Experimental study on the space charge properties in haze events

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ABSTRACT

In recent years, haze has posed a serious threat to the global climate change, ecological balance and human health. In this study, the laboratory experiments and field observations were performed and a possible charging mechanism was proposed to investigate the space charge properties in haze events. The laboratory experiments showed that the charge polarity of primary aerosol is determined by species of combustion fuels while the magnitude is dependent on the combustion completeness. The field observations revealed that the space charge of atmosphere aerosol in haze events differs from that of fair weather and is closely related to PM$_{2.5}$ concentration when Relative Humidity (RH) < 60%, with 1 to 2 orders of magnitude less than the case when RH $\geq$ 60%. The analysis of equivalent charge-to-mass ratio (ECTM) suggested that in haze events the space charge is governed by primary aerosol emitted by combustion of fossil fuel in a low relative humidity, whereas it is manipulated by the secondary chemical reaction of atmosphere aerosol in a high relative humidity. And we can identify the main pollutants in haze events according to the polarity of atmosphere aerosol and quickly take measures when RH < 60%. Accordingly, the dust-haze of RH $<$ 80% can be divided into dry-dust-haze when RH $<$ 60% and wet-dust-haze when 60% $\leq$ RH $<$ 80%. Our study firstly elucidated the space charge properties of atmosphere aerosol in haze events and can provide a new perspective for the prevention and control of air pollution.

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Introduction

Haze, which is defined as a weather phenomenon that numerous fine particulate matters from human production and life cause the atmospheric visibility less than 10 km, is throughout the whole process of human industrialization (Marzaccan et al., 2001; Ma et al., 2010; Chen et al., 2013; Guo et al., 2014; Wang and Chen, 2016). As an evil fruit of human activities combing with specific meteorological conditions, haze has severely affected the ecological balance and global climate change as well as human health (Guo et al., 2014; Zhang et al., 2010; Liu et al., 2014; Grantz et al., 2003; Ramanathan and Feng, 2009; Kim et al., 2015). The invasion of airborne particulate matters especially the inhalable fine particles into human body will wreak havoc on respiratory system, immune system, cardiovascular system and so on (Zhang et al., 2010; Kim et al., 2015; Koch and Amann, 2000). Worse still, the wide spread of haze events can pose a serious threat on people’s lives, for instance, the great smog incident in London, England in 1952 directly killed more than 4000 people (Met Office, 2016). Additionally, the Los Angeles photochemical “smog” between 1940s and 1960s and the
severe haze events in Beijing–Tianjin–Hebei Region, China in recent years make people trapped in traffic trouble and health problem (Ma et al., 2010; Zhang et al., 2010; Haagen-Smit, 1952; Gardner, 2014; Huang et al., 2014). As a result, haze pollution has attracted much attention of scholars nowadays.

Haze is mainly composed of particulate matter (PM) such as dust, smoke, vapor and gaseous pollutants such as SO$_2$, NH$_3$ and NO$_X$ in atmosphere (Liu et al., 2014; Fu et al., 2008). In previous studies, many scholars focused on two main aspects. From the macro perspective on the one hand, the source and formation as well as the regional and global transportation of haze were debated heatedly (Guo et al., 2014; Fu et al., 2008; Zheng et al., 2015). From the micro perspective on the other hand, the origins of pollutants and chemical components as well as the water-soluble ions of haze particles were analyzed (Marczanz et al., 2001; Koch and Amann, 2000; Huang et al., 2014). The fine particles (PM$_{2.5}$) in haze can be divided into primary (directly emitted by a source as particles and dispersed in the atmosphere) and secondary (indirectly formed by emitted gaseous pollutants such as SO$_2$, NH$_3$ and NO$_X$) particles (Koch and Amann, 2000; Huang et al., 2014; Zheng et al., 2015; Seinfeld and Pandis, 1998). The secondary species involve two distinct processes, i.e., nucleation process (gas-to-particle conversion) which produces high concentration of nano-sized particles through photochemical reactions, and growth process that yield numerous larger particles through a continuous size-growth over multiple days (Guo et al., 2014; Zheng et al., 2015). The ions analysis of PM$_{2.5}$ in Shanghai and Beijing, China evinced that SO$_4$$^2-$, NO$_3$ and NH$_4$ account for 46%, 18% and 17% in Beijing respectively and 44%, 25% and 16% in Shanghai respectively, which are the most abundant species in PM$_{2.5}$ (Yao et al., 2002), consequently, it implicated that the polarities of water-soluble ions are off-balanced in haze particles.

In recent years, some scholars discovered that the power equipment exposed in haze is threatened by flashover (Sun et al., 2015; Guo et al., 2016). Nizamuddin and Ramanadham (1983) have found that there are enhanced potential gradients during mist, haze and fog one century ago. Zhang et al. (2017a) found that the atmospheric electric field changes dramatically in haze events compared with the fair days. Studies of dust storms, volcanic eruptions, rainstorms and snowstorms demonstrated that particles in these events are charged particles which can generate a strong spatial electric field in atmosphere, and in turn the spatial electric field will change the trajectory and distribution of charged particles. Besides, the charged particles in atmosphere can affect electromagnetic wave propagation (Kok and Lacks, 2009; Mather and Harrison, 2006; Esposito et al., 2016; Zheng et al., 2003; Schmidt et al., 1999; Bohren and Hunt, 2011; Zhang et al., 2017b; Zhou et al., 2005).

All of the facts above suggest that the atmospheric aerosol in haze events may be charged. And the charged aerosol in haze events can generate an electric filed in space, which will greatly affect the formation and evolution of haze as well as the propagation of electromagnetic waves. However, the research about the charged properties of atmospheric aerosols during haze events is scarce. Hence, in this study, we firstly try to investigate the space charge properties in haze events, aiming at providing some valuable information for the prevention and control of haze pollution and for the optimization of instruments design based on electromagnetic wave propagation.

1. Materials and methods

1.1. Apparatus and measuring systems

1.1.1. The “Faraday box”

There are many techniques available to quantify the space charge density in atmosphere, among which the “potential gradient” method, the “Faraday cage” method and the “direct filtration” method are the most popular ones (Bent and Hutchinson, 1966; Anderson, 1966; Pawar and Kamra, 2000). But Pawar and Kamra (2000) pointed out that all of the three methods are not perfect, because both of the “potential gradient” method and the “Faraday cage” method have a disadvantage that they can only obtain an average value over an extended region. The “Faraday cage” method as a passive technique may cause experimental errors when the ions in atmosphere diffuse to the wire-mesh sides of the cage (Anderson, 1966). Another inherent error of the “Faraday cage” and the “direct filtration” method is that the presence of large metal cage or filter apparatus may distort the local atmospheric electric field and create a charge layer at the upper surface of the apparatus in low wind speed (Pawar and Kamra, 2000). Bent (1964) demonstrated that under the high relative humidity conditions such as rainfall, snowfall and mist, the “direct filtration” method is null but the “Faraday cage” method can work normally. In view of the elucidation of above techniques, the “Faraday box,” which combines the advantages of the “Faraday cage” method and the “direct filtration” method, is devised to achieve long-term, continuous and stable measurement of space charge density.

The schematic diagram of the “Faraday box” is shown in Fig. S1a. The 101 and 106 are collecting box and shielding box respectively. Collecting box is a stainless-steel box with 1 m × 1 m × 1 m. Shielded box is also a stainless-steel box with 1.1 m × 1.1 m × 1.1 m which is used to shield external effects and then guarantee the accuracy of the charge quantity. The two boxes share with the same center, and the distance between the surfaces of the two boxes is 50 mm. The 102 and 103 are inlet pipe and outlet pipe, respectively. The inner pipe links to the collecting box while the outer one links to the shielding box, and it is mutually insulating between inner pipe and outer pipe. The length, internal diameter and external diameter of the inner pipe are 50, 160 and 180 mm, respectively. The length, internal diameter and external diameter of the outer pipe are 350, 160 and 280 mm, respectively. The measuring pipe (104) which links to the aerosol monitors is used to measure the mass concentration of haze particles in collecting box. The length, inner diameter and outer diameter of the measuring pipe are 50, 10, 11 mm, respectively. 105 are the wires used to link the electrometer, with one wire installed at the bottom of collecting box, the other at the bottom of the shielding box.
1.1.2. Space charge density measuring system (SCDMS)
The major function of the space charge density measuring system (SCDMS) independently developed by Lanzhou University is to measure the space charge density (SCD) of charged matters in the atmosphere. The system is composed of five apparatus, i.e., electrometer, data gather computer, aerosol monitors, air pump and the “Faraday box.” The sampling frequency of electrometer and aerosol monitors is 1 Hz. The operation instructions of SCDMS:

1) As shown in Fig. S1b, connect the air pump with the outlet pipe (103) of “Faraday box,” connect the aerosol monitors with measuring pipe (104) of “Faraday box,” connect the positive and negative probes of the electrometer with two wires (105) of “Faraday box,” connect the data gathering computer with electrometer.
2) Open and debug all instruments to ensure they work properly.
3) Record the data of PM$_{2.5}$ concentration and charge quantity in the collection box when the gas flow is stable.

1.1.3. Environmental variable measuring system
As shown in Fig. S1c, S1d, the environment variable measuring system consists of temperature and relative humidity sensor, cup anemometer, sonic anemometer and CR3000 data-logger, with the sampling frequencies of ambient temperature, relative humidity, horizontal wind velocity and three-dimensional wind velocity are 1 Hz, 1 Hz, 1 Hz and 20 Hz, respectively.
Details of apparatus can be found in Table S1.

1.2. Experimental sites and performances
1.2.1. Laboratory experiment
The laboratory experiment includes two parts: (1) the SCDMS; (2) the firebox, a device generating smoke. The firebox links with the inlet pipe of the “Faraday box.” The laboratory experiments were conducted at Multifunctional Environmental Wind Tunnel Laboratory inside the Yuzhong campus, a branch of Lanzhou University (35°56.4′N, 104°9′E, and 1763 m ASL) from October 19, 2016 to November 13, 2016.

1.2.2. Field observation
As two of the largest cities in northern China, Beijing and Xi’an have witnessed a rapid growth in economy, population, vehicles and energy consumption in past three decades, and the severe haze pollution followed has not only aroused high vigilance of the Chinese government but also earned a sustained attention by the international community (Zheng et al., 2015; Yao et al., 2002; Cao et al., 2005; Shen et al., 2009). Hence, Beijing, located in the North China Plain, with a population of 21.7 million and Xi’an, located in the Guanzhong Plain, with a population of 8.7 million, were selected to be the best venues for our observations. The field observation was firstly conducted during severe winter haze from December 6, 2015 to December 19, 2015 and secondly from December 9, 2016 to December 26, 2016 at School of engineering, Peking University, Beijing, China (39°59.4′N, 116°19.2′E, 54 m ASL), and thirdly conducted in winter from December 7, 2017 to December 20, 2017 at North Street, Xi’an, China (34°16.2′N, 108°57′E, 404 m ASL). And all of the observations were performed on the roofs which are higher than 20 m. The field observation includes two parts. The first part is the SCDMS, where the inlet pipe is exposed in the air (Fig. S1b). The second part is the environment variable measuring system (Fig. S1c, S1d).

2. Results and discussion
2.1. Space charge in primary emissions
To investigate the space charge in primary emissions, the firebox was built in laboratory to generate the primary aerosol. There are many different phases of fuel combustion, and the most distinctive phases are ignition phase, combustion phase, and extinction phase (Jarosinski and Veysseyrie, 2009; Austin, 2008). In this paper, we define the ignition phase as Phase 1, the open fire combustion phase as Phase 2, and the stage that before extinction as Phase 3, respectively. In Phase 1, with a little flame in firebox, it can produce high smoke concentration. In Phase 2, the open fire is clear and visible, and a layer of black smoke which encircles the flame is emitted into the air. In Phase 3, the boundary between the flame and the air is not clear, and only a little smoke on the top of the fire can be observed. So the PM$_{2.5}$ concentration of smoke yielded by combustion of these fuels decreases from Phase 1 to Phase 3.

Fig. 1 shows the original data of SCD and PM$_{2.5}$ concentration of primary aerosol generated by combustion of coal, wood, plastic and engine oil in different combustion phases. When connect the inlet pipe of the “Faraday box” with firebox, the PM$_{2.5}$ concentration increases. When disconnect the inlet pipe of the “Faraday box” with firebox and expose the inlet and outlet pipe of the “Faraday box” in the air, the smoke in the “Faraday box” diffuses freely and the PM$_{2.5}$ concentration decreases. Since the ions in atmosphere may diffuse to the “Faraday box” thus cause experimental errors when the inlet and outlet of the “Faraday box” exposed in the air, the data in red solid line frames (the stage that PM$_{2.5}$ concentration increase constantly when connect the inlet pipe of the “Faraday box” with firebox) in Fig. 1 were selected to analyze the relationship between SCD and PM$_{2.5}$ concentration with linear regression method. In Figs. 1 and S2, the SCD of primary aerosol generated by coal, wood, and plastic combustion decreases with the increasing of PM$_{2.5}$ concentration in growth phase, and then increases with the decreasing of PM$_{2.5}$ concentration in attenuation phase. On the contrary, the SCD of primary aerosol generated by engine oil combustion increases with the increase of PM$_{2.5}$ concentration in growth phase, and then decreases with the decrease of PM$_{2.5}$ concentration in attenuation phase. This indicate that the primary aerosol generated by coal, wood, and plastic combustion is inversely proportional to PM$_{2.5}$ concentration in primary aerosol generated by coal, wood and plastic combustion,
while it is proportional to PM$_{2.5}$ concentration in the primary aerosol emitted by engine oil combustion. Assuming that all the charges are carried by the particles (in fact, total charges consists of ions freed in the atmosphere and ions attached to particle surface (Jayaratne and Verma, 2004; Law, 1963; Chalmers, 1929)), the slope of fitting lines represent the charge quantity of particulate matter per unit mass, so it can be referred as the equivalent charge-to-mass ratio (ECTM). The key parameters of fitting lines are shown in Table 1 and Table S2. The fitting precision, $R^2 > 0.8$ indicates that the SCD of primary aerosol may be mainly determined by the particulate matters. The results exposed that the ECTM of primary aerosol produced by the combustion of wood, coal and plastic are all negative, while the ECTM of primary aerosol emitted by engine oil combustion are all positive, which manifests that the charge polarity of primary aerosol is manipulated by species of combustion fuel. Moreover, the ECTM magnitudes of primary aerosol produced by the same fuels tend to increase from Phase 1 to Phase 3, which implies that the charge quantity of primary aerosol is governed by combustion phase. The more sufficient the combustion is, the larger the charge quantity of primary aerosol will be.

Fig. 1 – Time series of SCD and PM$_{2.5}$ concentration of primary aerosol generated by combustion of coal (a)–(c), wood (d)–(f), plastic (g)–(i) and engine oil (j)–(l) in different combustion phases.
Kousaka et al. (1981) concluded that the aerosol particles generated by condensation after evaporation, chemical reaction, drying after atomization and mechanical dispersion maybe higher than the charge of Boltzmann equilibrium depending on the particle fuels, reaction types and the solution state. Their statements are coinciding with ours that both the charged polarity and magnitude of SCD carried by primary aerosol are different, but they did not present the reason for these differences. Burtscher (1992) emphasized that the smoldering fire (Phase 1) can produce high smoke concentration but the charge on smoke particles are so weak which is much less than the equilibrium charge. However, highly sooting open fire (Phase 2) with little smoke concentration can produce high charges which are much higher than the equilibrium charge. This is in complete agreement with our experimental results that the charge of primary aerosol increases with the completeness of combustion. And Burtscher (1992) qualitatively attributed these properties to the strong convection of flames and the ionization process such as thermo-ionization, photo-ionization and chemi-ionization. Consequently, the primary aerosol generated by combustion is highly charged.

2.2. Space charge in fair weather

To reveal the space charge during haze events, it is necessary to make the charge nature of atmospheric aerosols in fair weather clear. Fair weather is considered as the day with wind speeds less than 4 m/s and clouds less than 3/8, absence of snowfall, rainfall, fog, lightning, clouds, thunderstorm and pollution, etc. (Harrison, 2004; Latha, 2003). PM$_{2.5}$ concentration as an important indicator for distinguishing fair weather from haze days cannot be equal to 0 μg/m$^3$. Haze

<table>
<thead>
<tr>
<th>Fuel</th>
<th>ECTM (μc/kg)</th>
<th>Fitting precision ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase 1</td>
<td>$-15.57$</td>
<td>0.93</td>
</tr>
<tr>
<td>Phase 2</td>
<td>$-737.43$</td>
<td>0.96</td>
</tr>
<tr>
<td>Phase 3</td>
<td>$-8310$</td>
<td>0.94</td>
</tr>
<tr>
<td>Wood</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase 1</td>
<td>$-17.47$</td>
<td>0.8</td>
</tr>
<tr>
<td>Phase 2</td>
<td>$-52.8$</td>
<td>0.95</td>
</tr>
<tr>
<td>Phase 3</td>
<td>$-609.35$</td>
<td>0.79</td>
</tr>
<tr>
<td>Plastic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase 1</td>
<td>$-109.47$</td>
<td>0.94</td>
</tr>
<tr>
<td>Phase 2</td>
<td>$-1160$</td>
<td>0.79</td>
</tr>
<tr>
<td>Phase 3</td>
<td>$-46700$</td>
<td>0.85</td>
</tr>
<tr>
<td>Engine oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase 1</td>
<td>$+19.29$</td>
<td>0.67</td>
</tr>
<tr>
<td>Phase 2</td>
<td>$+68.46$</td>
<td>0.8</td>
</tr>
<tr>
<td>Phase 3</td>
<td>$+2003$</td>
<td>0.8</td>
</tr>
</tbody>
</table>
event is defined as a weather condition that visibility is less than 10 km (Chinese Meteorological Administration). According to the results of Zhang et al. (2015) which PM$_{2.5}$ concentrations are all higher than 100 $\mu g/m^3$ when the visibility is less than 10 km, the PM$_{2.5}$ concentration which below 100 $\mu g/m^3$ was defined as the fair weather in this paper. Then a total of 6 days during field observation were selected for further analysis.

The SCD of atmosphere in fair weather appears a significant periodic variation within approximately 24 hr, which fluctuates sharply from 8:00 to 18:00 while calms down from 18:00 to 8:00 (Fig. 3a). The diurnal variation of the 30 min time-averaged SCD during fair weather (Fig. 3b, c) presents an oscillation pattern which differs from year to year at the same observation site. For example, the oscillation pattern appears a triple peak double valley configuration during 2015 in Beijing (Fig. 3b), whereas it is a double peak single valley configuration during 2016 in Beijing (Fig. 3c). And the first peak of SCD in December 14, 2016 and December 15, lagged half an hour compared of that in December 22, 2016 and December 23, 2016 (Fig. 3c) despite of the same period and the same site, which may be related to the time of sunrise. Meanwhile, the temperature on December 14, 2016 rises at 7:00 and drops at 15:00, two hours later than that of December 23, 2016 (Fig. 3d). The time of sunrise and sunset can be judged by the rise and fall of temperature to some extent, this is in accordance with the oscillation pattern of the SCD at the same time (Fig. 3b, d). Nichols (1916) once demonstrated that the electric charge in atmosphere is affected by sunrise and sunset. Therefore, it can be well concluded that the diurnal variation of SCD in fair weather differs in different sites at the same time on account of solar radiation.

The investigation on space charge in fair weather presents a similar diurnal variation with a 24-hr cycle pattern (Bent and Hutchinson, 1966; Pawar and Kamra, 2000; Law, 1963; Crozier, 1963; Dhanorkar et al., 1989; Kamra, 1982). Quantitatively, the outcome of Bent and Hutchinson (1966), Pawar and Kamra (2000), Crozier (1963) is in agreement with ours that the space charge density is negative by day and positive by night, while the observation results of Law (1963), Kamra (1982) and Dhanorkar et al. (1989) are opposite with ours. This difference can be explained from two aspects. On the one hand, the diurnal variation of Earth’s electric field and conduction current as well as space charge differs with the observation stations and the observation time (Chalmers, 1929; Brown, 1935). On the other hand, the vertical spatial distribution of

![Image](https://example.com/image1)

Fig. 3 – (a) Time series of the SCD in the atmosphere during fair weather; (b)-(c) the diurnal variation of the 30-min time-averaged SCD in the atmosphere during fair weather (gray dotted line represents the SCD = 0 $\mu c/m^3$); (d) the diurnal variation of the 1 hr time-averaged temperature during fair weather.
Fig. 4 – (a)–(h) Time series of vertical wind velocity in Xi'an, 2017; (i) power spectrum of vertical wind velocity at day time and night time; (j) energy spectrum of vertical wind velocity at day time and night time.
ions in fair weather is portrayed as decreased negative ions and increased positive ions with an increase of altitude owing to the electrode effect (Kamra, 1982; Smiddy and Chalmers, 1960; Harrison, 2010; Kim et al., 2005), i.e., the upper atmosphere tends to be positively charged whereas the lower thin layer at ground tends to be negatively charged, driving positive ions towards the ground and negative ions off the ground (Pawar and Kamra, 2000; Crozier, 1963). Moreover, the SCD fluctuates sharply during daytime and appears a conspicuous peak in early morning, and solar radiation may be responsible for this phenomenon. The studies in diurnal variation of ions concentration and ionization rates revealed that both of them arrive a peak in the morning hours, which are compatible with the diurnal variation of SCD, potential gradient, electric field and conductivity in atmosphere (Dhanorkar and Kamra, 1993; Dhanorkar and Kamra, 1994). And this peak was ascribed to the growth of some radioactive aerosol particles when the sun rises. So it can be inferred that there exists radiation ionization when sunlight shine on the earth.

To figure out the distribution of space charge density in fair weather, the atmospheric wind speed should be discussed firstly. Then the vertical wind velocity in Xi’an, 2017 was selected to illustrate the vertical convection of atmosphere. The time series of vertical wind velocity from 00:00 to 24:00 (Fig. 4a, b, c, d, e, f, g and h) indicate that the fluctuations of vertical wind velocity during day time is more intense than that of night time despite that the average value seldom changes. Then, the four-hour vertical wind velocity data (20 Hz) at day time and night time respectively were selected for spectrum analysis. The power spectrum (Fig. 4i) demonstrates that the energy density of vertical wind velocity during the day time is greater than that of night time. The energy spectrum (Fig. 4j) reveals that the peak energy of vertical wind velocity during the day time is five times as that of night time. All of the above demonstrate that the vertical convection of the atmosphere is enhanced during day time while it is suppressed at night time.

Then taking some meteorological conditions such as thermal convection and inversion layer into consideration, the vertical convection of the atmosphere is enhanced due to the presence of solar radiation during day time while it is suppressed on account of the absence of the solar radiation at night time. Then the space charge distribution in fair weather can be pictured as follows (Fig. 5), i.e., at night time, the typical electrode effect in atmosphere plays a major role under the stable atmospheric stratification. At sunrise, solar radiation may ionize molecules, with the positive ions move towards the ground while negative ions go towards the high altitude. After that, by absorbing solar energy, the increased surface temperature strengthens the vertical convection (thermal convection) and drives ions towards the air. This transfer of ions breaks the electrode effect and leads to the electrode inversion (in Law’s view, this electrode inversion phenomenon is governed by convection current (Law, 1963)). Next, sunset accompanied by a sudden drop in surface temperature leads to the formation of atmospheric inversion.
Fig. 6 - (a)–(c) The frequency distribution of SCD during 2015, Beijing, 2016, Beijing and 2017, Xi’an respectively; (d) the probability density and (e) the probability distribution of SCD in 2015, Beijing, 2016, Beijing, and 2017, Xi’an; (f) the variation of SCD with relative humidity, the red circles denote the 1-hr averaged data in 2016, Beijing, the black line denote the fitting line, the gray dash dot line denote RH = 60%.
Fig. 7 – (a)–(d) The relationship between average SCD and average PM$_{2.5}$ concentration when RH < 60%; (e)–(h) the relationship between average SCD and average PM$_{2.5}$ concentration when RH $\geq$ 60%; error bars are standard error.
layer. This inversion layer compresses the atmosphere towards the ground and forms a stable stratification and finally recovers the space charge to the typical distribution. The charging mechanism above exactly explicates the diurnal variation curve of SCD with an oscillation pattern in our observations, i.e., during fair weather nights at our observation sites, the SCD is positive because of the typical charge distribution, then it increases quickly and achieves a peak at morning due to the radiation ionization of solar, next it decreases and even becomes negative on account of the negative ions carried by thermal convection. Subsequently, it fluctuates severely at day time and doesn’t calm down until the sunset. Finally, it returns to the typical distribution for the presence of atmospheric inversion layer when night befalls.

2.3. Space charge in haze events

From the above analysis it can be concluded that the SCD fluctuates greatly during the day time due to the influence of solar radiation and human activities in downtown while it is relatively stable at night time. And concerning the fact that the PM$_{2.5}$ concentration will grow at night in haze days, the data during the night time was selected for further analysis. The key information of the selected data in haze events is shown in Table S3, and time series of PM$_{2.5}$ concentration, SCD, temperature and relative humidity are shown in Fig. S4 (the data of temperature and relative humidity in 2015 are missing due to instrument problems).

The atmosphere aerosol in haze events are mainly composed of primary aerosol and secondary aerosol (Koch and Amann, 2000; Huang et al., 2014; Zheng et al., 2015; Seinfeld and Pandis, 1998). The primary aerosol is the pollutants that directly emitted by stationary sources such as power plants, industrial furnaces, and heating boilers etc. (Fu et al., 2008; Guo et al., 2014). The secondary aerosol is the nano-sized particles produced by the secondary reactions of primary pollutants under the influence of light, moisture and temperature (Guo et al., 2014; Zheng et al., 2015). The results of laboratory experiments indicated that the primary aerosol are charged and the electric charge of primary aerosol is closely related the PM$_{2.5}$ concentration. Hence, the relationship between SCD and PM$_{2.5}$ concentration in field observations is discussed to investigate the space charge of primary aerosol. But the relationship among SCD, temperature and relative humidity in field observations is analyzed to investigate the influence of environmental factors on space charge of secondary aerosol.

The frequency distribution of the SCD of atmosphere aerosol in haze events obeys Gaussian distribution approximately (Fig. 6a, b, c). Then the probability density of SCD (Fig. 6d) was fitted by Gaussian function, from which it can be seen that there is some difference between the fitting median of SCD in haze events and the average SCD in fair weather (27.23, 43.72, 47.97 pc/m$^3$ in Beijing, 2015, Beijing, 2016 and Xi’an, 2017, respectively), suggesting that the pollutants can affect the space charge in atmosphere. In addition, it can be seen from Fig. 6f that the SCD of atmosphere aerosol varies linearly with the ambient relative humidity when RH < 60%, whereas it increase dramatically when RH > 60%, which indicates that the SCD of atmosphere aerosol in haze events is sensitive to

### Table 2 – Key parameter of linear fitting between SCD and PM$_{2.5}$ concentration in filed observations.

<table>
<thead>
<tr>
<th>Relative humidity (%)</th>
<th>Date</th>
<th>ECTM (μC/kg)</th>
<th>Fitting precision ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH &lt; 60%</td>
<td>2015/12/06 - 2015/12/18</td>
<td>-103</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>2016/12/09 - 2016/12/21</td>
<td>-71</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>2017/12/07 - 2017/12/14</td>
<td>124</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>2017/12/15 - 2017/12/19</td>
<td>-621</td>
<td>0.46</td>
</tr>
<tr>
<td>RH ≥ 60%</td>
<td>2016/12/12</td>
<td>4686</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>2016/12/17</td>
<td>1497</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>2016/12/18</td>
<td>3201</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>2016/12/24</td>
<td>8177</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Fig. 8 – (a) The relationship between average SCD and average ambient temperature when RH < 60%, (b) the relationship between average SCD and average ambient relative humidity when RH < 60%; error bars are standard error.
Fig. 9 – (a)–(d) Time series of SCD and relative humidity in the 4 events; (e)–(h) Time series of PM$_{2.5}$ concentration in the four events when RH $\geq 60%$. 
the ambient relative humidity. So the data were divided into RH > 60% and RH < 60% for further analysis.

When RH < 60%, as an important indicator of the pollution level in haze events, the PM$_{2.5}$ concentration is closely related to the SCD (Fig. 7) during haze nights, but the relevance between them is different in different haze events. For example, the SCD from December 6, 2015 to December 19, 2015 (Fig. 7a) and from December 9, 2016 to December 22, 2016 (Fig. 7b) at Beijing as well as from December 16, 2017 to December 20, 2017 (Fig. 7d) at Xi’an is negatively correlated with PM$_{2.5}$ concentration, while it is positively correlated with PM$_{2.5}$ concentration from December 7, 2017 to December 15, 2017 at Xi’an (Fig. 7c). This means that charge polarity of atmosphere aerosol in haze events are different. Besides, there is a good correlation between temperature and SCD (Fig. 8a) and between relative humidity and SCD (Fig. 8b), which implies that the environmental factors may influence the space charge of atmosphere aerosol through secondary reactions of primary pollutants.

The ECTM of atmosphere aerosol in haze events are shown in Table 2. Qualitatively, the polarities of ECTM are different in different haze events when RH < 60%, which indicates that the charge polarity of atmosphere aerosol are different in different haze events. Generally, the air pollution are mainly caused by the combustion of coal from power plants, industrial furnaces, and heating boilers etc. and the combustion of engine oil from vehicle (Cao et al., 2005; Andersson et al., 2015). The analysis of our laboratory experiments suggested that combustion products of coal are negatively charged, but the combustion products of engine oil are positively charged. Hence, we can identify the main pollutants according to the polarity of atmosphere aerosol in haze events. That is, the main source of pollutants is coal combustion if the space charge we measured in a haze event is negative (ECTM < 0), and the main source of pollutants is vehicle exhausts if the space charge we measured in a haze event is positive (ECTM > 0). Traditionally, the identification of pollutant sources lies on chemical experiments which experience a long period of sampling and elemental analysis. But we can identify the major sources of pollutants by real-time monitoring the space charge of atmosphere aerosol in haze events and quickly take measures. Quantitatively, the ECTM magnitude of atmosphere aerosol in haze events varies from 10 to 10$^7$ when RH < 60%, which is consistent with that of the primary aerosol produced by combustion of coal and engine oil in Phase 1 and Phase 2 in laboratory experiment. Since the coal and engine oil are almost burned completely in Phase 1 and Phase 2, the primary aerosol in atmosphere are mainly from these two phases. This result further confirmed that the primary aerosol play a dominant role in haze events when RH < 60%.

However, when RH ≥ 60%, the SCD are all positively correlated with PM$_{2.5}$ concentration and can reach 500, 250, 450 and 1100 pc/m$^3$ (Fig. 9a, b, c and d), respectively. And the ECTM of all atmosphere aerosols is positive in the four haze events (Fig. 7e, f, g and h, Table 2) which are one order of magnitude larger than the case of RH < 60%. It can be found from the time series of PM$_{2.5}$ concentration during these four events (Fig. 9e, f, g and h) that haze has experienced a long time before the occurrence of the four events, which indicates that the composition of ions and particulate matter in the air has been developed for a long time and may become very complicated before these four events. Therefore, it can be speculated that the sudden growth of SCD may be caused by the intensity of secondary chemical reaction under high humidity and complex aerosol, i.e., after a long period of development, the composition of ions and particulate matter in the air become quite complicated, and then the air polarities may change significantly.

Fig. 10 – The schematic diagram of a possible charging mechanism in haze events; red stars with sign “+” denote positive ions; green stars with sign “−” denote negative ions; blue stars with sign “+” and “−” denote the secondary water-soluble ions; khaki balls denote neutral particles; gray cycles denote gas pollutants; orange curve denotes variation of PM$_{2.5}$ and black curve denote the variation of SCD; red dotted line denotes SCD = 0 μc/m$^3$. 
humidity increases to more than 60%, causing the secondary chemical reaction of atmosphere aerosol more violent and then resulting in the rapid growth of SCD.

As a result, the relative humidity has a great effect on the space charge of atmosphere aerosol in haze events. When RH < 60%, the SCD of atmosphere aerosol is closely related to the PM$_{2.5}$ concentration, and the ECTM is consistent with the primary aerosol in laboratory experiment, which indicates that the primary aerosol play a dominant role in haze events. When RH > 60%, the SCD of atmosphere aerosol increases sharply, this suggests that the secondary chemical reaction of atmosphere aerosol is more violent in haze events. Thereby, the relative humidity can used to determine whether the primary aerosol or the secondary aerosol is the dominant factor in haze pollution. The discussion above indicate that RH = 60% remains a critical value in haze events. Dui (2008) investigated the standards for distinguish the fog, mist, and haze in different institutions, and defined the relative humidity near 100% as fog, 95% ≤ RH < 100% as mist, 80% ≤ RH < 95% as fog-haze and RH < 80% as dust-haze. Generally, in the haze-prone areas such as the North China Plain and the Guanzhong Plain, China, the relative humidity is impossible to reach 80% during winter. For instance, the relative humidity in our observations (Fig. S4) were all less than 80% except for periods of rainfall and snowfall. So it is inappropriate to classify RH ≤ 80% as dust-haze. In view of this, we further divide the dust-haze into dry-dust-haze when RH < 60% and wet-dust-haze when 60% ≤ RH < 80% according to the variation of SCD.

In addition, a possible charging mechanism in haze events can be drawn as follows (Fig. 10), i.e., in the formative stage, the chemi-ionization, the photo-ionization and the thermos-ionization in combustion process can produce many charged ions and then emit to air. In the development stage, the negative ions will go towards sky but positive ions may move towards the ground under the influence of electrode effect. After that, the photo-ionization and radiation ionization of solar may generate a lot of ions. Subsequently, the charge distribution in haze events in a low relative humidity (RH < 60%) is similar to that of the fair weather, while the gas-to-particle conversion of gaseous pollutants together with the scattering of haze particles may decrease the rate of ionization and furtherly diminish the SCD fluctuations during the day time. However, when 60% ≤ RH < 80%, the secondary chemical reaction of atmosphere aerosol may accelerate the chemi-ionization rate and finally contribute to the rapid increase of SCD in atmosphere. In the dissipation stage, a strong wind, rainfall or snowfall etc. will declare the death of haze event. It should be noted that this charging mechanism can exactly interpret the variations of SCD obtained in our observations.

### 3. Conclusions

In this study, the laboratory experiments and the field observations were performed to investigate the space charge of atmosphere aerosol in haze events. And a possible charging mechanism was proposed based on the charge properties of atmosphere aerosol in haze events. The results showed that both the primary aerosols produced by combustion and atmosphere aerosols in haze events are charged. In addition, the laboratory experiments revealed that the charge polarity of the primary aerosol generated by combustion is governed by species of fuels whereas the magnitude is manipulated by the combustion phase. The more sufficient the combustion is, the larger the charge of primary aerosol will be. The field observations demonstrated that the diurnal variation of SCD during fair weather presents an oscillation pattern with a period of approximately 24 hr, and the oscillation patterns differs in different years and different observation sites. These results are all well agreement with previous researches.

Then, taking the fact that PM$_{2.5}$ concentration and SCD during haze nights are relatively stable into account, the data during the haze nights was selected to elucidate the space charge property of atmosphere aerosol in haze events. The results confirmed that the SCD of atmosphere aerosol in haze events differs from that of fair weather and is closely related to PM$_{2.5}$ concentration when RH < 60%, with 1 to 2 orders of magnitude less than the case when RH ≥ 60%. When RH < 60%, the polarities of ECTM are different in different haze events, which indicates that the charge polarity of atmosphere aerosol are different in different haze events. Based on the results in laboratory experiments, we can identify the main pollutants in haze events according to the polarity of atmosphere aerosol and quickly take measures. That is, the main source of pollutants is coal combustion if the space charge we measured in a haze event is negative (ECTM < 0), and the main source of pollutants is vehicle exhausts if the space charge we measured in a haze event is positive (ECTM > 0). However, when RH ≥ 60%, the ECTM of atmosphere aerosol is one order of magnitude larger than the case that RH < 60%, which means that the space charge of atmosphere aerosol lies on the secondary chemical reaction when RH ≥ 60%. These results suggest that in haze events the space charge is governed by primary aerosol in a low relative humidity, whereas it is manipulated by the secondary aerosol in a high relative humidity. Accordingly, the dust-haze of RH < 80% can be divided into dry-dust-haze when RH < 60% and wet-dust-haze when 60% ≤ RH < 80% according to the mutation threshold of SCD in haze events.

Finally, a possible charging mechanism was proposed to interpret the variations of SCD in haze events obtained in our observations, i.e., in formative stage, the chemi-ionization, the photo-ionization and the thermos-ionization of solar may generate a lot of ions. Subsequently, the charge distribution in haze events in a low relative humidity (RH < 60%) is similar to that of the fair weather, while the gas-to-particle conversion of gaseous pollutants together with the scattering of haze particles may decrease the rate of ionization and furtherly diminish the SCD fluctuations during the day time. Nevertheless, when RH > 60%, the complex secondary chemical reaction can accelerate the chemi-ionization rate and further contribute to the rapid growth of SCD in atmosphere. Moreover, the
electrode effect may drive the positive ions towards ground and negative ions towards upper air and thus breakdown the electrode effect or even lead to the inversion of atmosphere electric field. In the dissipation stage, a strong wind, rainfall or snowfall etc. will re-shuffle the charge mode and distribution of space charge to fair weather. This charging mechanism can exactly interpret the variations of SCD obtained in our observations.

In a word, the atmosphere aerosol in haze events are charged, and the charged aerosol can generate an electric filed in space which will greatly affect the formation and evolution of haze. In addition, the scattering, reflection and absorption of the suspended charged aerosol will greatly influence the propagation of electromagnetic waves. Hence, an in-depth understanding in charge properties of atmosphere aerosol can not only give some valuable information for the transportation of haze pollutants and optimization of instruments design based on electromagnetic wave propagation, but also provide a new perspective for the prevention and control of air pollution. This study investigated the space charge of atmosphere aerosol and made people have a preliminary understanding in charge properties of atmospheric aerosol in haze events. However, as for the atmospheric electrical properties such as the space distribution of atmosphere electric field, the proportion of positively charged aerosol and negatively charged aerosol in atmosphere, as well as their effects on the formation and evolution in haze events and the like, are still need to be explored further.

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Appendix A. Supplementary data

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REFERENCES