Impact of diurnal variability and meteorological factors on the PM$_{2.5}$ - AOD relationship: Implications for PM$_{2.5}$ remote sensing

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ABSTRACT

PM$_{2.5}$ retrieval from space is still challenging due to the elusive relationship between PM$_{2.5}$ and aerosol optical depth (AOD), which is further complicated by meteorological factors. In this work, we investigated the diurnal cycle of PM$_{2.5}$ in China, using ground-based PM measurements obtained at 226 sites of China Atmosphere Watch Network during the period of January 2013 to December 2015. Results showed that nearly half of the sites witnessed a PM$_{2.5}$ maximum in the morning, in contrast to the least frequent occurrence (5%) in the afternoon when strong solar radiation received at the surface results in rapid vertical diffusion of aerosols and thus lower mass concentration. PM$_{2.5}$ tends to peak equally in the morning and evening in North China Plain (NCP) with an amplitude of nearly twice or three times that in the Pearl River Delta (PRD), whereas the morning PM$_{2.5}$ peak dominates in Yangtze River Delta (YRD) with a magnitude lying between those of NCP and PRD. The gridded correlation maps reveal varying correlations around each PM$_{2.5}$ site, depending on the locations and seasons. Concerning the impact of aerosol diurnal variation on the correlation, the averaging schemes of PM$_{2.5}$ using 3-h, 5-h, and 24-h time windows tend to have larger $R$ biases, compared with the scheme of 1-h time window, indicating diurnal variation of aerosols plays a significant role in the establishment of explicit correlation between PM$_{2.5}$ and AOD. In addition, high cloud fraction and relative humidity tend to weaken the correlation, regardless of geographical location. Therefore, the impact of meteorology could be one of the most plausible alternatives in explaining the varying $R$ values observed, due to its non-negligible effect on MODIS AOD retrievals. Our findings have implications for PM$_{2.5}$ remote sensing, as long as the aerosol diurnal cycle, along with meteorology, are explicitly considered in the future.

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1. Introduction

Aerosols have been extensively suggested to play an important role in climate change on regional and global scales, largely due to their significant but uncertain direct and indirect effects (e.g., Kaufman et al., 2002; Rosenfeld et al., 2008; Li et al., 2011; IPCC, 2013; Wang et al., 2014a; Guo et al., 2016a). In addition, PM$_{2.5}$ (particulate matter with an aerodynamic diameter smaller than 2.5 μm) is believed to be closely associated with a wide range of adverse health effects, including cardiovascular, respiratory diseases, and even premature death (e.g., Al-Saadi et al., 2005; Vidot et al., 2007; Wang et al., 2010; Apte et al., 2015; Schwartz et al., 2015). Therefore, the ability of getting accurate temporal and spatial distribution of ground-based PM$_{2.5}$ becomes an increasingly key prerequisite for the effective reduction and prevention of aerosol pollution (Wang and Christopher, 2003; Lin et al., 2015; Guo et al., 2016b).

Apart from the traditional surface PM$_{2.5}$ monitoring network,
The estimation methods of near-surface PM$_{2.5}$ from space-borne AOD can be classified into two categories: observation- and simulation-based methods (Lin et al., 2015). The observation-based methods largely rely on statistical relationships between AOD and surface-level PM$_{2.5}$ observations, which was initially conducted in the United States by Wang and Christopher (2003), who compared MODIS AOD with seven ground measured PM$_{2.5}$ concentrations in Alabama, United States, in 2002, and found that the correlation coefficient ($R$) between AOD and PM$_{2.5}$ differed by regions, with a maximum $R$ of 0.90. The correlation analyses based on MODIS AOD and PM$_{2.5}$ measurements were then extended throughout the contiguous United States (Engel-Cox et al., 2004), revealing a relatively moderate correlation ($R = 0.4$) between MODIS AOD with daily and hourly mean PM$_{2.5}$ concentration. A similar statistical regression study was performed in Europe as well (Koelemeijer et al., 2006). Recently, more sophisticated methods used to estimate PM$_{2.5}$ from space were developed by taking into account meteorological factors such as cloud cover, wind speed, the mixed layer height, and relative humidity (Guo et al., 2006; Liu et al., 2009; Wang et al., 2010; Zheng et al., 2015). As a consequence, the correlation coefficient between AOD and PM$_{2.5}$ or PM$_{10}$ improved significantly (e.g., Guo et al., 2009; van Donkelaar et al., 2010; Wang et al., 2010; Li et al., 2015).

As a side effect of fast economic development, China is currently suffering from serious aerosol pollution, which leads to increasingly attention paid to this region (Xia et al., 2006; Guo et al., 2009; Song, 2009; Wang et al., 2010, 2014b), and underscores the urgent need for real-time air pollution monitoring. However, few operational remote sensing algorithms have been developed to monitor large-scale surface PM$_{2.5}$ concentrations, despite the recent great advances in sophisticated nonlinear methods for PM$_{2.5}$ estimation from space-borne AOD products like multivariate linear models (Seo et al., 2015), back-propagation artificial neural network (e.g., Wu et al., 2012), and geographically weighted regression (GWR) statistical model (e.g., Song et al., 2014; van Donkelaar et al., 2015). This is in part caused by the inhomogeneous horizontal or vertical distributions (Huang et al., 2015), in addition to the meteorology effect in both ground-level PM$_{2.5}$ and satellite AOD retrievals (Li et al., 2015).

It is still challenging to directly estimate ground-level PM$_{2.5}$ due to difficulty in making comparison of a pixel-wise AOD value with a point observation of PM$_{2.5}$. Large-scale discrepancy between AOD and PM$_{2.5}$ might mask their smaller-scale correspondences (Hutchison et al., 2008; Kumar, 2010). This will be the case if we intentionally or unintentionally ignore the effect caused by the diurnal variation of aerosols. As we know, the diurnal cycle of PM$_{2.5}$ seems to be quite important due to its great impact on various applications, including radiative forcing computation, aerosol-cloud interaction, as well as public health (Smirnov et al., 2002; Arola et al., 2013; Xu et al., 2016), most of which are limited to studies of aerosol optical properties at local scale (Kuang et al., 2015; Xu et al., 2016). To the best of our knowledge, few studies have taken the diurnal variability of PM$_{2.5}$ into account when attempting to develop methods to estimate PM$_{2.5}$ over large scale from space.

Therefore, the objective of this study is to investigate the diurnal cycle of PM$_{2.5}$ based on long-term large-scale PM$_{2.5}$ observational network across China, in addition to conducting correlation analyses between PM$_{2.5}$ and AOD by considering the potential impact of aerosol diurnal cycle, ground-based cloud fraction (CF) and relative humidity (RH). The paper is organized as follows: descriptions of the MODIS-derived AOD, ground-based PM$_{2.5}$, RH and CF measurements in China are presented in section 2. The results concerning the correlation analysis between AOD and PM$_{2.5}$, and its influential factors are presented in section 3. Section 4 gives the major conclusions.

2. Data and method
2.1. PM$_{2.5}$ observations and their processing

Hourly ground-based PM$_{2.5}$ measurements during the period from January 1, 2013 to December 31, 2015 were obtained from 226 sites, which constitute one indispensible part of the China Atmosphere Watch Network (CAWNET) operated by the China Meteorological Administration (CMA). CAWNET was mainly designed to measure ambient aerosol loadings across China, and most of its sites are located in suburban areas, in sharp contrast to the urban settings of the PM$_{2.5}$ sites which belong to the observational network maintained by the Ministry of Environment Protection of China. The latter network takes continuous PM$_{2.5}$ measurements primarily from the Tapered Element Oscillating Microbalance (TEOM) with an accuracy of $\pm 5\mu g m^{-3}$ for 10 min-averaged data and $\pm 1.5\mu g m^{-3}$ for hourly averages. It is well known that PM$_{2.5}$ has to be measured at RH $< 40\%$ (e.g., Barnaba et al., 2010), and all the PM$_{2.5}$ data have undergone strict quality control according to the criteria described in detail by Guo et al. (2009).

All ground-based PM$_{2.5}$ measurements are recorded in Beijing time (BJT). In order to reflect the real effect of solar radiation on the diurnal variation in PM$_{2.5}$, the time coordinates have to be converted to local solar time (LST) using the following formula (Guo et al., 2014):

$$T_{LST} = T_{BJT} - 8 + Lon/15 \tag{1}$$

where $T_{LST}$ denotes the observational time in LST, $T_{BJT}$ denotes the original observational time recorded in BJT, and $Lon$ denotes the longitude for a given PM$_{2.5}$ site. To enhance visual interpretation, for a given PM$_{2.5}$ observation station, each daily 24-h period is divided into four 6-hourly intervals defined as follows: early morning (0000–0600 LST), morning (0600–1200 LST), afternoon (1200–1800 LST), and evening (1800–2400 LST).

The diurnal cycles of PM$_{2.5}$ concentration and frequency are determined on the basis of the daily average distribution of hourly time series for the whole period from January 2011 to December 2015. Following the similar methods proposed for characterizing the diurnal variation of precipitation (Guo et al., 2014), the averaged PM$_{2.5}$ at a particular hour of the day $PM_{2.5}(x,y,t)$ is expressed as

$$PM_{2.5}(x,y,t) = \frac{\sum_{d=1}^{d=day} PM_{2.5}(x,y,t,d)}{day} \tag{2}$$

where $PM_{2.5}(x,y,t,d)$ represents the PM$_{2.5}$ concentration at “t”
o’clock (r = 1, 2, 3 ..., 24) on the day of “d” for a particular site with coordinates (x, y), and “day” represents the total number of days during the three-year period. As such, 24 mean hourly PM$_{2.5}$ values were obtained, each of which was further examined to identify the hour with a maximum in PM$_{2.5}$ concentration (amplitude) and occurrence frequency (phase) for a given day. In this way, the time series of PM$_{2.5}$ concentration (amplitude) and occurrence frequency can be obtained for each site.

2.2. MODIS AOD

The MODIS level 2 AOD data (version 5.1, with a resolution of 10 km $\times$ 10 km) for the period January 2013 to December 2015 were downloaded from the Level 1 and Atmosphere Archive and Distribution System (LAADS, https://ladsweb.nascom.nasa.gov/data/search.html). For simplicity, only MODIS-Aqua AOD data which are retrieved at ~1330 LST are used. The MODIS AOD of this version is retrieved using the dual-channel Dark-Target algorithm, which has improved aerosol optical models for the AOD algorithm over land. The algorithm employs primarily three spectral channels centered at 0.47, 0.66, and 2.1 $\mu$m respectively. AOD is derived at 0.47 and 0.66 $\mu$m, and interpolated to 0.55 $\mu$m in order to make comparison with ground-based sun-photometer derived AOD (Anderson et al., 2012).

Extensive field validation campaigns (Wang et al., 2007; Levy et al., 2010) suggested that the MODIS level 2 AOD product has an accuracy of 0.05$\tau_a$±0.15 ($\tau_a$ represents AOD) over land, high enough for further correlation analyses in the following text.

2.3. Collocation between PM$_{2.5}$ concentration and MODIS AOD

Ground-based measurements are point values, while MODIS AOD is reported at a grid box of 10 km $\times$ 10 km (nominal). To investigate the relationship between columnar AOD and surface-level PM$_{2.5}$, both measures must be collocated in space and time. To accomplish realistic spatio-temporal collocation of MODIS AOD and ground-level PM$_{2.5}$, we averaged the original MODIS AOD product (10 km $\times$ 10 km) over 50 km $\times$ 50 km grid box centered at each PM$_{2.5}$ observational site shown in Fig. 1. Furthermore, continuous PM$_{2.5}$ measurements at each site were collocated with the MODIS-Aqua AOD retrievals within ±30 min of its overpass time. In this way, only the data that were spatially collocated and temporally matched at the MODIS overpasses were obtained and used in the following analyses.

To eliminate the potential influence caused by extreme atmospheric pollution, AOD values greater than 2, as well as PM measurements greater than 400 $\mu$g m$^{-3}$, are excluded. At the same time, only the sites with 30 or more valid pairs of satellite/ground observations (Wilks, 2011) were used to perform correlation analyses.

2.4. Ground-based meteorological observations

The meteorological observations considered here contain RH and total cloud cover (TCC), both of which are obtained from surface weather stations. All of these RH and TCC measurements are made simultaneously with PM$_{2.5}$ concentrations at the same 226 PM$_{2.5}$ sites, which provide an ideal testbed and foundation to investigate how meteorological conditions affect the association of ground-level PM$_{2.5}$ with MODIS AOD. Due to the increasingly deteriorating air quality during recent years (Li et al., 2007; Guo et al., 2011), further correlation analyses were focused on three regions of interest (ROIs): the North China Plain (NCP, 36°N $-$ 41°N, 114°E $-$ 119°E), the Yangtze River Delta (YRD, 30°N $-$ 35°N, 117°E $-$ 123°0'E), the Pearl River Delta (PRD, 20.5°N $-$ 25.5°N, 111.5°E $-$ 116.5°E), which respectively correspond to the red rectangles A, B, and C in Fig. 1b.

RH measurements were made at 3-h intervals each day: 0200 LST, 0500 LST, 0800 LST, 1100 LST, 1400 LST, 1700 LST, 2000 LST, and 2300 LST, respectively. Only 1400 LST RH observations were taken to make more genuine temporal collocation with MODIS-Aqua AOD. Table S1 (in the supplementary materials) shows the statistics with respect to the classification criteria of RH in NCP, YRD, and PRD, respectively. In NCP, the RH ranges of 0$-$24.5%, 4.5%$-$39.5%, and 39.5%$-$100% correspond to “Lowest”, “Medium”, and “Highest” RH conditions, respectively. In YRD, the “Lowest”, “Medium”, and “Highest” RH conditions are characterized with RH of 0$-$40.5%, 40.5%$-$54.5%, 54.5%$-$100%, respectively. Similar thresholds hold true for PRD, which have 0$-$45.5%, 45.5%$-$56.5%, and 56.5%$-$100%, respectively.

Cloud observations at weather sites operated by CMA include TCC and low cloud cover, both of which are measured by human observers. The observations are made at 1-h intervals at the national climate observation stations, and made at 3-h intervals at national basic weather observation stations (Xia, 2012). The TCC is the fraction of sky covered by clouds, ranging from 0 to 10. The observation with TCC of zero is referred to as clear and that with TCC of ten is referred to as overcast.

To facilitate the elucidation of how the TCC influences the correlation between AOD and PM$_{2.5}$, three TCC categories were defined (Table S2 in the supplementary materials): “Clear sky”, “Median cloudy”, and “High cloudy”, each of which contains an equal number of samples. The thresholds for these three TCC categories large vary by region.

3. Results and discussion

3.1. Spatial distribution of aerosol particles

As shown in Fig. 1a, the most populous regions like Pearl River Delta (PRD), North China Plain (NCP), and Sichuan Basin, which are generally characterized with high industrialization and intense anthropogenic emissions, have AOD values up to 1.2 or larger. Generally, regions with high PM$_{2.5}$ concentrations coincide with high AOD loadings (Fig. 1b), with the exception of southeastern China (e.g., PRD) and northwestern China. For instance, high AOD can be distinctly seen in northwestern China where dust or dust storms prevail, which generally results in high PM$_{10}$ concentrations. But relatively low PM$_{2.5}$ concentration can be seen in this region (Fig. 1b), indicating aerosol particles with a large aerodynamic diameter contribute to these high AOD values. On the whole, MODIS AOD exhibits a similar spatial pattern as PM$_{2.5}$. That is to say, the regions with great AOD typically correspond to those with high PM$_{2.5}$ concentrations.

Fig. S1 (in supplementary materials) shows the spatial distribution of valid MODIS-Aqua AOD samples (in percentage) for each 1° $\times$ 1° domain of China for spring (March-April-May), summer (June-July-August), fall (September-October-November), and winter (December-January-February). In terms of seasonal difference of valid MODIS samples, NCP can reach to as low as 20% in winter, in comparison with 60$-$80% in the other three seasons. PRD has relatively lower valid AOD samples (20$-$50%) compared to the other areas, depending on the seasons. What’s more interesting is that large climatological AOD is found in the PRD region, contrary to the relatively small PM$_{2.5}$ concentration. This is mostly likely due to the persistent high cloud coverage over this region (Wang et al., 2015), since cloud cover often exerts considerable contamination on the AOD, but can hardly affect the ground-based PM$_{2.5}$ measurements. The observed limited valid AOD samples over PRD, therefore, could at least in part account for the observed mismatch between the two quite different metrics for aerosol loadings: AOD...
versus PM$_{2.5}$.

3.2. Diurnal variability of PM$_{2.5}$

Fig. 2 presents the spatial distribution of diurnal phase and amplitude of PM$_{2.5}$ averaged during the period from January 2013 to December 2015 according to maximum mean PM$_{2.5}$ concentration and maximum occurrence frequency of PM$_{2.5}$ peak for each hour within the 24 h. To minimize the impact caused by the recorded time zone (BJT), all hourly PM$_{2.5}$ concentrations are subjected to the conversion procedures based on Eq. (1) in section 2.1. As such, the diurnal cycles of both PM$_{2.5}$ concentration and occurrence frequency can be determined.

Overall, among the 226 PM$_{2.5}$ observational sites, maximum PM$_{2.5}$ concentrations occur in the morning at 107 sites (about 47.3%), followed by 85 sites (37.6%) with peaks in the evening. On the other hand, only 12 sites (5.3%) have the afternoon peak, whereas 22 sites (9.8%) have the early morning peak. The story with
respect to the diurnal phase and amplitude of maximum frequency of PM$_{2.5}$ is almost the same (Fig. 2b). In terms of the spatial pattern, the timing of maximum PM$_{2.5}$ concentration agrees well with the diurnal cycle of its occurrence frequency. To be more specific, peak PM$_{2.5}$ generally occurs in the evening in the Pearl River Delta region (YRD in Fig. 1b) of southern China, where sporadic sites witness an afternoon or evening PM$_{2.5}$ maximum (Fig. 2a), with magnitude generally lower than 50 $\mu$g m$^{-3}$. By comparison, both morning and evening PM$_{2.5}$ peaks contribute almost equally to the diurnal cycle in the North China Plain region (NCP in Fig. 1b), with amplitude that is twice or three times that over southern China, indicative of the severe air pollution in northern China. Interestingly, observational sites in northeastern China also have large diurnal amplitude and the maximum PM$_{2.5}$ tends to occur in the morning and evening. This further bears out the AOD and PM$_{2.5}$ pattern observed in Fig. 1. Besides, morning PM$_{2.5}$ peak dominates the Yangze River Delta region (YRD in Fig. 1b), with amplitude lying between those of NCP and PRD.

### 3.3. The spatio-temporal variability of correlation between PM$_{2.5}$ and AOD

In order to better characterize the regional features, correlation analyses between PM$_{2.5}$ and AOD have been performed over all the sites shown in Fig. 1b, through downscaling to regional scale. Namely, we divided the 226 monitoring sites into 23 sub-domains, each of which has a domain size of 5’’ x 5’’. The scatter plots of ground-based in-situ PM$_{2.5}$ against AOD, as well as their concomitant correlation coefficients (R) in these 23 sub-domains are shown in Fig. 3. The R values range from 0.17 to 0.57, exhibiting large regional variability, which is in good agreement with the results found in United States (Li et al., 2015). In particular, R values in...
as black lines and red numbers, respectively. Note that the asterisk in the superscript attached to red numbers ($R$) means the regression is statistically significant ($p < 0.05$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Scatter plots of ground-based PM$_{2.5}$ against coincident MODIS-Aqua AOD for each 5’ × 5’ subdomain with enough PM$_{2.5}$ observations. The color shading represents frequency of occurrence for each bin of 0.1 AOD × 10$^{-9}$ PM$_{2.5}$. The regression line and its corresponding correlation coefficients between PM$_{2.5}$ and AOD are given in each subplot as black lines and red numbers, respectively. Note that the asterisk in the superscript attached to red numbers ($R$) means the regression is statistically significant ($p < 0.05$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

eastern China on average are higher than those in western China, where most of the domains have arid conditions and high surface albedos, thereby leading to highly uncertain AOD retrievals (Remer et al., 2005). This in turn results in large biases for the correlation analysis between PM$_{2.5}$ and AOD. A close-up look at sample density distributions (shaded color in Fig. 3) suggests that AOD values for most of the data-pairs are limited to less than 0.5, and PM$_{2.5}$ limited to less than 50 µg m$^{-3}$. This further supports the results shown in Fig. 3a.

Table 2 shows the results concerning correlation analyses between PM$_{2.5}$ concentration and AOD in different seasons throughout China. In terms of the seasonal variability of $R$, there exists a large spatial discrepancy. In particular, $R$ values generally range from 0.5 to 0.8 in Northeast China, NCP, and YRD, indicating that AOD is a good indicator of PM$_{2.5}$ pollution levels in these regions. In addition, we notice that $R$ is relatively low in areas with complex topography, such as southwestern China, which agrees with previous results (e.g., Xie et al., 2015). Also, the correlation coefficients in coastal areas can not be as high, which may be related to the difficulties in dealing with complex aerosol types and underlying surface albedo in the AOD inversion algorithm applied to the coastal areas (van Donkelaar et al., 2006; Anderson et al., 2012).

As shown in Table 1, the annually averaged $R$ over NCP can be as high as 0.54, gradually reduced to 0.46 over YRD and then dropping to as low as 0.37 over PRD, indicating $R$ values exhibit spatial dependence to some degree. Meanwhile, the MODIS-derived AOD is found to be most closely associated with the ground-based PM$_{2.5}$ pollution level in spring over NCP with the highest $R$ value (0.71). In contrast, the highest $R$ (0.55) occurs in winter over YRD, whereas it occurs in fall over PRD with $R = 0.45$.

3.4. Impact of various spatio-temporal average schemes on the correlation between AOD and PM$_{2.5}$

As previously demonstrated in section 3.2, significant diurnal variation in PM$_{2.5}$ has been widely observed. Here we selected three ROIs (NCP, PRD, and YRD) to further determine whether or not the diurnal cycle of PM$_{2.5}$ will influence the correlation analyses between AOD and PM$_{2.5}$, and how. As illustrated in Fig. 5, the occurrence time with the maximum averaged PM$_{2.5}$ values is quite different, depending on geographical locations. The PM$_{2.5}$ (112 µg m$^{-3}$) peaks at midnight over NCP, as compared with the evening peak (67 µg m$^{-3}$) over YRD, and the morning peak (36 µg m$^{-3}$) over PRD. In contrast, the lowest PM$_{2.5}$ values occur uniformly at 1400–1600 LST, irrespective of NCP, YRD, and PRD. This could be due to the increased incident solar radiation, which has been suggested to be closely linked to enhanced turbulence and buoyancy and elevated boundary layer height (Guo et al., 2016c).

It is intriguing to note that all the correlation coefficients (individual 1-h mean PM$_{2.5}$ versus MODIS-Aqua AOD) over three ROIs peaks at 1330 LST, then decreases slowly as the PM$_{2.5}$ observational time moves further away from 1330 LST. Therefore, except for the perennially high PM$_{2.5}$ values over NCP which deserves more attention, the impact of PM$_{2.5}$ diurnal variability on the remote sensing of ground-based PM$_{2.5}$ should be considered seriously.

Fig. 4 compares the correlation coefficients for the regression analyses between PM$_{2.5}$ concentration and AOD in different seasons throughout China. As previously demonstrated in section 3.2, significant diurnal variation in PM$_{2.5}$ has been widely observed. Here we selected three ROIs (NCP, PRD, and YRD) to further determine whether or not the diurnal cycle of PM$_{2.5}$ will influence the correlation analyses between AOD and PM$_{2.5}$, and how. As illustrated in Fig. 5, the occurrence time with the maximum averaged PM$_{2.5}$ values is quite different, depending on geographical locations. The PM$_{2.5}$ (112 µg m$^{-3}$) peaks at midnight over NCP, as compared with the evening peak (67 µg m$^{-3}$) over YRD, and the morning peak (36 µg m$^{-3}$) over PRD. In contrast, the lowest PM$_{2.5}$ values occur uniformly at 1400–1600 LST, irrespective of NCP, YRD, and PRD. This could be due to the increased incident solar radiation, which has been suggested to be closely linked to enhanced turbulence and buoyancy and elevated boundary layer height (Guo et al., 2016c).

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Table 2 shows the results concerning correlation analyses between PM$_{2.5}$ and AOD using different temporal averaging schemes of PM$_{2.5}$ centered over MODIS-Aqua observational time (about 1330 LST). The PM$_{2.5}$ concentrations were averaged over 1300 to 1400, 1200 to 1500, 1100 to 1600, and 0000 to 2400 LST and then compared with the corresponding MODIS-Aqua AOD values. Even though the magnitudes differ greatly, $R$ values are typically reduced from north to south, despite various temporal averaging schemes. More importantly, the more the closer the MODIS-Aqua overpass time to the time PM$_{2.5}$ was taken, the larger the $R$ values are. That is to say, the scheme with 3-h, 5-h, and 24-h time windows will result in large biases in constructing realistic regression equations, compared with the 1-h time window. This indicates that the large biases in part reflect the abovementioned temporal mismatch, and more careful attention should be paid to the temporal mismatch between AOD and PM$_{2.5}$, especially for the temporal averaging scheme for hourly PM$_{2.5}$ observations.

In the meanwhile, we have performed sensitive analyses over NCP, YRD, and PRD regarding the impact of MODIS AOD averaging scheme on the changes in correlation between ground-based PM$_{2.5}$ and collocated MODIS AOD, which corresponds to a spatial resolution of 10 km × 10 km, 30 km × 30 km, 50 km × 50 km,
respectively. As shown in both Table S3 and Figure S2 in the supplementary material, R values decrease with the size of grid box for averaging the original level 2 MODIS AOD (10 km) when matching AOD and coincident PM$_{2.5}$. This holds true over NCP, YRD, and PRD. Therefore, the correlation between PM$_{2.5}$ and AOD, to some extent, depends on spatial average scheme of MODIS AOD.

3.5. The potential impact of meteorology

Hygroscopic growth of aerosol particles was found to be
ubiquitous, which inevitably leads to uncertainties to varying degree in retrieving of AOD from satellite observations (e.g., Remer et al., 2005; Guo et al., 2009). In addition, cloud contamination often induces uncertain or artifact retrievals of satellite- or ground-based AOD (Jeong and Li, 2010; Määtä et al., 2014; Ford and Heald, 2016). Therefore, the effect of RH and cloud fraction on the correlation between PM$_{2.5}$ and AOD merits further detailed and explicit analyses in certain ROIs when PM$_{2.5}$ concentrations are to be estimated from satellite-based AOD (e.g., MODIS-derived AOD).

Fig. S3 (in the supplementary materials) presents the histograms of RH over NCP, YRD, and PRD averaged over the period from 1300 to 1400 LST, matching well with the MODIS-Aqua overpass time. The lowest and highest 30% quantiles of RHs are marked with red dashed lines in each subplot. More details on the criteria have been given for the determination of largest RH and smallest RH conditions. PRD is the most humid region, which is in sharp contrast to the driest NCP. Can this discrepancy in RH have any impact on the regional correlation coefficients derived from the regression analyses of PM$_{2.5}$ against AOD?

Fig. 6 shows the scatter plots of ground-based PM$_{2.5}$ (averaged over 1300 to 1400 LST) versus the collocated MODIS AOD under different levels of RH over NCP, YRD, and PRD. Overall, regardless of the geographical discrepancy, R exhibits a decreasing trend as the ambient atmosphere becomes more humid. For instance, R over NCP is reduced by 30% (from 0.62 to 0.44), as compared with a magnitude of reduction of 37.5% (42.2%) over YRD (PRD). Also, we also notice a distinct southward decrease in R. In other words, the smallest R can be seen over PRD (southernmost ROI) for all RH conditions, in sharp contrast to the largest R over NCP (northernmost ROI) and median R over YRD (central ROI). This signifies that RH exerts a significant influence on the correlation between PM$_{2.5}$ and AOD, and cannot be ignored, despite the existing differences in R values.

The effect of cloud fraction on correlation analyses between AOD and PM$_{2.5}$ is investigated by separating the matched samples into three equal-sample bins (Table S2). As shown in Fig. 7, R tends to become much higher when all samples are taken under clear sky conditions over NCP, YRD, and PRD, as compared with that under high cloudy conditions. The well-known cloud-induced artificial AOD due to aerosol humidification near clouds (e.g., Twomey et al., 2009), and light scattering from the side of clouds (e.g., Koren et al., 2007; Varnai and Marshak, 2009), generally result in large uncertainties in MODIS AOD retrievals, thereby leading to a deteriorated association of MODIS AOD with ground-based PM$_{2.5}$. Therefore, the confounding meteorological factors like cloud fraction and RH, if any, will make the direct retrieval of PM$_{2.5}$ from MODIS AOD almost impossible due to its adverse impact on R.

data across China were spatio-temporally collocated with MODIS-Aqua AOD data, combined with surface-observed cloud and humidity data to perform explicit correlation analyses.

The diurnal cycles of mass concentration and occurrence frequency of PM$_{2.5}$ are investigated across China. Roughly speaking, one half sites, among the 226 sites, have the maximum PM$_{2.5}$ concentration in the morning, in sharp contrast to the least frequent occurrence (about 5%) in the afternoon, which is most likely due to strong solar radiation received at the surface in the afternoon, thereby leading to the rapid diffusion of aerosol particles and lower mass concentration. Interestingly, the occurrence frequency of PM$_{2.5}$ has almost the same diurnal cycles, as well as its spatial pattern. In particular, PM$_{2.5}$ tends to peak equally in the morning and evening in NCP with amplitudes twice or three times that in PRD. The morning PM$_{2.5}$ peak dominates YRD with amplitudes lying between those of NCP and PRD.

The correlation between surface level PM$_{2.5}$ and MODIS varies greatly in China, both spatially and temporally, which is in good agreement with the previous results. In particular, correlation in eastern China is on average stronger than those in other domains. In terms of the seasonal variability of R, there still exists large spatial discrepancy. MODIS AOD can better represent the surface PM$_{2.5}$ in spring over NCP with the largest R value (0.71). By comparison, maximum correlation (R = 0.55) occurs in winter over YRD, whereas it occurs in fall over PRD with R = 0.45.

As far as the impact of aerosol diurnal variation on the correlation was concerned, we found that the schemes with 3-h, 5-h, and 24-h time windows have larger biases in constructing realistic regression equations, in comparison with the scheme using 1-h time window. This suggests that the large biases at least partly reflect the above-mentioned temporal mismatch. The impact of meteorology becomes one of the most plausible alternatives that can explain the relatively low R values observed in most sites of China, due to its non-negligible effect on MODIS AOD retrievals. The results have great implications for future PM$_{2.5}$ remote sensing from space.

Nevertheless, accurate estimation of the association of PM$_{2.5}$ with AOD remains extremely challenging because both PM$_{2.5}$ and AOD co-vary with meteorological conditions, including cloud fraction and relative humidity. Even though the effect of meteorological factors like CF and RH has been elucidated, the boundary layer height along with vertical structure of aerosols, among others, have been sufficiently recognized to be key to modulating the statistical relationship between PM$_{2.5}$ and AOD. Therefore, more work should be warranted in this regard. Furthermore, the aerosol types with differing light absorbing and scattering properties may affect the correlation analysis results to some extent, which merits more attention in the future.

4. Concluding remarks

In this study, three years (2013–2015) of ground-based PM$_{2.5}$

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**Appendix A. Supplementary data**

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.11.043.

**References**


