in several different ways. In paper I-III in this thesis, ship plume aerosols were measured at land-based sites. Ambient air was sampled, and due to the vicinity of ships, the influence of ship plumes was evaluated based on increased aerosol concentrations during favorable conditions, which supported the presence of plumes. There are other ways of studying exhaust emissions from shipping. Controlled experiments can be performed on test-bed engines in a lab environment, e.g. [82-84]. A test-bed engine provides the possibility of detailed control of engine and fuel parameters. Dilution of the exhaust aerosol is required to reach ambient concentrations. Another method for ship emission studies is to measure on-board, at the exhaust stack, or by following a sailing ship with another marine vessel or an aircraft, e.g. [85-88]. However, while these methods provide detailed observations of the fresh ship emissions from the selected engines and ships, they do not give information about the variety of particle properties between different ships. These methods can also be rather cost-intensive. Ambient studies make it possible to observe plumes from a large number of ships passing, and how these ship plumes have evolved during transport in the atmosphere. Land-based measurements are also relevant for estimating the real aerosol exposure in areas near shipping lanes and harbors. In paper I, the measurement site was positioned on the islet Risholmen in the entrance to the Port of Gothenburg (N57.6849, E11.838). The land-based aerosol sampling was hence performed as close to the shipping lane passing into the port as possible. This provided the possibility to sample a large number of fresh plumes, without influence of other nearby sources, during southerly and southwesterly winds. Ship plumes were studied at this site during both 2014 and 2015, with the aim to compare BC emissions from the same or a similar fleet, before and after ship fuel regulation. In paper II-III, the measurement site was positioned at the Falsterbo peninsula, at the southwestern tip of Sweden (N55.3843, E12.8164). This was also a suitable location for sampling semi-aged ship plumes, without much influence from other sources. During westerly and southerly winds, which is predominant in the region especially in wintertime, ship plumes are transported towards land and pass the measurement site.

Soot properties vary depending on source and atmospheric aging. Similarly to ship emissions, emissions from road traffic can be studied in both lab and ambient environments depending on the research question. In paper IV, the results from a field campaign at an urban and a rural are presented. At the urban site 'Dalaplan', in Malmö in southern Sweden, air quality monitoring has been ongoing since 2005. During 2018, the existing monitoring of PM, eBC, and health relevant gases was complemented with advanced aerosol instruments during a campaign of a few months. The aerosol sampling at Dalaplan is done at street level, and is hence suitable for observing fresh traffic emissions, as well as the urban background. At the ACTRIS supersite 'Hyltemossa', climate relevant aerosol measurements have been ongoing since 2017. At this rural background station, located in a spruce forest in southern Sweden, aerosol and greenhouse gas monitoring was complemented with more advanced aerosol instruments, just as in the urban site. At Hyltemossa, there are no nearby sources of BC, but the observations here provide information on aged BC-containing particles transported from distant sources. Specifically, two aerosol mass spectrometers (see Instrument section) were deployed simultaneously at the urban and rural site. This setup was planned in order to study exactly the same aerosol at two different locations, with a known transport time in between.

The locations for the soot study in paper IV were suited for comprehensive aerosol characterization due to the large number of aerosol parameters continuously measured at the monitoring stations. In contrast, a more polluted country than Sweden, but with less aerosol monitoring, is Poland. In paper V, measurements are presented from the rural European Monitoring and Evaluation Programme (EMEP) regional background monitoring station, Diabła Góra, and the nearby, coastal environmental pollution research station, Preila. Like Hyltemossa, Diabła Góra is located in a forested area, with no nearby emission sources. During southerly winds, air from the inland of Poland is transported to Diabła Góra, which is located near the northern country border. During the EMEP intensive measurement period in winter 2018, in addition to the standard monitoring, wavelength dependent aerosol absorption (see Instrument section) was performed during a limited campaign. This was done in order to perform source apportionment of the carbonaceous aerosol and, consequently, the exposure of this type of aerosol in the region.

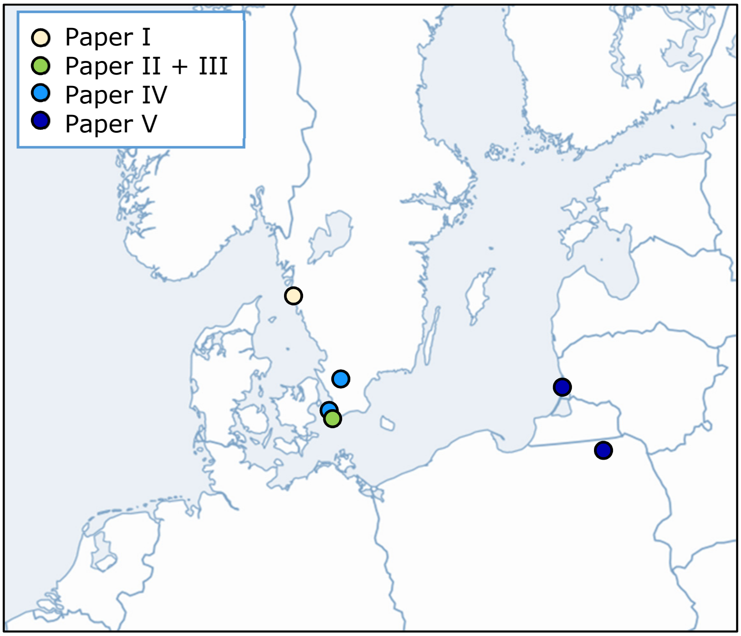


Figure 8.
Map of the Baltic region, including the locations of the measurement sites presented in the papers included in this thesis.

Instrumentation

The main instruments used for soot particle characterization in this thesis are described in more detail below. All instrumentation used for aerosol sampling in the papers, including main and auxiliary, are summarized in Table 2. All aerosol instruments described measure continuously, in-situ, and on-line, except for the off-line analysis of filter sampler for OC, EC, and levoglucosan quantification.

Aethalometer and Multi Angle Absorption Photometer

Equivalent black carbon (eBC) content was measured with two optical absorption methods, using a Multi Angle Absorption Photometer (MAAP, Thermo Fisher Scientific, λ = 637 nm) [89] and a seven wavelength aethalometer (model AE33, Magee Scientific, λ = 370, 470, 520, 590, 660, 880, and 950 nm) [90]. In short, these instruments are based on the principle of light absorption of the aerosol corresponding to atmospheric eBC mass concentrations. An aerosol flow is drawn through a filter tape on which all aerosol particles are deposited. The filter is irradiated with light from LED sources, and the light attenuation is measured by a photodetector on the opposite side of the filter. When the particle load reaches a threshold value, the filter tape roll automatically advances so that a new filter spot is used. The eBC concentration is derived from the light absorption coefficient (σ_{abs}) using a wavelength specific mass absorption coefficient (MAC),

$$[eBC]\ [\mu\mathrm{g\ m^{-3}}] = \frac{\sigma_{abs,\lambda}\ [\mathrm{Mm^{-1}}]}{MAC_{\lambda}\ [\mathrm{m^2\ g^{-1}}]} \tag{1}$$

In the MAAP, in addition to the attenuation, the back-scattered light from the particle loaded filter is also measured using four additional photodetectors at two different backscatter angles. This makes it possible to correct the measured attenuation for light scattering aerosols in order to get an improved measure of the aerosol absorbance. The uncertainty in measured absorbance for the MAAP has been estimated to 12-15 % [89, 91]. The aethalometer does not measure aerosol light scattering like the MAAP. However, sampling artefacts due to scattering of the particles collected on the filter, the so-called shadowing effect, is treated in real-time in the AE33 using a dual spot technique [90]. The attenuation is measured on two parallel spots on the filter, but with different sample flows and hence different particle loading rate. Scattering within the filter depends on the filter material and is corrected for by a constant factor of 1.57. The uncertainty in measured absorbance for the AE33 has been estimated to 35 % [91].

Aerosol Mass Spectrometer

The Soot Particle Aerosol Mass Spectrometer (SP-AMS, Aerodyne Research Inc.) measures the size dependent chemical composition of particles in the aerodynamic size range ~70 nm-1 µm [92]. An aerosol sample flow is passed through an aerodynamic lens which focuses the particles but not the gaseous compounds of the aerosol, to a narrow flow. A rotating disc with one or several slits, a chopper, is alternately used to let the particle beam pass, giving rise to size resolved particle properties due to the time-of-flight (ToF) of the differently sized particles. A chopper position which fully blocks the particle beam is used to measure the instrumental background. The particles are then vaporized at a heated tungsten plate, the vapors are ionized by electron ionization from a heated filament, and the ionized vapors are detected and categorized by a mass spectrometer. In the basic setup, the non-refractory particulate matter is measured, but not the compounds with higher (than ca 600 °C) vaporization temperatures such as rBC. In the SP-AMS set-up, an Nd:YAG laser (λ =1064 nm) is used to also vaporize the rBC [93].

Single particle soot photometer

The Single Particle Soot Photometer (SP2, Droplet Measurement Technology, Boulder, CO, USA) is an aerosol instrument for quantifying the rBC mass in single particles, using laser-induced incandescence [94-96]. The light scattering signal of particles is also measured, in order to obtain information on coating and on particles without rBC cores, i.e. non-refractory matter. The SP2 can quantify the rBC mass of individual particles in the range ~0.5-50 fg per particle, corresponding to rBC cores with mass equivalent diameters in the range ~80-500 nm. The aerosol flow passes the cavity of a continuous Nd:YAG laser (λ =1064nm) with an intensity of ~10^6 W cm^{-2}. BC containing particles absorb the radiation and are heated, causing vaporization of non-refractory matter if present, followed by vaporization of the rBC (at ca 4000 K). The thermal radiation emitted by the incandescent rBC is proportional to the rBC mass.

Table 2. Summary of instruments used for studying the ambient aerosol in this thesis.

Instrument	**Abbreviation**	**Model/Manufacturer**	**Method**	**Output**	**Used in paper** [a]
Soot particle aerosol mass spectrometer	SP-AMS	Aerodyne Research Inc.	Time-of-flight, heat and laser vaporization, and ionization	Size dependent mass and chemical composition	2,3(s,w),4
Single particle soot photometer	SP2	Droplet Measurement Techniques Inc.	Laser induced incandescence	rBC mass, non-refractory mass	4
Aethalometer	AE33	AE33, Magee Scientific	Optical absorption (7 wavelengths)	Wavelength dependent aerosol absorption (AAE, eBC and BrC mass).	2,3(s,w),4,5
Multi angle absorption photometer	MAAP	5012, Thermo Fisher Scientific	Optical absorption and back-scattering (637 nm)	eBC mass	1,3(s)
Aerosol particle mass analyzer	APM	Model 3600, Kanomax	Centrifugal and electrostatic force balance	Particle mass and effective density distribution	4
Condensation particle counter	CPC	3775, 3025, YSI Inc.	Light scattering after butanol condensation	Particle number concentration	2,3(s,w)
Scanning (or differential) mobility particle sizer spectrometer	SMPS (DMPS)	Custom-built	Charging, electrical size selection, and counting (by CPC)	Particle number and volume electrical mobility diameter size distribution (~10-550 nm)	2,3,4
Aerosol particle sizer	APS	3321, TSI Inc.	Light scattering and time-of-flight	Number and volume size aerodynamic equivalent diameter distribution (~0.5-20 µm)	2,3
Engine Exhaust Particle Sizer	EEPS	3090, TSI Inc.	Charging and multiple electrometer detectors	Number and volume electrical mobility diameter size distribution (5.6-600 nm)	1
NO_x monitor	-	CLD 700 AL, Eco Physics	Chemiluminescence	NO_x, NO, and NO_2 concentration	3(s,w)
SO_2 monitor	-	S.A AF22M, Environnement	UV fluorescence	SO_2 concentration	3
CO_2 monitor	-	LI840, LI-COR	IR spectroscopy	CO_2, and H_2O vapor concentration	1,2,3(s,w)
Filter sampling	-	-	Flame ionization detection (OC/EC), gas chromatography/ion trap mass spectrometry (LVG)	OC, EC, and levoglucosan concentration	5
Potential aerosol mass oxidation flow reactor	PAM-OFR	Pennsylvania State University	Aerosol oxidation	Secondary organic aerosol formation	3(s,w)

[a] s – summer campaign, w – winter campaign.

Data analysis

Ship plume extraction and analysis

In paper I-III, individual ship plumes were identified for calculation of the aerosol concentration within a single ship plume. Further, the use of AIS for ship identification gives additional information on the ship properties, such as ship type, size, and speed. The transportation of the plume from a ship to the measurement site was calculated using wind direction and wind speed, together with AIS data. A MATLAB script was created, and presented in Paper II, which follows a single ship plumes route from the AIS location to the coordinates of the measurement site, see example in Figure 9. When a plume is estimated to pass within 500 m of the measurement site, it is considered to affect the air at the site.

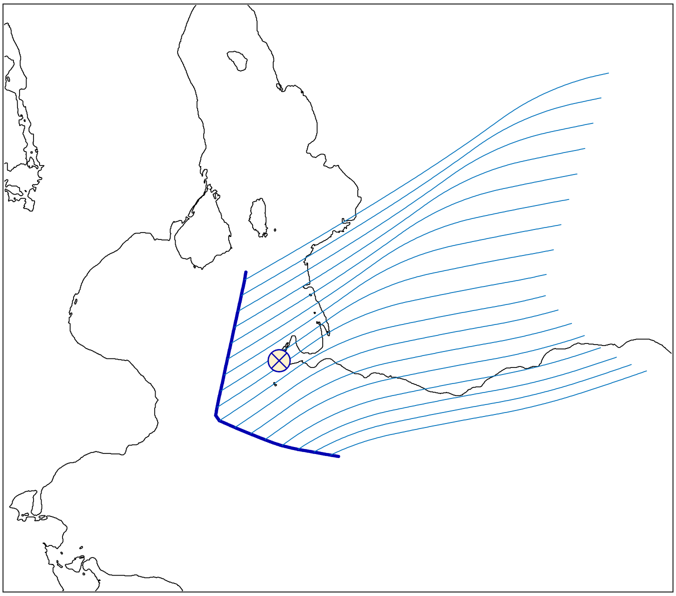


Figure 9.
Illustration of the method used for ship plume identification using AIS position data. The thick line shows the ship's geographical position every minute as it sails from the North and then makes an eastward turn. The blue, thin lines show the wind trajectory and assumed plume path every ten minutes. The measurement site is marked with a circle and cross.

Plumes were identified based on an increasing concentration of particle number concentration. A selection criterion for further analysis of plumes was that there should be no overlap of several plumes, in order to perform individual assessment of ship plumes. A schematic version of the Figure 4 in Paper II is shown in Figure 10. In Figure 10, a clearly observable species (1) is used as a marker of a ship plume. In the Port of Gothenburg this species was CO_2 and particle number concentration, and at the coast of Falsterbo, this was only particle number concentration. The species-1-time stamp which marks the start and end of a plume, is transferred to the time series of another species (2). Since a sliding percentile calculation for background concentrations (described in Paper I) is not suitable for species-2, but only for data with distinct peaks, the background was instead defined as the concentration in a time interval just before and after the plume time stamps. In order to estimate a daily and seasonal contribution from the shipping lane, the average plume concentrations were extrapolated using the average number of ship passages per day, and the average number of days per year on which the wind is carrying ship plumes from Øresund to Falsterbo.

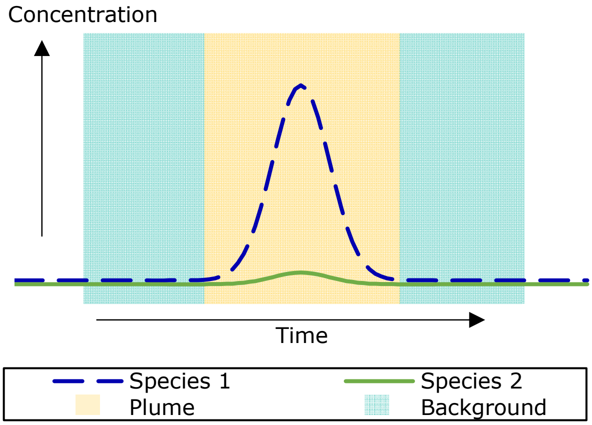


Figure 10.
Schematic illustration of the plume and background selection method for aerosol variables with high (1) and low (2) concentration, respectively.

Urban plume identification at a nearby rural site

A similar approach to the ship plume identification method was applied to the measurements described in Paper IV. The parallel measurements at an urban and at a nearby rural site, enabled a comparison of the same air mass which first passed the urban site and was then transported to the countryside. We used the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) with meteorological data from the Global Data Assimilation System (GDAS) to retrieve hourly seven days' air mass back trajectories from the Hyltemossa rural background site, including precipitation. A limited area including the cities of Malmö and Copenhagen was defined as the nearby source of urban influence. If the air mass had passed this region at any time during the last 48 hours prior to reaching the rural site, it was classified as an urban plume. We compared the aerosol properties during periods with and without such plumes. Further, the air masses were classified based on their main origin, namely northwesterly (NW), northeasterly (NE), southeasterly (SE), and southwesterly (SW).

Aethalometer model, biomass burning tracers and source apportionment

The source apportionment of the carbonaceous aerosol in Paper V is based on the aethalometer model, described in detail by Sandradewi *et al.* (2008) [97], and which has been used and developed by many others, e.g. [98-101]. The model builds on different sources having different wavelength dependent absorption patterns. The aerosol absorption Ångström exponent (AAE) was calculated based on the relationship between the σ_{abs} at different wavelengths, λ_i, as follows:

$$AAE = -\frac{\log\frac{\sigma_{abs,\lambda_1}}{\sigma_{abs,\lambda_2}}}{\log\frac{\lambda_1}{\lambda_2}} \qquad (2)$$

Traffic emissions were assumed to have an AAE of 1.03, typical for fresh BC. Wood and coal burning were assumed to both have an AAE of 1.93, that is stronger absorption at the shorter wavelengths, which is typical for biomass burning and BrC. The model was constrained with the assumption that the $CM_{coal+WB}$ was not allowed to be lower than the CM_{WB} obtained from source tracer analysis, described next.

In addition to the absorption wavelength dependence, the biomass burning trace molecule levoglucosan ($C_6H_{10}O_5$) was used to specifically quantify the daily biomass burning source, which at this field site is assumed to originate from household burning of wood. The wood burning contribution to the total carbonaceous matter (CM) was calculated as

$$CM_{WB} = CM\frac{[LVG]}{0.15 \cdot OC} \qquad (3)$$

where [LVG] is the levoglucosan concentration, OC is the organic carbon fraction (obtained from OC/EC analysis, described in the paper), and the conversion factor of 0.15 between OC and [LVG] is obtained from literature, e.g. [102-104]. Subtraction of CM_{WB} from the $CM_{coal+WB}$ obtained from the aethalometer model, provides apportionment of three separate sources instead of two. Levoglucosan is a commonly used tracer for biomass burning, since it is unique to pyrolysis of cellulose and hemicellulose and relatively stable in the atmosphere [105]. Filter samples for levoglucosan analysis were available for about a month of the three-month measurement campaign. For the nearby Lithuanian field site, Preila, levoglucosan samples were not available. Instead, the organic fraction of m/z 60 from aerosol chemical speciation monitor (ACSM) measurements, which is a type of aerosol mass spectrometer, was used as a proxy for the biomass burning marker [106].

The geographical origin of the different sources after apportionment was investigated with hourly air mass back trajectories, obtained from HYSPLIT with meteorological data from GDAS. The source dependent contribution for each air mass was added accumulatively on a gridded map to highlight source regions (see Paper V, Figure 4). Different spatial resolution was used to study the local and regional source regions, respectively.

Results and discussion

General observations

The common aim in all field campaigns has been to study anthropogenic BC and particle number size distributions of fine PM as part of the physicochemical characterization of the ambient aerosol.

BC properties have been measured with different techniques, as described in the methods section. In all campaigns, particle light absorption has been measured with either the MAAP, or the aethalometer, or both. In Table 3, the average eBC concentration for each field site is presented. Where the total particle mass ($PM_{2.5}$ or PM_1) was evaluated, the relative fraction of eBC is also given. The absolute eBC levels in Sweden were generally around half of those observed in Poland and Lithuania. Additionally, at the Coast of Falsterbo where both summer and winter observations were available, it can be seen that the concentration was higher in the winter. This difference is in line with more combustion emissions during the winter heating season. Within Sweden, the two urban sites (Port of Gothenburg and Dalaplan Malmö City) showed higher eBC concentrations than the rural site (Hyltemossa background station). It should be noted that all measurement campaigns are limited to a few weeks or months of observations. For a comprehensive and more general comparison between the geographical locations, at least a full year of measurements would be desirable in order to compare annual averages and seasonal variations.

Table 3. Average equivalent black carbon (eBC) concentrations at all field sites, including the fraction of eBC of the total PM mass.

Location and time			eBC±1 std ($\mu g\ m^{-3}$)	Fraction of $PM_{2.5}$ (%)	Fraction of PM_1 (%)
Sweden	Port of Gothenburg[a]	Oct 17-Nov 11 2014 Sep 24-Nov 5 2015	0.41 ± 0.25	not available	not available
	Coast of Falsterbo (summer)[a]	May 18-Jul 7 2016	0.26 ± 0.24	3.4	not available
	Coast of Falsterbo (winter)[a]	Jan 21-Mar 1 2016	0.48 ± 0,38	not available	not available
	Dalaplan Malmö City[b]	Sep 1-Oct 10 2018	0.49 ± 0.45	3.1	5.7
	Hyltemossa rural background station[b]	Jul 21-Aug 23 and Sep 25-Oct 11 2018	0.24 ± 0.23	not available	6.2
Poland/ Lithuania	Diabła Góra rural station[b]	Jan 17-Mar 19 2018	1.04 ± 0.61	5.6	9.1[d]
	Preila coastal background station[c]	Jan 17-Mar 19 2018	0.74 ± 0.58	not available	5.0

[a] Absorption instrument used: MAAP, MAC = 6.60 $m^2\ g^{-1}$ at 670 nm.

[b] Absorption instrument used: Aethalometer AE33, MAC = 7.77 $m^2\ g^{-1}$ at 880 nm.

[c] In Preila, another instrument model, AE31, was used instead of AE33, MAC = 16.6 $m^2\ g^{-1}$ at 880 nm.

[d] PM_1 concentrations were available for a subset of 10 days. The average eBC and the fraction of $PM_{2.5}$ is based on all 62 days.

The average particle number size distributions for each site and measurement campaign are shown in Figure 11. The corresponding volume size distributions are shown in Figure 12. The volume was calculated based on the electrical mobility diameters in Figure 11, assuming spherical particles. Four different instruments for particle sizing have been used at the different sites. An instrument inter-comparison is outside the scope of this thesis, but the EEPS has been compared to SMPS systems previously [107, 108].

At the urban site, the number size distribution was dominated by particles in the Aitken mode (10-100 nm) with an additional distinguishable mode around 100 nm. At the rural site, there was also an Aitken mode present. The maximum peak was at a larger size than at the urban site, around 45 nm compared to 20 nm. At the rural site, there was a relatively stronger accumulation mode (100-1000 nm) present. About 25 % of the particles were above 100 nm in rural size distribution, compared to about 10 % in the urban. At the Port site, an Aitken mode around 35 nm was significant, and a nucleation mode seems to be present (1-10 nm). We associate these two modes with the frequent ship plumes in the port [26]. In the volume size distribution (which is a proxy for mass), the distributions were all dominated by an accumulation mode, which extends outside of the upper range of these instruments (500-800 nm). The values are also uncertain for the largest sizes due to low counting frequency. In the Port site, a volume mode was present at about 80 nm, which was also seen when the contribution from ship plumes was isolated (see Figure 16).

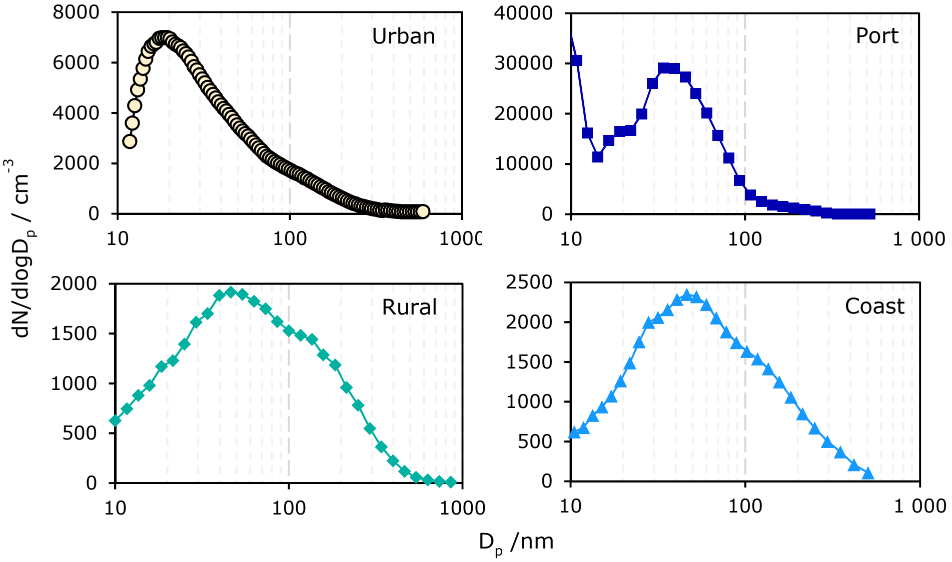


Figure 11.
Particle number size distributions from all Swedish sites, in the size range 10-500 nm. Different particle sizers have been used, urban and coast: SMPS, rural: DMPS, and port: EEPS. The data was collected during Sept-Oct, Sept-Oct, Sept-Nov, Jan-Feb, at the urban, rural, port, and coastal site, respectively. Data are not corrected for sampling losses.

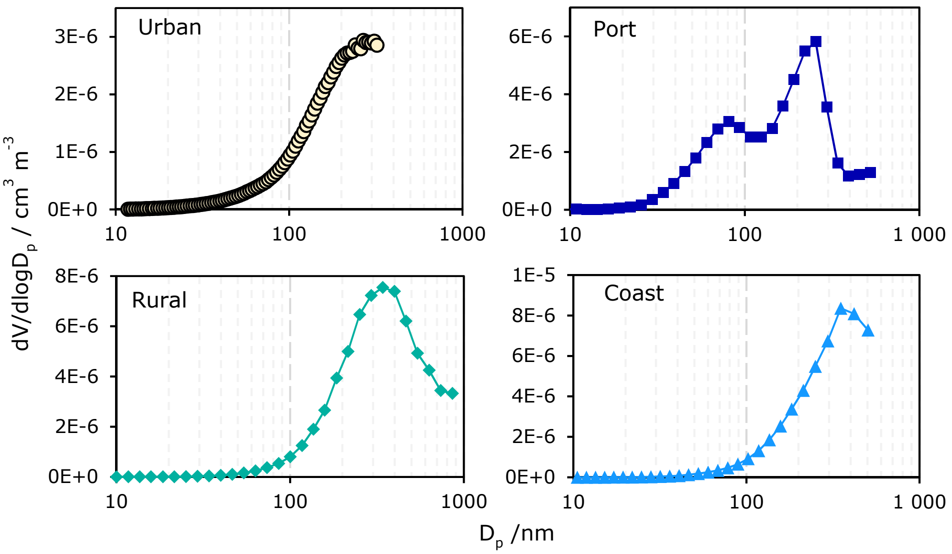


Figure 12.
Particle volume size distributions from all Swedish sites, in the size range 10-500 nm. The volume is calculated from the number size distributions in Figure 11, assuming spherical particles.

Up close - BC in ship plumes in a harbor

Land-based, extractive sampling of ship plumes was performed in the Port of Gothenburg, which is located within the North and Baltic Sea SECA. Ship emission plumes were clearly seen in the high frequency (1 Hz) time series of CO_2 and particle number size distribution. In the time series of eBC, with a time resolution of one minute, the ship plumes were occasionally visible to the eye, but not always. When no eBC plume could be visually distinguished, we used the novel method described in the "Data analysis" section to quantify the eBC contribution from individual ships. The sampled eBC plume was expected to have a longer duration than the corresponding ship plume visible from the CO_2 monitor. This was attributed to the difference in time resolution of the instruments, and smearing of the aerosol concentration in the different sampling lines. The large number of plumes with a distinct eBC peak acted as a template to predict the start and stop times of plumes without a discernable eBC peak. Hence, a larger uncertainty is associated with the emission factors of the low eBC containing plumes.

In the fresh plumes present in the harbor area, CO_2 was not too diluted and hence eBC emission factors (EF_{eBC}) could always be calculated. EF_{eBC} was determined for 346 ship plumes (Figure 13 a-b). About 10 % of the plumes had zero or close to zero (< 0.05 g (kg fuel)$^{-1}$) observed EF_{eBC}, within the detection limit of the instrument. The average observed EF_{eBC} was 29 % lower in 2015 than in 2014. The average EF_{eBC}, including one standard deviation, was 0.48±0.81 g (kg fuel)$^{-1}$ in 2014 and 0.34±0.40 g (kg fuel)$^{-1}$ in 2015 (Figure 13 c). The standard deviation here represents the variation within the sample, and is mainly due to large ship to ship variability. The uncertainty in the absolute values are dependent on the instrument detection uncertainty.

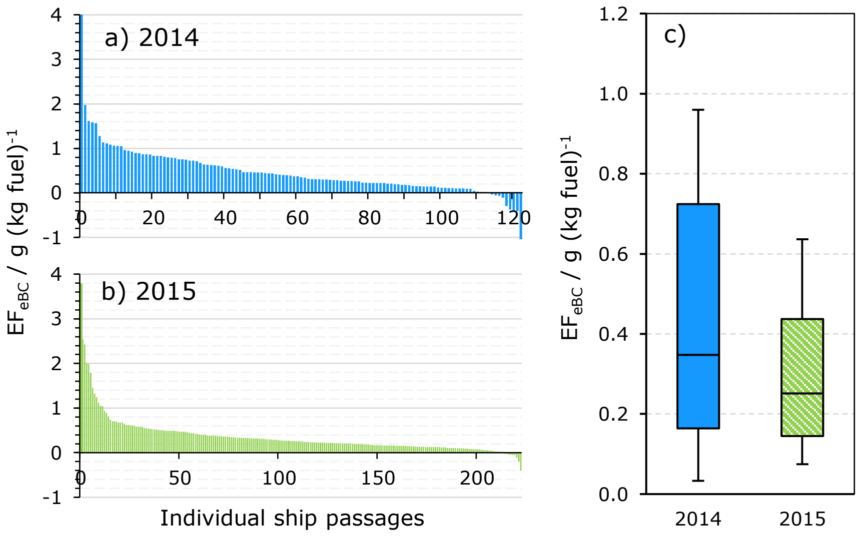


Figure 13.
Equivalent black carbon emission factors for all ship measured in 2014 (a) and 2015 (b), respectively. In 2015, one plume is outside the range of the y-axis, with an EF_{eBC} of 7.6 g (kg fuel)$^{-1}$. c) Median, 25th, 75th (box) and 10th and 90th (whiskers) percentile of the samples EF_{eBC}.

When looking at the distribution of emission factors of the ship samples in our campaigns (see Figure 13 a-b), the most frequently observed emission factors were in the range 0-0.4 g (kg fuel)$^{-1}$ during both years, but a larger fraction of the fleet was in this range in 2015 (37 % more than in 2014). In 2015, the fraction of ship plumes with an EF in the range 0.6-1.2 g (kg fuel)$^{-1}$ had decreased with 68 % compared to 2014. In addition to instrument precision, additional uncertainty lies in the number of plumes sampled. Fewer plumes were sampled in 2014 due to instrument malfunction (123 compared to 223 in 2015). Hence, the observed difference in EF_{eBC} could be skewed in any direction due to different ship types being present in the data set. AIS identification data was available for the period, but not all individual plumes could be associated with a specific ship, for various technical reasons. Since the number of AIS identified ships was relatively low during the periods when the absorption measurements were ongoing, it was not possible to compare entire fleets of ships.

From the subset of plumes which could be associated with individual ships, it can be seen that there seems to be a reduction in EF_{eBC} from passenger ships. In Figure 14 a, the total average EF_{eBC} including sample standard deviation is shown for different classes of ships, namely, passenger ships (7 identified in 2014 and 38 in 2015) and cargo and tanker ships (12 identified in 2014 and 55 in 2015). The relatively small number of identified ship plumes makes the comparison between the years difficult.

The apparent increase for the cargo and tanker ships is mainly due to a few tankers having very high EF_{eBC} values (see Figure 15). An argument for a real decrease in passenger ship emissions is seen in Figure 14 b, where the average EF_{eBC} is shown for two passenger ships ('P1 and P2'), which passed the site several times during both campaigns. Both showed a more than 50 % decrease in EF_{eBC}.

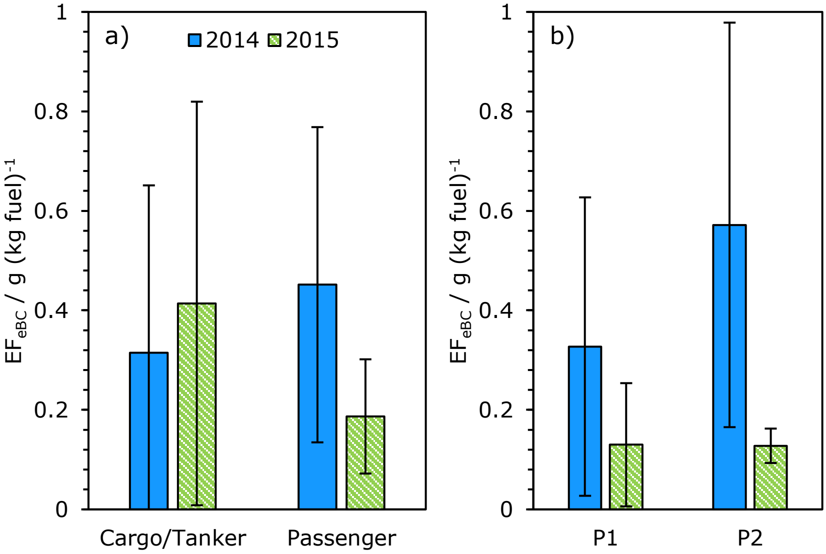


Figure 14.
Equivalent black carbon emission factors measured in 2014 and 2015, respectively. a) Average EF_{eBC} for all identified cargo ships, tankers and passenger ships (number of cargo/tanker: 12 and 55, respectively, number of passenger: 7 and 38 respectively). b) EF_{eBC} for two individual passenger ships, "P1 and P2" (3-5 passages per ship and year).

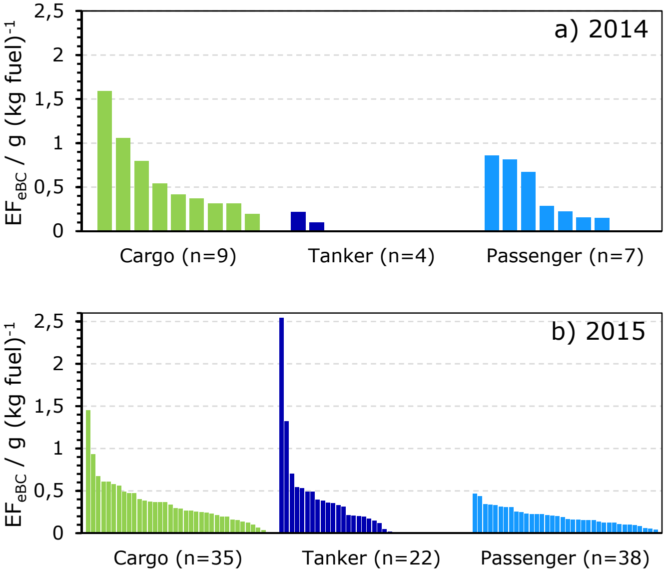


Figure 15.
Equivalent black carbon emission factors for all ships identified with AIS in 2014 and 2015, respectively, split up by ship type.

If these results are typical for the overall transition to lower sulfur emissions, the effect on global BC emissions will be significant. Just recently, on January 1st 2020, a global cap on sulfur was introduced, making the effect of improved fuels reach outside the designated emission control areas. For example, assuming a radiative forcing due to BC from shipping of +1.4 mW m^{-2} [8], a reduction by a third of this value would result in a change of about -0.5 mW m^{-2}. This would be less than 0.05 % of the total RF from all atmospheric BC, and less than 0.03 % of the total RF from CO_2. However, as the shipping traffic is expected to increase, and expand in the Arctic region, this can be of global importance. A continuous update of emission factors will be relevant for estimating future climate impact.

In Paper I, the plume travel distance was relatively short, hence the projected trajectory from the ship to the measurement site had a low uncertainty. On the other hand, the occasionally high ship traffic density, made it difficult to assign a specific ship to an individual plume due to the high frequency of ship plumes in the data. Further, in this study we were mainly interested in the ships that move over larger areas and contribute to emissions elsewhere than in the Port of Gothenburg. Hence, the occasionally frequent number of local vessels, such as tug boats and dredgers, were excluded from, or treated separately in, the analysis.

Due to data not overlapping perfectly in time (e.g. AIS information lacking while BC measurements were ongoing, in Paper I), there are several plumes included which are not identified with AIS. This should not result in an uncertainty in source (only ships give that kind of short peak during winds passing the Port entrance). However, we can be including the tug boats and dredgers occasionally. This is still important for evaluation of the local emissions, i.e. the shipping source in the Port of Gothenburg. However, it is not as representative for the e.g. the Baltic Sea as a whole.

Minutes downwind - Ship plume characteristics at a coastline

Land-based, extractive sampling of ship plumes were performed in the same SECA twice more. These times, of slightly more aged plumes at the Falsterbo peninsula in southern Sweden. Again, plumes were clearly seen in the high frequency (0.2 Hz) time series of particle number concentration. Figure 16 shows the particle volume size distribution for the port and coastal measurements. These average size distributions are obtained from the average of 113 and 200 ship plumes, from the port and coast respectively, and the background particle concentration was defined and subtracted according to the method shown in Figure 10 in the “Data analysis” section. Both the fresh and the slightly aged ship plumes contained a mode around 60-65 nm, and an additional mode was visible for the slightly aged plumes, at 110 nm. A direct comparison between the size distributions can be problematic, since they were sampled with different instrumentation, during different years. The instruments have not been calibrated against each other. The EEPS has been shown to underestimate particles larger than 100 nm, especially aggregate particles including fresh BC, and to have issues with non-unimodal distributions [107, 108].

In the literature there are many examples of observed number size distributions dominated by a nucleation or an Aitken mode, like we show in Figure 11, and a rBC mass mode around 120-180 nm [87, 109]. There are also reports on an additional mode of very large rBC particles from ships running on heavy fuel oil, in the range 300-640 nm [76, 88]. This mode is not observed in our coastal or port observations, which is potentially due to the relatively high fraction of distillate fuels used in the Baltic Sea (see Figure 4).

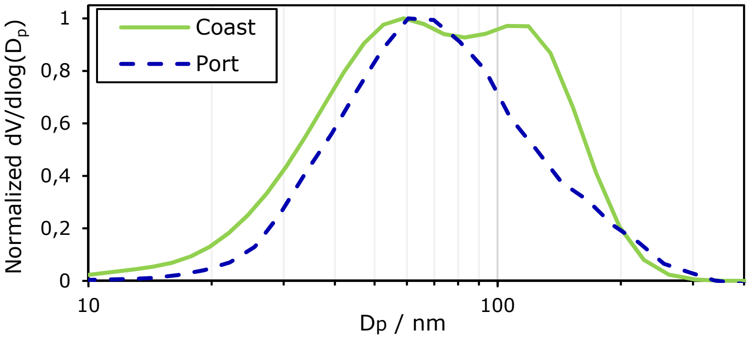


Figure 16.
Average ship plume particle volume size distribution, measured for 200 plumes with EEPS (Port) and 113 plumes with SMPS (Coast). The volume is calculated from number size distributions, assuming spherical particles, and the y-axis is normalized so that the maximum value is equal to 1 for both samples.

A conclusion from both summer and winter coastal observations was that the ship contribution to PM was rather small compared to the ambient background. A ship plume did on average contain 80 ng m^{-3} $PM_{0.5}$ (particulate matter below 500 nm diameter and assuming spherical particles of density 1.5 g cm^{-3}), and with the ship traffic density at that time this corresponded to a local annual average concentration of 18-37 ng m^{-3}. There were some differences in size distributions and daily aerosol contribution between summer and winter results as seen in Paper III.

A ship plume in Falsterbo did on average contain about 10 ng m^{-3} of eBC and 3.4 µg m^{-3} of NO_2, corresponding to an annual average of 3.5 ng m^{-3} and 1.2 µg m^{-3}, respectively. Hence, on average, a ship plume contained about 13 % eBC, by mass. But the eBC contribution is unevenly distributed and there is a generally large plume-to-plume variation for all aerosol species. The shipping lane in this study contributed to about 1.4 % of the local eBC levels. In the 33 ship plumes which were observed in the SP-AMS data, the average non-refractory PM_1 was 0.22 µg m^{-3}, composed of 56 % organics and 36 % sulfate.

There are recent examples from the literature of estimations of the contribution of BC to the air quality in the Baltic region. As presented by Karl *et al.* (2019), the modeled contribution to EC was 4-5 %. This is substantially higher than our 1.4 %. The discrepancy could be due to different years, and consequently different emission factors, or that our eBC data is limited to the winter season, which affects the background eBC concentration (see Table 2). It is also expected to observe a lower contribution from a single lane. Zanatta *et al.* (2019) measured an enhancement of rBC (from SP2) of 1.11 and of aerosol extinction (scattering + absorption) of 1.01 along shipping lanes. This strengthens the claim that the absorption of eBC from shipping is low compared to the background aerosol in the Baltic Sea.

Ramacher *et al.* (2019) estimated the urban population exposure of the total $PM_{2.5}$ from shipping to 1-3 % [110] and Karl *et al.* (2019) modelled average contribution to $PM_{2.5}$ levels in coastal land areas in the Baltic Sea region to be in the range of 3.1-5.7 %. This is similar to the results presented by Hammingh *et al.* (2012) [111], and illustrated in the review by Viana *et al.* (2014), see Figure 17 [112]. As can be seen in this figure, the PM emissions from shipping in the Baltic region are not very high compared to background concentrations. In contrast, the countries around the Mediterranean Sea are exposed to comparatively high PM levels from shipping. This region has been discussed as a potential future SECA [113]. According to our study and others, such an establishment could have a large impact on the air quality in Europe and specifically in the coastal areas in the Mediterranean region.

Despite low PM contribution, the contribution to particle number concentration was substantial, ~10-18 %. This is in line with previous literature which has shown that ship emissions are dominated by particles in the nucleation mode [26, 87, 88]. Karl *et al.* (2020) modeled the ultrafine particle number concentration in ship plumes, and found a factor of 2 increase compared to background concentrations 3.6 km downwind of the ship stack [114]. The ships we studied were 7-20 km away, and during days with ship influence, the number concentration increased by a factor of 1.14-1.25. Other ambient observations from the literature are similar our results, with elevated factors of ultrafine particle number concentration of 1.11-1.19 (25-60 km downwind) [115],1.25-2.97 (few 100 m downwind) [116] and 1.55 (airborne observations above a shipping lane) [88].

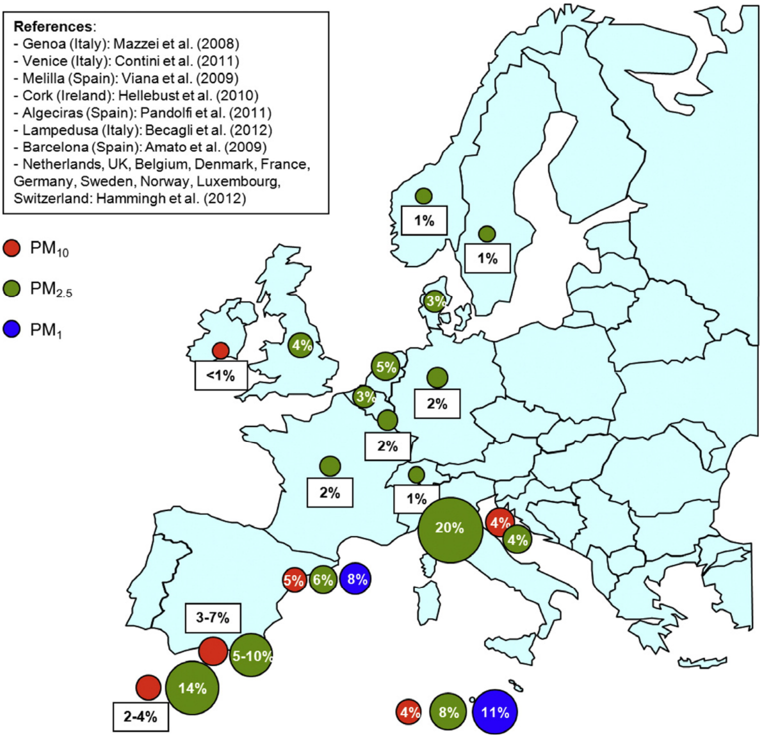


Figure 17.
Contribution from shipping emissions to PM$_1$, PM$_{2.5}$, and PM$_{10}$ across Europe. Larger circles represent higher contribution. Reprinted with permission from [112].

The ship plumes in this study were on the order of 30 minutes old. If there is additional condensation due to presence of VOCs and SO$_2$, secondary PM can be larger further downwind of the source. We used an oxidation flow reactor to simulate additional aging during parts of the summer campaign. Four times during a five-day period, significant secondary aerosol formation was observed (see Paper III). It was not possible to distinguish individual plumes when using the reactor, hence it is still not clear how much shipping could influence the total particle exposure. According to Viana *et al.* (2014), shipping contributions in Europe were 40–30% primary and 60–70% secondary in PM$_{2.5}$ mass concentrations, but a need for more studies was highlighted. Karl *et al.* (2019) showed that the SECA regulations have resulted in substantial decrease in both primary and secondary PM$_{2.5}$ from shipping [57], which could explain the difficulties in observing secondary aerosol formation, and the low PM contribution in general in Falsterbo in Paper II and III.

In Paper II and III, the plume travel distance was relatively long compared to Paper I. This posted a challenge in attributing the correct AIS signal to the corresponding ship, since the wind speed and direction were determining the time of the plume passage at our measurement site. This problem was solved through a method, which is described in detail in Paper I, and illustrated in Figure 9. Through this method, the AIS position of the ship was combined with wind data to calculate a plume trajectory and hence gave an estimate of the expected plume passage. Due to the relatively low frequency of ship passages, compared to the Port measurements, the attribution of a ship identity to individual plumes became rather straightforward.

Due to the longer plume travel distance in Falsterbo, there was also substantial dilution of the ship aerosol before detection at the measurement site. With the setup used in our field campaign, it was not possible to calculate a CO_2 concentration for any plumes, and only possible to calculate a chemically resolved particle mass contribution for 33 of the plumes.

Due to the dilution of the plumes and consequently the lack of CO_2 concentration, emission factors were not determined in Falsterbo. However, if we use the noise in the CO_2 measurements as an upper estimate of the plume concentration, we can calculate a theoretical 'minimum emission factor' of any plume variable (EF_X), using

$$EF_x = \frac{\Delta[\mathrm{X}]}{\Delta[\mathrm{CO_2}]} \cdot EF_{co_2} \tag{4}$$

where $\Delta[X]$ is the plume contribution of the variable X, and $\Delta[CO_2]$ is the variance of CO_2 observed in the time series. This variance is set to 0.8 ppm, corresponding to 3σ (the manufacturer states it to be less than 1ppm). The emission factor of CO_2, EF_{CO2}, is set to 3.2 kg (kg fuel)$^{-1}$ [26]. Using our typical observed values of plume contributions to particle number concentration (PN = 750 cm^{-3}), mass concentration ($PM_{0.5}$ = 80 ng m^{-3}), eBC (10 ng m^{-3}), and NO_2 (3.4 µg m^{-3}), gives the following minimum emission factors: $EF_{PN} = 1.7 \cdot 10^{15}$ (kg fuel)$^{-1}$, $EF_{PM0.5}$ = 0.18 g (kg fuel)$^{-1}$, EF_{eBC} = 0.022 g (kg fuel)$^{-1}$, and EF_{NO2} = 7.6 g (kg fuel)$^{-1}$. Note that these are based on the average concentration, and the heterogeneous nature of the ship plumes would give varying emission factors if calculated for individual ships.

The literature values on PM emission factors from ships are scattered and are shown to be highly dependent on engine load and fuel type. The EF_{PM} of the entire global fleet has been estimated to 6.0 g (kg fuel)$^{-1}$ in 2001 [117]. From later studies of single ships in the Baltic and North Sea, EF_{PM} from 0.06 to 5.3 g (kg fuel)$^{-1}$ are presented [53, 64]. To compare with our coastal observations, an average EF_{PM} from a large (n=734) sample of ship plumes is presented by Jonsson *et al.* (2011). They calculated the $EF_{PM0.560}$ to be 2.05 g (kg fuel)$^{-1}$, which is about a factor of ten larger than our coastal observations

[26]. For a discussion on literature EF_{eBC}, see paper I. Our estimated EF_{eBC} from the coastal measurements are less than 10 % of the EF_{eBC} observed in the Port of Gothenburg (see the previous section).

Beecken *et al.* (2014) present particle number and NO_x emission factors from ship plume sampling in the Baltic and North Sea SECA in 2011 and 2012, and also present emission factor values from the literature [118, and references therein]. EF_{PN} are in the range $0.32 \cdot 10^{16}$-$6.2 \cdot 10^{16}$ (kg fuel)$^{-1}$, and when only considering studies with large samples (>100) of ships, the EF_{PN} is typically in the range $0.8 \cdot 10^{16}$-$2.55 \cdot 10^{16}$ (kg fuel)$^{-1}$ [26, 118, 119]. Compared to this, the estimated minimum EF_{PN} from our coastal measurements is about a factor ten smaller.

Again, according to Beecken *et al.*, the literature EF_{NOx} are in the range 13-73 g (kg fuel)$^{-1}$ [118]. For the studies of ship fleets (> 100 ships), the range is more narrow, 50-70 g (kg fuel)$^{-1}$ [118-120]. Additionally, Betha *et al.* (2017) showed that a renewable ship fuel had an EF_{NOx} in the range 47-55 g (kg fuel)$^{-1}$, compared to 51-64 g (kg fuel)$^{-1}$ of an ultra-low sulfur diesel fuel [121]. All of these values are a factor of seven to ten larger than our calculated value.

Karl *et al.* (2020) describe how NO_x is diluted within a ship plume with travel distance with a power law function [114]. Assuming these parameters for CO_2, which is also an inert gas, and a CO_2 concentration at the ship stack of 5 % [65], we could expect to sample a ship plume CO_2 concentration of about 0.2-0.7 ppm in Falsterbo, 7-20 km downwind. If this is accurate, the minimum theoretical EFs calculated above could by increased by up to a factor 5. Of course, there should still be a large ship to ship variability in both CO_2 emissions and in plume dispersion, depending on meteorology. Hence, for measurements at such long distances (> 7 km), a highly sensitive CO_2 measurement method is recommended. For accurate emission factor measurements of ambient ship plumes, it could also be motivated to measure closer to the source.

Hours downwind - BC from city to rural

In Paper IV, the aim was to characterize the ambient aerosol at a rural and urban site, as well as the changes in aerosol properties during the transport between these nearby sites.

The total concentration was strongly correlated between the two sites, and the mass fractions of chemical compounds was similar during the period with parallel AMS measurements (see Paper IV, Figure 5). However, despite this close relationship, there was a major difference in the local traffic contribution at the urban site. This contribution is most frequent during traffic rush hours, and is mainly composed of BC and OA, and is seen as short (second to minutes) peaks on top of the urban background.

The eBC concentration was making up about 5 % of the total PM_1 at both sites, but the absolute concentration of eBC (and rBC) was about 2.2-2.5 times higher in the city than at the rural site (see Table 3). The average number of rBC containing particles was estimated to be about three times higher at the urban site, and higher during traffic rush hours. The relative number of rBC containing particles compared to the total particle number concentration was ca 13.4±5.5 % in the city, and 2.7±0.6 % at the rural site.

The mean diameter of the rBC cores was similar at the two sites, but slightly larger at the rural site (168±12 nm compared to 141±11 nm). Additionally, measurements of particle density showed two externally mixed mass modes of 150 nm sized particles at the urban site, which has previously been associated with fresh and agglomerated versus aged and dense combustion particles [122]. A larger fraction of the BC particles were also found to be more heavily coated at the rural site, which is in line with the rapid soot aging described by Eriksson *et al.* (2017) [123].

As described in the Methods section, we attempted to study the contribution of the urban region of Malmö and Copenhagen on the aerosol properties at the rural background site. Figure 18 shows a period of AMS and aethalometer measurements at the rural background site. The purple, shaded periods are influenced by the urban region, according to HYSPLIT air mass back trajectories. From Figure 18, it might appear as if the urban region has a large influence on the concentration of all aerosol species, with high concentrations during the second half overlapping with long periods of urban influence. However, when looking at the seven days' air mass back trajectories, it is rather the geographical origin before reaching Sweden, which causes the high concentration periods. This also became evident when analyzing eBC concentrations from a whole year. During 2018, there was no significant increase in eBC for air masses which had passed the urban region. However, if a subset of the data is considered, a significant contribution could be distinguished. This was the case for air masses of southwesterly origin, i.e. with relatively low background concentrations but with frequent passage over the urban region, which was associated with a factor of 1.1 higher eBC concentrations. It was also the case for all air masses with little wet scavenging through precipitation (< 1 mm), during which the eBC concentration was a factor 1.6 higher (corresponding to ~0.1 $\mu g\ m^{-3}$) during periods of urban influence. In general, southeasterly air masses were associated with eBC concentrations 3-6 times higher than for all other geographical origins.

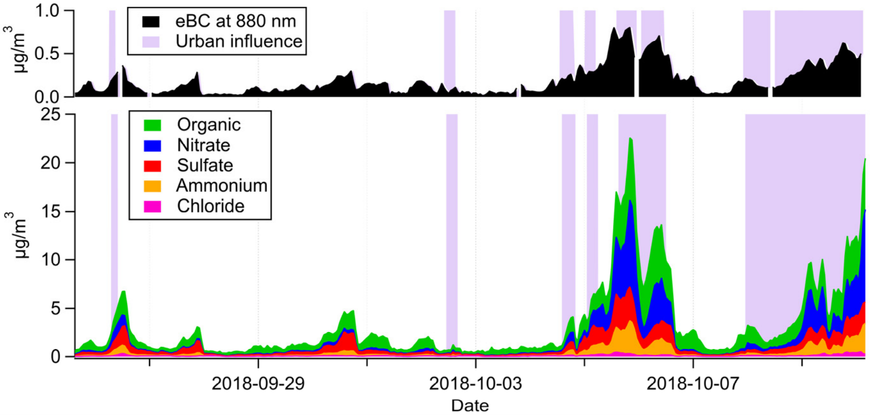


Figure 18.
Time series of eBC and non-refractory carbon mass from the HR-ToF-AMS during a period in autumn at the Hyltemossa rural background station. The shaded area marks periods when the air mass arriving at Hyltemossa had passed the area of Copenhagen and Malmö.

In order to examine the physicochemical properties of the urban aerosol upon reaching the rural site, the data from October 2nd was selected as a case study (from now on called the *urban plume*). This day was chosen due to the relatively clean air mass, originating from the North Sea, see Figure 19a. During this day, the air mass was sweeping over the urban area, resulting in urban plume influence at the rural site during approximately five hours. The hours before and after this passage are defined as a background. The background and the urban plume particle number size distributions are shown in Figure 19c. This figure also includes the size distribution from a day with southeastern (SE) air mass influence (October 11th, see Figure 19b) for comparison. The total number concentration was a factor 1.9 higher during urban influence compared to the background. Both in the background and in the urban plume, two particle modes were present, at 50 nm and 215 nm. Hence, there was no significant difference in particle size during urban influence. In contrast, the size distribution is dominated by larger particles during southeastern influence. The difference in diameter can be due to different particle sources, or can reflect the aging of the particles, with increasing diameters due to more condensation and coagulation during longer atmospheric aging. Compared to the size distribution sampled at the urban site (see Figure 11), the particles at the Hyltemossa rural site were typically larger than in Malmö (geometric mean diameter of 18 nm).

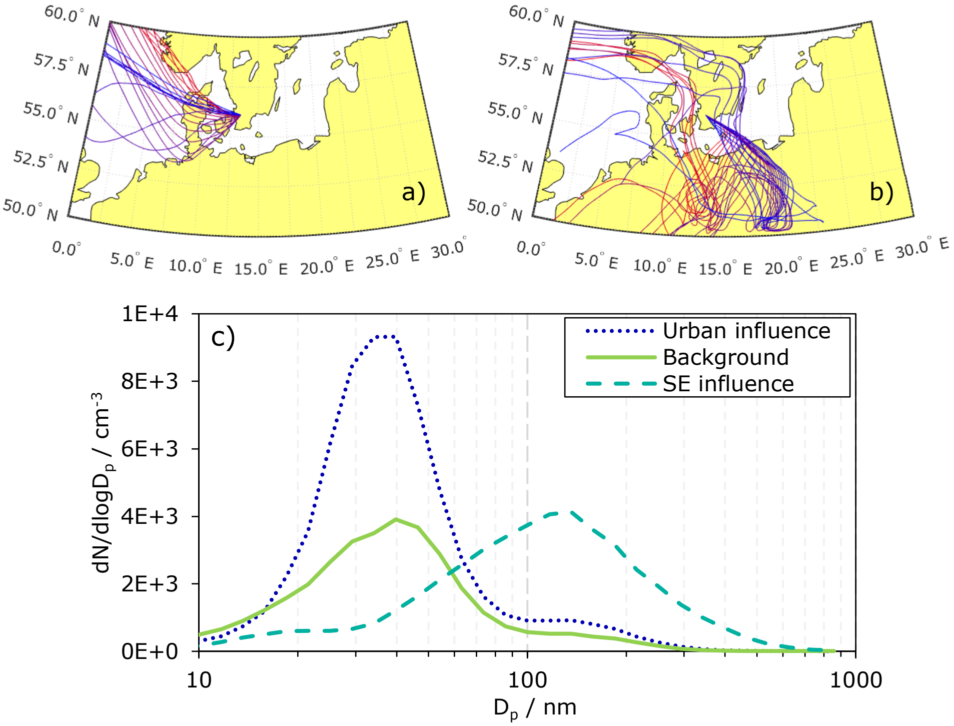


Figure 19.
A case study of the particle size distributions during two days in October. a) Seven days' air mass back trajectories for the day 2018-10-02. This air mass was of westerly, marine origin. b) Seven days' air mass back trajectories for the day 2018-10-11, the air mass had passed parts of eastern Europe. c) Particle number size distribution during Oct 2nd, separated into hours when the air mass had passed Malmö/Copenhagen (Urban influence), and not (background), and from Oct 11th (SE influence).

For the same case, October 2nd, the organic aerosol sampled with the AMS was examined at the rural site. Subtracting the background organic aerosol mass spectrum from the plume, resulted in a net urban plume contribution, which is shown in Figure 20 a. In this mass spectrum, the m/z 18, 28, and 44 are not included due to currently unsolved issues with water and carbon dioxide subtraction. Similarly, 90 traffic plumes from the AMS at the urban site were selected and the background (defined as a few minutes before and after a traffic peak, see Paper IV) was subtracted. The net urban traffic emission mass spectrum is shown in Figure 20 b for comparison. The urban traffic organic aerosol exhibits typical features of previously reported hydrocarbon-like organic aerosols, such as a high m/z 57 ($C_4H_9^+$) and generally a pattern of high $C_nH_{2n-1}^+$ and $C_nH_{2n+1}^+$, characteristic for traffic emissions [124, 125]. A similar pattern can be seen at the rural site during urban plume influence, indicating transported traffic emissions from the city. There are relatively more oxygenated species

($C_lH_mO^+$ and $C_lH_mO_o^+$) at the rural site, which is in line with atmospheric oxidation during transport.

Other days with urban influence were also examined, but the difference between background and plume aerosol was negligible. Hence, a conclusion from the study of these two nearby sites is that during periods of high background concentrations, the urban influence from the nearby region of Malmö/Copenhagen is not of a relatively high importance. Still, periods with cleaner background air masses can be used to study the influence and physicochemical properties of the Malmö/Copenhagen urban plume on the air quality at the rural site. We have done this for a case study of such an urban plume, but a longer measurement period would make it possible to quantify and characterize the contribution more accurately.

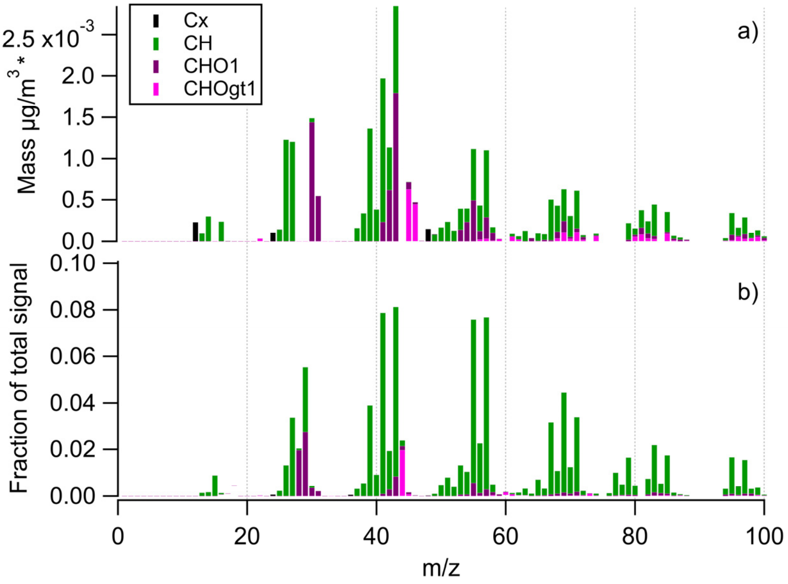


Figure 20.
Organic aerosol mass spectra from the AMS, C_x is pure carbon clusters, CH is hydrocarbons, CHO1 contains one oxygen atom, and CHOgt1 more than one oxygen atoms. a) Urban influence at the Hyltemossa rural background site, during Oct 2nd, with mass given as nitrate equivalent mass, and b) fresh traffic emissions measured at the urban site.

Long range transport - a case of BC source apportionment

As was evident from the measurements in southern Sweden, the air pollution in the region is largely dependent on in transport from other parts of Europe. Air masses from the southeast stood out as the ones contributing the most to high eBC levels in both urban and rural environments. This high contribution is partly due to meteorological effects, such as typically less precipitation with southeasterly winds, but also due to higher source emissions. It is therefore of interest to know more about the anthropogenic sources from this region, both for the understanding what affects the air quality in southern Sweden, as well as in the parts of Europe where these aerosols originate from. Particle source apportionment in Eastern Europe is rarely observed in peer-reviewed literature, and the sources are different from Western Europe.

A combination of standard source apportionment methods for the ambient carbonaceous aerosol were utilized to separate and quantify three combustion source components, contributing to wintertime air pollution in northern Poland. The aerosols light absorption properties were measured online, with high time resolution, and from this the absorption Ångström Exponent (AAE) (see the Section Instrumentation) was derived. The AAE is typically around 1 for the carbonaceous aerosol from traffic emission, or black carbon. Higher AAE values are associated with brown carbon, and typically biomass burning emissions. In the measurement site presented in Paper V however, we know that coal combustion is a large source of heating in the region. Hence, for measurements in Poland and similar places, the assumption of only two main carbonaceous aerosol sources (traffic and biomass burning) is insufficient. Household burning of coal has also been associated with higher AAE values in several studies [126-128]. Therefore, we assumed for this case that the eBC observed from absorption measurements was due to traffic sources, and the BrC was due to both coal and biomass burning sources. From offline chemical analysis of aerosol filters, the daily average concentration of the biomass burning tracer levoglucosan was quantified. From this concentration, a source fraction of biomass burning was apportioned to the total carbonaceous aerosol loading. The coal combustion was then derived from the fraction not attributed to either traffic or biomass burning. This resulted in an average winter source contribution of 3.3 µg m^{-3} (41 %) from domestic coal combustion, 2.9 µg m^{-3} (38 %) from traffic, and 1.63 µg m^{-3} (21 %) from biomass combustion. In this analysis, coal burning was assumed to have the same AAE as biomass burning. Accurate knowledge of the local coal burning AAE would strengthen the analysis. This information could be retrieved from measurements of well-defined local sources, or from detailed data on the typical coal usage in combination with literature AAE values.

Higher PM$_{2.5}$ concentrations were generally observed during periods with slower wind speeds, which is in agreement with the typical features of a stagnant boundary layer during calm, winter conditions. This is not a new finding, but it does again highlight the importance of uncontrollable, meteorological parameters on air pollution and consequently human exposure. A bit surprisingly, high biomass and coal burning contribution was not correlated with temperature. A higher concentration would be expected during colder periods, but this was not seen. There was a tendency towards a lag time in BrC, i.e. that an increased concentration was observed up to four days after a colder period. However, a longer measurement period would be needed for a complete analysis of seasonal and weather trends.

Figure 21 shows the carbonaceous aerosol source contribution during the whole measurement period. Levoglucosan filter data was not available for the entire period, hence, at the beginning and the end of time series the entire non-traffic fraction is shown as coal burning. As described in paper V, there was an event of agricultural grass burning at the end of the sampling period. The Figure 21b shows the fire count in the Baltic Region during this period. At both measurement sites, a distinct increase in carbonaceous aerosol occurs. While this is apportioned to both coal and biomass combustion in Diabła Góra, due to lack of biomass tracer measurements, mass spectrometry data from the other nearby sampling site, Preila, shows a corresponding increase in the biomass burning tracer m/z 60 ($C_2H_4O^+$) (see Paper V). This example of a re-occurring, annual event shows the importance of giving specific attention to events which differ from the typical source pattern for accurate source apportionment. Such events and other trends could be explained if there are long term measurements available, and data on specific source tracers.

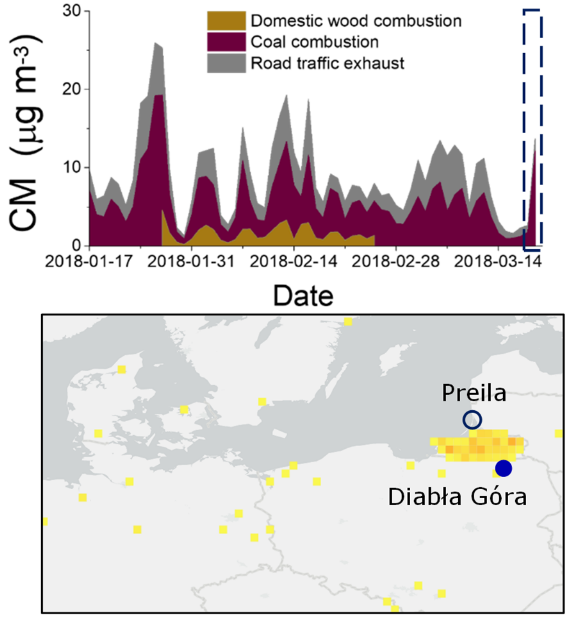


Figure 21.
Carbonaceous aerosol concentration from Diabła Góra, dashed line marks the grass burning event, and map with fire count during March 17-18 [129], and the location of Diabła Góra and Preila marked.

Outlook

In this thesis, I have characterized fresh and semi-aged ship emission plumes. But, there is more to be done for a detailed picture of what shipping emissions look like today, and how they will change in the future. From experience of land-based measurements, a harbor is a suitable location for further studies of fresh shipping PM. An oxidation flow reactor can be used to simulate further atmospheric aging of the plumes. Ambient observations of ship plumes over a longer time period should include multi-wavelength absorption measurements for investigating absorption properties, which is of high relevance for climate effects. Microscopy studies of the morphology and soot microstructure could also be useful for identifying typical ship BC types. Further deployment of OFR and SP-AMS at coastal sites would be valuable to estimate SOA formation, together with additional measurements of SOA precursors for enhanced process understanding.

Looking beyond the Baltic region, it is relevant to find accurate ways to translate observations to other geographical areas, or expand measurements to these areas. For example, the Arctic region is an area of particular interest, due to the potentially high relative increase of BC in an otherwise very clean environment. Another example is the Mediterranean region, an area with large population and lot of coastline, but no SECA. The ambitions of the International Maritime Organization to reduce CO_2 and BC from shipping will introduce significant adoption of other potential fuels. These fuels include LNG, methane, methanol, ammonia, or distillates of renewable origin. The physico-chemical properties of such emissions will be important to characterize for updated emission databases of a growing shipping sector.

Continued research is needed to identify and describe the key processes of the initial stages of atmospheric aging of soot. Further studies of urban plumes should include longer observations of these phenomena, and potentially at shorter distances (than 60 km), in several points along the air mass trajectory, and in combination aerosol dynamics and chemistry modeling.

The health effect of poor air quality and PM has largely focused on $PM_{2.5}$. For a better understanding of the health effects of anthropogenic combustion emissions, this should be expanded to also specifically target the toxicity and epidemiological effects of ultrafine particles, and subcategories of $PM_{2.5}$ such as black carbon.

Physiochemical characterization and emission factors of domestic coal appliances are needed for identification of new source tracers and estimation of AAE values, for accurate source apportionment in both rural and urban regions. Laboratory studies or ambient characterization inside residential areas with 100 % coal appliances could be performed to get better chemical source tracer marker characterization for domestic coal combustion.

For widespread air quality monitoring and source apportionment of BC, cheaper and less labor requiring methods are desirable, such as the light absorption methods. It will be important to understand how these compare to other methods which measure different BC properties (eBC, vs rBC, vs EC) in different environments. To develop source apportionment models, like the aethalometer model, which can differentiate between more than two main sources, will be important in regions affected by multiple sources. A suggestion could be the combination with aerosol mass spectrometry monitoring techniques (ACSM) for assessing the non-refractory aerosol chemical composition.

Acknowledgments

I would like to thank my main supervisor, Adam Kristensson. You have always been positive towards my ideas, and I value your constant optimism and kindness. My co-supervisors, Axel Eriksson, Birgitta Svenningsson, and Thomas Bjerring Kristensen. I diverse group of many experts, which I have had the pleasure to work with. An extra shout-out to Axel, without your AMS skills and talent for finding interesting results in every data set, this thesis would not have been what it is. Erik Ahlberg, I took my first trembling steps as a novice aerosol scientist in your Skrehalla-project, and you have since put so much work into many of my projects. I hope we are sort of even now, even if I don't think that is quite true.

Thank you, Göran Frank, Charlotta Nilsson, Dirk Rudolph, Jane Nilsson, Mari Lundberg, Yulia Lindholm, Anneli Nilsson-Ahlm, and Hanno Perrey for excellent administration of studies, teaching and other work-place related issues.

Mårten Spanne, thank you for your help and contribution in Falsterbo and at Dalaplan and for sharing your extensive experience in aerosol measurements. Moa Sporre, thank you for the discussions on meteorology, an inevitable task when doing ambient measurements. Julija Pauraite, thank you for your engagement in and input to the final paper of this thesis. And to all my other co-authors for your valuable contributions. Many thanks to team at Hyltemossa Research station, and the team at the "Big-Glenn" campaigns in Gothenburg, teamwork has indeed proven to be great for science.

I want to express gratitude to the ClimBEco research school for great opportunities to meet fellow PhD students and senior researchers, and for providing interesting courses. I have also been a teacher myself, in 14 courses (if counted correctly) during these years. Thanks to all the teaching colleagues at Nuclear Physics and to all students, you are a source of inspiration and motivation. Speaking of teaching, I want to take the opportunity to acknowledge all of my high school and upper secondary school science teachers for planting the seeds which led me onto the path of science and experiments.

To all my colleagues at KF and EAT over the years, especially John, Johan M., Oscar, Moa, Johan F., Cerina, Emilie, Malin, Christina, Jonas, Ville, Yuliya, Louise, Madeleine, Sara, Patrik, Christian, thank you for many lovely memories. Karin Lovén, we have shared office since the beginning. I don't think I could have had any better start and journey than that. Your sense of organization is a trait I appreciate and share, and you have been my steady bridge to the EAT community and for this I am very grateful.

Thank you Elna Heimdal Nilsson. I am very grateful for having had you as my supervisor during my undergraduate studies. Many of the tools I learnt during that time are still invaluable to me, both in work and in life in general. It has also been a pleasure to work with you later as a teacher. You were actually the one who recommended me to apply for this PhD student position, so I guess you are somewhat responsible also for the existence of this thesis.

Thank you to the Physics and Lasershow crew. Sometimes I can miss the adventures, we had a lot of them. Keep up the good work! Men akta, den är limmad… To P-O and Johan, in addition to being kind, smart, and humorous, you have taught me the immense importance of communicating science to everyone. And also a few party-tricks along the way.

To all my friends in Lund and beyond. Thank you for all the memorable moments outside of work and studies. What would these years have been without Rydbergs, board game evenings, celebrations, and just everyday things? You know who you are!

To my family, Yvonne, Kalju, and Erik. Thank you for your never-ending love, generosity, and support. You have always believed in me, probably more than I do myself. (And thank you for proofreading the popular summary for this thesis.)

Michael. Thank you for helping me through all the moments. If I can be just half as good a support to you as you have been to me when it is your turn, I will be proud. Let's continue to discover the world, life, and happiness together!

References

1. EEA, *Air quality in Europe 2019.* 2019. DOI: 10.2800/822355.
2. The Intergovernmental Panel on Climate Change (IPCC), *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.* 2013.
3. Corbett, J.J., Lack, D.A., Winebrake, J.J., Harder, S., Silberman, J.A., and Gold, M., *Arctic shipping emissions inventories and future scenarios.* Atmospheric Chemistry and Physics, 2010. **10**(19): p. 9689-9704.
4. Dalsøren, S.B., Samset, B.H., Myhre, G., Corbett, J.J., Minjares, R., Lack, D., and Fuglestvedt, J.S., *Environmental impacts of shipping in 2030 with a particular focus on the Arctic region.* Atmospheric Chemistry and Physics, 2013. **13**(4): p. 1941-1955.
5. Bond, T.C., Doherty, S.J., Fahey, D.W., Forster, P.M., Berntsen, T., DeAngelo, B.J., . . . Zender, C.S., *Bounding the role of black carbon in the climate system: A scientific assessment.* Journal of Geophysical Research: Atmospheres, 2013. **118**(11): p. 5380-5552.
6. Wittbom, C., Eriksson, A.C., Rissler, J., Carlsson, J.E., Roldin, P., Nordin, E.Z., . . . Svenningsson, B., *Cloud droplet activity changes of soot aerosol upon smog chamber ageing.* Atmospheric Chemistry and Physics, 2014. **14**(18): p. 9831-9854.
7. Yun, Y., Penner, J.E., and Popovicheva, O., *The effects of hygroscopicity on ice nucleation of fossil fuel combustion aerosols in mixed-phase clouds.* Atmospheric Chemistry and Physics, 2013. **13**(8): p. 4339-4348.
8. Balkanski, Y., Myhre, G., Gauss, M., Rädel, G., Highwood, E.J., and Shine, K.P., *Direct radiative effect of aerosols emitted by transport: from road, shipping and aviation.* Atmospheric Chemistry and Physics, 2010. **10**(10): p. 4477-4489.
9. Eyring, V., Isaksen, I.S.A., Berntsen, T., Collins, W.J., Corbett, J.J., Endresen, O., . . . Stevenson, D.S., *Transport impacts on atmosphere and climate: Shipping.* Atmospheric Environment, 2010. **44**(37): p. 4735-4771.
10. Sofiev, M., Winebrake, J.J., Johansson, L., Carr, E.W., Prank, M., Soares, J., . . . Corbett, J.J., *Cleaner fuels for ships provide public health benefits with climate tradeoffs.* Nature Communications, 2018. **9**(1): p. 406.
11. NASA Earth Observatory, *Ship Tracks in the Northern Pacific.* 2008. [Accessed: 2020-02-15]; Available from: https://earthobservatory.nasa.gov/images/20248/ship-tracks-in-the-northern-pacific.

12. Wilkins, E., *Air pollution and the London fog of December, 1952.* Journal of the Royal Sanitary Institute, 1954. **74**(1): p. 1-21.
13. Haagen-Smit, A.J., *Chemistry and Physiology of Los Angeles Smog.* Industrial & Engineering Chemistry, 1952. **44**(6): p. 1342-1346.
14. Hinds, W.C., *Aerosol technology: properties, behavior, and measurement of airborne particles.* 1999: John Wiley & Sons.
15. Rückerl, R., Schneider, A., Breitner, S., Cyrys, J., and Peters, A., *Health effects of particulate air pollution: A review of epidemiological evidence.* Inhalation Toxicology, 2011. **23**(10): p. 555-592.
16. Pope, C.A., 3rd, Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., and Thurston, G.D., *Lung Cancer, Cardiopulmonary Mortality, and Long-term Exposure to Fine Particulate Air Pollution.* JAMA, 2002. **287**(9): p. 1132-1141.
17. Hoek, G., Krishnan, R.M., Beelen, R., Peters, A., Ostro, B., Brunekreef, B., and Kaufman, J.D., *Long-term air pollution exposure and cardio- respiratory mortality: a review.* Environmental Health, 2013. **12**(1): p. 43.
18. International Agency for Research on Cancer (IARC), *IARC monographs on the evaluation of carcinogenic risks to humans: vol. 109, outdoor air pollution.* 2016: IARC Press Lyon, France.
19. Carey, I.M., Anderson, H.R., Atkinson, R.W., Beevers, S.D., Cook, D.G., Strachan, D.P., . . . Kelly, F.J., *Are noise and air pollution related to the incidence of dementia? A cohort study in London, England.* BMJ Open, 2018. **8:e022404**.
20. Lelieveld, J., Klingmüller, K., Pozzer, A., Pöschl, U., Fnais, M., Daiber, A., and Münzel, T., *Cardiovascular disease burden from ambient air pollution in Europe reassessed using novel hazard ratio functions.* European Heart Journal, 2019. **40**(20): p. 1590-1596.
21. Janssen, N.A.H., Gerlofs-Nijland, M.E., Lanki, T., Salonen, R.O., Cassee, F., Hoek, G., . . . Krzyzanowski, M., *Health effects of black carbon, The WHO European Centre for Environment and Health, Bonn, Germany.* World Health Organisation Regional Office for Europe, Copenhagen, Denmark, 2012.
22. Grahame, T.J., Klemm, R., and Schlesinger, R.B., *Public health and components of particulate matter: The changing assessment of black carbon.* Journal of the Air & Waste Management Association, 2014. **64**(6): p. 620-660.
23. Benbrahim-Tallaa, L., Baan, R.A., Grosse, Y., Lauby-Secretan, B., El Ghissassi, F., Bouvard, V., . . . Straif, K., *Carcinogenicity of diesel-engine and gasoline-engine exhausts and some nitroarenes.* The Lancet Oncology, 2012. **13**(7): p. 663-664.
24. Healy, R.M., O'Connor, I.P., Hellebust, S., Allanic, A., Sodeau, J.R., and Wenger, J.C., *Characterisation of single particles from in-port ship emissions.* Atmospheric Environment, 2009. **43**(40): p. 6408-6414.
25. Pirjola, L., Pajunoja, A., Walden, J., Jalkanen, J.P., Rönkkö, T., Kousa, A., and Koskentalo, T., *Mobile measurements of ship emissions in two harbour areas in Finland.* Atmospheric Measurement Techniques, 2014. 7(1): p. 149-161.

26. Jonsson, Å.M., Westerlund, J., and Hallquist, M., *Size-resolved particle emission factors for individual ships.* Geophysical Research Letters, 2011. **38**(13).

27. Corbett, J.J., Winebrake, J.J., Green, E.H., Kasibhatla, P., Eyring, V., and Lauer, A., *Mortality from Ship Emissions: A Global Assessment.* Environmental Science & Technology, 2007. **41**(24): p. 8512-8518.

28. Brandt, J., Silver, J.D., Christensen, J.H., Andersen, M.S., Bønløkke, J.H., Sigsgaard, T., . . . Hansen, K.M., *Assessment of past, present and future health-cost externalities of air pollution in Europe and the contribution from international ship traffic using the EVA model system.* Atmospheric Chemistry and Physics, 2013. **13**(15): p. 7747-7764.

29. Doney, S.C., Mahowald, N., Lima, I., Feely, R.A., Mackenzie, F.T., Lamarque, J.-F., and Rasch, P.J., *Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system.* Proceedings of the National Academy of Sciences, 2007. **104**(37): p. 14580.

30. Hassellöv, I.-M., Turner, D.R., Lauer, A., and Corbett, J.J., *Shipping contributes to ocean acidification.* Geophysical Research Letters, 2013. **40**(11): p. 2731-2736.

31. Hunter, K.A., Liss, P.S., Surapipith, V., Dentener, F., Duce, R., Kanakidou, M., . . . Zhu, T., *Impacts of anthropogenic SOx, NOx and NH3 on acidification of coastal waters and shipping lanes.* Geophysical Research Letters, 2011. **38**(13).

32. Odén, S., *The acidification of air and precipitation and its consequences on the natural environment.* 1968: State National Science Research Council, Sweden.

33. Likens, G.E., Wright, R.F., Galloway, J.N., and Butler, T.J., *Acid rain.* Scientific American, 1979. **241**(4): p. 43-51.

34. UNECE, *Protecting the Air We Breathe, 40 years of cooperation under the Convention on Long-range Transboundary Air Pollution.* http://www.unece.org/fileadmin/DAM/env/lrtap/Publications/1914867_E_ECE_EB_AIR_NONE_2019_3_200dpi.pdf United Nations Economic Commission for Europe.

35. EC-JRC/PBL, *Emission Database for Global Atmospheric Research (EDGAR).* [Accessed: 2020-02-03]; release EDGAR version 4.3.2:[Available from: http://edgar.jrc.ec.europa.eu/overview.php?v=432.

36. Crippa, M., Guizzardi, D., Muntean, M., Schaaf, E., Dentener, F., van Aardenne, J.A., . . . Janssens-Maenhout, G., *Gridded emissions of air pollutants for the period 1970–2012 within EDGAR v4.3.2.* Earth Syst. Sci. Data, 2018. **10**(4): p. 1987-2013.

37. OECD, *OECD Environmental Outlook to 2050 - The Consequences of Inaction.* 2012. DOI: http://dx.doi.org/10.1787/9789264122246-en.

38. The New York Times, *High Levels of Pollution Spur Paris to Action.* March 14, 2014 [Accessed: 2020-02-09]; Available from: https://www.nytimes.com/2014/03/15/world/europe/paris-suffers-a-spring-smog-attack.html.

39. Vieno, M., Heal, M.R., Twigg, M.M., MacKenzie, I.A., Braban, C.F., Lingard, J.J.N., . . . Reis, S., *Corrigendum: The UK particulate matter air pollution episode of March–April 2014: more than Saharan dust (2016Environ. Res. Lett.11044004).* Environmental Research Letters, 2016. **11**(5): p. 059501.

40. The New York Times, *Beijing, Bracing for 5 Days of Heavy Pollution, Issues Red Alert.* December 2016 [Accessed: 2020-02-09]; Available from: https://www.nytimes.com/2016/12/16/world/asia/beijing-air-pollution.html.

41. Hindustan Times, *Delhi's worst smog yet wakes up govt, emergency measures announced.* November 2016 [Accessed: 2020-02-09]; Available from: https://www.hindustantimes.com/delhi/delhi-sees-season-s-worst-air-quality-kejriwal-announces-emergency-steps/story-J11rGcyCdk2wn6T4jqxG2O.html.

42. Los Angeles Times, *Utah is the land of ski runs, pristine parks and a really bad smog problem*. February 2017 [Accessed: 2020-02-09]; Available from: https://www.latimes.com/nation/la-na-utah-smog-2017-story.html.

43. The Santiago Times, *Smog emergency in Santiago de Chile*. May 2018 [Accessed: 2020-02-09]; Available from: https://santiagotimes.cl/2018/05/30/smog-emergency-in-santiago-de-chile/.

44. SFS 2010:477, *Luftkvalitetsförordning*, S.M.-o. energidepartementet, Editor.

45. Naturvårdsverket, *Luftguiden*. 2019, Arkitektkopia AB, Bromma: Naturvårdsverket.

46. Review of Maritime Transport. 2019: United Nations Conference on Trade and Development.

47. Smith, T., Jalkanen, J., Anderson, B., Corbett, J., Faber, J., Hanayama, S., . . . Pandey, A., *Third IMO GHG Study 2014: Executive Summary and Final Report*. 2014: International Maritime Organization (IMO), London, UK.

48. IMO, *The International Convention for the Prevention of Marine Pollution from Ships, 1973 as modified by the Protocol of 1978 relating there to (MARPOL 73/78), Annex VI: Prevention of Air Pollution from Ships, 2008 Amendments*. 2008, International Maritime Organization: London, UK.

49. Jonson, J.E., Jalkanen, J.P., Johansson, L., Gauss, M., and Denier van der Gon, H.A.C., *Model calculations of the effects of present and future emissions of air pollutants from shipping in the Baltic Sea and the North Sea.* Atmospheric Chemistry and Physics, 2015. **15**(2): p. 783-798.

50. Mellqvist, J., Beecken, J., Conde, V., and Ekholm, J., *Surveillance of Sulfur Emissions from Ships in Danish Waters, Report.* 2017. DOI: 10.17196/DEPA.001.

51. Chu Van, T., Ramirez, J., Rainey, T., Ristovski, Z., and Brown, R.J., *Global impacts of recent IMO regulations on marine fuel oil refining processes and ship emissions.* Transportation Research Part D: Transport and Environment, 2019. **70**: p. 123-134.

52. Claremar, B., Haglund, K., and Rutgersson, A., *Ship emissions and the use of current air cleaning technology: contributions to air pollution and acidification in the Baltic Sea.* Earth System Dynamics, 2017. **8**(4): p. 901-919.

53. Zetterdahl, M., Moldanová, J., Pei, X., Pathak, R.K., and Demirdjian, B., *Impact of the 0.1% fuel sulfur content limit in SECA on particle and gaseous emissions from marine vessels.* Atmospheric Environment, 2016. **145**: p. 338-345.
54. Petzold, A., Lauer, P., Fritsche, U., Hasselbach, J., Lichtenstern, M., Schlager, H., and Fleischer, F., *Operation of Marine Diesel Engines on Biogenic Fuels: Modification of Emissions and Resulting Climate Effects.* Environmental Science & Technology, 2011. **45**(24): p. 10394-10400.
55. Burel, F., Taccani, R., and Zuliani, N., *Improving sustainability of maritime transport through utilization of Liquefied Natural Gas (LNG) for propulsion.* Energy, 2013. **57**: p. 412-420.
56. IMO, *Prevention of air pollution from ships, Information on NOX Emissions from Shipping in the Baltic Sea Area, MEPC 57/INF.14.* 2008, International Maritime Organization.
57. Karl, M., Bieser, J., Geyer, B., Matthias, V., Jalkanen, J.P., Johansson, L., and Fridell, E., *Impact of a nitrogen emission control area (NECA) on the future air quality and nitrogen deposition to seawater in the Baltic Sea region.* Atmospheric Chemistry and Physics, 2019. **19**(3): p. 1721-1752.
58. Tollefson, J., *UN agency targets black-carbon pollution from ships.* Nature, 2018. **554**(7691).
59. IMO, *UN body adopts climate change strategy for shipping.* 13/04/2018 http://www.imo.org/en/MediaCentre/PressBriefings/Pages/06GHGinitialstrategy.aspx The International Maritime Organization (IMO).
60. IMO, *AIS transponders*. 2020. [Accessed: 2020-02-22]; Available from: http://www.imo.org/en/OurWork/safety/navigation/pages/ais.aspx.
61. Eurostat, *Energy, transport and environment statistics* 2019. DOI: doi:10.2785/660147.
62. OECD, I., *Energy and Air Pollution: World Energy Outlook Special Report 2016.* 2016.
63. Matti Maricq, M., *Chemical characterization of particulate emissions from diesel engines: A review.* Journal of Aerosol Science, 2007. **38**(11): p. 1079-1118.
64. Moldanová, J., Fridell, E., Popovicheva, O., Demirdjian, B., Tishkova, V., Faccinetto, A., and Focsa, C., *Characterisation of particulate matter and gaseous emissions from a large ship diesel engine.* Atmospheric Environment, 2009. **43**(16): p. 2632-2641.
65. Khan, M.Y., Ranganathan, S., Agrawal, H., Welch, W.A., Laroo, C., Miller, J.W., and Cocker, D.R., *Measuring in-use ship emissions with international and U.S. federal methods.* Journal of the Air & Waste Management Association, 2013. **63**(3): p. 284-291.
66. Simpson, C.D., *Emission of Polycyclic Aromatic Hydrocarbons (PAHs) and Nitrated Polycyclic Aromatic Hydrocarbons (NPAHs) from Diesel Engines and Vehicles*, in *Polycyclic Aromatic Hydrocarbons: Environmental Behavior and Toxicity in East Asia*, K. Hayakawa, Editor. 2018, Springer Singapore: Singapore. p. 65-74.

67. Kim, K.-H., Jahan, S.A., Kabir, E., and Brown, R.J.C., *A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects.* Environment International, 2013. **60**: p. 71-80.

68. Streibel, T., Schnelle-Kreis, J., Czech, H., Harndorf, H., Jakobi, G., Jokiniemi, J., . . . Zimmermann, R., *Aerosol emissions of a ship diesel engine operated with diesel fuel or heavy fuel oil.* Environmental Science and Pollution Research, 2017. **24**(12): p. 10976-10991.

69. Corbin, J.C., Mensah, A.A., Pieber, S.M., Orasche, J., Michalke, B., Zanatta, M., . . . Gysel, M., *Trace Metals in Soot and PM2.5 from Heavy-Fuel-Oil Combustion in a Marine Engine.* Environmental Science & Technology, 2018. **52**(11): p. 6714-6722.

70. Canagaratna, M.R., Jayne, J.T., Ghertner, D.A., Herndon, S., Shi, Q., Jimenez, J.L., . . . Worsnop, D.R., *Chase Studies of Particulate Emissions from in-use New York City Vehicles.* Aerosol Science and Technology, 2004. **38**(6): p. 555-573.

71. Eichler, P., Müller, M., Rohmann, C., Stengel, B., Orasche, J., Zimmermann, R., and Wisthaler, A., *Lubricating Oil as a Major Constituent of Ship Exhaust Particles.* Environmental Science & Technology Letters, 2017. **4**(2): p. 54-58.

72. Smith, S.J., van Aardenne, J., Klimont, Z., Andres, R.J., Volke, A., and Delgado Arias, S., *Anthropogenic sulfur dioxide emissions: 1850–2005.* Atmospheric Chemistry and Physics, 2011. **11**(3): p. 1101-1116.

73. Petzold, A., Ogren, J.A., Fiebig, M., Laj, P., Li, S.M., Baltensperger, U., . . . Zhang, X.Y., *Recommendations for reporting "black carbon" measurements.* Atmospheric Chemistry and Physics, 2013. **13**(16): p. 8365-8379.

74. Pöschl, U., *Atmospheric Aerosols: Composition, Transformation, Climate and Health Effects.* Angewandte Chemie International Edition, 2005. **44**(46): p. 7520-7540.

75. Corbin, J.C., Czech, H., Massabò, D., de Mongeot, F.B., Jakobi, G., Liu, F., . . . Gysel, M., *Infrared-absorbing carbonaceous tar can dominate light absorption by marine-engine exhaust.* npj Climate and Atmospheric Science, 2019. **2**(1): p. 12.

76. Corbin, J.C., Pieber, S.M., Czech, H., Zanatta, M., Jakobi, G., Massabò, D., . . . Gysel, M., *Brown and Black Carbon Emitted by a Marine Engine Operated on Heavy Fuel Oil and Distillate Fuels: Optical Properties, Size Distributions, and Emission Factors.* Journal of Geophysical Research: Atmospheres, 2018. **123**(11): p. 6175-6195.

77. Kristensen, T.B., Müller, T., Kandler, K., Benker, N., Hartmann, M., Prospero, J.M., . . . Stratmann, F., *Properties of cloud condensation nuclei (CCN) in the trade wind marine boundary layer of the western North Atlantic.* Atmospheric Chemistry and Physics, 2016. **16**(4): p. 2675-2688.

78. Zhang, R., Khalizov, A.F., Pagels, J., Zhang, D., Xue, H., and McMurry, P.H., *Variability in morphology, hygroscopicity, and optical properties of soot aerosols during atmospheric processing.* Proceedings of the National Academy of Sciences, 2008. **105**(30): p. 10291.

79. Qiu, C., Khalizov, A.F., and Zhang, R., *Soot Aging from OH-Initiated Oxidation of Toluene.* Environmental Science & Technology, 2012. **46**(17): p. 9464-9472.

80. Kumar, N.K., Corbin, J.C., Bruns, E.A., Massabó, D., Slowik, J.G., Drinovec, L., . . . Prévôt, A.S.H., *Production of particulate brown carbon during atmospheric aging of residential wood-burning emissions.* Atmospheric Chemistry and Physics, 2018. **18**(24): p. 17843-17861.

81. Bond, T.C., Habib, G., and Bergstrom, R.W., *Limitations in the enhancement of visible light absorption due to mixing state.* Journal of Geophysical Research: Atmospheres, 2006. **111**(D20).

82. Anderson, M., Salo, K., Hallquist, Å.M., and Fridell, E., *Characterization of particles from a marine engine operating at low loads.* Atmospheric Environment, 2015. **101**: p. 65-71.

83. Kasper, A., Aufdenblatten, S., Forss, A., Mohr, M., and Burtscher, H., *Particulate emissions from a low-speed marine diesel engine.* Aerosol Science and Technology, 2007. **41**(1): p. 24-32.

84. Lyyränen, J., Jokiniemi, J., Kauppinen, E.I., and Joutsensaari, J., *Aerosol characterisation in medium-speed diesel engines operating with heavy fuel oils.* Journal of Aerosol Science, 1999. **30**(6): p. 771-784.

85. Chen, G., Huey, L.G., Trainer, M., Nicks, D., Corbett, J., Ryerson, T., . . . Fehsenfeld, F., *An investigation of the chemistry of ship emission plumes during ITCT 2002.* Journal of Geophysical Research: Atmospheres, 2005. **110**(D10).

86. Murphy, S.M., Agrawal, H., Sorooshian, A., Padró, L.T., Gates, H., Hersey, S., . . . Cocker III, D.R., *Comprehensive simultaneous shipboard and airborne characterization of exhaust from a modern container ship at sea.* Environmental Science & Technology, 2009. **43**(13): p. 4626-4640.

87. Petzold, A., Hasselbach, J., Lauer, P., Baumann, R., Franke, K., Gurk, C., . . . Weingartner, E., *Experimental studies on particle emissions from cruising ship, their characteristic properties, transformation and atmospheric lifetime in the marine boundary layer.* Atmospheric Chemistry and Physics, 2008. **8**(9): p. 2387-2403.

88. Zanatta, M., Bozem, H., Köllner, F., Schneider, J., Kunkel, D., Hoor, P., . . . Herber, A.B., *Airborne survey of trace gases and aerosols over the Southern Baltic Sea: from clean marine boundary layer to shipping corridor effect.* Tellus B: Chemical and Physical Meteorology, 2020. **72**(1): p. 1-24.

89. Petzold, A. and Schönlinner, M., *Multi-angle absorption photometry—a new method for the measurement of aerosol light absorption and atmospheric black carbon.* Journal of Aerosol Science, 2004. **35**(4): p. 421-441.

90. Drinovec, L., Močnik, G., Zotter, P., Prévôt, A., Ruckstuhl, C., Coz, E., . . . Wiedensohler, A., *The" dual-spot" Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation.* Atmospheric Measurement Techniques, 2015. **8**(5): p. 1965-1979.

91. Zanatta, M., Gysel, M., Bukowiecki, N., Müller, T., Weingartner, E., Areskoug, H., . . . Laj, P., *A European aerosol phenomenology-5: Climatology of black carbon optical properties at 9 regional background sites across Europe.* Atmospheric Environment, 2016. **145**: p. 346-364.

92. DeCarlo, P.F., Kimmel, J.R., Trimborn, A., Northway, M.J., Jayne, J.T., Aiken, A.C., . . . Jimenez, J.L., *Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer.* Analytical Chemistry, 2006. **78**(24): p. 8281-8289.

93. Onasch, T., Trimborn, A., Fortner, E., Jayne, J., Kok, G., Williams, L., . . . Worsnop, D., *Soot particle aerosol mass spectrometer: development, validation, and initial application.* Aerosol Science and Technology, 2012. **46**(7): p. 804-817.

94. Baumgardner, D., Kok, G., and Raga, G., *Warming of the Arctic lower stratosphere by light absorbing particles.* Geophysical Research Letters, 2004. **31**(6).

95. Schwarz, J.P., Gao, R.S., Fahey, D.W., Thomson, D.S., Watts, L.A., Wilson, J.C., . . . Aikin, K.C., *Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the boundary layer to the lower stratosphere.* Journal of Geophysical Research: Atmospheres, 2006. **111**(D16).

96. Stephens, M., Turner, N., and Sandberg, J., *Particle identification by laser-induced incandescence in a solid-state laser cavity.* Applied Optics, 2003. **42**(19): p. 3726-3736.

97. Sandradewi, J., Prévôt, A.S.H., Szidat, S., Perron, N., Alfarra, M.R., Lanz, V.A., . . . Baltensperger, U., *Using Aerosol Light Absorption Measurements for the Quantitative Determination of Wood Burning and Traffic Emission Contributions to Particulate Matter.* Environmental Science & Technology, 2008. **42**(9): p. 3316-3323.

98. Mohr, C., Lopez-Hilfiker, F.D., Zotter, P., Prévôt, A.S.H., Xu, L., Ng, N.L., . . . Thornton, J.A., *Contribution of Nitrated Phenols to Wood Burning Brown Carbon Light Absorption in Detling, United Kingdom during Winter Time.* Environmental Science & Technology, 2013. **47**(12): p. 6316-6324.

99. Favez, O., Cachier, H., Sciare, J., Sarda-Estève, R., and Martinon, L., *Evidence for a significant contribution of wood burning aerosols to PM2.5 during the winter season in Paris, France.* Atmospheric Environment, 2009. **43**(22): p. 3640-3644.

100. Wang, X., Heald, C.L., Sedlacek, A.J., de Sá, S.S., Martin, S.T., Alexander, M.L., . . . Artaxo, P., *Deriving brown carbon from multiwavelength absorption measurements: method and application to AERONET and Aethalometer observations.* Atmospheric Chemistry and Physics, 2016. **16**(19): p. 12733-12752.

101. Martinsson, J., Abdul Azeem, H., Sporre, M.K., Bergström, R., Ahlberg, E., Öström, E., . . . Eriksson Stenström, K., *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, 2017. **17**(6): p. 4265-4281.

102. Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., . . . Pio, C., *Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background.* Journal of Geophysical Research: Atmospheres, 2007. **112**(D23).

103. Utry, N., Ajtai, T., Filep, Á., Pintér, M., Török, Z., Bozóki, Z., and Szabó, G., *Correlations between absorption Angström exponent (AAE) of wintertime ambient urban aerosol and its physical and chemical properties.* Atmospheric Environment, 2014. **91**: p. 52-59.

104. Caseiro, A., Bauer, H., Schmidl, C., Pio, C.A., and Puxbaum, H., *Wood burning impact on PM10 in three Austrian regions.* Atmospheric Environment, 2009. **43**(13): p. 2186-2195.

105. Bhattarai, H., Saikawa, E., Wan, X., Zhu, H., Ram, K., Gao, S., . . . Cong, Z., *Levoglucosan as a tracer of biomass burning: Recent progress and perspectives.* Atmospheric Research, 2019. **220**: p. 20-33.

106. Alfarra, M.R., Prevot, A.S.H., Szidat, S., Sandradewi, J., Weimer, S., Lanz, V.A., . . . Baltensperger, U., *Identification of the Mass Spectral Signature of Organic Aerosols from Wood Burning Emissions.* Environmental Science & Technology, 2007. **41**(16): p. 5770-5777.

107. Xue, J., Li, Y., Wang, X., Durbin, T.D., Johnson, K.C., Karavalakis, G., . . . Jung, H.S., *Comparison of Vehicle Exhaust Particle Size Distributions Measured by SMPS and EEPS During Steady-State Conditions.* Aerosol Science and Technology, 2015. **49**(10): p. 984-996.

108. Wang, X., Grose, M.A., Caldow, R., Osmondson, B.L., Swanson, J.J., Chow, J.C., . . . Hu, S., *Improvement of Engine Exhaust Particle Sizer (EEPS) size distribution measurement – II. Engine exhaust particles.* Journal of Aerosol Science, 2016. **92**: p. 83-94.

109. Buffaloe, G., Lack, D., Williams, E., Coffman, D., Hayden, K., Lerner, B., . . . Onasch, T., *Black carbon emissions from in-use ships: a California regional assessment.* Atmospheric Chemistry and Physics, 2014. **14**(4): p. 1881-1896.

110. Ramacher, M.O.P., Karl, M., Bieser, J., Jalkanen, J.P., and Johansson, L., *Urban population exposure to NOx emissions from local shipping in three Baltic Sea harbour cities – a generic approach.* Atmospheric Chemistry and Physics, 2019. **19**(14): p. 9153-9179.

111. Hammingh, P., Holland, M., Geilenkirchen, G., and Maas, R., *Assessment of the environmental impacts and health benefits of a nitrogen emission control area in the North Sea*. 2012: PBL Netherlands Environmental Assessment Agency.

112. Viana, M., Hammingh, P., Colette, A., Querol, X., Degraeuwe, B., Vlieger, I.d., and van Aardenne, J., *Impact of maritime transport emissions on coastal air quality in Europe.* Atmospheric Environment, 2014. **90**: p. 96-105.

113. Cofala, J., Amann, M., Borken-Kleefeld, J., Gomez-Sanabria, A., Heyes, C., Kiesewetter, G., . . . Fagerli, H., *The potential for cost-effective air emission reductions from international shipping through designation of further Emission Control Areas in EU waters with focus on the Mediterranean Sea.* 2018.

114. Karl, M., Pirjola, L., Karppinen, A., Jalkanen, J.-P., Ramacher, M.O.P., and Kukkonen, J., *Modeling of the Concentrations of Ultrafine Particles in the Plumes of Ships in the Vicinity of Major Harbors.* International journal of environmental research and public health, 2020. **17**(3).

115. Kivekäs, N., Massling, A., Grythe, H., Lange, R., Rusnak, V., Carreno, S., . . . Glasius, M., *Contribution of ship traffic to aerosol particle concentrations downwind of a major shipping lane.* Atmospheric Chemistry and Physics, 2014. **14**(16): p. 8255-8267.

116. Lopes, M., Russo, A., Gouveia, C., and Ferreira, F., *Monitoring of Ultrafine Particles in the Surrounding Urban Area of In-Land Passenger Ferries.* Journal of Environmental Protection, 2019. **10**(06): p. 838-860.

117. Eyring, V., Köhler, H.W., van Aardenne, J., and Lauer, A., *Emissions from international shipping: 1. The last 50 years.* Journal of Geophysical Research: Atmospheres, 2005. **110**(D17).

118. Beecken, J., Mellqvist, J., Salo, K., Ekholm, J., and Jalkanen, J., *Airborne emission measurements of SO2, NOx and particles from individual ships using a sniffer technique.* Atmospheric Measurement Techniques, 2014. 7(7): p. 1957-1968.

119. Alföldy, B., Lööv, J.B., Lagler, F., Mellqvist, J., Berg, N., Beecken, J., . . . Hjorth, J., *Measurements of air pollution emission factors for marine transportation in SECA.* Atmospheric Measurement Techniques, 2013. **6**(7): p. 1777-1791.

120. Williams, E., Lerner, B., Murphy, P., Herndon, S., and Zahniser, M., *Emissions of NOx, SO2, CO, and HCHO from commercial marine shipping during Texas Air Quality Study (TexAQS) 2006.* Journal of Geophysical Research: Atmospheres, 2009. **114**(D21).

121. Betha, R., Russell, L.M., Sanchez, K.J., Liu, J., Price, D.J., Lamjiri, M.A., . . . Paulson, S.E., *Lower NO x but higher particle and black carbon emissions from renewable diesel compared to ultra low sulfur diesel in at-sea operations of a research vessel.* Aerosol Science and Technology, 2017. **51**(2): p. 123-134.

122. Rissler, J., Nordin, E.Z., Eriksson, A.C., Nilsson, P.T., Frosch, M., Sporre, M.K., . . . Swietlicki, E., *Effective Density and Mixing State of Aerosol Particles in a Near-Traffic Urban Environment.* Environmental Science & Technology, 2014. **48**(11): p. 6300-6308.

123. Eriksson, A.C., Wittbom, C., Roldin, P., Sporre, M., Öström, E., Nilsson, P., . . . Swietlicki, E., *Diesel soot aging in urban plumes within hours under cold dark and humid conditions.* Scientific Reports, 2017. 7(1): p. 12364.

124. Mohr, C., DeCarlo, P.F., Heringa, M.F., Chirico, R., Slowik, J.G., Richter, R., . . . Prévôt, A.S.H., *Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data.* Atmospheric Chemistry and Physics, 2012. **12**(4): p. 1649-1665.
125. Crippa, M., El Haddad, I., Slowik, J.G., DeCarlo, P.F., Mohr, C., Heringa, M.F., . . . Prévôt, A.S.H., *Identification of marine and continental aerosol sources in Paris using high resolution aerosol mass spectrometry.* Journal of Geophysical Research: Atmospheres, 2013. **118**(4): p. 1950-1963.
126. Bond, T.C., Bussemer, M., Wehner, B., Keller, S., Charlson, R.J., and Heintzenberg, J., *Light Absorption by Primary Particle Emissions from a Lignite Burning Plant.* Environmental Science & Technology, 1999. **33**(21): p. 3887-3891.
127. Bond, T.C., Covert, D.S., Kramlich, J.C., Larson, T.V., and Charlson, R.J., *Primary particle emissions from residential coal burning: Optical properties and size distributions.* Journal of Geophysical Research: Atmospheres, 2002. **107**(D21): p. ICC 9-1-ICC 9-14.
128. Sun, J., Zhi, G., Hitzenberger, R., Chen, Y., Tian, C., Zhang, Y., . . . Mo, Y., *Emission factors and light absorption properties of brown carbon from household coal combustion in China.* Atmospheric Chemistry and Physics, 2017. **17**(7): p. 4769-4780.
129. NASA Earthdata, *Fire information for resource management system (FIRMS)*. 2020. [Accessed: February]; Available from: https://firms.modaps.eosdis.nasa.gov/.

Pictures from the measurement sites.

Printed by Media-Tryck, Lund 2020 NORDIC SWAN ECOLABEL 3041 0903

LUND
UNIVERSITY

Faculty of Engineering
Department of Physic
Division of Nuclear Physics

ISBN 978-91-7895-470-4

9 789178 954704