Supplement of Atmos. Meas. Tech., 7, 2667–2681, 2014
http://www.atmos-meas-tech.net/7/2667/2014/
doi:10.5194/amt-7-2667-2014-supplement

Atmospheric Measurement Techniques
Open Access

Supplement of

Optimized method for black carbon analysis in ice and snow using the Single Particle Soot Photometer

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Supplementary Material

Equations and details for the calculations

Acronyms:

LDL: Lower detection limit

PSL: Polystyrene size standards

UDL: Upper detection limit

Table S1 – Symbols.

Symbol	Description	Unit
D	General symbol for particle diameter. Suffixes are used to specify the particular diameter type where needed (e.g. BC mass equivalent diameter, PSL diameter or mobility diameter)	µm
D_{BC}	BC mass equivalent diameter	µm
$D_{\mathrm{BC,min}}$, $D^{*}_{\mathrm{BC,min}}$	Minimal mass equivalent diameter of the BC cores in an aqueous sample (*standard)	µm
$D_{\mathrm{BC,max}}$, $D^{*}_{\mathrm{BC,max}}$	Maximal mass equivalent diameter of the BC cores in an aqueous sample (*standard)	µm
$D_{\mathrm{BC,LDL}}$	Lower cut-off diameter of the SP2 measurement in terms of BC core mass equivalent diameter ($D^{*}_{\mathrm{BC,LDL}}$ is assumed to be equal to $D_{\mathrm{BC,LDL}}$)	µm
$D_{\mathrm{BC,UDL}}$	Upper cut-off diameter of the SP2 measurement in terms of BC core mass equivalent diameter ($D^{*}_{\mathrm{BC,UDL}}$ is assumed to be equal to $D_{\mathrm{BC,UDL}}$)	µm
$D_{\mathrm{BC,ref}}$	Reference BC mass equivalent diameter for calculating the reference nebulizer efficiency, $\eta_{\mathrm{BC,ref}}$, for BC	µm

D_{PSL}	(Nominal) PSL diameter	µm
$D_{\mathrm{PSL,\,ref}}$	Reference PSL diameter for calculating the reference nebulizer efficiency, $\eta_{\mathrm{PSL,ref}}$, for PSLs	µm
D_{mob}	Mobility diameter of a BC core	µm
f_{bias}, f^{*}_{bias}	SP2 calibration bias for the BC type of an aqueous sample (*standard) expressed as a factor.	-
g_{mob2mev}	Diameter conversion function that calculates the mass equivalent diameter of a BC core from its mobility diameter. This conversion function depends on the BC particle type and is only defined for BC types with a fixed mobility diameter to mass relationship.	n.a.
C_{liq}, C^{*}_{liq}	BC mass concentration of an aqueous sample (*standard)	µg L^{-1}
M_{liq}, M^{*}_{liq}	Mass concentration of water-insoluble particulate matter in an aqueous sample (* standard)	µg L^{-1}
γ^{*}_{BC}	BC mass fraction in dried particles of a BC material that is used to prepare aqueous standard suspensions.	-
c_{air}, c^{*}_{air}	BC mass concentration of the aerosol from a nebulized aqueous sample (*standard)	µg m^{-3}
c_{SP2}, c^{*}_{SP2}	BC mass concentration of the aerosol as inferred from the SP2 measurement of a nebulized aqueous sample (*standard)	µg m^{-3}
$C^{\mathrm{x}}_{\mathrm{SP2}}$, $C^{\mathrm{x},*}_{\mathrm{SP2}}$	BC mass concentration in an aqueous sample (*standard) inferred from the SP2 measurement of the nebulized sample (with accounting for the absolute overall nebulizer efficiency). Note, the superscript "x" is a placeholder for indicating the approach that is used to calculate C_{SP2}. "x" can be S1, S2, Sη	µg L^{-1}
$C^{\eta}_{\mathrm{SP2,low}}$, $C^{\eta,*}_{\mathrm{SP2,low}}$	Lower limit of the BC mass concentration in an aqueous	µg L^{-1}

	sample (*standard) inferred from the SP2 measurement of the nebulized sample (calculated by using the upper limit for the overall nebulizer efficiency)	
$\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})$, $\frac{dC^{*}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})$	BC mass size distribution of an aqueous sample (*standard)	µg L^{-1}
$\frac{d\widetilde{C}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})$, $\frac{d\widetilde{C}^{*}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})$	Normalized BC mass size distribution of an aqueous sample (*standard)	-
$\frac{dc_{\mathrm{air}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})$, $\frac{dc^{*}_{\mathrm{air}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})$	BC mass size distribution of the aerosol from a nebulized aqueous sample (*standard)	µg m^{-3}
$\frac{dc_{\mathrm{SP2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})$, $\frac{dc^{*}_{\mathrm{SP2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})$	BC mass size distribution measured by the SP2 for a nebulized aqueous sample (*standard)	µg m^{-3}
$\frac{dC^{\eta}_{\mathrm{SP2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})$, $\frac{dC^{\eta,*}_{\mathrm{SP2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})$	BC mass size distribution of an aqueous sample (*standard) inferred from the SP2 measurement of the nebulized sample (with accounting for the nebulizer efficiency)	µg L^{-1}
$\Delta\widetilde{C}_{\mathrm{LDL}}$, $\Delta\widetilde{C}^{*}_{\mathrm{LDL}}$	Relative contribution to the total BC mass in an aqueous sample (*standard) from BC cores with sizes below the LDL of the SP2	-
$\Delta\widetilde{C}_{\mathrm{UDL}}$, $\Delta\widetilde{C}^{*}_{\mathrm{UDL}}$	Relative contribution to the total BC mass in an aqueous sample (*standard) from BC cores with sizes above the UDL of the SP2	-

$\eta(D), \eta^*(D)$	Overall nebulizer efficiency for insoluble particles as a function of the particle diameter during the measurement of a sample (*standard)	L m^{-3}
η_{max} , η^*_{max}	Maximum possible overall efficiency of a nebulizer during the measurement of an aqueous sample (*standard)	L m^{-3}
$\eta_{BC}(D_{BC})$, $\eta^*_{BC}(D_{BC})$	Overall nebulizer efficiency for BC as a function of BC mass equivalent diameter during the measurement of an aqueous sample (*standard)	L m^{-3}
$\eta_{BC,ref}$, $\eta^*_{BC,ref}$	Reference nebulizer efficiency for BC at the reference BC mass equivalent diameter D_{ref} during the measurement of an aqueous sample (*standard)	L m^{-3}
$\tilde{\eta}_{BC}(D_{BC})$, $\tilde{\eta}^*_{BC}(D_{BC})$	Normalized overall nebulizer efficiency for BC as a function of BC mass equivalent diameter (*standard)	-
$\hat{\eta}_{BC}(D_{mob})$	Overall nebulizer efficiency for BC as a function of the mobility diameter of the BC core.	-
$\eta_{PSL}(D_{PSL})$	Overall nebulizer efficiency for PSLs as a function of PSL diameter	L m^{-3}
$\eta_{PSL,ref}$	Reference nebulizer efficiency for PSLs at the reference PSL diameter $D_{PSL,ref}$	L m^{-3}
$\tilde{\eta}_{PSL}(D_{PSL})$	Normalized overall nebulizer efficiency for PSLs as a function of PSL diameter	-
$N_{liq,PSL}(D_{PSL})$	Number concentration of PSLs with nominal diameter D_{PSL} in an aqueous standard	L^{-1}
$n_{air,PSL}(D_{PSL})$	Number concentration of PSLs with nominal diameter D_{PSL} in the aerosol from a nebulized aqueous standard	cm^{-3}
$\varepsilon_{drop}, \varepsilon^*_{drop}$	Fraction of the supplied aqueous sample that is transformed into droplets and successfully transferred	-

	towards the aerosol sample outlet of the nebulizer during the measurement of an aqueous sample (*standard)	
$\varepsilon_{\mathrm{loss}}(D)$, $\varepsilon^{*}_{\mathrm{loss}}(D)$	Size-dependent factor accounting for all kind of losses during the measurement of a sample (*standard) in the complete nebulizer unit including everything between the sample vial and the SP2 inlet	-
$q_{\mathrm{air,supply}}, q^{*}_{\mathrm{air,supply}}$	Air flow rate at the purge air inlet of the nebulizer during the measurement of an aqueous sample (*standard)	L min^{-1}
$q_{\mathrm{air,aerosol}}, q^{*}_{\mathrm{air,aerosol}}$	Air flow rate of the aerosol outlet of the nebulizer during the measurement of an aqueous sample (*standard)	L min^{-1}
$q_{\mathrm{air,drain}}, q^{*}_{\mathrm{air,drain}}$	Air flow rate through the drain channel from the nebulizer chamber during the measurement of an aqueous sample (*standard)	L min^{-1}
$Q_{\mathrm{liq,supply}}, Q^{*}_{\mathrm{liq,supply}}$	Flow rate of the aqueous sample supplied to the nebulizer during the measurement of an aqueous sample (*standard)	mL min^{-1}
$Q_{\mathrm{liq,drain}}, Q^{*}_{\mathrm{liq,drain}}$	Flow rate of water that is drained from the nebulizer chamber without being nebulized during the measurement of an aqueous sample (*standard)	mL min^{-1}
ρ_{bulkBC}	Void free material density of BC	kg m^{-3}
$\rho_{\mathrm{eff,BC}}(D_{\mathrm{mob}})$	Effective density of BC particles as a function of particle mobility diameter	kg m^{-3}

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S.1 General definitions and equations

S.1.1 Nebulizer efficiency for BC

The size-dependent overall nebulizer efficiency for BC as a function of BC mass equivalent diameter during the measurement of an aqueous BC sample is defined as the ratio of the BC mass size distribution in the aerosol from the nebulized aqueous sample, $\frac{dc_{\mathrm{air}}}{d\log D_{\mathrm{BC}}}$, to the BC mass size distribution in the aqueous sample, $\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}$, at the same BC mass equivalent diameter, D_{BC}:

$$\eta_{\mathrm{BC}}(D_{\mathrm{BC}}) := \frac{\frac{dc_{\mathrm{air}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})}{\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})} \tag{S1}$$

The reference nebulizer efficiency for BC, $\eta_{\mathrm{BC,ref}}$, at the arbitrarily chosen BC mass equivalent reference diameter, $D_{\mathrm{BC,ref}}$, is defined as:

$$\eta_{\mathrm{BC,ref}} := \eta_{\mathrm{BC}}(D_{\mathrm{BC,ref}}) \tag{S2}$$

and the normalized overall nebulizer efficiency for BC as a function of BC mass equivalent diameter is defined as:

$$\tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}}) := \frac{\eta_{\mathrm{BC}}(D_{\mathrm{BC}})}{\eta_{\mathrm{BC,ref}}} \tag{S3}$$

Note, from Eqs. (S2) and (S3) follows: $\tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC,ref}}) = 1$.

Rearranging Eq. (S3) provides an alternative form for the overall nebulizer efficiency for BC (as a function of BC mass equivalent diameter):

$$\eta_{\mathrm{BC}}(D_{\mathrm{BC}}) = \eta_{\mathrm{BC,ref}}\,\tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}}) \tag{S4}$$

The definitions for the nebulizer efficiency during the measurement of an aqueous BC standard are equivalent to Eqs. (S1) to (S4) (obtained with substituting $\eta_{\mathrm{BC}}, \tilde{\eta}_{\mathrm{BC}}, c_{\mathrm{air}}$ and C_{liq} for η^*_{BC}, $\tilde{\eta}^*_{\mathrm{BC}}, c^*_{\mathrm{air}}$ and C^*_{liq}, respectively).

S.1.2 Nebulizer efficiency for PSLs

The size-dependent overall nebulizer efficiency for PSLs as a function of PSL diameter is defined as the ratio of the number concentration of PSLs in the aerosol from the nebulized aqueous standard, $n_{air,PSL}$, to the number concentration of PSLs in the aqueous standard, $N_{liq,PSL}$, with the same nominal diameter D_{PSL}:

$$\eta_{\mathrm{PSL}}(D_{\mathrm{PSL}}) := \frac{n_{\mathrm{air,PSL}}(D_{\mathrm{PSL}})}{N_{\mathrm{liq,PSL}}(D_{\mathrm{PSL}})} \cdot 10^6 \tag{S5}$$

where the factor 10^6 accounts for the units as defined in the list of all symbols. This definition for the nebulizer efficiency for PSLs is equivalent to the definition for the nebulizer efficiency for BC (Eq. S1). The reference nebulizer efficiency for PSLs, $\eta_{\mathrm{PSL,ref}}$, at the arbitrarily chosen reference PSL diameter, $D_{\mathrm{PSL,ref}}$, is defined as:

$$\eta_{\mathrm{PSL,ref}} := \eta_{\mathrm{PSL}}(D_{\mathrm{PSL,ref}}) \tag{S6}$$

and the normalized overall nebulizer efficiency for PSLs as a function of PSL diameter is defined as:

$$\tilde{\eta}_{\mathrm{PSL}}(D_{\mathrm{PSL}}) := \frac{\eta_{\mathrm{PSL}}(D_{\mathrm{PSL}})}{\eta_{\mathrm{PSL,ref}}} \tag{S7}$$

Note, from Eqs. (S6) and (S7) follows: $\tilde{\eta}_{\mathrm{PSL}}(D_{\mathrm{PSL,ref}}) = 1$

Rearranging Eq. (S7) provides an alternative form for the overall nebulizer efficiency for PSLs (as a function of PSL diameter):

$$\eta_{\mathrm{PSL}}(D_{\mathrm{PSL}}) = \eta_{\mathrm{PSL,ref}}\,\tilde{\eta}_{\mathrm{PSL}}(D_{\mathrm{PSL}}) \tag{S8}$$

S.1.3 Particle losses in a nebulizer and upper limit for the nebulizer efficiency

The efficiency of a nebulizer during the measurement of an aqueous BC sample depends on several factors. The overall nebulizer efficiency for insoluble particles in suspension, as defined in Eqs. (S1) and (S5) for BC and PSLs, respectively, can be written as:

$$\eta(D) = \frac{\varepsilon_{\mathrm{drop}} Q_{\mathrm{liq,supply}}}{q_{\mathrm{air,aerosol}}} \varepsilon_{\mathrm{loss}}(D) \tag{D9}$$

This equation is valid for nebulizers where the main nebulizer chamber only has two inputs for the aqueous sample and purge air supply and two outlets for the aerosol sample and the chamber drain (additional drains or vents between the aerosol sample outlet from the main chamber nebulizer chamber and the SP2 inlet such as e.g. drains from the dryer do not matter as they don't change the aerosol concentration). The factor ε_{drop} accounts for the fraction of the supplied aqueous sample, fed to the nebulizer with a flow rate of $Q_{liq,supply}$, that is transformed into droplets and successfully transferred towards the aerosol sample outlet of the nebulizer. $q_{air,aerosol}$ is the air flow rate at the aerosol outlet of the nebulizer. The factor ε_{loss} accounts for any kind of losses of insoluble particles in the complete nebulizer unit, i.e. between the sample vial and the SP2 inlet.

ε_{drop} can be expressed with the flow rate of water in the drain line, $Q_{liq,drain}$:

$$\varepsilon_{drop} = \frac{Q_{liq,supply} - Q_{liq,drain}}{Q_{liq,supply}} \quad \text{(S10)}$$

$Q_{liq,drain}$ is the flow rate of the portion of the supplied aqueous sample that leaves the nebulizer chamber directly through the drain line without giving a contribution to the aerosol at the nebulizer outlet. Any drain water from the dryer section of the nebulizer must not be included in $Q_{liq,drain}$.

$q_{air,aerosol}$ can alternatively be expressed with the flow rates of the purge air, $q_{air,supply}$, and the air in the drain line from the nebulizer chamber, $q_{air,drain}$:

$$q_{air,aerosol} = q_{air,supply} - q_{air,drain} \quad \text{(S11)}$$

$q_{air,drain}$ only includes the air flow that leaves the nebulizer chamber directly through the drain line. Any air flow at additional drain ports for e.g. removing water from the dryer section of the nebulizer must not be included in $q_{air,drain}$. Often, $q_{air,drain}$ is much smaller than $q_{air,supply}$, such that $q_{air,aerosol} \approx q_{air,supply}$.

ε_{loss} is the only unknown quantity in Eq. (D9) for any nebulizer type where $Q_{liq,supply}$, $Q_{liq,drain}$, and $q_{air,aerosol}$ can be measured. An upper limit for the maximal possible efficiency of a nebulizer, η_{max}, is:

$$\eta_{max} = \frac{\varepsilon_{drop} Q_{liq,supply}}{q_{air,aerosol}} = \frac{(Q_{liq,supply} - Q_{liq,drain})}{q_{air,aerosol}} \approx \frac{(Q_{liq,supply} - Q_{liq,drain})}{q_{air,supply}} \quad \text{(S12)}$$

Inserting Eq. (S12) into Eq. (D9) provides:

$$\eta(D) = \eta_{\max}\varepsilon_{\text{loss}}(D) \;\Leftrightarrow\; \varepsilon_{\text{loss}}(D) = \frac{\eta(D)}{\eta_{\max}} \tag{S13}$$

where η is the true efficiency of the nebulizer. Given the fact that $\varepsilon_{\text{loss}}(D) \leq 1$ confirms that $\eta_{\max}$ is indeed an upper limit for $\eta(D)$.

Note, $\varepsilon_{\text{loss}}(D)$ is likely to depend on the properties (density, shape, etc.) of the insoluble particles.

Equations (D9) to (S13) are equivalent for the measurement of an aqueous standard (obtained with substituting $Q_{\text{liq,supply}}$, $Q_{\text{liq,drain}}$, $q_{\text{air,supply}}$, $q_{\text{air,drain}}$, $q_{\text{air,aerosol}}$, $\varepsilon_{\text{drop}}$, $\varepsilon_{\text{loss}}$, η and $\eta_{\max}$ for $Q^*_{\text{liq,supply}}$, $Q^*_{\text{liq,drain}}$, $q^*_{\text{air,supply}}$, $q^*_{\text{air,drain}}$, $q^*_{\text{air,aerosol}}$, $\varepsilon^*_{\text{drop}}$, $\varepsilon^*_{\text{loss}}$, η^* and $\eta^*_{\max}$, respectively).

S.1.4 BC mass size distribution and mass concentration of an aqueous BC sample and the corresponding nebulized aerosol

The aim of measuring the aerosol from a nebulized aqueous sample with the SP2 is to determine the total BC mass concentration, C_{liq}, and the BC mass size distribution, $dC_{\text{liq}}/d\log D_{\text{BC}}$, in the aqueous sample. These two quantities are related as follows:

$$C_{\text{liq}} = \int_{D_{\text{BC,min}}}^{D_{\text{BC,max}}} \frac{dC_{\text{liq}}}{d\log D_{\text{BC}}}(D_{\text{BC}})\, d\log D_{\text{BC}} \tag{S14}$$

where $D_{\text{BC,min}}$ and $D_{\text{BC,max}}$ are the minimal and maximal BC core mass equivalent diameters in the sample.

The primary measurements of the SP2 are the total BC mass concentration, c_{SP2}, and the BC mass size distribution, $dc_{\text{SP2}}/d\log D_{\text{BC}}$, of the aerosol from the nebulized aqueous sample, which are related as follows:

$$c_{\text{SP2}} = \int_{D_{\text{BC,LDL}}}^{D_{\text{BC,UDL}}} \frac{dc_{\text{SP2}}}{d\log D_{\text{BC}}}(D_{\text{BC}})\, d\log D_{\text{BC}} \tag{S15}$$

$D_{\text{BC,LDL}}$ and $D_{\text{BC,UDL}}$ are the LDL and UDL of the SP2 in terms of BC mass equivalent diameter.

The detection efficiency of the SP2 is unity within its detection limits. BC cores smaller than the LDL of the SP2 may still be detected but with a detection efficiency below unity. BC cores larger than the UDL of the SP2 are properly counted but their BC mass cannot be quantified (due to detector saturation).

Any SP2 measurement of BC mass is potentially biased. The size-dependent calibration bias for BC mass, f_{bias}, can be defined as:

$$f_{\text{bias}}(D_{\text{BC}}) = \frac{\frac{dc_{\text{SP2}}}{d\log D_{\text{BC}}}(D_{\text{BC}})}{\frac{dc_{\text{air}}}{d\log D_{\text{BC}}}(D_{\text{BC}})} \tag{S16}$$

where $dc_{air}/d\log D_{BC}$ is the true BC mass size distribution of the aerosol from the nebulized aqueous sample. If the calibration bias is assumed to be a constant, i.e. independent of BC core size, within the detection range of the SP2, follows:

$$\frac{dc_{\text{SP2}}}{d\log D_{\text{BC}}}(D_{\text{BC}}) = f_{\text{bias}}\,\frac{dc_{\text{air}}}{d\log D_{\text{BC}}}(D_{\text{BC}}) \quad \forall \quad D_{\text{BC}} \in \left[D_{\text{BC,LDL}}\, D_{\text{BC,UDL}}\right] \tag{S17}$$

The normalized BC mass size distribution of the aqueous sample is defined as:

$$\frac{d\tilde{C}_{\text{liq}}}{d\log D_{\text{BC}}}(D_{\text{BC}}) := \frac{1}{C_{\text{liq}}}\frac{dC_{\text{liq}}}{d\log D_{\text{BC}}}(D_{\text{BC}}) \tag{S18}$$

The relative contribution from BC cores with sizes below the LDL of the SP2 to the total BC mass in the aqueous sample is (use Eq. S18 to obtain the right hand side):

$$\Delta\tilde{C}_{\text{LDL}} = \frac{1}{C_{\text{liq}}}\int_{D_{\text{BC, min}}}^{D_{\text{BC, LDL}}}\frac{dC_{\text{liq}}}{d\log D_{\text{BC}}}(D_{\text{BC}})d\log D_{\text{BC}} = \int_{D_{\text{BC, min}}}^{D_{\text{BC, LDL}}}\frac{d\tilde{C}_{\text{liq}}}{d\log D_{\text{BC}}}(D_{\text{BC}})d\log D_{\text{BC}} \tag{S19}$$

The relative contribution from BC cores with sizes above the UDL of the SP2 to the total BC mass in the aqueous sample is (use Eq. S18 to obtain the right hand side):

$$\Delta\tilde{C}_{\text{UDL}} = \frac{1}{C_{\text{liq}}}\int_{D_{\text{BC, UDL}}}^{D_{\text{BC, max}}}\frac{dC_{\text{liq}}}{d\log D_{\text{BC}}}(D_{\text{BC}})d\log D_{\text{BC}} = \int_{D_{\text{BC, UDL}}}^{D_{\text{BC, max}}}\frac{d\tilde{C}_{\text{liq}}}{d\log D_{\text{BC}}}(D_{\text{BC}})d\log D_{\text{BC}} \tag{S20}$$

From Eqs. (S14), (S18), (S19) and (S20) follows:

$$\int_{D_{\text{BC, LDL}}}^{D_{\text{BC, UDL}}}\frac{d\tilde{C}_{\text{liq}}}{d\log D_{\text{BC}}}(D_{\text{BC}})d\log D_{\text{BC}} = 1 - \Delta\tilde{C}_{\text{LDL}} - \Delta\tilde{C}_{\text{UDL}} \tag{S21}$$

From the above definition of the nebulizer efficiency for BC follows (Eqs. S1 and S4):

$$\frac{dc_{\mathrm{air}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) = \eta_{\mathrm{BC}}(D_{\mathrm{BC}})\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) = \eta_{\mathrm{BC,ref}}\tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}})\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \tag{S22}$$

Inserting Eq. (S17) into Eq. (S22) provides:

$$\begin{aligned}\frac{dc_{\mathrm{SP2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) &= f_{\mathrm{bias}}\eta_{\mathrm{BC}}(D_{\mathrm{BC}})\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \\ &= f_{\mathrm{bias}}\eta_{\mathrm{BC,ref}}\tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}})\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \\ &\qquad \forall\ D_{\mathrm{BC}} \in \left[D_{\mathrm{BC,LDL}}, D_{\mathrm{BC,UDL}}\right]\end{aligned} \tag{S23}$$

Inserting Eq. (S23) into Eq. (S15) provides the following relationship between the total BC mass concentration measured by the SP2 and the BC mass size distribution in the aqueous sample:

$$c_{\mathrm{SP2}} = f_{\mathrm{bias}}\int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}}\eta_{\mathrm{BC,ref}}\tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}})\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})d\log D_{\mathrm{BC}} \tag{S24}$$

The central equation for inferring the BC mass size distribution in an aqueous sample, $dC^{\eta}_{\mathrm{SP2}}/d\log D_{\mathrm{BC}}$, from the SP2 measurement of the nebulized sample, if the absolute nebulizer efficiency is known, is:

$$\frac{dC^{\eta}_{\mathrm{SP2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) := \frac{1}{\eta_{\mathrm{BC}}(D_{\mathrm{BC}})}\frac{dc_{\mathrm{SP2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) = \frac{1}{\eta_{\mathrm{BC,ref}}\tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}})}\frac{dc_{\mathrm{SP2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \tag{S25}$$

Inserting Eqs. (S17) and (S22) into Eq. (S25) provides:

$$\begin{aligned}\frac{dC^{\eta}_{\mathrm{SP2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) &= f_{\mathrm{bias}}\frac{1}{\eta_{\mathrm{BC}}(D_{\mathrm{BC}})}\frac{dc_{\mathrm{air}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \\ &= f_{\mathrm{bias}}\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \quad \forall \quad D_{\mathrm{BC}} \in \left[D_{\mathrm{BC,LDL}}, D_{\mathrm{BC,UDL}}\right]\end{aligned} \tag{S26}$$

This confirms that Eq. (S25) indeed provides the correct result for all BC core sizes within the detection range of the SP2, if the size dependent nebulizer efficiency for BC is known and if the potential SP2 calibration bias is small (i.e. $f_{\mathrm{bias}} \approx 1$).

The central equation for inferring the total BC mass concentration in an aqueous sample, C_{SP2}^{η}, from the SP2 measurement of the nebulized sample, if the absolute nebulizer efficiency is known, is obtained by integrating Eq. (S25):

$$\begin{aligned} C_{\mathrm{SP2}}^{\eta} &:= \int_{D_{\mathrm{BC,\,LDL}}}^{D_{\mathrm{BC,\,UDL}}} \frac{dC_{\mathrm{SP2}}^{\eta}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})\, d\log D_{\mathrm{BC}} \\ &= \int_{D_{BC,LDL}}^{D_{BC,UDL}} \frac{1}{\eta_{BC}(D_{BC})} \frac{dc_{SP2}}{d\log D_{BC}}(D_{BC})\, d\log D_{BC} \\ &= \int_{D_{BC,LDL}}^{D_{BC,UDL}} \frac{1}{\eta_{BC,ref}\tilde{\eta}_{BC}(D_{BC})} \frac{dc_{SP2}}{d\log D_{BC}}(D_{BC})\, d\log D_{BC} \end{aligned} \tag{S27}$$

Inserting Eqs. (S26), (S18), and (S21) into Eq. (S27) provides:

$$\begin{aligned} C_{\mathrm{SP2}}^{\eta} &= \int_{D_{\mathrm{BC,\,LDL}}}^{D_{\mathrm{BC,\,UDL}}} \frac{dC_{\mathrm{SP2}}^{\eta}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})\, d\log D_{\mathrm{BC}} \\ &= \int_{D_{\mathrm{BC,\,LDL}}}^{D_{\mathrm{BC,\,UDL}}} f_{\mathrm{bias}} \frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})\, d\log D_{\mathrm{BC}} \\ &= f_{\mathrm{bias}} C_{\mathrm{liq}} \int_{D_{\mathrm{BC,\,LDL}}}^{D_{\mathrm{BC,\,UDL}}} \frac{d\tilde{C}_{\mathrm{liq}}}{d\log D}(D_{\mathrm{BC}})\, d\log D_{\mathrm{BC}} = f_{\mathrm{bias}} C_{\mathrm{liq}} \left(1 - \Delta\tilde{C}_{\mathrm{LDL}} - \Delta\tilde{C}_{\mathrm{UDL}}\right) \end{aligned} \tag{S28}$$

This confirms that Eq. (S27) indeed provides the correct result for the total BC mass concentration of BC cores within the detection range of the SP2, if the size-dependent nebulizer efficiency for BC is known and if the potential SP2 calibration bias is small (i.e. if $f_{\mathrm{bias}} \approx 1$).

No aqueous BC standard is required as a reference for the approach with using Eq. (S27) for inferring the total BC mass concentration in the aqueous sample. However, Eq. (S27) can only be evaluated if the size-dependent overall efficiency of the nebulizer for BC is known and if it is different from zero in the size range between $D_{BC,LDL}$ and $D_{BC,UDL}$, i.e. if:

$$\tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}}) \neq 0 \quad \forall \quad D_{\mathrm{BC}} \in \left[D_{\mathrm{BC,LDL}}, D_{\mathrm{BC,UDL}}\right] \tag{S29}$$

For nebulizers with a sharp efficiency drop towards zero above a certain diameter, such as e.g. observed for the CETAC ultrasonic nebulizer, the integration in Eq. (S27) must be additionally restricted to diameters below which the nebulizer is sufficiently efficient (i.e. diameters for which Eq. (S29) is fulfilled). This would potentially increase the unaccounted

portion of BC mass, $C_{\mathrm{liq}}\Delta\widetilde{C}_{\mathrm{UDL}}$, if the nebulizer cut-off is below the upper end of the BC size distribution.

If the BC mass fraction of BC cores in the aqueous sample with sizes outside the detection range of the SP2 is small, i.e. if:

$$\Delta\widetilde{C}_{\mathrm{LDL}} + \Delta\widetilde{C}_{\mathrm{UDL}} << 1 \tag{S30}$$

then follows from Eq. (S28) that Eq. (S27) correctly provides the total BC mass concentration in the aqueous sample of BC cores with any core size, except for the potential calibration bias:

$$C_{\mathrm{SP2}}^{\eta} \approx f_{\mathrm{bias}} C_{\mathrm{liq}} \tag{S31}$$

Typically, the absolute nebulizer efficiency is not known. In such cases it is still possible to obtain an estimate of the lower limit of the total BC mass concentration in an aqueous sample, $C_{\mathrm{SP2,low}}$, from the SP2 measurement of the nebulized sample by substituting the true nebulizer efficiency (η_{BC}) with the upper limit of the nebulizer efficiency ($\eta_{\max}$) in Eq. (S27):

$$C_{\mathrm{SP2,low}}^{\eta} := \frac{1}{\eta_{\max}} \int_{D_{\mathrm{BC,\,LDL}}}^{D_{\mathrm{BC,\,UDL}}} \frac{dc_{\mathrm{SP2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) d\log D_{\mathrm{BC}} = \frac{1}{\eta_{\max}} c_{\mathrm{SP2}} \tag{S32}$$

With $\eta_{\max} \geq \eta_{\mathrm{BC}}(D_{\mathrm{BC}})$ follows:

$$C_{\mathrm{SP2,low}}^{\eta} \leq C_{\mathrm{SP2}}^{\eta} \tag{S33}$$

which confirms that Eq. (S32) indeed provides a lower limit for C_{SP2}^{η}.

Equations (S14) to (S33) are equivalent for the measurement of an aqueous BC standard (obtained with substituting C_{liq}, $D_{\mathrm{BC,min}}$, $D_{\mathrm{BC,max}}$, $dC_{\mathrm{liq}}/d\log D_{\mathrm{BC}}$, c_{SP2}, $dc_{\mathrm{SP2}}/d\log D_{\mathrm{BC}}$, etc. for C_{liq}^{*}, $D_{\mathrm{BC,min}}^{*}$, $D_{\mathrm{BC,max}}^{*}$, $dC_{\mathrm{liq}}^{*}/d\log D_{\mathrm{BC}}$, c_{SP2}^{*}, $dc_{\mathrm{SP2}}^{*}/d\log D_{\mathrm{BC}}$, etc., respectively).

S.2 Approach of using aqueous standards as a reference for the measurement of unknown samples

The nebulizer efficiency is often not known. In such cases it is common to relate the BC mass concentration measurement of an aqueous sample to the measurement of an aqueous BC standard of known concentration, C_{liq}^{*}. The assumption behind this approach is that the

nebulizer efficiency remains stable between the measurement of the sample and the standard, i.e.:

$$\eta_{\mathrm{BC}}(D_{\mathrm{BC}}) = \eta^{*}_{\mathrm{BC}}(D_{\mathrm{BC}}) \qquad \forall \quad D_{\mathrm{BC}} \tag{S34}$$

The following simple rule of proportion is then commonly used to infer the BC mass concentration, $C^{\mathrm{S1}}_{\mathrm{SP2}}$, of the aqueous sample of interest from the SP2 measurements of the nebulized sample and standard:

$$C^{\mathrm{S1}}_{\mathrm{SP2}} := c_{\mathrm{SP2}} \frac{C^{*}_{\mathrm{liq}}}{c^{*}_{\mathrm{SP2}}} \tag{S35}$$

Drifts of the aqueous sample and/or air flow rates between the measurement of the aqueous BC sample and standard (i.e. if $Q_{\mathrm{liq,supply}} \neq Q^{*}_{\mathrm{liq,supply}}$, $Q_{\mathrm{liq,drain}} \neq Q^{*}_{\mathrm{liq,drain}}$, $q_{\mathrm{air,supply}} \neq q^{*}_{\mathrm{air,supply}}$ and/or $q_{\mathrm{air,aerosol}} \neq q^{*}_{\mathrm{air,aerosol}}$), which can occur depending on the nebulizer type, will result in a drift of the overall nebulizer efficiency (see Eqs. D9 to S11), thus turning Eq. (S34) invalid. However, the particle losses in the nebulizer system may not be affected by moderate changes of the water and air flow rates, such that the factor $\varepsilon_{\mathrm{loss}}$may still be assumed to remain stable between the measurement of the sample and the standard, i.e.:

$$\varepsilon_{\mathrm{loss}}(D_{\mathrm{BC}}) = \varepsilon^{*}_{\mathrm{loss}}(D_{\mathrm{BC}}) \qquad \forall \quad D_{\mathrm{BC}} \tag{S36}$$

In such cases it is possible to account for drifts of $Q_{\mathrm{liq,supply}}$, $q_{\mathrm{air,aerosol}}$ and/or $\varepsilon_{\mathrm{drop}}$, for nebulizer types where these quantities can be monitored, by using the following equation (as an alternative to Eq. S35):

$$C^{\mathrm{S2}}_{\mathrm{SP2}} := C^{\eta}_{\mathrm{SP2,low}} \frac{C^{*}_{\mathrm{liq}}}{C^{\eta,*}_{\mathrm{SP2,low}}} \tag{S37}$$

From Eq. (S32) follows:

$$\frac{C^{\eta}_{\mathrm{SP2,low}}}{C^{\eta,*}_{\mathrm{SP2,low}}} = \frac{\eta^{*}_{\mathrm{max}}}{\eta_{\mathrm{max}}} \frac{c_{\mathrm{SP2}}}{c^{*}_{\mathrm{SP2}}} \tag{S38}$$

and by inserting Eqs. (S35) and (S37) into Eq. (S38) it follows that:

$$C^{\mathrm{S2}}_{\mathrm{SP2}} = \frac{\eta^{*}_{\mathrm{max}}}{\eta_{\mathrm{max}}} C^{\mathrm{S1}}_{\mathrm{SP2}} \tag{S39}$$

From Eq. (S39) follows that the approaches of using Eq. (S35) or (S37) are equal except for the factor $\eta^*_{\mathrm{max}}/\eta_{\mathrm{max}}$, which is normally close to unity (the factor $\eta^*_{\mathrm{max}}/\eta_{\mathrm{max}}$ reflects the slightly different underlying assumptions, i.e. Eq. S34 for Eq. S35 and Eq. S36 for Eq. (S37). If this factor was substantially different from unity, i.e. if the nebulizer system was operated with substantially different water and air flow rates when measuring the standard and the sample, then Eq. (S34) is not sufficiently well satisfied, thus turning Eq. (S35) invalid (see also below). In such cases, it is important to account for differences between η_{max} and η^*_{max} by applying Eq. (S37) instead. However, if the water and air flow rates differ substantially between measuring the standard and the sample, then it is also possible that Eq. (S36) is not fulfilled anymore, thereby potentially making the approach of Eq. (S37) imprecise or even invalid, too.

The use of Eqs. (S18) and (S24) as well as the assumption of Eq. (S34) yields:

$$\begin{aligned}\frac{c_{\mathrm{SP2}}}{c^*_{\mathrm{SP2}}} &= \frac{f_{\mathrm{bias}}\int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} \eta_{\mathrm{BC,ref}}\,\tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}})\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})d\log D_{\mathrm{BC}}}{f^*_{\mathrm{bias}}\int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} \eta^*_{\mathrm{BC,ref}}\,\tilde{\eta}^*_{\mathrm{BC}}(D_{\mathrm{BC}})\frac{dC^*_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})d\log D_{\mathrm{BC}}} \\ &= \frac{C_{\mathrm{liq}}}{C^*_{\mathrm{liq}}}\frac{f_{\mathrm{bias}}}{f^*_{\mathrm{bias}}}\frac{\int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} \tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}})\frac{d\tilde{C}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})d\log D_{\mathrm{BC}}}{\int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} \tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}})\frac{d\tilde{C}^*_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})d\log D_{\mathrm{BC}}}\end{aligned} \tag{S40}$$

Inserting Eq. (S40) into Eq. (S35) provides:

$$C^{\mathrm{S1}}_{\mathrm{SP2}} = C_{\mathrm{liq}}\frac{f_{\mathrm{bias}}}{f^*_{\mathrm{bias}}}\frac{\int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} \tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}})\frac{d\tilde{C}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})d\log D_{\mathrm{BC}}}{\int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} \tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}})\frac{d\tilde{C}^*_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})d\log D_{\mathrm{BC}}} \tag{S41}$$

Equation (S41) can be written as:

$$C^{\mathrm{S1}}_{\mathrm{SP2}} = C_{\mathrm{liq}}\frac{f_{\mathrm{bias}}}{f^*_{\mathrm{bias}}}k_{\mathrm{S1}} \tag{S42}$$

with:

$$k_{S1} := \frac{\int_{D_{BC,LDL}}^{D_{BC,UDL}} \tilde{\eta}_{BC}(D_{BC}) \frac{d\tilde{C}_{liq}}{d \log D_{BC}}(D_{BC}) d \log D_{BC}}{\int_{D_{BC,LDL}}^{D_{BC,UDL}} \tilde{\eta}_{BC}(D_{BC}) \frac{d\tilde{C}^{*}_{liq}}{d \log D_{BC}}(D_{BC}) d \log D_{BC}} \quad \text{(S43)}$$

From Eqs. (S39) and (S42) it follows that:

$$C_{SP2}^{S2} = C_{liq} \frac{f_{bias}}{f_{bias}^{*}} k_{S2} \quad \text{(S44)}$$

with:

$$k_{S2} := \frac{\eta_{max}^{*}}{\eta_{max}} k_{S1} = \frac{\int_{D_{BC,LDL}}^{D_{BC,UDL}} \varepsilon_{loss}(D_{BC}) \frac{d\tilde{C}_{liq}}{d \log D_{BC}}(D_{BC}) d \log D_{BC}}{\int_{D_{BC,LDL}}^{D_{BC,UDL}} \varepsilon_{loss}(D_{BC}) \frac{d\tilde{C}^{*}_{liq}}{d \log D_{BC}}(D_{BC}) d \log D_{BC}} \quad \text{(S45)}$$

The factor $\frac{f_{bias}}{f_{bias}^{*}} k_{S1}$ in Eq. (S42) quantifies the total error introduced when using the simple Eq. (S35) to infer the BC mass concentration of an aqueous sample from the SP2 measurements of the aqueous sample and an aqueous standard with known concentration (under the assumption of Eq. S34). Likewise, the factor $\frac{f_{bias}}{f_{bias}^{*}} k_{S2}$ in Eq. (S44) quantifies the total error introduced when using the simple Eq. (S37) to infer the BC mass concentration of an aqueous sample from the SP2 measurements of the aqueous sample and an aqueous standard with known concentration (under the slightly less stringent assumption of Eq. S36). From Eq. (S45) and the fact that $\eta_{max}^{*} / \eta_{max}$ is close to unity, follows that k_{S1} and k_{S2} are almost equal. Consequently, the conditions under which Eqs. (S35) and (S37) are valid are similar (the difference being the underlying assumptions, i.e. Eq. S34 for Eq. S35 and Eq. S36 for Eq. S37) and thus these conditions are only discussed for the approach of Eq. (S35) in the following.

The ratio f_{bias} / f_{bias}^{*} in Eq. (S42) quantifies the contribution of SP2 calibration error for the BC in the sample and the standard to the total error when using the simple Eq. (S35). The sensitivity of the SP2 can differ substantially between different BC types (see Moteki and Kondo, 2010, and Laborde et al., 2012) for a detailed discussion of SP2 sensitivity). The

factor $f_{\mathrm{bias}}/f^{*}_{\mathrm{bias}}$ only becomes unity if the correct SP2 calibration curves are applied to evaluate both the measurements of the sample and the standard, or if the calibration biases cancel each other by chance (i.e. if $f_{\mathrm{bias}} \approx f^{*}_{\mathrm{bias}}$). If the correct calibration is known for the standard only (i.e. $f^{*}_{\mathrm{bias}} \approx 1$), then the uncertainty introduced by the factor $f_{\mathrm{bias}}/f^{*}_{\mathrm{bias}}$ reduces to (f_{bias}). Likewise, if the correct calibration is known for the sample only (i.e. $f_{\mathrm{bias}} \approx 1$), then the uncertainty introduced by the factor $f_{\mathrm{bias}}/f^{*}_{\mathrm{bias}}$ reduces to $(f^{*}_{\mathrm{bias}})^{-1}$. If the SP2 sensitivity is neither known for the sample nor the standard, then the same internal SP2 calibration curve should be applied for evaluating the SP2 data from both the sample and standard. Using this strategy, the bias factor in the BC mass concentration inferred with Eq. (S35), which is introduced by the factor $f_{\mathrm{bias}}/f^{*}_{\mathrm{bias}}$ in Eq. (S42), will be unity, if the SP2 is equally sensitive to the BC in the sample and the standard, or it will otherwise reflect the ratio of the SP2 sensitivity to the sample and the standard, as the absolute magnitude of the sensitivities is cancelled.

When applying Eq. (S35), the factor k_{S1} in Eq. (S42) quantifies the error in the determination of the BC mass concentration of the aqueous sample that is associated with the differences in the shape of the mass size distributions of the sample and the standard (note that the values of $D_{\mathrm{BC,LDL}}$ and $D_{\mathrm{BC,UDL}}$ and the size dependence of the efficiency only matter if there is such a difference). Unfortunately, k_{S1} is generally not unity nor can it be evaluated if the BC mass size distributions and $\tilde{\eta}_{\mathrm{BC}}(D)$ are unknown. Equation (S42) thus shows that an error of unknown magnitude is introduced when using Eq. (S35) to infer the BC mass concentration of an aqueous sample from the SP2 measurements of the sample and standard. However, it will be shown in the following that it is possible to further constrain the factor k_{S1} under certain conditions such that Eq. (S35) (and Eq. S37) becomes a valid approach.

S.2.1 Nebulizers with size-dependent efficiency for BC

It has been shown above (Eq. S42) that working with aqueous BC standard suspensions is difficult if the nebulizer efficiency depends on BC size, i.e. if $\eta_{\mathrm{BC}}(D_{\mathrm{BC}}) \neq \mathrm{const}$. An exception is the special case when the shapes of the BC mass size distributions of the aqueous sample and the aqueous standard are equal, i.e. if:

$$\frac{d\tilde{C}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \approx \frac{d\tilde{C}^{*}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \quad \forall\ D_{\mathrm{BC}} \tag{S46}$$

In this case the factor k_{S1} becomes approximately equal to unity and Eq. (S35) becomes valid for any kind of size-dependent nebulizer efficiency. In principle, it is sufficient to relax the condition of Eq. (S46) to:

$$\frac{d\tilde{C}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \approx \frac{d\tilde{C}^{*}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \quad \forall\ D_{\mathrm{BC}} \in \left[D_{\mathrm{BC,LDL}}\,, D_{\mathrm{BC,UDL}}\right] \tag{S47}$$

However, the condition in Eq. (S47) is equivalent to the following pair of conditions (Eqs. S14, S18, S19, and S20):

$$\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \propto \frac{dC^{*}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) \quad \forall\ D_{\mathrm{BC}} \in \left[D_{\mathrm{BC,LDL}}\,, D_{\mathrm{BC,UDL}}\right] \tag{S48}$$

and

$$\Delta\tilde{C}_{\mathrm{LDL}} + \Delta\tilde{C}_{\mathrm{UDL}} \approx \Delta\tilde{C}^{*}_{\mathrm{LDL}} + \Delta\tilde{C}^{*}_{\mathrm{UDL}} \tag{S49}$$

These two conditions are hardly fulfilled if the shapes of the BC mass size distributions of the sample and the standard differ outside the detection range of the SP2. Thus the more restrictive condition (Eq. S46) of agreement between the size distribution shapes of sample and standard must essentially be fulfilled over the whole size range of BC cores for the validity of Eq. (S35), if the nebulizer efficiency is size-dependent.

The factor k_{S1} (Eq. S43) only contains the relative size dependence of the nebulizer efficiency, $\tilde{\eta}_{\mathrm{BC}}(D)$, while the factor for the absolute efficiency, $\eta_{\mathrm{BC,ref}}$, got cancelled. This indicates that using an aqueous standard as a reference can provide quantitative results if the relative size dependence of the nebulizer efficiency for BC is known. In such cases, the following equation can be used to infer the BC mass concentration, $C^{\mathrm{S}\eta}_{\mathrm{SP2}}$, in the aqueous sample of interest from the SP2 measurements of the nebulized sample and standard, taking into account the relative size dependence of the nebulizer efficiency:

$$C^{\mathrm{S}\eta}_{\mathrm{SP2}} := \int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} \frac{1}{\tilde{\eta}_{\mathrm{BC}}(D)} \frac{dc_{\mathrm{SP2}}}{d\log D}(D) d\log D \frac{C^{*}_{\mathrm{liq}}}{\int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} \frac{1}{\tilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}})} \frac{dc^{*}_{\mathrm{SP2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) d\log D_{\mathrm{BC}}} \tag{S50}$$

Inserting Eq. (S27) into Eq. (S50) in a first step and Eq. (S28) in a second step provides:

$$C_{\mathrm{SP2}}^{\mathrm{S}\eta} = C_{\mathrm{SP2}}^{\eta} \frac{C_{\mathrm{liq}}^{*}}{C_{\mathrm{SP2}}^{\eta,*}} = C_{\mathrm{liq}} \frac{f_{\mathrm{bias}}}{f_{\mathrm{bias}}^{*}} \frac{\left(1 - \Delta\widetilde{C}_{\mathrm{LDL}} - \Delta\widetilde{C}_{\mathrm{UDL}}\right)}{\left(1 - \Delta\widetilde{C}_{\mathrm{LDL}}^{*} - \Delta\widetilde{C}_{\mathrm{UDL}}^{*}\right)} \tag{S51}$$

Equation (S51) can be written as:

$$C_{\mathrm{SP2}}^{\mathrm{S}\eta} = C_{\mathrm{liq}} \frac{f_{\mathrm{bias}}}{f_{\mathrm{bias}}^{*}} k_{\mathrm{fract}} \tag{S52}$$

with:

$$k_{\mathrm{fract}} := \frac{1 - \Delta\widetilde{C}_{\mathrm{LDL}} - \Delta\widetilde{C}_{\mathrm{UDL}}}{1 - \Delta\widetilde{C}_{\mathrm{LDL}}^{*} - \Delta\widetilde{C}_{\mathrm{UDL}}^{*}} \tag{S53}$$

The factor $\frac{f_{\mathrm{bias}}}{f_{\mathrm{bias}}^{*}} k_{\mathrm{fract}}$ in Eq. (S52) quantifies the total error introduced when using Eq. (S50) to infer the BC mass concentration of an aqueous sample from the SP2 measurements of the aqueous sample and an aqueous standard with known concentration and with accounting for the relative size dependence of the nebulizer efficiency (note that the assumption of Eq. S34 needs to be satisfied for Eq. S52 to be valid). The ratio $f_{\mathrm{bias}} / f_{\mathrm{bias}}^{*}$ quantifies the contribution of SP2 calibration errors for the BC in the sample and the standard to the total error, as already discussed above. The factor k_{fract} quantifies the contribution to the total error associated with BC cores in the sample and/or standard outside the detection range of the SP2.

If the contribution of BC cores outside the detection range of the SP2 to the total BC mass is negligible for both the sample and the standard (Eq. S30 is fulfilled for the sample and the standard) then it follows that $k_{\mathrm{fract}} \approx 1$. Thus, Eqs. (S52) and (S53) show that Eq. (S50) can be used to accurately determine the BC mass in the aqueous sample, except for potential SP2 calibration errors, by relating it to the measurement of an aqueous BC standard, if the relative size dependence of the nebulizer efficiency for BC is known and if the SP2 measurement covers the full range of the BC mass size distributions in both the sample and the standard (i.e. if Eq. (S30) is fulfilled for the sample and the standard). Additionally, the nebulizer efficiency for BC must be different from zero across the measurement range of the SP2 (i.e. Eq. S29 must be fulfilled). Otherwise, the integration in Eq. (S50) must be restricted to the range across which the nebulizer is sufficiently efficient, thereby potentially increasing the unaccounted BC mass fraction of the sample and/or the standard.

If the BC mass size distribution of the aqueous sample extends beyond the detection range of the SP2 (Eq. S30 is not fulfilled for the sample), it follows from Eqs. (S52) and (S53) that Eq. (S50) still provides an accurate value for the BC mass concentration in the aqueous sample within the detection range of the SP2 (as long as Eq. S30 is fulfilled for the standard, i.e. if the aqueous standard fully falls within the detection range of the SP2).

It also follows from Eqs. (S52) and (S53) that the BC mass concentration in an aqueous sample within the detection range of the SP2 is overestimated by the factor $(1-\Delta\widetilde{C}^{*}_{\mathrm{LDL}}-\Delta\widetilde{C}^{*}_{\mathrm{UDL}})^{-1}$ when applying Eq. (S50) and using an aqueous standard with a substantial portion of the BC mass outside the detection range of the SP2 (Eq. S30 is not fulfilled for the standard).

S.2.2 Nebulizers with size-independent efficiency for BC

Nebulizers with size-independent efficiency for the nebulization of BC fulfill:

$$\begin{aligned}\eta_{\mathrm{BC}}(D_{\mathrm{BC}}) \approx \eta_{\mathrm{BC,ref}} \;&\Leftrightarrow \widetilde{\eta}_{\mathrm{BC}}(D_{\mathrm{BC}}) \\ &\approx 1 \;\forall\; D_{\mathrm{BC}} \in \left[\min(D_{\mathrm{BC,min}}, D^{*}_{\mathrm{BC,min}}), \max(D_{\mathrm{BC,max}}, D^{*}_{\mathrm{BC,max}})\right]\end{aligned} \tag{S54}$$

The assumption of Eq. (S54) together with Eqs. (S21), (S43) and (S53) yields:

$$k_{\mathrm{S1}} \approx \frac{\int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} \frac{d\widetilde{C}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})\, d\log D_{\mathrm{BC}}}{\int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} \frac{d\widetilde{C}^{*}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})\, d\log D_{\mathrm{BC}}} = \frac{1-\Delta\widetilde{C}_{\mathrm{LDL}}-\Delta\widetilde{C}_{\mathrm{UDL}}}{1-\Delta\widetilde{C}^{*}_{\mathrm{LDL}}-\Delta\widetilde{C}^{*}_{\mathrm{UDL}}} = k_{\mathrm{fract}} \tag{S55}$$

Equation (S42) then simplifies to:

$$C^{\mathrm{S1}}_{\mathrm{SP2}} \approx C_{\mathrm{liq}} \frac{f_{\mathrm{bias}}}{f^{*}_{\mathrm{bias}}} k_{\mathrm{fract}} \tag{S56}$$

where k_{fract} is defined in Eq. (S53).

The ratio $f_{\mathrm{bias}} / f^{*}_{\mathrm{bias}}$ in Eq. (S56) quantifies the contribution of SP2 calibration errors, as discussed above, for the BC in the sample and the standard to the total error when using the approach of Eq. (S35) for a size-independent nebulizer efficiency. If the contribution of BC cores outside the detection range of the SP2 to the total BC mass is negligible for both the sample and the standard (Eq. S30 is fulfilled for the sample and the standard), it follows that

$k_{\text{fract}} \approx 1$. Equation (S56) thus shows that Eq. (S35) can be used to determine the BC mass concentration of an aqueous sample from the SP2 measurements of the nebulized sample and standard, if the nebulizer efficiency is independent of particle size and if the BC cores smaller and larger than the LDL and UDL of the SP2, respectively, only give a negligible contribution to the total BC mass for both the aqueous sample and the aqueous standard.

If the BC mass size distribution of the aqueous sample extends beyond the detection range of the SP2 (Eq. S30 is not fulfilled for the sample), then follows from Eqs. (S53) and (S56) that Eq. (S35) still provides an accurate value for the BC mass concentration in the aqueous sample within the detection range of the SP2 (as long as Eq. S30 is fulfilled for the standard, i.e. if the aqueous standard fully falls within the detection range of the SP2).

It also follows from Eqs. (S53) and (S56) that the BC mass concentration in an aqueous sample within the detection range of the SP2 is overestimated by the factor $(1-\Delta\widetilde{C}^{*}_{\text{LDL}}-\Delta\widetilde{C}^{*}_{\text{UDL}})^{-1}$ when applying Eq. (S35) and using an aqueous standard with a substantial portion of the BC mass outside the detection range of the SP2 (Eq. S30 is not fulfilled for the standard). Thus, Eq. (S35) can generally not be applied for such standards without introducing a bias.

An exception, where Eq. (S35) is valid even if Eq. (S30) is not fulfilled for the standard, is when the shapes of the BC mass size distributions of the aqueous sample and the aqueous standard are equal for all diameters (i.e., Eq. (S46) is fulfilled, which also implies $D_{\text{min}} \approx D^{*}_{\text{min}}$ and $D_{\text{max}} \approx D^{*}_{\text{max}}$). In this case follows $1-\Delta\widetilde{C}_{\text{LDL}}+\Delta\widetilde{C}_{\text{UDL}} \approx 1-\Delta\widetilde{C}^{*}_{\text{LDL}}+\Delta\widetilde{C}^{*}_{\text{UDL}}$ and hence $k_{\text{fract}} \approx 1$, such that only potential calibration biases remain left in Eq. (S56):

$$C^{\text{S1}}_{\text{SP2}} \approx C_{\text{liq}} \frac{f_{\text{bias}}}{f^{*}_{\text{bias}}} \tag{S57}$$

S.3 Measurement of the nebulizer efficiency

S.3.1 Nebulizer efficiency for PSLs

It is quite straightforward to produce a PSL standard suspensions from PSL size standards (see Sect. 2.4.2 in main text), i.e. an aqueous suspension with known number concentration of PSL spheres, $N_{\text{liq,PSL}}$, of a well-defined diameter, D_{PSL}. The aerosol obtained by nebulizing such a standard contains the PSL spheres with diameter D_{PSL} and, for the most part, very

small particles that emerge from the residual solutes in each droplet. The residual particles can be distinguished from the PSL spheres based on their size. Therefore, the number concentration of the target PSL particles, $n_{air,PSL}$, can be measured by the SP2 using the light scattering detector (the SP2 has a detection efficiency of unity for purely scattering particles with sizes above the LDL of the light scattering detector). The nebulizer efficiency for PSLs is then directly obtained with Eq. (S5). Figure 2a in the main text shows the normalized overall nebulizer efficiency for PSLs, $\widetilde{\eta}_{\mathrm{PSL}}$, for the three investigated nebulizer types. Normalization was done according to Eqs. (S6) and (S7), where different reference diameters, $D_{\mathrm{PSL,\,ref}}$, are chosen for the different nebulizers in such a manner that $\widetilde{\eta}_{\mathrm{PSL}}$ is unity at the PSL diameter with maximal efficiency. The reference PSL diameters, normalization factors and coefficients for the fitted efficiency curves are provided in Table S2 for all nebulizers.

Logarithmic functions were used to fit the efficiency curves of the APEX and Collison-type nebulizers:

$$\widetilde{\eta}_{\mathrm{PSL}}^{\mathrm{APEX\text{-}PSI}}(D_{\mathrm{PSL}}) = c_0 + c_1 \ln\left(D_{\mathrm{PSL}}\right) \tag{S58}$$

and

$$\widetilde{\eta}_{\mathrm{PSL}}^{\mathrm{Collison\text{-}PSI}}(D_{\mathrm{PSL}}) = c_0 + c_1 \ln\left(D_{\mathrm{PSL}}\right) \tag{S59}$$

The efficiency curve of PSI's CETAC nebulizer was fitted with a skewed Gauss function:

$$\widetilde{\eta}_{\mathrm{PSL}}^{\mathrm{CETAC\text{-}PSI}}(D_{\mathrm{PSL}}) = 2\, f_{\mathrm{Gauss}}(D_{\mathrm{PSL}}, c_0, c_1, c_2)\, f_{\mathrm{GaussCDF}}(c_3(D_{\mathrm{PSL}} - c_2), c_1) \tag{S60}$$

with the Gauss function

$$f_{\mathrm{Gauss}}(x, N, \sigma, \bar{x}) = \frac{N}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-\bar{x})^2}{2\sigma^2}\right) \tag{S61}$$

and the cumulative Gauss function

$$f_{\mathrm{GaussCDF}}(x, \sigma) = \frac{1}{2}\left(1 + \mathrm{erf}\left(\frac{x}{\sigma\sqrt{2}}\right)\right) \tag{S62}$$

where erf denotes the error function.

The efficiency curve of CWU's CETAC nebulizer was fitted with a Hill-equation:

$$\tilde{\eta}_{\mathrm{PSL}}^{\mathrm{CETAC\text{-}CWU}}(D_{\mathrm{PSL}}) = c_0 + \frac{c_1 - c_0}{1 + \left(c_3 / D_{\mathrm{PSL}} \right)^{c_2}} \quad \text{(S63)}$$

Table S2 – Efficiency curves of the different nebulizers for PSLs.

Nebulizer	$D_{\mathrm{PSL,\,ref}}$ [µm]	$\eta_{\mathrm{PSL,ref}}$ [-]	c_0	c_1	c_2	c_3
APEX-PSI[a]	1.000	$3.16 \cdot 10^{-2}$	1	0.107	-	-
Collison-PSI[a]	0.100	$4.78 \cdot 10^{-3}$	0.356	-0.280	-	-
CETAC-PSI[a]	0.405	$4.80 \cdot 10^{-2}$	0.556	0.296	0.245	1.39
CETAC-CWU[b]	0.220	0.108	1	-0.0259	5.76	0.589

[a]valid for the PSL diameter range 0.1–1.0 µm

[b]valid for the PSL diameter range 0.22–1.025 µm

S.3.2 Quantifying the losses of PSL particles in the CETAC nebulizer

All relevant water and air flow rates, $Q_{\mathrm{liq,supply}}$, $Q_{\mathrm{liq,drain}}$, and $q_{\mathrm{air,aerosol}}$, can be measured when using a CETAC nebulizer, such that an upper limit for the overall nebulizer efficiency, $\eta_{\mathrm{max,CETAC}}$, can be calculated with Eq. (S12). Substituting $\eta_{\mathrm{max,CETAC}}$ for $\eta_{\mathrm{BC}}(D_{\mathrm{BC}})$ in Eq. (S27) thus provides a lower limit for the true BC mass concentration of the sample (Eq. S32). However, the true BC mass concentration will be substantially higher than the lower limit obtained in this way, as $\varepsilon_{\mathrm{loss,CETAC}}$ is substantially smaller than unity. Eqs. (S12) and (S13) were used to calculate $\varepsilon_{\mathrm{loss,CETAC}}$ from the overall nebulizer efficiency, $\eta_{\mathrm{PSL,CETAC}}(D_{\mathrm{PSL}})$, measured for the PSL standards (see above). Figure S1 reveals that the fraction of lost particles, $\varepsilon_{\mathrm{loss,CETAC}}$, differs significantly between the PSI- and CWU nebulizer. Consequently, it is not possible to rely on literature values for the CETAC nebulizer efficiency. Instead every nebulizer needs to be tested (and stable performance also needs to be ensured) if the shape and/ or absolute values of the nebulizer efficiency curve is relevant. Both nebulizers have in common that $\varepsilon_{\mathrm{loss,CETAC}}$ remains below ~0.2–0.3 at any diameter (i.e. at least 70–80% losses) and that $\varepsilon_{\mathrm{loss,CETAC}}$ sharply drops above PSL diameters of ~450–500 nm. $\varepsilon_{\mathrm{loss}}$ depends on (1) potential losses of insoluble particles between the aqueous sample and the point of

nebulization, (2) on the probability that an insoluble particle is incorporated into a droplet if the portion of aqueous sample where it resides is nebulized, i.e. that it is not lost during the process of droplet generation at e.g. the ultrasonic membrane of the ultrasonic nebulizer, as well as (3) on potential losses of insoluble particles between the point of nebulization and the aerosol outlet of the nebulizer unit including the dryer.

It is not possible to quantify the loss factor $\varepsilon_{\mathrm{loss}}$ for the APEX or Collison type nebulizers applied in this study in a similar manner, as not all aqueous and air flow rates required to calculate $\varepsilon_{\mathrm{loss}}$ are known.

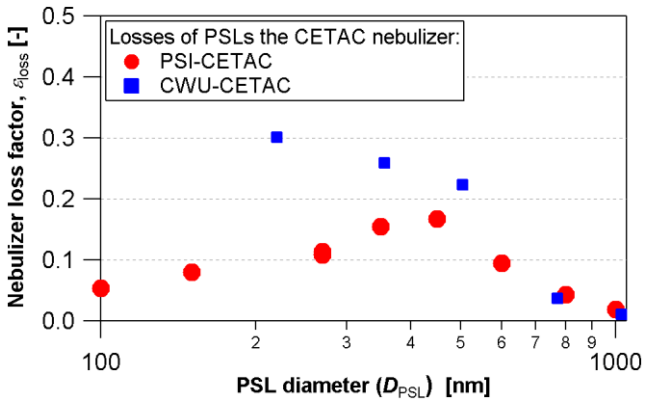

Figure S1 – Losses in the PSI- and CWU-CETAC nebulizer as derived from the measurements of the PSL standard suspensions.

S.3.3 Nebulizer efficiency for BC

Both PSL spheres and BC particles are insoluble in water, but they typically have a different material density and shape. Thus, the nebulizer efficiency for BC particles may potentially differ from that for PSL spheres. The loss processes in the nebulizer may for example depend on the mobility diameter, mass equivalent diameter or aerodynamic diameter of a particle. It is, therefore, not quite clear which type of diameter should be used to estimate the nebulizer efficiency for BC particles from the measured efficiency for PSL spheres.

The nebulizer efficiency for BC particles cannot be directly measured, as no aqueous standards containing a known number concentration of BC particles with a well-defined size are available. It is also not straightforward to infer it from measurements of the nebulizer efficiency for PSL spheres, as the loss processes in the nebulizer may depend on the mobility diameter, mass equivalent diameter, aerodynamic diameter and/or further particle properties.

Nevertheless, the aerosols produced with two different nebulizers from the same aqueous BC sample makes it possible to test whether BC particles behave similar to PSL particles. Taking the ratio of the BC mass size distributions measured by the SP2 for two nebulizers "neb1" and "neb2" and inserting Eq. (S23) provides:

$$\frac{\frac{dc_{\mathrm{SP2}}^{\mathrm{neb1}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})}{\frac{dc_{\mathrm{SP2}}^{\mathrm{neb2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})} = \frac{\eta_{\mathrm{BC}}^{\mathrm{neb1}}(D_{\mathrm{BC}})\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})}{\eta_{\mathrm{BC}}^{\mathrm{neb2}}(D_{\mathrm{BC}})\frac{dC_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})} \tag{S64}$$

Solving for $\eta_{\mathrm{BC}}^{\mathrm{neb1}}$ provides:

$$\eta_{\mathrm{BC}}^{\mathrm{neb1}}(D_{\mathrm{BC}}) = \eta_{\mathrm{BC}}^{\mathrm{neb2}}(D_{\mathrm{BC}})\frac{\frac{dc_{\mathrm{SP2}}^{\mathrm{neb1}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})}{\frac{dc_{\mathrm{SP2}}^{\mathrm{neb2}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})} \tag{S65}$$

Fortunately, the efficiency of the APEX nebulizer depends only weakly on particle size (see Sect. 3.1.1 in main text), such that it can be assumed that its efficiency for BC (as a function of BC mass equivalent diameter) is approximately equal to that for PSL spheres (as a function of PSL diameter), i.e.:

$$\eta_{\mathrm{BC}}^{\mathrm{APEX}}(D_{\mathrm{BC}}) \approx \eta_{\mathrm{PSL}}^{\mathrm{APEX}}(D_{\mathrm{PSL}}) \tag{S66}$$

From Eq. (S65) and (S66) (and defining the APEX as the second nebulizer) follows:

$$\eta_{\mathrm{BC}}^{\mathrm{neb1}}(D_{\mathrm{BC}}) \approx \eta_{\mathrm{PSL}}^{\mathrm{APEX}}(D_{\mathrm{PSL}})\frac{\frac{dc_{\mathrm{SP2}}^{\mathrm{neb1}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})}{\frac{dc_{\mathrm{SP2}}^{\mathrm{APEX}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})} \tag{S67}$$

Equation (S67) can be used to determine the efficiency of any nebulizer "neb1" expressed as a function of BC mass equivalent diameter (D_{BC}) to a degree of approximation which depends on the validity of the assumption made in Eq. (S66).

The mobility diameter, D_{mob}, of a BC particle normally differs from its mass equivalent diameter, D_{BC}, as they are typically non-spherical. The relationship between D_{BC} and D_{mob} can be expressed as:

$$D_{\mathrm{BC}} = D_{\mathrm{mob}}\left(\frac{\rho_{\mathrm{eff,BC}}(D_{\mathrm{mob}})}{\rho_{\mathrm{bulk,BC}}}\right)^{1/3} \tag{S68}$$

where $\rho_{\mathrm{bulk,BC}}$ is the void-free material density of BC (1'800 kg m^{-3}) and $\rho_{\mathrm{eff,BC}}$ is the size-dependent effective density of the BC particles as defined in Gysel et al. (2011).

The nebulizer efficiency for BC particles, $\hat{\eta}_{\mathrm{BC}}$, as a function of the mobility diameter of the BC core is related to the efficiency as a function of the mass equivalent diameter:

$$\hat{\eta}_{\mathrm{BC}}(D_{\mathrm{mob}}) = \eta_{\mathrm{BC}}\left(D_{\mathrm{mob}}\left(\frac{\rho_{\mathrm{eff,BC}}(D_{\mathrm{mob}})}{\rho_{\mathrm{bulk,BC}}}\right)^{1/3}\right) \tag{S69}$$

Inserting Eq. (S69) into Eq. (S65) provides:

$$\hat{\eta}_{\mathrm{BC}}^{\mathrm{neb1}}(D_{\mathrm{mob}}) = \hat{\eta}_{\mathrm{BC}}^{\mathrm{neb2}}(D_{\mathrm{mob}})\frac{\frac{dc_{\mathrm{SP2}}^{\mathrm{neb1}}}{d\log D}\left(D_{\mathrm{mob}}\left(\frac{\rho_{\mathrm{eff,BC}}(D_{\mathrm{mob}})}{\rho_{\mathrm{bulk,BC}}}\right)^{1/3}\right)}{\frac{dc_{\mathrm{SP2}}^{\mathrm{APEX}}}{d\log D}\left(D_{\mathrm{mob}}\left(\frac{\rho_{\mathrm{eff,BC}}(D_{\mathrm{mob}})}{\rho_{\mathrm{bulk,BC}}}\right)^{1/3}\right)} \tag{S70}$$

Similar to Eq. (S66), it can be argued that

$$\hat{\eta}_{\mathrm{BC}}^{\mathrm{APEX}}(D_{\mathrm{mob}}) \approx \eta_{\mathrm{PSL}}^{\mathrm{APEX}}(D_{\mathrm{mob}}) \tag{S71}$$

is likely fulfilled in good approximation. Combining Eqs. (S70) and (S71) provides:

$$\hat{\eta}_{\mathrm{BC}}^{\mathrm{neb1}}(D_{\mathrm{mob}}) \approx \eta_{\mathrm{PSL}}^{\mathrm{APEX}}(D_{\mathrm{mob}})\frac{\frac{dc_{\mathrm{SP2}}^{\mathrm{neb1}}}{d\log D}\left(D_{\mathrm{mob}}\left(\frac{\rho_{\mathrm{eff,BC}}(D_{\mathrm{mob}})}{\rho_{\mathrm{bulk,BC}}}\right)^{1/3}\right)}{\frac{dc_{\mathrm{SP2}}^{\mathrm{APEX}}}{d\log D}\left(D_{\mathrm{mob}}\left(\frac{\rho_{\mathrm{eff,BC}}(D_{\mathrm{mob}})}{\rho_{\mathrm{bulk,BC}}}\right)^{1/3}\right)} \tag{S72}$$

Equation (S72) can be used to determine the efficiency of any nebulizer "neb1" expressed as a function of the mobility diameter in good approximation, provided that Eq. (S71) is fulfilled and that the effective density is known for the BC sample that is used to test the nebulizers.

In this study AQ was used to determine the nebulizer efficiency for BC particles, as the effective density for AQ particles is available in the literature (Gysel et al., 2011). Equations (S67) and (S72) were then used to infer η_{BC} and $\hat{\eta}_{\mathrm{BC}}$, respectively, for the CETAC and Collision type nebulizers (see Sect. 3.1.1 in main text).

S.3.4 Testing the approach of using standards for the CETAC nebulizer

Above it has been shown that it is, under certain circumstances, possible to use standard suspensions with known BC concentrations as a reference for the measurement of aqueous BC samples of unknown concentration (Eqs. (S35) or (S37)). Some tests to confirm the validity of this approach include e.g. the measurement of different types of BC standards or of dilution series (i.e. equal BC material but variable concentration). This has been done using CWU's CETAC nebulizer in order to test whether or not the factor $C^{*}_{\mathrm{liq}} \big/ C^{\eta,*}_{\mathrm{SP2,low}}$ in Eq. (S37) is independent of BC standard concentration and standard material. The results provided in the main text (Sect. 3.2) revealed considerable differences in the factor $C^{*}_{\mathrm{liq}} \big/ C^{\eta,*}_{\mathrm{SP2,low}}$ determined with different BC standards. The reasons for this will be elucidated in the following.

From Eqs. (S14), (S32), and (S23) follows:

$$\frac{C^{*}_{\mathrm{liq}}}{C^{\eta,*}_{\mathrm{SP2,low}}} = \frac{\int_{D^{*}_{\mathrm{BC,min}}}^{D^{*}_{\mathrm{BC,max}}} \frac{dC^{*}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})\, d\log D_{\mathrm{BC}}}{\frac{1}{\eta^{*}_{\max}} \int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} f^{*}_{\mathrm{bias}} \eta^{*}_{\mathrm{BC}}(D_{\mathrm{BC}}) \frac{dC^{*}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})\, d\log D_{\mathrm{BC}}} \tag{S73}$$

Further inserting Eqs. (S13) and (S18) into Eq. (S73) provides:

$$\frac{C^{*}_{\mathrm{liq}}}{C^{\eta,*}_{\mathrm{SP2,low}}} = \frac{1}{f^{*}_{\mathrm{bias}}} \frac{1}{\int_{D_{\mathrm{BC,LDL}}}^{D_{\mathrm{BC,UDL}}} \varepsilon^{*}_{\mathrm{loss}}(D_{\mathrm{BC}}) \frac{d\widetilde{C}^{*}_{\mathrm{liq}}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}})\, d\log D_{\mathrm{BC}}} \tag{S74}$$

Equation (S74) can be simplified if the losses of particles in the whole nebulizer system are independent of particle size, i.e. if:

$$\varepsilon^{*}_{\mathrm{loss}}(D_{\mathrm{BC}}) \approx \varepsilon^{*}_{\mathrm{loss}} = \mathrm{const.} \qquad \forall \quad D_{\mathrm{BC}} \in \left[D_{\mathrm{BC,LDL}}, D_{\mathrm{BC,UDL}}\right] \tag{S75}$$

Inserting Eq. (S75) into Eq. (S74) provides (with inserting Eq. S21):

$$\frac{C_{\mathrm{liq}}^{*}}{C_{\mathrm{SP2,low}}^{\eta,*}} \approx \frac{1}{f_{\mathrm{bias}}^{*}} \frac{1}{\varepsilon_{\mathrm{loss}}^{*}} \frac{1}{\int_{D_{\mathrm{BC,\,LDL}}}^{D_{\mathrm{BC,\,UDL}}} \frac{d\widetilde{C}_{\mathrm{liq}}^{*}}{d\log D_{\mathrm{BC}}}(D_{\mathrm{BC}}) d\log D_{\mathrm{BC}}} = \frac{1}{f_{\mathrm{bias}}^{*}} \frac{1}{\varepsilon_{\mathrm{loss}}^{*}} \frac{1}{1-\Delta\widetilde{C}_{\mathrm{LDL}}^{*}-\Delta\widetilde{C}_{\mathrm{UDL}}^{*}} \quad . \tag{S76}$$

If there is no bias of the SP2 calibration for the BC type in the aqueous BC standard, one has:

$$f_{\mathrm{bias}}^{*} \approx 1 \Leftrightarrow {f_{\mathrm{bias}}^{*}}^{-1} \approx 1 \tag{S77}$$

If the whole BC mass size distribution of the aqueous standard falls within the detection range of the SP2, i.e. if Eq. (S30) is fulfilled for the BC standard, follows:

$$(1-\Delta\widetilde{C}_{\mathrm{LDL}}^{*}-\Delta\widetilde{C}_{\mathrm{UDL}}^{*})^{-1} \approx 1 \tag{S78}$$

If both Eqs. (S77) and (S78) are fulfilled, then Eq. (S76) finally simplifies to:

$$\frac{C_{\mathrm{liq}}^{*}}{C_{\mathrm{SP2,low}}^{\eta,*}} \approx \frac{1}{\varepsilon_{\mathrm{loss}}^{*}} \geq 1 \tag{S79}$$

Equation (S79) is independent of the choice made for the type of aqueous BC standard (independence of $\varepsilon_{\mathrm{loss}}^{*}$ on the type of BC is an assumption that is inherently required when working with BC standards), while this does not apply for Eqs. (S74) and (S76). This implies that applying Eq. (S37) cannot provide accurate results by using an aqueous BC standard unless the BC standard fulfills Eqs. (S77) and (S30) (i.e. there is no bias of the SP2 calibration to the BC type in the aqueous BC standard and the whole BC mass size distribution of the aqueous standard falls within the detection range of the SP2), and the nebulizer system fulfills Eq. (S75) (i.e. the nebulizer losses are independent of particle size). It further implies that Eqs. (S77) and (S30) are the only conditions to be fulfilled by an aqueous standard from a mathematical point of view (other reasons such as stability of the aqueous suspension also play a role when choosing a material for the aqueous BC standards).

Unknown sensitivity of the SP2 to the BC type of the aqueous BC standard results in an uncertainty of the magnitude ${f_{\mathrm{bias}}^{*}}^{-1}$ (see e.g. Moteki and Kondo, 2010, and Laborde et al., 2012, for a detailed discussion of SP2 sensitivity). If the aqueous BC standard contains substantial contribution to the total BC mass from BC cores with sizes outside the detection

range of the SP2 (i.e. Eq. S30 is not fulfilled for the standard), then the factor $(1-\Delta\widetilde{C}^{*}_{\mathrm{LDL}}-\Delta\widetilde{C}^{*}_{\mathrm{UDL}})^{-1}$ becomes greater than unity and it follows from Eq. (S76) that the BC mass concentration inferred with Eq. (S37) overestimates the true value.

Equation (S76) shows that the ratio $C^{*}_{\mathrm{liq}}/C^{\eta,*}_{\mathrm{SP2,low}}$ essentially characterizes the particle losses in the nebulizer system. However, if the particle losses in the nebulizer system depend on particle size (Eq. S75 is not fulfilled), then the ratio $C^{*}_{\mathrm{liq}}/C^{\eta,*}_{\mathrm{SP2,low}}$ contains a factor representing a "weighted average of $\varepsilon^{*}_{\mathrm{loss}}(D_{\mathrm{BC}})$ over all diameters between $D_{\mathrm{BC,LDL}}$ and $D_{\mathrm{BC,UDL}}$ with the shape of the BC mass size distribution of the standard as a weighting function" (see Eq. S74). The ratio $C^{*}_{\mathrm{liq}}/C^{\eta,*}_{\mathrm{SP2,low}}$ then becomes dependent on the choice of the aqueous BC standard, thereby introducing uncertainty when applying the approach of Eq. (S37). The conclusion drawn here about the factors that make the ratio $C^{*}_{\mathrm{liq}}/C^{\eta,*}_{\mathrm{SP2,low}}$ dependent on the choice of the aqueous BC standard, reflect a subset of the complete set of conditions under which the approaches of Eqs. (S35) and (S37) are valid (see earlier section).

S.4 Correct treatment of non-BC matter in BC standard materials

Not all BC materials available for preparing aqueous BC standard suspensions are pure BC. The BC mass fraction, γ^{*}_{BC}, of Fullerene Soot is almost 100% (Gysel et al., 2011; Moteki and Kondo, 2010), while of dried AQ particles it is only around 70.5% (this study; similar to the 76% found in Gysel et al. (2011). This fact must be considered when working with aqueous BC standards for the quantification of BC in aqueous samples using Eqs. (S35) or (S37), specifically when determining the factor $C^{*}_{\mathrm{liq}}/c^{*}_{\mathrm{SP2}}$ or $C^{*}_{\mathrm{liq}}/C^{\eta,*}_{\mathrm{SP2,low}}$, respectively. Practically, this means that the BC mass concentration of an aqueous BC standard (C^{*}_{liq}) must be calculated from the mass concentration of water-insoluble particulate matter in an aqueous standard (M^{*}_{liq}):

$$C^{*}_{\mathrm{liq}}=\gamma^{*}_{\mathrm{BC}}M^{*}_{\mathrm{liq}} \tag{S80}$$

At the same time, the SP2 response to the standard particles must be calibrated for the BC mass in the particles rather than the total particle mass, i.e. when selecting the standard particles by an aerosol particle mass analyzer to provide particles of a well defined mass to the SP2 during internal calibration of the SP2 (such as e.g. described in Gysel et al., 2011). It

is important to correct this nominal mass of the selected particles with the factor γ^*_{BC} in order to get the BC mass in these particles. The factor γ^*_{BC} gets cancelled in the ratio $C^*_{\mathrm{liq}}/c^*_{\mathrm{SP2}}$ or $C^*_{\mathrm{liq}}/C^{\eta,*}_{\mathrm{SP2,low}}$ because it shows up both in the nominator and the denominator. Consequently, it is also possible to ignore the factor γ^*_{BC} for the preparation of an aqueous BC standard and in the internal SP2 calibration curve applied in the analysis of the SP2 measurement of the standard. This reflects the fact that the ratio $C^*_{\mathrm{liq}}/c^*_{\mathrm{SP2}}$ or $C^*_{\mathrm{liq}}/C^{\eta,*}_{\mathrm{SP2,low}}$ is simply used to quantify the nebulizer efficiency for insoluble particles and it is in principle possible to use any insoluble material that is detectable by the SP2 in a quantitative manner and that fulfils the other requirements for preparing an aqueous standard. However, materials with a substantial mass fraction of water-soluble components are not suitable for preparing aqueous standards, because water-soluble matter is redistributed in an uncontrolled manner between droplets with/without insoluble inclusion, when producing an aerosol by nebulization of an aqueous suspension.

S.5 The SP2 sensitivity to different BC types and associated measurement uncertainties

The sensitivity of the SP2 to BC mass depends on the chemical structure of the BC, i.e. graphitic versus disordered. Previous studies (Laborde et al., 2012; Moteki and Kondo, 2010) indicate that the sensitivity of the SP2 to BC in diesel exhaust, wood combustion exhaust and atmospheric particles is similar to its sensitivity to fullerene soot, while it is more sensitive to AQ particles (i.e. ~40% more sensitive without accounting for the non-BC matter in AQ, ~80% more sensitive with accounting for this). Thus, fullerene soot has been recommended as an SP2 calibration material for atmospheric applications (Baumgardner et al., 2012).

The value c_{SP2} or $C^{\eta}_{\mathrm{SP2,low}}$ in Eqs. (S35) or (S37), respectively, must always be evaluated with an SP2 calibration that matches the SP2 sensitivity to BC mass of the BC type in the sample under investigation as close as possible (i.e. in order to keep the factor f_{bias} in Eqs. (S42) or (S44) as close as possible to unity). The SP2 has a broadband and narrowband incandescence detector. The signal ratio in the two channels, commonly referred to as band ratio or colour ratio, also differs between different BC types. Ambient BC often exhibits the same band ratio as fullerene soot, while that of AQ is different. However, the band ratio of ambient BC is occasionally more similar to that of AQ. Likewise, the band ratio of BC from ice core and

snow samples sometimes resembles that of fullerene soot, sometimes that of AQ. If the band ratio of a sample under investigation differs from the band ratio of the material used for internal calibration of the SP2, then follows that applying such calibration data will result in biased BC mass measurements for at least one incandescence channel (possibly even both). Inversely, it might be interpreted as evidence that a calibration material is suitable, if its band ratio matches that of the sample under investigation, though this is not a proof. Consequently, it is suggested to apply fullerene soot calibration curves for the evaluation of aqueous samples that exhibit the same band ratio as fullerene soot. If the band ratio of an aqueous sample is more similar to that of AQ, then it is suggested to apply an AQ calibration. Whether or not to correct the AQ calibration curve for the BC mass fraction in AQ particles is difficult to answer. From a conceptual point of view this correction should be done. However, the uncorrected AQ calibration falls in between the two extremes corresponding to fullerene soot calibration and the corrected AQ calibration (which differ by 80%). Thus, applying the uncorrected AQ calibration might be better in order the keep the potential calibration bias within ~±40% if the true calibration is not really known. If the band ratio is not available or does not give any indication for the choice of the calibration material, then it is suggested to apply the fullerene soot calibration as recommended by Baumgardner at al. (2012). However, the measurement bias in such cases may be as high as 40–80%. The discussion above solely affects the choice of the internal SP2 calibration curve that is to be applied for the evaluation of the measurements of the aqueous sample, i.e. to determine C_{SP2}^{η}, c_{SP2} or $C_{\mathrm{SP2,low}}^{\eta}$ when working with the approaches of Eqs. (S27), (S35) or (S37), respectively. However, it does not affect the choice of the BC material that is used to prepare aqueous BC standards. Any BC material with known SP2 sensitivity, which is suitable for preparing aqueous standards, can be used when working with the approaches of Eqs. (S35) or (S37), but it is important to apply the internal SP2 calibration curve for the standard material when calculating c_{SP2}^{*} or $C_{\mathrm{SP2,low}}^{\eta,*}$, respectively, in order to keep the factor f_{bias}^{*} in Eqs. (S42) or (S44) as close as possible to unity (see also previous discussion above). If the SP2 sensitivity to the BC type in the standard material is not known, then a measurement uncertainty of at least 40% is introduced.

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