Comparison of Filtration System and a Honeycomb Denuder-Based System for Sampling PM$_{2.5}$ in Tianjin, China

Shijian Zhang$^{1,2}$, Yaqin Ji$^{1,2,}$*, Zhenyu Zhu$^{1,2}$, Yangyang Li$^{1,2}$, Wen Yang$^3$

$^1$ College of Environmental Science and Engineering, Nankai University, Weijin Road 94, Tianjin, 300071, China
$^2$ State Environmental Protection Key Laboratory of Urban Ambient Air Particulate Matter Pollution Prevention and Control, Weijin Road 94, Tianjin, 300071, China
$^3$ Chinese research academy of Environmental Sciences, NO. 8, Dayangfang, Anwai, Chaoyang District, Beijing, 100012, China

ABSTRACT

To evaluate sampling artifacts of PM$_{2.5}$ with conventional filtration system (FS), a contrastive study between the FS and a honeycomb denuder system (HDS) in measuring atmospheric concentrations of PM$_{2.5}$ and its main water-soluble ions (Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$) was conducted at a urban site in Tianjin, China in both summer and winter. In this study, we confirmed the optimum concentration of absorbents of Na$_2$CO$_3$ and citric acid for HDS were 3% and 6% in summer experiments and 4% and 5% in winter experiments. Daily mean concentrations of Cl$^-$ obtained by HDS were higher than those by FS both in summer and winter. In contrast, the HDS gave lower daily mean SO$_4^{2-}$ concentrations than FS in both summer and winter. For NO$_3^-$ and NH$_4^+$, concentrations obtained by HDS were lower than those obtained by FS in winter. However, the HDS gave larger values of NO$_3^-$ and NH$_4^+$ than FS in summer. The different results of different ions were in response to the concentrations of interfering gases in ambient air and chemical characteristics of ionic species. In addition, the concentrations of PM$_{2.5}$ obtained by HDS were higher than those obtained by FS in summer, while virtually no significant difference between HDS and FS in winter. Our study points out that investigating optimum concentrations of coating solutions before denuder system sampling is necessary. Moreover, it is essential to make careful evaluation and modification when applying FS in highly polluted Environment, especially for PM$_{2.5}$ ions determining.

Keywords: Filtration system; Honeycomb denuder system; Acidic/Alkalic gases; Coating solution.

INTRODUCTION

Fine particulate matter (PM$_{2.5}$) is the main air pollutant in many cities of China. Water-soluble ions are the main components of atmospheric PM$_{2.5}$ (He et al., 2001; Gao et al., 2011). They can affect human heath, reduce visibility, acidify rain water, and alter the radiation balance of the atmosphere (Ding et al., 2008; Ostro et al., 2009; Polichetti et al., 2009; Cao et al., 2012; Robichaud and Ménard, 2014). Therefore, accurate measurements of atmospheric PM$_{2.5}$ and its compositions are essential for understanding aerosol properties and effects. Usually, the conventional measurement of PM$_{2.5}$ and its compositions is filtration system (FS), which includes a 2.5 μm cut inlet. Filters are used in FS samplers to collect PM$_{2.5}$. PM$_{2.5}$ concentrations are determined by weighing before and after sampling, and then main water-soluble ions in PM$_{2.5}$ are measured with subsequent chemical analysis.

When sampling particulate matters using FS as described above, possible sampling artifacts maybe exist. In FS, potentially interfering gases (such as SO$_2$, HNO$_3$, NH$_3$) are not removed prior to sampling, positive artifacts due to the adsorption of acidic and alkalic gases on filters can give rise to an overestimation of aerosol concentration, shown as Eqs. (1)-(5) (Pathak et al., 2004; Lin et al., 2010; Ohba et al., 2010; Pathak et al., 2010; Huang et al., 2011; Liu et al., 2013).

$$3\text{SO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{S} + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad (1)$$

$$4\text{SO}_2 + 4\text{H}_2\text{O} \leftrightarrow \text{H}_2\text{S} + 3\text{SO}_4^{2-} + 6\text{H}^+ \quad (2)$$

$$\text{HCl} \leftrightarrow \text{H}^+ + \text{Cl}^- \quad (3)$$

$$\text{HNO}_3 \leftrightarrow \text{H}^+ + \text{NO}_3^- \quad (4)$$

$$\text{H}^+ + \text{NH}_3 \leftrightarrow \text{NH}_4^+ \quad (5)$$

* Corresponding author.
Tel.: +86 22 23503397; Fax: +86 22 23503397
E-mail address: jiyaqin@nankai.edu.cn
On the other hand, the evaporation of semi-volatile compounds such as ammonium nitrate from collecting filter, which are called negative artifacts, can result in significant underestimation of their components via the following Eqs. (6)–(7) (Pathak et al., 2003, 2004; Chow et al., 2005; Pathak and Chan, 2005; Liu et al., 2014).

\[
\begin{align*}
\text{NH}_4^+ + \text{Cl}^- & \leftrightarrow \text{NH}_3 + \text{HCl} \quad (6) \\
\text{NH}_4^+ + \text{NO}_3^- & \leftrightarrow \text{NH}_3 + \text{HNO}_3 \quad (7)
\end{align*}
\]

Hence, the results obtained by FS may be uncertain. To solve these potential problems, some kinds of denuders have been used to separate and remove acidic/alkaline gases prior to collecting particulate matters, and a back-up filter is recommended to collect vapors (Possanzini et al., 1983; Koutrakis et al., 1993; Chow, 1995; Ashok and Gupta, 2012). A combination of honeycomb denuders and back-up filters for sampling of mutually convertible atmospheric species such as SO\(_2\) and SO\(_4^{2-}\), HNO\(_3\) and NO\(_3^-\), NH\(_3\) and NH\(_4^+\), HCl and Cl\(^-\) (Koutrakis et al., 1993; Pathak et al., 2003; Pathak et al., 2004; Nie et al., 2010; Huang et al., 2011), the so-called honeycomb denuder system (HDS), has been tested by many investigators. In their studies, the concentrations of adsorbents coated on denuders to collect acidic/alkaline gases are almost the same, despite of the spatial and temporal disparities. However, the concentrations of major interfering gases in ambient air such as SO\(_2\), HNO\(_3\), NH\(_3\) vary significantly with seasons and geographic locations (Ianniello et al., 2011). Therefore, confirming the optimum concentrations of coating solutions before sampling PM\(_{2.5}\) using HDS is essential, especially in China where the atmospheric concentrations of particulate matter are much higher. Despite of the existence of sampling artifacts, samplers without denuders and back-up filters are still widely used because of the cost-effective equipment and convenient operation (Louie et al., 2005; Shi et al., 2009; Tian et al., 2014).

This study confirmed the optimum concentrations of coating solutions of HDS in Tianjin, China and compared the measurement results of PM\(_{2.5}\) and major water-soluble ions from a FS and a HDS in both summer and winter.

**MATERIALS AND METHODS**

**Sampling Site**

The sampling site (39°05′N, 117°09′E) was in Tianjin, which is a large city near the capital of China, adjacent to the Bohai Sea. The area of Tianjin city is 11,200 km\(^2\) and the population is over ten million. PM\(_{2.5}\) is the main pollutant in Tianjin like many other north cities of China. Its temperate monsoon climate causes four distinct seasons. The location of the sampling site is provided in Fig. 1.

The samplers were set on the roof (20 m above ground level) of a building at the Nankai university campus, which is located in a large residential and educational area, and about 500 m away from a major road. There are no high buildings around and no special contamination.

**Instruments**

Two different methods, filtration system (FS) and honeycomb denuder system (HDS) were employed to measure PM\(_{2.5}\) and water-soluble ions. The experimental period ran from July 1 of 2013 to August 31 of 2013 (summer campaign) and January 1 of 2014 to February 24 of 2014 (winter campaign). During the sampling periods, most of the samples were collected for 22 h from 8 a.m to the next day 6 a.m, but a few shorter-time (6 h) samples were collected on heavy pollution days in winter.
Field Experiments
As shown in Optimum concentrations of coating solutions, the optimum concentrations of Na$_2$CO$_3$ and citric acid were 3% and 6% in summer, but 4% and 5% in winter, respectively. Therefore, the first denuder was coated with Na$_2$CO$_3$ (3% (w/v)) in summer campaign while 4% (w/v) in winter campaign) and 1% (w/v) glycerol in a 50% H$_2$O/50% methanol mixture (v/v) to absorb SO$_2$, HNO$_3$, and HCl gases. The second denuder was coated with citric acid (6% (w/v)) in summer campaign while 5% (w/v) in winter campaign) and 2% (w/v) glycerol in methanol to absorb NH$_3$ during the field experiments.

The filter pack was comprised of a 47 mm diameter Teflon filter (F$_1$) for particle collection, a nylon back-up filter (F$_3$) for absorbing evaporated HCl and HNO$_3$, and an addition Teflon back-up filter (F$_3$) coated with the citric acid solution for absorbing evaporated NH$_3$ (Pathak et al., 2004).

Analysis of Samples
Prior to sampling, all the filters were heated at 40°C for 2 h, and the sampled filters were stored at −4°C in order to minimize artifacts. For FS samples, the PM$_{2.5}$ mass was determined by Teflon filters using the standard gravimetric method. Before weighing, the filters were balanced for 2 h under the condition of constant temperature (20°C ± 1°C) and constant relative humidity (40% ± 5%). After gravimetric analysis of the filter samples, particulates on the Teflon were dissolved completely in an ultrasonic bath in 5 mL ultra-pure water (purified by Milipore Water Purification System) for 50 minutes (twice washed, 25 minutes each time). The extracts were stored at 4°C in a pre-cleaned tube before analysis. Ion chromatography (ICS-900, DIONEX) was used to analyze Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$.

For the HDS samples, the front Teflon filters were analyzed as described above, while the second nylon filters were extracted with 5 mL ultra-pure water to extract chloride and nitrate. The third citric coated Teflon filters were extracted with 5 mL ultra-pure water for ammonium analysis. All of these extracted samples were also analyzed by the IC.

Background contamination was routinely monitored through blank tests. Enough blank tests (nearly 10% of samples) were conducted and used to correct corresponding data. The pre-treatment procedure, chemical analysis can be referred to our previous works and other related studies (Bi et al., 2007; Kong et al., 2010; Shi et al., 2009; Tian et al., 2014). Fig. 3 illustrates a flow diagram of procedure of this study.

RESULTS AND DISCUSSION

Optimum Concentrations of Coating Solutions
Table 1 shows the efficiencies of the collections for various gases with different concentrations of coating solutions, in which the efficiency was expressed as W(D$_f$)/[W(D$_f$) + W(D$_s$)] × 100%, where W(D$_f$) and W(D$_s$) are the masses of the gaseous species collected by the first denuder and second denuder, respectively. Three sets of parallel tests have been carried out to determine the efficiencies of gas collections by the honeycomb denuder for each concentration of adsorbents during the prior period of the sampling campaign. The reported values of efficiencies are averages of the measurements of three parallel tests. No detectable amounts of Cl$^-$, SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ were found on blank denuders.

Fig. 2. Schematic of ChemComb 3500 honeycomb denuder system.

38mm Glass Spacer
First Denuder
Second Denuder
Spring
Teflon Filter
Nylon Filter

Air
Inlet

Honeycomb
Denuder

Spacer

To
Pump
From Table 1, it can be seen that the optimum concentrations of Na₂CO₃ and citric acid were 3% and 6% in summer, while optimum concentrations of Na₂CO₃ and citric acid were 4% and 5% in winter, respectively. The phenomenon, adsorption efficiencies are different when the coating solution concentrations are different, observed in this study were also found in Beijing (Li et al., 2010). The results indicated that the optimum concentrations of coating solution were not the same at different sampling periods, even though in the same sampling location. The difference may be due to the changes of temperature, relative humidity and concentrations of interfering gases. Therefore, investigating optimum concentrations of coating solutions before denuder system sampling is necessary.

Although denuders were installed in the HDS to remove interfering gases such as SO₂, NO₃, NH₄, it appeared that the SO₂, NH₄ levels in the site were so high that the gases could not be completely removed and thus penetrated the denuders (Wu and Wang, 2007). In Table 1, the efficiencies of the collections of various gases in winter were lower than those in summer. One reason could be the generally higher levels of interfering gases in winter.

Loss Aerosols from Collecting Filters

The HDS was used for determining the loss ratio \(L_r\) of unstable aerosol components on the Teflon filter. The extent of the negative sampling artifacts will be expressed in term of the \(L_r\). For instance, the \(L_r\) is expressed by

\[
L_r = \frac{F_b}{F_b + F_t}
\]

where, \(F_b\) and \(F_t\) stand for the mass of gaseous components on the back-up filters (Nylon filter and impregnated Teflon filter), and the concentrations on the Teflon filter, respectively. SO₄²⁻ is not volatile. Therefore, no detectable amounts of SO₄²⁻ were found on back-up filters. The calculation results using Eq. (8) and the data of \(L_r\) are shown in Table 2. The loss rates were higher in summer and lower in winter, and the \(L_s\) of aerosol were as follows: Cl⁻: 10.3%–76.2% (average: 26.2%), NO₃⁻: 27.3%–86.6% (45.6%), and NH₄⁺: 26.7%–53.9% (41.3%) in summer while Cl⁻: 1.5%–35.8% (9.4%) NO₃⁻: 2.5%–72.0% (18.8%), and NH₄⁺: 2.0%–18.5% (6.6%) in winter. These results indicated that remarkable negative artifacts existed during sampling PM₂.5 and main ionic species with FS sampler in Tianjin, especially during summer sampling.

Compared with the summer campaign, the evaporative losses of ionic species were lower in winter. On average, about 18% nitrate loss was observed from the Teflon filters, but much greater losses (~72%) were found at low concentrations (nitrate < 10 μg/m³). The conclusions were also drawn from the chlorate and ammonium. Similar results were found in other studies (Nie et al., 2010). Therefore, cautions should be taken on the potential under-determination of inorganic species and other semi-volatile compounds such as some forms of organic carbon.

The correlation between loss of NH₄⁺ (molar concentration) and loss of Cl⁻ + NO₃⁻ (molar concentration) was existent, with \(R^2 = 0.581\) and a slope of 1.08. Fig. 4 shows that these losses can be explained by the loss of NH₄NO₃ + NH₄Cl aerosol from the Teflon filters. Similar findings were reported elsewhere (Matsumoto and Okita, 1998).

Comparison of Ionic Concentration

Fig. 5 shows the concentrations of Cl⁻, NO₃⁻, SO₄²⁻ and NH₄⁺ obtained by the HDS and FS in both winter and summer in Tianjin. The concentrations of Cl⁻, NO₃⁻ and NH₄⁺ in PM₂.5 obtained by HDS can be estimated by adding the concentrations on the Teflon and the corresponding back-up filters. SO₄²⁻ is a non-evaporative specie. Its concentration was therefore taken from that on the Teflon filters only. There were obvious differences in concentrations of ionic species of NO₃⁻, SO₄²⁻ and NH₄⁺ between HDS and FS sampler.

As shown in Fig. 5(a), the daily mean concentrations of Cl⁻ obtained by HDS were higher (8.80 μg/m³ in winter and 1.81 μg/m³ in summer) than those by FS (8.33 μg/m³ in winter and 1.49 μg/m³ in summer) both in summer and winter, with slopes of 0.88 and 0.95, respectively. Therefore, negative artifacts, loss of chlorate due to evaporation, played a more important role than positive artifacts for Cl⁻ during PM₂.5 sampling. On average, the concentrations of Cl⁻ from FS were 94% of those from HDS in winter but only 76% in summer. Less volatilization of Cl⁻ in winter, which can be drawn in Loss aerosols from collecting filters, may lead to the difference.
Table 1. Efficiencies of collection of gaseous species by honeycomb denuder.

| Season   | Coating material of denuder | $W(D_f)/[W(D_f) + W(D_s)] \times 100$ (%) | Sampling conditions |
|----------|-----------------------------|------------------------------------------|---------------------|
|          |                             | $W(D_f)/[W(D_f) + W(D_s)] \times 100$ (%) | Temp. (°C) | RH (%) | Conc. (SO$_2$) ($\mu$g/m$^3$) |
| Summer   | 1% Na$_2$CO$_3$ $^a$        | 68.6                                      | 27         | 76     | 16.2                          |
|          | 2% Na$_2$CO$_3$ $^a$        | 60.7                                      | 29         | 69     | 14.5                          |
|          | 3% Na$_2$CO$_3$ $^a$        | 81.4                                      | 29         | 63     | 25.2                          |
|          | 4% Na$_2$CO$_3$ $^a$        | 75.1                                      | 30         | 61     | 31.9                          |
|          | 4% Citric acid $^b$         | 90.0                                      | 29         | 49     | 12.4                          |
|          | 5% Citric acid $^b$         | 93.1                                      | 27         | 54     | 9.1                           |
|          | 6% Citric acid $^b$         | 98.1                                      | 28         | 62     | 11.6                          |
|          | 7% Citric acid $^b$         | 97.1                                      | 28         | 66     | 20.6                          |
| Winter   | 1% Na$_2$CO$_3$ $^a$        | 60.5                                      | 1          | 25     | 139.7                         |
|          | 2% Na$_2$CO$_3$ $^a$        | 61.3                                      | 1          | 31     | 184.3                         |
|          | 3% Na$_2$CO$_3$ $^a$        | 72.1                                      | 2          | 43     | 189.2                         |
|          | 4% Na$_2$CO$_3$ $^a$        | 79.4                                      | 1          | 40     | 70.7                          |
|          | 5% Na$_2$CO$_3$ $^a$        | 67.7                                      | 1          | 52     | 85.4                          |
|          | 6% Na$_2$CO$_3$ $^a$        | 63.2                                      | 2          | 45     | 169.3                         |
|          | 1% Citric acid $^b$         | 62.4                                      | 1          | 43     | 164.8                         |
|          | 2% Citric acid $^b$         | 65.9                                      | 2          | 50     | 146.7                         |
|          | 3% Citric acid $^b$         | 65.4                                      | 1          | 48     | 172.7                         |
|          | 4% Citric acid $^b$         | 63.7                                      | 1          | 46     | 194.2                         |
|          | 5% Citric acid $^b$         | 93.7                                      | 2          | 39     | 144.6                         |
|          | 6% Citric acid $^b$         | 77.6                                      | 3          | 43     | 126.5                         |
|          | 7% Citric acid $^b$         | 78.2                                      | 3          | 45     | 75.0                          |

D$_f$: first denuder, D$_s$: second denuder;
$^a$ Coating solution with 1% (w/v) glycerol in a 50% H$_2$O/50% methanol mixture (v/v);
$^b$ Coating solution with 2% (w/v) glycerol in methanol.

The overall NO$_3^-$ comparison results between the HDS and the FS are shown in Fig. 5(b). The correlation between the two methods in summer was excellent, with $R^2 = 0.946$ and a slope of 0.64, indicating that the HDS gave larger NO$_3^-$ values (10.61 $\mu$g/m$^3$) than the FS samples (6.45 $\mu$g/m$^3$). As shown in Loss aerosols from collecting filters, the lower nitrate values in the FS could be attributed to evaporation loss of NO$_3^-$ from Teflon filter. In contrast to summer, data from winter showed an excellent overall adjustment ($R^2 = 0.974$) of NO$_3^-$ between the two methods, but overall slope was 1.05. The concentrations of NO$_3^-$ from HDS (33.30 $\mu$g/m$^3$) were lower than those from FS (35.18 $\mu$g/m$^3$). This phenomenon may be resulted from lower temperature, which leads to less evaporation of NO$_3^-$, and higher NO$_x$ and HNO$_3$ levels that can attributed to positive artifacts in winter (Wang et al., 2006; Kai et al., 2007).

The SO$_2^-$ concentrations are shown in Fig. 5(c). The HDS SO$_2^-$ was highly correlated with FS SO$_2^-$ in both summer campaign ($R^2 = 0.988$) and winter campaign ($R^2 = 0.994$), but the HDS gave lower daily mean SO$_2^-$ concentrations (32.81 $\mu$g/m$^3$ in winter and 15.18 $\mu$g/m$^3$ in summer) than FS (39.37 $\mu$g/m$^3$ in winter and 17.21 $\mu$g/m$^3$ in summer). In general, the HDS showed 88% of FS SO$_2^-$ in summer but only 83% in winter, with a slope of 1.09 for summer and 1.18 for winter. During winter campaign, much higher concentrations of SO$_2$ and PM$_{2.5}$ were observed. One possible explanation for the higher value from FS is the SO$_2$ absorption by the alkaline particles collected (Pathak and Chan, 2005; Wu and Wang, 2007), especially in winter with an average higher level of SO$_2$ in sampling site.

Fig. 5(d) shows the concentrations of NH$_4^+$ obtained from the HDS and FS. The correlation between the two methods was excellent in winter, with a $R^2 = 0.974$ and a slope of 0.58. In summer campaign, the daily mean concentration of NH$_4^+$ from HDS (8.47 $\mu$g/m$^3$) was higher than that of the FS (5.51 $\mu$g/m$^3$), indicating that higher temperature deduced higher NH$_4^+$ evaporation and leaded to a significant loss of NH$_4^+$. During winter campaign, the result was adverse. The FS gave a larger value of NH$_4^+$ (29.34 $\mu$g/m$^3$) than that of the HDS (26.80 $\mu$g/m$^3$). The phenomenon indicated that the absorption of NH$_4^+$ could have played a more important role than evaporation of NH$_4^+$, much less loss of NH$_4^+$ was observed in winter as mentioned previously.

Comparison of PM$_{2.5}$ Concentrations

Fig. 6 shows a comparison of the PM$_{2.5}$ measurements of the two systems (FS and HDS) in both summer and winter. The values of PM$_{2.5}$ obtained by HDS, included both the PM$_{2.5}$ concentration measured by the Teflon filter and evaporative gas concentrations from back-up filters. To compare the difference between the concentrations of PM$_{2.5}$ determined by HDS and FS, Wilcoxon Signed Ranks Test was applied, and the results showed that there were no significant statistical differences between them in winter while differences existed in summer ($P_{summer} = 0.001$, $P_{winter} = 0.773$). Data from air pollution monitoring station show that the daily mean concentration of SO$_2$ was 134.8 ± 75.5 $\mu$g/m$^3$ in winter campaign while 19.9 ± 21.5 $\mu$g/m$^3$ in summer.
Table 2. Losses of aerosols from collecting filter.

| Season | Date | Conc. loss Cl– (μg/m³) | Conc. loss NO3– (μg/m³) | Conc. loss NH4+ (μg/m³) |
|--------|------|-------------------------|-------------------------|-------------------------|
|        |      | Lr (%)                  | Lr (%)                  | Lr (%)                  |
|        |      |                          |                          |                          |
| Summer | 8.03 | 1.35                    | 0.34                    | 20.2                    |
|        | 8.04 | 0.62                    | 0.21                    | 25.3                    |
|        | 8.05 | 1.54                    | 0.39                    | 20.3                    |
|        | 8.07 | 0.56                    | 0.12                    | 17.5                    |
|        | 8.08 | 3.41                    | 0.43                    | 11.2                    |
|        | 8.10 | 1.52                    | 0.17                    | 10.3                    |
|        | 8.14 | 2.37                    | 0.41                    | 14.7                    |
|        | 8.17 | 0.16                    | 0.52                    | 76.2                    |
|        | 8.19 | 4.04                    | 0.78                    | 16.2                    |
|        | 8.20 | 2.37                    | 0.90                    | 27.5                    |
|        | 8.22 | 1.11                    | 0.13                    | 10.3                    |
|        | 8.25 | 0.08                    | 0.06                    | 41.6                    |
|        | 8.26 | 1.01                    | 0.41                    | 28.8                    |
|        | 8.28 | 1.46                    | 0.27                    | 15.4                    |
|        | 8.31 | 0.20                    | 0.28                    | 57.7                    |
|        | Avg  | 1.45                    | 0.36                    | 26.2                    |
| Winter | 2.09 | 4.38                    | 0.61                    | 12.2                    |
|        | 2.10 | 14.82                   | 0.55                    | 3.6                     |
|        | 2.11 | 37.06                   | 0.57                    | 1.5                     |
|        | 2.12 | 14.50                   | 0.42                    | 2.8                     |
|        | 2.13 | 11.06                   | 0.54                    | 4.7                     |
|        | 2.14 | 12.26                   | 0.23                    | 1.9                     |
|        | 2.15 | 13.54                   | 0.75                    | 5.3                     |
|        | 2.17 | 6.06                    | 0.47                    | 7.2                     |
|        | 2.18 | 6.11                    | 0.49                    | 7.4                     |
|        | 2.19 | 14.01                   | 0.40                    | 2.8                     |
|        | 2.20 | 10.08                   | 0.83                    | 7.6                     |
|        | 2.21 | 0.43                    | 0.24                    | 35.8                    |
|        | 2.22 | 0.67                    | 0.25                    | 26.7                    |
|        | 2.23 | 1.32                    | 0.19                    | 12.8                    |
|        | 2.24 | 7.24                    | 0.68                    | 8.6                     |
|        | Avg  | 10.24                   | 0.48                    | 9.4                     |

Conc.: Ft, loss: Fb, Lr: Fb/(Fb + Ft) × 100%.

Fig. 4. Relationship between NH4+ and Cl– + NO3– loss of aerosols.
Fig. 5. Scatter plots of Cl\(^{-}\) (a), NO\(_3\)\(^{-}\) (b), SO\(_4\)\(^{2-}\) (c) and NH\(_4\)\(^+\) (d) from HDS and FS in both summer and winter.

Fig. 6. Scatter plots of PM\(_{2.5}\) from HDS and FS in both summer and winter.
campaign. Therefore, the positive artifact level may be higher in winter than in summer. As to negative artifact, in Loss aerosols from collecting filters, the results of Nylon and second Teflon filter illustrate that the loss rates were higher in summer and lower in winter. In other words, the negative artifact level in summer was higher than in winter. The values of PM$_{2.5}$ concentrations from HDS (78.34 μg/m$^3$) were generally higher than those from FS (69.26 μg/m$^3$) in summer (Fig. 6(a)) when the negative artifact level accounted for a significant fraction. This phenomenon may be caused by higher volatilization of semi-volatile PM$_{2.5}$ due to higher temperature and lower concentrations of acidic/alkaline gases, which made the positive artifact level insignificant in summer. The very little differences between PM$_{2.5}$ (HDS, 223.37 μg/m$^3$) and PM$_{2.5}$ (FS, 226.37 μg/m$^3$) in winter (Fig. 6(b)) suggested that positive artifact concentrations found in the FS sampler were well balanced by the losses of evaporative species or non-evaporative species due to reaction and evaporation in winter.

CONCLUSIONS

Data of PM$_{2.5}$ and main water-soluble ions from two filter-based samplers (FS and HDS) were compared to assess the sampling artifacts of these techniques under very serious polluted conditions. Field studies were conducted at an urban site in Tianjin, China in both summer and winter. The main findings were summarized as follows.

1) The optimum concentrations of absorbents of Na$_2$CO$_3$ and citric acid were 3% and 6% in summer experiments while 4% and 5% in winter experiments, respectively.

2) The loss rate of semi-volatile PM$_{2.5}$ was higher in summer and lower in winter. The major volatile ammonium species were NH$_4$Cl and NH$_4$NO$_3$ in the Teflon filters of the HDS. Similar conclusion can be drawn for the FS sampler.

3) Concentrations of Cl$^-$ obtained by HDS were higher than those obtained by FS in both summer and winter. In contrast, the values of SO$_4^{2-}$ from FS were higher than those from HDS in both summer and winter. Concentrations of NO$_3^-$ and NH$_4^+$ obtained by HDS were lower than those obtained by FS in winter while inversion in summer.

4) The concentrations of PM$_{2.5}$ obtained by HDS were higher than those obtained by FS in summer, while virtually no significant difference in winter.

5) Even though differences of concentrations of ions and PM$_{2.5}$ between HDS and FS in both summer and winter, the concentrations of Cl$^-$, NO$_3^-$, NH$_4^+$ and PM$_{2.5}$ between the two methods were close in winter. In consideration of economy and handleability of sampling, it should be fine to use the FS system in winter when the SO$_4^{2-}$ was not emphasis of one study.

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