Laser Ablation ICP-MS of Size-Segregated Atmospheric Particles Collected with a MOUDI Cascade Impactor: A Proof of Concept

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Abstract. A widely used instrument for collecting size-segregated particles is the micro-orifice uniform deposit impactor (MOUDI). In this work, a 10-stage MOUDI (cutpoint dia. 10 µm to 56 nm) was used to collect ~~24~~ samples in Ljubljana, Slovenia and Martinska, Croatia. Filters, collected with and without rotation, were cut in half and analysed for nine elements (As, Cu, Fe, Ni, Mn, Pb, Sb, V, Zn) using laser ablation ICP-MS. Elemental image maps (created with ImageJ) were converted to concentrations using NIST SRM 2783. Statistical analysis of the elemental maps indicated that for submicron particles (stages 6–10), ablating 10 % of the filter (0.5 cm^2, 20 min ablation time) was sufficient to give values in good agreement (±10 %) to analysis of larger parts of the filter and with good precision (*RSE* < 1 %). Excellent sensitivity was also observed (e.g., 20 ± ~~8~~ 0.2 pg m^{-3} V). The novel use of LA ICP-MS, together with image mapping, provided a fast and sensitive method for elemental analysis of size-segregated MOUDI filters, particularly for submicron particles.

1 Introduction

Inhalation of particle-bound metals in atmospheric particulate can negatively impact human health (Chen and Lippmann, 2009). Particle-bound Fe, Ni, and V can lead to oxidative stress, pulmonary inflammation, cardiac effects, and cardiovascular and respiratory illnesses (Aust et al., 2002; Bell et al., 2009; Campen et al., 2002). Particle size is also a factor. Submicron particles pose the greatest health risks (Davidson et al., 2005), and particle-bound metals from anthropogenic sources (e.g., fossil fuel combustion and vehicle emissions) commonly partition to these smaller sizes (<1 µm) (Fang and Huang, 2011). A well-known instrument for the collection and speciation of size-segregated particles is the multi-orifice uniform deposit impactor (MOUDI) (Allen et al., 2001; Herner et al., 2006; Ntziachristos et al., 2007; Pekney et al., 2006; Singh et al., 2002). Particles are sorted by size into stages using cascade impaction and deposited on filters. Models with various flow rates (2-130 L min^{-1}) and stages (cutpoint dia. between 0.01 and 18 µm) are available, as well as rotating and non-rotating options (Marple, 1991; Marple et al., 2014). To determine elemental concentrations, filters are typically extracted with acid and analyzed by ICP-MS (Canepari et al., 2008; Herner et al., 2006; Li et al., 2012; Ntziachristos et al., 2007; Pekney et al., 2006) or ICP-AES (Fang and Huang, 2011), whereas in some cases direct analysis of the filters was performed by X-ray fluorescence spectrometry[11] or proton-induced X-ray emission (Brüggeman et al.,

2009). Detection limits using these methods are challenging due to low particle mass and contamination risks; after corrections have been made for blanks, elemental concentrations are often below detection limits (Pekney et al., 2006).

A promising alternative to acid extraction involves laser ablation ICP-MS (LA ICP-MS) (Aubriet and Carré, 2010). This method samples the filters via pulsed laser ablation, effectively removing the particles, thereby eliminating the need for harsh chemicals, offering faster sample preparation times, reducing contamination, and increasing sensitivity. Initial efforts using LA ICP-MS have been promising (Gligorovski et al., 2008; Triglav et al., 2010), although problems associated with spatial inhomogeneity (Brown et al., 2009), matrix-matched standards (Chin et al., 1999; Tanaka et al., 1998), and laser instabilities have been reported. Hsieh et al. (2011) optimized the LA-ICP-MS parameters suitable for analysis of nanometer- and submicrometer-sized airborne particulate matter sampled by an electrical low-pressure impactor. In this work, we addressed these problems by using a MOUDI for particle collection and a highly stable excimer laser (193 nm ArF*) for particle ablation. To our knowledge, we are the first to analyze MOUDI filters by LA ICP-MS. Filters collected both with and without rotation were analyzed. Concentrations of nine elements from ten MOUDI stages are reported with specific attention given to submicron particles (stages 6–10).

2 Materials and methods

2.1 Air Sampling

A 10-stage, micro-orifice uniform-deposit impactor (MOUDI, Model 110R with rotator, Applied Physics, Inc.) was used to collect four air samples where stages 1–10 correspond to 3, 10, 10, 20, 40, 80, 900, 900, 2000, 2000 nozzles and 50% cut-point dia. of 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10, and 0.0156 µm, respectively. Samples 1 (24 h, March 3 to 4, 2015) and 2 (72 h, Mar 31 to April 3, 2015) were collected in a residential area of Ljubljana, Slovenia. Samples 3 (May 6 to 7, 2015) and 4 (May 8 to 9, 2015) were collected at Martinska station, Croatia, an estuary on the Eastern Adriatic coast. Particles were collected on PTFE filters (Whatman, 46.2 mm, deposit area 4.91 cm^2). Samples 1, 2, and 4 were collected with rotation (depositing particles in concentric circles); sample 3 was collected without rotation (depositing particles in mounds or spots). The nominal flow rate was 30 L min^{-1}.

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2.2 Laser ablation ICP-MS

A quadrupole ICP-MS (Agilent Technologies 7900, Palo Alto, USA) interfaced with a laser ablation system (193 nm ArF* excimer, Analyte G2, Teledyne Photon Machines Inc.) was used to analyze nine nuclides (^{75}As, ^{63}Cu, ^{57}Fe, ^{55}Mn, ^{60}Ni, ^{208}Pb, ^{121}Sb, ^{51}V, ^{66}Zn). (See optimized parameters in Table 1.) Ablation took place in a HelEx 2-volume cell applying a laser beam size of 150 µm (square mask), a scanning speed of 300 µm s^{-1}, a repetition rate of 10 Hz, and a fluence of 1.21 J cm^{-2}. Ablated materials were transported from the ablation cell to the plasma with helium; argon was added as the make-up gas

before the ICP torch. Ions formed in the plasma were extracted and separated by their mass-to-charge (m/z) ratios. The mass spectrometer, in time-resolved analysis mode, measured one point per mass for the nine selected masses. The detection limit for each element was determined as 3 × *SD* of seven clean blanks (Table 2).

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2.3 Filter preparation and ablation

All 10 filters (stages 1–10) were ablated in samples 1 and 2 (Ljubljana, rotation), eight filters (stages 3–10) were ablated in sample 3 (Martinska, non-rotation), and four filters (samples 6–9) were ablated in sample 4 (Martinksa, rotation). Filters were cut in half and four or five were co-mounted on a single glass slide with double-sided tape (Fig. 1). For the rotated filters (Fig. 1A), the laser raster pattern comprised parallel lines that spanned the width and ran the length of the co-mounted half-filters. For the non-rotated filters (Fig. 1B), half-filters were ablated individually, except for stages 3 and 4, which were ablated spot-by-spot (5 of 10 spots in stage 3; 9 of 20 spots in stage 4). A standard reference material (NIST 2783, air particulate on filter media) with certified elemental areal mass densities (ng cm^{-2}) and a lab blank (an unexposed filter, taken directly from the box) were mounted alongside the exposed filters. At least 1 cm^2 of the NIST and blank filters were ablated with each set of four or five half-filters. LA ICP-MS stability was tested by ablating the NIST standard in four segments (0.25 cm^2 per segment), alternating with the sample filters. No loss in laser stability or ICP-MS drift was observed over 11 h.

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The laser beam energy was sufficient to remove several layers of the PTFE filter in each particle size range, and no particles were visible on the filters (100× magnification) following ablation; hence, we assume that most particles were removed during ablation. However, deeply impacted particles may have remained embedded in the filters, particularly for the smaller particles in the case of MOUDI sampling without rotation and high loading. Elemental concentrations were determined via ~~a~~ one-point calibration with the NIST standard.

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2.4 QA/QC

Filters from sample 1 (stages 6–10) were cut in half and analysed by laser ablation and wet-chemical ICP-MS (Agilent Technologies 7900). For wet-chemical analysis, standards were prepared by diluting certified, traceable, inductively coupled plasma-grade, single-element standards. Filters were placed in metal-free HDPE vials containing 10 mL of an acid mixture (5 % HNO_3 and 2.5 % HCl, *v*/*v*), mixed by a rotary shaker for 12 h, and centrifuged. Extracts were measured without dilution. Recovery rates (85–105%) were measured using NIST SRM 2783 as a reference standard. Good agreement was observed between wet chemical and laser ablation ICP-MS for As, Fe, Mn, Pb, V, and Zn (R = 0.94–0.99; m = 0.83–1.52). Poor agreement was observed for Cu, Ni, and Sb, attributed in part to low concentration levels in the extracts (low µg L^{-1}) (Table 3).

3 Results and discussion

3.1 Elemental image maps

Unlike wet chemical ICP-MS (a bulk technique), LA ICP-MS allows for microanalysis of solid samples. In this work, each laser pulse provided spatially resolved elemental data (in counts per second associated with a certain *m*/*z* value). Using ImageJ software (Schneider et al., 2012), these data were mapped into pixels. The pixels formed elemental image maps with pixel size P_{size} (μm^2):

$$P_{size} = ss \cdot t_{acq} \cdot d \quad (1)$$

where *ss* is the laser scanning speed ($\mu m\ s^{-1}$), t_{acq} is the ICP-MS acquisition time (s), and *d* is the laser beam dimension (μm). To obtain maps with square pixels we selected a scanning speed and an acquisition time so that $ss \times t_{acq} = d$; hence, $P_{size} = d^2$. In this work, P_{size} = 150 × 150 μm^2 (*ss* = 300 $\mu m\ s^{-1}$, t_{acq} = 0.5 s, *d* [square mask] = 150 μm). For an analyzed area A_{anal} (cm^2), the number of pixels *P* is given by $10^8 \times A_{anal}/d^2$.

For our half-filters, A_{anal} was nominally 2.4 cm^2 or 10,677 pixels (1 cm^2 = 4444 pixels). Image maps for Pb are shown in Figs. 1A (sample 1, rotated filters of stages 7–10) and 1B (sample 3, non-rotated filters of stages 6–9). (See Figs. S1 and S2 for maps of other elements in samples 1 and 3, respectively.) The false image map colors in Fig. 1 are brightness values, where each pixel *i* with element intensity I_i is converted by ImageJ to a brightness value B_i (dimensionless) using 65,536 pseudocolors (or 65,536 levels of gray).

3.2 Visual inspection of elemental maps

Elemental image maps offer a robust tool for observing details about particle deposition not detectable by bulk methods. For example, the 2-D image maps in Fig. 1A illustrate the concentric circles created by MOUDI rotation. A clogged nozzle is apparent in stage 7, where minimal deposition is observed near the center of the half-filter. Other images made apparent a thumb print, a scissors cut, and the edge of the mounting tape. The ability to "see" such errors made it straightforward to avoid these parts of the filter when selecting areas to analyze. The maps also offered insights into the deposition patterns of various elements. Most notable was Ni, which unlike other elements, deposited in mounds even when collected with rotation (Fig. S3).

Additional information can be gleaned from 3-D image maps. For example, 3-D maps of non-rotated filters gave direct evidence for particle bounce (Marple et al., 2014). Relative intensities, measured with ImageJ, indicated that 12 % of the signal for Pb (stage 5) was located between spots (Fig. S4). Bounce was less pronounced in stages 6–10 (due to more

nozzles). 3-D maps also made apparent "spikes" in the data, defined as values more than twice the median. Spikes were observed for most elements in sample filters (rotated), filter blanks, and gas blanks. In each case, outliers were replaced with the median of the pixels in the surrounding area (2 × pixel size). This correction was made in all filters (including blanks) except for non-rotated filters, where the much higher concentrations in the spots masked the spikes. Spike removal is illustrated in Fig. S5 for Zn (stages 6–10). After spike removal, the average relative standard deviation of the mapped area decreased from 300 to 30 %.

3.3 Statistical ~~analyses~~ analysis of elemental maps

The elemental brightness values associated with each pixel were analyzed statistically using ImageJ (after spike removal). First, we investigated how small an area could be ablated and still reproduce the mean half-filter value B_{half}. We measured (for rotated filters) mean elemental areal brightness values, B_{areal} (cm^{-2}) = $\sum B_i/A_{anal}$, for successively smaller areas A_{anal} (generally rectangular shapes, in different sections of the half-filter) and compared them to B_{half}. For stages 6–10, 10 % of the total filter deposit area (0.5 cm^2, 20 min ablation time) gave brightness values in good agreement (±10 %) to the half-filter values. Representative results for Pb (sample 1, stages 7–9) are shown in Fig. 2. For stages 1–5, 20 % of the filter deposit area (1 cm^2, 40 min ablation time) gave similar results. A notable exception was Ni, which had irregular deposition (Fig. S3). For non-rotated filters (without spike removal), good agreement (±10 %) to B_{half} was observed when (a) in stages 7–10, at least 15 % of the total deposit area was ablated and (b) in stages 5 and 6, areas containing 5 spots (of 40) and 8 spots (of 80), respectively, were ablated. In stages 3 and 4, where individual spots were ablated, we measured only the relative standard deviations across spots: 25 % (n = 5) and 23 % (n = 9), respectively.

Second, for rotated filters, where deposition is expected to be uniform, we measured the relative standard deviations (*RSD*) of the elemental areal brightness values for each MOUDI stage (after spike removal). For stages 1 to 3, *RSD* values were large (120 to 80 %, respectively) due to fewer particles and fewer nozzles at those stages. *RSD* values decreased in stage 4 (60 %), stage 5 (40 %), and stages 6–10 (all ~30 %). *RSD* values became constant at larger areas (more pixels); hence, *RSE* values (= *RSD*/√(number of pixels)) were also determined. Results are shown in Fig. 3, where both theoretical and experimental *RSE* values for Pb (sample 1) are plotted. For stage 4, an ablation area of 20 % (1 cm^2, 40 min ablation time) was sufficient for good precision (*RSE* = 1 %); for stages 5–10, only 10 % was required (0.5 cm^2, 20 min ablation time). In contrast to our previous findings (Gligorovski et al., 2008), in this work, the NIST standard also showed good precision for a 1 cm^2 (4444 pixels) ablation area (*RSD* = 22 %, *RSE* = 0.33 %).

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3.4 Elemental concentrations

Like wet chemical ICP-MS, the ultimate goal of LA ICP-MS is to measure elemental concentrations. Elemental image maps were converted to concentrations using the NIST standard. For rotated filters, B_{areal} (cm^{-2}) was converted to a mass density

M_{areal} (ng cm^{-2}) using $B_{areal,NIST}$ and $M_{area,NIST}$ (eq 2). B_{areal} values were blank corrected using the average elemental areal brightness value of seven clean blanks $B_{areal,BL}$:

$$M_{areal} = \frac{B_{areal} - B_{areal,BL}}{B_{areal,NIST}/M_{areal,NIST}} \quad (2)$$

Atmospheric elemental concentrations C_{air} (ng m^{-3}) were determined by multiplying M_{areal} by the filter exposure area (4.91 cm^2) and dividing by the air volume (43.2 m^3). Although half-filter areas were used in these calculations, as shown above, 10 % areas (stages 6–10) or 20 % areas (stages 1–5) gave comparable results (± 10 %). A corresponding approach was used for non-rotated filters, except that spikes were not removed. Also, in stages 3 and 4, elemental brightness values were determined per spot rather than per area, then multiplied by the total number of spots per filter.

Atmospheric elemental concentrations were highest in MOUDI stages 5–9 (1.0–0.1 µm); these concentrations are shown in Fig. 4A (Ljubljana, samples 1 and 2) and 4B (Martinska, samples 3 and 4). (See Tables S1 and S2 for all concentrations). Elemental concentrations (ng m^{-3}) are shown on the left; percentages (normalized to 100 %) are shown on the right. To facilitate comparison, the two Ljubljana samples (24 and 72 h) and the two Martinksa samples (both 24 h) are plotted side by side. Together, these graphs illustrate both the magnitude and relative contributions of the nine elements in each stage. Several trends are worth noting. First, at both sites, the largest concentrations were observed in stage 5 (cutpoint = 1 µm). In Ljubljana, the 24 h concentrations were generally greater than the 72 h values (except for stage 5), but the relative percentages in each stage were quite similar. These trends suggest a common major source for the elements, but one that varies in magnitude from day to day. Consistent with previous works (Grgić et al., 2009; Hitzenberger et al., 2006; Mirage, 1989; Pacyna and Pacyna, 2001), we attribute this source to traffic emissions. Fe and Zn were the major elements comprising 85 % of the total elemental mass in sample 1 (101 ng m^{-3} Fe; 44 ng m^{-3} Zn) and 90 % of the total elemental mass in sample 2 (127 ng m^{-3} Fe; 27 ng m^{-3} Zn). The other trace elements (e.g., Cu, Pb, V, and Mn) were also consistent with traffic emissions and vehicle exhaust or fossil fuel or biomass combustion (Mirage, 1989; Pacyna and Pacyna, 2001). We note the excellent sensitivity that was observed in detecting trace metals with 24 h concentrations as low as 20 (± ~~8~~0.2), 22 (± ~~8~~0.2), and 26 (± ~~4~~0.1) pg m^{-3} for V (stage 9), Mn (stage 10), and As (stage 10), respectively.

In Martinska (Figure 4B), the total elemental concentrations were lower than in Ljubljana by roughly a factor of two. The highest values were in stage 5 (36 ng m^{-3}), predominated by Fe (92 %) with smaller amounts of Zn (3 %), Mn (2 %), Pb (1 %), and V (1 %). In general, higher total concentrations were observed in sample 4 (day 2), and there was more variability in composition between the two days than in Ljubljana. The largest variability was observed for V in stage 8; concentrations varied from 1.92 (39 %) in sample 3 (day 1) to 1.36 ng m^{-3} (14 %) in sample 4 (day 2). Vanadium has been observed previously in marine aerosols (Turšič et al., 2006) and is attributed to continental pollution from oil combustion (Tolocka et al., 2004). The variability in the direction of continental winds on the two days of sampling may have influenced this signal.

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4 Conclusions

In this proof of concept paper, we have demonstrated the usefulness of LA ICP-MS as a tool for analysing the elemental composition of size-segregated atmospheric particles collected on filter-based media. ~~Two p~~Previous problems associated with LA ICP-MS were addressed: (1) MOUDI rotation sampling overcomes the lack of uniformity in particle deposition, creating a sample highly suitable for LA-ICP-MS 2D mapping, 2) the 2D mapping mode yields results which show a high degree of accuracy when larger areas are ablated and superior detection limits, and 3) quantification problems due to non-matrix matched standards are circumvented by ablating through the filter or obliterating the particles on the filters, warranting the reliable use of one-point calibrating on NIST SRM 2783. Together, these improvements allowed for an efficient and sensitive measurement of elemental composition. Although half-filters were analysed in much of this work, we showed that comparable results could be obtained by ablating only 1 cm^2 of filter or less. The ability to analyse a filter in roughly 40 min of instrument time makes feasible routine measurements of size-segregated particles. Compositional graphs of these particles, such as those shown in Fig. 4 for Ljubljana and Martinska, will be useful to the atmospheric community by allowing comparison of elemental profiles of particulate collected at diverse sites (e.g., urban industrial centres to remote background locations). Such profiles can be compared over days, months, or even years; short-term and long-term compositional changes can be used to monitor atmospheric changes such as a new pollution source, the impacts of pollution remediation, and the effects of climate change. A key limitation to this approach is the lack of a size-segregated reference standard; hence, measurements of absolute elemental concentrations is not yet feasible. Nonetheless, much can be learned from relative changes in elemental composition, which are easily measured by this technique.

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Supplementary material. Supplementary materials include (1) atmospheric elemental concentrations for MOUDI stages 1–5 (Table S1) and 6–10 (Table S2); (2) elemental image maps for stages 6–10 of sample 1 (Fig. S1), (3) elemental image maps for stages 6 and 9 of sample 2 (“spots”) (Fig. S2), (4) elemental image maps of Ni vs Pb (Fig. S3, stages 3–8), (5) illustration of particle bounce for Pb (Fig. S4), and (6) illustration of spike removal for zinc (Fig. S5, stages 6–10, sample 1).

Author contribution. M. S. Robinson collected samples, carried out experiments, and prepared the manuscript. V. S. Šelih and M. Šala ~~designed and~~ carried out experiments. I. Grgić collected samples and prepared the manuscript. M Bitsui collected samples. J. T. van Elteren designed and carried out experiments and prepared the manuscript.

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Table 1. Optimized operating conditions for the laser ablation ICP-MS system.

Laser ablation (Analyte G2)	
Wavelength	193
Pulse length	<4 ns
Beam size (square mask)	150 µm
Fluence	1.21 J cm^{-2}
Repetition rate	10 Hz
Scanning speed	300 µm s^{-1}
He carrier flow rate	0.5 L min^{-1} (cup) and 0.3 L min^{-1} (cell)
Ar make-up flow rate	0.8 L min^{-1}
ICP-MS (Agilent 7900)	
Rf power	1500 W
Sampling depth	9 mm
Acquisition time/mass	0.5–1.0 s
Measurement mode	time-resolved TRA(1)
Ar plasma gas flow rate	15 L min^{-1}
Ar auxiliary gas flow rate	0.7 L min^{-1}
No. of line scans/mapping sequence	70–150 (0.56–4.38 min line $scan^{-1}$)
Isotopes measured	^{75}As, ^{63}Cu, ^{57}Fe, ^{55}Mn, ^{60}Ni, ^{208}Pb, ^{121}Sb, ^{51}V, ^{66}Zn

Table 2. Detection limits DL (3 x SD) were determined from the mean standard deviations of seven clean blanks with ablation areas of 1.1 cm^2. DLs were converted to concentrations using the NIST standard and a theoretical air sampling period of 24 h at 30 LPM. All values were spike corrected. Units are in ng m^{-3}.

element	DL
As	0.019
Cu	0.009
Fe	0.370
Mn	0.016
Ni	0.114
Pb	0.004
Sb	0.019
V	0.003
Zn	0.160

Table 3. Correlation coefficient (R) and slope (m in y = mx) for concentrations measured by laser ablation ICP-MS (x) and wet-chemical ICP-MS (y) in MOUDI stages 6–10. Reasonable agreement was observed for the first six elements.

element	R	m
As	0.97	0.92
Fe	0.99	1.52
Mn	0.97	0.93
Pb	0.98	0.91
V	0.99	0.83
Zn	0.95	0.92
Cu	0.78	1.08
Ni	0.03	2.20
Sb	0.52	0.23

Figure captions.

Figure 1. Setups for LA ICP-MS of rotated (A, sample 1, stages 7–10) and non-rotated (B, sample 3, stages 6–9) filters; both optical and elemental images (pseudocolored image maps of Pb) for each filter are shown. Lab blanks (LB) and the NIST 2783 standard (STD) were analysed next to the filters.

Figure 2. Comparison of mean brightness values for smaller ablation areas (Bfraction) to the half-filter value (Bhalf) for Pb in sample 1 (stages 7–9). The blue bar shows that ablation of smaller areas agreed with the half-filter value to ±10 %.

Figure 3. Relative standard errors ($RSE = RSD/\sqrt{P}$) as a fraction of the number of pixels P (=21,822 pixels, associated with a total filter deposit area A_{tot} of 4.91 cm^2). Solid lines are theoretical values for RSD = 30, 40, and 60 %. Markers are experimental values for Pb in stages 4 (filled squares), 5 (filled triangles), and 7 and 8 (open squares and circles).

Figure 4. Elemental concentrations of (A) samples 1 (24 h) and 2 (72 h) in Ljubljana and (B) samples 3 (24 h) and 4 (24 h) in Martinska. Graphs on the left show atmospheric concentrations. Graphs on the right show corresponding percent composition. MOUDI stages 5–9 correspond to cutpoint dia. of 1.0, 0.56, 0.32, 0.18, and 0.10 μm, respectively.

FIG1

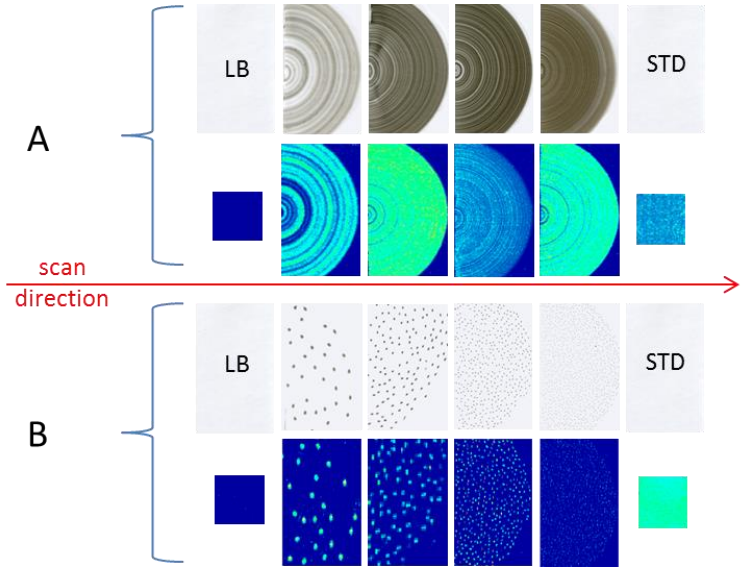


FIG2

5

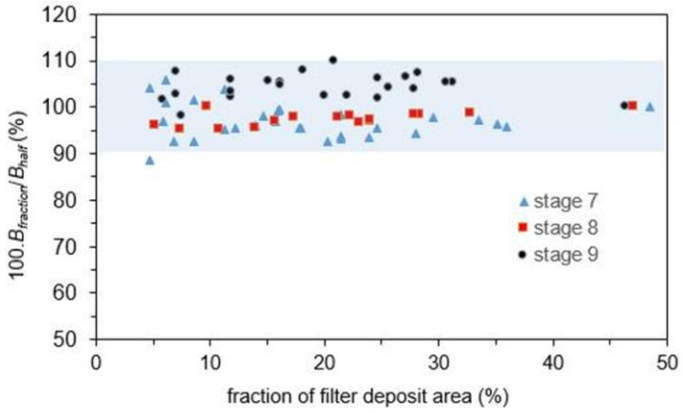

120
110
100
90
80
70
60
50
0
10
20
30
40
50
100.$B_{fraction}$/B_{half} (%)
fraction of filter deposit area (%)
stage 7
stage 8
stage 9

FIG3

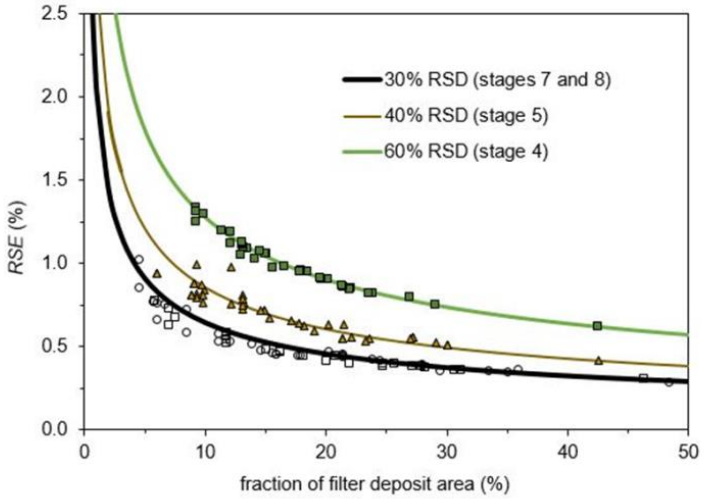
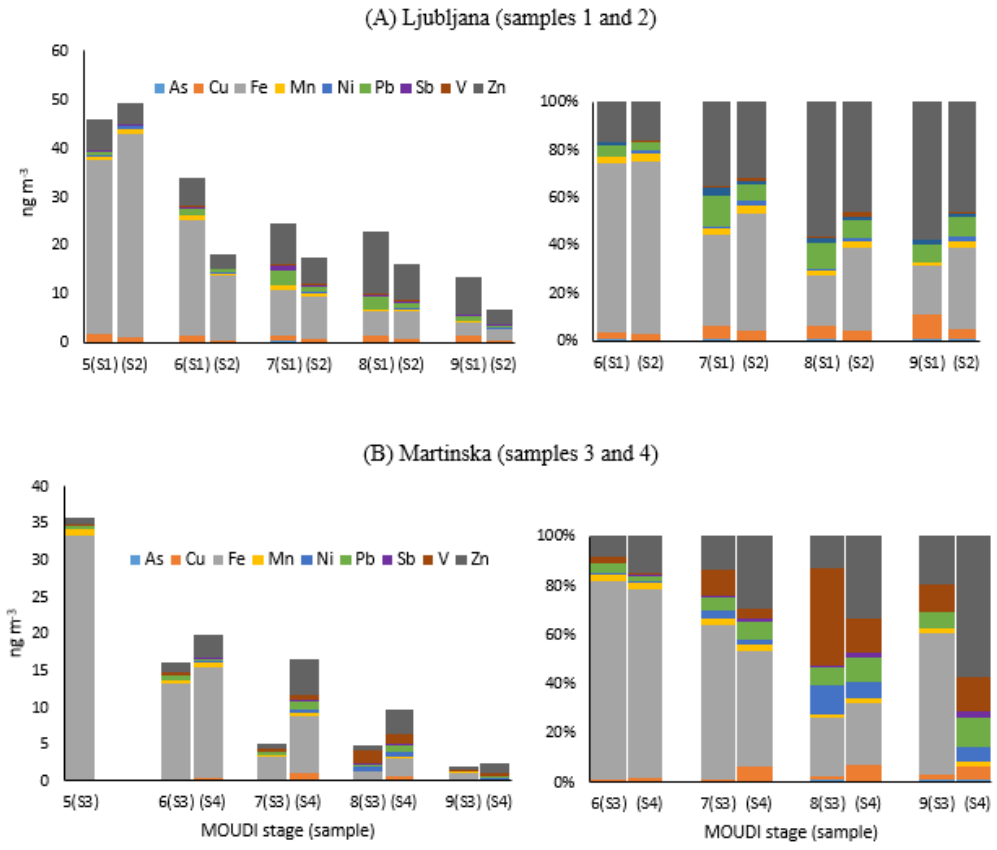

30% RSD (stages 7 and 8)
40% RSD (stage 5)
60% RSD (stage 4)
RSE (%)
fraction of filter deposit area (%)
0.0
0.5
1.0
1.5
2.0
2.5
0
10
20
30
40
50

FIG4


(A) Ljubljana (samples 1 and 2)
As Cu Fe Mn Ni Pb Sb V Zn
ng m-3
60
50
40
30
20
10
0
5(S1) (S2)
6(S1) (S2)
7(S1) (S2)
8(S1) (S2)
9(S1) (S2)
100%
80%
60%
40%
20%
0%
6(S1) (S2)
7(S1) (S2)
8(S1) (S2)
9(S1) (S2)
(B) Martinska (samples 3 and 4)
As Cu Fe Mn Ni Pb Sb V Zn
ng m-3
40
35
30
25
20
15
10
5
0
5(S3)
6(S3) (S4)
7(S3) (S4)
8(S3) (S4)
9(S3) (S4)
MOUDI stage (sample)
100%
80%
60%
40%
20%
0%
6(S3) (S4)
7(S3) (S4)
8(S3) (S4)
9(S3) (S4)
MOUDI stage (sample)

Reply to reviewers (original manuscript):

Responses to Reviewer #1

(1) ***Reviewer's comment:*** *This manuscript was previously submitted to another journals with other scope requirements different than the scope of AMT. In order to render the manuscript suitable for the AMT discussion some changes should be performed. For example, the conclusion section is completely missing.*

Authors' response: This paper was formatted initially for a journal with stricter page limitations; hence, much information was moved to Supplementary Materials. We have now moved three tables back into the manuscript (Tables 1–3) and added a Conclusions section. We also included two more samples (a 72 h sample from Ljubljana and a second 24 h sample from Martinska). The results of all four samples are now discussed and shared in a new figure (Fig. 4).

Authors' changes in manuscript: Addition of Tables 1–3 to manuscript; addition of Fig. 4 (which describes results of four MOUDI samples rather than two); addition of a Conclusions section.

(2) ***Reviewer's comment:*** *Comparison with other similar techniques to validate their method is also missing.*

Authors' response: Based on the concentration levels found in the filters, validation with similar imaging techniques like XRF, PIXE, etc. is questionable as LA-ICP-MS is the most sensitive technique for elemental microanalysis. However, by comparing the elemental concentration in size-segregated particles with a sensitive bulk analytical technique like ICP-MS, after digestion of the filter, an indirect comparison can be made as explained in section 2.4 and highlighted in Table 3. As such we feel that the LA-ICP-MS imaging method used yields accurate and precise data.

(3) ***Reviewer's comment:*** *The authors never mentioned what are the advantages and disadvantages of this method. Therefore, a discussion about atmospheric implications of this method should improve the quality of the manuscript and make it more interesting for the readers*

Authors' response: We agree with the reviewer and made changes to the text.

Authors' changes to manuscript: The Conclusions section now highlights the strengths and weaknesses of the approach and describe its potential usefulness to the atmospheric community.

(4) ***Reviewer's comment:*** *There are many tables and figures in the supplementary section while the manuscript on the other hand is way too short. I would recombine the manuscript and the supplementary material when possible.*

Authors' response: As noted in comment #1, we have now integrated Tables 1–3 into the manuscript.

Authors' changes to manuscript: Addition of Tables 1–3.

Responses to Reviewer #2

(1) ***Reviewer's comment:*** *The manuscript reports the analysis by LA ICP-MS of atmospheric particles collected with a MOUDI cascade impactor. This subject fit well with the scope of the AMT journal. However, this study which intended to demonstrate the value of this combination not treated and discussed a lot of keypoints that deserved the proof of concept:*

The main problem comes with the lack of a real reference material characterized for the different particle sizes tested here. The urban particulate matter of the SRM 2783 used as reference in this study has a median particle size of 3.2 µm and a size range of 2.5 µm and particles are collected on nuclepore polycarbonate membrane filters of 0.4 µm pore size. How it can be possible for the author to compare its response by LA ICPMS with what they obtained on their particulate samples of lower sizes, collected on PTFE filters? This is not discussed (influence of the particle size and the filter type on the laser ablation efficiency/influence of the laser beam mask size on the ablation efficiency and the mapping…)

Authors' response: We used NIST SRM 2783 as an absolute calibration standard, i.e. the LA-ICP-MS parameters were such that the laser beam completely penetrated the nucleopore filter, making matrix-matching unnecessary. The PTFE filters were not completely obliterated after ablation, probably due to the fact they were ticker, but the size-segregated particles on the filter were in most instances completely removed as observed by optical microscopy under 100× magnification, except maybe for the deepest impacted, smallest particles in the case of MOUDI sampling without rotation, making quantification by one-point calibration of the rotational filters on the NIST standard accurate. Since we use a laser beam diameter of 150 µm with a square mask it is obvious that the particles ablated are much smaller and as such the influence of particle size on the quantification is negligible.

Authors' changes to manuscript: We state that quantification is related to the use of NIST SRM 2783 as an absolute calibration standard and as such matrix-matching becomes unnecessary.

(2) ***Reviewer's comment:*** *The authors claimed that "The laser beam energy was sufficient to remove all of the particles during ablation, allowing elemental concentrations to be determined via a one-point calibration with the NIST standard" (P3L12). The authors have to prove that it is realistic. What about deep-impacted particles into filters?*

Authors' response: Visual inspection of the post-ablation filters under 100× magnification showed that the selected laser parameters (e.g., fluence/mask size/repetition rate) were sufficient to remove multiple layers of PTFE in each particle stage; hence, we assumed that the particles themselves were also ablated. However, it is possible that the deepest impacted particles were missed, especially in the smallest size ranges in the case MOUDI without rotation and high loading of particles. MOUDI with rotation prevents such potential problems altogether.

Authors' changes to manuscript: In Section 2.3 (Filter preparation and ablation), we now point out that although no particles were visible on the filters after ablation, that it is possible that small, deeply impacted particles may have remained embedded in the filters.

(3) ***Reviewer's comment:*** *As they mentioned in their previous paper published in Science of the Total Environment in 2008 ("A multi-element mapping approach for size-segregated atmospheric particles using laser ablation ICP-MS combined with image analysis") distribution of particulate matter in SRM 2783 is non-homogeneous.*

Authors' response: We are aware of the heterogeneity of the NIST standard as the certificate declares that a sampling area of 1 cm^2 is deemed necessary for reaching the certified uncertainty. In the current manuscript we routinely analyzed 1 cm^2 to comply with these requirements.

Authors' changes to manuscript: In section 3.3, we have now added the following: In contrast to our previous findings (Gligorovski et al., 2008), in this work, the NIST standard gave good precision for a 1 cm^2 (4444 pixels) ablation area (*RSD* = 22 %, *RSE* = 0.33 %).

(4) ***Reviewer's comment:*** *LA ICP-MS and "wet chemical" ICP-MS of several samples had been also compared for 5 samples which is informative but non-sufficient to understand the effect of the particulate size on the LA ICP-MS response.*

Authors' response: As stated in comment #1, we did not specifically examine the effect of particulate size on the LA ICP-MS response; however, we did optimize the laser parameters so that particles in all stages appeared to be ablated. Furthermore, section 2.4 (QA/QC) clearly shows that there is a good agreement between LA-ICP-MS and bulk ICP-

MS after digestion for most elements and for stages 6-10 with cut-point dia. of 0.56, 0.32, 0.18, 0.10, and 0.0156 µm, respectively.

Authors' changes to manuscript: None.

(5) ***Reviewer's comment:*** *Particulate collection is another keypoint of this particulate matter analysis. However, collection particle losses during MOUDI collection was not investigated (nozzle wall loss which is dependent on the size but also on the particle composition / clogging effects). Moreover, the effect of the rotation of the filter was studied by comparing the results got from two different cities, at different days and different climatic conditions…too much parameters varied to get really confident comparison.*

Authors' response: It is true that there may have been particle losses during MOUDI collection, but this was not our focus. Our focus was to use LA ICP-MS (as an alternative to wet-chemical ICP-MS) to determine the elemental composition of the particles that were successfully collected. We also used laser ablation to investigate the uniformity of the particles that were deposited when the MOUDI was rotated.

Authors' changes to manuscript: None.

(6) ***Reviewer's comment:*** *No conclusion was drawn on the proof of concept…*

Authors' response: We have now added a Conclusions section.

Authors' changes to manuscript: We have added a Conclusions section.

(7) ***Reviewer's comment:*** *I suggest conducting the proof of concept on a very well characterized particulate sample (size/composition by other analytical tools), to study systematically each critical parameter and compare with their previous work and the literature (one important paper in this field is missed: Hsieh, Chen et al. "Elemental analysis of airborne particulate matter using an electrical low-pressure impactor and laser ablation/inductively coupled plasma mass spectrometry" J.Anal.At.Spectrom., 2011, 26, 1502). Validation steps of the concept need also to be considered (repeatability integrating the collection step). Consequently, I recommend that authors go further in their analytical study before to be resubmitted for review in this journal.*

Authors' response: The current manuscript, although it does not study systematically each critical parameter, shows that LA-ICP-MS yields accurate data and superior detection limits for elemental analysis of size-segregated aerosols

collected by MOUDI in rotation mode. Please also see the response to comments # 1 and 4. We are confident that this progress will be of interest to the atmospheric community.

Authors' changes to manuscript: The reference mentioned was included in the manuscript. The importance of our findings is more clearly stated in the Conclusions section, which was lacking in the first submission.

Interactive comments and authors' response I:

The paper dedicated to the analysis by LA ICP-MS of atmospheric particles collected with a MOUDI cascade impactor fit well with the scope of the AMT journal. However, many questions arise. The study which intended to demonstrate the value of this combination (MOUDI / LA ICP-MS) not treated and discussed a lot of keypoints that deserved the proof of concept. The main problem comes with the lack of a real reference material characterized for the different particle sizes tested here. The urban particulate matter of the SRM 2783 used as reference in this study has a median particle size of 3.2 µm and a size range of 2.5 µm and particles are collected on nuclepore polycarbonate membrane filters of 0.4 µm pore size. How it can be possible for the authors to compare its response by LA ICPMS with what they obtained on their particulate samples of lower sizes, collected on PTFE filters? This is not discussed (influence of the particle size and the filter type on the laser ablation efficiency / influence of the laser beam mask size on the laser ablation efficiency and the mapping...)

Authors' response: We used NIST SRM 2783 as an absolute calibration standard, i.e. the LA ICP-MS parameters were such that the laser beam completely penetrated the nucleopore filter, making matrix-matching unnecessary. The PTFE filters were not completely obliterated after ablation, probably due to the fact they were thicker, but the size-segregated particles on the filter were in most instances completely removed as observed by optical microscopy under 100× magnification, except maybe for the deepest impacted, smallest particles in the case of MOUDI sampling without rotation, making quantification by one-point calibration of the rotational filters on the NIST standard accurate. Since we use a laser beam diameter of 150 µm with a square mask it is obvious that the particles ablated are much smaller and as such the influence of particle size on the quantification is negligible.

The authors claimed that "The laser beam energy was sufficient to remove all of the particles during ablation, allowing elemental concentrations to be determined via a one-point calibration with the NIST standard" (P3L12). The authors have to prove that it is realistic. What's about deep-impacted particles into filters? As they mentioned in their previous paper published in Science of the Total Environment in 2008 ("A multi-element mapping approach for size-segregated atmospheric particles using laser ablation ICP-MS combined with image analysis") distribution of particulate matter in SRM 2783 is non-homogeneous... Why is it not taking into account here?

Authors' response: Visual inspection of the post-ablation filters under 100× magnification showed that the selected laser parameters (e.g., fluence/mask size/repetition rate) were sufficient to remove multiple layers of PTFE in each particle stage; hence, we assumed that the particles themselves were also ablated. However, it is possible that the deepest impacted particles were missed, especially in the smallest size ranges in the case of MOUDI sampling without rotation and high loading of particles. MOUDI with rotation prevents such potential problems altogether. We are aware

of the heterogeneity of the NIST standard as the certificate declares that a sampling area of 1 cm^2 is deemed necessary for reaching the certified uncertainty. In the current manuscript we routinely analyzed 1 cm^2 to comply with these requirements.

LA ICP-MS and "wet chemical" ICP-MS of several samples had been also compared for 5 samples which is informative but non-sufficient to understand the effect of the particulate size on the LA ICP-MS response.

Authors' response: We did not specifically examine the effect of particulate size on the LA ICP-MS response; however, we did optimize the laser parameters so that particles in all stages appeared to be ablated. Furthermore, section 2.4 (QA/QC) clearly shows that there is a good agreement between LA CP-MS and bulk ICP-MS after digestion for most elements and for stages 6-10 with cut-point dia. of 0.56, 0.32, 0.18, 0.10, and 0.0156 μm, respectively.

Particulate collection is another keypoint of this particulate matter analysis. However, collection particle losses during MOUDI collection was not investigated (nozzle wall loss which is dependent on the size but also on the particle composition / clogging effects). Moreover, the effect of the rotation of the filter was studied by comparing the results got from two different cities, at different days and different climatic conditions...too much parameters varied to get really confident comparison.

Authors' response: It is true that there may have been particle losses during MOUDI collection, but this was not our focus. Our focus was to use LA ICP-MS (as an alternative to wet-chemical ICP-MS) to determine the elemental composition of the particles that were successfully collected. We also used laser ablation to investigate the uniformity of the particles that were deposited when the MOUDI was rotated.

Moreover, no validation data are given on this new measurement system. Validation steps of the concept should be considered (repeatability integrating the collection step).

Authors' response: Based on the concentration levels found in the filters, validation with similar imaging techniques like XRF, PIXE, etc. is questionable as LA ICP-MS is the most sensitive technique for elemental microanalysis. However, by comparing the elemental concentration in size-segregated particles with a sensitive bulk analytical technique like ICP-MS, after digestion of the filter, an indirect comparison can be made as explained in section 2.4 and highlighted in Table 3. As such we feel that the LA ICP-MS imaging method used yields accurate and precise data.

Why no conclusion was drawn on the proof of concept ...?

Authors' response: The current manuscript contains a "Conclusions" section.

I suggest conducting the proof of concept on a very well characterized particulate sample (size/composition by other analytical tools), to study systematically each critical parameter and compare with the author's previous work and the literature (one important paper in this field is missed: Hsieh, Chen et al. "Elemental analysis of airborne particulate matter using an electrical low-pressure impactor and laser ablation/inductively coupled plasma mass spectrometry" J.Anal.At.Spectrom., 2011, 26, 1502).

Authors' response: The current manuscript, although it does not study systematically each critical parameter, shows that LA ICP-MS yields accurate data and superior detection limits for elemental analysis of size-segregated aerosols collected by MOUDI in rotation mode. The mentioned reference is included in the current manuscript.

Interactive comments and authors' response II:

The paper investigates " Laser Ablation ICP-MS of Size-Segregated Atmospheric Particles Collected with a MOUDI Cascade Impactor: A Proof of Concept" The topic of the manuscript is very interesting and not yet investigated in literature to the best of my knowledge. The manuscript is concise and well written and conclusion adequately supported by experimental data. I suggest publication in Atmospheric Measurement techniques journal pending minor revision as noted: The developed method is quite promising for analysis of elemental composition of size-segregated atmospheric particles collected on filters. The authors compared this method with the "wet chemical" ICP-MS. However, a comparison with other techniques from the literature to validate their method is missing. For example, how this technique proofs useful compared with some instruments aimed for online analysis of the elemental composition in single atmospheric particles, such as A-TOF-MS, for instance. A-TOF-MS is also based on laser desorption technique

Authors' response: Based on the concentration levels found in the filters, validation with similar imaging techniques like XRF, PIXE, etc. is questionable as LA ICP-MS is the most sensitive technique for elemental microanalysis. However, by comparing the elemental concentration in size-segregated particles with a sensitive bulk analytical technique like ICP-MS, after digestion of the filter, an indirect comparison can be made as explained in section 2.4 and highlighted in Table 3. As such we feel that the LA ICP-MS imaging method used yields accurate and precise data. An instrument like A-TOF-MS is meant for the determination of single particle size and analysis individual particles and refractory materials such as sodium chloride, elemental carbon and mineral dust constituents. As such specific classes of particles are identified based on fingerprinting or combing peaks but true elemental composition analysis as achieved with our approach is not possible. Although we limited ourselves to a limited suite of elements, in theory most element of the periodic table can be measured routinely.

Furthermore, the authors should better explain what are really the advantages and disadvantages of their method. Therefore, a discussion about atmospheric implications of this method should improve the quality of the manuscript and make it more interesting for the readers. I suggest including a section "Atmospheric implications".

Authors' response: In this proof of concept paper, we have demonstrated the usefulness of LA ICP-MS as a tool for analysing the elemental composition of size-segregated atmospheric particles collected on filter-based media and have addressed these issues in the Conclusions section.

Previous problems associated with LA ICP-MS were addressed: (1) MOUDI rotation sampling overcomes the lack of uniformity in particle deposition, creating a sample highly suitable for LA-ICP-MS 2D mapping, 2) the 2D mapping mode yields results which show a high degree of accuracy when larger areas are ablated and superior detection limits, and 3)

quantification problems due to non-matrix matched standards are circumvented by ablating through the filter or obliterating the particles on the filters, warranting the reliable use of one-point calibrating on NIST SRM 2783. Together, these improvements allowed for an efficient and sensitive measurement of elemental composition. Compositional graphs of particles such as those shown in Fig. 4 for Ljubljana and Martinska, will be useful to the atmospheric community by allowing comparison of elemental profiles of particulate collected at diverse sites (e.g., urban industrial centres to remote background locations). Such profiles can be compared over days, months, or even years; short-term and long-term compositional changes can be used to monitor atmospheric changes such as a new pollution source, the impacts of pollution remediation, and the effects of climate change.

How was chosen the NIST standard? I this the best option for this kind of study? On which scientific basis were chosen the 9 elements in this study? On which basis the authors decided to cut the filters? How do we know for sure that the elements are homogenously distributed on the filters? I did not understand why some filters are ablated individually and some spot by spot? How was this decided?

Authors' response: We used NIST SRM 2783 as an absolute calibration standard as this seems to be the only "reliable" elements standard available for particulate matter although we are aware of the heterogeneity of the NIST standard as the certificate declares that a sampling area of 1 cm^2 is deemed necessary for reaching the certified uncertainty. In the current manuscript we routinely analyzed 1 cm^2 to comply with these requirements. We have chosen the most important trace elements based on inhalation risks associated with particle-bound metals as explained in the introduction.

Filters were not cut but we measured half-filters although measurement of areas of 1 cm^2 would suffice for accurate analytical results. Since the laser samples a statistically significant portion of the filter we can be confident that heterogeneity issues are circumvented. Using the MOUDI with and without rotation, generating homogeneously distributed particles and "particle spots", respectively, we show two approaches used for field collection of size-segregated particles and the limitations of both approaches, i.e. higher sensitivity and noisier data in the case of "particle spots" and lower sensitivity and better reproducibility in the case of homogeneously distributed particles.