**Chemical characteristics of PM2.5 during haze episodes in spring 2013 in Beijing**

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**Abstract:** A continuous daily PM2.5 sampling campaign for two months from 10 April till 8 June 2013, including three haze episodes, was conducted in Beijing. Chemical species, including elemental carbon, organic carbon, water-soluble ions and inorganic elements in PM2.5, were analysed by a thermal/optical carbon analyser, IC and ICP-MS, respectively. A comparison of air quality during such haze episodes in relation to clear air situations, as well as the differences between the haze episodes was emphasised. The results showed that the most important fractions of PM2.5 during the hazes were SO42-, NO3- and NH4+ (namely, SNA) which together accounted for 54-61% of the total PM2.5 mass. Estimated secondary organic carbon (SOC) was found to be increased during haze, too, but the relative increase compared to clear days was much lower than for SNA, leading to a decrease in relative contribution of SOC to PM2.5 in the observed haze events. Cluster analyses from back trajectories showed four air mass clusters during spring 2013 and air flow, which was from the south-easterly directions, might favour the accumulation of PM2.5, especially SNA and anthropogenic elements. All these results proved that the anthropogenic air pollution in the Southeast of Beijing was responsible for the formation of hazes in Beijing during spring 2013.

**Keywords:** haze, PM2.5 characteristics, PM2.5 chemical composition, SNA, back trajectory, cluster analyses

**1. Introduction**

Haze has progressively become a typical pollution event in Beijing ever since the severe haze pollution event occurred in Beijing in January 2013. Haze has a strong impact on a human’s life, not only with respect to visibility but also on human health, because it is usually accompanied by a high PM mass concentration (Zhao et al., 2013a). Many studies on haze pollution in Beijing were carried out in the past, but were mainly focused on summer haze (Li et al., 2010; Duan et al., 2012; Sun et al., 2013; Han et al., 2015) and winter haze, especially on the January 2013 haze pollution event (Ji et al., 2014; Tao et al, 2014; Wang et al., 2014a,b; Zhang et al., 2014a, b; Huang et al., 2015; Zheng et al., 2015). These studies pointed out that SO42-, NO3- and NH4+ (namely, SNA) were the dominant fraction of PM during haze. In addition, sources of PM during haze were summarised by Huang et al. (2015) as traffic, coal combustion, biomass burning, cooking, dust related as well as secondary particle formation.

Considering that dust storms frequently invade Beijing in spring (Guo et al., 2004), dust is another typical and important pollution event during spring and is also one kind of air pollution which can cause haze. The study of spring haze is important for distinguishing dust pollution and haze pollution caused by dust. As most studies about haze focused on winter and summer periods, the study of spring haze has thus been rare. Due to the existence of differences between hazes in different seasons, studies of spring haze are helpful for getting a clear and better understanding of characteristics and sources of particles during haze. In addition, finding out the differences between different haze pollutions in the same season is also helpful for developing strategies to improve air quality.

Therefore, a two-month continuous sampling campaign in spring 2013 is described and analysed in this study. A comparison of air quality during such haze episodes in relation to clear air situations, as well as the different characteristics of each haze episode in spring 2013, were investigated.

**2. Materials and methods**

2.1 Sampling strategy

Two high volume samplers A and B (HVS, nominal flow 500 l min-1, Digitel DHA-80, Hegnau, Switzerland) were installed on the roof of a two-storied building at the Institute of Atmospheric Physics (IAP, Figure 1), which is about 10 m above ground. The North-South G6 Jingzang Expressway and the East-West Beitucheng West Road are located 300 m to the East and 100 m to the North of the sampling site, respectively. Additionally, this site is surrounded by residential areas, parks, trees and institute buildings. This sampling site is operated as a network station of urban atmospheric environment since 2004. The sampling site is not a kerb site to determine high air pollution exposure but an urban site of Beijing. In addition, the representation of our sampling site was described in detail by Liu et al. (2015).

Daily mean PM2.5 samples (00:00 – 24:00, local time) were collected from 10 April 2013 till 8 June 2013. Quartz fibre filters with 150 mm diameter (Munktell T293, Falun, Sweden) were used as a collection substrate. Every two weeks, one blank filter was kept for comparison. This sampling site has been running as an observatory of the urban atmospheric environment since 2004 and many studies have shown that this site to be representative of an urban environment of Beijing (e.g., Wang et al., 2001; Sun et al., 2013; Liu et al., 2014, 2015).

In addition, PM2.5 and PM10 mass concentrations were obtained by a tapered element oscillating microbalance instrument (TEOM, TEOM Series 1400a, Thermo Fisher Scientific Environmental Instrument Co. Ltd) which is operated at the same sampling site and used for comparison. More details about the operating principle of TEOM can be found in Cyrys et al. (2001) and Green et al. (2006). All daily mean TEOM data in this study were averaged from hourly mean data.



Figure 1. The location of the sampling sites in Beijing (Source: http://map.baidu.com): IAP is the Institute of Atmospheric Physics of the Chinese Academy of Sciences; ZBAA is the code for the monitoring site from where one can obtain meteorological data on the website of the University of Wyoming, USA (<http://weather.uwyo.edu/upperair/sounding.html>).

2.2 Analytical methods for chemical compositions

Filters from sampler A were heated at 500℃ for 6 hours before sampling to remove organic compounds and were used for the elemental carbon (EC), organic carbon (OC), water soluble ions and inorganic elements analysis after sampling.

Filters from sampler B were only used for the gravimetric PM2.5 mass concentration determination following the guideline DIN-EN-14907EN (2005). An analytical balance (Mettler Analysenwaage AE240, reading precision 0.1 mg) was used to determine the filter mass before and after sampling. Before weighing, filters were equilibrated for 48 h in a conditioning room (temperature 22℃ ± 0.2, relative humidity 42% ± 0.5).

Organic carbon (OC) and elemental carbon (EC) were analysed by a thermal/optical carbon analyser (DRI Model 2001A, Desert Research Institute, USA) and the IMPROVE (Interagency Monitoring of Protected Visual Environments). A protocol with the thermal optical reflection method (TOR) is applied. More details about this method can be found in previous studies (Cao et al., 2007; Chow et al., 2007).

Eight water soluble ions, including Cl-, NO3-, SO42-, Na+, NH4+, K+, Mg2+ and Ca2+, were analysed by ion chromatography (IC, ICS-90, Dionex, USA). Loaded quartz fiber filter parts (30 mm round diameter) were shaken for 30 minutes with 25 ml de-ionized water (Milli-Q, 18.2 MΩ·cm) in an ultrasonic bath and then filtered by a syringe filter with a pore size of 0.22 μm (Xiboshi, China). A description of this method can be found in a previous work (Li et al., 2013).

The inorganic elements, K, Ca, Na, Mg, Al, Fe, V, Cr, Mn, Ni, Cu, Zn, As, Cd, Ba, Tl and Pb, were measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500a, Agilent, USA). Before analysis, filter parts (20 mm round diameter) were digested in Teflon vessels with 6 ml concentrated HNO3, 2 ml HCl and 0.2 ml HF by using a microwave digestion system (MARS 5, CEM Corporation, Matthews, NC, USA) and then diluted with de-ionized water to 50 ml. Quality control was done by a parallel analysis of the soil reference material GBW07403. This method was also described by Pan et al. (2013).

Field blank filters were measured and subtracted from the loaded filters in the above mentioned analysis.

2.3 Meteorological parameters

Temperature (T), atmospheric pressure (p), relative humidity (RH), visibility, wind speed (WS) and wind direction (WD) were obtained from an open source (<http://weather.uwyo.edu/upperair/sounding.html>) where the data of the weather station ZBAA (Figure 1) are available. The available maximum visibility data are only up to 10 km.

The mixing layer height (MLH) was measured by a ceilometer CL31 (Vaisala GmbH, Hamburg, Germany). All details about MLH determination by CL31 are described in previous studies (Münkel et.al, 2007; Emeis et al., 2008).

2.4 Backward trajectories analysis

The HYSPLIT4 (Hybrid Single Particle Lagrangian Integrated Trajectory, Version 4) model in which meteorological data from the Global Data Assimilation System (GDAS) (horizontal resolution 1°×1°) were applied was used to calculate backward trajectories of air flows (<http://ready.arl.noaa.gov/HYSPLIT.php>). In order to cover both horizontal and vertical scale transport, 72 h backward trajectories were chosen. Considering that pollutants are well mixed, a height of 500 m above ground level (AGL) at the ending point was selected. This height was used widely in previous studies (Zhang et al., 2009; Ji et al., 2014). The time ending at 06:00 UTC (14:00 local) was chosen for cluster analysis, because this MLH is the highest during the day and the conditions are favourable for the mixing of transported air pollutants down to the ground at this time.

2.5 Definition of haze, dust and clear days in this study

Haze is defined as a phenomenon with a visibility lower than 10 km caused by particulate matter in the air (Sun et al., 2006). As dust events can also cause a decrease in visibility, an additional definition of haze and dust will be given in this study to better differentiate haze from dust pollution. Because only polluted events were considered, a PM mass concentration higher than 75 μg m-3 (Chinese Ambient Air Quality Standard for 24 h PM2.5, Grade II) is the first threshold. Additionally, haze events are days with visibilities which are continuously lower than 5 km during at least six hours. Dust days, including dust storms from non-local sources and re-suspended dust events from local sources, were identified by no precipitation and six hour wind speeds continuously equal to or higher than 5 m s-1 that caused at least one hour decreased visibility during one day. For comparison, clear days are referred to those days during which visibility is equal to or more than 10 km.

**3. Results and discussion**

3.1 PM2.5 mass concentrations

The variation of PM2.5 mass concentrations from 10 April till 8 June 2013 is shown in Figure 2. The sample of 16 May was not collected due to an electricity supply failure. Daily mean PM2.5 mass concentration varied from 16 to 182 µg m-3 with an average of 89 µg m-3, which is much higher than the threshold for the annual average of the Chinese Ambient Air Quality Standard for PM2.5 (Grade II: 35 μg m-3) (China State Environmental Protection Administration (SEPA), 2012). In a previous study, PM2.5 mass concentration during spring (April) in 2009 was reported as 126 µg m-3 (Zhang et al., 2013), which indicated that PM2.5 was reduced after emission reduction measures for the Olympic Summer Games in 2008. In addition, the Beijing Municipal Environmental Protection Bureau (Beijing Environmental Statement 2013) reported average PM2.5 mass concentrations during April and May 2013 in Beijing of 65 µg m-3 and 80 µg m-3, respectively. We found higher values as they represent the urban area only, while data from the Beijing Municipal Environmental Protection Bureau depict the average of data from rural and urban areas in Beijing.

Figure 2. Daily mean PM2.5 mass concentrations determined by gravimetric analyses of PM sampled with HVS and by TEOM at the IAP from 10/04/2013 till 08/06/2013.

In addition, the variation of PM2.5 mass concentrations from TEOM was also shown in Figure 2. The correlation coefficient (R) between PM2.5 mass concentrations obtained from HVS and from TEOM is 0.81 with a slope of 0.76. This comparison shows that the PM2.5 mass concentrations determined by TEOM are underestimated by 24% when compared with gravimetric analyses of PM sample with HVS. This could be caused by the loss of volatile substances because the working temperature of TEOM is 50℃.

Three haze episodes (HE) were found during this study period which happened from 21 to 23 April (HE1), 5 to 8 May (HE2) and 2 to 8 June (HE3). The average daily mean PM2.5 mass concentration during HE1, HE2 and HE3 was 164 µg m-3, 164 µg m-3 and 125 µg m-3, respectively, while only 51 µg m-3 during clear days. This demonstrates that the haze episodes are associated with heavy PM pollution in comparison with clear days. In addition, TEOM data was used to calculate PM2.5/PM10 ratios to obtain differences of particle size fraction during haze and clear days. The PM2.5/PM10 ratios during HE1, HE2, HE3 and clear days are 0.6, 0.7, 0.6 and 0.4, respectively. That means the values during the three haze episodes were all higher than 0.5, indicating that PM was dominated by fine particles during haze, while by coarse particles during clear days. Even though high concentrations of fine particles are related to anthropogenic pollution events, PM2.5/PM10 ratio cannot be used to distinguish haze and dust. For instance, on 16 May, the PM2.5/PM10 ratio was even higher than during haze and reached 0.9, but the visibility on this day was 10 km.

3.2 Chemical species

3.2.1 Carbonaceous components

Daily mass concentrations of OC varied from 4.2 to 23.6 µg C m-3 with an average value of 11.4 ± 4.0 µg C m-3 , and the daily mass concentrations of EC varied from 1.0 to 7.6 µg C m-3 with an average value of 3.2 ± 1.3 µg C m-3 (Figure 3). These results agree well with the observed results from other areas of Beijing by Zhang et al. (2013). The average mass percentages of OC and EC in PM2.5 were 14% and 4%, respectively. OC and EC showed the same variation pattern as PM2.5 mass concentration, and all had peak values during haze events (Figures 2 and 3). Carbonaceous matter (CM) can be calculated by the sum of organic matter (OM) and EC, while OM is estimated through OC multiplied by 1.4 (Tian et al., 2014). The average fraction of CM in PM2.5 varied from 11% to 55% with an average value of 24%.

Figure 3. Variation of daily mean mass concentrations of EC, OC and SOC in PM2.5 at the IAP from 10/04/2013 till 08/06/2013.

OC originates not only from primary sources, but also from the secondary formation, which is the so-called secondary organic carbon (SOC). OC/EC ratios can be used to roughly estimate SOC when the OC/EC mass ratio is higher than 2 (Turpin et al., 1991; Chow et al., 1996; Cao et al., 2007). Compared with previous studies in Beijing in which OC/EC values of 2.7 in spring 2000 (He et al. 2001) and 3.0 in April 2009 (Zhao et al. 2013b) were reported, the average OC/EC ratio in the present study was found to be 3.8, which suggests that more SOC was formed during spring 2013.

According to previous studies (Turpin and Huntzicker, 1995; Castro et al., 1999, Lim and Turpin 2002), secondary organic carbon (SOC) was estimated by calculating the difference between total OC and primary OC (POC), which was calculated by EC and primary OC/EC ratio. A least‐squares regression was applied to calculate the primary OC/EC ratio (Cao et al., 2007; Zhao et al., 2013b). For this analysis days with the lowest potential impact from SOC should be selected. Therefore the days with lowest 10% of OC/EC ratio were selected. Days with rain or dust event were excluded from the analysis. As result of this analysis we found the slope of the regression to be 1.93 ± 0.14 and the intercept to be 1.10 ± 0.58. The coefficient of determination (r²) was 0.98.

As a result of this calculation, in average SOC in our study accounted for 42±8% of the OC and 34±7% of the total carbon (TC). All measured chemical component mass concentrations and percentages during haze episodes and clear days are listed in Table 1. When haze episodes were compared with clear days SOC was found to be increased by a factor 0.6 to 2. Because secondary inorganic compounds showed a much stronger increase in haze days (factor of 6 to 7 compared to clear days) the percentages of SOC contributions were found to decrease during all haze episodes. Figure 3 shows that SOC concentration varied as much as OC concentrations peaking in haze and non-haze periods, whereas EC showed little variation peaking in HE2 and HE3.

Table 1. Average values of all measured compounds from daily mean mass concentrations in PM2.5 samples at the IAP during haze episodes and clear days collected in spring 2013. MC: mass concentration (unit: µg m-3, from V to Pb unit: ng m-3); MP: mass percentage (unit: %)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Species  | HE1 | HE2 | HE3 | Clear |
| MC  | MP  | MC  | MP  | MC  | MP  | MC  | MP |
| PM2.5 | 164 |  | 164 |  | 125 |  | 51 |  |
| EC  | 3.8 | 2.3 | 6.0 | 3.6 | 5.0 | 4.0 | 2.2 | 4.3 |
| OC  | 16.6 | 10 | 19.8 | 12 | 12.6 | 10 | 9.0 | 18 |
| SOC | 8.6 | 5.3 | 7.3 | 4.4 | 2.5 | 2.0 | 4.4 | 8.6 |
| Cl- | 3.5 | 2.1 | 1.0 | 0.6 | 2.9 | 2.3 | 0.7 | 1.3 |
| NO₃- | 39.5 | 24 | 26.5 | 16 | 21.7 | 17 | 4.2 | 8 |
| SO₄2- | 32.3 | 20 | 40.2 | 24 | 32.6 | 26 | 5.7 | 11 |
| Na⁺ | 0.48 | 0.3 | 0.49 | 0.3 | 0.41 | 0.3 | 0.24 | 0.5 |
| NH₄⁺  | 20.3 | 12 | 21.8 | 13 | 21.5 | 17 | 3.2 | 6 |
| K⁺ | 1.2 | 0.7 | 1.1 | 0.7 | 1.2 | 1.0 | 0.4 | 0.9 |
| Mg²⁺ | 0.08 | 0.05 | 0.15 | 0.09 | 0.07 | 0.05 | 0.12 | 0.2 |
| Ca²⁺ | 1.0 | 0.6 | 1.2 | 0.7 | 0.5 | 0.4 | 1.5 | 2.9 |
| Na | 0.9 | 0.5 | 1.6 | 1.0 | 0.7 | 0.5 | 0.5 | 1.0 |
| Mg  | 0.50 | 0.3 | 0.74 | 0.4 | 0.23 | 0.2 | 0.68 | 1.3 |
| Al  | 0.95 | 0.6 | 1.83 | 1.1 | 0.58 | 0.5 | 1.5 | 2.9 |
| K  | 1.7 | 1.0 | 1.7 | 1.1 | 1.4 | 1.1 | 0.8 | 1.6 |
| Ca  | 1.7 | 1.0 | 2.1 | 1.3 | 1.7 | 1.4 | 2.0 | 3.9 |
| Fe  | 1.1 | 0.7 | 1.4 | 0.8 | 1.0 | 0.8 | 1.3 | 2.5 |
| V | 2.1 | 0.001 | 5.9 | 0.004 | 8.7 | 0.007 | 3.1 | 0.006 |
| Cr  | 6.2 | 0.004 | 7.6 | 0.005 | 9.2 | 0.007 | 5.4 | 0.011 |
| Mn  | 80 | 0.05 | 83 | 0.05 | 53 | 0.04 | 51 | 0.10 |
| Co  | 0.58 | 0.0004 | 1.29 | 0.0008 | 0.62 | 0.0005 | 0.55 | 0.0011 |
| Ni  | 2.4 | 0.001 | 7.7 | 0.005 | 7.0 | 0.006 | 2.6 | 0.005 |
| Cu  | 50 | 0.03 | 39 | 0.02 | 26 | 0.02 | 21 | 0.04 |
| Zn  | 647 | 0.39 | 389 | 0.24 | 415 | 0.33 | 117 | 0.23 |
| As | 91 | 0.06 | 32 | 0.02 | 17 | 0.01 | 10 | 0.02 |
| Cd  | 10.9 | 0.007 | 2.9 | 0.002 | 2.6 | 0.002 | 1.1 | 0.002 |
| Ba  | 44 | 0.03 | 95 | 0.06 | 75 | 0.06 | 24 | 0.05 |
| Tl  | 3.1 | 0.002 | 3.0 | 0.002 | 2.6 | 0.002 | 0.9 | 0.002 |
| Pb  | 423 | 0.3 | 298 | 0.2 | 295 | 0.2 | 90 | 0.2 |

3.2.2 Water soluble ions

All measured ions contributed an average value of 42% to the PM2.5 mass. SO42-, NO3-and NH4+(SNA) contributed an average value of 85% to the measured total ions mass, which is similar to results from previous studies (Yao et al., 2002; He et al., 2012). The variation of SNA is shown in Figure 4, which demonstrates that SNA had a pronounced variation, exhibiting peak values during haze periods, in good agreement with the variation of PM2.5 mass concentration and the correlation coefficient R between SNA and PM2.5 can reach 0.83. In addition, SNA had the same variation during the whole sampling period, which suggests that they have likely originated from similar processes.

Figure 4. Variation of daily mean mass concentrations of SO42-, NO3-and NH4+ in PM2.5 at the IAP from 10/04/2013 till 08/06/2013.

Compared with clear days (see Table 1), both mass concentrations and percentages of SNA in PM2.5 are enhanced sharply during haze, demonstrating the accelerated chemical formation of SNA under haze conditions. SNA mass percentages in PM2.5 increased sharply up to 56%, 54% and 61% during HE1, HE2 and HE3, respectively, from 26% during clear days. In general, the contributions of SNA to PM2.5 were more than 50% during all three haze episodes, indicating that SNA were the most important compounds for PM2.5 during haze in spring 2013.

Even though certain differences in the proportion of SNA in PM2.5 among these three haze episodes can be observed. NO3- and SO42- mass percentages varied in HE1, HE2 and HE3 (Table 1). HE1 had the highest NO3- mass percentage while HE2 and HE3 had higher SO42- mass percentages. Therefore, HE1 was affected much more by nitrate, while HE2 and HE3 were influenced much more by sulfate. It is interesting that these variations coincide with air temperature changes. During HE1, the mean temperature was 11°C but during HE2 and HE3, the mean temperatures were 22°C and 21°C, respectively. As NH4NO3 is more volatile, only small amounts of NO3- can be kept in PM under high temperatures. As a result, we believe that the air temperature, to a certain extent, had an influence on NO3- in PM2.5 during haze episodes.

The linear regression between NH4+ and SO42−, NH4+ and [SO42−+NO3−] equivalent concentrations (µeq m-3) in PM2.5 are shown in Table 2, respectively. The slope of NH4+ and SO42− is 1.58 which is higher than unity, revealing that SO42− was neutralized completely by NH4+ and an additional NH4+ was inferred to react with NO3-. Meanwhile, the slope of NH4+ and [SO42−+NO3−] is 0.98 which is smaller than unity, implying that nitrate can be present in not only NH4NO3, but also other chemical compounds such as Ca(NO3)2 and Mg(NO3)2 (Zhang et al., 2013). These micro-morphologies have been discovered in summer haze episodes using TEM (Li and Shao, 2009a). A significant correlation between [NH4++Ca2++Mg2+] and [NO3-+SO42−] can also be found in Table 2. This agrees well with the results from a previous study which pointed out that mineral particles can have heterogeneous reactions with the precursors of NO3−, such as NOx, HNO3 and N2O5 (Li and Shao, 2009b).

Table 2. Correlations between equivalent concentrations (µeq m-3) of ions in PM2.5 at the IAP during spring 2013.

|  |  |  |  |
| --- | --- | --- | --- |
| X | Y | Y=aX | R2 |
| SO42− | NH4+ | y=1.58x | 0.94 |
| SO42−+NO3− | NH4+ | y=0.98x | 0.94 |
| SO42−+NO3− | NH4++Ca2++Mg2+ | y=1.06x | 0.92 |

Cl-, Na+, K+, Ca2+ and Mg2+ were a minor faction of water soluble ions with an average mass contribution of 15%. Previous studies pointed out that the sources of Cl- might be coal combustion, biomass burning and sea salt (Yao et al., 2002; Li et al., 2007; Li et al., 2013). The impact from sea-salt was most probably not significant because the molar ratio of Cl- to Na+ was 2.1, which is much higher than that in sea water of 1.2 (Chester, 1990; Zhang et al., 2013), indicating that Cl- originated mostly from other sources. K+ mainly comes from biomass burning, sea salt and soil (Zhang et al., 2008; Li et al., 2013). The correlation coefficient (R) of Cl- and K+ is 0.89 during HE1, which suggests that biomass burning could be the source of Cl-. Moreover, Na+ had no large variation during the whole sampling period and a good correlation (r = 0.76) with K+, meaning that Na+ and K+ could have originated from similar sources. Compared with clear days (see Table 1), both Mg2+ and Ca2+ mass concentrations and percentages decreased during haze episodes. Mg2+ had a good correlation with Ca2+ (R=0.78) and the highest mass concentration on 19 May 2013 as caused by re-suspended dust, indicating that Mg2+ and Ca2+ probably came from mineral dust. Additionally, as with Cl-, the molar ratio of Mg2+/Na+ was 0.7, which was larger than the average ratio of 0.2 in sea water (Chester, 1990; Zhang et al., 2013), indicating that sea salt could not be a major source of Mg2+. Therefore, mineral dust could be the major source of Mg2+.

3.2.3 Inorganic elements

The most abundant element in PM2.5 was Ca with an average mass concentration of 2.2 µg m-3. Ca, Mg, Al and Fe showed similar variation patterns (Figure 5) and had no peak concentrations during haze, but had peak concentrations during the re-suspended dust event on 19 May 2013, indicating that they might have originated from similar sources like crustal sources, agreeing well with the above mentioned results from water soluble Ca and Mg. These four elements accounted for 67% of all measured elemental mass. Compared with clear days, mass percentages of these four elements decreased during haze episodes. However, mass concentrations during HE2 increased, probably due to a local source, such as reconstruction activities on the roof during corresponding sampling days.

Figure 5. Variation of daily mean mass concentrations of Mg, Al, Ca and Fein PM2.5 at the IAP from 10/04/2013 till 08/06/2013.

The most abundant trace element was Zn with an average mass concentration of 238 ng m-3. Zn, As and Pb followed a similar pattern, especially the peak concentrations during haze (Figure 6). The sources of Zn, As and Pb are mainly from the anthroposphere, such as traffic and industry (Li et al., 2004; Wang and Mulligan, 2006; Shi et al., 2010; Tian et al., 2010; Soriano et al., 2012; Xu et al., 2012). These trace elements tend to have potential health impact (Magari et al., 2002; Kang et al., 2011; Sun et al., 2014). Thus, anthropogenic sources play an important role in producing haze and might cause adverse influences on human health.

Figure 6. Variation of daily mean mass concentrations of Zn, As and Pbin PM2.5 at the IAP from 10/04/2013 till 08/06/2013.

3.3 Impact of meteorological parameters on haze formation and visibility

Meteorological parameters during haze and clear days are listed in Table 3. Temperature and air pressure had no significant differences between haze and clear days, except for temperature which was lower during HE1. Relative humidity during haze episodes was significantly higher than during clear days (31%). The previous studies pointed out that a high relative humidity could favour the formation of secondary inorganic ions (Sun et al., 2006). The lower wind speed (3.0, 2.3 and 2.1 m s-1 during HE1, HE2 and HE3, respectively) and MLH (680 m, 770 m and 530 m during HE1, HE2 and HE3, respectively) during haze episodes in comparison with clear days (wind speed: 4.1 m s-1; MLH: 1400 m) can accelerate the increase of pollutants which leads to a high mass concentration of particles and the formation of haze. In general, the main meteorological differences between haze and clear days were the relative humidity and MLH.

Table 3. Average values of PM2.5 mass concentration, meteorological parameters and visibility during haze episodes and clear days at the IAP.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | HE1 | HE2 | HE3 | Clear |
| PM2.5 (µg m-3) | 164 | 164 | 125 | 51 |
| Temperature (℃) | 11 | 21 | 21 | 18 |
| Relative Humidity (%) | 66 | 57 | 80 | 31 |
| Air pressure (hPa) | 1014 | 1014 | 1008 | 1011 |
| Wind speed (m s-1) | 3.0 | 2.3 | 2.1 | 4.1 |
| Mixing Layer Height (m) | 680 | 770 | 530 | 1400 |
| Visibility (km) | 4 | 5 | 4 | 10 |

Correlations between visibility and meteorological parameters were also investigated. Visibility showed a significant negative correlation with RH (correlation coefficient R=-0.84), indicating that visibility decreased with the increase in RH. In addition, visibility had a strong negative correlation with PM2.5 mass concentration (correlation coefficient R=-0.71), which meant that visibility decreased when PM mass concentration increased. Moreover, EC, Cl-, NO3-, SO42-, NH4+, K+, Zn and Pb had significant negative correlations with visibility. In general, visibility is highly correlated with most anthropogenic compounds.

3.4 Regional transport

Backward trajectories were calculated by applying HYSPLIT 4. Four trajectory clusters of air flow path were found (Figure 7). They are “Northerly flow” (cluster 1, N flow) which is air flow coming from the North, “Long-range Northwesterly flow” (cluster 2, long-range NW flow) which is air flow orignating from the Northwest of Beijing by long-range transport, “North-Southeasterly flow” (cluster 3, N-SE flow) which shows the air flow from the North but reaching Beijing from the Southeast and “Southeasterly flow” (cluster 4, SE flow) which expresses the air flow from the Southeast of Beijing, respectively. Consequently, N, long-range NW, N-SE, and SE flows accounted for 27%, 17%, 15% and 42% of all air flows in spring 2013, respectively.



Figure 7. Four clusters of backward trajectories at the IAP in spring 2013: cluster 1 (red line, Northerly flow), cluster 2 (dark blue line, long-range Northwesterly flow), cluster 3 (green line, North-Southeasterly flow) and cluster 4 (light blue line, Southeasterly flow).

All sampling days can be divided into four groups (Table 4) according to these four clusters. The highest PM2.5 mass concentration (117 µg m-3) was found in SE flow, followed by long-range NW flow (83 µg m-3), N-SE flow (70 µg m-3) and N flow (60 µg m-3). The SE flow was the shortest trajectory (Figure 7), indicating the presence of a relatively stagnant atmosphere favourable for the accumulation of air pollutants leading to high PM2.5 mass concentration.

Table 4. Summary of daily mean PM2.5 and chemical compounds mass concentrations from different directions in spring 2013 (unit: µg m-3, Zn and Pb: ng m-3).

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Direction | PM2.5 | PM2.5/PM10 | NO3- | SO42- | NH4+ | Zn | Pb |
| N | 60 | 0.4 | 5.6 | 6.5 | 3.9 | 116 | 90 |
| Long-range NW | 83 | 0.4 | 5.2 | 6.0 | 3.4 | 169 | 84 |
| N-SE | 70 | 0.6 | 11.9 | 10.9 | 7.1 | 196 | 167 |
| SE | 117 | 0.6 | 19.7 | 26.2 | 15.2 | 359 | 275 |

The discussion above pointed out that SNA, Zn and Pb were the most important compounds during haze episodes. Therefore, only these five compounds will be discussed here and are also divided into four groups on the basis of four clusters. Mass concentrations of these five compounds from different airflows are shown in Table 4. The highest mass concentration of these compounds was from SE air flows, followed by N-SE air flows. Therefore, particles from industry and secondary inorganic ions formation increased quickly when the air flow originated from the SE and N-SE. The ratio of PM2.5/PM10 (TEOM) showed the same variation (see Table 4). It increased from 0.4 to 0.6 when the direction of the cluster turned to the Southeast. Hence, more fine particles were contributed from southerly air flow.

In addition, the distribution of the four clusters of backward trajectory analyses during the three haze episodes and clear days are shown in Figure 8. All haze episodes were dominated by SE flow while clear days were characterized by N and long-range NW flows. Thus, Beijing was significantly affected by air pollutant emission sources (cities and industry) located in the South in the Hebei Province and Tianjin Municipality.

Figure 8. The distribution of the four clusters of backward trajectory analyses during the three haze episodes and clear days.

1. **Conclusions**

PM2.5 pollution was found to be heavy during spring haze episodes. Secondary organic carbon was estimated but did not play an important role in these spring haze events. Similar to other studies (Li et al., 2010; Ji et al., 2014; Tao et al, 2014; Wang et al., 2014a, b; Zhang et al., 2014a, b; Han et al., 2015; Huang et al., 2015; Zheng et al., 2015), SNA (SO42-, NO3- and NH4+) were the most important compounds in PM2.5 during spring haze in 2013 which can constitute more than 50% of PM2.5 mass concentrations. The characteristics and sources of PM in seasonal perspective are given in Shen et al. (2015). There was no haze found to be caused by dust invasion. The difference when compared to previous studies is even though most of haze events were contributed by southerly air flows, very small amount of haze events was found to be contributed by Northerly air flows. Besides this, anthropogenic elements, for instance Zn and Pb, were also important for spring haze. Even though SNA were the most important fraction of these three haze episodes, the differences between these three haze episodes were found. HE1 was affected much more by nitrate, while HE2 and HE3 were influenced much more by sulphate. This could be caused by the variation of air temperature. Regional transportation was another important factor for favouring the haze formation. Backward trajectories and cluster analysis showed that SNA, Zn, Pb and As during spring haze periods in 2013 were mainly transported from south-easterly located polluted industrial and urban regions to Beijing. Most haze happened when air was transported to Beijing from south-easterly regions. Therefore, in order to improve air quality, the reduction of the emissions of precursors of SNA, such as SO2, NOx and NH3 from south-easterly areas of Beijing, becomes increasingly important.

Consequently, this study gives comprehensive information on PM2.5 exposure during spring haze episodes in 2013 following the severest haze pollution event which happened in January 2013. Investigating the characteristics of particles during spring haze is useful to have a full understanding of haze in different seasons. It is also helpful to look into the agreements and differences between the different haze episodes. Thus, it may be helpful to develop different strategies to improve air quality in accordance with the corresponding sources during different haze episodes.

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