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Supplement of

Refractory black carbon mass concentrations in snow and ice: method evaluation and inter-comparison with elemental carbon measurement

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Size-dependence of the aerosolization efficiency

Figure S1 reports aerosolization efficiency determined for the APEX-Q nebulizer with mono-dispersed PSLs (3000 series nanosphere, Thermo scientific, USA) of known diameters: 150 nm, 200 nm, 240 nm, 350 nm and 600 nm.

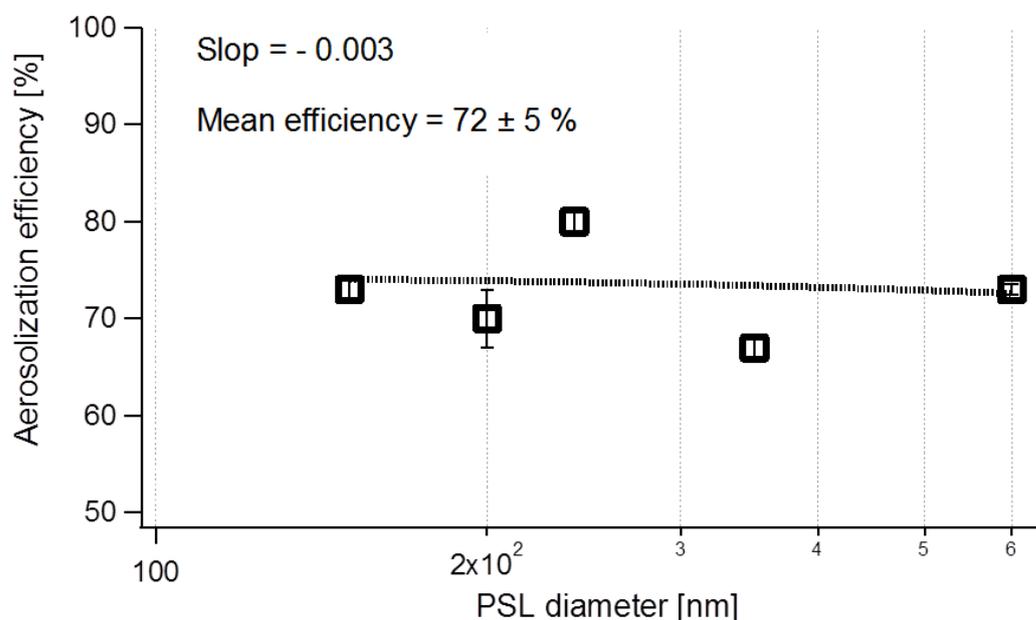


Figure S1. Aerosolization efficiency of the APEX-Q nebulizer determined for PSL particles of known diameter and number concentration. The whiskers stand for one standard deviation.

Fate of unaerosolized rBC particles in the APEX-Q

We investigated potential memory effect of the APEX-Q nebulizer. To do so, we sequentially analyzed Aquadag® (AQ) solutions (8.7 or 87 $\mu\text{g L}^{-1}$) and ultrapure water. Figure S2 reveals rBC residues of the AQ solutions lasting for ~10 minutes when measuring the ultrapure water. The total amount of measured rBC residues was about 6-12 % of the injected rBC concentrations, suggesting that ~6-12 % of the injected rBC mass adheres to the system surfaces between the sample injection tube and the SP2 optics. Such rBC residue may impact analysis of very clean, low rBC level-samples (e.g., rBC concentrations < $\sim 1.0 \mu\text{g L}^{-1}$), and cleaning the system with ultrapure water between analyses would then be required.

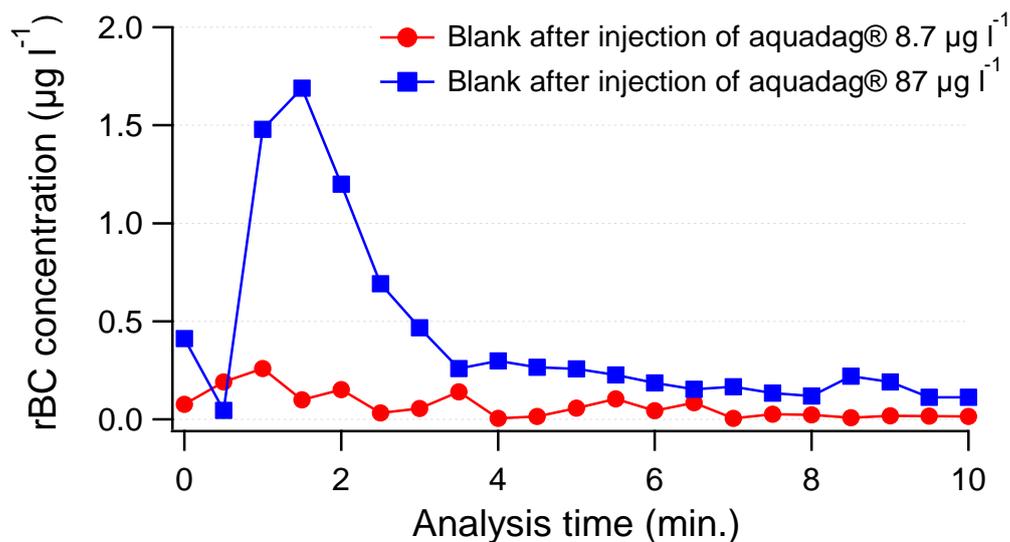


Figure S2. Measured rBC residues of aquadag® (AQ) solutions of 8.7 µg l⁻¹ and 87 µg l⁻¹ as a function of time during 10 minutes when ultrapure water is injected right after AQ solution analyses.

To fully understand the fate of rBC during aerosolization, we also analyzed the drain of AQ solutions measured. Surprisingly, less than 6% of injected rBC mass was found in the drain. Consequently, only a fraction of the rBC mass lost during aerosolization (i.e., ~12-18% over ~25% of initial sample mass) was identified in the drain or adhering on the surfaces of the nebulizer. The remaining rBC loss was not identified probably due to the following reasons; (i) no specific aerosolization calibration was applied when measuring drains and (ii) the flow rate of sample injection and drain might be too low to effectively clean out the surface area in the system.

Filtration and chemical decarbonation for thermal-optical method

The EUSAAR-2 protocol was applied to snow and firn by filtering melted samples on quartz fiber filters (Pall Tissuquartz™ filter, Pall corp.) using sample volumes of 0.16-2.00 liters. Insoluble EC particles initially present in snow and firn were collected on the filters introduced into the OC-EC analyzer. Evaluation of the filtration procedure was performed using the Col du Dôme (CDD) snow, and the following optimized procedure was applied to sample filtration. Melted snow and firn samples were carefully filtrated on a pre-heated quartz fiber filter (pre-heating conducted at 500 °C during 8 hours) by using a hand pump. The filtration of water-insoluble particles was achieved by using a filter unit equipped with a stainless steel mask allowing particles concentrated onto a circular spot of 10 mm diameter. We observed very negligible EC levels in back-up filters, thus a single filter was used. Filtration was performed twice on a filter, because we found twice-filtration was more efficient to

collect EC particles. At the end of filtration, a glass unit was rinsed with ultrapure water (e.g., ~100 mL) to ensure complete transfer of EC particles to filter. Filters were dried in a laminar flow cabinet all the night through, and then stored in a fridge until before analysis. Whole filters were analyzed, i.e. without punching a specific part of these filters since we observed inhomogeneous EC concentrations in punched areas of a filter, which differed up to around factor of two at a very low concentration, e.g., $< 1 \mu\text{g}$ EC. Filters were decarbonated chemically prior to analysis to avoid potential positive EC artifact from carbonate carbon (Karanasiou et al., 2011). Briefly, filters were acidified with 20 % HCl over-night and then neutralized with NaOH pellets for two days to reach a pH of 7 in a pre-cleaned glass container without air exchange. We observed that positive EC artifact from calcium carbonate ($\sim 6 \mu\text{g}$) was efficiently removed when this chemical decarbonation procedure was applied to a filter loaded with both AQ (10 μg) and calcium carbonate (200 μg , a level in the range frequently observed in CDD ice cores (Legrand et al., 2007; Preunkert et al., 2001).

Electron microscopy images dedicated to filtration efficiency estimation

A CDD sample was filtered on a quartz filter, and the liquid after this filtration was collected on filtered again on a 0.2- μm nucleopore. Figure S3 reports the observation of this nucleopore filter by the electron microscopy. The presence of BC aggregates with diameters ranging between 100 and 200 nm is visible, contrary to larger BC particles (Fig. S2). Such image confirms that small particles can easily pass through quartz filters during filtration.

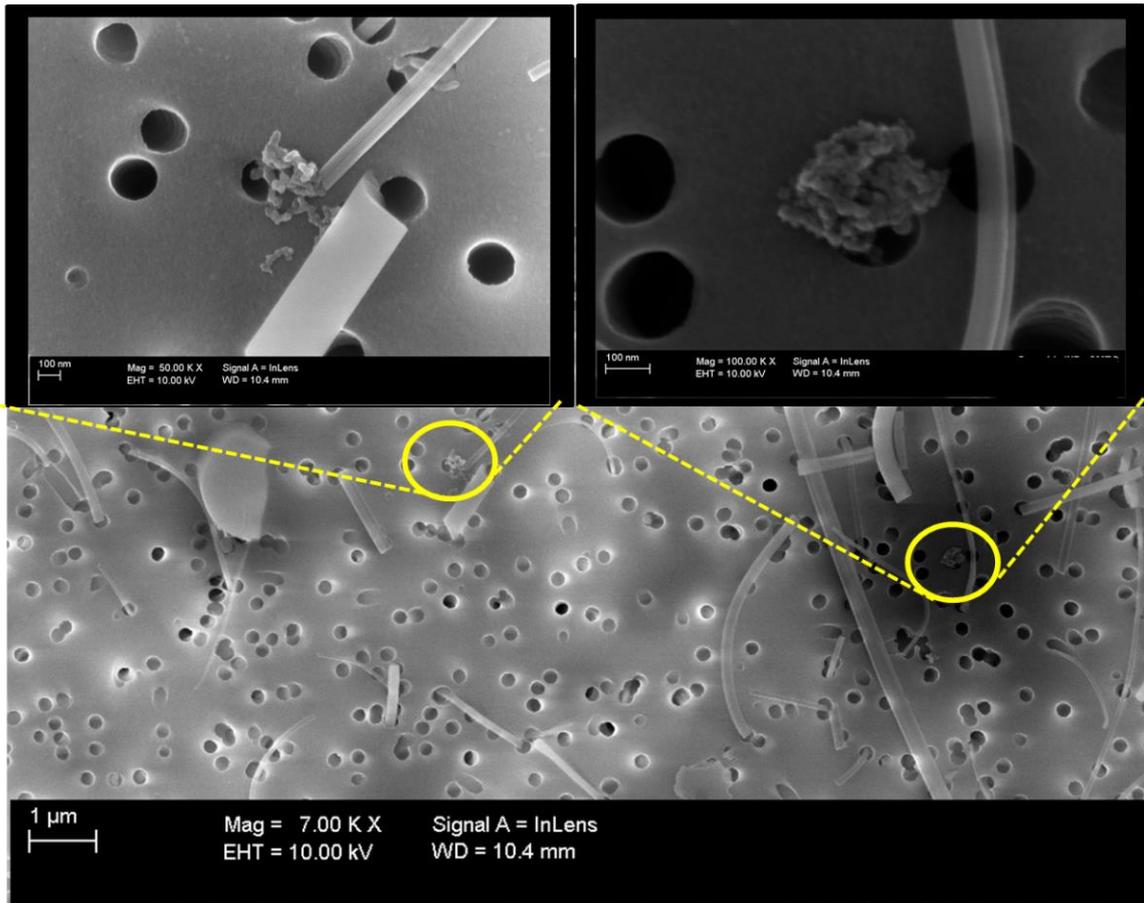


Figure S3. An electron microscope image showing BC aggregates retaining on a 0.2 μm -nuclepore filter after first filtration on a quartz fiber filter. 10-mL volume CDD surface snow sample was used to avoid artificial particle agglomeration on the filter.

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