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Characteristics of Atmospheric Small Ions and Their Application to Assessment of Air Quality in a Typical Semi-Arid City of Northwest China

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ABSTRACT

Observations of atmospheric air ions at most geographic areas have been undertaken, but there are still very few observations at middle-latitude semi-arid areas throughout the world. To quantify characteristics of small air ions in semi-arid areas of China, measurements of small air ions and particulate matter (PM_{10}) were conducted at 16 different sites in Xi'an (34°26′N, 108°94'E), China, from August 2009 to July 2010 along with meteorological parameters. The influences of meteorological parameters and PM_{10} concentration on small air ions as well as their influence mechanisms were discussed in detail. The results showed that both spatial and temporal distributions of small ions were uneven in Xi'an city. Spatially, the concentration of small ions increased gradually from city center to the suburbs. The mean annual concentration of small negative ions was in the range of 200–400 cm^{-3} with the mean value of 261 ± 39 cm^{-3} at urban areas, while more than 500 cm^{-3} at suburban areas. Significant seasonal variations of small ions were observed with highest level in summer, followed by spring and autumn, and lowest in winter at various types of sites. The positive correlations were found between small ions concentration and temperature as well as relative humidity, while negative correlation between the small ions concentration and PM_{10} concentration. Air ions concentration was also applied to the assessment of air quality in Xi'an. The assessment results indicated that the air quality was better at suburban areas than at urban areas, suggesting that the unipolarity model is reasonable to indicate air cleanness.

Keywords: Air ions; Meteorological parameters; Particulate matter; Air quality; Semi-arid areas.

INTRODUCTION

Atmospheric air ions exist everywhere in natural world. It is well known that neutral air molecules in the atmosphere may be ionized into pairs of positive ions and free electrons by cosmic rays from space and radiations from natural radioactive materials in soil and air. Generally, an electron can not exist freely in air at normal temperature and pressure, but readily attaches itself to hydrous or oxygen molecular in air, resulting in the formation of negative air ions (NAIs). These ions cannot remain stable in the atmosphere under normal conditions, and consequently are adsorbed to a number of neutral molecules or atoms and reach certain stability in the form of cluster ions, known as small ions (Pawar *et al.*, 2010). When these small ions are transported and dispersed in the atmosphere, they are prone to attachment to aerosol particles and then form so-called intermediate and large ions in the size range of2 nm–1 μm. Apparently, air ions not only determine the electrical state of atmosphere but also participate in different atmospheric processes such as cloud process, precipitation and aerosol particle formation (Yu and Turco, 2001; Lee *et al.*, 2003; Kulmala and Tammet, 2007; Hirsikko *et al.*, 2011). Therefore, the study of atmospheric air ions is significantly important to understand deeply their effects on global climate, air quality and human health.

During the last decade, the study of atmospheric air ions has become the subject of intense scientific activities. Most of those existing researches focused on the role of air ions in affecting climate and atmospheric aerosol formation based on large numbers of air ion measurements. Kulmala *et al.* (2004) and Hirsikko *et al.* (2011) gave their own excellent overview of such measurements, respectively, made in different environments such as continental boundary layer (Hirsikko *et al.*, 2007), marine boundary layer (Komppula *et al.*, 2007), upper troposphere and lower stratosphere (Lee *et al.*, 2003), Arctic and Antarctic (Virkkula *et al.*, 2007), boreal forests (Vana *et al.*, 2006), coastal regions (Siingh *et al.*, 2005), tropical rural region (Pawar *et al.*, 2010) and various urban outdoor environments (Retalis *et al.*, 2009; Ling *et al.*, 2010). The above studies revealed that the air ions were continuously generated and destroyed

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by various processes in the atmosphere. There were many natural and anthropogenic sources of atmospheric ions (lightning, waterfall, corona discharge, combustion etc.) and ion concentrations varied greatly in different environments.

According to Hirsikko *et al.* (2011), under steady conditions in the natural atmosphere, mean small ions concentration varied from about 300–400 cm^{-3} in clean environments to a few thousands cm^{-3} in the presence of waterfalls (Laakso *et al.*, 2006) and overhead power lines (Fews *et al.*, 1999; Jayaratne *et al.*, 2010). However, since small air ions rapidly got attached to aerosol particles and loosed their mobility or descended to the ground, it could be expected that small ions concentration in polluted environments was generally lower than in clean environments. This suggested that observation of air ions might offer indirect information on aerosol pollution, and air ions concentration might be used as an index of air quality assessment. More recently, several studies on urban air ions demonstrated that there was an inverse relationship between particle concentration and small ion concentration (Titta *et al.*, 2007; Retalis *et al.*, 2009; Jayaratne *et al.*, 2010; Ling *et al.*, 2013). However, in contrast to numerous studies on air ions in other geographic areas, the characteristics of air ions in arid or semi-arid areas have never been investigated, along with the relationship between the level of air ions and particulate matter concentration as well as meteorological conditions. Further, there is still lack of a deeper insight into influence mechanism of meteorological conditions on air ions. In addition, there are very few studies on the assessment of air quality based on air ions in various types of urban environments.

Consequently, the present study was carried out in a typical semi-arid city with the aim of addressing these gaps in our knowledge. For this purpose, the concentrations of small air ions and particulate matter were measured in Xi'an city of Northwestern China from August 2009 to July 2010 as well as some meteorological parameters (temperature and relative humidity). The spatial-temporal variation of air ions concentration in Xi'an was then determined. The relationship between the concentration of small air ions and meteorological parameters and its influence mechanism were analyzed in detail. Finally the air quality in Xi'an city was assessed based solely on measured concentrations of small ions.

METHODOLOGY

Description of Measurement Sites

The measurements of air ions were made at 16 different outdoor sites in Xi'an city (34°26′N, 108°94'E and 424 m above sea level, shown in Fig. 1), the capital of Shaanxi province, China. As the largest city in northwestern China, Xi'an occupies an area of about 9983 km^2, with a population of 8.468 million and a total number of vehicles more than 1.60 million. As a typical semi-arid inland city, Xi'an is located in the middle of the Yellow River valley and in the center of the Guanzhong Plain, surrounded by the Loess Plateau and Qingling Mountain. As representative of most cities in the north and northwest of China, Xi'an has four distinct seasons with long summer and winter and short spring and autumn. Further, it is hot, rainy and humid in summer and cold and dry in winter with an annual average temperature of 13.0–13.4°C and annual precipitation of 558–750 mm. The prevailing wind direction is North-East i.e., NE 12% and East–North–East i.e., ENE 8%.

Fig. 1 illustrated the location of 16 sampling sites for air ions measurement in this study. Along city's central east-west axis and north-south axis, a total of 13 sites were selected and were all within urban areas (inside outer-ring road). Twelve of these 13 sites were also along an inner-, middle- (Second-) and outer- (Third-) ring road, respectively. Because they were close to busy roads, and intersections, these 12 sites were grouped into the traffic areas. The site of Bell Tower (BT) was situated in the city centre, surrounded by business buildings, and thus, was classified as commercial areas. The site of Chang'an University (CAU) located in the suburbs had lots of greenery in the vicinity, surrounded by residential dwellings and teaching buildings. It stood for education/residential areas. The site of Chang-Ning Palace (CNP) was approximately 17 km away from the city centre. Its surrounding terrain was characterized by groups of trees, grass and agricultural land. The Gaoguan Park (GGP), situated in the northern slope of Qinling Mountain, about 50 km southwest of the city centre, was also selected as a special sampling site from which a waterfall is located around 30 m away. There were no specific pollution sources surrounding these sites of CAU, CNP and GGP.

Instrumentation

The air ions concentration was detected for two sites at a time by using two air ion counters (DLY-2G and DLY-4G, China) in which the ion collector and electrometer were designed in one assembly set. This instrument can discriminate the negative and positive ions by polarity, and can separate the ion size by mobility (Zhang and Yu, 2006; Li *et al.*, 2010). The resolution of both instruments is ±10 cm^{-3} with a measure range of $10 \sim 1.999 \times 10^9$ cm^{-3}. Their mobility may be adjusted as 1, 0.4 and 0.15 cm^2/V-s for DLY-4G; 0.15, 0.04 and 0.004 cm^2/V-s for DLY-2G, respectively. According to Hirsikko *et al.* (2011), the range of the detectable ion size is: small ions (< 1.6 nm) and intermediate ions (1.6–7.4 nm) for DLY-4G, and intermediate ions (1.6–7.4 nm) and large ions (> 7.4 nm) for DLY-2G, respectively.

A frmOMNI ambient air sampler (BGI, USA) was used to collect PM_{10} samples with a flow rate of 5 L/min. The sampler was equipped with a solar power battery to avoid power failure. In addition, the wind speed was monitored by a portable electronic anemometer (AZ8901, AZ Instrument Corp., Chinese Taiwan) and the ambient temperature and relative humidity were measured by a hygrometer (TES1364, TES Corp., Chinese Taiwan).

Sampling and Analysis

Monitoring for air ions was conducted over a period of one year from August 2009 to July 2010. Several continuous days in each season were chosen to make measurements at each site, except that the measurement at GGP was made

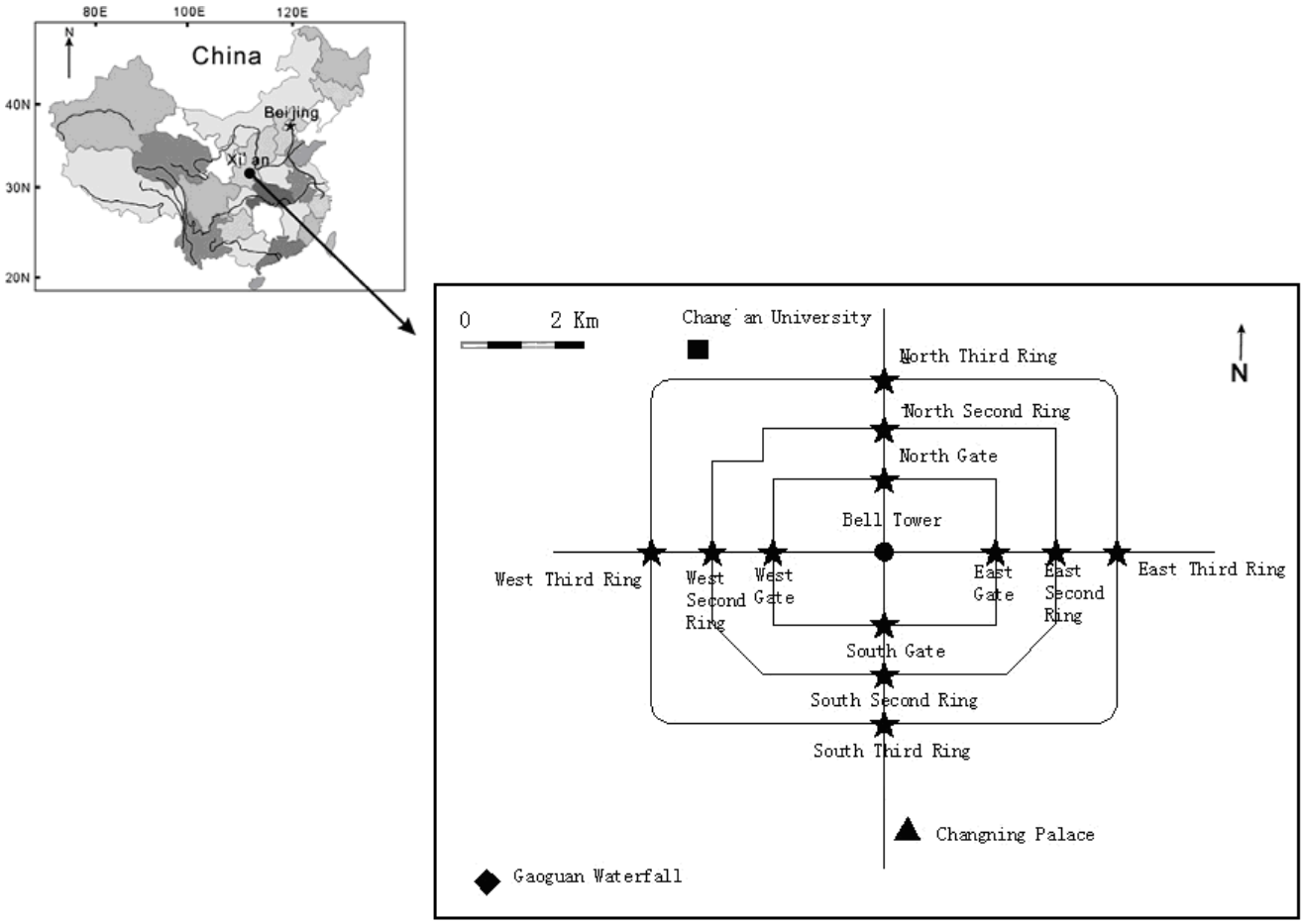

Fig. 1. Location of measurement sites for air ions in Xi'an. (● commercial areas; ■ education/residential areas; ▲ park areas; ★ traffic areas; ◆ reference site).

sporadically. Sampling was carried out at a height of about 1.0 m above the ground level. As suggested by Siingh *et al.* (2005), stability and accuracy of air ion counter were maintained by drying the insulators and checked by checking the zero-shift of each output before each measurement in the present study. In addition, to reduce the measurement uncertainty, three repetitive data in each of 4 perpendicular directions, and totally 12 data were recorded at each site each season. Therefore, a total of 48 data were analyzed for most sites.

For measurement of PM_{10} concentration, a continuous sampling was carried out at each site during the same period between 8:00 in the morning and 8:00 in the evening. A micro fiber quartz filter (Φ47 mm) was utilized to collect particulate matter. The filter was weighed 3 times before and after the samplings respectively. The aerosol mass concentrations were then determined gravimetrically using an electronic microbalance with 1 μg sensitivity (Sartorius, Germany). Before weighing, the quartz filter samples were equilibrated for 24 h at a constant temperature at 20–25°C and RH between 40%–45%. Each filter was weighted at least three times before and after sampling by a 24 h equilibration. The mean net mass for each filter was obtained by the average post-weight data subtracting the pre-weight.

During the sampling period, meteorological data, including ambient temperature, relative humidity (RH), wind speed, and wind direction were also recorded at each site.

The concentration values reported below were represented as the mean and standard deviation. The difference of air ion concentration at different sites was also compared by Student's t-test, in which p values of < 0.05 were considered to be statistically significant. Pearson's correlation analysis and multiple regression analysis were performed to evaluate the statistical significances of correlation between various environmental factors and concentrations.

RESULTS AND DISCUSSION

Concentrations of Small Air Ions

Table 1 shows the mean annual concentration of small air ions measured at different observation sites of Xi'an city. At urban environments inside the Third-ring Road, it can be seen that the mean concentration of small NAIs is 261 ± 39 cm^{-3}, while the concentration of small positive air ions (PAIs) is 449 ± 90 cm^{-3}. At suburban outside the Third-ring Road, the mean annual concentration of small NAIs and PAIs at CNP is 514 ± 105 cm^{-3} and 540 ± 177 cm^{-3}, respectively, while 1259 ± 114 cm^{-3} and 1753 ± 262 cm^{-3} at CAU. Particularly, the mean concentration of small NAIs and PAIs at GGP is up to 3675 ± 444 cm^{-3} and 738 ± 191 cm^{-3}, respectively.

Table 1. The mean annual concentration of small air ions at different sites of Xi'an city.

	Negative (n_-)		Positive (n_+)		n_+/n_-
	Mean	SD	Mean	SD	
Bell Tower (BT)	243[a]	± 39	361[a]	± 113	1.45
Inner-ring Rd (IRR)	250[a]	± 84	387[a]	± 134	1.55
Second-ring Rd (SRR)	264[a]	± 58	551[a]	± 120	2.09
Third-ring Rd (TRR)	295[a]	± 91	440[a]	± 155	1.49
Changning Palace (CNP)	514[b]	± 105	540[ab]	± 177	1.05
Chang`an University (CAU)	1259[c]	± 114	1753[c]	± 262	1.39
Gaoguan Park (GGP)	3675[d]	± 512	738[b]	± 191	0.20

a, b, c, d means that mean values within the column by the same letter are not significantly different ($p < 0.05$).

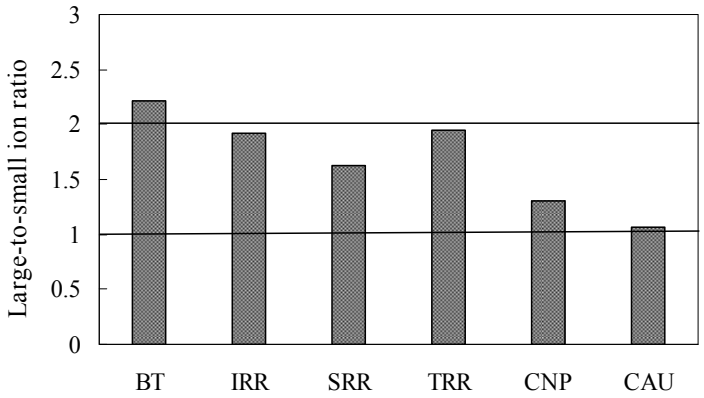

Fig. 2. The large-to-small ion ratio at different sites in Xi'an. (BT: Bell Tower; IRR: Inner-ring Road; SRR: Second-ring Road; TRR: Third-ring Road; CNP: Changning Palace; CAU: Chang'an Univrsity).

It can be also found that the mean concentration of small air ions increased gradually from city centre to the suburbs, reflecting that the spatial distribution of small air ions is uneven in Xi'an. At each site inside the Third-ring Road, the difference between ion concentrations with both polarities is not statistically significant ($p > 0.05$), but these concentrations are all significantly lower than those in the suburbs ($p < 0.05$). In addition, small ion concentration is also found significantly higher in the northern suburbs (CAU) than in the southern suburbs (CNP) ($p < 0.05$) due to the dominant wind frequency of northeast and north-northeast in Xi'an.

The present spatial variation in air ions is consistent with previous results in other cities worldwide obtained by Retalis *et al.* (2009), Pawar *et al.* (2012) and Ling *et al.* (2010). This may be attributed to air pollution and underlying surface conditions in urban and suburban areas. As stated by Pawar *et al.* (2010), humans built cities and covered the land with asphalt and concrete, which prevented the normal generation of ions from the ground. Moreover, air pollution would be greater in urban areas than in suburban areas due to a higher density of traffic and human activities in urban areas. Therefore, small ions are likely to be attached to aerosol particles presented in the polluted air and then loose their mobility or form large ions. This conclusion can be supported by the fact that large-to-small ion ratios are significantly higher in urban areas than in suburban areas shown in Fig. 2. The large-to-small ion ratio mirrors transformation rate of small ions into intermediate and large ions to some extent.

Table 2 represents a comparison of small ions concentration in different urban areas worldwide. Compared to the urban areas of Helsinki, Boulder and Brisbane reported by previous studies (Iida *et al.*, 2006; Hirsikko *et al.*, 2007; Ling *et al.*, 2010), small air ions detected in this investigation show lower level. An important reason might be due to the differences in geographic region of different observation locations. Xi'an city, the present observation locations, is located at middle-latitude zone and semi-arid areas, while Helsinki and Brisbane are coastal cities and Helsinki is also situated at high-latitude area. Therefore, climate characteristics and solar radiation are entirely different. Another main reason might be due to substantially strong air pollution accompanied by the rapid urbanization and industrialization in Xi'an over the past decade. Further, Xi'an has a semi-arid climate that may further aggravate pollution levels resulting in enormous levels of respirable aerosols. This explanation can be also supported by comparable concentrations of small ions detected in Tecamac, Mexico (Iida *et al.*, 2008), Pune, India (Pawar *et al.*, 2012) and Athens, Greece (Retalis *et al.*, 2009), as shown in Table 2. India and Mexico have experienced rapid urbanization and industrial expansion, resulting in increased air pollution during recent years. According to Retalis *et al.* (2009), high background aerosol concentrations at the polluted urban environment of Athens, acted as increased sinks for small ions. Therefore, small ion concentrations in the urban areas of Tecamac, Pune and Athens showed comparable level to our results.

Table 2. Comparison of small ion concentrations in different urban areas worldwide.

City	Location	Observation period	Small ion concentration (cm^{-3})		Reference
			Negative (n_-)	Positive (n_+)	
Xi'an, China	34°26'N, 108°94'E	Aug. 2009–Jul. 2010	Range: 200–400, Mean: 261	Range: 200–700, Mean: 449	Current study
Helsinki, Finland	60°10'N, 24°57'E	Jul. 2004–Sep. 2004	Mean: 683	Mean: 627	Hirsikko *et al.* (2007)
Boulder, USA	40°1'N, 105°17'W	Mar. 2004–Sep. 2004	Mean: 454	Mean: 515	Iida *et al.* (2006)
Tecamac, Mexico	19°40'N, 98°54'W	Mar. 2006	Mean: 209	Mean: 266	Iida *et al.* (2008)
Athens, Greece	37°58'N, 23°43'E	1968–1984	Mean: 151.1	Mean: 188.8	Retalis *et al.* (2009)
Pune, India	18°31'N, 73°55'E	Jul. 2009	Range: 100–200	Range: 300–1200	Pawar *et al.* (2012)
Brisbane, Australia	27°28'S,153°02'E	Mar. 2010–Nov. 2010	Median: 360–580	Median:460–860	Ling *et al.* (2013)

Note that the mean concentration of small positive ions is higher than that of small negative ions at each site except at GGP. As shown in the right column of Table 1, all ratios of small PAIs to small NAIs are larger than 1 except at GGP. This observation is also consistent with Retalis *et al.* (2009) and Pawar *et al.* (2012). Retalis *et al.* (2009) found that the n_+/n_- ratio was equal to 1.25 in Athens, Greece urban area. Pawar *et al.* (2012) reported that average positive to negative ion ratio is 2.8, 0.5 and 0.75 at urban, coastal and mountain site, India, respectively. According to them, this may be because more negative ions are combined with aerosols than positive ions due to pollution at the urban area. Further, the Earth's surface has generally a net negative charge. Therefore, it repels the negative ions and attracts the positive ions near surface so that the PAIs are much more than the NAIs near surface. At GGP, as mentioned earlier, there exists a waterfall close to this measurement point. When the water of waterfall is overshooting and impacting on the rock, the breaking up of water droplets will cause molecules which are torn from the water surface to bear a negative charge (small negative ions) whereas large drops of the entire mass of water are positive. This is known as the Lenard effect. As a result, it is not surprising that the ion concentration is significantly higher at GGP than other sites in the present study ($p < 0.01$). Similar phenomenon of waterfall or rainfall induced ions was also reported by Laakso *et al.* (2007) and Tammet *et al.* (2009), who found that waterfalls and rainfall produce high concentration of ions, especially negative ions smaller than 10 nm. These finds also suggested waterfalls are strong sources of small ions.

Seasonal Variations in Concentrations of Small Air Ions

Fig. 3 compares the average values of small NAIs and PAIs measured at four types of functional areas in different seasons. Although the spatial location is rather different and the type of functional area is also various at these sites selected, the seasonal variation of small ions with both polarities seems to be similar, that is, the highest concentration in summer, followed by spring and autumn, and lowest in winter. For example, as representative of traffic areas, average concentrations of NAIs at Second-ring Road are 223 ± 30, 273 ± 53, 232 ± 17 and 197 ± 39 cm^{-3}, respectively, in spring, summer, autumn and winter. Similarly, at CNP, the average concentrations of NAIs are 523 ± 39, 573 ± 50, 497 ± 25 and 442 ± 32 cm^{-3}, respectively, in four seasons.

These seasonal variations could be explained in terms of the meteorological features and their changes in different seasons. As summer is a hot, rainy and humid season in Xi'an, on the one hand, various plants flourish well and solar radiation intensity increases, resulting in more small ions produced due to plant transpiration of radon and thoron. On the other hand, during the summer, rain may clear the pre-existing particulate pollutants, which will reduce the sink due to ion-aerosol attachment process. In contrast, the winter is much-polluted and dusty period in Xi'an due to existence of frequent thick inversions, which leads to elevated ions attached to aerosols and thereby,

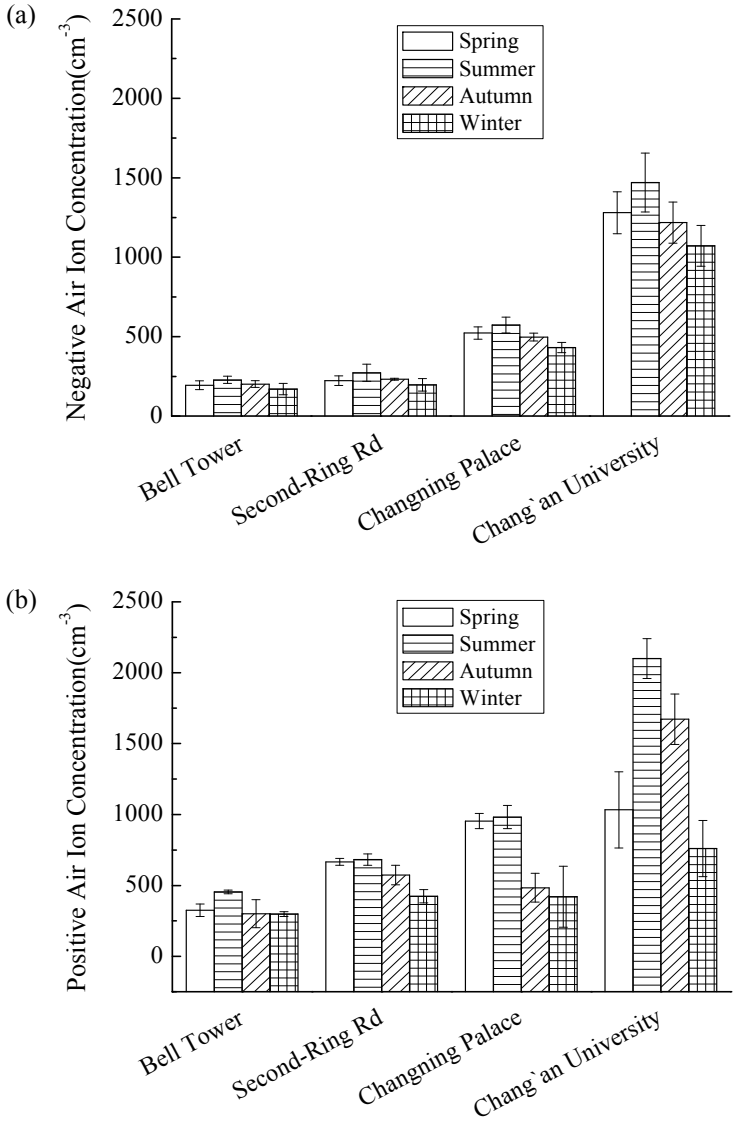

Fig. 3. Seasonal variations in (a) small negative ions and (b) small positive ions at various functional areas in Xi'an.

reducing the small ion counts. Another reason is that plant transpiration of radon and thoron is lowest due to most of trees and grass withered in winter.

Relationship between Small Air Ions and Meteorological Conditions

Fig. 4 shows the correlation between the concentration of small ions and relative humidity. Fig. 5 shows the correlation between the concentration of small ions and temperature. It can be seen that both of ambient temperature and relative humidity are positively correlated statistically with the concentration of small ions, reflecting that the concentration of small ions is high under the condition of high relative humidity or high temperature.

To better depict the influence of the meteorological parameters on the small ions concentration, a multiple regression analysis was also employed. The regression equations for NAIs and PAIs can be given as following, respectively:

$$n_{-} = 109.848 + 2.257T + 2.750RH \quad (1)$$

$$n_{+} = 71.271 + 2.866T + 3.182RH \quad (2)$$

where n_{-} and n_{+} represent the concentration of NAIs and PAIs, respectively; T and RH denote the temperature and relative humidity, respectively. Multiple regression analysis shows that the correlation between the concentration of small ions and two meteorological parameters is highly significant. The correlation coefficients are 0.952 ($p < 0.05$) for small NAIs and 0.869 ($p < 0.05$) for small PAIs, respectively.

The positive correlation between RH and ion concentrations can be explained simply from a radiant ionization standpoint. If a high-energy particle (such as α, β and γ) is captured by water molecule, the water molecule may be ionized. The amount of ionized molecules can be calculated as follow:

$$N = E/I \quad (3)$$

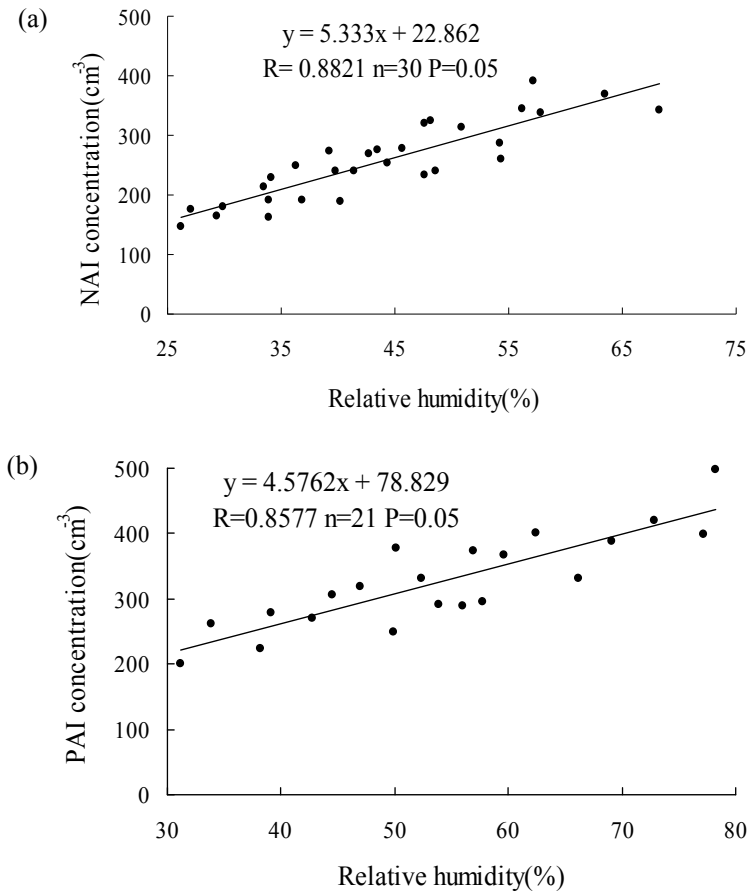

Fig. 4. Correlation between (a) small negative ions and (b) small positive ions concentration and relative humidity

where N is amount of ionized molecules; E and I denote the energy of high-energy particle and the ionization energy of the ionized molecule (eV), respectively. Using α-particle as an example, its energy is about 4–8 MeV. The ionization energy of water molecules and oxygen molecules is only 1.25 eV and 12 eV, respectively. Based on Eq. (3), one can obtain easily that the amount of ionized water and oxygen molecules is about 3.2×10^6–6.4×10^6 and about 3.3×10^5–6.6×10^5, respectively. As relative humidity increases, the amount of oxygen molecules per unit volume will decrease and the amount of water molecules per unit volume will increase. Consequently, the specified radiant energy will ionize more water molecules into ion pairs than oxygen molecules. As a result, the ion counts per unit volume increases. Moreover, the high relative humidity may cause high collision probability between water molecules, resulting in the improvement of collision ionization probability of water molecules.

Because the concentration of water molecules is much smaller than that of oxygen and nitrogen in atmospheric air, of course, the majority of ionized molecules will be oxygen or nitrogen. Therefore, such effect of RH on small ion concentration might be mainly due to an increase of nuclei condensation radius resulting to an increase of combination rate and to a decrease of small ions mobility (Retalis *et al*., 2009).

The lower ion counts with decreased temperature may be mainly attributed to the destruction of small ions by recombination with large ions (charged nuclei) and neutral nuclei. According to Retalis *et al.* (2009) and Hirsikko *et al.* (2011), the concentration of these nuclei increases because they are produced by different air polluting sources such as industries, lighting gas and vehicles, and because they are subjected to limited diffusion. With the concentration of condensation nuclei decreases considerably as they are transferred to higher atmospheric layers by upward motions due to soil heating, and by turbulent motions of the air. These latter motions become most intense in higher temperature. As the temperature and the intensity of upward motions decrease, the number of nuclei near the ground increases and, as a consequence, the rate of destruction of small ions increases. Moreover, based on the molecular kinetic theory, as ambient temperature increases, the velocity of molecules or atoms will increase, resulting in elevated collision probability and high collision ionization probability. Further, the ionization process of oxygen molecules will be strengthened as the temperature rises, with a result that the negative oxygen ions increase. In addition, with temperature increasing, water vapor pressure increases exponentially. For a specified relative humidity, the water molecular amount per unit volume will increase exponentially too. Therefore, according to the influence mechanism of humidity on the negative air ions discussed above, the concentration of air ions will increase.

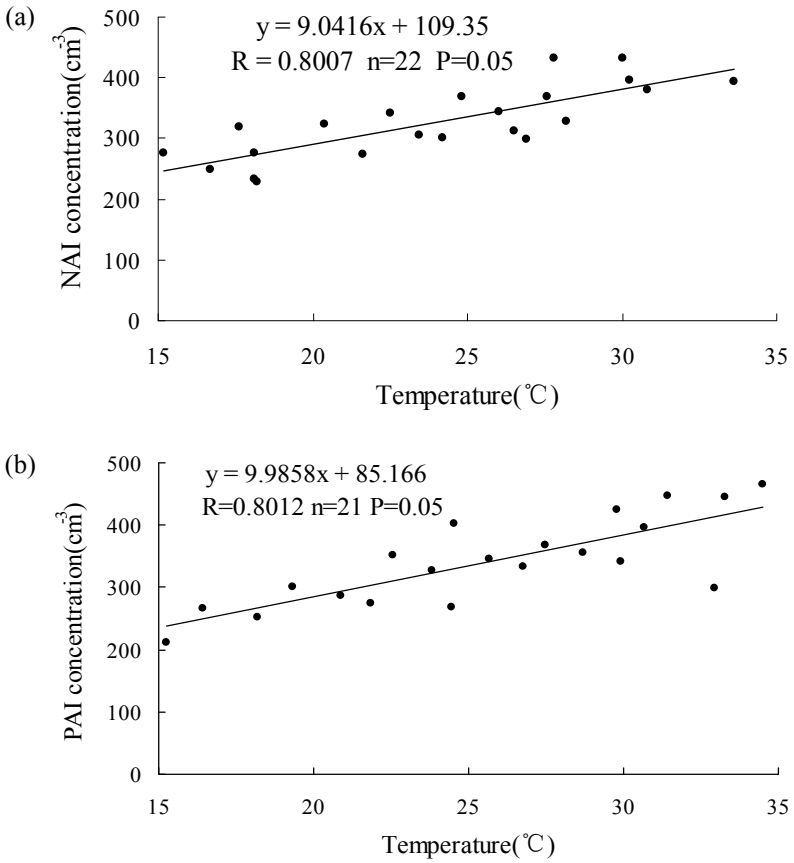

Fig. 5. Correlation between (a) small negative ions and (b) small positive ions concentration and temperature.

Relationship between Small Air Ions and PM_{10}

Fig. 6 represents the relationship between the air ions concentration and particulate matter (PM_{10}) concentration. It can be seen that there is significantly negative correlation between these two parameters (R = –0.9215, p = 0.05 for NAIs; R = –0.9023, p = 0.05 for PAIs), indicating that the concentration of NAIs and PAIs declines with increase of PM_{10}. Similar results were also reported by several previous studies at other urban sites (Retalis *et al.*, 2009; Pawar *et al.*, 2010; Ling *et al.*, 2013). The main reason may be that small air ions could be consumed by particulate pollutants. On the one hand, high particle density could increase collision probability between charged particles and air ions, and thus the air ions would lose their mobility by neutralization. On the other hand, the sedimentation of particle would be much easier by absorption charge from the collision between air ions and the particles without charge. The negative ions would be consumed by this way.

Air Quality Assessment

As discussed previously, air ions concentration depends on the formation and loss rates of the ions. Two major sinks for the ions are ion-ion recombination and ion-aerosol attachment. The former depends mainly on the ion concentrations themselves, but the latter depends on the aerosol number size distribution. As a result, in a more polluted environment, i.e., having higher sink due to attachment, the ion concentrations are lower. However, this could also be due to smaller formation rate of ions, which makes it difficult to assess air quality based only on small ions concentration. Fortunately, the negative and positive small ions have different mobilities, with the negative ones being more mobile than positive ones. Consequently, if the coagulation sink is high, i.e., in a polluted environment, the loss of negative ions is higher than that of positive ones resulting in a unipolarity factor, n_+/n_-, being above unity. Hence, the concentration of small ions may be used as an index of air pollution. At present, the uni-polarity factor, defined as the positive-to-negative ion ratio, is widely used to assess the air quality in urban environments. This ratio value beyond 1 means more polluted atmosphere and near 1 means that air is almost aerosol free (Kolarz *et al.*, 2009; Pawar, 2012).

According to this definition, the uni-polarity factor can be obtained at each site, also shown in Table 1. It can be observed that the uni-polarity factors at all urban sites inside the Third-ring Road are above 1 and also higher than those at suburban sites outside the Third-ring Road. That means that the air quality in the suburbs is better than in the urban area of Xi'an city. Therefore urban atmosphere is very harmful for human health as compared to suburban.

It is worthy of noting that the uni-polarity factor at GGP site is much less than 1. As mentioned earlier, there exists a very strong ion source at the waterfall location, resulting in more negative air ions produced. That means that the generation mechanism of air ions is different for different

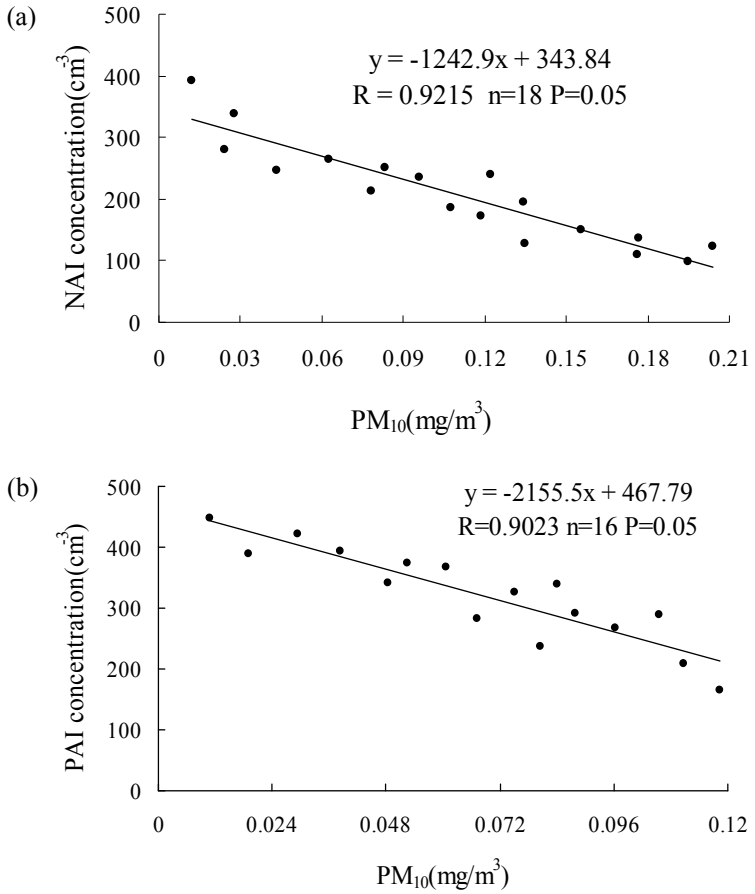

Fig. 6. Correlation between (a) small negative ions and (b) small positive ions concentration and PM_{10} concentration.

measurement points. Lots of negative small ions produced at GGP are not directly connected to air quality and the unipolarity factor is substantially influenced by the waterfall effect. Therefore, the present air quality assessment method may be not suitable for the GGP.

CONCLUSIONS

The concentration of atmospheric small ions varied at different observation sites near surface layer in Xi'an. Their spatial distribution showed obviously uneven characteristics. The small negative ions concentration increased gradually from urban center to suburbs. Statistically, no significant concentration differences between any two sites within urban areas were found ($p > 0.05$) while there was a significant concentration difference between urban and suburban sites ($p < 0.05$). As for seasonal variation, the concentration of small ions was highest in summer and lowest in winter for the whole year. Such temporal-spatial variation of small ions concentration was found to depend on ion production due to sources and on ion consuming due to sinks from weather conditions, plant transpiration and anthropogenic activity, etc.

The concentration of small negative and positive ions was found to be significantly affected by meteorological parameters and PM_{10} concentration. In this study there was a positive correlation between air ions concentration and temperature as well as humidity. In addition, PM_{10} was significantly negatively correlated with the concentration of small ions with both polarities.

Finally, the assessment results for air quality based on a simple unipolarity model showed that the air quality was better at suburban areas than at urban areas, suggesting that the present assessment model employed is reasonable and useful in air pollution studies.

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