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Spatial distribution of aerosol hygroscopicity and its effect on $PM_{2.5}$ retrieval in East China

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ABSTRACT

The hygroscopic properties of aerosol particles have strong impact on climate as well as visibility in polluted areas. Understanding of the scattering enhancement due to water uptake is of great importance in linking dry aerosol measurements with relevant ambient measurements, especially for satellite retrievals. In this study, an observation-based algorithm combining meteorological data with the particulate matter (PM) measurement was introduced to estimate spatial distribution of indicators describing the integrated humidity effect in East China and the main factors impacting the hygroscopicity were explored. Investigation of 1 year data indicates that the larger mass extinction efficiency α_{ext} values (>9.0 m^2/g) located in middle and northern Jiangsu Province, which might be caused by particulate organic material (POM) and sulfate aerosol from industries and human activities. The high level of POM in Jiangsu Province might also be responsible for the lower growth coefficient γ value in this region. For the inland junction provinces of Jiangsu and Anhui, a considerable higher hygroscopic growth region in East China might be attributed to more hygroscopic particles mainly comprised of inorganic salts (e.g., sulfates and nitrates) from several large-scale industrial districts distributed in this region. Validation shows good agreement of calculated $PM_{2.5}$ mass concentrations with *in situ* measurements in most stations with correlative coefficients of over 0.85, even if several defective stations induced by station location or seasonal variation of aerosol properties in this region. This algorithm can be used for more accurate surface level $PM_{2.5}$ retrieval from satellite-based aerosol optical depth (AOD) with combination of the vertical correction for aerosol profile.

1. Introduction

Hygroscopicity of atmospheric aerosol is a bridge to link its microphysical and chemical parameters, as well as its optical properties. Aerosol particles with water-soluble component grow under wet conditions and change their extinction feature (Deng et al, 2011). The hygroscopic properties of aerosol particles have strong impact on climate, as well as visibility in heavily polluted areas. Knowledge of the effect of relative humidity (RH) on aerosol optical properties is of great importance for assessment of climate forcing and adverse impacts on regional visibility and human health (Li et al., 2014).

Inorganic constituents such as sulfate, nitrate, ammonium, and sea salt as well as some particulate organic material (POM) are the typical hygroscopic particles (Hu et al, 2008; Liu, 2008). Under wet conditions, they may have different refractive indices, size, density, number size distribution, and extinction cross-section (Malm et al., 2000; Zhang and Shi, 2002). Hygroscopic growth could contribute more than 60% of visibility reduction in certain haze weather, exceeding the contribution from dry aerosol particle (Wang and Martin, 2007). For satellite retrievals of aerosol mass concentration based on extinction coefficients, significant uncertainty could be introduced if neglecting the hygroscopic growth.

The impact of air humidity on aerosol extinction coefficient can be described by hygroscopic growth factor f(RH), which is defined as the ratio of aerosol extinction coefficient under ambient humidity condition to that with RH < = 40% (Kotchenruther et al., 1999). f(RH) varies between 1.2 and 4.1 depending on the origin of the air masses, ambient humidity, geographic background, and aerosol types (Pan, 2007; Liu, 2008). Generally, f(RH) is highest for marine aerosol (f(80%) ~ 2.68), followed by urban and continental aerosol (~2.04), and it is lowest for biomass burning aerosol (~1.55), which is typically rich of hydrophobic black carbon (Liu, 2008). According to the different hygroscopic properties, aerosols are traditionally classified into three groups, i.e., hydrophobic particles, less hygroscopic particles, and more hygroscopic particles.

Many studies focused on hygroscopic growth properties using *in situ* measurements with the Hygroscopic Tandem Differential Mobility Analyzer (H-TDMA), Humidified Differential Mobility Particle Sizer (H-DMPS), or Tandem (Parallel) Nephelometer System. Swietlicki et al. (2008) summarized some of those studies using H-TDMA, while several field experiments (e.g. ACE-2 (Carrico et al., 2000), ACE-Asia

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(Kim et al., 2006), TARFOX (Kotchenruther et al., 1999), INDOEX (Sheridan et al., 2002), SCAR-B (Kotchenruther and Hobbs, 1998)) adopted the Tandem (Parallel) Nephelometer System. Offline measurements (sampling and laboratory analysis) of hygroscopic growth factors are more valuable and recommended because it can give more information on mixing state and chemical components of aerosols than *in situ* measurements (Boreddy et al., 2014a, 2014b). But the expensive cost and discontinuous monitoring makes offline measurement in low temporal and spatial resolution and limit its application on regional scale.

The aerosol hygroscopic properties have drawn much attention in East China in recent years due to increased frequency of haze episodes. Several field experiments for aerosol hygroscopic properties had been carried out in Beijing (Liu, 2008; Massling et al., 2008), Yangtze River Delta region (Xu et al., 2002; Ye et al., 2013), and Pearl River Delta region (Tan et al., 2013). However, most of those measurements were limited to a single station, thus the resulted f(RH) cannot represent the aerosol properties on a regional scale. Recently, Lin et al. (2015) proposed an observation-based algorithm that combines meteorological data with the particulate matter (PM) measurement to estimate spatial distribution of indicators describing the integrated humidity effect. In their study, only the ground measurements taken at 75 stations in China were used to obtain the spatial distribution of f(RH), which varies significantly with the geographical location and distance from aerosol source. Thus, a detailed validation and analysis of error source are essential before applying this algorithm to obtain the credible surface level $PM_{2.5}$ concentration.

The main goals of this work are to 1) characterize the hygroscopic scattering enhancement in East China, 2) find out the main factors impacting the hygroscopicity, and 3) estimate the dry aerosol concentration by using ambient aerosol optical properties. In this study, spatial distribution of f(RH) is derived based on 1 year long measurements. The retrieved $PM_{2.5}$ mass concentrations in same stations are also validated by using new *in situ* measurement data to avoid self-verification with the training set.

2. Methodology and data

2.1. Methodology

An algorithm was built by Lin et al. (2015) to present the f(RH) and mass extinction efficiency and a similar one was built in this study. According to the Mie theory, the physical correlation between $\sigma_{a,dry}$ and PM could be expressed like (Wang et al., 2010):

$$\sigma_{a,dry} = \alpha_{ext,a} \cdot PM = \alpha_{ext} \cdot PM_{2.5} + \alpha'_{ext} \cdot PM_{>2.5} \quad (1)$$

where $\sigma_{a,dry}$ represents aerosol extinction coefficient under dry condition, and $\alpha_{ext,a}$ represents the mean mass extinction efficiency. α_{ext} is introduced to denote the mass extinction efficiency of fine mode aerosol (≤2.5 μm in size) and α'_{ext} denotes that of coarse mode. Since fine mode particles contribute the dominant portion of aerosol extinction, especially for East China where the major aerosol type is urban/industrial aerosol, the relationship between $\sigma_{a,dry}$ and PM can be represented by the first term of Eq. (1) with acceptable uncertainty.

The aerosol extinction coefficients in ambient and under dry condition are used to fit the empirical function of aerosol hygroscopic growth factor f(RH) by (Emili et al., 2010; Guo et al., 2009; Kotchenruther et al., 1999; Randriamiarisoa et al., 2006):

$$f(RH) = \frac{\sigma_a}{\sigma_{a,dry}} = \left(\frac{1-RH}{1-RH_0}\right)^{-\gamma} \quad (2)$$

where γ is the Hänel growth coefficient. RH_0 represents the RH for dry aerosol with a value equals to 40%.

Combining Eqs. (1) and (2), it can be got

$$PM_{2.5} = \frac{1}{\alpha_{ext}} \cdot \frac{\sigma_a}{f(RH)} = \frac{\sigma_a}{\alpha_{ext}} \cdot \left(\frac{1-RH}{1-RH_0}\right)^{\gamma}. \quad (3)$$

Eq. (3) is nonlinear and includes two unknown parameters, α_{ext} and γ. Its linearized form is shown below:

$$\ln\frac{\sigma_{a,i}}{PM_{2.5,i}} = \ln\alpha_{ext,i} - \gamma_i \ln\left(\frac{1-RH_i}{1-RH_0}\right), \quad (4)$$

where i represents different station with *in situ* measurements of $PM_{2.5}$, σ_a and RH. The spatial distribution of parameter α_{ext} and γ can be derived by spatial interpolations.

The *in situ* surface extinction coefficient $\sigma_{a,i}$ can be obtained from observed visibility L using the empirical relationship $\sigma_{a,i} = 3.912/L$ when the threshold contrast of human visual perception is assumed to be 0.02 (Koschmieder, 1925).

2.2. Measurement data

Surface meteorological parameters of 82 stations, including visibility and RH, are acquired in the study region. Fig. 1 shows geography of the study region and key cities mentioned below. The temporal resolution of meteorological data is 3 hours. The data at 11:00 am LST are extracted. Hourly mean $PM_{2.5}$ concentration data measured on same or nearby stations from January 1 to December 31 during 2014 are used to build the visibility-$PM_{2.5}$ model. The $PM_{2.5}$ concentration was monitored using the tapered element oscillating microbalance (TEOM) technique or beta attenuation monitors (BAM or β-gauge) (Engel-Cox et al., 2013). The data are recorded hourly with an uncertainty of 0.75%. The meteorological and PM data measured on the same stations from January 1 to March 31 in 2015 are used to validate the estimated $PM_{2.5}$ mass concentrations.

3. Results and discussions

Fig. 2 presented the spatial distribution of (a) α_{ext}, (b) γ, and (c) f(80) in East China region. As the indicator of mean mass extinction, the α_{ext} represents the extinction ability of dry aerosol particles, which is relevant with the chemical composition, mixing state, and aged stage and is sensitive to the seasons due to the difference of emission sources. The α_{ext} here is obtained from the measurement of one whole year instead of individual season, which might smooth seasonal characteristics. However, it was found that in each season, there are few samples which increased the uncertainty of model parameters. In addition, it is not rigorous to distinguish aerosol properties (e.g. components and mixing state) by season due to the continuous temporal variation of most emissions (He et al., 2012). Unfortunately, the lack of aerosol chemical composition and mixing state measurement limited the accuracy of model parameters retrieval for different aerosol classification. Therefore, the parameters from 1 year long measurement data are reasonable to represent the general characteristics of aerosol in the study region.

It can be seen in Fig. 2a that the α_{ext} with smaller values (~2.0 m^2/g) are basically distributed in mountainous area and agricultural compact district of Fujian and Jiangxi Province, where the continental background aerosols are dominant with less extinction ability (Howell and Huebert, 1998). The α_{ext} with values larger than 7.0 m^2/g locate in the middle of Zhejiang, western and northern Anhui Province, especially in the middle and northern Jiangsu Province (>9.0 m^2/g). The results (~5.0 m^2/g) are close to several previous measurements in Lin'an (4.0 m^2/g by Xu et al. (2002) and 3.42 m^2/g by Zhang (2014)). Particles with higher extinction ability released from industrial emissions and human activities, such as POM and sulfate aerosol, might significantly contribute the larger α_{ext}. Meanwhile, modeling studies also showed