



Comparison among filter-based, impactor-based and continuous techniques for measuring atmospheric fine sulfate and nitrate

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ARTICLE INFO

Article history:

Received 19 April 2010

Received in revised form

22 July 2010

Accepted 23 July 2010

Keywords:

Particulate matter

Comparison

Denuded filter-pack system

AIM

Artifacts

Aluminum substrate

Evaporation loss

ABSTRACT

Filter-based methods for sampling aerosols are subject to great uncertainty if the gas–particle interactions on filter substrates are not properly handled. Sampling artifacts depend on both meteorological conditions and the chemical mix of the atmosphere. Despite numerous of studies on the subject, very few have evaluated filter-based methods in the Asian environments. This paper reports the results of a comparison of the performances of two filter-based samplers, including a Thermo Anderson Chemical Speciation Monitor (RAAS) and a honeycomb denuder filter-pack system, a Micro Orifice Uniform Deposit Impactor (MOUDI) and a real-time ambient ion monitor (AIM, URG9000B) in measuring atmospheric concentrations of PM_{2.5} sulfate and nitrate. Field studies were conducted at an urban site in Jinan, Shandong province, during the winter of 2007 and at a rural site near Beijing in the summer of 2008. The AIM was first compared with the honeycomb denuder filter-pack system which was considered to have minimal sampling artifacts. After some modifications made to it, the AIM showed good performance for both sulfate and nitrate measurement at the two sites and was then used to evaluate other instruments. For the un-denuded RAAS, the extent of sampling artifacts for nitrate on quartz filters was negligible, while that on Teflon filters was also minimal at high nitrate concentrations ($>10 \mu\text{gm}^{-3}$); however, loss through evaporation was significant ($\sim 75\%$) at low nitrate concentrations under hot summer conditions. The MOUDI using aluminum substrates suffered a significant loss of nitrate (50–70%) under summer conditions due to evaporation. Considering that the aluminum substrates are still being widely used to obtain size-resolved aerosol compositions because of their low cost and accurate mass weighed, caution should be taken about the potential significant under determination of semi-volatile components such as ammonium nitrate.

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1. Introduction

Sulfate and nitrate are the main components of atmospheric PM_{2.5} (particulate matter with an aerodynamic diameter less than or equal to 2.5 μm). They affect human health, reduce visibility, acidify rain water, and alter the radiation balance of the atmosphere, and therefore have been a major concern in both the scientific and regulatory communities (e.g., McMurry et al., 2004).

Collecting particulate matter on a filter or substrate with subsequent chemical analyses in laboratories is the conventional method for measuring the atmospheric concentrations of PM_{2.5}

sulfate and nitrate. In un-denuded systems, in which potentially interfering gases are not removed prior to sample collection, positive artifacts due to the absorption of acidic and alkalic gases on filters can give rise to an overestimation of aerosol concentration; on the other hand, the evaporation of semi-volatile compounds such as ammonium nitrate from filter substrates can result in significant underestimation of their components (Appel et al., 1979; Dasch et al., 1989; Koutrakis et al., 1992; Zhang and McMurry, 1992; Chow, 1995; Chow et al., 2005; Cheng and Tsai, 1997; Tsai and Perng, 1998; Schaap et al., 2004; Pathak et al., 2004; Pathak and Chan, 2005). The extent of sampling artifacts can be affected by many factors, including temperature, relative humidity, the loading and composition of the aerosol, the type of filter substrate and the structure of the collector used. Positive artifacts for sulfate, which are due to the absorption/reaction of SO₂ on the collected particles, have been found to be negligible for ammonium-poor samples, and to range from 7% to 11% in ammonium-rich ones (Tsai and Perng,

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1998; Pathak and Chan, 2005). The measurement of PM_{2.5} nitrate can also suffer from positive artifacts due to the absorption of gas-phase nitric acid on the filter (Appel et al., 1979; Chow, 1995). Of major concern is a negative bias for PM_{2.5} nitrate (Cheng and Tsai, 1997; Chow, 1995), which is due to the evaporation of ammonium nitrate collected on filters over the duration of sample collection. To minimize these sampling artifacts, denuders of various designs have been used to remove the interfering gases, and a back-up filter is recommended to collect the vapor (Chow, 1995). The Interagency Monitoring of Protected Visual Environments (IMPROVE) network, for example, uses a denuder and nylon filter to measure total (non-volatilized and volatilized) particulate nitrate (Chow and Watson, 1998). Nonetheless, samplers without denuders and back-up filters are still widely being used because of the lower cost in equipment and operations (Wang et al., 2005; Louie et al., 2005; Sharma and Maloo, 2005). Most of the previous evaluations of the sampling artifacts were conducted in North America and Europe, but few was carried out in Asia where the atmospheric concentrations of particulate matters are much higher.

MOUDI (Micro-Orifice Uniform Deposit Impactor) is the most popular cascade impactor for obtaining size-resolved aerosol compositions (Chow and Watson, 2007). Teflon and aluminum filters are commonly used in MOUDI. Samples collected on Teflon filters are normally analyzed for water-soluble ions and trace elements, and those collected on aluminum filters for organic and elemental carbon, as well as polycyclic aromatic hydrocarbons (PAH) (Chow and Watson, 2007). Because Teflon filters are far more expensive than aluminum ones, the latter are also widely used for analysing water-soluble ions in MOUDI (Moya et al., 2003, 2004; Malm et al., 2005; Márquez et al., 2005; Cheng et al., 2008; Lee et al., 2008). Previous evaluations of the sampling artifact of MOUDI mostly focused on the loss of particles resulting from impaction and bounce (Stein et al., 1994; Howell et al., 1998; Chang et al., 1999; Duan et al., 2005), and little is known about the degree of loss of semi-volatile components due to evaporation.

Several continuous and semi-continuous techniques have been developed in recent years (Weber et al., 2001; Drewnick et al., 2003) to overcome the shortcomings of the filter-based methods such as sampling artifacts and the poor time-resolution of data. Wu and Wang (2007) applied a real-time ion analyzer to two polluted sites near Beijing and Shanghai, respectively. The systems

contained a denuder to remove acidic and alkalic gases, a steam chamber to allow particles to grow to super-micron size, and two ion chromatographs for subsequent automatic analyses of cations and anions. They found positive interferences to sulfate at high SO₂ conditions (>30 ppbv) and negative bias at high aerosol loadings (sulfate > 20 μgm⁻³). There is thus a need for further evaluations of the newly developed real-time instruments under a wide range of chemical and meteorological conditions.

In the present study, we compare the measurement results of sulfate and nitrate obtained from an un-denuded filter-based sampler (RAAS), a Micro Orifice Uniform Deposit Impactor (MOUDI), a denuder filter-pack sampler (Harvard honeycomb denuder, Chemcomb Model 3500), and an on-line semi-continuous system (AIM). The data were obtained from two field campaigns in Jinan and Beijing in the highly polluted North China Plains. The present study addresses the artifacts and performance of these internationally adopted instruments under polluted conditions. We first compare the AIM with the Honeycomb system, and the AIM data are then used to evaluate the other two filter-based samplers (RAAS and MOUDI). The effects of mass loading, filter type, and sampling temperature are examined.

2. Methods

2.1. Sampling sites

The first site was in Heishanzai, Changping district, Beijing (in brief of “HSZ”; 40°22′N, 116°18′E, 303 m above sea level), where we found high ozone and nitrate in our previous study in 2005 (Wang et al., 2006; Pathak et al., 2009). The HSZ site is in a rural and mountainous area about 50 km from the center of the Beijing urban area. The other site was in Jinan (in brief of “JN”; 36°40′N, 117°03′E, 50 m above sea level). The samplers were set on the roof (15 m above ground level) of a building on the Shandong University campus, which is located 5 km northeast of downtown Jinan and surrounded by four streets with moderate traffic.

In order to illustrate the concentration regimes of the two sites, time series of the hourly measurements of PM_{2.5} sulfate and nitrate at HSZ and JN sites are shown in Fig. 1a and b. Very large concentration ranges were observed at both sites. The maximum hourly concentration of sulfate and nitrate was 130 μgm⁻³ and 60 μgm⁻³ at HSZ site and 260 μgm⁻³ and 60 μgm⁻³ at JN site, respectively.

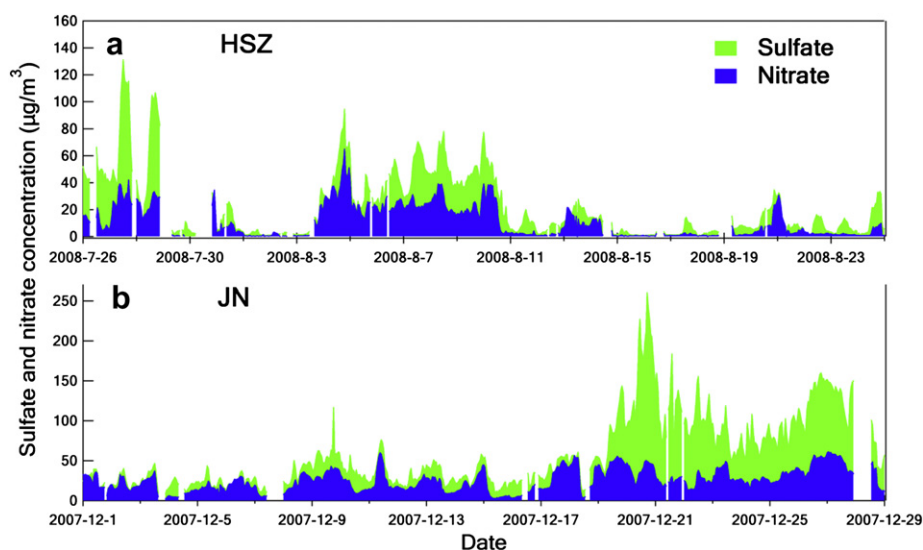


Fig. 1. Time series of hourly concentrations of PM_{2.5} sulfate and nitrate at (a) HSZ in summer 2008 and (b) JN in winter 2007.

Table 1
Instruments list and sampling periods at HSZ and JN.

Instruments	HSZ	JN
RAAS	Jul 8 to Aug 25, 2008	Dec 1 to 28, 2007
MOUDI	Jul 8 to Aug 25, 2008	Dec 2 to 28, 2007
HCD	Jul 26 to 31, 2008	Not employed
AIM	Jul 26 to Aug 25, 2008	Dec 1 to 28, 2007

Such higher concentrations of sulfate are rarely seen nowadays in developed countries.

2.2. Instruments descriptions

Four different instruments, RAAS, MOUDI, honeycomb denuder and AIM, were employed to measure PM_{2.5} sulfate and nitrate at HSZ site, while RAAS, MOUDI and AIM were used at JN site. Table 1 shows the instruments used and the sampling period at the two sites.

2.2.1. RAAS

A Thermo Andersen Chemical Speciation Monitor (Thermo Electron Corporation, RAAS 2.5–400) was used to collect PM_{2.5} samples on Teflon (Teflon™, 2 μm pore size and 47 mm diameter, Pall Inc.) and quartz (47 mm Pall quartz fibre filters) filters at a flow rate of 16.67 L min⁻¹ and 7.33 L min⁻¹, respectively. A detailed description of this sampler is given elsewhere (Wu and Wang, 2007). Prior to sampling, the Teflon filters were heated at 40 °C for 30 min, and the quartz filters were heated at 600 °C for 2 h. The sampled filters were stored at -5 °C in order to minimize artifacts. The PM_{2.5} mass was determined by Teflon filters using the standard gravimetric method. Before weighing, the filters were balanced for 48 h under the condition of constant temperature (20 °C ± 0.5 °C) and constant relative humidity (50% ± 2%). During the two campaigns, most of RAAS samples were collected for 24 h, but a few shorter-time (6 h) samples were collected on polluted days.

2.2.2. MOUDI

A MOUDI (MSP Company) was deployed in the HSZ and JN sites. The sample flow rate was 30 L min⁻¹. The impactor collected particles in eight size ranges: >18 μm (inlet), 10–18 μm, 5.6–10 μm, 3.2–5.6 μm, 1.8–3.2 μm, 1–1.8 μm, 0.56–1 μm, 0.32–0.56 μm, and 0.18–0.32 μm (Marple et al., 1991). Aluminum substrates (MSP Company) were used. The substrates were heated at 500 °C for 4 h in order to remove residual organic matters, and weighted using the same method as that used for the Teflon filters.

2.2.3. Harvard honeycomb denuder

The Harvard honeycomb denuder filter-pack system (Chemcomb Model 3500) uses two denuders in series to remove acidic and alkalic gases prior to the collection of particles on the filter. The first denuder was coated with 1% (w/v) Na₂CO₃ 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 a citric acid solution (4% (w/v) citric acid and 2% (w/v) glycerol in methanol) to absorb NH₃. The filter pack is comprised of a 47 mm diameter Teflon filter with 2 μm pores for particle collection, a nylon back-up filter for absorbing evaporated HCl and HNO₃, and an additional Teflon back-up filter coated with the citric acid solution for absorbing evaporated NH₃ (Pathak et al., 2004).

2.2.4. AIM

An ambient ion monitor (AIM, URG Corporation, URG9000B) was used to measure PM_{2.5} sulfate and nitrate on an hourly basis. Seven anions (F⁻, Cl⁻, Br⁻, NO₂⁻, NO₃⁻, SO₄²⁻, PO₄³⁻) were determined at the HSZ site, and 10 ions (Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺, F⁻, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻) were determined at the JN site. A detailed description of this instrument is given in Wu and Wang (2007). In order to avoid the positive interference by SO₂ and negative bias by high aerosol loadings (Wu and Wang, 2007), a sodium hydroxide solution was used as the denuder liquid at the JN site, and the flow rates to the analytical system of the AIM were from 3 L min⁻¹ to 2 L min⁻¹ at the HSZ site. At JN, a sodium hydroxide solution (5 mmol L⁻¹) was substituted for ultra-pure water as the denuder liquid to enhance the absorption of acidic gases such as SO₂ and HNO₃. At HSZ the sample flow rate through the cyclone was kept at original 3 L min⁻¹ in order to avoid changing the cut size of the cyclone; after the inlet (cyclone), the flow was divided to two branches: one has a flow rate of 2 L min⁻¹ which went into denuder, the mist chamber and the IC units; the other bypassed the system and went directly to the exhaust pump with the flow rate maintained at 1 L min⁻¹. This set-up therefore did not change the total flow rate through the cyclone (thus the sample cut size), but reduced the amount of sample entering into the analytical system by one-third.

2.3. Analysis of samples

After sample collection, particulates on the Teflon and quartz filters and aluminum substrates were dissolved completely in an ultrasonic bath in ultra-pure water of 18.2 MΩ cm (purified by Millipore Water Purification System) for 60 min (Teflon and quartz filters

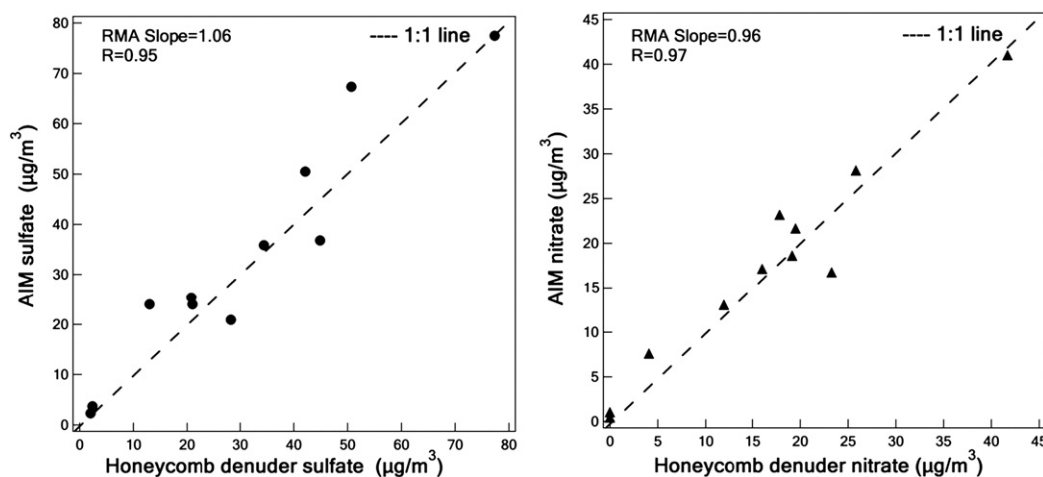


Fig. 2. Scatter plots of sulfate and nitrate from the AIM and Honeycomb denuder filter-pack sampler in HSZ, Beijing.

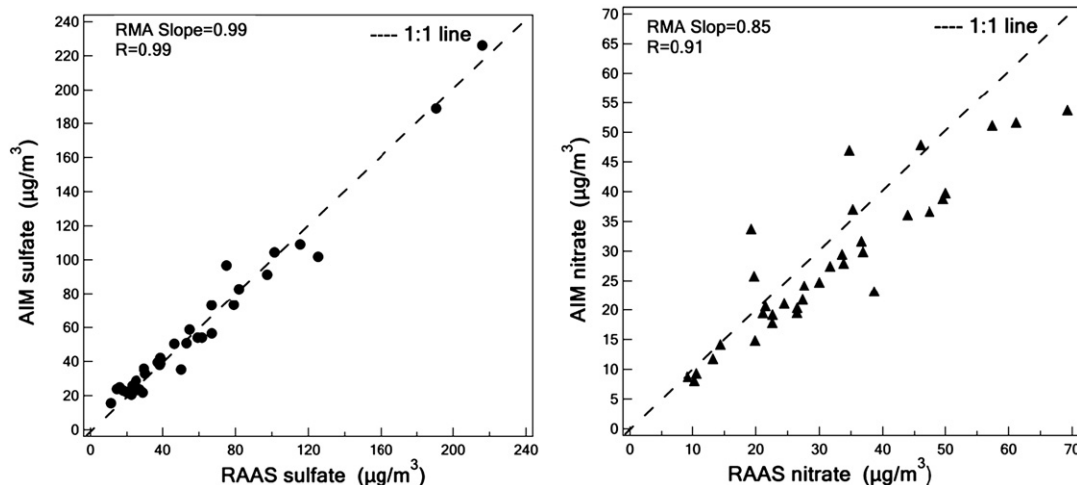


Fig. 3. Scatter plots of the 24 h sulfate and nitrate from the AIM and RAAS in JN, Shandong.

in 20 ml, aluminum substrates in 10 ml). The water extracts were filtered through a 13-mm filter with 0.2 µm pores (13JP020AN, ADVANTEC). Inorganic water-soluble ions including F^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} in the solution of samples were detected using Dionex IC 90 (Ionpac @ AS14A 4 × 250 mm Analytical Column, AMMS 300 4 mm suppresser and conductivity detector for anions; Ionpac @ CS12A 4 × 250 mm Analytical Column, CSRS Ultra II-4 mm suppresser and conductivity detector for cations).

3. Results and discussion

3.1. The performance of the AIM

Our previous study found sampling artifacts in the AIM measurements (Wu and Wang, 2007). Sulfate and nitrate were underestimated at high particle concentrations in Beijing, and sulfate was overestimated at elevated SO_2 levels (>30 ppbv) in Shanghai.

In the present study, the AIM was performed at a reduced flow rate ($2 L min^{-1}$ to the analytical system) in order to ensure adequate extraction of particles in the steam-particle mixing chamber. The AIM was first compared with the honeycomb denuder filter-pack system which is considered to have minimal sampling artifacts. Fig. 2

shows the comparison of $PM_{2.5}$ sulfate and nitrate concentrations in August 2008 at the HSZ site. The sampling duration ranged from 2 h to 12 h. The data of the two systems agreed very well with a regression slopes, using the reduced matrix axis (RMA) method (Hirsch and Gilroy, 1984), of 1.06 and 0.96 and a correlation coefficient of 0.95 and 0.97, respectively. A very large range in concentration was observed: 2–77 $\mu g m^{-3}$ for sulfate and 0–41 $\mu g m^{-3}$ for nitrate. Reducing the sampling flow rate of AIM appeared to have been successful in avoiding the underestimation of sulfate and nitrate at high aerosol loadings.

Another AIM instrument (same model) was deployed in JN in 2007. Fig. 3 shows the comparison of the sulfate and nitrate measurements using the RAAS and AIM in JN in December 2007, during which time very high concentrations of SO_2 were observed. As mentioned previously, a sodium hydroxide solution ($5 mmol l^{-1}$) was used as the denuder liquid to enhance the absorption of SO_2 and HNO_3 . Because the denuder filter-pack system was not used in JN, the RAAS (un-denuded filter-based sampler) was used to evaluate the performance of the AIM under high SO_2 conditions. It can be seen that the RAAS sulfate agreed very well with the AIM sulfate (Fig. 3), with an RMA slope of 0.99 and correlation coefficient of 0.99, indicating that the sodium hydroxide solution effectively removed SO_2 even when the SO_2 concentration was much higher than 30 ppbv.

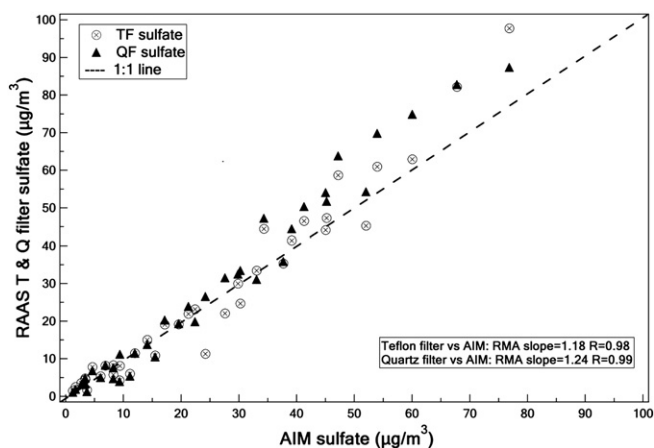


Fig. 4. Scatter plot of sulfate from the RAAS (Teflon and quartz filters) and AIM in HSZ, Beijing. TF and QF denote Teflon and quartz filters, respectively.

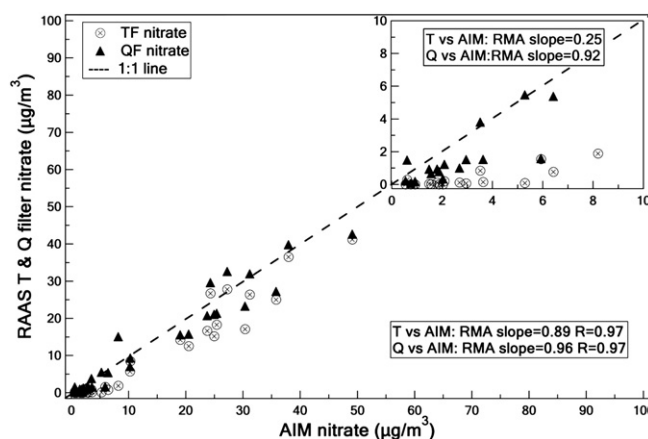


Fig. 5. Scatter plot of nitrate from the RAAS (Teflon and quartz filters) and AIM in HSZ, Beijing. TF and QF denote Teflon and quartz filters, respectively.

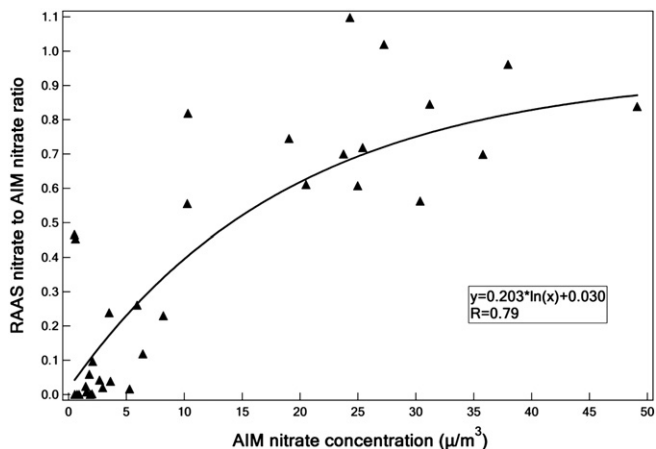


Fig. 6. The ratios of RAAS nitrate to AIM nitrate as a function of the AIM nitrate.

In summary, with the above mentioned modifications, the AIM was largely artifact free at the HSZ and JN sites. Hence it was subsequently used to evaluate the performance of other samplers which were operated in parallel with the AIM for longer periods of time than the Honeycomb system.

3.2. The performance of the RAAS

Fig. 4 shows a comparison of the sulfate data obtained by the RAAS on Teflon and quartz filters and the AIM at HSZ. Overall, the RAAS sulfate showed a good agreement with that from the AIM for both the Teflon and quartz filters. We notice that the filter data showed higher values for a few samples at higher concentrations. These samples were collected during the hazy and humid days, and the *in-situ* SO₂ concentrations were only slightly higher than those on clear days. One possible explanation for the higher values from filters is the SO₂ absorption by the alkaline particles collected (Tsai and Perng, 1998).

Fig. 5 shows a comparison of the nitrate measurements of the two systems at HSZ. On average, about 10% nitrate loss was observed on the Teflon filters, but much greater losses (~75%) were found at lower concentrations (nitrate < 10 µg m⁻³), as shown in the insert in Fig. 5. An examination of the scatter plot of ammonium and the sum of sulfate and nitrate in the RAAS PM_{2.5} showed that

ammonium was enough to neutralize the sum of sulfate and nitrate (figure not shown). This implied that the nitrate was present in the form of ammonium nitrate. Thus the differences of nitrate losses at high and low concentrations are mainly due to the difference in particle loadings. This phenomenon has been observed by other researchers (Wang and John, 1988; Cheng and Tsai, 1997; Chang et al., 2000), which is attributed to the formation of a particle cake on the filter thereby suppressing the evaporation of ammonium nitrate from the filter. Fig. 6 shows the ratio of RAAS nitrate (on the Teflon filter) to AIM nitrate, and a logarithmic fit to the data is: $y = 0.203 \ln(x) + 0.030$, $R = 0.79$. This relationship can be used to help correct the PM_{2.5} nitrate concentrations measured by an un-denuded system on Teflon filters in an environment similar to HSZ. Plotting the ratios as a function of the ambient temperatures did not reveal an obvious dependence of the ratios on the temperature (figure not shown).

In contrast, the quartz filters did not have such a large loss of nitrate at low concentrations (see Fig. 4). This could be due to the different textures of the two kinds of filters. Schaap et al. (2004) found that Teflon filters were more susceptible to the evaporation losses of nitrate than quartz filters during the INTERCOMP2000 campaigns conducted at Melpitz, Germany. Their study and that of Keck and Wittmaack (2005) showed that most of the nitrate loss occurred in the temperature range of 20–25 °C. The present study, however, showed no significant losses in the temperature range of 22–34 °C, which is consistent with the finding of a laboratory study that the evaporation loss of ammonium nitrate from quartz filters occurred only at temperatures higher than 35 °C (Schaap et al., 2004).

Fig. 3 shows a comparison of sulfate and nitrate between the AIM and RAAS (Teflon filter) in JN during the winter of 2007. As discussed in the previous section, the RAAS sulfate measurements matched excellently with those of the AIM. Unlike the case in summertime in Beijing, the RAAS nitrate experienced negligent loss in cold winter (daily maximum temperature ranged from 2 °C to 8 °C). It is also worth noting that the nitrate concentration rarely dropped below 10 µg m⁻³; thus, it is not possible for us to examine the extent of evaporative loss of nitrate at low concentrations under cold conditions.

3.3. MOUDI sampling artifacts

A MOUDI using aluminum substrates can experience loss of particles due to bounce and re-entrainment at RH below 70% when particles are dry (Stein et al., 1994; Chang et al., 1999;

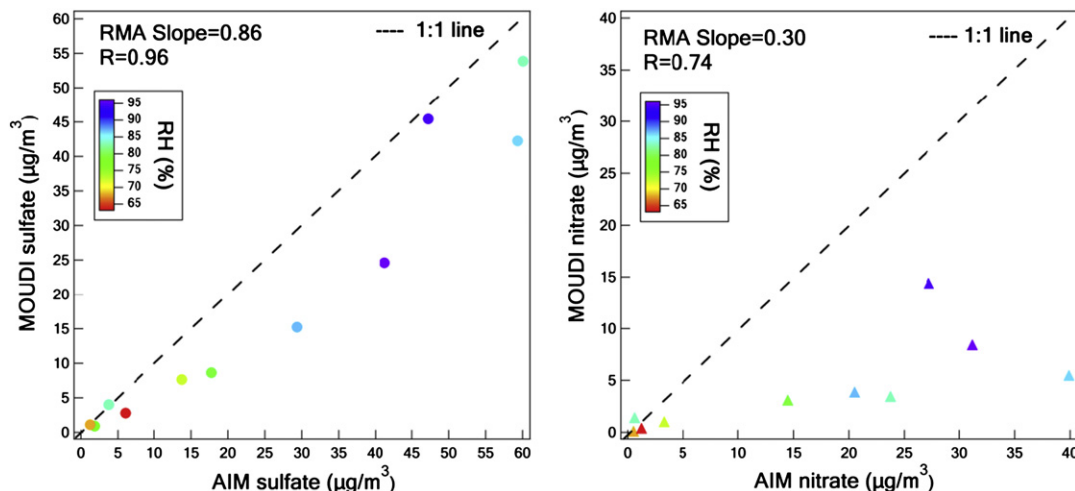


Fig. 7. Scatter plots of sulfate and nitrate from the MOUDI and AIM, HSZ, Beijing.

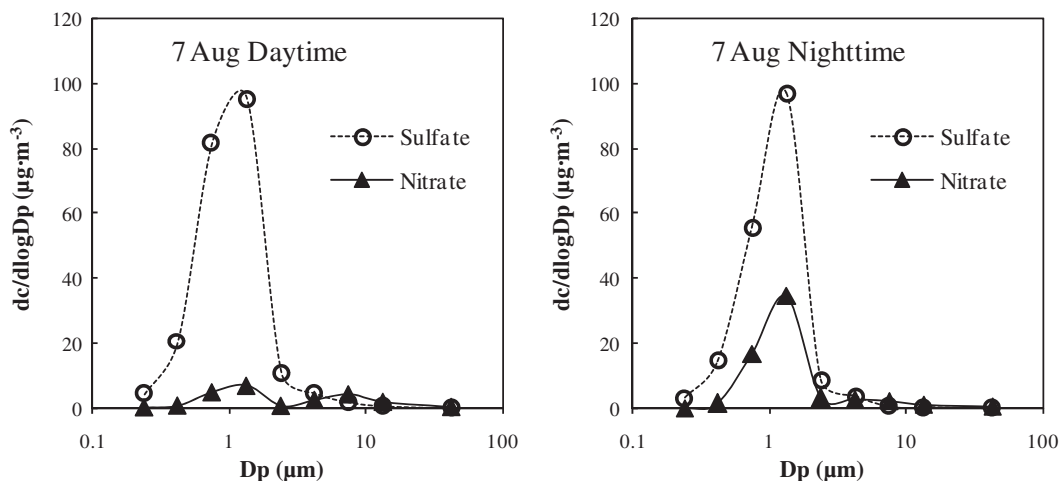


Fig. 8. The size-resolved concentrations of sulfate and nitrate on August 7, 2008, during daytime and nighttime.

Duan et al., 2005). Fig. 7 shows the sulfate and nitrate obtained by the MOUDI and AIM in HSZ in Beijing. Here, we added their mass measured by the MOUDI up to the size of $3.2 \mu\text{m}$. It can be seen that about 14% of sulfate and 70% of nitrate were lost in the MOUDI. A loss of sulfate was observed at RH higher than 70% and more than 10% loss of sulfate even at RH higher than 90%. As a non-volatile species, sulfate can be lost from the aluminum foil because of bouncing during sampling and the loss of particles during the handling and transport of the samples.

For nitrate, assuming the same 14% loss due to bounce and sample handling, the additional 50% of the loss can be attributed to the evaporation of ammonium nitrate in the fine mode ($<2.5 \mu\text{m}$). It is generally accepted that high RH will reduce the evaporation loss of ammonium nitrate. However, significant nitrate loss was observed in this study even at high RH (see Fig. 7). It is worth noting that aluminum substrates are also widely used for collecting organic matter (Chow and Watson, 2007; Timonen et al., 2008; Yang et al., 2006). Some of the organic compounds are also semi-volatile, and thus their sampling artifacts may also be significant in hot seasons.

Fig. 8 shows the size distributions of sulfate and nitrate during the daytime and nighttime on a polluted day (August 7, 2008). The concentrations and some meteorological parameters are listed in Table 2. Although the distributions of sulfate and coarse mode ($>3.2 \mu\text{m}$) nitrate were similar during the two times, large differences in the concentration of nitrate in the fine mode ($<3.2 \mu\text{m}$) were observed between the daytime and nighttime samples. Coarse mode nitrate, such as sodium nitrate and calcium nitrate, is non-volatile, whereas fine mode nitrate is mostly semi-volatile ammonium nitrate. The formation of ammonium nitrate is generally favored during nighttime because of the lower temperature and higher RH (Seinfeld and Pandis, 2006). However, the average daytime and nighttime ambient temperatures were similar (daytime: $26.7 \text{ }^\circ\text{C}$; nighttime: $25.5 \text{ }^\circ\text{C}$) and there was only a 10%

difference in RH (daytime: 84%; nighttime: 94%). These small differences in ambient temperature and RH cannot explain the large difference in fine mode nitrate loss between the daytime (86%) and nighttime (47%) samples. Therefore, we checked the temperature inside the MOUDI. A MOUDI sampler was set up on 6 October 2009 on the roof of a six-storey building on the campus of Hong Kong Polytechnic University in Hong Kong. A temperature sensor (a thermocouple) was placed at the third filter stage of the MOUDI and another one was placed in open ambient air. Fig. 9 shows the variations of temperature inside the MOUDI and in the ambient atmosphere. On that day, the ambient temperature ranged between $24 \text{ }^\circ\text{C}$ and $34 \text{ }^\circ\text{C}$, similar to that at the HSZ site ($22\text{--}34 \text{ }^\circ\text{C}$). It can be seen that the temperature inside the MOUDI was higher than the ambient temperature with a maximum difference of more than $4 \text{ }^\circ\text{C}$ from 14:00 to 16:00. No significant difference was found at nighttime. These results indicate that the body of the MOUDI sampler was heated during daytime under direct sunshine. The higher temperature inside the MOUDI may have caused higher nitrate evaporation during the daytime, leading to a significant loss of nitrate collected on the aluminum substrates. The significant loss of nitrate on aluminum substrates can be attributed to the fact that particles are not embedded into the aluminum filter metal. In comparison, much less loss (17%) was reported for a MOUDI using Teflon substrates in a study conducted in Los Angeles (Chang et al., 2000).

Table 2

Nitrate concentration of MOUDI and AIM samples during daytime and nighttime, on August 7, 2008.

Time	MOUDI Nitrate ($\mu\text{g}\cdot\text{m}^{-3}$)		AIM Nitrate ($\mu\text{g}\cdot\text{m}^{-3}$)	Temperature ($^\circ\text{C}$)	RH (%)
	PM _{3.2}	PM _{3.2-10}			
Daytime	3.4	1.7	23.8	26.5	84
Nighttime	14.4	1.4	27.3	25.5	94

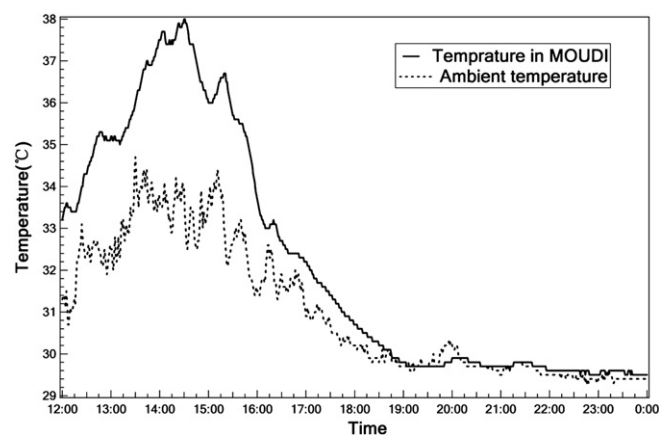


Fig. 9. Temperature inside the MOUDI and the ambient temperature during a test in Hong Kong in October 2009.

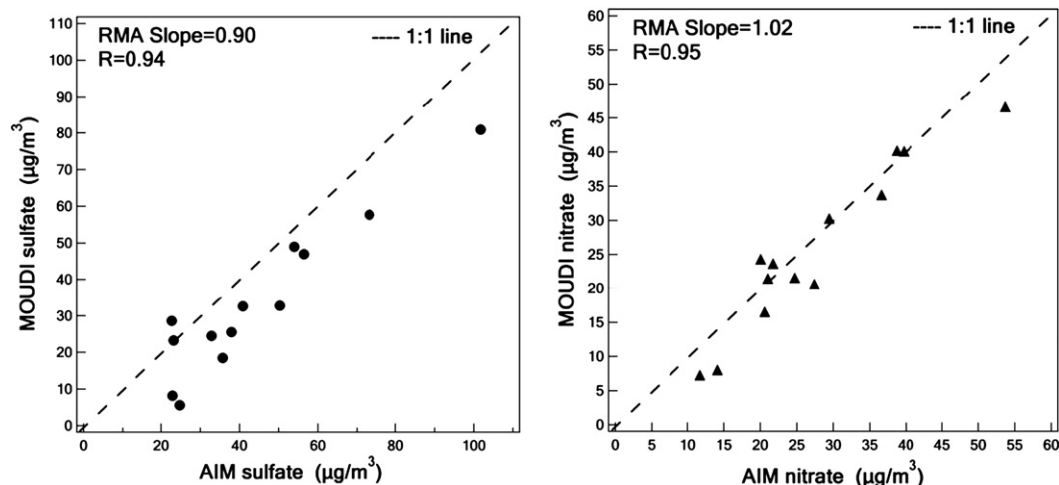


Fig. 10. Scatter plot of sulfate and nitrate concentrations from the MOUDI and AIM in JN, Shandong.

Much smaller loss of nitrate was observed in winter. Fig. 10 shows the concentrations of sulfate and nitrate obtained from the MOUDI and AIM in the JN winter study. Similar to the results at HSZ, the MOUDI sulfate measurement was 10% lower than that of the AIM. However, MOUDI nitrate was exactly the same as AIM nitrate. In this case, a positive artifact, that is, the absorption of nitric acid, could have occurred compensating for the loss of nitrate due to particle bounce.

4. Summary and conclusions

Atmospheric sulfate and nitrate data collected from two filter-based samplers (a RAAS and a denuder filter-pack system), an impactor (MOUDI), and a real-time ambient ion analyzer (AIM, URG9000B) were compared to assess the sampling artifacts of these techniques under polluted conditions. Field studies were conducted at an urban site in Jinan, Shandong province, during the winter of 2007, and at a rural site near Beijing in the summer of 2008. The main findings are summarized as follows.

- The modifications made to the AIM (i.e., reducing the sampling flow rate and changing the denuder liquid) were effective in avoiding the underestimation and overestimation problems found in our previous study (Wu and Wang, 2007).
- Teflon filters in the un-denuded filter-based sampler (RAAS) were shown to give excellent results for sulfate; evaporation loss of nitrate from Teflon filter in summer depended on the loading of particles on filters: small at high loading (nitrate > 10 µg m⁻³) but large (up to 75%) at low nitrate (<10 µg m⁻³). The evaporative loss of nitrate was minimal in winter. These results appear to indicate small to moderate sampling artifacts for conventional sampling methods (un-denuded and without a back-up filter) in a polluted environment of eastern China.
- Different from the results of previous studies, only small evaporation loss of nitrate (8%) from quartz filters was found at low concentration ranges in the present study.
- Because of the low cost and ease of weighing for mass determination, aluminum substrates have been widely used in MOUDI for the measurements of size-resolved ions. This study found significant loss of nitrate due to the evaporation on hot days. Therefore, cautions should be taken on the potential underdetermination of nitrate and other semi-volatile compounds such as some forms of organic carbon.

Acknowledgements

The authors would like to thank Jian Gao, Jing Wang, Steven Poon, Youping Shou, Chao Yuan, Zheng Xu, Yangchun Yu, Linlin Wang, Xuezhong Wang and Baoguo Jing for their contribution to the field work and sample analysis. We thank Aijun Ding, Xiaohuan Liu, Likun Xue, Yang Zhou and Zhe Wang for their suggestions regarding the data analysis. We thank Chak K. Chan for supplying the Honeycomb denuder filter-pack system. This study was funded by the National Basic Research Program of China (973 Program) (2005CB422203), the Haze Program of the Shandong Environmental Protection Bureau (2006045), the Niche Area Development Program of the Hong Kong Polytechnic University (1-BB94) and the Hong Kong Research Grants Council (PolyU 5294/07E).

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