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BLACK CARBON DEPOSITION IN THE EUROPEAN ARCTIC FROM THE PREINDUSTRIAL TO THE PRESENT

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ACADEMIC DISSERTATION

To be presented for public examination with the permission of the Faculty of
Biological and Environmental Sciences of the University of Helsinki
in Auditorium 2, Infocenter Korona, Viikki campus, Viikinkaari 11,
on the 10th of June 2015, at 12 o'clock noon.

Helsinki, 2015

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ISBN 978-951-51-1203-3 (print), ISBN 978-951-51-1204-0 (PDF)
(http://ethesis.helsinki.fi)
Dissertationes Schola Doctoralis Scientiae Circumiectalis, Alimentariae, Biologicae
ISSN 2342-5423 (print), ISSN 2342-5431 (Online)
Hansaprint, Vantaa, 2015
Cover photo: Meri M. Ruppel: Mountain ridges in Svalbard, Norway, March 2013

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I Rose, N. L., **Ruppel, M.** (2015) Environmental archives of contaminant particles. In: Blais, J. M., Rosen, M. R., Smol, J. P. (eds.), Environmental Contaminants – Using natural archives to track sources and long-term trends of pollution. Developments in Paleoenvironmental Research, vol. 18, Springer, Dortrecht, pp 187–221, doi: 10.1007/978-94-017-9541-8_9.

II **Ruppel, M.**, Lund, M. T., Grythe, H., Rose, N., Weckström, J., Korhola, A. (2013) Comparison of Spheroidal Carbonaceous Particle Data with Modelled Atmospheric Black Carbon Concentration and Deposition and Air Mass Sources in Northern Europe, 1850–2010. Advances in Meteorology, vol. 2013, Article ID 393926, doi:10.1155/2013/393926.

III **Ruppel, M. M.**, Isaksson, E., Ström, J., Beaudon, E., Svensson, J., Pedersen, C. A., Korhola, A. (2014) Increase in elemental carbon values between 1970 and 2004 observed in a 300-year ice core from Holtedahlfonna (Svalbard). Atmospheric Chemistry and Physics, 14, 11447–11460, doi:10.5194/acp-14-11447-2014.

IV **Ruppel, M. M.**, Gustafsson, Ö., Rose, N. L., Pesonen, A., Yang, H., Weckström, J., Palonen, V., Korhola, A. (2015) Spatial and temporal patterns in Black Carbon (BC) deposition in dated Fennoscandian Arctic lake sediments from 1830 to 2010. Under review at Environmental Science & Technology.

The publications are referred to in the text by their roman numerals.

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AUTHORS’ CONTRIBUTION TO THE PUBLICATIONS

The doctoral candidate’s independent contribution in the publications/article manuscripts is as follows:

I N. Rose acted as the corresponding author while both authors equally contributed to preparing the manuscript. In particular, M. Ruppel prepared the sections from “Black Carbon” through “Black carbon in lake sediments” (pages 192–202), as well as mostly section “Recent and future developments” (page 206).

II M. Ruppel designed the study. Lake sediments were collected by M. Ruppel and J. Weckström, or J. Weckström with others. M. Ruppel analyzed half of the sediments for BC, while previously published BC data for the other half was provided by N. Rose. M. Lund modelled BC deposition with the OsloCTM2 model, while H. Grythe performed air mass back trajectory analysis with the FLEXPART model, and both contributed associated text sections. M. Ruppel interpreted most of the results and wrote most of the paper while all authors commented and contributed.

III M. Ruppel and E. Isaksson planned the study. The ice core was collected and subsampled by E. Isaksson and others during the European Union Millennium project in 2005. M. Ruppel filtered the ice core samples, and analysed the ice core filter samples for BC, while C. Pedersen trained her in filtering and J. Svensson in thermal optical BC analysis. E. Beaudon provided previously published data on the dating, ion concentrations and melt index of the ice core. J. Ström was responsible for meteorological interpretations. M. Ruppel interpreted most of the results and prepared the manuscript while all authors commented and contributed.

IV M. Ruppel designed the study. Lake sediments were collected by M. Ruppel and J. Weckström, or J. Weckström with others. M. Ruppel prepared and analysed all samples for BC, while Ö. Gustafsson, A. Pesonen and V. Palonen lent support in methodological issues. M. Ruppel interpreted the results and prepared the manuscript while all authors commented and contributed.

ABSTRACT

The Arctic has been warming twice as fast as the rest of the world during the last decades of global warming. Reasons for the amplified Arctic warming are thought to partly relate to positive feedbacks affecting the radiative budget of the area. Black carbon (BC) is a light-absorbing particulate produced by incomplete combustion of biomass and fossil fuels. BC strongly warms the atmosphere, and its climate effects are amplified in the Arctic where its deposition on light surfaces decreases their reflectivity, resulting in elevated heat absorption and further hastening melt of snow and ice. Globally, BC is estimated to be the second most important climate-warming agent after carbon dioxide.

Historical information on BC deposition plays a significant role in the assessment of long-term climate effects of BC, but scarce data on this past variability has been available from the Arctic. Historical BC records can be attained from environmental archives, such as ice cores, peat deposits and marine and lake sediments, which store direct evidence of past BC deposition in chronological order. The objective of this thesis is to collect new spatial and temporal data on BC deposition in the European Arctic from the preindustrial to the present (i.e., the last ca. 300 years), and assess BC sources and climatic implications, by analysing five lake sediment cores from Arctic Finland and an ice core from Svalbard. No standard method exists to determine BC, and the precise definition of BC depends on the methodology used for its quantification. Here, three different analytical methods were used to quantify different components of BC. Spheroidal Carbonaceous Particles (SCP) and soot-BC (SBC) were analysed from the Arctic Finland lake sediments by SCP analysis and chemothermal oxidation at 375 °C, respectively, and elemental carbon (EC) from the Svalbard ice core with a thermal optical method.

The results suggest temporal variation in past BC trends, both between study sites and between methods. While SCPs show a marked trend with fluxes peaking around 1980 and declining afterwards, they represent only a minor fraction of total BC. SBC and EC are better suited to indicate general historical BC trends. SBC fluxes vary between sites but some regional patterns are noticeable. The two northernmost lakes indicate generally decreasing SBC fluxes during the latter half of the 20th century which is in line with previous data from Greenland ice cores, modelling studies and atmospheric measurements. However, two other lake sites indicate increasing SBC fluxes from ca. 1970 to the end of the records, likely caused by local emissions from the Kola Peninsula, Russia. Moreover, an increasing EC deposition trend from ca. 1970 to 2004 is also recorded in the Svalbard ice core. This increasing trend is unexpected and unparalleled among available arctic records. The observed increase in the ice core is likely caused by flaring emissions from northern Russia. The fact that a similar trend in BC fluxes and deposition is recorded in two separate environmental archives analysed with different methods and receiving atmospheric transport from mostly different source areas, highlights the plausibility of such a trend, and implies that it may also be observable at other locations in the Arctic. In such a case, BC may have exerted a significant impact on the radiative forcing and thereby past climatic warming of the Arctic, in the most recent three or four decades. However, the present study indicates that local results cannot necessarily be extrapolated over wider areas, and therefore further studies are required to establish regional BC deposition trends within the Arctic. In addition, the study highlights that BC results obtained using different analytical methods should be compared with caution.

ABBREVIATIONS

ACIA	Arctic Climate Impact Assessment
AMAP	Arctic Monitoring and Assessment Programme
BC	Black Carbon
CO_2	Carbon dioxide
CTO-375	Chemothermal oxidation at 375 °C
EC	Elemental Carbon
SBC	Soot Black Carbon
SCP	Spheroidal Carbonaceous Particle
SP2	Single Particle Soot Photometer
TO	Thermal Optical

1. INTRODUCTION

1.1 Arctic climate change and black carbon

Climate change is the most severe environmental problem at present causing global changes in physical conditions and ecosystem functions. Global temperatures have risen on average by 0.85 °C between 1880 and 2012 mostly due to forcing exerted by exponentially growing anthropogenic greenhouse gas emissions (IPCC, 2013). Climate models unambiguously indicate that the Arctic is the most vulnerable to the warming (e.g., ACIA, 2005). Impacts of climate change are first and most intensely seen in the Arctic where the annual average temperature has increased twice as fast compared to the rest of the world since 1980 (ACIA, 2005; Miller et al., 2010; AMAP, 2011a). The temperature increase has been accompanied by a decrease in sea-ice and snow cover extent and duration, increased permafrost temperatures, and a decline in multi-year sea ice, mountain glaciers, ice caps and the Greenland Ice Sheet (AMAP, 2011a). These processes have inevitable consequences for the functioning of the Arctic ecosystem which mainly relies on the undisturbed existence of the cryosphere (ACIA, 2005).

Reasons for the particularly strong warming in the Arctic, i.e. the Arctic amplification, are still partly unresolved. The Arctic is not only affected by global climate change but it also affects the global climate system itself. The fundamental role of the Arctic in the global climate system is to function as the heat sink of the northern hemisphere. In addition, the Arctic cools the Earth by reflecting incoming solar radiation back to space (AMAP, 2011a). The loss of snow and ice cover in the Arctic reduces the Earth's albedo, creating a self-accelerating positive feedback in which the increased heat absorption further reduces the snow and ice cover, with the end result of warming the region and thereby global climate (e.g., ACIA, 2005; Serreze et al., 2007; AMAP, 2011a). The Arctic amplification is thought to be mainly caused by the intensification of the above-described snow-albedo and other positive feedbacks (ACIA, 2005; Miller et al., 2010). Consequently, any factor affecting the reflectivity of the Arctic may have wide-ranging influence on global climate change.

In addition to the increased greenhouse gas concentration inflicted snow-albedo feedback, other natural and anthropogenic emissions may also perturb the surface radiative budget in the Arctic and contribute to the warming (e.g., Shaw, 1995; AMAP, 2011b). Black carbon (BC) is a fine particulate produced by incomplete combustion of biomass and fossil fuels. Due to its black colour and surface characteristics BC has the strongest visible light absorption per unit mass of all atmospheric aerosols and thereby warms the atmosphere effectively (Bond et al., 2013). Its climate impacts are amplified in the Arctic where even low BC deposition on high-reflectivity snow and ice may significantly lower the surface albedo (e.g., Warren and Wiscombe, 1980; AMAP, 2011b). The BC-induced albedo change can exert a large influence on Arctic climate by advancing the timing of snow and ice melt in spring, and triggering the snow-albedo feedback (Hansen and Nazarenko, 2004; Jacobson, 2004; Flanner et al., 2007, 2009). It seems that the equilibrium temperature response, per unit of radiative forcing, driven by

BC caused snow darkening, is several times greater than that of carbon dioxide (CO_2) (Hansen and Nazarenko, 2004; Flanner et al., 2007, 2009; Koch et al., 2009). Therefore, BC is potentially more important for Arctic warming and melting than greenhouse gases (e.g., Jacobson, 2001; Hansen and Nazarenko, 2004; Bond et al., 2013). The snow-albedo amplified effects of BC are not restricted to the Arctic, as BC has been linked to the climatologically premature retreat of mountain glaciers in both the European Alps (Painter et al., 2013) and the Himalayas (Xu et al., 2009). Globally, BC has been estimated to be the second most important climate warming agent after carbon dioxide (e.g., Jacobson, 2001; Ramanathan and Carmichael, 2008; Bond et al., 2013), with a total climate forcing of +1.1 W m^{-2} (+0.17 to +2.1 W m^{-2} range) (Bond et al., 2013).

1.2 Black carbon sources and transport to the Arctic

BC is formed by incomplete combustion, which can occur during natural grassland or forest fires, anthropogenic industrial combustion of biomass or fossil fuels, in diesel and gasoline engines, or during small-scale fire place burning (e.g., Goldberg, 1985). Consequently, BC consists of many different types of carbonaceous particles, depending on the combusted material and combustion temperature. Different BC particle types are further discussed in section 1.4. Generally, BC is uniquely identifiable among atmospheric particulates due to its morphology, strong absorption of solar radiation, stability at high temperatures (refractory nature) and insolubility in water (AMAP, 2011b; Bond et al., 2013).

Generally, BC is co-emitted with varying proportions of other particles, such as sulphate, organic carbon, trace metals and dust, which have differing light-absorption and scattering characteristics and may function as cloud condensation nuclei (e.g., Bond et al., 2013). Therefore, plumes containing BC may actually have climate-cooling effects, especially when the sulphate to BC ratio is high (e.g., Ramana et al., 2010; Bond et al., 2013). However, even the particles cooling the atmosphere exert significant climate-warming effects when deposited on snow by lowering the surface albedo (e.g., AMAP, 2011b; Bond et al., 2013). For instance, mineral dust is suggested to have a stronger effect on surface albedo, and therefore climate warming, in some parts of Greenland (Dumont et al., 2014) and Himalayan glaciers (Kaspari et al., 2014) than BC due to its much higher concentrations. Despite these facts, only BC is considered in this thesis.

As BC is emitted due to incomplete combustion, the emission amounts are not directly proportional to fuel use but are also affected by the combustion efficiency relating to advances in used technology. Thereby, BC emission amounts and their sources vary greatly between regions. According to bottom-up inventory methods, global BC emissions have increased markedly since 1850, which is used here as a reference point for the start of industrialization. In the early 20th century global BC emissions were dominated by emissions from the industrialized western countries, while in the latter half of the century, emissions from developing countries, such as China and India, prevailed (e.g., Novakov et al., 2003; Bond et al., 2007). This trend is illustrated in

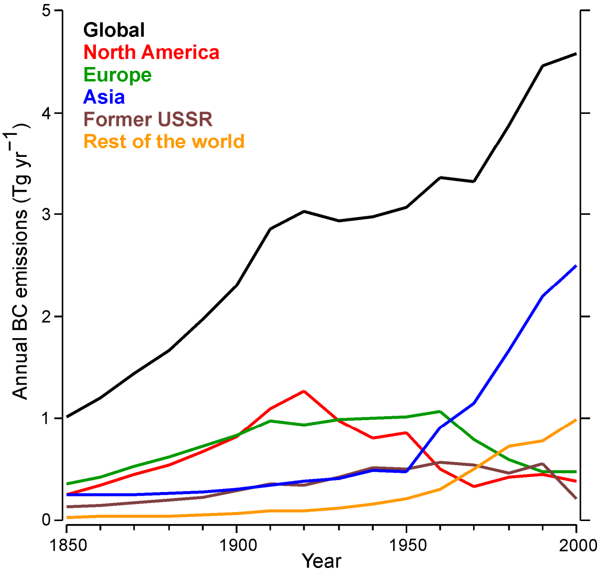


Figure 1. Global annual anthropogenic BC emissions (Tg yr^{-1}) by region (data: Bond et al., 2007).

Figure 1. According to updated inventory results, total global BC emissions in the year 2000 were 7500 Gg yr^{-1} (uncertainty range 2000 to 29000 Gg yr^{-1}). Most of the emissions (4800 Gg yr^{-1}) resulted from energy-related combustion, and the rest from open burning of forests, grasslands, and agricultural residues (Bond et al., 2013). In the year 2000, 60 to 80% of Asian and African BC emissions resulted from combustion of residential solid fuels (i.e. coal and biomass), while in Europe, North America and Latin America on-road and off-road diesel engines contributed about 70 % of BC emissions (Bond et al., 2013).

The atmospheric life-time of BC varies from a few days up to several weeks. Due to this short atmospheric lifetime its atmospheric concentrations are not uniform around the world and highest values are recorded above most polluting regions. However, BC may be transported from its emission source with prevailing winds over thousands of kilometres before being wet or dry deposited (Ramanathan & Carmichael, 2008; Bond et al., 2013), thereby being a global environmental threat.

Currently there are few BC emission sources within the Arctic. Most of BC observed in the Arctic is a result of long-range transport from source regions outside the Arctic or on its fringes (Stohl, 2006; Law and Stohl, 2007). Transport pathways of BC into the Arctic vary with seasons, and different source areas contribute varyingly to near surface (and middle or upper troposphere) atmospheric BC concentrations in different parts of the Arctic (e.g., Sharma et al., 2006; Stohl, 2006; Hirdman et al., 2010a). Arctic air masses are most sensitive to emissions of air pollutants over Siberia and Europe in winter and over oceans in summer (Stohl, 2006). Generally, BC emission sources north of 40°N are considered relevant for the Arctic (AMAP, 2011b). Highest atmospheric BC concentration in the Arctic are observed during winter and early spring (e.g., Sharma et al., 2006; Eleftheriadis et al., 2009) in connection to the Arctic haze phenomenon transporting a varying mixture of mostly anthropogenic particulate pollutants, such as sulphate, particulate organic matter, nitrate, ammonium, and dust and heavy metals in addition to BC, to the Arctic from lower latitudes (Quinn et al., 2002). Lowest BC concentrations on the other hand are measured in summer months. This seasonal pattern in atmospheric BC concentrations is caused by seasonality both in atmospheric transport pathways to the Arctic and in wet-scavenging of BC, i.e. wash-out of BC by precipitation (AMAP, 2011b).

1.3 Previous observational research on black carbon in the Arctic

Research on BC as a climate-warming agent is a relatively new area of climate research. The atmospheric presence of BC in remote locations (e.g., Andreae, 1983; Rosen et al., 1984) and the contribution of BC to the Arctic haze, as well as its effect on snow albedo (e.g., Warren and Wiscombe 1980; Hansen and Rosen, 1984; Clarke and Noone, 1985) were observed already in the 1980s. However, research on BC and its climate warming potency escalated only after Jacobson (2000) and Hansen et al. (2000) pointed out that BC may warm the atmosphere about one-third as much as carbon dioxide.

Continuous atmospheric measurements and systematic, published monitoring of BC in the Arctic started in Alert, Canada and Barrow, Alaska in 1989 (Sharma et al., 2004, 2006), and in Ny-Ålesund, Svalbard (Norway) in 1998 (Eleftheriadis et al., 2009). Recently, a 47-year data-set of weekly atmospheric BC observations in Kevo, northern Finland, was published (Dutkiewicz et al., 2014). The Alert, Barrow and Ny-Ålesund measurements indicate a 40 % decline in atmospheric BC concentrations from 1990 to 2009 (Sharma et al., 2013), while a 78 % decrease was observed at Kevo between 1971 and 2011 (Dutkiewicz et al., 2014). Additional shorter term atmospheric BC monitoring sites exist in e.g. Russia, Sweden, Greenland, and Finland (AMAP, 2011b).

Pioneering work on BC quantification in North-American and European Arctic snow packs by Clarke and Noone (1985) was followed by Doherty et al. (2010) analysing 1200 Arctic snow samples for BC with better geographical coverage than in Clarke and Noone (1985). The BC concentrations quantified by Doherty et al. (2010) were somewhat lower than those presented in Clarke and Noone (1985), and therefore Doherty et al. (2010) deduced that it was doubtful that BC in Arctic snow would have contributed to the rapid decline of Arctic sea ice observed since 1979 (e.g., AMAP, 2011a). Nevertheless, in an effort to establish the role of BC in current climate change, the number and spatial coverage of BC measurements from Arctic snow are further increasing (e.g., Forsström et al., 2009, 2013; Aamaas et al., 2011; Doherty et al., 2010, 2013). However, comparing individual snow BC results and establishing regional trends remain challenging because most snow measurements only represent a snap-shot of BC concentrations in space and time.

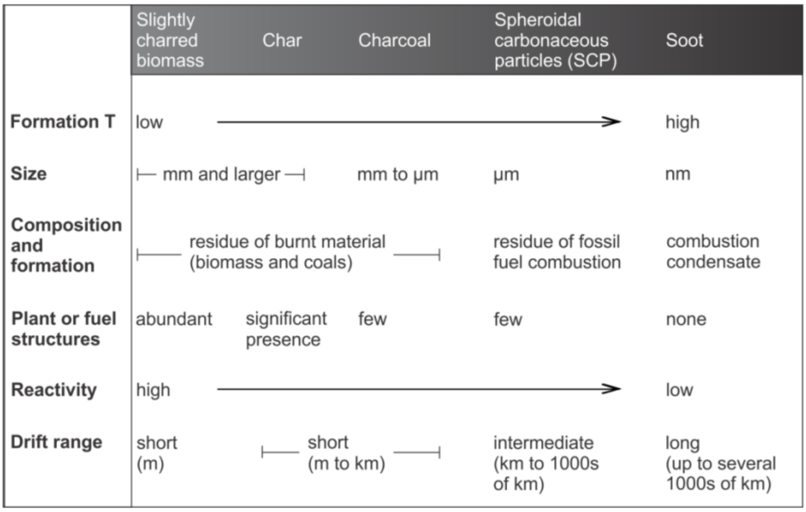
To comprehensively assess the role of BC in past, present and future Arctic climate change, and for hind-casting and predictive model validation, long-term BC records beyond the observational data are required. Such data can be obtained from environmental archives, such as ice cores, marine and lake sediments, and peats which contain evidence of atmospherically-deposited material in chronological and conformable order. Despite the significance of BC in Arctic climate warming, long-term records on its concentrations and deposition in the area are very limited at present (Fig. 3a). Ice and firn core records are available from the Greenland Ice Sheet (McConnell et al., 2007; McConnell and Edwards, 2008; McConnell, 2010; Keegan et al., 2014) which all record increasing BC concentrations from 1850, peaking around 1910, followed by a decline to almost pre-industrial levels after 1950 (see also Figure 9c, below). The trend is mainly explained by intense coal combustion in North America during the late 1800s and early 1900s, and subsequent technological advancements in combustion and changes in fuel sources, and finally the Clean Air Act (McConnell et al., 2007; McConnell and Edwards, 2008). However, McConnell et al. (2007) recognized that the BC deposition at the high-elevation sites (e.g., at 2713 and 2410 m a.s.l.) in Greenland could not be taken as representative of overall BC trends in lower elevation regions of the Arctic, which receive most of their BC loadings from Eurasia (e.g., Hirdman et al., 2010a; AMAP, 2011b). An ice core from Canada similarly shows increasing BC concentrations from 1850 to the early 1900s but the record only extends to 1950 (Holdsworth et al., 1996). In addition, carbonaceous particles have been studied from Arctic lake sediments (e.g., Doubleday et al., 1995; Rose et al., 2004) but these studies are analytically restricted, as discussed below, and do not illustrate general BC trends.

To get a better overall view on BC trends, sources and climate effects in the Arctic, further investigations on past BC concentrations and deposition are required from other locations in the region.

1.4 Black carbon terminology: the BC combustion continuum model

An important aspects of BC that needs to be introduced before more thorough scrutiny, is the BC terminology. The definition of BC is not straightforward, especially across research disciplines. BC is not a specifically determined chemical component. Rather, the term incorporates a variety of different types of charred material formed during oxygen-deprived combustion (e.g., Goldberg, 1985; Hedges et al., 2000). Generally, BC is composed of > 60 % carbon with accessory elements including hydrogen, oxygen, nitrogen and sulphur (Goldberg, 1985). BC (or carbonaceous particles) has been long studied in sedimentary archives as a proxy for fire (Whitlock and Larsen, 2001) and industrial development (e.g., Rose, 1990; Rose et al., 1999). BC is chemically very inert and strongly resists decomposition, and may therefore be preserved over long geological time scales (Goldberg, 1985; Schmidt and Noack, 2000; Forbes et al., 2006). However, the research on BC as a light-absorbing and climate-warming atmospheric component is rather young. There is no single accepted definition for BC, especially between disciplines. Terms such as black carbon, elemental carbon, soot, graphitic black carbon, pyrogenic carbon and refractory black carbon are often used interchangeably, and definitions for these are based on source processes, morphological characteristics, chemical composition and the optical properties of the material in question (Masiello, 2004; Andreae and Gelencsér, 2006). Recently Bond et al. (2013) defined BC very specifically as being a distinct type of carbonaceous material formed in flames and having a unique combination of physical properties. However, this definition applies mostly only for atmospheric sciences, and does not cover all BC particles included in soil and sediment studies. Furthermore, Bond et al. (2013) remark that in previous modelling and measurement studies, the term BC has not been limited to the material with the properties described by Bond et al. (2013), making comparisons challenging between studies.

To better illustrate the myriad of particles termed black carbon and their characteristics, Hedges et al. (2000) presented the so called “BC combustion continuum model” (Fig. 2). All particles of the continuum share their origin from incomplete combustion, black colour, and insolubility in water. Despite these similarities the particles differ greatly from another, mainly due to the combustion temperature at which they are formed, and the combusted material. The particles range from slightly charred biodegradable biomass, char and charcoal through to industrial particles formed at high temperatures (spheroidal carbonaceous particles (SCP)), and soot. In many cases, there are no clear cut boundaries between these classes (Seiler and Crutzen, 1980). Generally, the particles can be grouped into larger chars, which are residues reflecting the structure of the burned material, or the nature of the burning process, and smaller particles, soot, which are combustion condensates, i.e. formed from the vapour phase (Novakov, 1984; Elmquist et al., 2006). Both types can form simultaneously from a single combustion source (Goldberg, 1985; Elmquist et al., 2006). The purest form of black (or elemental) carbon is graphite, which consists of sp2–bonded carbon in planar layers. Graphite is formed over geological time-scales under conditions of high temperature and pressure. It is therefore not a combustion product and is not considered further here.



	Slightly charred biomass	Char	Charcoal	Spheroidal carbonaceous particles (SCP)	Soot
Formation T	low	→	→	→	high
Size	mm and larger		mm to µm	µm	nm
Composition and formation	residue of burnt material (biomass and coals)			residue of fossil fuel combustion	combustion condensate
Plant or fuel structures	abundant	significant presence	few	few	none
Reactivity	high	→	→	→	low
Drift range	short (m)	short (m to km)		intermediate (km to 1000s of km)	long (up to several 1000s of km)

Figure 2. Black carbon combustion continuum model (Paper **I**). Modified from Hedges et al. (2000) and Masiello (2004). Reproduced with permission of Springer Science+Business Media.

Soot differs from the other BC particles as it is a condensation product rather than a combustion residue. Atmospheric scientists mostly consider only soot as BC (e.g., Bond et al., 2013), most likely due to its small size that allows it to stay aloft for longer times, and its well-known optical (light absorbance) properties. Soot may be produced in large natural fires if sufficient temperature is attained, but it is also common in industrial processes, and during the combustion of natural gas, gasoline and diesel, which do not produce any other BC forms (e.g., Goldberg, 1985). Soot forms in flames by individual hydrocarbon spherules aggregating by rapid coagulation (Haynes and Wagner, 1981). The size of soot particles may vary from a few tens to hundreds of nanometres and it may be transported over several thousands of kilometres before deposition (Bond et al., 2013).

Another BC fraction easily identifiable among BC types is spheroidal carbonaceous particles (SCPs). SCPs are a component of fly ash and result only from the incomplete combustion of fossil fuels, mainly coal and oil, at high temperatures (greater than 1000 °C) in heavy industry and energy production. Morphologically they are the “skeletons” of the incompletely combusted fuel particle and owe their spheroidal form to the melted fuel particles. Their size is much bigger than that of soot, as their usual size range is 2–20 µm (diameter). In remote areas only particles smaller than 10 µm are found (Rose, 1994; Rose et al., 1999). SCPs have been used for decades as a tracer for industrial combustion and pollution deposited from the atmosphere (e.g., Doubleday et al., 1995; Rose et al., 2004) and have been studied widely in Europe (e.g., Wik and Renberg, 1996; Rose et al., 1999) but their role as climate warming particles has received less attention. Nevertheless, the climate-warming potential of SCPs is indisputable and may be wide-ranging, as they have been found far from their emission sources, for instance, in Greenland (Bindler et al., 2001), Svalbard (e.g. Rose et al., 2004; Hicks and Isaksson, 2006) and Antarctica (Martins et al., 2010). This should also be the case for other most condensed forms of char-type BC, such as charcoals (e.g., Hicks and Isaksson, 2006), and their inclusion in atmospheric studies of light-absorbing BC should be considered. In previous presentations of the BC combustion continuum (e.g., Hedges et al., 2000; Masiello, 2004; Elmquist et al., 2006) SCPs have not been described separately but likely as a component of char-type BC (under charcoal in Fig. 2). In this thesis SCPs are discussed separately from char-type BC, as they clearly differ from other char-type BC due to their specific formation conditions that make them more thermally resistant, and thereby analytically differently quantifiable from other char-type BC.

In this work, the term BC is used to refer to the broad spectrum as defined above, and when discussing a specific BC fraction, an appropriate further identifier/term is used.

1.5 Objectives and hypotheses

The overall objective of this thesis is to gather new spatial and temporal information on the long-term trend of BC concentrations and deposition in the European Arctic. For this, lake sediments from northern Finland and an ice core from Svalbard, Norway, are studied. While ice sheets are extremely valuable as archives of atmospheric pollutant deposition histories, they are only found on restricted areas in the Arctic. Local conditions, such as wind directions, topography and precipitation, can strongly effect BC deposition at a specific point in space. Lake sediments, on the other hand, can be found all around the Arctic and thereby play an irreplaceable role in depicting the spatial variance in BC deposition history in the region. In addition, the emission sources of BC in the Arctic and their temporal variation are roughly assessed by investigating different fractions of BC (SCPs and soot, Fig. 2). The acquired data may bring new insights on the importance of BC and different emission sources in the past climate warming of the Arctic, and may help to understand more specifically the role of BC in the present and future climate change.

More specific objectives of the study are:

1. to determine BC concentrations and fluxes to five Arctic Finland lake sediments during the last ca. 120 years;
2. to determine BC concentrations and deposition in a 300-year Svalbard ice core;
3. to compare BC results in the above environmental records in order to attempt regional synthesis of historical BC deposition and its possible climate implications in the European Arctic;
4. to analyse BC from environmental archives with different methods to see whether temporal trends agree between methods and between different environmental archives;
5. to assess whether BC analysed with different methods may be used to evaluate the significance of different BC sources in the European Arctic;
6. to assess the applicability of different analytical methods to quantify BC from Arctic environmental archives.

Main hypotheses of the study are:

1. Spatial and temporal variability in the past BC concentrations and deposition in the Arctic may be larger than expected based on ice core data from Greenland. The Greenland high-elevation data do not portray the BC deposition trend over other parts of the Arctic (especially the European Arctic) that are more prone to emissions from Eurasia rather than North America.
2. Emissions and deposition of BC in the European Arctic have declined since 1960s as a result of implemented air protection measures, as predicted by modelling exercises (e.g., Koch et al., 2011). However, a recent increase may be detected due to increasing emissions from eastern and southern Asia possibly reaching the Arctic, increased marine transportation and economic development (e.g., oil and gas extraction in Russia) in the Arctic, more intense boreal forest fires, and increasing use of diesel engines in European traffic. Diesel engines have much higher particulate matter emissions than gasoline engines, and total BC emissions from gasoline are less than 10 % of diesel BC emissions, although gasoline vehicles are more numerous (Bond et al., 2013).

3. Records of different BC fractions (e.g., SCPs and soot), acquired using different analytical methods, may indicate different spatial and temporal deposition trends in the same study area. These differences may reflect different emission sources and variation in the source strengths.
4. The past BC deposition trend in the European Arctic may differ from the trend suggested by atmospheric measurements at established monitoring stations since 1989 (and separate measurement at Kevo since 1964 (Dutkiewicz et al., 2014)), as about 85–90 % of Arctic BC is wet-deposited (Wang et al., 2011) and therefore not quantified by atmospheric measurements.

2. MATERIAL AND METHODS

2.1 Research sites, sampling and preparation for BC analysis

In this thesis, the term Arctic is used to refer to the Arctic area defined by the Arctic Monitoring and Assessment Programme (AMAP). In Europe, this means the area north of the Arctic Circle (66°32'N), as presented in Figure 3a.

2.1.1 Lake sediments

Five lakes from different parts of Finnish Lapland were selected for studies on BC deposition in the European Arctic. Details on the study lakes are given in Table 1 and their geographical location in Fig. 3b. The lakes Kuutsjärvi and Vuoskojärvi are situated

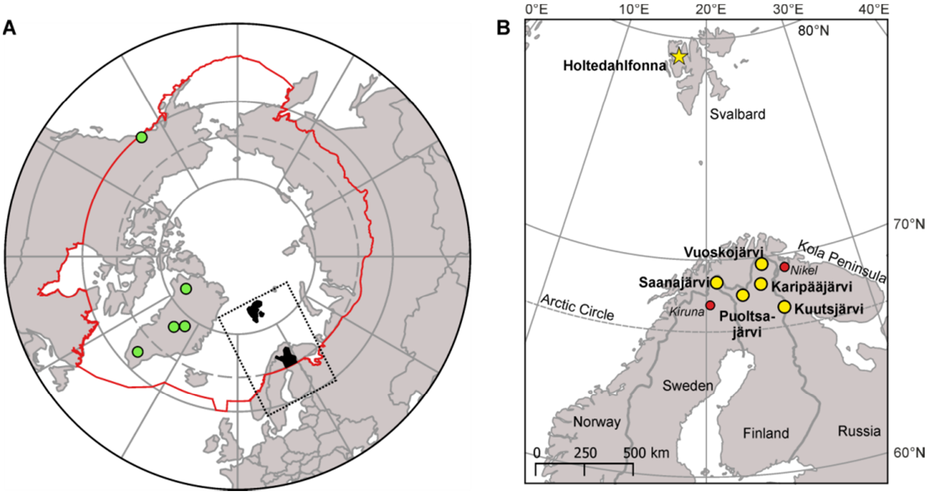


Figure 3. The Arctic and the location of study sites. A) A map of the Arctic as defined by AMAP (*red line*). The study areas in Svalbard and arctic Finland are highlighted in black. Also indicated are the locations of previously published ice core BC records from the Arctic (*green dots*) (Holdsworth et al., 1996; McConnell et al., 2007; McConnell and Edwards, 2008; McConnell et al., 2010; Keegan et al., 2014). B) Locations of study lakes (*yellow dots*), and Holtedahlfonna glacier (*yellow star*), and potential significant emission sources for the study lakes (*red dots*).

Table 1. Details on the study lakes.

Lake	Karipääjärvi (KPJ)	Kuutsjärvi (KJ)	Puoltsajärvi (PJ)	Saanajärvi (SJ)	Vuoskojärvi (VJ)
Location	68°49′N, 26°52′E	67°45′N, 29°37′E	68°26′N, 24°41′E	69°05′N, 20°52′E	69°44′N, 26°57′E
Altitude (m a.s.l.)	265	341	355	679	144
Size (ha)	32	0.67	17	70	17
Max. (coring) depth (m)	6.7	8.6	7	24	7.2
Coring year	2010	2009	2010	2013	2010

within strict nature reserve conservation areas where any human activity (apart from research) is forbidden. The other lakes are similarly located in remote areas where local pollution is not expected to dominate the recorded BC trends.

The sediments were collected from the deepest parts of the lakes using a HTH gravity corer (Renberg and Hansson, 2008). Lakes with simple bathymetry and as flat sediment beds as possible were preferred, as the sediment is expected to accumulate most undisturbed in these coring locations. Also, the relative contribution of material deposited directly from the atmosphere, rather than as secondary influx from the catchment area and/or the sediment bed, is expected to be highest at these coring locations. The top most 12.5 cm of the sediments was retrieved from each lake and sliced in 0.25 cm resolution into minigrip© plastic bags.

The sediments were dried in a vacuum-freeze-dryer, and sent for radiometric dating (^{210}Pb, ^{226}Ra, ^{137}Cs, and ^{241}Am) to the University College London Environmental Radiometric Facility or the Liverpool University Environmental Radioactivity Laboratory (Appleby and Oldfield, 1978; Appleby et al., 1986; Appleby et al., 1992).

2.1.2 Ice core

In addition to the lake sediments, BC was analysed from a 125 m deep ice core collected in March 2005 (within the European Union-funded Millennium project) from the Holtedahlfonna glacier (79°8′15″N, 13°16′20″E; Fig. 3b), Svalbard. The ice core was drilled at 1150 m a.s.l., at a saddle point where the lateral ice flow velocity (i.e. disturbance of vertical snow accumulation) was expected to be minimal (Sjögren et al., 2007). The ice core was retrieved in ca. 50–60 cm sections, packed into plastic bags, and stored frozen. The ice core was cut to subsamples in a cold room (−22°C) using a thin blade band saw, and each surface of the subsamples scraped with a stainless steel knife, after which the samples were placed in plastic bags and stored frozen. The inner part of the core, i.e. the part best protected from contamination during drilling and handling, was reserved for BC analyses. Dating of the ice core was performed using an age−depth scale based on the ice thinning model by Nye (1963) constrained by the 1963 radioactivity fallout layer at 28.5 m depth (van der Wel et al., 2011), and by counting of annual $\delta^{18}O$ layers (Divine et al., 2011). In addition, a dating method based on historical volcanic eruptions (Moore et al., 2012) complemented the other approaches. The Holtedahlfonna ice core was dated to cover approximately 300 years (Divine et al., 2011; Moore et al., 2012).

2.2 Black carbon analytical methods

2.2.1 General background on black carbon methodology

Black carbon is an operational term. This means that the precise definition of BC depends on the method used for its quantification, as at present, no individual method is able to quantify all fractions of the BC combustion continuum (Fig. 2) simultaneously. Moreover, no standard method is available for BC quantification. In many cases, it is not even possible to precisely define which components of the BC continuum are quantified with the used method. Consequently, comparisons of BC levels and trends measured using different methods are challenging.

BC quantification of atmospheric samples often relies on the light-absorbing qualities of BC (Petzold et al., 2013). However, atmospheric BC quantification methods are not ideal for soil and sediment studies (Hammes et al., 2007). This is unfortunate, as sediment record studies usually attempt to quantify BC particles that originate from the atmosphere. BC in sediments is surrounded by a complex matrix of organic and inorganic material from which, in many cases, it needs to be extracted prior to BC quantification. This procedure usually exerts qualitative selection on the analysed material, excluding some BC particles incorporated in atmospheric measurements, and possibly also including others that are not.

Methods most commonly used for BC quantification from environmental archives can be divided into five different main categories: (i) optical (Watson et al., 2005 and references therein); (ii) thermal (Watson et al., 2005 and references therein); (iii) microscopic (e.g., Stoffyn-Egli et al., 1997; Thevenon and Anselmetti, 2007; Rose, 1994; 2008); (iv) chemical (e.g., Masiello and Druffel, 1998); and (v) indirect (e.g. molecular markers; Glaser et al., 1998). Additionally, some mixed methods have been employed such as the thermo-optical (e.g., Chow et al., 1993) or chemo-thermal (e.g., Gustafsson et al., 1997; 2001) methods. Thermal methods developed for BC quantification in sediments and soils rely on the resistance of BC to degradation, in particular oxidation (Elmquist et al., 2006; Hammes et al., 2007). Chemical methods, on the other hand, determine BC as the component which resists chemical extraction during removal of organic material and inorganic minerals with acid treatments (Masiello and Druffel, 1998; Rose, 1994).

As the precise analytical windows of the methods may vary, it is not surprising that method comparisons show considerable discrepancies. Watson et al. (2005) showed typical differences by a factor of 2 between identical samples analysed for BC with different methods. Schmidt et al. (2001) reported variability by a factor of 500 between measured concentrations of BC in an inter-comparison study of soil samples. Such variation makes comparisons between studies using different analytical methods problematic and even inappropriate (Paper I). Exceptions occur where particle types can be more precisely defined by their morphology with specific identification criteria, such as SCPs (e.g., Rose, 2008). Therefore, the methodology and the BC particle fractions analysed in the thesis studies are described in detail in the following.

2.2.2 Black carbon quantification methods used in the thesis

Attention was paid to use as established and widely used methods as possible, to secure comparability to previous and future studies.

For Paper I no new BC analyses were performed but previous global BC observations in environmental archives were reviewed and compared.

In Paper II, a well-defined and clearly identifiable (e.g. Rose, 1994; Rose, 2008), and previously widely studied (e.g., Wik and Renberg, 1996; Rose et al., 1999; Inoue et al., 2014) BC fraction, spheroidal carbonaceous particles (SCPs) were studied (Figure 4). SCPs were extracted from the Karipääjärvi, Kuutsjärvi and Puoltsajärvi sediments (Fig 3b) following the method described in Rose (1994). The dried sediments were subjected to sequential acid treatments to remove unwanted sediment fractions leaving behind carbonaceous material. First, concentrated nitric acid (HNO_3) removed organic material, second, hydrofluoric acid (HF) removed silicates, and third, hydrochloric acid (HCl) removed carbonates. SCPs are composed mostly of elemental carbon and are chemically robust. Microscope slides with a known fraction of the resulting concentrated suspension of mainly carbonaceous material were made. The number of SCPs was counted under a light microscope at 400 times magnification following identification criteria described in Rose (2008), and per personal training given by Neil Rose (UCL). The accuracy of the used method was checked by preparing reference standard material samples with known SCP content (Rose, 2008) in each sample batch. Other SCP lake sediment records presented in the study (from Saanajärvi, Finland; Arresjøen, Svalbard; and Stepanovichjarvi, Russia) were analysed by Rose using the same methodology. Finally, SCP flux as g m^{-2} yr^{-1} was calculated for all sediment records, based on the number of SCPs counted per gram of sediment, sedimentation rate, and the weight estimation of a medium sized (20 μm) SCP (1.96×10^{-9} g; Rose, 2001).

In addition, Paper II presents various modelling results of e.g. BC deposition from 1850 to 2010 at the study sites, based on the OsloCTM2 chemical transport model, prepared by Dr. Marianne Lund (CICERO, Center for International Climate and Environmental Research - Oslo). Furthermore, M.Sc. Henrik Grythe (NILU, Norwegian Institute for Air Research) performed back trajectory modelling of air masses with a Lagrangian particle dispersion model (FLEXPART) to further explore the major source areas for SCPs and potential changes in the dominant transport patterns over the past decades to the study sites.

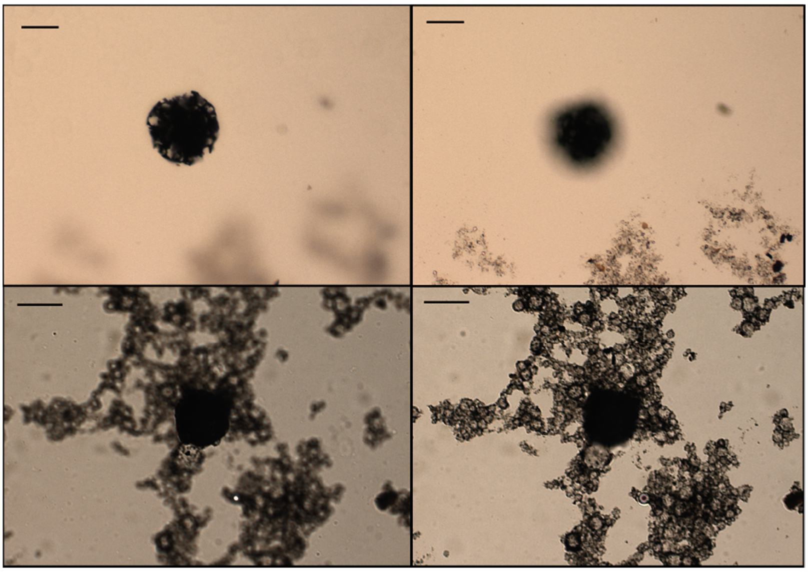


Figure 4. Spheroidal carbonaceous particles extracted from Karipääjärvi and Kuutsjärvi sediments under 400× magnification. The clearly identifiable rounded three-dimensional particles are SCPs (in focus on the left), whereas soot (quantified in Paper **IV**; in focus on the right) is seen as an amorphous mass in the background in addition to sporadic charcoal particles. Scale bars = 20 µm.

In Paper III, BC was quantified with a thermal-optical method from the ice core. Accordingly, the quantified BC is termed elemental carbon (EC), which is a proxy for BC. The thermal-optical (TO) method is a conventional method determining the carbonaceous aerosol fraction from atmospheric samples collected on quartz fibre filters (e.g., Birch and Cary, 1996; Cavalli et al., 2010). It has been recently applied to quantify EC also in precipitation (e.g. snow and ice) (e.g., Lavanchy et al., 1999; Forsström et al., 2009; Svensson et al., 2013). In this technique, organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC) are separately quantified due to their different volatilization temperature, by controlled temperature and atmosphere conditions, and an optical feature correcting for pyrolytically generated carbon (charring) (Birch and Cary, 1996).

In short, the ice was melted and immediately filtered through quartz fibre filters following the procedures described, for instance, in Forsström et al. (2009). The ice core samples were filtered in ca. 2–10 year resolution resulting in 88 filter samples (Fig. 5). After the filters had dried, a 1.5 cm^2 punch from each filter was analysed with the TO-method for EC with a Sunset Instrument (Sunset Laboratory Inc., Forest Grove, USA; Birch and Cary, 1996) at Stockholm University. The analysis was performed with the latest recommended thermal sequence EUSAAR_2 (Cavalli et al., 2010). Accordingly, in the first analysis stage, the filter punch is heated stepwise to 650 °C in a helium atmosphere, releasing OC and CC. In the second analysis stage, EC is released by heating the filter stepwise to 850 °C in an oxygen-helium atmosphere (Cavalli et al., 2010). During the second stage EC is released from the filter as CO_2 which is reduced to

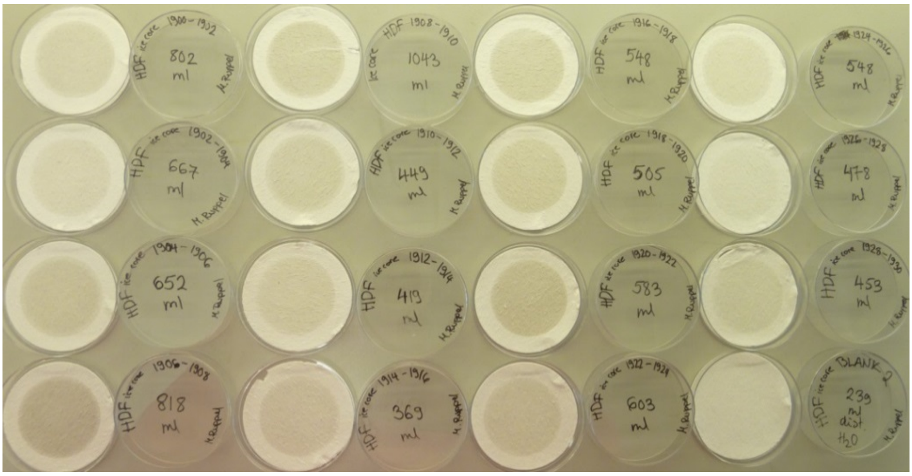


Figure 5. Ice core quartz fibre filter samples.

methane (CH_4) for detection by a flame ionization detector (FID) (Birch and Cary, 1996). During analysis, the transmittance of the filter is monitored using laser light (wavelength 678 nm), which allows for optical correction of charring, i.e. potential pyrolysis of OC to EC during the analysis (Cavalli et al., 2010). EC deposition to the ice core (g m^{-2} yr^{-1}) was calculated by dividing the total amount of EC in a (filter) sample by the (horizontal) cross section of the ice sample (ca. 10 cm^2) and the amount of years covered in one filtered ice sample. Extensive ion analyses discussed in Paper III were performed and reported by Beaudon et al. (2013).

In Paper IV, BC was analysed from the five Finnish Lapland lake sediments (Fig. 3b) as soot black carbon (SBC) with a chemothermal oxidation (CTO-375) method. The method has been specifically developed to quantify high-refractory soot in sediments and soils (Gustafsson et al., 1997, 2001). It is among the most commonly used BC quantification methods for soil and sediment samples (e.g., Elmquist et al., 2004; Hammes et al., 2007). It detects highly condensed SBC formed at high temperatures in the gas phase of combustion, irrespective of the combusted material (i.e. biomass or fossil fuels), when sufficient temperatures are attained (e.g., Elmquist et al., 2006).

Briefly, the dried lake sediments were ground to less than 100 µm particle size with a stainless steel ball grinder (Retsch, Mixer Mill 4000), and ca. 10 mg aliquots were weighed into silver capsules (8 × 5 mm). The CTO-375 method described in Gustafsson et al. (1997, 2001) includes the following three steps: 1. The sediment samples were placed in a home-build aluminium boat with 28 sample positions, and combusted in a custom made tube furnace at 375 °C for 18 hours under active airflow (200–300 mL min^{-1}). This step oxidises organic material, while highly condensed SBC and minerals are left behind. 2. After the samples had cooled down, in situ microscale acidification with 1M HCl was performed to remove carbonates. 3. The residual carbon content of the samples was determined and quantified as SBC with a Flash 2000 Organic Elemental Analyser (Thermo Fisher) at 1050 °C combustion temperature at the University of

Helsinki, Laboratory of Chronology. SBC fluxes (g m^{-2} yr^{-1}) were calculated by multiplying the retrieved SBC concentrations (g Dw^{-1}) with the radiometric dating inferred sediment accumulation rate (g cm^{-2} y^{-1}).

The ultimate aim of the thesis is to study the temporal and spatial trends in BC deposition from the atmosphere to the surface. Ice cores collect evidence of atmospherically deposited material more directly than lake sediments. Once BC is deposited on a snow or ice surface, it does not usually move laterally or vertically, if wind drift and strong melt are excluded. However, BC deposition to lake sediments is more complex. BC found in a sediment core may originate by direct deposition from the atmosphere or as lateral flux from other parts of the sediment bed or catchment area. Sediments may also be subject to mixing by bottom-dwelling organisms. Consequently, in case of lake sediments it is more challenging to assess how much of the BC originates directly from the atmosphere as opposed to ice cores. This shortcoming was avoided as much as possible by paying attention to the coring location, as described above. To acknowledge these differences, the term BC flux is used for lake sediments and BC deposition for the ice core.

2.2.3 Analytical windows of used methods and uncertainty assessment

The analytical methods used in this thesis determine partly different, but mostly overlapping BC fractions. The analytical windows of the used methods are presented in Figure 6.

The SCPs (Paper II) are the most clearly identifiable BC fraction studied here (Fig. 6). Potential uncertainties are small, and mostly related to the SCP identification skills of the analyst in question. If identification is correct, only SCPs and no other forms of BC are quantified. The mean recovery of SCPs is 95.2%, and detection limit 50–80 SCPs per gram dry mass (gDM^{-1}) (Rose, 1994). When SCP numbers are converted to SCP masses uncertainty is increased, as the medium size of SCPs may vary from one sample to the next, but the weight of a medium-sized SCP is used for the calculation.

Uncertainties related to the EC measurements from the ice core (Paper III) are comparably high. The analytical window of the method is not clear cut (Fig. 6). The method likely quantifies the widest spectrum of BC particles as EC, and it is possibly most effective in quantifying char-type BC. However, its efficiency in quantifying smallest BC particles in liquid samples is uncertain. While the quartz fibre filter is effective in collecting atmospheric aerosols of all size, its efficiency for small particles decreases for liquid samples (e.g., Forsström et al., 2013; Svensson et al., 2013; Torres et al., 2014). Smallest BC particles, most likely soot formed as a combustion condensate, may penetrate the filter in liquid samples. While the mass of particles penetrating the filter may be low due to the small size of the respective particles, their proportion to the quantified EC may vary between samples. The uncertainty related to this undercatch was estimated to be 22 % (Forsström et al., 2013). When other potential error sources (e.g. heterogeneous filter loading with EC) are included, the general uncertainty of the ice core EC quantification was estimated to 35–40% (Paper III).

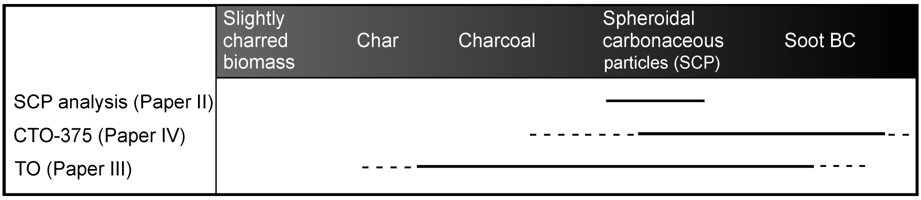


Figure 6. Conceptual analytical window of the used methods. The dashed lines at the end of the solid lines indicate the uncertainty in the range of the BC continuum that each method measures. Note that the length of the line portraying each BC fraction is not proportional to the potential mass of the BC fraction present in the samples. Modified after Hammes et al. (2007).

The BC fraction quantified with the CTO-375 method (Paper IV) is clear and extensively studied (e.g., Elmquist et al., 2006). The method detects carbon material of high thermal-oxidative resistance, i.e. soot (Elmquist et al., 2006), and likely some char-type BC, containing morphological features of the original fuel particle, formed in high-temperature combustion (Nguyen et al., 2004), such as SCPs (Rose et al., 1999) (Fig. 6). The BC quantified with the CTO-375 method is termed soot BC (SBC). Char-BC particles formed at lower combustion temperatures (i.e. less condensed forms of BC) have lower thermal-oxidative stabilities and have a lower recovery with the CTO-375 method (e.g., Elmquist et al., 2006). Therefore, the method gives an underestimation (or minimum value) of total BC present in the sediment samples. The CTO-375 method has also been shown to effectively exclude highly condensed and potentially interfering non-BC organic matter such as wood, melanoidin and pollen and thus avoid false positives effectively (Gustafsson et al., 2001; Nguyen et al., 2004; Hammes et al., 2007). Based on extensive duplicate to 23 times repeated analyses of identical lake sediment and standard reference material samples, the SBC quantification with the CTO-375 method showed 2.24 % relative standard deviation. The uncertainty of observed SBC concentrations is thereby very low, although some additional uncertainty is associated with the partly uncertain analytical window of the method.

Blanks were prepared during all BC analyses used in this thesis and showed undetectable BC concentrations in all cases. During the SCP and the SBC analyses, respective standard reference material samples were prepared to check for possible errors during the analysis procedures. A large majority of reference standard material results (6 for SCPs and 47 for SBC) gave results within the 95 % confidence interval of previously reported values, and thereby indicated the reliability of the presented results.

The above-described uncertainties apply only to the determined BC concentrations. Additional uncertainties are involved in the BC flux and deposition calculations due to dating uncertainties. Generally, these uncertainties are low at the top of the records, i.e. between 1963 (nuclear weapons testing peak in radionuclide deposition) and the surface, but increase in older parts of the records. As the dating affects the BC flux and deposition trends decisively, records where the dating seemed corporately unreliable, were excluded (Paper IV).

3. MAIN RESULTS AND DISCUSSION

3.1 Variation in black carbon flux trends in European Arctic lake sediments (Paper II and IV)

3.1.1 Spheroidal carbonaceous particle flux trends (Paper II)

The concentrations and the temporal trend of spheroidal carbonaceous particle (SCP) fluxes in the studied Finnish Lapland lake sediments (Paper II) are consistent with previously presented results from different parts of Europe (e.g., Wik & Renberg, 1996; Rose et al., 1999). First signs of SCP presence were detected at the end of the 19th or the beginning of the 20th century followed by a gradual increase. Around 1950, SCP values started to increase rapidly, peaking around 1980. Subsequently, the values have decreased towards the present. The trend is explained by increased power generation in Europe after the Second World War and the widespread use of fuel-oil in power stations then for the first time (Wik and Renberg, 1996; Rose et al., 1999). The SCP peak in the 1980s and subsequent decrease of SCP values is most likely explained by clean air legislation and improved particle arrestor technology. European SCP records show decreasing values after the 1970s or 1980s concurring with modelled industrial combustion derived sulphur deposition (Rose and Juggins, 1994). Furthermore, ice core records from Greenland illustrate the implementation of the Clean Air Act in the United States by lowered sulphur concentrations since the 1970s (McConnell et al., 2007).

The SCP flux trends show some variation in magnitudes between the sites (Fig. 7). The observed SCP fluxes are significantly higher in Saanajärvi, and notably higher in Kuutsjärvi, than the other sites. Back trajectory modelling of air masses reveals Saanajärvi to be more susceptible to air masses passing over Kiruna, a large iron mine in Sweden, whereas Kuutsjärvi is more prone to air masses coming from Nikel, a large nickel, palladium, and copper mine and smelter on the Kola Peninsula (Russia), than the

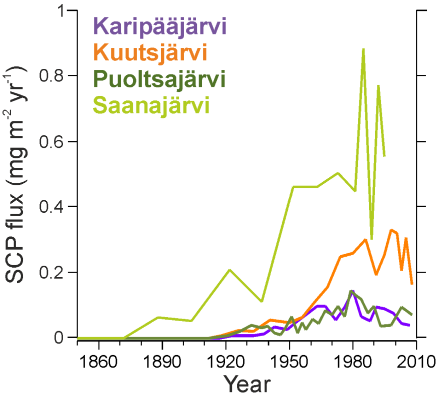


Figure 7. SCP flux (mg m^{-2} yr^{-1}) to Karipääjärvi, Kuutsjärvi, Puoltsajärvi and Saanajärvi between 1850 and 2010. SCPs were not analysed from Vuoskojärvi due to lack of sediment material.

other lakes. These large emission sources have a pronounced influence on nearby sediment records. The study underlines that even on a relatively small geographical scale SCP deposition can substantially vary due to prevailing wind directions transporting different air pollution to individual sites. Generally, the Finnish Lapland study sites receive atmospheric transport mainly from the south.

The resolution (100 × 100 km) of the used OsloCTM2 chemical transport model does not capture significant differences in BC deposition magnitudes observed between the sites. The OsloCTM2 model results show some agreement in energy and industry derived BC deposition trends to the study lakes with the SCP fluxes, as a similar peak in energy and industry derived BC model deposition is observed in 1980 as in SCP fluxes. However, modelled early 20th century trends do not agree with the SCP records, most likely because energy and industry related combustion did not reach sufficient temperatures for SCP production in that period. Generally, Paper II indicates that records of BC fractions, such as SCP, may prove useful for model validation while more records would be needed for meaningful model validation. The paper also highlights that the OsloCTM2 model may miss significant regional variation in BC deposition, and possibly underestimate local significant emission sources due to its coarse resolution.

As SCPs can be transported over long distances, the fuel use history and emission regulation of individual countries cannot explain trends found in the sediment records.

3.1.2 Spatial and temporal variation soot black carbon trends (Paper IV)

Previous results on soot black carbon (SBC) concentrations and fluxes during the last 150 years in Europe are much scarcer than those for SCPs. No previous SBC data were available for the Arctic. The results presented in Paper IV indicate generally very low SBC fluxes that are similar to preindustrial levels in a lake sediment core from southern Sweden (Elmquist et al., 2007). As opposed to SCPs, no generally common temporal trend in SBC fluxes is detectable for the five study lakes (Fig. 8a).

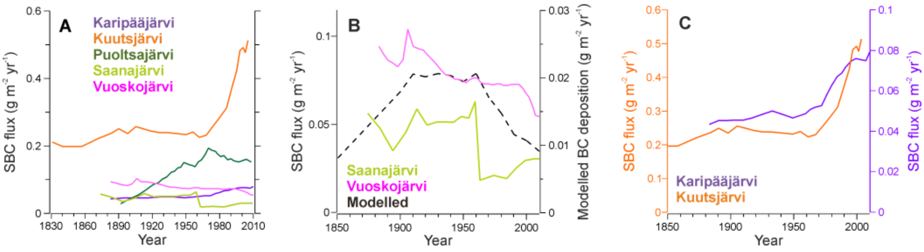


Figure 8. SBC flux (g m^{-2} yr^{-1}) to the lake sediments. A) SBC flux to all lake sediments. B) SBC flux to Saanajärvi and Vuoskojärvi, compared with modelled annual anthropogenic atmospheric BC deposition (g m^{-2} yr^{-1}) to Saanajärvi (data from Paper **II**). C) SBC flux to Karipääjärvi and Kuutsjärvi. Note that the y-axes are not identical.

However, some of the records suggest regional patterns in SBC fluxes. The two most northern lakes, Saanajärvi and Vuoskojärvi, indicate similarities in respective SBC fluxes with roughly higher values observed in 1910 to 1960 and a subsequent decrease to the present (Fig. 8b). The trend is similar to modelled BC deposition in the study area (Paper II) (Fig. 8b). In addition, the Vuoskojärvi sediment record shows declining SBC fluxes in the most recent decades similar to atmospheric BC measurements from 1964 to 2011 observed nearby to the lake (Dutkiewicz et al., 2014). The Saanajärvi SBC record is likely sensitive to BC emission changes from the Kiruna iron ore (Paper II), whereas Vuoskojärvi may be particularly sensitive to BC emissions from Nikel which is only ca. 100 km away from Vuoskojärvi (Fig. 3b).

In addition, SBC flux trends in Karipääjärvi and Kuutsjärvi, located closest to the Kola Peninsula and its several potential large emission sources, show similarities (Fig. 8c). The magnitude of SBC flux to Kuutsjärvi is significantly higher than to the other study lakes, but this is explained by sediment focussing in the lake, as evidenced by similarly significantly higher lead (^{210}Pb) fluxes to the sediment core (Supporting Information of Paper IV). Little variation in SBC fluxes in Karipääjärvi and Kuutsjärvi occur before ca. 1970 when a rapid increase of SBC fluxes starts in both records and continues to the top of the cores. Unfortunately, no historical BC emission data are available from the various ores and smelters on Kola Peninsula, and it may be difficult to link the SBC flux trends to any particular emission source. However, the fact that the trend is observed at more than one location increases its credibility, while the fact that the trend is only observable at the two sites, points to relatively local sources. The presence of local BC emission sources and their potential dominance over background values and trends in the Scandinavian Arctic was indicated also in snow BC measurements by Doherty et al. (2010).

A fifth SBC flux record (Puoltsajärvi) indicates yet another BC flux trend, but it may be driven by erroneous dating in the bottom parts of the sediment core. Significant variation in SBC flux trends in lakes within a relatively small region have been reported also previously (Muri et al., 2006; Bogdal et al., 2011), which may reflects that deposition of the very light SBC particles may also be influenced by quite local conditions (e.g., topography and wind directions). Therefore, if regional synthesis of SBC fluxes or deposition is attempted, trends only apparent in more than one record should be considered noteworthy.

3.1.3 Are the sediment BC records expressing changes in black carbon sources? (Paper IV)

As spheroidal carbonaceous particle (SCPs) and soot (Fig. 2; quantified as SBC in the lake sediments) are partly formed differently, their presence in environmental archives could potentially express different meaningful BC sources for the respective site. Whenever SCPs are formed, i.e. in heavy industry combustion at more than 1000 °C, soot is also formed. However, there are emission sources that may produce soot but no SCPs, such as wildfires and residential combustion. In addition, the combustion of natural gas, gasoline, and diesel do not produce any BC forms other than soot.

Consequently, tentative BC source analysis is possible based on the comparison of SCP and SBC values. Vuoskojärvi is not included in this comparison as no SCPs were analysed from this lake due to lack of material, and Saanajärvi is excluded because SCPs were analysed from a different sediment core (collected in 1996) than SBC (collected in 2013), which may potentially lead to errors in the comparison.

As described for Paper II, SCP fluxes in the study lakes increase after the 1950-60s and are highest at around 1980, and subsequently drop (Fig. 7), similar to the general SCP flux trend observed around Europe (e.g., Rose et al., 1999). Therefore, it may seem that BC emissions prior to 1950 in most important source areas of the study area related to other activity than industry, for example domestic combustion. However, in Paper II, the OsloCTM2 model predicted a pronounced peak in energy and industrial combustion derived BC deposition in the study area around 1900. It was inferred that if the modelled BC deposition is regarded as reliable, the most plausible reason for non-existent SCP fluxes around 1900 is likely due to industrial processes not reaching sufficient temperatures for SCP formation at that time. On the other hand, the temporal development of SCP fluxes since 1950 closely follows the trend suggested by the OsloCTM2 model for industry and energy sector derived BC deposition in the study area, with a peak around 1980 and a subsequent decrease. The post-1980 SCP flux decrease is mostly driven by advances in particle arrestor technology. Therefore, SCPs seem to reliably express BC emissions and deposition from industry and energy production after 1950.

Interestingly, however, as opposed to the other lakes, in Kuutsjärvi higher SCP fluxes are recorded in the 1990s and 2000s than during the 1980s peak (Fig. 7). This may indicate that particle arrestor technology has not been implemented and/or that industry related BC emissions have not decreased in the BC source area of Kuutsjärvi. Consequently, also the increase in SBC fluxes observed in Kuutsjärvi post-1970 (Fig. 8a, c) may be caused by polluted air masses being transported from industrial plants or smelters from Kola Peninsula which are not necessarily as efficiently regulated as European facilities. Moreover, Kuutsjärvi seems generally more affected by industrial BC emissions than Karipääjärvi and Puoltsajärvi as the correlation between SCP and SBC fluxes in Kuutsjärvi is higher ($r = 0.76$, $p < 0.005$) than in the other lakes ($r = 0.43$ and $r = 0.61$, respectively). This example indicates that SCP data could potentially help in SBC source apportionment, although the ratio of SCPs to SBC is very low, ca. 0.01–0.02 at most. Other potential causes for the increasing SBC fluxes in Karipääjärvi and Kuutsjärvi (and possibly even Saanajärvi) post-1970 may relate to BC emissions from the transport sector which is a growing BC source in western countries (Bond et al., 2013) and produces only soot. In addition, natural gas arrived in Finnish energy use only in 1974 (Keskinen, 1993). However, in the case of these latter or other distant potential emission sources, it is difficult to explain why these should be significant only for two of the five studied lakes.

To conclude, the present BC source analysis based on the different BC fractions analysed is not comprehensive. Better source apportionment may be achieved, for instance, by radiocarbon dating extracted or isolated BC. The radiocarbon proportion of

BC quantified in atmospheric, snow, ice or sediment samples reveals if the original combusted material was biomass (modern radiocarbon signal) or fossil (no radiocarbon left due to decay) or a combination of these. Such analysis is possible, for instance, by trapping (i.e. isolating) CO_2 formed during the final volatilization/quantification of respective EC or SBC in course of the thermal-optical and chemothermal oxidation methods (e.g., Gustafsson et al., 2009). This BC source apportionment is not able to exhaustibly indicate natural vs. anthropogenic BC emissions, as biomass combustion derived BC may result from both sources. However, the distinction is essential in discussion of the effect of BC on climate, as fossil fuel combustion derived BC has a 100 % stronger climate warming capacity than biofuel combustion derived BC due to co-emitted species (Ramana et al., 2010).

3.2 Elemental carbon values in the Holtedahlfonna ice core (Svalbard) (Paper III)

The elemental carbon (EC) concentrations recorded in the Holtedahlfonna ice core are significantly higher than BC concentrations measured with a different method in Greenland ice cores (McConnell et al., 2007; McConnell and Edwards, 2008), but compatible with EC concentrations quantified with the same/similar methods in European Alps ice cores (Lavanchy et al., 1999; Jenk et al., 2006). The temporal EC deposition trend, however, shows some similarities to BC values recorded in the Greenland ice cores (McConnell et al., 2007; McConnell and Edwards, 2008; McConnell, 2010) (Fig. 9). EC (as also BC) values start to increase around 1850, and peak around 1910 (Fig. 9). The BC values in the Greenland ice cores returned to almost preindustrial levels in the 1950s with very slow decrease continuing to the present (McConnell et al., 2007; McConnell and Edwards, 2008; McConnell, 2010) (Fig. 9c). Therefore, an increase in EC concentrations and deposition recorded in the Holtedahlfonna ice core from ca. 1970 to 2004 after a temporal low point in the 1960s (Fig. 9a, b) was quite unexpected. Moreover, this trend may seem inconsistent with decreasing atmospheric BC concentrations observed at several locations in the Arctic during the last decades (e.g., Sharma et al., 2013; Dutkiewicz et al., 2014).

Explanations for the diverging trends observed in the Greenland and Svalbard ice cores post-1970 may relate to the used measurement techniques quantifying partly different sized BC particles. The Single Particle Soot Photometer (SP2) used in the Greenland studies only quantifies high-refractory soot of ~ 80-500 nm core size (e.g., McConnell et al., 2007; Kaspari et al., 2011), while the EC measurements are most efficient for larger particle size due to possible filter undercatch of smallest particles (unknown size range) (e.g., Torres et al., 2014). Notably, with increasing Arctic temperatures BC particle size in snow and ice may have increased due to BC particle size growing with repeated snow melt and freeze cycles (Schwarz et al., 2013). However, more likely, the Greenland ice core records do not portray BC deposition over the rest of the Arctic at lower elevation, as McConnell et al. (2007) implicated. For instance, BC

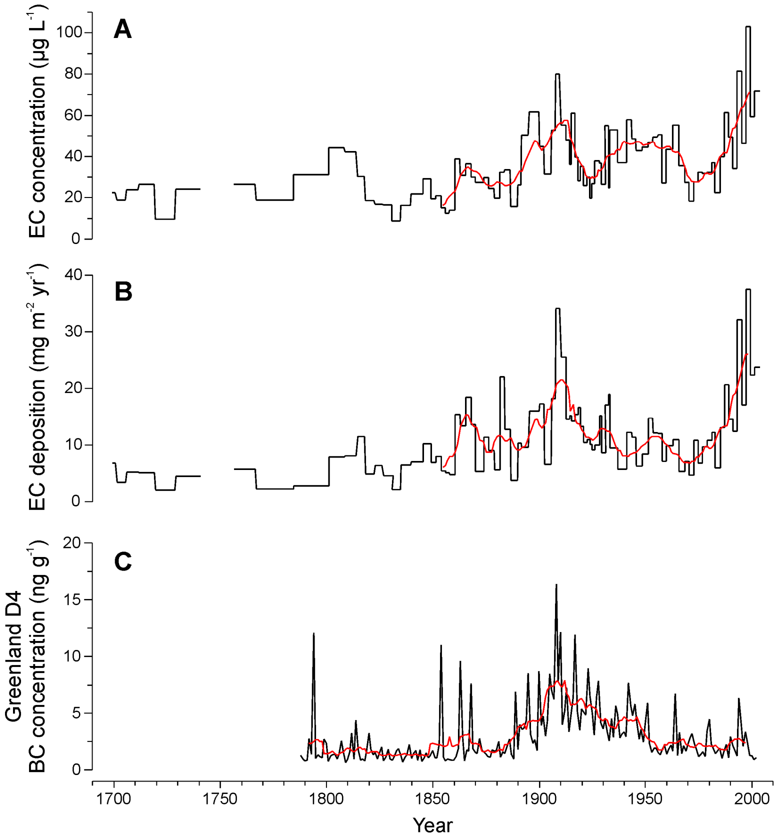


Figure 9. Elemental carbon (EC) concentrations and deposition in the Holtedahlfonna ice core compared to black carbon (BC) concentrations recorded in a Greenland (D4) ice core (McConnell et al., 2007). A) EC concentrations in µg L^{-1}, and B) EC deposition in mg m^{-2} yr^{-1}, with 10-year running averages (*red line*). The deposition trend (B) is different from the concentration trend (A) around 1930 to 1970 due to variations in the snow accumulation rates of the glacier. C) Annual BC concentration (ng g^{-1}) data (*black*) and 10-year running averages (*red*) in the Greenland D4 ice core (McConnell et al., 2007). BC deposition based on this data was presented in McConnell, 2010 showing a very similar trend as here, indicative for little temporal variation in snow accumulation rates at the D4 ice coring site.

emissions within the Arctic would not reach the high-elevation (e.g., at 2713 and 2410 m a.s.l.) Greenland coring sites due to restricted isentropic uplift (Stohl, 2006; Stohl et al., 2013). Such emissions could originate from natural gas flaring in northern Russia which have previously been significantly underestimated but are suggested to account for 42 % of mean annual atmospheric surface BC concentrations in the Arctic (Stohl et al., 2013). The intense flaring area in north-eastern European Russia and western Siberia (around the Yamal Peninsula) has been repeatedly shown to be a very significant source area for atmospheric BC observed Ny-Ålesund, Svalbard, only 40 km away from the Holtedahlfonna coring site (Eleftheriadis et al., 2009; Hirdman et al., 2010b; Stohl et al., 2013; Tunved et al., 2013). Flaring in the region may be projected to have started around 1970 when some of the reserves were found and oil and gas extraction started. These flaring emissions are likely to reach Svalbard but to miss Greenland ice coring sites.

The discrepancy between the post-1970 EC deposition trend in the ice core and decreasing atmospheric BC concentrations measured at Ny-Ålesund, could also be explained by changes in the scavenging efficiency of BC. Cozic et al. (2007) showed that BC scavenging during cloud formation increases when temperatures increase. Rising temperatures have been observed also on Svalbard in recent decades (Førland et al., 2011). Therefore, BC deposition may increase despite in tandem declining atmospheric concentrations. Moreover, 85-90 % of BC is wet-deposited in the Arctic (Wang et al., 2011), and may thereby not be caught by atmospheric measurements. Subsequently, temporal trends in atmospheric and snow BC concentrations and deposition may diverge.

3.3 Climatic and policy implications of the observed BC trends

Climatic implications of the recorded preindustrial to present BC flux and deposition trends in this thesis may be manifold.

First, the general conception of recent declining BC values in the Arctic is questioned. Previously information available from the Greenland ice cores (e.g. McConnell, 2010), atmospheric measurements (e.g. Sharma et al., 2013; Dutkiewicz et al., 2014), sporadic snow measurements (e.g. Doherty et al., 2010), and modelling (e.g. Koch et al., 2011; Paper II) indicate that atmospheric and snow BC concentrations and deposition in the Arctic have been declining during the recent decades. These results have led to deductions of substantial warming in the Arctic during the last 20 years despite declining BC values (such as in AMAP, 2011b). However, in the light of the results presented in this thesis these previous deductions may have been premature, as BC fluxes and deposition have increased in recent decades at least in some parts of the Arctic. A regional synthesis based on the results presented here would in fact show a generally increasing BC deposition trend from ca. 1970 to the present. This is indicated in Figure 10, with the ice core EC deposition trend (Fig. 10a) and the standardized SBC flux trend based on four of the five study lakes (Fig. 10b) showing surprisingly similar features between 1850 and 2010.

Second, the sources for the increased BC fluxes and deposition observed in the Svalbard ice core (Paper III) and some lake sediments in northern Finland (Paper IV) since ca. 1970 are likely located within the Arctic. High-latitude and possibly local sources would explain the observed differences in trends between sites, for instance, the Greenland vs. Svalbard ice cores, and different lake sediments in Finland, respectively. The presence of such high-latitude BC sources is alarming, as BC emissions originating within the Arctic travel at lower elevations in the atmosphere and have a higher probability to be deposited within the Arctic, resulting in an almost five times larger Arctic surface temperature response (per unit of emitted mass) compared to emissions at mid-latitudes (Sand et al., 2013a). In the Arctic the radiative forcing exerted by BC deposited on snow is significantly higher than that of atmospheric BC (Flanner et al., 2007, 2009; Skeie et al., 2011).

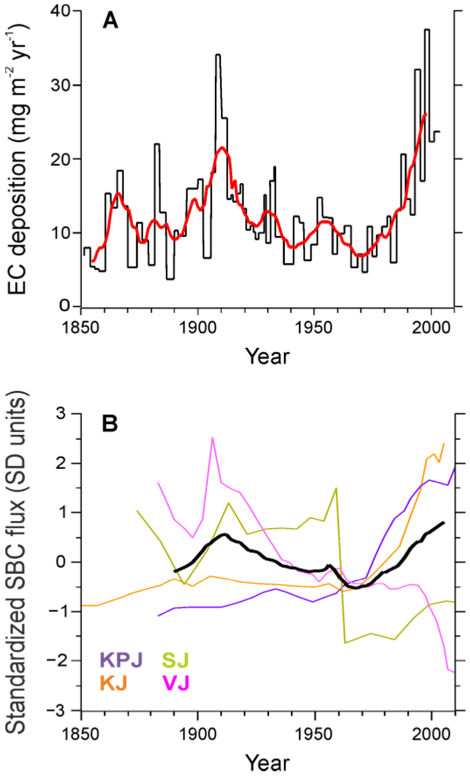


Figure 10. EC deposition to the Holtedahlfonna ice core compared to standardized SBC fluxes to the Finnish lake sediments. (Puoltsajärvi was not included in the analysis due to its potential dating errors and thus possibly biased flux trend (Paper **IV**)). The sediment records were standardized to avoid any single record dominating the general trend. A) EC deposition in mg m^{-2} yr^{-1}, with 10-year running averages (*red line*). B) Stacked SBC fluxes at Karipääjärvi (KPJ), Kuutsjärvi (KJ), Saanajärvi (SJ) and Vuoskojärvi (VJ) expressed as standard deviations from the mean. A LOESS smoother (*black curve*) (span = 0.15) is fitted to the data for the time intervals for which data is available from all lakes.

Third, as the increasing trend in post-1970 BC fluxes and deposition is visible in two independent environmental archives (ice core and lake sediments) in different locations receiving atmospheric transport from different source areas (e.g., Paper II and III), it could be presumed that a similar trend may possibly be observed also in other parts of the Arctic, especially as the post-1970 trend in the Svalbard ice core is not thought to be caused by local sources. Flaring in northern Russia, concentrated in north-eastern European Russia and western Siberia (around the Yamal Peninsula), is assumed to be a previously underestimated significant source of BC emission within the Arctic (Stohl et al., 2013). The extensive survey by Doherty et al. (2010) showed that snow BC concentrations were highest in Russia for the whole Arctic. While the cause for the observation was assumed to be the close proximity to towns and cities during sampling, and sublimation concentrating BC in surface snow during winter and spring (Doherty et al., 2010), the proximity to the intensive flaring areas could also be a possible explanation. If Russian flaring at the edge of the Arctic Ocean is in the future confirmed to be such a predominant BC source for the Arctic, as suggested by Stohl et al. (2013) and the Svalbard ice core observations (Paper III), these emissions could turn out to have been a great contributor to the accelerating retreat of the Arctic sea ice post-1970.

In general, more observations on past BC concentration and deposition trends are needed from the Arctic to assess general or regional trends in past BC values and their climatic and policy implications. In the meanwhile, efforts should be taken to decrease flaring related BC emissions in northern Russia. According to Elvidge et al. (2009), flaring is common in northern Russia due to missing infrastructure in the region to transport and utilize all extracted natural gas. Therefore, investments in improvements of the region's infrastructure could mitigate harm caused to the Arctic environment by oil and gas extraction. However, decreasing BC emissions in the region will be severely challenging, as extensive economic development is planned for the Arctic in the near future, including offshore oil and gas drilling (see e.g. the Yamal megaproject: http://www.gazprom.com/about/production/projects/mega-yamal/, webpage visited February 27th, 2015) and year-round shipping.

Although BC emissions within the Arctic present an imminent threat to the undisturbed functioning of the Arctic cryosphere as a key reflecting surface of the Earth, BC emissions outside the Arctic are also significant for the arctic climate. BC forcing exerted at mid-latitudes increases the atmospheric heat transport to the Arctic, warming the surface and causing retreat of the sea ice (Sand et al., 2013b). The increased surface temperatures increase the frequency of boreal wild fires (e.g. Kelly et al., 2013), which may themselves be an increasing source for BC in the Arctic (e.g., Bond et al., 2013). Therefore, to ameliorate Arctic climate warming, BC emissions outside the Arctic have to be managed as well (e.g., AMAP, 2011b).

When considering global and arctic climate change as a whole, reduction of carbon dioxide emissions needs to be the backbone of climate change mitigation. However, CO_2 has a long atmospheric lifetime and therefore even swift reductions in its emissions may not be able to delay ongoing melting and associated positive feedback processes in the Arctic. Thus, if it is a goal to contain the melting, the quickest results may be achieved by targeting BC (AMAP, 2011b). In recent years atmospheric scientists have proposed that in climate negotiations the main attention in *short time* mitigation of climate change should be directed towards cutting down BC emissions (Grieshop et al., 2009; Penner et al., 2010; Shindell et al., 2012). Fortunately, mitigation based on CO_2 and BC emission reductions support one another as both are mostly produced from same sources, and should therefore not be seen as competitive or exclusionary. For instance, the use of renewable biofuels, e.g. in energy production, reduces both CO_2 emissions and BC radiative forcing, as fossil fuel combustion derived BC warms the atmosphere more efficiently than biomass combustion derived BC (Ramana et al., 2010; Bond et al., 2013). Furthermore, BC is an important health issue. In the atmosphere, BC soaks up toxic organic material and heavy metals (from same or different sources than BC) that reach deep respiratory systems of humans. BC has been implicated in many cardiovascular and respiratory diseases and a major contributor to millions premature deaths per year (e.g., Shindell et al, 2012; WHO, 2013). Thus, mitigation of BC emissions offers an opportunity to address climate change and air pollution simultaneously (e.g., Jacobson, 2002; Ramanathan and Charmichael, 2008; Shindell et al., 2012).

3.4 Applicability of selected analytical methods for black carbon quantification in Arctic environmental archives

Paper I compared several historical BC records analysed from ice cores and lake sediments. The discussion highlighted that the comparison of data acquired using different analytical methods may be inappropriate. For instance, records obtained from two ice cores from a Himalayan glacier, with one analysed with the SP2 (Kaspari et al., 2011) and the other with the thermal optical (Ming et al., 2008) method, showed different temporal BC trends. According to Kaspari et al. (2011) the two ice cores were retrieved from the same drilling site, and therefore it is unlikely that the observed differences would be caused by depositional differences. Similar discrepancy is observed also in the European Alps where Lavanchy et al. (1999) and Thevenon et al. (2009) analysed BC from the same ice core using different methods and recorded partly differing trends (Paper III). Such discrepancies complicate the drawing of conclusions on regional BC trends and their climatic implications. Therefore, in future analyses it is crucial to clarify which methods are used, and furthermore, to acknowledge which fraction of the BC combustion continuum is quantified, as no method is able to quantify the total BC mass.

The lack of an exact definition for BC has hampered comparisons of BC results in atmospheric sciences also. The definition of BC in the highly influential summary of BC research in Bond et al. (2013) may reduce future discrepancies. At the same time, Bond et al. (2013) recognize that previous analyses and modelling results are not limited to the material that they define as BC, causing a lack of comparability among results. If future research of BC in environmental archives were restricted to material defined as BC in Bond et al. (2013), then approaches using the SP2 method for ice cores and the CTO-375 for soils and sediments would likely be the most appropriate. These methods quantify only high-refractory and most condensed forms of BC which generally are also the smallest in size (Fig. 2). Such an approach may be justified as the visible light absorption of BC particles decreases with increasing size (Schwarz et al., 2013), and as smaller particles have a longer atmospheric lifetime, and are therefore more likely to be observed in remote locations such as the Arctic. However, this thesis shows that bigger BC particles are also present in the Arctic, and they and their climate effects should not be overlooked, particularly as BC size may increase in snow and ice after deposition due to freeze-melt cycles (Schwarz et al., 2013). This poses challenges for the BC quantification by the SP2 method as it is restricted to smaller BC particles (e.g., McConnell et al., 2007; Kaspari et al., 2011; Schwarz et al., 2013). BC analysis with the CTO-375 method is not restricted by the size of the particles and is applicable for atmospheric filter samples (Zencak et al., 2007) and therefore likely also for snow and ice samples. However, comparably high BC concentrations, and therefore big samples from remote areas, are required to exceed the detection limit of the CTO-375 method, and it may therefore not be optimal for Arctic samples. To conclude, the most comprehensive data to account for the different BC particle types would be attained by using multiple analysis methods at the same time, while acknowledging the strengths and weaknesses of each method.

4. SUMMARY AND CONCLUSIONS

- In this thesis, past black carbon (BC) flux and deposition trends were studied from the European Arctic based on an ice core from Svalbard and five lake sediment cores from northern Finland. Three different BC analysis methods were used, resulting in three different BC fractions being quantified. The results indicate significant spatial variation in the preindustrial-to-present BC deposition trends, and also in BC trends quantified with different methods.
- Spheroidal carbonaceous particles (SCPs), which are only formed by high-temperature industrial fossil fuel combustion, show similar temporal flux trends in the lake sediments as previously reported in Europe: fluxes increase rapidly after the Second World War and peak around 1980 followed by decreasing fluxes due to implemented “Clean air” legislation. As SCPs represent a minor fraction of total BC mass, elemental carbon (EC) was analysed from the ice core and soot BC (SBC) from lake sediments. These BC fractions are expected to better illustrate general BC flux and deposition trends. Similar BC flux and deposition trends as previously presented in Greenland ice cores, atmospheric measurements and modelling studies are observed in some locations, while contrasting results are found in others.
- At two lake sites, SBC fluxes indicate a generally decreasing trend from ca. 1960 to the present which is in line with model results, atmospheric measurements, and Greenland ice core data. However, the Svalbard ice core and two lake sediment records show rapidly increasing EC and SBC deposition and fluxes from around 1970 to the end of the records (2004, 2005 and 2010, respectively). This increase is unexpected and unparalleled within the Arctic.
- The Svalbard ice core site receives atmospheric transport mostly from different source areas (predominately from east) compared to the Finnish lake sites (predominately from south). Therefore, the source for the increased SBC flux and EC deposition values is expected to be different for the ice core and the lake sediment sites. Flaring in northern Russia is likely responsible for the increase recorded in the ice core, while local sources are considered more probable for the lake sediment trends. If the same source affected both areas (Svalbard and northern Finland) the SBC flux trend in the lake sediments would be expected to be similar for all sites. The present thesis is not able to conclusively identify the specific sources for the observed increasing SBC flux and EC deposition trends. Thus, further source investigation is needed.

- The observed results cannot be extrapolated over wider areas. More records from other parts of the Arctic are required to confirm a regional trend in past BC deposition in the area. However, the fact that increasing BC flux and deposition trends were observed in different environmental archives analysed by different methods, and likely receiving atmospheric transport from different source areas, implies that a similar trend may be observed also over other parts of the Arctic. If that were the case, regardless of the cause for the increasing BC flux and deposition trends, BC may have exerted a significant impact on the radiative forcing and thereby past climate warming of the Arctic in the most recent three or four decades.
- An important observation indicated by the Svalbard ice core record is that EC deposition may not necessarily be proportional to measured atmospheric BC concentrations trends. Explanations for such observations are that, a) most of BC is wet-deposited in the Arctic and is thereby not detected by atmospheric measurements, and b) BC scavenging efficiency may change over time causing discrepancies between atmospheric measurements and deposition observations. On the other hand, similar trends of atmospheric BC measurements and recorded SBC fluxes to lake sediments were observed over more than forty years in northern Finland, highlighting the significance of local conditions.
- As BC is an operational term, caution should be exercised when comparing BC results attained using different methods. However, the possibility to quantify different BC fractions separately may enable tentative BC source identification. Generally, to get a comprehensive view on total BC concentrations, deposition and their trends, BC should be analysed with as many different methods as possible from the same samples.

5. FUTURE PERSPECTIVES

The BC flux and deposition results presented in this thesis are from a restricted geographical area in the European Arctic. Therefore, the BC deposition history over the wider Arctic, e.g. Russian and Canadian Arctic and Alaska, is still unresolved and may entail many unexpected results. Future research on historical BC deposition in the Arctic should focus, for instance, on deciphering the spatial and temporal patterns of past BC deposition in a broader geographical context, clarifying BC sources present within the Arctic, and sources (whether high or mid-latitude) of BC observed in the Arctic, and method comparison. These research directions could further contribute to the assessment of the importance of BC in past, present and future climate change in the Arctic.

The following detailed contributions for this task are planned (or already started) by the author:

1. Confirmation of the recorded BC deposition trend in the Holtedahlfonna (Svalbard) ice core

Generally, ice cores reliably accumulate evidence of particles deposited directly from the atmosphere, especially when the coring location is carefully selected within the accumulation zone of the glacier. However, it is difficult to entirely rule out the possibility of local conditions (e.g., wind drift or precipitation patterns) dominating the recorded trends. To confirm the recorded BC trend in Holtedahlfonna, another ice core was collected from the glacier in April 2015, close to the 2005 drilling site. In addition, one ca. 10 m deep ice cores was drilled from Kongsvegen glacier, ca. 40 km southwest from Holtedahlfonna. The objectives are:

1. to confirm whether the same BC concentration and deposition trend is recorded in the new Holtedahlfonna ice core as in the 2005 ice core.
2. to see whether the increasing BC deposition trend between 1970 and 2004 observed in the 2005 Holtedhlfonna ice core has continued in the most recent 10 years or not.
3. to tentatively establish whether similar BC concentrations, depositions and their trends are observed at a glacier (Kongsvegen) nearby to Holtedahlfonna.
4. to test whether the same BC concentration and deposition trends are recorded by quantifying BC with different methods.

First, to ensure comparability, BC (in this case EC) is analysed in all ice cores with the same thermal optical method as in Paper III. Secondly, BC is analysed at least from the new Holtedahlfonna ice core with the Single Particle Soot Photometer (SP2), according to methodology described e.g. in McConnell et al. (2007), Kaspari et al. (2011) and Wendl et al. (2014). Samples analysed with the SP2 will be identical, i.e. aliquots, of those analysed with the thermal optical method. The test will clarify whether different BC trends may be quantified with different methods, as hypothesized in Paper I and III. In this case, the different trends would be explained in varying trends of different sized BC particles, as the thermal optical method is most efficient in quantifying comparably large and the SP2 method small BC particles. In addition, the undercatch of the thermal optical method will be assessed by analysing the ice core melt water filtered through the quartz fibre filters with the SP2 for BC.

2. Assessment of the climatic effect of recorded BC concentrations through albedo reductions

The next step following BC quantifications in arctic snow and ice is to assess the climate impact of the recorded concentrations. A straightforward way to do this is to estimate the albedo reductions caused by the reported concentrations. As no spectral snow albedo measurements are available from the Holtedahlfonna ice core site, the spectral albedo in snow at the study site must be inferred from modelling results (e.g. Warren and Wiscombe, 1980; Hansen and Nazarenko, 2004), as has been done, e.g. in Kaspari et al. (2014). The radiative forcing, i.e. the climatic effect of BC in snow and ice, can then be calculated based on these estimates of snow BC concentration inflicted albedo changes (e.g. Hansen and Nazarenko, 2004; Skeie et al., 2011; Bond et al., 2013). This work will be done in collaboration with the Finnish Meteorological Institute and Center for International Climate and Environmental Research – Oslo.

3. Comparison of lake sediment BC records attained using different analytical methods

Sediments collected from three Finnish Lapland study lakes (Vuoskojärvi, Saanajärvi and Karipääjärvi) which are already analysed for SBC with the chemothermal oxidation (CTO-375) method, will be analysed for EC with the thermal-optical method at the State University of New York at Albany, Atmospheric Sciences Research Center. The thermal-optical method applied for sediments follows wet chemical *ex situ* extraction of BC from surrounding sediment material, as described in Husain et al. (2008) and Khan et al. (2009). Unpublished results are already available for Vuoskojärvi and indicate partially different results between the methods, as a much more pronounced early 20th century peak is detected in EC values than in SBC, but the records concur in showing declining values towards the present. These preliminary results highlight that the methods indeed quantify different fractions of the BC continuum.

4. Source apportionment of BC recorded in environmental archives of the European Arctic

The source of BC recorded in selected samples from the five lake sediment cores from northern Finland will be analysed by radiocarbon analysis (Gustafsson et al., 2009). The analysis will reveal how much of the recorded BC resulted from biomass combustion. Bond et al. (2013) suggested that the ratio of biomass-derived BC may be increasing in the northern hemisphere in response to increasing intensity of boreal wildfires due to climatic warming (Kelly et al., 2013). Such analysis will also be attempted for the new Svalbard ice core.

ACKNOWLEDGEMENTS

My journey in the unfamiliar and mysterious world of BC research has been full of surprises, occasional desperation, successes and setbacks, excitement and tension, but most importantly, joy. For this joy I owe big thanks to the wonderful colleagues, friends and family around me.

My supervisors and I were in the beginning completely puzzled about BC, as it was a new research field for all of us. In the end, I think we have learned a lot. I thank Atte Korhola and Jan Weckström for the encouragement they have given me and for showing strong confidence in me. I feel particularly deep gratitude towards Neil Rose, whom I call my mentor, for introducing me to the world of SCPs with unforeseen dedication, and for showing unexpected trust in me by inviting me to co-author a book chapter, at a point when I had yet little to show for my scientific abilities. I am also thankful for Minna Väliranta and Markku Oinonen for being in my thesis advisory committee and for showing interest in my work and lending helpful guidance. Furthermore, I am happy to have worked at ECRU, and I thank all my fellow PhD students and colleagues there for the good and inspiring working environment. I also warmly thank my thesis reviewers Susan Kaspari and John Smol for their helpful comments.

One of the most important connections and research directions I have taken was getting involved in the Nordic Centre of Excellence CRAICC. I am deeply grateful for Jaana Bäck and Sanna Sorvari for ushering me in that direction. Through CRAICC, I got to know wonderful Nordic scientists, to name the most important: Elisabeth Isaksson and colleagues at the Norwegian Polar Institute; Johan Ström, Örjan Gustafsson and Henrik Grythe at Stockholm University; and Aki Virkkula, Outi Meinander and Jonas Svensson at the Finnish Meteorological Institute. Elisabeth warm-heartedly introduced me to Tromsø, gave me the invaluable opportunity to work with an ice core and brought me along on unforgettable adventures in Svalbard (thank you also Ewa Lind, Anne Hormes, Trine Holm, Henrik Rasmussen, Jørn Dybdahl), while the others have had inspiring collaboration with me, and exciting future projects are arising in each direction. I am particularly moved by Johan Ström and Örjan Gustafsson finding the time and interest to give me indispensable insights and guidance in my research. I also warmly thank all the other co-authors without whose expertise I could not have managed: Marianne Lund, Emilie Beaudon, Christina Pedersen and Handong Yang.

Finding appropriate methods for black carbon analysis in lake sediments, and especially getting these to work with the available laboratory setups, has proven to be surprisingly difficult. The staff at the Laboratory of Chronology (including Vesa Palonen), have accompanied me in my endeavours to overcome methodological challenges, and have lent extraordinary support, assistance and friendship in the process. The ambiance of the laboratory is one filled with good humour and warmth, which have eased my work tremendously. In particular, I am forever thankful to Antto Pesonen for helping and encouraging me throughout the years.

At last, I want to thank all of my dear friends for the comfort and support they have given me in my life. I would not have made it without the joy and relaxation that you have brought me. Furthermore, I thank my mother for letting me vent all my frustration and annoyance at her while still maintaining a good spirit, and my father for always supporting and encouraging me when I needed it the most. My brother I have always looked up to, and his music has supported and guided me through difficulties and given me incessant joy. My husband I deeply thank for being there for me on every imaginable level, and for his unwavering confidence in me.

I express my profound gratitude towards the Arctic Doctoral Programme ARKTIS (University of Lapland), the NordForsk Top-level Research Initiative Nordic Centre of Excellence CRAICC (Cryosphere–Atmosphere Interactions in a Changing Arctic Climate), and the Academy of Finland (grant 257903) for funding my research. In addition, the financial support for running costs granted by the Finnish Cultural Foundation, Emil Aaltonen Foundation, and the University of Helsinki Heinonsalo Fund is warmly acknowledged.

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