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Concentrations of total arsenic and arsenic species in $PM_{2.5}$ in Nanjing, China: spatial variations and influences of local emission sources

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Abstract

The aim of this study was to assess the spatial variation in the concentrations of total arsenic (As_{total}), arsenite (As(III)), arsenate (As(V)), monomethylarsonic acid (MMAs(V)), and dimethylarsinic acid (DMAs(V)) in fine particulate matter ($PM_{2.5}$) and to explore the influence of local emission sources based on the monitoring data from 18 sampling sites in Nanjing, China. The results showed that the average concentration of As_{total} in the $PM_{2.5}$ was 6.81 ng/m^3 in Nanjing, which exceeded the standard limit of 6 ng/m^3 in China. As(V) was the dominant species and varied between 71 and 81% of water-extractible As in the $PM_{2.5}$. The results of the spatial variation coefficients (CVs) showed that As_{total}, As(III), and As(V) displayed moderate levels of spatial heterogeneity (CV = 0.23), while DMAs(V) a considerably high level (CV = 0.60). The concentrations of As_{total} and As species can be arranged in the following order: urban background ~ urban street < suburban < rural < industrial sampling sites. This pattern was connected to the influence of three local emission sources (industrial source, road traffic, and biovolatilization), which were quantified by multiple linear regression. Results showed that local road traffic sources had the smallest value of standardized regression coefficient (0.26) among these three sources, indicating that local road traffic sources contributed less to the concentration of As in $PM_{2.5}$ than industrial source emissions and biovolatilization. Our findings indicate that the spatial heterogeneity of As species should be considered in exposure assessments and As biovolatilization is linked to the high heterogeneity.

Keywords Arsenic · Particulate matter · Metalloid · Chemical speciation · Source

Capsule: The level of spatial heterogeneity was moderate for As_{total}, As(III) and As(V) and was considerably high for DMAs(V).

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Introduction

Spatial variations are the extent to which the concentrations that are measured at multiple spatial locations vary over a sampling area (US EPA 1997). Understanding the spatial variations in chemical components of airborne particle matter with an aerodynamic diameter of less than or equal to 2.5 μm ($PM_{2.5}$) is critical (Minguillón et al. 2014) because inadequate consideration of spatial variations can lead to exposure misclassification in epidemiological and exposure studies (Pinto et al. 2004). Among the components of particle matter, arsenic (As) has generated considerable research interest because it is considered the most toxic metal(loid) to health worldwide (IARC 2017). Humans are exposed to As via three main pathways: drinking water, food, and inhalation (Wang et al. 2014). Arsenic pollution in groundwater has been a serious health threat to the public human in parts of the world (Wang et al. 2014). Compared with drinking As-contaminated water, contact with ambient air may involve more areas and larger populations, because As biovolatilization process which is a widespread phenomenon can release stable volatile As species into the atmosphere (Jakob et al. 2010) and thus enables As transferring via the atmosphere (Wang et al. 2014).

The cancer risk caused by total arsenic (As_{total}) in $PM_{2.5}$ is not negligible (Li et al. 2015). However, measuring only As_{total} is not sufficient to characterize human health risks because the toxicity of As is determined by its chemical form: arsine (AsH_3) is the most toxic form, followed by water-soluble As (inorganic species as arsenite (As(III)) and arsenate (As(V)) > organic compounds). Arsenic in the air is mainly found in atmospheric particulate matter with As(V) as the predominant species accompanied by a small amount of organic compounds, including trimethylarsine oxide (TMAs(V)O), dimethylarsinic acid (DMAs(V)), and monomethylarsonic acid (MMAs(V)) (Hughes et al. 2011; Sánchez de la Campa et al. 2008; Tziaras et al. 2015). Moreover, the more toxic inorganic species are more distributed in $PM_{2.5}$ (Lewis et al. 2012).

However, these studies collected only airborne particle samples at one or two sampling sites or at one type of sampling site (e.g., urban, industrial, rural sites) and cannot provide sufficient information to assess the spatial variation in As species (Lewis et al. 2012). A study in the European region demonstrated that the As_{total} levels in total suspended particulate (TSP) matter can be arranged in the following order: certain industrial >> traffic ~ urban > rural >> remote sites (EC 2000). However, this study did not discuss the reasons for this spatial trend, and the unexpectedly high levels of several rural sampling sites were not well explained.

To better explain these issues, it is necessary to combine the local emission sources of As because the concentration of As in the atmosphere is affected by the degree of local pollution (Sarkar and Paul 2016). Local emission sources with an influence scale from micro (~ 10 m) to urban (~ 5 to 50 km) scales are important for within-city variability of $PM_{2.5}$ and its constituents (Pinto et al. 2004), while long-range transport of pollutants can result in spatial homogeneity across city areas (Yadav 2013). Sources of As in the atmosphere include anthropogenic and natural sources (Chen et al. 2016). Industrial emissions (especially, coal consumption, nonferrous metal smelting, and non-metallic minerals manufacturing) are the major anthropogenic sources of atmospheric As in China (Wang et al. 2015). The biological volatilization process occurring in water/soil/sediment is a natural source of widespread As in the atmosphere (Faust et al. 2016; Jakob et al. 2010). This process can generate volatile As species, including AsH_3 and methylarsines (mono-, di-, and trimethylarsine), which can then be converted into their respective nonvolatile, oxidized compounds, e.g., AsH_3 to As(III) or As(V) and dimethylarsine (Me_2AsH) to DMAs(V) (Faust et al. 2016; Mestrot et al. 2013; Jakob et al. 2010). These oxidized compounds are water-soluble and can be adsorbed onto particulate matter; thus, As, especially organic species in particulate matter, are attributed to biovolatilization (Savage et al. 2019).

Multiple linear regression, typically land use regression (LUR), is a method that can link local emission sources to spatial variations. LUR has been increasingly used to model the spatial distribution of air pollutants (Gulliver et al. 2018; Zhang et al. 2015). Dependent variables of LUR models include the concentrations of air pollutants, which are obtained from a number of purpose-designed monitoring sites and thus represent the spatial variation in pollutants. Expected pollutant sources, mainly local traffic and other land use–correlated sources within the study area, have been indirectly characterized in LUR models as independent variables, which can be obtained by geospatial analysis (Gulliver et al. 2018; Zhang et al. 2015). By using the standardized regression coefficients of independent variables that represent the local emission sources in LUR models, the relative importance of the emission sources with regard to the concentrations can be assessed (Zhang et al. 2015).

In this work, we present the temporal variation and descriptive statistics of the concentrations of As and As species in $PM_{2.5}$ samples collected at eighteen sites (including industrial, rural, suburb, urban background, and urban street sites) in Nanjing, China. Then, the spatial variation coefficients are used to assess the spatial variation in the As_{total} and As species. The independent variables, which are related to local industrial point sources, local road traffic and As biovolatilization (farmland and water bodies), are extracted using GIS methods. Multiple linear regression models that use these spatial variables as independent variables are constructed. The influence of local emission sources on the concentrations across the study area is quantified using the standardized regression coefficients and relative importance of the independent variables. The purpose of this study is to assess the spatial variation in the concentrations of As_{total} and As species in $PM_{2.5}$ and explore the influence of local emission sources on the concentrations across the study area.

Study area and methods

Study area

Nanjing is the capital of Jiangsu Province, China (Fig. 1). It is the second largest city in the East China region, with an area of approximately 6600 km^2 and a population of approximately 8.3 million. It is the main transportation hub in the Yangtze River Delta. It is also an important industrial area of petrochemical, iron and steel, and power production, and the locations of the important industry with large air pollutant emissions are shown in Fig. 1. Nanjing is characterized by a subtropical monsoon climate, and the wind direction is predominantly southeast in summer and northwest in winter. Its

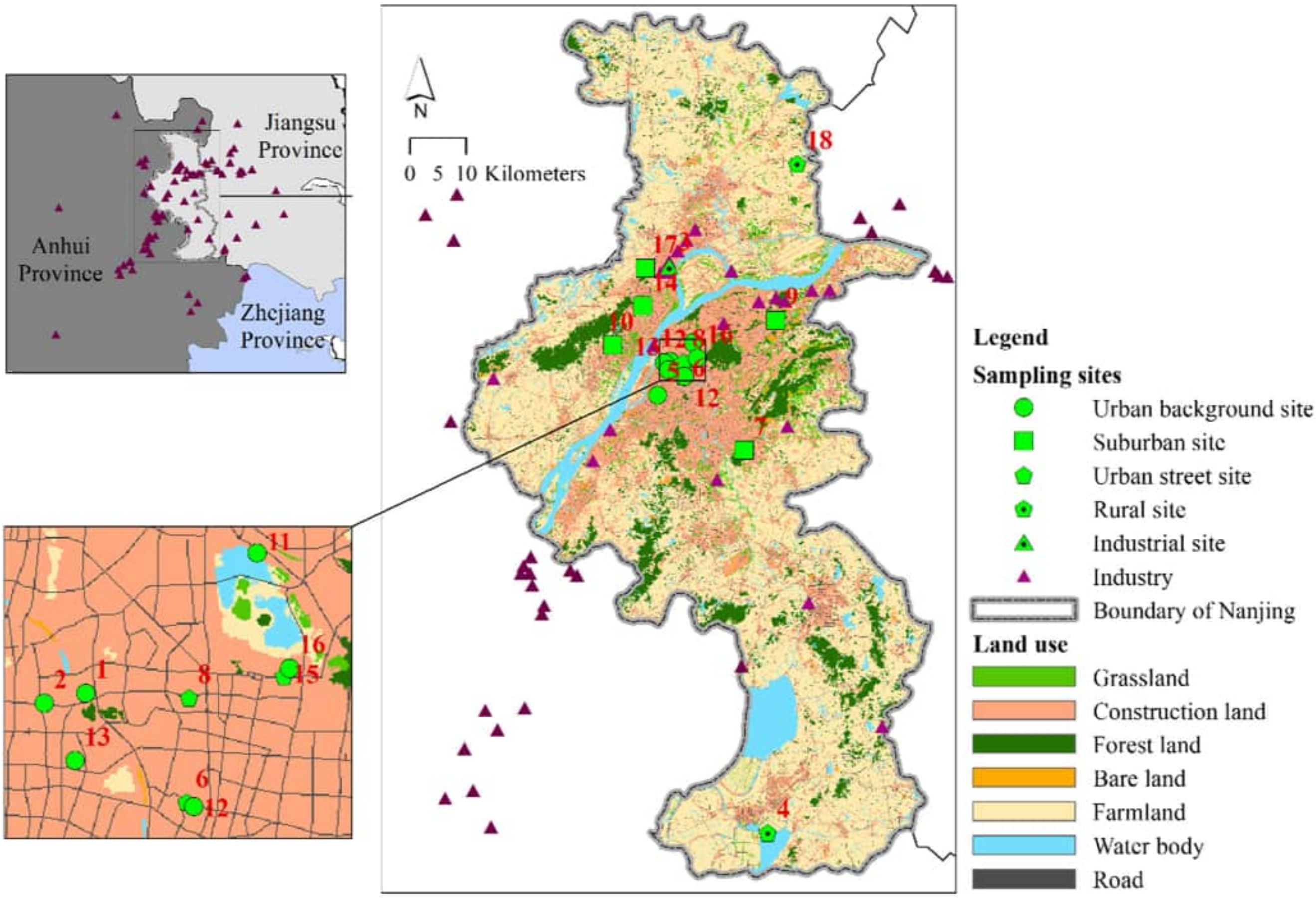

Fig. 1 Study area, sampling sites numbered from 1 to 18, and industrial source distribution

average annual precipitation is 1106 mm, and its average annual temperature is 15.4 °C. More meteorological factors are listed in Table S1 in the Supplementary Information (SI).

Sample collection

A purpose-designed monitoring method is adopted based on the previous LUR studies (Gulliver et al. 2018; Zhang et al. 2015). $PM_{2.5}$ samples were collected at eighteen sampling sites in Nanjing (Fig. 1) between summer 2016 and spring 2017 (Table S2 and Table S3) to assess the spatial variation in the As_{total} and As species. These sites included one industrial site, two rural sites, five suburban sites, three street sites, and seven urban background sites (details provided in the SI). Due to the availability of the sampling equipment, a maximum of six sites were monitored concurrently, and one urban background site was used as a reference site, which was operated continuously throughout the sampling schedule. The reference site (numbered 1 in Fig. 1) was a national air pollutant monitoring site (urban background site) with fewer than 3000 vehicles per day passing within a 50-m radius. It was carefully selected to ensure that the selected site was not subjected to local emission sources. More details of the site can be found in Table S2. Samples were collected from each site for a 2-week period in each season, and an interval sampling method was used. Medium-flow (100 L/min) atmospheric particulate samplers (Qingdao Xuyu, XY-2200) were applied to collect $PM_{2.5}$ samples using 90-mm quartz filters (Whatman, 1851-090). A total of 87 samples were obtained. The samples were stored at − 20 °C in a refrigerator prior to chemical analyses. More detailed information on the sample collection can be found in the SI.

Chemical analyses

Sample treatment and analysis for As_{total} in $PM_{2.5}$ samples

A HNO_3:H_2O_2 mixture microwave assistant method was applied to digest the samples to determine the As_{total} in $PM_{2.5}$ (Hu et al. 2012). Inductively coupled plasma mass spectrometry (ICP-MS) was used for the As_{total} determination because it has low detection limits while providing the capability of multi-elemental analysis. Briefly, ¼ sections of the filters were cut. The filters were extracted in Teflon tubes by adding 5 mL HNO_3 (69%) and 1 mL H_2O_2 (30%) and subsequent microwave digestion (25 min at 190 °C). After cooling, the digestion solutions were filtered through 0.22-μm syringe filters, diluted to 25 mL with ultrapure deionized water, and then stored at 4 °C and analyzed within 48 h. Before analysis, 1 mL of the solutions was diluted 10-fold and analyzed using an XSeries2 ICP-MS (Thermo Fisher Scientific, Waltham, USA).

The QA/QC of the analytical process regarding As_{total} was estimated by analyzing the certified reference material NIST SRM 1648a (urban particulate matter). Briefly, 10 mg of the reference material was added to a ¼ portion of a blank filter, which was submitted to the same chemical treatment and analysis as that used for the samples. The determined As_{total} concentration was within 90% of the certified value. Blank filters were also analyzed, and the concentration of As_{total} was below the low detection limits.

Sample treatment and analysis for As chemical speciation in $PM_{2.5}$ samples

As(III), As(V), DMAs(V), and MMAs(V) in $PM_{2.5}$ samples were extracted with a similar procedure as that described in (Tziaras et al. 2015) by ultrasonication with ultrapure deionized water at 50 °C. The As species were detected by coupling a 1260 infinity HPLC system (Agilent Technologies, Santa Clara, USA) to a 7700x ICP-MS (Agilent Technologies, Santa Clara, USA), which is similar to the method used by Jakob et al. (2010). Briefly, a ¼ section of the filter was cut and placed into centrifuge tubes and extracted using 10 mL of ultrapure deionized water. The tubes were sealed tightly and ultrasonicated for 1 h at 50 °C, and then the extracts were moved to another tube. These procedures were repeated twice. Afterward, the extracts were filtered through 0.45-μm syringe filters, kept in capped 2-mL chromatographic vials, and then stored at 4 °C and analyzed within 48 h (Tziaras et al. 2015). An anion-exchange column (Hamilton PRP-X100, 250 × 4.1 mm, pore size of 10 μm) was used in the HPLC system. The mobile phase was a mixture of 25 mM $NH_4H_2PO_4$ and 2% (v/v) methanol, adjusted to pH 8 using aqueous ammonia. The flow rate was 1 mL/min, and the sample volume was 100 μL. External calibration solutions containing As (0.5 to 50 ng/mL) as As(III), DMAs(V), MMAs(V), and As(V) were prepared. Arsenic species in the samples were identified by comparing their chromatographic peak retention time with those of the standards and quantified by external calibration curves with peak areas.

For quality control purposes, several different approaches were followed. The extraction efficiency was calculated as the sum of the As species concentrations to the As_{total} concentration (Tanda et al. 2019; Tziaras et al. 2015). The mean extraction efficiency for As was determined to be 72 ± 16% ($n = 93$). Currently, there are no CRMs with certified As species in PM. Therefore, the trueness of the methods was evaluated by adding mixed standards of As(III), As(V), DMAs(V), and MMAs(V) with concentrations of 2 and 10 ng/mL to ¼ portions of the blank filters. The determined concentrations of As species were 90–110% of the added concentrations. In addition, filter blanks were processed and analyzed in parallel with the samples, and As species were not detected. Limits of detection (LODs) of the employed method were calculated using the US EPA method (details provided in the SI). Limits of detection were 0.07 ng/m^3 for As(III), 0.03 ng/m^3 for DMAs(V), 0.04 ng/m^3 for MMA, and 0.04 ng/m^3 for As(V).

Annual average concentration calculations

The four 2-week samples were used to calculate the annual average concentrations of the As_{total} and As species at each site, which were then used to measure the spatial variation. As mentioned in the "Sample collection" section, the samples were not concurrently collected at all sites; as a result, the arithmetic average of the concentrations in the four sampling periods reflected both the spatial and the temporal variation over the measurement period if the temporal variation was substantial. Therefore, adjusting for the temporal variation was critical for characterizing only the spatial variation. The reference site was used to adjust the temporal variation by the difference method (details provided in the SI), as has been described earlier in LUR studies (Gulliver et al. 2018; Zhang et al. 2015). For comparison with the difference method, the annual averages were also computed by a ratio method (Hoek et al. 2002). We assessed the precision of the annual average concentrations by the standard error of the mean (SEM), as described in Hoek et al. (2002).

Spatial variables representing local emission sources

We assessed the influences of emission sources on concentrations based on the results of multiple linear regression models. In this study, local emission sources were operationally defined as sources within the study area. The spatial variables that were used to represent the local emission sources were extracted and then used as independent variables of multiple linear regression models in accordance with LUR studies (Zhang et al. 2015). We generated 36 variables in 3 categories at different circular buffer radii around each sampling site (Table S4). These categories, characterizing major contributors to atmospheric As in the study area, included industrial point sources, road networks, and biovolatilization sources, which were indirectly represented by farmland and water bodies because biovolatilization may occur in water/soil/sediment (Mestrot et al. 2013). Each independent variable was first given an expected sign of the regression coefficient (i.e., positive or negative). The details of the data input and GIS methods used to extract these spatial variables can be found in the SI.

Statistical analysis

The spatial coefficient of variation (CV) was used to measure the spatial variation of the concentrations, which was the same as the method used by He et al. (2017). The CVs of the temporal adjusted annual average concentrations from the 18 sampling sites in the study area were calculated for As_{total} and each As species, as shown in Equation (1):

$$CV = \frac{SD}{\overline{x}} \quad (1)$$

where SD and $\overline{x}$ are the standard deviation and the mean of the temporally adjusted annual average concentrations from the 18 sampling sites, respectively.

Multiple linear regression was applied to explore the influence of local emission sources on the concentrations. The annual average concentrations of As_{total} and the individual As species in $PM_{2.5}$ were used as dependent variables. A normal distribution of the dependent variables was ascertained using the Shapiro-Wilks test and QQ plots, and non-normally distributed dependent variables were logarithmically transformed before regression. Principal component analysis (PCA) and varimax rotation were used to construct multiple linear regression models based on Abdul-Wahab et al. (2005). We added the following step following the procedures of Abdul-Wahab et al.: conduct linear regression with each spatial variable to rule out the spatial variables that were inconsistent with the expected sign of the regression coefficient shown in Table S4. More details on these methods can be found in Abdul-Wahab et al. (2005).

The influence of each type of local emission source on the concentration was quantified as the relative importance of the independent variable representing each source type in the multiple linear regression models. The relative importance was measured by the standardized coefficient of the regression models and the LMG metric recommended by Grömping (2015).

All of the statistical analyses were conducted using RStudio software, mainly using the functionalities of the "psych" package for PCA and "relaimpo" for the calculation of the LMG metric.

Results and discussion

Temporal variation

As expected, the temporal variation was substantial, as shown in Fig. 2. DMAs(V) was detected only in summer samples (Fig. 2). As(III) had a significant positive correlation with DMAs(V) (Table S5), and therefore, it also had the highest concentration in summer. The ratio of As(III) to As(V) (As(III)/As(V)) had the highest value in the rainy season of Nanjing (summer) (Fig. 2). This is linked with As(V) concentration decrease in rainfall which may produce a preferential dissolution of As(V) (Sánchez de la Campa et al. 2008). The substantial seasonal variation indicates the need for a temporal adjustment to remove the effects of time variations. The Pearson's correlation coefficients between the unadjusted and adjusted averages with the difference and ratio methods were between 0.68 and 0.91, respectively (Table S5). The precision of the annual averages that were measured by the SEM was improved by both adjustment methods, especially for As(V) and $PM_{2.5}$, and the difference method resulted in a slightly better precision than that obtained using the ratio method (Table S6), which is similar to the results of Hoek et al. (2002). Therefore, the annual average concentrations calculated by the difference method were adopted in this study unless otherwise stated.

Descriptive statistics of As_{total} and As species in $PM_{2.5}$

Descriptive statistics for the annual average concentrations of the 18 sampling sites are displayed in Table 1. The average concentration of As_{total} was 6.81 ± 2.18 ng/m^3, which exceeded the standard limit of As_{total} (6 ng/m^3) set by the Ambient Air Quality Standard in China (GB3095-2012). This result indicates that there is $PM_{2.5}$ As pollution in Nanjing, and the public may face certain exposure risks to As. The concentrations of As_{total} and As species were compared with the previous studies at the same sites and sites of other cities (Table S7). The comparison results with the same sites showed that the As_{total} concentrations in spring were similar to Li et al. (2015); the annual averages were smaller than those of Li et al. (2016) and larger than Leng et al. (2018). The differences may be related to the temporal variation in the concentrations because the sampling periods of these studies were not exactly the same. The As_{total} concentration was lower than these that measured in two Northern cites of China (Taiyuan and Baoding) where coal is the main energy source (Liu et al. 2020; Xie et al. 2019) and was higher than Lagos (Nigeria) (Alani et al. 2019) and New York (Schachter et al. 2016). The annual averages of As(III) and As(V) were lower than an industrial site in Spain (Sánchez de la Campa et al. 2008) and higher than an urban traffic site of Poland (Widziewicz et al. 2016).

The results of As chemical speciation in $PM_{2.5}$ samples showed that the concentrations of MMAs(V) in all samples were below the LOD (0.04 ng/m^3). The average concentrations of As(III), As(V), and DMAs(V) at all sites were 1.01 ± 0.23 ng/m^3, 3.21 ± 0.75 ng/m^3, and 0.04 ± 0.02 ng/m^3, respectively, and the As(III) / As(V) ratio was 0.32 ± 0.05 (Table 1).

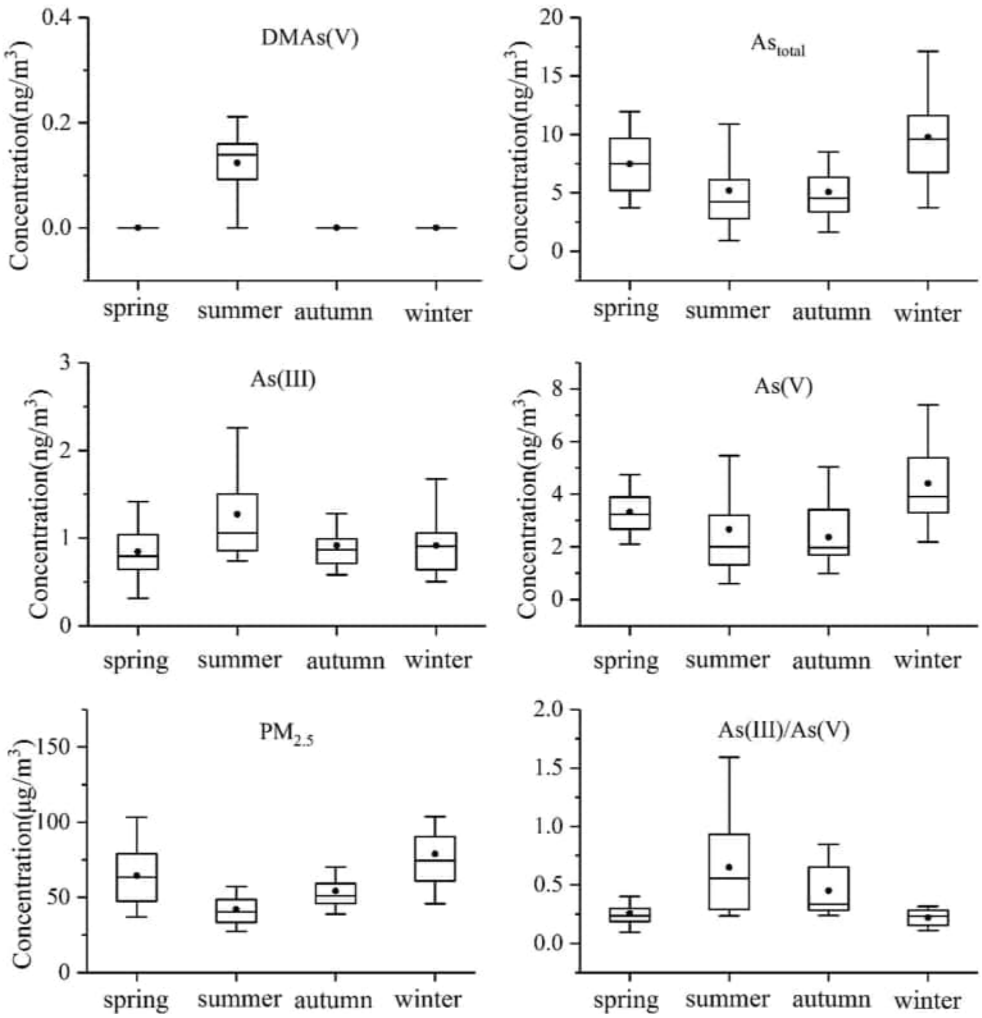

Fig. 2 Seasonal variations in As_{total}, As species, and $PM_{2.5}$ and the ratio of As(III) to As(V) (As(III)/As(V))

These results are in agreement with the results obtained in the previous studies, which suggested that inorganic As, especially As(V), was the dominant species of the water-extractible As in atmospheric particulate matter (EC 2000; Sánchez de la Campa et al. 2008; Tziaras et al. 2015). Some studies (Jakob et al. 2010; Tanda et al. 2019; Tziaras et al. 2015) have detected TMAs(V)O in airborne particle matter. Without any additional chromatography or intentional species conversion, we cannot separate TMAs(V)O from As(III) using the Hamilton PRP-X100 anion-exchange column (Tziaras et al. 2015). More details of this limitation and future work are provided in the SI.

Table 1 Descriptive statistics of the annual average concentrations [a] (n = 18)

Variable	Mean	Min	Max	Skew	Kurtosis	SD[b]	Spatial CV[c]
$PM_{2.5}$	60.54	43.6	95.22	1.02	0.54	12.77	0.21
As_{total}	6.81	4.04	11.57	0.63	− 0.55	2.18	0.32
As(III)	1.01	0.71	1.62	1.01	0.66	0.23	0.23
As(V)	3.21	2.28	4.55	0.67	− 1.06	0.75	0.23
DMAs(V)	0.04	0.02	0.08	0.87	− 1.02	0.02	0.6
As(V)/water-extractible As	0.75	0.71	0.81	− 0.25	− 1.04	0.03	0.04

[a] Unit of concentration: $PM_{2.5}$ μg/m^3 , others ng/m^3

[b] Standard deviation

[c] Coefficient of variation

Spatial variation in concentrations

Comparison of spatial variation for As_{total} and As species

Previous studies have not provided sufficient information to evaluate the spatial variation in As species in air because they did not include enough sampling sites (Lewis et al. 2012). Based on the annual average concentrations of the 18 sampling sites, we calculated the spatial CVs for As_{total} and the individual As species to evaluate their spatial variations. The spatial CVs of As_{total} and the individual As species in Nanjing were above 0.2, which were higher than that of the $PM_{2.5}$ (Table 1). These CVs of As indicate spatial heterogeneity according to the US EPA (1997), which suggests that CVs larger than 0.1 are desirable indicators of spatial heterogeneity. The spatial heterogeneity can be arranged in the following order: DMAs(V) (CV = 0.60) >> As_{total} (CV = 0.32) > As(III) = As(V) (CV = 0.23). He et al. (2017) suggested that the spatial variation was largest for SO_2, with a CV of 0.6, and was smallest for O_3, with a CV of 0.19, in major Chinese cities. Compared with the results of He et al., our results confirmed that As_{total}, As(III), and As(V) had medium levels of spatial heterogeneity, and DMAs(V) had a considerably high level of spatial heterogeneity, which was related to biovolatilization (explained in the "Influence of biovolatilization on concentrations" section). This is the first study to quantify the spatial variation in As species in $PM_{2.5}$.

Concentration contrasts among sampling sites

A study in the European region demonstrated that the As_{total} levels in TSP can be arranged in the following order: certain industrial >> traffic ~ urban > rural >> remote sites (EC 2000). We found different spatial trends than those found in this European study. In our study, as illustrated in Fig. 3, the As_{total} and As species concentrations can be arranged in the following order: urban background ~ urban street < suburban < rural < industrial sampling sites. The independent-sample *t* test calculations showed that the suburbs had statistically significantly higher mean values than the urban area for the concentrations of As_{total}, As(III), and DMAs(V), but there was no statistically significant difference between the suburbs and urban areas regarding the concentrations of As(V) (Table S8). The industrial sampling site (Fig. 1) was located in a power plant that was close to iron and steel smelting and petrochemical plants. This site had the highest concentrations of DMAs(V) and As(III) and relatively high concentrations of As(V) and As_{total}, as shown in Fig. 3. In this study, *t* tests were not performed for the industrial and rural sites because the sample sizes were too small. More sampling sites should be located in industrial and rural areas in future research.

The major difference between our results and those of the European study (EC 2000) was the order of the urban and rural sites. We found that the concentrations of the rural sites were unexpectedly high; conversely, the concentrations of urban sites were unexpectedly low. These differences may be linked to the contributions of pollution sources. In our study, rural sites are surrounded by farmland and/or water bodies. In particular, the southern rural site located near open water (Fig. 1) had the highest level of As_{total}, which was related to biovolatilization (explained in the "Influence of biovolatilization on concentrations" section). Conversely, the urban area in our study area was far from both industrial and natural sources. Although road traffic is of general intensity in urban areas, the local road traffic emissions had less of an impact on the concentrations of As in $PM_{2.5}$, as indicated by the street/urban background ratios (ST/UB) that were only slightly larger than 1 (Table S8). This result is consistent with that of the European study. It should, however, be noted that there were outliers with high values (not shown). These outliers were from an urban street site, which was approximately 200 m from two road sections with frequent heavy traffic congestion. This result indicates that the influence of local traffic sources on the concentration of As in $PM_{2.5}$ may be related to the traffic flow, which requires further investigation.

Influence of local emission sources on concentrations

Results of multiple linear regression

In this study, PCA and varimax rotation were used to construct multiple linear regression models, which were applied to explore the influence of local emission sources on concentrations. To counter the significant amount of multicollinearity among the spatial variables, they were first transformed into seven principal components with eigenvalues greater than or equal to 1 (Table S9). After the transformation, varimax rotation was used to maximize the loading of the spatial variables on one component (Table S9). The scores of the seven principal components were used as the independent variables in stepwise regression to choose principal components, and the results are summarized in Table S10. We then matched each of these chosen principal components to a spatial variable with the largest absolute loading shown in bold in Table S9. Finally, the selected spatial variables were used as the independent variables in stepwise regression to obtain the final multiple linear regression models, as summarized in Table 2. The variance inflation factors (VIFs) for all the regression models were far less than 10, indicating no significant collinearity.

The adjusted coefficient of determination (R^2) was used to assess the performances of the regression models, as in prior LUR studies (Gulliver et al. 2018). Our regression model explained approximately 46% of the spatial variation in the concentrations of As_{total} (adjusted R^2 ~ 0.46) (Table 2). This adjusted R^2 value indicates a moderate performance according to

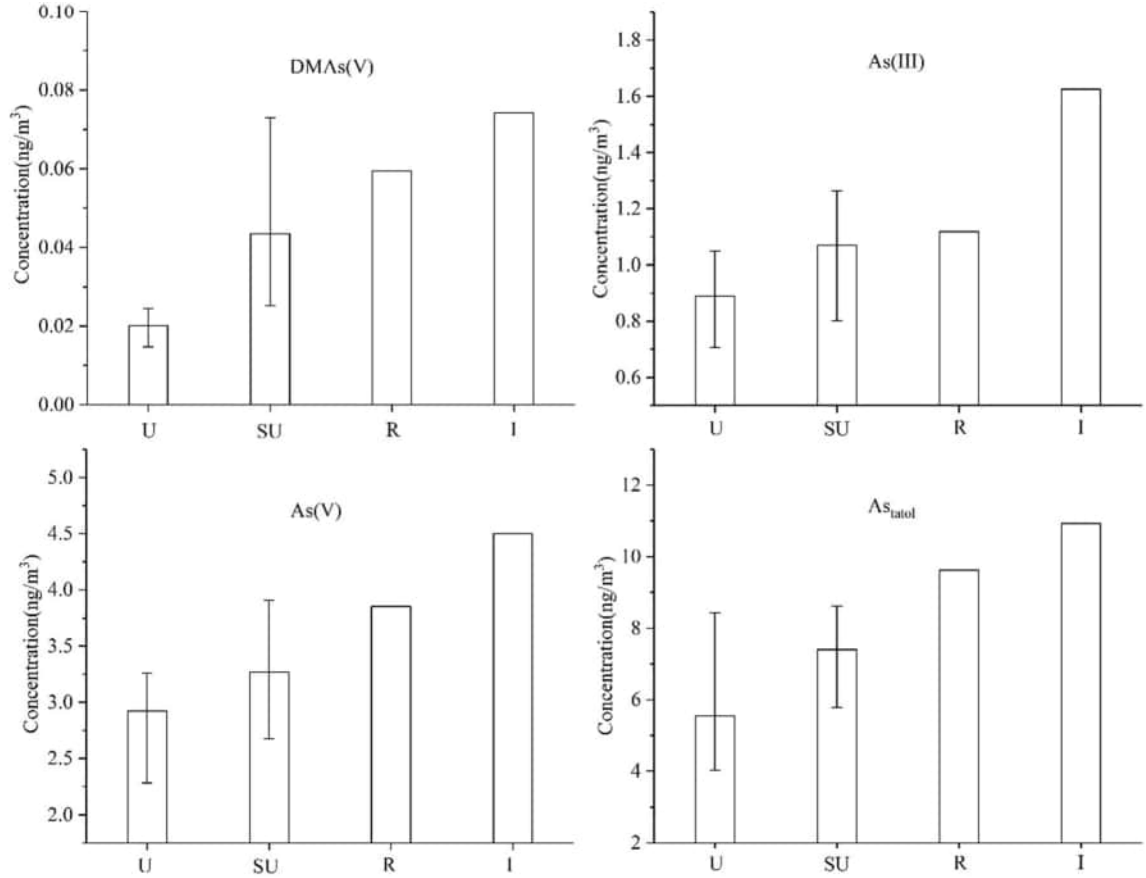

Fig. 3 Distribution of annual average concentrations of As_{total} and the individual As species for industrial (I) ($n = 1$), rural (R) ($n = 2$), suburban (SU) ($n = 5$), and urban (U) ($n = 10$) sampling sites

Gulliver et al. (2018). The regression model of As(III) had a good performance (adjusted $R^2 \sim 0.70$) (Table 2). This result indicates that the concentration of As(III) was mainly influenced by local sources. However, for DMAs(V) and As(V), the adjusted R^2 values were only 0.24 and 0.28, respectively (Table 2), indicating that DMAs(V) and As(V) were affected by important factors other than only local sources. This result may be associated with the secondary formation of As(V) and DMAs(V) because the concentrations of secondary atmospheric pollutants are significantly affected by meteorological conditions and regional diffusion (Monn 2001).

Influence of industrial point sources on concentrations

Industrial sources are the major anthropogenic sources of As in the atmosphere, but to our knowledge, the influence of industrial point sources on the concentrations of As species in $PM_{2.5}$ have not been quantitatively assessed based on monitoring data from multiple sampling sites. In our study, the influence was quantified by the standardized coefficient of the regression models (β) and the LMG metric, as listed in Table 2. All of the multiple linear regression models summarized in Table 2 contained an independent variable PI_7500m representing industrial point sources, as shown in Table S4. The estimated regression coefficients of PI_7500m were larger than 0, which means that there were more industrial plants within 7.5 km of the sampling site, which caused the higher concentrations of As_{total} and As species in the sampled $PM_{2.5}$. For the concentrations of As(III), As_{total}, and As(V), PI_7500m was the independent variable with the highest value of β and LMG (Table 2), indicating that PI_7500m was the most important predictor for them. This finding is in line with that of a previous study (Zhang et al. 2015). The major industrial plants in our study include coal combustion, which is the main anthropogenic source of atmospheric As in China (Chen et al. 2016). This result indicates that primary emissions of coal combustion from industrial sources are major sources of As in $PM_{2.5}$ in Nanjing.

Influence of local road traffic emissions on concentrations

As mentioned earlier, there was no significant difference in the As concentrations between streets and urban backgrounds. This result is consistent with the results of

Table 2 Final multiple linear regression models

Dependent variable	Independent variable	Regression coefficient	P value	Standardized coefficients β	LMG	VIF
log(As(III))	Constant	− 0.24	0			
	PI_7500m	18.45	0	0.73	49	1.12
	LUW_1000m	0.6	0.03	0.35	12	1.14
	LUC_1000m	0.23	0.17	0.21	4	1.2
	IDR	0.39	0.08	0.26	12	1.06
	Adjusted coefficient of determination (R^2) = 0.70					
log(As(V))	Constant	1.01	0			
	PI_7500m	14.38	0.02	0.54	28	1.01
	LUW_1000m	0.58	0.14	0.33	9	1.01
	Adjusted coefficient of determination (R^2) = 0.28					
log(DMAs(V))	Constant	− 3.85	0			
	PI_7500m	25.94	0.09	0.4	11	1.06
	LUC_1000m	1.41	0.03	0.52	21	1.06
	Adjusted coefficient of determination (R^2) = 0.24					
As_{total}	Constant	4.86	0			
	PI_7500m	162.55	0	0.62	32	1.06
	LUW_1000m	6.06	0.09	0.34	14	1.14
	LUC_1000m	3.73	0.1	0.34	10	1.2
	Adjusted coefficient of determination (R^2) = 0.46					

[a] Relative importance matrix

[b] Variance inflation factor

multiple linear regressions. Only the regression model of As(III) included a traffic-related variable, the inverse of the distance to the nearest road (IDR) (Table 2). The IDR variable had an LMG value of 12 and a β value of 0.26, which were smaller than those of other independent variables representing industrial sources or biovolatilization (Table 2). This result is consistent with the results obtained in Wang et al. (2015), which found that the contribution of liquid fuel combustion to As in air in China was less important than that of industrial coal consumption and was in line with the results of Johansson et al. (2009), who found that As was not the main metal element attributed to road traffic emissions. Therefore, this study indicates that local road traffic sources are less important than industrial sources and biovolatilization in terms of the As pollution in $PM_{2.5}$.

Influence of biovolatilization on concentrations

Volatile As species generated from biovolatilization process occurring in water/soil/sediment can be converted into water-soluble species and adsorbed onto particulate matter (Mestrot et al. 2013; Jakob et al. 2010). As shown in Table 2, the regression models contain one or two independent variables representing biovolatilization sources: LUW_1000m and LUC_1000m (Table S4). The regression coefficients of LUW_1000m and LUC_1000m in the regression models were larger than 0 (Table 2), indicating that the larger the area of water and/or farmland was within 1 km around the sampling site and the higher the concentrations of As_{total} and As species in $PM_{2.5}$ will be at the sampling site. These results indicate that biovolatilization is an important source of As_{total} and the individual As species in $PM_{2.5}$ across the study area. This may be the cause of the unexpectedly high concentrations of As_{total} and the individual As species in the southern rural site because farmland and/or water (where biovolatilization may occur) surrounded this site, and the nearest industrial sources were approximately 50 km away (Fig. 1). For the regression model of DMAs(V), both β and the LMG metric were larger for LUC_1000m than for PI_7500m (Table 2), indicating that biovolatilization contributed more to DMAs(V) than industrial sources. This result is in line with the previous studies, which attributed organic As species in particulate matter to biovolatilization (Savage et al. 2019).

The influence of biovolatilization may be the cause of the seasonal variations (detected only in summer) in DMAs(V). As mentioned in "Temporal variation" section, DMAs(V) was only detected in summer samples. This seasonality is consistent with the active biovolatilization of As in summer, which is the rainy season in Nanjing. Frequent rain can decrease the soil redox potential, which makes methylation and biovolatilization of As occur more readily (Faust et al. 2016). The volatile Me_2AsH generated from biovolatilization can be oxidized to DMAs(V), which are photo-oxidative reactions, presumably with OH radicals (Jakob et al. 2010). Therefore, the higher atmospheric oxidation levels in summer can promote the conversion of Me_2AsH to DMAs(V) (Jakob et al. 2010; Faust et al. 2016).

As the most influential source for DMAs(V) (Table 2), biovolatilization, which is commonly viewed as a local source driving spatial variations in organic As deposition (Savage et al. 2019), may also be the driver of the considerably high levels of spatial heterogeneity of DMAs(V) in this study. In addition, previous studies (Jakob et al. 2010) have found that methylarsines are more active than AsH_3. In other words, DMAs(V) can be formed more rapidly from Me_2AsH than As(III) and As(V) from AsH_3. The shorter the reaction time to form secondary pollutants is, the more heterogeneous the spatial distribution of the secondary pollutants will be (Monn 2001); therefore, the spatial distribution of secondary DMAs(V) may be more heterogeneous than that of secondary As(III) and As(V).

Conclusions

This study has revealed that the spatial heterogeneity of As species (especially DMAs(V)) in $PM_{2.5}$ should be considered in exposure assessments. The concentrations of As in $PM_{2.5}$ of the rural sites were unexpectedly high; conversely, the concentrations of the urban sites were unexpectedly low. This spatial pattern is consistent with the results of multiple linear regression, which indicates that industrial source emissions and biovolatilization play more important roles in the pollution of As in $PM_{2.5}$ than local road traffic sources. In particular, As biovolatilization is critical for the spatial heterogeneity, which will be the focus of further research.

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