UC Davis
UC Davis Previously Published Works

Title
Characterization of the 8-stage Rotating Drum Impactor under low concentration conditions

Permalink
https://escholarship.org/uc/item/8v55b62p

Authors
Venecek, Melissa A
Zhao, Yongjing
Mojica, Jose
et al.

Publication Date
2016-10-01

DOI
10.1016/j.jaerosci.2016.07.007

Peer reviewed

Characterization of the 8-stage Rotating Drum Impactor under low concentration conditions

Melissa A. Venecek [a], Yongjing Zhao [b], Jose Mojica [c], Charles E. McDade [c], Peter G. Green [d], Michael J. Kleeman [d], Anthony S. Wexler [a,b,c,d,*]

[a] Department of Land, Air and Water Resources, University of California, Davis, United States
[b] Air Quality Research Center, University of California, Davis, United States
[c] Crocker Nuclear Laboratory, University of California, Davis, United States
[d] Department of Civil and Environmental Engineering, University of California, Davis, United States

ARTICLE INFO

ABSTRACT

The Rotating Drum Impactor (RDI) is designed to collect samples of airborne particulate matter that are resolved by aerodynamic particle diameter as a function of time. The purpose of this study is to characterize the accuracy and precision of measurements for particulate matter less than 2.5 μm (PM2.5) from the latest generation of the RDI sampler for use in relatively low concentration environments. Nominal RDI size cuts were used to interpret the results; a laboratory calibration of the RDI was not undertaken. Airborne particulate matter was collected on the campus of the University of California at Davis during the winter and summer of 2013. Two RDI samplers operating with 1 h resolution, two IMPROVE samplers operating 21 h per day, and one MOUDI sampler operating 42 h every two days were deployed for both seasons to enable a comparison of co-located measurements. The RDI samples were scanned using synchrotron X-rays from the Advanced Light Source (ALS), Lawrence National Berkeley Laboratory, to obtain X-ray Fluorescence (XRF) spectra. IMPROVE and MOUDI samples were analyzed using Panalytical XRF instruments using the IMPROVE protocol, then analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent 7500i. Repeated measurements from the same samplers and analytical techniques were compared to elucidate precision; inter-comparisons between measurements made with different sampler and analytical technique combinations were used to indirectly evaluate accuracy.

The IMPROVE XRF analysis technique gave similar repeated measurements for 78% of the elements present above stated Minimum Detection Limits (MDLs) in winter and 42% of elements above MDL in summer. The MOUDI XRF analysis technique gave similar repeated measurements for 33% and 37% of the elements above stated MDLs in winter and summer, respectively. The MOUDI, ICP-MS analysis technique was the most repeatable method tested, yielding similar repeated measurements for 62% and 91% of elements above stated MDLs in winter and summer, respectively. The RDI, XRF analysis technique was the least repeatable method tested, yielding similar repeated measurements for 35–40% and 5–20% of elements above stated MDLs in winter and summer, respectively.

PM2.5 measurements from IMPROVE samplers were in better agreement with integrated size-resolved measurements made by MOUDI samplers than RDI samplers in the summer season, however with higher concentrations in the winter season both instruments performed with similar accuracy when using the XRF analysis method. MOUDI samples analyzed by ICP-MS had the best agreement overall with IMPROVE samples

---

* Correspondence to: University of California, One Shields Avenue, Davis, CA 95616, United States.

analyzed by ICP-MS. These results suggest that MDLs should be reassessed for all methods and a longer collection time should be considered under low concentration conditions.

1. Introduction

Accurate measurements of the composition and size distribution of airborne particulate matter (PM) are import due to the complex role of PM in climate change, visibility and health. Airborne particles influence climate by scattering and absorbing solar radiation and via their role as cloud and ice condensation nuclei (CCN). Particle size and composition strongly influences their optical properties and CCN formation potential (Bucher et al., 2013). Many studies have been conducted on the effects of PM on health and the link between PM and cardiovascular disease (Pope & Dockery, 2006). Recent work has focused on the health effects of individual chemical components or sources of airborne particles (Brunekreef & Forsberg, 2005; Franklin, Koutrakis, & Schwartz, 2008; Ostro, Broadwin, Green, Feng, & Lipsett, 2006). In addition, ultrafine particles (particles with an aerodynamic diameter less than 0.1 μm) are of increasing interest because of their ability to translocate from the airways to the blood and extrapulmonary organs such as the liver (Oberdorster, Oberdorster, & Oberdorster, 2005). Accurate and precise aerosol samplers that measure composition and size distribution of particles are needed to support studies in all of the areas outlined above.

Many kinds of instruments can be used to characterize particle size, composition, concentration and other properties, each with their own strengths and weaknesses in terms of cost, temporal resolution, and Method detection limit (MDL). Cascade impactors, such as the micro orifice uniform deposit impactor (MOUDI), have been designed to collect size resolved PM (Marple, Rubow, & Behm, 1991), however operation of the MOUDI can be expensive due to the manual labor needed for filter changing and for chemical analyses that are performed after sample collection. Other instruments such as the Aerosol Mass Spectrometer (AMS, Aerodyne, Billerica, MA) have been developed to measure real time chemical composition and size resolution (Jayne et al., 2000); however these instruments can be quite costly to purchase and/or operate.

Many different generations of Lundgren style impactors (e.g., the Rotating Drum Impactor (RDI); the Davis Rotating-drum Unit for Monitoring (DRUM)) have been developed to collect time resolved and size-segregated PM by impacting aerosol particles on rotating cylinders, instead of onto impaction substrates (Lundgren, 1967). In 1988, Raabe et al. developed and characterized the first DRUM impactor that measures continuous, size resolved PM at relatively low-cost instrumentally and operationally (Raabe, Braaten, Axelbaum, Teague, & Cahill, 1988). Since then, the 8-stage RDI has been developed and modified at the University of California-Davis (UC Davis) following the original DRUM design (Zhao et al., 2014).

In recent years, a number of studies have used the latest generation of the 8-stage RDI to measure continuous, size resolved PM (Atwood et al., 2013; VanCuren et al., 2012; Zhao et al., 2014) however none have investigated the accuracy and precision of the size resolved aerosol concentration collected against co-located measurements from other PM samplers. Thus, although numerous 8-stage RDI data sets have been produced containing near continuous measurements of size resolved particulate elements for months at a time, the accuracy and precision of the measured size distributions are not well characterized.

The purpose of this study is to investigate the accuracy and precision of measurements from the latest generation of the 8-stage RDI sampler in terms of time, size and elemental quantification. Aggregated PM2.5 and size resolved measurements of the RDI were compared to two other forms of PM sampling instruments. RDI PM2.5 concentrations were compared to measurements made by the IMPROVE sampling modules developed at UC Davis, while RDI size resolved concentrations were compared to measurements made by a MOUDI. RDI samples were analyzed exclusively by X-ray fluorescence spectroscopy (XRF) while IMPROVE and MOUDI samples were analyzed by both XRF and inductively coupled plasma mass spectrometry (ICP-MS) to obtain elemental concentrations.

2. Methods

Airborne particulate matter samples were collected at the IMPROVE sampling station on the roof of Ghausi Hall on the main campus of the University of California, Davis, during the winter (January 11–February 12) and summer (July 10–August 12) of 2013. Two 8-stage RDI samplers (UC Davis), two IMPROVE samplers (UC Davis) and two MOUDI samplers (model 110R, MSP Corp., Shoreview, MN) were deployed for both seasons.

The 8-stage RDI collects particulate matter on rectangular strips of Mylar film fixed to 8 rotating drums downstream of 8 jets (slit design) with theoretical 50% cut-off collection aerodynamic diameters (Dp50) of 5 μm, 2.5 μm, 1.15 μm, 0.75 μm, 0.56 μm, 0.34 μm, 0.26 μm, and 0.1 μm and a programmable time resolution between 0.4 and 48 h (Zhao et al., 2014). The cut points for each stage in the RDI were derived based on theoretical calculations of aerodynamic collection efficiency (Zhao et al., 2014). Nominal RDI size cuts were used to interpret the results; a laboratory calibration of the RDI was not undertaken. The RDI employs an inlet with a 10 μm cut point and particles smaller than 0.1 μm are collected on an after-filter. Figure 1
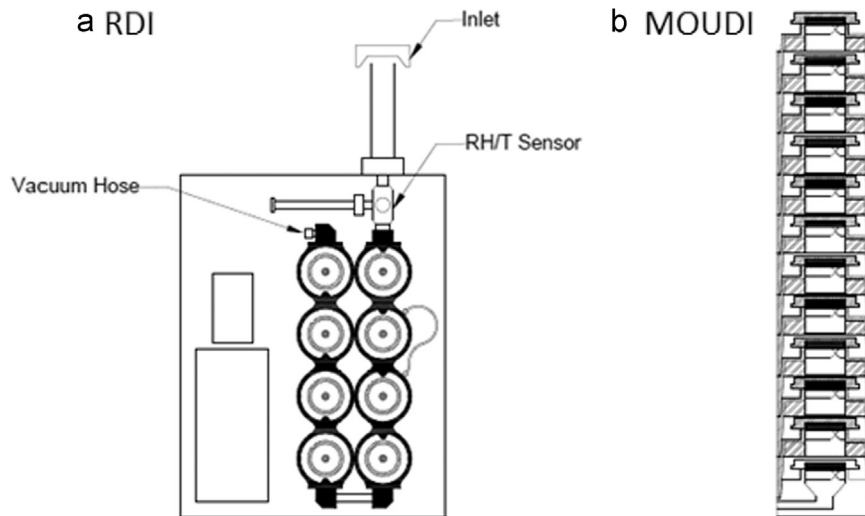
Fig. 1. Cross sectional area of RDI (a) and MOUDI (b) impaction sights.

(a) shows the cross sectional image of the flow path through the RDI. The RDI operates continuously with a flow rate of 16.7 L/min drawn by an external pump. Summation of PM collected on stages 3–8 (2.5–0.1 μm) was used as the aggregated RDI PM2.5 measurement that was compared to the IMPROVE PM2.5 measurement. After completing sampling campaigns in both seasons, it was observed that the stage 5 orifice was installed in the stage 6 location and vice versa in both RDI samplers. As a result, the material deposited on stage 5 encompassed what should have deposited on stage 5 and 6. In order to provide useful data, stage 5 and 6 were binned to yield what would have been collected over a larger size range (0.34–0.75 μm) essentially broadening the two stages into one. To ensure this binning did not introduce other artifacts into what was collected on these and other stages of the RDI a 3 week comparison test was performed in March 2016, wherein two RDIs where operated side-by-side, one with the orifices in the correct position and the other with orifices 5 and 6 swapped as occurred in our original study. The results of this test are provided in the Supporting Information and show that the other stages size distributions are not affected.

The 10-stage MOUDI 110R is a cascade impactor that collects particulate matter on Teflon or foil substrates downstream of multiple cylindrical jets produced by orifice plates. One MOUDI was loaded with Teflon substrates in the current study and these samples were used for comparison to other instruments. The second MOUDI was loaded with foil substrates and results will be reported in a future publication. Figure 1(b) shows the cross sectional image of the 11 stage MOUDI. The measured Dp50 for each MOUDI stage are 10 μm, 5.6 μm, 3.2 μm, 1.8 μm, 1.0 μm, 0.56 μm, 0.32 μm, 0.18 μm, 0.1 μm, and 0.056 μm. As operated in this study, the MOUDI inlet was a cyclone separator with a nominal cut size of 1.8 μm at the target flow rate of 30 L/min. This inlet removed larger particles (prone to bounce) from the sample stream. Therefore only the six bottom stages (5–10) on the MOUDI collected meaningful samples. Particles smaller than 0.056 μm are collected by an after-filter. Summation of PM collected on stages 5–10 (1.8–0.056 μm) was used as the aggregated PM1.8 measurement and compared to IMPROVE PM2.5 and RDI PM2.5 in the current study.

The Interagency Monitoring of Protected Visual Environments (IMPROVE) sampler consists of four modules (labeled A, B, C and D) used to collect particulate matter on three different sampling media; for this study, only Module A was used to collect PM2.5 on Teflon filters. Module A achieves its PM2.5 size cut using a cyclone with a Dp50 at 2.5 μm and a flowrate of 23 L/min. The IMPROVE sampler also includes a controller which records flow rate and temperature readings every minute in order to obtain a 15 min average. Detailed information on the IMPROVE sampling network can be found at the IMPROVE Website (University of California, 2015). Two identical IMPROVE A modules were mounted adjacent to one another on the Ghausi rooftop sampling platform in order to provide measurements that could be used to check precision.

Figure 2 shows the configuration of all samplers. RDI and MOUDI inlets were placed as close as possible to the IMPROVE samplers. All inlets were similar in height to minimize artifacts associated with sampling different air streams. A meteorological tower operated by the department of Land, Air and Water Resources at the Campbell Tract, (approximately 6.5 km from the sampling site), measured temperature, relative humidity, wind speed and direction during the campaign. Prevailing winds were generally from the south (bottom of Fig. 2a, left side of Fig. 2b) or the north (top of Fig. 2a; right side of Fig. 2b) but occasionally from the west (straight ahead in Fig. 2b). Figure 3 shows a regional map of the sampling site, including proximity to PM sources such as interstate 80 and the distance from the meteorological tower.

Collections were performed in discrete periods synchronized between all three samplers. Each period started at noon on day 1, paused between 9 a.m. and noon on day 2, and then resumed collection ending at 9 a.m. on day three. Each 48 h period therefore included 42 h of active sample collection. The PM2.5 IMPROVE samplers collected two Teflon filters during each 2 day sampling period (from noon on the first day to 9 a.m. on the next day for two consecutive days). The MOUDI
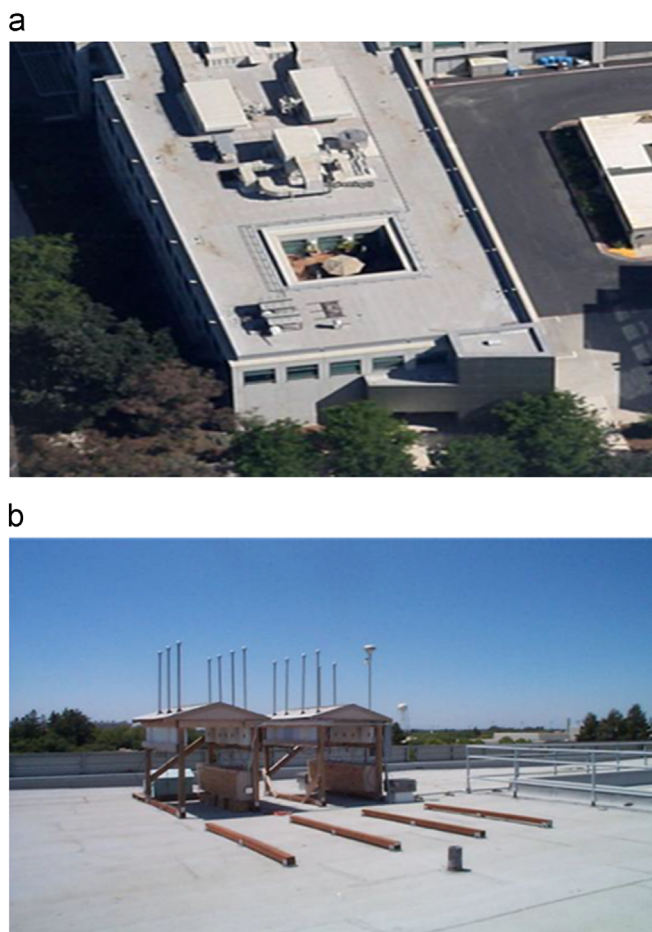
a

b

Fig. 2. (a) Roof of Ghausi Hall showing the location of the IMPROVE sampling station where the method intercomparison was conducted. (b) Height of IMPROVE, MOUDI and RDI inlets.

collected one set of Teflon filters from noon on the first day to 9 a.m. on the next day, paused sampling while IMPROVE filters were changed, and then resumed sampling from noon on the second day until 9 a.m. on the third day. The RDI operated continuously for the two sampling periods with 3-h resolution. RDI measurements were not used during periods when other samplers were not operating. A total of 15, two-day average measurements were collected for all three of the samplers in the winter and in the summer.

Two co-located RDI samplers (named 3a and 7a) and two identical co-located IMPROVE samplers (named RONS and ROSN) were deployed at the site for an instrument precision analysis. Only one MOUDI sampler was used for the current analysis. Instrument precision analysis of the MOUDI was performed by comparing MOUDI PM1.8 to the co-located bulk PM2.5 collected by the IMPROVE sampler.

The RDI samples were analyzed by XRF using a broad spectrum X-ray beam generated on beam line 10.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL) yielding concentrations for 20 elements. The MOUDI and IMPROVE filters were analyzed by XRF (Epsilon 5 EDXRF analyzer, Panalytical, The Netherlands) at Crocker Nuclear Laboratory (CNL) located at UC Davis producing concentrations for 24 elements. In addition, the MOUDI and IMPROVE filters were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500i ICP-MS, Santa Clara, CA). ICP-MS samples were extracted from filters using a 3:1 mixture of acetone and 1 N nitric acid following the method developed by Herner et. al (Herner, Green, & Kleeman, 2006). The ICP-MS quantitatively analyzed 48 elements, however it was found by Herner et al. that only 21 elements were above MDLs under typical ambient conditions (Herner et al., 2006). XRF was performed twice, on the same day, on a subset of both the RDI samples and MOUDI filters in order to quantify method and instrument precision. ICP-MS was also performed twice, on the same day, on a subset of the MOUDI and IMPROVE filters to quantify method and instrument precision. ICP-MS analysis was not possible with the RDI because the PM collected during a 90-min sampling period occupied only about 1 mm on the collection strips, which could not be effectively cut and analyzed by ICP-MS.

Method detection limits (MDLs) for each type of analysis on each sampler were calculated using the procedure recommended by the U.S. Environmental Protection Agency (Waste, 1994) and are provided in the Supporting Information.
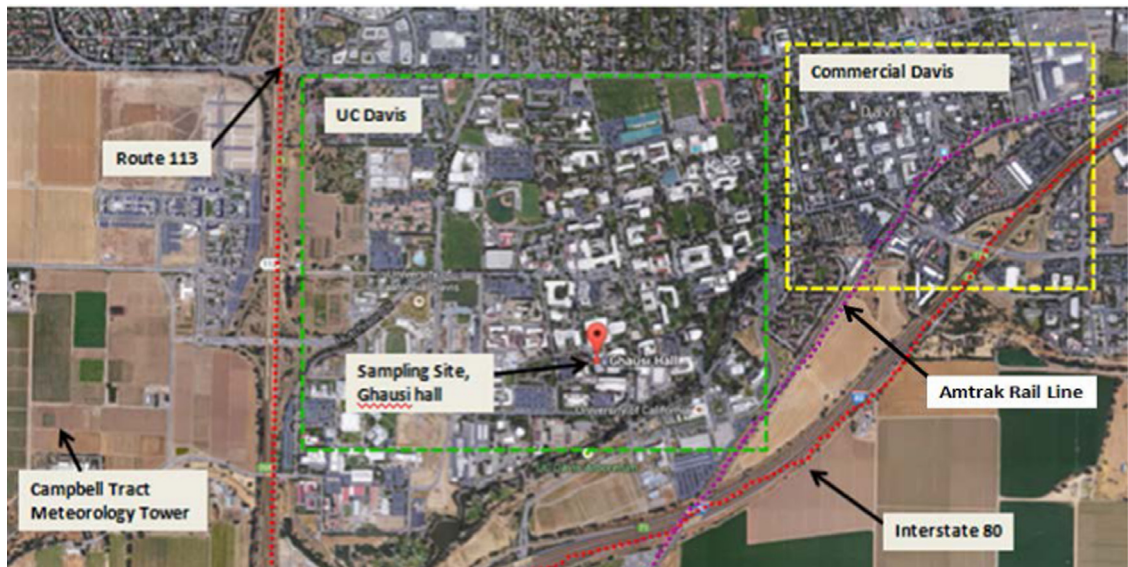
Fig. 3. Regional map of the city of Davis where the sampling was conducted. IMPROVE sampling site at Ghausi Hall is indicated by a red marker. A yellow dashed line represents the outline of Downtown Davis, while a green dashed line represents the outline of the UC Davis main campus. Interstates and highways are indicated by a red dashed line.The amtrack rail line is indicated by purple dashed line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
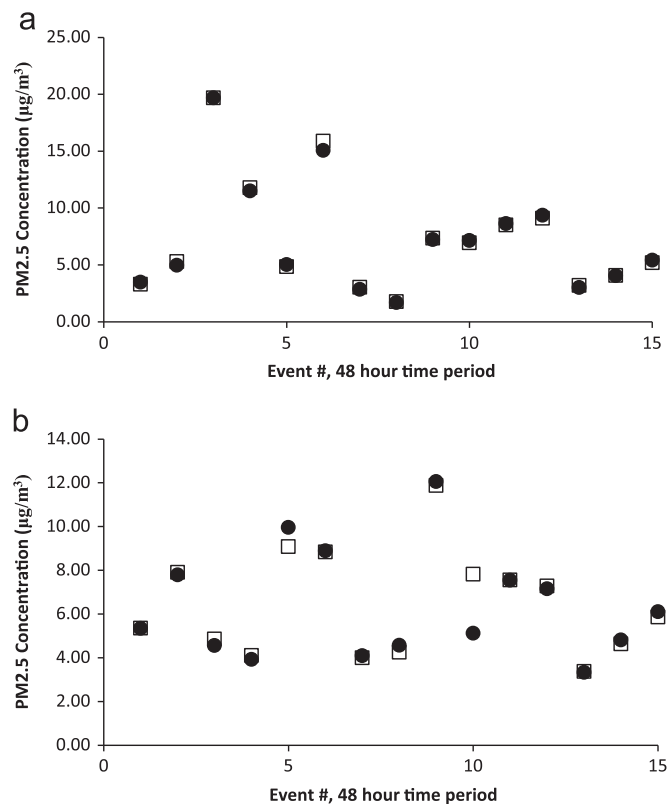
Fig. 4. PM2.5 concentration time series over 15, 48 h periods in (a) winter and (b) summer 2013 measured by two, co-located IMPROVE samplers (RONS=black circles, ROSN=white squares).

Any elemental measurement below MDL was not included in the comparison. It was observed that the ICP-MS MDLs for the 21 target elements were typically much lower, by 1–2 orders of magnitude, than the 19 XRF MDLs when comparisons could be performed. This was similar to results described by Herner et al. (2006).

Table 1a
Tiered comparison for IMPROVE (RONS and RONS), RDI (3 and 7) and MOUDI samplers analyzed by XRF in Winter 2013.

Tier		1. Comparison to duplicate XRF analysis			2. Comparison to co-located sampler			3. Comparison between SAMPLER and IMPROVE measurement		
Sampler	Element	RSQ	Slope	Intercept/avg	RSQ	Slope	Intercept/avg	RSQ	Slope	Intercept/avg
IMPROVE RONS PM2.5	**Na**	N/A			**0.979**	**1.180**	**−0.003**	N/A		
	Mg				**0.906**	**1.063**	**0.167**			
	Al				**0.948**	**0.908**	**0.17**			
	Si				**0.959**	**0.895**	**0.043**			
	P				**0.856**	**0.989**	**0.049**			
	S				**0.997**	**1.061**	**−0.021**			
	Cl				**0.991**	**0.993**	**−0.006**			
	K				**0.996**	**1.019**	**0.004**			
	Ca				**0.966**	**0.964**	**−0.005**			
	Ti				**0.927**	**0.951**	**0.030**			
	V				< MDL	< MDL	< MDL			
	Cr				0.218	0.536	0.522			
	Mn				**0.645**	**0.806**	**0.265**			
	Fe				**0.968**	**0.969**	**−0.001**			
	Ni				< MDL	< MDL	< MDL			
	Cu				**0.877**	**1.033**	**0.020**			
	Zn				**0.968**	**1.047**	**−0.014**			
	Se				0.221	0.527	0.545			
	Br				**0.923**	**0.925**	**0.084**			
RDI 3A PM2.5	**Na**	**0.986**	**1.046**	**−0.005**	**0.984**	**0.733**	**0.117**	**0.940**	**1.525**	**−2.11**
	Mg	**0.927**	**0.966**	**−0.031**	0.480	0.514	0.859			
	Al	**0.996**	**1.002**	**0.010**	**0.915**	**0.830**	**−0.53**	**0.900**	**0.443**	**0.132**
	Si	**0.998**	**1.013**	**−0.007**	**0.681**	**0.829**	**0.617**	**0.659**	**0.320**	**−0.194**
	P	**0.986**	**1.016**	**−0.005**	0.007	−0.085	0.928	**0.690**	**1.120**	**−0.087**
	S	**0.981**	**1.022**	**0.007**	**0.703**	**0.803**	**0.082**	**0.978**	**0.768**	**0.028**
	Cl	**0.998**	**1.081**	**−0.001**	**0.998**	**0.786**	**0.061**	**0.909**	**1.099**	**0.001**
	K	**0.993**	**1.024**	**0.013**	**0.876**	**0.667**	**0.169**	**0.868**	**0.440**	**−0.204**
	Ca	**0.998**	**0.998**	**0.002**	**0.925**	**0.964**	**0.195**	**0.950**	**0.262**	**−0.065**
	Ti	**0.996**	**1.003**	**0.015**	**0.944**	**0.894**	**0.019**			
	V	**0.989**	**1.002**	**0.022**	**0.905**	**0.760**	**−0.031**			
	Cr	**0.997**	**0.994**	**0.024**	**0.875**	**0.864**	**−0.114**	**0.927**	**0.509**	**0.029**
	Mn	**0.994**	**1.019**	**−0.051**	**0.713**	**0.666**	**1.547**			
	Fe	**0.998**	**1.004**	**0.015**	**0.925**	**0.928**	**−0.037**	**0.889**	**0.560**	**−0.600**
	Ni	**0.938**	**0.752**	**0.089**	0.005	−0.150	1.727	**0.882**	**0.711**	**−0.559**
	Cu	**0.999**	**0.998**	**−0.008**	**0.919**	**0.865**	**0.206**			
	Zn	**0.997**	**1.026**	**0.003**	**0.825**	**0.865**	**0.020**			
	Se	**0.834**	**0.928**	**0.051**	**0.794**	**0.800**	**0.228**			
	Br	**0.957**	**1.102**	**−0.074**	**0.667**	**0.707**	**0.227**	**0.810**	**1.393**	**−1.805**
MOUDI PM1.8	**Na**	**0.660**	**0.649**	**0.100**	N/A			**0.970**	**1.582**	**0.206**
	Mg	**1.00**	**0.966**	**0.004**				0.004	−0.015	0.478
	Si	**0.998**	**0.958**	**0.043**				0.008	−0.078	0.810
	P	0.386	0.906	−0.041				**0.500**	**1.050**	**0.325**
	S	**0.991**	**0.891**	**0.107**				**0.870**	**1.062**	**−0.261**
	Cl	**0.998**	**1.031**	**−0.308**				**0.963**	**1.770**	**−0.588**
	K	**0.996**	**1.065**	**−0.056**				**0.936**	**1.070**	**−0.068**
	Ca	**1.00**	**1.049**	**−0.020**				0.137	0.533	0.797
	Ti	**0.960**	**0.878**	**0.079**				0.015	−0.128	1.004
	V	**0.939**	**0.817**	**−0.058**						
	Cr	**0.996**	**1.097**	**−0.120**						
	Mn	**0.972**	**0.978**	**0.059**				0.060	−0.050	0.355
	Fe	**0.997**	**0.981**	**0.028**				0.051	0.302	0.589
	Ni	**0.994**	**0.982**	**0.008**						
	Cu	**0.986**	**0.969**	**0.042**				0.137	−0.040	0.231
	Zn	**0.938**	**0.917**	**0.080**				0.362	0.410	0.054
	Se	0.235	0.479	0.296						
	Br	**0.817**	**0.872**	**0.274**				**0.761**	**0.951**	**0.521**

Statistical analysis was performed on measurements from all collection devices and analysis techniques to determine precision and accuracy of the aggregated elemental masses collected with the IMPROVE sampler and the size resolved measurements collected with the RDI and MOUDI samplers.

Table1b
Tiered comparison for IMPROVE (RONS and ROSN), RDI (3 and 7) and MOUDI samplers analyzed by XRF in Summer 2013.

| Tier		1. Comparison to duplicate XRF analysis			2. Comparison to co-located sampler			3. Comparison between SAMPLER and IMPROVE measurement		
Sampler	Element	RSQ	Slope	Intercept/avg	RSQ	Slope	Intercept/avg	RSQ	Slope	Intercept/avg
IMPROVE RONS PM2.5	**Na**	N/A			**0.898**	**0.954**	**0.102**	N/A		
	Mg				**0.798**	**0.800**	**0.181**			
	Al				0.550	0.391	0.475			
	Si				0.445	0.346	0.513			
	P				< MDL	< MDL	< MDL			
	S				**0.847**	**0.837**	**0.188**			
	Cl				**0.852**	**1.020**	**0.083**			
	K				**0.844**	**0.822**	**0.149**			
	Ca				**0.651**	**0.565**	**0.359**			
	Ti				0.476	0.338	0.545			
	V				0.344	0.564	0.431			
	Cr				0.013	0.016	0.483			
	Mn				0.037	0.133	0.727			
	Fe				0.471	0.315	0.565			
	Ni				0.109	0.134	0.694			
	Cu				0.394	0.423	0.496			
	Zn				**0.613**	**0.644**	**0.210**			
	Se				0.371	0.581	0.213			
	Br				**0.808**	**0.830**	**0.163**			
RDI 3A PM2.5	**Na**	**0.935**	**0.877**	**0.089**	0.635	0.607	0.323	**0.917**	**1.298**	**0.040**
	Mg	**0.953**	**0.986**	**−0.013**	0.046	0.236	0.698			
	Al	**0.752**	**0.900**	**0.102**	0.028	0.264	0.718			
	Si	**0.859**	**0.987**	**0.010**	0.014	0.177	0.826			
	P	**0.817**	**1.165**	**−0.140**	0.004	0.033	0.964			
	S	**0.974**	**1.023**	**−0.006**	**0.747**	**0.649**	**0.290**	**0.556**	**0.604**	**0.060**
	Cl	**0.903**	**0.879**	**0.037**	**0.861**	**0.839**	**0.084**	**0.817**	**0.524**	**0.029**
	K	**0.982**	**0.979**	**0.031**	0.424	0.596	0.373			
	Ca	**0.953**	**0.914**	**0.075**	0.221	0.517	0.491			
	Ti	**0.815**	**0.859**	**0.147**	0.043	0.298	0.690			
	V	**0.903**	**0.922**	**0.079**	0.070	0.320	0.571			
	Cr	**0.669**	**1.321**	**−0.251**	0.017	0.204	0.793			
	Mn	**0.898**	**0.931**	**0.049**	0.198	0.570	0.5697			
	Fe	**0.799**	**0.861**	**0.147**	0.061	0.396	0.612			
	Ni	**0.875**	**0.795**	**0.044**	0.329	0.603	0.552			
	Cu	**0.931**	**1.076**	**−0.097**	0.351	0.996	0.077			
	Zn	**0.841**	**0.983**	**0.036**	0.221	0.517	0.482			
	Se	**0.711**	**0.913**	**0.081**	0.098	0.418	0.64			
	Br	**0.984**	**0.957**	**0.054**	**0.814**	**0.747**	**0.231**	**0.577**	**1.065**	**0.002**
MOUDI PM1.8	**Na**	**0.965**	**1.034**	**0.017**	N/A			**0.879**	**1.293**	**0.026**
	Mg	**0.874**	**0.897**	**−0.106**				**0.869**	**1.167**	**0.034**
	Si	**0.999**	**1.077**	**−0.112**						
	P	< MDL	< MDL	< MDL						
	S	**0.997**	**0.999**	**0.002**				**0.749**	**0.670**	**0.078**
	Cl	**1.000**	**0.982**	**−0.004**				**0.945**	**1.582**	**−0.177**
	K	**0.996**	**1.021**	**−0.019**				**0.624**	**1.181**	**−0.071**
	Ca	**0.997**	**1.020**	**−0.011**				**0.633**	**1.357**	**0.027**
	Ti	**0.838**	**0.949**	**−0.224**						
	V	**0.782**	**0.094**	**−0.125**						
	Cr	**0.995**	**1.127**	**−0.038**						
	Mn	**0.994**	**1.268**	**0.181**						
	Fe	**0.990**	**1.107**	**−0.115**						
	Ni	**0.993**	**1.135**	**−0.100**						
	Cu	**0.489**	**0.309**	**0.642**						
	Zn	**0.916**	**1.015**	**0.081**				0.044	−0.011	0.036
	Se	0.047	0.381	0.168						
	Br	**0.940**	**1.146**	**0.114**				**0.551**	**0.592**	**0.332**
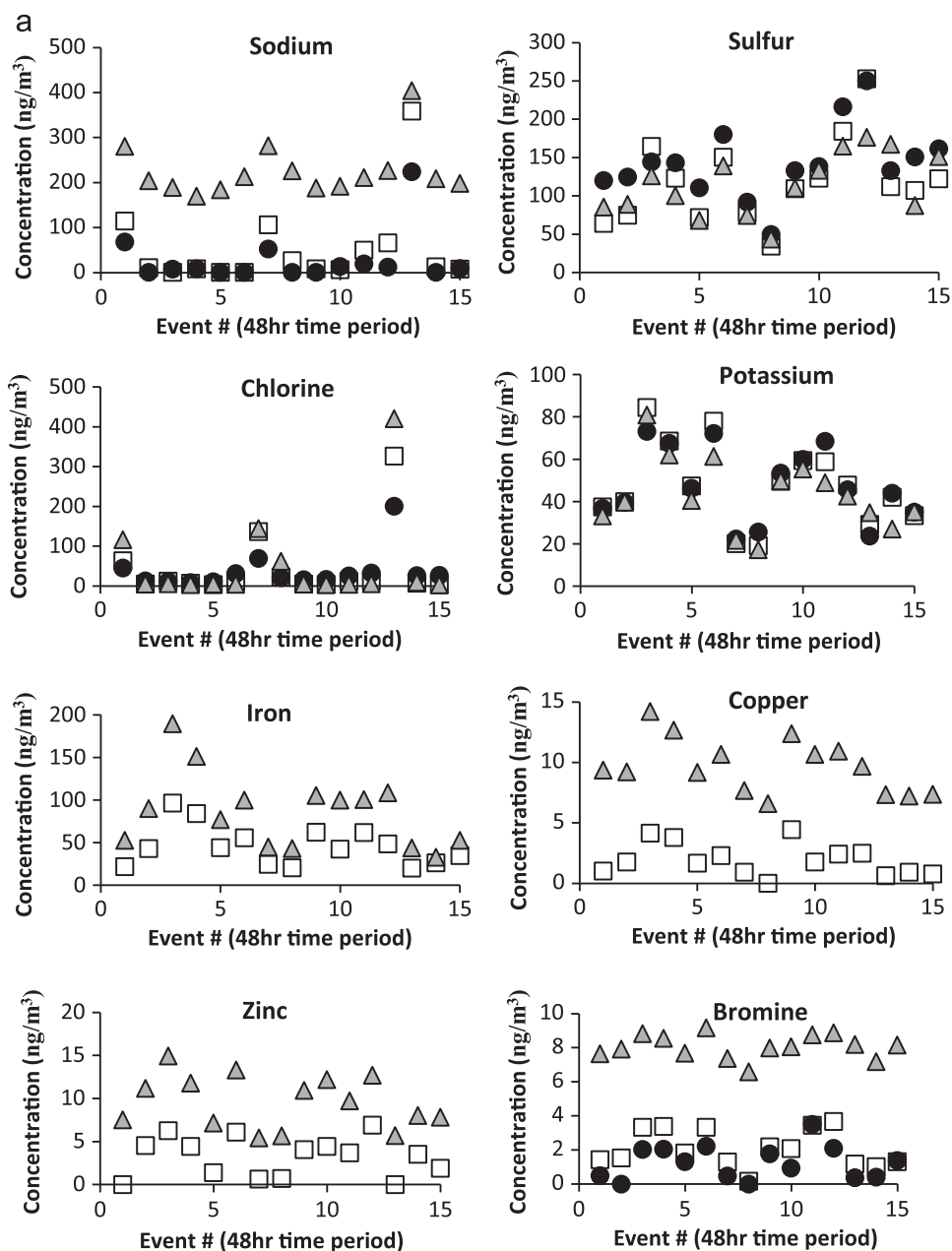
Fig. 5. (a) Time series plots for 15 sampling events (each 48 h duration) in winter 2013 comparing IMPROVE PM2.5 (white squares), RDI PM2.5 (gray triangles) and MOUDI PM1.8 (black circles). The elements that did not pass tier 3 in Tables 1a and 1b were not included in the time series comparison. (b) Time series plots for 15 sample events (each 48 h) in summer 2013 comparing IMPROVE PsM2.5 (white squares), RDI PM2.5 (gray triangles) and MOUDI PM1.8 (black circles). The elements that did not pass tier 3 in Tables 1a and 1b were not included in the time series comparison.

3. Results and discussion

Figure 4a and b show the ambient PM2.5 concentration measured by two IMPROVE samplers in winter and summer, respectively. Atmospheric concentrations for PM2.5 were found to be low, or at clean levels, for both the winter and summer episodes.

Evaluation of the precision and accuracy for each collection device and analysis method was carried out in successively more challenging tiers of comparison. In tier 1, samples collected by the same instrument were analyzed on two different occasions as a precision check of the analytical instruments and methods. In tier 2, samples collected by identical co-located samplers were analyzed and compared as a precision check. In tier 3, samples collected on cascade impactors were summed to form estimates for PM2.5 concentrations that were then compared to measurements from co-located IMPROVE samplers.
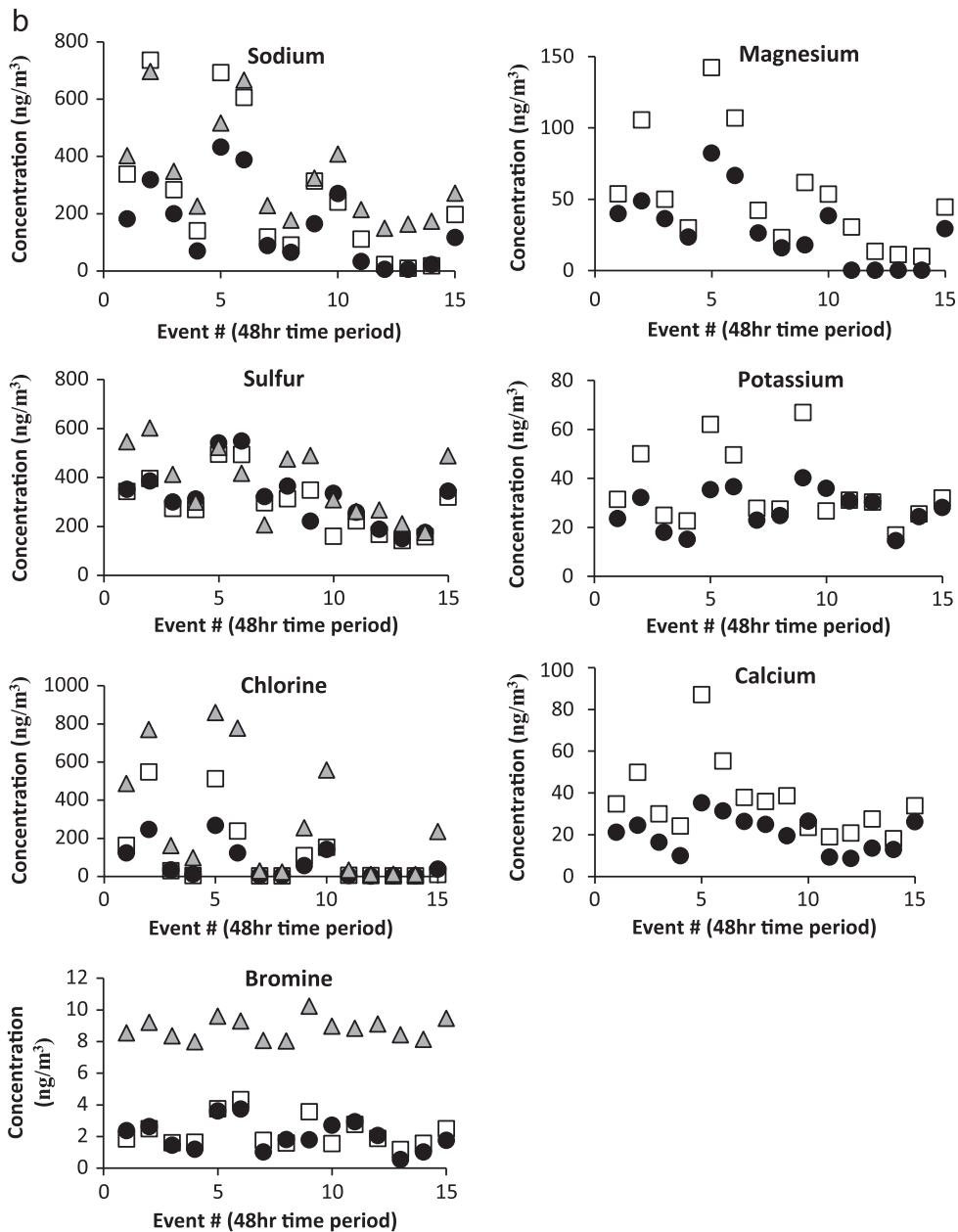
Fig. 5. (*continued*)

This final check quantifies both precision and accuracy, since typical sampling errors manifest differently in cascade impactors vs. filter samplers.

Tables 1a and 1b show the tier comparison for IMPROVE, RDI and MOUDI samplers analyzed by XRF in winter and summer 2013, respectively. Moving left to right, the first column shows a duplicate XRF analysis comparison, followed by a comparison to identical co-located samplers, then a comparison of the impactor (RDI or MOUDI) to the IMPROVE sampler. If an element's R^2 (RSQ, the correlation for the comparison listed at the top of the three comparison columns) was larger than 0.5 and slope was in between the values of 0.5 and 2, that element "passed" the comparison test and moved on to the next tier of comparison. Elements and statistical values that pass are in bold. N/A represents a comparison that was not measured or not applicable. < MDL represents an element with a concentration lower than the stated method detection limit.

Tier 1 evaluates the precision of XRF chemical analyses by comparing duplicates. Out of the 24 elements analyzed by the Panalytical XRF at CNL and 20 elements analyzed by the XRF at LBNL, 19 elements were consistent. Therefore 19 elements were compared for the RDI and IMPROVE samples. Only 18 out of the 19 elements were compared for the MOUDI samples due to the fact that aluminum (Al) is frequently used in the MOUDI sampling process and typically produces unreliable data.

Table 2a

Tiered comparison for IMPROVE (RONS) and MOUDI samplers analyzed by ICP-MS in Winter 2013.

Tier		1. Comparison to duplicate ICP-MS analysis			3. Comparison between IMPACTOR and IMPROVE measurement		
Sampler	Element	RSQ	Slope	Intercept/avg	RSQ	Slope	Intercept/avg
IMPROVE RONS PM2.5	Li	< MDL	< MDL	< MDL	N/A		
	S	0.973	0.930	−0.008			
	K	N/A	N/A	N/A			
	Ti	< MDL	< MDL	< MDL			
	V	0.857	1.025	0.023			
	Mn	0.865	1.064	0.156			
	Fe	0.971	0.930	0.023			
	Ga	0.997	0.956	0.067			
	Ge	< MDL	< MDL	< MDL			
	As	0.967	0.945	0.097			
	Se	0.976	0.982	0.028			
	Br	0.952	0.944	0.096			
	Rb	< MDL	< MDL	< MDL			
	Sr	0.957	1.03	0.092			
	Cd	< MDL	< MDL	< MDL			
	Sn	0.979	0.998	0.012			
	Sb	0.850	0.873	0.075			
	Ba	0.999	0.976	0.087			
	Tl	< MDL	< MDL	< MDL			
	Pb	0.993	0.964	0.024			
	Bi	N/A	N/A	N/A			
MOUDI PM1.8	Li	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	S	0.993	0.980	−0.004	0.237	0.675	0.403
	K	N/A	N/A	N/A	N/A	N/A	N/A
	Ti	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	V	0.887	1.005	0.099	0.783	2.000	−0.437
	Mn	0.845	1.034	0.123	0.453	1.043	0.036
	Fe	0.961	0.960	0.054	0.500	1.813	−0.080
	Ga	0.987	0.986	0.031	0.151	0.143	0.899
	Ge	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	As	0.977	0.975	0.041	0.594	1.588	0.562
	Se	0.936	0.942	0.068	0.542	2.076	0.647
	Br	0.982	0.9744	0.035	0.626	0.986	0.879
	Rb	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	Sr	0.997	1.006	0.016	0.005	−0.010	0.306
	Cd	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	Sn	0.999	0.991	0.009	0.774	0.852	1.096
	Sb	0.880	0.899	0.092	0.729	1.588	1.200
	Ba	0.949	0.980	0.063	0.451	1.960	0.607
	Tl	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	Pb	0.996	0.971	0.018	0.103	0.802	0.817
	Bi	N/A	N/A	N/A	N/A	N/A	N/A

No duplicate XRF analysis was performed on the IMPROVE filters, so no tier 1 comparison was performed. For the RDI, all of the elements passed the tier 1 duplicate XRF comparison in both the summer and winter. Of the 18 elements that were compared for the MOUDI samples, 18 elements were above stated XRF MDL in the winter and 17 elements were above the stated XRF MDL in the summer. The tier 1 duplicate analysis for XRF MOUDI samples showed that 16 out of 18 passed the comparison test in the winter and 17 out of 18 passed the comparison test in the summer. From these results it can be noted that there is good precision of the analytical instrument (XRF) for both the RDI and MOUDI samples.

Tier 2 evaluates sampler precision by comparing results from co-located samplers. Elements that did not pass tier 1 were not compared in tier 2. Because the IMPROVE samples did not have an applicable tier 1 comparison, all 19 elements were compared in tier 2. Of the 19 elements, 14 elements passed the tier 2 precision test between the two co-located IMPROVE samplers (RONS and ROSN) in the winter but only 8 passed in the summer. Since in the winter only 2 elements were below the stated MDL and in the summer only 1 was below, the stated MDLs for the IMPROVE sampler with XRF analysis appear to be optimistic. Uncertainty associated with the IMPROVE sampler collection efficiency also may have skewed the measurement comparison between the two samplers, a known shortcoming of the IMPROVE sampler (Hyslop & White, 2011; White et al., 2005). All elements for the RDI tier 1 comparison passed so were then compared in the tier 2 comparison. 16 out of 19 elements passed the RDI (3 and 7) co-located comparison test in the winter but only 4 of the19 passed in the summer. Only one MOUDI sampler was deployed for both the winter and summer sampling seasons, therefore tier

Table 2b
Tiered comparison for IMPROVE (RONS) and MOUDI samplers analyzed by ICP-MS in Summer 2013.

Tier		1. Comparison to duplicate ICP-MS analysis			2. Comparison between IMPACTOR and IMPROVE measurement		
Sampler	Element	RSQ	Slope	Intercept/avg	RSQ	Slope	Intercept/avg
IMPROVE RONS PM2.5	Li	< MDL	< MDL	< MDL	N/A		
	S	**0.929**	**0.965**	**−0.003**			
	K	N/A	N/A	N/A			
	Ti	< MDL	< MDL	< MDL			
	V	**0.889**	**1.024**	**0.059**			
	Mn	**0.963**	**0.946**	**0.003**			
	Fe	**0.985**	**0.986**	**0.023**			
	Ga	**0.978**	**0.994**	**−0.019**			
	Ge	< MDL	< MDL	< MDL			
	As	**0.975**	**1.054**	**−0.096**			
	Se	**0.945**	**1.043**	**−0.003**			
	Br	**0.934**	**1.004**	**−0.093**			
	Rb	< MDL	< MDL	< MDL			
	Sr	**0.888**	**0.867**	**0.012**			
	Cd	< MDL	< MDL	< MDL			
	Sn	< MDL	< MDL	< MDL			
	Sb	< MDL	< MDL	< MDL			
	Ba	**0.969**	**0.987**	**0.086**			
	Tl	< MDL	< MDL	< MDL			
	Pb	**0.939**	**0.932**	**−0.023**			
	Bi	N/A	< MDL	N/A			
MOUDI PM1.8	**Li**	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	S	**0.999**	**0.972**	**−0.001**	**0.471**	**1.607**	**1.226**
	K	N/A	N/A	N/A	N/A	N/A	N/A
	Ti	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	V	**0.859**	**1.003**	**0.049**	**0.816**	**1.189**	**0.045**
	Mn	**0.939**	**0.920**	**0.010**	**0.617**	**1.070**	**0.209**
	Fe	**0.995**	**0.981**	**0.003**	**0.911**	**0.677**	**0.253**
	Ga	**0.989**	**0.984**	**−0.012**	0.243	1.940	1.022
	Ge	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	As	**0.962**	**1.000**	**−0.037**	**0.654**	**0.856**	**0.423**
	Se	**0.999**	**1.009**	**−0.019**	**0.691**	**0.707**	**0.750**
	Br	**0.984**	**1.008**	**−0.024**	**0.524**	**1.278**	**0.492**
	Rb	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	Sr	**0.878**	**0.844**	**0.040**	**0.782**	1.896	**0.727**
	Cd	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	Sn	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	Sb	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	Ba	**0.986**	**0.966**	**0.017**	**0.486**	**1.344**	**0.716**
	Tl	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
	Pb	**0.972**	**0.992**	**−0.023**	**0.757**	**1.830**	**0.555**
	Bi	N/A	< MDL	N/A	N/A	N/A	N/A

2 evaluation is not possible for the MOUDI samples, and all elements passing tier 1 comparisons were subjected to tier 3 comparisons as discussed below.

Tier 3 evaluates both accuracy and precision of the RDI and MOUDI samplers by comparing them to the co-located IMPROVE PM2.5 sampler. Tables 1a and 1b show RDI 3 but not RDI 7 results; all other data are included in the Supporting Information. Comparison was made between elements that passed tier 1 and 2 for both the RDI and IMPROVE samplers, such that comparisons for the XRF RDI samples were carried out for 12 elements in the winter and 4 elements in the summer. RDI 3 passed this test for 7 of the 12 elements in the winter and all 4 elements in the summer while RDI 7 passed this test for 8 of the12 elements in the winter and only 1of 4 elements in the summer. The causes for the different performance between the co-located RDI samplers are unknown.

MOUDI samples were summed to yield a PM1.8 concentration that was then compared to the co-located PM2.5 measurement from the IMPROVE sampler in the tier 3 comparison. Comparison was made between elements that passed tier 1 and 2 for both the MOUDI and IMPROVE samplers, such that comparisons for the MOUDI XRF samples were carried out for a total of 14 elements in the winter and 8 elements in the summer. Of these, 6 of the 14 elements passed tier 3 comparisons in the winter and 7 of the 8 elements passed in the summer. The failure of additional elements during the tier 3 comparison for the XRF MOUDI analysis may reflect the need for appropriate size resolved correction factors to account for XRF response to different particle diameters on different impactor stages (Formenti et al., 2010). No size-resolved MOUDI XRF corrections were applied in the current study.
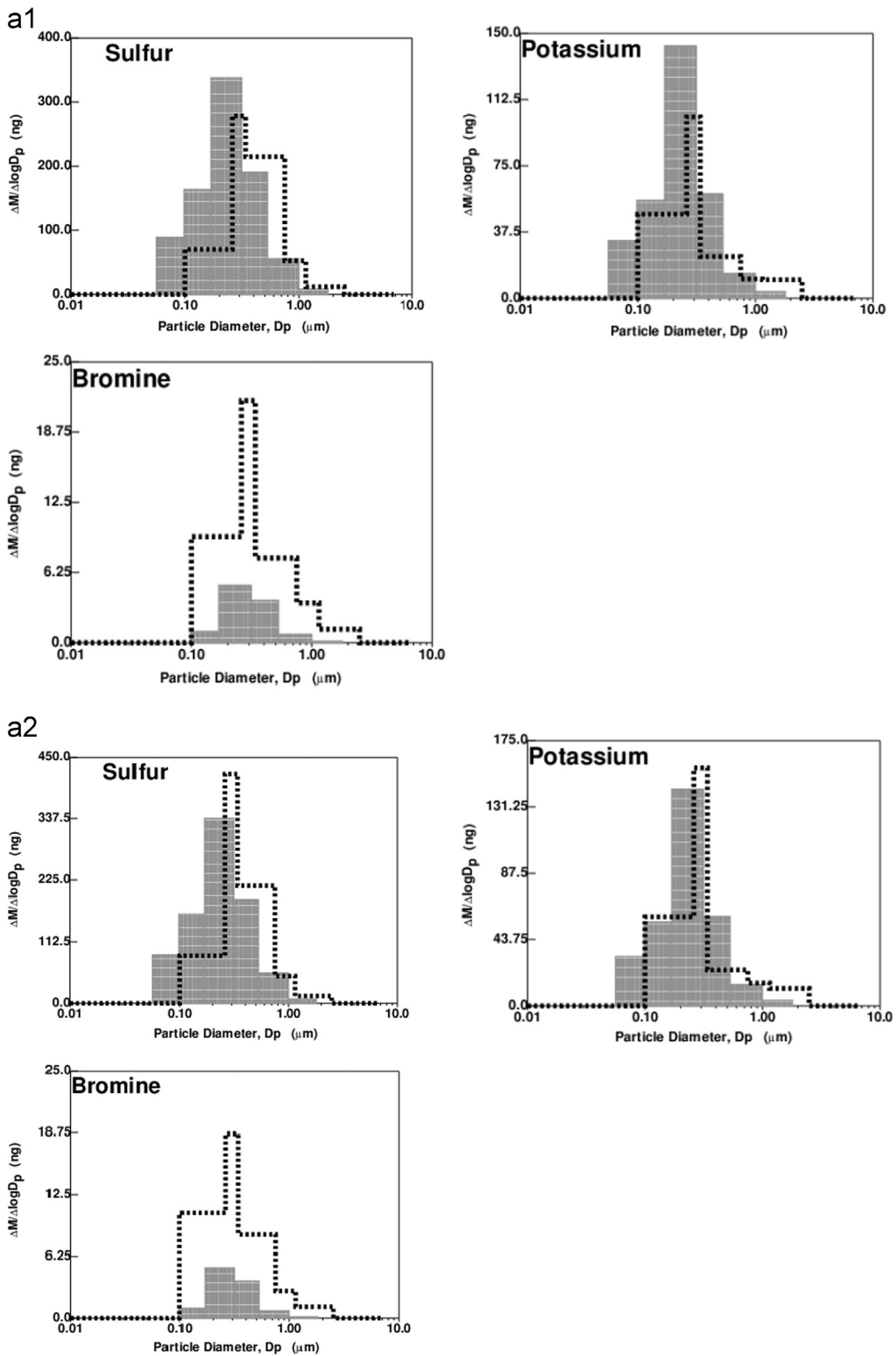
Fig. 6. a1 Winter RDI 3a (dashed black dots) size distribution compared to MOUDI (gray block) size distributions for elements S, K, and Br. a2 Winter RDI 7a (black dash dots) size distribution compared to MOUDI (gray blocks) size distributions for elements S, K, and Br. b1 Summer RDI 3a (black dashed dot) size distribution compared to MOUDI (gray block)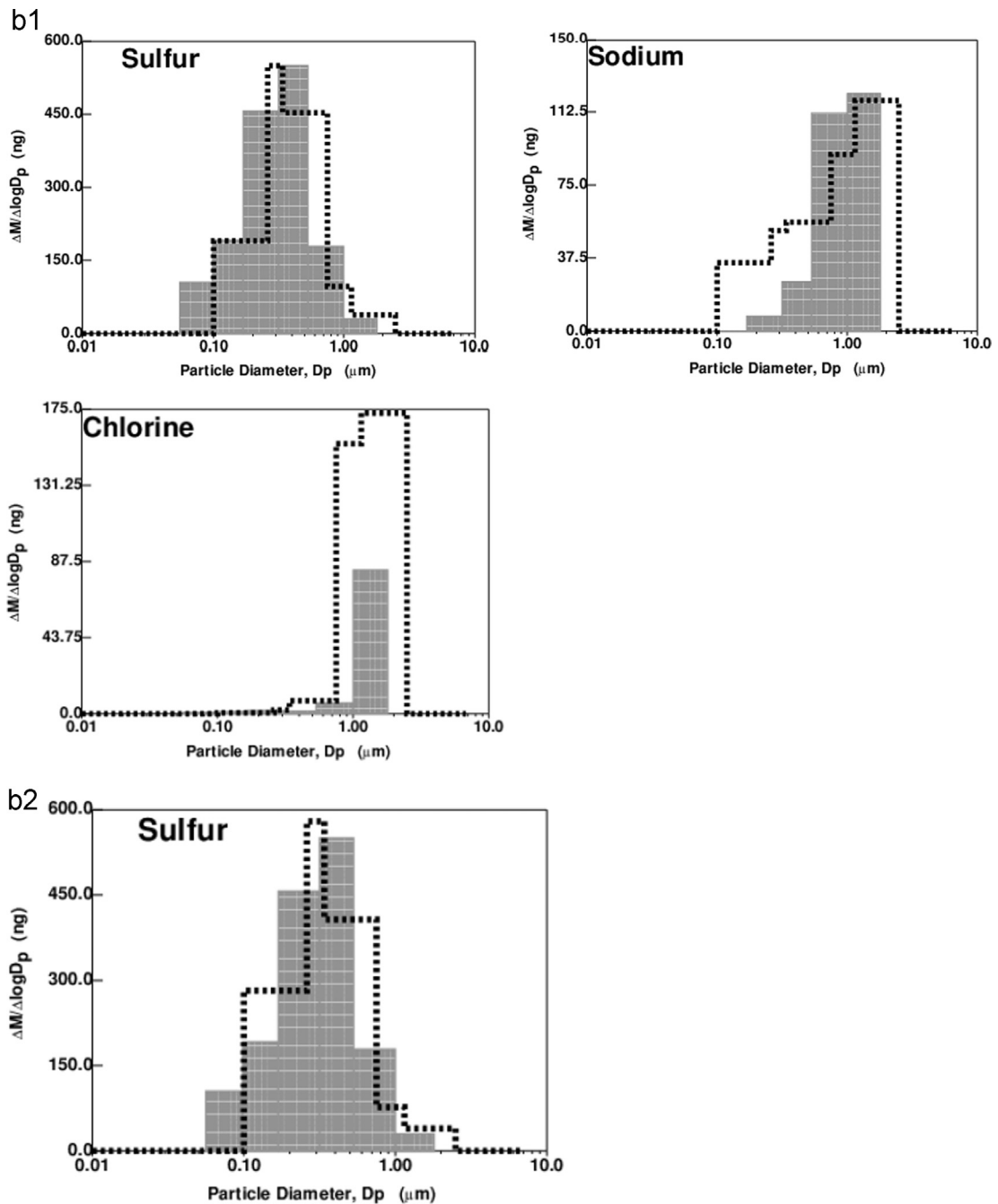 size distributions for elements S, Na, Cl. b2 Summer RDI 7a (dashed black dots) size distribution compared to MOUDI (gray block) size distributions for element S.

Fig. 6. (continued)

Figure 5a and b compare the time series of elemental concentrations collected by the IMPROVE (PM2.5), RDI (PM2.5) and MOUDI (PM1.8) samplers for the winter and summer sampling periods, respectively. The time series plots reveal that the RDI does not measure all elements accurately despite passing the tier 1–3 comparisons summarized previously. The RDI temporal patterns generally match those of other instruments but the reported concentrations are higher than values measured by the IMPROVE and MOUDI samplers for multiple elements. For example, silicon and sodium concentrations reported by the RDI in Fig. 5a show a strong correspondence in temporal patterns but are higher than the values measured by the IMPROVE and MOUDI samplers. This is not a flow rate calibration problem because other RDI elements such as sulfur and chlorine match IMPROVE and MOUDI measurements quite well, but may be due to the insufficient background subtractions. In all cases, MOUDI measurements of elemental concentrations are in equal or better agreement with IMPROVE measurements than RDI samples despite the fact that MOUDI samples were PM1.8 while IMPROVE samples were PM2.5.

Tables 2a and 2b show the tier 1 and tier 3 comparisons for IMPROVE and MOUDI samplers analyzed by ICP-MS in Winter and Summer 2013, respectively. As noted previously, tier 2 comparisons were not possible because only one MOUDI sampler was equipped with Teflon collection substrates. Moving left to right, the first column shows a duplicate ICP-MS analysis comparison, followed by a comparison of the MOUDI to the IMPROVE sampler. If an element's R^2 was larger than 0.5 and slope was in between the values of 0.5 and 2, that element passed and moved on to the next tier of comparison. Statistical values for passing elements are in bold. N/A (underlined) represents a comparison that was not measured or not applicable. N/A (not underlined) is listed when an element's external standard did not pass QA/QC checks. < MDL represents an element with a concentration lower than the method detection limit.

A total of 21 elements were measured by ICP-MS under typical conditions in central California during previous studies (Herner et al., 2006). It is expected that greater uncertainty may be present in the current study because the Teflon filters for both the MOUDI and IMPROVE samplers underwent handling for non-destructive XRF analysis prior to ICP-MS analysis, which generally increases background contamination. Of the 21 target elements, 13 elements were above stated MDLs in the winter and 11 elements were above MDLs in the summer. All elements above MDL passed the tier 1 duplicate analysis for both the MOUDI and IMPROVE samplers. Comparing ICP-MS results between the MOUDI and IMPROVE samplers, 8 out of 13 elements passed the tier 3 analysis in the winter and 10 out of the 11 elements passed the tier 3 analysis in the summer. The closer agreement between the expected MDLs and the actual performance of the co-located MOUDI and IMPROVE samplers suggests that the ICP-MS MDLs are more realistic than the stated XRF MDLs.

Figure 6a and b compare the particle size distributions for elements that successfully pass tier 1–3 comparisons for winter and summer 2013, respectively. In both RDI samplers, the orifices for stages 5 and 6 were inadvertently swapped during installation, so that the material deposited on stage 5 included material that should have deposed on stages 5 and 6. RDI stages 5 and 6 were therefore combined in all subsequent data analysis in the current study. Figure 6a illustrates a slight shift towards larger diameter for sulfur and potassium collected by the RDI sampler relative to the MOUDI during winter months. A similar comparison for bromine is complicated by the poor agreement between the magnitude of the RDI and MOUDI measurements. Figure 6b illustrates similar size distributions between sulfur, sodium, and chlorine size distributions measured with the RDI and MOUDI.

4. Conclusion

The IMPROVE XRF analysis technique reliably measured 78% of elements present above stated MDLs in winter and 42% in summer under the low concentration conditions present during this study. The MOUDI XRF analysis technique reliably measured 33% and 37% of elements above stated MDLs in winter and summer, respectively. The RDI XRF analysis technique precisely measured 35–40% and 5–20% of elements above stated MDLs in winter and summer, respectively, but concentrations for several of these elements appeared to have low accuracy compared to the reference IMPROVE and MOUDI measurements (which were in good agreement). Overall, the RDI XRF and MOUDI XRF measurements had similar accuracy throughout the winter season while in the summer season the MOUDI performed with higher accuracy and precision. The MOUDI ICP-MS analysis technique reliably measured 62% and 91% of elements above stated MDLs in winter and summer, respectively. Based on this simple metric, the MOUDI ICP-MS technique outperforms all XRF analysis techniques for the analysis of size-resolved airborne particulate matter, but it is important to note that the elements measured well by XRF are different than the elements measured well by ICP-MS. Overall, MDLs should be reassessed for all methods and a longer collection time should be considered under low concentration conditions so that collected PM concentrations are above MDLs. An additional study performing a formal calibration of the RDI would be beneficial for future assessment but is beyond the scope of the present study.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jaerosci.2016.07.007.

References

Atwood, S. A., Reid, J. S., Kreidenweis, S. M., Cliff, S. S., Zhao, Y., Lin, N., & Westphal, D. L. (2013). Size resolved measurements of springtime aerosol particles over the northern South China Sea. *Atmospheric Environment, 78*, 134–143.

Brunekreef, B., & Forsberg, B. (2005). Epidemiological evidence of the effects of coarse airborne particles on health. *The European Respiratory Journal, 26*, 309–318.

Bucher, O., Randall, D., Artaxo, P., Bretherton, C., Feingold, G., Forster, P., & Zhang, X. Y. (2013). *Clouds and aerosols. Climate change 2013: the physical science basis. Contribution of working group 1 to the fifth assessment report of the intergovernmental panel on climate change*. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press.

Formenti, P., Nava, S., Prati, P., Chevaillier, S., Klaver, A., Lafon, S., & Chiari, M. (2010). Self-attenuation artifacts and correction factors of light element measurements by X-ray analysis: implication for mineral dust composition studies. *Journal of Geophysical Research: Atmospheres, 115* (DI).

Franklin, M., Koutrakis, P., & Schwartz, P. (2008). The role of particle composition on the association between PM2.5 and mortality. *Epidemiology, 19*(5), 680–689.

Herner, J. D., Green, P. G., & Kleeman, M. J. (2006). Measuring the trace elemental composition of size resolved airborne particles. *Environmental Science and Technology, 40*, 1925–1933.

Hyslop, N. P., & White, W. H. (2011). Identifying sources of uncertainty from the inter-species covariance of measurement errors. *Environmental Science and Technology, 45*, 4030–4037.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., & Worsnop, D. R. (2000). Development of an aerosol mass spectrometer for size and composition analysis of submicron particles. *Aerosol Science and Technology, 33*, 49–70.

Lundgren, D. A. (1967). An Aerosol Sampler for Determination of Particle Concentration as a Function of Size and Time. *Journal of the Air Pollution Control Association, 17*(4), 225–229.

Marple, V. A., Rubow, K. L., & Behm, S. M. (1991). A micro orifice uniform deposit impactor (MOUDI): description, calibration and use. *Aerosol Science and Technology, 14*(4), 434–446.

Oberdorster, G., Oberdorster, E., & Oberdorster, J. (2005). Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. *Environmental Health Perspectives, 113*(7), 823–839.

Ostro, B., Broadwin, R., Green, S., Feng, W.-Y., & Lipsett, M. (2006). Fine particulate air pollution and mortality in nine California counties: results from CALFINE. *Environmental Health Perspectives, 114*(29–33).

Pope, C. A., & Dockery, D. W. (2006). Health effects of fine particulate air pollution: lines that connect. *Journal of Air and Waste Management, 56*(6), 709–742.

Raabe, O. G., Braaten, D. A., Axelbaum, R. L., Teague, S. V., & Cahill, T. A. (1988). Calibration studies of the drum impactor. *Journal of Aerosol Science, 19*(2), 183–195.

Waste, E. S. (1994). *Method 6020 inductively coupled plasma-mass spectrometry*. SW-846 Test methods for evaluating solid waste, physical/chemical methods.

University of California, D. (2015). Interagency montering of protected visual environments. *IMPROVE standard operating protocols*.

VanCuren, R. A., Cahill, T., Burkhart, J., Barnes, D., Zhao, Y., Perry, K., & McConnell, J. (2012). Aerosols and their sources at Summit Greenland – first results of continuous size- and time-resolved sampling. *Atmospheric Environment, 52*, 82–97.

White, W. H., Feeney, P. J., McDade, C. E., Perley, B. P., Shadoan, D. J., & Wakabayashi, P. H. (2005). *Behavior of fine-particle elemental data near the detection limit. Crocker Nuclear Laboratory Internal Report*. Davis: University of California.

Zhao, Y., Cliff, S. S., Wexler, A. S., Javed, W., Perry, K., Pan, Y., & Mitloehner, F. M. (2014). Measurements of size- and time-resolved elemental concentrations at a California dairy farm. *Atmospheric Environment, 94*, 773–781.