Roles of Relative Humidity in Aerosol Pollution Aggravation over Central China during Wintertime

Lin Zang 1, Zemin Wang 1,*, Bo Zhu 2 and Yu Zhang 3

1 Chinese Antarctic Centre of Surveying and Mapping, Wuhan University, Wuhan 430079, China; zanglin2018@whu.edu.cn
2 Hubei Environmental Monitoring Centre, Wuhan 430079, China; zhubo125@whu.edu.cn
3 School of Remote Sensing and Information Engineering, Wuhan University, Wuhan 430079, China; zhangyu543@whu.edu.cn
* Correspondence: zmwang@whu.edu.cn

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Abstract: Aerosol pollution elicits considerable public concern due to the adverse influence on air quality, climate change, and human health. Outside of emissions, haze formation is closely related to meteorological conditions, especially relative humidity (RH). Partly due to insufficient investigations on the aerosol hygroscopicity, the accuracy of pollution prediction in Central China is limited. In this study, taking Wuhan as a sample city, we investigated the response of aerosol pollution to RH during wintertime based on in-situ measurements. The results show that, aerosol pollution in Wuhan is dominated by PM2.5 (aerodynamic particle size not larger than 2.5 µm) on wet days (RH ≥ 60%), with the averaged mass fraction of 0.62 for PM10. Based on the RH dependence of aerosol light scattering (f(RH)), aerosol hygroscopicity was evaluated and shows the high dependence on the particle size distribution and chemical compositions. f (RH = 80%) in Wuhan was 2.18 (±0.73), which is comparable to that measured in the Pearl River Delta and Yangtze River Delta regions for urban aerosols, and generally greater than values in Beijing. Ammonium (NH4+), sulfate (SO42−), and nitrate (NO3−) were enhanced by approximately 2.5-, 2-, and 1.5-fold respectively under wet conditions, and the ammonia-rich conditions in wintertime efficiently promoted the formation of SO42− and NO3−, especially at high RH. These secondary ions play an important role in aggravating the pollution level and aerosol light scattering. This study has important implications for understanding the roles of RH in aerosol pollution aggravation over Central China, and the fitted equation between f(RH) and RH may be helpful for pollution forecasting in this region.

Keywords: aerosol pollution; hygroscopicity; relative humidity; secondary formation

1. Introduction

Atmospheric aerosols, consisting of large amounts of solid and liquid particles, could directly or indirectly affect the climate system [1–4]. The Intergovernmental Panel on Climate Change (IPCC) reports that aerosols are consistently the leading contributors to the uncertainty of global climate change [5,6]. What is more, numerous epidemiological studies have indicated that the suspended particles in the atmosphere, especially those with an aerodynamic diameter not larger than 2.5 µm (PM2.5), would produce serious adverse effects on human bodies, hence increasing deaths from cardiovascular and respiratory diseases and even lung cancer [7,8]. As such, aerosols have drawn considerable concern [9–11]. In recent years, numerous studies have been conducted to investigate the formation mechanisms of aerosol pollution, and some of them implied the important role of relative humidity (RH) in this issue because of the aerosol hygroscopicity [12,13].
On the one hand, the volume of hydrophilic aerosols increases after water uptake, thereby enhancing light scattering and, consequently, affecting horizontal visibility and the earth–atmosphere radiation budget [14,15]. To assess the effect of aerosols on the radiation budget, numerous in-situ measurements of aerosol light scattering are carried out. However, these measurements are commonly performed under dry conditions through heating air mass samples. It is necessary to transform the measured dry aerosol optical properties into corresponding values at ambient RH [16]. In order to quantify the relationship between the two aerosol scattering properties, the scattering hygroscopic growth factor, \( f(RH) \), was established to picture the response of aerosol optical properties to the different ambient RH [17]. Notably, the value of \( f(RH) \) presents significant spatial variety [16]. Quantifying \( f(RH) \) is necessary to estimate the aerosol direct radiative forcing.

On the other hand, the increased conserved water could accelerate the gas–liquid–solid reactions of gaseous precursors with particles, thereby strengthening the hygroscopicity of aerosols [14,18]. Since the 1980s, China has witnessed rapid urbanization and industrialization accompanied by a continuous increase in total emissions of air pollutants and gradual deterioration of air quality [19–21]. Specifically, traditional coal–smoke air pollution, which includes sulfur dioxide (SO\(_2\)) and particles as the main components, remains severe due to the coal-dominated energy structure of China [22]. Furthermore, the concentration of photochemical precursors in the atmosphere, such as NO\(_x\) and volatile organic compounds, has continued to increase with vehicle ownership [23]. Other than primary emissions, secondary particle generation has become another notable cause of haze formation in the country, and may even play a decisive role occasionally [13,24,25]. Understanding the aerosol hygroscopicity is vital to further explain the physicochemical processes in the atmosphere and local haze pollution.

Notably, aerosol hygroscopicity not only has significant impacts on climate and environment, but also aggravates the threats to human health by affecting the transmission and deposition of inhaled particles into the respiratory system [26,27]. Therefore, it has elicited wide research attention, especially in the Beijing–Tianjin–Hebei (BTH) region [28–30], the Yangtze River Delta (YRD) region [25,31,32], and the Pearl River Delta (PRD) region [33,34]. For example, Xie et al. (2017) [25] focused on a wintertime haze episode in Shanghai in 2014, and found that both hygroscopicity and effective density of the particles increased with particle size, indicating the key role of secondary particles generated from the gaseous precursors in the particle growth. However, to the best of our knowledge, systemic studies on the aerosol hygroscopicity and its impact on pollution aggravation in Central China, one of the most polluted areas in the country, are still quite limited. Herein, observations from an environmental monitoring facility in Wuhan were adopted to explore the hygroscopic growth distributions and response of aerosol pollution to RH variations in Central China.

2. Data and Methods

2.1. Data

Observations from an environmental monitoring super site (114.37° E, 30.53° N) of the Hubei Environmental Monitoring Centre located in Wuhan, China, were adopted. This site is surrounded by commercial blocks and dwelling quarters, and can be considered a representative urban site. Various aerosol-related observation instruments are installed at this site, including the ambient particulate monitor (Model TEOM-1405, USA), nephelometer (Model Ecotech-Aurora1000, Australia), online ion chromatographic analyzer (Model METROHM-MAGAR 1S, Holland), automatic organic carbon (OC) and elemental carbon (EC) analyzer (Model RT4, USA), various gas analyzers and meteorological monitors, etc. The datasets used here included ground-based concentration measurements of solid and gaseous pollutants, chemical compositions in particles, and aerosol light scattering. Meteorological parameters, such as RH (%) and T (°C), were also obtained from in-situ measurements. Only data that met the quality requirements established by the local environmental
agency were adopted, and data recorded with RH > 95% were excluded from this study to avoid the influence of wet deposition. The sampling time range was from December 2017 to February 2018.

The mass concentrations of PM$_1$, PM$_{2.5}$, and PM$_{10}$, that is, particles with aerodynamic diameters not larger than 1.0, 2.5 and 10 µm, were measured using the micro-oscillation balance method with a time resolution of 1 h. Mass concentrations of main water-soluble ionic components in PM$_{2.5}$, including cations (e.g. NH$_4^+$, Na$^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$) and anions (e.g. SO$_4^{2-}$, NO$_3^-$, and Cl$^-$), were measured via the ion chromatography method with a sampling velocity of 1 m$^3$/h. OC and EC were monitored based on the thermal–optical transmittance method with a measuring sensitivity of 0.5 µgC/m$^3$. Aerosol scattering coefficients (SC) were monitored using the integral method with a minimum detection limit of 0.3 Mm$^{-1}$ by the nephelometer. During the experiment, the RH of sampled aerosols was controlled by a heating process. The mass concentrations of gas pollutants, namely, SO$_2$, nitrogen dioxide (NO$_2$), and ozone (O$_3$), were measured through fluorescence analysis, chemi-luminescence method, and ultraviolet spectrophotometry, respectively.

In order to evaluate the influence of hygroscopic growth on aerosol observations measured by satellite remote sensing, aerosol optical depth (AOD) data provided by Himawari-8 was also used in this work. Himawari-8 is a stationary orbit satellite, which was launched in October 2014 and is operated by the Japan Aerospace Exploration Agency. Until now, only two kinds of AOD products (L2 and L3) have been published, and they have the same spatial resolution of 0.05$^\circ$. However, the temporal resolution of L2 products is 10 min and that of L3 products includes 1 h, 1 day, and 1 month. There are four confidence levels, namely, very good, good, marginal, and no confidence for AOD quality assurance. Herein, hourly AOD data with the highest confidence level from L3 were adopted.

2.2. Method

2.2.1. Parameterization of Scattering Hygroscopic Growth

The RH dependence of aerosol light scattering is one of the physical parameters commonly applied to describe aerosol hygroscopicity, and could be characterized by the scattering hygroscopic growth factor, denoted by $f(RH)$, which is defined as the ratio of aerosol light scattering coefficient at a given RH ($\sigma_{RH}$) and under dry conditions ($\sigma_{dry}$), which is usually defined as RH < 40% [14,17]. This factor is used to represent the overall aerosol light scattering enhancement and is determined by the particle size distribution, chemical composition, density, and refractive index [14,35]. Several models, such as the exponential [35] and binomial models [29], have been developed to describe the relationship between $f(RH)$ and RH. Herein, two widely used models, namely, the two-parameter fit equation [36,37] and the kappa equation [37,38], were adopted to investigate the hygroscopic growth for light scattering in Central China:

1. Two-parameter fitting equation

$$f(RH) = a \left(1 - \frac{RH}{100}\right)^{-b}$$

where $a$ and $b$ are empirical fitting parameters. The scattering growth in this equation is normalized by the parameter of $a$, and the magnitude of the hygroscopic increase in the scattering coefficient is represented by the parameter of $b$ [37,39]. This equation is related to both particle size and chemical composition.

2. Kappa equation

$$f(RH) = 1 + k \left(\frac{RH}{100 - RH}\right)$$

where $k$ is a fitting parameter, related to the average water activity of aerosol components [37]. The hygroscopic growth of aerosol scattering in this equation is theoretically expressed in terms of volume growth based on the Mie equation [37,38].
Under the condition of low RH, the change of \( f(RH) \) is not obvious, while at high RH, \( f(RH) \) changes greatly with the increase of RH. Based on the aircraft measurements, Beyersdorf et al. (2016) [40] concluded that at low RH, aerosol loadings and hygroscopic growth accounted for about 88% and 10% of the extinction variability respectively, while when \( RH > 60\% \), 95% of the extinction diurnal variability and 62% of the spatial variability should be attributed to aerosol water uptake. Chen et al. (2014) [14] also indicates that when \( RH < 60\% \), the influence of aerosol water uptake on the \( f(RH) \) is indistinct. Therefore, in order to better analyze the influence of aerosol hygroscopicity on local pollution, particular attention was paid to aerosol distribution and optical properties when \( RH \geq 60\% \), defined as wet conditions here.

2.2.2. Evaluation of Secondary Aerosols

Here, analysis of secondary aerosol formation focused on sulfate (SO\(_4^{2-}\)), nitrate (NO\(_3^-\)), and ammonium salt (NH\(_4^+\)), generally considered as the main composition of secondary inorganic aerosols, remarkably contributing to the moisture absorption of atmospheric particles [41]. The oxidation of gaseous precursors is the main chemical pathway for secondary particle formation. Among them, the oxidation property of gaseous precursors (SO\(_2\) and NO\(_2\)) can be evaluated by the oxidation ratio, calculated following Li et al. (2013) [42] and Pani et al. (2018) [43]:

\[
\begin{align*}
\text{SOR} &= \frac{n(\text{SO}_4^{2-})}{n(\text{SO}_4^{2-}) + n(\text{SO}_2)} \\
\text{NOR} &= \frac{n(\text{NO}_3^-)}{n(\text{NO}_3^-) + n(\text{NO}_2)}
\end{align*}
\]

where SOR and NOR are the sulfur oxidation ratio and nitrogen oxidation ratio respectively, indicating the conversion degree of gas-phase SO\(_2\) and NO\(_2\) to particulate sulfate (SO\(_4^{2-}\)) and nitrate (NO\(_3^-\)). \( n(\text{SO}_4^{2-}) \), \( n(\text{SO}_2) \), \( n(\text{NO}_3^-) \), and \( n(\text{NO}_2) \) are the molar concentration of each component. Previous studies have indicated that the value of SOR (NOR) is generally less than 0.10 in the primary pollutants, and a higher SOR (NOR) denotes the significant generation of sulfates (nitrates) in the atmosphere [44,45].

3. Results and Discussion

3.1. Overview

During the sampling period, the averaged concentrations of PM\(_1\), PM\(_{2.5}\), and PM\(_{10}\) were 29.89, 51.87, and 95.39 \( \mu g/m^3 \), respectively, and the mean mass fraction of PM\(_{2.5}\) in PM\(_{10}\) was 0.55. Compared with dry conditions (\( RH \leq 40\% \)), although the average concentration of PM\(_{10}\) only increased by 14% on wet days (\( RH \geq 60\% \)), the mean contents of PM\(_1\) and PM\(_{2.5}\) almost doubled, which resulted in a remarkable increase in the proportion of fine particles, with the ratio of PM\(_{2.5}/\text{PM}_{10}\) increasing from 0.38 to 0.62 (Table 1). When \( RH \leq 70\% \), the concentrations of PM\(_1\) and PM\(_{2.5}\) both increased with RH increasing, as shown in Figure 1a,b. However, when \( RH > 70\% \), the concentration of PM\(_1\) decreased, whereas that of PM\(_{2.5}\) continued to increase. The above results suggest that the enhancement of PM\(_{2.5}\) concentration at high RH is dominated by particles with aerodynamic diameters between 1.0 and 2.5 \( \mu m \).
was fitted by the two-parameter fitting equation and the kappa equation respectively, as shown in Figure 2a,b. Aerosol hygroscopic growth was inconspicuous at low RH. Here, the aerosol hygroscopicity on the extinction for light. Here, the RH dependence of light scattering, f(RH), was fitted by the two-parameter fitting equation and the kappa equation respectively, as shown in Figure 2a,b. Aerosol hygroscopic growth was inconspicuous at low RH, only leading to slight changes in f(RH). With the increase of RH, especially when RH > 60%, aerosol hygroscopic growth leads to significant changes in light scattering.

Table 1. Variation statistics of particles under dry and wet conditions.

| Items       | PM₁ (µg/m³) | PM₂.₅ (µg/m³) | PM₁₀ (µg/m³) | PM₁/PM₂.₅ | PM₂.₅/PM₁₀ |
|-------------|-------------|---------------|--------------|------------|------------|
| Average     | 29.89       | 51.87         | 95.39        | 0.59       | 0.55       |
|             | (13.78)     | (24.03)       | (37.65)      | (0.19)     | (0.16)     |
| Dry (RH ≤ 40%) | 16.11       | 31.44         | 84.83        | 0.51       | 0.38       |
|             | (9.57)      | (13.36)       | (29.59)      | (0.19)     | (0.10)     |
| Wet (RH ≥ 60%) | 33.56       | 57.25         | 96.40        | 0.60       | 0.62       |
|             | (13.04)     | (20.22)       | (38.19)      | (0.17)     | (0.14)     |
| Increase    | 17.45       | 25.81         | 11.57        | 0.09       | 0.24       |

Note: Numbers in parentheses represent the standard deviation.

Figure 1. Variation in (a) PM₁, (b) PM₂.₅ and (c) mass fraction of PM₂.₅ in PM₁₀ with increasing RH during winter.

3.2. Aerosol Scattering Hygroscopic Growth

The ambient aerosols absorb or lose water in response to the change of ambient RH and consequently the particle size and refractive index change, altering the aerosol scattering properties ultimately [16]. Compared with dry conditions (RH ≤ 40%), the averaged SC enhanced by 228.26 Mm⁻¹ on wet days (RH ≥ 60%), from 189.71 Mm⁻¹ to 441.99 Mm⁻¹, which indicates the remarkable impact of aerosol hygroscopicity on the extinction for light. Here, the RH dependence of light scattering, f(RH), was fitted by the two-parameter fitting equation and the kappa equation respectively, as shown in Figure 2a,b. Aerosol hygroscopic growth was inconspicuous at low RH, only leading to slight changes in f(RH). With the increase of RH, especially when RH > 60%, aerosol hygroscopic growth leads to significant changes in light scattering.

Figure 2. Parameterization of aerosol scattering hygroscopic growth based on (a) the two-parameter fitting equation and (b) the kappa equation. (c) Hygroscopic correction of satellite-based AOD during winter. Measured PM₂.₅ is dry PM₂.₅, and corrected PM₂.₅ is dry PM₂.₅ multiplied by hygroscopic growth factor.
Comparison of the fitting performance between two models indicates that the two-parameter fitting equation was more suitable for representing the actual hygroscopic growth in Wuhan in terms of a higher determination coefficient ($R^2 = 0.97$). Therefore, the final parametric form of $f(RH)$ is presented as follows:

$$f(RH) = 0.95 \cdot \left(1 - \frac{RH}{100}\right)^{-0.49}$$ (5)

Based on the parametric form above, the correlation between satellite AOD from Himawari-8 and the concentration of dry particles observed from the ground stations improved from 0.56 to 0.65 after a simple hygroscopic correction considering scattering hygroscopic growth ($AOD \sim PM_{2.5}^{dry} \times f(RH)$), as shown in Figure 2c.

So far, researchers in China have conducted numerous studies investigating the hygroscopic factor for aerosol scattering. In order to further analyze the difference of aerosol hygroscopicity between Central China and other regions in the country, we focused on the parameter of $f(RH = 80\%)$, which has been widely used to compare the aerosol hygroscopicity in different regions or different pollution levels, and it was summarized in Table 2. Comparisons implied that the hygroscopicity of aerosols varies in different regions with various pollution levels and aerosol types. In this study, $f(RH = 80\%)$ is 2.18 ($\pm 0.73$), which is comparable to 2.4 measured in Nanjing and 2.0 ($\pm 0.3$) measured in Guangzhou for urban aerosols, but it was generally greater than that measured in BTH regions. This is partly due to drier conditions and a higher dust fraction in BTH regions. Additionally, it could be found that $f(RH)$ of urban aerosols is higher than that of rural aerosols. This may be because of the higher mass fraction of anthropogenic hydrophilic inorganic salts, organic acids, and/or organic acid salts, which need to be further investigated. The marine aerosols show the strongest hygroscopicity because of the high solubility of sea salt, which is more than twice as strong as dust aerosols.

**Table 2.** Summary of scattering hygroscopic growth factors at $RH = 80\%$ in different regions.

| Study Area   | Site          | Study Period | Aerosol Type | $f(RH = 80\%)$ | Reference            |
|--------------|---------------|--------------|--------------|----------------|----------------------|
| YRD          | Nanjing      | 2012.11      | Urban        | 2.4            | Cui et al. (2016) [46]|
| YRD          | Shanghai     | 2011.5–2012.4| Mixed        | 3.5            | Cui et al. (2016) [44]| Cheng et al. (2013) [47]|
| PRD          | Guangzhou    | 2006.7       | Mixed        | 2.3 ($\pm 0.3$) | Liu et al. (2012) [33]|
|              |              |              | Marine       | 2.7 ($\pm 0.6$) |                      |
|              |              |              | Dust         | 1.20 ($\pm 0.02$) |                      |
| BTH          | Rural site   | 2006.4–2006.5| Clean        | 1.31 ($\pm 0.03$) | Pan et al. (2009) [48]|
|              | of Beijing   |              | Urban        | 1.57 ($\pm 0.02$) |                      |
| BTH          | Urban site   | 2007.10–2007.11| Urban        | 1.9 ($\pm 0.3$) | Liu et al. (2013) [28]|
|              | of Beijing   |              |              |                |                      |
| BTH          | Wuqing       | 2009.10–2010.1| Clean        | 1.46 ($\pm 0.15$) | Chen et al. (2014) [14]|
|              |              |              | Polluted     | 1.58 ($\pm 0.19$) |                      |
| BTH          | Raoyang      | 2014.6–2014.8| Polluted     | 2.28 ($\pm 0.69$) | Wu et al. (2017) [29]|
| Central China| Wuhan        | 2017.12–2018.2| Urban        | 2.18 ($\pm 0.73$) | This study            |

Herein, a sensitivity analysis of particulate scattering hygroscopic growth at $RH = 80\%$ was further conducted (Figure 3). There is a high linear correlation between $f(RH = 80\%)$ and the mass fraction of $PM_{2.5}$ in $PM_{10}$, with the correlation coefficient of 0.85, as presented in Figure 3a. With the mass fraction of inorganic salts (including $NH_4^+$, $SO_4^{2-}$, $NO_3^-$, $Ca^{2+}$, $Na^+$, $K^+$, $Mg^{2+}$, and $Cl^-$) in $PM_{2.5}$ increasing, $f(RH = 80\%)$ showed an increasing tendency, with the correlation coefficient of 0.57. Rather, a gradual decrease was observed with the enhanced mass fraction of organic matter in $PM_{2.5}$. This is because most organic particles are hydrophobic. The similar findings were also noted by Wu et al. (2017) [29] and Chen et al. (2014) [14]. These statistical results indicate the high dependence of $f(RH)$ on the aerosol particle size distribution and hygroscopicity, which is correlated to chemical compositions.
Wuhan exhibits ammonia-rich conditions in wintertime. That is, SO\(_4^{2-}\) winter, further suggesting were significantly correlated to particle hygroscopic growth, while other inorganic ions (Ca\(^{2+}, Na^{+}, K^{+}, M^{2+}\), and Cl\(^{-}\)) showed little correlation. Therefore, we focus on the variation of NH\(_4^+\), SO\(_4^{2-}\), and NO\(_3^-\) to further investigate the relationship between aerosol chemical compositions and RH in Wuhan.

During the sampling period, the averaged concentrations of NH\(_4^+\), SO\(_4^{2-}\), and NO\(_3^-\) were 10.71, 7.53, and 6.01µg/m\(^3\), respectively (Table 3). Compared with dry conditions (RH ≤ 40%), the mean concentrations of NH\(_4^+\), SO\(_4^{2-}\), and NO\(_3^-\) increased by about 2.5-, 2-, and 1.5-fold on wet days, respectively. Figure 4 shows the detailed variation of SO\(_4^{2-}\) and NO\(_3^-\) with the increase of RH during winter, further suggesting RH plays an important role in the transformation and evolution of secondary sulfate and nitrate. SOR (Figure 4d) and NOR (Figure 4e) indicate strong oxidation during humid conditions in Wuhan, especially when RH > 80% and T < 10 °C.

Table 3. Variation statistics of secondary inorganic salts and gaseous precursors during winter (µg/m\(^3\)).

| Item          | NO\(_3^-\) | NH\(_4^+\) | SO\(_4^{2-}\) | SO\(_2\)  | NO\(_2\) |
|---------------|------------|------------|---------------|----------|----------|
| Average       | 10.71      | 7.53       | 6.01          | 14.47    | 60.11    |
|               | (7.56)     | (6.40)     | (4.82)        | (11.85)  | (25.99)  |
| Dry (RH ≤ 40%)| 5.55       | 2.68       | 2.43          | 17.54    | 51.10    |
|               | (3.03)     | (1.96)     | (1.21)        | (8.94)   | (25.69)  |
| Wet (RH ≥ 60%)| 12.91      | 9.67       | 7.50          | 12.41    | 61.72    |
|               | (8.32)     | (6.97)     | (5.32)        | (12.63)  | (25.75)  |
| Increase      | 7.36       | 6.99       | 5.07          | -5.13    | 10.62    |

Note: Numbers in parentheses represent the standard deviation.

The averaged molar ratio of NH\(_4^+\) to SO\(_4^{2-}\) was 6.7 during the sampling period, implying that Wuhan exhibits ammonia-rich conditions in wintertime. That is, SO\(_4^{2-}\) and NO\(_3^-\) could be neutralized by NH\(_4^+\), and particulate sulfate and nitrate could be generated by gas-phase reactions of acid precursors with NH\(_3\) [50]. In accordance with Pathak et al. (2009) [51], herein we applied the excess ammonium (excess [NH\(_4^+\)] = ([NH\(_4^+\)] / [SO\(_4^{2-}\)] - 1.5) × [SO\(_4^{2-}\)] as a function to show the reaction between ammonia and nitric acid, and the other formation processes of nitrate in different (relative) concentrations of sulfate (Figure 4c). The result shows that the nitrate concentration increased with an almost similar increase in excess ammonium, suggesting the neutralizing process related to NH\(_4^+\) plays an important role in the formation of SO\(_4^{2-}\) and NO\(_3^-\).

3.3. Secondary Aerosol Formation

On the basis of aerosol chemical composition measurements, Liu et al. (2014) [49] reported that three inorganic ions of NH\(_4^+\), SO\(_4^{2-}\), and NO\(_3^-\), mainly generated by secondary processes, were significantly correlated to particle hygroscopic growth, while other inorganic ions (Ca\(^{2+}, Na^{+}, K^{+}, M^{2+}\), and Cl\(^{-}\)) showed little correlation.

Figure 3. Hygroscopic growth of aerosol scattering at RH = 80% as a function of (a) mass fraction of PM\(_{2.5}\)/PM\(_{10}\), and (b) mass fraction of inorganic aerosols, as well as (c) organic matter in PM\(_{2.5}\).
from December 2017 to February 2018, and the main findings are as follows: RH distributions and response of aerosol pollution to RH. These secondary ions would further promote the pollution level and light scattering. 

\[ \text{PM}_{2.5} \text{ aerosols are mainly enriched in PM}_{2.5}, \text{ especially in particles with aerodynamic diameters between 1.0 and 2.5 } \mu\text{m}, \text{ which could partly explain why PM}_{2.5} \text{ and PM}_{1} \text{ presented different trends with RH in Figure 1. These secondary ions would further promote the pollution level and light scattering.} \]

The correlation between secondary aerosol ions and particles of different sizes (i.e., PM\(_1\), PM\(_{2.5}\) , and PM\(_{10}\)) under wet conditions (RH > 60%) was assessed, as presented in Figure 5. The results show that secondary aerosol ions (i.e. the sum of NH\(_4^+\), SO\(_4^{2-}\), and NO\(_3^-\)) varied more consistently with PM\(_{2.5}\) (R = 0.72) than with PM\(_1\) (R = 0.24), or PM\(_{10}\) (R = 0.44). This phenomenon implies that secondary aerosols are mainly enriched in PM\(_{2.5}\), especially in particles with aerodynamic diameters between 1.0 and 2.5 \(\mu\)m, which could partly explain why PM\(_{2.5}\) and PM\(_1\) presented different trends with RH in Figure 1. These secondary ions would further promote the pollution level and light scattering.

\[ \text{The averaged molar ratio of NH}_4^+ \text{ to SO}_4^{2-} \text{ was 6.7 during the sampling period, implying that } \text{SO}_4^{2-} \text{ as a function to show the reaction between NH}_4^+ \text{, and particulate sulfate and nitrate could be generated by gas-phase reactions of acid} \]

\[ \text{The correlation between secondary aerosol ions and particles of different sizes (i.e., PM}_{1}, \text{ PM}_{2.5}, \text{ and PM}_{10} \text{ under wet conditions (RH > 60%) was assessed, as presented in Figure 5. The results show that secondary aerosol ions (i.e. the sum of NH}_4^+, \text{ SO}_4^{2-}, \text{ and NO}_3^- \text{) varied more consistently with PM}_{2.5} \text{ (R = 0.72) than with PM}_{1} \text{ (R = 0.24), or PM}_{10} \text{ (R = 0.44). This phenomenon implies that secondary aerosols are mainly enriched in PM}_{2.5}, \text{ especially in particles with aerodynamic diameters between 1.0 and 2.5 } \mu\text{m}, \text{ which could partly explain why PM}_{2.5} \text{ and PM}_{1} \text{ presented different trends with RH in Figure 1. These secondary ions would further promote the pollution level and light scattering.} \]

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\text{4. Conclusions} \]

Quantification of aerosol scattering hygroscopic growth is critical for determining the response of aerosol optical properties on various ambient RH and then modeling the aerosol direct radiative effects. In this study, in-situ measurements in Wuhan were adopted to explore the hygroscopic growth distributions and response of aerosol pollution to RH variations in Central China during wintertime from December 2017 to February 2018, and the main findings are as follows:
(1) Aerosol pollution in Wuhan is dominated by fine particles at high RH. Compared with dry conditions (RH ≤ 40%), the mean contents of PM$_1$ and PM$_{2.5}$ on wet days (RH ≥ 60%) almost doubled, and the averaged mass fraction of PM$_{2.5}$ in PM$_{10}$ increased to 62% from 38%. The ratio of PM$_{2.5}$/PM$_{10}$ presented significant increase with RH, however, compared with conditions of RH ≤ 70%, the enhancement of PM$_{2.5}$ concentrations when RH > 70% should be mainly attributed to the particles with aerodynamic diameters between 1.0 and 2.5 µm, rather than PM$_1$.

(2) Aerosol scattering hygroscopic growth could be well fitted by the two-parameter equation, and the correlation between satellite-based AOD and in-situ particle measurements increased from 0.56 to 0.65 after a simple hygroscopic correction based on the fitting equation, further indicating the influence of particle water uptake in the light extinction. $f$ (RH = 80%) in Wuhan was 2.18 (±0.73), comparable to that measured in the Pearl River Delta and Yangtze River Delta regions for urban aerosols.

(3) The atmosphere showed a high oxidation property under wet conditions, especially when RH > 80% and T < 10 ºC. Compared with dry conditions, the averaged concentrations of NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$ on wet days increased by approximately 2.5-, 2-, and 1.5-fold, respectively, which were mainly enriched in PM$_{2.5}$. The ammonia-rich conditions in wintertime played an important role in the formations of SO$_4^{2-}$ and NO$_3^-$.

This study has important implications for understanding the roles of relative humidity in aggravating aerosol pollution over Central China, and the fitted equation between $f$ (RH) and RH may be helpful for pollution forecasting and evaluating aerosol radiative forcing in this region. The parameter $f$ (RH) presents the high dependence on the aerosol particle size distribution and chemical compositions. Therefore, the new parameterization scheme for $f$ (RH) in terms of the size distribution and chemical compositions should be developed in the future.

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