An Empirical Correction Factor for Filter-based Photo-absorption Black Carbon Measurements

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MEASUREMENTS

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1 **Abstract**

2 Filter-based BC measurement techniques such as the Continuous Soot
3 Monitoring System (COSMOS) are particularly well suited to long-term observations
4 of black carbon (BC) due to their relative robustness and reliability. However, caution
5 is required when determining the threshold transmittance, Tr_{thresh} (roughly
6 proportional to the time interval between filter changes), in order to ensure that
7 acceptable measurement accuracy is maintained throughout the sampling period. We
8 present a new, empirically derived transmittance-dependent correction factor used to
9 interpret the response characteristics of filter-based aerosol absorption measurements
10 performed by COSMOS. Simultaneous measurements of ambient BC aerosol mass
11 (M_{BC}) were conducted in Tokyo, Japan, using two identical COSMOS instruments
12 operated with different threshold transmittance, Tr_{thresh} , values, of 0.95 and 0.6. The
13 derived values for M_{BC} were consistently underestimated by the COSMOS operating
14 at lower Tr_{thresh} , as a function of decreasing filter transmittance. The 1-hour averaged
15 values of M_{BC} were underestimated by around 10 %, incorporating measurements
16 across the entire range of filter transmittance (1-0.6), with a maximum
17 underestimation at around 17 % immediately preceding filter advancement (i.e. $Tr =$
18 ~ 0.6). An empirical correction factor was derived from these ambient measurements,
19 and was applied to M_{BC} as a function of filter transmittance, resolving the instruments
20 to within 2 %.

21 Further to the transmittance-based correction, the operational performance of
22 COSMOS was tested for two types of quartz fibre filter (PALLFLEX and HEPA).
23 Agreement in derived values of M_{BC} for two COSMOS using the same type of filter
24 was around 2 %, however a comparison of the PALLFLEX and HEPA filters
25 demonstrated a systematic overestimation of M_{BC} derived when using HEPA filters,

26 of around 6 - 8 %. A sensitivity study of a radiative transfer model indicated that this
27 enhanced absorption was primarily a result of the increased thickness of the HEPA
28 filter.

29 1. INTRODUCTION

30 1.1. Long-term measurements of black carbon mass concentrations

31

32 Long-term continuous on-line measurements of black carbon (BC) mass
33 concentrations (M_{BC}) are a fundamental requirement for constraining atmospheric
34 models, providing valuable information, such as seasonal trends, that may not be
35 observed during short-term field deployments. However, such measurement
36 techniques require significant labour and infrastructure costs, and are typically not as
37 quantitatively detailed when compared to short-term measurements due to the
38 methods used (e.g. either poor or zero size-resolution). Filter-based techniques are
39 intrinsically limited by: measurement artefacts due to particle concentration, changes
40 in morphology due to deposition, and the optical interaction of deposited particles due
41 to their penetration depth (Moosmüller et al. 2009). There are a number of widely-
42 used filter-based photometers commercially available, such as the Aethalometer
43 (Magee Scientific, Berkeley, CA) (Hansen et al., 1984; Weingartner et al. 2003),
44 Particle Soot Absorption Photometer (PSAP; Radiance Research, Seattle, WA, USA)
45 (Bond et al. 1999; Virkkula et al. 2005), Multi-Angle Absorption Photometer
46 (MAAP; Thermo Scientific, Waltham, MA, USA) (Petzold et al. 2005), and
47 Continuous Soot Monitoring System (COSMOS; KANOMAX, Inc., Japan) (Kondo et
48 al. 2009; 2011).

49 Aethalometer and PSAP measure the transmission of light through a loaded
50 filter at specified wavelengths and compare it to the transmission of light through a
51 clean filter, resulting in the derivation of M_{BC} , which requires careful correction for
52 non-absorbing (light scattering) aerosol. Measurements of M_{BC} by the Aethalometer
53 and PSAP require additional data (e.g. from nephelometers) for specific treatments to

account for the optical influences of non-absorbing (non-BC) compounds present within the ambient aerosol, which significantly impact on their light extinction properties.

MAAP was designed to reduce the uncertainties in BC measurements caused by aerosol scattering. The optical absorption coefficient of aerosol collected on a filter is determined by radiative transfer considerations, which include multiple scattering effects and absorption enhancement due to reflections from the filter (Petzold et al. 2005). However, the accuracy of M_{BC} measured by MAAP is not well quantified (Kanaya et al. 2013).

COSMOS allows for a fully automated, high-sensitivity, continuous measurement of light absorption by BC aerosol (Miyazaki et al. 2008). COSMOS measures changes in transmittance between a clean and exposed section of automatically advancing quartz filter tape using a light-emitting diode (LED) at a wavelength of 565 nm (Miyazaki et al. 2008). The aerosol sample air stream enters COSMOS on the side of the unit, and is introduced to the surface of the quartz filter. The quartz filter will remove all aerosol particles, and the resultant particle-free sample air passes through the back of the reference portion of the quartz filter. COSMOS includes a heated inlet to effectively volatilise non-refractory aerosol components internally mixed with BC (Kondo et al., 2011), and provides automated filter changes according to a pre-determined threshold transmittance value. The measurements of M_{BC} by COSMOS have been estimated to be about 10 % (Kondo et al. 2011).

A transmittance-dependent correction factor is used in deriving M_{BC} by COSMOS, based on the experiments using polydisperse nigrosine ($C_{48}N_9H_{51}$; Bond et al. 1999). However, it is not obvious if the same factor can be applied to BC particles.

79 There has been no measurement of the correction factor for BC thus far. In this work,
80 we have derived such a correction using ambient BC in Tokyo.

81 Until now, COSMOS instruments have routinely utilised PALLFLEX quartz
82 filters (E70-2075W, hereafter simply referred to as PALLFLEX; the same filter used
83 for PSAP), but due to a change in supplier, an alternative quartz filter (HEPA L-
84 371M; hereafter referred to as simply HEPA) has been proposed for use in future
85 measurements. The PALLFLEX filters were used for the original characterisation of
86 COSMOS (Miyazaki et al., 2008), and have shown good agreement with other
87 techniques used to measure ambient M_{BC} (e.g. Kondo et al., 2011). However, the
88 performance of the HEPA filter is unknown, and there is a urgent need to characterise
89 it. In this study, we also assess the applicability of the HEPA filter for use with
90 COSMOS.

91

92 **2. MEASUREMENTS AND METHODS**

93 **2.1 Experimental Setup**

94

95 We performed a series of experiments using ambient COSMOS measurements
96 to (a) assess the impact of filter transmittance deterioration on BC measurements (for
97 both PALLFLEX and HEPA filters), and (b) test the suitability of the HEPA filters
98 for COSMOS measurements, by directly comparing the HEPA and PALLFLEX
99 filters (resulting in the HP-factor). For these tests, two COSMOS were operated in
100 parallel, in the configuration outlined in Figure 1a.

101 The aforementioned sampling procedure takes place within the ‘optical block’,
102 which is heated to a temperature of 50 °C to minimise the influence of high ambient
103 relative humidity fluctuations on the measurement (a source of uncertainty with PSAP

measurements). Another key advantage of COSMOS, is that COSMOS automatically advances the quartz filter by 20 mm when the light transmission value recorded by the instrument falls below a predefined threshold value (Tr_{thresh}).

The COSMOS measurements took place downstream of an inlet heater, or thermal denuder, and a particle impactor (with a size-cut of 2 μm), as shown in Figure 1. Following the results from detailed laboratory experiments performed by Irwin et al. (2013), an operational temperature of 300°C was chosen for the inlet heater. COSMOS operates with a high-consistency constant flow rate of 0.7 STP LPM $\pm$ 1 %, controlled by a Mass Flow Controller (MFC; SEC-E40MK3, HORIBA ESTEC, Kyoto, Japan). During these experiments, the number and mass distributions of ambient BC were periodically measured by an SP2, simultaneous with COSMOS measurements.

2.2 COSMOS operating principle

COSMOS records values of light transmission (Tr) at 1 kHz based on the transmittance of a section of blank filter (I_0), and the transmittance of the filter area bisecting the aerosol flow at time t , (I_t):

$$Tr = I_0 / I_t \quad (1)$$

Data is provided as 1 minute integrated data of BC mass concentration (M_{BC}) in units of $\mu\text{g m}^{-3}$ at standard temperature and pressure (STP; 273.15K and 1013 hPa), which is derived from the absorption coefficient, b_0 . Absorption coefficients of BC particles collected on filters are not the same as those for suspended BC particles, due

129 to multiple scattering within the filter medium. Therefore, a raw absorption
 130 coefficient, b_0 , is operationally determined using the following equation:

131

$$132 \quad b_0 = (A/V_s) \ln[I_{t-\Delta t}/I_t] \quad (2)$$

133

134 where A is the collection area of the sample spot, V_s is the sample volume
 135 during a given time period Δt (between $t-\Delta t$ and t), and $I_{t-\Delta t}$ and I_t are the average
 136 transmittances. The flow rate of the COSMOS instrument is typically set to 0.7 litres
 137 min^{-1} at STP.

138 Unlike PSAP, COSMOS makes use of a heated inlet to vaporise semi-volatile
 139 material, which negates the requirement for a correction to account for scattering due
 140 to coating on BC particles, and scattering due to the co-existence of non-BC
 141 compounds within the filter medium (Kondo et al., 2009). However, there are
 142 correction factors to account for the multiple scattering in the filter medium, which
 143 must be applied to the raw absorption coefficient b_0 to convert it into the absorption
 144 coefficient, b_{abs} , as shown in the following equation:

145

$$146 \quad b_{abs} = f_{fil} b_0 \quad (3)$$

147

148 where f_{fil} accounts for the multiple scattering of light in the filter medium. Bond
 149 et al. (1999) derived the following equation for f_{fil} using polydisperse nigrosine:

$$150 \quad f_{fil}(Tr) = \frac{1}{[1.0796 Tr + 0.71] \times B} \quad \text{for } Tr \geq 0.7 \quad (4)$$

151

152 where B is a constant scaling factor of 1.22 (Bond et al., 1999). The correction
 153 factor for multiple scattering, $f_{fil}(Tr)$ is dependent on the aerosol size distribution, as

154 f_{fil} varies with the penetration depth of aerosol into the filter (Kondo et al., 2009). As
 155 it is difficult to perform a detailed analysis of transmittance-based factors using
 156 ambient BC with PSAP instruments, the majority of earlier studies investigating these
 157 absorption coefficients typically did so via laboratory experiments using either poly-
 158 or monodisperse aerosol in conjunction with PSAP instruments (e.g. Bond et al.,
 159 1999; Sheridan et al, 2005), and to this effect, different values of B have been used
 160 depending on the value of the mass absorption cross-section used at the time of
 161 measurement (for further discussion on this topic, see the Appendix). Here, we
 162 present a detailed comparison between two COSMOS instruments measuring ambient
 163 BC, by effectively fixing the transmittance values of one instrument and comparing it
 164 to the other operating under normal conditions.

165 The mass absorption cross-section (σ_{abs} , with units of $m^2 g^{-1}$) of BC can be
 166 derived from simultaneous measurements of b_0 (i.e. COSMOS) and the mass
 167 concentration of black carbon, M_{BC} (e.g. by a single particle soot photometer, SP2;
 168 Droplet Measurement Technology, Boulder, CO, USA);

169

$$170 \quad \sigma_{abs} = b_{abs}/M_{BC} (SP2) = f_{fil} (Tr) b_0/M_{BC} (SP2) \quad (5)$$

171

172 Kondo et al. (2011) evaluated the uncertainty of σ_{abs} associated with changes in
 173 size distribution of ambient BC. Once σ_{abs} is determined for a typical BC size
 174 distribution, M_{BC} (COSMOS) is derived from b_0 :

$$175 \quad M_{BC} = f_{fil} (Tr) b_0/\sigma_{abs} = F \times b_0 \quad (6)$$

$$176 \quad F = f_{fil} (Tr)/\sigma_{abs}$$

177 From the factory, COSMOS firmware contains values of $B = 1.22$, and $\sigma_{abs} = 10$.

178 Kondo et al. (2011) showed that the same BC mass concentration is derived from the

179 same value of b_0 , providing the correct associated pairs of B and σ_{abs} are used (i.e. $B =$
180 1.22 for $\sigma_{\text{abs}} = 10$, and $B = 1.397$ for $\sigma_{\text{abs}} = 5.9$; see Appendix). The absolute accuracy
181 of M_{BC} is determined by the uncertainty of F , not the uncertainty of σ_{abs} . The accuracy
182 of F is determined by the measurement accuracies of b_0 , M_{BC} (SP2), and the
183 functional form of $f_{\text{fil}}(Tr)$.

184 At present, COSMOS derives M_{BC} utilising equation (4), providing values of Tr
185 ≥ 0.7 . Depending on instrument location and the aerosol concentration, it is
186 advantageous to operate COSMOS with $Tr_{\text{thresh}} \leq 0.7$ to minimize the frequency of
187 filter changes. In this study, we performed a re-evaluation of the functional form of f_{fil}
188 (Tr) to enable accurate measurements of M_{BC} at lower values of Tr .

189 In this study, we performed a re-evaluation of the functional form of $f_{\text{fil}}(Tr)$ to
190 enable accurate measurements of M_{BC} using BC in Tokyo. We also assessed the
191 applicability of the new HEPA filter for use with COSMOS. A radiative transfer
192 model, originally presented by Moteki et al. (2010), was used validate to the
193 instrument response to the new filters. Furthermore, we derive a simple
194 HEPA/PALLFLEX correction factor (subsequently referred to as the HP-factor)
195 suitable for bringing average values of M_{BC} in-line with the original, validated,
196 COSMOS measurements using the PALLFLEX filter.

197

198 **3. RESULTS**

199 **3.1. Transmittance-based correction**

200

201 In order to evaluate the functional form of $f_{\text{fil}}(Tr)$, two COSMOS instruments
202 were operated in parallel, but with COSMOS 1 set to filter advance at $Tr_{\text{thresh}} = 0.95$
203 and COSMOS 2 set to advance its filter at a threshold transmittance of $Tr_{\text{thresh}} = 0.6$

204 using HEPA and PALLFLEX filters. Operating COSMOS 1 with a threshold
 205 transmittance of 0.95 results in a rapid filter advance (to the order of a few minutes),
 206 as only a small amount of BC is collected on the filter before reaching the threshold
 207 transmittance required for advancement. In doing so, values of M_{BC} will be derived
 208 from COSMOS 1 in the near-constant filter transmittance range 1-0.95.

209 The measurements took place in central Tokyo between 27 September and 2
 210 October 2013, using the setup shown in Figure 1. Figure 2 shows examples of the 1-
 211 day averaged number-size distribution ($dN/d\log D_{BC}$) and mass-size distribution
 212 ($dM/d\log D_{BC}$) values, and lognormal fitted curves, measured by the SP2 on 3 October
 213 2013. The results are consistent with previous SP2 measurements in central Tokyo,
 214 with a peak in the mass-size distribution at around $D_{BC} = 140$ nm. A lognormal fit was
 215 applied to the number-size distribution after assuming the count median diameter
 216 (CMD) to be around 60 - 70 nm, based on previous results of ambient Tokyo BC
 217 mass- and number-size distributions (e.g. Kondo et al. 2011).

218 Table 1 shows the results of the slope and r^2 correlation between the two
 219 COSMOS, separated according to different filter transmittance regimes of COSMOS
 220 2. When both COSMOS are operating within the transmittance range 1-0.9 the
 221 agreement is almost 1:1. Values of M_{BC} derived from the two COSMOS diverge with
 222 increasing values of Tr , as shown in Table 1. Throughout the measurement period,
 223 there was almost no change in the r^2 correlation, indicating that this divergence of
 224 M_{BC} values is a function of filter transmittance.

225 A correction factor dependent on Tr can be derived by plotting the BC ratio,
 226 $M_{BC}(Tr_{0.6})/M_{BC}(Tr_{0.95})$, against the corresponding filter transmittance value of
 227 COSMOS 2 (for which $Tr_{thresh} = 0.6$) at the time of measurement. Figure 3 shows the
 228 BC ratio plotted against the filter transmission of COSMOS 2 (where $Tr_{thresh} = 0.6$)

229 using HEPA filters, visualising the transmittance dependence of M_{BC} . The empty
 230 circles in Figure 3 show the mean BC ratio (at transmittance intervals of ~ 0.05) of the
 231 original, uncorrected data decreasing almost linearly with reducing filter transmittance.
 232 Provided systematic instrumental biases are negligible, this ratio can be used to derive
 233 a correction factor, $g(Tr)$, where Tr is the transmittance at the time of measurement.
 234 With a good approximation, $g(Tr)$ can be expressed as,

235

$$236 \quad g(Tr) = m(1 - Tr) + 1 \quad (7)$$

237

238 The gradient m was determined to be 0.462 for HEPA filter by ordinary least
 239 squares regression. The same experiment was also performed for PALLFLEX filters,
 240 for which $m = 0.398$, as shown in Table 2. The full circles in Figure 3 show the values
 241 of the BC ratio after applying the transmittance-based correction outlined by Eq. 8.
 242 Table 3 shows the slope and r^2 correlation of the uncorrected and corrected values of
 243 M_{BC} for each COSMOS. After applying the correction, the agreement between the
 244 two COSMOS instruments is $\sim 1\%$, across the entire tested transmittance range.

245 The correction factor $g(Tr)$ can then be used to directly derive corrected values
 246 of M_{BC} (corr):

247

$$248 \quad M_{BC}(\text{corr}) = g(Tr) \times M_{BC} \quad (8)$$

249

250 where M_{BC} is the original value of BC mass concentration, as derived using
 251 equation (4). The correction factor g can also be used to correct $f_{fil}(Tr)$:

252

$$253 \quad f_{fil}(\text{corr}, Tr) = \frac{1}{[1.0796 Tr + 0.71][g(Tr) \times B]} \quad (9)$$

254 which can be re-written as:

255
$$f_{fil}(corr, Tr) = \frac{1}{[-0.429681 Tr^2 + 1.2267 Tr + 0.99258] \times B} \quad (10)$$

256 or

257
$$f_{fil}(corr, Tr) = \frac{1}{[-0.498775 Tr^2 + 1.25036 Tr + 1.03802] \times B} \quad (11)$$

258

259 for PALLFLEX or HEPA filters, respectively. The functional forms of these two
260 equations are shown in Figure 4, alongside those similarly derived from PSAP
261 measurements by Ogren (2010) and Virkkula (2010). Though the shapes of these
262 functions are quite different, there is around 20% agreement in all cases except for
263 data at low filter transmittance, with low average single scattering albedo (i.e. where
264 $\langle SSA \rangle = 0.239$), suggesting that as the filter loading increases $f_{fil}(Tr)$ becomes more
265 sensitive to absorbing aerosols. However, instruments are rarely used at such low
266 filter transmittances (typically no lower than 0.7), and within this region all
267 approaches to $f_{fil}(Tr)$ agree to within ~20 %.

268 Finally, $g(Tr)$ can be used to derive a corrected mass absorption cross section,
269 $\sigma_{abs}(corr)$:

270

271
$$\sigma_{abs}(corr) = \sigma_{abs} / g(Tr) \quad (12)$$

272

273 **3.2. Filter Comparisons**

274 **3.2.1. Systematic Bias**

275

276 To assess the instrumental bias between instruments, both COSMOS
277 instruments were operated with identical inlet configurations (Figure 1), and with the
278 same Tr_{thresh} value of 0.7. Figure 5 shows the results of this comparison for hourly

mean values of M_{BC} for a) PALLFLEX and b) HEPA filters for an ambient measurement period of 72 hours. The data presented are corrected, based on filter transmittance. The error bars represent the average standard deviation at $\sim 0.1 \mu\text{g m}^{-3}$ increments. It should be noted that the standard deviation incorporates the natural variability of the ambient BC concentration over the averaging period (of one hour). The results show that reported values of M_{BC} from parallel COSMOS measurements with PALLFLEX and HEPA filters are consistent to within around 1-2 %, with no evidence for a systematic bias between the two COSMOS instruments. The uncorrected data had an almost identical slope, but a slightly larger standard deviation (results not shown).

3.2.2. PALLFLEX and HEPA filter comparison

After assessing the experimental setup for systematic bias, the COSMOS instruments were then operated under typical conditions (i.e. $Tr_{thresh} = 0.7$) with one COSMOS installed with a PALLFLEX filter and the second COSMOS installed with a HEPA filter. In order to incorporate any systematic bias between filter types, the filters were swapped in the respective instruments after 5 days of continuous measurement. Figure 6 shows a comparison of the total results from the 10 days of simultaneous measurements, before (empty circles and dashed line) and after (solid circles and solid line) the application of the correction factor. These results indicate that a COSMOS installed with a HEPA filter will consistently report values of M_{BC} around 8 % higher than a COSMOS installed with a PALLFLEX filter (with both datasets corrected), most likely due to differences in the physical parameters between the two filters as described in Section 3.1. If only uncorrected data are considered,

values of M_{BC} derived from HEPA are just 6 % higher than from PALLFLEX. Table 4 shows the impact of the correction on the agreement between the two datasets. The best agreement is for an uncorrected-uncorrected comparison (with an agreement of around 6 %). The larger discrepancy between measurements using the different filters after the correction is a result of the numerically larger correction factor applicable to HEPA filters (averaging ~6 %) when compared to that applied to the PALLFLEX filters (averaging ~4 %), which therefore increases the difference between derivations of M_{BC} from the two filters after correction. Therefore, for either pairing (i.e. corrected-corrected, or uncorrected-uncorrected), a simple and constant HP-factor of $M_{BC} = 0.94 \times M_{BC_HEPA}$ would be sufficient to bring the 1-hour mean values of M_{BC} derived from at least one single Tr cycle (i.e. at least one filter advance) of the HEPA filter to within ~2 % of the PALLFLEX filter measurements. It should be noted that the r^2 correlation improves slightly from 0.976 to 0.992 after correction.

317

318 **4. SENSITIVITY OF LIGHT ABSORPTION TO FILTER PARAMETERS**

319

The absorption coefficient b_{abs} was originally derived for the PALLFLEX filter type, and was shown to agree to within around 10% (precision) via comparison with the SP2 (Kondo et al., 2011), after the absolute normalization discussed above. Values of $g(Tr)$ are expected to vary between different filters (though for the same filter type, this variation was measured to be typically less than 2%), due to changes in the physical properties between filters. The correction $g(Tr)$ was therefore derived for the new HEPA filter. To validate the response of light absorption to different filter parameters, we used the radiative transfer model presented in detail by Moteki et al. (2010), which provides a filter-based absorption coefficient B_{abs_filter} , analogous to the

329 absorption coefficient, b_{abs} , derived from COSMOS measurements.

330 The radiative transfer model is described in detail by Moteki et al. (2010), but in
331 brief, the model makes use of five parameters used to calculate the radiative transfer
332 response of fibrous filters to particle loadings: sample spot area, A ; fibre diameter, D_f ;
333 refractive index, n ; thickness, L ; and solidity, α (these terms are included in the
334 derivation of transmissivity). The sample spot size is a constant for each COSMOS
335 instrument, and is thus not changed. Due to the low density of the filters, a scanning
336 electron microscope (SEM) could not be used to accurately derive fibre parameters
337 such as diameter, thickness, and solidity.

338

339 **4.1. Dependence on filter thickness**

340

341 The HEPA filter is made from similar quartz material to the PALLFLEX filter,
342 but is approximately twice as thick at $310 \pm 10 \mu\text{m}$ (PALLFLEX filters are 150 ± 10
343 μm in thickness). An increase in filter thickness will change the physical
344 characteristics of the filter (such as particle penetration depth, light transmissivity),
345 and thus the derived values of b_{abs} and M_{BC} . The increased thickness of the HEPA
346 filter does not change the sample flow rate, which is separately controlled by a mass
347 flow controller.

348 B_{abs_filter} was derived for filter thicknesses between 50 - 500 μm , for a constant
349 particle number concentration of BC particles of 100 nm in diameter, and the results
350 are shown in Table 5. A peak in B_{abs_filter} was observed for a filter thickness of 310 μm
351 (equivalent to the HEPA filter thickness), around 13 % higher than the derived
352 absorption for filters of 150 μm in thickness (equivalent to PALLFLEX filter
353 thickness). Further increasing the filter thickness up to 500 μm results in a plateau of

354 B_{abs_filter} at around 7×10^{-5} , whereas reducing the filter thickness down to 50 μm results
355 in a decrease of B_{abs_filter} by a factor of 2. The time (in minutes) taken to reach Tr_{thresh}
356 0.7 was around 116 min for a filter thickness of 150 μm compared to 102 min for a
357 filter thickness of 310 μm , corresponding to a reduction of around 13 % when using
358 the thicker filter. A reduction of similar magnitude was observed during simultaneous
359 ambient measurements; the COSMOS using a HEPA filter will advance the filter ~
360 10% sooner than the COSMOS using a PALLFLEX filter.

361

362

363 **4.2. Dependence on filter solidity**

364

365 A filter's efficiency with respect to particle interception increases with
366 increasing fibre diameter (both PALLFLEX and HEPA filters are comprised of quartz
367 fibres of diameter 0.5 μm), as the fibre occupies a larger space. However, in addition
368 to filter thickness, a major factor behind filter efficiency is its packing density, or
369 solidity (α), where α = fibre volume/total volume. Filter solidity plays an increasingly
370 dominant role as the number of fibres per unit area increases, increasing the
371 probability of particle capture. In order to assess the dependence of filter collection to
372 solidity, the value of solidity was changed within the radiative transfer model between
373 typical values of 0.01 and 0.3 (Hinds, 1999).

374 The radiative transfer model was used to derive filter transmittance as a function
375 of sampling time, for a sample airflow with a constant concentration of 100 nm
376 particles. The gradient of this graph was derived, and is hereafter referred to as the
377 Transmittance Loss Rate (TLR, s^{-1}). Table 6 shows the TLR calculated for both
378 PALLFLEX and HEPA filters (determined by changing only the filter thickness in the

model) as a function of filter solidity (α) in the expected range of 0.01 - 0.30 (Hinds, 1999). For reference, a filter solidity of $\alpha = 0.1$ was used in model simulations for a similar purpose in the original presentation of the model by Moteki et al. (2010), and agreed well with experimental results. For a sparse filter ($\alpha = 0.01$), particles are not collected efficiently, and the TLR is relatively low. The TLR reaches its apparent peak with a solidity of 0.1, and slowly decreases as the filter becomes increasingly dense. For $\alpha = 0.1$, the difference in TLR between the two filters is around 9 %. As the experimental results from the filter comparison are within an agreement of around 8 % (as shown in Section 4.), it is therefore likely that the solidity of the two filters is comparable, and that filter thickness is the dominant factor affecting b_{abs} .

5. APPLICATION TO LONG TERM DATA SET

In order to assess the applicability of the transmittance-based correction to a long-term dataset, the correction was applied to ambient M_{BC} data collected with a HEPA filter, taken in Tokyo between 25th August 2013 and 18th October 2013, inclusive. COSMOS 1 was operated with $Tr_{thresh} = 0.95$ and COSMOS 2 with $Tr_{thresh} = 0.6$. Both COSMOS 1 and COSMOS 2 track the variability in the BC concentration well, throughout the entire measurement period. The percentage difference between the uncorrected and corrected values of M_{BC} from COSMOS 2 reached a maximum at the time of filter advancement, i.e. when $Tr = 0.6$, of around 17 %. For the typical operational range of Tr values (1-0.70), the average underestimate of M_{BC} was around 6 %, whereas across the entire tested range of Tr values (1-0.6), the average underestimate was ~ 10 %. After applying the correction to the data, the agreement between reported values of M_{BC} was brought to within around 2 %. Figure 7 shows

the uncorrected and corrected datasets over a 24-hour period. The solid line shows M_{BC} for COSMOS 1, and the wide dashes for the uncorrected data from COSMOS 2. The narrow dashed lines represent the corrected values of COSMOS 2, showing good agreement when compared to COSMOS 1. The BC ratio ($M_{BC}(TR0.6)/M_{BC}(TR0.95)$) is shown on the top panel of Figure 7, showing that after the correction, the agreement between the two COSMOS measurements is greatly improved.

The correction was applied to COSMOS data collected in Tokyo in September 2009, originally presented by Kondo et al. (2011). During this sampling period COSMOS was operated with a standard Tr_{thresh} value of 0.7, alongside an SP2 (an example of this configuration is shown in Figure 1b). The correction using a value of 0.398 for the slope (Section 3.1. and Table 2) was applied to the 1-minute COSMOS data (originally shown in Figure 12 by Kondo et al., 2011), and is shown as 15-minute averaged data plotted against the SP2 data in Figure 8a as solid black circles (uncorrected data is empty circles). The slope between the original COSMOS and SP2 data was 0.971, and after the application of the correction, the slope became 1.009. This same procedure was performed for ambient COSMOS (PALLFLEX filter, $Tr_{thresh} = 0.7$) and SP2 data in Tokyo in late 2013. The CMD of BC mass-size distribution between 2009 and 2013 was ~130 nm (Figure 2), producing a similar increase in the average M_{BC} of ~4 %, as shown in Table 7. This average ~4 % increase in average M_{BC} is consistent with the results from the COSMOS-COSMOS comparison derived from PALLFLEX filters (Section 3.2.1.). It should be noted that the r^2 correlation only increases slightly from 0.974 to 0.982, and the scatter in the data is likely to be due to a combination of factors (e.g. variations in the BC mass-size distribution, instrumental noise). Figure 8b shows the BC ratio, $M_{BC}(Tr0.7)/M_{BC}(SP2)$ against the Tr value at the time of measurement. The dashed grey line shows

429 the slope derived from COSMOS PALLFLEX measurements (Table 2). After
430 application of the correction to the original COSMOS data, the BC ratio is ~1 across
431 the Tr range. This further demonstrates the trivial applicability of the correction to
432 pre-existing COSMOS data collected with PALLFLEX filters.

433 These results show that M_{BC} can be successfully corrected for changes in filter
434 transmittance, for ambient aerosol measured in Tokyo. It is known that there is some
435 size dependence associated with the derivation of M_{BC} from COSMOS, and so data
436 collected in other regions may show slightly different agreement. However, such
437 differences are likely smaller than the overall uncertainty of COSMOS measurements
438 (total systematic errors are ~12 %).

439 6. SUMMARY AND CONCLUSIONS

440 A transmittance-dependent correction factor to M_{BC} was derived following the
441 comparison of two parallel COSMOS measurements, using the same filter type. A
442 trend was observed whereby the difference in reported BC mass concentrations
443 between the two COSMOS widened for decreasing values of Tr , though the data
444 remained tightly correlated ($r^2 \sim 0.99$). An empirical correction factor, $g(Tr)$, was
445 derived from this data, using equation (7). Corrected values of BC mass can be
446 derived directly from COSMOS data using the following equation: $M_{BC}(\text{corr}) = g$
447 $(Tr) \times M_{BC}$. After application of the correction, the two data sets agreed to within 2 %.

448 The application of the correction to COSMOS data obtained with the use of
449 PALLFLEX filters was shown to correct values of M_{BC} by around 4% on average.
450 The application of the correction should be considered when high-resolution
451 COSMOS data is required, for use in comparisons with other instrumentation and
452 methods. However, it was found that the correction factor g is dependent on filter-
453 type. This correction was applied to long-term ambient data sampled using HEPA
454 filters in Tokyo, and resulted in a similar agreement between the two COSMOS
455 instruments of ~2 %. A sensitivity study was performed using a radiative transfer
456 model, suggesting that the increased thickness of the HEPA filter is the parameter
457 most likely to affect the filter absorption efficiency.

458 It was deduced that the HEPA filters consistently overestimated the values of
459 M_{BC} derived from PALLFLEX filters by around 6 %, if no correction is made.
460 Therefore, a simple correction to long-term averaged values taking the form of $M_{BC} =$
461 $0.94 \times M_{BC}(\text{HEPA})$ is sufficient to bring 1-hour averaged COSMOS measurements
462 using the new HEPA filter into ~2 % agreement with the original, validated,
463 PALLFLEX filter COSMOS measurements.

APPENDIX

A.1. The scaling factor B and its relation to σ_{abs}

In this section, we provide a more detailed description of the scaling factor B , and its relation to σ_{abs} , with attention focussed on COSMOS measurements. As explained in Section 1.2, COSMOS operationally determines the raw absorption coefficient, b_0 .

$$b_0 = (A/V_s) \ln[I_{t-\Delta t}/I_t] \quad (\text{A.1})$$

where A is the collection area of the sample spot (for COSMOS, this value is provided on a per-instrument basis from the factory), V_s is the sample volume during a given time period Δt (between $t-\Delta t$ and t), and $I_{t-\Delta t}$ and I_t are the average transmittances. The flow rate of the COSMOS instrument is typically set to 0.7 litres min^{-1} at STP.

This absorption coefficient must be corrected for the multiple scattering of light within the filter medium, in order to derive the absorption coefficient, b_{abs} . This correction takes the form of a light-transmittance dependent function, with a constant scaling factor B . The equation derived by Bond et al. (1999) took form:

$$f_{fil} = [1/(1.0796 Tr + 0.71)]/B \quad \text{for } Tr \geq 0.7 \quad (\text{A.2})$$

where B is the aforementioned scaling factor, and has a value of 1.22. The equation (A.1) was derived using poly-disperse nigrosin ($\text{C}_{48}\text{N}_9\text{H}_{51}$) of diameters $< 1 \mu\text{m}$. Due to a difference in the exposed filter area, A , in PSAP firmware compared to that determined by the manufacturer and used by Bond et al. (1999), Sheridan et al. (2005) corrected B by a factor of 0.873, to a final value of 1.397.

Nakayama et al. (2010) used the latter value of B (1.397), when exploring the size-dependence of f_{fil} in more detail, resulting in the following equation:

$$f_{fil} = [1/(1.0796 Tr + 0.71)]/[B \times E (MMD)] \quad (A.3)$$

495

496 where $E (MMD)$ is a size-dependent scaling factor.

497 M_{BC} is derived from COSMOS measurements in the following equation:

498

$$M_{BC} = f_{fil} (Tr) b_0 / \sigma_{abs} \quad (A.4)$$

500

501 where σ_{abs} is the mass absorption cross section. The value of σ_{abs} depends on the
 502 size distribution of BC. Kondo et al. (2011) examined this relationship in more detail,
 503 and found that the same BC mass concentration is derived from the same value of b_0 ,
 504 providing the correct associated values of B and σ_{abs} are used (i.e. $B = 1.22$ with σ_{abs}
 505 $= 10$ and $E = 1$, and $B = 1.397$ with $\sigma_{abs} = 5.9$ and $E = 1.554$).

506 From the factory, COSMOS firmware contains values of $B = 1.22$, and $\sigma_{abs} = 10$
 507 m^2/g , and as the size-distribution cannot be derived directly from COSMOS
 508 measurements (and the exposed filter area A is provided for each COSMOS), we base
 509 the correction to f_{fil} in this study on these values.

510

511

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518

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Figure Captions

Figure 1: Schematic diagram showing the experimental setup used for a) the COSMOS – COSMOS experiments, and b) COSMOS – SP2 experiments. Heaters were operated at a temperature of 300°C, removing non-BC components from the aerosol.

Figure 2: Plots showing 1-day mean ambient BC number and mass size distributions as measured by the SP2 in Tokyo on 3 October 2013

Figure 3. The ratio of BC mass, $M_{BC}(Tr_{0.6})/M_{BC}(Tr_{0.95})$, plotted as a function of filter transmittance (for the COSMOS with $Tr_{thresh} = 0.6$). The empty circles represent the uncorrected BC ratio, and the solid circles represent the BC ratio after the application of the correction. The vertical bars represent the standard deviation.

Figure 4. The transmission correction function $f_{fil}(Tr)$ as a function of filter transmission (Tr), derived for PALLFLEX and HEPA filters. The figure also shows the similar PSAP-derived functions presented by Ogren (2010) and Virkkula (2010) for comparison ($\langle SSA \rangle$ = average single-scattering albedo of the data).

Figure 5. Transmittance-corrected values of hourly averaged ambient BC Mass concentrations from 72-hour a) PALLFLEX and b) HEPA filter comparisons, showing good agreement between COSMOS instruments. The vertical and horizontal bars show an averaged standard deviation for the hourly mean BC measurement (at roughly $0.1 \mu\text{g m}^{-3}$ increments), and include natural variations

610 in concentration.

611

612 Figure 6. Original (empty circles) and corrected (solid circles) values of hourly
613 averaged ambient BC Mass concentrations from 10 days of measurement.

614

615 Figure 7. Top panel: the BC Ratio, $M_{BC}(Tr_{0.6})/M_{BC}(Tr_{0.95})$, for original (dashed) and
616 corrected (solid) data. Middle panel: Time series of uncorrected and corrected
617 long-term measurement data in Tokyo, with the values of Tr represented by the
618 grey scale in the bottom panel.

619

620 Figure 8a) Correlation plots of BC mass concentrations measured by COSMOS (using
621 PALLFLEX) and an SP2 in 2009, using 15-min average data. The original data
622 presented by Kondo et al. (2011) is denoted by empty circles, and its least
623 squares fitted line is denoted by a dashed line. The solid black circles represent
624 the data after application of the correction to the COSMOS data, with a least
625 squares fit denoted by a solid black line.

626

627 Figure 8b) The ratio of BC mass, $M_{BC}(Tr_{0.7})/M_{BC}(SP2)$, plotted as a function of filter
628 transmittance (for the COSMOS with $Tr_{thresh} = 0.7$). The empty circles represent
629 the uncorrected BC ratio (data from Kondo et al. 2011), and the solid circles
630 represent the BC ratio after the application of the correction. The vertical bars
631 represent the standard deviation.

- 1 Table 1. The slope and r^2 correlation of different transmittance regimes, for two
- 2 COSMOS using HEPA filters.

Transmittance Regime	Slope (Tr _{0.6} / Tr _{0.95})	r^2
1 — 0.9	0.988	0.99
0.9 — 0.8	0.954	0.99
0.8 — 0.7	0.897	0.99
0.7 — 0.6	0.833	0.99
ALL	0.901	0.97

1 Table 2. Empirically derived values of m , for PALLFLEX and HEPA filters.

Filter Type	m
PALLFLEX	0.398
HEPA	0.462

2

- 1 Table 3. The slope and r^2 correlation of BC mass data uncorrected and corrected for
- 2 changes in filter transmittance, for two COSMOS using HEPA filters.

Data state	Slope ($\text{Tr}_{0.6} / \text{Tr}_{0.95}$)	r^2
Uncorrected	0.915	0.99
Corrected	1.008	0.99

3

- 1 Table 4. The slope and r^2 correlation between values of M_{BC} measured using
- 2 PALLFLEX (P) and HEPA (H) filters before (_{UNCOR}) and after (_{COR}) correction.

Correction state	Slope	r^2
P _{UNCOR} /H _{UNCOR}	0.944	0.976
P _{UNCOR} /H _{COR}	0.880	0.982
P _{COR} /H _{COR}	0.914	0.992

- 1 Table 5. The relationship of filter thickness to $B_{\text{abs_filter}}$ and the time required to reach
- 2 $Tr_{\text{thresh}} = 0.7$.

	Filter thickness (μm):					
	50	100	150	310	400	500
$B_{\text{abs_filter}}$ ($\times 10^{-5}$)	3.978	5.386	6.441	7.279	6.955	7.067
Time to $Tr_{0.7}$ (min)	192	133	116	102	100	97

- 1 Table 6. Calculated transmittance loss rates (s^{-1}) as a function of filter solidity (α) for
- 2 HEPA and PALLFLEX filters, for 100 nm particles supplied at a constant flow.

Solidity (α)	Rate (s^{-1})	
	HEPA	PALLFLEX
0.01	-0.049	-0.024
0.05	-0.150	-0.113
0.1	-0.151	-0.138
0.2	-0.135	-0.131
0.3	-0.128	-0.126

- 1 Table 7. The slope and r^2 correlation between values of M_{BC} measured using
- 2 COSMOS (PALLFLEX) and an SP2, in Tokyo in 2009 and 2013.

Data state	2009 (Kondo et al. 2011)		2013	
	Slope	r^2	Slope	r^2
	$M_{BC}(\text{Tr}_{0.7})/M_{BC}(\text{SP2})$		$M_{BC}(\text{Tr}_{0.7})/M_{BC}(\text{SP2})$	
Uncorrected	0.971	0.974	0.979	0.989
Corrected	1.008	0.982	1.012	0.993

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8