



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

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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⁻, NO₃⁻, SO₄²⁻ and NH₄⁺) 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 Na₂CO₃ 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 SO₄²⁻ concentrations than FS in both summer and winter. For NO₃⁻ and NH₄⁺, concentrations obtained by HDS were lower than those obtained by FS in winter. However, the HDS gave larger values of NO₃⁻ and NH₄⁺ 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.

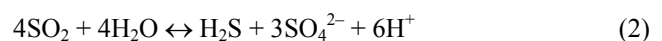
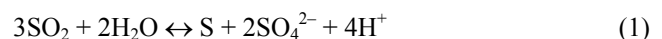
Keywords: Filtration system; Honeycomb denuder system; Acidic/Alkalic gases; Coating solution.

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 health, 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.

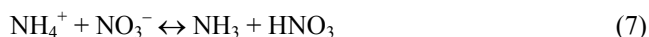
When sampling particulate matters using FS as described above, possible sampling artifacts maybe exist. In FS, potentially interfering gases (such as SO₂, HNO₃, NH₃) are not removed prior to sampling, positive artifacts due to the adsorption of acidic and alkalic gases on filters can give rise to an 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).



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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).



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/alkalic 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/alkalic 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 km² and the population is over ten million. $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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.

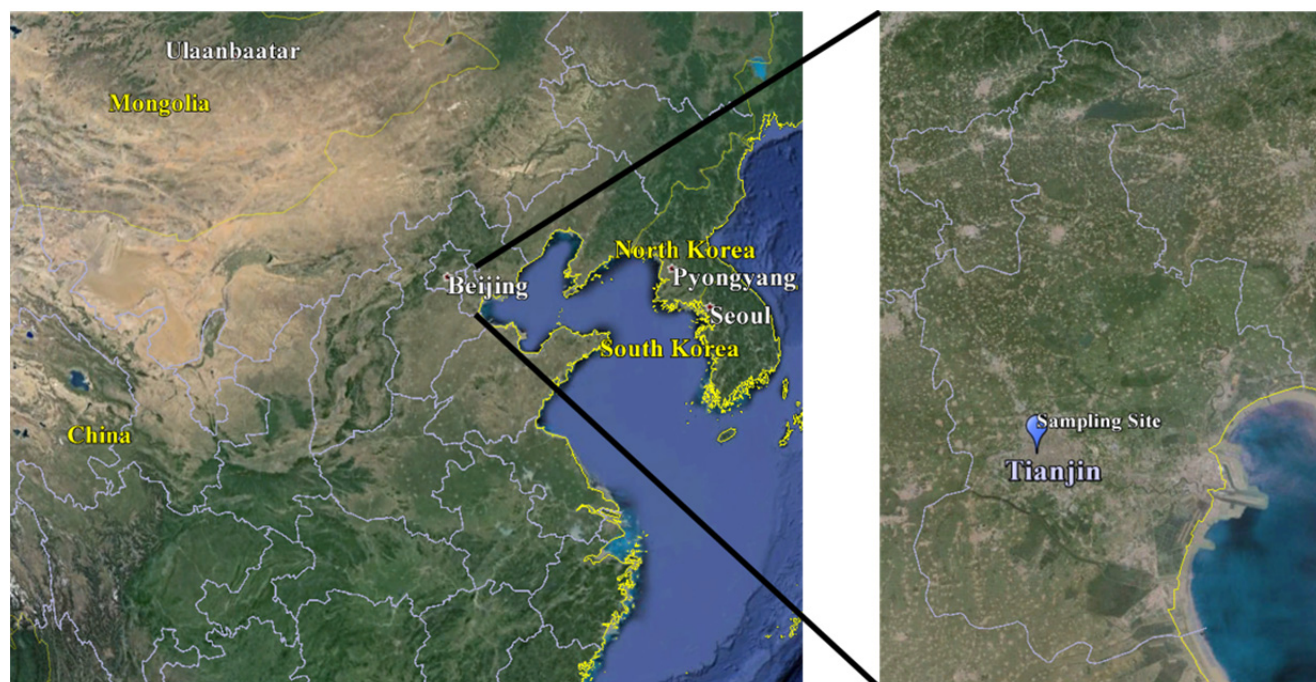


Fig. 1. Location of the sampling site in Tianjin, China.

FS

A medium volume sampler (MSV6, Sven Leckel, Berlin, Germany) equipped with a PM_{2.5} inlet was used to collect PM_{2.5} samples on Teflon filters (2 μm pore size and 47 mm diameter, Pall Inc.) at a flow rate of 2.3 m³/h. The same model number of sampler can be found in other literatures (Škrdlíková *et al.*, 2011).

HDS

The Harvard honey denuder filter-pack system (Chemcomb Model 3500) (Fig. 2) uses two denuders in series to remove acidic and alkalic gases prior to collecting particles on the filter. More introduction about HDS can be found in other studies (Koutrakis *et al.*, 1993; Sioutas *et al.*, 1996).

Optimum Concentrations of Coating Solutions

During the prior period of the sampling campaign, we should determine the optimum concentrations of Na₂CO₃ solution and citric acid solution coated on honeycomb denuders for absorbing acidic and alkalic gases. On the basis of previous studies (Chen *et al.*, 2003; Pathak *et al.*, 2004; Lin *et al.*, 2010; Huang *et al.*, 2011), the concentration gradients of Na₂CO₃ in this study were set as 1%, 2%, 3%, 4% in summer and 1%, 2%, 3%, 4%, 5%, 6% in winter; for citric acid solution they were 4%, 5%, 6%, 7% in summer and 1%, 2%, 3%, 4%, 5%, 6%, 7% in winter. Coating and extraction procedures of the HDS system followed those described by the Koutrakis (1992) and Lee (1993). When determining the optimum concentration of Na₂CO₃ solution (citric acid solution), the two denuders were coated same concentration of Na₂CO₃ solution (citric acid solution), and then using a medium volume sampler (MSV6) sampling ambient air. The species were extracted from Na₂CO₃ coated on denuders into 0.3% (v/v) aqueous H₂O₂ solution to oxidize sulfite to sulfate. Ion chromatography (ICS-900, DIONEX) was applied to determine the water soluble ions (Cl⁻, NO₃⁻, SO₄²⁻ and NH₄⁺) in the aqueous extracts of the denuders.

Field Experiments

As shown in *Optimum concentrations of coating solutions*, the optimum concentrations of Na₂CO₃ and citric acid were

3% and 6% in summer, but 4% and 5% in winter, respectively. Therefore, the first denuder was coated with Na₂CO₃ (3% (w/v) in summer campaign while 4% (w/v) in winter campaign) and 1% (w/v) glycerol in a 50% H₂O/50% methanol mixture (v/v) to absorb SO₂, HNO₃, 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 NH₃ during the field experiments.

The filter pack was comprised of a 47 mm diameter Teflon filter (F₁) for particle collection, a nylon back-up filter (F₂) for absorbing evaporated HCl and HNO₃, and an addition Teflon back-up filter (F₃) coated with the citric acid solution for absorbing evaporated NH₃ (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 72 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⁻, NO₃⁻, SO₄²⁻ and NH₄⁺.

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 $W(D_f)/[W(D_f) + W(D_s)] \times 100\%$, 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⁻, SO₄²⁻, NO₃⁻ and NH₄⁺ were found on blank denuders.

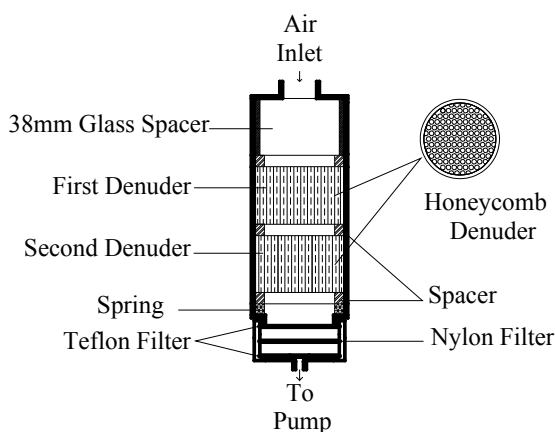


Fig. 2. Schematic of ChemComb 3500 honeycomb denuder system.

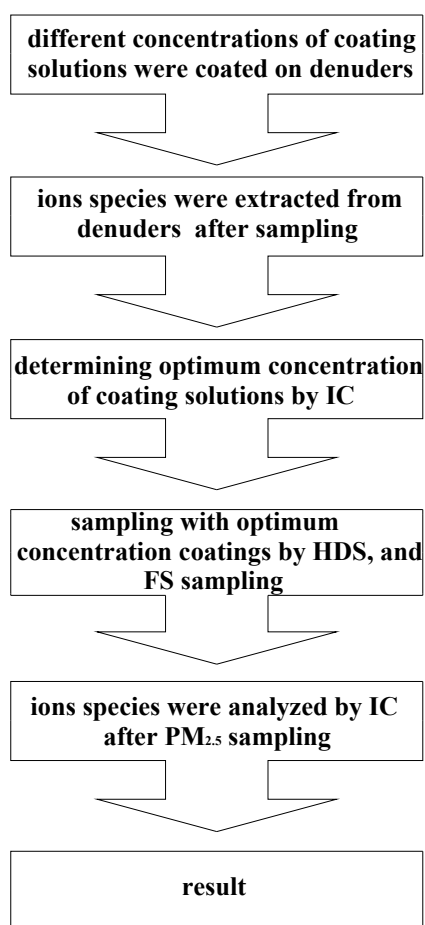


Fig. 3. Flow diagram of the procedure.

From Table 1, it can be seen that the optimum concentrations of Na_2CO_3 and citric acid were 3% and 6% in summer, while optimum concentrations of Na_2CO_3 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 SO_2 , NO_3 , NH_3 , it appeared that the SO_2 , NH_3 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

$$L_r = F_b / (F_b + F_t) \quad (8)$$

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. SO_4^{2-} is not volatile. Therefore, no detectable amounts of SO_4^{2-} 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_r s of aerosol were as follows: Cl^- : 10.3%–76.2% (average: 26.2%), NO_3^- : 27.3%–86.6% (45.6%), and NH_4^+ : 26.7%–53.9% (41.3%) in summer while Cl^- : 1.5%–35.8% (9.4%) NO_3^- : 2.5%–72.0% (18.8%), and NH_4^+ : 2.0%–18.5% (6.6%) in winter. These results indicated that remarkable negative artifacts existed during sampling $\text{PM}_{2.5}$ 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 < $10 \mu\text{g}/\text{m}^3$). 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 NH_4^+ (molar concentration) and loss of $\text{Cl}^- + \text{NO}_3^-$ (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 $\text{NH}_4\text{NO}_3 + \text{NH}_4\text{Cl}$ 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^- , NO_3^- , SO_4^{2-} and NH_4^+ obtained by the HDS and FS in both winter and summer in Tianjin. The concentrations of Cl^- , NO_3^- and NH_4^+ in $\text{PM}_{2.5}$ obtained by HDS can be estimated by adding the concentrations on the Teflon and the corresponding back-up filters. SO_4^{2-} 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 NO_3^- , SO_4^{2-} and NH_4^+ between HDS and FS sampler.

As shown in Fig. 5(a), the daily mean concentrations of Cl^- obtained by HDS were higher ($8.80 \mu\text{g}/\text{m}^3$ in winter and $1.81 \mu\text{g}/\text{m}^3$ in summer) than those by FS ($8.33 \mu\text{g}/\text{m}^3$ in winter and $1.49 \mu\text{g}/\text{m}^3$ 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 $\text{PM}_{2.5}$ 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			
		HCl	HNO ₃	SO ₂	NH ₃	Temp. (°C)	RH (%)	Conc. (SO ₂) (µg/m ³)	
Summer	1% Na ₂ CO ₃ ^a	68.6	79.8	69.9		27	76	16.2	
	2% Na ₂ CO ₃ ^a	60.7	98.0	85.7		29	69	14.5	
	3% Na ₂ CO ₃ ^a	81.4	97.3	94.3		29	63	25.2	
	4% Na ₂ CO ₃ ^a	75.1	83.5	84.7		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	77.8	69.8		1	25	139.7
		2% Na ₂ CO ₃ ^a	61.3	60.1	78.8		1	31	184.3
		3% Na ₂ CO ₃ ^a	72.1	71.5	79.9		2	43	189.2
		4% Na ₂ CO ₃ ^a	79.4	91.4	79.7		1	40	70.7
		5% Na ₂ CO ₃ ^a	67.7	70.0	78.9		1	52	85.4
		6% Na ₂ CO ₃ ^a	63.2	74.1	80.0		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% H₂O/50% methanol mixture (v/v);

^b Coating solution with 2% (w/v) glycerol in methanol.

The overall NO₃⁻ 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 NO₃⁻ values (10.61 µg/m³) than the FS samples (6.45 µg/m³). As shown in *Loss aerosols from collecting filters*, the lower nitrate values in the FS could be attributed to evaporation loss of NO₃⁻ from Teflon filter. In contrast to summer, data from winter showed an excellent overall adjustment ($R^2 = 0.974$) of NO₃⁻ between the two methods, but overall slope was 1.05. The concentrations of NO₃⁻ from HDS (33.30 µg/m³) were lower than those from FS (35.18 µg/m³). This phenomenon may be resulted from lower temperature, which leads to less evaporation of NO₃⁻, and higher NO_x and HNO₃ levels that can attributed to positive artifacts in winter (Wang et al., 2006; Kai et al., 2007).

The SO₄²⁻ concentrations are shown in Fig. 5(c). The HDS SO₄²⁻ was highly correlated with FS SO₄²⁻ in both summer campaign ($R^2 = 0.988$) and winter campaign ($R^2 = 0.994$), but the HDS gave lower daily mean SO₄²⁻ concentrations (32.81 µg/m³ in winter and 15.18 µg/m³ in summer) than FS (39.37 µg/m³ in winter and 17.21 µg/m³ in summer). In general, the HDS showed 88% of FS SO₄²⁻ 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 SO₂ and PM_{2.5} were observed. One possible explanation for the higher value from FS is the SO₂ absorption by the alkalic particles collected (Pathak and Chan, 2005; Wu and Wang, 2007), especially in winter

with an average higher level of SO₂ in sampling site.

Fig. 5(d) shows the concentrations of NH₄⁺ obtained from the HDS and FS. The correlation between the two methods was excellent in summer, with a $R^2 = 0.974$ and a slope of 0.58. In summer campaign, the daily mean concentration of NH₄⁺ from HDS (8.47 µg/m³) was higher than that of the FS (5.51 µg/m³), indicating that higher temperature deduced higher NH₄⁺ evaporation and led to a significant loss of NH₄⁺. During winter campaign, the result was adverse. The FS gave a larger value of NH₄⁺ (29.34 µg/m³) than that of the HDS (26.80 µg/m³). The phenomenon indicated that the absorption of NH₃ could have played a more important role than evaporation of NH₄⁺, much less loss of NH₄⁺ was observed in winter as mentioned previously.

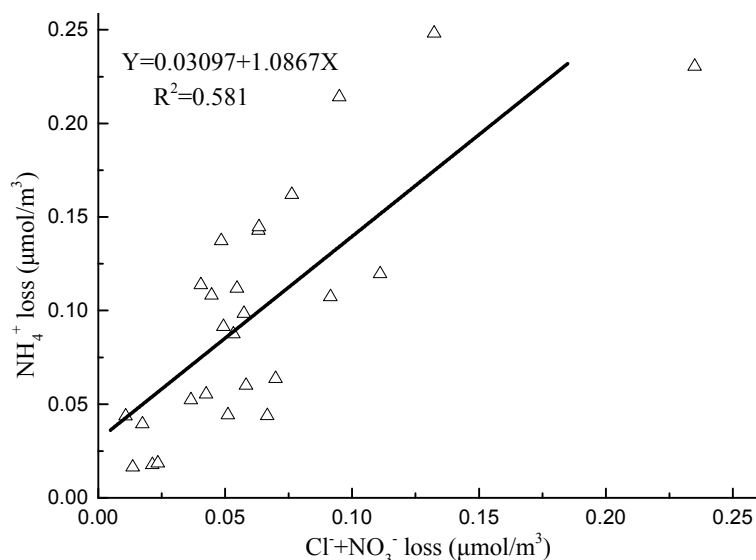
Comparison of PM_{2.5} Concentrations

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 ($P_{\text{summer}} = 0.001$, $P_{\text{winter}} = 0.773$). Data from air pollution monitoring station show that the daily mean concentration of SO₂ was 134.8 ± 75.5 µg/m³ in winter campaign while 19.9 ± 21.5 µg/m³ in summer

Table 2. Losses of aerosols from collecting filter.

Season	Date	Cl ⁻			NO ₃ ⁻			NH ₄ ⁺			Temp. (°C)
		Conc. $\mu\text{g}/\text{m}^3$	loss	L_r (%)	Conc. $\mu\text{g}/\text{m}^3$	loss	L_r (%)	Conc. $\mu\text{g}/\text{m}^3$	loss	L_r (%)	
Summer	8.03	1.35	0.34	20.2	6.21	4.13	40.0	4.87	2.92	37.5	27
	8.04	0.62	0.21	25.3	5.18	3.02	36.8	3.61	2.01	35.8	27
	8.05	1.54	0.39	20.3	17.77	7.52	29.7	7.48	4.47	37.4	28
	8.07	0.56	0.12	17.5	1.78	0.87	32.9	1.95	0.71	26.7	27
	8.08	3.41	0.43	11.2	8.43	3.17	27.3	6.82	2.57	27.4	28
	8.10	1.52	0.17	10.3	6.09	5.58	47.8	3.59	3.85	51.8	30
	8.14	2.37	0.41	14.7	4.12	2.29	35.8	3.08	2.47	44.5	31
	8.17	0.16	0.52	76.2	0.87	5.63	86.6	0.32	0.16	33.7	32
	8.19	4.04	0.78	16.2	13.37	7.56	36.1	12.00	9.82	45.0	31
	8.20	2.37	0.90	27.5	14.94	13.00	46.5	6.79	4.15	37.9	30
	8.22	1.11	0.13	10.3	1.30	2.28	63.7	3.20	2.05	39.0	27
	8.25	0.08	0.06	41.6	0.15	0.54	78.5	4.51	5.26	53.9	30
	8.26	1.01	0.41	28.8	4.08	3.21	44.1	3.55	2.61	42.4	27
	8.28	1.46	0.27	15.4	8.30	7.18	46.4	9.60	11.12	53.7	29
	8.31	0.20	0.28	57.7	0.38	0.18	32.4	0.70	0.79	52.7	28
	Avg		1.45	0.36	26.2	6.20	4.41	45.6	4.80	3.66	41.3
Winter	2.09	4.38	0.61	12.2	11.30	1.57	12.2	10.56	1.00	8.6	3
	2.10	14.82	0.55	3.6	84.56	2.60	3.0	49.49	1.77	3.5	2
	2.11	37.06	0.57	1.5	70.52	1.77	2.5	57.62	1.95	3.3	-1
	2.12	14.50	0.42	2.8	64.49	2.88	4.3	52.42	1.08	2.0	0
	2.13	11.06	0.54	4.7	50.07	4.72	8.6	38.96	1.93	4.7	2
	2.14	12.26	0.23	1.9	49.20	2.66	5.1	37.79	1.65	4.2	1
	2.15	13.54	0.75	5.3	36.33	5.57	13.3	28.07	2.15	7.1	1
	2.17	6.06	0.47	7.2	12.15	1.45	10.7	11.62	0.94	7.5	0
	2.18	6.11	0.49	7.4	21.97	2.31	9.5	23.19	0.80	3.3	0
	2.19	14.01	0.40	2.8	27.98	2.61	8.5	36.58	1.57	4.1	1
	2.20	10.08	0.83	7.6	26.20	2.87	9.9	22.00	1.15	5.0	1
	2.21	0.43	0.24	35.8	0.35	0.90	72.0	1.41	0.32	18.5	2
	2.22	0.67	0.25	26.7	0.49	1.03	67.6	2.58	0.33	11.4	3
	2.23	1.32	0.19	12.8	2.16	0.51	19.0	3.57	0.30	7.6	2
2.24	7.24	0.68	8.6	5.41	2.94	35.3	8.38	0.79	8.6	1	
Avg		10.24	0.48	9.4	30.88	2.43	18.8	25.62	1.18	6.6	1.2

Conc.: F_t , loss: F_b , L_r : $F_b/(F_b + F_t) \times 100\%$.

**Fig. 4.** Relationship between NH₄⁺ and Cl⁻ + NO₃⁻ loss of aerosols.

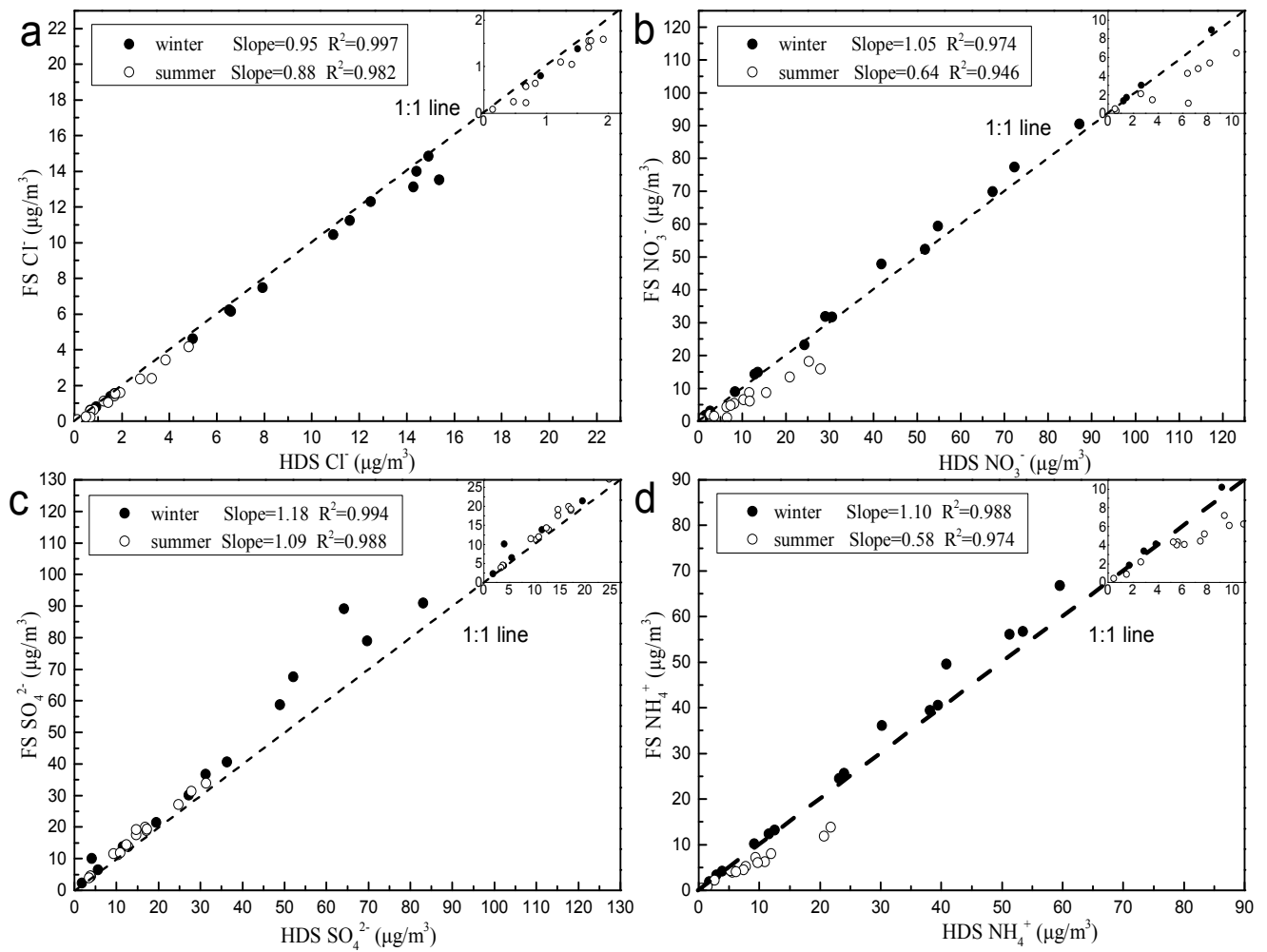


Fig. 5. Scatter plots of Cl⁻ (a), NO₃⁻ (b), SO₄²⁻ (c) and NH₄⁺ (d) from HDS and FS in both summer and winter.

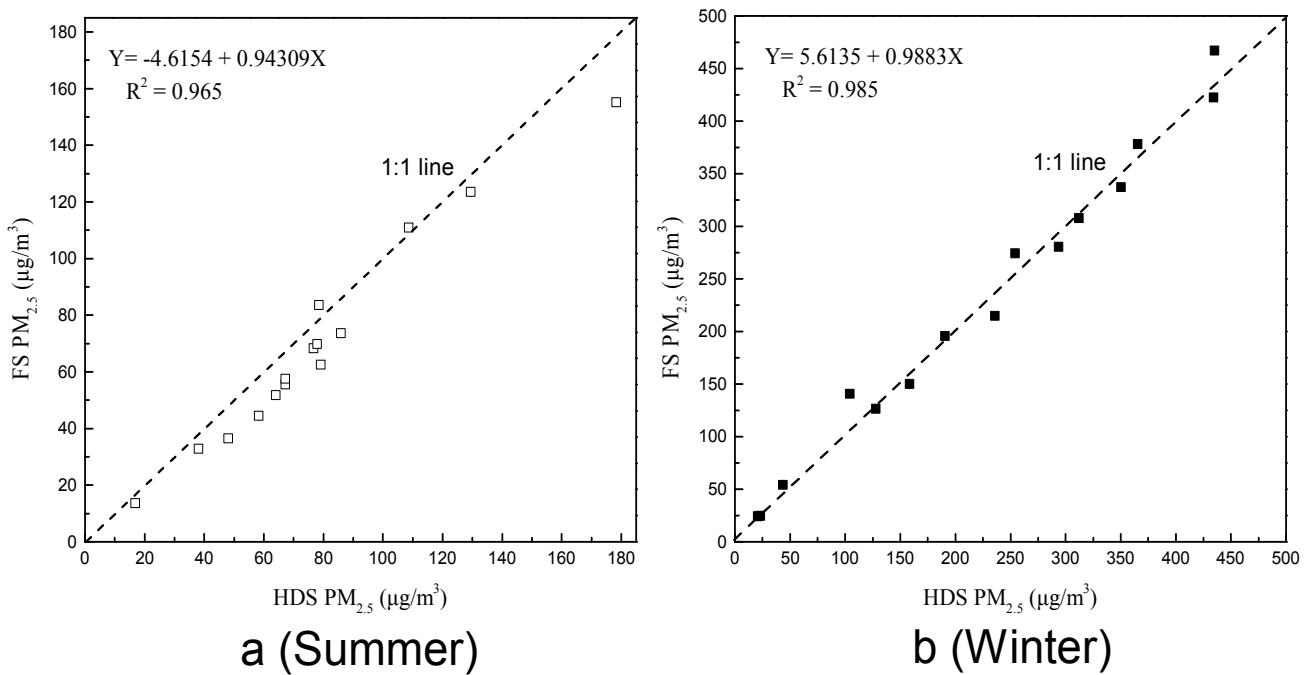


Fig. 6. Scatter plots of PM_{2.5} from HDS and FS in both summer and winter.

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/m³) were generally higher than those from FS (69.26 µg/m³) 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/alkalic gases, which made the positive artifact level insignificant in summer. The very little differences between PM_{2.5} (HDS, 223.37 µg/m³) and PM_{2.5} (FS, 226.37 µg/m³) 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 Na₂CO₃ 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 NH₄Cl and NH₄NO₃ 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 SO₄²⁻ from FS were higher than those from HDS in both summer and winter. Concentrations of NO₃⁻ and NH₄⁺ 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⁻, NO₃⁻, NH₄⁺ 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 SO₄²⁻ was not emphasis of one study.

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Received for review, January 7, 2015

Revised, March 2, 2015

Accepted, March 9, 2015