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Gravimetric analysis for $PM_{2.5}$ mass concentration based on year-round monitoring at an urban site in Beijing

Yanli Wang[1], *Wen Yang*[1], *Bin Han*[1], *Wenjie Zhang*[1], *Mindong Chen*[2], *Zhipeng Bai*[1,*]

1. *State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China. E-mail: wangyl@craes.org.cn*

2. *Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Nanjing University of Information Science & Technology, Nanjing 210044, China*

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ABSTRACT

Daily $PM_{2.5}$ (particulate matter with an aerodynamic diameter of below 2.5 μm) mass concentrations were measured by gravimetric analysis in Chinese Research Academy of Environmental Sciences (CRAES), in the northern part of the Beijing urban area, from December 2013 to April 2015. Two pairs of Teflon (T1/T2) and Quartz (Q1/Q2) samples were obtained, for a total number of 1352 valid filters. Results showed elevated pollution in Beijing, with an annual mean $PM_{2.5}$ mass concentration of 102 μg/m^3. According to the calculated $PM_{2.5}$ mass concentration, 50% of our sampling days were acceptable ($PM_{2.5}$ < 75 μg/m^3), 30% had slight/medium pollution (75–150 μg/m^3), and 7% had severe pollution (> 250 μg/m^3). Sampling interruption occurred frequently for the Teflon filter group (75%) in severe pollution periods, resulting in important data being missing. Further analysis showed that high $PM_{2.5}$ combined with high relative humidity (RH) gave rise to the interruptions. The seasonal variation of $PM_{2.5}$ was presented, with higher monthly average mass concentrations in winter (peak value in February, 422 μg/m^3), and lower in summer (7 μg/m^3 in June). From May to August, the typical summer period, least severe pollution events were observed, with high precipitation levels accelerating the process of wet deposition to remove $PM_{2.5}$. The case of February presented the most serious pollution, with monthly averaged $PM_{2.5}$ of 181 μg/m^3 and 32% of days with severe pollution. The abundance of $PM_{2.5}$ in winter could be related to increased coal consumption for heating needs.

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Introduction

To confront the unresolved pollution issue involving comparatively high densities of $PM_{2.5}$ (particulate matter with an aerodynamic diameter of below 2.5 μm), over the past few years, large numbers of studies on $PM_{2.5}$ were carried out in China. Among these studies, mass concentration has been one of the most commonly measured aerosol properties (He et al., 2001; Ye et al., 2003), and the most important one for health and environmental effects. There is a growing body of epidemiological data suggesting that elevated levels of $PM_{2.5}$ are associated with an array of human health hazards, such as lowered immune systems to aggravation of asthma or chronic coughs, even triggering heart attacks, which may cause a significant increase in human mortality (Koop and Tole 2006; Vedal et al., 2009).

* *Corresponding author*. E-mail: baizp@craes.org.cn (Zhipeng Bai).

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In response to the clamor of public health concern, the Ministry of Environmental Protection announced a new index standard, which includes the measurement of $PM_{2.5}$ and ozone. For over 3 years, China's environmental authorities have reported $PM_{2.5}$ to the public as the new key index for air quality (Pui et al., 2014; Shi et al., 2014). According to the Ambient Air Quality Standards (GB3095-2012), air quality monitoring of 74 cities/regions as the pioneer sites, including 3 key industrial regions (Beijing–Tianjin–Hebei region, Yangtze River Delta and Pearl River Delta), 4 municipalities and 27 provincial capitals, has been conducted since 2012. Among these, Beijing is of special concern, not only as the capital, but also because of its dense population and severe $PM_{2.5}$ pollution (Yuan et al., 2008).

Easing air pollution in China during its development phase is a massive systematic project; but first of all, accurate monitoring data on mass concentration is needed, before further analysis of chemical composition or any specific property can be carried out (He et al., 2001; Wang et al., 2002; Ye et al., 2003; Duan et al., 2006). True mass concentrations are the major basis for further calculations, such as of chemical compositions (including water-soluble ions, carbonaceous species and inorganic elements) and isotopic content (Ye et al., 2003; Yin et al., 2012; San et al., 2015; Wang et al., 2015).

There are numerous potential problems that may affect the calculation of $PM_{2.5}$ mass concentration (Feng et al., 2014; San et al., 2015), such as collection efficiency, stability of sampling flow rate, filter types, and weighing accuracy (Pui et al., 2014), among which the selection of a filter substrate is our specific concern. Teflon filters are chemically inactive and resistant, providing background levels of elements an order of magnitude lower than Quartz, and are thus recommended for gravimetric and elemental analyses by the interagency monitoring of protected visual environments (IMPROVE) program, after more than 25 years of modification and improvement (Pui et al., 2014). As the standard $PM_{2.5}$ measuring method, gravimetric measurement with Teflon filters as recommended was conducted national wide, and thus parallel comparisons were also carried out since $PM_{2.5}$ was listed as a criteria pollutant in the Chinese Ambient Air Quality Standard (Yin et al., 2012; Feng et al., 2014; Liu et al., 2014; Zhang et al., 2015).

Here in our study, the measurements were carried out with great caution, including regular calibration and cleaning. Weighing protocols were also developed to ensure comparability of the mass concentrations measured, with an automatic weighing system (using a high sensitivity electro-balance and strictly controlled temperature/relative humidity). Aiming to gain additional knowledge on gravimetric analysis, a careful investigation of year-round monitoring for $PM_{2.5}$ mass concentration was conducted, to grasp the true level and long term evolution of $PM_{2.5}$ in Beijing.

1. Methods

The observation site was located in the courtyard of Chinese Research Academy of Environmental Sciences (CRAES, 40°04′N, 116°42′E), at Lishuiqiao, South of Beiyuan Road (outside of the 5th ring), in the northern part of the Beijing urban area (Fig. 1). The sampling height was about 5 m above the ground. There are no large industrial pollution sources or tall buildings near the sampling site, which is representative of the typical urban environment in Beijing. More information can be found in a previous publication (Tao et al., 2015).

Fine particulate matter ($PM_{2.5}$) was collected daily in CRAES, during the period of December 2013 to April 2015. The aerosol sampler instruments were imported from Leckel (MVS6, Sven Leckel, Germany, conforming to European Standard), equipped with a $PM_{2.5}$ size-segregating impactor, operated at a flow rate of 38.3 L/min. To conduct a differential analysis of filter types, we chose two typical types, Quartz (Q, Whatman, England) and Teflon filters (T, Whatman, England), which are widely employed for the sampling of $PM_{2.5}$, both 47 mm in diameter. Four individual sampler instruments (Leckel), with filters for each group in parallel, were sorted as Teflon group (T1/T2) and Quartz group (Q1/Q2).

All 4 sampler instruments were set to run on sampling schedules of 23 hr, with nominal start times at 9:00 am to 8:00 am the next day. Prior to weighing and sampling, the Teflon filters were heated at 60°C for 0.5 hr, while the Quartz filters were baked at 800°C for 3 hr to remove any organic compounds that may be present on the filters. Filter blanks were assessed in the same manner as the loaded filters.

Before and after sampling, the empty or loaded filters were weighed twice by the same automatic weighing system (AWS-1, COMDE DERENDA, Germany, approved by European Standard) which is equipped with an electro-balance with sensitivity of 0.001 mg (WZA26-CW, Sartorius, Germany). Before this study, we carried out a thorough check of the AWS-1 to ensure the weighing accuracy. As humidity fluctuations may skew the filters' weights, our test evaluated the influence of temperature and relative humidity on aerosol mass concentrations, and determined the optimal parameters, with controlled temperature (20 ± 1°C) and humidity (50% ± 5%). The filters were equilibrated in the AWS-1 under that specific condition for at least 24 hr before the weighing process (He et al., 2001; Martuzevicius et al., 2004; Pui et al., 2014).

Meteorological parameters (temperature, relative humidity, and wind speed) were also obtained with a micrologger (CR21, Campbell Scientific, USA) at the same site. The 24 hr averaged relative humidity (RH) was calculated by averaging the raw data (with a time resolution of 30 min) according to the start and stop time of each sampling event. Daily reported online $PM_{2.5}$ mass concentrations and RH were gathered from the nearby Olympic Sports Center Monitoring Station (http://www.aqistudy.cn) and Weather Underground (http://www.wunderground) at the same time.

2. Results and discussion

With regular calibration to insure that ambient datasets meet with good quality assurance and quality control (QA/QC) standards, much attention was paid to instrument maintenance, background noise and basic signal analysis. A total number of 1352 normal samples were obtained, with 338 days of parallel T and Q groups. There were another 79 days, when the Q group samples were collected full time but the T group got interrupted, which could not be employed as valid samples. The

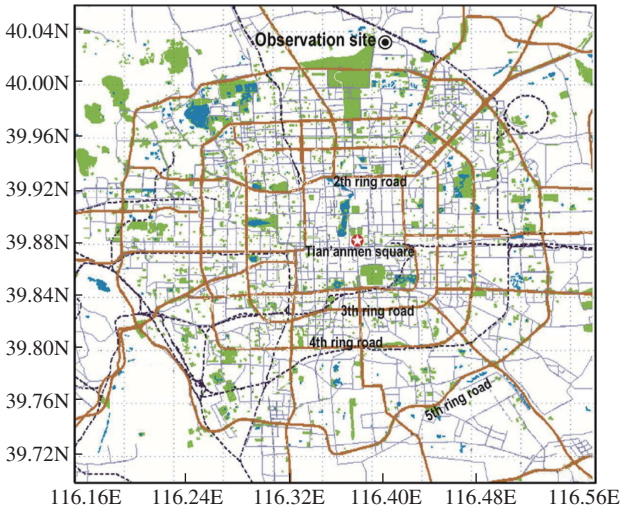

Fig. 1 – Map and location of observation site in Beijing.

sampling interruptions, with sampling time less than 18 hr or sampling volume less than 40 m^3 in standard state (San et al., 2015), may have been due to power outage or personnel interference, but disorderly shutdown happened much more frequently in the T group than the Q group, the reason for which deserved investigation.

The results showed that $PM_{2.5}$ in Beijing was nearly three times the interim target-2 standard for annual mean $PM_{2.5}$ recommended by the Ambient Air Quality Standards (GB3095-2012), with annual mean $PM_{2.5}$ mass concentration reaching 102 μg/m^3. In comparison with an earlier study of Beijing (Fig. 2), the year 2006 suffered more severe pollution; since then, the level of $PM_{2.5}$ has shown a slight decline (He et al., 2001; Zhao et al., 2009; Zhang et al., 2013). This study has demonstrated that the air quality of Beijing appears to be improving, as a series of control measures have been implemented (Liu et al., 2012). The energy source structure has been gradually changed by increased use of clean fuels and low-sulfur coal (Yuan et al., 2008). Emission control measures for vehicle exhausts were also adopted, such as implementation of new emission standards and conversion of diesel buses to compressed natural gas (Wu et al., 2015).

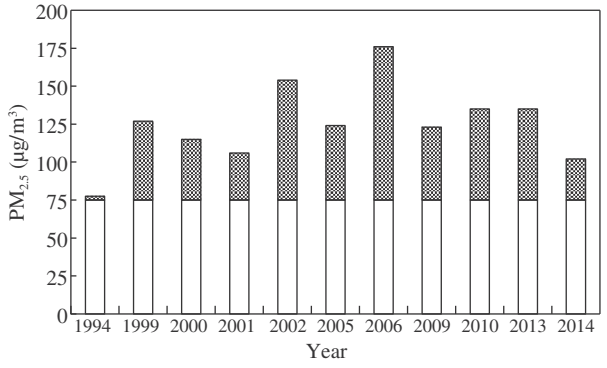

Fig. 2 – Historical monitoring data of $PM_{2.5}$ (particulate matter with an aerodynamic diameter of below 2.5 μm) in Beijing.

2.1. Analysis of sampling interruption

As sorted into 4 pollution levels, distribution analysis was conducted on all samples (Fig. 3a). The results showed that 50% of sampling days were acceptable (< 75 μg/m^3), 30% had slight/medium pollution (75–150 μg/m^3), 13% had serious pollution (150–250 μg/m^3) and 7% had severe pollution (>250 μg/m^3).

According to the detailed sampling record, the T group samples were sorted into three classes with sampling duration of 23, 18–23 and <18 hr, respectively. Most of the time, about 79%, the monitoring instrument of the T group obtained acceptable samples; another 3% had running time more than 18 hr but less than 23 hr, and the last 18% of samples were collected for less than 18 hr (Fig. 3b).

The samples with T interruptions were singled out for further check, and the distribution of pollution level was determined. As shown in Fig. 3b, all of the interruptions occurred on polluted days, with $PM_{2.5}$ exceeding the threshold of 75 μg/m^3, among which 26% occurred during severe pollution (>250 μg/m^3). There were 8 days encountering severe pollution during the last 6 months (from November 2014 to April 2015), and interruption occurred for 6 of these days. The dates of the other 2 with full time sampling were 27 December 2014 and 14 April 2015, with $PM_{2.5}$ mass concentrations of 255 and 318 μg/m^3 respectively; the latter one was recently reported as a sand storm.

To correlate with the pollution level, the RH of the corresponding dates were also divided into four grades, as 0%–40%, 40%–60%, 60%–80% and >80%. Fig. 3 shows the number and frequency of interruptions, in each category of RH and $PM_{2.5}$ pollution level. A noticeable feature was that the interruptions mainly followed the pattern of $PM_{2.5}$ level (Fig. 4). Under the same RH, severe $PM_{2.5}$ pollution led to higher frequency of interruption.

Because of the hygroscopicity of fine particles, the measured mass may include particle-bound water. Furthermore, hygroscopicity has been demonstrated to be a key factor regulating the cloud condensation nuclei activity of aerosol (Cheng et al., 2015); thus, high RH could enhance the formation of secondary components, which was responsible for the $PM_{2.5}$ episodes. Laboratory experiments have demonstrated that the gas precursors and water-soluble organic matter (OM) were likely to become more reactive with high RH and form water-soluble particles (Favez et al., 2008). Both the sulfur and nitrogen oxidation ratios have been shown to correlate strongly with RH (Sun et al., 2006; Cheng et al., 2015).

Previous studies found that the airflow velocity decreased with increasing loaded particle mass on the filter, and high $PM_{2.5}$ combined with high RH gave rise to a thicker particle cake formed on the filter, which blocked Teflon filters (Malm et al., 2011; Liu et al., 2014). To unravel the complex issue of filter-promoted reactions during sampling of $PM_{2.5}$, our further analysis investigated the effects of filtration velocity, particle size distribution, and loaded particle mass on the extent of evaporation loss during sampling.

2.2. Correlation of T and Q data

To insure an accurate interpretation of $PM_{2.5}$ levels, we performed diagnostics and parallelism checks on the data before any analysis (Zheng et al., 2005). After elimination of

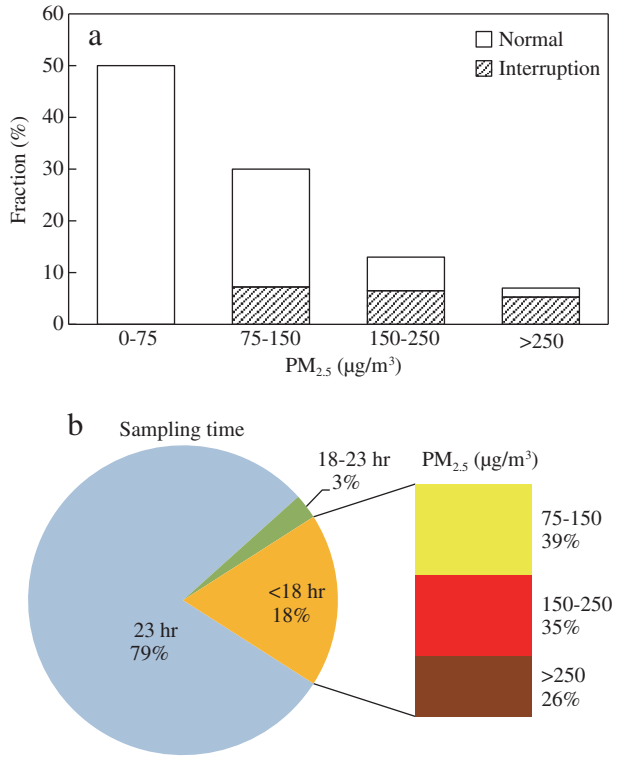

Fig. 3 – (a) Distribution of normal and interruption samples and (b) statistical analysis of Teflon filters' sampling time.

samples with interruptions, 338 parallel samples for each group of T and Q filters were counted. Correlation of T and Q samples showed that the data could be grouped in four different ranges of RH (Fig. 5), and that the T/Q ratio was not a fixed value, but exhibited variations.

By comparing the results, we derived linear parameters in a simple dose–response function. The most positive correlation between T and Q was found in RH > 80%, with $y = 0.99\ x$ and $R^2 = 0.97$, while the group of RH < 40% had $y = 1.00\ x$ and $R^2 = 0.93$. As RH increased, in the range of 40%-60%, the Q group showed a slightly higher $PM_{2.5}$ mass concentration than the T group, with $y = 0.98\ x$ and $R^2 = 0.84$. With RH in the range of 60%-80%, the T/Q showed an opposite discrepancy, with $y = 1.02\ x$ and $R^2 = 0.89$; most of the T interruptions fell into this section. The T group data could then be complemented using the slope of the linear regression and the correlation coefficient, as sorted into specific ranges of RH. In view of the good agreement between T and Q groups, it is desirable to perform parallel measurements on Quartz filters at the same time, to better determine the true mass concentration of $PM_{2.5}$ when interruption of data collection on Teflon filters occurs.

2.3. Pollution level distribution

Ranges, means and associated standard deviations for the ambient $PM_{2.5}$ mass concentrations, as divided into four seasons, are given in Table 1.

Taking the T group as an example, it is shown clearly in Table 1 that the $PM_{2.5}$ mass concentrations were higher in winter (113 ± 92 μg/m^3) than in summer (75 ± 40 μg/m^3), with the peak value in February (422 μg/m^3) and lowest value in June (7 μg/m^3).

To investigate the distribution of $PM_{2.5}$ pollution level based on daily average values, 4 categories were established with reference to the classification standards of China Environmental Monitoring Stations, which are acceptable

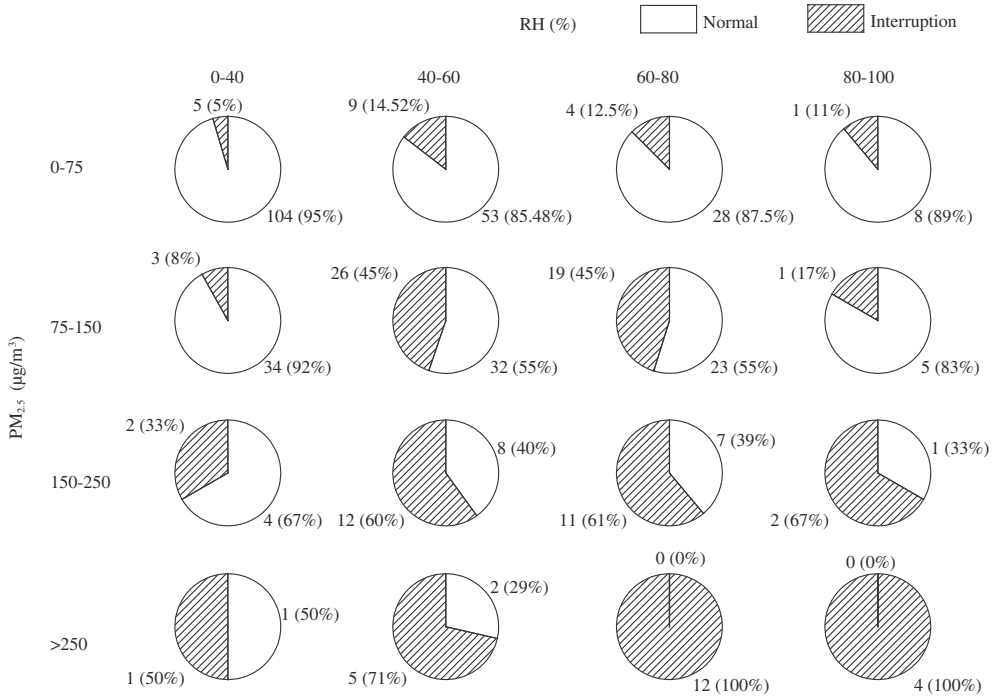

Fig. 4 – Frequency of interruption in each category of relative humidity (RH) and $PM_{2.5}$. Numbers in pie plots refer to interruption time, and the numbers in bracket refer to the percentage of interruption to overall sampling.

day (<75 μg/m^3), slight/medium pollution (75–150 μg/m^3), serious pollution (150–250 μg/m^3) and severe pollution (>250 μg/m^3). Here the normal samples of the T group were analyzed for temporal evolution.

The monthly distribution of pollution level (Fig. 6) showed that from May to August, the typical summer period, least severe pollution events were observed, with high precipitation levels accelerating the process of wet deposition to remove $PM_{2.5}$. The case of February presented the most serious pollution, with monthly averaged $PM_{2.5}$ of 181 μg/m^3 and 32% of the days having severe pollution. The abundance of $PM_{2.5}$ in winter could be related to changes in emission patterns, such as increased coal consumption for heating needs. Moreover, during the Chinese New Year period (from 30th January 2014 to 14th February 2014), a large amount of fireworks were set off, which might also contribute (Kong et al., 2015).

In addition, meteorological factors, such as ambient temperature, may affect the temperature-dependent partition between gaseous and aerosol phases, as well as thermal and photochemical reactions in the atmosphere. Particle matters are accumulated continuously because the atmospheric boundary layer becomes more stable (Silkoff et al., 2005; Wang et al., 2008). The decrease in ground temperature in winter, along with the lower atmospheric mixing heights, favored the transfer of more available nitric acid to the particulate phase after reaction with ammonia to form ammonium nitrate (Pu et al., 2011; Tiwari et al., 2015). By contrast, owing to the higher temperature, it remains mostly in the gas phase as nitric acid vapor in summer (Zhao et al., 2009).

3. Conclusions and suggestions

As the standard measurement method, gravimetric analysis was conducted in CRAES throughout almost one and half years. With two pairs each of Teflon and Quartz filters, and 338 days of valid sampling, a total number of 1352 filters were obtained for $PM_{2.5}$ mass concentration measurements. There were another 79 days when Q group samples were collected full time but the T group experienced interruptions. Strict data analysis was carried out to insure accurate interpretation of $PM_{2.5}$, and the key outcomes of this study can be summarized as follows:

(1) The results showed that $PM_{2.5}$ in Beijing was nearly three times the interim target-2 standard for annual mean $PM_{2.5}$ recommended by the Ambient Air Quality Standards (GB3095-2012), with annual mean reaching 102 μg/m^3. However, in comparison with earlier studies, the pollution level of $PM_{2.5}$ showed a slight decline. According to the calculated $PM_{2.5}$ mass concentration, 50% of our sampling days were acceptable ($PM_{2.5}$ < 75 μg/m^3), 30% had slight/medium pollution (75–150 μg/m^3), 13% had serious pollution (150–250 μg/m^3) and 7% had severe pollution (>250 μg/m^3).

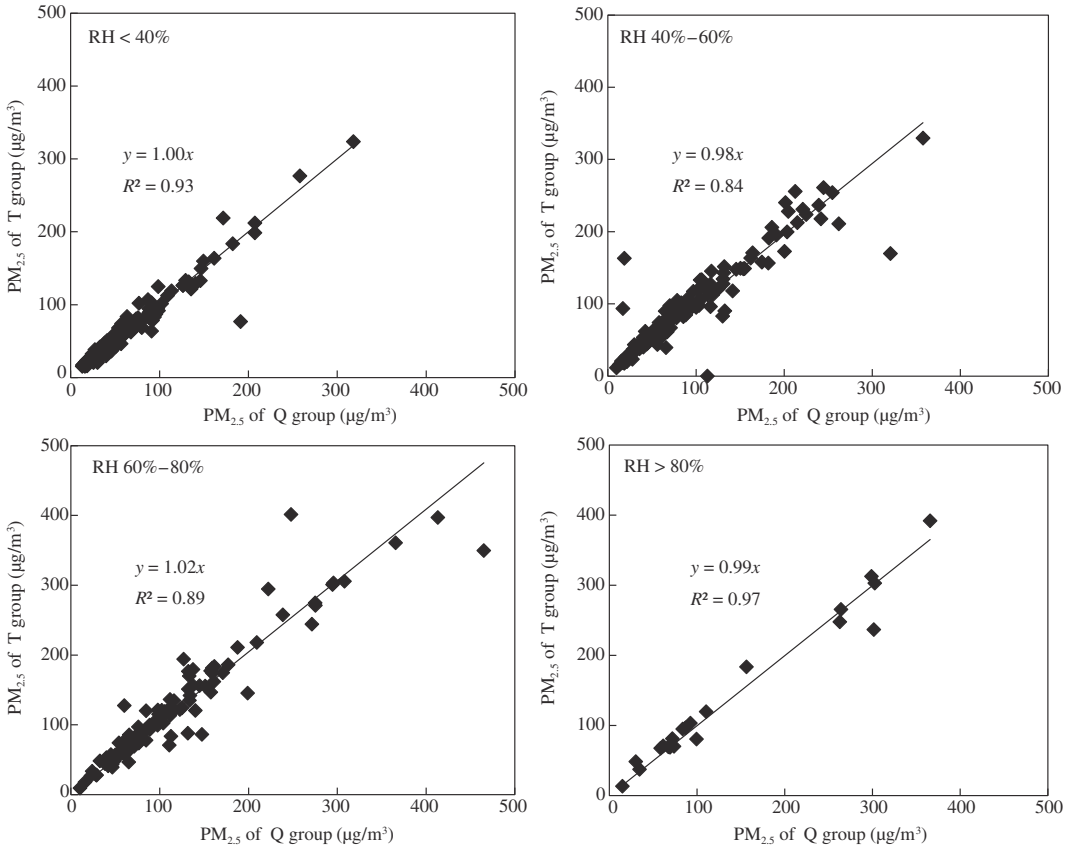

Fig. 5 – Correlation analysis of Teflon (T) group and Quartz (Q) group in different ranges of RH.

Table 1 – Statistical summary of $PM_{2.5}$ mass concentrations (units: μg/m³).

	$PM_{2.5}$	Teflon group	Quartz group	Reported data
Annual	Ranges	10–413	12–422	5–401
	Means (±SD)	104 ± 71	105 ± 76	96 ± 73
Spring	Ranges	18–358	18–366	10–288
	Means (±SD)	93 ± 65	92 ± 67	86 ± 58
Summer	Ranges	10–213	11–217	11–213
	Means (±SD)	75 ± 40	78 ± 42	75 ± 48
Autumn	Ranges	13–366	12–374	5–343
	Means (±SD)	102 ± 87	105 ± 89	94 ± 77
Winter	Ranges	15–413	16–422	15–401
	Means (±SD)	113 ± 92	117 ± 94	112 ± 86

$PM_{2.5}$: particulate matter with an aerodynamic diameter of below 2.5 μm; SD: standard deviation.

(2) As recommended for gravimetric analyses, Teflon filters were reliable most of the time, but often failed under heavy load, with running time less than 18 hr. All of the interruptions took place during polluted days, with $PM_{2.5}$ exceeding the threshold of 75 μg/m³, among which 26% were during severe pollution (>250 μg/m³).

(3) Positive relationship between our gravimetric analysis data and the daily reported online $PM_{2.5}$ was found, and seasonal variation of $PM_{2.5}$ showed higher values in winter, lower in summer. From May to August, the typical summer period, the least severe pollution events were observed, with high precipitation levels accelerating the process of wet deposition to remove $PM_{2.5}$. The abundance of $PM_{2.5}$ in winter could be related to increased coal consumption for heating needs.

Since high $PM_{2.5}$ mass concentrations associated with high RH might bring about T interruption, it is suggested that shorter sampling time segments be set during heavy polluted periods. In addition, close monitoring of instruments is necessary, so that once an interruption occurs, a fresh Teflon filter can be installed. The true $PM_{2.5}$ mass concentrations then may be determined using the sum of the weight increases on the filters and the known volume of ambient air. In view of the good agreement found between the T and Q groups, it is desirable to perform parallel measurements on Quartz filters at the same time, to help determine the true mass concentration of $PM_{2.5}$ when interruption of data collection on Teflon filters occurs.

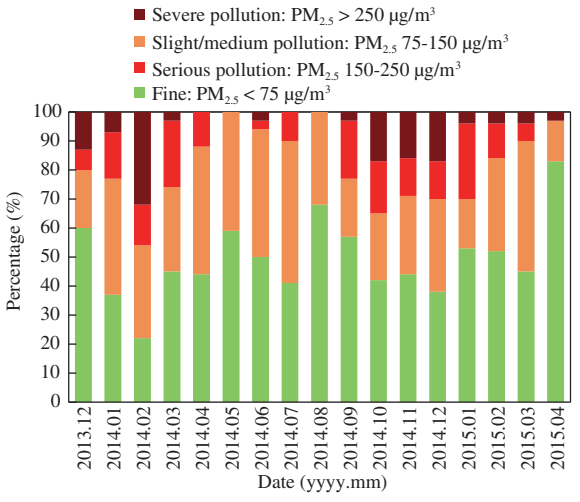

Fig. 6 – Pollution level distribution of each month during December 2013 and April 2015.

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