Size-resolved measurement of the mixing state of soot in the megacity Beijing, China: diurnal cycle, aging and parameterization

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Measurement of the mixing state of soot in the megacity Beijing

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Abstract

Soot particles are regarded as the most efficient light absorbing aerosol species in the atmosphere, playing an important role as a driver of global warming. Their climate effects strongly depend on their mixing state, which significantly changes their light absorbing capability and cloud condensation nuclei (CCN) activity. Therefore, knowledge about the mixing state of soot and its aging mechanism becomes an important topic in the atmospheric sciences.

The size-resolved (30–320 nm diameter) mixing state of soot particles in polluted megacity air was measured at a suburban site (Yufa) during the CAREBeijing 2006 campaign in Beijing, using a Volatility Tandem Differential Mobility Analyzer (VTDMA). Particles in this size range with non-volatile residuals at 300 °C were considered to be soot particles. On average, the number fraction of internally mixed soot in total soot particles (F_{in}), decreased from 0.80 to 0.57 when initial \( D_p \) increased from 30 nm to 320 nm. Further analysis reveals that: (1) \( F_{in} \) was well correlated with the aerosol hygroscopic mixing state measured by a CCN counter. More externally mixed soot particles were observed when particles showed more heterogeneous features with regard to hygroscopicity. (2) \( F_{in} \) had pronounced diurnal cycles. For particles in the accumulation mode (\( D_p \) at 100–320 nm), largest \( F_{in} \) were observed at noon time, with “apparent” turnover rates (\( k_{ex\rightarrow in} \)) up to 7.8 % h\(^{-1}\). (3) \( F_{in} \) was subject to competing effects of both aging and emissions. While aging increases \( F_{in} \) by converting externally mixed soot particles into internally mixed ones, emissions tend to reduce \( F_{in} \) by emitting more fresh and externally mixed soot particles. Similar competing effects were also found with air mass age indicators. (4) Under the estimated emission intensities, actual turnover rates of soot (\( k_{ex\rightarrow in} \)) up to 20 % h\(^{-1}\) were derived, which showed a pronounced diurnal cycle peaking around noon time. This result confirms that (soot) particles are undergoing fast aging/coating with the existing high levels of condensable vapors in the megacity Beijing. (5) Diurnal cycles of \( F_{in} \) were different between Aitken and accumulation mode particles, which could be explained by the faster size shift of smaller particles in the Aitken mode.
To improve the $F_{\text{in}}$ prediction in regional/global models, we suggest parameterizing $F_{\text{in}}$ by an air mass aging indicator, i.e., $F_{\text{in}} = a + bx$, where $a$ and $b$ are empirical coefficients determined from observations, and $x$ is the value of an air mass age indicator. At the Yufa site in the North China Plain, fitted coefficients ($a, b$) were determined as (0.57, 0.21), (0.47, 0.21), and (0.52, 0.0088) for $x$ (indicators) as $[\text{NO}_2]/[\text{NO}_y]$, $[\text{E}]/[\text{X}]$ ([ethylbenzene]/[m,p-xylene]) and $([\text{IM}] + [\text{OM}])/[\text{EC}]$ ([inorganic + organic matter]/[elemental carbon]), respectively. Such a parameterization consumes little additional computing time, but yields a more realistic description of $F_{\text{in}}$.

1 Introduction

Soot particles are generally regarded as the most efficient light absorbing component of atmospheric aerosols (Hansen et al., 1979; Japar et al., 1986; Horvath, 1993; Bergstrom et al., 2007). They are produced by incomplete combustion of fossil fuel and biomass and they consist mainly of black or elemental carbon but may also contain some refractory organic matter (Horvath, 1993; Smith and O’Dowd, 1996; Burtscher et al., 2001; Novakov et al., 2003; Pöschl, 2005; Sadezky et al., 2005; Andreae and Gelencsér, 2006; Kondo et al., 2006, 2010; Rose et al., 2006; Frey et al., 2008; Cheng et al., 2009; Wehner et al., 2009). In the atmospheric science literature, the terms black carbon (BC), elemental carbon (EC), pyrogenic carbon are frequently used as synonyms for soot (e.g., Kondo et al., 2006, 2009; Pöschl et al., 2010). More discussion on this topic can be found in Andreae and Gelencsér (2006).

Soot particles, after emission, are generally undergoing aging processes by condensation (Smith et al., 1989), coagulation (Riemer et al., 2004, and references therein), as well as oxidation (Ivleva et al., 2007) and cloud/fog processing; and gradually become internally mixed (coated) with other chemical compounds. Depending on their mixing state, soot particles can be classified as internally mixed (coated) or externally mixed (uncoated). The mixing state of soot particles has a great influence on their climate effects. The light absorbing capability of soot (related to their direct radiative
effects) can be enhanced by a factor of 1.5 to 3 when soot is coated by or internally mixed with other aerosol components including sulfate, nitrate, organics and water (Jacobson, 2000; Lesins et al., 2002; Bond et al., 2006; Cheng et al., 2006, 2008a,b, 2009; Shiraiwa et al., 2008, 2010). Moreover, the coating of soot particles can significantly enhance their ability to be activated as cloud condensation nuclei (CCN) (Rose et al., 2011) and hence influence the cloud formation processes (related to their indirect radiative effects) and the removal of soot particles from the atmosphere. For these reasons, the mixing state is a crucial parameter for soot particles, uncertainty about which has been made difficult the accurate assessment of soot’s climatic impact (Jacobson, 2001).

In global/regional climate models, the turnover rate ($k_{\text{ex} \rightarrow \text{in}}$) is used to describe the conversion rate of externally mixed to internally mixed soot particles. Due to limited knowledge and computational limits, a constant $k_{\text{ex} \rightarrow \text{in}}$ was taken in most studies, varying from 1.25% h$^{-1}$ to 2.5% h$^{-1}$ (Cooke and Wilson, 1996; Cooke et al., 1999, 2002; Lohmann et al., 2000; Jacobson, 2001; Koch, 2001). To obtain a more realistic $k_{\text{ex} \rightarrow \text{in}}$, several aerosol modeling studies have been carried out to examine quantitatively $k_{\text{ex} \rightarrow \text{in}}$ of soot particles (Riemer et al., 2004, 2010). However, it is challenging to validate the modeling results against atmospheric conditions, since modeling of the soot mixing state is almost equivalent to modeling all physicochemical processes in the gas and aerosol phases.

Decades ago, information about the soot mixing state relied on particle morphology measurements by Transmission Electron Microscopy (Katrinak et al., 1992, 1993; Hasegawa and Ohta, 2002). This technique does not always give reliable information, as volatile coatings may be lost, or thin coatings may not be evident. Later on, several online instruments with high time resolution were developed, i.e., volatility tandem differential mobility analyzer (VTDMA) (Philippin et al., 2004), single particle soot photometer (SP2) (Stephens et al., 2003) and aerosol time-of-flight mass spectrometer (ATOFMS) (Moffet and Prather, 2009). Among these methods, only the VTDMA is able to determine particle smaller than 0.1 µm. Based on these online methods, several
field studies have been carried out in recent years at regional (Engler et al., 2007), suburban (Shiraiwa et al., 2007; Cheng et al., 2009; Wehner et al., 2009), and urban sites (Rose et al., 2006), and by aircraft measurements (Moteki et al., 2007). The aging of soot particles was found to be well correlated with several air mass age indicators, e.g., ratios of C$_2$H$_4$ to C$_2$H$_2$ (Moteki et al., 2007), 2-pentyl nitrate (2- acetone peroxinate) to $n$-pentane ($n$-C$_5$H$_{12}$) (Shiraiwa et al., 2007) and OC/EC (organic carbon/elemental carbon) (Cheng et al., 2006). Under certain assumptions on the air mass history and OH concentrations, increase rates of $F_{in}$ (number fraction of internally mixed soot particles) of about 1 % h$^{-1}$ to 2.3 % h$^{-1}$ were derived (Moteki et al., 2007; Shiraiwa et al., 2007).

In the summer of 2006, measurements of the mixing state of non-volatile particles (here taken to be “soot particles”, see discussion in Sect. 2.2) were carried out at a suburban site of Beijing in the North China Plain by using a VTDMA (Cheng et al., 2009; Wehner et al., 2009). In this study, we perform an in-depth analysis of VTDMA results, focusing on the following topics: (1) comparison of the mixing state of soot measured by a VTDMA and the aerosol hygroscopicity mixing state determined by a CCN (cloud condensation nuclei) counter; (2) diurnal variation and evolution of soot mixing state at different size ranges; (3) calculation of $k_{ex-in}$ and the influence on it of emissions; and (4) potential parameterization methods.

2 Methods

2.1 Overview of the campaign

As part of the “Campaign of Air Quality Research in Beijing and Surrounding Region 2006” (CAREBeijing 2006), air pollutants including aerosol and gases were comprehensively measured at a suburban site, Yufa (39.51467° N, 116.30533° E, ~ 25 m above ground level), during the summer of 2006. The Yufa site is located in the south of Beijing, roughly 50 km away from the urban center. One major road passes east of the
measurement site, at a distance of less than 200 m. Figure S1 (in the Supplement) shows the meteorological conditions at the Yufa site from 15 August to 9 September. During this period, the averages (± one standard deviation) of temperature, relative humidity (RH) and wind speed were $26.2 \pm 3.7^\circ$C, $68 \pm 17\%$ and $1.6 \pm 1.4$ m s$^{-1}$, respectively (based on 5-min resolution meteorological data, see Supplement Fig. S1).

2.2 VTDMA measurement

A Volatility Tandem Differential Mobility Analyzer (VTDMA) (Orsini et al., 1996; Philippin et al., 2004) was used to measure the number size distributions of the non-volatile residuals of pre-selected mono-disperse particles that were heated at 300°C (7 selected particle diameters in the range of 30 nm to 320 nm; time resolution of 1 h for a complete cycle of 7 diameters). In the thermal chamber (i.e., at 300°C) of the VTDMA, the coating materials undergo volatilization leaving behind the non-volatile cores. Details about the VTDMA measurements at the Yufa site in 2006 can be found in Cheng et al. (2009) and Wehner et al. (2009). The volatilization results in a change of particle size, where unchanged particles indicate no coating material while big changes indicate a large fraction of coating materials. In continental polluted megacity air, the material of sub-micrometer particles that is non-volatile at this temperature (i.e., 300°C) is considered to be mostly “soot” (Smith and O’Dowd, 1996; Burtscher et al., 2001; Kondo et al., 2006, 2010; Rose et al., 2006; Frey et al., 2008; Cheng et al., 2009; Wehner et al., 2009), which consists mainly of black or elemental carbon but may also contain some refractory organic matter (Pöschl, 2005; Sadezky et al., 2005; Andreae and Gelencsér, 2006). Since the VTDMA actually measures non-volatile-core containing particles (NVP), the notation “soot (NVP)” was mostly used instead of “soot” when referring to the VTDMA results.

In VTDMA measurements, the size distribution of nonvolatile residuals is classified into three groups according to $D_{p,300^\circ C}/D_p$, where $D_p$ is the initial diameter of the sampled dry particles and $D_{p,300^\circ C}$ is the diameter of the particle residual after being heated at 300°C. Following Wehner et al. (2009), (1) particles with $D_{p,300^\circ C}/D_p < 45\%$
were denoted as “high-volatile” and not considered as soot particles; (2) particles with 45% < \(D_{\text{p,300 °C}}/D_{\text{p}}\) < 82% were denoted as “medium-volatile” and considered as internally mixed (coated) soot particles; and (3) Particles with 82% < \(D_{\text{p,300 °C}}/D_{\text{p}}\) were denoted as “low-volatile” and considered as externally mixed (uncoated) soot particles.

\(F_{\text{in}}\), the number fraction of internally mixed soot particles (among all soot-containing particles), was intensively used for discussion in this paper and calculated as,

\[
F_{\text{in}} = \frac{n_{\text{in}}}{n_{\text{in}} + n_{\text{ex}}}
\]

where \(n_{\text{in}}\) is the number concentration of internally mixed soot (NVP) particles, and \(n_{\text{ex}}\) is the number concentration of externally mixed soot (NVP) particles.

2.3 The turnover rate of soot particles

The turnover rate, \(k_{\text{ex→in}}\), is a parameter describing the conversion rate of the externally mixed soot to internally mixed particles:

\[
\left(\frac{\partial n_{\text{ex}}}{\partial t}\right)_{\text{ex→in}} = \left(\frac{\partial n_{\text{ex}}}{\partial t}\right)_{\text{cond}} + \left(\frac{\partial n_{\text{ex}}}{\partial t}\right)_{\text{coag}} = -k_{\text{ex→in}}n_{\text{ex}} + \left(\frac{\partial n_{\text{ex}}}{\partial t}\right)_{\text{coag}}\]

(2)

where \(\left(\frac{\partial n_{\text{ex}}}{\partial t}\right)_{\text{ex→in}}\) is the rate of change of \(n_{\text{ex}}\) due to aging (conversion) processes. The two major aging processes are the condensation of sulfuric acid and organic compounds and the coagulation of particles. For large particles or during daytime, the condensation dominates the aging processes (Jacobson, 1997; Riemer et al., 2004), which converted equal amounts of externally mixed soot to internally mixed. Then the rate of change of \(n_{\text{in}}\) due to aging (conversion) processes is

\[
\left(\frac{\partial n_{\text{in}}}{\partial t}\right)_{\text{ex→in}} \approx -\left(\frac{\partial n_{\text{ex}}}{\partial t}\right)_{\text{ex→in}} = k_{\text{ex→in}}n_{\text{ex}}
\]

(3)

The values of \(n_{\text{ex}}\) and \(n_{\text{in}}\) measured in field campaigns can be subject to other processes, e.g., horizontal/vertical transport (\(\text{Tran}_{\text{ex}}\) and \(\text{Tran}_{\text{in}}\)), emission (\(\text{Emis}_{\text{ex}}\) and...
\begin{equation}
\frac{\partial n_{\text{ex}}}{\partial t} = \text{Tran}_{\text{ex}} + \text{Emis}_{\text{ex}} + \text{Depo}_{\text{ex}} + \left( \frac{\partial n_{\text{ex}}}{\partial t} \right)_{\text{ex} \rightarrow \text{in}}
\end{equation}

\begin{equation}
\frac{\partial n_{\text{in}}}{\partial t} = \text{Tran}_{\text{in}} + \text{Emis}_{\text{in}} + \text{Depo}_{\text{in}} + \left( \frac{\partial n_{\text{in}}}{\partial t} \right)_{\text{ex} \rightarrow \text{in}}
\end{equation}

When aging is the only or dominant process affecting \( n_{\text{ex}} \) and \( n_{\text{in}} \),

\begin{equation}
\frac{\partial n_{\text{ex}}}{\partial t} \approx \left( \frac{\partial n_{\text{ex}}}{\partial t} \right)_{\text{ex} \rightarrow \text{in}} = -k_{\text{ex} \rightarrow \text{in}}n_{\text{ex}}
\end{equation}

\begin{equation}
\frac{\partial n_{\text{in}}}{\partial t} \approx \left( \frac{\partial n_{\text{in}}}{\partial t} \right)_{\text{ex} \rightarrow \text{in}} = k_{\text{ex} \rightarrow \text{in}}n_{\text{ex}}
\end{equation}

\begin{equation}
\left( \frac{\partial n_{\text{tot}}}{\partial t} \right)_{\text{ex} \rightarrow \text{in}} = \left( \frac{\partial n_{\text{ex}}}{\partial t} \right)_{\text{ex} \rightarrow \text{in}} + \left( \frac{\partial n_{\text{in}}}{\partial t} \right)_{\text{ex} \rightarrow \text{in}} = 0
\end{equation}

where \( \partial n_{\text{tot}}/\partial t \) is the rate of change of total (ex + in) soot particles. \( (\partial n_{\text{tot}}/\partial t)_{\text{ex} \rightarrow \text{in}} = 0 \) indicates that \( n_{\text{tot}} \) is constant in the aging (ex \( \rightarrow \) in) process dominated by the condensation.

In aging processes, the rate of change of \( F_{\text{in}} \) (\( F_{\text{in}} = n_{\text{in}}/n_{\text{tot}} \)) is

\begin{equation}
\left( \frac{\partial n_{\text{tot}}}{\partial t} \right)_{\text{ex} \rightarrow \text{in}} = k_{\text{ex} \rightarrow \text{in}}n_{\text{ex}}
\end{equation}

\begin{equation}
\left( \frac{\partial F_{\text{in}}}{\partial t} \right)_{\text{ex} \rightarrow \text{in}} = k_{\text{ex} \rightarrow \text{in}}(1 - F_{\text{in}})
\end{equation}

Then the turnover rate \( k_{\text{ex} \rightarrow \text{in}} \) can be calculated by

\begin{equation}
k_{\text{ex} \rightarrow \text{in}} = \frac{(\partial F_{\text{in}}/\partial t)_{\text{ex} \rightarrow \text{in}}}{(1 - F_{\text{in}})} \approx \frac{(\partial F_{\text{in}}/\partial t)}{(1 - F_{\text{in}})} \approx \frac{(\Delta F_{\text{in}}/\Delta t)}{(1 - F_{\text{in}})}
\end{equation}
When aging \((\text{ex} \rightarrow \text{in})\) dominates the variation of \(F_{\text{in}}\), \(k_{\text{ex} \rightarrow \text{in}}\) can be determined by Eq. (11). When other processes become significant, this conclusion will not hold and \(k_{\text{ex} \rightarrow \text{in}}\) determined by Eq. (11) is called the “apparent” turnover rate. Increase rates \((\Delta F_{\text{in}} / \Delta t)\) of 1.0–2.3 % \(\text{h}^{-1}\) and \(F_{\text{in}}\) of 0.2–0.6 were reported in previous studies (Moteki et al., 2007; Shiraiwa et al., 2007), corresponding to “apparent” \(k_{\text{ex} \rightarrow \text{in}}\) of 1.3–5.8 % \(\text{h}^{-1}\).

### 2.4 CCN measurement and hygroscopicity (\(\kappa\)) distribution

Size-resolved CCN efficiency spectra (activation curves) were measured with a Droplet Measurement continuous flow CCN counter (DMT-CCNC) coupled to a Differential Mobility Analyzer (DMA; TSI 3071) and a Condensation Particle Counter (CPC; TSI 3762). The CCNC was operated at a total flow rate of 0.5 l \(\text{min}^{-1}\) with a sheath-to-aerosol flow ratio of 10. The effective water vapor supersaturation \((S)\) was regulated by the temperature difference between the upper and lower end of the CCNC flow column \((\Delta T)\) and calibrated with ammonium sulfate aerosol as described by Rose et al. (2008). For a detailed description of CCN measurements in the campaign, see Gunthe et al. (2011).

Size-resolved CCN efficiency spectra can be used to derive the cumulative distribution function of particle hygroscopicity, \(H(\kappa, D_p)\), which is defined as the number fraction of particles with a given dry diameter, \(D_p\), and with an effective hygroscopicity parameter smaller than the parameter \(\kappa\) (Su et al., 2010). The data conversion from \(S-D_p\) space to \(\kappa-D_p\) space is achieved by solving the \(\kappa\)-Köhler model equation (Petters and Kreidenweis, 2007).

By fitting \(H(\kappa, D_p)\) with a cumulative single-mode lognormal distribution function (CDF), the following parameters were calculated: \(\overline{\kappa}_g\), the geometric mean of \(\kappa\) in the fitted mode; and \(\sigma_{\kappa,g}\), the geometric standard deviation of \(\kappa\) in the fitted mode. The spread of the \(\kappa\) distribution, e.g., \(\sigma_{\kappa,g}\), reflects the mixing state of aerosols: under internally mixed conditions, all particles have the same composition and a uniform hygroscopicity mode, while under externally mixed conditions, particles can have distinct hygroscopicity modes (see Fig. 1).
2.5 Air mass age indicator

The aging of soot particles results in a change of their mixing state, i.e., conversion of externally mixed to internally mixed soot. An aged air mass has a larger fraction of internally mixed soot than a fresh air mass. Therefore, correlations can be expected between an air mass age indicator and the soot mixing state parameter (e.g., $F_{in}$). If such a correlation is significant, the soot mixing state could be parameterized by the air mass age indicators.

The age of air mass is a concept under the Lagrangian system. Ideally, the most fresh air mass is assigned an age of zero and its age will increase as the air mass becomes aged. The longer the air mass travels in the atmosphere, the older it will be. However, this does not mean that the age of an air mass can become infinitely large, and injection of fresh emissions into the air mass would reduce its age.

To quantify air mass ages, several indicators have been proposed. They are based on the fact that the aging will change the chemical compositions of air masses and parameters reflecting such changes can indicate the aging stage. Three indicators were used in this study.

\[
\frac{[NO_z]}{[NO_y]}
\]

In a fresh air mass from combustion sources, NO$_x$ (NO$_x$=NO + NO$_2$) are the dominant components of NO$_y$ (the total odd nitrogen compounds in the atmosphere). As photochemical reactions proceed, NO$_x$ evolves to other N-containing compounds such as HNO$_3$ and PAN, and the ratio of $[NO_z]/[NO_y]$ (NO$_z$=NO$_y$−NO$_x$) will increase. In this study, the nitrogen oxides (NO$_x$) and total reactive nitrogen (NO$_y$) were measured using a NO-O$_3$ chemiluminescence detector combined with a photolytic converter and a gold tube catalytic converter (Takegawa et al., 2006)

\[
\frac{[E]}{[X]}
\]

The ratios of hydrocarbons have been used as measures of photochemical age since Calvert (1976). Different reactivities of hydrocarbons result in different removal rates
and monotonic change of their ratios in the aging process. We used the ratio of ethylbenzene and m,p-xylene ([E]/[X]) in this study. Ethylbenzene and m,p-xylene were measured by an online GC-PID (gas chromatograph-photo ionization detector) system, as detailed by Xie et al. (2008).

\[ ([\text{IM}]+[\text{OM}])/[\text{EC}] \]

As an air mass ages, more secondary aerosol is produced, which reduce the mass fraction of soot particles. \( ([\text{IM}]+[\text{OM}])/([\text{EC}]) \) could hence be used as an indicator, in which \([\text{IM}]=[\text{NH}_4^+] + [\text{NO}_3^-] + [\text{SO}_4^{2-}] + [\text{Cl}^-] \) (inorganic ions in PM\(_1\) measured by aerosol mass spectrometer, AMS) and \([\text{OM}]\) was the organic matter mass (in PM\(_1\)) determined by AMS. An online Sunset EC/OC analyzer was used to measure the mass concentrations of EC, [EC]. Details about the EC/OC analyzer and AMS can be found in Takegawa et al. (2009).

3 Results and discussion

3.1 The mixing state of soot and hygroscopicity

Table 1 summarizes statistics of \( F_{in} \) measurements from this campaign. The \( F_{in} \) values show a decreasing trend as the particle size \( D_p \) increases, ranging from an \( \overline{F_{in}} \) of 0.80 ± 0.075 at \( D_p = 30 \text{ nm} \) to \( \overline{F_{in}} \) of 0.57 ± 0.102 at \( D_p = 320 \text{ nm} \) (arithmetic mean ± standard deviation). Figure 2 shows a comparison of hourly \( F_{in} \) data with \( \sigma_{\kappa,g} \) (the geometric standard deviation in a lognormal \( \kappa \) distribution, as detailed in Sect. 2.4., and Su et al., 2010). The \((1−F_{in})\) is the number fraction of externally mixed soot (NVP) particles. The two parameters, \( \sigma_{\kappa,g} \) and \((1−F_{in})\), are well correlated. This means that more externally mixed soot (NVP) particles were observed when particles showed more heterogeneous features in their hygroscopicity distributions (large \( \sigma_{\kappa,g} \)). Such consistence gives confidence about the robustness of both parameters and the reliability of the measuring systems.
3.2 Diurnal cycle of the soot mixing state

Figure 3 shows a pronounced diurnal cycle of $F_{in}$, which also has a strong size dependence. For accumulation mode particles (i.e., 100 nm to 320 nm, Fig. 3b), similar diurnal profiles of $F_{in}$ can be found, with a maximum at $\sim$ 13:00 LT (local time) and two minimums, in the early morning $\sim$ 7:00 LT and at night $\sim$ 21:00 LT, respectively. As the day progresses, an increase in $F_{in}$ (8:00–13:00 LT) is observed for accumulation mode particles with “apparent” turnover rates of 6.7–7.8 % h$^{-1}$.

In the Aitken mode, however, the variation of $F_{in}$ is different to that in the accumulation mode (Fig. 3a). The maximum of $F_{in}$ appears earlier at $\sim$ 8:00 LT (at $D_p = 30$ nm) and 12:00 LT (at $D_p = 50$ nm), and the afternoon minimum $F_{in}$ appears earlier as well. The distinct behaviors of Aitken mode particles are shown by the correlation matrix in Table 2, where $F_{in}$ of Aitken mode particles show poor correlations with the accumulation mode particles. The reasons for such correlations will be further discussed in Sect. 3.5.

For accumulation mode particles presented in Fig. 3b, $F_{in}$ shows a peak around noon time. Such a diurnal cycle indicates that ground-based measurements were subject to competing effects from physico-chemical aging and the introduction of fresh emissions. While the aging increases $F_{in}$ by turning externally mixed particles into internally mixed ones, the fresh emissions, with low $F_{in}$, tend to reduce the $F_{in}$ values. Similar competing effects can also be found in the diurnal courses of the air mass age indicators (e.g., $[\mathrm{NO}_2]/[\mathrm{NO}_y]$, $[\mathrm{E}]/[\mathrm{X}]$ and $([\mathrm{IM}]+[\mathrm{OM}])/[\mathrm{EC}]$ in Fig. 4) and aerosol single scattering albedo as reported in Garland et al. (2008).

3.3 Estimation of soot emission rate

Emissions have a significant impact on the measured $F_{in}$ and the “apparent” $k_{\text{ex}} \rightarrow \text{in}$ (soot turnover rate). Before determining the actual $k_{\text{ex}} \rightarrow \text{in}$, we need to first quantify the emissions.
Figure 5 shows the diurnal cycles of three parameters: (1) normalized EC concentrations during the campaign, (2) normalized total (ex + in) soot emission rates, and (3) the ratio of normalized emission rate to EC concentrations. The EC concentrations were determined by an online Sunset EC/OC analyzer (Takegawa et al., 2009); and the (total) soot emission rate was supposed to be proportional to the CO emissions in Beijing (Zhou et al., 2010). The normalized parameters were defined as the ratio of the individual parameter to its daily average value. For example, given [EC] of 9 µg cm\(^{-3}\) at 9:00 LT and a daily mean ([EC]) of 10 µg cm\(^{-3}\), the normalized EC concentration ([EC]*) at 9:00 LT is then 0.9 (i.e., 0.9 = 9 µg cm\(^{-3}\)/10 µg cm\(^{-3}\)).

The sum of Eqs. (4) and (5) gives the total (ex + in) emissions of soot particles

\[
\text{Emis}_{\text{tot}} = \frac{\Delta n_{\text{tot}}}{\Delta t} - \text{Tran}_{\text{tot}} - \text{Depo}_{\text{tot}} \quad \text{and} \quad \text{Emis}_{\text{tot},m} = \frac{\Delta m_{\text{tot}}}{\Delta t} - \text{Tran}_{\text{tot},m} - \text{Depo}_{\text{tot},m}
\]

where \text{Emis}_{\text{tot},m} is the mass emission rate of soot, and \text{m}_{\text{tot}} is the mass concentration of soot.

To obtain an optimal estimate of \text{Emis}_{\text{tot}} (or \text{Emis}_{\text{tot},m}), we adopted the following criteria, eliminating days with average wind speed > 2 m s\(^{-1}\) (20, 22 August, 3, 4, 5, 6 and 8 September), excluding the time periods from 8:00 to 19:00 LT, and choosing periods with large \text{Emis}_{\text{tot},m}/\text{m}_{\text{tot}}. The goal is to minimize the impact of horizontal/vertical transport and deposition, and choosing low wind speeds and night-time periods avoid large influence of horizontal transport and vertical mixing. Large \text{Emis}_{\text{tot},m}/\text{m}_{\text{tot}} ensures that the emission term could dominate the variation of \text{m}_{\text{tot}}.

In practice, we first calculated the diurnal variation of the three parameters (normalized \text{m}_{\text{tot}} = [\text{EC}]*, \text{Emis}_{\text{tot},m}*, \text{and} \text{Emis}_{\text{tot},m}/\text{m}_{\text{tot}}*) on days with average wind speed < 2 m s\(^{-1}\). Then we looked for the highest ratios of \text{Emis}_{\text{tot},m}/\text{m}_{\text{tot}} (labeled as “emission/concentration” in Fig. 5) in the period of 20:00–7:00 LT. In the end, the optimal emission rate was determined by \text{Emis}_{\text{tot},m} = \Delta[\text{EC}]/\Delta t \text{ at 20:00 LT, when the selected Emis}_{\text{tot},m}/\text{m}_{\text{tot}} data reached its maximum. The ratio of the mean (mass) emission rate to mean (mass) concentration, \text{Emis}_{\text{tot},m}*[\text{EC}], can then be determined by
\[ \frac{\text{Emis}_{\text{tot},m}}{[\text{EC}]} = \frac{\text{Emis}_{\text{tot},m}}{[\text{EC}]} \times \frac{[\text{EC}^*]}{\text{Emis}_{\text{tot},m}} \approx \frac{\Delta [\text{EC}]/\Delta t}{[\text{EC}]} \times \frac{[\text{EC}^*]}{\text{Emis}_{\text{tot},m}} \text{ at } 20:00 \text{ LT } \approx 13\% \text{ h}^{-1} \quad (13) \]

In the following analysis, we took the same value (13% h⁻¹) for the estimated ratio of the mean (number) emission rate to mean (number) concentration, \( \text{Emis}_{\text{tot}}/n_{\text{tot}} \).

### 3.4 Actual turnover rate of soot

In this section, a conceptual model was used to analyze the observed variation of \( F_{\text{in}} \). Since \( F_{\text{in}} \) of particles of all sizes in the accumulation mode (i.e., 100–320 nm) showed similar behaviors, \( F_{\text{in}} \) at 150 nm is taken as an example and will be discussed through this section.

Two processes were considered in the model: the aging process converting externally mixed particles into internally mixed particles, and the addition of fresh emissions. Equations (4) and (5) can be simplified as:

\[
\frac{\Delta n_{\text{in}}}{\Delta t} = \left( \frac{\partial n_{\text{in}}}{\partial t} \right)_{\text{ex} \rightarrow \text{in}} + \text{Emis}_{\text{in}} = k_{\text{ex} \rightarrow \text{in}} n_{\text{ex}} + \text{Emis}_{\text{in}} \quad (14)
\]

\[
\frac{\Delta n_{\text{ex}}}{\Delta t} = -k_{\text{ex} \rightarrow \text{in}} n_{\text{ex}} + \text{Emis}_{\text{ex}} \quad \text{and} \quad \frac{\Delta n_{\text{tot}}}{\Delta t} = \text{Emis}_{\text{tot}} \quad (15)
\]

where \( k_{\text{ex} \rightarrow \text{in}} \) denotes the turnover rate of externally mixed into internally mixed soot, \( n_{\text{tot}} \) is the number concentration of all soot particles (including both internally and externally mixed ones), \( \text{Emis}_{\text{in}} \), \( \text{Emis}_{\text{ex}} \), and \( \text{Emis}_{\text{tot}} \) are the emission rates of internally mixed, externally mixed, and total soot particles, respectively.

In Eqs. (14) and (15), we assumed that all (or most) particles stayed in the same size bin after the 1-h aging process. This assumption, to a large extent, simplified the following analysis, and could at least be valid for a broader size bracket, e.g., [100 nm, 350 nm]. The transport and dry deposition processes were supposed not to significantly change \( F_{\text{in}} \) (assuming \( n_{\text{in}} \) and \( n_{\text{ex}} \) have the same gradient and dry deposition velocity) and were therefore ignored in this analysis.
The variation of $F_{\text{in}}$ in the time interval $\Delta t$ can be derived by combining Eqs. (14) and (15):

$$
\Delta F_{\text{in}} = \frac{n_{\text{in}} + \Delta n_{\text{in}}}{n_{\text{tot}} + \Delta n_{\text{tot}}} - F_{\text{in}} = \frac{n_{\text{in}} + (k_{\text{ex} \rightarrow \text{in}}(n_{\text{tot}} - n_{\text{in}}) + \text{Emis}_{\text{in}})\Delta t}{n_{\text{tot}} + \text{Emis}_{\text{tot}}\Delta t} - F_{\text{in}}
$$

Then $k_{\text{ex} \rightarrow \text{in}}$ can be expressed as a function of $n_{\text{tot}}$, $F_{\text{in}}$, $\text{Emis}_{\text{tot}}$ and $\text{Emis}_{\text{in}}$,

$$
k_{\text{ex} \rightarrow \text{in}} = \frac{(\Delta F_{\text{in}} + F_{\text{in}})(1 + \frac{\text{Emis}_{\text{tot}}\Delta t}{n_{\text{tot}}}) - F_{\text{in}} - \frac{\text{Emis}_{\text{in}}\Delta t}{n_{\text{tot}}}}{(1 - F_{\text{in}})\Delta t}
$$

where, $n_{\text{tot}}$ and $F_{\text{in}}$ can be determined by VTDMA measurements. $\text{Emis}_{\text{tot}}$ can be calculated by multiplying a generic diurnal cycle of emissions in Beijing (Fig. 5) by the estimated emission intensity ($\text{Emis}_{\text{tot}}/n_{\text{tot}}$) of 13 % h$^{-1}$ (details in Sect. 3.3). $\text{Emis}_{\text{in}}$ can be calculated by multiplying $\text{Emis}_{\text{tot}}$ with an emission factor, $\beta = \text{Emis}_{\text{in}}/\text{Emis}_{\text{tot}}$. The minimum $F_{\text{in}} \sim 0.6$ can be considered as the upper limit of $\beta$, and we also chose several other $\beta$ values (0.2 and 0.4) for sensitivity studies.

Figure 6 shows the diurnal cycles of campaign-averaged $k_{\text{ex} \rightarrow \text{in}}$ calculated for particles at 150 nm with different $\beta$. Compared to a fixed $k_{\text{ex} \rightarrow \text{in}}$ value commonly used in regional and global models, the observation-constrained $k_{\text{ex} \rightarrow \text{in}}$ shows higher values with a maximum around 11:00–15:00 LT, and low values in the early morning and late afternoon. Such a diurnal course always holds, even after varying $\text{Emis}_{\text{tot}}$ by a factor of two (6.5–26 % h$^{-1}$). The cycle of the turnover rate, $k_{\text{ex} \rightarrow \text{in}}$, supports previous results in modeling studies (Riemer et al., 2004, 2010), which show high daytime $k_{\text{ex} \rightarrow \text{in}}$ dominated by condensation processes, and low $k_{\text{ex} \rightarrow \text{in}}$ contributed by both slower condensation and coagulation processes in the early morning and late afternoon. Although $k_{\text{ex} \rightarrow \text{in}}$ were also calculated for night-time periods, attention should be paid to these values. Because the coagulation-induced aging would become more important than the condensation, which violates the assumption of our model calculations.

Since the condensation-induced turnover rate is proportional to the condensable vapor pressure, the derived daytime $k_{\text{ex} \rightarrow \text{in}}$ implies a peak of condensable vapor pressure...
at the same period (11:00–15:00 LT). It is already known that gaseous sulfuric acid (precursor of sulfate in particles) often shows a peak around noon time. Our results indicate that even the potentially present unidentified condensable vapors might have similar diurnal cycles as sulfuric acid. Instead of complete characterizations of these unidentified vapors, the similarity in their diurnal variations enables the use of a simple parameterization method as an alternative solution in aerosol modeling studies, as will be discussed below.

Due to the presence of primary emission sources, the actual turnover rate of soot, $k_{\text{ex-in}}$, is higher than the “apparent” $k_{\text{ex-in}}$. The freshly emitted particles contain more externally mixed soot than the aged ambient air. The observed “aging” of soot (NVP) is to a certain extent compensated by the fresh emissions, the extent of which depends on the emission intensity. For the estimated emission intensity $(\frac{\text{Emis}_{\text{tot}}}{n_{\text{tot}}})$ of 13 % h$^{-1}$ and $\beta = 0.6$, $k_{\text{ex-in}}$ values reached up to 20 % h$^{-1}$ (see Fig. 6), much faster than the apparent $k_{\text{ex-in}}$ of 6.7–7.8 % h$^{-1}$.

The aging process in Beijing is also much faster than $k_{\text{ex-in}}$ of 1.3–5.8 % h$^{-1}$ in previous field measurements (Moteki et al., 2007; Shiraiwa et al., 2007) and 1.25–2.5 % h$^{-1}$ in modeling studies (Cooke and Wilson, 1996; Cooke et al., 1999, 2002; Lohmann et al., 2000; Jacobson, 2001; Koch, 2001; Tsigris and Kanakidou, 2003; Riemer et al., 2004). The fast turnover rate in the polluted megacity air is consistent with the observed rapid particle growth in the same area (Wiedensohler et al., 2009), both of which can be attributed to the fast formation and condensation of secondary aerosols in the megacity. The flow of soot particles from megacities influences the global background of soot to a large extent. If those soot particles are already coated or internally mixed in a very short time due to strong condensation, the background soot should be mostly internally mixed, as has been suggested by Andreae and Rosenfeld (2008).

Figure 6 also shows that the absolute value of $k_{\text{ex-in}}$ strongly depends on the choice of the emission factor $\beta$, while the relative variation of $k_{\text{ex-in}}$ does not. Smaller $\beta$ values (large fraction of externally mixed soot in emissions) require faster $k_{\text{ex-in}}$ to explain the
observed $F_{\text{in}}$ variations. For example, $\beta = 0.2$ requires $k_{\text{ex} \rightarrow \text{in}}$ up to 70% h$^{-1}$ to meet the observations. On the other hand, $k_{\text{ex} \rightarrow \text{in}}$ up to 20% h$^{-1}$ require a large $\beta = 0.6$, which means that 60% of the emitted soot particles should have already been internally mixed when they arrive at the measurement site.

### 3.5 Distinct diurnal variations of $F_{\text{in}}$ for Aitken and accumulation mode particles

In the conceptual model, we assume that particle growth will not lead to significant change in $n_{\text{tot}}$ and $n_{\text{ex}}$, which means no significant shift of the particle size distribution occurs over a short time. While such an assumption is valid for large particles in the accumulation mode (i.e., > 100 nm), it might be violated by the faster growth of small particles (e.g., 30 nm) in the Aitken mode, which was reflected by the different diurnal cycles of $F_{\text{in}}$ at smaller diameters (see Fig. 3).

To describe the rate of change of a particle size distribution $n(D_p)$ resulting from condensation, we adopted a general condensation equation (Seinfeld and Pandis, 2006, pp. 591) in the form

$$\frac{\partial n}{n \partial t} = - \frac{\partial}{n \partial D_p}(n \frac{4DM}{RTD_p \rho_p} f(Kn, \alpha) P)$$

(18)

where $n$ denotes the particle number concentration at $D_p$, $M$ is the molecular weight for the condensable species, $D$ is its diffusion coefficient in air, $R$ is the molar gas constant, $T$ is the temperature (in Kelvin), $\rho_p$ is the density of the particles, $P$ is the supersaturated vapor pressure of the condensable species, $Kn$ is the Knudsen number ($Kn = 2\lambda/D_p$), $\lambda$ is the mean free path of the condensable species in air, and $\alpha$ is the accommodation coefficient of the condensable species. $f(Kn, \alpha)$ is the correction due to non-continuum effects and imperfect surface accommodation and can be calculated by

$$f(Kn, \alpha) = \frac{0.75\alpha(1 + Kn)}{Kn^2 + Kn + 0.283Kn\alpha + 0.75\alpha}$$

(19)
Dividing both sides of Eq. (18) by \( A = 4DMP/(RT\rho_p) \), we get a parameter \( k_{\text{shift}} \):

\[
k_{\text{shift}} = \frac{1}{A} \frac{\partial n}{n \partial t} = -\frac{\partial}{n \partial D_p} \left( \frac{n}{D_p} f(Kn, \alpha) \right)
\]  

\( k_{\text{shift}} \) differs from \( (\partial n/\partial t)/n \) in Eq. (18) by a factor of \( A \), which is generally mostly independent of particle sizes. So, \( k_{\text{shift}} \) is equivalent to \( (\partial n/\partial t)/n \) in representing the size dependence of the rate of change of \( n \) due to condensation. By taking the measured \( n(D_p) \) and \( \lambda = \lambda_{\text{air}} \) (298 K, 1 atm) = 65.1 nm (Seinfeld and Pandis, 2006, p. 399), \( k_{\text{shift}} \) can be calculated for each \( D_p \).

Figure 7 shows \( k_{\text{shift}} \) as a function of the particle size \( D_p \), calculated with Eqs. (18)–(20) for the CAREBeijing 2006 campaign. The (mean) size distributions of the internally (externally) mixed soot (NVP) particles were used in the calculation (Wehner et al., 2009). Since VTDMA measurements covered only a limited size range (from 30 nm to 320 nm), nearest neighbor extrapolation were performed for out of range values, i.e. [1 nm, 30 nm) and (320 nm, 1000 nm] as shown in Fig. 7. \( k_{\text{shift}} \) shows positive values roughly on the right side of the peak of the particle size distributions and negative values on the left side. Positive \( k_{\text{shift}} \) (at \( D_p \) in shaded areas) indicate condensation-induced increases in \( n(D_p) \) while negative \( k_{\text{shift}} \) (at \( D_p \) in un-shaded areas) indicate condensation-induced decreases in \( n(D_p) \). Since the peaks of the \( n_{\text{in}}(D_p) \) and \( n_{\text{ex}}(D_p) \) distributions appears at sizes smaller than 100 nm, the condensation growth generally increases \( n_{\text{in}}(D_p) \) in the accumulation mode and reduces \( n_{\text{in}}(D_p) \) at the \( D_p \) of 30 nm.

Equation (21) describes the rate of change of internally mixed soot particles due to the condensational growth

\[
\frac{\Delta n_{\text{in}}}{\Delta t} = A n_{\text{in}} k_{\text{in,shift}}
\]  

where \( k_{\text{in,shift}} \) represent \( k_{\text{shift}} \) of internally mixed soot particles.

For externally mixed soot particles, the condensational growth results in a rate of change in the opposite direction of Eq. (21). Laboratory experiments showed that...
(externally mixed) soot agglomerates after sulfuric acid exposure (condensation) exhibit a considerable restructuring and shrinking to a more compact form (Zhang et al., 2008). By assuming a shrink speed (of \( n_{\text{ex}} \)) similar to the growth speed (of \( n_{\text{in}} \)), the rate of change of externally mixed soot particles due to condensational growth can be expressed by Eq. (22), in which \( \varepsilon \) is the conversion coefficient of the growing to shrinking speed.

\[
\frac{\Delta n_{\text{ex}}}{\Delta t} = -A\varepsilon n_{\text{ex}} k_{\text{ex,shift}}
\]

\[
\frac{\Delta n_{\text{tot}}}{\Delta t} = \frac{\Delta n_{\text{in}} + \Delta n_{\text{ex}}}{\Delta t} = A n_{\text{in}} k_{\text{in,shift}} - A\varepsilon n_{\text{ex}} k_{\text{ex,shift}}
\]

According to Eqs. (22) and (23), the condensation-induced shift of size distributions tends to reduce \( F_{\text{in}} \) of Aitken mode particles (a decrease in \( n_{\text{in}} \) and an increase in \( n_{\text{ex}} \)) while the emissions begin to counteract (or buffer) the influence of condensation. In Fig. 3a, the variation of \( F_{\text{in}} \) at \( D_p = 30 \text{ nm} \) is a good example of such competition: the condensation overwhelmed the emissions at 8:00–15:00 LT causing a decrease in \( F_{\text{in}} \), while the emission became more important from 15:00 to 19:00 LT resulting in an increasing \( F_{\text{in}} \). For particles at \( D_p = 50 \text{ nm} \), \( k_{\text{in,shift}} \) is not as fast as that at 30 nm. So the emissions and \( n_{\text{ex}} \rightarrow n_{\text{in}} \) needed to be considered along with \( k_{\text{in,shift}} \), which results in an intermediate variation of \( F_{\text{in}} \).

### 3.6 Size-resolved parameterizations of \( F_{\text{in}} \)

Because of our insufficient knowledge on mixing states and their change and the computational costs associated with explicit modeling of the mixing processes, it is still difficult to explicitly and accurately predict the variation of \( F_{\text{in}} \) in regional/climate models. In an aging air mass, the change of soot mixing state is generally accompanied by the change of other indicators representing the air mass age. We suggest parameterizing the mixing state of soot by using these correlations. If the other indicators...
are easier to measure and model, such parameterizations might provide an alternative solution, narrowing down the differences between ambient and modeled soot mixing state without significant additional computational costs.

The proposed parameterization approach involves two steps to calculate $F_{in}$ from other indicators. First, the average diurnal values of $F_{in}$ and other parameters (as shown in Figs. 3 and 4) are adopted to calculate a linear fit, resulting in the parameterization Eqs. (24)–(26). The reason for using average values is to smooth out fluctuations which may greatly reduce the correlation coefficient $R$ and introduce large uncertainties into the fitting results. $F_{in}$ at certain diameter (i.e., 150 nm) can be predicted by parameterization Eqs. (24)–(26). Figure 8a–c shows comparisons of $F_{in}$ at 150 nm with individual indicators, namely, $[\text{NO}_2]/[\text{NO}_y]$, $[\text{E}]/[\text{X}]$ and $([\text{IM}]+[\text{OM}])/[\text{EC}]$.

$$F_{in}(150 \text{ nm}) = 0.572 + 0.209\frac{[\text{NO}_2]}{[\text{NO}_y]}$$ \hspace{1cm} (24)

$$F_{in}(150 \text{ nm}) = 0.468 + 0.212\frac{[\text{E}]}{[\text{X}]}$$ \hspace{1cm} (25)

$$F_{in}(150 \text{ nm}) = 0.522 + 0.0088\frac{[\text{IM}]+[\text{OM}]}{[\text{EC}]}$$ \hspace{1cm} (26)

Secondly, the size-resolved $F_{in}$ in the accumulation mode can be calculated by the following equation from $F_{in}$ at 150 nm:

$$F_{in}(D_p) = (a\log_{10}(D_p/1 \text{ nm}) + b)F_{in}(150 \text{ nm})$$ \hspace{1cm} (27)

where $a$ and $b$ are constant parameters.

Fitting Eq. (27) to the measured $F_{in}$ over the diameter range 100 nm to 320 nm, we got $a = -0.353$ ($-0.370$, $-0.336$) (coefficients with 95% confidence bounds), $b = 1.78$ ($1.74$, $1.82$), and $R^2 = 0.80$. Figure 9 and Table 3 shows that Eq. (27) performs well in predicting the size-resolved $F_{in}$ over the size range between 100 nm and 320 nm. There is no systematic underestimation (or overestimation) and the fitted slope $k$ is almost
the same as the 1 : 1 line. Most variations, i.e., up to 77 %, of $F_{in}$ can be predicted by the parameterization.

4 Conclusions

Analysis of VTDMA results from the megacity Beijing shows a pronounced diurnal variation of $F_{in}$ with different time courses in the Aitken and accumulation modes. For accumulation mode particles, maxima of $F_{in}$ were observed at 12:00–13:00 LT, which can be explained by competing effects of physicochemical conversion and direct emissions. The distinct diurnal cycles of $F_{in}$ of Aitken and accumulation mode particles are likely to be caused by faster growth of smaller Aitken mode particles.

To calculate the actual turnover rate of soot from external to internal mixture ($k_{ex\rightarrow in}$), measurement data were analyzed by a conceptual model, which considered both direct emissions and the aging process. The analysis shows that the actual $k_{ex\rightarrow in}$ has high values during daytime, i.e., a maximum around 11:00–15:00 LT, and low values during the night-time. Turnover rates reached values of 20–70 % h$^{-1}$ around mid-day, which implies that soot (NVP) particles are present to a large extent as internal mixtures by the time they leave the urban environment. This enables them to act as CCN and also facilitates their removal by wet deposition (Andreae and Rosenfeld, 2008). The cycle of $k_{ex\rightarrow in}$ supports previous modeling results implying that the unidentified condensable vapors might have similar diurnal variations as sulfuric acid and other short life-time compounds produced by photochemistry. We also found that due to injection of fresh emissions, the “apparent” turnover rates derived from the variation in $F_{in}$ were much smaller than the actual $k_{ex\rightarrow in}$.

In this study, the calculated $k_{ex\rightarrow in}$ might be subject to potential uncertainties due to: (1) the estimation of $Emis_{tot}$ (soot emission intensity) and $\beta$ (number fraction of internally mixed soot particles in emissions); (2) the effect of transport process; and (3) the influence of particle growth and coagulation. To better understand the soot aging process, we suggest measuring $\beta$ in some emission studies, combining regional
models to quantify the transport effects, and implementing aerosol dynamic models instead of the current conceptual model.

$F_{in}$ shows a similar diurnal course as the other air mass age indicators (e.g., $[NO_2]/[NO_3]$, $[E]/[X]$ and $([IM]+[OM])/[EC]$), which are subject to competing effects between emissions and aging processes as well. The good agreement of their correlations can be expressed as a linear relationship. Given the difficulty of making direct measurements of soot mixing state ($F_{in}$), these relationships might be of great practical value in regional/global-scale studies on the influence of the various direct and indirect soot aerosol effects on climate, as it provides an easily measured proxy that does not consume significant additional computing time. However, such parameterizations require caveats because considerable variability can be expected between different sites or even at a given site, like the scattered data shown in Figs. 8 and 9. To validate the parameterization methods, improve our understanding and refine the range of the fitting parameters, more measurements should be carried out in other environments. In addition, validation for particles larger than 320 nm needs to be performed in future studies.

Appendix A

See Tables A1 and A2 for acronyms and symbols.

Supplementary material related to this article is available online at:

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References


Measurement of the mixing state of soot in the megacity Beijing

Y. F. Cheng et al.


Kondo, Y., Sahu, L., Kuwata, M., Miyazaki, Y., Takegawa, N., Moteki, N., Imaru, J., Han, S.,


Shiraiwa, M., Kondo, Y., Moteki, N., Takegawa, N., Miyazaki, Y., and Blake, D. R.: Evolution


Table 1. Statistics of $F_{in}$ at different diameters (429 data points).

<table>
<thead>
<tr>
<th>$F_{in}$</th>
<th>30 nm</th>
<th>50 nm</th>
<th>100 nm</th>
<th>150 nm</th>
<th>200 nm</th>
<th>260 nm</th>
<th>320 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arithmetic mean</td>
<td>0.80</td>
<td>0.74</td>
<td>0.70</td>
<td>0.64</td>
<td>0.60</td>
<td>0.62</td>
<td>0.57</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.075</td>
<td>0.078</td>
<td>0.084</td>
<td>0.090</td>
<td>0.100</td>
<td>0.100</td>
<td>0.102</td>
</tr>
</tbody>
</table>
Table 2. Correlation matrix of $F_{\text{in}}$ at different diameters (429 data points).

<table>
<thead>
<tr>
<th>$R$</th>
<th>30 nm</th>
<th>50 nm</th>
<th>100 nm</th>
<th>150 nm</th>
<th>200 nm</th>
<th>260 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 nm</td>
<td>0.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 nm</td>
<td>-0.12</td>
<td>0.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150 nm</td>
<td>-0.09</td>
<td>0.25</td>
<td>0.86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200 nm</td>
<td>-0.04</td>
<td>0.24</td>
<td>0.73</td>
<td>0.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>260 nm</td>
<td>-0.01</td>
<td>0.24</td>
<td>0.65</td>
<td>0.87</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>320 nm</td>
<td>0.00</td>
<td>0.28</td>
<td>0.58</td>
<td>0.80</td>
<td>0.89</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Table 3. Correlation of measured and predicted $F_{in}$ (429 data points for individual size bins; 2145 data points for all size bins).

<table>
<thead>
<tr>
<th>$D_p$</th>
<th>100 nm</th>
<th>150 nm</th>
<th>200 nm</th>
<th>260 nm</th>
<th>320 nm</th>
<th>all</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k^*$</td>
<td>0.99 ± 0.01</td>
<td>1.01 ± 0.00</td>
<td>1.02 ± 0.01</td>
<td>0.96 ± 0.01</td>
<td>1.00 ± 0.01</td>
<td>0.99</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.75</td>
<td>1.00</td>
<td>0.80</td>
<td>0.68</td>
<td>0.41</td>
<td>0.77</td>
</tr>
</tbody>
</table>

$k$ is the fit parameter in the equation: $F_{in}^{(predicted)} = kF_{in}^{(measured)}$. 
Table A1. Acronyms.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS</td>
<td>Aerosol mass spectrometer</td>
</tr>
<tr>
<td>ATOFMS</td>
<td>Aerosol time-of-flight mass spectrometer</td>
</tr>
<tr>
<td>CAREBeijing</td>
<td>Campaign of air quality research in Beijing</td>
</tr>
<tr>
<td>CCN</td>
<td>Cloud condensation nuclei</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential mobility analyzer</td>
</tr>
<tr>
<td>EC</td>
<td>Elemental carbon</td>
</tr>
<tr>
<td>GC-PID</td>
<td>Gas chromatography-photo ionization detector</td>
</tr>
<tr>
<td>OC</td>
<td>Organic carbon</td>
</tr>
<tr>
<td>PAN</td>
<td>Peroxyacetyl nitrates</td>
</tr>
<tr>
<td>PM$_1$</td>
<td>Particles of 1 µm or less in aerodynamic diameter</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>Particles of 10 µm or less in aerodynamic diameter</td>
</tr>
<tr>
<td>SP2</td>
<td>Single particle soot photometer</td>
</tr>
<tr>
<td>Soot (NVP)</td>
<td>Non-volatile-core containing particles, measured by the VTDMA,</td>
</tr>
<tr>
<td></td>
<td>and taken as soot particles</td>
</tr>
<tr>
<td>VTDMA</td>
<td>Volatility tandem differential mobility analyzer</td>
</tr>
</tbody>
</table>
Table A2. Symbols.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit*</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>m$^2$ s$^{-1}$</td>
<td>Diffusion coefficient for species in air</td>
</tr>
<tr>
<td>$D_p$</td>
<td>nm</td>
<td>Dry particle diameter</td>
</tr>
<tr>
<td>$D_{p,300}$</td>
<td>nm</td>
<td>Particle diameter after being heated at 300 °C in the VTDMA</td>
</tr>
<tr>
<td>[E]</td>
<td>ppb</td>
<td>Concentration of ethylene</td>
</tr>
<tr>
<td>[EC]</td>
<td>µg m$^{-3}$</td>
<td>Concentration of elemental carbon</td>
</tr>
<tr>
<td>$\text{Emis}_{in}$</td>
<td>cm$^{-3}$ h$^{-1}$</td>
<td>Number emission rate of internally mixed soot particles</td>
</tr>
<tr>
<td>$\text{Emis}_{tot}$</td>
<td>cm$^{-3}$ h$^{-1}$</td>
<td>Number emission rate of all soot particles</td>
</tr>
<tr>
<td>$\text{Emis}_{tot,m}$</td>
<td>µg m$^{-3}$ h$^{-1}$</td>
<td>Mass emission rate of all soot particles</td>
</tr>
<tr>
<td>$F_{in}$</td>
<td></td>
<td>Number fraction of internally mixed soot particles (medium volatile particles measured by VTDMA)</td>
</tr>
<tr>
<td>$f(Kn, \alpha)$</td>
<td>µg m$^{-3}$</td>
<td>Correction due to non-continuum effects and imperfect surface accommodation</td>
</tr>
<tr>
<td>[IM]</td>
<td>µg m$^{-3}$</td>
<td>[IM]=[$\text{NH}_4^+$]+[$\text{NO}_2^-$]+[$\text{SO}_4^{2-}$]+[$\text{Cl}^-$] (inorganic mass in PM$_1$ measured by aerosol mass spectrometer, AMS)</td>
</tr>
<tr>
<td>$Kn$</td>
<td></td>
<td>Knudsen number</td>
</tr>
<tr>
<td>$k_{ex\rightarrow in}$</td>
<td>h$^{-1}$</td>
<td>Turnover rate of soot, the rate of conversion of externally mixed to internally mixed soot</td>
</tr>
<tr>
<td>$k_{shift}$</td>
<td>nm$^{-2}$</td>
<td>Parameter representing the rate of change of particle number concentrations at certain size bin due to the condensational growth</td>
</tr>
<tr>
<td>$k_{ex,shift}$</td>
<td>nm$^{-2}$</td>
<td>$k_{shift}$ of externally mixed soot particles</td>
</tr>
<tr>
<td>$k_{in,shift}$</td>
<td>nm$^{-2}$</td>
<td>$k_{shift}$ of internally mixed soot particles</td>
</tr>
<tr>
<td>$M$</td>
<td>kg mol$^{-1}$</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>$[\text{NO}_x]$</td>
<td>ppb</td>
<td>Concentration of NO + NO$_2$</td>
</tr>
<tr>
<td>$[\text{NO}_y]$</td>
<td>ppb</td>
<td>Concentration of total reactive nitrogen</td>
</tr>
<tr>
<td>$[\text{NO}_z]$</td>
<td>ppb</td>
<td>$[\text{NO}_y]-[\text{NO}_x]$</td>
</tr>
<tr>
<td>$n_{in}$</td>
<td>cm$^{-3}$</td>
<td>Number concentration of internally mixed soot particles</td>
</tr>
<tr>
<td>$n_{ex}$</td>
<td>cm$^{-3}$</td>
<td>Number concentration of externally mixed soot particles</td>
</tr>
<tr>
<td>$n_{tot}$</td>
<td>cm$^{-3}$</td>
<td>Number concentration of total soot particles</td>
</tr>
<tr>
<td>[OM]</td>
<td>µg m$^{-3}$</td>
<td>Mass concentration of organic matter (in PM$_1$ measured by aerosol mass spectrometer, AMS)</td>
</tr>
<tr>
<td>$P$</td>
<td>Pa</td>
<td>Supersaturated vapor pressure of condensable species</td>
</tr>
<tr>
<td>$R$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
<td>Molar gas constant (unless specified)</td>
</tr>
<tr>
<td>$S$</td>
<td>%</td>
<td>Supersaturation of water vapor</td>
</tr>
<tr>
<td>$T$</td>
<td>K</td>
<td>Kelvin temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>s</td>
<td>Time</td>
</tr>
<tr>
<td>$[X]$</td>
<td>ppb</td>
<td>Concentration of m,p-xylene</td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td>Accommodation coefficient</td>
</tr>
<tr>
<td>$\beta$</td>
<td></td>
<td>$\beta = \text{Emis}<em>{in}/\text{Emis}</em>{tot}$</td>
</tr>
<tr>
<td>$\sigma_{p,\kappa}$</td>
<td></td>
<td>Geometric standard deviation in a lognormal $\kappa$ distribution</td>
</tr>
<tr>
<td>$\kappa$</td>
<td></td>
<td>Hygroscopicity parameter</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>m</td>
<td>Mean free path of the condensable species in air</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td></td>
<td>Conversion coefficient of the growing to shrinking speed for externally mixed soot particles</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>kg m$^{-3}$</td>
<td>Particle density</td>
</tr>
</tbody>
</table>

* if not specified.
Fig. 1. Evolution of the mixing state and hygroscopicity ($\kappa$) in the aging process. Solid lines refer to $dH/d\log\kappa$, the normalized number distributions of particle hygroscopicity. The areas of the pie diagrams refer to the abundance of individual chemical components (EC: elemental carbon, Org: organics, Inorg: inorganics). After aging, the externally mixed particles become internally mixed (coated).
Fig. 2. Comparison of aerosol and soot (NVP) mixing state parameters during the CAREBeijing-2006 campaign. The parameter $\sigma_{\kappa, g}$ was calculated from the aerosol hygroscopicity (i.e., $\kappa$) distribution measured at supersaturation $S = 0.26\%$ (Su et al., 2010); and the $(1 - F_{in})$ was determined for particles of diameters at 100 nm by the VTDMA measurements. Note that the mean activation diameter observed at $S = 0.26\%$ is 85 nm (Gunthe et al., 2011).
Fig. 3. Average diurnal variation of $F_{in}$ at different size bins (30, 50, 100, 150, 200, 260, and 320 nm). Symbols represent arithmetic mean values and error bars represent the standard deviation. Since transport might significantly affect the evolution of $F_{in}$ days with average wind speed $> 2 \text{ m s}^{-1}$ (20, 22 August, 3, 4, 5, 6 and 8 September) were completely removed in the analyses.
Fig. 4. Averaged diurnal variation of $[\text{NO}_z]/[\text{NO}_y]$, $[E]/[X]$ and $([\text{IM}]+[\text{OM}])/[\text{EC}]$. Symbols represent arithmetic mean values and error bars represent the standard deviation.
Fig. 5. Diurnal variation of normalized parameters: (a) emission rates from traffic in Beijing (according to CO emission intensity in the work of Zhou et al., 2010) (green dashed lines); (b) EC concentrations measured by an online Sunset EC/OC analyzer (red dotted lines); and (c) ratio of emission rate to EC concentration (black solid lines). Shaded areas represent the time period of 8:00–19:00 LT when vertical mixing is supposed to significantly affect EC concentrations.
Fig. 6. The actual turnover rate of soot (NVP), $k_{\text{ex}\rightarrow\text{in}}$, assuming different emission factors $\beta$ (number fraction of internally mixed soot particles to total soot particles in the emissions).
Fig. 7. The size dependence of the particle size distribution $n(D_p)$ variation due to condensation growth. $k_{\text{shift}}$ equals $(\partial n/\partial t)/n$ due to condensation growth divided by a constant (in Eq. 20). $k_{\text{shift}}$ can either be positive or negative, which indicates increases and decreases of $n(D_p)$ due to condensation growth, respectively. The shaded areas (with gray and light gray for $n_{\text{in}}$ and $n_{\text{ex}}$, respectively) indicate the size ranges where $k_{\text{shift}}$ are positive while $k_{\text{shift}}$ are negative in the un-shaded ranges.
Fig. 8. Correlations between $F_{in}$ and (a) $[\text{NO}_2]/[\text{NO}_y]$, (b) $[E]/[X]$, and (c) $([\text{IM}]+[\text{OM}])/[\text{EC}]$. The open circles are measurement data with a time resolution of 1 h; while the colored solid dots are average diurnal data. The average diurnal data can be linearly fitted by equation “$y = a + bx$” (dashed line) with $R$ being the correlation coefficient.
Fig. 9. Measured and predicted $F_{in}$ over 100 nm to 320 nm (2145 data points). The dashed line represents the 1:1 line.