

1 **Supplementary Material**

2 **Equations and details for the calculations**

3 **Acronyms:**

4 LDL: Lower detection limit

5 PSL: Polystyrene size standards

6 UDL: Upper detection limit

7

8 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)	$\mu\text{m}$
$D_{\text{BC}}$	BC mass equivalent diameter	$\mu\text{m}$
$D_{\text{BC,min}}, D_{\text{BC,min}}^*$	Minimal mass equivalent diameter of the BC cores in an aqueous sample (*standard)	$\mu\text{m}$
$D_{\text{BC,max}}, D_{\text{BC,max}}^*$	Maximal mass equivalent diameter of the BC cores in an aqueous sample (*standard)	$\mu\text{m}$
$D_{\text{BC,LDL}}$	Lower cut-off diameter of the SP2 measurement in terms of BC core mass equivalent diameter ( $D_{\text{BC,LDL}}^*$ is assumed to be equal to $D_{\text{BC,LDL}}$ )	$\mu\text{m}$
$D_{\text{BC,UDL}}$	Upper cut-off diameter of the SP2 measurement in terms of BC core mass equivalent diameter ( $D_{\text{BC,UDL}}^*$ is assumed to be equal to $D_{\text{BC,UDL}}$ )	$\mu\text{m}$
$D_{\text{BC,ref}}$	Reference BC mass equivalent diameter for calculating the reference nebulizer efficiency, $\eta_{\text{BC,ref}}$ , for BC	$\mu\text{m}$

$D_{\text{PSL}}$	(Nominal) PSL diameter	$\mu\text{m}$
$D_{\text{PSL,ref}}$	Reference PSL diameter for calculating the reference nebulizer efficiency, $\eta_{\text{PSL,ref}}$ , for PSLs	$\mu\text{m}$
$D_{\text{mob}}$	Mobility diameter of a BC core	$\mu\text{m}$
$f_{\text{bias}}, f_{\text{bias}}^*$	SP2 calibration bias for the BC type of an aqueous sample (*standard) expressed as a factor.	-
$g_{\text{mob2mev}}$	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.
$C_{\text{liq}}, C_{\text{liq}}^*$	BC mass concentration of an aqueous sample (*standard)	$\mu\text{g L}^{-1}$
$M_{\text{liq}}, M_{\text{liq}}^*$	Mass concentration of water-insoluble particulate matter in an aqueous sample (* standard)	$\mu\text{g L}^{-1}$
$\gamma_{\text{BC}}^*$	BC mass fraction in dried particles of a BC material that is used to prepare aqueous standard suspensions.	-
$c_{\text{air}}, c_{\text{air}}^*$	BC mass concentration of the aerosol from a nebulized aqueous sample (*standard)	$\mu\text{g m}^{-3}$
$c_{\text{SP2}}, c_{\text{SP2}}^*$	BC mass concentration of the aerosol as inferred from the SP2 measurement of a nebulized aqueous sample (*standard)	$\mu\text{g m}^{-3}$
$C_{\text{SP2}}^x, C_{\text{SP2}}^{x,*}$	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 $C_{\text{SP2}}$ . “x” can be S1, S2, S $\eta$	$\mu\text{g L}^{-1}$
$C_{\text{SP2,low}}^{\eta}, C_{\text{SP2,low}}^{\eta,*}$	Lower limit of the BC mass concentration in an aqueous	$\mu\text{g L}^{-1}$

sample (\*standard) inferred from the SP2 measurement of the nebulized sample (calculated by using the upper limit for the overall nebulizer efficiency)

$$\frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}), \quad \text{BC mass size distribution of an aqueous sample } \mu\text{g L}^{-1} \text{ (*standard)}$$

$$\frac{dC_{\text{liq}}^*}{d \log D_{\text{BC}}}(D_{\text{BC}})$$

$$\frac{d\tilde{C}_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}), \quad \text{Normalized BC mass size distribution of an aqueous sample (*standard) -}$$

$$\frac{d\tilde{C}_{\text{liq}}^*}{d \log D_{\text{BC}}}(D_{\text{BC}})$$

$$\frac{dc_{\text{air}}}{d \log D_{\text{BC}}}(D_{\text{BC}}), \quad \text{BC mass size distribution of the aerosol from a nebulized aqueous sample } \mu\text{g m}^{-3} \text{ (*standard)}$$

$$\frac{dc_{\text{air}}^*}{d \log D_{\text{BC}}}(D_{\text{BC}})$$

$$\frac{dc_{\text{SP2}}}{d \log D_{\text{BC}}}(D_{\text{BC}}), \quad \text{BC mass size distribution measured by the SP2 for a nebulized aqueous sample } \mu\text{g m}^{-3} \text{ (*standard)}$$

$$\frac{dc_{\text{SP2}}^*}{d \log D_{\text{BC}}}(D_{\text{BC}})$$

$$\frac{dC_{\text{SP2}}^{\eta}}{d \log D_{\text{BC}}}(D_{\text{BC}}), \quad \text{BC mass size distribution of an aqueous sample } \mu\text{g L}^{-1} \text{ (*standard) inferred from the SP2 measurement of the}$$

$$\frac{dC_{\text{SP2}}^{\eta,*}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \quad \text{nebulized sample (with accounting for the nebulizer efficiency)}$$

$$\Delta\tilde{C}_{\text{LDL}}, \Delta\tilde{C}_{\text{LDL}}^* \quad \text{Relative contribution to the total BC mass in an aqueous sample (*standard) from BC cores with sizes below the LDL of the SP2 -}$$

$$\Delta\tilde{C}_{\text{UDL}}, \Delta\tilde{C}_{\text{UDL}}^* \quad \text{Relative contribution to the total BC mass in an aqueous sample (*standard) from BC cores with sizes above the UDL of the SP2 -}$$

$\eta(D), \eta^*(D)$	Overall nebulizer efficiency for insoluble particles as a function of the particle diameter during the measurement of a sample (*standard)	$L m^{-3}$
$\eta_{\max}, \eta_{\max}^*$	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	$cm^{-3}$
$\mathcal{E}_{drop}, \mathcal{E}_{drop}^*$	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)	
$\varepsilon_{\text{loss}}(D)$	, 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	-
$\varepsilon_{\text{loss}}^*(D)$		
$q_{\text{air,supply}}, q_{\text{air,supply}}^*$	Air flow rate at the purge air inlet of the nebulizer during the measurement of an aqueous sample (*standard)	$\text{L min}^{-1}$
$q_{\text{air,aerosol}}, q_{\text{air,aerosol}}^*$	Air flow rate of the aerosol outlet of the nebulizer during the measurement of an aqueous sample (*standard)	$\text{L min}^{-1}$
$q_{\text{air,drain}}, q_{\text{air,drain}}^*$	Air flow rate through the drain channel from the nebulizer chamber during the measurement of an aqueous sample (*standard)	$\text{L min}^{-1}$
$Q_{\text{liq,supply}}, Q_{\text{liq,supply}}^*$	Flow rate of the aqueous sample supplied to the nebulizer during the measurement of an aqueous sample (*standard)	$\text{mL min}^{-1}$
$Q_{\text{liq,drain}}, Q_{\text{liq,drain}}^*$	Flow rate of water that is drained from the nebulizer chamber without being nebulized during the measurement of an aqueous sample (*standard)	$\text{mL min}^{-1}$
$\rho_{\text{bulk,BC}}$	Void free material density of BC	$\text{kg m}^{-3}$
$\rho_{\text{eff,BC}}(D_{\text{mob}})$	Effective density of BC particles as a function of particle mobility diameter	$\text{kg m}^{-3}$

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## 1 **S.1 General definitions and equations**

### 2 **S.1.1 Nebulizer efficiency for BC**

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

6 BC mass size distribution in the aqueous sample,  $\frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}$ , at the same BC mass equivalent  
7 diameter,  $D_{\text{BC}}$ :

$$8 \quad \eta_{\text{BC}}(D_{\text{BC}}) := \frac{\frac{dc_{\text{air}}}{d \log D_{\text{BC}}}(D_{\text{BC}})}{\frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}})} \quad (\text{S1})$$

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

$$11 \quad \eta_{\text{BC,ref}} := \eta_{\text{BC}}(D_{\text{BC,ref}}) \quad (\text{S2})$$

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

$$14 \quad \tilde{\eta}_{\text{BC}}(D_{\text{BC}}) := \frac{\eta_{\text{BC}}(D_{\text{BC}})}{\eta_{\text{BC,ref}}} \quad (\text{S3})$$

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

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

$$18 \quad \eta_{\text{BC}}(D_{\text{BC}}) = \eta_{\text{BC,ref}} \tilde{\eta}_{\text{BC}}(D_{\text{BC}}) \quad (\text{S4})$$

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

### 1 **S.1.2 Nebulizer efficiency for PSLs**

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

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

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

$$11 \quad \eta_{\text{PSL,ref}} := \eta_{\text{PSL}}(D_{\text{PSL,ref}}) \quad (\text{S6})$$

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

$$14 \quad \tilde{\eta}_{\text{PSL}}(D_{\text{PSL}}) := \frac{\eta_{\text{PSL}}(D_{\text{PSL}})}{\eta_{\text{PSL,ref}}} \quad (\text{S7})$$

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

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

$$18 \quad \eta_{\text{PSL}}(D_{\text{PSL}}) = \eta_{\text{PSL,ref}} \tilde{\eta}_{\text{PSL}}(D_{\text{PSL}}) \quad (\text{S8})$$

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

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

$$23 \quad \eta(D) = \frac{\varepsilon_{\text{drop}} Q_{\text{liq,supply}}}{q_{\text{air,aerosol}}} \varepsilon_{\text{loss}}(D) \quad (\text{D9})$$

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

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

$$12 \quad \varepsilon_{\text{drop}} = \frac{Q_{\text{liq, supply}} - Q_{\text{liq, drain}}}{Q_{\text{liq, supply}}} \quad (\text{S10})$$

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

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

$$19 \quad q_{\text{air, aerosol}} = q_{\text{air, supply}} - q_{\text{air, drain}} \quad (\text{S11})$$

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

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

$$27 \quad \eta_{\text{max}} = \frac{\varepsilon_{\text{drop}} Q_{\text{liq, supply}}}{q_{\text{air, aerosol}}} = \frac{(Q_{\text{liq, supply}} - Q_{\text{liq, drain}})}{q_{\text{air, aerosol}}} \approx \frac{(Q_{\text{liq, supply}} - Q_{\text{liq, drain}})}{q_{\text{air, supply}}} \quad (\text{S12})$$



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

$$2 \quad \eta(D) = \eta_{\max} \varepsilon_{\text{loss}}(D) \Leftrightarrow \varepsilon_{\text{loss}}(D) = \frac{\eta(D)}{\eta_{\max}} \quad (\text{S13})$$

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

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

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

#### 10 **S.1.4 BC mass size distribution and mass concentration of an aqueous BC** 11 **sample and the corresponding nebulized aerosol**

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

$$15 \quad C_{\text{liq}} = \int_{D_{\text{BC, min}}}^{D_{\text{BC, max}}} \frac{dC_{\text{liq}}}{d \log D_{\text{BC}}} (D_{\text{BC}}) d \log D_{\text{BC}} \quad (\text{S14})$$

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

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

$$21 \quad c_{\text{SP2}} = \int_{D_{\text{BC, LDL}}}^{D_{\text{BC, UDL}}} \frac{dc_{\text{SP2}}}{d \log D_{\text{BC}}} (D_{\text{BC}}) d \log D_{\text{BC}} \quad (\text{S15})$$

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

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

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

$$7 \quad f_{\text{bias}}(D_{\text{BC}}) = \frac{\frac{dc_{\text{SP2}}}{d \log D_{\text{BC}}}(D_{\text{BC}})}{\frac{dc_{\text{air}}}{d \log D_{\text{BC}}}(D_{\text{BC}})} \quad (\text{S16})$$

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

$$11 \quad \frac{dc_{\text{SP2}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) = f_{\text{bias}} \frac{dc_{\text{air}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \quad \forall D_{\text{BC}} \in [D_{\text{BC,LDL}} D_{\text{BC,UDL}}] \quad (\text{S17})$$

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

$$13 \quad \frac{d\tilde{C}_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) := \frac{1}{C_{\text{liq}}} \frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \quad (\text{S18})$$

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

$$16 \quad \Delta\tilde{C}_{\text{LDL}} = \frac{1}{C_{\text{liq}}} \int_{D_{\text{BC,min}}}^{D_{\text{BC,LDL}}} \frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) d \log D_{\text{BC}} = \int_{D_{\text{BC,min}}}^{D_{\text{BC,LDL}}} \frac{d\tilde{C}_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) d \log D_{\text{BC}} \quad (\text{S19})$$

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

$$19 \quad \Delta\tilde{C}_{\text{UDL}} = \frac{1}{C_{\text{liq}}} \int_{D_{\text{BC,UDL}}}^{D_{\text{BC,max}}} \frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) d \log D_{\text{BC}} = \int_{D_{\text{BC,UDL}}}^{D_{\text{BC,max}}} \frac{d\tilde{C}_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) d \log D_{\text{BC}} \quad (\text{S20})$$

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

$$21 \quad \int_{D_{\text{BC,LDL}}}^{D_{\text{BC,UDL}}} \frac{d\tilde{C}_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) d \log D_{\text{BC}} = 1 - \Delta\tilde{C}_{\text{LDL}} - \Delta\tilde{C}_{\text{UDL}} \quad (\text{S21})$$

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

$$2 \quad \frac{dc_{\text{air}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) = \eta_{\text{BC}}(D_{\text{BC}}) \frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) = \eta_{\text{BC,ref}} \tilde{\eta}_{\text{BC}}(D_{\text{BC}}) \frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \quad (\text{S22})$$

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

$$4 \quad \begin{aligned} \frac{dc_{\text{SP2}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) &= f_{\text{bias}} \eta_{\text{BC}}(D_{\text{BC}}) \frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \\ &= f_{\text{bias}} \eta_{\text{BC,ref}} \tilde{\eta}_{\text{BC}}(D_{\text{BC}}) \frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \end{aligned} \quad (\text{S23})$$

$\forall D_{\text{BC}} \in [D_{\text{BC,LDL}}, D_{\text{BC,UDL}}]$

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

$$8 \quad c_{\text{SP2}} = f_{\text{bias}} \int_{D_{\text{BC,LDL}}}^{D_{\text{BC,UDL}}} \eta_{\text{BC,ref}} \tilde{\eta}_{\text{BC}}(D_{\text{BC}}) \frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) d \log D_{\text{BC}} \quad (\text{S24})$$

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

$$12 \quad \frac{dC_{\text{SP2}}^{\eta}}{d \log D_{\text{BC}}}(D_{\text{BC}}) := \frac{1}{\eta_{\text{BC}}(D_{\text{BC}})} \frac{dc_{\text{SP2}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) = \frac{1}{\eta_{\text{BC,ref}} \tilde{\eta}_{\text{BC}}(D_{\text{BC}})} \frac{dc_{\text{SP2}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \quad (\text{S25})$$

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

$$14 \quad \begin{aligned} \frac{dC_{\text{SP2}}^{\eta}}{d \log D_{\text{BC}}}(D_{\text{BC}}) &= f_{\text{bias}} \frac{1}{\eta_{\text{BC}}(D_{\text{BC}})} \frac{dc_{\text{air}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \\ &= f_{\text{bias}} \frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \quad \forall D_{\text{BC}} \in [D_{\text{BC,LDL}}, D_{\text{BC,UDL}}] \end{aligned} \quad (\text{S26})$$

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

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

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

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

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

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

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

$$15 \quad \tilde{\eta}_{BC}(D_{BC}) \neq 0 \quad \forall \quad D_{BC} \in [D_{BC,LDL}, D_{BC,UDL}] \quad (S29)$$

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

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

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

$$5 \quad \Delta \tilde{C}_{\text{LDL}} + \Delta \tilde{C}_{\text{UDL}} \ll 1 \quad (\text{S30})$$

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

$$9 \quad C_{\text{SP2}}^{\eta} \approx f_{\text{bias}} C_{\text{liq}} \quad (\text{S31})$$

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

$$14 \quad C_{\text{SP2,low}}^{\eta} := \frac{1}{\eta_{\text{max}}} \int_{D_{\text{BC,LDL}}}^{D_{\text{BC,UDL}}} \frac{dc_{\text{SP2}}}{d \log D_{\text{BC}}} (D_{\text{BC}}) d \log D_{\text{BC}} = \frac{1}{\eta_{\text{max}}} c_{\text{SP2}} \quad (\text{S32})$$

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

$$16 \quad C_{\text{SP2,low}}^{\eta} \leq C_{\text{SP2}}^{\eta} \quad (\text{S33})$$

17 which confirms that Eq. (S32) indeed provides a lower limit for  $C_{\text{SP2}}^{\eta}$ .

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

## 21 **S.2 Approach of using aqueous standards as a reference for the** 22 **measurement of unknown samples**

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

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

$$3 \quad \eta_{BC}(D_{BC}) = \eta_{BC}^*(D_{BC}) \quad \forall D_{BC} \quad (S34)$$

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

$$7 \quad C_{SP2}^{S1} := c_{SP2} \frac{C_{liq}^*}{c_{SP2}^*} \quad (S35)$$

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

$$15 \quad \varepsilon_{loss}(D_{BC}) = \varepsilon_{loss}^*(D_{BC}) \quad \forall D_{BC} \quad (S36)$$

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

$$19 \quad C_{SP2}^{S2} := C_{SP2,low}^{\eta} \frac{C_{liq}^*}{C_{SP2,low}^{\eta,*}} \quad (S37)$$

20 From Eq. (S32) follows:

$$21 \quad \frac{C_{SP2,low}^{\eta}}{C_{SP2,low}^{\eta,*}} = \frac{\eta_{max}^*}{\eta_{max}} \frac{C_{SP2}}{C_{SP2}^*} \quad (S38)$$

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

$$23 \quad C_{SP2}^{S2} = \frac{\eta_{max}^*}{\eta_{max}} C_{SP2}^{S1} \quad (S39)$$

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

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

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

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

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

16 Equation (S41) can be written as:

$$C_{\text{SP2}}^{\text{S1}} = C_{\text{liq}} \frac{f_{\text{bias}}}{f_{\text{bias}}^*} k_{\text{S1}} \tag{S42}$$

18 with:

$$1 \quad k_{S1} := \frac{\int_{D_{BC,LDL}}^{D_{BC,UDL}} \tilde{\eta}_{BC}(D_{BC}) \frac{d\tilde{C}_{liq}}{d \log D_{BC}}(D_{BC}) d \log D_{BC}}{\int_{D_{BC,LDL}}^{D_{BC,UDL}} \tilde{\eta}_{BC}(D_{BC}) \frac{d\tilde{C}_{liq}^*}{d \log D_{BC}}(D_{BC}) d \log D_{BC}} \quad (S43)$$

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

$$3 \quad C_{SP2}^{S2} = C_{liq} \frac{f_{bias}}{f_{bias}^*} k_{S2} \quad (S44)$$

4 with:

$$5 \quad k_{S2} := \frac{\eta_{max}^*}{\eta_{max}} k_{S1} = \frac{\int_{D_{BC,LDL}}^{D_{BC,UDL}} \epsilon_{loss}(D_{BC}) \frac{d\tilde{C}_{liq}}{d \log D_{BC}}(D_{BC}) d \log D_{BC}}{\int_{D_{BC,LDL}}^{D_{BC,UDL}} \epsilon_{loss}(D_{BC}) \frac{d\tilde{C}_{liq}^*}{d \log D_{BC}}(D_{BC}) d \log D_{BC}} \quad (S45)$$

6 The factor  $\frac{f_{bias}}{f_{bias}^*} k_{S1}$  in Eq. (S42) quantifies the total error introduced when using the simple

7 Eq. (S35) to infer the BC mass concentration of an aqueous sample from the SP2  
8 measurements of the aqueous sample and an aqueous standard with known concentration

9 (under the assumption of Eq. (S34)). Likewise, the factor  $\frac{f_{bias}}{f_{bias}^*} k_{S2}$  in Eq. (S44) quantifies the

10 total error introduced when using the simple Eq. (S37) to infer the BC mass concentration of  
11 an aqueous sample from the SP2 measurements of the aqueous sample and an aqueous  
12 standard with known concentration (under the slightly less stringent assumption of Eq. (S36)).

13 From Eq. (S45) and the fact that  $\eta_{max}^*/\eta_{max}$  is close to unity, follows that  $k_{S1}$  and  $k_{S2}$  are  
14 almost equal. Consequently, the conditions under which Eqs. (S35) and (S37) are valid are  
15 similar (the difference being the underlying assumptions, i.e. Eq. (S34) for Eq. (S35) and  
16 Eq. (S36) for Eq. (S37)) and thus these conditions are only discussed for the approach of  
17 Eq. (S35) in the following.

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



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

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

### 24 **S.2.1 Nebulizers with size-dependent efficiency for BC**

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

$$1 \quad \frac{d\tilde{C}_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \approx \frac{d\tilde{C}_{\text{liq}}^*}{d \log D_{\text{BC}}}(D_{\text{BC}}) \quad \forall D_{\text{BC}} \quad (\text{S46})$$

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

$$5 \quad \frac{d\tilde{C}_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \approx \frac{d\tilde{C}_{\text{liq}}^*}{d \log D_{\text{BC}}}(D_{\text{BC}}) \quad \forall D_{\text{BC}} \in [D_{\text{BC,LDL}}, D_{\text{BC,UDL}}] \quad (\text{S47})$$

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

$$8 \quad \frac{dC_{\text{liq}}}{d \log D_{\text{BC}}}(D_{\text{BC}}) \propto \frac{dC_{\text{liq}}^*}{d \log D_{\text{BC}}}(D_{\text{BC}}) \quad \forall D_{\text{BC}} \in [D_{\text{BC,LDL}}, D_{\text{BC,UDL}}] \quad (\text{S48})$$

9 and

$$10 \quad \Delta\tilde{C}_{\text{LDL}} + \Delta\tilde{C}_{\text{UDL}} \approx \Delta\tilde{C}_{\text{LDL}}^* + \Delta\tilde{C}_{\text{UDL}}^* \quad (\text{S49})$$

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

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

$$23 \quad C_{\text{SP2}}^{S\eta} := \frac{\int_{D_{\text{BC,LDL}}}^{D_{\text{BC,UDL}}} \frac{1}{\tilde{\eta}_{\text{BC}}(D)} \frac{dc_{\text{SP2}}}{d \log D}(D) d \log D}{\int_{D_{\text{BC,LDL}}}^{D_{\text{BC,UDL}}} \frac{1}{\tilde{\eta}_{\text{BC}}(D_{\text{BC}})} \frac{dc_{\text{SP2}}^*}{d \log D_{\text{BC}}}(D_{\text{BC}}) d \log D_{\text{BC}}} \frac{C_{\text{liq}}^*}{C_{\text{liq}}} \quad (\text{S50})$$

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

$$2 \quad C_{\text{SP2}}^{S\eta} = C_{\text{SP2}}^{\eta} \frac{C_{\text{liq}}^*}{C_{\text{SP2}}^{\eta,*}} = C_{\text{liq}} \frac{f_{\text{bias}}}{f_{\text{bias}}^*} \frac{\left(1 - \Delta\tilde{C}_{\text{LDL}} - \Delta\tilde{C}_{\text{UDL}}\right)}{\left(1 - \Delta\tilde{C}_{\text{LDL}}^* - \Delta\tilde{C}_{\text{UDL}}^*\right)} \quad (\text{S51})$$

3 Equation (S51) can be written as:

$$4 \quad C_{\text{SP2}}^{S\eta} = C_{\text{liq}} \frac{f_{\text{bias}}}{f_{\text{bias}}^*} k_{\text{fract}} \quad (\text{S52})$$

5 with:

$$6 \quad k_{\text{fract}} := \frac{1 - \Delta\tilde{C}_{\text{LDL}} - \Delta\tilde{C}_{\text{UDL}}}{1 - \Delta\tilde{C}_{\text{LDL}}^* - \Delta\tilde{C}_{\text{UDL}}^*} \quad (\text{S53})$$

7 The factor  $\frac{f_{\text{bias}}}{f_{\text{bias}}^*} k_{\text{fract}}$  in Eq. (S52) quantifies the total error introduced when using Eq. (S50) to

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

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

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

6 It also follows from Eqs. (S52) and (S53) that the BC mass concentration in an aqueous  
 7 sample within the detection range of the SP2 is overestimated by the factor  
 8  $(1 - \Delta\tilde{C}_{LDL}^* - \Delta\tilde{C}_{UDL}^*)^{-1}$  when applying Eq. (S50) and using an aqueous standard with a  
 9 substantial portion of the BC mass outside the detection range of the SP2 (Eq. (S30) is not  
 10 fulfilled for the standard).

## 11 **S.2.2 Nebulizers with size-independent efficiency for BC**

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

$$13 \quad \eta_{BC}(D_{BC}) \approx \eta_{BC,ref} \Leftrightarrow \tilde{\eta}_{BC}(D_{BC}) \quad (S54)$$

$$\approx 1 \quad \forall \quad D_{BC} \in [\min(D_{BC,min}, D_{BC,min}^*), \max(D_{BC,max}, D_{BC,max}^*)]$$

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

$$15 \quad k_{SI} \approx \frac{\int_{D_{BC,LDL}}^{D_{BC,UDL}} \frac{d\tilde{C}_{liq}}{d \log D_{BC}}(D_{BC}) d \log D_{BC}}{\int_{D_{BC,LDL}}^{D_{BC,UDL}} \frac{d\tilde{C}_{liq}^*}{d \log D_{BC}}(D_{BC}) d \log D_{BC}} = \frac{1 - \Delta\tilde{C}_{LDL} - \Delta\tilde{C}_{UDL}}{1 - \Delta\tilde{C}_{LDL}^* - \Delta\tilde{C}_{UDL}^*} = k_{fract} \quad (S55)$$

16 Equation (S42) then simplifies to:

$$17 \quad C_{SP2}^{S1} \approx C_{liq} \frac{f_{bias}}{f_{bias}^*} k_{fract} \quad (S56)$$

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

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

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

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

11 It also follows from Eqs. (S53) and (S56) that the BC mass concentration in an aqueous  
 12 sample within the detection range of the SP2 is overestimated by the factor  
 13  $(1 - \Delta\tilde{C}_{\text{LDL}}^* - \Delta\tilde{C}_{\text{UDL}}^*)^{-1}$  when applying Eq. (S35) and using an aqueous standard with a  
 14 substantial portion of the BC mass outside the detection range of the SP2 (Eq. (S30) is not  
 15 fulfilled for the standard). Thus, Eq. (S35) can generally not be applied for such standards  
 16 without introducing a bias.

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

$$22 \quad C_{\text{SP2}}^{\text{S1}} \approx C_{\text{liq}} \frac{f_{\text{bias}}}{f_{\text{bias}}^*} \quad (\text{S57})$$

### 23 **S.3 Measurement of the nebulizer efficiency**

#### 24 **S.3.1 Nebulizer efficiency for PSLs**

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

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

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

$$14 \quad \tilde{\eta}_{\text{PSL}}^{\text{APEX-PSI}}(D_{\text{PSL}}) = c_0 + c_1 \ln(D_{\text{PSL}}) \quad (\text{S58})$$

15 and

$$16 \quad \tilde{\eta}_{\text{PSL}}^{\text{Collison-PSI}}(D_{\text{PSL}}) = c_0 + c_1 \ln(D_{\text{PSL}}) \quad (\text{S59})$$

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

$$18 \quad \tilde{\eta}_{\text{PSL}}^{\text{CETAC-PSI}}(D_{\text{PSL}}) = 2f_{\text{Gauss}}(D_{\text{PSL}}, c_0, c_1, c_2) f_{\text{GaussCDF}}(c_3(D_{\text{PSL}} - c_2), c_1) \quad (\text{S60})$$

19 with the Gauss function

$$20 \quad f_{\text{Gauss}}(x, N, \sigma, \bar{x}) = \frac{N}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x - \bar{x})^2}{2\sigma^2}\right) \quad (\text{S61})$$

21 and the cumulative Gauss function

$$22 \quad f_{\text{GaussCDF}}(x, \sigma) = \frac{1}{2} \left( 1 + \operatorname{erf}\left(\frac{x}{\sigma\sqrt{2}}\right) \right) \quad (\text{S62})$$

23 where erf denotes the error function.

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

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

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

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

3 <sup>a</sup>valid for the PSL diameter range 0.1–1.0  $\mu\text{m}$

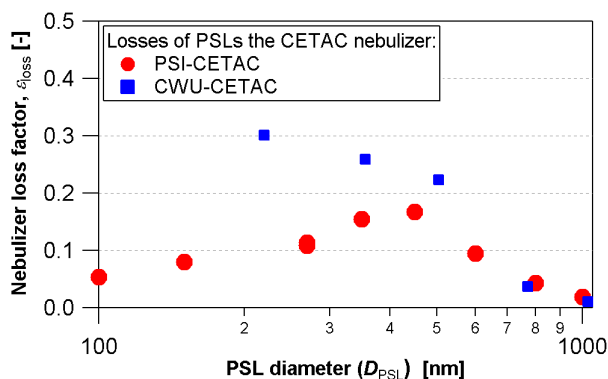
4 <sup>b</sup>valid for the PSL diameter range 0.22–1.025  $\mu\text{m}$

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

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

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

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



9  
10 Figure S1 – Losses in the PSI- and CWU-CETAC nebulizer as derived from the  
11 measurements of the PSL standard suspensions.

### 12 **S.3.3 Nebulizer efficiency for BC**

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

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



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

$$5 \frac{\frac{dc_{SP2}^{neb1}(D_{BC})}{d \log D_{BC}}}{\frac{dc_{SP2}^{neb2}(D_{BC})}{d \log D_{BC}}} = \frac{\eta_{BC}^{neb1}(D_{BC}) \frac{dC_{liq}}{d \log D_{BC}}(D_{BC})}{\eta_{BC}^{neb2}(D_{BC}) \frac{dC_{liq}}{d \log D_{BC}}(D_{BC})} \quad (S64)$$

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

$$7 \eta_{BC}^{neb1}(D_{BC}) = \eta_{BC}^{neb2}(D_{BC}) \frac{\frac{dc_{SP2}^{neb1}(D_{BC})}{d \log D_{BC}}}{\frac{dc_{SP2}^{neb2}(D_{BC})}{d \log D_{BC}}} \quad (S65)$$

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

$$12 \eta_{BC}^{APEX}(D_{BC}) \approx \eta_{PSL}^{APEX}(D_{BC}) \quad (S66)$$

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

$$14 \eta_{BC}^{neb1}(D_{BC}) \approx \eta_{PSL}^{APEX}(D_{BC}) \frac{\frac{dc_{SP2}^{neb1}(D_{BC})}{d \log D_{BC}}}{\frac{dc_{SP2}^{APEX}(D_{BC})}{d \log D_{BC}}} \quad (S67)$$

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

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

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

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

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

$$6 \quad \hat{\eta}_{\text{BC}}(D_{\text{mob}}) = \eta_{\text{BC}} \left( D_{\text{mob}} \left( \frac{\rho_{\text{eff,BC}}(D_{\text{mob}})}{\rho_{\text{bulk,BC}}} \right)^{1/3} \right) \quad (\text{S69})$$

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

$$8 \quad \hat{\eta}_{\text{BC}}^{\text{neb1}}(D_{\text{mob}}) = \hat{\eta}_{\text{BC}}^{\text{neb2}}(D_{\text{mob}}) \frac{\frac{dc_{\text{SP2}}^{\text{neb1}}}{d \log D} \left( D_{\text{mob}} \left( \frac{\rho_{\text{eff,BC}}(D_{\text{mob}})}{\rho_{\text{bulk,BC}}} \right)^{1/3} \right)}{\frac{dc_{\text{SP2}}^{\text{APEX}}}{d \log D} \left( D_{\text{mob}} \left( \frac{\rho_{\text{eff,BC}}(D_{\text{mob}})}{\rho_{\text{bulk,BC}}} \right)^{1/3} \right)} \quad (\text{S70})$$

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

$$10 \quad \hat{\eta}_{\text{BC}}^{\text{APEX}}(D_{\text{mob}}) \approx \eta_{\text{PSL}}^{\text{APEX}}(D_{\text{mob}}) \quad (\text{S71})$$

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

$$12 \quad \hat{\eta}_{\text{BC}}^{\text{neb1}}(D_{\text{mob}}) \approx \eta_{\text{PSL}}^{\text{APEX}}(D_{\text{mob}}) \frac{\frac{dc_{\text{SP2}}^{\text{neb1}}}{d \log D} \left( D_{\text{mob}} \left( \frac{\rho_{\text{eff,BC}}(D_{\text{mob}})}{\rho_{\text{bulk,BC}}} \right)^{1/3} \right)}{\frac{dc_{\text{SP2}}^{\text{APEX}}}{d \log D} \left( D_{\text{mob}} \left( \frac{\rho_{\text{eff,BC}}(D_{\text{mob}})}{\rho_{\text{bulk,BC}}} \right)^{1/3} \right)} \quad (\text{S72})$$

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

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

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

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

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

$$17 \frac{C_{liq}^*}{C_{SP2,low}^{\eta,*}} = \frac{\int_{D_{BC,min}^*}^{D_{BC,max}^*} \frac{dC_{liq}^*}{d \log D_{BC}}(D_{BC}) d \log D_{BC}}{\frac{1}{\eta_{max}^*} \int_{D_{BC,LDL}}^{D_{BC,UDL}} f_{bias}^* \eta_{BC}^*(D_{BC}) \frac{dC_{liq}^*}{d \log D_{BC}}(D_{BC}) d \log D_{BC}} \quad (S73)$$

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

$$19 \frac{C_{liq}^*}{C_{SP2,low}^{\eta,*}} = \frac{1}{f_{bias}^*} \frac{1}{\int_{D_{BC,LDL}}^{D_{BC,UDL}} \varepsilon_{loss}^*(D_{BC}) \frac{d\tilde{C}_{liq}^*}{d \log D_{BC}}(D_{BC}) d \log D_{BC}} \quad (S74)$$

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

$$22 \varepsilon_{loss}^*(D_{BC}) \approx \varepsilon_{loss}^* = \text{const.} \quad \forall D_{BC} \in [D_{BC,LDL}, D_{BC,UDL}] \quad (S75)$$

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

$$\begin{aligned}
\frac{C_{\text{liq}}^*}{C_{\text{SP2,low}}^{\eta,*}} &\approx \frac{1}{f_{\text{bias}}^*} \frac{1}{\varepsilon_{\text{loss}}^*} \frac{1}{\int_{D_{\text{BC,LDL}}}^{D_{\text{BC,UDL}}} \frac{d\tilde{C}_{\text{liq}}^*}{d \log D_{\text{BC}}} (D_{\text{BC}}) d \log D_{\text{BC}}} \\
2 & \\
&= \frac{1}{f_{\text{bias}}^*} \frac{1}{\varepsilon_{\text{loss}}^*} \frac{1}{1 - \Delta\tilde{C}_{\text{LDL}}^* - \Delta\tilde{C}_{\text{UDL}}^*}
\end{aligned} \tag{S76}$$

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

$$4 \quad f_{\text{bias}}^* \approx 1 \Leftrightarrow f_{\text{bias}}^{*-1} \approx 1 \tag{S77}$$

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

$$7 \quad (1 - \Delta\tilde{C}_{\text{LDL}}^* - \Delta\tilde{C}_{\text{UDL}}^*)^{-1} \approx 1 \tag{S78}$$

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

$$9 \quad \frac{C_{\text{liq}}^*}{C_{\text{SP2,low}}^{\eta,*}} \approx \frac{1}{\varepsilon_{\text{loss}}^*} \geq 1 \tag{S79}$$

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

21 Unknown sensitivity of the SP2 to the BC type of the aqueous BC standard results in an  
22 uncertainty of the magnitude  $f_{\text{bias}}^{*-1}$  (see e.g. Moteki and Kondo, 2010, and Laborde et al.,  
23 2012, for a detailed discussion of SP2 sensitivity). If the aqueous BC standard contains  
24 substantial contribution to the total BC mass from BC cores with sizes outside the detection

1 range of the SP2 (i.e. Eq. (S30) is not fulfilled for the standard), then the factor  
 2  $(1 - \Delta\tilde{C}_{LDL}^* - \Delta\tilde{C}_{UDL}^*)^{-1}$  becomes greater than unity and it follows from Eq. (S76) that the BC  
 3 mass concentration inferred with Eq. (S37) overestimates the true value.

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

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

16 Not all BC materials available for preparing aqueous BC standard suspensions are pure BC.  
 17 The BC mass fraction,  $\gamma_{BC}^*$ , of Fullerene Soot is almost 100% (Gysel et al., 2011; Moteki and  
 18 Kondo, 2010), while of dried AQ particles it is only around 70.5% (this study; similar to the  
 19 76% found in Gysel et al. (2011)). This fact must be considered when working with aqueous  
 20 BC standards for the quantification of BC in aqueous samples using Eqs. (S35) or (S37),  
 21 specifically when determining the factor  $C_{liq}^*/c_{SP2}^*$  or  $C_{liq}^*/C_{SP2,low}^{\eta,*}$ , respectively. Practically,  
 22 this means that the BC mass concentration of an aqueous BC standard ( $C_{liq}^*$ ) must be  
 23 calculated from the mass concentration of water-insoluble particulate matter in an aqueous  
 24 standard ( $M_{liq}^*$ ):

$$25 \quad C_{liq}^* = \gamma_{BC}^* M_{liq}^* \quad (S80)$$

26 At the same time, the SP2 response to the standard particles must be calibrated for the BC  
 27 mass in the particles rather than the total particle mass, i.e. when selecting the standard

1 particles by an aerosol particle mass analyzer to provide particles of a well defined mass to  
2 the SP2 during internal calibration of the SP2 (such as e.g. described in Gysel et al., 2011). It  
3 is important to correct this nominal mass of the selected particles with the factor  $\gamma_{BC}^*$  in order  
4 to get the BC mass in these particles. The factor  $\gamma_{BC}^*$  gets cancelled in the ratio  $C_{liq}^*/c_{SP2}^*$  or  
5  $C_{liq}^*/C_{SP2,low}^{\eta,*}$  because it shows up both in the nominator and the denominator. Consequently, it  
6 is also possible to ignore the factor  $\gamma_{BC}^*$  for the preparation of an aqueous BC standard and in  
7 the internal SP2 calibration curve applied in the analysis of the SP2 measurement of the  
8 standard. This reflects the fact that the ratio  $C_{liq}^*/c_{SP2}^*$  or  $C_{liq}^*/C_{SP2,low}^{\eta,*}$  is simply used to  
9 quantify the nebulizer efficiency for insoluble particles and it is in principle possible to use  
10 any insoluble material that is detectable by the SP2 in a quantitative manner and that fulfils  
11 the other requirements for preparing an aqueous standard. However, materials with a  
12 substantial mass fraction of water-soluble components are not suitable for preparing aqueous  
13 standards, because water-soluble matter is redistributed in an uncontrolled manner between  
14 droplets with/without insoluble inclusion, when producing an aerosol by nebulization of an  
15 aqueous suspension.

## 16 **S.5 The SP2 sensitivity to different BC types and associated measurement** 17 **uncertainties**

18 The sensitivity of the SP2 to BC mass depends on the chemical structure of the BC, i.e.  
19 graphitic versus disordered. Previous studies (Laborde et al., 2012; Moteki and Kondo, 2010)  
20 indicate that the sensitivity of the SP2 to BC in diesel exhaust, wood combustion exhaust and  
21 atmospheric particles is similar to its sensitivity to fullerene soot, while it is more sensitive to  
22 AQ particles (i.e. ~40% more sensitive without accounting for the non-BC matter in AQ,  
23 ~80% more sensitive with accounting for this). Thus, fullerene soot has been recommended as  
24 an SP2 calibration material for atmospheric applications (Baumgardner et al., 2012).

25 The value  $c_{SP2}$  or  $C_{SP2,low}^{\eta}$  in Eqs. (S35) or (S37), respectively, must always be evaluated with  
26 an SP2 calibration that matches the SP2 sensitivity to BC mass of the BC type in the sample  
27 under investigation as close as possible (i.e. in order to keep the factor  $f_{bias}$  in Eqs. (S42) or  
28 (S44) as close as possible to unity). The SP2 has a broadband and narrowband incandescence  
29 detector. The signal ratio in the two channels, commonly referred to as band ratio or colour  
30 ratio, also differs between different BC types. Ambient BC often exhibits the same band ratio

1 as fullerene soot, while that of AQ is different. However, the band ratio of ambient BC is  
2 occasionally more similar to that of AQ. Likewise, the band ratio of BC from ice core and  
3 snow samples sometimes resembles that of fullerene soot, sometimes that of AQ. If the band  
4 ratio of a sample under investigation differs from the band ratio of the material used for  
5 internal calibration of the SP2, then follows that applying such calibration data will result in  
6 biased BC mass measurements for at least one incandescence channel (possibly even both).  
7 Inversely, it might be interpreted as evidence that a calibration material is suitable, if its band  
8 ratio matches that of the sample under investigation, though this is not a proof. Consequently,  
9 it is suggested to apply fullerene soot calibration curves for the evaluation of aqueous samples  
10 that exhibit the same band ratio as fullerene soot. If the band ratio of an aqueous sample is  
11 more similar to that of AQ, then it is suggested to apply an AQ calibration. Whether or not to  
12 correct the AQ calibration curve for the BC mass fraction in AQ particles is difficult to  
13 answer. From a conceptual point of view this correction should be done. However, the  
14 uncorrected AQ calibration falls in between the two extremes corresponding to fullerene soot  
15 calibration and the corrected AQ calibration (which differ by 80%). Thus, applying the  
16 uncorrected AQ calibration might be better in order to keep the potential calibration bias  
17 within  $\sim\pm 40\%$  if the true calibration is not really known. If the band ratio is not available or  
18 does not give any indication for the choice of the calibration material, then it is suggested to  
19 apply the fullerene soot calibration as recommended by Baumgardner et al. (2012). However,  
20 the measurement bias in such cases may be as high as 40–80%. The discussion above solely  
21 affects the choice of the internal SP2 calibration curve that is to be applied for the evaluation  
22 of the measurements of the aqueous sample, i.e. to determine  $C_{SP2}^\eta$ ,  $c_{SP2}$  or  $C_{SP2,low}^\eta$  when  
23 working with the approaches of Eqs. (S27), (S35) or (S37), respectively. However, it does not  
24 affect the choice of the BC material that is used to prepare aqueous BC standards. Any BC  
25 material with known SP2 sensitivity, which is suitable for preparing aqueous standards, can  
26 be used when working with the approaches of Eqs. (S35) or (S37), but it is important to apply  
27 the internal SP2 calibration curve for the standard material when calculating  $c_{SP2}^*$  or  $C_{SP2,low}^*$ ,  
28 respectively, in order to keep the factor  $f_{bias}^*$  in Eqs. (S42) or (S44) as close as possible to  
29 unity (see also previous discussion above). If the SP2 sensitivity to the BC type in the  
30 standard material is not known, then a measurement uncertainty of at least 40% is introduced.  
31

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