



Technical Note

## Analytic Expression for the Aerosol Mass Efficiencies for Polydispersed Accumulation Mode

Chang H. Jung<sup>1\*</sup>, Junshik Um<sup>2</sup>, Soo Ya Bae<sup>3</sup>, Young Jun Yoon<sup>4</sup>, Seoung Soo Lee<sup>5</sup>, Ji Yi Lee<sup>6</sup>, Yong Pyo Kim<sup>7</sup>

<sup>1</sup> Department of Health Management, Kyungin Women's University, Incheon 21041, Korea

<sup>2</sup> Department of Atmospheric and Environmental Sciences, Pusan National University, Busan 46241, Korea

<sup>3</sup> Korea Institute of Atmospheric Prediction Systems, Seoul 07071, Korea

<sup>4</sup> Korea Polar Research Institute, Incheon, Korea

<sup>5</sup> Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20740, USA

<sup>6</sup> Department of Environmental Science and Engineering, Ewha Womans University, Seoul 03760, Korea

<sup>7</sup> Department of Chemical Engineering and Materials Science, Ewha Womans University, Seoul 03760, Korea

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### ABSTRACT

Aerosol mass efficiencies for extinction, scattering, and absorption are important parameters to understand aerosol optical properties. Although the mass efficiency is functions of the refractive index and particle size distribution, due to the complexity of the efficiency, mass efficiency parameters are usually regarded as a size independent and assumed to depend mainly on the chemical composition of aerosols. In this study, we calculated the mass efficiencies of polydispersed aerosols based on different aerosol types. An analytical approach to the approximated formula of the mass efficiency of each chemical species was developed and evaluated by fitting the results to those of the Mie theory that calculated the optical properties of chemical species based on the refractive index and size. We used the lognormal size distributions and external mixture approximations that represent the polydispersity of aerosol particles. Size ranges of 0.5–2.5  $\mu\text{m}$  in the geometric mean diameter were considered for five different chemical species. The parameters of fitting curves were generalized for polydispersed aerosols as functions of the geometric mean diameter and the geometric standard deviation. The results of the newly developed analytic approach showed a good agreement with those of the Mie theory. The proposed approach provides an effective means to estimate the mass extinction efficiency of polydispersed multi-component aerosols.

**Keywords:** Analytical approach; Polydisperse aerosol particles; Mass scattering efficiency; Mass absorption efficiency; Mie theory.

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### INTRODUCTION

Atmospheric aerosols play an important role in regulating earth's radiation budget and this regulation depends strongly on their optical properties. Light scattering and absorption characteristics of atmospheric aerosols, which affect their optical properties, depend on several factors, such as the wavelength of the incident light, the size distribution, shape, chemical composition and the mixing state of aerosol particles, and relative humidity (RH) that determines the aerosol water content (Piliinis *et al.*, 1995).

Among many physical and optical parameters that

characterize aerosol properties, coefficients and efficiencies of extinction, scattering, and absorption are the most important ones to understand aerosol optical properties. Note that the aerosol mass efficiency is functions of aerosol mass density, refractive index, and particle size distribution. For the mass efficiency, we have considered different density for different aerosol species. However, because of the complexity of considering all these aerosol physico-chemical characteristics, the mass efficiency is often considered as a size-independent parameter and assumed to depend only on the chemical composition of aerosol particles. For example, the Interagency Monitoring of Protected Visual Environments (IMPROVE) network measures light scattering coefficients using a nephelometer with an assumption that mass scattering and absorption efficiencies are constant over different sizes of aerosol particles (Malm *et al.*, 1994; Malm and Day, 2000, 2001; Malm *et al.*, 2004, 2005, 2011; Chen *et al.*, 2016). Although several modifications have been

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\* Corresponding author.

Tel.: 82-32-540-0166; Fax: 82-32-540-0167

E-mail address: jch@kiwu.ac.kr

made on the Malm's reconstructed extinction coefficient, the main idea to compute aerosol extinction coefficient from mass extinction efficiency and mass concentration is not altered. For example, according to Malm and Hand (2007), a scattering and absorption coefficient can be expressed as

$$\begin{aligned} b_{scat} &= (3.0)(C_{[(NH_4)_2SO_4]} + C_{[NH_4NO_3]})f_{AS}(RH) + (4)C_{[OMC]} + \\ &(1)C_{[SOIL]} + 0.6 C_{[CM]} + 1.37f_{SS}(RH) C_{[SS]} \\ b_{abs} &= (10.0)C_{[LAC]} \end{aligned} \quad (1)$$

Here,  $b_{scat}$  and  $b_{abs}$  (in  $Mm^{-1}$ ) are the reconstructed scattering and absorption coefficients, respectively;  $f(RH)$  is the relative humidity scattering enhancement factor, which is the ratio between dry and wet scattering as a function of RH;  $f_{AS}(RH)$  and  $f_{SS}(RH)$  are the enhancement factors for ammonium sulfate  $[(NH_4)_2(SO)_4]$  and sea salt (NaCl), respectively;  $C_{[(NH_4)_2SO_4]}$  and  $C_{[NH_4NO_3]}$  are fully neutralized ammonium sulfate and ammonium nitrate ( $NH_4NO_3$ ) mass concentrations in  $\mu g m^{-3}$ , respectively;  $C_{[OMC]}$ ,  $C_{[SOIL]}$ ,  $C_{[CM]}$ , and  $C_{[SS]}$  are the mass concentrations of organic carbon, soil, coarse mass (CM), and fine sea salt (SS), respectively. The aerosol mass extinction efficiency (MEE) is the ratio between aerosol extinction and mass concentration, while mass scattering efficiency (MSE) is the ratio between aerosol scattering and mass concentration. Mass absorption efficiency (MAE) is the ratio between the aerosol absorption coefficient and the aerosol mass concentration in a unit volume of air (Malm et al., 2000; Hand and Malm, 2007).

One of the main weaknesses of the Malm's equations is that these equations are not able to express size-dependent mass efficiencies. In Eq. (1), the scattering coefficient is approximated solely by a combination of mass concentrations of various chemicals. Such approximation does not take into account the information on the size distribution of chemical compounds and this causes visibility degradation. Thus,  $b_{scat}$  in Eq. (1) is identical for aerosol particles as long as their mass concentration is identical, although they have their different size distributions. To overcome this weakness, several modifications have been made on the Malm's equation shown in Eq. (1). For example, Pitchford et al. (2007) revised the IMPROVE equation for fine and coarse particles using the Mie theory. They used a bimodal aerosol size distribution with geometric mean diameters (geometric standard deviation) of 0.2  $\mu m$  (2.2) and 0.5  $\mu m$  (1.5) for fine and coarse modes, respectively. However, these modified expressions still cannot fully describe the size dependent mass efficiencies.

Many previous studies showed that the scattering and absorption properties of aerosols are both size and composition dependent (e.g., Lowenthal et al., 2000; Malm et al., 2000; Jung et al., 2015). For example, the efficiency of absorbing carbon is dependent on its chemical characteristics and how it is measured. According to Malm et al. (1994), theoretical calculations of carbon absorption efficiencies yield values between 8 and 12  $m^2 g^{-1}$  based on the study by Horvath (1993). Horvath (1993) reviewed a number of studies that measured MAE of soot and black carbon, as well as the theoretical calculations of the MAE that used a variety of refractive indices and densities. The

measured MAEs were between 3.8 and 17  $m^2 g^{-1}$ , while the theoretically calculated counterparts were between 8 and 12  $m^2 g^{-1}$  (Malm et al., 1994). According to Horvath (1993), the mass absorption coefficient depends on the particle size and the refractive index. The largest mass absorption coefficient of  $\sim 10 m^2 g^{-1}$ , which is commonly used to represent the MAE of elemental carbon (EC), can be obtained only for monodisperse carbon particles with a radius of 0.08  $\mu m$ . Values below 1  $m^2 g^{-1}$  can be obtained for particle sizes greater than 2–3  $\mu m$ .

The experimental results in Dillner et al. (2001) showed that at a wavelength of 550 nm, the MEE of EC ranged from 9.3 to 1.7  $m^2 g^{-1}$  for particles with diameters between 0.14 and 3.7  $\mu m$ . One of the main reasons for using the constant MEE is its simplicity. In order to consider the effects of polydispersity on mass extinction, scattering, and absorption efficiencies, the Mie theory is commonly used. However, the application of the Mie theory is restricted, because there are variations in particle sizes and further the Mie theory is only applicable to spherical aerosol particles. Thus, it is important to develop a simple parameterized expression that accounts for the polydispersity and chemical composition of aerosols in the calculation of mass efficiency.

In this study, an analytic approach to the approximated formula for the MEE of each aerosol chemical component was developed by fitting the formula results to those calculated by the Mie theory. To take into account the aerosol size effect, MEE, MSE, and MAE of polydisperse aerosols were calculated analytically. Geometric mean diameters of 0.5–2.5  $\mu m$  and geometric standard deviations of 1.2–2.2 were used assuming lognormal size distribution for all aerosol species. The MEE based on the Mie theory was parameterized analytically using a polynomial approximation for each composition. Finally, mass efficiencies of different mixtures were compared, and water content was calculated using an aerosol thermodynamic model (SCAPE II, Kim et al., 1993a, b) and the calculated results were compared with those of the Mie theory.

## METHODOLOGY

### *Aerosol Optical Properties*

A physical relationship between light extinction and atmospheric particle compositions can be established if both the particle concentration and the size distribution of each chemical species are known (Sloane, 1984; Sloane et al., 1991). Theoretically, an extinction coefficient,  $b_{ext}$ , can be calculated using the Mie theory as follows:

$$b_{ext} = \sum_i b_{ext,i} \quad (2)$$

and

$$b_{ext,i} = \int_0^{d_p^{max}} \frac{\pi d_p^2}{4} Q_{ext,i}(d_p, \lambda, m) n(d_p) dd_p, \quad (3)$$

where  $b_{ext,i}$  is the extinction coefficient associated with the

$i^{\text{th}}$  species in  $\text{Mm}^{-1}$ . The particles are assumed to be spherical. The  $n(d_p)$  is the particle number concentration ( $\mu\text{m}^{-1}\text{cm}^{-3}$ ) at a particle diameter  $d_p$  ( $\mu\text{m}$ ) and  $Q_{\text{ext}}(d_p, \lambda, m)$  is the extinction efficiency of a particle with  $d_p$  and refractive index  $m$  at a wavelength  $\lambda$  ( $\mu\text{m}$ ).

With this definition of the MEE, the extinction coefficient of  $i^{\text{th}}$  chemical species is expressed as follows:

$$b_{\text{ext},i} \cong C_i \times MEE_i \quad \text{and} \quad MEE_i = \frac{b_{\text{ext},i}}{C_i}, \quad (4)$$

$$b_{\text{ext}} = \sum_i b_{\text{ext},i} = \sum_i [C_i \times MEE_i] \quad (5)$$

where  $MEE_i$  is the mass extinction efficiency (in  $\text{m}^2 \text{g}^{-1}$ ) and  $C_i$  is the mass concentration of the  $i^{\text{th}}$  chemical species (in  $\mu\text{g m}^{-3}$ ). Then, the extinction coefficient for all aerosol species (i.e.,  $b_{\text{ext}}$ ) that are externally mixed in a unit volume of air is calculated as in Equation (5) (Malm et al., 1994; Malm et al., 2000; Malm and Hand, 2007).

The extinction coefficient is also calculated by using scattering and absorption efficiencies as follows (Malm and Day, 2001; Hand and Malm, 2007):

$$\begin{aligned} b_{\text{ext}} &= \sum_i b_{\text{ext},i} = \sum_i (b_{\text{sca},i} + b_{\text{abs},i}) = \sum_i (MEE_i + C_i) \\ &= \sum_i (MEE_i + MAE_i) \times C_i \end{aligned} \quad (6)$$

Here, the MSE and MAE are:

$$MSE_i = \frac{b_{\text{sca},i}}{C_i}, \quad b_{\text{sca}} = \sum_i b_{\text{sca},i} = \sum_i [C_i \times MSE_i], \quad (7)$$

and

$$MAE_i = \frac{b_{\text{abs},i}}{C_i}, \quad b_{\text{abs}} = \sum_i b_{\text{abs},i} = \sum_i [C_i \times MAE_i], \quad (8)$$

where  $b_{\text{ext}}$ ,  $MEE_i$ ,  $MSE_i$ , and  $MAE_i$  are a function of size distribution. We used the refractive indices at the wavelength of 550 nm and aerosol densities for each  $i^{\text{th}}$  component listed in Table 1.

## RESULTS

### Analytic Expression for Aerosol Mass Efficiencies as a Function of Geometric Mean Diameter

Regardless of their mixture type (i.e., internal or external mixture), aerosols scatter or absorb a specific fraction of radiant energy that can be calculated theoretically by invoking several assumptions on the chemical and physical properties of aerosols. Aerosols in the atmosphere are polydispersed with a wide range of particle sizes. The optical properties of individual aerosol particles vary with the diffraction and refraction properties of individual

particles. This variation of optical properties is also closely related to aerosol size distributions because extinction coefficients vary with the aerosol size. In this study, the size distribution of ambient polydispersed aerosols is represented by a lognormal distribution function:

$$n(\ln d_p) = \frac{N}{\sqrt{2\pi} \ln \sigma_g} \exp \left[ \frac{-\ln^2 (d_p/d_g)}{2 \ln^2 \sigma_g} \right], \quad (9)$$

where  $d_p$  is the diameter of the particle,  $d_g$  is the geometric mean diameter,  $\sigma_p$  is the geometric standard deviation, and  $N$  is the total number concentration of aerosol particles. We use the lognormal size distributions to represent the polydispersity of externally-mixed aerosol particles with varying geometric mean diameters (0.5–2.5  $\mu\text{m}$ ) and geometric standard deviations (1.2–2.2).

Aerosol mass concentration and chemical composition data from Jung et al. (2015) used for a case study. The mass concentration, refractive index, and density of each chemical component used in this study are summarized in Table 1. All mass scattering, absorption, and extinction efficiencies of polydisperse aerosols were approximated using a power law relationship:

$$ME = ad_g^b. \quad (10)$$

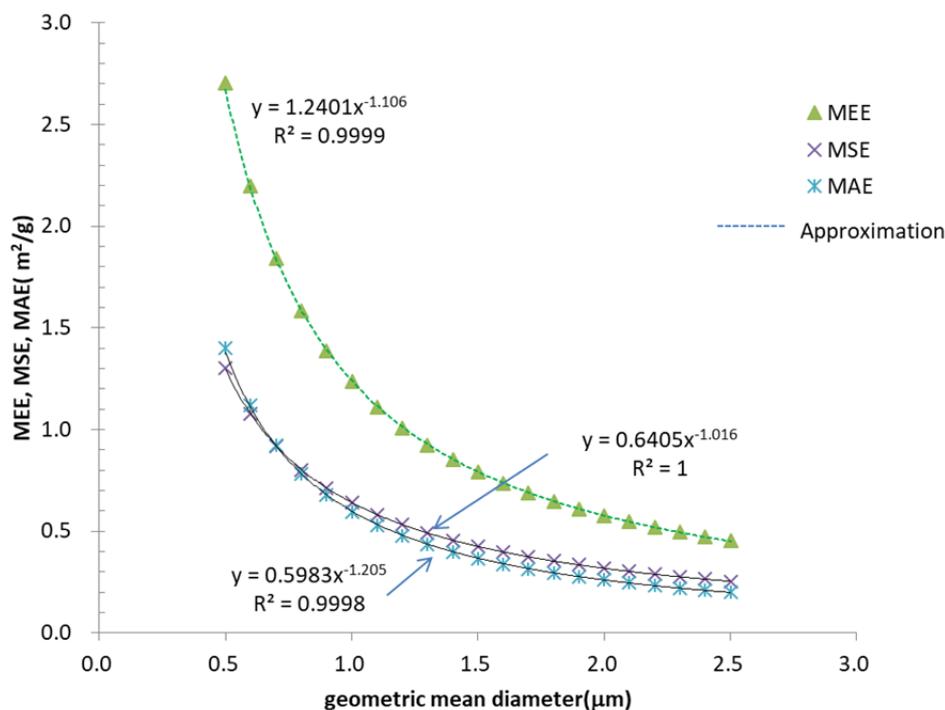
Here, the ME stands for mass efficiency. Coefficients  $a$  and  $b$  represent the coefficients of the best-fitting curves. We determined the power law relationship (i.e., Eq. (10)) as a function of geometric mean diameter based on the calculated mass efficiencies which were obtained by using the Mie theory. The original values calculated using the Mie theory and those determined by the best-fitting curves are closely related, which indicates that the approximated formula represents the calculated Mie data well for all the MEE, MAE, and MSE.

In order to determine the coefficients ( $a$  and  $b$ ) for polydisperse aerosols more efficiently, we used a two-step approach. First, we established the power law relationship for a geometric standard deviation of 1.5. Then, we calculated relationships of  $a$  and  $b$  that vary with the varying geometric standard deviations as a way of accounting for aerosol polydispersity. Fig. 1 shows the MEE (triangles), MSE (crosses), and MAE (asterisks) of Elemental Carbon (EC) as a function of geometric mean diameter, which were calculated using the Mie theory and the corresponding best-fitting curves (broken lines). For the geometric mean diameter range of 0.5–2.5  $\mu\text{m}$ , the MEE of EC was between 0.533 and 3.18  $\text{m}^2 \text{g}^{-1}$ , while MAE of EC was between 0.297 and 1.53  $\text{m}^2 \text{g}^{-1}$ . The MSE of EC was between 0.236 and 1.65  $\text{m}^2 \text{g}^{-1}$ . All mass efficiency values decreased as the geometric mean diameter increased (Fig. 1).

The same approach was applied to other chemical species, such as  $(\text{NH}_4)_2\text{SO}_4$  (herein, AMS),  $\text{NH}_4\text{NO}_3$  (herein, AMN), OC, and residual. Fig. 2 shows the comparison of the calculated mass scattering efficiency using the Mie theory with the best-fitting curves of other aerosol chemical

**Table 1.** Mass concentration, refractive index, and density of externally mixed aerosols (Sloane, 1983, 1984; Sloane and Wolff, 1985; Jung et al., 2015).

	Mass Concentration ( $\mu\text{g m}^{-3}$ )	$m_r$	$m_i$	Density ( $\text{g cm}^{-3}$ )
EC	3.225	1.90	0.60	2.00
$(\text{NH}_4)_2\text{SO}_4$	7.841	1.53	0.00	1.76
$\text{NH}_4\text{NO}_3$	3.113	1.55	0.00	1.73
OM	14.05	1.55	0.00	1.4
NaCl	2.317	1.51	0.00	2.165
Residue	30.40	1.62	0.00	2.300
Water	6.674	1.33	0.00	1.000

**Fig. 1.** Calculated mass extinction efficiency (MEE), mass scattering efficiency (MSE), and mass absorption efficiency (MAE) of EC as a function of geometric mean diameter ( $\sigma_{g0} = 1.5$ ,  $\lambda = 550$  nm), and the corresponding best-fitting curves (broken lines).

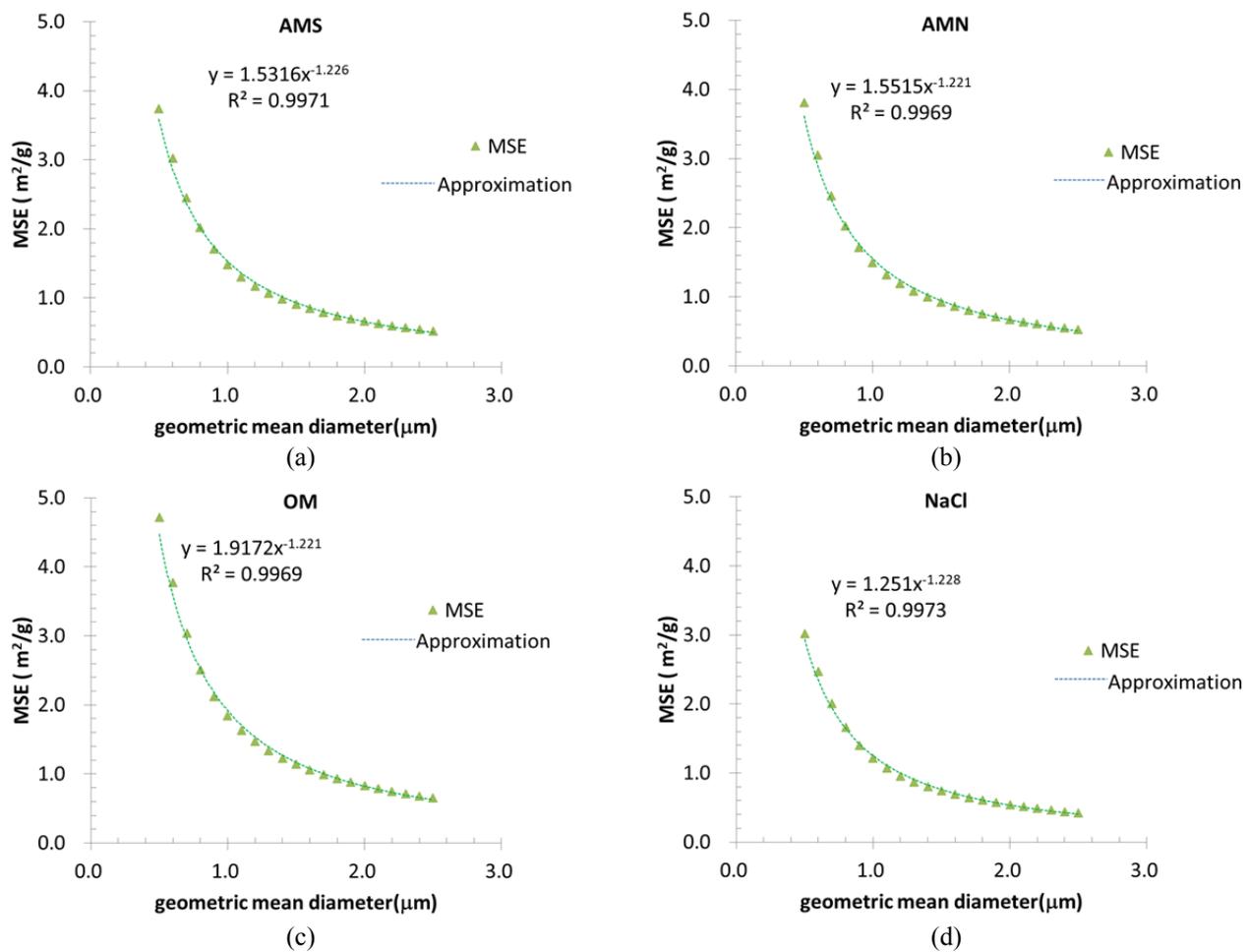
components. The calculated and approximated data are correlated well with correlation coefficients ( $R^2$ ) larger than 0.98 for all aerosol species. These approximations cover a range of accumulation mode particle sizes (0.5–2.5  $\mu\text{m}$  in geometric mean diameter) at any given geometric standard deviation. The approximations shown in Fig. 2 provide mass efficiency values across a wide range of geometric mean diameters in the aerosol accumulation mode.

#### **Analytic Expression for Aerosol Mass Efficiencies as a Function of Geometric Mean Diameter with Geometric Standard Deviation**

The approximations for aerosol mass efficiencies as a function of geometric mean diameter are not able to accommodate the changes in the geometric standard deviation for polydisperse aerosols and, in result, the approximations are not able to construct the general formula for the mass efficiencies. The general formula should include polydispersity parameters for aerosol particles, such as the

geometric standard deviation, as well as a parameter representing the geometric mean diameter. Eq. (10) can be transformed into the general formula that covers aerosol size distributions with geometric standard deviations of 1.1–1.7 and a geometric mean diameters of 0.5–2.5  $\mu\text{m}$ . For this transformation, the parameters  $a$  and  $b$  need to be a function of geometric standard deviation.

Table 2 shows the fitting coefficients ( $a$  and  $b$ ) of each aerosol component for varying geometric standard deviations. For EC, the fitting coefficients of MSE and MAE are also listed. These fitting coefficients are then generalized for polydisperse aerosols as functions of geometric standard deviation and geometric mean diameter. For aerosol components other than EC, we assumed MEE to be the same as MSE due to the absence of absorption. In Table 2,  $a$  decreases and  $b$  increases with an increase in the geometric standard deviation. The magnitude of these decreases and increases depend on the chemical composition, which is related to the refractive index.



**Fig. 2.** Mass scattering efficiency (MSE) for  $\sigma_{g0} = 1.5$  over geometric mean diameters and the corresponding best-fitting curves (solid lines). The MSE and the curve for AMS (Ammonium Sulfate), AMN (Ammonium Nitrate), OM (Organic matter), and NaCl are shown in panels (a), (b), (c), and (d), respectively.

**Table 2.** Coefficients (*a* and *b*) for Mass Efficiency (ME) of each aerosol component ( $ME = ad_g^b$ ).

Type	<i>a</i>				<i>b</i>			
	1.1	1.3	1.5	1.7	1.1	1.3	1.5	1.7
$\sigma_g$								
EC (MEE)	1.8913	1.607	1.2401	0.9045	-1.122	-1.115	-1.106	-1.096
EC (MSE)	0.9482	0.8156	0.6405	0.4761	-1.015	-1.016	-1.016	-1.015
EC (MAE)	0.9406	0.7895	0.5983	0.4276	-1.233	-1.222	-1.205	-1.187
AMS (MEE)	2.4607	2.0528	1.5316	1.0885	-1.353	-1.292	-1.226	-1.175
AMN (MEE)	2.4932	2.078	1.5515	1.1042	-1.351	-1.287	-1.221	-1.171
OC (MEE)	3.0809	2.5678	1.9172	1.3645	-1.351	-1.287	-1.221	-1.171
NaCl (MEE)	2.0057	1.6763	1.251	0.8884	-1.351	-1.294	-1.228	-1.176
Residue (MEE)	1.8423	1.5338	1.1505	0.823	-1.312	-1.263	-1.201	-1.158

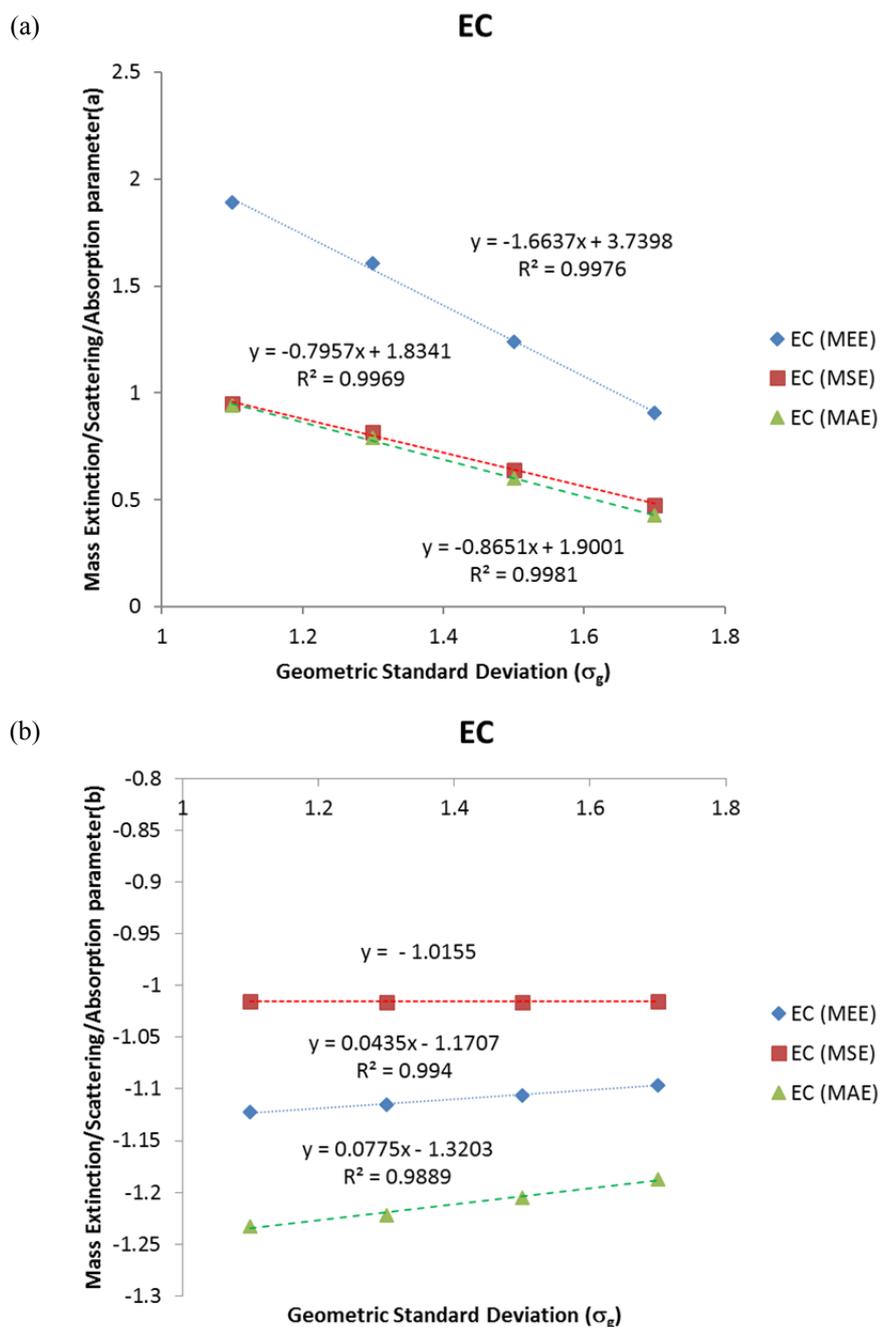
Fig. 3 shows the fitting coefficients *a* and *b* that represent the MEE, MSE, and MAE of EC as a function of geometric standard deviation. With the first order regression, the parameters *a* and *b* for MEE are represented by the following linear equations with  $R^2$  of 0.9976 and 0.994, respectively:

$$a = -1.6637\sigma_g + 3.7398 \quad (11)$$

$$b = 0.0435\sigma_g - 1.1707 \quad (12)$$

Using these linear equations for *a* and *b*, ME in Eq. (10) is now functions of geometric mean diameter and geometric standard deviation. For example, the MEE for polydisperse EC is expressed as follows:

$$MEE(EC) = (-1.6637\sigma_g + 3.7398)d_g^{(0.0435\sigma_g - 1.1707)} \quad (13)$$



**Fig. 3.** (a) coefficient  $a$  and (b) coefficient  $b$  in the power law relationships ( $ME_i = a_i d_g^{b_i}$ ) that represent the mass extinction efficiency (MEE), the mass scattering efficiency (MSE), and the mass absorption efficiency (MAE) of EC. These coefficients are shown over geometric standard deviations.

The same procedure can be applied to estimate other components. Fig. 4 shows the coefficients  $a$  and  $b$  for the MEE of other chemical compounds (Ammonium Sulfate (AMS), Ammonium Nitrate (AMN), Organic Carbon (OC), NaCl, and the residue) as a function of geometric standard deviation. In Table 2,  $a$  decreases and  $b$  increases linearly with the increasing geometric standard deviation.

Using these equations, we can calculate ME with no use of the Mie theory in a way that the analytic expressions for the mass efficiency of polydisperse aerosols are functions

of the geometric mean diameter and the geometric standard deviation as follows:

$$ME_i = a_i d_g^{b_i}, \quad (14)$$

where

$$a_i = \theta_{1,i} \sigma_g + \theta_{2,i}, \quad b_i = \vartheta_{1,i} \sigma_g + \vartheta_{2,i}, \quad (15)$$

and

$$ME_i = (\theta_{1,i}\sigma_g + \theta_{2,i})d_g^{b_i\theta_{1,i}\sigma_g + \theta_{2,i}} \quad (16)$$

$$b_{ext,EC} = b_{sca,EC} \times b_{abs,EC} \quad (17c)$$

Table 3 summarizes the resultant parameters used in estimating the ME. Likewise, the resultant extinction coefficient can be expressed using the following formulas and applying the coefficients derived in Eqs. (14)–(16):

$$b_{ext,AMS} = a_2 d_g^{b_2} \times [AMS] \quad (17d)$$

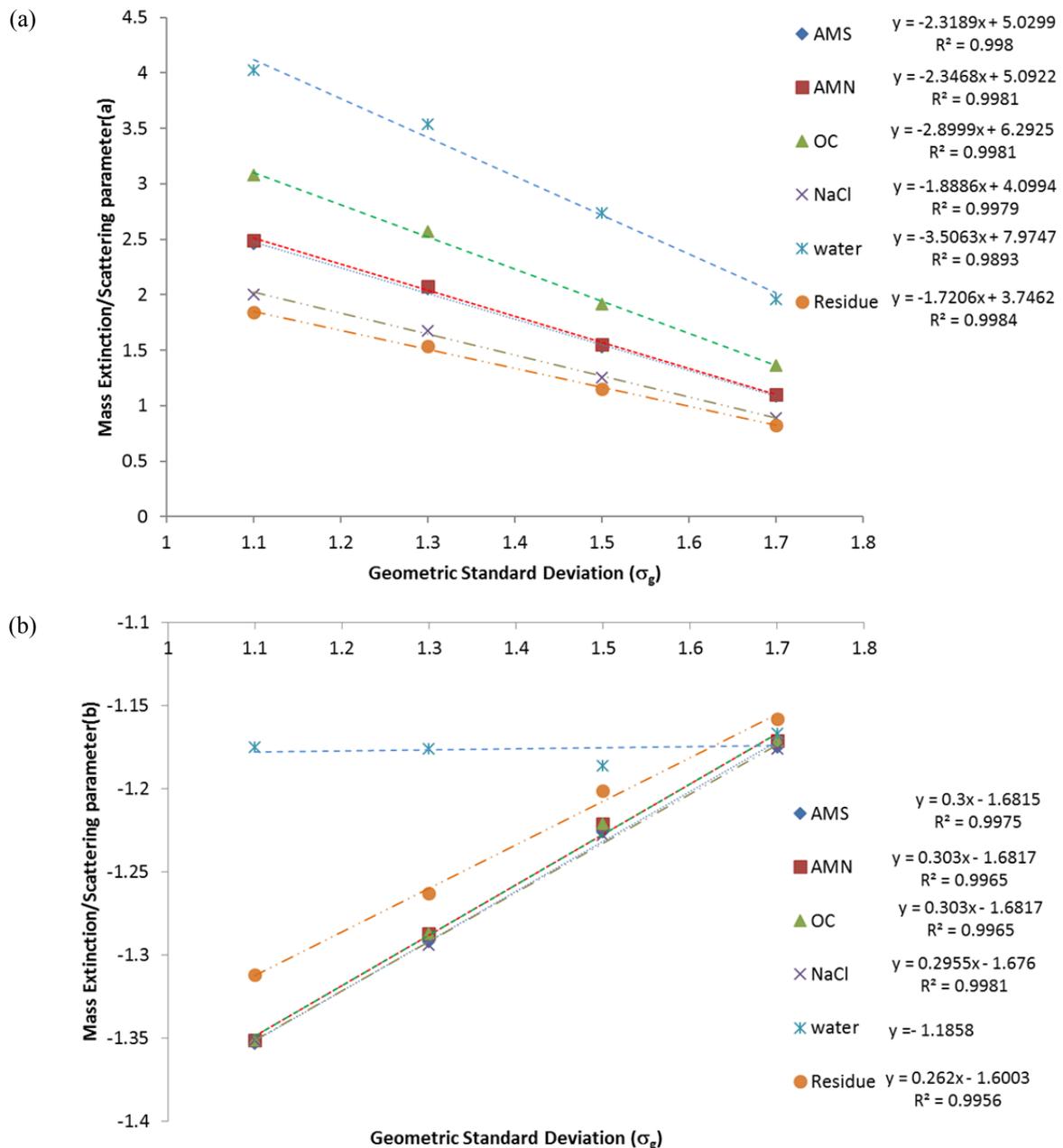
$$b_{ext,AMN} = a_3 d_g^{b_3} \times [AMN] \quad (17e)$$

$$b_{sca,EC} = a_1 d_g^{b_1} \times [EC] \quad (17a)$$

$$b_{ext,OC} = a_4 d_g^{b_4} \times [OC] \quad (17f)$$

$$b_{abs,EC} = c_1 d_g^{b_1} \times [EC] \quad (17b)$$

$$b_{ext,SS} = a_5 d_g^{b_5} \times [SS] \quad (17g)$$



**Fig. 4.** (a) coefficients  $a$  and (b) coefficient  $b$  in the power law relationships ( $ME_i = a_i d_g^{b_i}$ ) that represent the mass scattering and extinction efficiencies of AMS (Ammonium Sulfate), AMN (Ammonium Nitrate), OM (Organic matter), NaCl, water, and residue.

**Table 3.** Generalized parameters representing mass extinction efficiency parameters ( $a$  and  $b$ ) as a function of geometric standard deviation.

Composition	$i$	$a_i = \theta_{1,i} \sigma_g + \theta_{2,i}$		$b_i = \vartheta_{1,i} \sigma_g + \vartheta_{2,i}$	
		$\theta_{1,i}$	$\theta_{2,i}$	$\vartheta_{1,i}$	$\vartheta_{2,i}$
EC (MEE)	1	-1.6637	3.7398	0.0435	-1.1707
EC (MSE)		-0.7957	1.8341	0	-1.0155
EC (MAE)		-0.8651	1.9001	0.0775	-1.3203
AMS	2	-2.3189	5.0299	0.3	-1.6815
AMN	3	-2.3468	5.0922	0.303	-1.6817
OC	4	-2.8999	6.2925	0.303	-1.6817
NaCl	5	-1.8886	4.0994	0.2955	-1.676
Residue	6	-1.7206	3.7462	0.262	-1.6003
Water	7	-3.5063	7.9747	0	-1.1858

$$b_{ext,Residue} = a_6 d_g^{b_6} \times [Residue]. \quad (17h)$$

The resultant extinction coefficient can be expressed as follows:

$$b_{ext,dry} = (a_1 d_g^{b_1} + c_1 d_g^{d_1}) \times [EC] + a_2 d_g^{b_2} \times [AMS] + a_3 d_g^{b_3} \times [AMN] + a_4 d_g^{b_4} \times [OC] + a_5 d_g^{b_5} \times [SS] + a_6 d_g^{b_6} \times [Residue] \quad (18)$$

$$b_{ext,wet} = b_{ext,dry} + a_7 d_g^{b_7} \times [Water] \quad (19)$$

The parameter  $b_{ext,dry}$  is the extinction coefficient of dry aerosol particles and  $b_{ext,wet}$  is the extinction coefficient of aerosols that contain water. These coefficients are based on their chemical composition and RH and will be described in Section 4. The same approach can be applied to the calculations of the MAE and the MSE (Table 2).

### Mixture Types and Water Contents

Fig. 5 shows a comparison between the extinction coefficients of internal and external aerosol mixtures. The extinction coefficient for the internal mixture ( $b_{ext,int}$ ) is as follows:

$$b_{ext,int} = C \times MEE_{int} \quad (20)$$

or

$$MEE_{int} = \frac{b_{ext,int}}{C}, \quad (21)$$

where  $MEE_{int}$  is the MEE for the internal mixture and  $C$  is mass concentration. In the internal mixture, all participating species have an identical composition for the specific size range. Here, the refractive index, and the density of aerosols are calculated by a volume-averaged method for the internal mixture (Levoni et al., 1997; Jung et al., 2015). To produce Fig. 5, we used the composition and mass concentration data that are collected in Seoul, Korea in 2006 (Jung et al., 2015) (see Table 1).

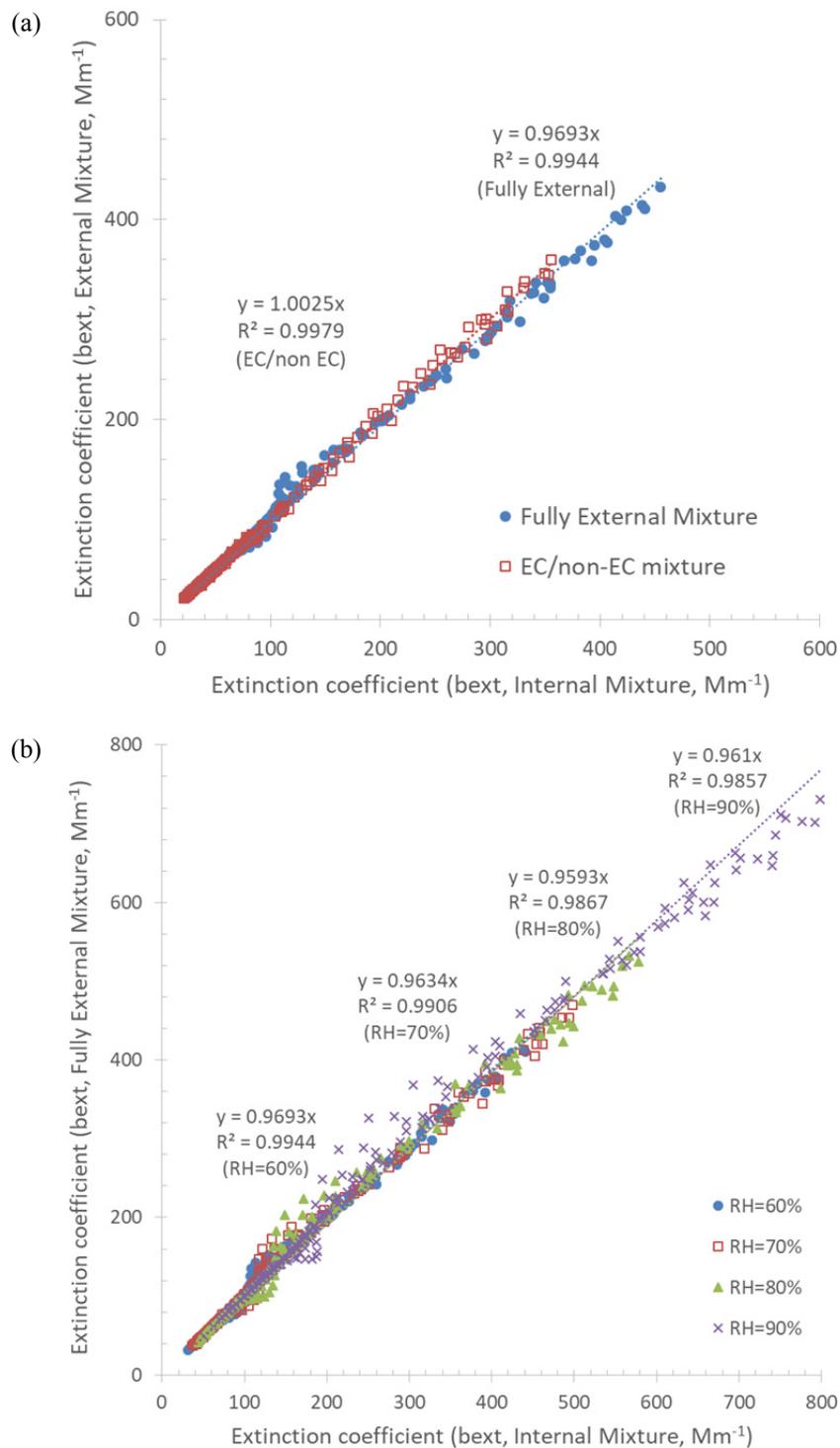
In Fig. 5, the externally mixed aerosols (i.e., those whose components exist separately) and EC/non-EC mixtures are

also considered. In EC/non-EC mixtures, EC particles exist separately from the other particles, whereas the other particles are internally mixed. The refractive indices of other particles are, therefore, calculated as a volume average of external particles. Here, geometric mean diameters of 0.5–2.5  $\mu\text{m}$  are used with a geometric standard deviation of 1.5. Fig. 5 shows high correlations between internal and external mixtures with a slope of 0.9693 and  $R^2$  of 0.9944. A high level of agreement between an internal mixture and a two-phase EC/non-EC external mixture is also observed with a slope of 1.0025 and  $R^2$  of 0.9979.

One of the important factors for the calculations of aerosol optical properties is the water content in aerosol particles, which depends on RH and hygroscopicity. For both external and internal mixtures, water co-exists in the solution with water-soluble aerosols. We calculate the MEE by considering the water content for the external mixture and compared the results from the calculation with those for the internal mixture.

Aerosol particles absorb water as RH increases and this absorption affects the particle diameter as well as the chemical composition, refractive index, and thus, the optical properties of aerosols. In this study, the water content in aerosols is calculated using the thermodynamic equilibrium model, which is Simulating Composition of Atmospheric Particles at Equilibrium II (SCAPE II, Kim et al., 1993a, b; Meng et al., 1998), for a given condition (aerosol composition, aerosol mass concentration, temperature, and relative humidity). Jung et al. (2015) developed a size resolved model to determine the optical properties of organic aerosols by combining the thermodynamic hygroscopic growth model and the aerosol dynamics model. SCAPE II uses the following ions: sodium, sulfate, ammonium, nitrate, chloride, potassium, calcium, magnesium, and carbonates. In this study, the MEs are computed using the Mie theory as functions of refractive index, the geometric mean diameter, and the geometric standard deviation. Based on the water content simulated by SCAPE II, we calculate the hygroscopic growth factor (HGF), which determines the particle growth behavior, using the volume ratio of dry and wet particles (Jung et al. 2015).

Fig. 5 shows a comparison between the calculated extinction coefficients of a full internal mixture and those



**Fig. 5.** Comparisons between the calculated extinction coefficients for an internal mixture and those for an external mixture ((a): upper panel: fully external mixture and EC/non-EC mixture, (b): lower panel: relative humidity sensitivity).

of a full external mixture over the varying RH. This comparison shows that the slopes of best linear-fitting curves are between 0.9593 and 0.9693 for RH between 60% and 90% with high correlations ( $R^2 > 0.99$ ). The extinction coefficients for an internal mixture are approximately 3% larger than those for an external mixture that contains moisture.

## DISCUSSION

The developed analytic formula can be applied to the size-resolved optical properties by considering chemical mass concentrations. For example, the simple forcing efficiency (SFE) in W/g based on the direct aerosol radiative forcing (RF) at the top of the atmosphere (TOA) is

as follows (Chylek and Wong, 1995; Bond and Bergstrom, 2006):

$$SFE_i (W/g) = -\frac{S_0}{4} T_{atm}^2 (1-N) \left[ (1-\alpha)^2 2\beta MSE_i - 4\alpha MAE_i \right] \quad (22)$$

where

$S_0$ : Solar constant,  $1,370 (W m^{-2})$ ;

$S_0/4$ : The globally averaged incident solar flux at the top of the atmosphere;

$T_{atm}$ : Transmittance of the atmosphere above the aerosol layer, 0.76;

$N$ : Fraction of sky covered by clouds (0.6);

$\alpha$ : Albedo of underlying surface, 0.15;

$\beta$ : Fraction of radiation scattered by aerosols into the upper hemisphere, 0.125.

According to Eqs. (7), (8), and (17), SFE (Eq. (22)) is rewritten as a function of the polydisperse aerosol size distribution with no consideration of the Mie theory:

$$SFE_i = -\frac{S_0}{4} T_{atm}^2 (1-N) \left[ (1-\alpha)^2 2\beta a_i d_g^{bi} - 4\alpha c_i d_g^{di} \right], \quad (23)$$

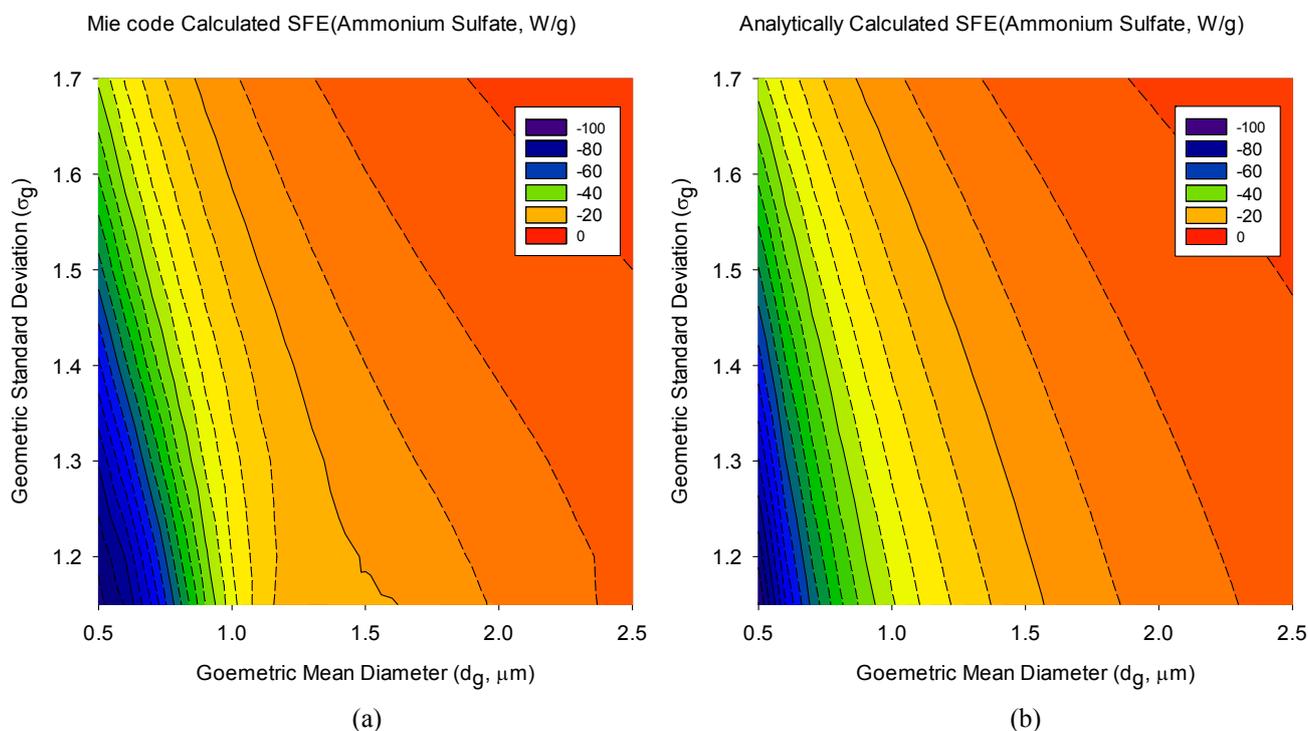
where  $MSE_i = a_i d_g^{bi}$  and  $MAE_i = c_i d_g^{di}$  for the  $i^{th}$  component and  $a$ ,  $b$ ,  $c$ , and  $d$  are the estimated coefficients of the ME which are described in Eq. (17).

Fig. 6 shows a comparison of the contour plots of the SFE of polydisperse aerosols that is calculated by the

newly developed simple approach (i.e., Eq. (14)) and that by the method using the Mie theory. This comparison is over geometric mean diameters and geometric standard deviations for ammonium sulfate. The reasonable agreement (mean error of 5.21%) between the approach and the method in Fig. 6 demonstrates that the SFE of polydisperse aerosols can be calculated using the analytic formula which does not involve the Mie calculation. Hence, this study provides a convenient way of obtaining the MEs of polydisperse aerosols with no calculations which involve the Mie theory.

## CONCLUSION

For a given wavelength, MEs (e.g., MEE, MSE, and MAE) are generally considered constant over the particle sizes and associated standard deviations of the particle-size distributions. However, a constant ME is not able to accurately represent aerosol polydispersity due to the dependence of the ME on the geometric mean diameter and the geometric standard deviation. Note that the geometric mean diameter and the geometric standard deviation represent the polydispersity of aerosol particles. Therefore, the size distributions of aerosol particles should be considered in the calculations of the ME based on the Mie theory as a process of taking the polydispersity into account, when the scattering properties of aerosols are computed for the varying sizes of aerosol particles. However, such calculations require a large amount of computational resources and do not produce analytic solutions.



**Fig. 6.** Contour plot of simple forcing efficiency (SFE, W/g) for polydisperse aerosols as functions of geometric mean diameter and geometric standard deviation for ammonium sulfate. Panel (a) shows the plot based on the Mie-code calculation, while panel (b) shows the plot based on the analytic solution.

In this study, the MEE, the MSE, and the MAE of polydispersed aerosols are calculated for particles with geometric mean diameters of 0.5–2.5  $\mu\text{m}$  and geometric standard deviations of 1.1–1.7. An analytic approach to the approximation of a formula for the MEE in consideration of the chemical composition is developed by fitting the results that are obtained by using the Mie theory under the assumptions of the lognormal size distribution and the external mixing.

The calculated MEs of all aerosol components are shown as a function of the geometric mean diameter and in the form of a power law formula. The determined coefficients of the power law formula are further generalized as a function of the geometric standard deviation. Thus, the obtained aerosol MEs are shown as functions of the geometric mean diameter, the mass concentration, and the geometric standard deviation for each chemical component that comprises an aerosol particle (i.e., EC,  $(\text{NH}_4)_2(\text{SO}_4)$ ,  $\text{NH}_4\text{NO}_3$ , OC, and NaCl). The resulting analytically approximated optical properties of external mixtures are compared with those of the internal mixtures and with those of the EC/non-EC external mixtures and this comparison showed a good agreement with good confidence. The MEE depends on particle sizes. For example, the general trend of the MEE increases as a particle diameter increases for nuclei mode. For accumulation mode, however, the MEE decreases as a particle diameter increases. Hence, different approximations should be proposed for different size ranges. It should be noted that the approximated expression for the MEE proposed in this study is valid for an accumulation mode with the geometric mean diameters of 0.5–2.5  $\mu\text{m}$ . Future work should concentrate on developing approximated expressions for wider size ranges including nuclei mode and coarse mode. It should also be noted that the analytically driven MEs from this study is valid for a wavelength of 550 nm which is ubiquitous in aerosol optical studies. For other wavelengths, the optical properties (e.g., extinction coefficient), show different values, which indicates that we need another expression for a given wavelength. However, the methodology to obtain an analytic expression developed this study should be valid and applicable to other wavelengths.

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