Distribution and chemical speciation of arsenic in different sized atmospheric particulate matters

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ABSTRACT

The distribution and chemical speciation of arsenic (As) in different sized atmospheric particulate matters (PMs), including total suspended particles (TSP), PM_{10}, and $PM_{2.5}$, collected from Baoding, China were analyzed. The average total mass concentrations of As in TSP, PM_{10}, and $PM_{2.5}$ were 31.5, 35.3, and 54.1 µg/g, respectively, with an order of $PM_{2.5}$ > PM_{10} > TSP, revealing that As is prone to accumulate on fine particles. Due to the divergent toxicities of different As species, speciation analysis of As in PMs is further conducted. Most of previous studies mainly focused on inorganic arsenite (iAs^{III}), inorganic arsenate (iAs^V), monomethylarsonate (MMA), and dimethylarsinate (DMA) in PMs, while the identification and sensitive quantification of trimethylarsine oxide (TMAO) were rarely reported. In this study, a high-performance liquid chromatography coupled to inductively coupled plasma mass spectrometry system was optimized for As speciation including TMAO in PMs. An anion exchange column was used to separate MMA, DMA and iAs^V, while a cation exchange column to separate TMAO and iAs^{III}. Results showed that iAs^V was the dominate component in all the samples, corresponding to a portion of 79.2% ± 9.3% of the total extractable species, while iAs^{III}, TMAO and DMA made up the remaining 21%. Our study demonstrated that iAs^{III} accounted for about 14.4% ± 11.4% of the total extracted species, with an average concentration of 1.7 ± 1.6 ng/m^3. It is worth noting that TMAO was widely present in the samples (84 out of 97 samples), which supported the assumption that TMAO was ubiquitous in atmospheric particles.

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Introduction

Arsenic (As) is a toxic element that is widely present in the natural environment. Acute and chronic exposure studies reveal that As is related to cancers and a series of cardiovascular and neurological diseases (Jomova et al., 2011). Nearly every organ in the human body can be attacked by As exposure (Carlin et al., 2016). The International Agency for Research on Cancer (IARC) also listed As and its inorganic compounds as the group 1 human carcinogens (IARC, 2016), which incurred increasing concerns among the scientific community, governments, and the general public.

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During the past years, a great number of regions in China suffered from severe air pollution. Atmospheric particulate matters (PMs) have attracted particular attentions due to the health effects and association with haze (Duan et al., 2014; Zhou et al., 2014). A recent study reported the discovery of exogenous combustion-derived nanoparticles in human serum and pleural effusion samples, proving the direct evidence of the entering of PMs into the human body (Lu et al., 2020). Meanwhile, the large surface area enables PMs to adsorb numerous organic pollutions and heavy metals (Li et al., 2013; Wu et al., 2020). Inhalable of PMs is an important way for the exposure of As, as more than 90% of atmospheric As was reported to be present in the particulate form (Huang et al., 2018). It is commonly accepted that the smaller PMs are, the deeper they can penetrate into the human body. PM_{10} can get access to pharynx, larynx, trachea, and lower respiratory tract, and $PM_{2.5}$ can reach the alveoli, while ultrafine particles can even penetrate the alveolar and translocate into the blood circulatory (Zwozdziak et al., 2016). Therefore, to accurately assess the health risks caused by As, the determination of size-dependent distribution of As species in PMs is needed.

Although studies on atmospheric As have been reported extensively, most of them focused on the total concentrations. Only a few studies concentrated the chemical speciation of As in PMs, even though As toxicity is dependent not only on the total content but also on species. Generally, inorganic As is more toxic than the organic ones, and inorganic arsenite (iAs^{III}) is more harmful than inorganic arsenate (iAs^V) (Huang et al., 2018). To fully understand the real pollution of As in the air and the related health effects, chemical speciation of As in PMs is highly demanded. Liquid chromatography coupled with inductively coupled plasma mass spectrometry (ICP-MS) was frequently used to separate different As species. Up to now, five As species, including iAs^{III}, iAs^V, monomethylarsonate (MMA), dimethylarsinate (DMA), and trimethylarsine oxide (TMAO), were reported to be present in atmospheric particles. However, the majority of the related studies only mentioned the first four species, while the identification and sensitive quantification of TMAO, first reported in the 1970s (Johnson and Braman, 1975; Tziaras et al., 2015), in PMs was rarely reported. As far as we know, only very few studies demonstrated the determination of TMAO in atmospheric particles (Jakob et al., 2010; Tanda et al., 2020, 2019; Tziaras et al., 2015), partly because neither TMAO nor iAs^{III} can be retained by the commonly used anion exchange column. During the chromatographic separation process, the two species would co-elute from the column, making the separation and detection of them rather complicated. Some study even speculated that iAs^{III}, reported to be frequently detected in atmospheric particles might sometimes be TMAO by mistaken (Tziaras et al., 2015).

For the accurate determination of TMAO, a complementary cation exchange column is always needed. Tziaras et al. (2015) developed a chromatographic approach to connect an anion exchange column and a cation exchange column in series, which enabled the separation of the five As species in a single run. However, they stated that the sensitivity was a problem, so they changed the commonly used pneumatic nebulizer introduction system into an arsine generation system, which may be rather complicated. In a recent study, to distinguish TMAO and iAs^{III}, PM samples were extracted with H_2O_2 to oxidize iAs^{III} into iAs^V. A twice separation was performed that once was using an anion exchange column to detect MMA, DMA and iAs^V, and once with a cation exchange column to identify and analyze TMAO (Tanda et al., 2020). Though the occurrence and seasonal trends of TMAO in the PM samples can be monitored, information about iAs^{III} was missing due to the oxidation by H_2O_2, which hindered the accurate assessment of health risks. A more general analytical method for the separation of different As species in atmospheric particles is urgently needed.

Baoding is a typical industrial city in North China, located in the Beijing-Tianjin-Hebei region. It developed rapidly in recent years, and the heavy coal consumption and fast growth of vehicles make it one of the most air-polluted cities in China. The speciation analysis of As in atmospheric PMs in Baoding would be conducive to fully understand the current As pollution situation in air in the Beijing-Tianjin-Hebei region, and to reasonably assess the potential health impacts. Therefore, 97 PM samples, including $PM_{2.5}$, PM_{10}, and total suspended particles (TSP), were collected in Baoding urban areas in this study. The aims of our work are: (1) gain the real As pollution levels in PMs from Baoding; (2) discriminate As speciation (iAs^{III}, iAs^V, MMA, DMA and TMAO) in PMs, especially the analysis of TMAO; (3) investigate the As species distribution in different sized particles.

1.   Materials and methods

1.1.   Chemicals and standards

Nitric acid (65%), and methanol were purchased from Merck (Darmstadt, Germany). High purity orthophosphoric acid, hydrofluoric acid, hydrogen peroxide, and ammonium bicarbonate were supplied from Sinopharm Chemical Reagent Co. (Beijing, China). Formic acid (≥98%) and pyridine (≥99.9%) were obtained from Sigma-Aldrich (St. Louis, USA). MMA and DMA standard solutions were from the National Institute of Metrology (Beijing, China). Inorganic As^{III} and As^V standard solutions were prepared by dissolving sodium arsenite and sodium arsenate into ultrapure water. All the reagents used in this study were analytical grade or better. Ultrapure water (18.2 MΩ•cm) was used throughout the experiment.

1.2.   Sampling

All atmospheric PM samples, including 32 $PM_{2.5}$ samples (9 samples in the spring, 5 samples in the summer, 8 samples in the autumn, and 10 samples in the winter), 33 PM_{10} samples (9 samples in the spring, 5 samples in the summer, 9 samples in the autumn, and 10 samples in the winter), and 32 TSP samples (9 samples in the spring, 5 samples in the summer, 7 samples in the autumn, and 11 samples in the winter), were taken from the campus of North China Electric Power University in Baoding, Hebei Province, China, during October 2017 to August 2018. The sampling site is situated on the roof of a teaching building on the campus near an atmospheric environmental monitoring station of the National Environmental Protection Agency, China. PM sampling was conducted by using medium

volume air samplers (Wuhan Tianhong Instruments Co. Ltd., China) with $PM_{2.5}$, PM_{10}, or TSP inlets, respectively, and a calibrated flow rate at 100 L/min for 23.5 hr was operated. Samples were collected on quartz microfiber filter papers (90 mm, Whatman, UK), which were pre-heated at 100 °C for an hour to remove any interferences and balanced in a desiccator for 24 hr before and after sampling. Filters were weighed before and after sampling, and then wrapped in sealed polyethylene bags and kept at 4 °C.

1.3. Total As measurements

Each filter paper was equally separated into eight parts, of which three were used for total As measurements and three were used for the speciation analysis. For the total As measurements, a subsample of the paper was placed into a PTFE tube, and 4 mL of HNO_3, 1 mL of HF and 1 mL of H_2O_2 were added for microwave digestion. After pre-digested in the fume hood for 10 hr, the samples were digested at 180 °C for 15 min and then diluted with ultrapure water for further analysis. An Agilent 7700 ICP-MS (Santa Clara, USA) was used to determine the total As concentration. Blank filters were also subjected to microwave digestion to determine background As, and all the data given have subtracted the As contents in blank filters.

1.4. Sample extraction and preparation

For the sample extraction, each subsample was cut into small pieces and placed in a centrifuge tube. Three milliliters of ultrapure was added as the extracting agent, and the tube was sonicated for 30 min at room temperature. Afterword, the tube was centrifuged at 5000 r/min for 30 min, and the supernatant was collected. The extraction procedure was repeated three times, with another 3 mL of ultrapure water. Finally, the supernatant was mixed, went through a 0.22 µm filter membrane, and kept at 4 °C for the subsequent speciation analysis of As within 48 hr.

1.5. Speciation analysis of As

A high-performance liquid chromatography system (HPLC, Agilent Technologies, USA) coupled with ICP-MS (LC-ICP-MS) was used to analyze different species of As in atmospheric PMs. The extracts were analyzed twice with different chromatographic columns. An anion exchange column (Hamilton PRP-X100, 10 mm, 250 mm × 4.1 mm) with a mobile phase of 90 mmol/L NH_4HCO_3 at pH 8.6 (adjusted with an ammonia solution) was used to separate MMA, DMA and iAs^V, while a cation exchange column (Hamilton PRP-X200, 10 mm, 150 mm × 4.1 mm) with a mobile phase of 4 mm pyridine at pH 2.8 (adjusted with formic acid) was conducted to separate iAs^{III} and TMAO. The flow rate was 1.0 mL/min, and the injection volume was 50 µL. The collision cell mode with He as the gas was used and the ion signal at m/z 75 (^{75}As) was monitored in time-resolved analysis mode. The As standards were prepared by directly diluting the stock solutions with ultrapure water, and external calibration curves were used to quantify different As species. The limit of detection (LOD, S/N = 3) of iAs^{III}, iAs^V, MMA, DMA, and TMAO were 0.25, 0.24, 0.29, 0.20 and 0.32 ng/mL, respectively. The concentrations of five As

species in the blank filter extraction were all below the LODs of the method. The extraction efficiency of PMs and the HPLC column recovery were not evaluated separately. The speciation analysis recovery of PM samples, defined as a combination of the extraction efficiency and the HPLC column recovery, was calculated by dividing the sum of the five As species derived from LC-ICP-MS by the total As contents given by ICP-MS. Three independent experiments were carried out for each sample to determine the concentrations of total As and As species, and average values were given.

2. Results and discussion

2.1. Mass concentrations of PMs

In our study, 97 atmospheric PM samples, containing 32 TSP samples, 33 PM_{10} samples, and 32 $PM_{2.5}$ samples, were determined. The mass concentrations of TSP, PM_{10}, and $PM_{2.5}$ were ranging from 70.7 to 490.2, 75.7 to 414.4, and 24.8 to 299.3 µg/m^3, with average levels of 216.2 ± 97.0, 171.1 ± 84.1, 116.5 ± 62.5 µg/m^3, respectively. Comparing with the data in our previous study that analyzing PMs in Baoding during 2016–2017 (Xie et al., 2019), the average mass concentrations of all the three different sized PM samples declined. The severe haze pollution in recent years has been a big concern. The burning of fossil fuels was regarded as a primary source of atmospheric PMs, so the government implemented a policy of "burning gas instead of coal" (BGiC) in 2017 in North China, aiming to improve the air quality (Xie et al., 2020b). By September 2017, Baoding had shut down or renovated more than 4000 coal-fired boilers, resulting in a sharp drop in the coal consumption in this city since the winter of 2017 (Xie et al., 2020a). The decrease of mass concentrations of TSP, PM_{10}, and $PM_{2.5}$ showed that the implement of BGiC policy had achieved remarkable results. Nevertheless, the average mass concentrations of TSP, PM_{10}, and $PM_{2.5}$ were still higher than the primary national standard (GB 3095–2016, 120, 50, and 35 µg/m^3 in 24 hr on average for TSP, PM_{10}, and $PM_{2.5}$, respectively), indicating that besides coal combustion, other sources such as building and soil dust and motor vehicle emission also contribute to the high concentration of PMs in the atmosphere (Soleimani et al., 2018).

2.2. Size distribution of the total As

The total concentrations of As in TSP, PM_{10}, and $PM_{2.5}$ were in the range of 1.5–27.7, 1.3–34.1, 1.2–17.7 ng/m^3, with average values of 6.2 ± 5.8, 5.9 ± 5.8, and 5.6 ± 4.0 ng/m^3, respectively, which was dramatically decreased compared with As contents in 2016–2017 (Xie et al., 2019) before the implementation of BGiC policy, revealing that coal-burning was a key source of atmospheric As (Duan et al., 2012; George et al., 2020). According to a previous survey of heavy metals in the atmosphere of more than 44 cities in China, the average concentration of atmospheric As was 51.0 ± 67.0 ng/m^3 in China (Duan and Tan, 2013). Zhang et al. reported an atmospheric As level of 58 ng/m^3 on the campus of Tsinghua University in Beijing from 2001 to 2006 (Okuda et al., 2008), while a much higher

concentration of As (130 ng/m^3) in PMs was presented in a research institution in Beijing from 2009 to 2011 (Yang et al., 2012). In our study, the concentrations of As in more than 60% of the PM samples werebelow the national air quality standard (6 ng/m^3, GB3095–2012), showing the positive effects of BGiC policy on the improvement of air conditions. However, compared with atmospheric As levels in other countries, such as Greece (0.03–0.7 ng As/m^3 in different sized samples) (Tziaras et al., 2015), southeastern Austria (0.06–3.32 ng As/m^3 in PM$_{10}$) (Tanda et al., 2020), and Spanish (0.7–2.8 ng As/m^3 in PM$_{10}$) (Garcia-Aleix et al., 2014), the particulate As values in China are still high.

The size distribution of As in PMs was analyzed. The Pearson correlation analysis showed that the correlation coefficients were 0.933 between TSP and PM$_{10}$, 0.829 between PM$_{10}$ and PM$_{2.5}$, and 0.822 between TSP and PM$_{2.5}$, indicating that As in TSP, PM$_{10}$ and PM$_{2.5}$ may come from similar sources. Meanwhile, total contents of As in PM$_{10}$ versus PM$_{2.5}$, and PM$_{10}$ versus TSP (Fig. 1a and 1b) showed good correlation, with the correlation coefficients (R^2) of 0.87 and 0.71, respectively. The slopes of the linear regression lines were close to 1, implying that As is more likely to be present in fine particles.

We further recalculated the mass concentrations of As per gram of PMs to elucidate the accumulation patterns. As shown in Fig. 1c, the average mass concentrations of As in TSP, PM$_{10}$, and PM$_{2.5}$ were 31.5, 35.3, and 54.1 µg/g, respectively, showing apparent orders of PM$_{2.5}$ > PM$_{10}$ > TSP. The accumulation of As in fine-sized particles was also reported in previous studies (Garcia-Aleix et al., 2014; Huang et al., 2018; Lu et al., 2012), probably due to that the surface areas of small particles are larger than the big ones, and thus provide much more sites for the adsorption of emitted As in the air. Considering that the smaller the size of PM particles, the greater the capacity to enter human bodies through the respiratory system, the enrichment of As in fine-sized particles indicated that small atmospheric PMs would pose a more significant threat for the human health.

2.3. Extraction of As species

Different extraction agents, such as H$_3$PO$_4$, NH$_2$OH•HCl, and CH$_3$OH, have been reported to extract As in atmospheric PMs (Oliveira et al., 2005). Since the presence of Cl$^-$ may interfere with the detection of ^{75}As by ICP-MS, H$_3$PO$_4$ and CH$_3$OH were tried in our study. Though high concentrations of agents could extract most of As in PMs, they affected the separation process and resulted in the distortion of chromatograms. To minimize the influence of extraction agents on As speciation, ultrapure water was evaluated. Ten TSP samples were used to calculate the extraction efficiency due to their homogeneous As distribution. Results revealed that the extraction efficiencies were between 69.6% and 104.3%, and the majority showed recoveries higher than 75%. Thus, ultrapure water was used in the following experiment.

2.4. As separation and determination

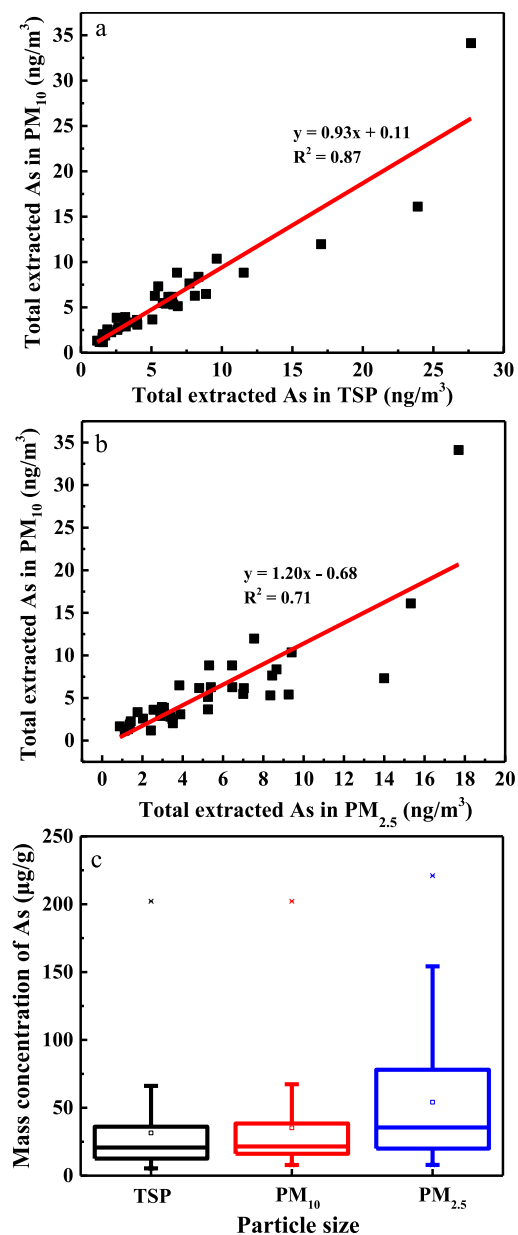Like most reported studies, we initially aimed to use the Hamilton PRP-X100 column to separate four familiar As

Fig. 1 – Scatter diagrams of arsenic (As) in total suspended particles (TSP)-PM$_{10}$ (a), PM$_{2.5}$-PM$_{10}$ (b), and the mass concentrations of As in different sized particulate matters (PMs), expressed as the concentrations of As per gram of PMs (c).

species (iAs^{III}, iAs^V, MMA and DMA) in atmospheric PMs. However, the chromatogram of the PM extracts showed that there were two non-retained peaks with very close retention times (Fig. 2a). Mixed standard solutions containing the four As species were added into the sample extracts, and four single standards were also analyzed for comparison. The area of the first peak did not change, indicating that it belonged to none of the four As species (Fig. 2b-f). As Tziaras et al. (2015) reported that TMAO, which may also be present in the atmospheric PMs, did not retain by the anion exchange column, we further added the TMAO standard solution into the sample
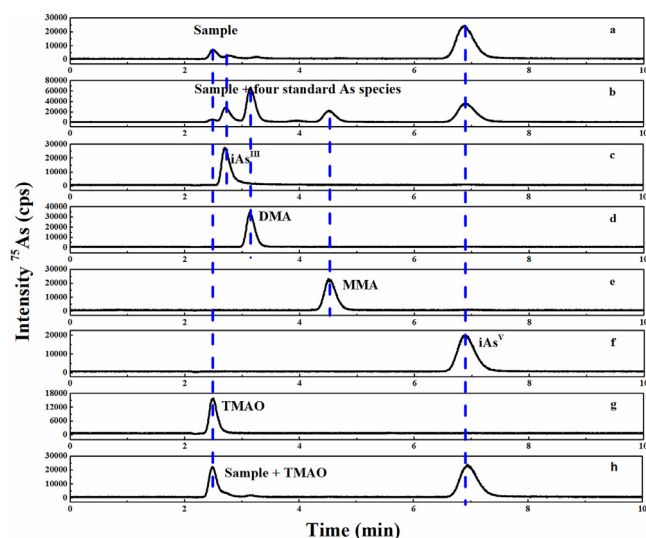
Fig. 2 – Anion exchange inductively coupled plasma mass spectrometry (ICP-MS) chromatograms of As species in atmospheric particle extracts (a), atmospheric particle extracts with the addition of four standard As species (b), the inorganic arsenite (iAs^{III}) standard (c), the dimethylarsinate (DMA) standard (d), the monomethylarsonate (MMA) standard (e), the inorganic arsenate (iAs^V) standard (f), the trimethylarsine oxide (TMAO) standard (g), and atmospheric particle extracts with the addition of TMAO (h).
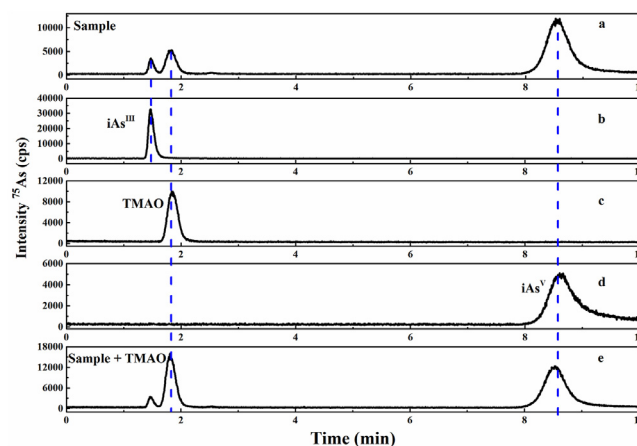

Fig. 3 – Cation exchange ICP-MS chromatograms of As species in atmospheric particle extracts (a), the iAs^{III} standard (b), the TMAO standard (c), the iAs^V standard (d), and atmospheric particle extracts with the addition of TMAO (e).

extracts. As shown in Fig. 2g and h, the area of the unknown peak largely increased, with the retention time matching the TMAO standard, implying that it may be TMAO. Further identification is needed.

MMA, DMA, and iAs^V in the PM extracts could be readily separated and determined. However, this unknown As species cannot be fully separated from iAs^{III}, which hindered the accurate determination of iAs^{III}. Tziaras et al. (2015) developed an approach that connected an anion exchange column and a cation exchange column in series to separate of all the five As species in a single run, which would be an ideal choice for the confirmation of TMAO. However, a modification of the sample introduction system is needed to achieve satisfying sensitivity, which is not allowed for our instrument. As TMAO can be retained by the cation exchange column, and iAs^{III} showed no retention at proper pH, a cation exchange column was introduced in the subsequent experiment. Under the optimized conditions, iAs^{III} and TMAO can be well separated, and the presence of other As species did not disturb their determination. The chromatogram of the sample extracts separated by the cation exchange column was showed in Fig. 3. The retention time of the unknown As species was in line with that of the TMAO standard. By adding TMAO standards into the extracts, the area of the unknown peak significantly increased, confirming the presence of TMAO. Therefore, for the following determination of As species in PMs, the extracts were separated twice, once with an anion exchange column to determine MMA, DMA and iAs^V, and once with a cation exchange column to analyze TMAO and iAs^{III}. Without the modifica-

tion of the sample introduction system, this twice-separation method would be more applicable.

2.5. As speciation analysis in different sized PM extracts

After water extraction of PMs, the extracts were directly subjected to LC-ICP-MS to analyze diverse As species. For all of the samples, the water extractable As (sum of all the extractable species) was in the range of 1.7–36.2 ng/m^3. The speciation analysis recovery of PM samples, defined as a combination of the extraction efficiency and the HPLC column recovery, was also calculated, as shown in Appendix A Fig. S1. Among all of the samples, iAs^V was found to be the major fraction in atmospheric PMs, accounting for 79.2% ± 9.3% of the total water-extractable As concentrations, followed by iAs^{III}, TMAO and DMA. The percentage of each As species was similar in different sized PMs (Table 1). DMA was only detected in 6 of the 97 samples at relatively low concentrations, while the concentration of MMA was below the limit of detection for all the samples.

The dominating component of iAs^V in PMs was in consistent with previous studies that sampling at other countries and locations (Tanda et al., 2019; Tziaras et al., 2015; Yang et al., 2012). However, different from Tziaras et al. (2015)'s result that iAs^{III} only contributed little (1%± 1%) to the total PM As, our study showed that iAs^{III} accounted for about 14.4% ± 11.4% of entire extracted species, second only to iAs^V. Inorganic As^{III} was present in 30 of TSP samples, 28 of PM$_{10}$ and 26 of PM$_{2.5}$ samples, with the average concentration of 1.8 ± 1.3, 1.5 ± 1.4 and 1.6 ± 1.1 ng/m^3, respectively. Compared with iAs^{III} concentrations in TSP samples from Beijing, China (4.7 ± 3.6 ng/m^3) (Yang et al., 2012), our detected values were much lower. However, they were 2–3 orders magnitude higher than that detected in PM$_{10}$ samples from Greece (2.2–10.8 pg/m^3), revealing that the air pollution in China is still severe. It is well known that iAs^{III} is carcinogenic, with the toxicity much higher than iAs^V. The non-negligible amounts of

	iAs^V	iAs^{III}	TMAO	DMA
Table 1. – Chemical speciation of As in TSP, PM_{10} and $PM_{2.5}$ samples.				
TSP				
Concentration range (ng As/m^3)	2.2–33.0	0.3–8.1	0.02–1.9	/
Average $\pm$ SD (ng As/m^3)	10.1 $\pm$ 6.8	1.8 $\pm$ 1.3	0.6 $\pm$ 0.5	/
Percentage (%)	78.7	15.4	5.9	/
PM_{10}				
Concentration range (ng As/m^3)	1.5–30.0	0.3–5.1	0.1–2.3	0.2–0.3
Average $\pm$ SD (ng As/m^3)	9.4 $\pm$ 6.6	1.5 $\pm$ 1.4	0.6 $\pm$ 0.5	0.2 $\pm$ 0.2
Percentage (%)	79.9	13.3	6.6	0.1
$PM_{2.5}$				
Concentration range (ng As/m^3)	1.7–22.0	0.2–7.0	0.1–1.6	0.2–0.5
Average $\pm$ SD (ng As/m^3)	9.6 $\pm$ 6.5	1.6 $\pm$ 1.1	0.6 $\pm$ 0.5	0.3 $\pm$ 0.1
Percentage (%)	78.9	14.4	6.3	0.3

iAs^{III} in the atmospheric PMs may be a significant threat to humans.

TMAO was detected in almost all the PM sample, with 31 of TSP samples, 30 of PM_{10} and 31 of $PM_{2.5}$ samples. The concentration of TMAO was in the range of 0.02–1.9, 0.1–2.3 and 0.1–1.6 ng As/m^3 for TSP, PM_{10} and $PM_{2.5}$, respectively, with the mean values of 0.6 $\pm$ 0.5 ng As/m^3. No significant difference was observed between different sized atmospheric PMs. Although limited studies have presented the presence of TMAO in PMs, based on the reported results, TMAO was detected in atmospheric PMs from Japan (Mukai and Ambe, 1987b), Greece (Tziaras et al., 2015), Argentina (Jakob et al., 2010), and Austria (Tanda et al., 2020). Our study, for the first time, demonstrated that TMAO was commonly found in PMs from North China, which supported the assumption that TMAO was ubiquitous in atmospheric particles (Tziaras et al., 2015). Similar levels of TMAO were reported in PM_{10} samples taken from Austria (17 $\pm$ 13 pg As/m^3) (Tanda et al., 2020), Argentina (20.3 $\pm$ 15.8 and 16.2 $\pm$ 11.5 pg As/m^3 collected from two sites) (Jakob et al., 2010) and Greece (36 $\pm$ 25 pg As/m^3 in PM_{10}) (Tziaras et al., 2015). Tziaras et al. (2015) speculated that the concentration of TMAO in the atmosphere might be constant, which was stemmed from the biovolatilization of naturally occurring As and existed as a background As species in the atmosphere. However, an earlier study showed a seasonal variation of TMAO concentrations in the atmospheric particles in Japan. Comparable concentrations of TMAO (6–66 pg As/m^3) were detected in winter, while much higher concentrations (162–604 pg As/m^3) were detected in summer (Mukai and Ambe, 1987a). Our detected TMAO concentrations were much higher than these studies, suggesting that besides the naturally occurring As, other exogenous As contributed to the biomethylation processes. In our study, we also found that TMAO concentrations in PM particles were seasonally dependent (Appendix A Fig. S2). The average concentrations of TMAO were the lowest in winter (0.1 $\pm$ 0.1 ng As/m^3) and the highest in summer (1.2 $\pm$ 0.4 ng As/m^3). In comparison, comparable concentrations were detected in spring (0.7 $\pm$ 0.3 ng As/m^3) and autumn (0.8 $\pm$ 0.5 ng As/m^3), showing a similar trend with atmospheric TMAO concentrations in Japan. Mukai and Ambe (1987a) speculated that the origin of TMAO in PMs was from biomethylation processes which were favored in summer with high temperature and humidity.

DMA was only detected in 2 PM_{10} and 5 $PM_{2.5}$ samples with an average concentration of 0.3 $\pm$ 0.1 ng As/m^3, all of which were collected in summer. No MMA was detected in all the samples. The limited amounts of MMA were also reported by Tziaras et al.(2015). In 81 atmospheric samples collected in Greece, MMA was only detected in 6 out of 33 PM_{10} samples with the concentration ranging from 2.0 to 5.3 pg As/m^3, while the concentrations of MMA were below the limit of detection in all the $PM_{2.5}$ and $PM_{2.1}$ samples (Tziaras et al., 2015). Comparable levels of MMA was also detected in atmospheric PMs from Argentina (Jakob et al., 2010). Though earlier studies demonstrated a considerable concentration of MMA (up to 1.4 ng As/m^3) was detected in atmospheric PMs taken from Japan (Mukai and Ambe, 1987a), it was mainly originated from the pollution of an alkylarsenic pesticide (iron methane arsonate) applied in surrounding paddy fields. Baoding city is an industrialized city, and the sampling site was located on a campus, which excluded the pesticide contamination.

3. Conclusions

In this study, 97 atmospheric PM samples ($PM_{2.5}$, PM_{10}, and TSP) were collected from Baoding in China, during October 2017 to August 2018, after the implement of BGiC policy in North China. By analyzing the total As concentrations and different As species in the samples, our results showed that both the mass concentrations of PMs and the total As concentration in the atmospheric particles dramatically decreased compared with samples taken during 2016–2017, proving the positive effects of this policy. Arsenic is more likely to concentrate on fine particles, implying that small atmospheric PMs would pose a more significant threat to human health. Inorganic As^V was the major fraction in PMs, corresponding to 78.7% $\pm$ 9.7%, 79.9% $\pm$ 8.5%, 78.9% $\pm$ 9.8% of the total extractable As in TSP, PM_{10}, and $PM_{2.5}$, followed by iAs^{III}, TMAO and DMA. No MMA was detected in all the samples. The wide detection of TMAO in PMs, along with their ubiquity in atmospheric particles taken from Japan, Greece, Argentina, and Austria, reminds us that TMAO would be an important component in the atmosphere that has been long-neglected. Further studies are needed to identify the primary sources of TMAO and predict their potential risks.

Acknowledgments

Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2021.02.010.

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