

## Research Article

# Comparison of Spheroidal Carbonaceous Particle Data with Modelled Atmospheric Black Carbon Concentration and Deposition and Air Mass Sources in Northern Europe, 1850–2010

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Received 8 March 2013; Accepted 9 July 2013

Academic Editor: Junji Cao

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Spheroidal carbonaceous particles (SCP) are a well-defined fraction of black carbon (BC), produced only by the incomplete combustion of fossil fuels such as coal and oil. Their past concentrations have been studied using environmental archives, but, additionally, historical trends of BC concentration and deposition can be estimated by modelling. These models are based on BC emission inventories, but actual measurements of BC concentration and deposition play an essential role in their evaluation and validation. We use the chemistry transport model OsloCTM2 to model historical time series of BC concentration and deposition from energy and industrial sources and compare these to sedimentary measurements of SCPs obtained from lake sediments in Northern Europe from 1850 to 2010. To determine the origin of SCPs we generated back trajectories of air masses to the study sites. Generally, trends of SCP deposition and modelled results agree reasonably well, showing rapidly increasing values from 1950, to a peak in 1980, and a decrease towards the present. Empirical SCP data show differences in deposition magnitude between the sites that are not captured by the model but which may be explained by different air mass transport patterns. The results highlight the need for numerous observational records to reliably validate model results.

## 1. Introduction

The term black carbon (BC) was first introduced by Novakov [1] and incorporates a wide spectrum of charred material formed by incomplete combustion of biomass and fossil fuels [2]. Generally, BC can be grouped into larger chars, which are aromatic residues reflecting the structure of the burned material or the nature of the burning process, and smaller particles, soots, which are combustion condensates formed in the vapour phase [1–5]. The precise definition of BC depends

on the method used for its quantification [6]; therefore, no single definition has been widely accepted, especially across disciplines.

However, within this imprecise myriad of carbonaceous particles, spheroidal carbonaceous particles (SCPs) are a clearly identifiable component of BC. 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. They have no natural sources [7] and consist mainly of elemental

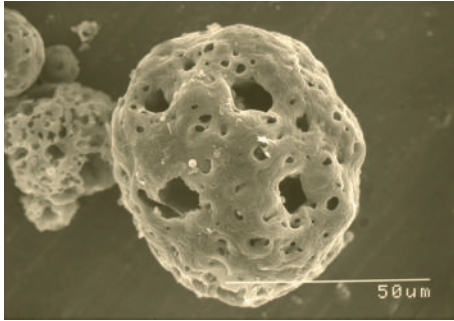


FIGURE 1: Scanning electron microscope picture of a spheroidal carbonaceous particle (picture by Neil Rose).

carbon making them chemically inert. Morphologically they are the spheroidal “skeletons” left by the incomplete combustion of fuel particles (coal) and droplets (oil) (see Figure 1). They thereby physically resemble char BC although their other characteristics are more typical of soot BC (highly refractory, chemically inert, and hydrophobic). The usual size range of SCPs in the environment is 2–20  $\mu\text{m}$  (diameter), but the largest particles can reach  $>50 \mu\text{m}$ . In remote areas only particles smaller than 10  $\mu\text{m}$  are found [8].

The atmospheric lifetime of BC particles smaller than 2.5  $\mu\text{m}$  is around a week [9], which should also be the case for the smallest SCPs, whereas particles of the size range of  $\geq 10 \mu\text{m}$  are probably transported only on a regional scale [10]. SCPs are removed from the atmosphere by wet or dry deposition and are abundant in urban areas close to industrial sources [11, 12]. However, they have been recorded even in remote areas such as Svalbard [13, 14], Greenland [15], the Canadian High Arctic [16], and Antarctica [17, 18] far removed from any local or regional emission sources. SCPs have been used for decades as a tracer for industrial combustion and pollution deposited from the atmosphere (e.g., [13]) and their spatial distribution is in good agreement with patterns of sulphur deposition [11, 12] as well as polycyclic aromatic hydrocarbon (PAH) distribution [19].

Examples of long-term monitoring of SCPs in the atmosphere are very few [20]. In the absence of long-term monitoring data, environmental archives, such as glacial ice, peat deposits, and lake and marine sediments, are the only means by which long-term trends of contaminant deposition can be ascertained. Accumulating sediments store direct evidence of atmospheric deposition of pollutants in chronological and conformable order thereby providing an *in situ* record of atmospheric contamination. Furthermore, SCPs strongly resist decomposition and therefore their sediment record is both robust and reliable [21].

In addition to sedimentary records of SCPs and BC, historical trends can also be estimated using models. Much of the understanding about the present and future impact of BC is based on modelling studies but, to be credible, models need to be evaluated and validated against historical data. Sedimentary records can supplement modeled data by providing spatial and temporal information on atmospheric contamination patterns. A few modelling studies

have explored the historical concentration of BC in the atmosphere using estimates of historical emissions [22–24]. These studies compare modelled BC concentrations to ice core records from Greenland [25–27] and show very good agreement with both temporal trends and magnitudes of the BC concentrations. In addition, Lee et al. [24] compare results of eight models [28] to eight ice cores from the Alps, Tibetan Plateau, and Antarctica. While models are able to capture the relative increase in BC from preindustrial times to the present in the Antarctic ice cores, they fail to reproduce the temporal trends from Tibetan Plateau records. This shows that good agreement between modelled and empirical data in one location cannot necessarily be expected in others for the same model. Hence, comparisons of models with observational data require large spatial coverage. Records from single locations may also include characteristics that prohibit upscaling. For example, McConnell et al. [25] recognized that their Greenland ice cores mainly represented emissions from North America and, located in the free troposphere (ca. at 2500 m asl), did not reflect BC deposition at sea level altitudes.

Current estimates rank BC as the second most important contributor to climate warming with a total climate forcing of  $+1.1 \text{ W m}^{-2}$  ( $+0.17$  to  $+2.1 \text{ W m}^{-2}$ ). It has an especially strong climate warming efficiency in the Arctic where BC aerosols can significantly reduce the albedo when deposited on snow covered surfaces (see [29] and references therein). Until recently, measurements of past BC concentrations and deposition have been scarce, and with the exception of the ice core records of McConnell et al. [25, 26] no long-term records of total BC or EC (elemental carbon) exist from the Arctic. However, historical SCP records have been studied in Arctic regions [13–16, 30].

This paper focuses on arctic Europe since a number of SCP records were available within a small geographical area, and although remote, the area is of special interest due to the nearby industrialized area on the Kola Peninsula, Russia. Also, the European sector is clearly the area with highest elemental carbon (EC) concentrations measured from modern snow in the Arctic [31] and is therefore an important area with respect to Arctic climate change.

The ultimate objective of this paper is to use direct sedimentary records to provide support for models reconstructing historical BC concentrations. Accurate measurements of SCP trends in remote locations, enabled by the sedimentary records, will help improve models to better capture the large spatial and temporal variations in BC, informing climate science, health, and policy. We use the chemistry transport model OsloCTM2 (e.g., [22, 32, 33]) to model historical time series of BC concentration and deposition from energy and industrial sources and compare these to sedimentary measurements of SCPs to show the usefulness of sedimentary data in the validation and possible improvement of models. In addition to the evolution of industrial and energy emissions, the SCP record is also a manifestation of variation in precipitation and wind direction patterns. We therefore generate back trajectories of air masses from the study sites. This information may provide data on the origin

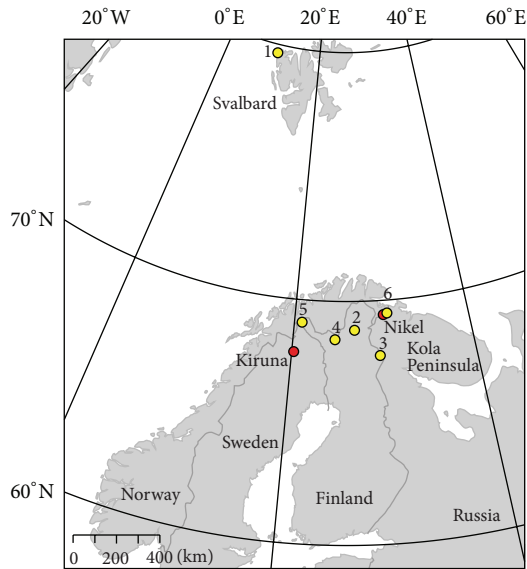


FIGURE 2: Location of lake coring sites and nearby large emission sources, Kiruna (Sweden) and Nickel (Kola Peninsula, Russia). The numbers refer to the study lakes listed in Table 1.

of the deposited material at each site and the likely sources of SCPs. In addition, analysis of transport patterns over time may disentangle whether changes in SCP deposition could have been caused by possible trends in transport.

## 2. Material and Methods

### 2.1. SCP Data

**2.1.1. Study Sites and Sample Collection.** In order to determine the past concentration and deposition of SCPs in the European Arctic, lake sediments were collected from six sites in arctic and subarctic Europe (Figure 2 and Table 1). The four lakes in Finland and one on Svalbard were chosen because they are remote from sources and have no direct human impact and therefore their SCP records are not dominated by local sources. By contrast, the lake on the Kola Peninsula was selected in order to provide a site near major emission sources in the Arctic. This lake is situated ~20 km northeast of Nickel, a small town supporting a large nickel, palladium, and copper mine and smelter. In addition to Nickel, only an iron mine in Kiruna, Sweden, presents a possibly significant emission source for SCPs in the region.

In general the lakes are small and have simple bathymetries. The sediments were collected from the deepest part of the sediment accumulation area. The uppermost 10–20 cm of sediment representing ca. the last two centuries were collected with an HTH gravity corer [34] or a Glew corer [35]. The sediments from three sites in Finland were retrieved in 2009 and 2010 (Kuutsjärvi, Puoltsajärvi, and Karipääjärvi), whereas the other sediments were collected in 1992 (Stapanovichjarvi), 1993 (Arresjøen), and 1995 (Saanajärvi). The sediments were subsampled at high-resolution intervals: 0.2 cm for Saanajärvi; 0.25 for the other

Finnish lakes, and Arresjøen and 0.5 cm for Stepanovichjarvi, and stored in plastic bags. The sediments were freeze-dried prior to analysis.

**2.1.2. Radiometric Dating.** Sediment cores were dated radiometrically. Lead-210 (half-life 22.3 years) is a naturally produced radionuclide, derived from atmospheric fallout (termed unsupported  $^{210}\text{Pb}$ ). Cesium-137 (half-life 30 years) and  $^{241}\text{Am}$  are artificially produced radionuclides, introduced to the study areas by atmospheric fallout from nuclear weapons testing and nuclear reactor accidents. Dried sediment samples were analysed for  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ ,  $^{137}\text{Cs}$ , and  $^{241}\text{Am}$  by direct gamma assay using ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detectors. Lead-210 was determined via its gamma emissions at 46.5 keV, and  $^{226}\text{Ra}$  by the 295 keV, and 352 keV gamma rays emitted by its daughter isotope  $^{214}\text{Pb}$  following three weeks storage in sealed containers to allow radioactive equilibration. Cesium-137 and  $^{241}\text{Am}$  were measured by their emissions at 662 keV and 59.5 keV, respectively [36]. The absolute efficiencies of the detector were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self-absorption of low energy gamma rays within the sample [37]. This method allows sediment chronologies to be produced for the most recent ca. 150 years. The sediment of Saanajärvi, Kuutsjärvi, Karipääjärvi, and Arresjøen was analysed in the Liverpool University Environmental Radioactivity Laboratory and the sediment of Puoltsajärvi in the Environmental Radiometric Facility at University College London. The sediment of Stepanovichjarvi on the Kola Peninsula was not dated.

**2.1.3. SCP Analysis.** SCPs were extracted following the method developed by Rose [38]. The sediments were subjected to sequential chemical attack using  $\text{HNO}_3$ , HF, and HCl to remove organic material, silicates, and carbonates, respectively. 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. The detection limit of the method is 50–80 SCPs per gram dry mass ( $\text{g DM}^{-1}$ ) with a mean recovery of 95.2% [38]. Identification criteria for SCP counting are described in Rose [39].

The concentrations of SCPs in the sediment were calculated as “number of particles per gram dry mass of sediment” ( $\text{g DM}^{-1}$ ). The flux of SCPs to the sediment was calculated as “number of SCPs per square metre per year” ( $\text{SCP m}^{-2} \text{yr}^{-1}$ ) for all lakes that were dated and the sediment accumulation rate known. The weight of a medium sized ( $20 \mu\text{m}$ ) SCP has been estimated to be  $1.96 \times 10^{-9} \text{g}$  [21]. This estimation was used to calculate the flux of the SCPs as “gram per square metre per year” ( $\text{g m}^{-2} \text{yr}^{-1}$ ).

### 2.2. Modeling Experiments

**2.2.1. The OsloCTM2.** OsloCTM2 is a global off-line 3-dimensional chemistry transport model with transport

TABLE I: Details on the study lakes.

Number (in Figure 2)	1	2	3	4	5	6
Lake	Arresjøen	Karipääjärvi	Kuutsjärvi	Puoltsajärvi	Saanajärvi	Stepanovichjarvi
Location	79°40'N, 10°45'E	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°28'N, 30°40'E
Altitude (m a.s.l.)	15	265	341	355	679	200
Size (ha)	34	32	0.67	17	70	Unknown
Maximum depth (m)	31	6.7	8.6	7	24	14
Coring year	1993	2010	2009	2010	1995	1992

driven by meteorological data generated by the Integrated Forecast System (IFS) model at the European Center for Medium Range Weather Forecast (ECMWF). The horizontal resolution is  $2.8^\circ \times 2.8^\circ$  and there are 60 vertical layers from the surface to 0.1 hPa. The advection of tracers in the model is calculated by the second order moment method [40]. Vertical mixing is based on Tiedtke [41] and the turbulent mixing in the boundary layer is treated following the Holtslag K-profile scheme [42].

Time-slice simulations for 1850 and for every 10th year from 1900 to 2010 are performed using meteorological data for 2006. For the purpose of our study we focused only on BC in the model runs. Historical anthropogenic and biomass burning emissions are from Lamarque et al. [23], while anthropogenic emissions for 2010 are from the Representative Concentration Pathway 4.5 [43]. These emissions are consistent with the historical inventory by Lamarque et al. [23]. Biomass burning emissions for 2000 are used for 2010. SCPs have limited emission sources and for the best possible comparison of modelled BC and measured SCP, we perform additional simulations where all BC emissions other than those from energy and industrial sectors are switched off.

The carbonaceous aerosols are parameterized using a bulk scheme based on Cooke et al. [44]. BC particles are assumed to be 20% hydrophilic and 80% hydrophobic upon emission. Conversion from hydrophobic to hydrophilic mode, where particles are assumed to be hygroscopic and available for wet removal, is given by constant aging times depending on latitude and season [22]. This aerosol aging scheme is based on results using the full tropospheric chemistry version of the OsloCTM2 with the microphysical aerosol module M7 [32] and is an improvement on the traditional approach of using one constant exponential lifetime to represent aging. The M7 [45] allows for a more realistic representation of aerosols than the bulk scheme by including size distribution and mixing state and allowing for aging and growth by particle interaction. BC aerosols are aged through coating by condensation and coagulation of sulfate and aging thus varies seasonally and regionally depending on the availability of sulfate. Using M7 leads to significant differences in BC distribution and lifetime [32] compared to the bulk scheme. However, simulations with the M7 in the OsloCTM2 are very demanding in terms of computing resources and do not allow separation of energy/industry BC from the total and are hence not used in this study.

Particles are removed by dry deposition and large-scale and convective precipitation. The dry deposition velocity for hydrophilic particles is  $0.025 \text{ cm s}^{-1}$  over land and  $0.2 \text{ cm s}^{-1}$  over ocean [44]. For hydrophobic aerosols a velocity of  $0.025 \text{ cm s}^{-1}$  is applied over all surfaces. Hydrophilic aerosols are removed according to the fraction of liquid plus ice water content of a cloud that is removed by precipitation. Aerosols are assumed to be 100% absorbed in cloud droplets for convective precipitation. For large-scale precipitation, 100% scavenging is assumed for liquid clouds and 12% for ice clouds [22].

*2.2.2. Back Trajectories.* To further explore the major source areas for SCPs and potential changes in the dominant transport patterns over the past decades, we calculated back trajectories of air masses to the study sites. Back trajectories were used to investigate air mass histories at all study sites, except Stepanovichjarvi, for which there is no information on depositional fluxes of SCP. The back trajectories were made with FLEXPART [46], a Lagrangian Particle Dispersion Model (LPDM). Trajectories tracing the air were run from each of the study sites. The model computes trajectories of particles in the atmosphere following the mean flow and random motion in order to take turbulence into account. Turbulence is parameterized as Gaussian and solved using the Langevin equations [47]. The model has been applied and validated in a wide range of aerosol studies on several scales, including volcanic ash [48], power plant plumes [49], and arctic transport [50].

For the period from January 2000, the model was driven by operational reanalysis of wind fields from ECMWF, with analyses at 00, 06, 12, and 18 UTC and three-hour intermediate forecasts. The horizontal resolution of the fields used was  $1^\circ$  by  $1^\circ$  with 91 vertical levels [51]. For the period 1983–2000, ECMWF ERA-40 reanalysis [52] data with the same horizontal and temporal resolution and 61 vertical levels were used to drive the model.

At each study site 25,000 trajectories were started in the boundary layer each day in the period 1983–2007, each trajectory running back in time for seven days. The years 1990 and 1999 missed input data from wind fields and are therefore excluded from the analysis. The model has daily output with a spatial resolution of  $1^\circ$  by  $1^\circ$  and is a count of the time spent in each grid cell by the tracer trajectories. This provides sufficient statistics on movements of the air

masses before reaching the study sites, thereby providing a 25-year record of transport to each site. The trajectories were run as air tracers and thus no atmospheric loss processes were taken into account, since such specific information is not available for SCPs. The wide spread in sizes for the SCPs makes different loss processes important. For the larger SCPs ( $r_d = 10\text{--}50\ \mu\text{m}$ ) gravitational settling is increasingly important with size and weight, while for smaller particles wet/dry deposition dominates.

Using air tracing trajectories will not provide information when, in the air mass history, emissions of SCP are significant. Losses during transport will deplete a source's importance relative to an air tracer with increasing transport time. Also, for SCPs that are relatively large particles, gravitation is influential and the path of a SCP in the atmosphere may deviate from that of an air tracer. Consequently, the air tracers will not give direct information on SCP sources but are rather a measure of where the air has been and thus where potential sources of SCPs may be located.

### 3. Results and Discussion

*3.1. The SCP Record in Lake Sediments.* SCP accumulation data has been previously published for Saanajärvi [53], Arresjøen, and Stepanovichjärvi [30], whereas the results for Kuutsjärvi, Karipääjärvi, and Puoltsajärvi are presented here for the first time (Figure 3). The older sediment records are used in this study for comparative purposes. The radiometric dating of the sediments provides chronologies with typical uncertainties of  $\pm 0\text{--}5$  years in recent decades, but uncertainties increase in older sediments reaching  $\pm 20$  years in the 19th century.

The SCP concentration profiles in the study lakes are generally in good agreement with previous trends across Europe (e.g., [54]). The first signs of SCP deposition in this study were recorded in Saanajärvi, Finland, in the 1870s, but not until the 1910s in the other Finnish lakes. These differences might be caused by analytical detection limits at low SCP concentrations and possible dating errors. On Svalbard SCP concentrations only exceeded the detection limit for the first time in the 1960s. With the exception of Saanajärvi the SCP concentrations initially increased quite moderately and more rapidly after the 1950s in common with many other European lakes. This trend is explained by a post-war expansion in the power generation industry in Europe and by the widespread usage of fuel-oil in power stations for the first time [54]. Coincidentally the smelter at Nikel also started operation in 1946 [55], suggesting that the earlier SCPs recorded in the study lakes may originate from either smaller scale regional activity or long-range transport. Peak values in SCP concentrations in all the dated sediment profiles were reached around the 1980s. Maximum concentrations for the Finnish lakes are 1400–3000 particles  $\text{g DM}^{-1}$ , and a little less for Arresjøen on Svalbard (ca. 1200 SCP  $\text{g (DM}^{-1})$ ). These concentrations are consistent with results from comparable sites, for example, Wik and Renberg [11] typically found concentrations of 100–2000 SCP  $\text{g (DM}^{-1})$  in northern Sweden in surface sediments in the late 1980s and Rose et al. [13] found

concentrations of 200–1000 SCP  $\text{g (DM}^{-1})$  in numerous surface sediments collected in Svalbard in 1995. In our study lakes SCP concentrations decreased from peak values, such that concentrations in 2010 were similar to those in the early 1950s. The peak in the 1980s and subsequent decrease of SCP concentration is most likely explained by clean air legislation and improved particle arrestor technology. In the Finnish lakes the start of the decrease of SCP concentrations seems to also coincide with the fall of the USSR in 1991.

Stepanovichjarvi on the Kola Peninsula shows significantly higher concentrations (up to 12000 SCP  $\text{g DM}^{-1}$ ). The overall shape of the SCP concentrations is similar to the other lakes. It is thus likely that the peak values of SCP concentrations were also reached in the 1980s. The prevailing wind patterns arrive at Stepanovichjarvi from the south west so it is situated downwind from the smelter in Nikel and received high contamination deposition. The high SCP concentrations for this region are supported by concentrations of  $>8000$  SCP  $\text{g DM}^{-1}$  in 1980 found in a northeastern Finnish lake ca. 40 km west of the Nikel smelter area [56].

SCP concentrations in lake sediments cannot be converted to concentrations for the atmosphere over the study area, since they are always influenced by sedimentary processes. However, converting SCP sediment concentrations to depositional fluxes facilitates a better comparison with modelled BC deposition.

*3.2. SCP Deposition and Comparison with Modelled BC Deposition.* Figure 4(a) shows the depositional fluxes of SCPs to the lakes and takes into account changes in the sediment accumulation rate. The sediment accumulation rates vary according to the input of both allochthonous organic and inorganic material and autochthonous biogenic material. SCP deposition is also shown on a decadal basis (Figure 4(b)) to provide similar results to the modelled time slices.

In general trends in SCP depositional fluxes differ from observed sediment concentrations due to higher sediment accumulation rates in some lakes. This is evident when comparing the SCP concentration (Figure 3) and flux profiles (Figure 4(a)) of Saanajärvi and Kuutsjärvi, respectively. In Saanajärvi (Figure 4(a)) conversion to depositional fluxes emphasises the 1980s peak with respect to concentration data (Figure 3). By contrast, in Kuutsjärvi SCP flux is higher in the late 1980s and 1990s (Figure 4(a)). In the other lakes trends in concentrations seem to show good agreement with flux rates which is explained by relatively constant sediment accumulation rates.

Although the SCP concentrations (Figure 3) were quite similar in the Finnish lakes some of the depositional flux values differ quite dramatically. In Karipääjärvi and Puoltsajärvi SCP fluxes were low and reached only ca.  $0.15\ \text{mg m}^{-2}\ \text{yr}^{-1}$ , whereas in Kuutsjärvi it was more than twice as high and in Saanajärvi almost an order of magnitude higher ( $0.9\ \text{mg m}^{-2}\ \text{yr}^{-1}$ ) (Figure 4(a)). In Arresjøen, on Svalbard, the SCP depositional flux was the lowest which is expected due to its remoteness. However despite these differences in scale of contaminant inputs to the lake sediments, temporal patterns are similar.

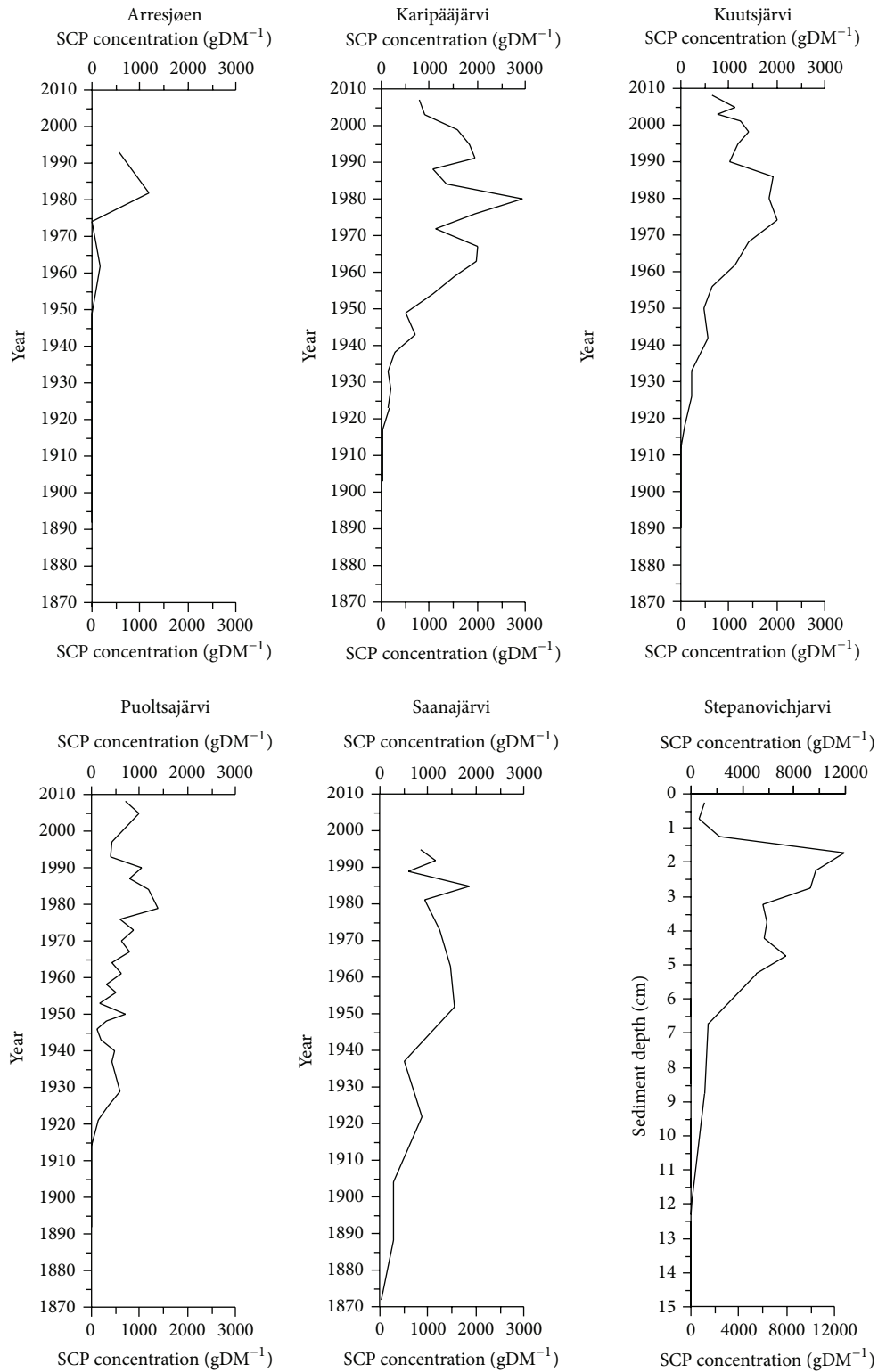


FIGURE 3: SCP concentration profiles for dated sediments taken from Arresjøen, Svalbard, Kuutsjärvi, Karipääjärvi, Puoltsajärvi, and Saanajärvi from Finland and Stepanovichjarvi on the Kola Peninsula. Note that the Stepanovichjarvi profile is given on a sediment depth axis since the core is not dated and that it has a larger scale on the  $x$ -axis than the other lakes.

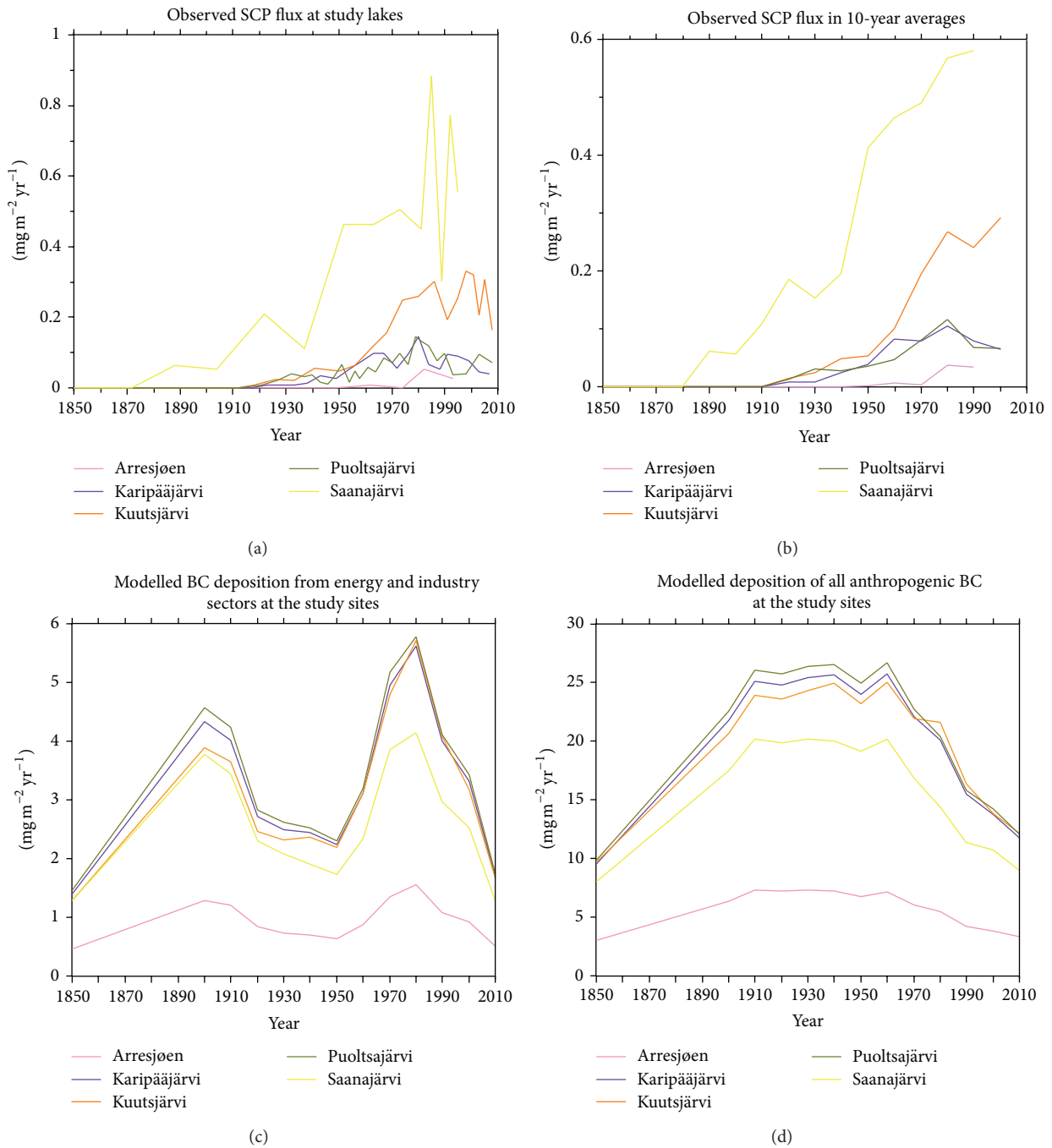


FIGURE 4: Observed depositional fluxes of SCP and modelled BC deposition at the study sites from 1850 to 2010. Results are given in milligrams per square meter per year ( $\text{mg m}^{-2} \text{yr}^{-1}$ ). (a) SCP depositional flux for the five dated study lakes, (b) SCP depositional flux for the lakes in 10-year averages, (c) modelled time slice simulations of BC deposition from the industry and energy sectors at the study lakes, and (d) modelled time slice simulations of all anthropogenic BC deposition at the study lakes. The model results for 1850 to 1900 are linear interpolations. The SCP deposition results are also linear interpolations between dated observations. Note that the y-axes are not the same in all panels.

As with the concentration data, all lakes show a peak in SCP flux around 1980 and this peak is also clearly apparent in the 10-year averages (Figure 4(b)). Kuutsjärvi and Saanajärvi are an exception from the other lakes as they show no decline after 1980. This is apparently due to differences in coring date and the fact that in most cases the last available deposition

observation in the records falls outside the last full 10-year period used for averaging and thus the most recent trend is not seen in Figure 4(b).

Figure 4 also shows the modelled deposition of BC at each of the lakes. In Figure 4(c) the results are shown for BC deposition resulting from the industrial and energy sectors

whereas in Figure 4(d) deposition from all anthropogenic sources is shown. Model values are interpolated between the four grid boxes closest to each of the study lakes. Values of BC deposition resulting from the industrial and energy sectors (Figure 4(c)) are mostly of the order of 2 to 5 mg m<sup>-2</sup> yr<sup>-1</sup> for the four lakes in northern Finland. The model resolution is quite coarse (approx. 100 km × 100 km in the horizontal) and since the lakes are relatively close together the model is not capable of capturing significant variability between them. At Arresjøen, which is more remote, model values are around 0.50–1.5 mg m<sup>-2</sup> yr<sup>-1</sup> (Figure 4(c)).

Deposition rates for BC from industrial and energy sectors are much higher than the measured SCP depositional fluxes. SCPs make up only part of the emissions from energy and industry, while modelled BC is more representative of elemental carbon (EC). Comparing the magnitude of deposition is therefore not possible without an estimate of the fraction of SCPs in BC emissions. To the best of our knowledge, Muri et al. [57] is the only study to include both SCP and soot BC deposition in the same lakes. The soot BC was measured with the chemothermal oxidation method [58, 59], which probably represents EC measured in atmospheric studies quite well. Based on these results and assuming a mass of  $1.96 \times 10^{-9}$  g for a medium (20 μm) sized SCP, it can be estimated that SCPs make up 0.01–2.66% of total BC in these studied sediments. However, this value is highly variable in time and space and is based on only one study. Our study indicates that SCPs might represent approximately ≤5% of the modelled BC from the industrial and energy sectors and therefore, despite some assumptions, modelled and measured deposition would appear to agree quite well at several sites. Saanajärvi has a much higher measured depositional flux value than the other Finnish lakes, which may be explained by different transportation routes (see below).

Due to this limited knowledge about the fraction of SCP of total BC, we focus more on the temporal evolution in deposition rates than on their magnitudes. The general trends (Figures 4(a), 4(b) and 4(c)) seem to agree reasonably well. The measured peak in SCP deposition in 1980 (Figures 4(a) and 4(b)) is captured very well in the modelled time series of BC deposition (Figure 4(c)). After 1980, modelled deposition of BC from industrial and energy sectors declines significantly, to 1850 levels. Sediment data also show a decrease in this period but less significantly than the modelled data. The rapid increase leading up to the 1980 peak starts in 1950 in the model, which also agrees well with the SCP measurements. However, in the first part of the 20th century, modelled deposition of industrial and energy combustion derived BC reveals a local maximum around 1900 followed by a decrease until 1940 (Figure 4(c)). The increase from 1850 to the local maximum in 1900 is not seen in any of the lake sediments although they are analysed for SCP back to ca. 1850. This could suggest that the estimated energy and industrial emissions might be too high in the late 19th and early 20th centuries and uncertainties in regional BC emissions may be expected to be as large as a factor of two [23, 60, 61]. Furthermore, differences may arise due to the spatial distribution of emissions or

the transport from emission source to the study lakes in the model. However, the most plausible explanation for the divergence is that the BC peak in 1900 depicted by the model represents other forms of BC than SCP as combustion in the energy and industrial sector in the early 20th century did not always reach the temperatures required for SCP formation. This inference is supported by measurements of high refractory soot BC and pyrolysis-derived contaminant polycyclic aromatic hydrocarbons (PAH) in a lake sediment core from southern Sweden, ca. 1100 km southwest from the study area [62]. The 700-year record shows maximum soot BC and rapidly increasing PAH fluxes to the sediment in 1922–1928 in an area that might at least in part have same source areas for smaller, long-range transported particles as our Finnish study sites (see also Figure 6).

BC deposition from all anthropogenic emissions is shown in Figure 4(d). Both trends and magnitudes (values between 10 and 25 mg m<sup>-2</sup> yr<sup>-1</sup>, but lower for Arresjøen) are completely different than for the SCP and modelled industrial and energy sector derived BC deposition. This is probably mainly due to domestic combustion dominating the development of anthropogenic BC emissions, that is, much of the difference between total anthropogenic BC emissions and the industrial and energy sector seen in Figure 5(a) represents the domestic sector. The BC deposition for all anthropogenic BC (Figure 4(d)) seems to have increased at the study sites until 1900, stayed quite constant until 1960, and declined subsequently reaching almost preindustrial levels at present. This trend clearly illustrates the importance of choosing appropriate BC components when validating comparative studies between observed and modelled results.

As explained earlier, the changes in modelled deposition are governed by changes in emissions since we use constant meteorology in the model simulations. Figure 5(a) shows the time series of global annual BC emissions in the model from 1850 to 2010 for the energy and industrial sectors. For comparison we also show the total anthropogenic BC emissions. There is a continuous increase in emissions after 1950. However, the modelled deposition shows a significant decline in deposition at the measurement sites after 1980, despite the increase in emissions. This is explained by the geographical shift in major emission source regions. Figure 5(b) shows zonal mean distribution of energy and industrial emissions for selected years. There has been a significant southward shift in maximum emissions from 50–60°N towards 30°N during the industrial era. While emissions in Europe and North America have declined in the last decades of the 20th century, they have increased strongly in developing countries like China and India, although emissions from these regions are expected to have contributed little to the BC deposition in Finland and Svalbard [32, 63].

Modelled surface concentrations of BC at the study sites are shown in Figure 5(c) and exhibit the same trend as deposition. Concentrations range from 5 to 25 ng m<sup>-3</sup> during 1850–2010 at the Finnish lakes and 1–4 ng m<sup>-3</sup> at Arresjøen. Comparison of present-day surface concentrations of BC from the OsloCTM2 with observed data shows a reasonable agreement at Pallas (northern Finland, close to



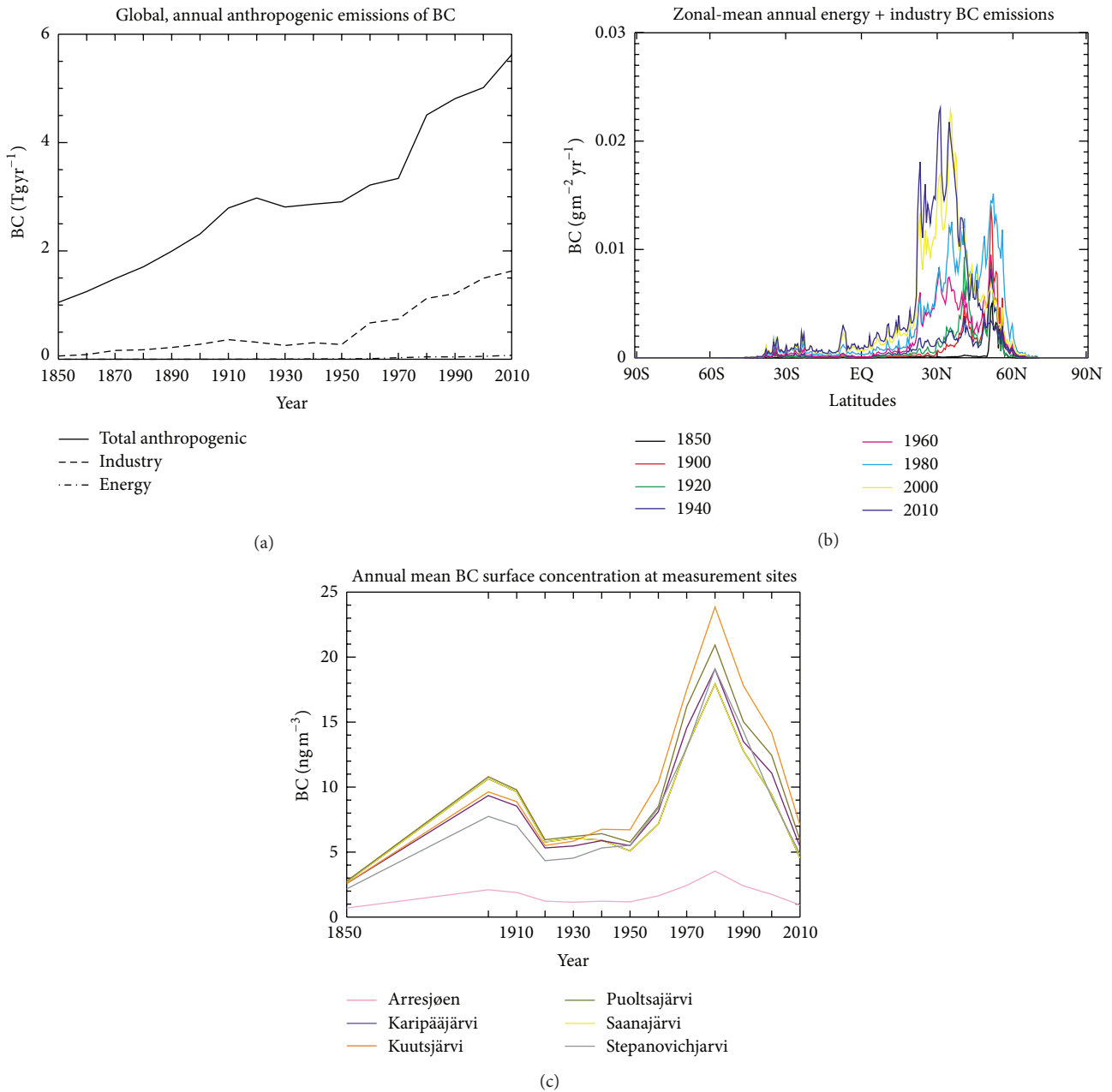


FIGURE 5: (a) Time series of annual energy and industrial emissions of BC used as input to the OsloCTM2. Also shown for comparison is the total anthropogenic emissions. (b) Zonal-mean annual BC emissions from the energy plus industrial sectors for selected years. (c) Time series of annual-mean surface concentration of BC from energy and industrial emissions at the six lakes.

Puoltsajärvi) and an underestimation at Zeppelin (Svalbard, close to Arresjøen), particularly during spring [22, 24, 32]. At Stepanovichjärvi, SCP deposition fluxes are not available because the sediment core was not dated. While the SCP concentrations at this site show much larger values than at the other sites, the model does not capture this. This might be due to the resolution of the model, but it is also probable that emissions from point sources such as the Nikel smelter, which is a likely source of pollution for the site, are underestimated or not captured in the model.

3.3. *Back Trajectories.* Figure 6 shows the direction and distance for which air, as a percentage, has spent time less than 100 m above the surface for 1983–2007. Only air below 100 m above the surface is considered because SCP and BC particles are produced only in this layer of air. The direction from each study lake to a grid cell centre was calculated using the Haversine formula and the distance is the great circle distance in kilometres. The area spanned by each segment in Figure 6 is thus the relative frequency that air has spent close to the surface in the direction of the segment. The colour scale

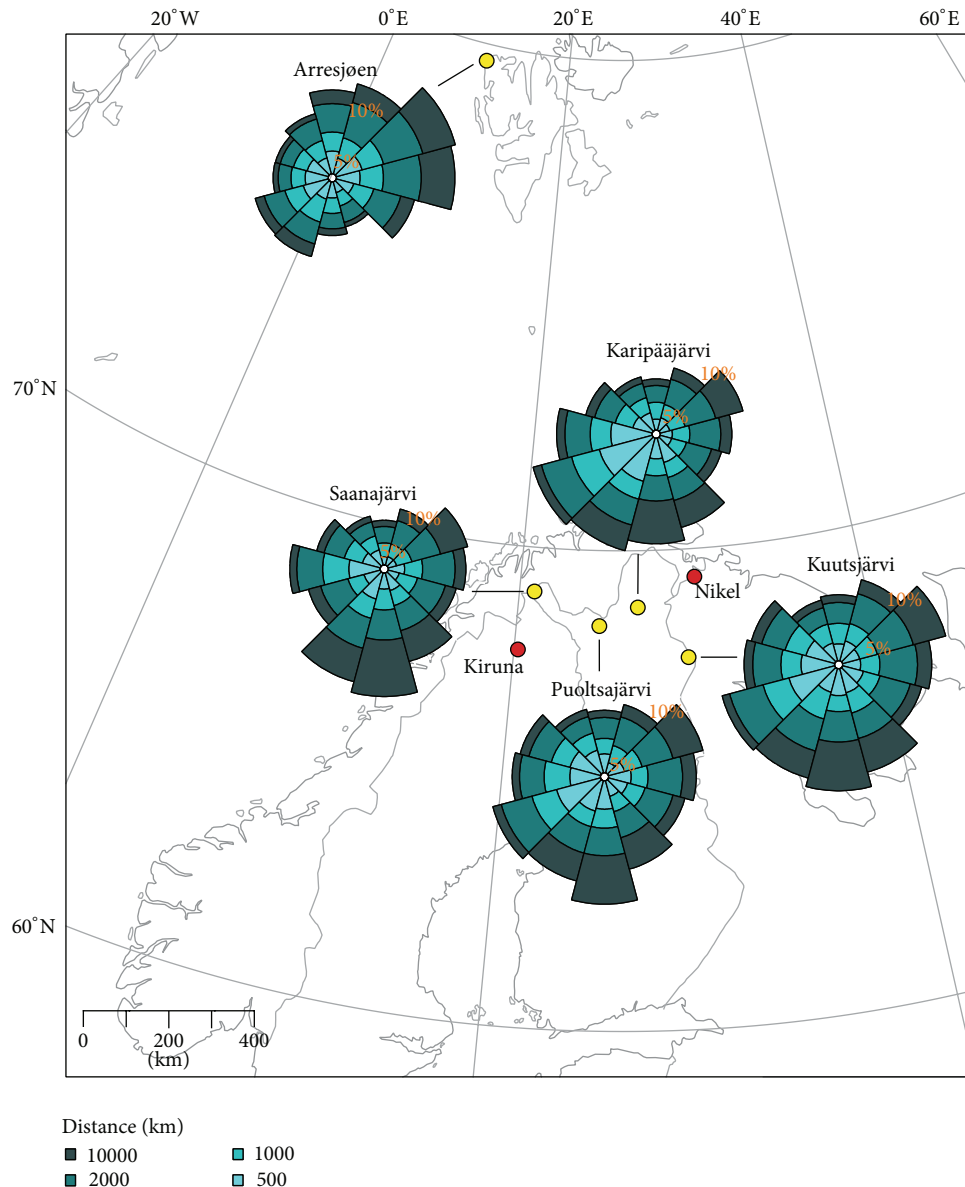


FIGURE 6: Frequency of direction and distance of trajectories for each of the study sites. Each segment size shows the frequency of air coming from the compass direction towards which it points. A light colouring indicates short distance (km) from the study site, whereas dark colours show a long travel distance. The yellow dots indicate the study lakes and the red dots the coal mine in Kiruna, Sweden, and the smelter in Nickel on the Kola Peninsula, Russia. The plotted data is based on the frequency of trajectories spending time near the surface within 7 days of arriving at the lakes in the interval 1983–2007.

of the segments reflects the distance the air has travelled over the previous seven days.

Karipääjärvi, Kuutsjärvi, and Puoltsajärvi seem to have quite similar transport patterns. Most air is transported from the south and east and from similar distances to the lakes. Saanajärvi on the other hand, while being geographically close to the other Finnish sites, has a somewhat different transport pattern. More of the air masses reaching it come from further away and more from the south and southwest compared to the other lakes in Finland. Arresjøen on Svalbard also has a diverging transport pattern. Much more of the

transport is coming from longer distances than to the other sites and mainly either from the southeast or northwest. This division between the lakes on the mainland and on Svalbard is probably due to the seasonal cycle of air circulation patterns and whether the lake is inside the polar dome or not.

The interannual or decadal variability of the source regions for the lakes can be calculated by subtracting a year/decade to that of another, and the absolute residual is then the variability in source regions for each lake coring site. The variability for all lakes is less than 10%, with Arresjøen displaying a somewhat larger variability than the other sites.

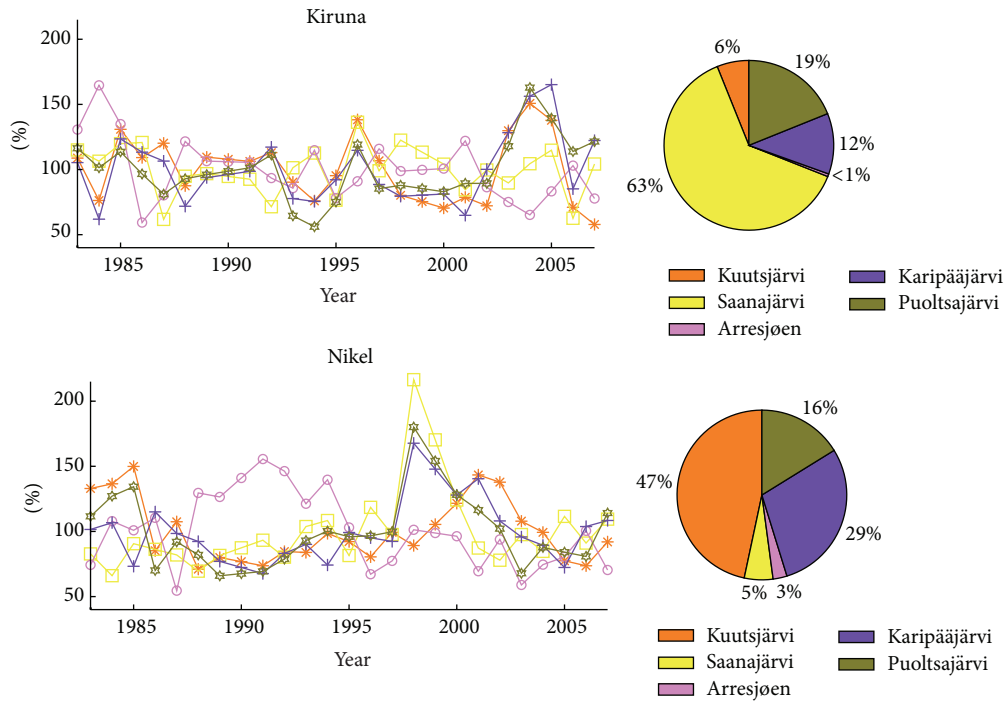


FIGURE 7: Left panel: time series of how transport to the coring sites changes over time from Kiruna (top) and Nickel (bottom). 100% is the 25-year average and years with higher % are years where there is more transport from Nickel/Kiruna to the lakes than on average. The years 1990 and 1999 have been linearly interpolated between neighbouring years. Right panel: pie charts showing the amount of transport from Kiruna (top) and Nickel (bottom) to the study lakes.

There has been no discernible trend pointing towards a change in transport to any of the study lakes during the period between 1983 and 2007.

Figure 7 relates the transport patterns of the five lakes to two expected significant emission sites in the region, Nickel and Kiruna. While the overall change in transport from year to year is small for all study sites, there is much stronger variability when looking at transport to the lakes from Nickel and Kiruna. As can be seen in Figure 7 (left panel), the transport to the lakes from Nickel and Kiruna vary annually by more than  $\pm 50\%$ . There are no significant signs of transport patterns changing over yearly or decadal time scales, from either Nickel or Kiruna. However, in terms of transport frequency, Kiruna is a more significant source area for the studied lakes since the total annual average time air masses spend before arriving at any study site is  $\sim 52000$  seconds above Kiruna compared to  $\sim 32000$  seconds above Nickel.

According to our results, the study lakes situated quite close to each other on the European mainland receive atmospheric transportation from relatively different sources. Figure 7 (right panel) compares the transport from Nickel and Kiruna to the study lakes. According to these results, Saanajärvi receives only about a third of the transport from Nickel compared to the other lakes on the mainland (Karipääjärvi, Kuutsjärvi, and Puoltsajärvi). Therefore, a more likely source for SCPs at Saanajärvi is the large iron mine in Kiruna, from where emissions are frequently transported towards Saanajärvi.

While the average transport patterns to Karipääjärvi, Kuutsjärvi, and Puoltsajärvi look quite similar (Figure 6), the lakes differ in both the direction and distance to strong sources. The distance seems to be the dominant factor determining air mass transport between Nickel and Kiruna and the study lakes. Arresjøen is located far from the polluting sources and receives very little transport from Northern Europe and transport from both Kiruna and Nickel is infrequent compared to the other lakes. Therefore, it seems that SCP deposition in Arresjøen could result from small local sources such as the power stations in Isfjorden as suggested in Rose et al. [13] while long-range transport from other sources in both Eurasia and North America is possibly contributing as well. For the remaining lakes both Nickel and Kiruna are probably the dominant sources since there is no other large scale fossil fuel based industrial activity in the area. Transport from Nickel has the strongest impact on SCP deposition in Kuutsjärvi and Karipääjärvi whereas Kiruna has the strongest impact on Saanajärvi.

Consequently it seems that variations in the magnitude of SCP deposition to the lakes (Figures 4(a) and 4(b)) can be mostly explained by Kuutsjärvi and especially Saanajärvi receiving greater amounts of polluted air masses from nearby large emission sources than the other study lakes. These lakes have two common features: they are located close to the pollution sources and are heavily impacted by prevailing winds coming from the direction of those sources. These are evident causes for the observed high deposition (Figures 4(a)

and 4(b)). The strong impact of Kiruna might also explain the earlier start of the SCP record in Saanajärvi than in the other study lakes (Figures 3, 4(a) and 4(b)) since mining started there in the 1870s. This analysis emphasises that even on a relatively small geographical scale, prevailing wind directions can be quite different and affect SCP and therefore also BC deposition to individual sites substantially.

*3.4. The Feasibility of Using SCPs and Lake Sediments in the Evaluation of BC Model Results.* Comparisons of observational measurements of BC with modelled results should be performed carefully since numerous methods to quantify BC and therefore BC definitions exist. Furthermore, studies investigating past concentrations, approximating to the complete BC spectrum from sedimentary records, are not yet available in large numbers, especially in the Arctic. Therefore, in order to get sufficient records, ice core data should additionally be used where available. With regard to comparisons with models, promising methods used for BC quantification from environmental records are variations of the thermal/optical methods which have been applied for soils and sediments by Han et al. [64, 65] and Husain et al. [66]. These Thermal Optical Transmittance/Reflectance (TOT and TOR) methods quantify EC in sediments and soils after chemical extraction and use the same instrument that measures EC from atmospheric samples. The application of this approach by Husain et al. [66] has shown consistency in EC measured from lake sediments and the atmosphere at the same site between 1978 and 2005. However, the application is very elaborate and time consuming and entails numerous known error sources [66]. Another promising method is the chemothermal oxidation method developed for soot BC quantification in sediments [58, 59] which can also be applied to atmospheric samples [67]. Unfortunately it is not known exactly how representative the soot BC concentrations retrieved with this method are of BC used in models, and this complicates any comparison. The emission factors used in the inventories of anthropogenic BC emissions represent a more EC-like carbonaceous compound than BC [68]. Several laboratory studies have shown EC and BC concentrations to differ significantly, up to a factor 7 between different methods (see [68] and references therein).

Our study, however, indicates the possibility of comparing historical observational data of a widely studied and clearly defined BC fraction, SCPs, with modelled BC trends albeit with the caveat that SCPs are only derived from industrial fossil-fuel combustion. Therefore, they cannot be used for comparison beyond the industrial era and neither for biomass burning reconstruction. However, reasonable comparisons are facilitated by the knowledge of the exact emission sources of SCP and emissions from these sectors can be selected for model runs. Since SCPs represent a well-defined fraction of BC, they could potentially be a useful tool for model evaluation. Currently, however, assessments of models based on SCP data alone are restricted as information on SCP source strength and the fraction of total BC represented by SCPs is unknown. Ideally, BC records from lake sediments would, in future consist of soot

BC or EC measurements (e.g., [64–66]), since these best represent EC measured in the atmosphere. However, until these measurements are readily available, SCP records may represent a useful tool for the validation and improvement of models. There are numerous SCP records available all around Europe and in some areas (e.g., UK) these exist in high numbers and distribution densities.

According to the recent specific definition of refractory black carbon in the atmosphere by Bond et al. [29], SCPs do not represent BC, since they are not an aggregate of small carbon spherules. Nonetheless, other properties (strong visible light absorption, refractoriness, and insolubility in water) are similar, although the exact mass absorption cross-section of SCPs is currently unknown. BC particles found in sediments are those that have been deposited from the atmosphere. Therefore, in order to facilitate BC model validation or to find natural background levels of contamination, it is crucial that a general definition of BC should also include particles readily studied in natural archives, such as SCPs.

## 4. Conclusions

In general we found a good agreement between the temporal records of SCP in lake sediments and modelled industrial and energy sector derived BC deposition. Discrepancies in the results are most likely explained by SCPs not representing all BC formed by these sectors but only a relatively small fraction. This explains the differences in magnitude as well as the model capturing a possible BC concentration and deposition peak in the early decades of the 20th century that is not observed in sedimentary SCP data.

Despite generally good agreement between SCP concentration and flux trends between lakes, some differences in the magnitude of depositional fluxes are evident. In general trends in deposition follow trends in emissions, as implied by the OsloCTM2-model. According to back trajectories of air masses it seems that trends in SCP deposition to the study sites are not caused by changes in general air mass transportation patterns, at least not during the last 25 years. On the contrary, differences in observed magnitudes of SCP deposition seem to be caused by differing quantities of polluted air masses being transported to the sites from nearby emission sources.

Our study also points to the fact that models might easily miss quite significant regional variation in BC concentrations and deposition both due to the coarse resolution of the model and possibly underestimation of local emission sources. The modelled trends are a manifestation of changes in emission strengths and geographical patterns. On a smaller geographical scale, however, the lack of detailed information on air mass transport patterns in the model becomes apparent. For example, the model cannot predict the higher SCP concentrations observed in a lake (Stepanovichjarvi) close to a known large emission source and it fails to capture the higher SCP deposition values in lakes receiving air masses from more polluted areas (Saanajärvi and Kuutsjärvi).

Our results underline the fact that significant variation in BC deposition can be recorded within a small geographical

area. The concentrations, deposition, and trends of BC may vary at a specific site for many reasons. These include factors that are captured by the OsloCTM2 model, local conditions that affect the sediment records ability to capture atmospheric deposition that the model cannot account for, and variation in transport patterns of air masses to the study sites. Therefore, numerous observational records are required to credibly validate and improve models. While ice sheets are extremely valuable as archives of atmospheric pollutant deposition histories, they are only found in restricted regions. Lake sediments can be found almost anywhere around the world and can play an important role in recording deposition history of BC and other pollutants.

Although the emissions of BC, specifically SCP, from industrial sectors have declined in Europe and North America during recent decades, emissions are increasing in Asian countries. Therefore, SCPs must also be considered as a significant component in climate change mitigation strategies in the future.

## Acknowledgments

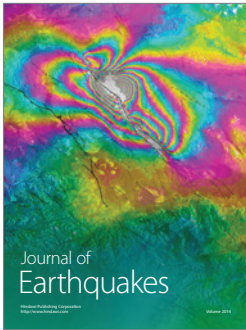
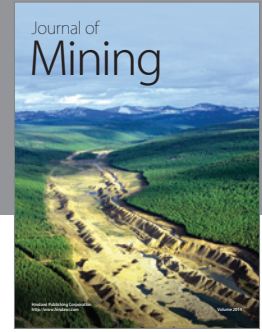
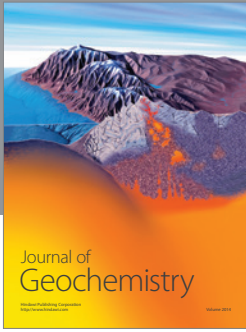
The work was inspired and set in motion by collaboration with the NordForsk Top-Level Research Initiative Nordic Centre of Excellence CRAICC (Cryosphere-atmosphere interactions in a changing Arctic climate). M. Ruppel's work was funded by the Arctic Doctoral Programme ARKTIS of the University of Lapland, by CRAICC and the Academy of Finland Center of Excellence Program (Project 1118615) and by the Academy of Finland Project 257903. M. T. Lund's contribution was supported by the Norwegian Research Council within the project "Climate and Health Impacts of Short-Lived Atmospheric Components (SLAC)". Some of the model results are based on previous work by Ragnhild B. Skeie at CICERO. H. Grythe acknowledges the funding by CRAICC.

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