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RESEARCH ARTICLE

Impact of emission control on $PM_{2.5}$ and the chemical composition change in Beijing-Tianjin-Hebei during the APEC summit 2014

Wei Wen[1,2] · **Shuiyuan Cheng**[1,3] · **Xufeng Chen**[4] · **Gang Wang**[1] · **Song Li**[1] · **Xiaoqi Wang**[1] · **Xiaoyu Liu**[1]

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Abstract The success of the emission reduction measures undertaken by authorities in the Asia-Pacific Economic Cooperation summit 2014 demonstrated that the Beijing-Tianjin-Hebei air quality can be improved by introducing integrated emission reduction measures. This paper combines observation data, emission reduction measures, and air quality simulations that were applied before, during, and after the emission control measure implement to analyze the chemical composition change and relationship between emissions and concentrations of pollutants in region. The 24-h $PM_{2.5}$ samples were collected in the city Beijing, Shijiazhuang, and Tangshan during the period of 20 October to 25 November, 2014. The total $PM_{2.5}$ mass was measured. $PM_{2.5}$ samples were used for the analysis of inorganic elements, selected ions, and organic carbon (OC) and element carbon (EC). $PM_{2.5}$ concentrations during the emission control period were decreased. Total $PM_{2.5}$ concentrations were reduced by 54, 26, and 39 % when compared to non-emission control period in Beijing, Shijiazhuang, and Tangshan. The average element concentrations were reduced significantly by 75 % in Beijing, 37 % in Shijiazhuang, and 36 % in Tangshan. After the Asia-Pacific Economic Cooperation (APEC) conference, the average element concentration increased. At both cities, the concentration secondary water-soluble ions, primary carbon, and element carbon were reduced. However, the concentration of secondary carbon species increased in Beijing due to photochemical oxidants change. More stringent control of regional emissions will be needed for significant reductions of fine particulate pollution in the region to continue to improve air quality.

Keywords AEPC summit · $PM_{2.5}$ emission control · Chemical composition · Emission control assessment

Responsible editor: Philippe Garrigues

✉ Shuiyuan Cheng
chengsy@bjut.edu.cn; bjutpaper@gmail.com

[1] College of Environmental and Energy Engineering, Beijing University of Technology, Beijing, People's Republic of China 100124

[2] Environmental Meteorology Forecast Center of Beijing-Tianjin-Hebei, Chinese Meteorological Administration, Beijing 100089, China

[3] Collaborative Innovation Center of Electric Vehicles, Beijing 100081, China

[4] Tangshan Environmental Monitoring Station, Tangshan 063000, China

Introduction

In 2014, "APEC blue" has become a catchphrase with citizens. APEC blue was blue skies overhanging Beijing during the 2014 Asia-Pacific Economic Cooperation (APEC) Leaders' Meeting. The strictest pollution control measures were enforced for the APEC summit to significantly improve the city's air quality. The details of the measures have been presented elsewhere (Beijing Municipal Environmental Protection 2014). The measures were effective for every activity that was a potential pollution source, including vehicle emissions, industry, construction, and so forth. APEC blue provided us with an invaluable opportunity to understand the pollution reduction potential in Beijing-Tianjin-Hebei. During the 2 November 2014 to 12 November 2014, the emission control measure implemented. The average $PM_{2.5}$ concentration was 43 $\mu g/m^3$ in Beijing during the measure implement period. Corresponding to the same periods in 2013, the concentration was 95 $\mu g/m^3$ (CNEMC 2014). This event condensed a comprehensive air quality management plan into a short-term

aggressive abatement and reveals the air quality improvements' potential under comprehensive control.

In the past decades, $PM_{2.5}$ pollution has become a severe environmental challenge facing China. The Chinese government made great efforts to reduce the air pollution. A series of air pollution control plans have been issued by both central and local Chinese governments in order to effectively control regional $PM_{2.5}$ pollution and to improve air quality. For example, on 12 September 2013, a plan titled "National Action Plan for Air Pollution Prevention and Control" was released by the central government of China. According to this plan, the key regions need to reduce the annual average concentration of $PM_{2.5}$ by 25 % in 2017 (compared to their 2012 $PM_{2.5}$ concentration levels) (China State Council 2013). Beijing and Hebei Province also released its own Provincial Air Pollution Prevention and Control Action Plan, which is even more stringent than the national control target. The plan requires the city of Beijing to reduce its annual average $PM_{2.5}$ concentrations in 2017 within 60 $\mu g/m^3$ (The Government of Beijing 2013). The plan of Hebei requires the key cities in the region to reduce its annual average $PM_{2.5}$ concentrations by 33 % instead of 25 % in 2017 (Provincial Government of HeBei 2013). The goal of $PM_{2.5}$ concentration reduction will be enforced as the part of the evaluation standards in the annual performance review of the local governments. With the case study of emission control measures for APEC, our understanding of the source control and dynamics affecting pollutants in the Beijing-Tianjin-Hebei environment could be improved. To learn from the success of the emission control event of APEC is critically important for further air quality management. It will benefit not only for Beijing-Tianjin-Hebei (BTH) but also for other regions of China.

Several field studies have investigated the effect of the pollution control measures on the surrounding environment. For example, in 2008, the Beijing Olympic Games Zhou et al. (2012) focus on assessing the effects of different restriction policies implemented during and after the 2008 Olympic Games. Wang et al. (2010) reveal different responses of secondary pollutants to the control measures from primary pollutants. Okuda et al. (2011) investigated the difference in the concentrations of air pollutants between the period of the Beijing 2008 Olympic Games and the same periods in the prior 3 years. Also in Guangzhou during the Asian Games, Liu et al. (2013) combines observation data, emission reduction measures, and air quality simulations that were applied in Guangzhou to analyze the relationship between emissions and concentrations of pollutants during the Asian Games. It is found that the reductions of 19-day average NO_2, SO_2, and PM_{10} concentration in Guangzhou are 58.9 $\mu g/m^3$ (51.3 %), 66.3 $\mu g/m^3$ (66.8 %), and 21.2 $\mu g/m^3$ (21.4 %), respectively. However, it was still very difficult to resolve the complex effects between the changing emissions and $PM_{2.5}$ concentration. As non-linear chemical and physical processes was important for secondary $PM_{2.5}$ formation. Also, meteorological conditions had a great impact on the air quality during the emission control.

These aggressive intervention emission control measures offer a good opportunity to understand if the complex relationship between emission reduction and air quality improved. The purposes of this study are to present the first results of the long-term measurements of chemical compositions of $PM_{2.5}$ in Beijing, Tangshan, and Shijiazhuang before, during, and after the emission control for APEC and to assess how great an impact pollution control had on the air quality of the region, especially on the chemical composition of the particulate matter so that we could get a much clearer understanding of emission reduction potential and complex effects between the changing emissions and $PM_{2.5}$ concentration. It would help to formulate a long-term strategy for reducing the air pollution of china.

Methodology

Emission reduction in different control strategies

To improve air quality during the APEC meetings, BTH government has taken several steps in different strategies to implement emission control measure. In total, forth phases of new policies were implemented during 2 to 12 November 2014. Beijing from 2 to 12 November, mandatory restrictions were implemented for personal vehicles, permitting them on roads only on alternate days depending on license plate numbers (odd-numbered vehicles on odd-numbered days and even-numbered vehicles on even-numbered days). During the conference, all construction activities were placed on hold. Point sources in Beijing were supervised strictly to reduce emissions. Trucks transporting mud, stone and chemicals, and heavy-emission vehicles are not permitted to drive on Beijing roads during the summit (BMEPU 2014). Based on the above reduction plan, the emission factor method applied to calculate the reductions of pollutant (SO_2, NO_x, $PM_{2.5}$, VOCs) emission. Moreover, the no-reduction emission inventory was updated to 2013 based on inventory of Beijing 2012. Compared to the no-reduction emission inventory, the emission reduction rates were 53 % of SO_2, 50 % of NO_x, 55 % of $PM_{2.5}$, and 27 % of VOCs. The emission inventory update methods were described by our colleagues study (Lang et al. 2013). Since, it has been shown that Beijing's air quality problems also have regional effects (Wang et al. 2010). Emission controls on large industrial sources were also applied in surrounding cities from 2 November. Local governments of Hebei and Tianjin have ordered companies, such as cement factories, iron and steel mills, and coking plants, to stop or limit production. Around 1000 factories in Hebei Province have been ordered to stop production temporarily, and 881 construction sites have been closed for the meetings. Since 6 November, several cities plus strengthened measures for improving air quality. For example,

several municipal areas take on the odd-and-even-license plate rules to restrict vehicles on roads. More factories in Hebei Province have been ordered to stop production. Table 1 shortly summarizes the emission reductions from each phase.

Modeling description

In this present work, $PM_{2.5}$ is simulated using the Models-3/Community Multiscale Air Quality (CMAQ) modeling system (Version 4.7.1), developed by the US EPA (Binkowski and Roselle 2003). The CMAQ model has received many applications and evaluations in China (Zhang et al. 2012; Liu et al. 2010a, b). The meteorological circulation was simulated by the Weather Research Forecast model (WRF, v3.3). The physical options used in this study include WRF single-moment 3-class microphysics scheme, rapid radiative transfer model (RRTM) long wave radiation scheme (Mlawer et al. 1997), Dudhia shortwave radiation scheme (Dudhia 1989), NOAH land surface model (Chen and Dudhia 2001), Yonsei University planetary boundary layer scheme (Hong et al. 2006), and Kain-Fritsch cumulus parameterization scheme (Kain 2004). The initial and boundary conditions for the WRF simulation were prepared using the 1 × 1 resolution final global tropospheric analyses data (FNL) which was produced by National Centers for Environmental Prediction's (NCEP) Global Forecast System (GFS).

Model application

In this study, a two-level nested-grid architecture was designed for the implementation of the coupled modeling system. The modeling domain 1 (i.e., Do1) was with a spatial resolution of 27 km. The modeling domain 2 (i.e., Do2) was with a spatial resolution of 9 km, which covers the Beijing-Tianjin-Hebei region and parts of its surrounding provinces (including the provinces of Shanxi, Shandong, Henan, Liaoning, and Inner Mongolia). The vertical dimension of CMAQ simulation was divided into 14 layers from the ground surface to planetary boundary layer (PBL). The corresponding sigma levels are 1.00000, 0.99300, 0.98300, 0.97000, 0.95400, 0.93400, 0.90900, 0.82958, 0.67830, 0.32385, 0.22827, 0.12129, 0.06938, and 0.00000. The CB05 (Carbon Bond mechanism) was chosen as the gas-phase chemistry mechanism. The raw emission data were mainly obtained from local environmental protection bureaus or administrations. The data were calculated based on the categories of activities and their emission coefficients by our colleagues. More detailed descriptions of the complete emission inventory can be found in previous works published by our colleagues (Cheng et al. 2012; Lang et al. 2013).

Table 1 Summaries of the emission reductions from each phases

Beijing					Hebei			
Step	SO_2	NO_x	$PM_{2.5}$	VOCs	SO_2	NO_x	$PM_{2.5}$	VOCs
1~2	53 %	50 %	55 %	27 %	30 %	24 %	27 %	18 %
3~5					30 %	28 %	28 %	21 %
6					30 %	31 %	28 %	23 %
7~12					67 %	53 %	39 %	39 %

Sampling program

The 24-h (09:00 to 09:00 local time) $PM_{2.5}$ samples were collected at Beijing, Tangshan, and Shijiazhuang (as shown in Fig. 1). These sampling sites were all placed on the building rooftop with even atmospheric mixing in order to reflect the condition of regional atmospheric pollution. The sampling heights are 35, 15, 20 above ground level at the Beijing Normal University (BNU), the Environmental Monitoring Station (EMS) of Tangshan, and the sampling site of Shijiazhuang. The BNU site is located between the North 2nd Ring Road and North 3rd Ring Road, with more intensive traffic but little industrial activities. The Environmental Monitoring Station (EMS) of Tangshan is surrounded by offices and residential buildings, while two roads with heavy traffic are located 20 and 700 m away in the east and the south, respectively. The sampling site of Shijiazhuang is surrounded by residential building and traffic roads. The three sites represent the urban area condition as location surrounded by mixed commercial, traffic, and residential condition. The samples were collected during the period of 20 October to 25 November. The filters used in the samplers are Whatman 41 filters (Whatman Inc. Maidstone, UK) and the quartz filters (Whatman Inc. Maidstone, UK). All the samplers (Wuhan Instrument Cooperation Ltd.) were operated at a flow rate of 100 L/min. The sample measurements were conducted in a certified lab (Key Laboratory of Beijing on Regional Air Pollution Control, Beijing). The laboratory had carried out lots of research on $PM_{2.5}$ in recent years (Lang et al. 2013; Wang et al. 2015). All the filters were weighed before and after sample collections in the lab using 1 over 10,000 analytical balance. The filters were equilibrated in constant temperature (20±5 °C) and humidity (40±2 %) chamber for 48 h. Before placing the filters back into the samplers, all flow meters were calibrated and the sampler needed to pass the tightness test. The inorganic elements were measured by inductively coupled plasma-mass spectrometry (ICP-MS, 7500a, Agilent). The ions were analyzed by ion chromatograph (Metrohm 861 Advanced Compact IC). During the laboratory analysis, blank filter fiber and standard chemical samples were tested by ICP-MS and ion chromatograph to ensure the data quality. Quartz fiber filter samples were extracted for the analysis of the organic carbon (OC) and element carbon (EC). The OC and EC were measured using a thermal/optical carbon analyzer (DRI, Model 2001). The blank Quartz fiber filters were also analyzed for validating the sample results.

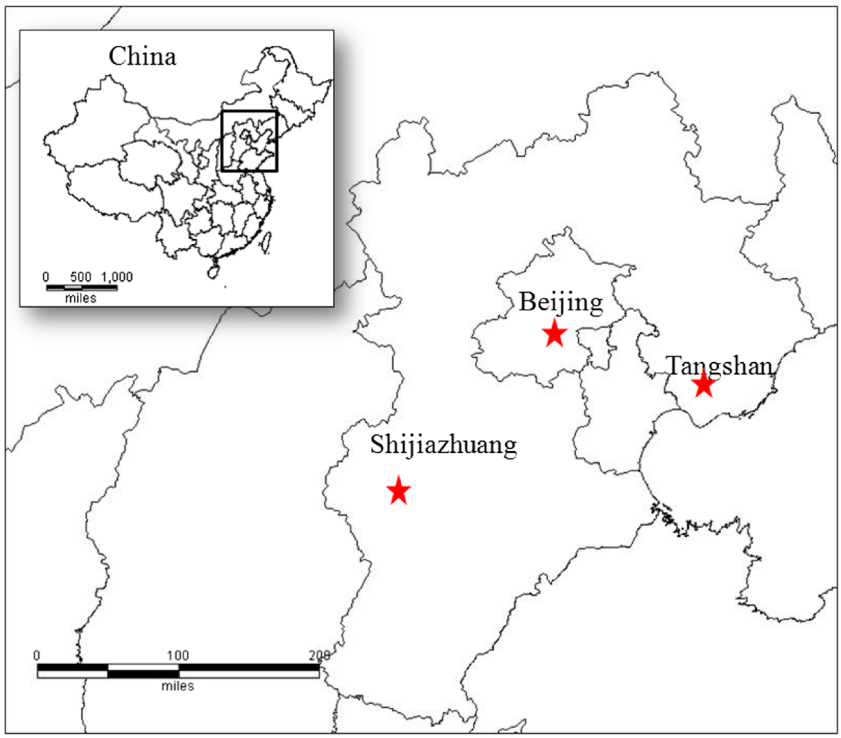

Fig. 1 The location of observation station

Results and discussion

Spatial and temporal variations of $PM_{2.5}$

The sampling program generated 36-day samples at Beijing, Shijiazhuang, and Tangshan, which is from 20 October to 25 November. The sampling program missed two samples, onw sample, and three samples at the Beijing, Tangshan, and Shijiazhuang sites due to mechanical failure (power blackout). The total $PM_{2.5}$ mass was measured for each sample, and they were plotted in Fig. 2.

It indicates that similar trends of $PM_{2.5}$ changes with time in Beijing, Shijiazhuang, and Tangshan sampling sites. Both sites experienced similar $PM_{2.5}$ pollution processes. The fact

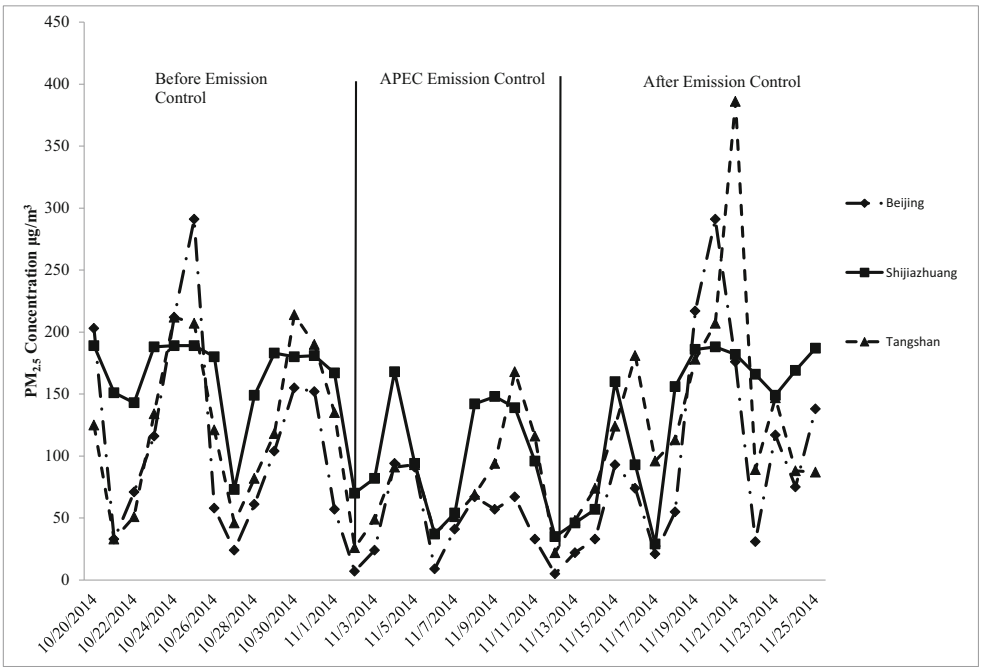

Fig. 2 Plot of temporal variations of $PM_{2.5}$ concentration at different cities

demonstrated that the $PM_{2.5}$ pollution could possibly be characterized as a regional issue. It is found that the $PM_{2.5}$ concentration has decreased trend at the region as the emission control measure implement.

The mean concentrations of $PM_{2.5}$ for each city (from 20 October to 25 November) were calculated. The Beijing sampling site had a value of 91 μg/m^3, which was 1.2 times of $PM_{2.5}$ Level II National Air Quality Standard (75 μg/m^3) (NAAQS). The $PM_{2.5}$ concentration in Shijiazhuang and Tangshan sampling sites were 135 and 116 μg/m^3, which was 1.8 and 1.5 times of the same standard. Figure 2 also shows that the $PM_{2.5}$ concentrations in Shijiazhuang sampling site were generally higher than that in the Beijing and Tangshan. The meteorological condition, emission, and terrain could be the obvious reason. However, according to emission inventory, the $PM_{2.5}$ emission in Shijiazhuang (142,319 t/year) was less than Tangshan (274,010 t/year) and it is greater than Beijing (82,465 t/year). The terrain and meteorological condition could be the main reason. Shijiazhuang is located in Taihang piedmont. The average wind speed in Shijiazhuang was relatively low during sampling period as Fig. 3 have shown. It was 7.2 m/s in Shijiazhuang, comparing with 8.2 and 9.5 m/s in Beijing and Tangshan, respectively. This unique meteorological tends to trap $PM_{2.5}$ emissions as well as the precursor gases formed to secondary nitrate and sulfate within the region.

According to the data measured, before emission control, average concentrations of $PM_{2.5}$ at Beijing, Shijiazhuang, and Tangshan sampling sites were 123, 166, and 127 μg/m^3. The concentrations were 46, 102, and 79 μg/m^3 during the emission control period in Beijing, Shijiazhuang, and Tangshan sampling sites. These pollutants have been simply reduced as a result of the pollution control measures. However, after the conference, the $PM_{2.5}$ concentration increased rapidly, which was 110 μg/m^3 in Beijing sampling site, 143 μg/m^3 in Shijiazhuang sampling site, and 147 μg/m^3 in Tangshan sampling site. It is mainly due to that the emission control measures are ended. Moreover the "heating season" began in north of China. The average $PM_{2.5}$ concentrations are decreased 54, 26, and 39 %, respectively, compared with the non-emission control days in Beijing, Shijiazhuang, and Tangshan sampling sites.

Characterization of inorganic elements and secondary water-soluble ions

Figure 4 presents the concentrations of inorganic elements in $PM_{2.5}$ at Beijing, Shijiazhuang, and Tangshan sampling sites. It shows a total of 18 inorganic elements from the $PM_{2.5}$ during the sample period.

Figure 4 shows that the concentrations of all inorganic elements at the Shijiazhuang site were higher than that of the Beijing and Tangshan in the sampling period. It also shows that the concentrations of elements in $PM_{2.5}$ were reduced when compared to the non-emission reduction period. Comparing the element concentrations before and during the emission control period, the average element concentrations were reduced significantly by 75 % in Beijing sampling site, 37 % in Shijiazhuang sampling site, and 36 % in Tangshan site. After the APEC summit, the average element concentration increased. It is increased by 62, 42, and 14 % in Beijing, Shijiazhuang, and Tangshan sampling sites.

Figure 5 shows scatter plots of the variation rate of element concentrations of inorganic elements. During emission control

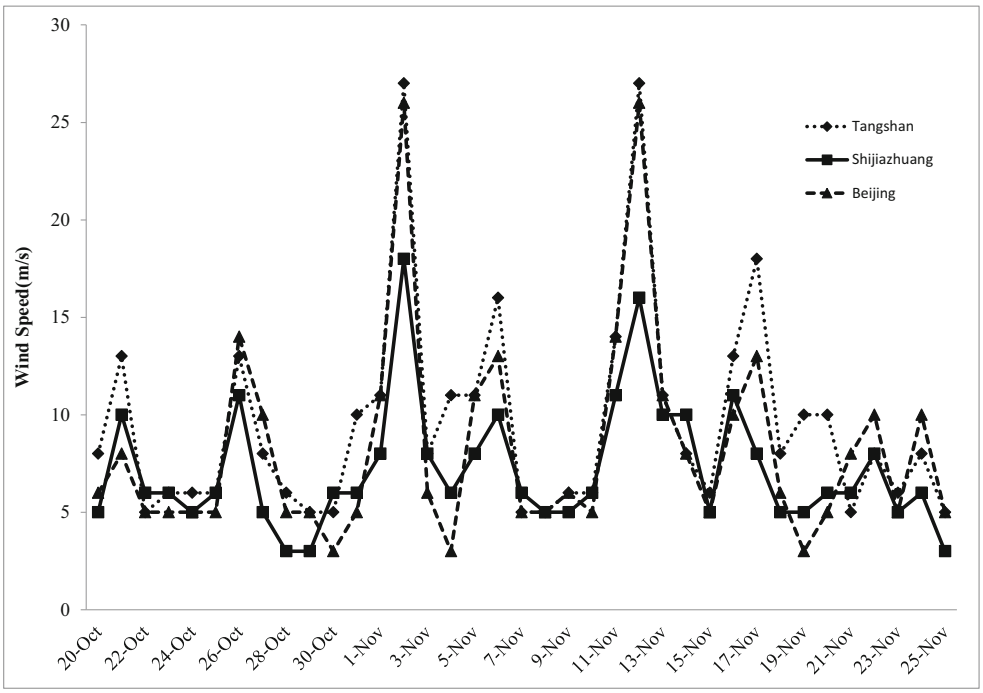

Fig. 3 Wind speed in different cities

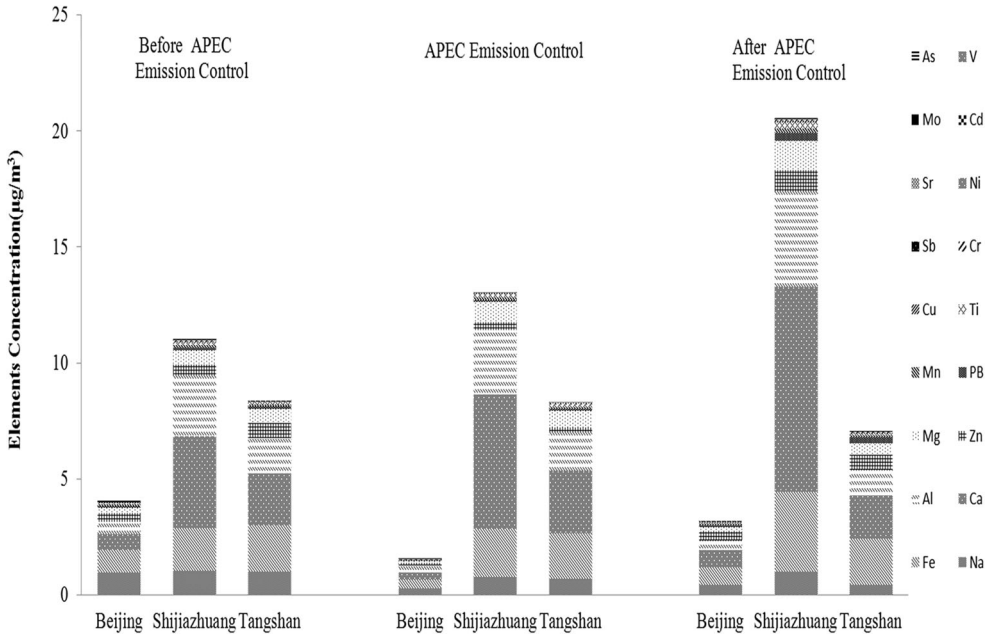

Fig. 4 The average concentrations of inorganic elements

implementation period, all of the inorganic element concentrations in Beijing site had decreased comparing with the concentration before emission control. Elements of V, Cr, and Sr were originated from metal smelting process (Gu et al. 2011); elements of Mn, Cu, Zn, and Pb came from the ceramic production, road traffic, and copper and zinc metallurgy (Querol et al. 2007). There were a number of emission reduction measures undertaken in Beijing. Halting production in polluting factories and power plant, which brought element Pb, Zn, decreased. More elements from the earth on the construction sites (such as Ca, Al, Mg, Ti) and from the diesel fuel consumed by transportation vehicles (such as V) to the residential subdivision were decreased by suspending work at construction sites and taking half of the city's vehicles off the road. While after the conference, all the element concentration increased apparently.

It was found that more difference in the pattern of inorganic element pollution phenomenon exists in Tangshan and Shijiazhuang. It is shown that some element concentrations (such as Ca, Al, Mg, Ti) were increased during the emission control period. It is understood that those elements were mainly form soil dust. The meteorogical data (the wind speed) were calculated of the sampling site, as Fig. 3 have shown. During the sampling period, especially 2, 11, and 12 November, the wind speed were relatively large. In this case, the fugitive dust emissions from the bare land were increased. The high concentration of elements (Ca, Al, Mg, Ti) caused by the strong winds. It also indicates that Tangshan and Shijiazhuang had poor control effects of unorganized dust comparing with Beijing.

Secondary water-soluble ions (SWSI) include SO_4^{2-}, NO_3^-, and NH_4^+. They were the major water-soluble ions in the $PM_{2.5}$ samples collected from the period. The sum of SWSI concentration was accounting for 27~53 % in $PM_{2.5}$ mass ratio, during the APEC summit in the region. Figure 6 presents the average concentrations of SWSI in each period at three cities.

NO_3^- had the highest concentrations in Beijing site and the lowest in Tangshan site during sampling period. SO_4^{2-} concentration in Shijiazhuang was highest. It was the lowest in Beijing site. Before, during, and after emission reduction, NO_3^- and SO_4^{2-} concentrations have the same spatial variation trend. However, the NH_4^+ spatial variation in different emission control stage was quite different. Comparing emission reduction with noreduction days, the SO_4^{2-}, NO_3^-, and NH_4^+ concentration in Beijing site reduced by 67, 55, and 57 %, respectively. In Tangshan, those three ions reduced by 54, 34, and 39 %. In Shijiazhuang site, the SO_4^{2-}, NO_3^-, and NH_4^+ reduced by 57, 52, and 57 %. SO_4^{2-} had the highest reduction rate at the region. This fact demonstrated that the halting coal burning is an effective method to control pollution in region. The low SWSI concentration associated mainly with the emission reduction as well as the better atmospheric conditions for air pollutant dispersion during the emission reduction period.

Carbon species and $PM_{2.5}$ mass balance

The carbon species were important chemical components of $PM_{2.5}$ in the region. The carbon species are usually classified into OC and EC. OC is composed of primary OC (POC) and secondary OC (SOC). Figure 7 presents the monthly average POC, SOC, and EC concentrations from all samples.

The average OC concentrations before emission reduction period were 15.05, 18.66, and 24.17 μg/m^3 in Beijing, Tangshan, and Shijiazhuang sampling sites. During the emission control days, the main carbon source (such as coal burning,

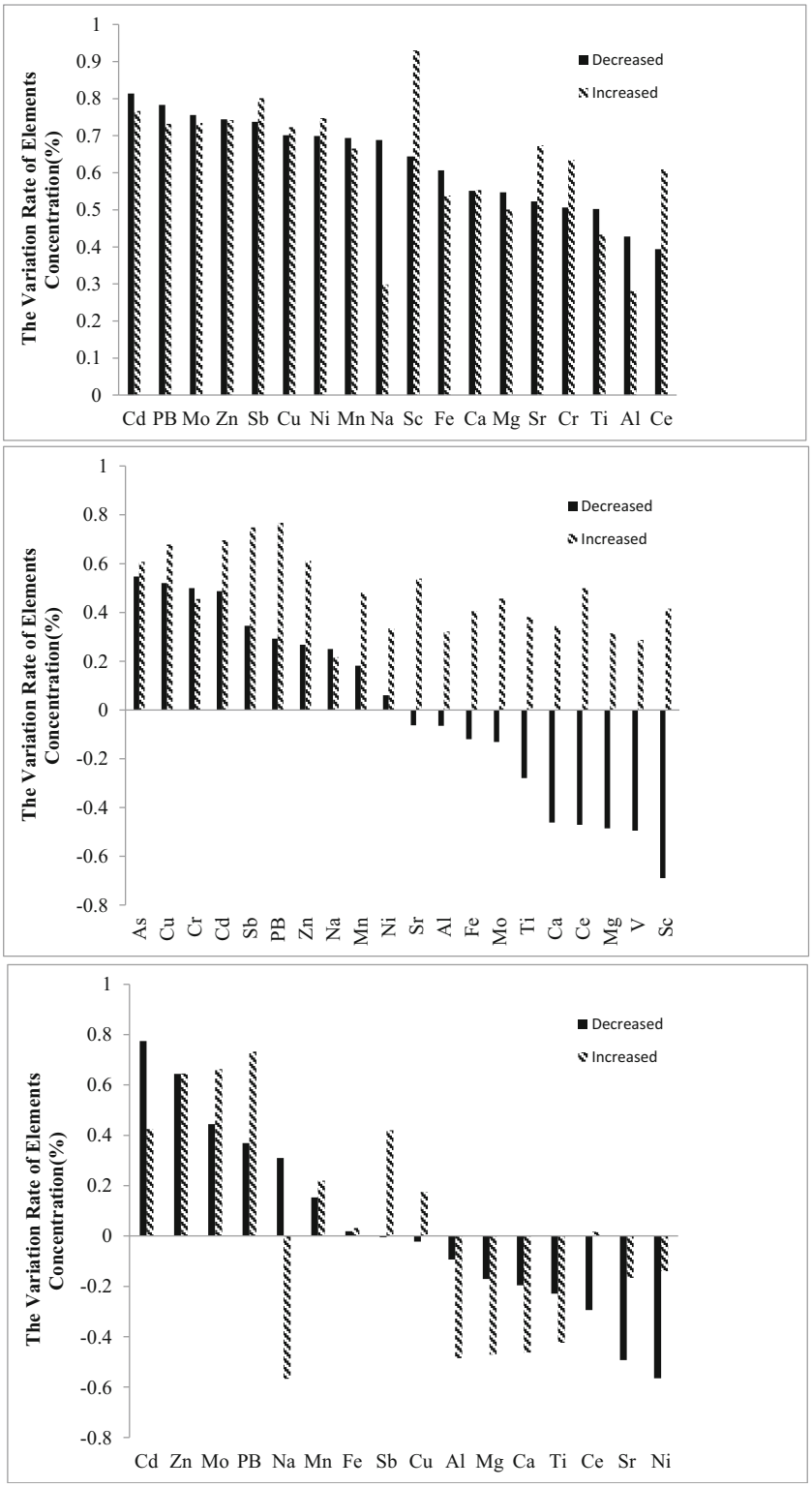

Fig. 5 Variation of element concentrations in different regions. (*Decreased*: comparing average element concentrations before and during control measure implement; *Increased*: comparing average element concentrations during and after control measure implement)

vehicle, etc.) reduced. As a result, the OC concentration in emission control period is with an average reduction rate of 54, 15, and 41 % in Beijing, Tangshan, and Shijiazhuang sites. It is shown that there was similar decreasing trend between OC and EC. The average EC concentrations before emission control were in the range 4.14~6.4 μg/m^3 in BTH region (average concentration of Beijing, Tangshan, and Shijiazhuang sites). The average reduction rates were 54, 19, and 44 %, respectively, in Beijing, Tangshan, and Shijiazhuang sites. However, after APEC, the carbon species concentration

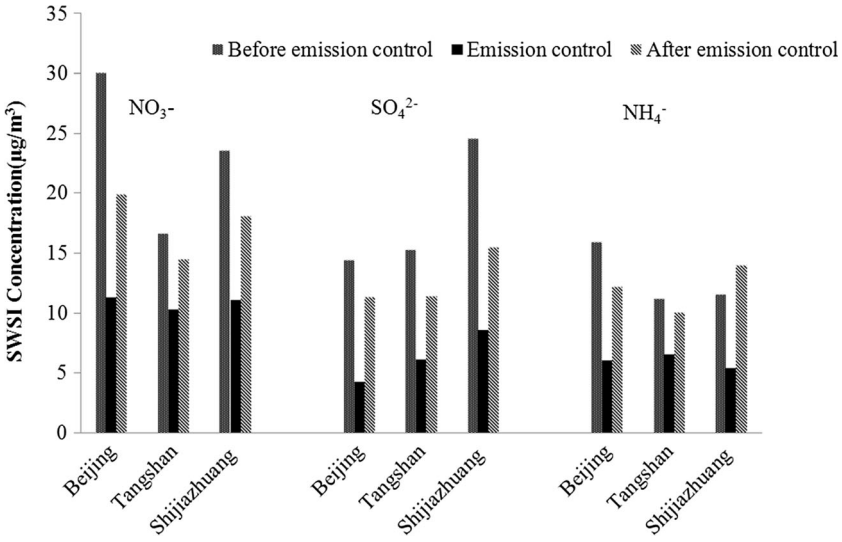

Fig. 6 The average concentrations of SWSI in each period

increased to varying degrees. The concentrations of carbon species were also larger than it was before emission control days. It is because odd-and-even-license plate rules of restrict vehicles are over. The heating season also began since 15 November. The coal usage for heating was increased by residential. It increased carbon emissions largely. Comparing concentrations after and during control measure implement period, OC and EC concentration increased 58 and 61 % in Beijing. In Tangshan, OC concentration increased 16 %, while EC concentrations increased 42 %. The OC and EC in Shijiazhuang site had substantial growth, in which ratios were 69 and 80 %. The different variation of carbon concentration is because the growth number of vehicle was different. Meanwhile, the way of heating that was different in cities leads to the different pollutant emission. For example, in Beijing, the measure of heating is to take gas boiler by central heating system. However, due to the underdeveloped economy in Heibei Province, coal burning is the main measure of heating.

The ratio of OC/EC was often used to evaluate the formation of SOC. Usually, the SOC can be formed when the ratio of OC/EC is over 2 (Chow et al. 1996). SOC was calculated by EC tracer method (Castro et al. 1999). The average SOC concentration was 3.2, 4.7, and 4.5 μg/m^3 at the Beijing, Tangshan, and Shijiazhuang, respectively. The SOC concentration decreased in Tangshan and Shijiazhuang by 19 and 44 %. However, the SOC concentration was increased by 50 % at Beijing sampling site when emission reduction undertaken during 2 to 12 November. It is mainly because photochemical oxidant capacity changed, subsequently affecting the formation of secondary components of $PM_{2.5}$. The average O_3 concentrations in Beijing was increased by 36 % comparing before (20 October to 2 November) and during emission control measure implement period (2 to 12 November) (CNEMC 2014). It might indicate a potential impediment to further $PM_{2.5}$ reduction in the region.

In this study, total $PM_{2.5}$ mass balance during emission reduction period was calculated. The mass balance was classified into primary compositions and secondary compositions. Primary compositions included soil dust, primary organic matter, elemental carbon, and pollution elements (He et al. 2011). The secondary compositions included secondary

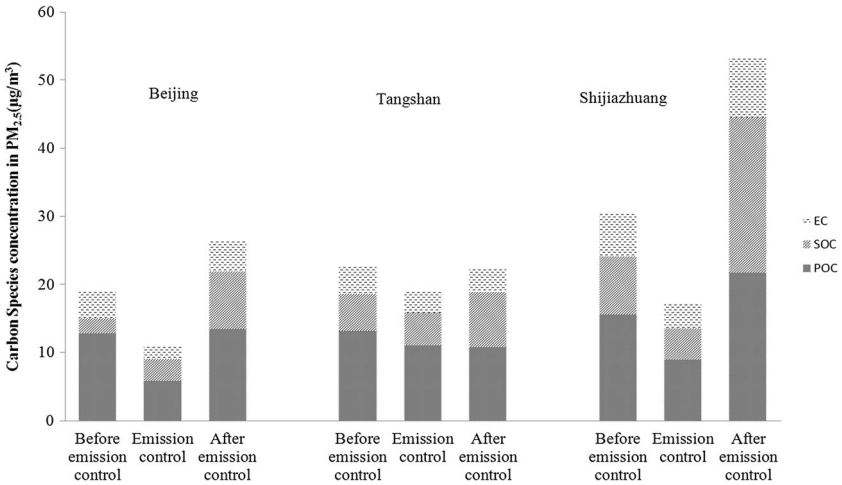

Fig. 7 The average POC, SOC, and EC concentrations

organic matter, SO_4^{2-}, NO_3^-, and NH_4^+. The mass of soil dust was estimated using the oxides of Al, Ca, Ti, Fe, Mg, Na, and K, and the equation is given below (Kim et al. 2001):

$$\text{Soil dust} = 2.20 \times \text{Al} + 2.49 \times \text{Si} + 1.63 \times \text{Ca} + 2.42 \times \text{Fe} + 1.94 \times \text{Ti} \quad (1)$$

In this study, Si was not measured due to lack of standard solution and method for this element, and its concentration was estimated to be four times of Al concentration (Yuan et al. 2008). Secondary organic aerosol (SOA) and primary organic aerosol (POA) can be converted from SOC and POC by multiplying a coefficient of 1.6 (Chow et al. 1996). Pollution elements contain the inorganic elements (As, V, Mo, Cd, Sr, Ni, Sb, Cr, Cu, Mn, Pb, Zn) which related to anthropogenic activity. Figure 8 gives the chemical compositions in mass percentage for the $PM_{2.5}$ samples collected at Beijing, Tangshan, and Shijiazhuang.

In Tangshan and Shijiazhuang, the soil dust had the highest mass percentage in the $PM_{2.5}$ total mass, which were 23 and 27 % separately. It is due to poor control of unorganized dust in those cities. Among all the compositions, POA and element carbon were accounting for 23, 29, and 16 % in $PM_{2.5}$ mass concentration. Coal burning was the main source of carbon species. The total coal consumption in Tangshan was 98.112 million tons in 2011 (BST 2012). It was 22.698 million tons and 54.08 million tons in Beijing and Shijiazhuang (BSB 2012; BSS 2012). The mass percentage of secondary compositions out of the total $PM_{2.5}$ ranged from 38~65 %, with the highest appearing in Beijing site. The percentage of NO_3^- was highest in all the secondary particulates. The percentages of NO_3^- were 22, 11, and 14 % in Beijing, Tangshan, and Shijiazhuang sites. Vehicle was the major source of NO_3^-. While, industrial was the main source of SO_4^{2-}. During the APEC summit, the industry emission was largely reduced in the region. The contribution of industrial to $PM_{2.5}$ decreased and the contribution of vehicle increased correspondingly.

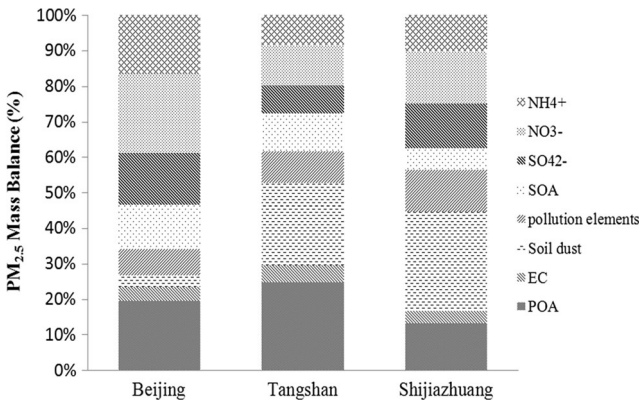

Fig. 8 Chemical compositions in mass percentage for the $PM_{2.5}$

Model verification

In this study, the normalized mean bias (NMB), normalized mean gross error (NME), and correlation coefficient (RC) were used to assess the performance of the CMAQ simulation (USEPA 2007). The simulated concentrations of $PM_{2.5}$ and the three inorganic particle components in (SO_4^{2-}, NO_3^-, NH_4^+) were compared with the monitoring data for target simulation period. The model verification results are presented in Table 2. The $PM_{2.5}$ mass simulated results and monitored data were plotted in Fig. 9.

Table 2 gives the statistical results through comparing the simulated and monitored 24-h average concentrations of $PM_{2.5}$. Specifically in Beijing, Shijiazhuang, and Tangshan sites, the NMB values for the simulation of $PM_{2.5}$ in those three cities were −13, −6, and 2 %. It is slightly underestimated at the Beijing site and Shijiazhuang site while overestimated at city of Tangshan. The model slightly underpredicted $PM_{2.5}$ concentrations in Beijing site (91.2 μg/m^3 monitoring vs simulation 79.5 μg/m^3) and Shijiazhuang site (135.1 μg/m^3 monitoring vs simulation 125.0 μg/m^3), which may be due to an underestimation of regional emissions and also model issue. The model usually did not perform well in heavy pollution. For example, in 19 November, Beijing $PM_{2.5}$ observation concentration was 217 μg/m^3. However, the simulation results only appeared 146 μg/m^3.

The NME values for the simulation of $PM_{2.5}$ in the different cities were 30, 23, and 34 %, respectively. The NME values from the simulation were generally large, and the errors might be from the following: (1) Emission inventories could be highly uncertain at individual sites, which would affect the accuracy of simulation results; (2) the uncertainties associated with the meteorology simulation could also affect the results.

Table 2 Comparison of monitored data with simulated results (24-h average concentrations: %)

		Monitor	Simulation	NMB	NME	RC
$PM_{2.5}$	Beijing	91.2	79.5	−13	30	81
	Shijiazhuang	135.1	125.0	−6	23	75
	Tangshan	116.2	118.1	2	34	68
SO_4^{2-}	Beijing	6.1	5.5	−3	46	74
	Shijiazhuang	11.1	7.5	−15	48	50
	Tangshan	7.5	10.3	39	65	50
NO_3^-	Beijing	18.3	17.1	−7	59	59
	Shijiazhuang	14.0	13.9	−4	68	31
	Tangshan	11.2	16.3	45	72	64
NH_4^+	Beijing	9.9	7.1	−24	50	62
	Shijiazhuang	9.7	8.4	−13	66	36
	Tangshan	8.7	7.1	−19	49	49

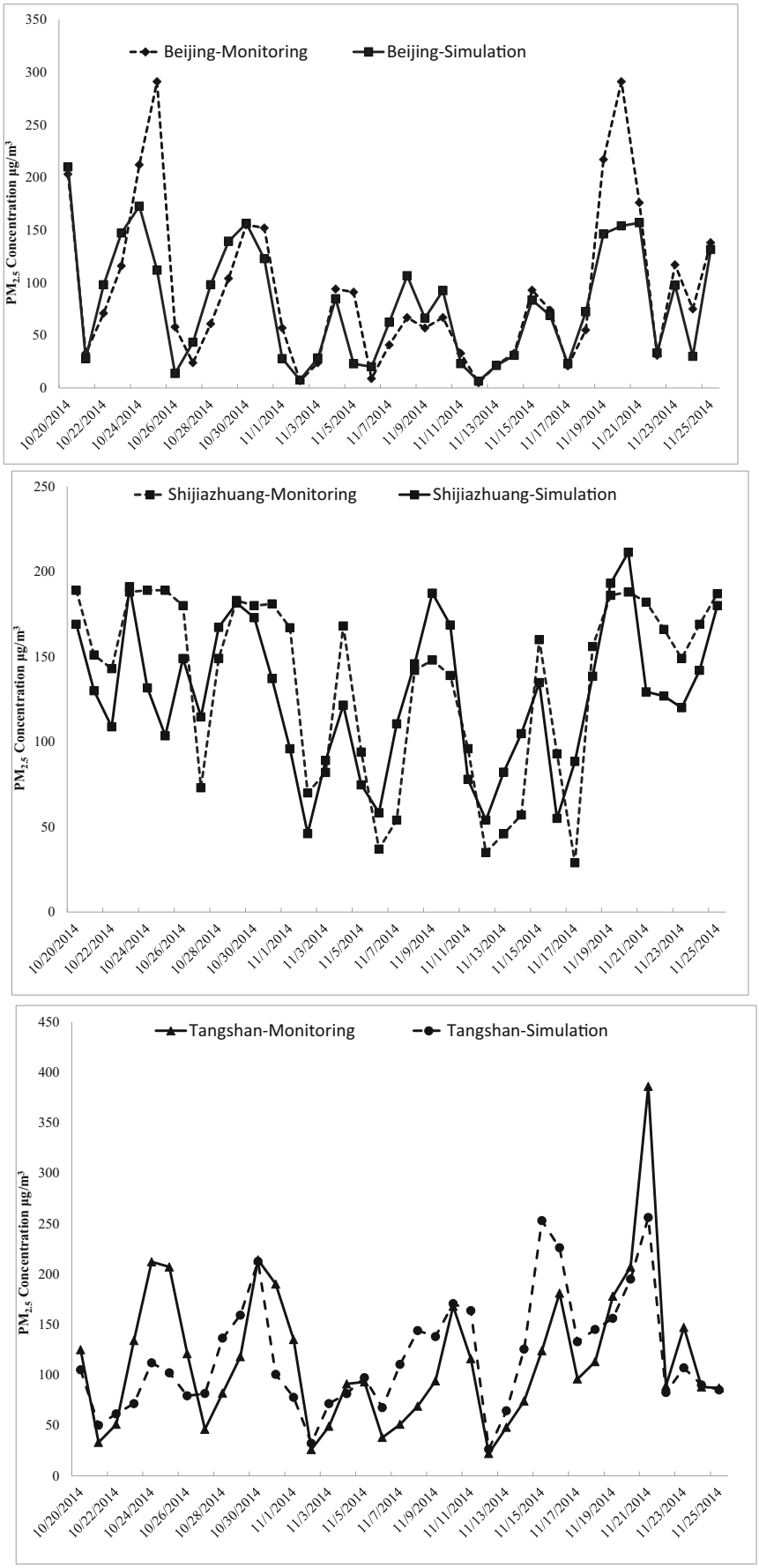

Fig. 9 Plot of $PM_{2.5}$ simulated results and monitored data at different cities

In general, the correlation coefficients of $PM_{2.5}$ between modeled and observed data were good. The correlation coefficients between the simulated and observed concentrations were 81, 75, and 68 %.

Generally, most of the NMB value of secondary components were ranging from −24 to 45 %. The simulation NME values of secondary components were relatively larger than $PM_{2.5}$ concentration. Most of correlation coefficients (SO_4^{2-}, NO_3^-, NH_4^+) between simulation and monitored data were strong, except NO_3^- and NH_4^+ results in Shijiazhuang and Tangshan. Considering the inherent uncertain nature of meteorological and air quality simulation and comparing with other related studies, the simulation results in this study were acceptable (Zhang et al. 2013; Liu et al. 2010a). It is indicated that the simulation performance was acceptable.

The effect of emission control assessment

The WRF/CMAQ model was used to analyse air quality for the APEC emission control measure implement period (2 to 12 November) and assess the emission control effects for $PM_{2.5}$ reduction. The extent of the effectiveness of emission reductions varies spatially. It indicates that if no control was taken, in Beijing, Shijiazhuang, and Tangshan, the $PM_{2.5}$ concentration was 66, 143, and 112 μg/m^3 under the same weather condition. The differences were due to the controlled source emission measure in different cities and the non-linear responses toward complicated atmospheric physical and chemical processes (Cohan and Napelenok 2011). The model predicted that the emission control effect was 33 % in Beijing, 29 % in Shijiazhuang, and Tangshan was 30 %. This result indicated a significant success for the proposed air pollution abatement policy for the APEC guarantee.

In this study, the CMAQ models were also used to investigate the effect of control measures on SWSI concentrations and its precursor gases change. Based on the model simulation results, it is shown that SO_4^{2-} concentrations in Beijing, Tangshan, and Shijiazhuang were decreased by 28, 27, and 29 %. With emission reductions, the NO_3^- concentration decreased 18, 12, and 15 % in Beijing, Shijiazhuang, and Tangshan. The precursor gases (SO_2, NO_2) had much higher reduction, in which average rates were 40 % (SO_2) and 24 % (NO_2) in BTH region. The much higher reduction rate of SO_2 found in the BTH region implied that the control measures of the time were effective. The $PM_{2.5}$ precursors SO_2 and NO_x and secondary ion particulate matters SO_4^{2-} and NO_3^- decreased ratio in different cities as shown in Table 3.

The non-linear reduction rate between precursor gases and secondary particle matter was obvious. The SO_2 and NO_x concentrations decreased more rapidly than those of the SO_4^{2-} and NO_3^-. It is found that in every 1 % decrease in SO_2 surface concentration, SO_4^{2-} surface concentration decreased by 0.65, 0.75, and 0.69 % in Beijing, Shijiazhuang, and Tangshan. Previous studies have reported that the relationship between decreased concentration of SO_2 and SO_4^{2-} was non-linear. Manktelow et al. (2007) found that for every 1 % decrease in SO_2 surface concentration, SO_4^{2-} surface concentration decreased by 0.55 % across Western Europe and by 0.58 % across the USA. Fu et al. (2014) data showed that each 1 % reduction in SO_2 concentration resulted in a 0.59 % decrease in SO_4^{2-} concentration in the PRD region. Specifically, every 1 % decrease in NO_x concentration resulted in a 0.60, 0.55, and 0.65 % decrease in NO_3^- concentration in the Beijing, Shijiazhuang, and Tangshan. Specifically, Fu et al. also found that every 1 % increase in NO_x concentration resulted in a 0.97 % increase in NO_3^- concentration in the PRD region. NO_x change also leads to an alteration in atmospheric oxidizing capacity and subsequently affects the formation of secondary components of $PM_{2.5}$. The different response of reduction in different cities was due to the conversion efficiency of precursor gases to secondary particulate matter.

Table 3 The decreased ratio of $PM_{2.5}$, secondary particulate, and its precursor gases

	$PM_{2.5}$	SO_2	NO_2	SO_4^{2-}	NO_3^-
Beijing	33	43	30	28	18
Shijiazhuang	29	36	18	27	12
Tangshan	30	42	23	29	15

Conclusions

This paper reports the monitoring and modeling results of $PM_{2.5}$ concentration and its chemical compositions before, during, and after emission reduction for APEC summit 2014. The $PM_{2.5}$ monitoring program was conducted to collect $PM_{2.5}$ samples in the cities of Beijing, Tangshan, and Shijiazhuang. The paper focuses on the characterization of $PM_{2.5}$ chemical composition during emission control period and non-emission control period. Also, the CMAQ model was applied to assess the effect of emission control measure in the region. The emission reductions were 55 % of SO_2, 50 % of NO_x, 55 % of $PM_{2.5}$, and 27 % of VOCs in Beijing and 30~67 % of SO_2, 24~53 % of SO_2, 27~39 % of $PM_{2.5}$, and 18~39 % of VOCs in Hebei Province when compared to the non-emission control period. These pollutants were reduced as a result of emission controls on large industrial sources and vehicle in Beijing and surrounding regions. Total $PM_{2.5}$ concentrations were reduced by 54, 26, and 39 % when compared to emission control and non-emission control period in Beijing, Shijiazhuang, and Tangshan.

Comparing the element concentrations before and during emission control period, the average element concentrations

were reduced significantly by 75 % in Beijing site, 37 % in Shijiazhuang site, and 36 % in Tangshan site. After the APEC conference, the average element concentration increased. It is increased by 62, 42, and 14 % in Beijing site, Shijiazhuang site, and Tangshan site. However, due to metrological condition, the elements from fugitive dust emissions (Ca, Al, Mg, Ti) were increased in Tangshan and Shijiazhuang sites. It also indicates that Tangshan and Shijiazhuang's local governments need to strengthen the control of unorganized dust. The SWSIs were the major water-soluble ions in the $PM_{2.5}$ samples. Comparing with non-emission reduction days, the SO_4^{2-}, NO_3^-, and NH_4^+ reduced by 67, 55, and 57 %; 54, 34, and 39 %; and 57, 52, and 57 % in Beijing, Tangshan, and Shijiazhuang sites. The OC and EC concentrations in APEC emission reduction period were with an average reduction rate of 54, 15, and 41 % and (54, 19, and 44 %, respectively, in Beijing, Tangshan, and Shijiazhuang sites. However, after APEC, the carbon species concentration increased to varying degrees. In Tangshan and Shijiazhuang, the soil dust had the highest mass percentage in the $PM_{2.5}$ total mass. In Beijing site, the mass percentage of secondary compositions out of the total $PM_{2.5}$ was highest, which accounts for 65 %. The WRF/CMAQ modeling results showed that if no control was taken, in Beijing, Shijiazhuang, and Tangshan, the $PM_{2.5}$ concentration would increase by 33, 29, and 30 % under the same weather condition. The model simulation results showed that the precursors SO_2 and NO_x concentrations obviously decreased more rapidly than SO_4^{2-} and NO_3^-. Every 1 % decrease in NO_x concentration resulted in a 0.60, 0.55, and 0.65 % decrease in NO_3^- concentration in the Beijing, Shijiazhuang, and Tangshan. Every 1 % decrease in SO_2 concentration resulted in a 0.65, 0.75, and 0.69 % decrease in SO_4^{2-} concentration in Beijing, Shijiazhuang, and Tangshan.

Although $PM_{2.5}$ pollution has been reduced in the BTH region during the APEC summit, to continue the APEC blue, more stringent controls of regional sources are needed to further improve the air quality in Beijing and the surrounding regions. Particularly secondary component will be extremely challenging in the future.

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