Optical, radiative and chemical characteristics of aerosol in Changsha city of Central China

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ABSTRACT

Industrial pollution has a significant effect on aerosol properties in Changsha City, a typical city of Central China. Therefore, year-round measurements of aerosol optical, radiative and chemical properties from 2012 to 2014 at an urban site in Changsha were analyzed. During the observation period, the energy structure was continuously optimized, which was characterized by the reduction of coal combustion. The aerosol properties have obvious seasonal variations. The seasonal average aerosol optical depth (AOD) at 500 nm ranged from 0.49 to 1.00, single scattering albedo (SSA) ranged from 0.93 to 0.97 and

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aerosol radiative forcing at the top of the atmosphere (TOA) ranged from -24.0 to 3.8 W m\(^{-2}\). The chemical components also showed seasonal variations. Meanwhile, the scattering aerosol such as organic carbon (OC), SO\(_4^{2-}\), NO\(_3^-\), and NH\(_4^+\) showed a decrease and elemental carbon (EC) increased. Compared with the observation in winter 2012, AOD and TOA decreased by 0.14 and -1.49 W m\(^{-2}\) in winter 2014. The scattering components SO\(_4^{2-}\), NO\(_3^-\) and NH\(_4^+\) decreased by 12.8 μg m\(^{-3}\) (56.8%), 9.2 μg m\(^{-3}\) (48.8%) and 6.4 μg m\(^{-3}\) (45.2%) respectively. The atmospheric visibility and pollution diffusion conditions improved. The extinction and radiative forcing of aerosol significantly controlled by the scattering aerosol. The results indicate that Changsha is an industrial city with strong scattering aerosol. The energy structure optimization had a marked effect on controlling pollution, especially in winter (strong scattering aerosol).

**Key words:** Aerosol; Optical; Radiative forcing; Chemical composition.

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**Article Highlights:**

- The high-concentration industrial aerosol was strongly cooling the atmosphere-surface system.
- Inorganic ions and carbonaceous aerosol occupied the main position of particulate matters.
- The extinction and radiative forcing of aerosol was significantly controlled by the scattering aerosol.
- The adjustment of the energy structure obviously played a role in the control of atmospheric pollution.
1. Introduction

Aerosols affect many physical and chemical processes in the atmosphere, and which further impact on weather and climate changes. Aerosol particles prevent radiation from reaching the ground through scattering or absorption. In addition, the scattering and absorption of solar radiation affect visibility. Apart from this, aerosol particles can be retained in the human respiratory tract, even deeply into the lungs. This directly affects people's health and living environment (Charlson et al., 1992; Kaufman, 1993; Wang et al., 2005; Lohmann et al., 2005; Mukai et al., 2006; Carslaw et al., 2010; Reisen et al., 2013; Sheng et al., 2013; Logan et al., 2013, 2014; Chen et al., 2014; IPCC 2014; Xin et al., 2015; Ma et al., 2016). Meanwhile, chemical compositions in different regions varies greatly due to different emissions and they show different radiative effects. Generally speaking, anthropogenic aerosols such as sulfate and nitrate have strong scattering characteristics and mainly exhibit cooling effects; while black carbon (BC) aerosol clearly shows heating effects due to strong absorption characteristics; sea salt aerosol which is natural aerosol exhibits heating effect; dust aerosol exhibits strong heating in short wave range and cooling effect in long wave range (Qian et al., 1998; Zhang et al., 2002; Zhang et al., 2008; Che et al., 2009; Li et al., 2009; Wang et al., 2010; Singh et al., 2012; Xu et al., 2013; Koepke et al., 2015; Tian, 2015; Tian et al., 2016; Huang, 2016; Zhang et al., 2016). As a heavily polluted region in the world, China has a major impact on global climate change and human health. However, there are huge differences in the physical and chemical characteristics of atmospheric particles in different types of sites in different regions of China (Xin et al., 2007, 2015, 2016; Zhang et al., 2012; Zhao et al., 2013; Tian, 2015; Cao et al., 2016; Huang, 2016). Therefore, it is necessary to study the optical,
radiative and chemical properties of aerosol and know the relationship between them, which is helpful for the further pollution control.

There had been many studies concentrated in the industrially developed and heavily polluted areas, such as the Beijing-Tianjin-Hebei region, the Yangtze River Delta region and the Pearl River Delta region in China (Zhao et al., 2013a; Gong et al., 2014; Kong et al., 2014; Zhao et al., 2013b, 2015; Shao et al., 2016; Kong et al., 2017; Tang et al., 2018; Zhao et al., 2018; Zhang et al., 2018). Up to today, we know aerosol optical depth (AOD) is relatively large in central and south-eastern China. Furthermore, there are many anthropogenic aerosol emissions in the southeast so that many areas in eastern China have shown the nature of contaminants and mixed mineral and smoke aerosols (Xin et al., 2007; 2015; 2016; Che et al., 2009; 2015). However, few researchers have focused on Central China, although the extinction effect of aerosol was strong there. Central China (including Henan, Hubei, and Hunan Province) is located in the centre of China, the middle reaches of the Yellow River and the Yangtze River. It is surrounded by the Beijing-Tianjin-Hebei region, the Yangtze River Delta, the Pearl River Delta, the Sichuan Basin and the Guanzhong Plain, and connects the entire country. The existing researches show that, the average AOD in Central China was 0.61 between 2003 and 2012, which was higher than that in North China (0.57) and the Pearl River Delta (0.41) (Chen, 2014). Furthermore, AOD at 500 nm in Wuhan was approximately 0.88, 1.07, 1.11, 1.38, 1.02, 0.92 and 1.07 for the years 2007, 2008, 2009, 2010, 2011, 2012 and 2013, respectively, and were slightly higher than those in Beijing, which were 0.79, 0.75, 0.85, 0.74, 0.86 and 1.06 during 2002-2007. Respectively, the year average of Ångström exponent (AE) was approximately 1.22, which showed the domination of fine particle pollution. The monthly variation of single
scattering albedo (SSA) was closely related to hygroscopic growth of aerosols, fossil fuels and biomass burning (Wang et al., 2015). The annual average of AOD at 440 nm in Zhengzhou was 0.89±0.57 in 2008, and the Ångström exponent was 1.47, which showed urban industrial aerosol particles were still the main controlled particles in Zhengzhou (Tian et al., 2010). The annual mean PM$_{2.5}$ in Zhengzhou were 191, 185, 150 µg m$^{-3}$ in 2013, 2014 and 2015, which was still higher than that in the Yangtze River Delta (59.7 µg m$^{-3}$) (Nan, et al., 2017). The annual average concentration of PM$_{2.5}$ was 82.81 µg m$^{-3}$ in 2013 and 76.38 µg m$^{-3}$ in 2014 in Changsha; the corresponding pollution day ratio (PM$_{2.5}$$>$75 µg m$^{-3}$) was 44.11% and 39.45% (Wang, 2016). The annual mean of AOD and the Ångström exponent was 0.95±0.52 and 1.06±0.31 from 2012 to 2013 (Xin et al., 2015).

The annual average concentration of PM$_{10}$ had been in a steady decline in China during the period of 2004-2012. However, PM$_{10}$ showed a large increase in almost all regions in 2013. Above all, we can know that Central China is a highly polluted area, and there are not many researches about deeper analysis on properties of aerosols in Central China. Therefore, studying properties of aerosols in Central China has significance.

Changsha is an important central city in the middle reaches of the Yangtze River. It is located between 27.81° N and 28.68° N, 111.88° E and 114.25° E in the north of Hunan Province and the middle of Xiangjiang Valley. The unique geography and topography make air pollutants difficult to spread and affect the environmental quality in Changsha. In addition, Changsha-Zhuzhou-Xiangtan forms a triangular industrial zone, so the atmosphere may also be affected by atmospheric pollutants emitted by other cities in the triangle zone. The long-term coal-based energy structure causes soot-type pollution, with SO$_2$ and NO$_2$ as the main pollutants. At the same time, dust is also a major pollutant.
Furthermore, Changsha was in the process of energy structure adjustment during 2012-2014. Therefore, we study the optical, radiative and chemical properties of aerosol in Changsha during 2012-2014 in this paper. In our research, we analyse the seasonal variations of optical (such as AOD, AE), radiative (SSA and radiative forcing) and chemical (including OC, EC and the water-soluble ions) properties in Changsha during 2012-2014. Meanwhile, we compare the changes in three years. Then, we do backward trajectory and potential source area analysis to know the impact of air mass transmission. At last, we study the relationship between optical, radiative and chemical properties.

2. Date and methods

The Changsha station (28.2°N, 113.067°E) of CARE-China is located in the east of Changsha, with an altitude of 58 m. It represents a typical urban station influenced by intensive human activities. The geographical location of Changsha Station and the distribution of AOD monitored by MODIS over Central China during 2012-2014 is shown in Fig. 1. We can see that Changsha is in the polluted area.

In this paper, the basic optical parameter, aerosol optical depth (AOD) was observed by the Microtops II solar photometer, manufactured by Solar Light, USA. The photometer has 5 spectral channels: 440 nm, 500 nm, 675 nm, 870 nm and 936 nm. All the channels can be used to determine aerosol optical depth according to the Lambert–Beer law. Ångström exponent (AE) representing the size of aerosol particles was calculated with AOD in three channels: 440 nm, 500 nm and 675 nm. Single scattering albedo (SSA) and values of radiative forcing (TOA: Aerosol radiative forcing at the top of the atmosphere; ATM: In the atmosphere; SFC: At the bottom of atmosphere) were calculated by the Santa Barbara DISORT Atmospheric Radiative Transfer (SBDART) software. We chose the mid-latitude
atmospheric profile in SBDART. The input part consists of the aerosol parameters, including AOD, SSA, asymmetric parameters and AE, and surface albedo of MODIS. The results were combined with MODIS observations. The more detailed descriptions were reflected in our previous articles (Gong, 2014; Xin et al., 2016; Gong et al., 2017). SSA represents the ratio of aerosol scattering to its total extinction (scattering plus absorption) (Xia et al., 2013; Koo et al., 2016; Ram et al., 2016; Gong, 2014; Gong et al., 2017; Palancar et al., 2017). AOD and SSA mentioned in this paper are all 500 nm results. The calculated results were under clear-sky conditions, and the relevant effects of the cloud layer on the results were not considered in this paper. The absorption aerosol optical depth (AAOD) and scattering aerosol optical depth (SAOD), respectively indicating the degree of aerosol absorption and scattering, were calculated with AOD and SSA \((\text{AAOD} = (1-\text{SSA}) \times \text{AOD}; \text{SAOD} = \text{SSA} \times \text{AOD})\) (Zhao et al., 2018). Apart from this, the meteorological data is provided by China Meteorological Data Network (http://www.nmic.cn/). It provides daily average data such as relative humidity, wind speed, wind direction, etc.

The mass concentration of PM\(_{2.5}\) was obtained by online atmospheric particulate matter monitoring system (TEOM 1400a) based on tapered element oscillating microbalance (TEOM). The PM\(_{2.5}\) data was output every minute. The atmospheric particulate matter was collected using an Anderson impact grading sampler (Series 20-800 Mark II), manufactured by American Thermoelectric Corporation to study the concentration and spectral distribution of chemical compositions. PM\(_{2.1}\) obtained by Anderson sampling is significantly linearly correlated \((R^2=0.89, p<0.05)\) with online PM\(_{2.5}\) (Tian, 2015). The atmospheric particulate matter was divided into nine particle size segments: <0.43 \(\mu\)m,
0.43~0.65 µm, 0.65~1.1 µm, 1.1~2.1 µm, 2.1~3.3 µm, 3.3~4.7 µm, 4.7~5.8 µm, 5.8~9.0 µm and >9.0 µm. The sampling frequency was one sampling per week and collected continuously for 48 h each time. The water-soluble ions were analyzed by ion chromatography (Dionex ICS-90, United States) and a thermal/optical carbon analyzer (DRI Model 2001A, Desert Research Institute, United States) was used to determine EC and OC (Tian, 2015; Su, 2018). The analysis method of the thermal/optical carbon analyzer adopts IMPROVE_A. Furthermore, we used the EC tracer method to estimate the mass concentration of secondary organic carbon (SOC) and primary organic carbon (POC) (SOC=OC_{tot}-(OC/EC)_{pri}×EC, POC=(OC/EC)_{pri}×EC) (Hu et al., 2016). And we estimated organic matter (OM) through the equation OM=1.4×OC (Srinivas et al., 2014; Tian, 2015; Shao, 2016).

We employed the TrajStat (Trajectory Statistics) model for seasonal backward trajectory clustering. The TrajStat model is the software developed by National Oceanic and Atmospheric Administration (NOAA) HYSPLIT users, using the same trajectory calculation module as HYSPLIT (Wang et al., 2009). The endpoint of trajectory was Changsha station, and the backward time was 72 hours. Meanwhile, we computed the potential source contribution function (PSCF) and concentration weighted trajectory (CWT) analyses according the PM$_{2.5}$ data. The meteorological data input was from the NCEP (National Centers for Environmental Prediction reanalysis dataset from NOAA).

3. Results and discussion

3.1 Basic properties of aerosol
Fig. 2 presents the seasonal mean changes of wind speed (V), relative humidity (RH), PM$_{2.5}$, AE and AOD between 2012 and 2014. V varied from 1.6 m s$^{-1}$ to 2.3 m s$^{-1}$ in Changsha. It expressed a large V in 2013 summer corresponding to a low PM$_{2.5}$ and AOD. More details were in Fig. S1. The seasonal RH varied from 58% to 81% in Changsha, providing enough water vapor for atmospheric reactions. The annual PM$_{2.5}$ was 77.8±27.4 µg m$^{-3}$ (shown in Table S1), which was more than Beijing (66±54 µg m$^{-3}$), Shenyang (71±55 µg m$^{-3}$) from 2012 to 2013 (Xin et al., 2016). PM$_{2.5}$ was obviously higher in winter and lower in summer, ranging from 41.4 µg m$^{-3}$ to 108.9 µg m$^{-3}$ in seasonal means. Besides, the mass concentration of PM$_{2.5}$ in winter 2014 decreased by 19.4 µg m$^{-3}$ (19.0%) compared with winter 2012. The annual average AOD and AE were 0.81±0.19 and 1.00±0.11, respectively (Table S1). The annual AOD value was almost the same as those of other industrial cities, such as Shenyang (0.61±0.13), Tangshan (0.80±0.26) and Lanzhou (0.74) (Zhang et al., 2017; Gong et al., 2017; Zhao et al., 2018). We could know that it had similar aerosol properties with the industrial cities. In three-year average, AOD had larger values in spring and winter (~0.90), while AE showed smaller values (0.93) in spring, which was identical to the results in Zhengzhou (Tian et al., 2010). However, this seasonal change was different with the observation around the Bohai Rim, such as in Beijing and Tangshan, which was summer > spring > autumn > winter (Zhang et al., 2017). In 2012-2014, AOD had a similar seasonal difference. AOD was larger in winter and spring. Comparing to winter 2012, AOD decreased by 0.14 in winter 2014. AE showed smaller values in spring because of dust aerosol. And it showed a growth trend during 2012-2014. It should be noted that all the seasonal means were more than 0.75, indicating that aerosol particles in Changsha were dominated by the fine particle mode. To sum up,
we could know that AOD and PM$_{2.5}$ decreased and AE overall increased in energy structure optimization in Changsha.

Fig. 3 shows seasonal average changes of SSA, AAOD, SAOD and radiative forcing at the top of the atmosphere (TOA), in the atmosphere (ATM) and at the surface (SFC) from 2012 to 2014. For the three-year average, SSA values were all larger than 0.94, which showed obvious urban characteristics (Gong et al., 2017). Seasonal mean values of SSA were all greater than 0.93, which showed the scattering effect of aerosol was very strong, and man-made scattering aerosol such as sulfate and nitrate was dominant in Changsha. SAOD and AAOD showed a highest value in winter due to the emissions. The overall trend of SAOD was similar to AOD. It can be seen that TOA in Changsha was basically negative, apart from summer 2013 (3.8 W m$^{-2}$), ranging from -24.0 W m$^{-2}$ to -1.1 W m$^{-2}$. ATM and SFC changed from 37.9 W m$^{-2}$ to 59.8 W m$^{-2}$ and -79.1 W m$^{-2}$ to -34.1 W m$^{-2}$. All radiative forcing had the largest values in winter, and small values in summer. Furthermore, the variation of TOA was different from that in Beijing, showing the cooling effect was weaker in winter and spring and relatively stronger in summer and autumn (Gong, 2014). In summer, the scattering effect weaken because of rainfall and reduced anthropogenic aerosol emissions. Therefore, the cooling effect of aerosol was weak in summer. Correspondingly, the cooling effect was strong in winter due to more anthropogenic aerosol emissions. In the three-year trend, the cooling effect of aerosol showed a small decrease. It was related to the decrease in scattering aerosol emissions during the energy structure optimizing process. This trend is expected to reduce the atmospheric stability and promote pollutant diffusion. From the results, we could see anthropogenic aerosol had a strong
scattering effect in Changsha, and there might be differences in aerosol types with northern regions. The energy structure optimization measures improved diffusion conditions.

Fig. 4 shows seasonal averages of mass concentration of OC, EC and water-soluble inorganic ions (SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Na$^+$, Cl$^-$, K$^+$, NO$_2^-$, Mg$^{2+}$ and F$^-$) in nine particle size segments from 2012 to 2014 in Changsha. From the three-year average, the average of the total chemical components (including OC, EC and water-soluble inorganic ions) was higher in winter (89.3 $\mu$g m$^{-3}$) than in other seasons (spring: 58.5 $\mu$g m$^{-3}$, summer: 44.4 $\mu$g m$^{-3}$ and autumn: 58.9 $\mu$g m$^{-3}$) in PM$_{2.1}$, due to the intensity of the emissions and weather conditions. The concentrations of PM$_{2.5}$ and EC, OC, SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ in PM$_{2.1}$ in winter were 1.8, 2.0, 1.6, 1.4, 5.9, and 2.6 times higher than those in summer (in Table S1). From Fig. 4, we can see that OC was greater than EC in almost nine particle size segments. Furthermore, OC and EC presented a bimodal distribution in 0.43-0.65 $\mu$m and 4.7-5.8 $\mu$m. EC was concentrated in PM$_{0.43}$, contributing approximately 20%-59%. The seasonal averages of OC ranged from 9.5 $\mu$g m$^{-3}$ to 25.8 $\mu$g m$^{-3}$ in PM$_{2.1}$, from 5.1 $\mu$g m$^{-3}$ to 18.9 $\mu$g m$^{-3}$ in PM$_{2.1-100}$. While EC ranged from 2.0 $\mu$g m$^{-3}$ to 7.4 $\mu$g m$^{-3}$, from 0.9 $\mu$g m$^{-3}$ to 4.1 $\mu$g m$^{-3}$ correspondingly (shown in Fig. S2 and Fig. S3). Both were higher than those in Tangshan and Beijing (Zhang et al., 2017). All of the above results indicated that carbonaceous aerosol pollution was heavy. Human emissions such as coal combustion, motor vehicle exhaust and biomass combustion were significant (Seinfeld and Pandis, 1998; Kirkevåg et al., 1999; Jacobson et al., 2001; Cao et al., 2005; Huan et al., 2005). Furthermore, OC showed a decrease from 2012 to 2014 because of more biomass burning and less fossil fuel burning (Fig. S5 and Fig. S6). The total water-soluble ions ranged from 20.4 $\mu$g m$^{-3}$ to 66.5 $\mu$g m$^{-3}$ in PM$_{2.1}$. The water-soluble ions were centrally distributed in
PM$_{0.43-2.1}$, contributing from 53% to 70%. Secondary inorganic ions (SIA, including SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$), the most important water-soluble inorganic ions in atmospheric particles accounted for 77%~92% in seasonal averages, indicating that secondary aerosol pollution played an important role in Changsha. The high SO$_4^{2-}$ indicated that atmospheric particulate matters were affected by coal combustion in Changsha. Apart from differences in seasonal emissions, the concentration of NO$_3^-$ and NH$_4^+$ in winter was greater than that in summer might be because of the influence of temperature on the state of particulate matter in a less extent (Guo et al., 2010; Russell et al., 1983; Cao et al., 2016). The concentration of SO$_4^{2-}$ and NH$_4^+$ decreased from spring to winter in 2014. Besides, we could find that OC and SO$_4^{2-}$ had a downward trend overall. Comparing with the values in winter, SIA, SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ decreased 28.4 μg m$^{-3}$ (51.1%), 12.8 μg m$^{-3}$ (56.8%), 9.2 μg m$^{-3}$ (48.8%) and 6.4 μg m$^{-3}$ (45.2%) respectively from 2012 to 2014. Human emissions such as fuel combustion had been reduced year by year. Energy structure was gradually optimized and the second pollution reduced, which was verified by Fig. S6 and Fig. S7. In Fig. S7, we can see that OM (organic matter) and SOM (secondary organic matter) showed a downward trend while POM (primary organic matter) increased during 2012-2014. Therefore, the mass concentrations of chemical components were high and the results showed there was serious secondary pollution in Changsha. Energy structure optimization changed the proportions of chemical components. Secondary aerosols decreased and pollution was controlled to a certain extent.

Fig. 5 shows seasonal mean variations of OC/EC and NO$_3^-$/SO$_4^{2-}$ in fine particle size segments (<0.43 μm, 0.43~0.65 μm, 0.65~1.1 μm and 1.1~2.1 μm) from 2012 to 2014 in Changsha. In this paper, we used the ratio of OC/EC to initially determine the source of
carbonaceous aerosols (Ram and Sarin, 2010) and the ratio of \( \text{NO}_3^-/\text{SO}_4^{2-} \) to compare the contribution of fixed sources (such as coal) and mobile sources (such as motor vehicles) to particulate matters in the atmosphere (Watson et al., 1994; Huang et al., 2014; Su et al., 2018). It can be seen in Fig. 5 that the OC/EC values were generally greater than 2.0, apart from the \(<0.43\) particle size segment, which showed it mainly based on secondary organic carbon (SOC) emissions in Changsha. In PM\(_{0.43}\), the percent of OC/EC<2 was 75%, showing that primary organic carbon (POC) was dominant in this particle size segment. The OC/EC values ranged from 1.1 to 19.3 in fine modes, which indicated that coal-fire emissions and biomass burning emissions existed (Jiang, 2017). The ratio of OC/EC had obvious seasonal changes with a larger value in summer, and a smaller value in winter. The low temperature in winter caused photochemical reactions to weaken, so OC/EC was generally lower in winter than in summer (Pio et al., 2011). Also, the type of pollutant and plant discharge made this result. There were exuberant plant emissions with more OC in summer and more coal combustion in winter. We guessed there was a lot of biomass burning so the values of OC/EC were high in 2012, as indicated by the fire point data in Fig. S5. From the three-year trend, it can be seen that OC had decreased, EC had increased and the OC/EC values showed a decline. This phenomenon illustrated that secondary emissions had been controlled. The ratio of \( \text{NO}_3^-/\text{SO}_4^{2-} \) had obvious seasonal changes; the highest in winter and the lowest in summer, followed by spring and autumn. The values of \( \text{NO}_3^-/\text{SO}_4^{2-} \) were mostly lower than 1, which showed coal still played a leading role in the energy structure and fixed sources was dominated than mobile sources. Meanwhile, the overall trend has risen because the energy structure was continuously optimized and fossil energy consumption continued to decrease (Fig. S6). The ratios in coarse mode had a
contrasting trend (Fig. S3): high in summer and low in winter, and it was almost all greater than 1, showing that the contribution of the moving sources in the coarse mode was large. A possible reason is that nitric acid gas could be adsorbed by coarse particles to form NO$_3^-$, and SO$_4^{2-}$ reacted with cloud droplets or droplets when the relatively humidity was high (Cao et al., 2016; Huang et al., 2013).

To sum up, there were obviously industrial aerosol characteristics with strong scattering effect in Changsha. Coal consumption reduced and natural gas consumption increased during the energy structure optimizing process from 2012 to 2014. Besides, AOD, particle matters and radiative forcing had been decreased. The extinction of aerosol declined and the visibility improved. TOA expressed a weaker cooling effect and pollutant diffusion conditions improved. AE showed an increasing trend while coarse particles were firstly controlled during the pollution control process. The degree of change on each component was not consistent. The mass concentrations of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and OC decreased in autumn and winter while EC increased. Comparing the results of optical, radiative and chemical properties of aerosol, we could know that, with the energy structure optimization and the control of government, chemical compositions had changed, while the extinction and radiative forcing of aerosol decreased with it. Anthropogenic emissions such as fossil fuel and secondary aerosol reduced and there was improvement in pollution control.

### 3.2 Backward trajectory and potential source area analysis

Fig. 6 represents the backward trajectories of aerosol in four seasons, as well as meteorological factors and optical, physical and chemical properties of aerosol corresponding to each trajectory. The route and direction of the trajectory indicates the area where the air mass passed before reaching the observation site. From Fig. 6(a), the
clustering results of the backward trajectories in spring consisted of 4 categories, three
(Type-I (21%), Type-II (37%), Type III (29%)) of which moved slowly and polluted more
seriously, which PM$_{2.5}$ was 77.96 $\mu$g m$^{-3}$, 72.77 $\mu$g m$^{-3}$ and 83.47 $\mu$g m$^{-3}$. Type-IV (13%)
originated from marine air masses. Correspondingly, the concentrations of all chemical
compositions and PM$_{2.5}$ (45.10 $\mu$g m$^{-3}$) were lower and AOD was smaller than the other.
The clustering results were classified into 6 categories in summer (Fig. 6(b)), which could
be divided into two categories, according to the direction: south (52%) and north (48%). It
can be found that the concentrations of chemical compositions and PM$_{2.5}$ originating from
the southern air mass (Type-II, Type-III and Type-V) were low, and AOD was also small.
Furthermore, TOA and SFC exhibited weak cooling effects because of the wet and clean
air mass from the south with less anthropogenic scattering aerosols. The clustering results
in autumn shown in Fig. 6(c) consisted of 5 categories: Type-I, Type-II, Type-III and Type-
IV, which were derived from the northeast, while Type-V (5%) was from the northwest.
The relative humidity of the Type-V air mass, the concentration of SIA and PM$_{2.5}$ were
lower than others, as well as AOD and AE, indicating that the northwest region transmitted
dry, coarse mode particles and less effect of anthropogenic aerosols. Other than this, the
cooling effect of TOA was smaller because of natural aerosol such as dust. The clustering
results in winter are shown in Fig. 6(d), and are similar to the direction in autumn, from the
northeast (90%) and northwest (10%). The properties of the air mass in winter originating
from the northwest were similar to those in autumn, but its corresponding AE was greater
than 1, indicating fine mode particles were dominant in winter. From the results of the
backward trajectory and the potential source area (Fig. S8), it was easy to see that the
atmospheric pollution in Changsha was greatly affected by local pollution as well as air
mass transportation in neighboring provinces and cities. These caused high concentrations of PM$_{2.5}$ and high AOD in Changsha. Meanwhile, the air mass from ocean or northwest would improve diffusion conditions and weakened air pollution. Therefore, governing local pollution in Changsha is an effective method. Collaboration across regions is also important.

3.3 Relationship between optical, radiative and chemical properties

Fig. 7 shows the relationship between AOD, PM$_{2.5}$, SSA, TOA and chemical components in seasonal means. And the color code represents relative humidity (RH) because of the hygroscopic growth of aerosols. As PM$_{2.5}$ increased, AOD performed an increase and TOA performed stronger cooling effect. Meanwhile, with the increase of OM and SIA, TOA performed a decrease. We all know that when the mass concentrations of PM$_{2.5}$ increased, the ratio of anthropogenic aerosol emissions would increase in urban cities and aerosol would displayed larger extinction, stronger scattering effects and cooling effects. All chemical compositions worked together on optical and radiative properties. The degree of optical and radiative changes caused by different compositions was different. In autumn and winter, chemical compositions had a more pronounced effect on AOD and TOA because of anthropogenic aerosol emissions and poor meteorological diffusion conditions. Besides, the hygroscopic growth of aerosols would affect aerosol properties. So there were some discrete points in Fig. 7. In some time, although OM was not large TOA exhibited a strong cooling effect with the large SIA. Therefore, the scattering aerosols played an important role in aerosol direct radiative forcing. Above all, PM$_{2.5}$ had an important contribution to AOD and TOA. Meanwhile, SIA was the important component
Furthermore, controlling SIA components in PM$_{2.5}$ remains an important step to control the atmospheric aerosol pollution.

4. Conclusions

By analyzing the optical, physical and chemical properties of aerosol in Changsha, it can be seen that there was obviously industrial pollution characteristics. Overall, AOD showed large values in spring and winter while there was a downward trend. AE indicated that aerosol particles mainly existed as fine-mode and coarse mode particles reduced. SSA were all more than 0.90 and the radiative forcing was almost negative, indicated that they were dominated by anthropogenic scattering aerosols. OC and EC generated by human emissions and secondary emissions were greater. OC and SOM showed a downward trend. The average concentration of total water-soluble ions was highest in winter, while secondary inorganic ions (SIA, including SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) occupied the main position in atmospheric particles. Coal combustion still played a leading role in the energy structure, as indicated by the higher concentrations of SO$_4^{2-}$ than NO$_3^-$. The extinction and radiative forcing of aerosol was significantly controlled by chemical compositions apart from the mass concentration of particulate matters. Besides, SIA was the important component to affect optical and radiative properties. Chemical components decreased in winter and caused lower AOD and weaker cooling effects in energy structure optimization. SIA had decreased 51.1% and AOD decreased 14.2%. The backward trajectories and the potential source area indicated that the atmosphere in Changsha was affected by local pollution and neighboring provinces and cities. Governing local pollution in Changsha is an effective method. In summary, it was greatly affected by industrial aerosol in Changsha with strong scattering effect. Atmospheric visibility improved and pollution was controlled.
to some extent during the energy structure optimizing process from 2012-2014. Further control of local anthropogenic pollution is still necessary.

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Fig. 1. Geographical location of the Changsha Station and the distribution of AOD monitored by MODIS over Central China from 2012 to 2014.
Fig. 2. Seasonal means of wind speed (V), relative humidity (RH), mass concentration of fine particle matters (PM$_{2.5}$), Ångström exponent (AE) and aerosol optical depth (AOD) during the observation period (2012-2014) in Changsha station (The columns represent seasonal means of each parameter, and the black error bar is the standard deviation of seasonal means calculated by monthly values).
Fig. 3. Seasonal means of single scattering albedo (SSA), absorption aerosol optical depth (AAOD), scattering aerosol optical depth (SAOD) and radiative forcing (TOA: Aerosol radiative forcing at the top of the atmosphere; ATM: In the atmosphere; SFC: At the bottom of atmosphere) during the observation period (2012-2014) in Changsha station (The columns represent seasonal means of each parameter, and the black error bar is the standard deviation of seasonal means calculated by monthly values).
Fig. 4. Seasonal means of total chemical compositions including organic carbon (OC), elemental carbon (EC) and water–soluble inorganic ions and their corresponding ratios in nine particle size segments during the observation period (2012-2014) in Changsha station (From left to right, the columns represent the mass concentration of chemical compositions with the diameter <0.43 µm, 0.43~0.65 µm, 0.65~1.1 µm, 1.1~2.1 µm, 2.1~3.3 µm, 3.3~4.7 µm, 4.7~5.8 µm, 5.8~9.0 µm and >9.0 µm).
Fig. 5. Seasonal mean variations of OC/EC (a) and NO$_3^-$/SO$_4^{2-}$ (b) in fine particle size segments (From left to right, the columns represent the values with the diameter <0.43 µm, 0.43~0.65 µm, 0.65~1.1 µm and 1.1~2.1 µm) during the observation period (2012-2014) in Changsha station (The blue dotted line represents a critical value: it means that secondary organic carbon occupies the main role when OC/EC>2, on the contrary, the primary organic carbon occupies the main role in Fig. 5(a); the contribution of fixed sources (such as coal) is more than that of mobile sources (such as motor vehicles) when NO$_3^-$/SO$_4^{2-}$<1 in Fig. 5(b)).
Fig. 6. Backward trajectory clustering and characteristics and meteorological factors of aerosols under different trajectory types in spring (a), summer (b), autumn (c) and winter (d) (The mass concentration of chemical compositions including water–soluble inorganic ions, EC, and OC in PM$_{2.1}$ in (I), AOD and the mass concentration of PM$_{2.5}$ in (II), radiative forcing at the top of the atmosphere (TOA), in the atmosphere (ATM) and at the surface (SFC) in (III), AE ($\alpha$) and RH in (IV)).
**Fig. 7.** Relationship between optical, radiative and chemical properties in seasonal averages during the observation period (2012-2014) in Changsha station (The blue line is the fitted straight line from Least squares. The color scale represents the relative humidity, the blue circles in the lower RHs while the red circles in the higher RHs.).