

**Long-term effects of mitigation measures and
meteorological conditions on aerosol characteristics in Beijing, China**

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Master of Science Yuan Chen

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Hauptreferent: Prof. Dr. S. Norra

Korreferent: Prof. Dr. K. Schäfer

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Karlsruhe den 28.05.2016

Yuan Chen

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Abstract

Due to the influences on climate, economy and human health, air pollution has become a significant concern of both scientists and the public all over the world, especially in the developing countries. Beijing, the capital of China, a typical megacity in Asian countries, has been suffering from severe air pollution owing to high loads of aerosol particulates. The swift growth of population, economy and number of automobiles was accompanied by the increase in total energy consumption and pollutants emission. To improve air quality, series of intervention measures were established by the government. And in order to hold a 'Green' Olympic Games in 2008, the most intensive mitigation measures were put into force in Beijing. This large 'experiment' performed by the government provided unique opportunity to study the impact of the intervention measures on air quality.

These intervention measures included particular mitigation measures on specific pollution sources, such as improved emission standards, traffic restriction, construction limitation and afforestation, and macro intervention policies such as energy structure transformation. In this context, with long-term sampling and analyses of atmospheric particulates from 2005 to 2014, the main aims of this dissertation were 1) to study the characteristics of the aerosol particulates and define their sources, 2) to evaluate and quantify the effects of various governmental measures on air quality, 3) to analyze the effects of meteorological conditions, such as precipitation and sand-dust weather, on aerosol distribution, 4) and to provide a substantial scientific contribution to aerosol study, human health research related to air pollution, as well as policy-making for improving air quality in China.

The annual mean concentration of PM_{2.5} from 2005 to 2014 was 65.6 µg/m³ and the annual mean of TSP from 2007 to 2014 was 227 µg/m³. They both exceeded the annual mean standards (level II) for PM_{2.5} (35 µg/m³) and TSP (200 µg/m³) according to the Ambient Air Quality Standard (GB3095-2012) in China. The concentrations of most elements of PM_{2.5} in Beijing were higher than the corresponding concentrations in other studies in European or American countries. Of the four elemental concentrations mentioned in the

Ambient Air Quality Standard, only As average concentration of $PM_{2.5}$ exceeded the standard (2.5 times), based on nine-year (2005-2013) measured data.

Principle component analysis (PCA) was performed to categorize and identify the main sources of fine particles according to the element associations: typical anthropogenic sources (i.e. traffic and smelting), geogenic dust, agriculture sources (i.e. fertilizers), coal combustion, steel-related industry, comprehensive combustion emission and diffuse urban pollution.

Concentrations of traffic-related elements, such as Pb, Sb and Sn, varied with the strictness of traffic restriction measures. The pollution level was inversely correlated with the intensity of the measures. The introduction of license plate lottery policy for car registration since the beginning of 2011 in Beijing led to the largest annual growth during the ten years of total amount of vehicles from 2009 to 2010. This was considered as a contributor to the relatively high concentrations of traffic-related elements in 2010 compared to 2009, especially in summer time when other sources for these elements played a minor role.

Chromium (Cr), Co and Ni were used to evaluate the influence of the relocation of the Capital Steel Company. Annual mean concentrations of Cr, Co, Ni decreased in 2010 compared to those in 2008 if only three-year measured data were analyzed. However, from the view of nine-year (2005-2013) data, the decrease in Cr, Co and Ni between 2008 and 2010 did not continue but reversed slightly between 2011 and 2013, which was attributed to the nearby relocation with the recovery of production.

Temporal distribution of black carbon (BC) showed a distinct declining trend from 2005 to 2013, which was well correlated to the declining consumption of coal and coke. Gallium (Ga) was recommended as a tracer for coal combustion for the first time, due to its strong correlation with BC and coal consumption, as well as its concentration variation between the heating- and non-heating periods. From a long-term perspective, particulate mercury (HgP) concentration fell even with increasing total energy consumption and growing total

vehicle number. The strong correlations between HgP and BC/Ga in winter, together with the success of energy structure transformation on reducing BC/Ga suggested the effectiveness of this transformation on HgP emission control. The effects of this macro intervention measure in improving air quality were quantified according to the reduced concentrations of these relative pollutants.

Mass concentrations of different size fractions of coarse particles (2.5-80 μm) all showed slightly decreasing trends during the long-term observation period. Most of the peaks correlated to the sand dust or dust storms. The Olympic Games period displayed lower concentrations than the rest of the sampling time, demonstrating the effectiveness of mitigation measures on reducing coarse particles. The different size distribution patterns during different pollution days provide reference information for the enactment of mitigation measures on aerosol particles.

Precipitation had direct scavenging effects on aerosol particles. Thus periods with similar precipitation were selected for comparison when studying the effects of mitigation measures. $\text{PM}_{2.5}$ and BC were responsible for visibility deterioration. Temperature had an indirect effect on aerosol distribution, as the heating activity – mainly coal combustion – occurred with low temperature in winter and led to high aerosol load. Wind condition affected aerosol distribution by re-suspending local dust or introducing aerosol pollution from the surrounding areas. Wind carrying dust from the north and the northwest with high wind velocity triggered sand dust or dust storms, especially in spring. Year-by-year variations of temperature and wind conditions were similar from the ten-year observation and played a minor role in aerosol distribution.

The year 2008 was a milestone for air quality improvement during the ten years. Effective governmental mitigation measures for specific sources (e.g. traffic restriction measures) and macro intervention measures (e.g. energy structure transformation) are recommended to be continued and improved in order to obtain more “blue sky” days in the future. On the one hand, industry relocation is not recommended as a long-term effective measure to mitigate air pollution, but on the other hand the concurrent improved emission standards

are considered promising. For both environmental sustainability and human health, aerosol pollution is a crucial issue to be mitigated in Beijing and more efforts are required for better air quality.

Zusammenfassung

Aufgrund der Einflüsse auf Klima, Wirtschaft und Gesundheit ist die Luftverschmutzung für die Wissenschaftler und Öffentlichkeit der ganzen Welt ein bedeutender Grund zur Sorge geworden, insbesondere in den Entwicklungsländern. Peking ist als Hauptstadt von China eine typische Megastadt in asiatischen Ländern. Aufgrund der hohen Belastung durch Aerosolpartikeln ist Peking von schwerer Luftverschmutzung betroffen. Mit dem schnellen Wachstum von Bevölkerung, Wirtschaft und Anzahl an Fahrzeugen nimmt auch gleichzeitig der Energieverbrauch und die Emission der Schadstoffe zu. Zur Verbesserung der Luftqualität wurde eine Reihe von Maßnahmen durch die Regierung durchgeführt. Um ‚grünen‘ olympische Spiele im Jahr 2008 abhalten zu können, wurden intensivste Schutzmaßnahmen in Peking durchgesetzt. Dieses von Regierung durchgeführte große ‚Experiment‘ bietet die einzigartige Gelegenheit, die Auswirkungen dieser Interventionsmaßnahmen auf die Luftqualität zu untersuchen.

Die Interventionsmaßnahmen enthalten besondere Schutzmaßnahmen zu spezifischen Verschmutzungsquellen, z.B. verbesserte Emissionsstandards, Verkehrssteuerung, Baubeschränkung, Aufforstung, und Makrointerventionspolitik, wie z.B. Innovation der Energiestruktur. Unter diesem Gesichtspunkt und des langfristigen Probenahme und Analyse der atmosphärischen Partikel von 2005 bis 2014 sind die Hauptziele dieser Dissertation 1) die Untersuchung der Eigenschaften der Aerosolpartikel und die Feststellung ihrer Quellen, 2) die Bewertung und Quantifizierung der Auswirkungen verschiedener staatlicher Maßnahmen auf die Luftqualität, 3) die Analyse der Auswirkungen der meteorologische Bedingungen, wie z.B. Niederschläge und Sandstürme, auf die Aerosolverteilung, 4) und das Liefern eines erheblichen wissenschaftlichen Beitrags zur Aerosolforschung, Gesundheitsforschung bezüglich der Luftverschmutzung sowie Politikgestaltung zur Verbesserung der Luftqualität in China.

Die mittlere jährliche PM_{2.5}-Konzentration von 2005 bis 2014 war 65.6 µg/m³ und die mittlere jährliche TSP-Konzentration von 2007 bis 2014 war 227 µg/m³. Beide überschritten die mittleren jährlichen Standards (Stufe II) für die PM_{2.5}- (35 µg/m³) und TSP- (200 µg/m³) Konzentration, anhand vom Umgebungsluftqualitätsstandard (GB3095-2012) in China. Die meisten PM_{2.5}-Elementkonzentrationen in Peking sind höher als die entsprechenden Konzentrationen in anderen Untersuchungen in europäischen

oder amerikanischen Ländern. Von den vier Umgebungsluftqualitätsstandard erwähnten Elementkonzentrationen überschreitet, basierend auf den neunjährigen Messdaten (2005-2013), nur die durchschnittliche As-Konzentration von $PM_{2,5}$ den Standard (Faktor 2.5).

Eine Hauptkomponentenanalyse (PCA) wurde durchgeführt, um die wichtigsten Quellen des Feinstaubes je nach Elementgruppierung zu kategorisieren und zu identifizieren. Die wichtigsten Quellen enthalten typische anthropogene Quellen (z.B. Verkehr, Verhüttung), geogenen Staub, Landwirtschaftsquellen, (z.B. Düngemittel), Kohleverbrennung, Stahlherstellungs-und-verarbeitungsindustrie, Gesamtemissionen aus Verbrennung und diffuse Städtische Luftverschmutzung.

Die Konzentrationen der verkehrsbezogenen Elemente, wie z.B. Pb, Sb und Sn, variieren je nach Strenge der Verkehrssteuerungsmaßnahmen. Der Verschmutzungsgrad war invers mit der Intensität der Maßnahmen korreliert. Die Einführung der Nummernschild Lotterienpolitik für Kfz-Zulassungen seit Anfang des Jahres 2011 in Peking führte von 2009 bis 2010 zum größten jährlichen Wachstum der Fahrzeuggesamtmenge in zehn Jahren. Besonders in der Sommerzeit, wenn andere Quellen für diese verkehrsbezogenen Elemente eine kleine Rolle spielten, wird dies als Beitrag zu den relativ hohen Konzentrationen von verkehrsbezogenen Elementen in 2010, Vergleichen mit 2009, betrachtet.

Chrom (Cr), Co und Ni werden zur Bewertung des Einflusses der Verlegung des Hauptstädtischen Stahlunternehmens. Wenn nur dreijährige Messdaten analysiert wurden, sanken die mittleren jährlichen Konzentrationen von Cr, Co, Ni im Jahr 2010, im Vergleich zu 2008. Aber aus der Sicht von neunjährigen (2005-2013) Daten nehmen Cr, Co und Ni zwischen 2008 und 2010 ab und nehmen dann leicht zwischen 2011 und 2013 zu. Dies wurde der nahegelegenen Verlegung und der Wiederaufnahme der Produktion zugeschrieben.

Die zeitliche Verteilung des schwarzen Kohlenstoffs (BC) zeigt eine deutliche rückläufige Tendenz zwischen 2005 und 2013, die gut mit dem rückläufigen Verbrauch von Kohle und Koks korreliert. Aufgrund seiner starken Korrelation mit BC, Kohleverbrauch und seiner Konzentrationsschwankung zwischen den Heiz- und Nicht Heizperioden wird Gallium (Ga) als Tracer für die Verbrennung von Kohle zum ersten Mal empfohlen. Aus einer

langfristigen Perspektive sank die partikuläre Quecksilberkonzentration (HgP), trotz erhöhtem Gesamtenergieverbrauch und wachsendes Fahrzeugegesamtzahl. Die starken Korrelationen zwischen HgP und BC/Ga im Winter zusammen mit dem Erfolg der Energiestruktur Umwandlung auf die BC/Ga-reduktion weisen auf die Effektivität dieser Umwandlung auf die HgP-Emissionskontrolle. Die Auswirkungen dieser Makrointerventionsmaßnahme zur Verbesserung der Luftqualität wurden anhand der reduzierten Konzentrationen dieser relativen Schadstoffe quantifiziert.

Die Massenkonzentrationen verschiedener Größenfraktionen Groberpartikel (2.5-80 μm) zeigten alle im langfristigen Beobachtungszeitraum leichte Abwärtstrends. Die meisten Peaks korrelieren mit Sandstaub oder Staubstürmen. Die im Zeitraum der olympischen Spiele Konzentrationen waren niedriger als die während der restlichen Abtastzeit gemessenen. Die Wirksamkeit der Abhilfemaßnahmen zur Verringerung der groben Partikel wurde dadurch bewiesen. Die unterschiedlichen Größenverteilungsmuster an verschiedenen Verschmutzungstagen liefern Referenzinformationen für den Erlass von Minderungsmaßnahmen bezüglich Aerosolpartikel.

Niederschlag hatte direkte reinigende Auswirkungen auf die Aerosolpartikel. Deshalb wurden Perioden mit ähnlichem Niederschlag zum Vergleich ausgewählt, um die Auswirkungen von Risikominderungsmaßnahmen zu untersuchen. $\text{PM}_{2.5}$ und BC waren für die Verschlechterung der Sichtbarkeit verantwortlich. Die Temperatur hatte eine indirekte Wirkung auf die Aerosolverteilung, da die Heizaktivität – hauptsächlich Kohleverbrennung – bei niedriger Temperatur im Winter auftritt und zu einer hohen Aerosolbelastung führt. Die Windbedingung beeinflusste die Aerosolverteilung durch Resuspension lokalen Staubs oder Eintrag von Aerosolbelastung aus der Umgebung. Die Winde mit hohen Windgeschwindigkeiten aus dem Norden und Nordwesten brachten Sandstaub oder Staubstürmen, besonders im Frühling. Aus der zehnjährigen Beobachtung sind die Schwankungen von Temperatur- und Windbedingungen von Jahr zu Jahr ähnlich und spielen bei der Aerosolverteilung nur eine kleine Rolle.

Das Jahr 2008 war ein Meilenstein für die Verbesserung der Luftqualität innerhalb der zehn Jahre. Es wurde empfohlen, effektive staatliche Minderungsmaßnahmen für bestimmte Quellen (z.B. Verkehr-Beschränkungsmaßnahmen) und Makrointerventionsmaßnahme (z.B. Energiestruktur Umwandlung), fortzusetzen und zu verbessern, um mehr Tage mit ‚blauem Himmel‘ in der Zukunft zu erhalten. Einerseites

kann der industrielle Standortwechsel nicht als langfristig wirksame Maßnahme zur Milderung der Luftverschmutzung empfohlen werden, aber andererseits werden die gleichzeitigen verbesserten Emissionsstandards als aussichtsreich angesehen. Sowohl für die ökologische Nachhaltigkeit, als auch für die menschliche Gesundheit, ist die Aerosolver Verschmutzung ein Schlüsselproblem, welches in Peking vermindert werden muss und es werden mehr Anstrengungen gefordert um eine bessere Luftqualität zu erhalten.

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1 Context of this dissertation

1.1 Purposes and the whole structure of this dissertation

Air pollution has become one of the greatest environmental concerns of both the public and scientists. It impacts human health via different ways, especially via respiratory tracts. Beijing, the Capital of China, a typical Asian megacity, has been suffering serious air pollution. To hold a ‘Green’ Olympic Games in 2008, the municipal government took a series of mitigation measures, covering industry, traffic, construction and afforestation, to control pollutant emission. Meantime, energy structure transformation has been in progress in all of China, and particularly in Beijing, by increasing cleaner energy and reducing coal consumption. This large ‘experiment’ performed by the government provided unique opportunity to study the impact of the intervention policies on air quality.

In this context, with long-term sampling and analyses of atmospheric particulates from 2005 to 2014 in Beijing urban area, this dissertation aims to 1) study the characteristics of the aerosol particulates and define their sources, 2) to evaluate and quantify the effects of various governmental measures on air quality including specific mitigation measures such as traffic control and industry relocation, and macro intervention policies such as energy structure transformation, 3) to analyze the effects of meteorological conditions, such as the precipitation and the sand-dust weather, on aerosol distribution, 4) and to provide a substantial scientific contribution to aerosol study, human health research related to air pollution, as well as mitigation-policy making in China.

This dissertation is based on the accumulation of seven scientific publications (sections 2.1 - 2.4 and 3.1 - 3.3) and two other parts: particulate mercury (HgP) study (section 4) and coarse particles study (section 5). I am the first and the corresponding author for four of these publications (sections 2.1 - 2.4) and a co-author for the other three (sections 3.1 - 3.3). The four first-authorships include three research papers and one conference paper published by Springer, while the co-authorships include the other three research papers. All the papers are based on sample collection, physical and chemical analyses, bio- and

mineral-analyses and experiments that were performed and gained within the frame of the aerosol study on basis of China-German cooperation for the ten years.

This background of the study area was illustrated in the following section 1.2 in order to better understand the purposes of this study. All the experiments and methods used in this study were summarized in the section 1.3 so as to get an overview of the contents of this study.

1.2 Study area: Beijing, China

1.2.1 Beijing and its surroundings

Beijing, the capital of the People's Republic of China, lies on the northwest border of the North China Plain and is surrounded by the Yanshan Mountains clockwise from southwest to northeast (Fig. 1.1-a, 1.1-b). There are vast deserts and loess areas especially to the north, northwest, west and southwest of Beijing, which are the principal domestic sources of sand dust or dust storms occurred in Beijing (Fig. 1.1-a). The urban traffic system consists of six ring roads in Beijing with additional streets and expressways (like G1) connecting to neighboring provinces (Fig. 1.1-b).

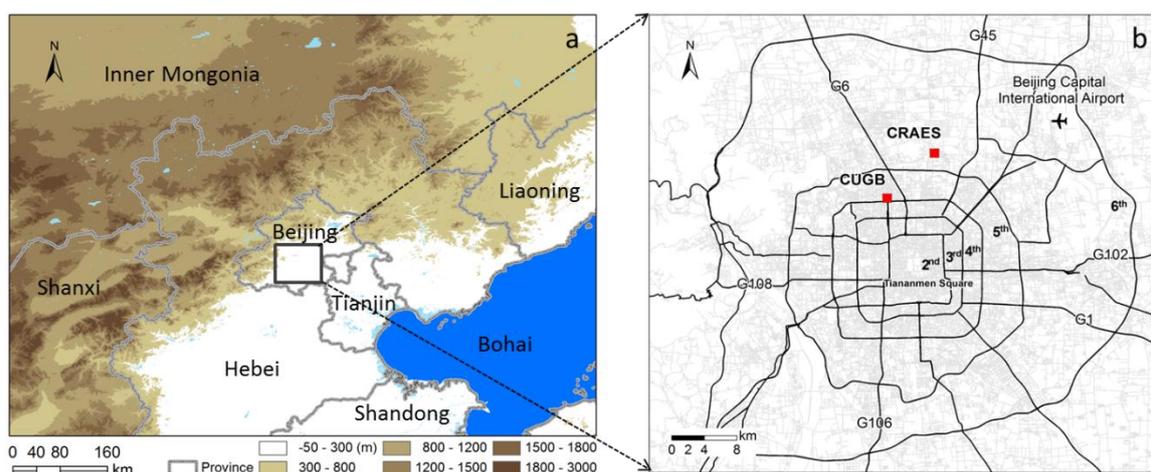


Fig. 1.1 Dimensional topography of the surround area of Beijing and the sampling sites (CUGB and CRAES) and the main traffic network of Beijing urban area, including the 2nd-6th ring roads (Fig. 1.1-a, data sources: National Geomatics Center of China and SRTM 90 m Digital Elevation Data, Fig. 1.1-b, source of the map: OpenStreetMap, produced with ArcGIS 10.2 Desktop).

The region of Beijing-Tianjin-Hebei (BTH) is one of three major rapidly developing economic zones in China (Xin et al., 2010). Beijing and Tianjin are directly administrated municipalities by the national government, surrounded by the Hebei province. It contributed to 10.9% of national Gross Domestic Product (GDP) and 7.8% of national population in 2010 (Zhao et al., 2013). With the speedy development of economy, BTH has become a major study region with respect to air pollution in China.

In 2014, permanent resident population was approximately 24.5 million in Beijing. The green land coverage percentage in 2014 was 47.4%, higher than 42.0% in 2005, and it was over 2 times of 22.3% in 1978. The forest coverage rate in 2014 was 41.0%, higher than 35.9% in 2006 (data in 2005 unavailable). All these statistic data were from Beijing Bureau of Statistics (2015).

1.2.2 Development of Beijing

The development of population, vehicles (civil automobiles) and GDP of Beijing was incredibly fast during the past decades (Fig. 1.2). For the ten years from 2005 to 2014, the permanent population increased from 15.4 to 21.5 million, the total amount of motor vehicles doubled from 2.5 to 5.6 million, and the GDP boomed from 697 to 2130 billion Yuan (the Chinese currency) (Fig. 1.3).

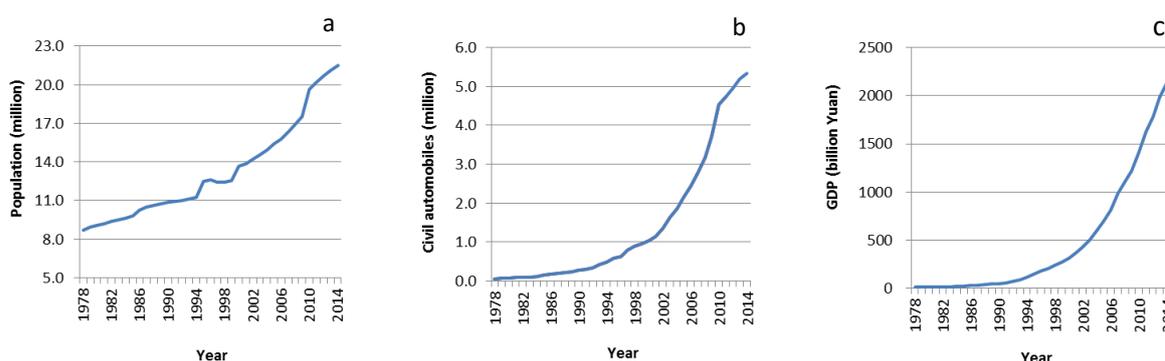


Fig. 1.2 Population, vehicles (civil automobiles) and GDP of Beijing from 1978 to 2014.

Car registrations have been being allocated by a license plate lottery policy since the beginning of 2011 in Beijing. Voluminous citizens purchased cars in 2010 before this

policy took effect. Consequently, the growth of the total amount of vehicles from 2009 to 2010 was the steepest during the ten years with an upswing of 0.79 million, and the growth was slow from 2010 to 2011 with only an increase of 0.17 million (Fig. 1.3).

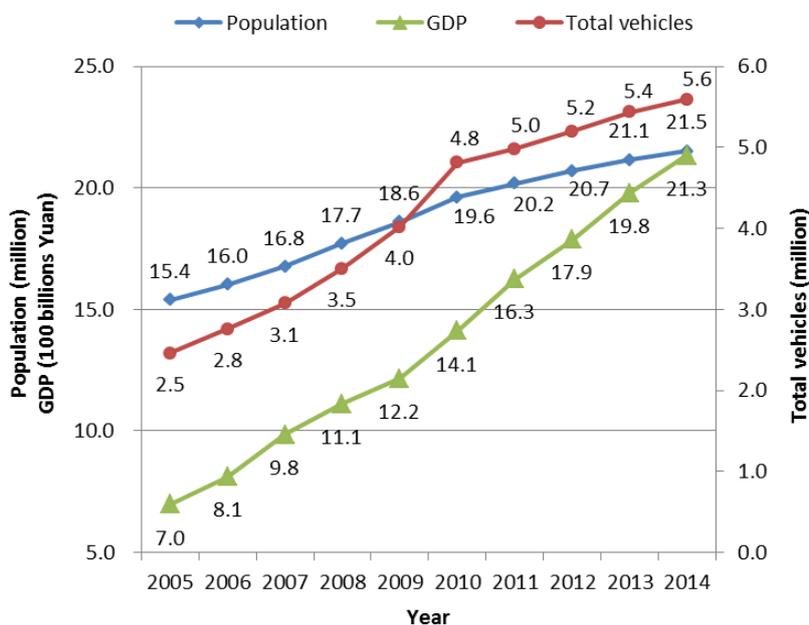


Fig. 1.3 Population, total vehicles and GDP of Beijing from 2005 to 2014 (observation period of this study). Data sources: Beijing Bureau of Statistics, 2006-2015.

1.2.3 Energy consumption in Beijing

Total energy consumption increased (Fig. 1.4) with the rapid development of motorization and industrialization in Beijing.

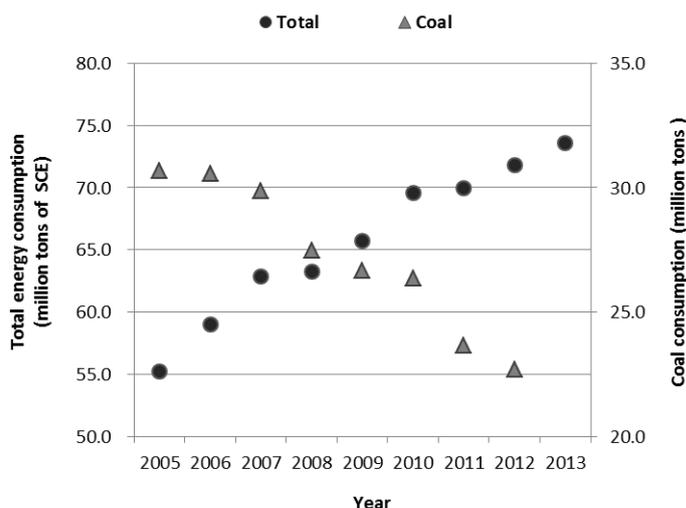


Fig. 1.4 Total energy consumption and coal consumption in Beijing. Data sources: Beijing Bureau of Statistics, 2006-2014.

The energy consumption structure shifted toward less coal and coke, more gas, more renewable energy such as wind energy and water energy, and more nuclear energy. Under this energy transformation policy, coal consumption in Beijing decreased gradually from 30.7 million tons SCE

(Standard Coal Equivalent) in 2005 to 22.7 million tons SCE in 2012 (Fig. 1.4). However, coal is still the predominant fuel for industrial processes and domestic life in Beijing and the surrounding area, although it has been gradually being replaced by natural gas in Beijing urban area since 1999 (Beijing Environmental Protection Bureau, 2012). The energy consumption data has been calculated based on new approach according to National Bureau of Statistics since 2013. Total energy consumption until 2013 and coal consumption data until 2012 are available with the old statistic approach. Here only data with the same statistic approach is used to compare.

1.2.4 Variation of air pollutants during the last decade

Daily averages of inspiratory particulate matter (PM₁₀), Sulfur oxides (SO_x) and nitrogen oxides (NO_x) from 2005 to 2014 were available from the Beijing Municipal Bureau of Environmental Protection (Fig. 1.5). For the three air pollutants, average concentrations in the years after 2008 was relatively lower than those before 2008. The year 2008 became a

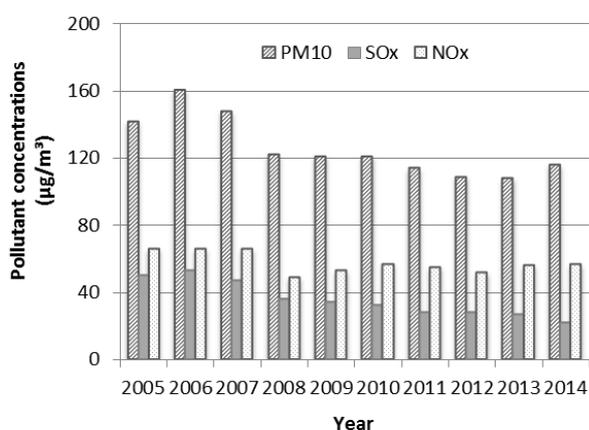


Fig. 1.5 Annual means of daily concentrations of PM₁₀, SO_x and NO_x from 2005 to 2014 in Beijing. Data sources: Beijing Bureau of Statistics, 2015.

milestone for improving air quality in Beijing. Annual mean PM₁₀ concentration kept decreasing from 2005 to 2013; however, it slightly increased from 2013 to 2014. Sulfur dioxide shows a decreasing trend for the ten years, while NO_x concentrations increased again after 2008 but still lower than those before 2008.

1.3 Synoptic summary of experiments and methods

Samples were collected at two sites in Beijing urban area: one was installed near the main entrance of the China University of Geosciences, Beijing (CUGB) at a height of 1.5 m, and the other one was set up on the roof of the Chinese Research Academy of

Environmental Sciences (CRAES) at a height of about 20 m (Fig. 1.1-b).

Atmospheric particulates, including $PM_{2.5}$ ($<2.5 \mu m$), TSP (total suspended particles) and coarse particles ($2.5-80 \mu m$) were studied within this dissertation. The study contents, the applied techniques and instruments were introduced in Table 1.1.

Table 1.1 The study contents, the applied techniques and instruments within this dissertation.

Content	Technique	Instruments	Particulate types	Sampling site
Particle mass	gravimetric analysis	Microbalance (Sartorius SE 2-F, Göttingen, Germany)	$PM_{2.5}$ & TSP	CUGB CRAES
Chemical elements	inductively coupled plasma mass spectrometer (ICP-MS)	High-Resolution (HR)-ICP-MS Axiom (VG Elemental, USA)	$PM_{2.5}$	CUGB
			$PM_{2.5}$ & TSP	CRAES
BC	optical transmission technique	SPECORD 50 and SPECORD 50 PLUS (Analytic Jena AG, Jena, Germany).	$PM_{2.5}$	CUGB CRAES
HgP	cold vapor atomic absorption spectrometry (CVAAS)	Direct Mercury Analyzer (Milestone DMA-80, Italy)	$PM_{2.5}$	CUGB
			$PM_{2.5}$ & TSP	CRAES
Particle species	scanning electron microscopy and electron dispersive X-ray fluorescence spectrometry (SEM-EDX)	Quanta FEG 650 (FEI, USA) coupled to EDXRF	coarse particles	CUGB
Size distribution and mass concentration	a PC-aided automatic image analysis system	An optical microscope (ZEISS Axioplan 2), an adapted automatic scanning stage (Prior Scientific), a high-resolution CCD camera (SVS-VISTEK) with the image analysis system Digitrace V.3.4 (IMATEC)	coarse particles	CUGB

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Xin, J., Wang, Y., Tang, G., Wang, L., Sun, Y., Wang, Y., Hu, B., Song, T., Ji, D., Wang, W., Li, L., Liu, G., 2010. Variability and reduction of atmospheric pollutants in Beijing and its surrounding area during the Beijing 2008 Olympic Games. *Chinese Science Bulletin*, 55(18), 1937-1944.

Zhao, P. S., F. Dong, D. He, X. J. Zhao, X. L. Zhang, W. Z. Zhang, Q. Yao, H. Y. Liu., 2013. Characteristics of concentrations and chemical compositions for PM_{2.5} in the region of Beijing, Tianjin, and Hebei, China. *Atmospheric Chemistry and Physics*, 13(9), 4631-4644.

2 First author scientific publications

2.1 The influence of governmental mitigation measures on contamination characteristics of PM_{2.5} in Beijing

Authors: Yuan Chen, Nina Schleicher, Yizhen Chen, Fahe Chai, Stefan Norra

In: Science of the Total Environment, 2014, 490, 647-658. DOI:

<http://dx.doi.org/10.1016/j.scitotenv.2014.05.049>

Authorship statement

This peer-reviewed scientific journal article was written by me and is based on data obtained from the CRAES site from 2007 to 2010. The data included PM_{2.5} mass concentrations, and concentrations of 25 elements in PM_{2.5} samples. I was responsible for gravimetric analyses of part of the loaded filters and performed the corresponding chemical analyses in the laboratories at KIT-AGW with the support from the technicians Cornelia Haug for filter digestions and Claudia Möbner for ICP-MS analyses. The



statistical analysis of all data and influence evaluation of governmental mitigation measures on PM_{2.5} were finalized by me. Nina Schleicher contributed to sample preparation, data processing and communication with CRAES. Yizhen Chen and Fahe Chai were the responsible scientists and primary cooperation partners from CRAES. They

offered the possibility of long-term aerosol sampling at CRAES and arranged all the sampling work in China. Stefan Norra designed and supervised the whole study structure. All co-authors critically reviewed the manuscript and agreed to the publication in Science of the Total Environment.

Abstract

Beijing, the capital of China, has become one of the most air-polluted cities due to its rapid economic growth. Weekly PM_{2.5} samples – collected continuously from 2007 to 2010 – were used to study the contamination characteristics of atmospheric particles and effects of governmental mitigation measures especially since the 2008 Summer Olympic Games. PM_{2.5} mass concentrations during the sampling period were reduced compared to the previous studies before 2005, although they were still too high in comparison with environmental standards of China and many other countries as well as WHO standards. Results of principle component analysis show that elements of primary anthropogenic origin had an obvious decline while elements mainly from the natural environment kept a relatively stable course. The governmental macro-control measures influenced both anthropogenic and geogenic sources, but they also led to some pollution peaks prior to implementation of the respective measures. Some element concentrations correlated to the restrictiveness of relative measures, especially during different traffic restrictions. The comparison with other countries and international standards shows that there is a long way to go in order to improve air quality in Beijing, and that governmental mitigation measures need to be continued and reinforced.

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2.2 Long-term variation of black carbon and PM_{2.5} in Beijing, China with respect to meteorological conditions and governmental measures

Authors: Yuan Chen, Nina Schleicher, Mathieu Fricker, Kuang Cen, Xiu-li Liu, Uwe Kaminski, Yang Yu, Xue-fang Wu, Stefan Norra

In: Environmental Pollution, 2016, 212, 269-278, DOI:

<http://dx.doi.org/10.1016/j.envpol.2016.01.008>

Authorship statement

This peer-reviewed scientific journal article was written by me and is based on data obtained from the CUGB site from 2005 to 2013. The data included PM_{2.5} and black carbon mass concentrations with meteorological data collected from a meteorological station in Beijing registered at the World Meteorological Organization (WMO) with the code 54511. I was responsible for part of the sampling, gravimetric analyses of the unloaded and loaded filters and performed the corresponding black carbon analyses in the laboratory at the

German Meteorological Service (DWD) with the support from Mathieu Fricker and Uwe Kaminski. Furthermore, all the scientific data evaluation was performed by me. Mathieu Fricker and Uwe Kaminski were the responsible scientists and primary research partners from DWD. They offered the instruments for black carbon analysis. Nina Schleicher and Yang Yu contributed to part of the sample preparation and data processing. Kuang Cen was responsible for the long-term running of the CUGB site. Xiu-li Liu and Xue-fang Wu



contributed to sample collection at the CUGB site. Stefan Norra designed and supervised the whole study structure. All co-authors critically reviewed the manuscript and agreed to the publication in Environmental Pollution.

Abstract

Black carbon (BC) and PM_{2.5} were studied for nine years from 2005 to 2013 in the Beijing urban area. The overall weekly average mass concentrations of BC and PM_{2.5} were 4.3 and 66.8 µg/m³. PM_{2.5} annual means of the nine years are around 2 times of the standard (GB3095-2012) in China, and are 5-7 times higher than the WHO standard. The Beijing Olympic Games in 2008 was a milestone to mitigate aerosol pollution. Temporal distribution of BC shows a distinct declining trend, and annual mean mass concentrations of PM_{2.5} after 2008 were lower than those before 2008 but increased from 2011 to 2013. Wind rose plots show that high BC concentrations are usually associated with low wind speed of northeastern or southwestern winds, generally causing poor visibility. Governmental mitigation measures such as traffic restriction despite increased motor vehicle numbers and gasoline consumption and industry relocation with declining consumption of coal and coke were successful in reducing BC emissions. Annual mean of BC was reduced by 38% in 2013 compared to 2005. However, BC contamination in Beijing is still severe when compared to other urban areas around the world.

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2.3 Evaluation of impact factors on PM_{2.5} based on long-term chemical components analyses in the megacity Beijing, China

Authors: Yuan Chen, Nina Schleicher, Kuang Cen, Xiuli Liu, Yang Yu, Volker Zibat, Volker Dietze, Mathieu Fricker, Uwe Kaminski, Yizhen Chen, Fahe Chai, Stefan Norra

In: Chemosphere, 2016, 155, 234-242, DOI: 10.1016/j.chemosphere.2016.04.052

Authorship statement

This peer-reviewed scientific journal article was written by me and is based on data obtained from the CUGB site from 2005 to 2013. This data was used to compare with the data obtained from the CRAES site. I was responsible for part of the sampling, gravimetric analyses of the unloaded and loaded filters and performed the corresponding chemical analyses (27 elements) in the laboratories at KIT-AGW with the support from the technicians Cornelia Haug for filter digestions and Claudia Mößner for ICP-MS analyses.



Furthermore, all the scientific data statistics and evaluation of impact factors on PM_{2.5} were performed by me. Nina Schleicher and Yang Yu contributed to part of the sample preparation and data processing. Kuang Cen was responsible for the long-term running of the CUGB site. Xiu-li Liu contributed to sample collection at the CUGB site. Volker Dietze, Mathieu Fricker and Uwe Kaminski were the responsible scientists and primary research partners from DWD. Yizhen Chen and Fahe Chai were the responsible scientists and primary research partners from CRAES. Stefan Norra designed and supervised the

whole study structure. All co-authors critically reviewed the manuscript and agreed to the publication in Chemosphere.

Abstract

Nine years of sampling and analyses of fine particles (PM_{2.5}) were performed in Beijing from 2005 to 2013. Twenty-seven chemical elements and black carbon (BC) in PM_{2.5} were analyzed in order to study chemical characteristics and temporal distribution of Beijing aerosols. Principle component analysis defined different types of elemental sources, based on which, the influences of a variety of anthropogenic activities including governmental intervention measures and natural sources on air quality were evaluated. For the first time, Ga is used as a tracer element for heating activities mainly using coal in Beijing, due to its correlation with BC and coal combustion, as well as its concentration variation between the heating- and non-heating periods. The traffic restrictions effectively reduced emissions of relevant heavy metals such as As, Cd, Sn and Sb. The expected long-term effectiveness of the steel smelters relocation was not observed due to the nearby relocation with increased capacity. Firework display during every Chinese spring festival season and special events such as the Olympic Games resulted in several times higher concentrations of K, Sr and Ba than other days and thus they were proposed as tracers for firework display. The impacts of all these factors were quantified and evaluated. Sand dust or dust storms induced higher concentrations of geogenic elements in PM_{2.5} compared to non-dust days. Sustainable mitigation measures, such as traffic restrictions, are necessary to be continued and improved to obtain more “blue sky” days in the future.

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2.4 The effect of government policies on the temporal development of contamination characteristics within the aerosol distribution in Beijing, China

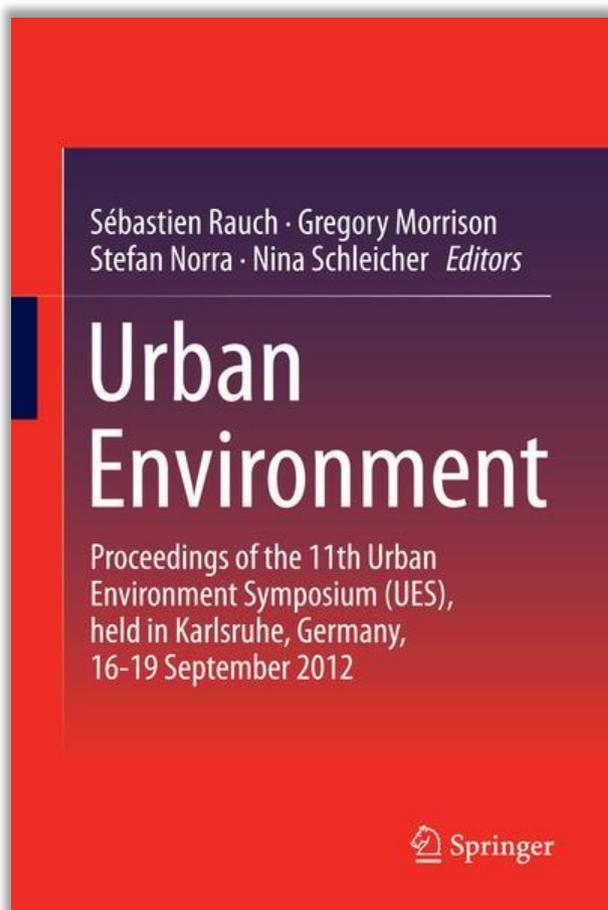
Authors: Yuan Chen, Nina Schleicher, Yizhen Chen, Fahe Chai, Shulan Wang, Stefan Norra

In: Rauch, S., Morrison, G., Norra, S., Schleicher, N., (eds.), *Urban Environment*, Springer, 2013, 313-321. DOI: 10.1007/978-94-007-7756-9_27

Authorship statement

This scientific article was written by me and is based on data obtained from the CRAES site from 2007 to 2010. I was responsible for gravimetric analyses of part of the loaded filters and performed the corresponding chemical analyses (7 elements) in the laboratories at KIT-AGW with the support from the technicians Cornelia Haug for filter digestions and Claudia Mößner for ICP-MS analyses. Nina Schleicher contributed to sample preparation, data processing and communication with CRAES. Yizhen Chen and Fahe Chai were the responsible scientists and primary

research partners from CRAES. They offered the possibility of long-term aerosol sampling at CRAES and arranged all the sampling work in China. Shulan Wang contributed to



sample collection at the CRAES site. Stefan Norra designed and supervised the whole study structure. All co-authors critically reviewed the manuscript and agreed to its publication.

Abstract

To host Green Olympic Games, the Beijing municipal government took comprehensive measures to improve air quality in 2008, which partly are still in force in 2012. The aim of this study is to investigate the temporal distribution of aerosol contamination characteristics and their variations under different government intervention policies. PM_{2.5} samples were collected continuously from 2007 to 2010 in the north of Beijing City. Element concentrations were analyzed by HR-ICP-MS. Results showed that concentrations of traffic-related elements such as Sn, Sb and Pb varied with the strength of traffic restrictions. Elements like Cr, Co and Ni, which are correlated with industries, were reduced under special policies like the relocation of Capital Steel Company. In general, the improving air quality demonstrates the success of government intervention policies although still the concentrations are too high if compared to international threshold values.

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3 Co-authored related scientific publications

3.1 Atmospheric particulate mercury in the megacity Beijing: Efficiency of mitigation measures and assessment of health effects

Authors: Schleicher, N.J., Schäfer, J., **Chen, Y.**, Blanc, G., Chai, F., Cen, K. and Norra, S.

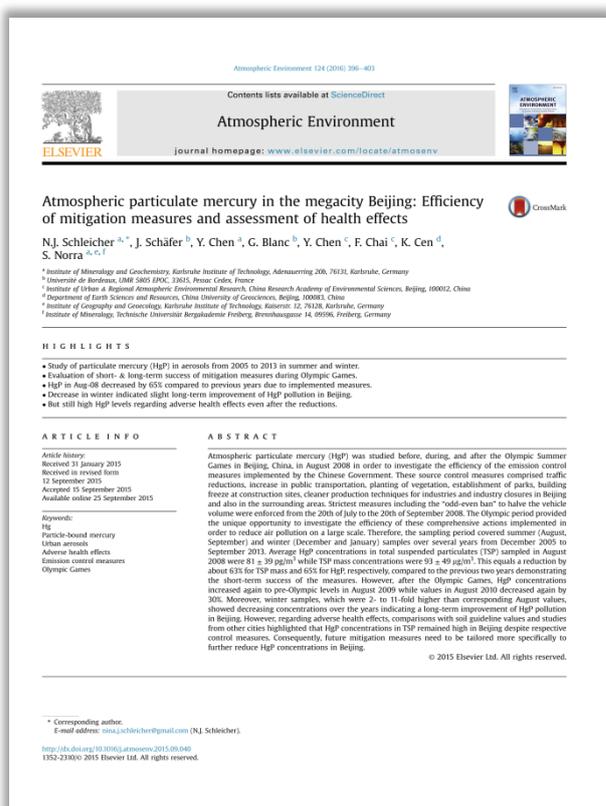
In: Atmospheric Environment, 2016, 124, 396-403, DOI: <http://dx.doi.org/10.1016/j.atmosenv.2015.09.040>

Authorship statement

This peer-reviewed scientific journal article is based on atmospheric particulate mercury (HgP) analysis of samples collected at the CRAES site and a site in the southeast of Beijing. Specifically, I prepared part of the TSP samples for HgP analysis. Furthermore, I contributed to part of the TSP mass concentration calculation. In total my contribution to this article amounts to around 15%.

Abstract

Atmospheric particulate mercury (HgP) was studied before, during, and after the Olympic Summer Games in Beijing, China, in August 2008 in order to investigate the efficiency of the emission control measures implemented by the Chinese Government. These source control measures comprised traffic reductions, increase in public transportation, planting of vegetation, establishment of parks, building freeze at construction sites, cleaner production techniques for industries and industry closures in Beijing and also in the surrounding areas. Strictest measures including the "odd-even ban" to halve the vehicle volume were enforced from the 20th of July to the 20th of September 2008. The Olympic period provided the unique opportunity to investigate the efficiency of these comprehensive actions implemented in order to reduce air pollution on a large scale. Therefore, the sampling period covered summer (August, September) and winter (December and January) samples over several years from December 2005 to September 2013. Average HgP concentrations in total suspended particulates (TSP) sampled in August 2008 were $81 \pm 39 \mu\text{g}/\text{m}^3$ while TSP mass concentrations were $93 \pm 49 \mu\text{g}/\text{m}^3$. This equals a reduction by about 65% for TSP mass and 65% for HgP, respectively, compared to the previous two years demonstrating the short-term success of the measures. However, after the Olympic Games, HgP concentrations increased again to pre-Olympic levels in August 2009 while values in August 2010 decreased again by 20%. Moreover, winter samples, which were 2- to 11-fold higher than corresponding August values, showed decreasing concentrations over the years indicating a long-term improvement of HgP pollution in Beijing. However, regarding adverse health effects, comparisons with soil guideline values and studies from other cities highlighted that HgP concentrations in TSP remained high in Beijing despite respective control measures. Consequently, future mitigation measures need to be tailored more specifically to further reduce HgP concentrations in Beijing.



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3.2 Seasonal dynamics of coarse atmospheric particulate matter between 2.5 μm and 80 μm in Beijing and the impact of 2008 Olympic Games

Authors: Stefan Norra, Yang Yu, Volker Dietze, Nina Schleicher, Mathieu Fricker, Uwe Kaminski, **Yuan Chen**, Doris Stüben, Kuang Cen

In: Atmospheric Environment, 2016, 124, 109-118, DOI: <http://dx.doi.org/10.1016/j.atmosenv.2015.08.029>

Authorship statement

This peer-reviewed scientific journal article is based on size distribution data of coarse particles (2.5-80 μm) samples collected at the CUGB site. Specifically, I collected part of the samples and meteorological data. Further, I contributed to the revision and correction of the draft manuscript. In total my contribution to this article amounts to around 5%.

Abstract

Beijing is well known as a megacity facing severe atmospheric pollution

problems. One very important kind of pollution is the high amount of particles in Beijing's atmosphere. Numerous studies investigated the dynamics of fine particles smaller 10 μm . Less information is available on the coarse particle fraction larger 10 μm , although geogenic dusts, which often are composed by those coarser particles, frequently affect the air quality in Beijing. Therefore, systematic sampling and analysis of size fractionated particulate matter between 2.5 and 80 μm was performed in Beijing from April 2005 till



October 2009. Atmospheric particles were collected in the North-West of Beijing using a cost-effective passive sampling method called Sigma-2. Altogether, 200 weeks could be analysed and assessed. Concentrations and size distribution of atmospheric coarse particles were determined by automated microscopic single particle analysis. Seasonal variability of the total mass of different size fractions was identified as follows: spring > winter > autumn > summer. High concentrations of transparent mineral particles indicate the activity of geogenic sources in spring and winter time, due to asian dust events and resuspension of soil from local bare land during dry and windy periods. The percentage of opaque particle components differs seasonally with relatively high values in winter, confirming combustion of fossil fuels for heating purposes as a predominant pollution source in this season. The influence of meteorological conditions on concentrations and size distribution of atmospheric particulate matter between 2.5 and 80 μm is demonstrated for the whole sampling period. Lowest pollution by coarse aerosols occurred during the period of the 2008 Olympic Summer Games. A general trend of decreasing total coarse particle mass concentrations was observed. Due to frequently observed high total coarse particle mass concentrations of several $100 \mu\text{m}\cdot\text{m}^{-3}$ it is strongly recommended to enhance research and observation regarding these air pollutants to gain a better understanding of their dynamics, health effects, well-being impacts on Beijing inhabitants and the effectiveness of mitigation measures.

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3.3 Characteristics and sources of PM in seasonal perspective – A case study from one year continuously sampling in Beijing

Authors: Rongrong Shen, Klaus Schäfer, Jürgen Schnelle-Kreis, Longyi Shao, Stefan Norra, Utz Kramar, Bernhard Michalke, Gülcin Abbaszade, Thorsten Streibel, Mathieu Fricker, **Yuan Chen**, Ralf Zimmermann, Stefan Emeis, Hans Peter Schmid

In: Atmospheric Pollution Research, 2016, 7, 235-248, DOI: <http://dx.doi.org/10.1016/j.apr.2015.09.008>

Authorship statement

This peer-reviewed scientific journal article is based on comprehensive chemical analyses of aerosol particle samples collected at the CUGB site with different instruments from this dissertation. Specifically, I contributed to the establishment of the sampling point at the CUGB site. Further, I contributed to inorganic chemical analysis with ED-XRF. In total my contribution to this article amounts to around 5%.

Abstract



Daily mass concentrations and chemical compositions (elemental carbon, organic carbon, water soluble ions, chemical elements and organic species) of PM were measured continuously in Beijing for one year from June 2010 to June 2011 (365 samples). The seasonal variation of PM mass concentration followed the order of spring 2011 > winter 2010 > summer 2010 > autumn 2010. Organic matter (OM) and secondary inorganic aerosol components (SNA: SO₄²⁻, NO₃⁻ and NH₄⁺) were the two major fractions of PM

during the whole year. Source apportionment by PMF performed on the basis of a full year of data, including both inorganic and organic species, showed that biomass burning, secondary sulfate and nitrate formation, mineral dust, industry, coal combustion and traffic were the main sources of PM in Beijing during 2010-2011. Specifically, comparison among the four seasons shows that the contribution of secondary sulfate and biomass burning, secondary nitrate formation, mineral dust, and coal combustion were the dominating sources of PM in summer, autumn, spring and winter, respectively. The contributions of industry to PM was distributed evenly in four seasons, while traffic contributed more in summer and autumn than in winter and spring. Backward trajectory analysis was applied in combination with PMF and showed that air flow from the South contributed mostly to high PM mass concentrations in Beijing. Meteorological parameters (temperature, wind speed, wind direction, precipitation and mixing layer height) influence such a variation. In general, high relative humidity and low mixing layer height can raise PM mass concentration, while high wind speed and precipitation can reduce pollutants. In addition, wind direction also plays a key role in influencing PM because different wind directions can bring different pollutants to Beijing from different regions.

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4 Particulate Mercury (HgP)

4.1 Introduction and background

Mercury in the atmosphere generally exists in three species: gaseous elemental Hg (GEM), reactive gaseous Hg (RGM), and particulate-bound Hg (HgP). GEM accounts for > 95% of the total atmospheric mercury while RGM together with HgP account only for < 5% (cf. Schroeder and Munthe, 1998). The residence time of GEM was estimated to be several months to up to two years due to the low chemical reactivity and water solubility, and thus GEM was considered as a global pollutant (Schroeder and Munthe, 1998). GRM and HgP have shorter residence time, hours to days and hours to weeks, respectively, and thus represent the local pollution or small-scale regional sources (HgP) (Lindqvist and Rodhe, 1985; Schroeder and Munthe, 1998).

Anthropogenic Hg emissions in China mainly attribute to fossil fuel combustion, cement production, metal mining and smelting, waste incineration and biomass burning (Zhao et al., 2015). Atmospheric Hg can be input to terrestrial and aquatic ecosystems by dry or wet deposition and adversely affects human health via bioaccumulation (Lindqvist et al., 1991; Zhu et al., 2014). It became a research hot point not only for natural scientists but also for pathologists.

China is the largest mercury emitting country (AMAP and UNEP, 2008), especially for HgP, which was considered to be higher in China than in the rest of the world due to coal combustion (Streets et al., 2005). In Beijing, coal combustion was reported as the major HgP source, while traffic, industrial and metallurgical activities and the red pigment from historical buildings contributed as minor sources (Schleicher et al., 2015). Heating supply in Beijing which usually starts in Mid-November and ends in the following Mid-March (cover the whole winter) is one of the major applications of coal consumption. In order to mitigate the influences of urban air pollutants emitted by coal-based heating, Chinese authorities have been promoting the transformation of coal into natural gas for heating

system in major cities since 1999 (Wu and Wang, 2014; Zhao et al., 2013). However, this action alone was not enough for eliminating the pollution (Liang et al., 2015). Energy structure transformation has been in progress in all of China, and particularly in Beijing, by increasing cleaner energy and reducing coal consumption (Chen et al., 2016a, 2016b). Traffic restriction measure according to the digit of the license plates, higher emission standards for industries and even relocation of industries were implemented to improve air quality as well.

This study evaluated the meteorological impact factors and the mitigation measures on HgP emissions based on long-term measurement data together with black carbon (BC) and Gallium (Ga) emissions which were also used to study the efficiency of energy structure transformation in Beijing in the sections 2.2 and 2.3 (Chen et al., 2016a, 2016b). To the authors' knowledge, only limited studies have investigated long-term HgP distribution of aerosol particles in Asian megacity and the long-term effects of mitigation measures on HgP. This study will contribute to both scientific researches and policy-making of pollution control measures.

4.2 Methodology

4.2.1 Sampling

Aerosol samples were collected at two sampling sites: one was installed near the main entrance of the China University of Geosciences, Beijing (CUGB) at a height of 1.5 m, and the other one was set up on the roof of the Chinese Research Academy of Environmental Sciences (CRAES) at a height of about 20 m. CUGB site was located near the 4th ring road in the urban area and CRAES site was located between the 5th ring road and the 6th ring road (Fig. 1.1). All samples were collected on quartz fiber filters (Whatman Inc., Maidstone, UK) actively. PM_{2.5} samples were collected by Mini-Volume Samplers (Leckel, Berlin) with a flow-rate of 200 L/h at the CUGB site, while TSP samples were collected by a TSP-Sampler (Leckel, Berlin) with a flow-rate of 1 m³/h at the CRAES site.

4.2.2 Analytic methods

Particulate mass on filters were obtained by subtraction of loaded filter mass to unloaded filter mass which were determined with a microbalance (Satorius SE 2-F, Göttingen, Germany). All the gravimetric analyses were carried out at constant temperature ($22 \pm 3^\circ\text{C}$) and relative humidity ($40 \pm 3\%$). Filter blanks and laboratory blanks were used for quality control and accuracy improvement. Each filter was weighed at least triplicates before and after sampling, respectively, at the Institute of Applied Geosciences, Karlsruhe Institute of Technology (AGW-KIT), Germany.

Four or six circles (diameter 5 mm) were punched out from the each filter sample and then placed in a metal sample carrier, ready for analysis without any further preparation. A Direct Mercury Analyzer (Milestone DMA-80, Italy) equipped with a cold vapor atomic absorption spectrometry (CVAAS) was used for analyzing HgP in aerosol samples. Firstly samples were combusted in an O_2 stream. Then the released Hg vapor was collected in a gold amalgamator and was transported to a heated cuvette for HgP analysis with the CVAAS.

Standard protocols included the use of filter blanks, laboratory blanks, and an external reference standard IAEA 433 (marine sediment, International Atomic Energy Agency) for all HgP analyses for quality control and quality assurance purpose.

The HgP contents (91 pg in 6 circles) in blank filters (N=28) were in the same range as the measurements (86 pg) of the laboratory blanks (N=184) which refer to empty metal carriers without any sample inside. The values of filter blanks were subtracted from the sample filters to improve the accuracy of HgP concentration calculation. The certified concentration of IAEA 433 is 168 ± 17 ng/g. The average concentration of this reference material throughout the measurements was 148 ± 19 ng/g (N=70). The measured results were corrected with a factor of 1.135 (ratio of certified value to measured average value of the reference standard material). Moreover, some $\text{PM}_{2.5}$ samples (N=6) and TSP samples (N=5) were analyzed triplicates. The average standard deviation of these triplicates was 8 pg/m^3 and 20 pg/m^3 perceptively.

4.2.3 Meteorological data

Meteorological data were obtained from the German Meteorological Service (DWD). The 3-hourly parameters including precipitation, wind direction and wind speed were collected from a meteorological station in Beijing registered at the World Meteorological Organization (WMO) with the code 54511.

4.3 Temporal distribution of HgP in aerosol particles (PM_{2.5} and TSP)

To observe the variation during a year, HgP analysis was performed with weekly aerosol samples collected from Dec. 2012 to Nov. 2013. To observe the long-term variation of HgP, aerosol samples in Augusts from 2005 to 2013 were used for HgP analysis to represent summer variation, while aerosol samples in Januaries from 2006 to 2013 were used for HgP analysis to represent winter variation.

During a year (from Dec. 2012 to Nov. 2013), HgP concentrations in PM_{2.5} particle samples ranged from 500 to 4150 ng/g (ng (HgP) per g (particles)), from 13 to 529 pg/m³ (pg (HgP) per m³ (air volume)). The annual average HgP concentration in PM_{2.5} was 2010 ± 1030 ng/g (136 ± 111 pg/m³).

At the same time, HgP concentrations in TSP particle samples ranged from 454 to 2590 ng/g, from 73 to 862 pg/m³. The annual average HgP concentration in TSP was 1160 ± 428 ng/g (297 ± 179 pg/m³).

4.3.1 Monthly and seasonal variation of HgP in aerosol particles

According to the meteorological conditions in China, winter includes the months December, the following January and February, spring includes March, April and May, summer covers June, July and August, and autumn covers September, October and November. The monthly variation (Fig. 4.1) shows that the highest HgP concentration in both PM_{2.5} and TSP occurred in January and the lowest occurred in July. The highest TSP and PM_{2.5} mass concentrations were also in January, and the lowest TSP and PM_{2.5} mass concentrations were in July with most precipitation (there was no TSP data in August due

to sampler error). Most precipitation occurred in summer (Fig. 4.1, Fig. 4.2). The lowest seasonal concentration occurred in summer with maximum precipitation and the highest occurred in winter with minimum precipitation. Therefore, precipitation was a significant factor to wash out aerosol particulates and thus leads to low HgP concentration in aerosols as well.

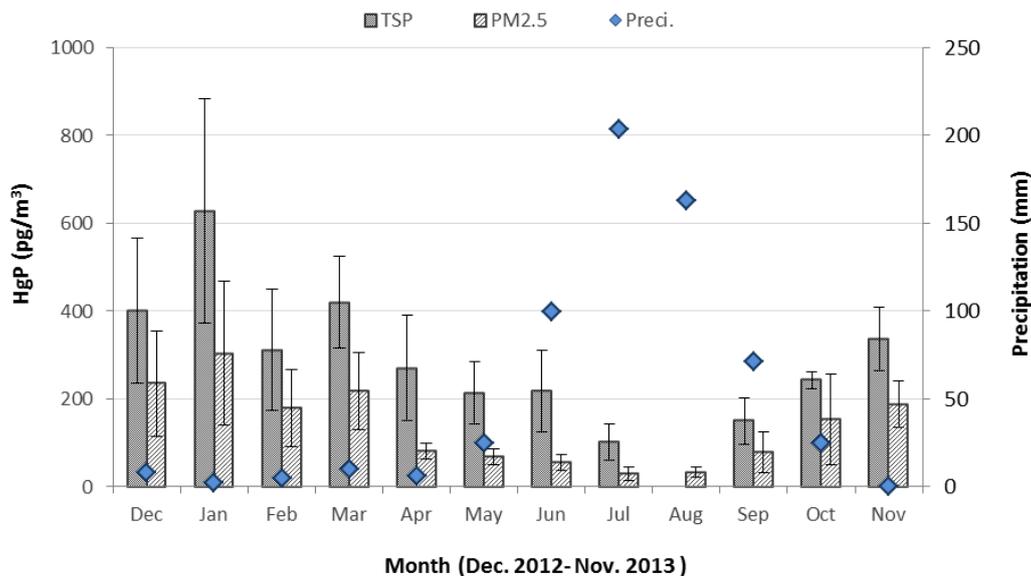


Fig. 4.1 HgP monthly variation in TSP and PM_{2.5} with precipitation. The whiskers represent standard deviations.

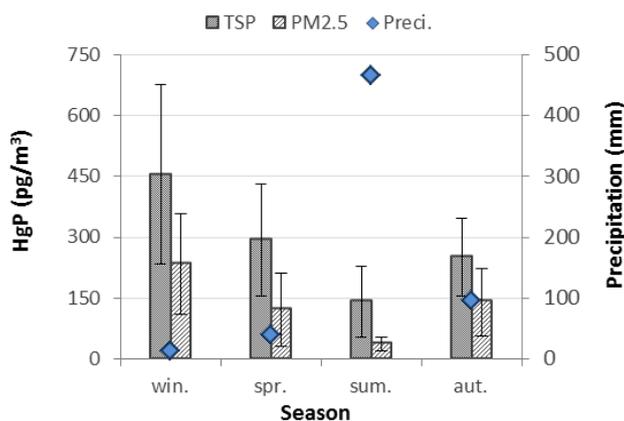


Fig. 4.2 HgP seasonal variation in TSP and PM_{2.5} with precipitation. The whiskers represent standard deviations.

4.3.2 Long-term variation of HgP in aerosol particles from 2005 to 2013

The Pearson correlation coefficient of HgP concentration in winter and in January was 0.98 (data in ng/g) and 0.91 (data in pg/m^3). January was used to represent for winter. August was used to represent for summer. The $\text{PM}_{2.5}$ samples during 2008 Olympic Games were used out for other chemical analyses and thus there was no HgP data for August 2008.

For $\text{PM}_{2.5}$ samples, average HgP concentration ($352 \text{ pg}/\text{m}^3$) of the eight successive Januaries from 2006 to 2013 was around 5 times of HgP ($74 \text{ pg}/\text{m}^3$) of the eight Augusts from 2005 to 2013 (besides August 2008). In general, the Olympic year 2008 was a turning point for HgP winter concentration (Fig. 4.3). In winter, HgP average concentration after 2008 was 57% of that before 2008. HgP concentrations in August did not show obvious decreasing or increasing trend from 2005 to 2013 (Fig. 4.3-b). The concentrations in August 2012 and 2013 sharply reduced compared to those before 2012 (Fig. 4.3-b).

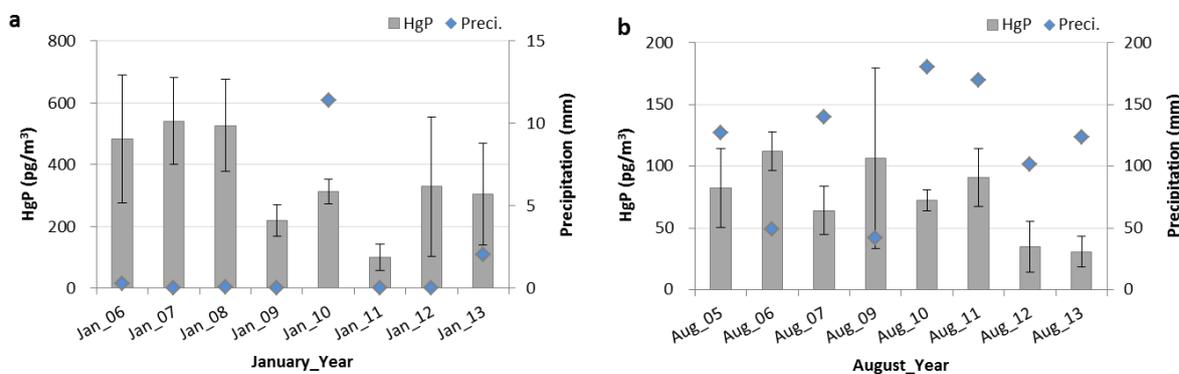


Fig 4.3. HgP concentrations in $\text{PM}_{2.5}$ with precipitation in January and August from 2005 to 2013. The whiskers represent standard deviations.

For TSP samples, average HgP concentration of the six successive winters from 2007 to 2013 was $458 \text{ pg}/\text{m}^3$, it was around 1.6 times that in $\text{PM}_{2.5}$ ($294 \text{ pg}/\text{m}^3$) in the same time. In general, HgP concentrations in winter show a slightly declining trend during the observation periods (Fig. 4.4). HgP average concentration in Win_12/13 was 61% of that in Win_07/08. The concentration in Win_11/12 was lower than that in Win_07/08 with

similar precipitation to Win_11/12 (Fig. 4.4). HgP concentrations in August/September from 2005 to 2013 were reported by Schleicher et al. (2016). The lowest concentration was observed in August 2008 (Olympic Games period) but no long-term decrease or increase trend was observed for summer months with two sites data.

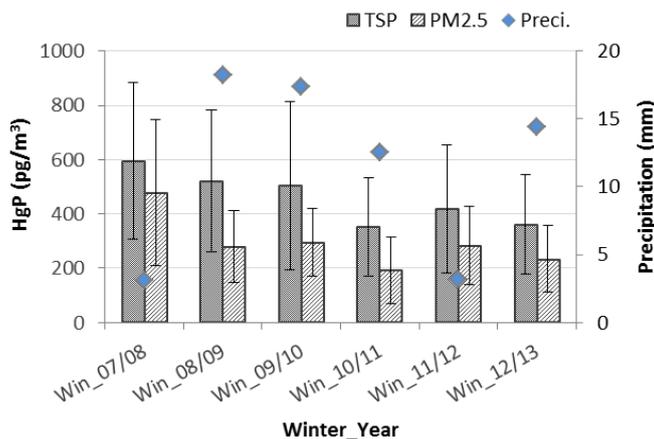


Fig 4.4. HgP winter concentrations in TSP and PM_{2.5} with precipitation from 2007 to 2013. The whiskers represent standard deviations. The X-axis represents the winter in different years; for example, Win_07/08 means winter from 2007 to 2008, namely Dec. 2007, Jan. 2008 and Feb. 2008.

4.4 Influence of meteorological conditions

Beside the direct wash out effects of precipitation as described in the section 4.3, wind direction and wind speed can also play roles on aerosol distribution (Chen et al., 2016b), thus can affect HgP concentrations.

Aerosol samples were collected weekly in this study. During a week, wind direction usually changed several times and the weekly average wind direction did not reflect the real wind direction at every time point. Therefore, 3-hourly meteorological data and the weekly mean concentration for each of the 3-h in a week were used to interpret the correlation. Wind directions were defined briefly as N (north), NE (northeast), E (east), SE (southeast), S (south), SW (southwest), W (west), and NW (northwest). Based on the meteorological data for a whole year from Dec. 2012 to Nov. 2013, the main wind directions were from NE and SW. Wind from NW and N mainly occurred in winter, spring

and autumn. And most of the high wind speed mainly occurred with wind from NW and N, some from SW in spring. These seasonal variations were similar to the results with nine year data from 2005 to 2013 in the section 2.2 (Chen et al., 2016b), which means that the predominating wind condition were relatively parallel from a long-term perspective. Seasonal variation of HgP with wind direction was presented in Fig. 4.5. Wind from N and NW with relatively higher HgP concentration occurred more frequently in winter and autumn than in spring and summer. High or low HgP concentration in a certain season can occur with winds from different directions. Through a whole year, wind seasonal variation could affect HgP concentration to some extent (sources seasonality could also play a part at the same time). However, wind condition was considered to play only a small role in HgP distribution from the long-term perspective.

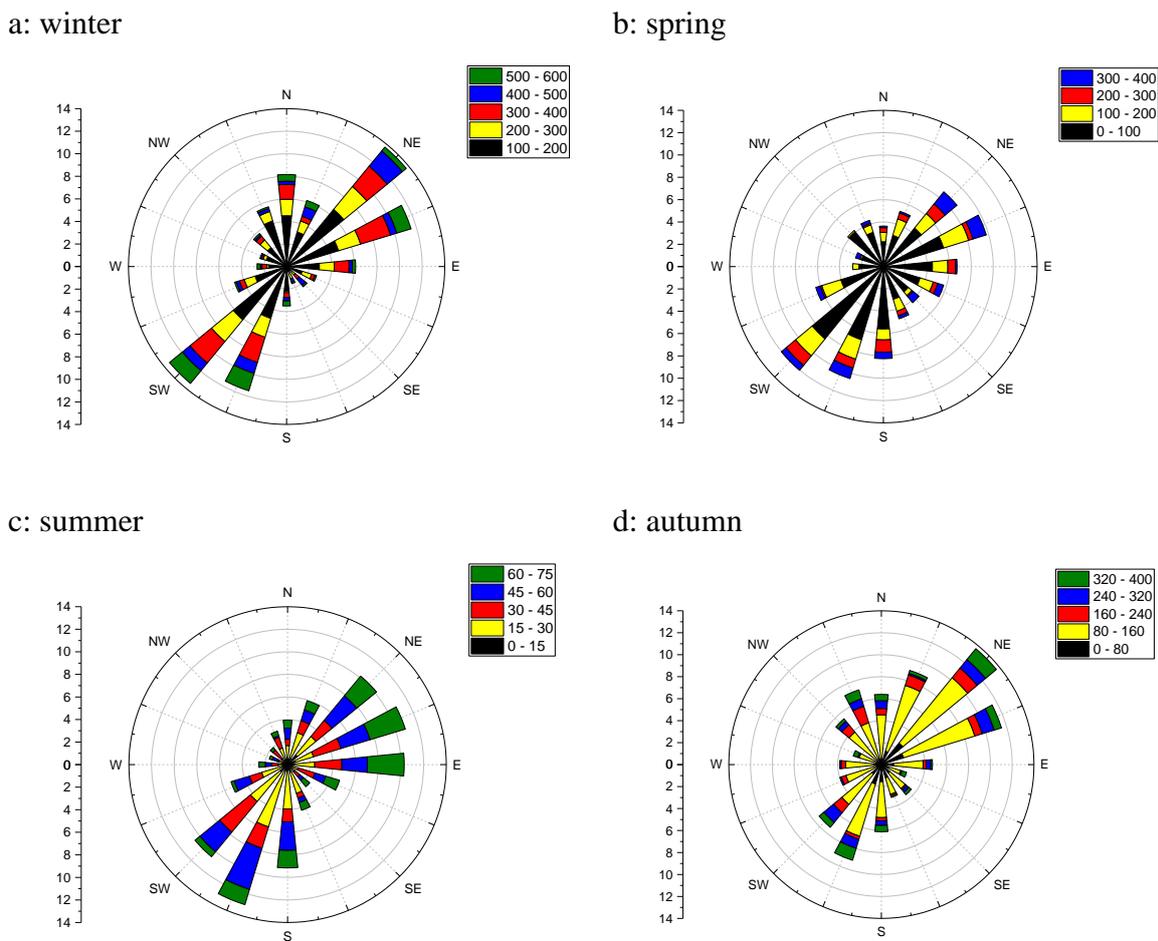


Fig. 4.5 HgP concentrations in $\text{PM}_{2.5}$ and wind direction during four seasons from Dec. 2012 to Nov. 2013. The legends display HgP concentration ranges in pg/m^3 and the left scales display the percentage frequencies.

4.5 Influence of governmental mitigations

Coal combustion is a major source for HgP emission in Beijing (Schleicher et al., 2015). Heating supply in winter is one of the major consumes of coal. However, the coal consumption quantity for heating in each winter was unavailable, hence the direct correlation between HgP and coal consumption cannot be calculated. In the sections 2.2 and 2.3 (Chen et al., 2016a, 2016b), black carbon (BC) and Ga concentrations were reported to well correlate to coal combustion with nine years data. And Ga had good correlation with BC as well, especially in the heating period which covers the whole winter (Chen et al., 2016a). Energy structure transformation policies (less coal and more clean energy) in Beijing have being been implemented and were demonstrated to be effective to reduce BC and Ga in aerosols. Correspondingly, correlations between HgP and BC/Ga were investigated to help to interpret the influence of coal consumption on HgP.

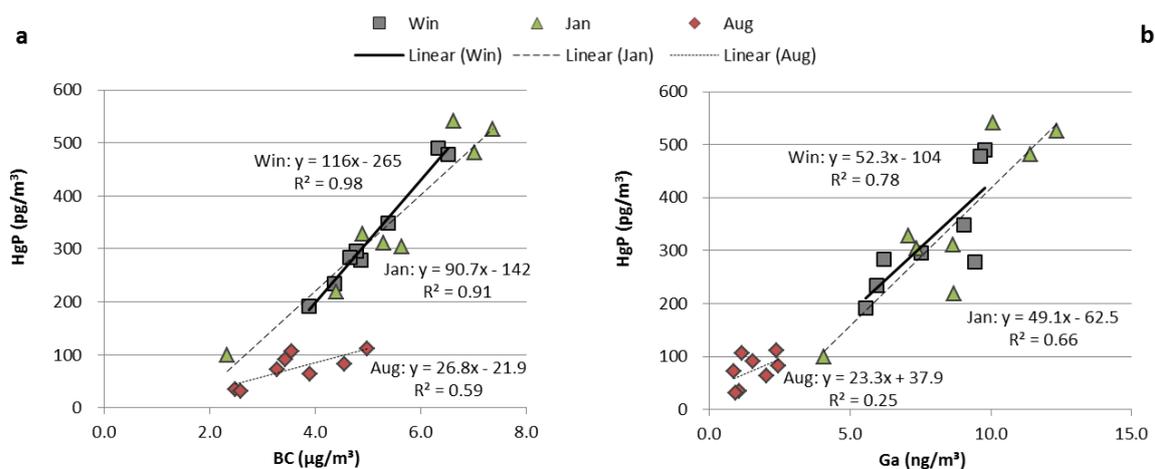


Fig. 4.6 Correlations between HgP and BC (Fig. 4.6-a)/Ga (Fig. 4.6-b) concentrations in PM_{2.5} during winter (Win), January (Jan) and August (Aug) from 2005 to 2013.

Fig. 4.6-a shows the correlations between HgP and BC during the whole winter, January and August for PM_{2.5}. The strongest correlation was observed between HgP and BC during winter. January shows similar correlation to winter. The correlations between HgP and Ga (Fig. 4.6-b) were similar to the correlations between HgP and BC but relatively weaker. This seasonal difference of these correlations depends on the sources seasonality of HgP. The effectiveness of energy structure transformation on reducing BC/Ga (Chen et al.,

2016a, 2016b) together with the strong correlations between HgP and BC/Ga in winter (Fig. 4.6) suggested the effectiveness of reduced coal consumption on HgP emission control.

For TSP, the lowest HgP concentration (pg/m^3) in August 2008 during the summer months from 2005 to 2013 demonstrated the short-term intensive governmental mitigation measures on HgP reduction but no long-term effect of the mitigation measures on HgP observed for summer months due to the relative stable sources in summer (Schleicher et al., 2016).

The lowest HgP concentrations in both TSP and $\text{PM}_{2.5}$ in winter were observed in Win_10/11 (Dec. 2010, Jan. 2011 and Feb. 2011) (Fig. 4.4). And the lowest HgP concentration in January occurred in Jan_11 (Fig. 4.3). These attribute to the largest annual decline of coal and coke consumption from 2010 to 2011 during the observation period (Beijing Bureau of Statistics, 2015).

Besides the energy structure transformation as a governmental macro intervention policy, specific mitigation measures during specific periods should be considered as well, for example, the relocation of the Capital Steel Company (CSC) and traffic restriction measures. They played a role along a whole year not mainly in winter.

The relocation project of the CSC started in 2005 and was completed at the end of 2010 in Beijing. The new company in Caofeidian, which is around 225 km to the southeast of the former location in Beijing, went into operation in the middle of 2010, and has gradually recovered the capacity at the new location. The sections 2.1 and 2.4 (Chen et al., 2013, 2014) reported the short-term effectiveness of this relocation project in reducing steel-related elements in $\text{PM}_{2.5}$ from 2008 to 2010. However, from a long-term perspective, the reduction did not continue and an increase of these elements was found since 2011, especially in 2012 and 2013 which was illustrated in the section 2.3 (Chen et al., 2016a). This is parallel to the higher HgP concentrations in Jan_12 and Jan_13 (Fig. 4.3) and could be also a reason for the higher HgP concentrations in Win_11/12 and Win_12/13 than in

Win_10/11 (Fig. 4.4).

The total amount of vehicles kept increasing over the entire investigation time (Fig. 1.3). The license plate lottery policy for car registration since the beginning of 2011 in Beijing caused the largest annual growth of total amount of vehicles from 2009 to 2010 (Fig. 1.3). This might contribute to the higher HgP concentration in Jan_10 (even with more precipitation) than in Jan_09 (Fig. 4.3). The average concentration in Aug_10 was lower than in Aug_09, which might attribute to the more precipitation in Aug_10 than in Aug_09 (Fig. 4.3).

4.6 Summary

In conclusion, for the long-term observation period from 2005 to 2013, meteorological conditions as well as mitigation measures can affect HgP distribution. Precipitation has direct scavenging effects on aerosol particles and thus reduced HgP. Wind condition plays a small role in HgP distribution from the long-term perspective, besides in the seasonal variation. Long-term HgP distribution was predominated by the control measures.

In winter, HgP average concentration in PM_{2.5} after 2008 was 57% of that before 2008, and the concentration in TSP in Win_12/13 was 61% of that in Win_07/08. Under the rapid economic and industrial developments in China, the total energy consumption kept increasing while the coal consumption reduced due to the energy structure transformation. HgP concentration fell from a long-term perspective even under the rapid development with increasing total energy consumption and growing total vehicle number. This demonstrated the effectiveness of the macro energy structure transformation policy and the specific mitigation measures on improving air quality and thus on HgP distribution. The Olympic year 2008 was a turning point for HgP winter concentrations.

This is not only an HgP case study, but also a representative mercury study in China, which reflect the mercury atmospheric pollution in developing countries. Improved technique to control HgP emission and governmental intervention measures are still on

demand to mitigate atmospheric mercury pollution in China.

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5 Coarse particles (2.5-80 μm)

5.1 Introduction and background

Aerosol particles can be collected with both active samplers and passive samples. One disadvantage of active samplers is the requirement of auxiliaries such as power supply and air-flow meters, which leads to application inconvenience in the field. Passive samplers can be installed in various environments, even at quite remote locations. Due to the cost-efficient property, they can be employed as a network for large-scale air quality monitoring (Guéguen et al., 2012). However, sampling interval with passive samplers should be considered according to sampling purposes and local aerosol pollution levels. For example, to collect sufficient material for trace element and isotope analysis in France, 1-4 weeks sampling time was necessary depending on the different environments (Guéguen et al., 2012); to analyze the size distribution and mass concentrations of coarse particles in Beijing, a megacity and the capital of China, 3-4-day interval was utilized to avoid excessively high loads and superimpositions of particulates (Norra et al., 2016).

For the recent decade, increasing studies about fine particles were published with growing attention due to the adverse health impacts, environmental and climatic effects, especially in developing countries. In Beijing, the highest concentrations of aerosol particles mostly correlated to the dust events (Chen et al., 2016; Norra et al., 2016) which resulted in an increase of aerosol particulates predominantly in coarse fraction (Zhang et al., 2009). Sand dust or dust storms have direct impacts on visibility and thus affect residents' commute (Zhao et al., 2007; Akhlaq et al., 2012; Cao et al., 2014); they can also affect human health (Chen and Yang, 2005; Honda et al., 2014) and even act as conveyance medias of anthropogenic pollutants (Kim et al., 2012). Therefore, coarse particles were significant as well when investigating air pollution.

Within this dissertation, $\text{PM}_{2.5}$ and TSP were collected with active samplers which were studied in the former sections (section 2, 3 and 4), while coarse particles were collected

with a passive sampler from 2005 to 2012, which were studied in this section. This study is the first study of long-term variation of size distribution of coarse particles and the effects of mitigation measures on different size fractions.

5.2 Methodology

5.2.1 Sampling

Coarse particle ($>2.5 \mu\text{m}$) samples were collected using a passive sampling device Sigma-2 (Grobéty et al., 2010, VDI, 2013) at the CUGB site. Technical details can be found in the guideline VDI 2119:2013-06 (VDI, 2013) and sampler description can be found in Norra et al. (2016). Particles were collected on highly transparent collection plates for optical microscopy (Norra et al., 2016). Generally, two samples in each week were collected in interval of three and four days in order to prevent too high loads and superimpositions of particulates from 2005 to 2012. To investigate the effects of the special governmental policies during the Olympic Games period in 2008, daily samples were collected in August and September 2008 (Schleicher et al., 2011, 2012). Weekly averages were calculated with daily samples or 3-4-day samples in one week. Part of the data (2005-2009) was used for studying the seasonal dynamics of opaque and transparent particles in different size intervals in Norra et al. (2016). Over the entire observation period, 763 samples were analyzed, and a few samples ($N=77$) were not available due to external errors such as sampler problem and sampling absence, accounting for 9% of total samples.

$\text{PM}_{2.5}$ samples and TSP samples used for comparison and evaluation were collected at the CUGB site and the CRAES site, respectively. Detail information can be found in the former sections (section 2, 3 and 4).

5.2.2 Analytic methods

5.2.2.1 Types and morphology of coarse particles

Scanning Electron Microscopy (SEM) was used to study the morphology of minerals and

other solid particles in aerosol. With a Quanta FEG 650 (FEI, USA) coupled to electron dispersive X-ray fluorescence spectrometry (EDX), particle composition and type were identified at the Laboratory for Electron Microscopy (LEM) at KIT by comparing the spectrograms of particles provided by Reed (2005). The excitation energy was 10 kV.

5.2.2.2 Size distribution and mass concentration

The method collected coarse particles up to 160 μm (geometrical equivalent diameter). Mass concentrations of different size fractions can be analyzed in intervals of 2.5-5, 5-10, 10-20, 20-40, 40-80 and 80-160 μm . For 92% of the samples (N=447) which were analyzed in all the intervals, the mass concentrations of particles larger than 80 μm were less than 0.5% of mass concentrations of particles between 2.5 and 80 μm . The largest particles usually occurred when the mass concentrations of particles between 2.5 and 80 μm were larger than 300 $\mu\text{g}/\text{m}^3$, especially during sand dust or dust storms. Thus the size fraction >80 μm was neglected within this study. The five size fractions in this study were defined as SF1 (2.5-5 μm), SF2 (5-10 μm), SF3 (10-20 μm), SF4 (20-40 μm) and SF5 (40-80 μm).

A computer-aided automatic image analysis system Digitrace V.3.4 (IMATEC) together with a motorized optical microscope (ZEISS Axioplan 2), an adapted automatic scanning stage (Prior Scientific) and a CCD-digital-camera (SVS-VISTEK) were used for quantitative optical microscopic analysis of single particles at the German Meteorological Service (DWD) in Freiburg, Germany. Technical details of this method were depicted by Dietze et al. (2006). Mass concentrations were calculated as described in Dietze et al. (2006) and Schleicher et al. (2010).

5.2.3 Meteorological data

Meteorological data were obtained from the German Meteorological Service (DWD). The 3-hourly parameters including precipitation, temperature, visibility, wind direction and wind speed were collected from a meteorological station in Beijing registered at the World Meteorological Organization (WMO) with the code 54511.

5.3 Types and morphology of coarse particles

SEM combined with EDX analysis of coarse particles identified particles types from various sources, including geogenic, anthropogenic and biogenic. During sand dust or dust storms which often occurred in spring but also were contingent in other seasons, geogenic mineral particles predominated, for example, quartz, mica, feldspar (albite), amphibole, dolomite, and clay minerals (Fig. 5.1). These minerals were less frequent during non-dust days. Special biogenic particles, such as pollen and diatoms (Fig. 5.2-a, Fig. 5.2-b) were found to accumulate in spring especially during sand dust or dust storm events with high wind velocity. Organic remains of different morphology were also observed (Fig. 5.2-c, Fig. 5.2-d). Soot chains, fly ash and iron oxides (Fig. 5.3) were the leading anthropogenic particles in most Beijing aerosol samples. Particles containing Fe-Cr-Ni were also observed, and they mostly attributed to steel-related work. Carbon fibers (Fig. 5.3-f) were found in some samples, which might come from car brakes. A number of particles agglomerated with each other, which caused uncertainly when counting particle numbers of different size fractions.

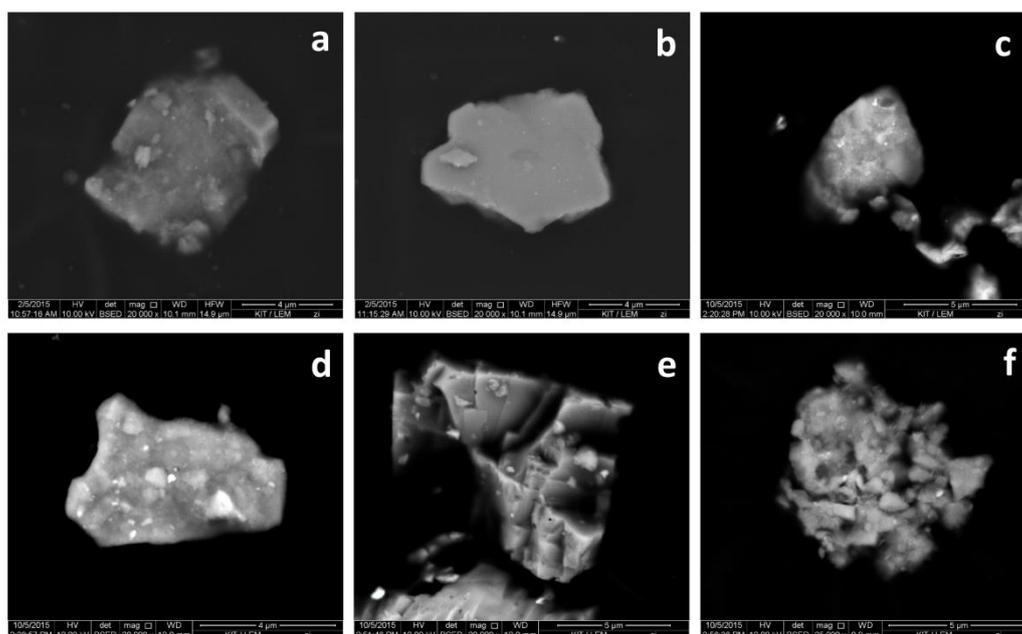


Fig. 5.1 Typical geogenic aerosol particles during sand dust or dust storms: a) quartz; b) mica; c) feldspar (albite); d) amphibole; e) dolomite; f) clay minerals.

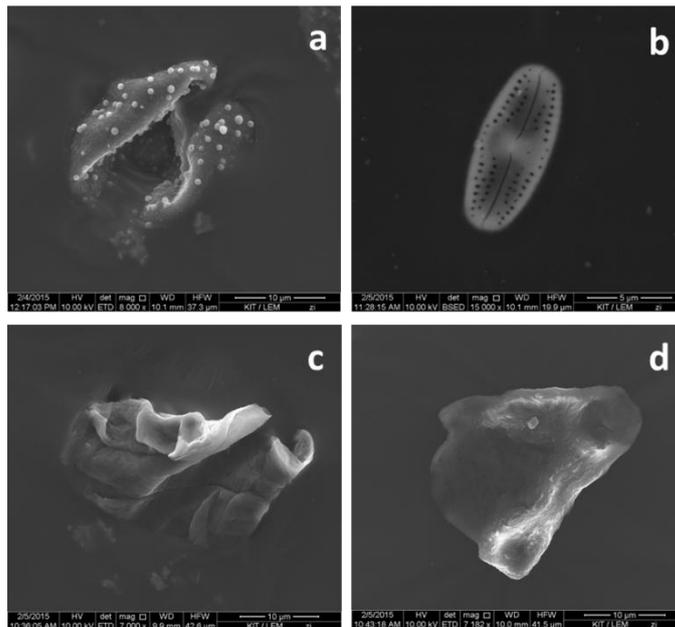


Fig. 5.2 Biogenic particles: a) pollen; b) diatom; c) and d) organic remains.

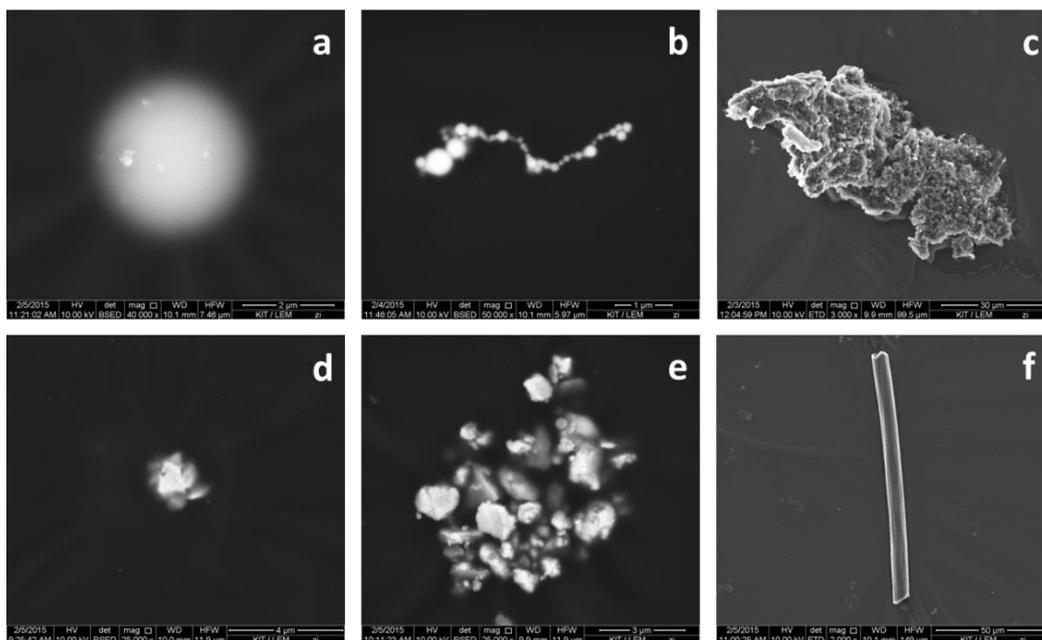


Fig. 5.3 Anthropogenic aerosol particles: a) fly ash; b) soot chain with iron oxides; c) soot chains with Fe-Cr-Ni; d) chromium oxide; e) iron oxides agglomerated on clay minerals; f) carbon fiber.

In general, geogenic particles contributed most to the total coarse particles in Beijing. Biogenic particles appeared seldom and only played a minor role in coarse particles. Anthropogenic particles appeared more frequently than biogenic particles but less than geogenic particles.

5.4 Comparison with TSP and $\text{PM}_{2.5}$ data

For long-term period, the calculation method of mass concentration with coarse particles collected by Sigma-2 was not compared with other methods. To evaluate this method, mass concentrations of $\text{PM}_{2.5}$ and TSP samples were used for comparison. The sum of mass concentrations of total coarse particles (2.5-80 μm) from the passive sampler and $\text{PM}_{2.5}$ (<2.5 μm) from an active sampler at the same sampling site was used to compare with the mass concentrations of TSP from an active sampler.

TSP and $\text{PM}_{2.5}$ samples were collected from different sampling sites. And for some weeks, the sampling periods of the two sites were not identical with one- or two-day malposition (earlier or later). This should be considered when discussing the comparison results of passive and active methods. Weighted mean of mass concentration ($C_{(n)\text{wm}}$) of a week (week number n) was calculated according to $C_{(n)\text{wm}} = (C_{(n-1)} + 2C_{(n)} + C_{(n+1)})/4$ and was used for comparison (Fig. 5.4).

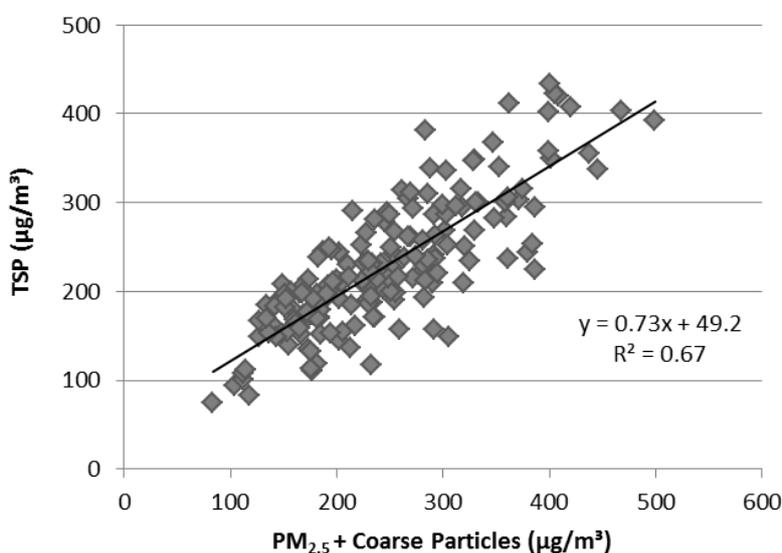


Fig. 5.4 Comparison of mass concentrations between TSP and the sum of $\text{PM}_{2.5}$ and coarse particles (2.5-80 μm).

For 62% of the sampling weeks (N=179) when three kinds of aerosol samples were all available, the sum concentration of $\text{PM}_{2.5}$ and coarse particles was larger than TSP mass concentration. On average, TSP mass concentration was $96\% \pm 19\%$ of the sum of $\text{PM}_{2.5}$ and coarse particles.

For 85% of spring weeks and 70% of winter weeks, TSP mass concentrations were usually less than the sum concentration. These weeks covered all the sand dust or dust storm events in spring. This indicated that the passive sampler overestimated the particles compared to the active samplers. The average overestimated concentration was 50.7, 36.1, 23.6, 57.9 $\mu\text{g}/\text{m}^3$, accounting for 21%, 28%, 14%, 26% of the average concentration of coarse particles for these weeks in spring, summer, autumn and winter, respectively. For the weeks with underestimated concentrations by the Sigma-2 system, 72 % were from summer and autumn. The average underestimated concentration was 20.1, 21.8, 22.2, 27.7 $\mu\text{g}/\text{m}^3$, accounting for 10%, 17%, 12%, 16% of the average concentration of coarse particles for these weeks in spring, summer, autumn and winter, respectively. On the whole, the underestimation extent was not as strong as the overestimation. It went through all the four seasons with a similar level (around 20 $\mu\text{g}/\text{m}^3$).

Overlapping of particles could lead to underestimation of particle number. Particle superimposition was a major problem when calculating the mass concentrations of particles from different size factions. Additional errors also existed during active sampling and filter analyses. For examples, too high aerosol loads during extremely polluted days can reduce the air flow. The sampler can even automatically stop when the filter is totally loaded and the air flow cannot pass through the filter. This can also result in underestimation of particle concentrations by active sampling.

In general, analytical results of samples from the passive sampler and those from active samplers were comparable from the long-term perspective (Fig. 5.4). For Beijing, one of the most polluted megacities, short interval (one day if possible) is recommended for size distribution study due to high loads of particles.

5.5 Temporal distribution of coarse particles and weather condition

Beijing hosted the Summer Olympic Games (8-24th in August) and the Paralympic Games (6-17th in September) in 2008. The corresponding weeks included calendar week (CW) 32/08 to CW34/08 and CW36/08 to CW38/08, respectively. These two periods together were called the Olympic Games period in this study.

From the long-term perspective, mass concentrations of different size fractions show slightly decreasing trends during the whole observation period. The Olympic Games period displayed lower concentrations compared to the other sampling time (Fig. 5.5). Most of the peaks correlated to the sand dust or dust storms. In most cases, wind from the north and the northwest with high wind velocity carrying dust triggered sand dust or dust storms especially in spring.

With increased planting and afforestation to prevent desertification and dust erosion, the day number of sand-dust weather (including sand dust and dust) showed a decreasing trend since the 1950s but only on a long term time sequence (An and Liu, 2004; Zhou et al., 2002) whereas year-to-year variations were not stable. According to the Sand-Dust Weather Almanacs for 2005-2012 (CMA, 2007-2014), there was no obvious increasing or decreasing trend for day number of sand-dust weather. The Beijing Observatory observed most days of sand-dust weather in 2006, which all occurred in spring. The highest peaks for mass concentrations of all size fractions during the whole observation period (Fig. 5.5) were observed with the most intensive sand-dust days in spring 2006.

This intensive sand-dust weather was triggered by several factors. The area around Beijing, including the east of Northwest China, the central and the north of North China, the most area of Inner Mongolia and the north of Northeast China, which covered the main areas of sand-dust domestic sources, had less precipitation in summer and autumn 2005 compared to the same periods in previous years, and the precipitation reduction in some areas was more than 50% (CMA, 2008). The prolonged drought in these areas from summer to autumn 2005 which attribute to El Niño resulted in decreased soil moisture and negatively

impacted land vegetation growth and thus impaired the ability of vegetation to retain soil. And relatively higher temperature (1-2°C higher) in spring 2006 compared to the same periods of previous years, which contributed to more evaporation of soil moisture, also resulted in soil loosening in the surrounding areas of Beijing. Furthermore, in early spring 2006, low precipitation with relatively high temperature thickened the surface dry soil layer. These all provided advantaged conditions for the high frequency of sand-dust weather, especially under windy circumstance (CMA, 2008). Therefore, climate and weather conditions in the areas around Beijing played an important role in sand-dust weather which could lead to high pollution of coarse particles.

Seasonal variation was characterized as the mass concentrations in sequence from high to low in: spring, winter, autumn and summer for the total coarse particles and also for all the five size fractions. This seasonal characteristic was identical to those of $\text{PM}_{2.5}$ and TSP. Among the 31 investigation season periods, summer 2012 presented the lowest concentrations for all size factions with the maximum precipitation. Spring 2006 presented the highest concentrations due to the frequent sand-dust weather but not with the least precipitation. If spring 2006 with extreme weather events was excluded for the long-term observation, the former slightly decreasing trends for mass concentrations of different size fractions get weaker. This should be considered when long-term study was conducted.

Coarse particles (2.5-80 μm)

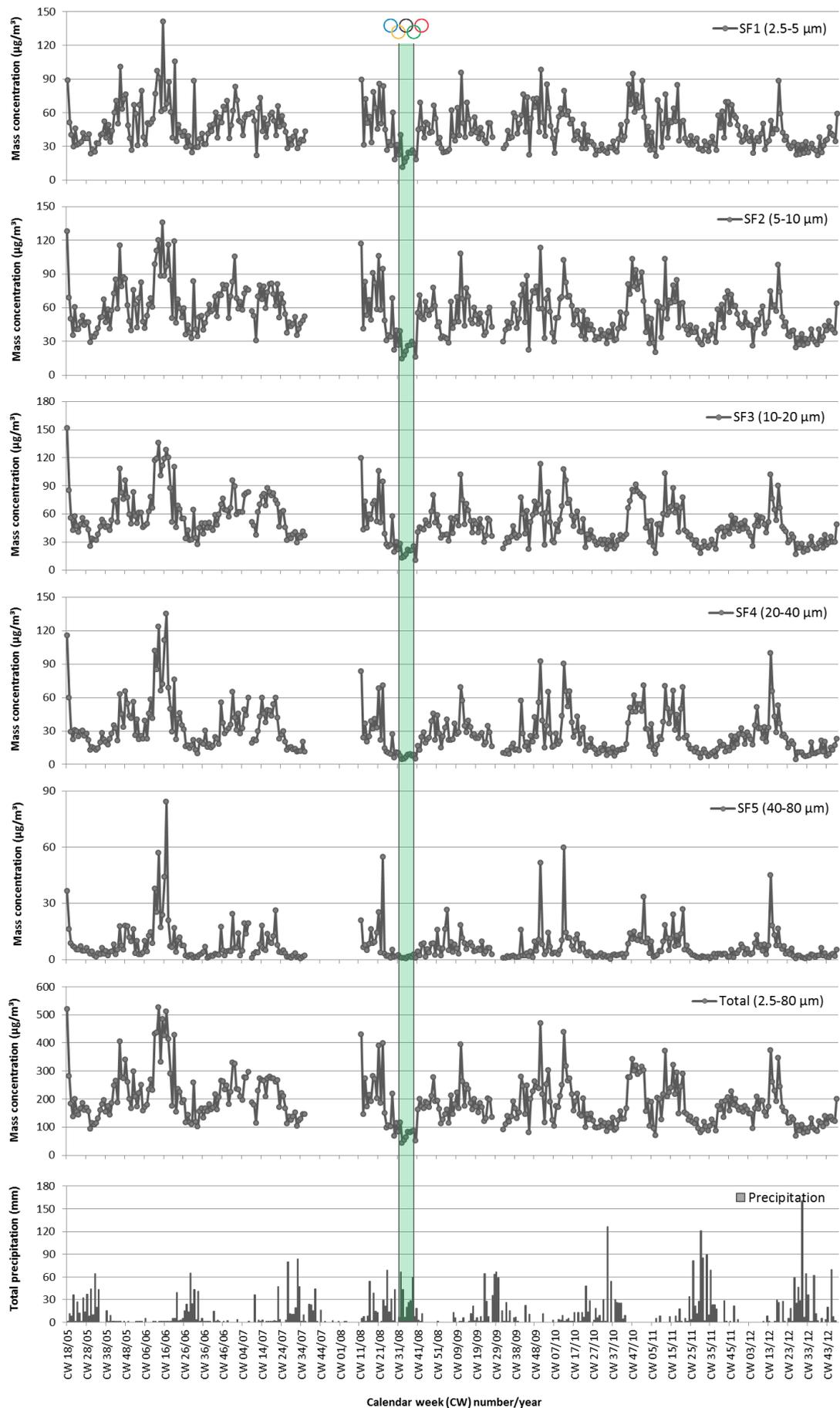


Fig. 5.5 Temporal distribution of coarse particle mass concentrations in different size fractions SF 1-5, The Olympic Rings indicate the period from CW32/08-CW38/08 which covered the whole Olympic Games period, including the Olympic Summer Games (8-24th in August, CW32/08 to CW34/08) and the Paralympic Games (6-17th in September, CW36/08 to CW38/08) in 2008.

From yearly variation perspective, temperature and wind condition were similar from 2005 to 2012. Annual mean mass concentrations of total coarse particles were well correlated with precipitation (Fig. 5.6). High mass concentrations of total coarse particles in 2005 and 2006 occurred with the low precipitation. Precipitation was a significant factor for scavenging coarse particles. However, mass concentrations of total coarse particles in 2009 were lower than that in 2007 with similar precipitation (Fig. 5.6), which might attribute to the mitigation measures which will be discussed in the following section.

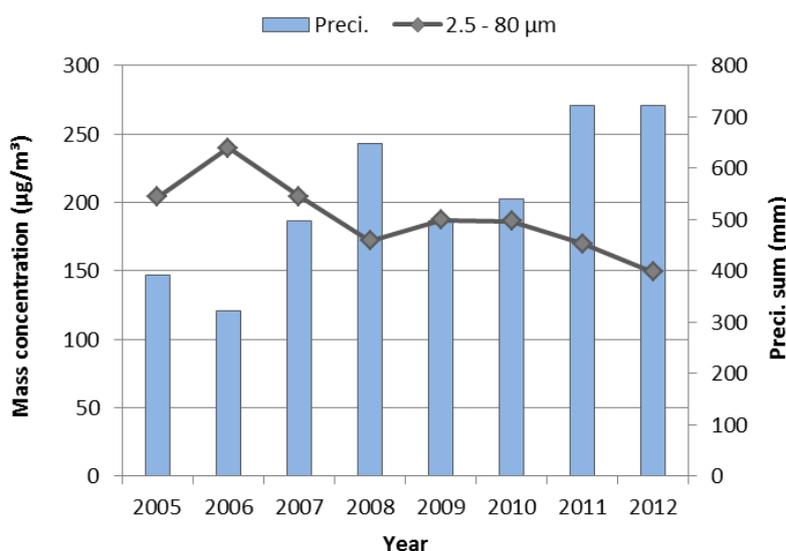


Fig. 5.6 Annual mean mass concentrations of total coarse particles (2.5-80 μm) with overall precipitation in each period.

5.6 Evaluation of governmental mitigations on coarse particles

To host a “Green” Olympic Games in 2008 in Beijing, a series of governmental measures for improving air quality were put into force step by step, including improvement of emission standards, restriction measures on traffic and construction, industry relocation

and afforestation to prevent desertification and sand dust erosion (Chen et al., 2013, 2014; Schleicher et al., 2011, 2012; Wang et al., 2009, 2010). The most intensive mitigation measures were implemented during the Olympic Games.

For the five size fractions of the coarse particles, the lowest monthly-average mass concentrations during the eight successive Augusts from 2005 to 2012 all occurred in Aug_2008 (Fig. 5.7), when the Summer Olympic Games took place. Average mass concentrations of different size fractions were calculated with four week data for seven Augusts except Aug_2009 only with three-week data due to sampler problem. TSP and $\text{PM}_{2.5}$ mass concentrations were calculated all with four week data in every August. Precipitation presented in Fig. 5.7 was the total precipitation in every August. Other meteorological parameters, such as temperature, visibility, wind direction and wind speed were similar for the eight Augusts and thus did not play a significant role for the long-term variation of coarse particle concentrations.

Compared to the average concentration in Augusts before 2008 (2005-2007), the mass concentration of total coarse particles (2.5-80 μm) in Aug_2008 was reduced by 47%, namely 60.6 $\mu\text{g}/\text{m}^3$. In Aug_2009, mass concentrations of all size fractions increased by 65% (45.1 $\mu\text{g}/\text{m}^3$) compared to Aug_2008. However, average concentrations of all size fractions after 2008 (2009-2012) were still lower in comparison with the averages in Augusts before 2008 (2005-2007). The average mass concentration of total coarse particles in Augusts after 2008 was reduced by 24.4 $\mu\text{g}/\text{m}^3$ compared to that before 2008. The reduction mainly fell to the coarse fraction ($>5 \mu\text{m}$) of the coarse particles, which was identical to the results of Schleicher et al. (2011) with short-term observation.

Precipitation was an important factor for scavenging aerosol particles. Therefore, periods with similar precipitation were selected for comparison in order to study the effects of mitigation measures. Aug_2008 had similar precipitation to Aug_2005 and Aug_2007, while their mass concentrations of all size fractions were higher than those in Aug_2008 (Fig. 5.7). Aug_2010 and Aug_2011 had more precipitation than Aug_2008; however,

concentrations of the former period were much higher than those in Aug_2008 (Fig. 5.6). These documented the effects of mitigation measures on reducing coarse particles.

The largest decline in 2008 and the continuous decline of mass concentrations of all size fractions of coarse particles indicated the effectiveness of the measures on improving air quality, especially reducing coarse fractions. The intensity of the mitigation measures determined the reduction of coarse particles.

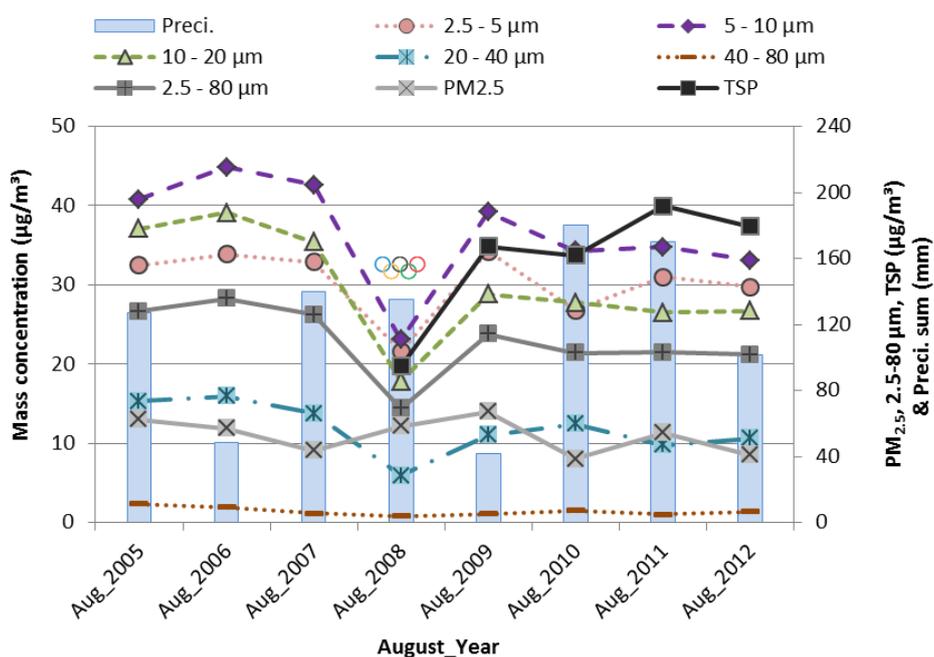


Fig. 5.7 Monthly average mass concentrations of coarse particles (2.5-80 μm) in different size fractions, together with $\text{PM}_{2.5}$, TSP and precipitation in August from 2005 to 2012. The Olympic Rings indicate the Olympic Games period in Aug_2008.

5.7 Cases study of size distribution patterns

According to the previous sections (section 2, 3 and 4), sand dust or dust storms and heating supply were investigated to represent the heavy pollution caused by natural sources and anthropogenic sources respectively. Calendar week 17, 34, 44 and 51 with similar precipitation (to diminish the scavenging effects of precipitation on coarse particles) were selected to represent for days with sand dust storm in spring, normal days in summer, normal days without heating in autumn and days with heating in winter. Fig. 5.8 shows the size distribution of the five size fractions during these weeks.

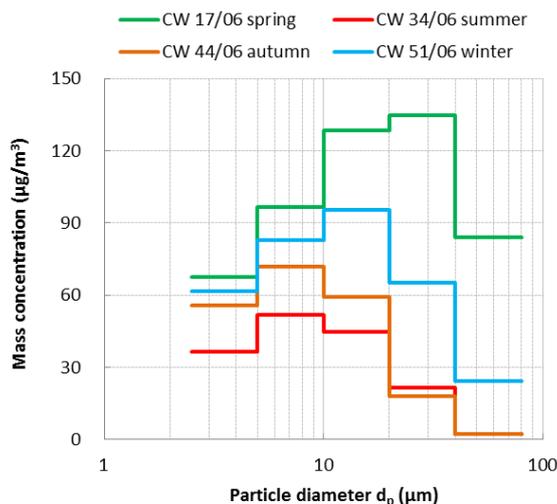


Fig. 5.8 Size distribution of coarse particles in four representative weeks from four seasons.

Coarse particles in CW 17/06 with sand dust storm were predominated by the coarse fraction SF3 and SF4 (10-40 μm). Compared to other weeks, mass concentrations increased in all size fractions. The increased percentage for each size fraction grew with the particle size. Coarse particles in CW 51/06 with heating activities were predominated by SF2 and SF3 (5-20 μm). During normal days in summer and autumn (CW 34/06 and CW 44/06), SF2 (5-10 μm) contributed most to the coarse particles. The different size distribution patterns during different pollution days provide reference information for the enactment of mitigation measures on aerosol particles by the government.

5.8 Summary

Various kinds of aerosol particles were observed, including geogenic particles which contributed most to the total coarse particles in Beijing, a small number of biogenic particles and anthropogenic particles which appeared more frequently than biogenic particles but less than geogenic particles.

With a long-term sampling and analyses, the comparable mass concentration data from active samplers (TSP and $\text{PM}_{2.5}$) and the passive sampler Sigma-2 (coarse particles) demonstrated the feasibility of the passive sampler system for aerosol study for the first time.

From the long-term perspective, mass concentrations of different size fractions show slightly decreasing trends during the whole observation period. Precipitation was an important contributor for this. The Olympic Games period displayed lower concentrations compared to the other sampling time. Most of the peaks correlated to the sand dust or dust storms. The highest peaks for mass concentrations of all size fractions were observed with the most intensive sand-dust days in spring 2006 due to global climate change caused by El Niño.

Seasonal variation was characterized as the mass concentrations in sequence from high to low in: spring, winter, autumn and summer for the total coarse particles and also for all the five size fractions.

During the eight successive Augusts from 2005 to 2012, the lowest monthly average mass concentrations for the five size fractions all occurred in Aug_2008. Compared to the average concentration in Augusts before 2008 (2005-2007), the mass concentration of total coarse particles (2.5-80 μm) in Aug_2008 was reduced by 47%, namely 60.6 $\mu\text{g}/\text{m}^3$. From the long-term perspective, the average mass concentration of total coarse particles in Augusts after 2008 was reduced by 24.4 $\mu\text{g}/\text{m}^3$ compared to that before 2008. These all demonstrated the effectiveness of the mitigation measures on improving air quality. And the most intensive measures led to the highest air quality.

During sand dust days, mass concentrations increased in all size fractions compared to other weeks. The increased percentage for each size fraction grew with the particle size. The different size distribution patterns during different pollution days provide reference information for the enactment of mitigation measures on aerosol particles by the government.

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6 Synoptic conclusions

As the capital of China, Beijing, a typical megacity in Asian countries, has been suffering from severe air pollution owing to high loads of aerosol particulates. To improve air quality, series of control measures were implemented by the government. And in order to hold a ‘Green’ Olympic Games in 2008, the most intensive mitigation measures were put into force in Beijing. With long-term sampling and analyses of atmospheric particulates from 2005 to 2014, this dissertation aims to study the characteristics of the aerosol particulates in Beijing and the effects of the mitigation measures in improving air quality with consideration of meteorological influences.

6.1 Air quality in Beijing

The annual mean concentration of PM_{2.5} from 2005 to 2014 was 65.6 µg/m³ and the annual mean of TSP from 2007 to 2014 was 227 µg/m³. They both exceeded the annual mean standards (level II) for PM_{2.5} and TSP according to the Ambient Air Quality Standard (GB3095-2012) in China and were several times higher than the standards from other countries and World Health Organization (WHO) (Table 6.1). The concentrations of most elements of PM_{2.5} in Beijing were higher than the corresponding concentrations in other studies in European or American countries. Of the four elemental concentrations mentioned in the Ambient Air Quality Standard, only As average concentration of PM_{2.5} exceeded the standard (2.5 times), based on nine-year (2005-2013) measured data. Elemental concentrations of Pb, Cd and As in Table 6.1 were measured with the PM_{2.5} samples from 2005 to 2013 from the CUGB site. Since only particulate-bound mercury (HgP) was measured within this study, annual mean (from Dec. 2012 to Dec.2013) of total atmospheric Hg concentration was estimated to 12 ng/m³ according to the mean fraction 2.5% of HgP in total atmospheric Hg in urban area of China (Fu et al., 2015).

During the entire observation period, TSP concentrations did not present an obvious increasing or decreasing trend. Annual mean mass concentrations of PM_{2.5} after 2008 were

lower than those before 2008 but it increased from 2011 to 2013, with the lowest annual mean concentration in 2011.

The main sources of fine particle were categorized and identified by factor analysis according to the element associations: typical anthropogenic sources (i.e. traffic and smelting), geogenic dust, agriculture sources (i.e. fertilizers), coal combustion, steel-related industry, comprehensive combustion emission and diffuse urban pollution. Temporal distributions of different sources were investigated based on the variations of factor scores.

Table 6.1 Annual mean concentrations of pollutants in this study and corresponding air quality standards from different countries and WHO.

	TSP ($\mu\text{g}/\text{m}^3$)	PM_{2.5} ($\mu\text{g}/\text{m}^3$)	Pb (ng/m^3)	Cd (ng/m^3)	Hg (ng/m^3)	As (ng/m^3)
This study	227	65.6	145 ^(a)	3 ^(a)	12 ^(b)	15 ^(a)
China Standard	200 (level II)	35 (level II)	500	5	50	6
EU Standard	-	25	500	5	-	6
USA Standard	75	15 (secondary)	150	-	-	-
Australia Standard	-	8	500	-	-	-
WHO AQG	-	10	500 ^(c)	5 ^(c)	-	-

^(a) elemental concentrations measured with the PM_{2.5} samples from 2005 to 2013 from the CUGB site

^(b) estimated annual mean concentration of total atmospheric Hg (from Dec. 2012 to Dec.2013)

^(c) WHO AQG for Europe (WHO, 2000)

Based on the data base collected in this dissertation, the yearly cycle of Beijing air pollution can be characterized as follows: occasional dust or sand dust storms in January or February in winter, firework-related pollution during the Chinese spring festival and the lantern festival, usually in January or February, typical dust or sand dust storms in spring, especially in March and April, biomass burning after harvest season in later summer and autumn, heating activities usually from Mid-November to the following Mid-March in

addition to the pollution baseline by traffic, industry production, construction activities and residential emission throughout a whole year.

6.2 Effects evaluation of mitigation measures and meteorological conditions

Precipitation had direct scavenging effects on aerosol particles. For the long-term observation period, precipitation played a significant role in aerosol particle distribution, especially in reducing coarse particles. In the sections 2, 4 and 5, aerosol pollutants during periods with similar precipitation but different mitigation measures were investigated and the effectiveness of these measures on mitigating certain sources were reported and quantified. The slightly reduced precipitation from 2011 to 2013 might be a contributor to the slightly increased PM_{2.5} and TSP concentrations.

PM_{2.5} and BC were responsible for visibility deterioration. High BC concentrations were usually associated with low wind speed of northeastern or southwestern winds. Temperature had an indirect effect on aerosol distribution, as the heating activity mainly using coal occurred with low temperature in winter and led to high aerosol load. Wind condition affected aerosol distribution by re-suspending local dust or introducing aerosol pollution from the surrounding areas. Wind from the north and the northwest with high wind velocity carrying dust triggered sand dust or dust storms, especially in spring. Year-by-year variations of temperature and wind conditions were similar from the ten-year observation and played a minor role in aerosol distribution.

With long-term sampling and analyses of atmospheric particulates from 2005 to 2014, effects of mitigation measures were evaluated according to the concentration variations of pollutants in the sections 2, 4 and 5. The year 2008 was a milestone for air quality improvement during the ten years. Concentrations of pollutants during periods before and after 2008 were used for comparison (Table 6.2). When evaluating the differences before and after 2008, the meteorological conditions should be considered as well.

Concentrations of traffic-related elements, such as Pb, Sb and Sn, varied with the strictness of traffic restriction measures. The pollution level was inversely correlated with the intensity of the measures. The introduction of license plate lottery policy for car registration since the beginning of 2011 in Beijing led to the largest annual growth during the ten years of total amount of vehicles from 2009 to 2010. This was considered as a contributor to the relatively high concentrations of traffic-related elements in 2010 compared to 2009, especially in summer time when other sources for these elements played a minor role. August 2007 had similar precipitation to August 2008. Concentrations of Sn, Sb and Pb in August 2008 were reduced by 53%, 50% and 59% respectively with the most intensive traffic restrictions, compared to concentrations in August 2007 without any restrictions.

Table 6.2 Concentrations of pollutants and variations in Beijing aerosols.

	Data periods	Years before 2008	Years after 2008	Reduction	Augusts Before 2008	Augusts After 2008	Reduction	
PM _{2.5} mass concentration (µg/m ³)	2005-2014	71.7	60.3	16%	54.3	47.2	13%	
TSP mass concentration (µg/m ³)	2008-2014	-	226	-	-	176	-	
Coarse particles mass concentration (µg/m ³)	2005-2012	216	173	20%	130	105	19%	
Toxic heavy metal elements (e.g. Pb, Sb) in PM _{2.5} (ng/m ³)	Pb	2005-2013	165	138	16%	130	102	22%
	Sb		11.4	7.92	30%	9.80	5.92	40%
BC (µg/m ³)	2005-2013	5.44	3.75	31%	4.47	3.07	31%	
HgP (pg/m ³) ^(a)	2005-2013	300	182	39%	86.3	67.1	22%	
Ga (ng/m ³)	2005-2013	4.80	3.05	37%	2.30	1.13	51%	

^(a) annual mean concentrations according to the average of PM_{2.5} samples in January and August each year from 2005 to 2013 from the CUGB site

Chromium (Cr), Co and Ni were used to evaluate the influence of the relocation of the Capital Steel Company. Annual mean concentrations of Cr, Co, Ni decreased in 2010 compared to those in 2008 if only three-year measured data were analyzed. However, from the view of nine-year (2005-2013) data, the decrease in Cr, Co and Ni between 2008 and 2010 did not continue but reversed slightly between 2011 and 2013, which was attributed to the nearby relocation with the recovery of production.

BC mass accounted for 7% of $PM_{2.5}$ mass on average. Temporal distribution of black carbon (BC) showed a distinct declining trend from 2005 to 2013, which was well correlated to the declining consumption of coal and coke. Gallium (Ga) was recommended as a tracer for heating-activities mainly using coal for the first time, due to its strong correlation with BC and coal consumption, as well as its concentration variation between the heating- and non-heating periods. From a long-term perspective, particulate mercury (HgP) concentration fell even with increasing total energy consumption and growing total vehicle number. The strong correlations between HgP and BC/Ga in winter, together with the success of energy structure transformation on reducing BC/Ga suggested the effectiveness of this transformation on HgP emission control. For BC and Ga (in $PM_{2.5}$), concentrations in August 2008 were reduced by 48% and 30% respectively with the most intensive mitigation measures, compared to concentrations in August 2007 with similar precipitation.

Mass concentrations of different size fractions of coarse particles (2.5-80 μm) all showed slightly decreasing trends from 2005 to 2012. Precipitation was an important contributor for this. Most of the peaks correlated to the sand dust or dust storms. The highest peaks for mass concentrations of all size fractions were observed with the most intensive sand-dust days in spring 2006 due to global climate change caused by El Niño. The Olympic Games period displayed lower concentrations than the rest of the sampling time, demonstrating the effectiveness of mitigation measures on reducing coarse particles. The diverse size distribution patterns during different pollution days provide reference information for the enactment of mitigation measures on aerosol particles.

During the observation periods, aerosol pollution was controlled in Beijing even with increasing total energy consumption and growing total vehicle number. Pollution peaks before implementation of the corresponding measures were observed as well. Effective governmental mitigation measures for specific sources (e.g. traffic restriction measures) and macro intervention measures (e.g. energy structure transformation) are recommended to be continued and improved in order to obtain more “blue sky” days in the future. On the one hand, industry relocation is not recommended as a long-term effective measure to mitigate air pollution, but on the other hand the concurrent improved emission standards are considered promising. For both environmental sustainability and human health, aerosol pollution is a crucial issue to be mitigated in Beijing and more efforts are required for better air quality.

6.3 Estimation for effects of aerosol pollution on human health

Risk estimates for effects of long-term exposure to particulate matter on the mortality associated with a $10 \mu\text{g}/\text{m}^3$ increase in the concentration of $\text{PM}_{2.5}$ were 1.14 and 1.07, according to Dockery et al. (1993) and Pope et al. (1995). The average risk estimate 1.105 was used for estimation in this study. For the annual mean $65.6 \mu\text{g}/\text{m}^3$ of $\text{PM}_{2.5}$ concentration, 1.73 times mortality due to $\text{PM}_{2.5}$ pollution was estimated in Beijing compared to the areas where meet the WHO standard.

The estimation method of WHO was used to assess the morbidity effects due to long-term exposure to air pollution. The effect on children bronchitis symptoms was estimated as an example. According to WHO (2000), assuming that 20% of one million population are children, a baseline prevalence of 5% among children are assumed to have bronchitis symptoms. Then 3,350 additional children were estimated to be affected per year with a $10 \mu\text{g}/\text{m}^3$ increase in $\text{PM}_{2.5}$ concentration above a background level of $10 \mu\text{g}/\text{m}^3$ (WHO, 2000). Based on this estimation precondition, from 2009 to 2014, in total 335,000 children per year were assessed to be affected by bronchitis for the 20-million population in Beijing (average after 2008) due to the annual mean $60 \mu\text{g}/\text{m}^3$ of $\text{PM}_{2.5}$ concentration after 2008 in

Beijing. Compared to the years before 2008 (2005-2007) with a 16-million average population, 13,600 children per year were exempted from bronchitis symptoms due to $10 \mu\text{g}/\text{m}^3$ reduction of annual $\text{PM}_{2.5}$ concentration after 2008.

The effects of unmeasured risk factors cannot be excluded with certainty and the regional differences such as population density and health situation, should be considered in the future work.

6.4 Outlook

Because governmental mitigation measures were enforced to reduce the adverse effects of air pollution on environment and human health, this dissertation focused on sampling aerosol particles in Beijing. Non-elemental indicators such as gas pollutants were not included in this study and thus emissions from industry could not be separated from traffic-related emissions. This resulted in uncertainty when evaluating the effects of specific mitigation measures such as traffic restrictions and industry relocation. For further work, gas pollutants data and aerosol particulates data can be combined for comprehensive study on air pollution in Beijing.

Aerosol pollution in a small scale can be affected by regional synoptic conditions and even by global climate change. Within this study, sand-dust weather in Beijing could be triggered by both regional meteorological condition and global climate change. Further study about synoptic conditions can help to interpret the influence of global climate change on regional aerosol distributions.

The effects of toxic elements in aerosol particles on human health could be estimated based on the long-term observation data of pollutants within this study together with more epidemiological data. More accurate risk-estimates could be carried out for effects of long-term exposure to particulate matters on the local morbidity and mortality.

This study is a first step towards the long-term systematical research for effects of mitigation measures on aerosol pollution with consideration of meteorological influences.

For further research, an integrated aerosol-climate-human health program could enable efficient decisions on pollution mitigation measures.

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Appendix

A —Full papers of first author scientific publications

A.1 The influence of governmental mitigation measures on contamination characteristics of PM_{2.5} in Beijing



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The influence of governmental mitigation measures on contamination characteristics of PM_{2.5} in Beijing

Yuan Chen ^{a,*}, Nina Schleicher ^a, Yizhen Chen ^b, Fahe Chai ^b, Stefan Norra ^{a,c}^a Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology, 76131, Karlsruhe, Germany^b Institute of Urban and Regional Atmospheric Sciences, Chinese Research Academy of Environmental Sciences, 100012, Beijing, China^c Institute of Geography and Geoecology, Karlsruhe Institute of Technology, 76131, Karlsruhe, Germany

HIGHLIGHTS

- The influence of governmental mitigation measures on PM_{2.5} was investigated.
- Source apportionment of PM_{2.5} was analyzed by principle component analysis.
- Concentrations of traffic-related elements varied with the restrictiveness of measures.
- Steel-related elements were reduced after relocation of the Capital Steel Company.
- Pollution peaks before implementation of the respective measures were observed.

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ABSTRACT

Beijing, the capital of China, has become one of the most air-polluted cities due to its rapid economic growth. Weekly PM_{2.5} samples—collected continuously from 2007 to 2010—were used to study the contamination characteristics of atmospheric particles and effects of governmental mitigation measures especially since the 2008 Summer Olympic Games. PM_{2.5} mass concentrations during the sampling period were reduced compared to the previous studies before 2005, although they were still too high in comparison with environmental standards of China and many other countries as well as WHO standards. Results of principle component analysis show that elements of primary anthropogenic origin had an obvious decline while elements mainly from the natural environment kept a relatively stable course. The governmental macro-control measures influenced both anthropogenic and geogenic sources, but they also led to some pollution peaks prior to implementation of the respective measures. Some element concentrations correlated to the restrictiveness of relative measures, especially during different traffic restrictions. The comparison with other countries and international standards shows that there is a long way to go in order to improve air quality in Beijing, and that governmental mitigation measures need to be continued and reinforced.

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1. Introduction

With the rapid industrialization and motorization of the world, air pollution has become one of the greatest environmental concerns of both, the public and scientists (Schleicher et al., 2011a; Sun et al., 2004). Fine particles in particular, as in aerosols with an aerodynamic diameter smaller than 2.5 μm (PM_{2.5}), are responsible for adverse effect on human's health, like deterioration of the pulmonary and respiratory system (e.g. Dockery and Pope, 1994; Schwartz et al., 1996). These problems cumulate worldwide in many cities, especially of the

developing world, where governance is often overstrained by the economic development. Consequently, severe air pollution is reported from many megacities worldwide, such as Mexico City, Sao Paulo, Cairo, Lagos, Istanbul, Bombay, Dhaka, Shanghai, or Chongqing. Large cities in so-called developed countries, such as New York, Rome or Tokyo, are affected by air pollution problems as well. Two smog types are named after western cities: London and Los Angeles. Thus, the world's urbanization increasingly affects substance fluxes of the atmosphere and of other spheres such as the pedosphere, hydrosphere and the biosphere. The sustainable control of element and substance fluxes of the astosphere (Norra, 2009), which is the sphere of the global network of urban systems within the anthroposphere (Baccini and Brunner, 1991), is crucial for the future of the environmental conditions human beings live in. Having faced environmental issues, air pollution problems in particular, developed countries are pioneering in

* Corresponding author at: Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology, Adenauerring 20b, Geb. 50.40, 76131, Karlsruhe, Germany. Tel.: +49 721 608 47356; fax: +49 721 608 47247.

E-mail address: yuan.chen@kit.edu (Y. Chen).

mitigation measures against air pollution. The adaptability and transfer of those measures but also the development of local air cleaning approaches are of great importance for decision makers in the field of urban development in the developing countries.

During the last decades China, the country that comprises most megacities worldwide, increasingly developed its economy with the typical negative effects on air quality. In consequence, China is struggling with the competition between industrial development and reduction of air pollution. One of the largest cities in China is the capital Beijing, which is encountering severe air contamination that poses a huge threat to the health of its more than 19 million inhabitants (Beijing Statistical Yearbook, 2012). The 2008 Olympic Games in Beijing have been a landmark for developing methods for reducing air pollution in China.

To achieve abatement of air pollution for the Olympic Games, the Beijing Municipal Government took measures to control pollutant emission. These mitigation measures covered industry, traffic, construction, and afforestation (Chen et al., 2013; Schleicher et al., 2011a, 2012; Wang et al., 2009, 2010). Up to now, some of these measures such as the traffic restriction measures are still ongoing and their effects on improving air quality have been considered a hot spot of aerosol study. Therefore, this study will focus on the efficiency of the implemented measures during but also after the Olympic Games period.

Several studies reported air quality improvements during the Olympic Games in Beijing. For example, Wang and Xie (2009) estimated the on-road concentrations of PM₁₀, CO, NO₂ and O₃ before and during the Olympic Games by Operational Street Pollution Model and proved the air quality improvement. Schleicher et al. (2011a) showed that mass concentrations of particles of different size classes within the coarse mode (2.5 to 80 μm) during this period were lower than before and later, and that the coarse particles were reduced more efficiently than the fine ones. A study by Li et al. (2012) reported that pollution levels of trace elements and water-soluble ions in aerosols declined strongly during the Olympic Games. Okuda et al. (2011) compared chemical compositions of TSP and PM_{2.5} between the period during the Olympic Games and the same periods in the prior three years 2005–2007 to assess the sustainable effectiveness of the governmental mitigation measures. Schleicher et al. (2012) showed that elements predominantly from anthropogenic sources, such as S, Cu, As, Cd, or Pb were reduced by 50 to 70% during the Olympic Games, whereas elements mainly from geogenic sources, such as Fe, Rb, and Sr were reduced by only 30 to 50%.

Most of the mentioned studies assessing the success of emission reduction measures in Beijing are mainly based on selected short periods and their inter comparisons. In this study, however, mass concentration, element concentration and their correlations with the governmental mitigation policies are discussed based on long term sampling and measurement over several years before and after the Olympic Games, which can be used for evaluation of mitigation measures, for long-term aerosol studies, and for governmental policymaking. Results of this study demonstrate the success of this big experiment of reduction measures carried out by the government but also show that further improvement of Beijing's air quality still requires much effort.

2. Experimental

2.1. Study area and sampling procedure

Beijing, located at the northwestern border of the North China Plain, is surrounded clockwise by mountain ridges from the southwest to the northeast. Generally, westerly wind and the Asian monsoon that provides warm humid southeast wind in summer and cold dry northwest wind in winter dominate the large-scale wind system of this region (Okuda et al., 2008). This typical U-shape terrain surrounding Beijing City provides the possibility to trap the aerosol particles from the south and southeast in the city and can result in poor air quality

under stagnant conditions with weak wind (Zhang et al., 2012). The main traffic network of Beijing is constituted by the main ring roads (2nd–6th ring roads) with additional streets and expressways (like G1) connecting to neighboring provinces (Fig. 1).

The sampling site is set up on the roof of the Chinese Research Academy of Environmental Sciences (CRAES) at a height of about 20 m. This CRAES site is located between the 5th and the 6th ring roads. A Mini-Volume Sampler at a flow rate of 200 L/h is used to collect weekly PM_{2.5} samples on quartz fiber filters (Whatman Inc., Maidstone, UK). During the Olympic Games, samples with higher time-resolution (12-hourly samples) were collected in August and September 2008. Detailed results of that intensive campaign are reported in Schleicher et al. (2012). This study analyzed the samples from Sep. 30th, 2007 to Jan. 4th, 2011. For the 171 weeks during the studied period, 158 valid weekly samples were collected, accounting for 92% of all samples. Here, higher time-resolution samples in one week during the 2008 Olympic Games were calculated as weekly mean.

2.2. Mass concentration analysis

Filters were acclimatized and stored in the laboratory for at least 48 h under the same conditions before and after sampling. They were weighed for at least three times with a microbalance (Sartorius SE 2-F, Göttingen, Germany) at a constant temperature (22 ± 3 °C) and relative humidity (40 ± 2%) before and after sampling, respectively. Accuracy control was implemented by blank filters, which were also sent to Beijing but sent back to Germany unused for analysis. The increased or decreased mass on blank filters was subtracted from the mass of loaded samples to improve the accuracy of the loaded mass. The gravimetric analysis was carried out at the Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology (IMG-KIT), Germany.

2.3. Chemical element analysis

For element concentration analysis, one quarter of each filter sample was cut out, weighed and digested with concentrated HNO₃, HF and HClO₄ (Merck, suprapur) in Teflon vessels. The samples were diluted twice with HNO₃ (1%) and analyzed by a high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS, Axiom, VG Elemental). Blank solution and blank samples were determined to provide good analytical accuracy. All samples were measured three times and mean values were taken as analytical results. Methodological blank values of the blank samples were subtracted from analytical results of PM_{2.5} samples. Additionally, standard reference material SRM 1648 (urban particulate matter) and GXR 2 (soil sample) from the National Institute of Standards & Technology (NIST, USA) were analyzed to control analytical quality. Element concentrations of standard materials were generally within ±10% of the certified values. All analyses were performed at the IMG-KIT. A more detailed description of the analytical procedures and can be found in previous studies of the same project (Schleicher et al., 2011b, 2012; Yu et al., 2011).

3. Results and discussion

3.1. Mass concentration evaluation

The weekly mass concentration of PM_{2.5} during the period studied ranged from 22.5 μg/m³ to 226 μg/m³ with an average of 86.1 μg/m³. In this study, annual means of PM_{2.5} mass concentration from 2008 to 2010 were 88.7, 80.5, and 80.9 μg/m³, respectively.

Since the 1990s, more and more studies have been published about PM_{2.5} mass concentration in Beijing: 136 μg/m³ from one week of daily sampling in June 1999 (Bergin et al., 2001), an annual mean of 125 μg/m³ from weekly sampling in 1999–2000 (Yang et al., 2005), 102 μg/m³ from weekly sampling in 2001–2002 (Duan et al., 2006), 106 μg/m³ at Beijing Normal University site from daily

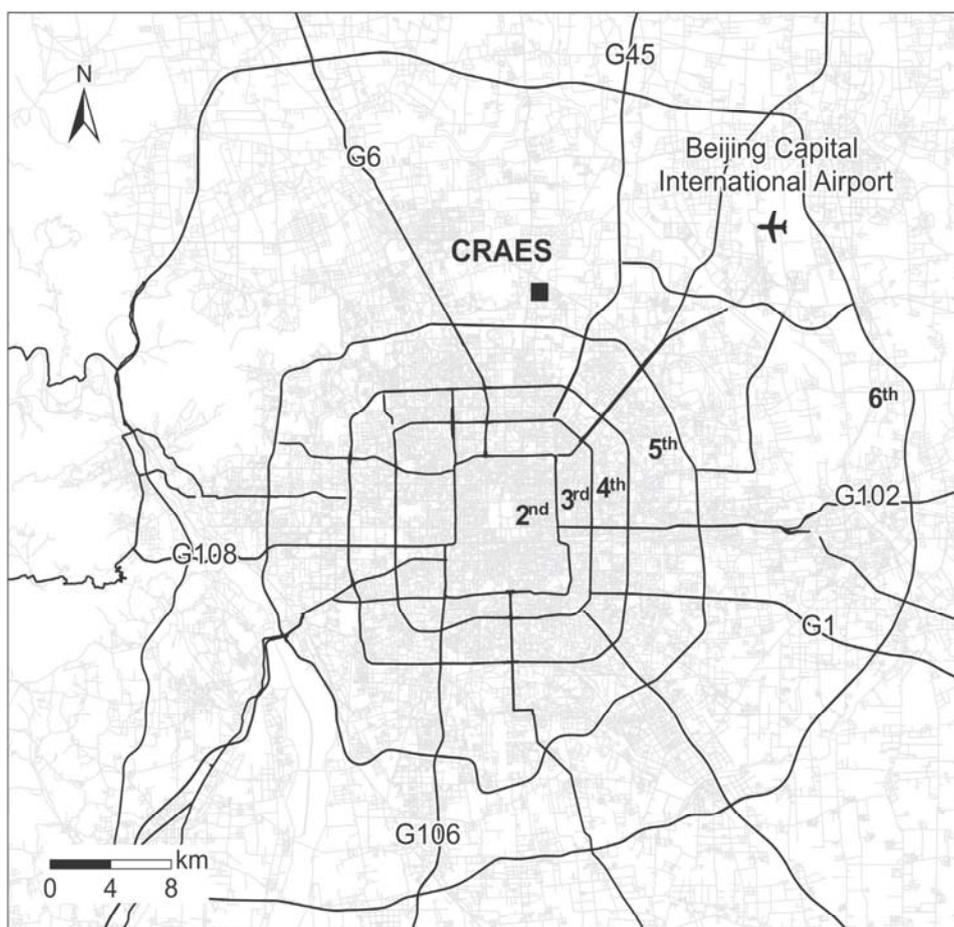


Fig. 1. Sampling site CRAES and the main traffic network of Beijing urban area, including 2nd–6th ring roads (Source of the map: OpenStreetMap).

sampling in winter and summer seasons in 2002 and 2003 (Sun et al., 2004), $104 \mu\text{g}/\text{m}^3$ at five sites crossing the whole Beijing City in 2004 (Yu et al., 2009), $91.5 \mu\text{g}/\text{m}^3$ at five sites in 2006 (Schleicher et al., 2010), and annual means of 86.5, 93.5 and $84.4 \mu\text{g}/\text{m}^3$ from hourly averages from 2005 to 2007 (Zhao et al., 2009). From a time perspective, average mass concentration of $\text{PM}_{2.5}$ was higher than $100 \mu\text{g}/\text{m}^3$ before 2005, and dropped to around $80 \mu\text{g}/\text{m}^3$ in 2010.

However, the $\text{PM}_{2.5}$ pollution level in Beijing is still too high compared to the World Health Organization's (WHO) annual mean threshold for $\text{PM}_{2.5}$ ($10 \mu\text{g}/\text{m}^3$) (WHO, 2006) and other annual mean standards from Environmental Protection Agency (EPA) in the United States of America (USA) ($15 \mu\text{g}/\text{m}^3$) (EPA-USA, 2013), European Union (EU) ($25 \mu\text{g}/\text{m}^3$) (EU, 2008) and Australia ($8 \mu\text{g}/\text{m}^3$) (DEH-Australia, 2004). At the beginning of 2012, a new Ambient Air Quality Standard (GB3095-2012) was published by the Ministry of Environmental Protection (MEP) of China, which established a standard for $\text{PM}_{2.5}$ mass concentration of $35 \mu\text{g}/\text{m}^3$ for the annual mean and of $75 \mu\text{g}/\text{m}^3$ for the 24-hour-mean (level II) (MEP-China, 2012). The annual $\text{PM}_{2.5}$ mass concentration in this study was 2.5 times higher than this new standard. Particle concentrations that significantly exceeded standards revealed the pollution severity of fine particles in Beijing and the necessity of macro-control by the government.

3.2. Source apportionment for $\text{PM}_{2.5}$ and variation of sources

3.2.1. Enrichment factors (EFs)

The enrichment factor of a certain element is defined as the ratio of the element concentration in the sampled particles compared to that in

the upper continental crust (ucc) of the earth. Anthropogenic pollutants in aerosols can be assessed by means of enrichment factors (EFs). As Ti is very stable in the process of transportation and mainly originates from

Table 1
Element concentrations ($\mu\text{g}/\text{g}$) and enrichment factors.

	N	Mean	Stdev	$\text{EF}_{\text{Ti}}(\text{ucc})$
Al	157	23800	14300	1
Sc	158	3.50	2.43	1
Y	156	8.29	5.64	1
Ti	158	1240	747	1
Fe	158	17500	9180	1
Sr	158	225	155	2
V	158	43.5	21.4	2
Mg	153	10300	6170	2
K	158	22000	11500	2
Na	146	26300	37600	2
Co	158	11.8	11.9	3
Ca	155	37500	25500	3
Li	158	30.4	15.4	4
Mn	158	976	643	4
Ni	153	65.5	55.4	8
Cr	158	136	117	10
P	145	6880	13300	20
Sn	158	114	138	50
Cu	158	574	433	56
Zn	158	4940	3600	168
Pb	158	1710	996	207
As	158	176	175	285
Cd	153	59.0	150	1460
Sb	152	155	106	1880

the crust (Duan et al., 2006), it was selected as the reference element in this study (Eq. (1)). Here, the average values of element concentrations of all samples are compared to element concentrations in the upper crust as given by Taylor and McClellan (1985) with the exception of the concentration of P, which is taken from Yaroshevsky (2006).

$$EF_{Ti(ucc)} = (Element/Ti)_{particles} / (Element/Ti)_{ucc} \quad (1)$$

(according to Zoller et al., 1974)

The average concentrations of all determined elements together with their EFs are shown in Table 1. The elements are arranged in order of their EFs and can, therefore, be more easily separated into groups with similar EFs. Generally, elements with small EFs < 5 (like Sc, Y and Ti) predominately originate from the upper continental crust while elements with relatively high EFs > 50 (like Pb, As, and Sb) dominantly originate from anthropogenic pollution.

3.2.2. Factor analysis

Factor analysis was performed to identify the main sources of fine particles using the software package STATISTICA 8.0 (StatSoft Inc., Tulsa, USA). Five factors with eigenvalues larger than 1 were extracted by principle component analysis (PCA) applying varimax standardized rotation (Fig. 2). These five extracted factors accounted for 88% of the total explained variance. Factor scores of each sample were calculated to present the proportions of the factors to reveal the major aerosol sources along the time period of investigation.

Factor 1 has high factor loadings for Ti, Sc, Y, Fe, V, Al, Ca, Mg, Li, Mn and MC (PM_{2.5} mass concentration) in order of decreasing factor loadings, explaining 35% of the variance (Fig. 2). Most of these elements have EFs around 1, while some elements like Ca, Li and Mn have only slightly higher EFs between 2 and 4. These elements are generally considered to be of geogenic origin. Construction activities and resuspended dust form local sources also could contribute to these elements. Moreover, the mass concentration of PM_{2.5} is included in this factor, which means that the geogenic material is the largest constituent of mass in aerosol particles.

The factor scores show some variation over the time period with maximum values up to more than two (Fig. 3). These high factor scores usually come up with dust days, and the peaks correlate with sand dust storms, such as the sand dust storms in the 11th and 12th weeks in March 2008, 2009 and 2010 with extremely high PM_{2.5} mass concentration of 206, 226 μg/m³ (2008), 123, 143 μg/m³ (2009), and 212, 117 μg/m³ (2010), respectively (Fig. 4). Some peaks in winter occur due to sand dust storms with strong wind, for example, during the 52nd week in December 2009 with a mass concentration of 211 μg/m³ (Fig. 4).

Factor 2 is strongly correlated with Sb, Pb, Sn, As, Cs, Zn, Cu and Cd, accounting for 24% of the total variance (Fig. 2), and covers all the elements with EFs larger than 50. Cs with EF of 9 in natural environments comes from the geogenic dust and rock weathering. Its EF is much higher than EFs of elements of crustal origin which are aggregated in Factor 1, suggesting that for Cs, anthropogenic sources are more dominant than geogenic sources for PM_{2.5}. The dominating anthropogenic sources of Cs are catalyst and nuclear leakage accidents (Reimann and Caritat, 1998). Since there was no nuclear leakage accident reported during the sampling period, the catalyst usage might be the main releasing mode of Cs into aerosol. Antimony, Pb, and Zn were recommended as markers of motor vehicle emissions (Huang et al., 1994; Wongphatarakul et al., 1998). Wearing of tires and brakes also contributes to the load of Sb, Sn, Zn and Cu in aerosol particles (Cyrys et al., 2003; Sternbeck et al., 2002; Wählin et al., 2006). Cadmium could come from both of these two sources (Reimann and Caritat, 1998). The local pollution level of As in aerosols is predominately associated with smelters, local traffic, coal combustion, and insecticide (Hedberg et al., 2005; Wang and Mulligan, 2006). Schleicher et al. (2011b) showed that coal combustion is an important source in Beijing especially for Cd, As, and Pb concentrations. The six elements of this factor could also originate from industrial sources including metallurgical activities, incineration, and material abrasion and so on. Therefore, this factor could be interpreted to represent anthropogenic pollution, mainly traffic and industry pollution including coal combustion. However, emissions from industry could not be separated from traffic-related

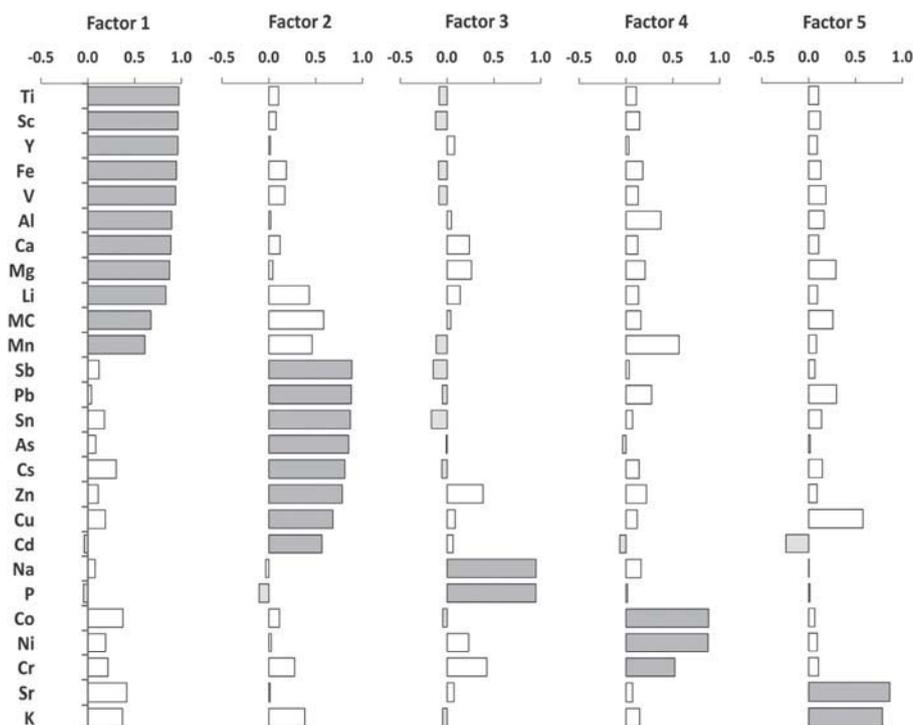


Fig. 2. Factor loadings of 5 extracted factors of all elements and mass concentration (MC) (using principal component analysis, varimax standardized rotation, 119 samples).

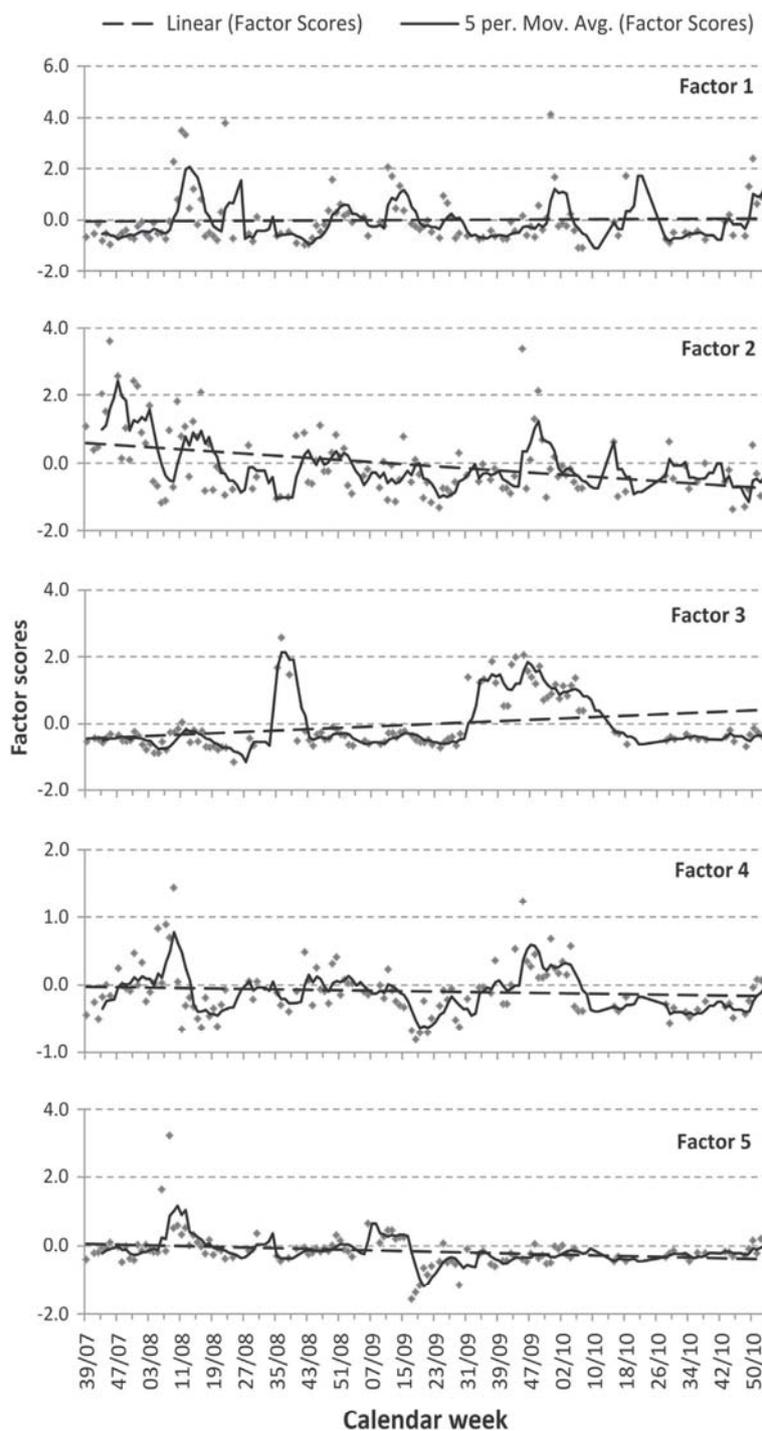


Fig. 3. Factor scores of each of the 5 factors of every sample (5 per moving average was calculated by the formula: $ACW_{(n)} = (CW_{(n-4)} + CW_{(n-3)} + CW_{(n-2)} + CW_{(n-1)} + CW_{(n)})/5$; $ACW_{(n)}$: 5 per moving average of aerosol concentration of calendar week n , $CW_{(n)}$: mean aerosol concentration of week n).

emissions because there is no non-elemental indicator included in this Factor (Vallius et al., 2005).

Factor scores for this factor show a decreasing trend for the whole sampling period (Fig. 3), proving the declining human contamination level under pollution-controlling policies by the municipal government. Despite this trend, however, factor scores significantly increase in Factor 2 (Fig. 3) one or two weeks before the central heating, which is supplied mainly by coal combustion.

Sodium and P show high positive loadings (both 0.95) in Factor 3 (Fig. 2) and explain 10% of the total variance. Mass concentration has small factor loadings in this factor and, thus, shows only little correlation with these elements. Phosphorus is widely used in fertilizers and, thus, agricultural areas around Beijing might contribute to this element association. But chemical industry is also a possible anthropogenic source for P (Reimann and Caritat, 1998). Firework displays might be a short-term source for P (Moreno et al., 2010). Also Na is often

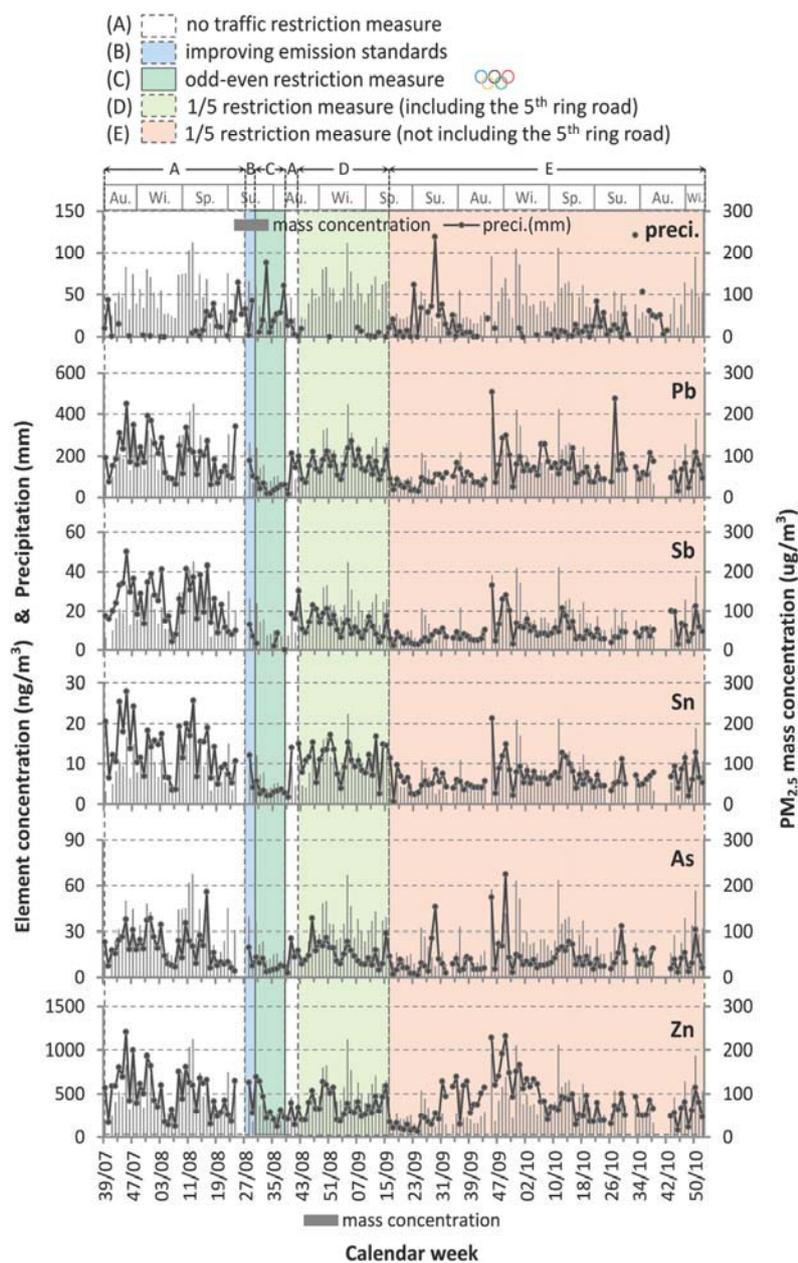


Fig. 4. Weekly element concentrations and $PM_{2.5}$ mass concentration at site CRAES under different traffic restriction policies during the observation period (Sp.: spring, Su.: summer, Au.: autumn, Wi.: winter).

associated with fertilizers (Reimann and Caritat, 1998). Other sources for Na are sea spray as a natural source and waste water as an anthropogenic one (Reimann and Caritat, 1998).

There are two periods with high factor scores during the whole sampling time (Fig. 3) while other factor scores are relatively stable. One appears during the Olympic Games 2008, and the other one is found from August 2009 to February 2010. These two periods imply that there is a certain pollution source or pollution point for each period. They might come from two nearby sewage treatment plants (Reimann and Caritat, 1998), Qinghe Sewage Treatment Plant and Beixiaohe Sewage Treatment Plant which are respectively located in the west and east of the sampling site. Therefore, more detailed research is necessary to analyze impacts of these two sewage treatment plants on $PM_{2.5}$.

Cobalt, Ni and Cr are the dominating elements in Factor 4 (Fig. 2), and also explain 10% of the total variance. The main pathways of these three elements to the atmosphere are primarily fossil fuel (oil and coal) combustion and steel works (Reimann and Caritat, 1998). Aggregations of these elements fall into the fine particles' fraction rather than into the coarse particles' fraction and have been found to go deep into people's lungs causing respiratory tract damage (ATSDR, 1997). They can originate from other anthropogenic sources such as waste incineration, as well as geogenic sources. Due to heating activities mainly using coal in Beijing, some high factor scores with high element concentrations show up in winter while small factor scores appear in spring when the geogenic sources prevail (Fig. 3). Manganese is not included in this factor but has relatively high factor loadings which

indicate combustion sources. Therefore, this factor can be explained by anthropogenic sources from combustion and steel works.

Factor 5 is dominated by high loadings for K and Sr (Fig. 2), explaining 9% of the total variance. Their possible sources are mainly from weathering, geogenic dust and sea spray. The course of factor scores for this factor is stable over the whole sampling period (Fig. 3), meaning that the sources of these two elements are relatively settled. Potassium mainly comes from the weathering of granitic rock which is one of the main rock types in Beijing (Yu et al., 2011) and chrysanthemum stone in Western Hills of Beijing is rich in strontium (celestite, SrSO₄); therefore, the local rock weathering could be an important source for this factor.

From the end of October 2009 to the beginning of February 2010, Factor 1, Factor 2, Factor 3 and Factor 4 all present high factor scores, except for Factor 5 (Fig. 3). During this period, the sand dust or dust with strong wind mainly contributes to the high scores of Factor 1; the heating supply, industries and traffic are the dominated contributors for the high scores of the other 3 factors.

3.3. Variation of specific element concentrations and influence of governmental mitigation measures

Specific elements can serve as fingerprints for different sources of fine particles. Therefore their pollution characteristics and variation were analyzed to understand the influence of different governmental mitigation measures on different sources of PM_{2.5}. In the following, especially the traffic mitigation measures and their efficiency will be discussed.

3.3.1. Influence of traffic mitigation measures

Elements like Pb, Sb, Sn, As and Zn which were grouped in Factor 2 (Section 3.2.2) with EFs higher than 50 (Table 1), are usually used to serve as tracers for traffic sources of fine particles (Cyrus et al., 2003; Huang et al., 1994; Sternbeck et al., 2002; Wählin et al., 2006; Wongphatarakul et al., 1998). Fig. 4 shows weekly averages of the respective element concentrations, PM_{2.5} mass concentration and precipitation with different traffic restriction policies made by the government over the observation period. Obviously, precipitation is an important way of washing out particles and, therefore, the reduction by wet deposition and the reduction due to the mitigation measures need to be distinguished. Traffic restriction measures included: (1) improving emission standards so vehicles not meeting the European Euro I standard for exhaust emissions were banned from the roads (Wang et al., 2010), (2) odd–even restriction measure which means private vehicles could only operate on odd or even days according to the last digit of their license plates, and (3) 1/5 restriction measures on weekdays, which were implemented depending on the last digit of license plates (for example vehicles with the last digit 1 or 6 are banned from roads on Monday and vehicles with the last digit 2 or 7 are banned from roads on Tuesday).

Element concentrations started decreasing after the government improved emission standards which were implemented from July 1st, 2008 for vehicles. For all these traffic-related elements, the lowest concentrations occurred during the 29th Olympic Games in August and September 2008 when the “odd–even restriction measure” was employed, which cut down about half of the motor vehicles every day. Precipitation during this period is another reason for the strong particle reduction. However, when comparing two periods of similar precipitation, June to July 2009 with August to September 2008, element concentrations were lower in August and September 2008. This indicates that the intensive policies during the Olympic Games did play a significant role in mitigating the pollution.

After the “odd–even restriction measure” during the Olympic Games, there was a short pause without any traffic restriction measures from September 20th to October 10th, 2008 (three sampling weeks, week number 39–41/08). In comparison with the previous three weeks (week number 36–38/08 during the Olympic Games with

“odd–even restriction measure”), the average concentrations of the investigated five traffic-related elements in these three weeks ascended by 126% (Pb), 302% (Sb), 143% (Sn), 103% (As), and 13% (Zn), respectively, due to the pause with an increase of 16% of PM_{2.5} mass concentration (Fig. 4).

Then from October 10th, 2008 to April 10th, 2009, the “1/5 restriction measure” (including the 5th ring road) followed, which cut down around 1/5 of private cars from roads and was implemented only during weekdays to mitigate traffic jams. Compared to element concentrations during the same period from 2007 to 2008 without traffic restriction measures, PM_{2.5} mass concentration was only reduced by 2% while element concentrations were reduced by 27% (Pb), 50% (Sb), 25% (Sn), 28% (As), and 37% (Zn) respectively (Fig. 4). From April 10th, 2009 to the end of the observation period, the “1/5 restriction measure” was performed on weekdays but did not include the 5th ring road anymore. As the sampling site was near to the 5th ring road, this policy might have been a reason for the slightly higher concentrations of both, PM_{2.5} mass and traffic-related elements Pb and Sb in 2010 than those in 2009, which increased by 1%, 11% and 8%, respectively.

In 2010, the government published a new policy which took effect in January 2011 to limit the amount of private vehicles: a lottery drawing policy for car license plates. Residents can purchase cars but need to apply for license plates via lottery. The resulting pre-2011 rush on cars with license plates in 2010 led to a sharp increase in the amount of vehicles, exceeding 4.8 million at the end of 2010 in Beijing (Beijing Statistical Yearbook, 2012). This might also have contributed to the relatively high Pb and Sb concentrations in 2010 compared to 2009. The same trend can be seen for As and Sn during summer time, when traffic is their major emitter and less energy has to be produced for heating purposes than during winter time. The annual mean and summer mean concentration of Zn was slightly lower in 2010 than that in 2009 since it also originates from combustion and other industrial sources including metallurgical activities, incineration, and material abrasion (Reimann and Caritat, 1998; Schleicher et al., 2011b).

Although the pollution level for some elements (Pb and Sb) was slightly higher in 2010 than in 2009, compared to the period before Olympic Games, the pollution of traffic-related elements was mitigated by the traffic restriction policies. Average concentrations of Pb, Sb, Sn, As and Zn in October, November and December in 2007 were reduced by 53%, 47%, 53%, 55% and 56% during this period in 2010.

In general, the pollution of these toxic elements varied with the strength of traffic restriction measures, and stricter measures brought in less pollution. This demonstrated the significance and effectiveness of the traffic restriction measures. However, peaks of element concentrations during winter time due to heating energy production by coal combustion are still an issue.

3.3.2. Influence of relocating project of the Capital Steel Company

The Capital Steel Company was one of the biggest steel companies in North China. Step by step, it was moved out of Beijing and relocated to the southeast of Beijing in Hebei Province near to Beijing.

Kuang et al. (2004) already documented the environmental impact of this steel plant. For metal processing industry, especially steel-related work, it is recommended to use fingerprinting on the indicator elements Co, Ni and Cr (Kuang et al., 2004; Nath et al., 2007; Schleicher et al., 2012). These three elements were grouped in Factor 4 by factor analysis (Section 3.2.2) and were used for evaluation of the relocating project of the Capital Steel Company.

Fig. 5 shows the weekly element concentrations. Since the capacity of the Capital Steel Company was reduced gradually from 2007, pollution levels dropped since then. In 2010, the relocation project was completed and the annual means of Co, Ni and Cr concentrations in 2010 reached their minimum (Chen et al., 2013). Compared to the concentrations in 2008, the annual means of Co, Ni and Cr concentrations in 2010 were reduced by 47%, 24% and 57% respectively. However, precipitation (Fig. 4) is an assignable impact factor as well. As the

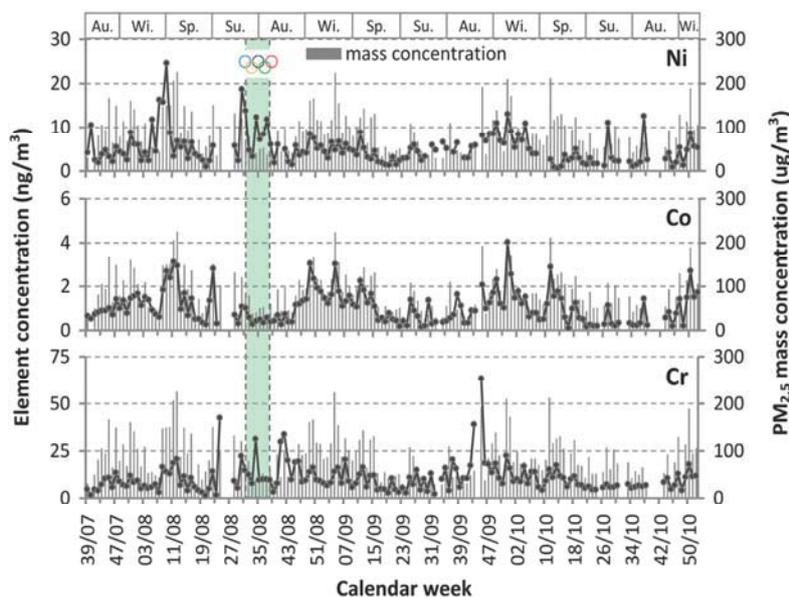


Fig. 5. Weekly concentrations of Ni, Co and Cr with PM_{2.5} mass concentration over the observation period.

concentrations during the Olympic Games with strict traffic restriction measures were not the minimum values, this means that traffic was not their main source. In conclusion, relocation significance was shown toward reducing fine particle pollution, in particular concerning elements related to combustion and steel industry.

3.3.3. Elements from predominately geogenic sources

While success was demonstrated on reducing elements from special anthropogenic sources during the sampling period, how about the elements that dominantly originate from geogenic sources? According to the findings of factor analysis (Section 3.2.2), Ti, Sc, Y, V and Mg

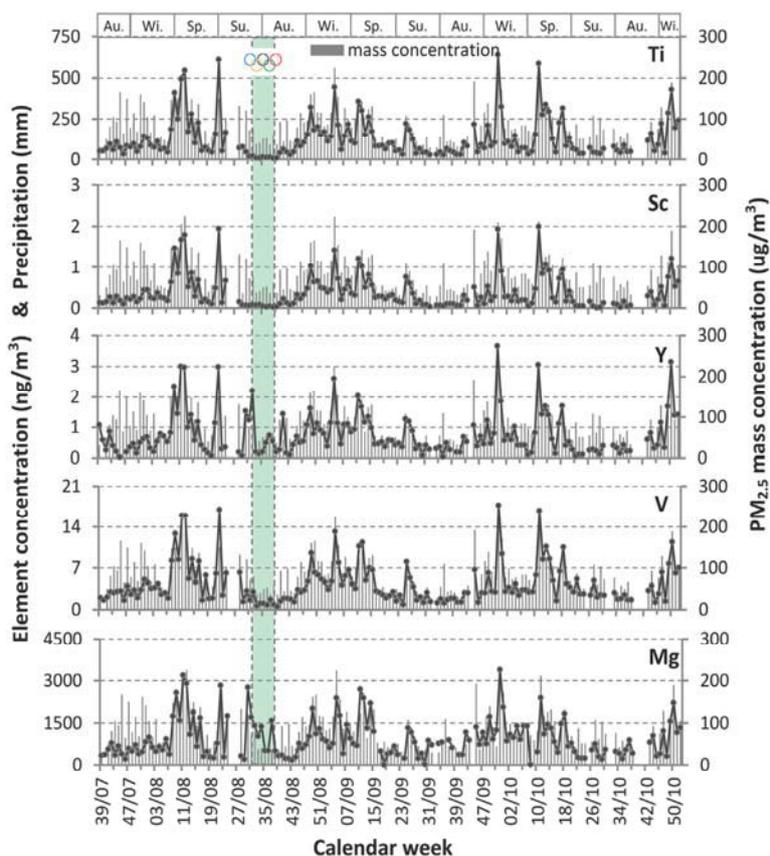


Fig. 6. Weekly concentrations of typical geogenic elements with PM_{2.5} mass concentration during the observation period.

with EFs around 1 (Table 1), were selected as geogenic tracers to observe the variation of geogenic sources during the whole sampling period. Fig. 6 shows that the concentration peaks of these elements usually coincided with sand dust storms or dust days in spring and winter while the low concentrations occurred in summer with precipitation (Fig. 4). With increased planting and afforestation to control local dust and sand dust storms, the number of days with sand dust or sand dust storms showed a decreasing trend since the 1950s but only on a long term time sequence (An and Liu, 2004; Zhou et al., 2002) whereas year-to-year variations were not stable. The annual means of the five elements did not decrease like the concentrations of anthropogenic elements. In the three sampling years, they stayed in a relatively stable range with average means of $131 \pm 1.69 \text{ ng/m}^3$ (Ti), $0.38 \pm 0.03 \text{ ng/m}^3$ (Sc), $0.79 \pm 0.07 \text{ ng/m}^3$ (Y), $4.44 \pm 0.18 \text{ ng/m}^3$ (V), and $969 \pm 99.3 \text{ ng/m}^3$ (Mg), respectively.

Since the government asked for suspension of construction activities during the Olympic Games, most of the construction sites were in operation day and night in order to finish certain goals before the Olympic Games. Therefore there was an increase in concentrations of geogenic elements like Mg related to construction activities in the summer shortly before the Olympic Games (week number 22–31/08) (Fig. 6), except for the days with much precipitation, which washed out aerosol particles.

In general, geogenic element concentrations did not show an obviously decreasing trend over the observation period with the mitigation measures. The suspension policy for construction activities for the Olympic Games even exacerbated the pollution situation of elements mainly from geogenic sources. Therefore, natural sources of fine particles, especially sand dust storms and local construction activities are still of major concern for the government.

3.4. The international context

To investigate the differences of aerosol pollution between Beijing and other cities and countries, studies about $\text{PM}_{2.5}$ mass concentration and chemical element composition are summarized in Table 2. However, to find identical sampling periods and techniques for each city during previous research was not feasible due to practical considerations and differences between cities from different countries with distinct development and government backgrounds.

Compared to other studies before 2007 in Beijing (Duan et al., 2006; Sun et al., 2004), concentrations of typical geogenic elements like Mg, Al, Ca and Ti in this study increased to some extent while concentrations of typical anthropogenic elements including combustion & steel-related elements and traffic-related elements like Cr, Ni, Co, Cu, Zn, As, Cd, Sb and Pb were significantly reduced. The $\text{PM}_{2.5}$ mass concentration was temporally reduced in Beijing.

$\text{PM}_{2.5}$ mass concentration in Beijing was higher than that in many other cities; i.e. more than 8 times higher than in Helsinki, Finland (Vallius et al., 2005). Compared to the results of over 200 different cities in the United States (Thurston et al., 2011), all element concentrations in Beijing were much higher.

Most element concentrations in Beijing were higher than the corresponding concentrations in other studies in European or American countries. Compared to these studies, concentrations of traffic-related elements, for example Sb, Pb, As, Zn, Cu and Cd in this study are much higher. For instance, Pb concentration was 346 times higher than that in Córdoba, Argentina, where daily samples were collected (López et al., 2011). It was 15 times higher compared to that in Toulouse, France (Calvo et al., 2008) where the same analytical method ICP-MS and also weekly sampling were employed, and it was 5 times the concentration in Zurich, Switzerland (Hueglin et al., 2005), which is a one of the world's financial centers and has much traffic. Antimony concentrations in $\text{PM}_{2.5}$ mainly from traffic sources in Beijing were 25 times the concentration of that in Zurich (Hueglin et al., 2005) and 7 times of that in Sao Paulo (Degobbi et al., 2011). This data only shows

a trend since the occurring concentrations also depend on the specific locations of the respective samplers.

Average concentrations of elements primarily originating from geogenic sources, such as Ti, Al, Ca, Mg and Mn, also exceeded the relative concentrations of other studies but not as much as the traffic-related elements during the sampling periods.

Concentrations for Cr, Co and Ni related to fuel combustion and steel work, as well as vanadium were lower in this study than those of some studies of other cities in European or American countries. For example, concentrations of these 4 elements (just the available data) in Toulouse, France (Calvo et al., 2008), Izmir, Turkey (Yatkin and Bayram, 2007) and San Paulo, Brazil (Degobbi et al., 2011) were all higher than concentrations in Beijing $\text{PM}_{2.5}$ (Table 2).

Most countries are tightening the standards for $\text{PM}_{2.5}$. But up until now there are no comprehensive standards for all chemical elements in aerosols or $\text{PM}_{2.5}$ yet. The maximum (ambient) concentration of Pb in air was set to 500 ng/m^3 in China (MEP-China, 2012) and Australia (DEH-Australia, 2004). Air Quality Standards in the European Union (EU, 2008) cover Ni (20 ng/m^3), As (6 ng/m^3), Cd (5 ng/m^3) and Pb (500 ng/m^3). The Chinese new Ambient Air Quality Standard (GB3095-2012) also gives reference standards for As and Cd, 6 ng/m^3 and 5 ng/m^3 respectively (MEP-China, 2012). According to the comparison between element concentrations in Beijing $\text{PM}_{2.5}$ and their limits required by the government, most of the concentrations meet the standards except for As which mainly originates from combustion and traffic. In the United States of America, EPA set a much stricter criterion for lead: 150 ng/m^3 (EPA-USA, 2013). If compared to this standard by EPA-USA, the average concentration in this study slightly exceeded the limit.

Conclusively, $\text{PM}_{2.5}$ was slightly polluted in the exemplarily selected cities of Europe and the United States, and a little worse in Latin America or some countries across Asia and Europe like Turkey, while $\text{PM}_{2.5}$ contamination was serious in Beijing although it is getting better on a long-term perspective.

4. Conclusions

Long-term sampling and analyses of $\text{PM}_{2.5}$ enabled the detailed investigation of temporal distribution of mass and chemical element concentrations in $\text{PM}_{2.5}$ in the megacity Beijing during a time when the government carried out an enormous experiment with mitigation measures to improve air quality since the successful bidding for the 29th Olympic Games. Especially in 2008, the government implemented some unique policies including traffic restrictions in order to mitigate air pollution.

$\text{PM}_{2.5}$ mass concentration decreased compared to the previous studies. Five main sources of elements were extracted by factor analysis. Results of factor analysis show that factor scores of anthropogenic element association displayed a decreasing trend under the government intervention policies while factor scores of elements of natural origin retained a relatively stable trend over the sampling period.

Temporal variations of element concentrations correlated with different governmental intervention measures. Measures like traffic restriction, improved emission standards for industry and relocation of the Capital Steel Company all contributed to mitigation of $\text{PM}_{2.5}$ contamination. Concentrations of traffic-related elements varied with the strength of traffic restriction measures. The pollution level was inversely correlated with the intensity of the measures. The “odd–even restriction measure” effected lowest concentrations of Pb, Sb, Sn, As and Zn. Due to the pause of the traffic restriction measures from September 20th to October 10th, 2008, their concentrations ascended by 126%, 302%, 143%, 103%, and 13%, respectively with 16% increased $\text{PM}_{2.5}$ mass concentration. The element concentrations were reduced by 27%, 50%, 25%, 28%, and 37% respectively during the “1/5 restriction measure” (including the 5th ring road) from October 10th, 2008 to April 10th,

Table 2
Average PM_{2.5} mass concentration ($\mu\text{g}/\text{m}^3$) and element concentrations (ng/m^3) in different cities.

Reference	Vallius et al., 2005	Hueglin et al., 2005	Calvo et al., 2008	Yatkin and Bayram, 2007	López et al., 2011	Degobbi et al., 2011	Thurston et al., 2011	Duan et al., 2005	Sun et al., 2004	This study
Location	Helsinki, Finland	Zürich, Switzerland	Toulouse, France	Izmir, Turkey ^a	Córdoba, Argentina ^b	Sao Paulo, Brazil	over 200 sites, U.S.	Beijing, China ^c	Beijing, China ^c	Beijing, China
N/duration	164, 24 h	79, 24 h	52, weekly	50, 24 h (weekly data used)	24 h	39, 24 h	24 h	40, 24 h	40, 24 h	Weekly
Sampling period	Nov 1998–Apr 1999	Apr 1998–Mar 1999	Mar 2004–Feb 2005	Jun 2004–May 2005 (winter & summer)	Jul 2009–Apr 2010	Apr 8–Jul 2008	Feb 2000–Dec 2005	Aug 2001–Sep 2002	Summer & winter in 2002, 2003	Sep 2007–Jan 2011
Analytical method	ED-XRF	ICP-MS	ICP-MS	ICP-OES	SR-XRF	ED-XRF	Several ^d	XRF	ICP-AES	ICP-MS
Mass concentration	10.6	20.0	11.0	67.5	68.6	32.9	14.2	102		88.5
Na		96.0		1040		1290	65.9	500	770	1830
Mg		17.0		104		70.9	9.0	215	270	955
Al	28.7	48.0	174	858	8.5	407			820	2400
K	53.1	223		548	198	732	68.2	2680		2220
Ca	32.3	54.0		1780	262	210	54.9	1260	1210	3410
Ti	2.27		7.43		17	26.6		75	50	131
V	6.56	1.1		12.6	6.5	13	2.0		10.8	4.38
Cr	3.42	3.5	36.0	23.9	3.75	14.5			20	11.3
Mn	66.7	124	7.50	16.4	13.5	56.1	3.6		55	88.5
Fe			325	397	335	444	87.3	1180	845	1790
Co					0.65	3.13			3.72	1.21
Ni	2.9	3.1	35.2	17.6	2.9	30.4	1.7		70	5.64
Cu	1.64	6.1	11.5	39.6	8.5	75.1	3.9	50	60	49.5
Zn	16.8	0.5	16.6	180	31	198	16.2	490	450	448
As						4.14	1.3	60	30	15.8
Sr			0.88	2.6					20	24.4
Cd			0.25	1.35					7.45	3.75
Sb			0.6							14.9
Pb	5.79	21.0	9.70	97.8	0.45	2.24	4.7	190	210	156

ED-XRF: energy-dispersive X-ray fluorescence spectrometry; ICP-MS: inductively coupled plasma mass spectrometer; ICP-OES: inductively coupled plasma optical emission spectrometer; SR-XRF: synchrotron-radiation X-ray fluorescence spectrometry; ICP-AES: inductively coupled plasma atomic emission spectroscopy.

^a Urban data.

^b Two sampling sites.

^c Beijing Normal University, BNU site.

^d Different chemical analyses performed according to local measurements.

2009, compared to the concentrations during the same period from 2007 to 2008 without any traffic restriction measures.

2010 annual mean concentrations of the steel-related elements, Co, Ni and Cr, compared to the values in 2008, were reduced by 47%, 24% and 57% inter alia due to the relocation project of the Capital Steel Company. However, elements predominately from geogenic sources did not show an obviously decreasing trend like the other anthropogenic elements, which means that the geogenic part of the fine particles is not mitigated like the anthropogenic part and is not easily controlled by artificial methods. Dust and sand dust from both local and external sources are still of major concern for the government. Pollution peaks before measures, such as construction-related elements before the Olympic Games or traffic-related elements before the lottery policy for the purchase of license plates were also observed.

It is a big challenge for Beijing to reach the WHO standard for PM_{2.5} in a short time due to its special geographic and meteorological conditions, as well as the variety of numerous sources and the continuous growth of industry, energy consumption and traffic fleet. It is therefore necessary to continue and intensify the macro-control measures by the government including limiting emission from anthropogenic contamination sources and mitigating geogenic sources. Both the government and the citizens have the responsibility and obligation to reduce emission of air pollutants and to obtain more “blue sky days” in the future.

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Yuan Chen is a PhD student from the Institute of Mineralogy and Geochemistry (IMG) at Karlsruhe Institute of Technology (KIT) of Germany. She did her bachelor and master study about environmental pollution in China University of Geosciences (Beijing). Her PhD study topic is “Long term aerosol dynamics and the effects of mitigation measures on mass concentration and chemical composition of particulate aerosols in Beijing”. Her expertise lies in studying aerosol pollution in Beijing and analyzing chemical compositions of aerosol samples for several years.

Nina Schleicher is a postdoctoral researcher at the Institute of Mineralogy and Geochemistry of the Karlsruhe Institute of Technology (KIT). As a geochemist, she has several years of experience with air quality topics in China and published several peer-reviewed articles. During her PhD thesis she investigated the chemical, physical and mineralogical properties of atmospheric particulate matter in the megacity Beijing. Her thesis was awarded the “Sparkassen-Umweltpreis” by the KIT and the foundation of the Sparkasse Karlsruhe Ettlingen. Currently, she is the investigator for air quality studies in Karlsruhe with focus on carbon sources and the impact of nearby construction sites.

Yizhen Chen is a professor from the Chinese Research Academy of Environmental Sciences (CRAES); he specializes in long term research on detection experiments of the boundary layer, air quality simulation, atmospheric environment process and planning. Nearly ten years as a project leader and technical backbone he joined many projects including the National Basic Research Development Program of China (973 Program) and the National High Technology Research and Development Program of China (863 Program), and has published more than fifty papers in magazines both domestic and international.

Fahe Chai, vice president and professor of the Chinese Research Academy of Environmental Sciences (CRAES), has wide knowledge and sufficient ability to undertake environmental science research and consultancy, especially in field of atmospheric environment. He has been very successful in the field of atmospheric environment, environmental management, environmental planning. As project manager or main research fellow, he was in charge of many national key research projects and other important projects including the National Basic Research Development Program of China (973 Program) and the National High Technology Research and Development Program of China (863 Program).

Stefan Norra is the head of the inter-institutional “Working group of Environmental Mineralogy and Environmental System Analysis” at the Institute of Mineralogy and Geochemistry (IMG) and the Institute of Geography and Geoecology (IFGG) of the Karlsruhe Institute of Technology (KIT). He is the speaker of the Topic Urban Systems within the KIT Center for Climate and Environment. He has established the research field Urban Geochemistry at IMG and teaches Urban Ecology at the IFGG. Moreover, he is a visiting professor at the Technische Universität Bergakademie Freiberg.

A.2 Long-term variation of black carbon and PM_{2.5} in Beijing, China with respect to meteorological conditions and governmental measures



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Long-term variation of black carbon and PM_{2.5} in Beijing, China with respect to meteorological conditions and governmental measures[☆]



Yuan Chen^{a,*}, Nina Schleicher^a, Mathieu Fricker^b, Kuang Cen^c, Xiu-li Liu^c,
Uwe Kaminski^b, Yang Yu^c, Xue-fang Wu^c, Stefan Norra^{a,d,e}

^a Institute of Applied Geosciences, Working Group for Environmental Mineralogy and Environmental System Analysis, Karlsruhe Institute of Technology, 76131, Karlsruhe, Germany

^b Air Quality Department, Research Center Human Biometeorology, German Meteorological Service, 79104, Freiburg i. Br., Germany

^c School of the Earth Sciences and Resources, China University of Geosciences, 100083, Beijing, China

^d Institute of Geography and Geoecology, Karlsruhe Institute of Technology, 76131, Karlsruhe, Germany

^e Institute of Mineralogy, Technische Universität Bergakademie Freiberg, Brennhausgasse 14, 09596, Freiberg, Germany

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ABSTRACT

Black carbon (BC) and PM_{2.5} were studied for nine years from 2005 to 2013 in the Beijing urban area. The overall weekly average mass concentrations of BC and PM_{2.5} were 4.3 and 66.8 μg/m³. PM_{2.5} annual means of the nine years are around 2 times of the standard (GB3095-2012) in China, and are 5–7 times higher than the WHO standard. The Beijing Olympic Games in 2008 was a milestone to mitigate aerosol pollution. Temporal distribution of BC shows a distinct declining trend, and annual mean mass concentrations of PM_{2.5} after 2008 were lower than those before 2008 but increased from 2011 to 2013. Wind rose plots show that high BC concentrations are usually associated with low wind speed of northeastern or southwestern winds, generally causing poor visibility. Governmental mitigation measures such as traffic restriction despite increased motor vehicle numbers and gasoline consumption and industry relocation with declining consumption of coal and coke were successful in reducing BC emissions. Annual mean of BC was reduced by 38% in 2013 compared to 2005. However, BC contamination in Beijing is still severe when compared to other urban areas around the world.

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1. Introduction

Black carbon (BC) is formed by incomplete combustion of fossil fuels, biofuels, and biomass. It is emitted directly into the atmosphere, mainly in the form of fine particles (PM_{2.5}) (United States Environmental Protection Agency, 2012). In China in particular, it originates from the usage of coal, diesel, and biofuels (Streets et al., 2001). China is the largest contributor to BC emissions throughout the world. Around 17% of global annual emissions of BC are estimated to be from China (Chameides and Bergin, 2002).

Black carbon contributes to visibility degradation (Wolff, 1981; Zhou et al., 2012), global warming (Hansen et al., 2000; Jacobson, 2001), and climate changes (Bond et al., 2011; McConnell et al.,

2007; Menon et al., 2002; Ramanathan and Carmichael, 2008). It is the main component of visible light absorption by particulate matter. For other substances, e.g. iron oxides, the absorption of visible light can be negligible in most cases compared to BC (Heintzenberg, 1982). Diminished crop yields in China were demonstrated to relate to reduced solar radiation reaching the earth (Chameides et al., 1999). As a constituent of PM_{2.5}, BC is responsible for respiratory and cardiovascular diseases (Geng et al., 2013; Jansen et al., 2005; Janssen et al., 2011; Straif et al., 2000). However, there are limited monitoring data on BC for epidemiologic analyses (Geng et al., 2013), especially in developing countries.

Historical records of 1952 Great Smog in London showed disastrous impacts on human health and life expectancy. The main reason of coal pollution aroused increased attention to BC research in the following decades (Penner and Novakov, 1996). In previous long-term studies, BC was usually estimated based on modeling and emission factors with energy consumption data, mainly for emission inventory studies (Bond et al., 2004; Cao et al., 2006; Lu

[☆] This paper has been recommended for acceptance by Baoshan Xing.

* Corresponding author. Institute for Applied Geosciences, Karlsruhe Institute of Technology, Adenauerring 20b, Geb. 50.40, 76131, Karlsruhe, Germany.

E-mail address: yuan.chen@kit.edu (Y. Chen).

et al., 2011; Ohara et al., 2007; Streets et al., 2001; Zhang et al., 2009). The emission factors were calculated by particulate matter (PM) measurements and BC/PM ratios. This results in great uncertainty in BC emissions. To the authors' knowledge, the present study is the first black carbon study with actual measurement data for such a long-term period in China, or even in Asian developing countries, which simultaneously explores the correlations between BC and meteorological factors and governmental mitigation measures. Nine years of sampling and measuring within this study can not only provide useful data with high precision for modeling and calculation, but also reference information for human health research and policy-makers.

2. Materials and methods

2.1. Study area and sampling procedure

Beijing, the capital of the People's Republic of China, lies on the northwest border of the North China Plain and is surrounded by the Yanshan Mountains clockwise from southwest to northeast (Fig. 1). The sampling site was located in the campus of the China University of Geosciences, Beijing (CUGB) (Fig. 1). It was in a distance of

approximately 15 m from the 4th ring road and shielded by a hedge in the north-eastern urban area of Beijing. Therefore, it cannot be regarded as a traffic site but an urban site.

Weekly PM_{2.5} samples were collected on quartz fiber filters (Whatman Inc., Maidstone, UK) with Mini-Volume Samplers (Leckel, Berlin) at a height of 1.5 m. The flow rate of the samplers was set up to 200 L/h and was continuously inspected with a rotameter. To investigate the effects of the special governmental policies for the Olympic Games period, samples with higher time-resolution (24-hourly samples at the CUGB site) were collected in August and September 2008. Higher time-resolution samples in one week during 2008 Olympic Games were considered as one weekly sample. The observation period of this study comprised the sampling period from 2005 to 2013. There were 440 valid samples in total during the 459 weeks of observation time.

2.2. Mass concentration analysis

Filters were weighed before and after sample collection for mass concentration calculation. They were equilibrated for at least 48 h under identical conditions before weighing, and were then measured at least three times with a microbalance (Sartorius SE 2-

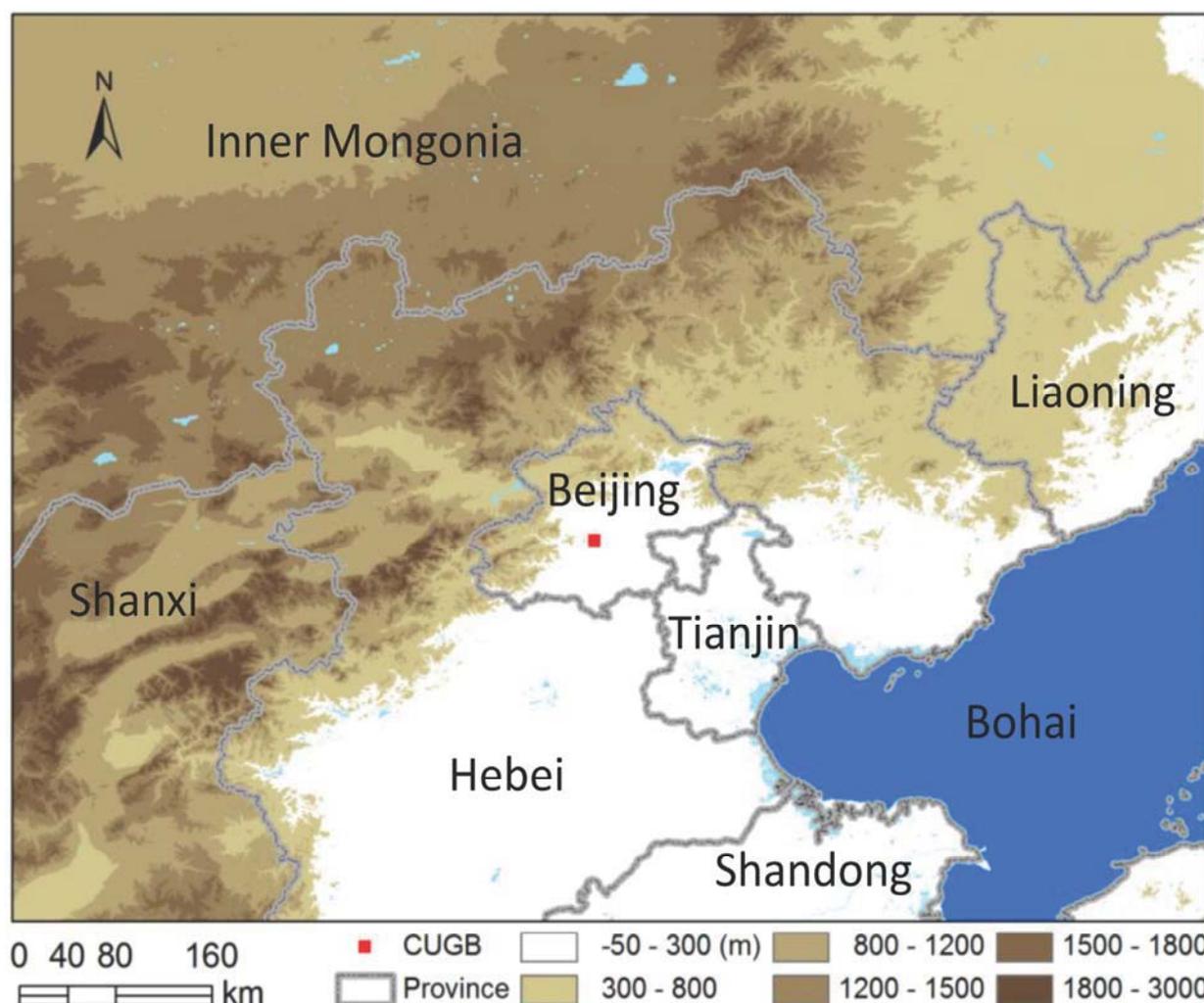


Fig. 1. dimensional topography of the surround area of Beijing and the sampling site (CUGB) in the urban area of Beijing (data sources: SRTM (Shuttle Radar Topographic Mission) 90 m Digital Elevation Data, <http://srtm.csi.cgiar.org/>, produced with ArcGIS 10.2 Desktop).

F, Göttingen, Germany) at a constant temperature (22 ± 3 °C) and relative humidity ($40 \pm 3\%$) before and after sampling, respectively. Standard protocols included the use of filter blanks, laboratory blanks, and externally certified standard weights for all gravimetric analyses for quality control and quality assurance purpose. Filter blanks were sent to Beijing and sent back to Germany like filter samples without being used. The increased or decreased mass on filter blanks was subtracted from the mass of loaded samples to improve the accuracy of the loaded mass. All gravimetric analyses were carried out at the Institute of Applied Geosciences, Karlsruhe Institute of Technology (AGW-KIT), Germany.

2.3. Black carbon analysis

Black Carbon is usually measured with non-destructive optical techniques, which is fast and cost-effective. In this study, BC concentrations were analyzed with an optical transmission technique of Ballach et al. (2001) modified by Fricker and Schultz (2002). A standard thermal analysis method (VDI, 1999) was used to link light absorption by the filter samples to elemental carbon (EC) concentration. Quartz fiber filters were immersed in a fluid, ProTaq Paramount (quartett GmbH, Berlin, Germany). Therefore, scattering effects at the internal interfaces in particle samples were minimized due to the similar refractive index, as is often done for microscopy purposes. Light absorption at a constant wavelength of 650 nm was measured by two spectrometers; CUGB samples from 2005 to 2012 ($N = 433$, in total with blank filters) were measured with a SPECORD 50 (Analytic Jena AG, Jena, Germany), and CUGB samples from 2012 to 2013 ($N = 98$, in total with blank filters) were measured with a SPECORD 50 PLUS (Analytic Jena AG, Jena, Germany). To compare the results of both spectrometers, twenty samples from 2012 were measured with both SPECORD 50 and SPECORD 50 PLUS. The difference of each sample was less than 5%.

For each sample, five measurements were performed from different areas within the filter. Average values were used for BC concentration calculations. Randomly selected samples ($N = 76$, in total) were analyzed three times for quality control. The standard deviation of this triple analysis was less than $0.2 \mu\text{g}/\text{m}^3$. To improve accuracy of the BC data, blank filters were also sent to Beijing and sent back to Germany unused for BC analysis. The analysis results of blank filters were subtracted from the results of loaded filters.

2.4. Meteorological data

Meteorological data were obtained from the German Meteorological Service (DWD), Offenbach, Germany. The data were collected from a meteorological station in Beijing registered at the World Meteorological Organization (WMO) with the code 54511.

3. Results

The overall weekly average mass concentration of $\text{PM}_{2.5}$ from 2005 to 2013 was $66.8 \mu\text{g}/\text{m}^3$, the weekly minimum was $13.1 \mu\text{g}/\text{m}^3$, and the weekly maximum was $275.6 \mu\text{g}/\text{m}^3$ (Fig. 2). The weekly average mass concentration of BC in $\text{PM}_{2.5}$ ranged from 1.0 to $12.9 \mu\text{g}/\text{m}^3$, with an average of $4.3 \mu\text{g}/\text{m}^3$ during the corresponding period (Fig. 2). Black carbon mass accounted for 7.0% of the $\text{PM}_{2.5}$ mass on average, varying between 1.5% and 15.8%.

During the nine-year period of investigation, the average $\text{PM}_{2.5}$ mass concentrations were $69.2 \mu\text{g}/\text{m}^3$ in spring, $57.4 \mu\text{g}/\text{m}^3$ in summer, $62.0 \mu\text{g}/\text{m}^3$ in autumn and $76.1 \mu\text{g}/\text{m}^3$ in winter, while BC mass concentrations were 3.8, 3.4, 5.0 and $5.1 \mu\text{g}/\text{m}^3$, respectively (Fig. 3). Generally, relatively high $\text{PM}_{2.5}$ mass concentrations occurred in spring and winter, mainly due to sand dust storms and heating activities with stagnant air condition, respectively (Fig. 3),

which was also reported by previous studies (Chen et al., 2013; Yu et al., 2011). Although $\text{PM}_{2.5}$ mass concentrations were high in spring, BC mass concentrations were low due to inactive sources. Relatively high BC concentrations occurred in late autumn and winter mainly due to heating activities (Figs. 2 and 3). Domestic heating in Beijing usually starts in Mid-November and ends in the following Mid-March. During this period, high concentrations of fine particles and BC were observed every year (Fig. 2). Average concentrations of $\text{PM}_{2.5}$ and BC during the heating period were 77.2 and $5.2 \mu\text{g}/\text{m}^3$, while they were 61.4 and $3.9 \mu\text{g}/\text{m}^3$ during the non-heating period. Most rainfall occurred during summer (Fig. 2). This is an important mechanism that washes out particles leading to low $\text{PM}_{2.5}$ and BC concentrations. Therefore, $\text{PM}_{2.5}$ and BC concentration were generally low in summer. However, $\text{PM}_{2.5}$ mass concentration was very high in summer in 2008, with high concentrations in June ($87.1 \mu\text{g}/\text{m}^3$) and July ($116.4 \mu\text{g}/\text{m}^3$) and a relatively low concentration in August ($58.2 \mu\text{g}/\text{m}^3$). Meanwhile, BC showed low concentration during the whole summer (average $2.7 \mu\text{g}/\text{m}^3$). Generally, the standard deviations of both $\text{PM}_{2.5}$ and BC concentrations were relatively lower in summer than those in other seasons, due to the relatively stable sources. However, the standard deviation of $\text{PM}_{2.5}$ in summer in 2008 presents the highest during all seasons (Fig. 3). According to the sampling record, there was road reconstruction activity near the sampling site during that time. To obtain better air quality for the Olympic Games, the government asked for suspension of construction activities beginning from August. Therefore, lots of construction companies intensified their activities before August, especially during June and July. Consequently, the intensive construction activities near the sampling site might be the main reason for the abnormally high concentration of $\text{PM}_{2.5}$ in June and July.

4. Discussion

4.1. Assessment of time variation

Fig. 4 shows the yearly variation of average BC and $\text{PM}_{2.5}$ mass concentration from 2005 to 2013. The year 2008 is a critical milestone for air quality improvement in Beijing. To achieve “Green” Beijing Olympic Games in 2008, many governmental mitigation measures were put into force step by step to improve air quality, including restriction measures on traffic and construction, industry relocation and afforestation to prevent desertification and sand dust erosion (Chen et al., 2013, 2014; Schleicher et al., 2011, 2012; Wang et al., 2009, 2010). Annual means of $\text{PM}_{2.5}$ mass concentrations after 2008 were lower than those before 2008. The lowest annual mean concentration occurred in 2011, and then it increased from 2011 to 2013 (Fig. 4-a). BC shows an obvious decreasing trend during the observation period, especially from 2007 to 2008 (Fig. 4-a). Annual mean of BC was reduced by 38% in 2013 compared to 2005. Annual mean reduction of BC mass concentration from 2005 to 2013 was $2.1 \mu\text{g}/\text{m}^3$. The relatively large standard deviation of $\text{PM}_{2.5}$ in 2008 resulted from the unique anthropogenic intervention during this year, which was described in Section 3. The yearly medians, the 1st quartile, the 3rd quartile, minimum and maximum can be found in Fig. 4-b.

According to the Ambient Air Quality Standard (GB3095-2012) in China, the threshold for annual mean of $\text{PM}_{2.5}$ mass concentration is $35 \mu\text{g}/\text{m}^3$ (level II). $\text{PM}_{2.5}$ annual means of the nine years within this study (Fig. 4) all exceed this standard, and they are around 2 times of it. They are 5–7 times higher than the World Health Organization's (WHO) annual mean threshold for $\text{PM}_{2.5}$ ($10 \mu\text{g}/\text{m}^3$). However, there is no standard for BC from WHO and China at the present time.

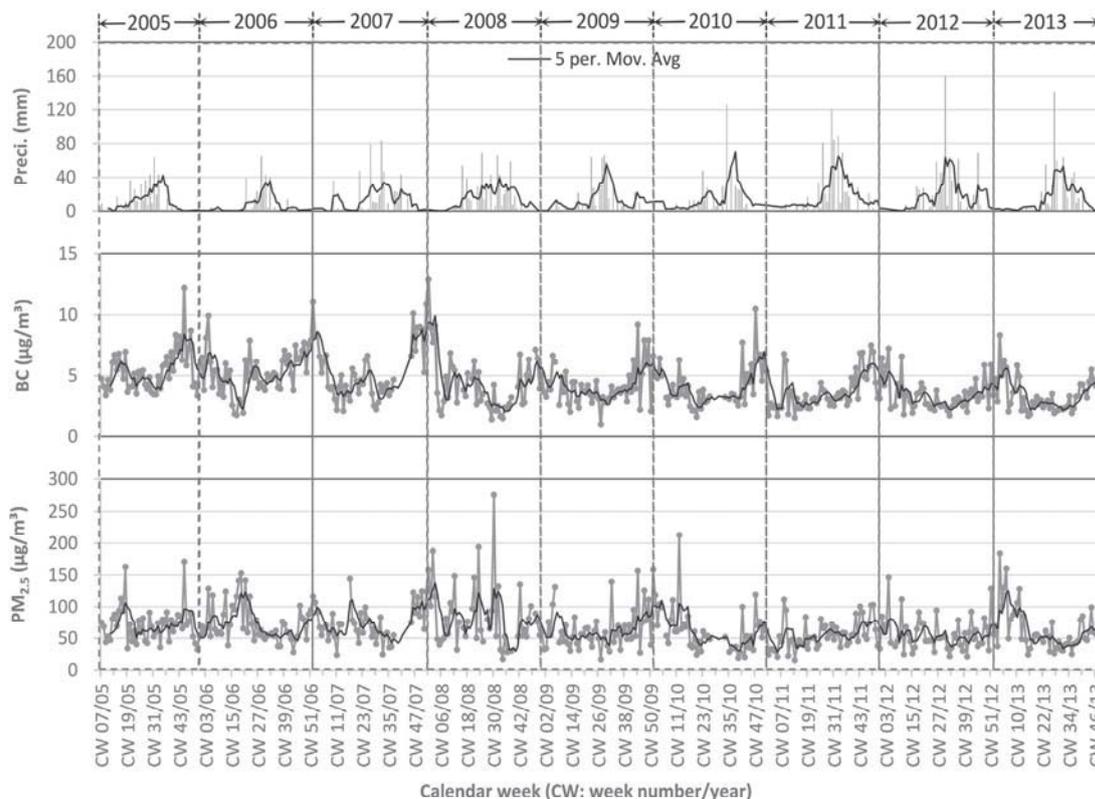


Fig. 2. weekly variation of precipitation (Preci.), BC and PM_{2.5} average mass concentration (in µg/m³) in Beijing urban area from 2005 to 2013.

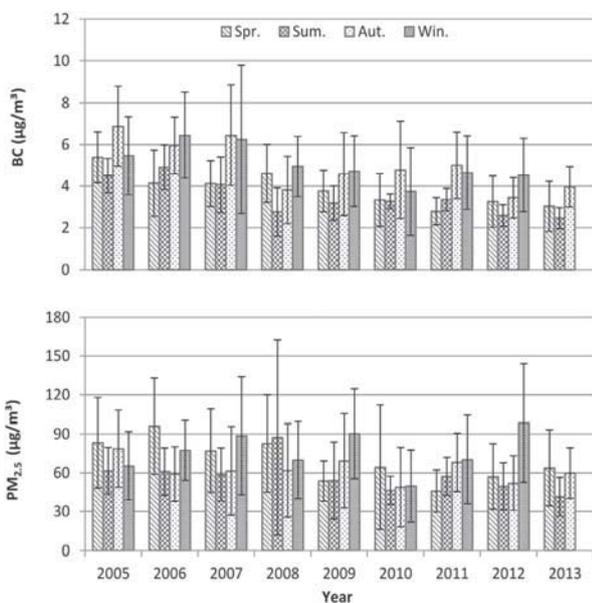


Fig. 3. seasonal variation of BC and PM_{2.5} average mass concentrations (in µg/m³) in Beijing urban area from 2005 to 2013. The whiskers represent the standard deviation.

4.2. Influence of meteorological conditions

Pearson correlation coefficients (*r*) between BC mass concentration and PM_{2.5} mass concentration and various meteorological

factors were calculated separately for the whole observation period, the heating period, and the non-heating period. In Table 1, PM_{2.5} mass concentration (MC) was positively correlated to BC concentration. BC showed negative correlation with all the meteorological factors, precipitation (Preci.), wind speed (WS), wind direction (WD), temperature (Temp.) and visibility (Vis.) during the whole nine-year period of investigation. As discussed in Section 3, precipitation is an important mechanism of washing out particles as well as black carbon. High speed wind as well as wind from the northwest and north facilitated the diffusion of aerosol particles (Chen et al., 2010) and led to less particle and BC pollution, especially during the heating period. Temperature had an indirect effect on BC concentration because when temperatures were low in winter, heating systems which mainly ran on coal combustion led to more BC emission. High BC (>6 µg/m³) and PM_{2.5} (>100 µg/m³) mass concentrations usually occurred together with relatively low visibility (<20 km) during the heating period (Fig. 5). And on some hazy days, for example at the end of October 2011, the high BC concentration with poor visibility even affected people's commuting. However, BC concentrations below 6 µg/m³ were not explicitly linked to low visibility and, therefore other causalities must play a role as well.

Wind rose plots were used to study the influence of wind direction (WD) on PM_{2.5} (Fig. 6) and BC concentrations (Fig. 7). In this study, the samples were collected weekly. During a week, wind direction usually changed several times and the weekly average wind direction did not reflect the real wind direction at every point in time. Therefore, we used 3-hourly meteorological data and the weekly mean concentration for each of the 3-h in a week to interpret the correlation. Wind directions: North (N), NE (North-east), E (east), SE (southeast), S (south), SW (southwest), W (west)

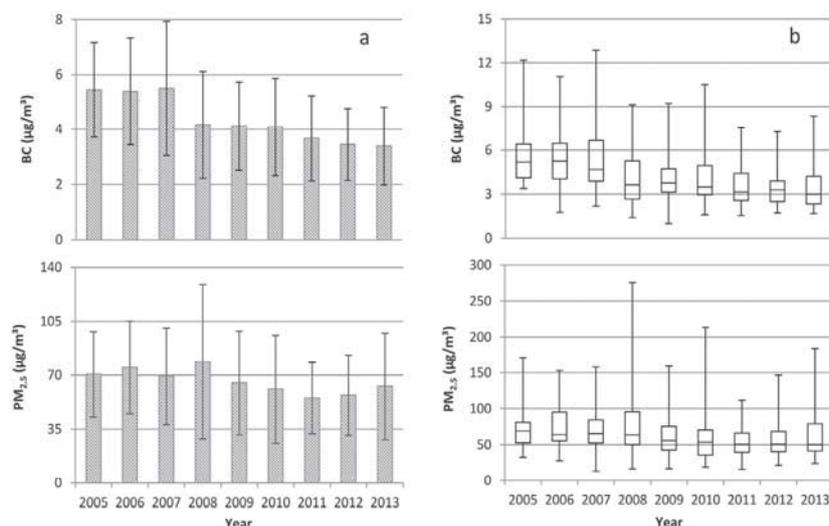


Fig. 4. yearly variation of BC and $PM_{2.5}$ mass concentrations (in $\mu\text{g}/\text{m}^3$) in Beijing urban area from 2005 to 2013. Fig 4-a shows the yearly average concentrations, the whiskers represent the standard deviation. Fig 4-b shows the median with the line in the box, the lower and upper line of the box represent the 1st quartile and the 3rd quartile, respectively, the lower and upper whiskers represent minimum and maximum respectively for each year.

Table 1

Pearson correlation coefficients (r) between average BC and $PM_{2.5}$ mass concentration (MC) and meteorological factors from 2005 to 2013.

r (BC)	Whole period	Heating period	Non-heating period
MC	0.61	0.64	0.54
Preci.	-0.27	-0.09	-0.25
WS	-0.31	-0.50	-0.23
WD	-0.22	-0.44	-0.18
Temp.	-0.32	0.13	-0.22
Vis.	-0.32	-0.60	-0.18

from N–E and SW–W; generally accompanied by poor visibility and low wind speed which is a disadvantage for pollutants diffusion. Open biomass burning from the North China Plain was considered to be an important source of BC (Dan et al., 2004; Duan et al., 2004; Guinot et al., 2007; Ni et al., 2014), even though its major emission product was organic carbon (OC). It is suggested to discontinue open biomass burning in the area around Beijing. However, most farmers still burn crop stalks directly on the fields after harvest. This is one of the contributors of high BC concentrations in autumn

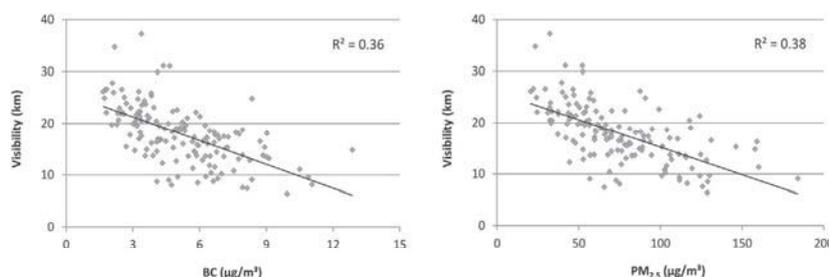


Fig. 5. correlation between BC/ $PM_{2.5}$ and visibility during the heating period.

and NW (northwest). Wind direction range was described clockwise, for example, S–W indicates wind range from S to W clockwise. The main wind directions were from NE and SW (Figs. 6 and 7). In spring and winter, wind from NW and N occurred more frequently than in summer and autumn.

In addition to the main wind directions, in spring, high $PM_{2.5}$ concentrations were transported to Beijing with wind from E and NW–N with high wind speed, accompanied by sand dust or sand dust storms, low BC concentration and poor visibility. Low $PM_{2.5}$ concentrations also coincided with high-speed NW winds not carrying sand dust, which dispersed the aerosol in the city. In summer, relatively high $PM_{2.5}$ concentrations coincided with winds from NE and SE–SW usually along with high BC concentrations. In these directions there are the primary industry areas of North China. In autumn, high BC concentrations also coincided with wind

in Beijing. In winter, high BC concentrations were dominantly associated with the main wind directions from N–E and S–W. Low BC concentrations mainly came from S–W as well as N. Low concentrations from N were usually associated with good visibility and high wind speed, which helped aerosol pollutant diffusion. High $PM_{2.5}$ concentrations mainly coincided with the wind from N–E and S–W. The air masses with low speed reaching Beijing from SW in particular caused poor visibility.

4.3. Assessment of governmental mitigation measures

Details of governmental mitigation measures to improve air quality for “Green” Olympic Games were described in the previous study (Chen et al., 2014). Some mitigation measures are effective long-term, such as the relocation measure of the Capital Steel

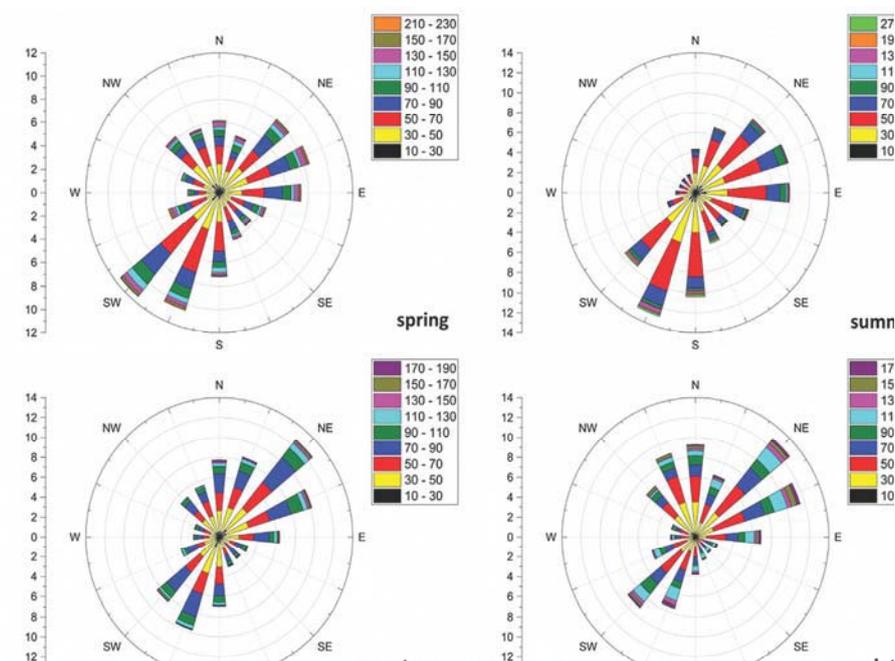


Fig. 6. weekly average PM_{2.5} mass concentrations with wind direction during four seasons. The scales display the percentage frequencies of wind directions. The legends display PM_{2.5} mass concentrations (in µg/m³).

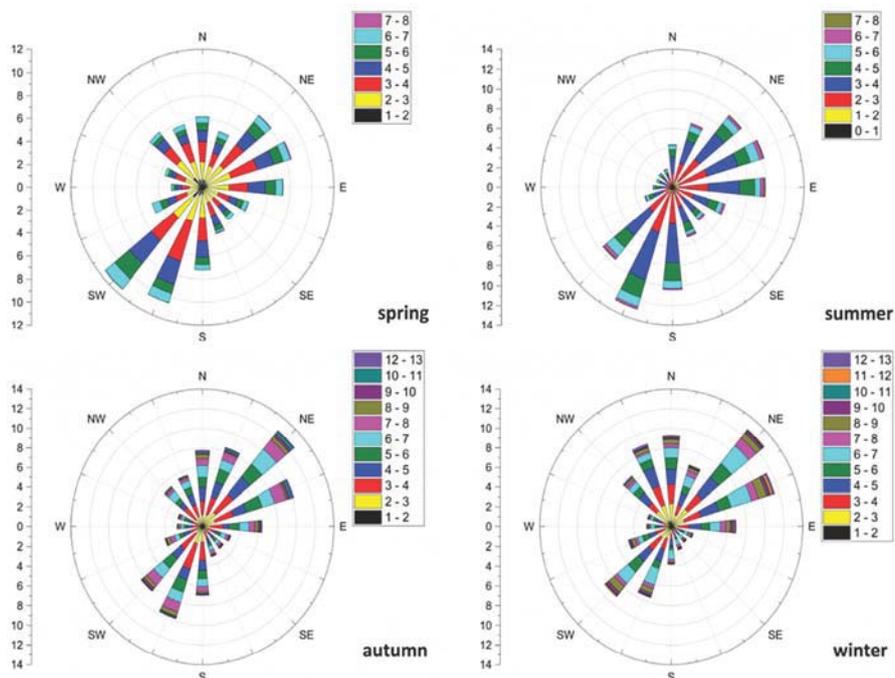


Fig. 7. weekly average BC mass concentrations with wind direction during four seasons. The scales display the percentage frequencies of wind directions. The legends display BC mass concentrations (in µg/m³).

Company; some mitigation measures are still under implementation in Beijing, for example the traffic restriction measures with lower strength after the Olympic Games. And some measures like construction limitation during the Olympic Games ended after the Olympic Games.

The intensive mitigation measures during the Olympic Games, covering i.e. traffic, factories and construction, resulted in the least anthropogenic chemical pollution (Chen et al., 2014). The unique traffic mitigation measures and industry relocation projects have been research hot points for scientists and governmental policy

makers. Within this study, BC was used as a tracer for the impact of combustion processes from industry and traffic during the period with governmental mitigation measures in Beijing.

The intensity of traffic restrictions varied during different periods (Chen et al., 2014). In August 2008 (Aug-2008), during the Olympic Games held in Beijing, all mitigation measures were put into force rigorously. The “odd-even restriction measure” according to which the last digit of the license plate (odd or even number) is used to allow driving on only odd or even days, respectively, cut down about half of the motor vehicles every day during the Olympic Games. The average BC concentration in Aug-2008 was, therefore, the lowest during the nine Augusts along the observation period although the precipitation was not the most and $PM_{2.5}$ concentration was not the lowest (Fig. 8). It was much less in comparison with BC in Aug-2007 and Aug-2013 with similar precipitation, implying that precipitation was not the main reason for the difference. BC concentration in Aug-2008 was only 45% of BC in Aug-2005. However, the average BC concentration in Aug-2009 became much higher again, but still lower than years before the Olympic Games. In the meantime, the total amount of motor vehicles kept rising in Beijing, from 2.58 million in 2005 (Beijing Statistical Yearbook, 2006) to 5.44 million in 2013 (Beijing Statistical Yearbook, 2014). As the dominant energy source of motor vehicles, yearly gasoline consumption correspondingly increased from 2.35 million tons to 4.16 million tons from 2005 to 2012 (Beijing Statistical Yearbook, 2014). BC concentration in Aug-2013 was reduced by 43% in comparison with BC concentration in Aug-2005. On the whole, BC concentrations decreased under the governmental mitigation measures even with increased motor vehicle number and gasoline consumption, which documented the efficiency of the traffic restriction measures by the municipal government.

The relocation project of the Capital Steel Company, one of the biggest steel companies in North China, started 2005 (Nr. 5 iron-smelting blast furnace shut down) and was completed in 2010 (all smelting and hot-rolling capability shut down). It was moved out of Beijing City and relocated to the southeast of Beijing in Hebei Province near Beijing. Previous studies (Chen et al., 2013, 2014) demonstrated the effectiveness of this relocation project in reducing steel-related elements in $PM_{2.5}$.

The raw material for smelting iron and steel in blast furnaces is coal. In China, including Beijing, coal is the major source of energy, accounting for 70% of the total energy consumption on average from 2005 to 2013 (China Statistical Yearbook, 2013). Total energy

consumption in Beijing accounted for 55.2 and 73.5 million tons of Standard Coal Equivalent (SCE) in 2005 and 2013, respectively. Although total energy consumption increased, coal consumption and its share in total energy consumption decreased from 2005 to 2013 (Beijing Statistical Yearbook, 2014). Coal consumption reduced gradually from 30.7 million tons SCE in 2005 to 22.7 million tons SCE in 2012 (Figs. 9-d) (Beijing Statistical Yearbook, 2014). Coke consumption dropped from 3.97 to 0.32 million tons SCE, respectively (Figs. 9-d). In 2011 it dramatically fell to 0.33 million tons SCE from 2.20 million tons SCE in 2010 (Beijing Statistical Yearbook, 2014). Correspondingly, BC concentration exhibited the largest annual decline from 2010 to 2011 during the observation period, with the exception of the special Olympic year 2008 (Beijing Statistical Yearbook, 2014). Pearson correlation coefficients (r) between annual mean BC concentration and coal and coke consumption were 0.962 and 0.944. The relocation of the Capital Steel Company was one of the major contributors to reduction of coal and especially coke consumption. And the improved heating system is conducive to reduce aerosol particulates (Wang et al., 2010), which could also contribute to BC emission decline. In this study, declining BC concentrations and their good correlation to coal and coke consumption (Fig. 9) revealed the efficiency of moving out large-scale industries of Beijing in mitigating pollution. It also demonstrated the success of governmental policies in improving air quality and abating BC emission by transforming the energy consumption structure.

Although coal has been gradually being replaced by natural gas and other relatively clean energy sources in urban areas of Beijing since 1999 (Beijing Environmental Protection Bureau, 2012), the energy consumption in suburban and rural areas of Beijing are still dominated by coal (Zhao et al., 2013). This should be improved in the future energy transformation to mitigate air pollution.

4.4. Comparison with other urban areas

In order to get a better understanding of the BC contamination situation in Beijing, in this study, study cases from previous research in Beijing and other cities all over the world were selected for BC comparison (Table 2). In some studies, elemental carbon (EC) was measured by thermal methods, and in other studies, BC was determined by optical methods as in this study. Essentially they are identical forms of carbon and show comparability for scientific research (Hitztenberger et al., 2006). Due to the various analytical techniques used by different researchers, caution must be exercised when comparing BC concentrations (Wolff, 1981). Different measurement methods produced different results even at the same sampling site (Kanaya et al., 2008). And the wave-length of the light adopted in the optical measurements was also one of the reasons for uncertainty when surveying BC. These influence factors should be considered when comparing different studies.

In spite of progressing energy consumption and a growing vehicle fleet, carbon concentrations followed a decreasing trend during the last two decades in comparison to previous studies about BC in Beijing (Chen et al., 1994; He et al., 2001; Lou et al., 2007; Schleicher et al., 2013; Song et al., 2013; Wang et al., 2005). Schleicher et al. (2013) measured BC concentrations at 4 sites using the same sampling and measurement methods as this study in Beijing. Compared to their results, BC displayed a reduction trend during the last several years of this study. Xi'an, the capital of Shanxi province, which is a major coal-producing area in China, shows much higher BC concentration than Beijing (Cao et al., 2009). Nevertheless, BC concentrations in the Beijing urban area were still higher than that in Hefei (Zhang et al., 2015), the capital of Anhui province, and Shanghai (Feng et al., 2014), a city which is comparable to Beijing with regard to traffic, population and economy. In

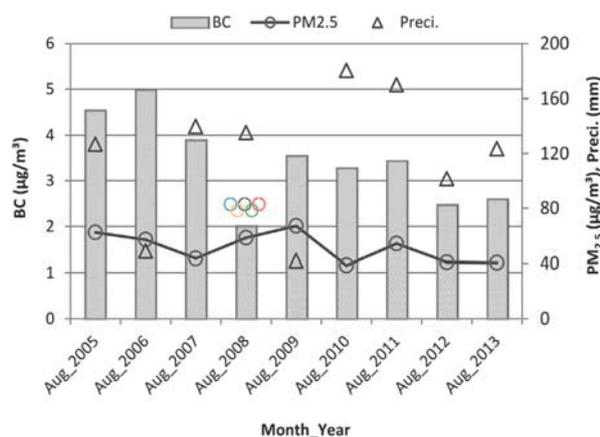


Fig. 8. average BC and $PM_{2.5}$ mass concentration (in $\mu\text{g}/\text{m}^3$) with precipitation (mm) in August every year during the observation period.

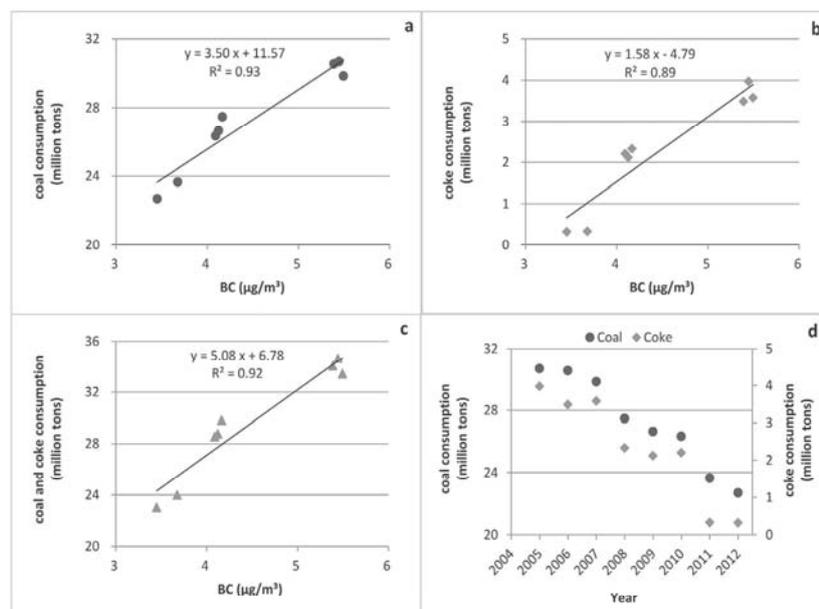


Fig. 9. the correlation between coal and coke consumption and BC emission.

Table 2

BC mass concentrations ($\mu\text{g}/\text{m}^3$) in different cities (spring (sp.), summer (su.), autumn (au.), and winter (wi.)).

City/Area, Country	Size	Type	Time period	Remark	Concentrations	References
Beijing, China	PM _{2.5}	BC	02/2005–12/2013	CUGB site	4.3 sp.: 3.8, su.: 3.4, au.: 5.0, wi.: 5.1	This study
Beijing, China	PM _{2.5}	BC	09/2005–08/2007	4 sites	6.01	Schleicher et al., 2013
Beijing, China	TSP	BC	2009	urban site	su.: 8.1 wi.: 16.1	Song et al., 2013
Beijing, China		BC	07/2003–01/2004	urban site	su.: 8.80 ± 2.59 wi.: 11.40 ± 8.18	Lou et al., 2007
Beijing, China		BC	every late autumn 1996–2004	urban site	20.0	Wang et al., 2005
Beijing, China	PM _{2.5}	EC	07/1999–09/2000	2 sites	9.4	He et al., 2001
Beijing, China	PM _{2.5}	EC	05/1989–05/1990	urban site (west)	18.6	Chen et al., 1994
Xi'an, China	PM _{2.5}	BC	09/2003–08/2005	urban site	14.7 ± 9.5	Cao et al., 2009
Hefei, China		BC	06/2012–05/2013	urban site	3.5 ± 2.5	Zhang et al., 2015
Shanghai, China	PM _{2.5}	BC	01/2010–12/2011	urban site	3.55 (average of 2 years)	Feng et al., 2014
Pearl River Delta Region, China	PM _{2.5}	EC	01-02/2002	8 sites	6.1 ± 4.0	Cao et al., 2003
Hong Kong, China	PM _{2.5}	EC	11/2000–02/2001 & 06–08/2001	urban site	wi. 6.4 ± 1.2 su. 5.9 ± 0.3	Ho et al., 2006
Seoul, Korea	PM _{2.5}	EC	03/2003–02/2005	urban site	4.1 ± 2.6	Kim et al., 2007
Tokyo, Japan	PM _{2.5}	BC	2003&2010	urban site	2.6 ± 0.5 (annual mean)	Kondo et al., 2012
Pune, India		BC	01/2005–12/2005	urban site	4.1	Safai et al., 2007
Granada, Spain		BC	12/2005–11/2008	urban site	3.0 ± 1.5	Lyamani et al., 2011
Helsinki, Finland		BC	11/1996–06/1997	urban site	1.38	Pakkanen et al., 2000
Zürich, Switzerland		BC	01/1998–03/1999	urban site	1.66	Putaud et al., 2003
Fresno, USA		BC	01/2000–12/2000	urban site	1.28 ± 1.06	Watson and Chow, 2002

the Pearl River Delta Region including Hong Kong, as one of main hubs of China's economic growth, BC pollution was severe as well (Cao et al., 2003; Ho et al., 2006). In comparison to the other two capital cities in Asian countries, Seoul in Korea and Tokyo in Japan, BC in Beijing was remarkable (Kim et al., 2007; Kondo et al., 2012). The annual mean of BC in 2005 in Beijing within this study was $5.5 \mu\text{g}/\text{m}^3$. That was higher than BC in Pune, India, during that period (Safai et al., 2007). It was also up to 3-fold higher compared to studies from some European and American cities even one decade ago (Lyamani et al., 2011; Pakkanen et al., 2000; Putaud et al., 2003; Watson and Chow, 2002).

In general, BC concentration was reduced depending on the intensity of governmental mitigation measures as described section

4.3. However, compared to other urban areas around the world, Beijing is still suffering from severe BC contamination.

5. Conclusions

This study presented the first clear evidence of a significant reduction in BC emissions in Beijing during 21st century from long-term measurement. The Chinese government has been adopting a wide variety of intervention measures to reduce emissions of air pollutants and the continuous abatement of BC mass concentration during the investigated nine years from 2005 to 2013 documented the effectiveness of these measures in reducing BC emissions. The "Green" Beijing Olympic Games in 2008 became a milestone in

reducing BC emissions.

BC mass accounted for 7.0% of PM_{2.5} mass on average. It showed a distinct declining trend during the nine years. Annual mean mass concentrations of PM_{2.5} after 2008 were lower than those before 2008 but it increased from 2011 to 2013, with the lowest annual mean concentration in 2011. PM_{2.5} annual means of the nine years are around 2 times of the corresponding standard in China, and are 5–7 times higher than the WHO standard. Annual mean of BC was reduced by 38% in 2013 compared to 2005. Annual mean reduction from 2005 to 2013 was 2.1 μg/m³.

High PM_{2.5} concentrations occurred in spring and winter due to heating, sand-dust storm and sand dust, while high BC concentrations occurred in autumn and winter due to open biomass burning, heating and other combustion sources. Average concentrations of PM_{2.5} and BC during the heating period were much higher than during the non-heating period.

High BC concentrations were usually associated with relatively poor visibility, especially during some hazy-day events. Wind rose plots showed that high BC concentrations were usually associated with wind from N–E and S–W clockwise, generally with poor visibility and low wind speed.

Assessment of governmental mitigation measures, such as traffic restriction measures and industry relocation, indicated the effectiveness in reducing BC emission. Under rigorous governmental abatement policies during the Olympic Games (August 2008), BC displayed the lowest monthly concentration during the nine-year investigation period. BC in August 2013 was reduced by 43% compared to BC in August 2005 even with increased motor vehicle number and gasoline consumption.

The relocation of the Capital Steel Company was considered an important contributor for decreasing BC emission, which was well correlated to the declining consumption of coal and coke, demonstrating the success of the transformation of energy structure to improve air quality.

However, compared to other urban areas around the world, BC contamination in Beijing is still severe, the control of emission sources and improvement of energy structure is still required to be reinforced in the future.

The special interplay of energy structure and industrial growth with environmental mitigation measures in China was observed within this study. It provides significant measurement data and evaluation information not only for scientists but also for policy-makers.

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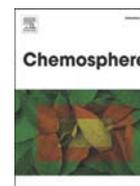
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A.3 Evaluation of impact factors on PM_{2.5} based on long-term chemical components analyses in the megacity Beijing, China



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Evaluation of impact factors on PM_{2.5} based on long-term chemical components analyses in the megacity Beijing, China



Yuan Chen^{a,*}, Nina Schleicher^a, Kuang Cen^b, Xiuli Liu^b, Yang Yu^b, Volker Zibat^c,
Volker Dietze^d, Mathieu Fricker^d, Uwe Kaminski^d, Yizhen Chen^e, Fahe Chai^e,
Stefan Norra^{a,f,g}

^a Institute of Applied Geosciences, Working Group for Environmental Mineralogy and Environmental System Analysis, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

^b School of the Earth Sciences and Resources, China University of Geosciences, 100083 Beijing, China

^c Laboratory for Electron Microscopy, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

^d Air Quality Department, Research Center Human Biometeorology, German Meteorological Service, 79104 Freiburg i. Br., Germany

^e Institute of Urban and Regional Atmospheric Sciences, Chinese Research Academy of Environmental Sciences, 100012 Beijing, China

^f Institute of Geography and Geoecology, Working Group for Environmental Mineralogy and Environmental System Analysis, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

^g Institute of Mineralogy, Technische Universität Bergakademie Freiberg, Brennhausgasse 14, 09599 Freiberg, Germany

HIGHLIGHTS

- Chemical components of aerosol particulates were analyzed in Beijing for nine years.
- Different sources of PM_{2.5} were defined by principle component analysis.
- The influences of mitigation measures on air quality were quantified and evaluated.
- For the first time, gallium (Ga) was used as a tracer for coal combustion in China.

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ABSTRACT

Nine years of sampling and analyses of fine particles (PM_{2.5}) were performed in Beijing from 2005 to 2013. Twenty-seven chemical elements and black carbon (BC) in PM_{2.5} were analyzed in order to study chemical characteristics and temporal distribution of Beijing aerosols. Principle component analysis defined different types of elemental sources, based on which, the influences of a variety of anthropogenic activities including governmental intervention measures and natural sources on air quality were evaluated. For the first time, Ga is used as a tracer element for heating activities mainly using coal in Beijing, due to its correlation with BC and coal combustion, as well as its concentration variation between the heating- and non-heating periods. The traffic restrictions effectively reduced emissions of relevant heavy metals such as As, Cd, Sn and Sb. The expected long-term effectiveness of the steel smelters relocation was not observed due to the nearby relocation with increased capacity. Firework display during every Chinese spring festival season and special events such as the Olympic Games resulted in several times higher concentrations of K, Sr and Ba than other days and thus they were proposed as tracers for firework display. The impacts of all these factors were quantified and evaluated. Sand dust or dust storms induced higher concentrations of geogenic elements in PM_{2.5} compared to non-dust days. Sustainable mitigation measures, such as traffic restrictions, are necessary to be continued and improved to obtain more “blue sky” days in the future.

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* Corresponding author. Institute for Applied Geosciences, Karlsruhe Institute of Technology, Adenauerring 20b, Geb. 50.40, 76131 Karlsruhe, Germany.
E-mail address: yuan.chen@kit.edu (Y. Chen).

1. Introduction

Beijing, the capital of the People's Republic of China, is the country's economic, cultural and political center. It is a typical Asian

megacity with a population of more than 21 million (Beijing Statistical Yearbook, 2015). However, rapid industrialization and urbanization is accompanied by air pollution, especially in the urban area. It has become one of the greatest environmental concerns of both the public and scientists in the 21st century. Aerosol particles occur over a wide range of size from nanometer scale to micrometer scale. Fine particles, such as those finer than 2.5 μm ($\text{PM}_{2.5}$), have adverse impacts on human health since they can be inhaled deep into the lungs and even reach the alveolus, where the smallest particles can pass the blood barrier (e.g. Dockery and Pope, 1994; Schwartz et al., 1996). Thus $\text{PM}_{2.5}$ is made responsible for a wide variety of diseases, especially of the respiratory tract and the cardiovascular system. The global burden of disease (GBD) due to urban air pollution occurs dominantly in developing countries; developing Asia is estimated to contribute approximately two-thirds of the global burden (Cohen et al., 2005). In China, the GBD estimates 1.2 million premature deaths; in Beijing City mortality due to $\text{PM}_{2.5}$ is about 22,000–30,000 persons per year (Zheng et al., 2015). The impacts of air pollution on human health are the predominant driver toward implementing air quality regulations.

Previous studies have investigated chemical constituents and their variations of aerosol particles in Beijing. For some examples, daily observations of hazardous trace metal concentrations in aerosols were conducted to describe their temporal distributions from 2001 to 2006 (Okuda et al., 2008). Crustal elements did not show clear increases while hazardous trace metals, such as Cd and Pb concentrations increased remarkably (Okuda et al., 2008). $\text{PM}_{2.5}$ and total suspended particulate (TSP) were studied in spring by a 4-year campaign (2001–2004) in order to understand the variation of characteristics and formation mechanisms of aerosols on dust, haze, and clear days in Beijing (Wang et al., 2006).

Beijing hosted the Olympic Summer Games (8th–24th in August) and the Paralympic Games (6th–17th in September) in 2008. The corresponding week numbers are calendar week (CW) 32/08 to CW34/08 and CW36/08 to CW38/08, respectively. These two periods together are called the Olympic Games period in this study. To improve air quality during the Games, the Beijing municipal government enforced a series of mitigation measures including traffic restriction, industry relocation and construction limitation (Chen et al., 2013, 2014). Previous studies documented the effectiveness of these actions during the Olympic Games in mitigating air pollution, covering reduced $\text{PM}_{2.5}$, PM_{10} , TSP, CO, NO_2 , O_3 , trace elements and water-soluble ions (Wang and Xie, 2009; Okuda et al., 2011; Schleicher et al., 2011b; Li et al., 2012). However, very few publications represented long-term effects of these measures. Besides these specific measures on particular sources, the government enacted macro policies to mitigate pollution. For instance, energy structure transformation has been in progress in all of China, and particularly in Beijing, to improve air quality by increasing clean energy and reducing coal consumption (Chen et al., 2016).

In this study, twenty-seven chemical elements in $\text{PM}_{2.5}$ were analyzed to detect chemical pollution, its sources and its long-term variation to assess the mitigation measures. Nine years of sampling and measurements provided referential data for not only air studies but also pathological research and policy-making.

2. Sampling and methods

2.1. Study area and samples collection

Weekly $\text{PM}_{2.5}$ samples were collected at two sampling sites: one is installed near the main entrance of the China University of Geosciences, Beijing (CUGB) at a height of 1.5 m, and the other one is set up on the roof of the Chinese Research Academy of

Environmental Sciences (CRAES) at a height of about 20 m. The former was located near the 4th ring road in the urban area and the latter was located between the 5th ring road and the 6th ring road (Fig. 1). Samples were collected on quartz fiber filters (Whatman Inc., Maidstone, UK) with Mini-Volume Samplers (Leckel, Berlin). $\text{PM}_{2.5}$ particles are isolated by the jet impactor with a size selective inlet. The flow rate of the samplers was set up to 200 L/h and was continuously inspected with a rotameter.

To investigate the effects of the special governmental policies for the Olympic Games period, samples with higher time-resolution (12-hourly samples at the CRAES site and 24-hourly samples at the CUGB site) were collected in August and September 2008 (Schleicher et al., 2011b, 2012). Higher time-resolution samples in one week during Olympic Games were considered as one weekly sample. The observation period of this study comprises the sampling period from 2005 to 2013 at the CUGB site and the period from 2007 to 2010 at the CRAES site. There are 440 valid samples from CUGB and 158 valid samples from CRAES.

The aerosol samples analyzed in this study are mainly from the CUGB site. $\text{PM}_{2.5}$ samples of the CRAES site were studied with same methods and were published in Chen et al. (2014). The former results of the CRAES site were used for comparison with the data from the CUGB site throughout this study.

2.2. Mass concentration analysis

Filters were equilibrated for at least 48 h at a constant temperature (22 ± 3 °C) and relative humidity ($40 \pm 3\%$) and then were weighed at least three times for mass concentration calculation before and after sample collection with a microbalance (Sartorius SE 2-F, Göttingen, Germany). Filter blanks, laboratory blanks and externally certified standard weights were used for all gravimetric analyses for quality assurance. A more detailed description of weighing procedures can be found in previous studies of the same project (Chen et al., 2013, 2014). All gravimetric analyses were performed at the Institute of Mineralogy and Geochemistry, which recently became a part of the Institute of Applied Geosciences, Karlsruhe Institute of Technology (AGW-KIT), Germany.

2.3. Chemical analysis

One quarter of each filter sample was used for element concentration analysis. The filter quarters were digested with concentrated HNO_3 , HF and HClO_4 (Merck, suprapur) in Teflon vessels. Twice-diluted samples with HNO_3 (1%) were analyzed by a high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS, Axiom, VG Elemental). Standard protocols included measurements of filter samples, filter blanks, laboratory blanks, and externally certified reference materials for analytical accuracy control. All samples were measured in triplicates and mean values were used as analytical results. Methodological blank values of the filter blanks were subtracted from analytical results of $\text{PM}_{2.5}$ filter samples. Element concentrations of certified reference materials, SRM 1648 (urban particulate matter) and GXR 2 (soil sample) from the National Institute of Standards & Technology (NIST, USA), were generally within $\pm 10\%$ of the certified values. All analyses were performed at the AGW-KIT. A more detailed description of the analytical procedures and can be found in previous studies of the same project (Schleicher et al., 2011a, 2012).

Black carbon (BC) was measured with a SPECORD 50 and a SPECORD 50 PLUS (Analytic Jena AG, Jena, Germany) by the optical transmission technique. A standard thermal analysis method (VDI, 1999) was used to link light absorption by the filter samples to elemental carbon concentrations, detailed information about the method was published in Chen et al. (2016).

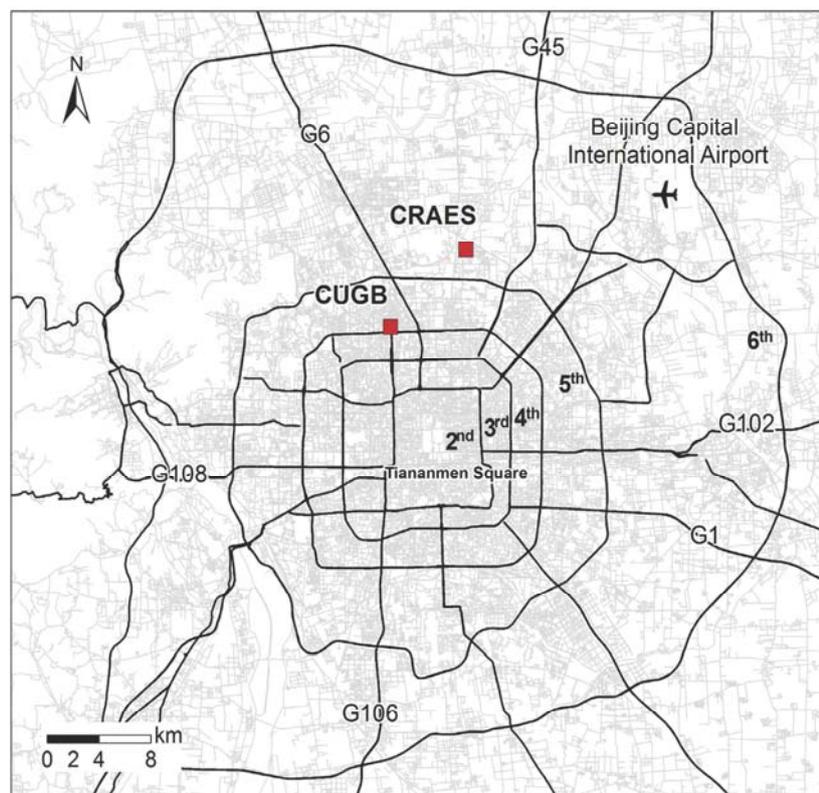


Fig. 1. Sampling sites and the main traffic network of the Beijing urban area, including 2nd–6th ring roads. (Source of the map: OpenStreetMap.)

2.4. Meteorological data

Meteorological data were obtained from the German Meteorological Service (DWD). The 3-hourly parameters including precipitation, temperature, visibility, wind direction and wind speed were collected from a meteorological station in Beijing registered at the World Meteorological Organization (WMO) with the code 54511. As weekly samples were analyzed in this study, average of 3-hourly data in each week was used in the following sections. Wind direction usually changed time after time and the weekly average wind direction did not reflect the real wind direction at every point in time. Therefore, it was only considered when discussing a certain time period.

3. Results

The average concentrations of all determined elements at the CUGB site are shown in Table 1 in order of increasing enrichment factors (EFs). Year-by-year data for the chemical composition of $PM_{2.5}$ from 2005 to 2013 can be found in supplementary materials (Table S1). EFs were calculated to distinguish between elements originating from natural sources or anthropogenic sources, to thus estimate the level of anthropogenic pollution. The enrichment factor for each element (X) in the fine particles (ptc), relative to the upper crust (ucc), can be calculated using the ratio between that element's concentration C_X and the concentration of the reference element titanium C_{Ti} (Eq. (1)).

$$EF_{Ti(ucc)} = (C_X/C_{Ti})_{ptc} / (C_X/C_{Ti})_{ucc} \text{ (according to Zoller et al., 1974) (1)}$$

Table 1

Element concentrations ($\mu\text{g/g}$) and enrichment factors (EFs).

	CUGB site, this study				CRAES site (Chen et al., 2014)			
	N	Mean	Stdev	EFs(ucc)	N	Mean	Stdev	EFs(ucc)
Al	395	15,700	17,100	1	157	23,800	14,300	1
Sc	402	2.8	2.4	1	158	3.5	2.43	1
Ti	417	985	667	1	158	1240	747	1
Y	294	7.6	7.1	1	156	8.3	5.64	1
Fe	417	17,300	8500	2	158	17,500	9180	1
Mg	373	7120	11,100	2	153	10,300	6170	2
Sr	417	191	243	2	158	225	155	2
Na	366	19,500	66,600	2	146	26,300	37,600	2
V	396	50.9	29.7	3	158	43.5	21.4	2
K	417	24,500	13,900	3	158	22,000	11,500	2
Ca	372	31,800	41,700	3	155	37,500	25,500	3
Rb	417	124	55.5	3				
Co	417	14.9	21.9	5	158	11.8	11.9	3
Mn	417	1040	456	5	158	976	643	4
Ba	406	1190	3210	7				
Ga	396	59.4	43.3	11				
Cs	417	18.3	9.7	15				
Cr	350	183	170	16	158	136	117	10
P	276	7390	35,100	24	145	6880	13,300	20
Ni	347	181	250	28	153	65.5	55.4	8
Cu	417	594	266	72	158	574	433	56
Sn	377	147	81.8	81	158	114	138	50
Zn	416	5360	3600	230	158	4940	3600	168
Pb	417	2340	882	357	158	1710	996	207
As	417	243	147	493	158	176	175	285
Cd	417	43.5	20.3	1350	153	59.0	150	1460
Sb	417	151	62.6	2300	152	155	106	1880

Element concentrations in the upper crust were published by

Taylor and McLennan (1985), except for the concentration of P, which is obtained from Yaroshevsky (2006).

Generally, elements with small EFs <5, such as Al, Sc, Y and V, are likely associated with a source largely derived from the upper continental crustal material, while elements with relatively high EFs >50, such as Cd, Sb, As and Pb, predominantly originate from anthropogenic pollution. This method was also used in Chen et al. (2014) for CRAES PM_{2.5} samples. The elements with both small EFs (<5) and high EFs (>50) in the current work are identical with the results of Chen et al. (2014) (Table 1).

There are no comprehensive standards for all chemical elements in aerosols or PM_{2.5} yet. The Chinese Ambient Air Quality Standard (GB3095-2012) provides reference standards for As (6 ng/m³), Cd (5 ng/m³) and Pb (500 ng/m³) (MEP-China, 2012). Based on the chemical analyses of CUGB PM_{2.5} samples (N = 417), their weekly average concentrations are 15 ng/m³, 3 ng/m³ and 145 ng/m³, respectively. Arsenic concentration of PM_{2.5} reached 2.5 times of the ambient air quality standard. Inhalable As-containing particles have a direct inverse influence on health via respiration (Álvarez et al., 2004). Epidemiological studies have demonstrated the association between long-term exposure to inorganic As and increased the risk of lung and skin cancers (Bates et al., 1992; Chiou et al., 1995).

4. Discussion

4.1. Source appointment of fine particles by factor analysis

To investigate aerosol sources, factor analysis of CUGB PM_{2.5} samples was conducted with the software package STATISTICA 8.0 (StatSoft Inc., Tulsa, USA) for the concentrations of 27 elements, PM_{2.5} mass concentrations, BC mass concentrations and the meteorological parameters. Seven factors with eigenvalues larger than 1 were extracted by principle component analysis (PCA) applying varimax standardized rotation, accounting for 77% of the explained variance (Expl. Var.). The factor loadings are listed in Table 2.

Cadmium, As, Sn, Pb, Zn, Cu, Cs and Sb show high positive loadings in **Factor 1** (Table 2) and account for 14% of the variance. They had high EFs up to 2300 (Table 1). Their typical anthropogenic sources are coal combustion and traffic (Huang et al., 1994; Reimann and Caritat, 1998; Wongphatarakul et al., 1998; Sternbeck et al., 2002; Cyrus et al., 2003; Wählin et al., 2006). Smelting (Cd, As, Pb, Zn, Cu and Sb), sewage sludge (As, Sn, Pb, Zn, Cu and Sb) and waste incineration (Sn and Pb) are also important pathways to atmospheric environment for them (Reimann and Caritat, 1998). These eight elements were associated in CRAES PM_{2.5} samples as well and were interpreted to represent anthropogenic pollution, primarily traffic and industry pollution including coal combustion (Chen et al., 2014).

Factor 2 comprises several elements with high positive loadings (Table 2) and accounts for 18% of the variance. These elements are Sc, Ti, Fe, Al, V, Y, Mn and Rb. They are typical geogenic elements with EFs close to 1 and smaller than 5 (Table 1). Wind speed also has high positive loading in this factor. High speed wind from the north or the northwest accompanying by sand dust or sand dust storms can transport high PM_{2.5} concentrations to Beijing (Chen et al., 2016). Sand dust days are always along with high factor scores, for example sand dust or dust days in the 12th weeks in March 2008, 2009 and 2010. High factor scores in the factor which represented geogenic sources were also observed at the CRAES site during the same weeks (Chen et al., 2014). Consequently, factor 2 can be interpreted to represent primarily geogenic influences.

Sodium, P, Mg and Ca show high positive loadings in **Factor 3** (Table 2) with low EFs (<10) except P with EF 24 (Table 1),

accounting for 11% of the variance. The common sources of those elements are fertilizers. Thus, agricultural areas in and around Beijing might be a major contributor to this element association. They can also originate from geogenic dust and construction activities. The factor scores curve was stable over the whole time span with only one extremely high peak during the Olympic Games and a small peak during the 60th anniversary of the founding of the People's Republic of China. Sodium and P can be transported to the atmosphere due to waste waters treatment (Reimann and Caritat, 1998). In a previous study of PM_{2.5} source apportionment at the CRAES site, there were two peaks of factor scores of Na and P as well (Chen et al., 2014), which corresponded to the two peaks of this study. Two sewage treatment plants nearby were considered to be possible contributors. Barium also shows relative high loading in this factor (Table 2). Barium (Wang et al., 2007; Huang et al., 2012) and P (Moreno et al., 2010) can originate from the firework displays. Consequently, firework displays during these two periods can be contributors to the peaks of factor scores.

Only Ga, with EF 11, has high positive loadings in **Factor 4** (Table 2). Furthermore, with a lower loading relative to Ga (Table 2), BC is also included in this factor. As illustrated in Fig. 2, Ga is well correlated with BC (Spearman correlation coefficient of 0.71, N = 396), especially during the heating period (usually from Mid-November to the following Mid-March) where the EF of Ga is 20. Negative loadings for precipitation and temperature were observed. They were reversely correlated to Ga and BC. Generally, low Ga and BC concentrations correlated with more rainfall and higher temperature in summer, while high Ga and BC concentrations correlated with less rainfall and low temperature in winter. The main common source for Ga and BC is coal combustion (Reimann and Caritat, 1998; Streets et al., 2001). Factor scores were much higher in winter than in other seasons, especially during the heating period. Gallium is enriched in coal geogenically and emitted into the aerosols in fly ash from coal combustion (Fang and Gesser, 1996; Dai et al., 2012; Mastalerz and Drobnik, 2012). The Ga content in Chinese coals and world coals is 6.55 µg/g (Dai et al., 2012) and 5.8 µg/g (Ketris and Yudovich, 2009). Ga-rich coal deposits (>30 µg/g) were suggested to be potential resources for Ga recovery as a by-product of coal combustion (Dai et al., 2012). BC can result from incomplete combustion of various fossil fuels, biofuels and biomass, while coal combustion is the primary anthropogenic source for Ga except Al–Mn–Cr–Fe production. Additionally, Ga displays seasonality connected to the heating activities mainly using coal. Therefore, Ga was used as a tracer for residential heating activities in Beijing in the following study in Section 4.2.2. Cadmium and As can also be released by coal combustion as described in the beginning of this section (discussion about Factor 1), however, they don't show high factor loadings in this factor. This might be attributed to their multiple sources such as traffic and industry (e.g., smelting) over the whole year, which did not present seasonal variety like Ga and BC.

Cobalt, Ni and Cr are the dominating elements in **Factor 5** (Table 2) with EFs of 5, 28 and 16, respectively (Table 1). Their common anthropogenic sources include steel works, smelters and fuel combustion. They were recommended as fingerprint for metal processing industry, especially for steel works (Kuang et al., 2004; Nath et al., 2007; Chen et al., 2014). Cobalt and Ni also indicate emissions from crude oil processing in refineries (Norra and Stüben, 2004; Speight, 2014). Yanshan Refinery of China Petroleum & Chemical (Sinopec) is located in the suburb of Beijing. Its capacity reached up to 10 million tons with production of Euro IV standard oil product in 2007. As the first 10-million-ton refining base in China, it accounts for around two thirds of the gasoline market in Beijing. (source: Sinopec official webpage). Consequently, oil refining was regarded as one source of this factor. Waste

Table 2

Factor loadings of seven extracted factors of elements, mass concentrations (MC), BC and meteorological parameters such as wind speed (WS), temperature (Temp.), visibility (Vis.) and precipitation (Preci.) for PM_{2.5} samples by principal component analysis, varimax standardized rotation, together with explained variance (Expl. Var.). High loadings are marked in bold.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
Cd	0.88	0.06	0.08	-0.07	-0.13	0.04	0.04
As	0.79	0.02	0.09	0.10	-0.01	0.01	-0.01
Sn	0.75	0.15	-0.01	-0.14	0.13	0.07	0.10
Pb	0.70	-0.07	-0.03	0.02	0.12	0.02	0.51
Zn	0.58	0.13	0.49	-0.21	0.14	-0.06	0.33
Cu	0.55	0.11	0.10	0.16	0.41	0.07	0.51
Cs	0.52	0.44	0.27	-0.06	0.14	-0.07	0.52
Sb	0.52	0.00	-0.02	0.32	0.31	-0.12	-0.44
Sc	-0.13	0.94	-0.02	0.07	-0.07	0.05	-0.01
Ti	-0.14	0.92	0.04	0.13	0.05	0.10	-0.08
Fe	0.15	0.90	0.14	0.03	0.24	0.06	0.13
Al	0.13	0.82	0.34	-0.01	0.15	-0.03	0.32
V	0.14	0.76	0.09	-0.09	0.12	-0.04	0.30
Y	0.20	0.64	0.24	-0.06	-0.07	0.18	-0.13
Mn	0.32	0.60	0.10	0.28	0.30	0.23	0.21
Rb	0.44	0.58	0.11	-0.03	0.10	-0.11	0.48
Na	0.00	0.07	0.93	0.01	0.17	0.05	0.04
P	0.20	0.05	0.86	-0.15	-0.01	-0.02	0.19
Mg	-0.10	0.46	0.74	0.03	0.03	0.14	0.03
Ba	0.25	0.22	0.61	-0.02	0.09	-0.06	0.65
Ca	0.11	0.42	0.58	0.04	0.55	0.07	0.00
Ga	0.11	0.11	0.04	0.80	0.25	-0.09	0.20
BC	-0.03	0.05	-0.15	0.39	-0.16	-0.77	-0.13
Preci.	-0.03	-0.08	0.07	-0.64	0.42	-0.07	0.02
Temp.	0.17	0.05	0.10	-0.89	-0.01	0.02	-0.07
Co	0.08	0.18	-0.01	-0.07	0.87	-0.08	0.02
Ni	-0.07	0.08	0.07	0.11	0.83	0.08	0.04
Cr	0.25	0.00	0.32	-0.10	0.55	0.04	0.15
Vis.	-0.08	0.29	0.05	0.21	-0.14	0.81	0.02
WS	-0.12	0.42	-0.17	0.10	-0.17	0.62	-0.08
MC	-0.40	0.14	-0.07	0.11	-0.26	-0.70	-0.03
K	0.10	0.03	-0.01	0.08	-0.03	0.04	0.82
Sr	0.03	0.21	0.32	0.25	0.16	0.10	0.79
Expl. Var. (%)	14	18	11	8	9	7	11

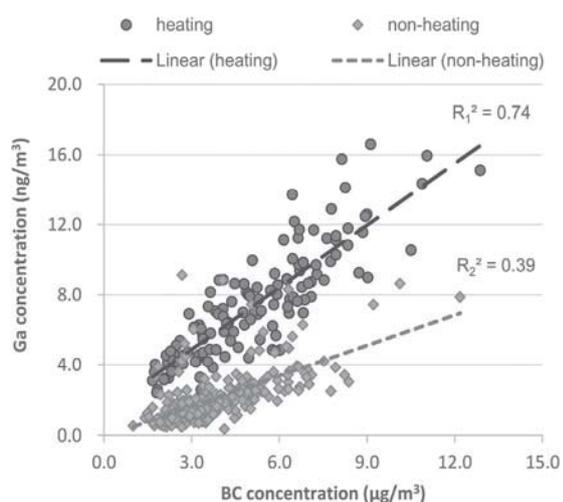


Fig. 2. Correlation between Ga and BC during the heating period (R_1^2) and the non-heating period (R_2^2).

incineration was a contributor of Ni and Cr as well (Nriagu and Pacyna, 1988; Reimann and Caritat, 1998). Copper shows relatively high loadings in this factor which can also originate from steel work and smelters (Reimann and Caritat, 1998). Therefore, this element association was interpreted as industry origins represented by steel works. More than half of the high factor scores (larger than 1) occurred in August and September with wind from

the southwest and the northeast.

Factor 6 has high positive loadings for visibility and wind speed and negative loadings for fine particles and BC mass concentrations (Table 2). The high factor scores (larger than 1) mostly occurred in spring and winter, few in autumn and none in summer, which indicated not only that precipitation effects aerosol pollution, but also that wind speed has an impact on it as well. In spring and winter, low concentrations of PM_{2.5} and BC from the north and the northwest were usually associated with good visibility and high wind speed, which helped aerosol pollutant diffusion during normal days without sand dust or dust storms (Chen et al., 2016). Wind direction also played a significant role in aerosol dispersion. Long-term study of BC and PM_{2.5} with respect to meteorological conditions refers to Chen et al. (2016).

Potassium, Sr and Ba are included in **Factor 7**. Cesium, Cu and Pb also show relative high factor loadings in this factor (Table 2). Firework displays were short-term contributor for K, Sr, Ba, Cu and Pb in the atmosphere during the Chinese spring festival and lantern festival (Huang et al., 2012; Wang et al., 2007). The influence of fireworks will be discussed in Section 4.2.4. Construction materials were also interpreted as possible sources for Sr and Ba (Norra et al., 2008). In general, this factor was interpreted as diffuse urban pollution.

4.2. Evaluation of influences of anthropogenic impact factors

4.2.1. Evaluation of the traffic restriction measures

Based on the source apportionment, As, Cd, Sn and Sb, which were assembled in factor 1 and show very low factor loadings in

other factors, were chosen to represent traffic-related elements. Former studies by Wang et al. (2010) and by Chen et al. (2014) with CRAES data demonstrated the effectiveness of different traffic mitigation measures during different periods. The odd-even traffic restriction measure during the Olympic Games period cut down about half of the motor vehicles every day. After the Olympic Games period, lower intensity traffic measures, e.g. 1/5 restriction measures on weekdays, reduced by around 20% of the civil vehicles on the roadways.

Within this study, average concentrations of three elements of nine consecutive Augusts (from 2005 to 2013) were calculated. Cadmium, Sn and Sb in August 2008 show the lowest concentrations among the nine Augusts (Fig. 3). Arsenic concentrations in August 2012 and 2013 were lower than the concentrations in August 2008. This might have resulted from the decreasing of other sources of As such as coal combustion.

Due to the scavenging effect of precipitation, periods with similar precipitation were selected for comparison study. August 2007 had similar precipitation to August 2008. Concentrations of As, Cd, Sn and Sb in August 2008 were reduced by 31%, 45%, 53% and 50% respectively with the most intensive traffic restrictions, compared to concentrations in August 2007 without any restrictions. August 2010 and 2011 had more precipitation than August in 2008. However, compared to concentrations in August 2008, concentrations of As, Cd, Sn and Sb increased by 108%, 117%, 71% and 49% in 2010 and increased by 131%, 260%, 149% and 11% in 2011, respectively, due to the lower intensity of traffic restriction measures. Precipitation in 2012 and 2013 was less than that in 2008. Element concentrations of Cd, Sn and Sb in 2012 and 2013 were slightly higher than those in 2008. Compared to 2008, both less precipitation and restriction measures with lower intensity can be contributors to increased element concentrations in 2012 and 2013.

In general, the concentrations after 2008 with traffic restriction measures were much lower compared to those before 2008 without any traffic restrictions (Fig. 3). The Olympic Games in 2008 became a milestone for the evaluation of the traffic restriction measures.

4.2.2. Evaluation of the influence of heating activities

Weekly mean concentration of Ga during the nine years was $59.4 \pm 43.3 \mu\text{g/g}$ (μg (Ga) per g (particles)) and was calculated to $3.9 \pm 3.3 \text{ ng/m}^3$ (ng (Ga) per m^3 (air volume)). Nine distinct peaks in total were observed over the whole sampling time span.

Eight noticeable peaks displayed during every heating period (HP) (Fig. 4). Weekly Ga mean concentrations were $108 \pm 37.9 \mu\text{g/g}$ ($7.5 \pm 3.1 \text{ ng/m}^3$) and $34.8 \pm 19.1 \mu\text{g/g}$ ($2.1 \pm 1.9 \text{ ng/m}^3$) during the heating period (HP) and the non-heating period (NHP). Weekly

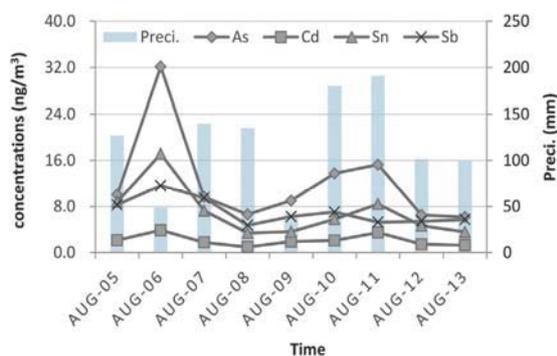


Fig. 3. Elemental concentrations of As, Cd, Sn and Sb in August from 2005 to 2013.

mean during HP was more than 3 times to the weekly mean during NHP. At the end of the sampling time, in November 2013 when the heating systems started to run, Ga concentrations started to increase as well. Gallium concentrations displayed decreasing trends during both HPs and NHPs from 2005 to 2013 (Fig. 4, Fig. S1).

Each year, coal consumption in Beijing declined under the energy transformation policy. It decreased gradually from 30.7 million tons SCE (Standard Coal Equivalent) in 2005 to 20.2 million tons SCE in 2013 (Beijing Statistical Yearbook, 2015). BC in Beijing aerosol was demonstrated to correlate well with the declining consumption of coal and coke (Chen et al., 2016). In this study, Ga was positively related to coal consumption as well (Fig. S2). Weekly mean Ga concentration during NHP in 2013 was only 55.3% of the weekly mean during NHP in 2006. And the weekly mean during HP (2012–2013) was only 47.7% of the weekly mean during HP (2005–2006). According to Beijing Statistical Yearbook (2015), the year 2008 was a turning point for energy structure transform in Beijing for a ‘Green’ Olympic Games. Gallium average concentration during NHPs after 2008 was less than half compared to that before 2008 (Fig. S1). When compare all the HPs from 2005 to 2013, the reduction can be observed since HP-08/09 (the heating period from Nov. 2008 to Mar. 2009). The sharp reduction from HP-09/10 to HP-10/11 (Fig. S1) might be associated with the conspicuous decrease of coal consumption from 2010 to 2011 (from 26.4 to 23.7 million tons SCE) (Beijing Statistical Yearbook, 2015). This also demonstrated the success of the energy structure transform in controlling pollutants emissions.

The other peak occurred from CW37/08 to CW 41/08, directly after the Paralympic Games (6th–17th of September, 2008) (Fig. 4). Many heavy element concentrations in aerosol particles increased dramatically in the meantime (Chen et al., 2014). After the Paralympic Games, most of the compulsory mitigation measures ceased; industries and factories restarted and recovered their capacities immediately, which led to more energy consumption, especially coal combustion. That might be the reason for this peak.

On the basis of nine-year data, Ga correlated well with BC, especially during the heating period, and displayed a strong variation between heating- and non-heating periods. It also correlated well with coal combustion in Beijing. Accordingly, this study is the first to use Ga as a tracer element for heating activities mainly due to coal combustion in Beijing.

4.2.3. Evaluation of the relocation of the Capital Steel Company

In 2005, the Capital Steel Company began its relocation to Caofeidian, which is around 225 km to the southeast of the former location in Beijing. Its activity in Beijing ceased at the end of 2010. It went into operation in the middle of 2010, and has gradually recovered capacity in Caofeidian.

At the CRAES site, annual mean concentrations of Cr, Co, Ni and in 2010 were reduced by 57%, 47% and 24%, respectively, when compared to the concentrations in 2008 (Chen et al., 2014). The short-term effectiveness of the relocation of the Capital Steel Company was documented (Chen et al., 2014). Within this study, if only the data from 2008 to 2010 were considered, they were reduced by 23%, 34% and 2.0%. However, from the view of nine-year measured data, the decrease in Cr, Co and Ni between 2008 and 2010 in Chen et al. (2014) was not continued but slightly reversed between 2011 and 2013 in this study (Fig. S3). This is attributed to the nearby relocation with the recovery of production. The concentration of Cr in 2008 was much higher than the previous two years (2006 and 2007) and following three years (2009, 2010 and 2011). It rose up again after 2011, and it was even higher in 2012 and 2013 than in 2008. The concentration of Co remained relatively stable during these years. Nickel in 2013 was reduced by more than half compared to 2006 and its highest concentration occurred in

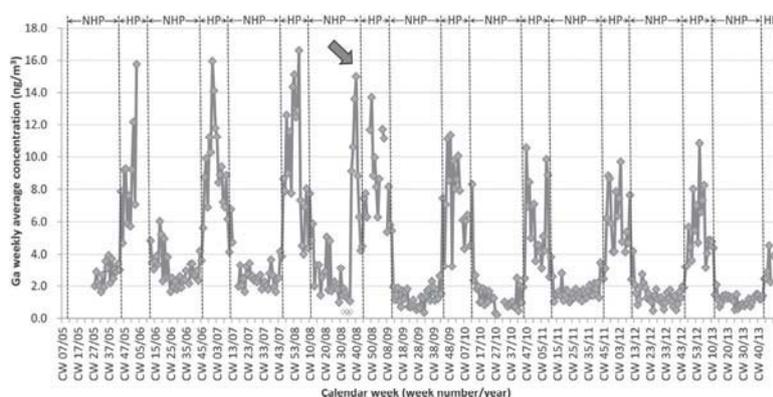


Fig. 4. Weekly average Ga concentrations from 2005 to 2013, HP: the heating period, NHP: the non-heating period.

2009.

4.2.4. Evaluation of short-term impacts of firework displays

Firework display is officially permitted since 2006 by the municipal government in the Beijing urban area (Wang et al., 2007). It is only allowed during some special events like Olympic Games and festivals like the Chinese spring festival. Within this study, the sampling period covered nine Chinese spring festivals and nine lantern festivals (together called the spring festival season), which are in the first three weeks of every year, according to the Chinese lunar calendar, usually in January or February.

Factor 7 was interpreted to characterize firework display in Section 4.1. There are in total nine significant peaks of the factor scores during the observation of nine years (Fig. 5). Seven peaks are in correspondence with seven Chinese spring festival seasons from 2007 to 2013 (P1 to P7 in Fig. 5). The highest factor score 6.3 appeared during the 2008 Olympic Games (P8 in Fig. 5). The remaining one occurred in July 2007 (P9 in Fig. 5), probably as a result of a local firework display close to the sampling site. There is only a small peak (P0 in Fig. 5) during the spring festival season in 2005. This might be due to the official banning of fireworks at that time. Only small amounts of residents in rural areas used fireworks. Aerosol samples were not available during the 2006 spring festival season due to the absence of sampling activity at the CUGB site. Wang et al. (2007) reported that concentrations of K, Sr and Ba were 22, 17 and 82 times higher on the lantern festival night with fireworks in 2006 compared to other days in Beijing. The average concentrations of K, Sr and Ba during the spring festival season were 3, 6 and 5-times higher than the averages during the other days in this study.

Schleicher et al. (2012) found out that the concentrations of K, Sr and Ba at the opening ceremony on 8th August 2008 were 3-times higher compared to the average concentration of the previous fourteen days in TSP samples at the CRAES site. The 2008 Olympic Summer Games started from the second half of CW32/08 to CW34/08. This three-week average was taken to represent the air situation during this event. The weekly average concentrations of K, Sr and Ba were 16,300, 440 and 4160 ppm, respectively. They are respectively 2, 4 and 2-times higher in comparison with the average concentrations of the previous 3 weeks.

On average, K concentration during the 2008 Olympic Games was similar to the average during the same three weeks throughout the other eight years, which might result from its various sources, while Sr and Ba were 4 times higher. Therefore, when long-term average concentrations were studied, Sr and Ba were recommended as tracers for studying the impacts of firework display.

4.3. Evaluation of the influence of sand dust or dust storms

The provenances of sand dust or dust storms in Beijing are primarily the deserts, Gobi and sandy lands in/to the north and northwest of China. They are in arid and semiarid regions, which cover 13.6% of China's area (Zhu et al., 1986). Sand dust or dust storms usually occur in spring and sometimes in winter with high wind velocity. They can trigger visibility deterioration which interrupted transportation and aviation and even affected residents' commute (Zhao et al., 2007; Akhlaq et al., 2012; Cao et al., 2014).

Sand dust or dust storms dominantly contribute to coarse particles rather than fine particles (Zhang et al., 2009). Mass

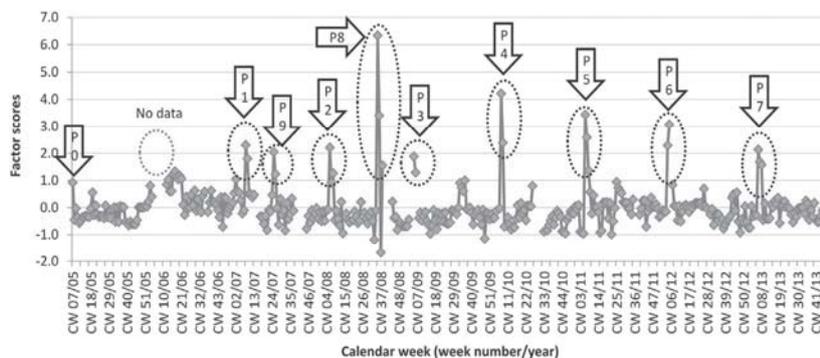


Fig. 5. Factor scores of Factor 7 (K, Sr and Ba) from 2005 to 2013.

concentrations of total suspended particles (TSP) can reach up to 30 times those on normal days (Zhuang et al., 2001). Within this study, aerosol samples were taken every week, so the average elemental concentrations were not much higher compared to those on individual dust days. Over the observed nine years, the average weekly mass concentration of PM_{2.5} during typical sand dust and dust days was 124 µg/m³; it was close to 2 times of the weekly mean, 63 µg/m³, during other normal days.

In Section 4.1, Factor 2 is comprised of elements which primarily originate from geogenic sources. Scandium, Ti, Fe, Al and Y with EFs smaller than 3 were selected to evaluate sand dust or dust storms. During typical sand dust and dust days, the concentrations (in µg/m³) were 0.56, 3.81, 2.85, 4.03 and 1.33 times of the mean values on normal days, respectively.

5. Conclusions

Long term sampling and analyses in this study defined the detailed chemical characteristics of PM_{2.5} and displayed temporal variations of aerosol pollution in the Beijing urban area, based on which, the impacts of a variety of governmental mitigation measures and natural sources on aerosol pollution were evaluated. The Olympic Games in 2008 offered a unique influence with rigorous mitigation measures on air quality. Most of anthropogenic elements displayed the lowest concentrations during the Olympic Games period. However, certain pollution sources, such as fireworks, also resulted in heavy contamination of relevant elements like Sr, and Ba in aerosols.

Aside from meteorological influences, seven types of sources of atmospheric particles were defined according to the element association by principal component analysis: typical anthropogenic sources like traffic and smelting, geogenic dust, fertilizers, coal combustion, steel works and chemical industry, comprehensive combustion emission and diffuse urban pollution. The element analyses with the related governmental mitigations proved the effectiveness of corresponding measures. For example, under the most intense traffic restrictions, average concentrations of traffic-related elements such as Cd, Sn and Sb in August 2008 showed the lowest concentrations among the nine Augusts. Steel-related elements such as Cr, Co and Ni did not continue to decrease on the long term which is attributed to the nearby relocation with the recovery of production.

Gallium displayed significant variation between heating- and non-heating periods and is used as a tracer element for heating activities mainly due to coal combustion in Beijing for the first time. Firework displays resulted in heavy pollution with high concentrations of Sr and Ba during the Chinese spring festivals and the lantern festivals since 2006 when they were legally permitted in the urban area. Dust or sand dust storms produced high particle concentrations.

Based on the data of this study, effective governmental mitigation measures (e.g. traffic restriction measures) and energy structure transformation (e.g. replacement of coal by gas) were recommend to be continued and improved in order to obtain more “blue sky” days in the future.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2016.04.052>.

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A.4 The effect of government policies on the temporal development of contamination characteristics within the aerosol distribution in Beijing, China

The Effect of Government Policies on the Temporal Development of Contamination Characteristics Within the Aerosol Distribution in Beijing, China

Yuan Chen, Nina Schleicher, Yizhen Chen, Fahe Chai, Shulan Wang and Stefan Norra

Abstract To host Green Olympic Games, the Beijing municipal government took comprehensive measures to improve air quality in 2008, which partly are still in force in 2012. The aim of this study is to investigate the temporal distribution of aerosol contamination characteristics and their variations under different government intervention policies. PM_{2.5} samples were collected continuously from 2007 to 2010 in the north of Beijing City. Element concentrations were analyzed by HR-ICP-MS. Results showed that concentrations of traffic-related elements such as Sn, Sb and Pb varied with the strength of traffic restrictions. Elements like Cr, Co and Ni, which are correlated with industries, were reduced under special policies like the relocation of Capital Steel Company. In general, the improving air quality demonstrates the success of government intervention policies although still the concentrations are too high if compared to international threshold values.

Introduction

Atmospheric aerosol pollution has increased dramatically since the preindustrial period [5, 12] and has become one crucial part of air environment study. Atmospheric particulate aerosols play a significant role in the climate change [3, 4, 11] and could have deleterious influence on human health [1, 7, 9, 19].

Y. Chen (✉) · N. Schleicher · S. Norra
Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology,
76131 Karlsruhe, Germany
e-mail: yuan.chen@kit.edu

N. Schleicher · S. Norra
Institute of Geography and Geoecology, Karlsruhe Institute of Technology,
76131 Karlsruhe, Germany
e-mail: yuan.chen@kit.edu

Y. Chen · F. Chai · S. Wang
Institute of Urban and Regional Atmospheric Sciences, Chinese Research Academy of
Environmental Sciences, 100012 Beijing, China

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Particles with an aerodynamic diameter smaller than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$), which can be inhaled into the lung with toxic materials and hence affect human health, have been one of the most concerns of the scientist and the public.

In Beijing, the capital of China, approximately 20 million people [2] are living and suffering from aerosol pollution. In late October 2011, for example, hazy days lasted for more than one week in Beijing and, as a consequence, the chief culprit $\text{PM}_{2.5}$ was identified and became one of the topics of people's daily life. Based on the public's voice, the Chinese government drafted a standard for $\text{PM}_{2.5}$ concentration with an annual mean limit value 35 and $75\ \mu\text{g}/\text{m}^3$ for 24 h mean (level II) [14]. This threshold values is scheduled to be implemented in 2016.

In preparation for 2008 Beijing Olympic Games, the Beijing Municipal Government took a series of emission control measures to improve the air quality and protect the air environment. The main ones consisted of relocating heavy polluters (e.g., the Capital Steel Company), improving emission standards for power plants and heating factories, afforestation outside and inside Beijing City and controlling traffic. Up to now, numerous of studies show that these measures have been operated successfully and had a positive effect on aerosol reduction [13, 17, 18, 22].

However, most of these investigations focused on the period of the 2008 Olympic Games and compared it with the situation before or a short period after the Olympics. To the authors' knowledge, only few articles about longtime comprehensive study around this event were published.

In this study, systematic sampling and measurement for more than 3 years was implemented so the influence of the government policies on fine particle reduction and the variation of chemical composition can be observed over a long time sequence in Beijing urban area. This study discusses mass concentration, temporal distribution of elements and correlations between element pollution levels and government mitigation policies. Results shown in this study are an example of the profound insights on the characteristics of the fine particles and the effects of government intervention policies on them.

Experimental

Sampling

The sampling site is located in the north of Beijing City, between the 5th ring road and 6th ring road, and is set up on the roof of the Chinese Research Academy of Environmental Sciences (CRAES) at a height of about 20 m (Fig. 1). From Sep. 30th 2007 to Jan. 4th 2011, $\text{PM}_{2.5}$ weekly samples were collected continuously on quartz fiber filters (Whatman Inc., Maidstone, UK) with an active Mini-Volume Sampler (Leckel, Berlin) at a flow rate of 200 L/h. During 2008 Olympic Games, in August and September, intensive sampling was implemented with a higher time-resolution

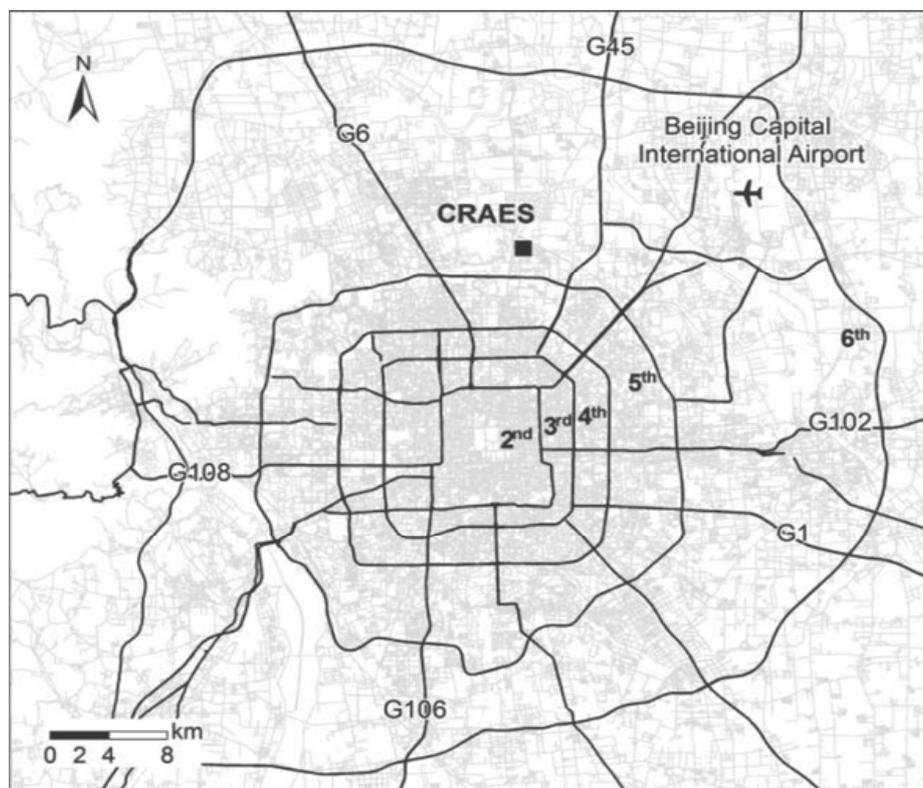


Fig. 1 Sampling site (CRAES) and the main traffic network of Beijing urban area, including 2nd–6th ring roads (Data source: OpenStreetMap)

of 12 h intervals to show more details about the fine particles reduction [18]. Here we calculated the weekly concentrations from these 12-hourly samples for a whole week in order to get the corresponding weekly average. For the 171 weeks during the sampling time, we obtained 158 valid weekly samples (14 of the 12-hourly samples in one week during 2008 Olympic Games were considered as one weekly sample), accounting for 92.4% of all samples.

Mass Concentration Analysis

Mass concentrations were calculated by gravimetric analysis of filters carried out with a microbalance (Sartorius SE 2-F, Göttingen, Germany) for three times after at least 48 h equilibration in constant temperature ($22 \pm 3\%$) and humidity ($40 \pm 2\%$) at the Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology (IMG-KIT), Germany. Accuracy control was implemented by blank filters which were also sent to Beijing but not used and sent back to Germany for analysis.

Chemical Analysis

Element concentrations were determined by a high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS, Axiom, VG Elemental). One quarter of each filter was cut down to digest for ICP-MS analyses. Details of digestion of samples can be found in previous studies of the same project [16, 24]. Standard reference material SRM 1648 (urban particulate matter) and GXR 2 (soil sample) from NIST (National Institute of Standards & Technology, USA) were additionally analyzed to control analytical quality. Element concentrations of standard material were usually within $\pm 10\%$ of the certified values. Methodological blank values of the blank samples were determined and subtracted from analytical results of $PM_{2.5}$ samples. All analysis was performed at the IMG-KIT.

Results and Discussion

Mass Concentration and Meteorological Condition

The weekly mass concentration of $PM_{2.5}$ during the whole sampling period (Fig. 2) ranged from 22.5 to 226 $\mu\text{g}/\text{m}^3$, and the average concentration in the whole period was 86.1 $\mu\text{g}/\text{m}^3$, which was 5.7 times to the USA standard (15 $\mu\text{g}/\text{m}^3$) and about 2.5 times to the drafted annual limit value (35 $\mu\text{g}/\text{m}^3$) in China. This was a slightly higher than the average particle concentration (65.6 $\mu\text{g}/\text{m}^3$) reported by Yu et al. [24] for a different site in the North-West of Beijing City. Particle concentrations that exceeded standards revealed the pollution severity of fine particles in Beijing and the necessity of macro-control by government.

In general, $PM_{2.5}$ pollution level began to decrease since 2008 when government strengthened the enforcement of measures, such as the traffic restriction measures, afforestation and greening and improving emissions standards.

During the heating season from November 15th to March 15th in the second year, average mass concentration of $PM_{2.5}$ (104.4 $\mu\text{g}/\text{m}^3$) was higher than that during non-heating period (74.3 $\mu\text{g}/\text{m}^3$) (Fig. 2). Seasonal pattern showed that spring and winter usually had higher concentrations than summer and autumn mainly due to sand dust storms and the heating activities respectively (Fig. 3), which was also reported by previous studies [6, 16, 24].

The statistic correlation between particle concentration and meteorology has already revealed the precipitation had a direct and rapid influence on reducing particle concentration [6]. In this study the particle concentration obviously showed a negative correlation with precipitation. Thus, wet deposition was the principal way of washing out particles in aerosol (Fig. 2).

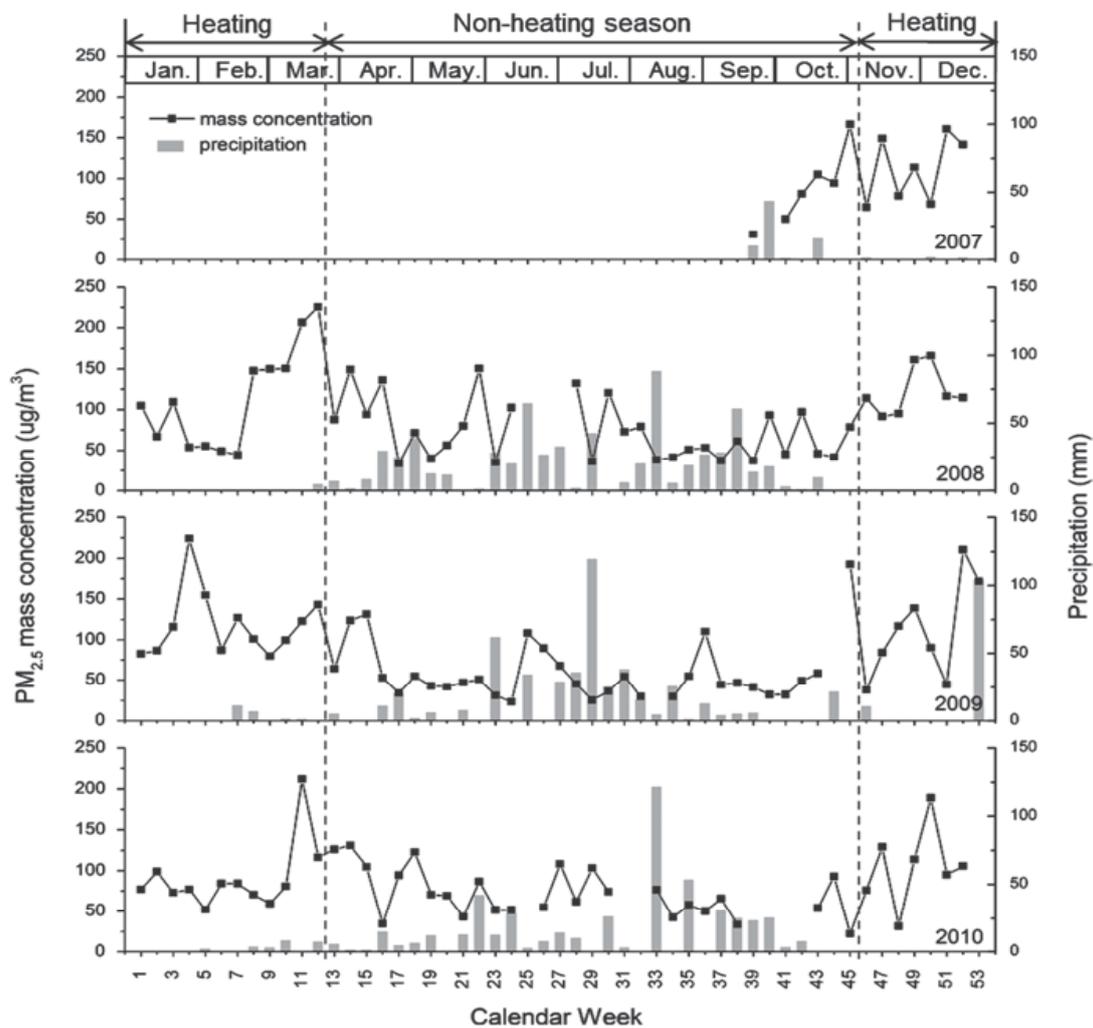
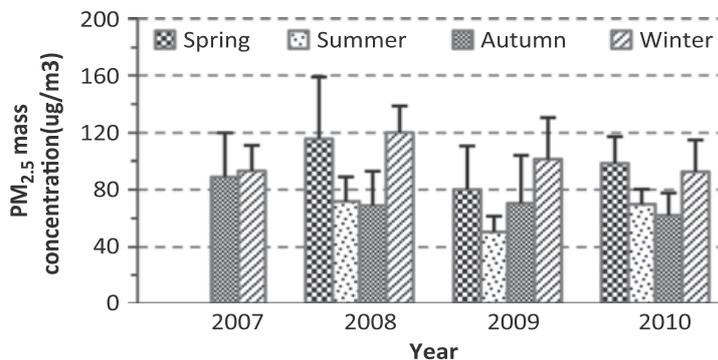


Fig. 2 PM_{2.5} weekly mass concentration from 2007 to 2010 with precipitation

Fig. 3 Seasonal variation of PM_{2.5} mass concentration (average and standard deviation)



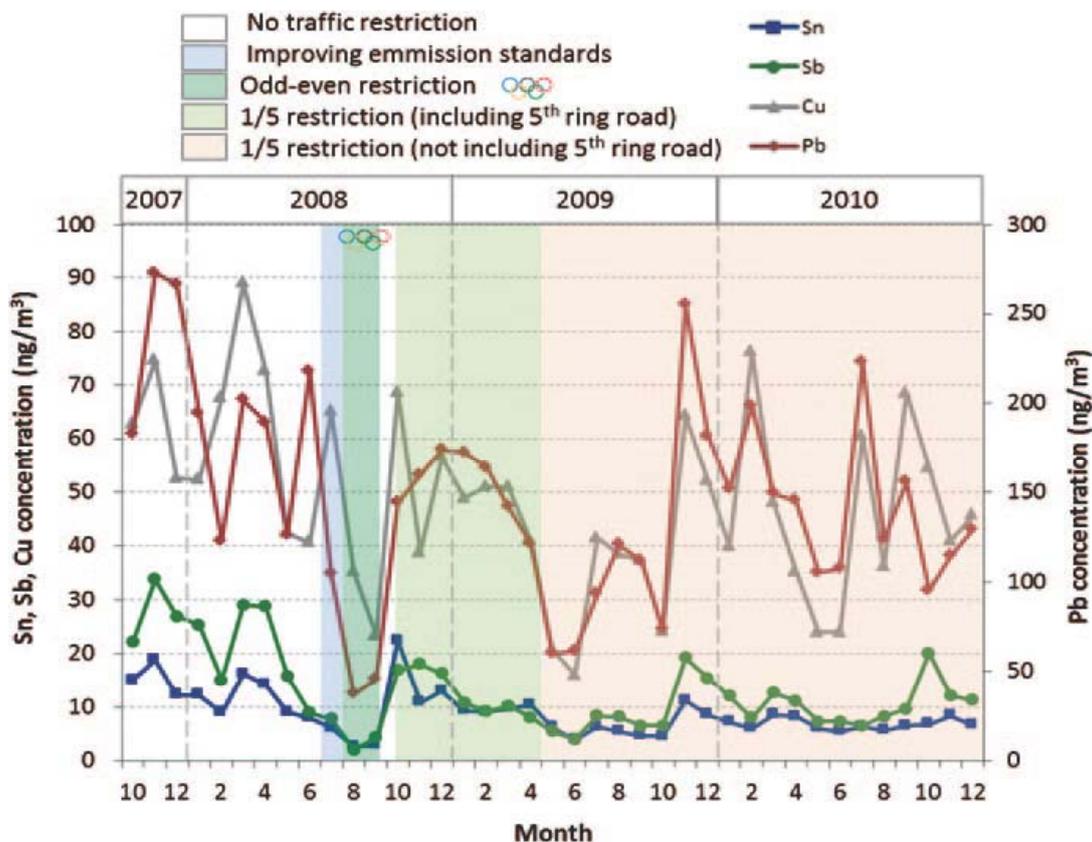


Fig. 4 Concentration of traffic-related elements under different traffic restriction measures

Effects of Government Intervention Policies on Contamination Characteristics of Chemical Element Composition

Influence evaluation of Traffic Restriction Measures on $PM_{2.5}$

In previous studies [8, 10, 20, 21, 23], Sb, Pb, Sn and Cu were recommended for markers of motor vehicle emissions. Their concentrations varied with the strength of traffic restriction policies according to the last number of license plates (Fig. 4). During the Olympic Games, the government implemented “odd-even restriction” policy which reduced around half of the vehicles on roads and brought the lowest element concentrations for the whole sampling period. After a short pause (October 2008) of intervention policies with obvious increasing concentrations (Fig. 4), 1/5 restriction police (including 5th ring road) was put into force on weekdays. This cut down around 1/5 of total number of vehicles running on roads.

From April 2009 and still in effect at the end of 2012, 1/5 restriction police (not including 5th ring road) is under way on weekdays. Since the sampling site (CRAES) is near to the 5th ring road, this policy could be one reason of increasing

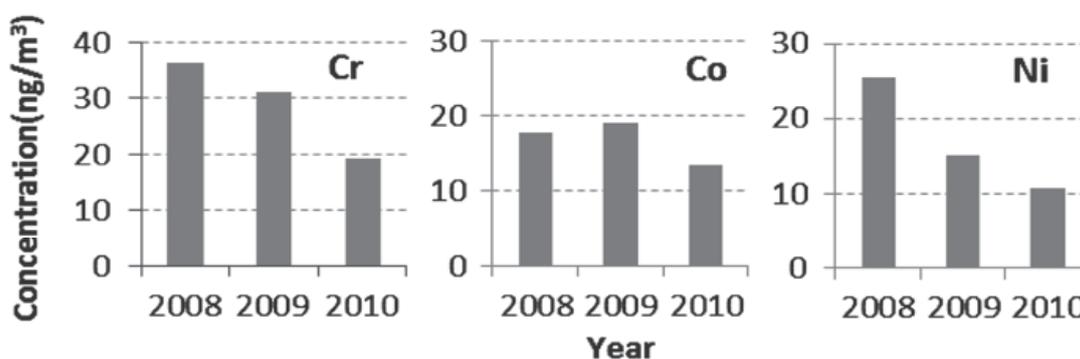


Fig. 5 Annual concentration variation of steelwork-related elements in PM_{2.5}

element concentrations in 2010 compared with concentrations in 2009. In January 2011 a lottery drawing for car license plates in Beijing started and lots of people purchased cars in 2010, which led to a sharp increase in the amount of vehicles exceeding 4.8 million at the end of 2010 in Beijing [2]. This government intervention policy also contributes to the elevation of traffic-related element concentrations in 2010 before its execution. But the contamination level in 2010 was still lower compared to the period before Olympic Games (Fig. 4).

Influence Evaluation of Policies on Capital Steel Company on PM_{2.5}

Among the government policies to control industry emissions, the relocating project of Capital Steel Company (moving it out of Beijing and relocating in Hebei Province which is near to Beijing) was the biggest one and of most influence. At the beginning of 2008, Capital Steel Company shut down its capacity step by step and its relocation program was finally finished in 2010. According to Reimann and Caritat [15], Co, Ni and Cr had common anthropogenic sources released to the atmosphere, primarily from fossil fuel (oil and coal) combustion and steel works, and, therefore, they were taken for evaluation of these policies within this study. Figure 5 shows that the element contamination level declined since 2008 and had in 2010 the minimum concentrations within the three years, which stated the effectiveness of the relocation project on reducing relevant toxic elements in PM_{2.5}.

Conclusions

PM_{2.5} pollution level began to decrease since 2008 when government strengthened the enforcement of measures. After the Olympic Games the concentrations increased again but remained lower than prior to the control measures. Decreasing concentrations of elements, such as Sn, Sb, Cu and Pb, demonstrated the effectiveness of

traffic restriction measures of government on controlling relevant compositions in $PM_{2.5}$. Reducing concentrations of Cr, Co and Ni proved the success of policies on controlling emissions, especially the relocation project of Capital Steel Company. Since some of the government intervention policies are not in effect anymore but some are still in force, it is necessary to continue this study on the effects of government policies on the temporal development of contamination characteristics of chemical compositions of $PM_{2.5}$ in Beijing City.

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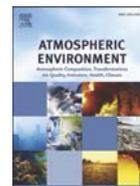
B —Full papers of co-authored scientific publications

B.1 Atmospheric particulate mercury in the megacity Beijing: Efficiency of mitigation measures and assessment of health effects



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Atmospheric particulate mercury in the megacity Beijing: Efficiency of mitigation measures and assessment of health effects



N.J. Schleicher^{a,*}, J. Schäfer^b, Y. Chen^a, G. Blanc^b, Y. Chen^c, F. Chai^c, K. Cen^d, S. Norra^{a, e, f}

^a Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology, Adenauerring 20b, 76131, Karlsruhe, Germany

^b Université de Bordeaux, UMR 5805 EPOC, 33615, Pessac Cedex, France

^c Institute of Urban & Regional Atmospheric Environmental Research, China Research Academy of Environmental Sciences, Beijing, 100012, China

^d Department of Earth Sciences and Resources, China University of Geosciences, Beijing, 100083, China

^e Institute of Geography and Geoecology, Karlsruhe Institute of Technology, Kaiserstr. 12, 76128, Karlsruhe, Germany

^f Institute of Mineralogy, Technische Universität Bergakademie Freiberg, Brennhausgasse 14, 09596, Freiberg, Germany

HIGHLIGHTS

- Study of particulate mercury (HgP) in aerosols from 2005 to 2013 in summer and winter.
- Evaluation of short- & long-term success of mitigation measures during Olympic Games.
- HgP in Aug-08 decreased by 65% compared to previous years due to implemented measures.
- Decrease in winter indicated slight long-term improvement of HgP pollution in Beijing.
- But still high HgP levels regarding adverse health effects even after the reductions.

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ABSTRACT

Atmospheric particulate mercury (HgP) was studied before, during, and after the Olympic Summer Games in Beijing, China, in August 2008 in order to investigate the efficiency of the emission control measures implemented by the Chinese Government. These source control measures comprised traffic reductions, increase in public transportation, planting of vegetation, establishment of parks, building freeze at construction sites, cleaner production techniques for industries and industry closures in Beijing and also in the surrounding areas. Strictest measures including the “odd-even ban” to halve the vehicle volume were enforced from the 20th of July to the 20th of September 2008. The Olympic period provided the unique opportunity to investigate the efficiency of these comprehensive actions implemented in order to reduce air pollution on a large scale. Therefore, the sampling period covered summer (August, September) and winter (December and January) samples over several years from December 2005 to September 2013. Average HgP concentrations in total suspended particulates (TSP) sampled in August 2008 were 81 ± 39 pg/m³ while TSP mass concentrations were 93 ± 49 µg/m³. This equals a reduction by about 63% for TSP mass and 65% for HgP, respectively, compared to the previous two years demonstrating the short-term success of the measures. However, after the Olympic Games, HgP concentrations increased again to pre-Olympic levels in August 2009 while values in August 2010 decreased again by 30%. Moreover, winter samples, which were 2- to 11-fold higher than corresponding August values, showed decreasing concentrations over the years indicating a long-term improvement of HgP pollution in Beijing. However, regarding adverse health effects, comparisons with soil guideline values and studies from other cities highlighted that HgP concentrations in TSP remained high in Beijing despite respective control measures. Consequently, future mitigation measures need to be tailored more specifically to further reduce HgP concentrations in Beijing.

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* Corresponding author.

E-mail address: nina.j.schleicher@gmail.com (N.J. Schleicher).

1. Introduction

Mercury transport in the atmosphere occurs predominantly as gas (volatilized Hg) but also adsorbed on particulate matter/aerosols (Fang et al., 2011) and its distribution covers the global hemisphere scale. The atmospheric residence time of gaseous elemental mercury (GEM) is at least a few months or even one to two years and, thus, it is much greater than for reactive gaseous mercury (RGM) with a few hours or days and for particulate mercury (HgP) with a residence time of a few weeks (e.g. Lindqvist and Rodhe, 1985; Schroeder and Munthe, 1998). Consequently, GEM can be transported over long distances, whereas HgP and RGM reflect more local and regional sources (e.g. Wängberg et al., 2003; Wang et al., 2006; Xiu et al., 2009). While HgP may constitute, in general, a small percentage by mass of total atmospheric mercury, it can be a very important form of atmospheric Hg under certain conditions, and play a strong role in the deposition of mercury to terrestrial and aquatic ecosystems (Lu and Schroeder, 1999). Most researchers agree that HgP is critical in understanding the mercury cycle in the environment (Fang et al., 2001). In China, HgP normally constitutes a high proportion of urban airborne Hg, which during episodes may approach 10% (Fu et al., 2012). Streets et al. (2009) examined the effect of possible future scenarios (projections for 2050) on relative emissions of the different species of Hg. The authors concluded that there would be a relative trend toward reduced long-range transport and enhanced local deposition of Hg. Studies focusing on PHg will therefore gain further importance in future.

Globally, artisanal and small-scale gold mining and coal burning are the major sources of anthropogenic mercury emissions to air (UNEP, 2013). China accounts for three-quarters of East and Southeast Asian anthropogenic Hg emissions, or about one third of the global total (UNEP, 2013). Streets et al. (2005) provide an inventory of Hg emissions from anthropogenic sources in China and estimated that in 1999 45% of the Hg came from non-ferrous metals smelting, 38% from coal combustion, and 17% from miscellaneous activities, of which battery and fluorescent lamp production and cement production were the largest. Particulate mercury emissions are high in China due to heavy burning of coal in residential and small industrial settings without PM controls (Streets et al., 2005). Streets et al. (2009) predict a further increase in Hg emission for the future with Asia as the main driving force. Sources for HgP are abundant in a Chinese megacity like Beijing. Coal combustion for industrial and residential use as well as coal-fired power plants constitutes a major source. Coal still is the dominant energy source in China, covering about 70% of the total energy consumption, which accounted for 2.6 billion tons Standard Coal Equivalent (SCE) in 2007 (National Bureau of Statistics of China, 2009). In Beijing, coal consumption reached almost 30 million tons of SCE in 2007 (Beijing Municipal Bureau of Statistics, 2009). Other potential sources are non-ferrous metal smelting, cement production, Hg mining, biofuel and biomass combustion (Fu et al. 2012). The manufacture of cement contributed about 10% (190 t) to the total global emissions of mercury to air from anthropogenic sources in 2005 and China, as the main contributor, was responsible for 45% of total emissions from cement manufacturing (UNEP, 2010). Mercury emissions from Zn production were estimated to be 80.7–104.2 t per year in China from 2002 to 2006 (Li et al., 2010). Also municipal solid waste incineration is a potential Hg source, which plays an important role in China (Chen et al., 2013).

The main focus of this study lies on the Olympic Summer Games in August 2008 in Beijing with its strictly enforced mitigation measures. The Olympic period (8th–24th of August 2008) provided the unique opportunity to investigate the efficiency of these comprehensive actions implemented in order to reduce air pollution on a large scale. The emission control measures comprised

traffic reductions, increase and improvements in public transportation, planting of vegetation, establishment of parks, building freeze at construction sites, cleaner production techniques for industries and industry closures in Beijing and also in the surrounding areas (Fang et al., 2009; Schleicher et al., 2012). Strictest measures including the “odd-even ban” to halve the vehicle volume was enforced from the 20th of July to the 20th of September 2008. Several studies investigated the efficiency of the governmental control measures on precursor gases (Sun et al., 2011), black carbon (BC) (Wang et al., 2009a; Okuda et al., 2011; Schleicher et al., 2011a), and also metal concentrations (Schleicher et al., 2012; Chen et al., 2014). All these studies reported that mitigation measures were successful in improving air quality but had different effects on distinct air pollutants. For example, Schleicher et al. (2011a) showed that mass concentrations of particles of different size classes within the coarse mode (2.5–80 μm) during this period decreased, and that the coarser particles were reduced more efficiently than the finer ones. Another study by Schleicher et al. (2012) reported a reduction by 50–70% for elements predominantly from anthropogenic sources, such as S, Cu, As, Cd, or Pb, whereas elements mainly from geogenic sources, such as Fe, Rb, and Sr were reduced by only 30–50% during the Olympic Games. Chen et al. (2014) showed that concentrations of traffic-related elements, such as Pb, Sb, Sn, and Zn, varied with the strength of traffic restriction measures.

To the authors' knowledge, no study investigated how control measures affected HgP concentrations during the Olympic Games in Beijing. Wang et al. (2013) studied the effect of the shutdown of a large coal-fired power plant located in Rochester, New York, USA, on ambient mercury species. The authors reported a decrease of 25% for GEM, 74% for RGM, and 50% for HgP after its closedown for four months. However, it is of special interest to evaluate to what extent the comprehensive set of control measures during the Olympic Games, which was designed to reduce particulate air pollution but not HgP concentrations specifically, affected HgP pollution levels in Beijing. Therefore, the data set presented here includes weekly TSP samples of each August from 2006 to 2010 in order to gain detailed knowledge about HgP concentrations before, during, and after the Olympic Games period and, thus, to examine the efficiency of mitigation measures under realistic conditions. In August 2008, TSP samples were collected with a higher time-resolution of 24 h in order to assess day-to-day differences. Additionally, September samples until 2013 were analyzed in order to investigate the longer development after the Olympic Games. Furthermore, winter samples (December, January) from various years before and after the Olympic Games (winter 2005/2006 to 2010/2011) are included since HgP concentrations in Beijing are highest during winter season (Wang et al., 2006; Schleicher et al., 2015). With this comprehensive approach it was possible to estimate the short- and long-term effects of the emission control measures on HgP concentrations and to assess the health benefits for the affected population.

2. Methodology

2.1. Sampling

The sampling site, labeled as CRAES, is located in the north of the inner city of Beijing close to the Central Olympic District (COD, Fig. 1). The site is placed on the roof of the Chinese Research Academy of Environmental Sciences (CRAES) at a height of about 20 m. At this site, weekly TSP samples were collected continuously since October 2007. Weekly samples represent filters that were collected over the complete 168 h, i.e. integrating the whole period. In August 2008, sampling was carried out with a higher time-

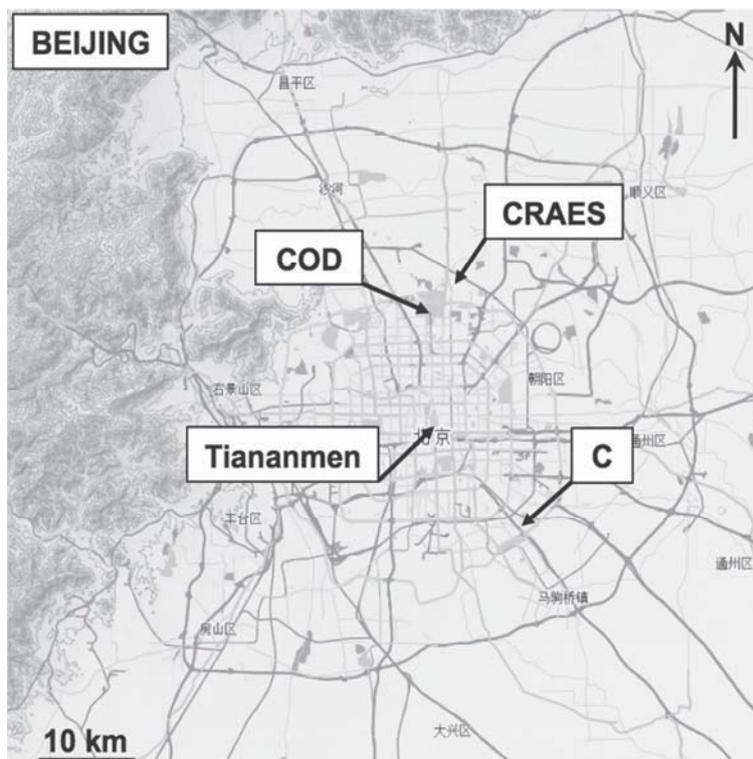


Fig. 1. City map of Beijing (www.openstreetmap.org; © OpenStreetMap contributors) with the location of the two sampling sites (site C and site CRAES), the central Tiananmen Square, and the Central Olympic District (COD) with the stadium.

resolution of 24-h. All samples were collected actively with a TSP-Sampler (Leckel, Berlin, Germany) at a flow-rate of $1 \text{ m}^3/\text{h}$ on quartz fiber filters (Whatman, Maidstone, UK). Previous to October 2007, weekly TSP samples were already collected with the same instrument at another site in Beijing (site C) for two years from September 2005 to August 2007. Some samples of site C were additionally included in this study for comparison.

Collecting HgP by pulling air through a filter and defining the trapped portion operationally as HgP is a widely used method (Lynam and Keeler, 2002). Nevertheless, it has to be kept in mind that uncertainties and positive as well as negative artifacts with the method are known (Lynam and Keeler, 2002, 2005; Pandey et al., 2011). Measured HgP concentrations will vary depending on the chemistry of the aerosol, the atmosphere, and GOM chemistry along with physical conditions of the atmosphere, such as temperature and relative humidity (Gustin et al., 2015). A known bias associated with filter-based methods is interaction between particles adsorbed on the filter and gaseous Hg species in the air stream (Pandey et al., 2011). Positive artifacts from RGM uptake were observed in several studies (e.g. Landis et al., 2002; Talbot et al., 2011). Conversely, during long sampling times, as air is being continuously pulled through the filter, evaporation of water or desorption of weakly bound species may lead to losses of Hg from the filter (Lynam and Keeler, 2002). Brown et al. (2015) report HgP data from 10-year time series during Hg monitoring in the UK and conclude that while absolute values obtained must be treated with caution due to the mentioned artifacts, the trend analyses were not affected due to their consistent approach over the years and that the artifacts are expected to be small compared to the uncertainties of the overall measurement. In our case, sampling artifacts cannot be excluded but are minimized since i) all samples were collected identically, ii) field blanks were analyzed, and iii) the same time

periods (summer and winter months, respectively) from different years were compared so that influencing factors like temperature and humidity can also be neglected.

2.2. Analytical procedure

Mass concentrations were determined gravimetrically with a microbalance (readability: $0.1 \mu\text{g}$, Satorius SE 2-F, Göttingen, Germany). Filters were weighed for three times at room conditions at a constant humidity of $42 \pm 3\%$ relative humidity. August samples from five successive years (2006–2010), as well as winter samples (December 2005 to 2010 as well as January 2006 to 2011) were chosen for HgP analysis. Additionally, September samples from 2009 to 2013 are included.

Total particulate mercury (HgP) was analyzed by cold vapor atomic absorption spectrometry (CVAAS) after calcination in an O_2 stream and amalgamation on an Au trap using a Direct Mercury Analyzer (DMA-80, Milestone, Italy). External calibration of the system was performed by analyzing a range of solutions prepared from a HgCl_2 stock solution, followed by the analysis of Certified Reference Materials (CRM: CRM 320, PACS-1, SL-1), providing results that were consistently within the certified concentration intervals. For HgP analysis, two circular filter punches (diameter: 5 mm) of TSP filter samples were used. These dry filter punches were placed in the metal sample boats and analyzed without any further preparation.

An additional CRM (LKSD-4, lake sediment, Lynch, 1990) with a certified concentration of 190 ng/g Hg, was used for quality control repeatedly throughout the measurements. The accuracy of the measurements of this CRM ($N = 154$) was 92.1% with a precision of 3.7% (relative standard deviation, 1^*RSD). Results were therefore corrected with a factor of 1.088 (calculated as the certified

concentration of CRM LKSD-4 divided by the average measured concentration of 174.6 ng/g). Blank filters were treated like loaded filters and also analyzed for HgP. These blank values were in the same range as measurements of metal boats without any sample (11 pg HgP, N = 35). Thus, the detection limit calculated as $AVG_{\text{blank}} + 3\sigma$ of method blanks was 41 pg HgP. Moreover, some filters were analyzed as triplicates. The average 1σ for these triplicates was 22 pg/m³ (N = 7).

3. Results

Particulate Hg concentrations in August 2008 at site CRAES (Fig. 1) ranged from 37 to 224 pg/m³ with an average value of 81 ± 39 pg/m³ (N = 30, daily samples). During the Olympic Games from the 8th to 24th of August, HgP concentrations were slightly lower (69 ± 27 pg/m³). Average HgP concentrations during Augusts of the previous 2 years at site C (Fig. 1) were 242 ± 85 pg/m³ for 2006 (N = 4, weekly samples) and 217 ± 76 pg/m³ for 2007 (N = 4, weekly samples), respectively. In August 2009 average HgP concentrations at site CRAES were similar to the pre-Olympics level with 227 ± 20 pg/m³ (N = 4, weekly samples) whereas in August 2010 lower concentrations of 157 ± 31 pg/m³ (N = 4, weekly samples) were measured. September HgP concentrations were similar to August values (Fig. 3). From 2009 to 2011, September concentrations increased from 160 to 190 and then to almost 250 pg/m³ and then decreased again to 180 pg/m³ in 2012 and then to 130 pg/m³ in 2013. December and January concentrations were significantly higher than respective August values before and also after the Olympic Games ($p = 0.0023$; Mann–Whitney U-test). Mercury concentrations for the respective years are listed in Table 1. Highest HgP concentrations during winter were measured in December 2006 and January 2007. In the years following the Olympic Games HgP values for December are monotonically decreasing, and a comparable decrease is also seen for January. Moreover, confidence intervals for 2007 and 2010 are not overlapping for December or for January, and hence the reduction of TSP values can be regarded as statistically significant between 2007 and 2010.

4. Discussion

4.1. Mercury concentrations during the Olympic Games

Some authors, e.g. Wang et al. (2009b) and Schleicher et al.

Table 1

Particulate mercury (HgP) concentrations (average \pm single standard deviation) in TSP samples at the two sampling sites in Beijing (site C from Dec-05 to Aug-07 and site CRAES from Dec-07 to Jan-11): (A) concentrations in ng/m³, (B) concentrations in ng/g.

A (ng/m ³)	Jan	Aug	Dec
2005	–	–	0.728 \pm 0.301
2006	1.105 \pm 0.337	0.242 \pm 0.085	1.805 \pm 0.474
2007	1.172 \pm 0.296	0.217 \pm 0.076	0.869 \pm 0.250
2008	0.645 \pm 0.186	0.081 \pm 0.039	0.831 \pm 0.167
2009	0.357 \pm 0.141	0.227 \pm 0.020	0.545 \pm 0.240
2010	0.404 \pm 0.092	0.157 \pm 0.031	0.283 \pm 0.192
2011	0.215 \pm 0.071	–	–
B (ng/g)	Jan	Aug	Dec
2005	–	–	2150 \pm 482
2006	2620 \pm 452	955 \pm 325	3120 \pm 654
2007	2650 \pm 756	841 \pm 246	2480 \pm 464
2008	1860 \pm 482	972 \pm 408	2790 \pm 299
2009	1870 \pm 768	1380 \pm 199	1730 \pm 165
2010	2070 \pm 794	981 \pm 172	973 \pm 559
2011	1750 \pm 450	–	–

(2011a, 2012), reported that meteorological conditions, especially rainfall, were responsible for parts of the strong particle reductions a few days after the Olympic Games started. In order to investigate this influence on HgP concentrations, daily HgP together with TSP mass concentrations as well as precipitation in August 2008 are shown in Fig. 2. Particulate mercury concentrations peaked on August 5th, three days previous to the opening day of the Olympic Games on the 8th of August. Concentrations decreased again on the following day, three days before the precipitation started and four days before overall TSP mass concentrations decreased (Fig. 2). Wet-deposition further reduced HgP concentration. However, the observation that HgP concentrations decreased prior to precipitation events unlike TSP mass suggests that wet deposition was not the only reason for HgP reductions.

During the Olympic Games, HgP concentrations remained below 100 pg/m³, except for two days (13th and 19th of August, Fig. 2). On August 13th, TSP mass concentrations were high with almost 140 $\mu\text{g}/\text{m}^3$ (Fig. 2). On August 19th, HgP concentrations were only slightly elevated with 105 pg/m³. Generally, HgP concentrations showed a different course compared to other elements during the Olympic Games period (see Schleicher et al., 2012 for detailed information about other elements), which is reflected by low correlation factors. Between the 8th and the 24th of August, significant correlations were found only with Cr (Pearson $r = 0.55$) and to a lower degree with Mn ($r = 0.35$) and Fe ($r = 0.31$). Common sources for this element association are geogenic dust on the one hand and steel works, as an anthropogenic source, on the other hand (Reimann and Caritat, 1998). Waste incineration and sewage sludge is a further source for Cr as well as HgP (Reimann and Caritat, 1998).

4.2. Evaluating the efficiency of the implemented mitigation measures

It is important to keep in mind that only HgP was investigated within this study but GEM and RGM were not considered. Besides being directly emitted from the source, HgP can also be formed through gas-to-particle partitioning (Seigneur et al., 1998; Rutter and Schauer, 2007a,b; Kim et al., 2012). Therefore, a possible speciation shift between the gas and particle phase needs to be taken into account when discussing the efficiency of emission control measures on HgP concentrations. Rutter and Schauer (2007a) found that gas–particle-partitioning coefficients for reactive Hg (RM, including RGM and HgP) in dry urban and laboratory aerosol were found to strongly depend on ambient temperature. Moreover, the authors were the first to demonstrate that gas-particle partitioning of RM varies with particle composition in synthetic atmospheric aerosol (Rutter and Schauer, 2007b). Amos et al. (2012) found that elevated HgP was mostly associated with high aerosol loads. In the following we will compare samples of the same months (summer and winter, respectively) before and after the Olympic Games since HgP concentrations in Beijing show a strong seasonal variation within each year (Wang et al., 2006; Schleicher et al., 2015) and that the influence of meteorological conditions can be neglected and, thus, also the effect of gas-particle partitioning should only play a minor role.

4.2.1. Comparison of summer samples from various years

Fig. 3a displays monthly summer (August, September) HgP concentrations from 2006 to 2013. For this comparison, it is important to highlight that the sampling site during the years 2006 and 2007 was different (site C, Fig. 1). However, a previous study from Beijing showed that HgP concentrations were clearly higher in the inner city within the 3rd ring road but quite similar at three other sampling sites outside this inner circle (Schleicher et al., 2015) and, therefore, no large difference between the two sites is

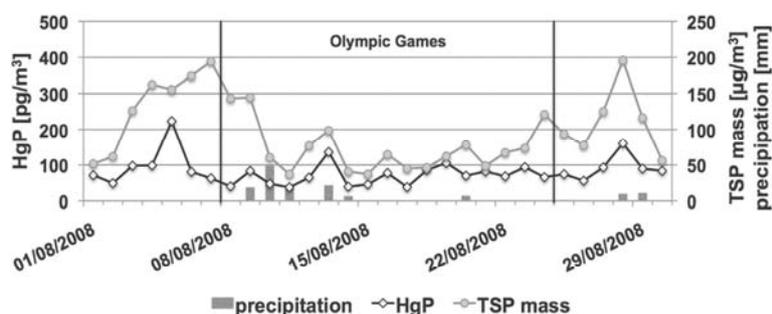


Fig. 2. Daily HgP and TSP mass concentrations as well as precipitation in August 2008 at site CRAES.

expected. Nevertheless, the limitations of using two different sampling sites to describe year-to-year variations need to be kept in mind. On average, HgP in August 2008 was reduced by about 65% compared to Augusts of the previous two years. This observation indicates that the implemented mitigation measures during the Olympic Games successfully reduced HgP concentrations. However, after the Olympic Games, in August 2009, HgP increased again to pre-Olympic levels. In August 2010, concentrations were 30% lower compared to August 2009 but still almost 50% higher than in August 2008. September concentrations increased after the Olympic Games from 2009 to 2011 and decreased in the successive two years again. Consequently, no long-term effect from the mitigation measures can be observed for summer months.

While the volume-related HgP concentrations expressed in pg/m^3 showed a clear minimum for August 08, the comparison is different when HgP values expressed in mass related values in ng/g were taken into account (Fig. 3b). It is remarkable that HgP concentrations expressed in ng/g remain on a similar level for all years with slightly higher values in August 2009. This observation indicates that overall TSP concentrations were strongly reduced in August 2008 whereas HgP concentrations were not reduced as much as it was the case for other components. Consequently, the efficiency of the implemented mitigation measures was not as high for HgP than for overall mass concentrations and most other elements. Since coal combustion is the major source for HgP in Beijing (Schleicher et al., 2015) the mitigation measures that were most

effective for HgP reductions during the Olympics were probably the relocation of many factories, especially those that used a lot of coal, to other provinces and the fact that 19 major pollutant industries around Beijing were ordered to cut 2008 emissions by 30% (Stone, 2008). On the contrary, other measures, like the traffic restrictions, which were a success for reducing other element concentrations such as Cu, Zn, Sn, Sb, and Pb (Schleicher et al., 2012; Chen et al., 2014), did not affect HgP concentrations strongly.

4.2.2. Comparison of winter samples from various years

In Beijing, air quality is better during summer months due to wet deposition and the lack of certain sources, such as coal combustion for heating purposes (He et al., 2001; Schleicher et al., 2010a,b, 2011b). Schleicher et al. (2015) reported HgP concentrations in Beijing were up to 15-fold higher during winter compared to summer months. Therefore, not only the concentrations during August, but also during winter months (December, January) for the years before and after the Olympic Games were compared (Fig. 4). For both, December and January, HgP concentrations were highest in winter 2006/2007 and then decreased almost continuously till winter 2010/2011.

Compared to pre-Olympic December (2007), a decrease of 5, 60 and 200% was observed for the successive years (2008–2010), respectively. Reductions for January were quite similar with 81, 60, and 200% for January 2009 to 2011, respectively, with the only difference that the decrease was already higher in the first winter

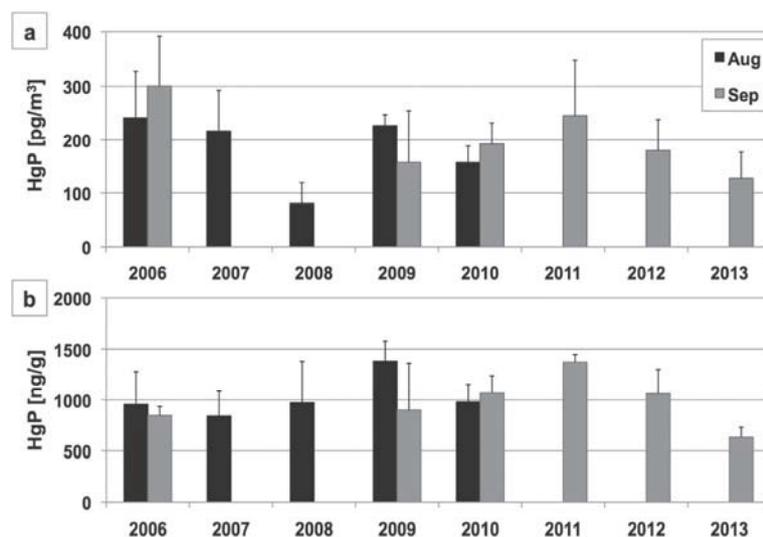


Fig. 3. Average HgP concentrations at site C (Aug-06, Sep-06 and Aug-07) and site CRAES (Aug-08 to Aug-10 and Sep-09 to Sep-13).

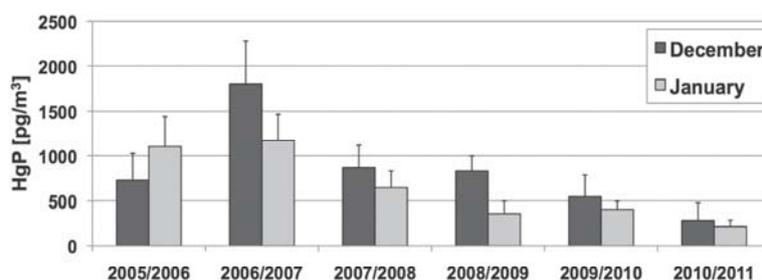


Fig. 4. Average HgP concentrations at site C (winter-05/06 and winter-06/07) and site CRAES (winter-07/08 to winter-10/11).

after the Olympic Games. The decreasing HgP concentrations in wintertime indicate a general improvement of HgP pollution in Beijing not only during the Olympic Games but also in the long-term view. Long-term emission control measures, which might contribute to this reduction, comprise further traffic restrictions (Chen et al., 2014), cleaner production techniques for industries (Fang et al., 2009), the permanent relocation of heavily polluting enterprises including the Capital Iron and Steel Company and the Yanshan Petrochemical Plant (Yang et al., 2010), afforestation, and an increase and enhancement of public transport (Fang et al., 2009). Nevertheless, this decreasing trend in Beijing is surprising since several studies have pointed out that Hg emissions from various anthropogenic sources were increasing over recent years in most regions in China (e.g. Zhang et al., 2015; Cheng et al., 2015; Tian et al., 2012, 2010; Li et al., 2010) and the HgP levels in ambient air in Beijing may be also influenced by regional Hg emissions in addition to local sources. The present study indicates a strong dominance of local HgP sources that could be tackled by local pollution control measures. For example, Tian et al. (2014) showed the co-benefit of installing removal devices into Chinese coal-fired power plants also on Hg emissions. The authors reported a peak of Hg emissions from coal-fired power plants in 2006 and a decrease by 4% during the following years until 2010. Zhao et al. (2015) reported that Hg emissions were decreasing in the three Chinese regions with highest population density and economic activity, including the Jing-Jin-Ji region with Beijing, Tianjin and Hebei, as well as the Yangtze River Delta region, and the Pearl River Delta Region. This decrease of Hg emissions was contrary to the observed trends in other regions in China. Consequently, Beijing might be one of the cities in China with further decreasing Hg (including HgP) concentrations in the near future. However, winter and summer didn't show a uniform picture in our study and the sampling period is still not long enough to clearly observe long-term trends. Therefore, continuous monitoring of HgP together with gaseous Hg in Beijing is urgently needed.

4.3. Assessment of health effects

Inhalation and non-dietary ingestion can be considered as the two relevant exposure routes for HgP in aerosols. Contrary to dietary exposure, which can be controlled by limiting the intake of certain types of food, it is almost impossible to limit the duration and strength of exposure to airborne particles. Inhalation is the dominant process but also mouth breathing and swallowing of larger particles play a role especially during physical exercise, while speaking or if the nasal airways are obstructed (Bowes and Swift, 1989). Ingestion of dust was found to constitute a relatively minor pathway of Guangzhou residents' exposure to Hg (Huang et al., 2012). The values used by the authors in the respective calculations are comparable to those from our study in Beijing and, therefore, a similar outcome can be assumed. However, especially young

children are vulnerable to ingestion of soil and dust through hand-to-mouth or object-to-mouth behavior (Moya et al., 2004). The amount ingested varies with the child's behavior, and daily ingestion rates have been calculated to be between 39 and 270 mg day⁻¹ (Ljung et al., 2007). We did not measure solid partitioning of Hg in particles or soils. However, typical values obtained from chemical selective extractions (H₂O₂ or HCl 1 M) suggest that in river Suspended Particulate Matter (SPM) and sediments (both derived from soil erosion) typical "potentially bioavailable" Hg fractions (extracted by HCl 1 M; Sutherland and Tack, 2008) are in the range of 60–80% and mainly associated with organic matter or sulphides (Castelle et al., 2007; Sahuquillo et al., 2003). Accordingly, we would expect the major part of Hg in soils from the study area to be "potentially bioavailable".

Guideline values for HgP concentrations exist for soils, but not for HgP in the atmosphere. Nonetheless it is instructive to compare HgP concentrations in TSP samples from Beijing with these guideline values, since direct connections between contaminated soils and particles can be imagined. On the one hand, a possible health hazard of contaminated soils leading to non-dietary exposure is the release of particles with high HgP values into the ambient air, and on the other hand, airborne particles with high HgP values may be deposited on the ground causing its contamination. We expect that the limit values for soil possess a similar order of magnitude and are therefore helpful for assessing the health effects of atmospheric particles as well. Average August HgP concentrations were 955, 841, 972, 1380, and 981 ng/g for the years 2006–2010, respectively. These summer values from Beijing are in the same magnitude as the soil guideline value of 1000 ng/g Hg for residential areas in the UK (DEFRA and Environment Agency, 2009) or the Chinese Grade II guideline value (Chen et al., 2010) of equally 1000 ng/g. Compared to the national background value for soil in China of 38 ng/g (Wang et al., 2007), the HgP values in August TSP samples were 22- to 36-fold higher and still about 3 times the maximum permissible concentration of potential toxic elements for agricultural soils in China of 300 ng/g for Hg (Liu et al., 2012). Higher winter values with average HgP concentrations of 2240 ± 846 for December 2005 to 2010 and 2110 ± 663 ng/g for January 2006 to 2011 are in the range of the guideline value for commercial areas in UK of 2600 ng/g (DEFRA and Environment Agency, 2009) and the USEPA soil ingestion screening level for Hg of 2300 ng/g.

Compared to August 2007 and 2006, particulate mercury concentrations during the Olympic Games in August 2008 were reduced by 160 and 140 ng/m³. These amounts of reduction are certainly not negligible, as they are of the same order of magnitude as the overall HgP concentrations at locations such as such as Taichung, Taiwan (70 ± 40 pg/m³, Fang et al., 2010), or Changchun City, China, during the non-heating period (145 pg/m³, Fang et al., 2001). As discussed in Section 4.2.2, winter HgP concentrations decreased after the Olympic Games during the three successive years.

Compared to December 2007, HgP concentrations in December 2008, 2009, and 2010 were reduced by a total amount of 40, 320, and 590 pg/m^3 . A similar reduction of 290 (January 2009), 240 (January 2010), and 430 (January 2011) pg/m^3 was observed during the same time period for January. Again, these reduction amounts are similar to concentrations at higher polluted cities such as Shanghai (560 ± 220 and 330 ± 90 pg/m^3 , respectively at two different sites, Xiu et al., 2009) or Changchun City during the heating period (461 pg/m^3 , Fang et al., 2001). The reduction of HgP during the Olympic Games shows the potential of mitigation measures, but the comparison with other cities also highlights that the concentration of HgP remains high despite respective pollution control measures.

Generally, this study showed that the burden of HgP pollution for the environment and the inhabitants of Beijing was still high and that further monitoring and emission reductions are necessary. Future mitigation measures need to be tailored more specifically to further reduce HgP concentrations in Beijing, which would necessarily include a reduction in coal combustion. The switching to natural gas for domestic heating purposes, which was started in preparation of the Olympic Games (Wang et al., 2010), will probably not be sufficient because of a high and increasing industrial usage of coal. Until now, China relies heavily on its coal supply, although natural gas consumption has been growing quickly in recent years (Lin et al., 2010). Given the low proportion of natural gas and high proportion of coal in China's energy resource reserves, using natural gas as fuel has always been a controversial topic since it was argued that i) natural gas should be used as a raw material for the chemical industry; and ii), clean-coal technology is the most cost-effective method of improving air quality (Mao et al., 2005). The proportions of coal, oil, and natural gas consumption in China in 2006 were 73%, 24%, and 3%, respectively (Lin et al., 2010) and it is likely that coal combustion will remain on high levels in China for the next decades (Streets et al., 2009). Furthermore, even with enhanced production techniques in many enterprises since the Olympic Games it is necessary to thoroughly investigate industrial Hg emissions in Beijing and include the most pollutant ones in any future urban planning efforts.

5. Conclusions

This study showed that average HgP concentrations of 81 ± 39 pg/m^3 in August 2008, the Olympic Games period with strictly enforced mitigation measures in Beijing and the surrounding areas, were about 65% lower compared to the same months during the previous years. It was further shown that wet deposition didn't have a strong influence on HgP reductions unlike on the decrease of overall particulate mass concentrations during the Olympics. Consequently, the emission control measures, especially the reduction of coal combustion emissions, were successful in reducing HgP concentrations in the short term. However, it was also shown that the measures were not as successful for HgP concentrations as for many other elements from anthropogenic sources.

After the Olympic Games period, HgP concentrations increased again to pre-Olympic values in August 2009. Then values decreased again in the following year (August 2010) by 30%, but were still almost 50% higher than in August 2008. Winter concentrations (December and January), which were 2- to 11-fold higher than corresponding August values, continuously decreased over the studied years. Consequently, the decreasing winter values indicate a slight improvement also in the long-term view. In order to assess the development of HgP concentrations for a longer period, further measurements and a close monitoring in Beijing during the successive years would be desirable.

Regarding health effects, comparisons with soil guideline values and concentrations in other cities showed that the burden for the environment and inhabitants in Beijing was still high. The reduction amount of HgP during the Olympic Games showed the potential of mitigation measures, but long-term improvements are needed. Therefore, future urban planning and new mitigation measures need to be tailored more specifically to further reduce HgP concentrations in Beijing.

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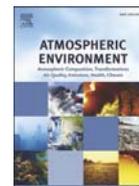
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B.2 Seasonal dynamics of coarse atmospheric particulate matter between 2.5 μm and 80 μm in Beijing and the impact of 2008 Olympic Games



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Seasonal dynamics of coarse atmospheric particulate matter between 2.5 μm and 80 μm in Beijing and the impact of 2008 Olympic Games



Stefan Norra^{a, b, c, *}, Yang Yu^{a, d}, Volker Dietze^e, Nina Schleicher^a, Mathieu Fricker^e, Uwe Kaminski^e, Yuan Chen^a, Doris Stüben^a, Kuang Cen^d

^a Institute of Applied Geosciences, Karlsruhe Institute of Technology, Adenauerring 20, 76131 Karlsruhe, Germany

^b Institute of Geography and Geoecology, Karlsruhe Institute of Technology, Kaiserstr. 12, 76128 Karlsruhe, Germany

^c Institute of Mineralogy, Technische Universität Bergakademie Freiberg, Brennhausgasse 14, 09596 Freiberg, Germany

^d Department of Geology and Mineral Resources, Chinese University of Geosciences, Xueyuan Road 29, Beijing 100083, China

^e Research Center Human Biometeorology, Air Quality Department, German Meteorological Service, Stefan-Meier-Str. 4, 79104 Freiburg i. Br, Germany

H I G H L I G H T S

- Assessment of coarse particles between 2.5 and 80 μm in Beijing.
- This study covers a long period from 2005 till 2009.
- Seasonal and source variations of mass concentrations are identified.
- Influences of Asian dust and the 2008 Olympic Games are described.
- A long term decrease of coarse particle mass concentrations was detected.

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A B S T R A C T

Beijing is well known as a megacity facing severe atmospheric pollution problems. One very important kind of pollution is the high amount of particles in Beijing's atmosphere. Numerous studies investigated the dynamics of fine particles smaller 10 μm . Less information is available on the coarse particle fraction larger 10 μm , although geogenic dusts, which often are composed by those coarser particles, frequently affect the air quality in Beijing. Therefore, systematic sampling and analysis of size fractionated particulate matter between 2.5 and 80 μm was performed in Beijing from April 2005 till October 2009. Atmospheric particles were collected in the North-West of Beijing using a cost-effective passive sampling method called Sigma-2. Altogether, 200 weeks could be analysed and assessed. Concentrations and size distribution of atmospheric coarse particles were determined by automated microscopic single particle analysis. Seasonal variability of the total mass of different size fractions was identified as follows: spring > winter > autumn > summer. High concentrations of transparent mineral particles indicate the activity of geogenic sources in spring and winter time, due to Asian dust events and resuspension of soil from local bare land during dry and windy periods. The percentage of opaque particle components differs seasonally with relatively high values in winter, confirming combustion of fossil fuels for heating purposes as a predominant pollution source in this season. The influence of meteorological conditions on concentrations and size distribution of atmospheric particulate matter between 2.5 and 80 μm is demonstrated for the whole sampling period. Lowest pollution by coarse aerosols occurred during the period of the 2008 Olympic Summer Games. A general trend of decreasing total coarse particle mass concentrations was observed. Due to frequently observed high total coarse particle mass concentrations of several 100 $\mu\text{g}\cdot\text{m}^{-3}$ it is strongly recommended to enhance research and observation regarding these air pollutants to gain a better understanding of their dynamics, health effects, well being impacts on Beijing inhabitants and the effectiveness of mitigation measures.

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* Corresponding author. Institute of Applied Geosciences, Karlsruhe Institute of Technology, Kaiserstr. 12, 76128 Karlsruhe, Germany.
E-mail address: stefan.norra@kit.edu (S. Norra).

1. Introduction

More than half of the world population now is living in urban environments. These systems consume and process enormous amounts of energy and mineral resources causing environmental pollution potentially harming the health of its inhabitants. From the geoscientific point of view, urban systems form a world wide connected entity, the astysphere (Norra, 2009, 2014a), showing beside local also a severe global environmental impacts (Baccini and Brunner, 2012; UNEP, 2012; Norra, 2014b). The atmosphere is one compartment of the astysphere with specific chemical compositions and aerodynamic properties due to characteristic urban land uses and pollution sources. Highest pollution levels are often reached in so called megacities such as Rio de Janeiro (Quiterio et al., 2004), Hong Kong (Lee et al., 2007), Delhi (Mandala et al., 2014) or also Beijing (Schleicher et al., 2010a). According to a certain global similarity of megacity systems regarding their sub-systems such as industry, housing and traffic, experiences about air pollution dynamics from one megacity contribute also to the knowledge about possible atmospheric pollution dynamics in other megacities, and help to identify potential threads and optimal mitigation measures. Within this special issue of Atmospheric Environment, Beijing, Tianjin and the surrounding Hebei province are in the focus of presenting research results on atmospheric pollution dynamics. Beijing in particular is an ideal region to study the impact of geogenic coarse particles and its interactions with anthropogenic emitted particulate matter due to frequently occurring dust storms transported from western deserts to Beijing and surrounding dry areas, which additionally act as particle sources (Schleicher et al., 2011a,b; Schleicher et al., 2012). Tianjin is only located about 100 km southeast of Beijing at the ocean and both cities are continuously growing together forming a metacity in the near future (UN Habitat, 2007). Furthermore, during periods of dominating winds from north-west Tianjin potentially is affected by atmospheric pollution generated in Beijing and during times of dominating winds from south-east Beijing potentially is affected by air pollution from Tianjin. However, since main wind directions in Beijing are south-east and north-west, this mutual impact on air quality is to some extent limited yet. Beijing, the capital of China, comprises over 20 million inhabitants (Beijing statistical yearbook 2012, <http://www.bjstats.gov.cn>). Together with Tianjin this metacity agglomeration will host more than 30 million inhabitants. Both urban plumes (Puxbaum et al., 2004) will grow together with consequences for urban air quality not known in detail yet. Thus, there is an urgent need on comprehensive knowledge on the dynamics of air pollution in this region to develop regionally adapted mitigation measures to improve the living conditions of the urban dwellers.

Studies on Beijing aerosol pollution in the past have been mainly focused on monitoring PM_{2.5} and PM₁₀, and were carried out for certain limited periods (Guinot et al., 2007; Chan and Yao, 2008; Quan et al., 2014; Li et al., 2013; Wang et al., 2013; Zhang et al., 2013). Some studies also considered coarser particle loads. Dillner et al. (2006) comprehensively investigated the dust storm event between March 22nd and April 1st in 2001. This study combined the analyses of total suspended particulates (TSP) with PM_{2.5} and particle size fractions between 0.056 and 1.8 μm sampled by 10 stage micro orifice uniform deposit impactors (MOUDI). During this dust event TSP concentrations reached about 900 $\mu\text{g}/\text{m}^3$ and declined to about 200 $\mu\text{g}/\text{m}^3$ at non dust event days. Between 2001 and 2004, PM_{2.5} and TSP concentrations in Beijing's air were recorded by Wang et al. (2006). Sampling was carried out by a medium-volume sampler during day time. Within the sample period altogether 315 samples were taken and classified according to dust, haze and clear days. Maximum TSP concentrations reached

about 10,000 $\mu\text{g}/\text{m}^3$ and the average was 2000 $\mu\text{g}/\text{m}^3$ for 40 samples representing dust days. A further study (Zhang et al., 2006) on a similar period from July 2001 to April 2003 also surveyed TSP, PM₁₀ and PM_{2.5} and recorded similar concentrations as Wang et al. (2006). The mobility of trace elements in TSP from Beijing collected in the period February 2005 to September 2007 was subject of a study by Schleicher et al. (2011a). Here, it was demonstrated that trace metal mobility varies throughout the year. A study on size fractionated coarse particles in Beijing's atmosphere was published by Norra et al. (2007). This study used the passive sampler technique Sigma-2 (VDI, 2013) and distinguished pollution during day and night for a short period in January 2005. Maximum concentrations of particles of the size fraction between 3 and 96 μm reached 500 $\mu\text{g}/\text{m}^3$. First insights into the successful reduction of different size fractions of coarse particles by mitigation measures enforced during the Olympic Games were presented by Schleicher et al. (2011b). The chemical composition of single coarse particles, collected by the SIGMA-2 method, was analysed at μm scale by means of μ -Synchrotron X-ray fluorescence (Schleicher et al., 2010b). These studies underline the important meaning of studies on coarse particles in Beijing, which still are a potential threat to the inhabitant's well-being. A detailed understanding of the sources and temporal dynamics of coarse particle is indispensable for the development of sustainable mitigation measures.

Also in this study, the passive sampler Sigma-2 (Schleicher et al., 2010; Guéguen et al., 2012; VDI, 2013) was applied in order to collect the coarse particles for subsequent particulate matter measurements ranging from 2.5 μm to 80 μm in diameter in intervals of 2.5–5, 5–10, 10–20, 20–40 and 40–80 μm . The aim of this paper is to study not only the size distributed mass concentration of coarse particles but also the seasonal variations and meteorological effects during a long term continuous sampling period (from April 2005 till October 2009) at an urban site in N–E Beijing.

2. Methods

2.1. Sampling

Coarse atmospheric particles were sampled with the passive sampling device Sigma-2 (Grobéty et al., 2010). Technical details of the instrument are described in the guideline VDI 2119:2013–06 (VDI, 2013). The Sigma-2 sampler consists of a protective antistatic plastic head covering an inner tube. The interior of the sampler contains a carrier with an inlaid sampling plate located at the bottom of the tube. Airborne particles are allowed to enter the tube through four rectangular windows in the head and the tube, as well but twisted against one another. Due to this construction the inside of the sampler is widely protected against the impact of precipitation and wind. In the claimed interior of the tube, particles are settling down onto the highly transparent collection plate suitable for optical microscopy. The particles are fixed on the surface of the collection plate, which is covered by a weather resistant adhesive.

Microscopic analyses of collection plates provide deposition rates of particles of sizes between 2.5 and 80 μm (geometrical equivalent diameter, d_p). By assuming spherical shape and unit density for all particles, a size-fractionated mass deposition rate of particles can be calculated. From these mass deposition rates, a size-fractionated particle mass concentration can be calculated by approximating individual particle deposition velocity by its settling velocity assumed under the calmed conditions in the interior of the Sigma-2 passive sampler (Schleicher et al., 2010b; VDI, 2013).

Sampling was conducted from April 25th 2005 till November 2nd 2009 (Table 1). Each week was separated into two sampling periods for three and four days to avoid too high loads and

superimpositions of particles on the adhesive collection plates. After microscopic analyses, the weekly concentrations of aerosols were calculated from these both samples. Unfortunately, logistic problems caused a gap of several weeks of samples from autumn 2007 and winter 2007/2008. Altogether, 15.3% of the samplings were interrupted by external errors. Sampling was carried out at the east gate of China University of Geosciences Beijing (CUGB) near to the 4th ring road (Fig. 1) (about 10 m west from the street kerb). The sampling site belongs to the north-western part of Beijing and represents a typical “urban site”. The sampler is installed at a height of 1.5 m above ground, which is an average standard height for the exposure of humans.

2.2. Measurement

An automatic image analysis system consisting of a Zeiss optical microscope (ZEISS Axioplan 2) with an adapted automatic scanning stage (Prior Scientific), a high-resolution CCD camera (SVS-VISTEK) and a PC-aided image analysis system Digitrace V.3.4 (IMATEC) was used to carry out measurement object-specific features of individual particles at the German Meteorological Service (DWD) in Freiburg, Germany. This approach provided the mass concentration of particles in the size range between 2.5 and 80 μm (geometrical equivalent diameter, d_p). Concurrently, particles were differentiated into transparent and opaque particles. Transparent particles typically are mineral particles from geogenic sources, such as quartz, feldspars or calcite. Furthermore, salt particles e.g. from sea spray belong to this particle group. However, due to the methodological needs of the optical analysis the sample has to be embedded into an aqueous immersion fluid which dissolves water soluble salts. Opaque particles often are characteristic for anthropogenic sources, such as combustion residues or tyre abrasion. Mass concentrations were calculated as described in Dietze et al. (2006) and expressed in fractions of size intervals of 2.5–5 μm (SI1), 5–10 μm (SI2), 10–20 μm (SI3), 20–40 μm (SI4) and 40–80 μm (SI5).

2.3. Meteorological data

Meteorological data (three hourly data) was obtained from China Meteorological Data Sharing Service System (<http://cdc.cma.gov.cn>). Wind roses were produced with WRPLOT View Freeware (Lakes Environmental, Ontario, Canada). Seasons are classified here according to meteorological definitions: Spring – March, April, May; Summer – June, July, August,; Autumn – September, October, November; Winter – December, January, February.

3. Results

Summary statistics of mass concentrations of total particles (TP) and transparent particles (TRP) between 2.5 and 80 μm differentiated for the size intervals SI1: 2.5–5 μm , SI2: 5–10 μm , SI3: 10–20 μm , SI4: 20–40 μm , SI5: 40–80 μm are reported in Table 2. Weekly concentrations of TP (2.5–80 μm) varied from 43.5 to 528 $\mu\text{g}\cdot\text{m}^{-3}$. The coarsest fraction analysed from 40 to 80 μm shows the lowest concentrations, whereas highest mass concentrations

were found in the size fractions of 5–20 μm . Average mass concentrations still are high in the size fraction of 2.5–5 μm , and lower in the size fraction of 20–40 μm . The same order of average mass concentrations was found for TRP. Thus, the general order of mass concentrations of the different fractions is: SI2, SI3 > SI1 > SI4 > SI5. SI2 shows a slight trend of higher concentrations as SI3. Transparent particles highly dominate opaque particles and account for about 90% of the whole particle mass concentrations, indicating the high meaning of geogenic particle sources for air quality in Beijing.

The time series are similar for the different size fractions during the period of sampling (Fig. 2), and follow the same temporal trend of high concentrations in spring and winter and lowest concentrations in summer (Fig. 3). Two periods differ obviously from the rest of the investigation period. Highest concentrations in all particle classes were monitored during the asian dust event in spring 2006 in the period of calendar week 10–22. Lowest concentrations occurred during the Olympic and Paralympic Games in summer and autumn 2008 from calendar week 32–38.

4. Discussion

4.1. Size distribution and seasonal variability

The average concentrations of coarse particles analysed in this study are in the same magnitude (201 $\mu\text{g}/\text{m}^3$) as Schleicher et al. (2010a) reported for total suspended particles (TSP) sampled by an active sampling measurement in Southeast Beijing. This study resulted in an average TSP concentration of 370 $\mu\text{g}/\text{m}^3$ for the period from August 2005 till August 2007. In contrast to TP as analysed in this study, TSP also includes the PM2.5 fine particle fraction. The sum concentrations of coarse particles between 2.5 and 80 μm in diameter exceeds those of PM2.5 concentrations. For the period of September 2007 till January 2011, Chen et al. (2014) reported average PM2.5 concentrations of 88.5 $\mu\text{g}/\text{m}^3$ at a site in north east Beijing. For the same site as investigated in this study (CUGB), Yu et al. (2011) calculated average annual PM2.5 concentrations between 63.3 and 65.6 $\mu\text{g}/\text{m}^3$ for the period between 2005 and 2007. Thus, PM2.5 concentrations only account for less than half of the mass concentrations of the particle size fractions between 2.5 and 80 μm . Also in this study, the average mass concentration of the finest particle size interval 2.5–5 μm (SI1) of the coarse particle fractions never was the highest one within the four seasons (Fig. 3). Conclusively, these results indicate that coarser particles, and especially those up to 40 μm in diameter, represent considerable air pollution in Beijing, needing more attention to be paid for, since those are able to negatively affect the well-being and the respiratory tract of humans (Guthrie and Mossmann, 1993; Guthrie, 1997) and influence local climate (Tandon et al., 2010).

The high concentrations in spring can be explained by the occurrence of Asian dust events, showing different intensities over the years. During these periods air masses transport high loads of particles from dry areas like Takla Makan and Gobi eastwards to the densely populated coastal regions of China where inhabitants of megacities such as Beijing and Tianjin consequently are suffering by reduced air quality (Qian et al., 2002; Shao et al., 2007; Yu et al., 2011; Schrader et al., 2013). Here, we show that concentrations

Table 1
List of all sampling weeks.

	Number (weeks)	Percentage of total weeks	Calendar weeks (week/year)
Weeks with operational errors	36	15.3	06/07–08/07, 36/07–11/08, 03–03/09, 28/09–31/09
Weeks without operational errors	200	84.7	All the others
Total weeks	236	100	17/05–44/09

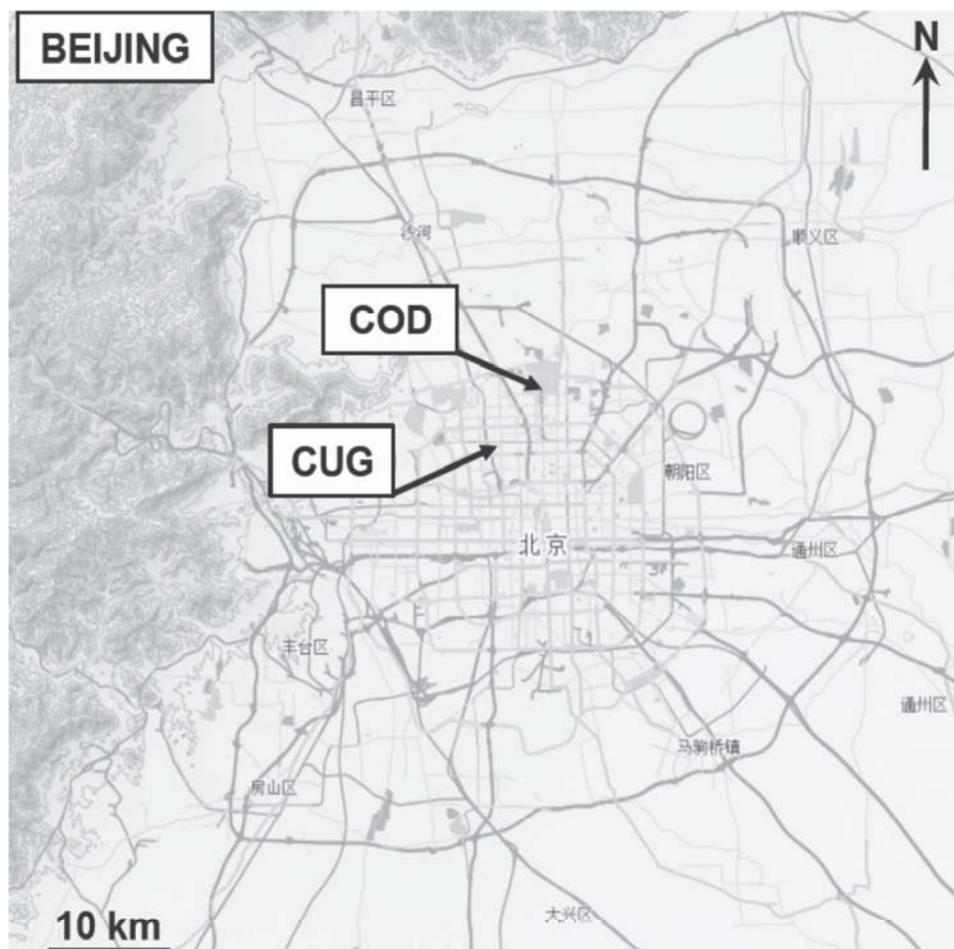


Fig. 1. Location of sampling site at the China University of Geosciences, Beijing (CUGB), and of the Central Olympic District (COD) (© OpenStreetMap contributors).

for particles of sizes between 2.5 and 80 μm even exceed 500 $\mu\text{g}/\text{m}^3$ for the weekly mean value. Together with the particle size fraction smaller 2.5 μm concentrations above 1000 $\mu\text{g}/\text{m}^3$ can occur as reported by Schleicher et al. (2010a). Especially spring 2006 faced an intensive dust storm, whereas the other springs which have been monitored faced lower dust storm intensities (Fig. 2).

Table 2

Mass concentrations ($\mu\text{g}\cdot\text{m}^{-3}$) for the different size intervals for total particles (TP) and transparent particles (TRP), respectively (N = 200).

Size interval (μm)	Mean	Stdev	Median	Max	Min
TP					
2.5–5 (SI1)	48.0	19.4	43.6	141	11.2
5–10 (SI2)	58.4	22.5	54.1	135	14.3
10–20 (SI3)	55.6	24.9	50.6	152	12.8
20–40 (SI4)	31.2	21.7	25.6	135	4.30
40–80 (SI5)	7.68	10.0	4.62	84.2	0.45
2.5–80	201	90.8	184	528	43.5
2.5–10	106	41.5	99.7	277	25.5
TRP					
2.5–5 (SI1)	43.3	18.3	39.6	135	9.38
5–10 (SI2)	52.1	21.6	48.2	129	10.9
10–20 (SI3)	50.3	23.9	45.6	146	9.01
20–40 (SI4)	28.5	20.8	22.7	132	3.26
40–80 (SI5)	7.04	9.60	4.19	80.9	0.32
2.5–80	181	87.3	162	506	33.4
2.5–10	95.4	39.5	88.4	264	20.2

The season with the second highest coarse aerosol mass concentration is winter when substantial heating processes emit combustion residues to the atmosphere (Schleicher et al., 2010a; Chen et al., 2014). This trend is traceable for all size fractions (Fig. 3). Lowest mass concentrations occur for each size fraction during summer, when combustion of fossil fuels for heating purposes is less necessary, dust storms do not occur due to other wind directions (Fig. 4), wind velocity is low and most precipitation is recorded (Fig. 5). Rainfall is able to wash out aerosol particles from the atmosphere, which is a well-known phenomenon. Beside precipitation also wind velocity is particularly able to influence the concentration of coarse particles. Coarse particles need stronger impulses to be suspended and resuspended into the atmosphere in comparison to smaller aerosol fractions (Shao and Lu, 2000; Alfarao and Gomez, 2001; Xuan and Sokolik, 2002). The correlation between wind velocities and concentrations of coarser particles is demonstrated in Fig. 5. In addition to spring, higher wind velocities occur during late autumn and early winter, which is the period of a second peak of coarse particle mass concentrations in Beijing (Fig. 5). Thus, strong wind at dry days can resuspend considerable amounts also of local coarse particles from streets, bare land and other surfaces. Conclusively, with respect to all size fractions, the respective mass concentrations follow the same seasonal trend: spring > winter > fall > summer (Fig. 3).

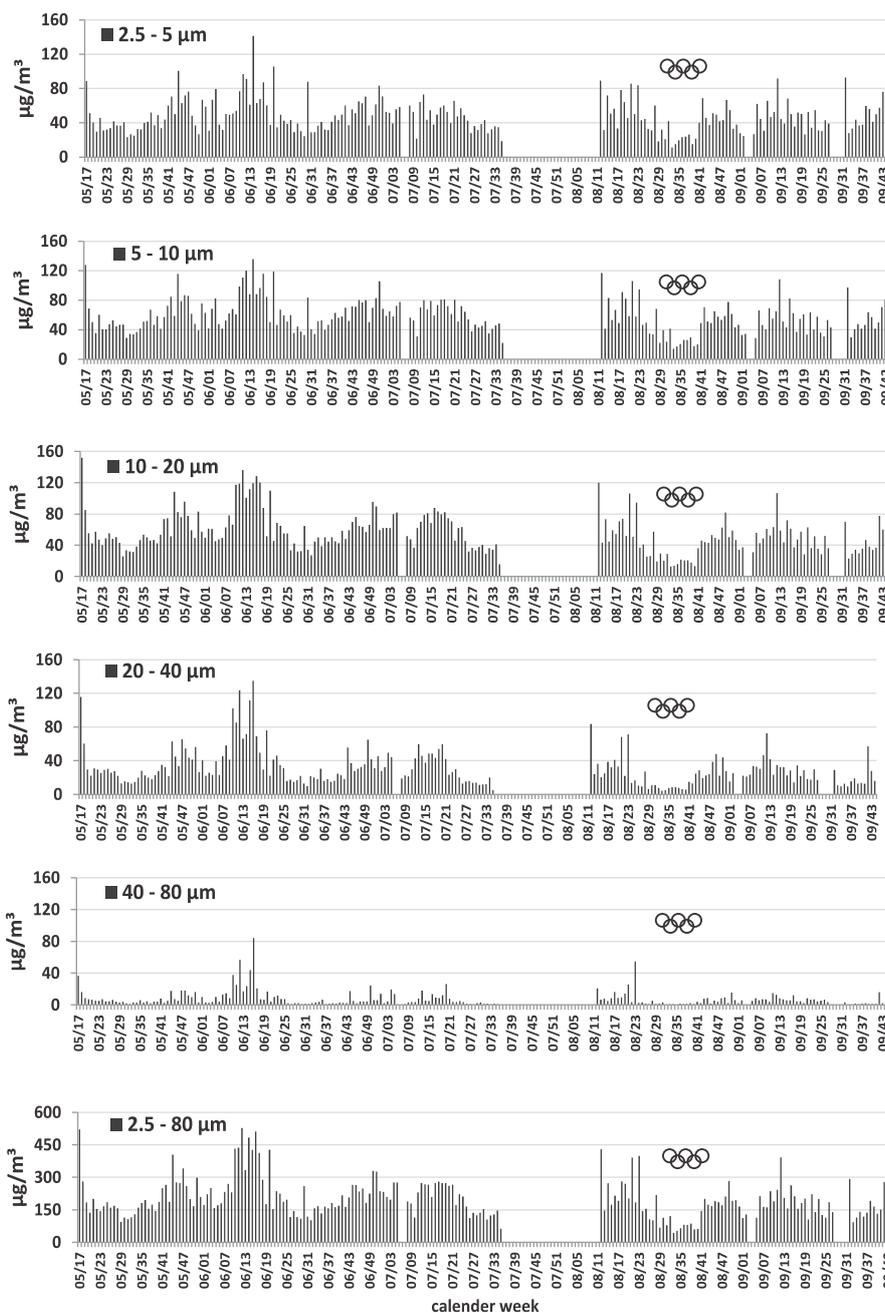


Fig. 2. Time series of coarse atmospheric particulate mass concentrations for TP total (2.5–80 µm) and the different size intervals SI1–SI5 (calendar week: year/week). The Olympic Rings indicate the period of the Olympic Games.

4.2. Evaluation of the origin: geogenic or anthropogenic

The Sigma-2 passive sampling technique in combination with the subsequent automated microscopic analysis does not only provide results for total particle concentrations but also for opaque (OP) and transparent particles (TRP). The described analysis directly obtains a size fractionated particle number deposition rate of low light absorbing transparent particles and of highly light absorbing opaque particles often characterized by considerable content of elemental carbon (Fiebig-Wittmaack et al., 2006). Examples for such particles are shown in Fig. 6. The opaque particles represent predominantly

anthropogenic aerosol sources such as soot from combustion processes and rubber particles from tyre wear while transparent particles are frequently refer to a geogenic origin, such as soil and sediment particles (Grobty et al., 2010). In order to evaluate the contributions from anthropogenic or geogenic origin, the concentrations of opaque and transparent particles in the size intervals between 2.5 and 80 µm geometric diameter are plotted in Fig. 7. Interestingly, concentrations of OP and TRP significantly discern in different seasons. Generally, concentrations of opaque particles are much lower by a factor of 5–15 in comparison to the concentrations of transparent particles. Both, opaque and transparent particles show

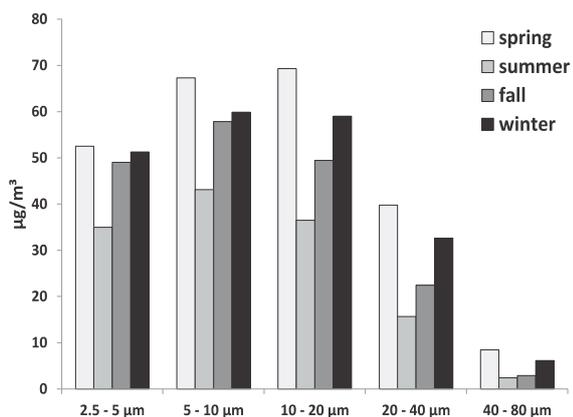


Fig. 3. Medians of seasonal coarse atmospheric particulate mass concentrations for different size fractions for the period April 2005 till October 2009.

highest concentrations for the size fraction of 5–20 µm (SI2, SI3). The smaller fraction SI1 of opaque and transparent particles already shows lower concentrations as SI2 and SI3 but still higher ones as those of SI4 and SI5, which is in accordance to the distribution of total particles (Fig. 3). Seasonal distribution of concentrations of opaque and transparent particles differs, since geogenic particles more contribute to the transparent particle fraction and combustion processes to the opaque particle fraction. Therefore, highest concentrations of opaque particles occur in winter and lowest in summer. Autumn and spring concentrations of opaque particles show intermediate values but change their order at 20 µm. In autumn, the mass concentrations of opaque particles of the fraction below 20 µm is higher as in spring. Opaque particles with diameters above 20 µm behave vice versa, most probably because the dust storms are able to transport some opaque coarse minerals, such as hornblende, chlorite or illite (Liu et al., 2004; Shao et al., 2007, 2008) and resuspend more anthropogenic particles from the surfaces due to higher wind velocities. This behaviour does not occur for transparent particles. In this case, the order of TRP concentrations follows spring > winter > autumn > summer for all size fractions (Fig. 7), which is the

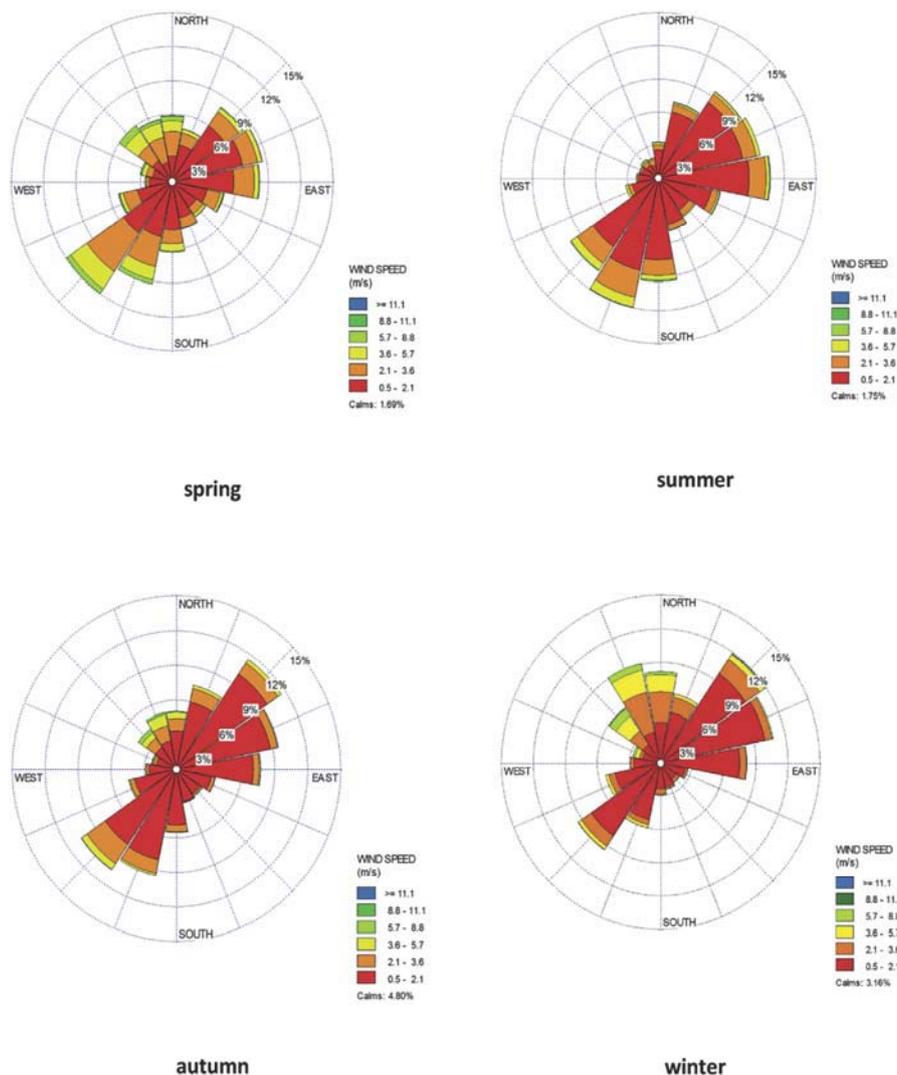


Fig. 4. Wind roses for different seasons (2005–2009) in Beijing (based on three-hourly data obtained from <http://cdc.cma.gov.cn>).

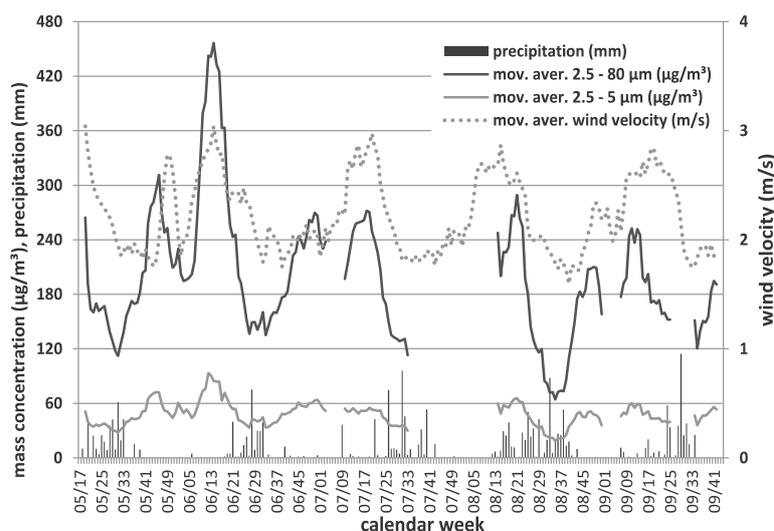


Fig. 5. Annual courses of wind velocities, precipitation and coarse aerosol mass concentrations. For moving averages, the mean of values of five days were used. (Meteorological data are obtained from China Meteorological Data Sharing Service System, <http://cdc.cma.gov.cn>).

same order as for TP. For OP the order of seasonal mass concentrations follows the sequence winter > spring, autumn > summer (Fig. 8).

4.3. Long term trend of mass concentrations and the influence of the Olympic Games

The time series of the single size fractions for the whole sampling period is shown in Fig. 2. To analyse the long term trend of mass concentration development, the medians of the size fraction 2.5–5 µm (SI1) and the agglomerated size fraction 2.5–80 µm (SI_{tot}) are depicted in Fig. 9 for the single seasons. Here, the smallest size fraction is used as indicator for anthropogenic emissions, whereas whole mass concentration is much more influenced by geogenic particle sources. For all seasons, a certain variance of SI1 mass concentrations is obvious but for the years 2005–2009 no clear trend can be alluded on basis of the available data. Contrarily, SI_{tot} shows a trend of decreasing mass concentrations over time for spring, summer and autumn, but not for winter. The lack of a temporal trend in winter can be caused the limited available data only allowing to calculate the median for three seasons. Thus, more

data of an even longer time series is necessary. The distribution of seasonal medians for spring periods is dominated by the severe asian dust event in spring 2006. But since then, median concentrations are steadily decreasing from medians of 426 µg·m⁻³ in 2005 to 202 µg·m⁻³ in 2009. In case of summer seasons the medians decrease from 157 µg·m⁻³ in 2005 to 125 µg·m⁻³ in 2009, and for fall seasons from 249 µg·m⁻³ in 2005 to 158 µg·m⁻³ in 2009.

The trends indicate that mitigation measures to reduce particulate air pollution in Beijing was more successful with respect to the reduction of coarse particle mass concentrations as with respect to the reduction of fine particle mass concentrations. This is in correspondence to the seasonal ratios of SI1 to SI_{tot} as demonstrated in Fig. 10. From 2005 to 2009 the ratios of SI1/SI_{tot} show for most seasons a trend of a slight increase indicating a growing share of smaller particles within the total particulate load. Only during winter the ratios stay fairly stable indicating no relative decrease of larger particle fractions.

The effects of the various mitigation measures during the Olympic Games (Chen et al., 2014) are visible in the temporal minima of median particle mass concentrations in summer 2008

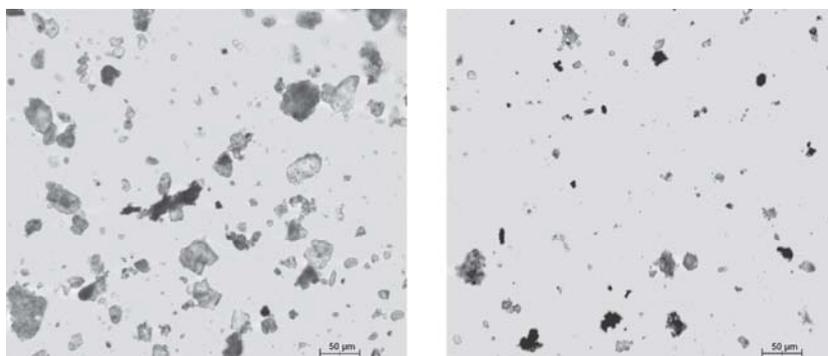


Fig. 6. Microscopic pictures of atmospheric particles sampled by SIGMA-2 method. Left: typical picture from spring season, calendar week 12, March 2006; Right: a typical picture from winter season, calendar week 52, December 2006. Transparent particles are often minerals such as quartz, whereas opaque particles often are tyre rubber or soot. The spring picture is dominated by coarse particles with a relative high number of transparent particles. The winter picture is dominated by smaller particles and a relative high number of opaque particles.

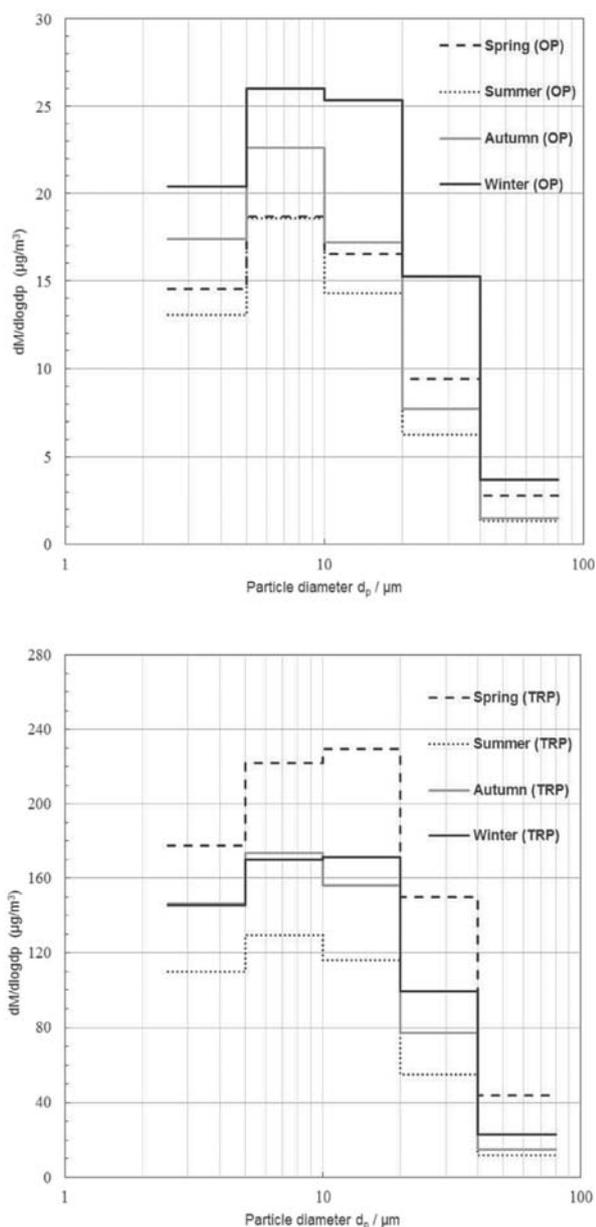


Fig. 7. Average size distributions of each season of the years 2005–2009 of OP and TRP concentrations (upper: average concentration of opaque particles, lower: average concentration of transparent particles).

(Figs. 2 and 9). This effect becomes even more visible if only focussing on the respective time period of the Olympic Games comprising the period from August 7th till September 17th, which falls into the calendar weeks 32–38 in 2008. Table 3 summarizes the median values of this specific period for TP. It is obvious that TP was reduced for all size classes relative to previous years and the following year. This indicates that reduction measures were effective for anthropogenic emissions of coarse transparent particles as e.g. emitted during construction activities, which were extremely predominant all over Beijing before 2008. Furthermore, the Olympic Games period in 2008 from August 7th till September 17th showed the highest precipitation with 207.6 mm in comparison to this period in the other years of this survey (2005: 77.5 mm; 2006: 44.5 mm; 2007: 74.5 mm; 2009: 53.2). Thus, this humid period

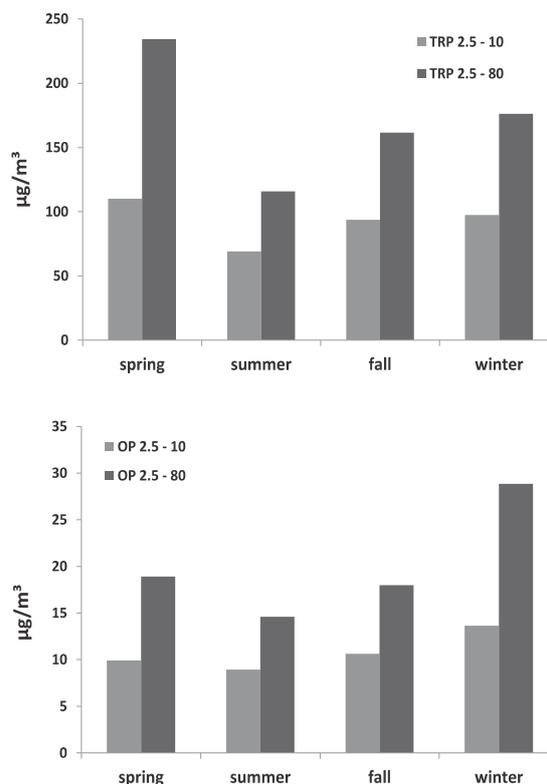


Fig. 8. Seasonal dynamics of TRP and OP coarse atmospheric particulate matter mass concentrations (medians) for agglomerated size fractions of 2.5–10 µm and 2.5–80 µm and for the period April 2005 to November 2009.

especially affected the abundance of coarse geogenic particles in the ambient Beijing atmosphere and supported a relative low mass concentration of coarse particles in Beijing's ambient air.

5. Conclusions

The technique of size distributed particle sampling by the Sigma-2 device combined with detailed automatic microscopic single particle analysis provided valuable results of size distribution and seasonal variation of different size fractions of coarse atmospheric particles between 2.5 and 80 µm. A noteworthy insight is presented into the coarse particles' temporal dynamics within the urban area of Beijing and their contribution to air pollution.

Mass concentrations and seasonal variations of particulate matter of 2.5–80 µm, also distinguished into opaque and transparent particles in different size intervals, were provided by this study for a long time period from April 2005 till October 2009. Highest mass concentrations occurred for the particle sizes between 5 and 20 µm. The mass concentrations in all size fractions follow the same seasonal trend: spring > winter > fall > summer. If differentiating the particles into transparent and opaque particles, transparent particles account for the lion's share of the total particle concentrations. However, the seasonal course of mass concentrations of opaque particles differed from transparent particles with highest mass concentrations in all size fractions during winter and not in spring.

A long term trend for the reduction of predominantly anthropogenic emitted particles was not obvious for small size fractions such as S11 (2.5–5 µm) and opaque particles. Nevertheless, such a trend was recorded for fractions of larger particles and transparent

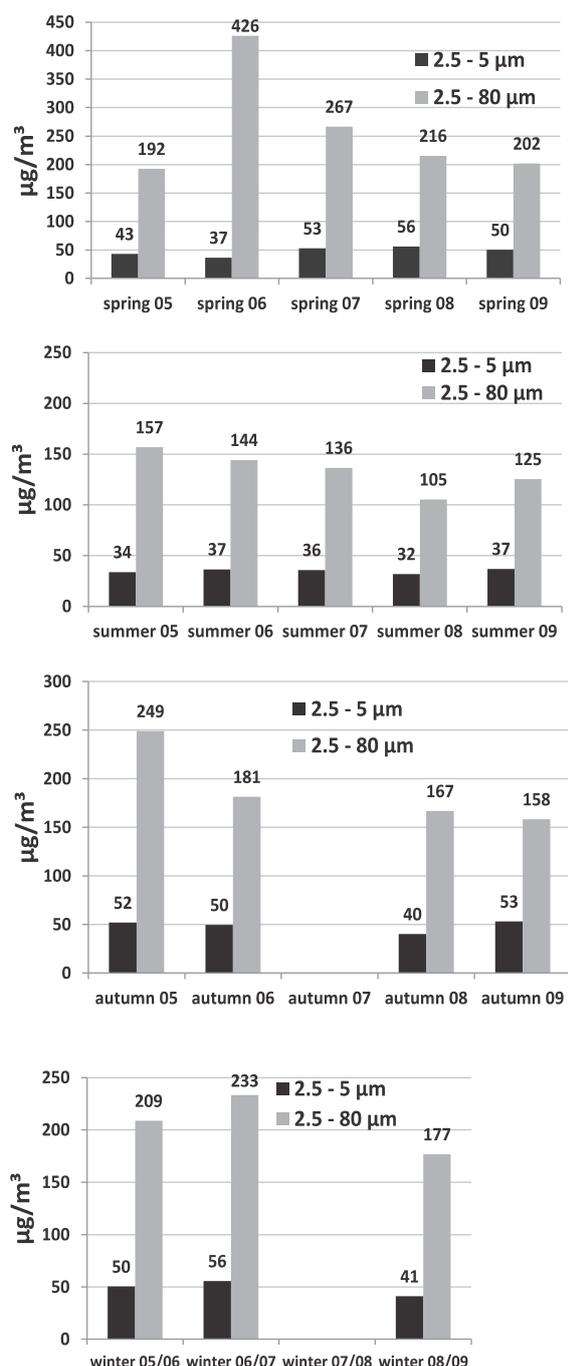


Fig. 9. Seasonal courses of medians of coarse atmospheric particulate matter mass concentrations of size fractions 2.5–5 μm and 2.5–80 μm.

particles for the seasons spring, summer and fall from 2005 till 2009. The asian dust event in 2006 caused an extremely high average weekly mass concentration of up to more as 500 μg·m⁻³ for the sum of all size fractions. Mitigation measures accompanying the period of Olympic Summer Games in 2008 especially were effective for larger particles. These mitigation measures were substantially supported by the highest precipitation amounts for years. Beside precipitation also wind speed effects particle concentrations contributing to lower mass concentrations of coarse particles

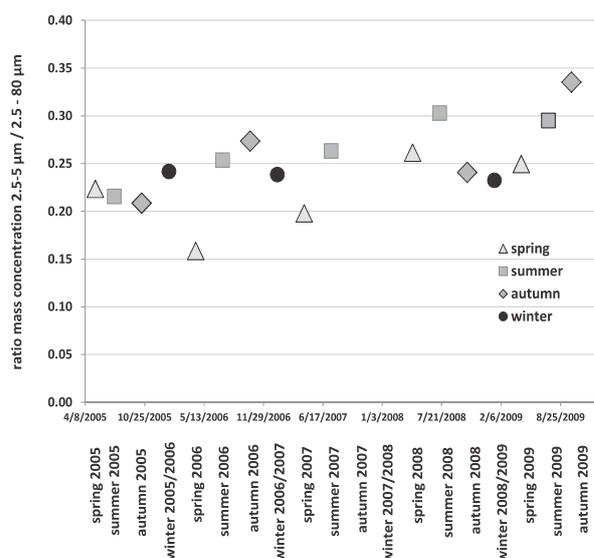


Fig. 10. Course of seasonal ratios of coarse atmospheric particulate matter mass concentrations of size fractions 2.5–5 μm and 2.5–80 μm.

Table 3

Medians of the mass concentrations (μg·m⁻³) for the different size intervals for total particles (TP) for the period of the Olympic Games in different years.

	2.5–5 μm	5–10 μm	10–20 μm	20–40 μm	40–80 μm	2.5–80 μm
TP						
2005	38.6	48.8	46.1	19.7	3.2	157
2006	34.2	49.1	44.8	19.0	2.7	157
2008	23.1	26.2	20.5	7.4	0.9	80.3
2009	37.8	46.5	34.5	12.5	1.6	137

during summer and higher concentrations during the other seasons with higher average wind speeds.

The results of this study prove an intensive urban air pollution in Beijing by coarse particles between 2.5 and 80 μm, exceeding the mass of PM2.5. Till today not many studies are available on the dynamics of coarse particles and especially of size fractionated coarse particles in the ambient air of Beijing and of megacities in general. Neither the meaning of the various coarse particles for scavenging small particles is comprehensively understood (Schleicher et al., 2010a, b) nor the influence of coarse particles on the local climate. Thus, it is highly advised to intensify the monitoring and reduction measures for this pollutant not only in Beijing but also in other megacities facing severe air pollution.

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B.3 Characteristics and sources of PM in seasonal perspective – A case study from one year continuously sampling in Beijing

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Characteristics and sources of PM in seasonal perspective – A case study from one year continuously sampling in Beijing



Rongrong Shen^{a,*}, Klaus Schäfer^a, Jürgen Schnelle-Kreis^b, Longyi Shao^c, Stefan Norra^{d,e,f}, Utz Kramar^e, Bernhard Michalke^g, Gülcin Abbaszade^b, Thorsten Streibel^h, Mathieu Frickerⁱ, Yuan Chen^e, Ralf Zimmermann^{b,h}, Stefan Emeis^a, Hans Peter Schmid^a

^a Institute of Meteorology and Climate Research, Atmospheric Environmental Research, Karlsruhe Institute of Technology (KIT/IMK-IFU), 82467 Garmisch-Partenkirchen, Germany

^b Joint Mass Spectrometry Centre, Comprehensive Molecular Analytics, Helmholtz Zentrum München (HMGU/CMA), 85764 Neuherberg, Germany

^c School of Geoscience and Surveying Engineering, China University of Mining and Technology (Beijing) (CUMTB), 100083 Beijing, PR China

^d Institute of Geography and Geoecology, Karlsruhe Institute of Technology (KIT/IGG), 76128 Karlsruhe, Germany

^e Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology (KIT/IMG), 76128 Karlsruhe, Germany

^f Institute of Mineralogy, TU Bergakademie Freiberg (TUBF), 09596 Freiberg, Germany

^g Research Unit Analytical BioGeoChemistry, Helmholtz Zentrum München (HMGU/ABGC), 85764 Neuherberg, Germany

^h Joint Mass Spectrometry Centre, Chair of Analytical Chemistry, University of Rostock (UR/IC), 18059 Rostock, Germany

ⁱ Research Center Human Biometeorology, Air Quality Department, Deutscher Wetterdienst (DWD/AQD), 79104 Freiburg, Germany

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ABSTRACT

Daily mass concentrations and chemical compositions (elemental carbon, organic carbon, water soluble ions, chemical elements and organic species) of PM were measured continuously in Beijing for one year from June 2010 to June 2011 (365 samples). The seasonal variation of PM mass concentration followed the order of spring 2011 > winter 2010 > summer 2010 > autumn 2010. Organic matter (OM) and secondary inorganic aerosol components (SNA: SO_4^{2-} , NO_3^- and NH_4^+) were the two major fractions of PM during the whole year. Source apportionment by PMF performed on the basis of a full year of data, including both inorganic and organic species, showed that biomass burning, secondary sulfate and nitrate formation, mineral dust, industry, coal combustion and traffic were the main sources of PM in Beijing during 2010–2011. Specifically, comparison among the four seasons shows that the contribution of secondary sulfate and biomass burning, secondary nitrate formation, mineral dust, and coal combustion were the dominating sources of PM in summer, autumn, spring and winter, respectively. The contributions of industry to PM was distributed evenly in four seasons, while traffic contributed more in summer and autumn than in winter and spring. Backward trajectory analysis was applied in combination with PMF and showed that air flow from the South contributed mostly to high PM mass concentrations in Beijing. Meteorological parameters (temperature, wind speed, wind direction, precipitation and mixing layer height) influence such a variation. In general, high relative humidity and low mixing layer height can raise PM mass concentration, while high wind speed and precipitation can reduce pollutants. In addition, wind direction also plays a key role in influencing PM because different wind directions can bring different pollutants to Beijing from different regions.

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1. Introduction

PM, as the major air pollutant in Beijing, has been widely studied on the general chemical characteristics (Song et al., 2012; Zhao et al., 2013a) and certain specific species, such as carbonaceous components (Yang et al., 2011; Zhao et al., 2013b), inorganic elements (Shi

* Corresponding author. Tel.: +49 8821 183192; fax: +49 8821 73573.

E-mail address: Rongrong_Shen@sina.com (R. Shen).

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et al., 2005; Yang et al., 2012), inorganic ions (Yao et al., 2002; Ianniello et al., 2011), organic matter (Sun et al., 2012; Wang et al., 2012) as well as on health effects (Shao et al., 2006, 2007; Li et al., 2010; Dimitrova et al., 2012), and influence on visibility (Jung and Kim, 2006; Cao et al., 2012) and global climate (IPCC, 2013).

In order to improve air quality, source apportionment of PM in Beijing was also widely performed by different receptor models, such as chemical mass balance (CMB), positive matrix factorization (PMF) and principal component analysis (PCA). However, in the receptor models mentioned above, PMF is discussed to be the most suitable tool for source apportionment. The reason is that PMF does not need a priori information on source emission profiles when compared with CMB, and PMF can constrain the factors and their loadings to be non-negative in value and handle missing data (Paatero and Tapper, 1994; Paatero, 1997) when compared with PCA. Even though lots of studies on source apportionment of PM in Beijing have been done by PMF (Lei et al., 2004; Song et al., 2006, 2007; Zhang et al., 2007; Wang et al., 2008, 2009; Yu et al., 2013; Wu et al., 2014), these studies only used either inorganic or organic compounds to perform source apportionment and the durations of sampling were comparably short or discontinuous. Sources and characteristics of PM samples from a short or discontinuous sampling period cannot be satisfactorily representative of the whole year. A previous study (Zhang et al., 2009a) pointed out that not less than 90 samples should be analyzed to obtain robust PMF results when 48 chemical species were included in the analysis. Of course more observations increase the robustness of source contribution analysis.

Consequently, a full year of continuous data was investigated to obtain more robust source apportionment and to investigate the temporal variation of source contributions. Source apportionment of PM in Beijing with continuous long-term inorganic and organic compounds has not previously been reported. Here, for the first time, data from a sampling campaign covering a full year of PM sampling are investigated. Both inorganic and organic composition was analyzed in this study and source apportionment based on a full year of continuous data was conducted.

Daily PM samples were collected continuously for one year from June 2010 until June 2011. Elemental carbon (EC), organic carbon (OC), inorganic elements, water soluble ions, PAHs, hopanes and levoglucosan were quantified. Source apportionment of PM was performed by PMF on the basis of these chemical compounds. The objectives of this paper are: (1) to investigate PM level at the height for exposure to humans; (2) to study the annual and seasonal variation of inorganic and organic species mass concentrations; (3) to obtain the more robust source apportionment results based on a large data set; (4) to look into the seasonal variation of different sources contribution to PM; (5) to examine the contribution of different sources in different air flows; (6) to discuss typical PM chemical characteristics during the four seasons together with meteorological influences.

2. Materials and methods

2.1. Sampling methods

Two sequential High-Volume Samplers (HVS, nominal flow 500 l min^{-1} , Digital DHA-80, Hegnau, Switzerland), sampler A and sampler B, were installed at the campus of the China University of Geosciences (Beijing) (CUGB) (Fig. 1). PM samples (00:00–24:00) were collected in parallel from 21 June 2010 till 20 June 2011. Quartz fiber filters (Munkstell T293, Falun, Sweden) with 150 mm diameter were used as the collection substrate. One field blank sample from both samplers was collected every second week. The sampler inlet tubes were installed at a height of 2 m above ground, which is a typical height for the exposure of humans.

2.2. Analytical methods

Filters of sampler A were heated at $500 \text{ }^\circ\text{C}$ for 6 h before sampling and analyzed for EC, OC, water soluble ions and organic compounds. Filters of sampler B were weighed by an analytical balance (Mettler Analysenwaage AE240, reading precision 0.1 mg) before and after sampling for gravimetric PM mass concentration determination. A 48 h equilibration of filters at a temperature of $22 \text{ }^\circ\text{C} \pm 0.2 \text{ }^\circ\text{C}$ and a relative humidity (RH) of $42\% \pm 0.5\%$ in a conditioning room was conducted before weighing. Filters of sampler B were also used for inorganic elements analysis.

OC and EC were analyzed by a thermal/optical carbon analyser (DRI Model 2001A, Desert Research Institute, USA). The IMPROVE (Interagency Monitoring of Protected Visual Environments) A protocol and the thermal optical reflection method (TOR) are applied. Round filter parts with 8 mm diameter were punched from each loaded sample and heated gradually at different temperatures for measuring different OC (OC1, OC2, OC3 and OC4) and EC fractions (EC1, EC2 and EC3). OC and EC have been corrected by the value of optical pyrolyzed carbon (OPC) ($\text{OC} = \text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OPC}$; $\text{EC} = \text{EC1} + \text{EC2} + \text{EC3} - \text{OPC}$). More details of this method can be found in previous studies (Chow et al., 2007; Li et al., 2012a).

Inorganic elements, including K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sn, Sb, Ba and Pb, were measured by polarized energy dispersive X-ray fluorescence (PEDXRF, Epsilon 5, PANalytical, The Netherlands). All loaded filters were analyzed as thin layer samples, using for calibration 30 filters of different load, which were previously analyzed by Inductively coupled plasma mass spectrometry (ICP-MS). More details of this method are described by Kramar (1999).

Cl^- , NO_3^- and SO_4^{2-} were analyzed by ion chromatography (IC) (ICS-1500, Dionex, USA) and NH_4^+ by a continuous flow analyser (CFA) (Scan⁺⁺, Skalar, The Netherlands). Round filter parts with 25 mm diameter were punched from loaded filters and extracted by 5 ml de-ionized water (Milli-Q, 18.2 M Ω cm) in an ultrasonic bath for 15 min. The extraction was taken for three times and the solution was filtered by 0.45 μm syringe filter after each extraction. 15 ml extracted solution was obtained for each sample in total.

Levoglucosan, eleven Hopane substances and fifteen PAHs were measured by in-situ derivatisation direct thermal desorption gas chromatography time-of-flight mass spectrometry (IDTD-GC-TOFMS). An Agilent 6890 gas chromatograph (Agilent, USA) attached to a Pegasus III time of flight mass spectrometer (Leco, USA) was used. The eleven Hopane substances are 18 α (H)-22,29,30-Trisnorhopane (Ts), 17 α (H)-22,29,30-Trisnorhopane (Tm), 17 β (H)-22,29,30-Trisnorhopane (27b), 17 α (H)21 β (H)-30-Norhopane (29ab), 17 β (H)21 α (H)-30-Norhopane (29ba), 17 α (H)21 β (H)-Hopane (30ab), 17 β (H)21 α (H)-Hopane (Moretan) (30ba), 22S-17 α (H)21 β (H)-Homohopane (31abS), 22R-17 α (H)21 β (H)-Homohopane (31abR), 22S-17 α (H)21 β (H)-Bishomohopane (32abS), and 22R-17 α (H)21 β (H)-Bishomohopane (32abR). The fifteen PAHs are Phenanthrene (PHE), Anthracene (ANT), Pyrene (PYR), Fluoranthene (FLU), Benz[a]anthracene (BAA), Chrysene (CRY), sum of Benzfluoranthenes (BBKF), Benzo[e]pyrene (BEP), Benzo[a]pyrene (BAP), Perylene (PER), Dibenz[a,h]anthracene (DAH), Indeno[1,2,3-cd]pyrene (IND), Picene (PIC), Benzo[ghi]perylene (BGH), and Coronene (COR). However, PHE, ANT, PYR and FLU are considered to be semi-volatile and thus mainly present in the gas phase. As the mass concentrations of these compounds determined in PM samples are highly driven by the gas phase concentrations during the last minutes of sampling, PHE, ANT, PYR and FLU are excluded from discussion in this study. More details of this method are described by Orasche et al. (2011).

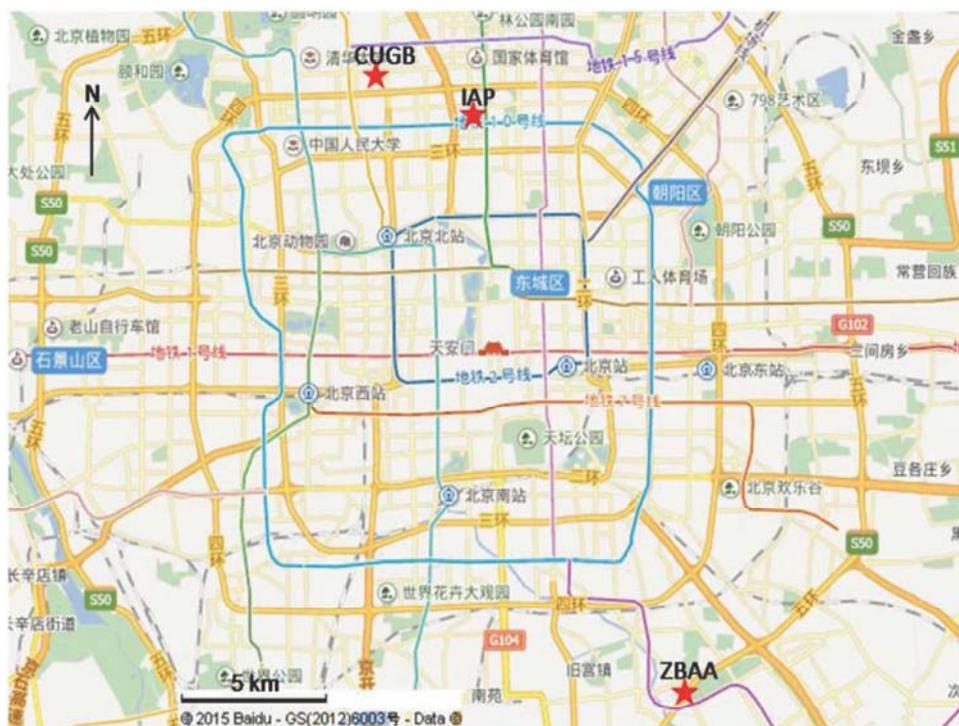


Fig. 1. The location of the sampling sites in Beijing (Source: <http://map.baidu.com>): CUGB is the China University of Geosciences (Beijing); IAP is the Institute of Atmospheric Physics of the Chinese Academy of Sciences; ZBAA is the code for the monitoring site from where one can obtain meteorological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

2.3. Meteorological parameters

Meteorological data, including temperature (T), atmospheric pressure (p), relative humidity (RH), visibility, wind speed (WS) and wind direction (WD), were collected from the internet page of the University of Wyoming, USA (<http://weather.uwyo.edu/upperair/sounding.html>) where the data of the weather station ZBAA (Fig. 1) is available. The available maximum visibility data is only up to 10 km. Wind roses were produced from ZBAA half hourly wind data with WRPLOT View Freeware (Lakes Environmental, Ontario, Canada).

Mixing layer height (MLH) was determined by a ceilometer CL31 (Vaisala GmbH, Hamburg, Germany), a laser-based remote sensing system (mini lidar), at the IAP (Institute of Atmospheric Physics) (Fig. 1). All details about methods of MLH calculation from particle backscatter intensities are described in previous studies (Münkel et al., 2007; Emeis et al., 2008).

2.4. Positive matrix factorization (PMF)

PMF is one kind of multivariate factor analysis methods which uses a matrix of measured data and a matrix of known uncertainties of individual data points to produce two matrices: factor profiles and factor contributions. So PMF can be written as:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (1)$$

where x_{ij} is the measured concentration of compound j in sample i ($\mu\text{g m}^{-3}$), p is the total number of factors, g_{ik} is the contribution of factor k to sample i ($\mu\text{g m}^{-3}$), f_{kj} is the profile of compounds j of

factor k (g g^{-1}), and e_{ij} is the residual for the compounds j in sample i ($\mu\text{g m}^{-3}$).

The aim of the PMF method is to find the minimum weighted sum of the squared residual function Q value (Equation (2)) by using least-squares fitting (Paatero and Tapper, 1993, 1994). The solution obtained at the minimum Q value is considered to be a reasonable result. The equation is as follows:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]^2 \quad (2)$$

Here, u_{ij} is the uncertainty of x_{ij} , n is the total number of samples, and m is the total number of measured compounds. The value of p , m , and n are restricted as $p < m$ and $n > m$. More details about PMF are described by previous studies (Paatero and Tapper, 1993; Paatero and Hopke, 2003; Reff et al., 2007; Norris et al., 2008).

Input data x_{ij} lower than or equal to the limit of quantification (LOQ) were replaced by half of the LOQ and their uncertainties u_{ij} were set as 5/6 of the LOQ (Polissar et al., 1998). But if x_{ij} is higher than the LOQ, u_{ij} were calculated by following equation (Norris et al., 2008):

$$u_{ij} = \left(((\text{Error Fraction}) * x_{ij})^2 + \text{LOQ}_{ij}^2 \right)^{0.5} \quad (3)$$

where error fraction (%) is estimated from both sampling error and analytical error. In this study, an error fraction of 8–10% for trace elements, 8% for EC and OC, 12–15% for water soluble ions, and 12–20% for organic compounds were estimated for the PMF analysis.

The missing data were replaced by the mean values of that species and the uncertainties were set as three times of the mean value (Gu et al., 2011). LOQ of all species are shown in the Table S1 of the Supporting Material. The modeling uncertainty, which is caused by other errors, such as variation of source profile and chemical transformation, was set as 5% in this study according to the suggestion from Norris et al. (2008).

In this study, species were discarded from the model if the sum of the number of missing data and the number of data with values below the LOQ was more than 1/3 of the samples.

Signal to Noise (S/N) ratios were used to categorize a species, and according to S/N ratios (Paatero and Hopke, 2003), three categories were obtained: “bad” ($S/N < 0.2$), “weak” ($0.2 < S/N < 2$), and “strong” ($S/N > 2$). “Bad” means this species will be excluded from the PMF model. “Weak” means the uncertainty of this species will be increased by model in order to reduce the influence of this species. Further information about S/N ratios of each input species are listed in Table S2 of the Support Material. 321 PM samples with 31 species (OC, EC, Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, K, Ca, Ti, Mn, Fe, Cu, Zn, As, Ba, Pb, 29ab, 29ba, 30ba, 30ab, 31abS, 31abR, BAA, CRY, BBKF, BEP, BAP, IND, PIC, BGH and levoglucosan) were used in the final PMF analysis ($n = 321$ and $m = 32$). The PM₄ mass concentration was also included but marked as a “total variable” which was grouped into the “weak category” automatically by the model in order to reduce its influence on the PMF solution. PMF was run several times with different factor numbers (4–12) to determine the most reasonable number of factors. The Q values (see equation (2)), which are goodness-of-fit parameters, are checked first to assess how well the model fits. The Q values in all runs converged and Q-robust was close to Q-true, indicating that the model fit well with the input data and the global minimum Q was found. In addition, the G-space plot (factor versus another factor) showed no edges in all factors, indicating that there is no rotational ambiguity. Therefore $F_{peak} = 0$ was used in this study. Finally, six factors were determined to be the most meaningful result. After a reasonable solution was selected, a 100 bootstrap was run (minimum $R^2 = 0.6$) to check its stability. Of the 100 runs, factor 1, factor 2 and factor 6 only had 2, 2 and 3 bootstraps unmapped, respectively, while all the remaining three factors had all bootstraps mapped. The correlation R^2 between modeled PM₄ mass concentrations by PMF and measured PM₄ mass concentrations reached 0.93 with a slope of 0.96, showing that model can adequately reproduce the measured PM₄ mass concentration. Therefore, the solution with six factors was considered as a stable result.

2.5. Backward trajectory analysis

The HYSPLIT4 (Hybrid Single Particle Lagrangian Integrated Trajectory, Version 4) model was used to calculate backward trajectories of air flows (<http://ready.arl.noaa.gov/HYSPLIT.php>) with meteorological data from Global Data Assimilation System (GDAS). In order to cover both horizontal and vertical scale transport of air flows, 72 h backward trajectories were selected (Zhu et al., 2011; Li et al., 2012b). 500 m height above ground level (AGL) at the ending point was chosen because in general pollutants are well mixed up to this height. The same application can also be found in previous studies (Zhang et al., 2009b; Ji et al., 2014). The time ending at 06:00 UTC (14:00 local) was chosen for calculating backward trajectories indicative of each day because the MLH is the highest at this time during the day and the conditions are favorable for mixing of air pollutants.

In order to obtain the possible source locations, cluster analysis based on backward trajectories was performed by multiple iterations. The aim of cluster analysis is to sort all backward trajectories which have similar movements into the same group, a so-called

cluster. During iteration, the cluster spatial variance (SPVAR) and the total spatial variance (TSV) among trajectories were calculated. SPVAR is the sum of the squared distances between the endpoints of the trajectories and corresponding cluster-mean, while TSV is the sum of SPVAR of all clusters (Draxler et al., 2009). At the initial step, one trajectory is considered as one cluster. With iterations, two trajectories with the lowest increase in STV are paired into the same cluster. Iterations continue until the rapid increase in STV is found. The detail about cluster analysis can be found in previous studies (Draxler et al., 2009; Kelly et al., 2012).

2.6. Quality assurance/quality control (QA/QC)

All filter holders and rings were cleaned by de-ionized water twice in an ultrasonic bath before being used. A time of 20 min was used for each cleaning. The holders and rings were then washed by de-ionized water individually once more and baked at 110 °C in an oven for 1 h. The tweezers were also first cleaned by de-ionized water and then by methanol once more before each time using. All loaded filters were stored at -20 °C before the chemical analysis, while all experimental results were corrected by deducting the blank filter values.

A not instantly perceived fault during installation of the devices led to a decreased collection air flow of 167 l min⁻¹ in both samplers. Meanwhile, the size of the collected particles on the filters was changed with the reduction of flow volume of samplers.

According to the impactor design theory (Gussman, 1969; Marple and Liu, 1974; Marple and Willeke, 1976), the equation is given as:

$$Stk_{50} = \frac{4\rho_p QCD_{50}^2}{9\pi\eta\mu W^3} \quad (4)$$

Here, Stk_{50} is the stokes number at 50% collection efficiency, ρ_p is the particle density ($\rho_p = 1 \text{ g cm}^{-3}$), Q is the total volume passing through the sampler, C is the Cunningham slip correction factor, D_{50} is particle diameter at 50% collection efficiency, n is the number of nozzles ($n = 10$), μ is the flux viscosity ($\mu = 1.81 \times 10^{-4} \text{ kg s}^{-1} \text{ m}^{-1}$) and W is the jet width (5.6 mm).

Because Stk_{50} is relatively constant when the ratio of jet-to-plate distance to jet width (S/W) is larger than 1.0 (Marple and Willeke, 1976) (in our study, $S/W = 3.6$), the cut-off size of particles $C^{0.5}D_{50}$ can be recalculated as PM₄ (aerodynamic diameter of PM is less than 4 μm), which is still meaningful and can be represented as respirable particulate matter (Fromme et al., 2005; Keil et al., 2010). The most important point is that the variation trend of PM₄ is supported by simultaneous PM_{2.5} TEOM data at CAS/IAP (Institute of Atmospheric Physics, Chinese Academy of Sciences) (Xin et al., 2014).

3. Results

3.1. PM₄ mass concentrations

Annual variation of PM₄ mass concentrations from 18 to 321 μg m⁻³ with an annual average value of 83 μg m⁻³ is shown in Fig. 2. Significant variation of monthly PM₄ mass concentrations was observed. PM₄ mass decreased continuously from June 2010 till September 2010, then increased from October 2010 till November 2010, and decreased again after December 2010, reached the lowest monthly average value (44 μg m⁻³) in January 2011, and the highest monthly average value of 117 μg m⁻³ in April 2011 (Fig. S1 of the Supporting material). The seasonal variation of PM₄ mass concentration was also examined. Considering the heating periods, the seasons are defined as summer from June till August, autumn in

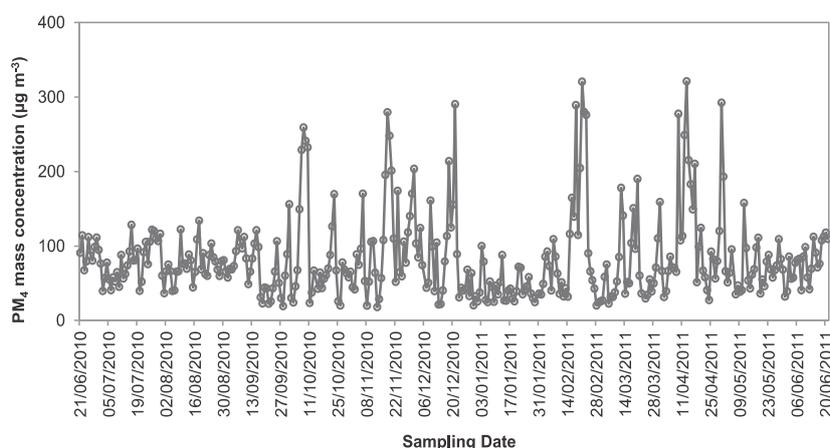


Fig. 2. Annual variation of daily mean $PM_{4.0}$ mass concentrations at the CUGB from 2010.06.21 till 2011.06.20.

September and October, winter from November till March, and spring in April and May. Only 20 days were investigated in summer 2011 (from 1 June till 20 June 2011), which cannot be representative for summer 2011. So in this paper, the data of these 20 samples will not be discussed with respect to seasonal variation. $PM_{4.0}$ mass concentrations are found to reach the highest value of $95 \mu\text{g m}^{-3}$ during spring 2011, decrease through the winter 2010 ($83 \mu\text{g m}^{-3}$), summer 2010 ($82 \mu\text{g m}^{-3}$) and show the lowest values in autumn 2010 ($80 \mu\text{g m}^{-3}$).

3.2. Mass concentrations of chemical species in $PM_{4.0}$

In order to assess air quality, seasonal average mass concentrations of chemical compounds in $PM_{4.0}$ are listed in Table 1.

3.2.1. EC and OC

The variation of daily EC and OC are shown in Fig. S2(a) of the Supporting material. Daily EC and OC mass concentrations varied from 0.5 to $11.6 \mu\text{g C m}^{-3}$ and from 5.4 to $70.1 \mu\text{g C m}^{-3}$ with annual average mass concentrations of 3.8 ± 2.1 (mean \pm standard deviation, similarly hereinafter) $\mu\text{g C m}^{-3}$ and $18.9 \pm 10.9 \mu\text{g C m}^{-3}$, respectively. EC had the highest mass concentration in autumn 2010 ($4.3 \pm 2.2 \mu\text{g C m}^{-3}$) and the lowest mass concentration in spring 2011 ($3.2 \pm 1.8 \mu\text{g C m}^{-3}$), while the seasonal average concentration of OC was the highest of $19.2 \pm 13.5 \mu\text{g C m}^{-3}$ in winter 2010 and the lowest of $18.0 \pm 9.7 \mu\text{g C m}^{-3}$ in spring 2011. The mass percentages of EC and OC in $PM_{4.0}$ showed no large variation in different seasons, 5.2%, 5.9%, 5.4% and 4.3% for EC and 26%, 26%, 25% and 24% for OC in summer 2010, autumn 2010, winter 2010 and spring 2011, respectively. The annual average contributions of EC and OC to $PM_{4.0}$ mass were 5.3% and 26%, respectively.

Carbonaceous matter (CM) was estimated applying the following equation (Turpin and Lim, 2001).

$$CM = OM + EC = 1.6 \times OC + EC \quad (5)$$

where OM is organic matter which can be estimated from OC. The ratio between OM and OC was found to range from 1.4 to 1.8 depending on the oxidative state of the aerosol which may lead to a seasonally dependent ratio. In this study, an average ratio of 1.6 was used (Turpin and Lim, 2001).

CM contributed 45%, 48%, 46% and 38% to $PM_{4.0}$ mass in summer 2010, autumn 2010, winter 2010 and spring 2011, respectively with the annual average mass percentage of 46%. It shows that CM is an important constituent in $PM_{4.0}$.

A ratio of OC/EC higher than 2 is an indicator for the presence of secondary organic carbon (SOC) (Chow et al., 1996). OC/EC mass ratio in Fig. S2(a) of the Supporting material showed that all OC/EC ratios during the whole year were higher than 2, which indicated that SOC formation in Beijing PM is common. SOC can be estimated from OC and EC but an uncertainty exists which is not easily evaluated. Therefore, estimation of SOC was not conducted in this study. OC/EC ratios varied from 2.7 to 48.6 with an average value of 5.3. The seasonal variation showed that the lowest OC/EC ratio was 4.4 in autumn 2010 and the highest value was 5.6 in spring 2011. The highest OC/EC value (48.6) was found on 1 May 2011 caused by dust storm on 1 May 2011 which transported organic soil material with high OC concentration (Zhao et al., 2013a) to Beijing.

3.2.2. Organic compounds

Levoglucosan shown in Fig. 2S(b) of the Supporting material was the dominant compound in all measured organic species and mass concentrations varied from 8 to 2443 ng m^{-3} with an annual average value of 406 ng m^{-3} and contributed 0.6% to $PM_{4.0}$ mass. The seasonal variation of levoglucosan mass concentration (Table 1) showed the highest mass concentration in summer 2010 (667 ng m^{-3}), followed by autumn 2010 (568 ng m^{-3}), winter 2010 (369 ng m^{-3}), and the lowest was in spring 2011 (176 ng m^{-3}).

Most of hopanes, except Ts, 30ab and 31abS, had the highest mass concentration in winter 2010 (Table 1). The dominant substances were 29ab and 30ab in all hopane compounds (Fig. 2S(b)), which contributed 23% and 24% to the hopane pattern, respectively.

The daily sum of PAH mass concentrations were in the range of 1 – 332 ng m^{-3} . The lowest PAH mass concentration was found in summer 2010, followed by spring 2011 and autumn 2010, and increased rapidly during winter time as also observed in previous studies (He et al., 2006; Huang et al., 2006).

3.2.3. Water soluble ions

SO_4^{2-} showed the highest mass concentration of $21.9 \mu\text{g m}^{-3}$ in summer 2010 and the lowest mass concentration of $9.9 \mu\text{g m}^{-3}$ in spring 2011. NO_3^- had the highest mass concentration at $11.7 \mu\text{g m}^{-3}$ in winter 2010 and the lowest mass concentration in summer 2010 ($1.7 \mu\text{g m}^{-3}$). Seasonal variation of NH_4^+ mass concentration showed the highest value in autumn 2010, followed by summer 2010, winter 2010, and spring 2011. The contribution of SO_4^{2-} , NO_3^- and NH_4^+ (SNA) to $PM_{4.0}$ mass concentration ranged from 2% to 85% with an annual average value of 24%, and 33%, 26%, 23% and 20% in summer 2010, autumn 2010, winter 2010 and spring 2011,

Table 1Seasonal average mass concentrations of chemical compounds in PM₄ at the CUGB from 2010.06.21 till 2011.06.20 (unit: from EC to NH₄⁺: μg m⁻³; from Fe to COR: ng m⁻³).

Species	Annual average	Summer 2010	Autumn 2010	Winter 2010	Spring 2011
EC/OC					
EC	3.8 ± 2.1	3.8 ± 0.9	4.3 ± 2.2	4.0 ± 2.6	3.2 ± 1.8
OC	18.9 ± 10.9	18.2 ± 2.8	18.8 ± 10.6	19.2 ± 13.5	18.0 ± 9.7
Ions					
Cl ⁻	2.0 ± 3.0	0.07 ± 0.2	0.5 ± 0.7	3.0 ± 3.5	0.9 ± 1.7
NO ₃ ⁻	8.6 ± 21.2	1.7 ± 1.0	9.9 ± 17.4	11.7 ± 28.8	7.5 ± 11.3
SO ₄ ²⁻	12.8 ± 19.3	21.9 ± 16.3	12.8 ± 16.3	10.9 ± 23.7	9.9 ± 10.7
NH ₄ ⁺	4.6 ± 8.6	5.6 ± 4.3	5.8 ± 9.9	4.6 ± 10.6	2.8 ± 4.0
Elements					
Fe	1455 ± 1198	1155 ± 368	1227 ± 605	1494 ± 1169	2103 ± 2013
K	1569 ± 1740	1163 ± 827	1070 ± 771	1899 ± 2318	1585 ± 1370
Ca	2340 ± 2048	1534 ± 544	1747 ± 862	2540 ± 1898	3587 ± 3494
Ti	102 ± 101	67.3 ± 22.9	72.6 ± 36.8	107 ± 77.6	175 ± 190
Mn	52.3 ± 37.4	37.6 ± 13.1	46.8 ± 23.3	61.0 ± 42.8	60.7 ± 48.9
Cr	16.3 ± 13.0	17.5 ± 11.0	14.3 ± 8.7	17.8 ± 15.5	14.3 ± 11.4
Ni	1.0 ± 0.7	0.9 ± 0.6	0.7 ± 0.5	1.1 ± 0.8	1.0 ± 0.7
Cu	35.5 ± 30.9	28.8 ± 16.8	37.0 ± 28.3	39.9 ± 37.8	31.0 ± 27.5
Zn	326 ± 301	350 ± 219	328 ± 296	313 ± 351	326 ± 295
As	15.6 ± 19.6	13.1 ± 13.1	12.7 ± 13.4	17.2 ± 24.6	16.8 ± 19.9
Sn	5.3 ± 3.6	5.0 ± 3.5	4.1 ± 3.3	5.3 ± 3.5	6.0 ± 3.8
Sb	2.8 ± 1.9	2.6 ± 2.0	2.7 ± 2.0	3.0 ± 2.0	2.7 ± 1.8
Ba	22.5 ± 18.8	17.8 ± 5.8	18.9 ± 9.5	23.1 ± 18.4	32.6 ± 31.5
Pb	105 ± 98.8	96.6 ± 56.2	97.3 ± 80.6	116 ± 122	99.2 ± 103
Organic compounds					
Levogluconan	406 ± 352	667 ± 462	568 ± 451	369 ± 262	176 ± 131
Hopanes					
Ts	1.5 ± 1.0	1.5 ± 0.9	1.7 ± 0.9	1.3 ± 0.9	1.5 ± 0.9
Tm	2.4 ± 2.2	1.1 ± 0.5	1.6 ± 0.8	3.4 ± 2.7	1.3 ± 0.6
29ab	5.6 ± 4.2	4.6 ± 1.6	5.3 ± 2.3	6.6 ± 5.5	3.4 ± 1.9
29ba	2.9 ± 3.2	0.9 ± 0.5	1.3 ± 0.5	4.5 ± 3.7	0.9 ± 0.8
30ab	5.6 ± 3.7	5.2 ± 1.8	6.0 ± 2.5	5.7 ± 4.4	4.0 ± 2.7
30ba	2.6 ± 3.0	0.8 ± 0.3	1.4 ± 0.5	4.0 ± 3.6	0.9 ± 0.6
31abS	2.1 ± 1.1	2.3 ± 0.6	2.4 ± 0.8	1.9 ± 1.1	1.5 ± 0.9
31abR	1.9 ± 1.1	1.7 ± 0.4	1.7 ± 0.6	2.2 ± 1.4	1.2 ± 0.9
32abS	1.6 ± 0.9	1.4 ± 0.4	1.6 ± 0.4	1.8 ± 1.0	1.0 ± 0.9
32abR	1.4 ± 0.9	1.3 ± 1.0	1.1 ± 0.4	1.5 ± 0.9	0.9 ± 1.0
PAHs					
BAA	2.1 ± 4.0	0.1 ± 0.1	0.4 ± 0.4	4.4 ± 5.1	0.3 ± 0.2
CRY	5.6 ± 8.6	0.8 ± 0.4	1.9 ± 1.9	10.8 ± 10.8	1.4 ± 1.0
BBKF	7.5 ± 10.8	1.3 ± 0.5	3.6 ± 2.9	14.0 ± 13.5	2.2 ± 1.8
BEP	2.3 ± 3.3	0.4 ± 0.2	1.2 ± 0.9	4.2 ± 4.1	0.7 ± 0.6
BAP	2.6 ± 3.8	0.3 ± 0.2	1.1 ± 1.0	4.7 ± 5.0	1.2 ± 0.5
PER	0.7 ± 0.9	0.06 ± 0.03	0.4 ± 1.1	1.0 ± 0.9	0.2 ± 0.1
DAH	0.7 ± 0.8	0.2 ± 0.1	0.4 ± 0.3	1.1 ± 0.8	1.1 ± 1.3
IND	3.4 ± 4.4	0.8 ± 0.5	2.0 ± 1.4	5.9 ± 5.4	1.3 ± 1.0
PIC	0.9 ± 0.8	0.1 ± 0.05	0.5 ± 0.3	1.2 ± 0.8	0.5 ± 0.5
BGH	2.5 ± 3.2	0.6 ± 0.2	1.6 ± 1.2	4.3 ± 3.9	1.0 ± 0.9
COR	2.6 ± 2.4	1.0 ± 0.8	1.4 ± 1.2	3.8 ± 2.6	1.0 ± 0.8

respectively. Cl⁻ was a minor fraction (2%) in PM₄ in comparison with SNA and it showed noticeably high mass concentration of 3.0 μg m⁻³ during winter 2010 compared with summer 2010.

3.2.4. Inorganic elements

In all measured metals, Ca had the highest annual average mass concentration (2340 ng m⁻³) while the lowest was Ni with 1.0 ng m⁻³. Fe, Ca, Ti and Ba, which are discussed to be related to the crustal sources (Yang et al., 2005), accounted for 67% of all elemental mass, and showed similar variation patterns over the whole year with many similar peaks in mass concentration. For instance, the highest mass concentrations of these four elements occurred in spring 2011 which was likely due to a dust storm contribution (Fig. 3S(a) of the Supporting material). The annual average mass concentration of [Fe + Ca + Ti + Ba] was 3913 ng m⁻³, and showed the seasonal average mass concentration of 2774, 3037, 4163 and 5898 ng m⁻³ in summer 2010, autumn 2010, winter 2010 and spring 2011, respectively. The other non-crustal elements, such

as Zn, As and Pb, which are generally considered to originate from anthropogenic sources (Shi et al., 2010; Tian et al., 2010; Soriano et al., 2012; Xu et al., 2012), followed a similar pattern during the whole sampling period and showed no large differences from season to season ([Zn + As + Pb]: 460 ng m⁻³ in summer 2010, 432 ng m⁻³ in autumn 2010, 446 ng m⁻³ in winter 2010 and 441 ng m⁻³ in spring 2010) except significant lower mass concentrations in January 2011 (Fig. 3S(b) of the Supporting material), which corresponds to relatively low PM₄ mass concentration.

3.3. PM₄ mass balance

The mass balance of PM₄ is shown in Fig. 3. Organic matter was calculated by 1.6 times OC (Formula 5) and was the largest fraction of PM₄ with a mass contribution of 41%. SO₄²⁻, NO₃⁻ and NH₄⁺ (SNA) contributed 25% to PM₄ mass. Crustal elements were described by the sum of Fe, Ca, Ti and Ba and contributed 5% to PM₄ mass. Trace elements including Cr, Ni, Zn, As, Pb, Sn, Cu and Sb, only were 1% of

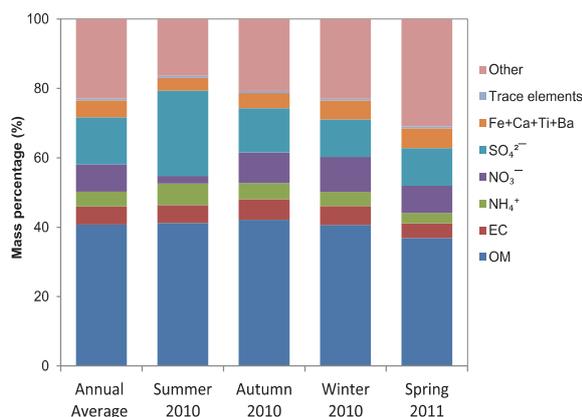


Fig. 3. Mass balance of PM₄ on the basis of daily mean samples in different seasons at the CUGB during 2010–2011.

PM₄ mass. The other unknown part was the third highest fraction of PM₄ mass with the contribution of 23%.

Seasonal mass balance of PM₄ is also shown in Fig. 3. Both OM and EC had the lowest contribution of 37% and 4% to PM₄ in spring 2010, respectively. NO₃⁻ showed the highest values (10%) in winter 2010 while SO₄²⁻ and NH₄⁺ had the highest contribution (25% and 6%) in summer 2010 on the contrary. The sum of Fe, Ca, Ti and Ba showed the clearly highest contribution in spring 2011 (6%). The exception was trace elements had no large variation during the four seasons.

3.4. Source apportionment

Six factors that can be explained as sources were determined by PMF (see discussion below). The species mass concentration (g g^{-1} , the species mass contained in 1 g particles in each factor) and mass percentage (%), the species mass concentration contained in one factor divided by the total mass concentration in all factors) are shown in Fig. 4. The time series variation of each factor mass concentration is shown in Fig. 5. The seasonal mass contributions of six factors are listed in Table 2.

4. Discussions

4.1. Organic compounds

Levoglucosan is widely used as an indicator for biomass burning (Zhang et al., 2008; Wagener et al., 2012), so the contribution of biomass burning to OC can be implied by the mass ratio of levoglucosan to OC (Zhang et al., 2008). Levoglucosan had much higher mass concentrations in summer and autumn than in winter and spring (Table 1), while the seasonal average mass ratios of levoglucosan to OC also showed the highest values in summer 2010 (0.04), followed by autumn 2010 (0.03), then winter 2010 (0.02) and spring 2011 (0.01). All these indicated that biomass burning contributed significantly to the particle loading in summer and autumn in Beijing. This agrees well with previous studies which pointed out that biomass burning, such as the combustion of agricultural waste and fallen leaves, usually happens in summer and autumn in Beijing and its surrounding area (Huang et al., 2012).

Fossil fuel combustion, such as coal combustion and vehicle emissions, is considered to be the main source of hopanes (He et al., 2006; Schnelle-Kreis et al., 2007). The hopane patterns, such as hopane index or homohopane index, are usually used to distinguish mineral oil based sources like vehicle emission from coal

combustion sources (Oros and Simoneit, 2000). The hopane index, 30ab/(30ab + 30ba), was found to be 0.1 for lignite coal, 0.5 for bituminous coal, 0.6 for brown coal (Oros and Simoneit, 2000) and greater than 0.9 for crude oil (El-Gayar et al., 2002). In this study, it varied from 0.29 to 0.95 with an annual average value of 0.72, and had the highest value of 0.86 in summer 2010, followed by autumn 2010 (0.83), spring 2011 (0.82) and the lowest values in winter 2010 (0.61). The homohopane index, 31abS/(31abS + 31abR), was found to be about 0.1 for lignite coal, 0.4 for bituminous coal, and 0.6 for fuel oil combustion (Oros and Simoneit, 2000; Schnelle-Kreis et al., 2007). In PM₄, it ranged from 0.14 to 0.78 with an annual average value of 0.53 and had a value of 0.57, 0.58, 0.47 and 0.56 in summer 2010, autumn 2010, winter 2010 and spring 2010, respectively. So both indexes in winter had lower values in comparison to other seasons, indicating that hopanes in spring, summer and autumn mainly originated from fuel oil consumption while coal combustion had a greater contribution to hopanes during winter.

PAHs had the highest mass concentrations in winter (Table 1). The reasons could be low temperatures, weak solar radiation (He et al., 2006) and the increase in coal combustion. PIC in PAHs, a tracer for coal combustion (Oros and Simoneit, 2000), had the highest mass concentration with the value of 1.2 ng m^{-3} in winter 2010, followed by autumn 2010 and spring 2011 which had the same value of 0.5 ng m^{-3} and much higher than in summer 2010 (0.1 ng m^{-3}). This supported that coal combustion contributed a large amount to PAHs during winter.

4.2. Interpretation of factors from PMF results

The first factor contained 65% of SO₄²⁻, 50% of NH₄⁺ and 55% of levoglucosan (Fig. 4). As discussed in Section 4.1, levoglucosan is widely used as a tracer for biomass burning (Zhang et al., 2008; Wagener et al., 2012). From Fig. 5 and Table 2, the time series variation and seasonal variation show that this factor had the highest mass concentration during summer ($35.8 \text{ } \mu\text{g m}^{-3}$) and followed by autumn with the value of $13.7 \text{ } \mu\text{g m}^{-3}$. This is because biomass burning usually happens during summer and autumn in Beijing and its surrounding areas (Huang et al., 2012) and the secondary sulfate is easily formed under strong solar radiation and high temperature, especially in summer (Seinfeld and Pandis, 2006). In addition, previous studies showed that SO₄²⁻ mass concentration increased during biomass burning episodes (Cheng et al., 2014; Rastogi et al., 2014). Therefore this factor can be explained by biomass burning and secondary sulfate formation.

The second factor was characterized by high concentrations of nitrate and ammonium, which can be explained as a secondary nitrate formation. The time series (Fig. 5) and Table 2 show that this factor concentrated during autumn ($13.2 \text{ } \mu\text{g m}^{-3}$) and winter ($10.4 \text{ } \mu\text{g m}^{-3}$) but had the lowest concentration during summer ($0.8 \text{ } \mu\text{g m}^{-3}$). The low values during summer may be biased because ammonium nitrate is semi-volatile and high temperatures in summer could have caused losses from the filters.

The third factor was mainly contributed by Fe (58%), Ca (59%), Ti (67%), Mn (48%), and Ba (59%) (Fig. 4). The main source of all these elements is considered as soil. The time series (Fig. 5) and seasonal variation (Table 2) showed that high concentrations of this factor were concentrated during spring with the value of $53.6 \text{ } \mu\text{g m}^{-3}$ when dust storms occurred. For instance, this factor had a peak value on 30 April 2011 when a dust storm happened. Therefore, this factor is indicative of mineral dust, including dust storm, road dust and construction dust.

The fourth factor was characterized by relative high contributions of As (79%), Zn (66%), Pb (57%), Cu (45%) (Fig. 4). As was found to be originated from smelter and base-metal refinery industries (Wang and Mulligan, 2006). Zn and Cu are originated

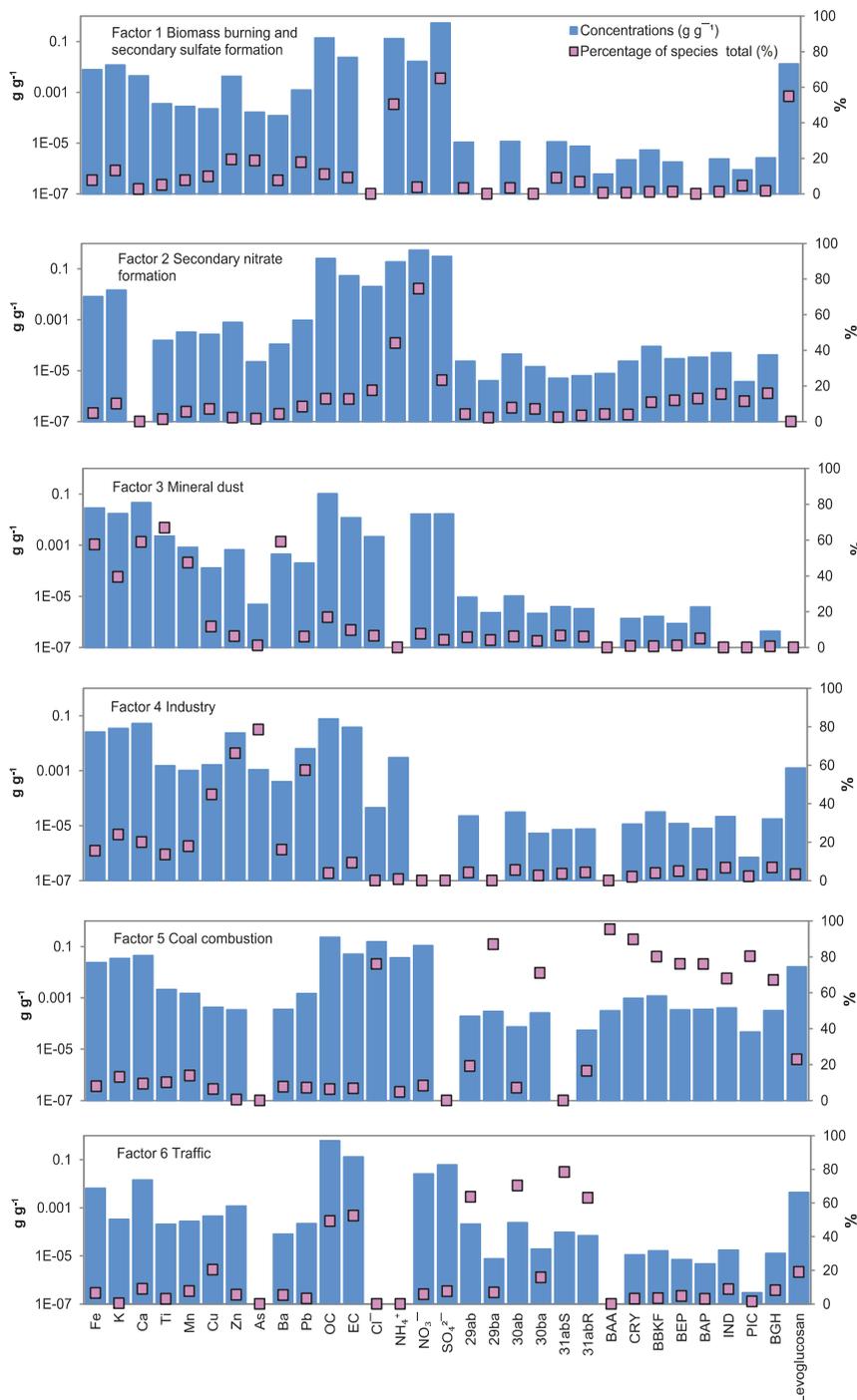


Fig. 4. PMF factor profiles from chemical compounds data in PM₄ during 2010–2011 at the CUGB.

from industrial metallurgical process (Xu et al., 2012). Tangshan city and Tianjin Municipality are important industrial cities which are located to the Southeast of Beijing. The main industry in Tangshan is iron and steel. In Tianjin, metalworking is one kind of important industry. Pb was considered to have originated from the ceramic industry, the manufacturing of insecticides, paints, glass and storage batteries (Soriano et al., 2012). Porcelain is another important industry in Tangshan city and producing

photovoltaic cells is an important industry in Baoding city which is located to the Southwest of Beijing. In addition to surrounding cities, the smelter industry is also located inside of Beijing, to the Northwest of CUGB, which is called “Changping smelter”. All above mentioned support that this factor can be representative of industrial based sources. The time series (Fig. 5) shows that the contribution of this factor to PM₄ is stable during the whole year, except in January 2011 where the lowest mass concentration was

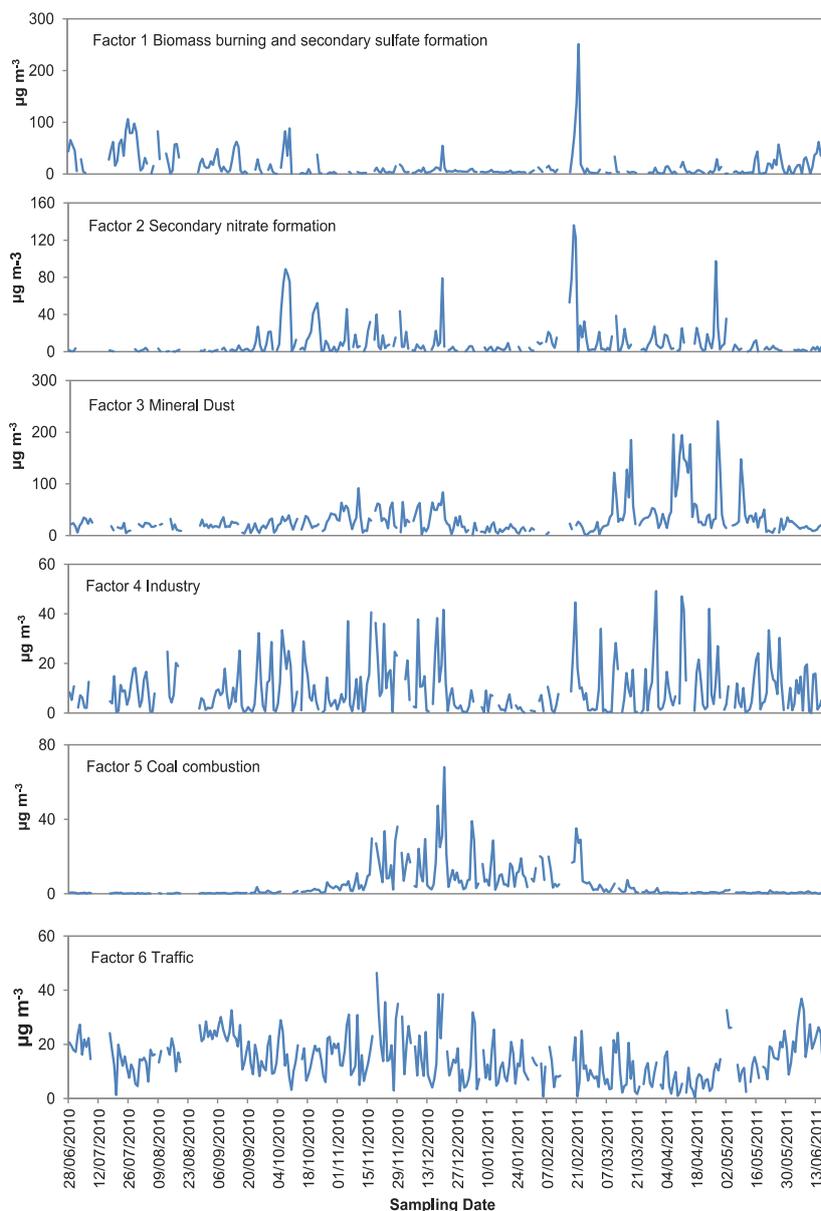


Fig. 5. Daily mean contributions of six sources from the PMF analysis for PM₄ at the CUGB in Beijing during 2010–2011.

found, which is supported by the lowest PM₄ mass concentration at the same period. The reason could be it was influenced by meteorological parameters and the decrease in human activities during winter holiday period.

The fifth factor in Fig. 5 was dominated by PAHs (95% of BAA, 90% of CRY, 80% of BBKF, 76% of BEP, 76% of BAP, 68% of IND, 80% of PIC and 67% of BGH), 29ba (87%), 30ba (70%), Cl⁻ (76%), and levoglucosan (23%). Levoglucosan was found not only from biomass

Table 2
Seasonal contributions of 6 factors to PM₄ during 2010–2011 (unit: µg m⁻³).

	Factor 1 Secondary sulfate formation and biomass burning	Factor 2 Secondary nitrate formation	Factor 3 Mineral dust	Factor 4 Industry	Factor 5 Coal combustion	Factor 6 Traffic
Annual average	14.1	8.6	29.1	8.8	4.8	14.4
Summer 2010	35.8	0.8	17.1	7.3	0.3	16.3
Autumn 2010	13.7	13.2	20.7	9.0	1.1	17.5
Winter 2010	8.6	10.4	27.7	8.9	10.2	13.4
Spring 2011	8.5	8.1	53.6	9.9	0.7	9.8

burning, but also from lignite combustion (Fabbri et al., 2008, 2009). Even though levoglucosan could also be caused by biomass burning for heating in winter, this form of heating is less common in the Beijing-Tianjin-Hebei region in comparison with coal combustion. Therefore, levoglucosan in this factor was most probably from coal combustion. Cl^- also can originate from coal combustion (Yao et al., 2002) and PIC is also used as a tracer for coal combustion (Oros and Simoneit, 2000). In this factor, the hopane index $30ab/(30ab + 30ba)$ is 0.2. As discussed in Section 4.1, this factor can be interpreted as coal combustion. In addition, contribution of this factor was found to be concentrated during winter (Fig. 5 and Table 2), indicating that coal combustion for heating during winter is the main reason. Most of PAHs were found to have a high contribution in this factor, showing that most of the very health hazardous PAHs are associated with coal combustion.

The sixth factor found in Fig. 5 was characterized by EC (52%), OC (49%), 29ab (64%), 30ab (70%), 31abS (78%) and 31abR (63%). In this factor, the homohopane index $31abS/(31abS + 31abR)$ was 0.6 and the hopane index $30ab/(30ab + 30ba)$ was 0.9. Both indexes indicated that this factor can be explained by oil combustion. Hopanes are considered to be an organic tracer for the lubricating oil which is usually used for gasoline or diesel engine vehicles (Rogge et al., 1993; Phuleria et al., 2006; Kleeman et al., 2009). Therefore this factor can be considered as traffic.

The six factors can be interpreted as a mixture of secondary sulfate formation and biomass burning, secondary nitrate formation, mineral dust, industry, coal combustion and traffic. These sources contributed the average value of 14.1, 8.6, 29.1, 8.8, 4.8 and $14.4 \mu\text{g m}^{-3}$ to PM_{10} mass and constitute 18%, 11%, 36%, 11%, 6% and 18% of PM_{10} mass, respectively (Table 2). The major sources of $\text{PM}_{2.5}$ in Beijing from previous studies (Song et al., 2007; Wang et al., 2008; Yu et al., 2013) can be listed as: dust, biomass burning, coal combustion, industry, vehicle emission and secondary particles formation. The difference to these studies is that the contribution of each source is different. In particular, the contribution of mineral dust to PM is much higher in this study and mineral dust is found to be an important source in Beijing, especially in spring. The reason could be that the size of PM_{10} is coarser than $\text{PM}_{2.5}$. On the other hand, the sampler inlet tubes were installed at a height of 2 m above ground, which is a typical height for the exposure of humans and is closer to the ground which can be more influenced by road dust.

The results from source apportionment illustrate the seasonal variation of each source and the dominant source of PM in each season (Table 2). In general, secondary sulfate formation and biomass burning contributions were concentrated in summer, while secondary nitrate formation concentrated in autumn and winter. PM from mineral dust had a relative high concentration during the whole year, especially in spring. Industry distributed relatively consistently throughout the whole year. Coal combustion for heating clearly had an obvious high contribution in winter. PM from traffic had a relative higher concentration in summer and autumn.

Considering source markers usually have more than one possible source, using single source marker or one category of species to trace the source is not complete. In this study, source apportionment was performed using a full year of data from both of inorganic and organic species for the first time to obtain more reasonable source identifications. In doing so it was possible to identify contributions from, e.g., coal combustion separated from traffic emissions. On the other hand it was not possible to un-mix sources with very similar variations in time like secondary sulfate formation and biomass burning.

4.3. Regional transportation indicated by back trajectories and cluster analysis

HYSPLIT4 was used to calculate 72 h backward trajectories at 500 m AGL prior to arriving in Beijing at 14:00 local time each day. Four trajectory clusters were obtained (Fig. 6).

Clusters 1, 2, 3 and 4 expressed the air flow from the South, the North, the Northwest and the Northwest with a long range transport of Beijing, respectively. These clusters are called the “South flow” (S flow), the “North flow” (N flow), “Northwest flow” (NW flow) and Long-range Northwest flow” (Long-range NW flow) and they accounted for 33%, 17%, 35% and 15% of all air flows, respectively. Long-range NW flow was longer than NW flow which indicated that Long-range NW flow had higher wind speeds in comparison with NW flow. In all clusters, the S flow was the shortest trajectory by far, which can be explained by the presence of relatively stagnant conditions.

According to these four clusters, all sampling days were also classified into four groups (Table 3). The highest PM_{10} mass concentration was from the S flow ($103 \mu\text{g m}^{-3}$), followed by the long-range NW flow ($95 \mu\text{g m}^{-3}$), the NW flow ($63 \mu\text{g m}^{-3}$) and the N flow ($57 \mu\text{g m}^{-3}$). The mixture of secondary sulfate formation and biomass burning, secondary nitrate formation and industry sources were mainly from S flows with the highest mass concentrations of 33.5, 14.2 and $12.8 \mu\text{g m}^{-3}$, respectively. In other words, the precursors of secondary inorganic ions, such as SO_2 and NO_x , were transported mainly from the cities which are located in the South of Beijing, such as Tianjin Municipality and Tangshan city. Both of these two cities are important heavy industrial cities. This indicates that cities located in the South of Beijing play an important role in PM pollution in Beijing. The highest contributions from mineral dust ($43.9 \mu\text{g m}^{-3}$) and coal combustion ($10.8 \mu\text{g m}^{-3}$) were found to be from long-range NW flows, the longest trajectory, which means this cluster was accompanied by the highest wind speed. In addition, this air flow passed Russia, Mongolia, Inner Mongolia and Hebei Province to Beijing. Therefore, high wind speeds could transport the dust particles from Gobi desert in Mongolia and sandy lands in Inner Mongolia to Beijing, leading to the increase in the mass concentration of mineral dust. Coal is widely used for heating during winter in Mongolia, Inner Mongolia and Hebei

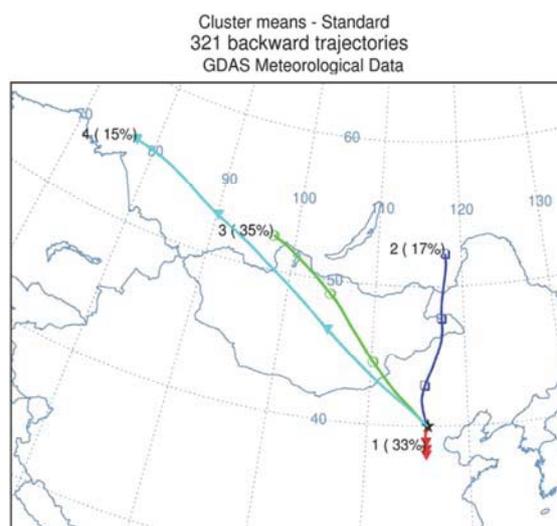


Fig. 6. Clusters of backward trajectories during 2010–2011.

Table 3

Summary of source distribution to PM₄ and corresponding PM₄ mass concentration on different directions of air flows during 2010–2011 (unit: μg m⁻³). S is South, etc.

Direction	Secondary sulfate formation and biomass burning	Secondary nitrate formation	Mineral dust	Industry	Coal combustion	Traffic	PM ₄
S flow	33.5	14.2	22.6	12.8	3.3	16.7	103
N flow	5.5	5.9	23.6	6.6	2.5	12.6	57
NW flow	3.4	4.7	31.6	5.9	4.7	13.0	63
Long-range NW flow	6.9	8.8	43.9	9.5	10.8	15.1	95

Province, and Zhangjiakou fossil-fuel power station, which mainly used coal, is also located on route where the long-range NW flow passed. 75% of sampling days from long-range PM₄ flows were found to be in winter. Therefore, the highest contribution from coal combustion was found from long-range NW flows coincidentally. Traffic showed little variation in all four backward trajectory clusters, indicating that it was mainly from local sources.

4.4. Influences of meteorological parameters and effect on visibility

Previous studies have pointed out that meteorological parameters were key factors affecting PM loading (Schäfer et al., 2006, 2011, 2014; Deng et al., 2012). The correlation coefficients between PM₄ and meteorological parameters such as T, WS, RH and MLH are listed in Table S3 of the Supporting Material.

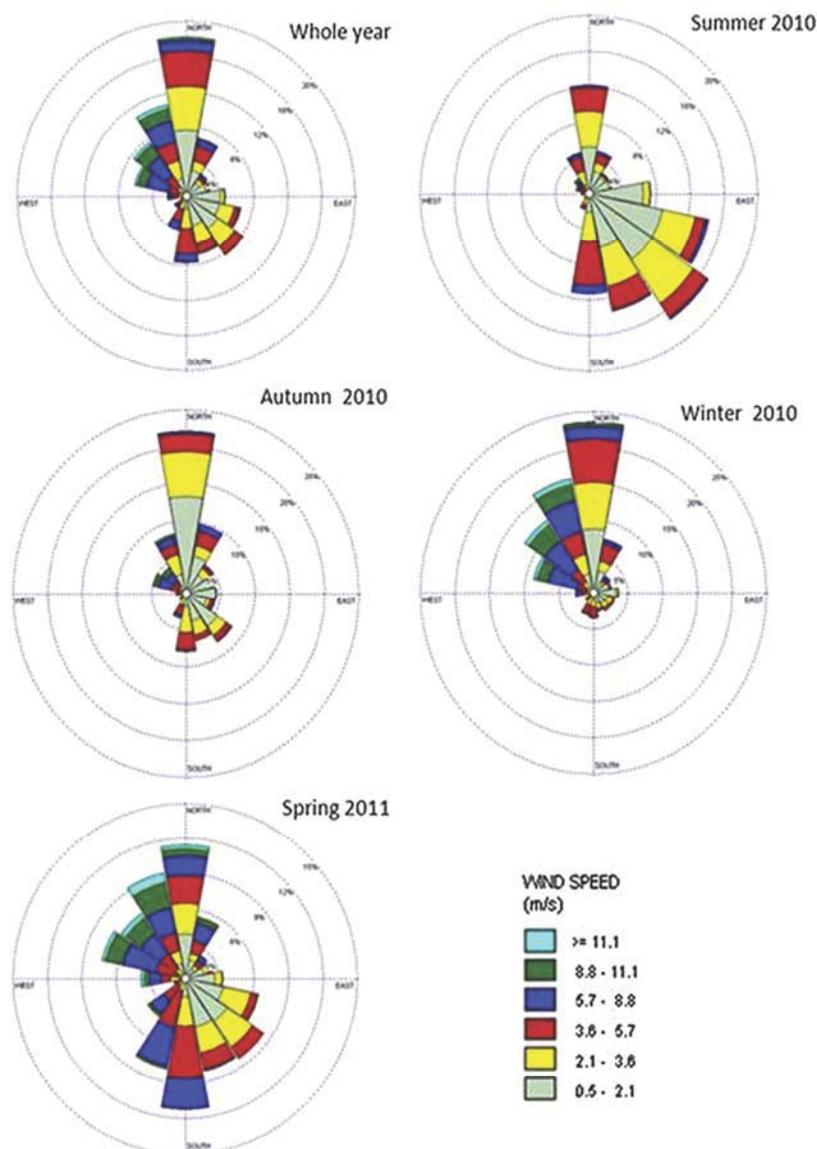


Fig. 7. Wind rose (WRPLOT View Freeware, Lakes Environmental, Canada) for PM₄ sampling at the CUGB, Beijing (data obtained from ZBAA) from half hourly mean data during different seasons.

Temperature had no significant correlation with PM₄ and most of its compounds except Cl⁻, all PAHs, Tm, 29ba and 30ba. Coal combustion for heating is one important source of Cl⁻ (Yao et al., 2002) and PAHs. Therefore, it was expected that the decrease in ambient temperatures may lead to the increase in coal combustion and increasing contribution from related emission constituents to PM in Beijing. On the other hand, stronger solar radiation accompanied by higher temperatures can accelerate the photochemical degradation of PAHs.

RH had a weakly positive correlation with PM₄ mass concentrations which indicated a high RH could favor the growth of the particles. This could be caused by hygroscopicity of particles which can lead to the increase in PM mass concentration. Especially, EC, NH₄⁺, SO₄²⁻, Zn, 31ab5 and levoglucosan were found to have a positive correlation with RH. EC contains char and soot (Han et al., 2009), and aged soot is hydrophilic (Niu et al., 2011).

Generally, wind speed had a negative correlation with PM₄ mass concentration and almost all compounds which supported that high wind speed could enhance the dispersion of pollutants. However in some cases, a high wind speed can also cause high PM mass concentration, such as a dust storm. Therefore, the threshold value of wind speed should be considered. In this study, this threshold cannot be determined because the influence on PM is often inferred from other meteorological parameters.

The MLH was found to have a negative correlation with PM₄ and most compounds which illustrated that a lower MLH could accelerate the accumulation of pollutants from local and regional sources.

Wind direction and precipitation are other two very important factors for influencing PM mass concentrations in Beijing. The wind conditions in this study are shown in Fig. 7. In spring, the prevailing wind directions were from the North, Northwest, South and Southeast. Therefore, dust storms which were from north and northwest can bring more particles into Beijing and then cause particularly higher PM concentrations in spring than in other seasons. In winter, the dominant wind direction was blown from the North and brought fresh air into Beijing, thus leading to PM₄ mass concentration during winter lower than during spring. In summer and autumn, the PM₄ concentration was relatively low because 59% and 30% of precipitation happened during these two seasons which can cause the wet deposition of particles leading to the decrease in PM mass concentration.

Visibility had negative correlations with all chemical compounds, especially strong negative correlations with PM, OC, EC, SO₄²⁻, NH₄⁺, Cu, Zn, Pb and levoglucosan, which meant visibility decreased with the increase in the PM mass concentration and is highly correlated with anthropogenic compounds. In addition, visibility was also significantly affected by RH (correlation coefficient R = -0.70).

5. Conclusions

The temporal variations of PM and its compounds were investigated and the results showed that the PM mass concentrations at the height for exposure of humans after the emission reduction measures during the Olympic Summer Games 2008 were still high with an average value of 83 μg m⁻³, which is much higher than annual average of Chinese Ambient Air Quality Standard for PM_{2.5} (Grade II: 35 μg m⁻³) (China State Environmental Protection Administration (SEPA), 2012). The influence of PM on human health is still serious.

The mass balance showed that OM and SNA were two major fractions of PM in Beijing during the whole year with the contribution of 41% and 25% to PM mass, respectively, which means anthropogenic PM is a very important part of the total PM.

Sources of PM were obtained by performing source apportionment, using PMF. They were industry, secondary nitrate formation, secondary sulfate formation, coal combustion, traffic, dust and biomass burning. These results were totally supported by the analysis of seasonal variation and characteristics of chemical species.

The seasonal variation of different sources points out the dominant source in each season: secondary sulfate formation, biomass burning contributions and secondary nitrate formation in summer, secondary nitrate formation in autumn, mineral dust in spring and coal combustion in winter. This is helpful for policy makers for the purpose of improving air quality according to the corresponding dominant PM source in each season.

Regional transportation can contribute significantly to the air pollution in Beijing. Backward trajectories, in combination with cluster analysis, demonstrated that the southerly air flow (S flow) is responsible for the high SNA and emission from the biomass burning and industry and it is the direction which transported the most PM to Beijing.

Meteorological parameters were the important factors influencing PM and its compound mass variations. In general, high relative humidity and low MLH can raise PM mass concentration, while high wind speed and precipitation can reduce pollutants. In addition, wind direction also plays a key role in influencing PM because different wind directions can bring different pollutants to Beijing from different regions.

Conflict of interest

There is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apr.2015.09.008>.

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