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# Source identification of individual soot agglomerates in Arctic air by transmission electron microscopy

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ABSTRACT

Individual soot agglomerates collected at four different locations on the Arctic archipelago Svalbard (Norway) were characterised by transmission electron microscopy and energy-dispersive X-ray microanalysis. For source identification of the ambient soot agglomerates, samples from different local sources (coal burning power plants in Longyearbyen and Barentsburg, diesel and oil burning for power generation in Sveagruva and Ny Ålesund, cruise ship) as well as from other sources which may contribute to Arctic soot concentrations (biomass burning, aircraft emissions, diesel engines) were investigated.

Diameter and graphene sheet separation distance of soot primary particles were found to be highly variable within each source and are not suited for source identification. In contrast, concentrations of the minor elements Si, P, K, Ca and Fe showed significant differences which can be used for source attribution. The presence/absence of externally mixed particle groups (fly ashes, tar balls, mercury particles) gives additional hints about the soot sources.

Biomass/wood burning, ship emissions and coal burning in Barentsburg can be excluded as major source for ambient soot at Svalbard. The coal power plant in Longyearbyen is most likely a major source of soot in the settlement of Longyearbyen but does not contribute significantly to soot collected at the Global Atmosphere Watch station Zeppelin Mountain near Ny Ålesund. The most probable soot sources at Svalbard are aircraft emissions and diesel exhaust as well as long range transport of coal burning emissions.

## 1. Introduction

Soot originates from incomplete combustion and is an important constituent of the atmospheric aerosol due to its strong light absorption efficiency (e.g., Horvath, 1993). In the present paper, the term soot is used for fractal-like agglomerates of primary particles consisting of graphene-like layers of carbon (Buseck et al., 2014). When measured by optical techniques, soot is often called black carbon (BC) (e.g., Moosmüller et al., 2009) although the use of the latter term has been criticised as imprecise (Buseck et al., 2014). A review of terminology used for carbonaceous particles is given by Lack et al. (2014). Soot/BC influences the Arctic climate via four different mechanisms (Quinn et al., 2011): (a) direct forcing by absorption of solar radiation, (b) reduction of albedo after deposition on snow, (c) indirect and semi-direct forcing by changing properties of clouds, and (d) radiative forcing outside the Arctic leading to changes in energy transport by the atmosphere and oceans.

It is long known that soot concentrations in Arctic air are highly elevated from late fall to early spring (e.g., Rosen et al., 1981; Heintzenberg, 1982). The highest average equivalent black carbon (EBC) concentrations in late winter/early spring (February–April) are on the order of 80–100 ng/m$^3$, in contrast to summer/autumn (July–October) with values around 5–15 ng/m$^3$ (e.g., Sharma et al., 2006; Eleftheriadis et al., 2009).

General downward trends of annual mean EBC concentrations at the three Arctic monitoring stations Alert (Nunavut, Canada), Barrow (Alaska,USA), and Zeppelin (Svalbard, Norway) were reported by Hirdman et al. (2010a). At Barrow a change of $-2.1 \pm 0.4$ ng/(m$^3$ * yr) (years 1989–2008) was observed, and $-1.4 \pm 0.8$ ng/(m$^3$ * yr) (years 2002–2009) at Alert and Zeppelin, respectively. A somewhat

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smaller value of −0.95 ng/(m$^3$ * yr) (years 2001–2007) at Zeppelin was reported by Eleftheriadis et al. (2009).

Based on trajectory analysis and transport models, the main source region for BC in the Arctic seems to be northern Eurasia (e.g., Polissar et al., 2001; Sharma et al., 2006; Eleftheriadis et al., 2009; Hirdman et al., 2010b; Huang et al., 2010; Wang et al., 2011). In contrast, it was suggested by Koch and Hansen (2005) that the predominant sources of Arctic BC are from south Asia (industrial and biofuel emissions) and from biomass burning.

The contribution of different sources to BC in the Arctic was determined either based on emission inventories (e.g., Quinn et al., 2011; Stohl et al., 2013) or based on chemical tracers measured at the receptor (e.g., Polissar et al., 1998; Hegg et al., 2009; Yttri et al., 2014). In the latter case, results are usually obtained from bulk chemical analysis.

In contrast, a single particle approach for source identification is elaborated in the present contribution. First, it is attempted to identify sources based on properties of individual soot agglomerates including size and nanostructure of primary particles, chemical composition (minor elements) as well as presence of heterogeneous inclusions. Such a single particle approach for source identification of soot was already suggested by Vander Wal et al. (2010) and Palotás (2013) but not applied systematically to ambient aerosols. Second, the presence of additional particle groups externally mixed with soot is used for source discrimination.

We have investigated individual soot agglomerates from local sources on Svalbard (coal burning, diesel and oil aggregates for power generation, ship emissions) as well as sources which can be expected to significantly contribute to Arctic soot concentrations (biomass burning, diesel engines, and aircraft emissions). Soot agglomerates from these sources are compared to ambient soot agglomerates collected at various locations at Svalbard.

## 2. Experimental

### 2.1. Sampling

Particles were collected on Ni or Cu transmission electron microscopy grids covered with Formvar foil (Plano S162 N9 and S147-4, Wetzlar, Germany) using (with one exception) a two-stage micro inertial cascade impactor (Kandler et al., 2007). Particles emitted from an airplane were collected on Cu grids with an ESPnano model 100 (Dash Connector Technology Inc., Spokane, WA, USA) electrostatic precipitator (Miller et al., 2010).

Three different kinds of samples were investigated (Table 1). Ambient samples were collected in the settlements of Longyearbyen and Ny Ålesund (at sea level), at the global atmospheric watch (GAW) station Zeppelin Mountain (474 m asl) near Ny Ålesund as well as during a balloon campaign in Ny Ålesund (950 m asl). Local sources were sampled either directly at the stack (diesel and oil burning aggregates in Ny Ålesund), a few meters away from the stack (diesel aggregate at Sveagruva, coal burning in Barentsburg) or a few hundred meters downwind within the visible emission plume (coal burning in Longyearbyen, ship emissions in Ny Ålesund).

The group of other sources includes emissions from a jet engine airplane (Boeing 737) in idling position (Gardermoen Airport, Oslo, Norway) and from a diesel passenger car (VW Golf). Biomass burning particles were collected with an airplane in the vicinity of the Cape Verde Islands at an altitude of 100 m (22nd Jan. 2008) and 900 m (23rd Jan. 2008) above sea level (for details see Lieke et al., 2011; samples

**Table 1**
Sampling.

| Location/source | Sample code | Date | Local time | Duration (minutes) |
|---|---|---|---|---|
| **Ambient samples** | | | | |
| Longyearbyen settlement | A-LB | 19.03.2010 | 16:14 | 60 |
| | | 22.03.2010 | 12:54 | 30 |
| Ny Ålesund settlement | A-NA | 11.03.2010 | 14:40 | 60 |
| | | | 16:30 | 60 |
| | | | 20:13 | 30 |
| Ny Ålesund balloon | A-NAB | 26.03.2014 | 19:40 | 60 |
| Zeppelin Station, Ny Ålesund | A-ZS | 07.10.2008 | 10:55 | 210 |
| | | 07.11.2008 | 11:20 | 165 |
| | | 22.11.2008 | 08:20 | 160 |
| **Local sources** | | | | |
| Barentsburg downwind power plant | L-BBPP | 27.03.2010 | 13:54 | 34 |
| Longyearbyen downwind power plant | L-LBPP | 22.03.2010 | 10:31 | 60 |
| | | 25.03.2010 | 14:35 | 30 |
| Ny Ålesund downwind cruise ship | L-NACS | 16.07.2007 | 16:05 | 30 |
| Ny Ålesund diesel aggregate | L-NADA | 26.03.2014 | 14:30 | 1 |
| Ny Ålesund oil burning | L-NAOB | 26.03.2014 | 14:30 | 1 |
| Sveagruva diesel aggregate | L-SGDA | 10.03.2014 | 13:45 | 5 |
| | | | 13:55 | 5 |
| **Other sources** | | | | |
| Airplane | O-AP | 09.04.2014 | 06:00 | 5 |
| Biomass burning (airborn sampling) | O-BB | 22.01.2008 | 15:13 | 3 |
| | | 23.01.2008 | 16:52 | 3.5 |
| Diesel car | O-DC | 26.04.2012 | 10:35 | 5 |

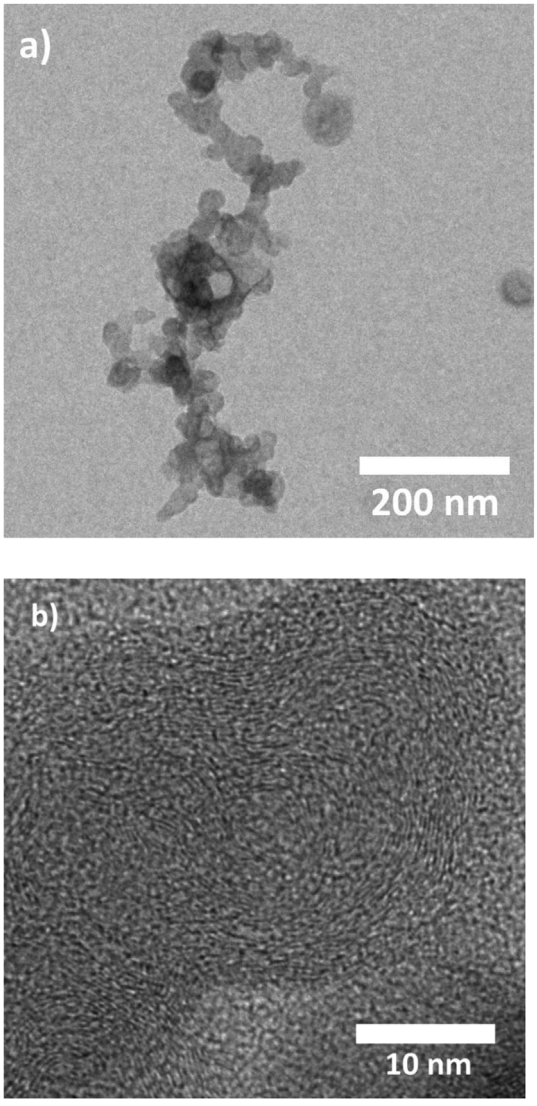


**Fig. 1.** TEM bright field image of a typical soot agglomerate from the coal burning power plant in Barentsburg (a), and high-resolution TEM image showing the typical onion-shell nanostructure (b).