SUPPLEMENTARY INFORMATION FOR

Evaluation of 213 nm and 193 nm laser ablation ICPMS for the elemental characterization of particulate matter on quartz fibre filters

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SI in numbers: 13 pages, 8 tables, and 7 Figures

Table S1 Element specific dwell times used for both LA systems

Element	Measured mass/ isotope	Dwell time (msec)
Al	27	5
K	39	3
Ti	47	24
V	51	20
Cr	52	20
Mn	55	10
Fe	56	3
Co	59	35
Ni	60	40
Cu	63	5
Zn	66	10
As	75	80
Rb	85	20
Mo	95	30
Cd	111	50
Sn	118	20
Sb	121	20
Ba	137	10
Tl	205	20
Pb	208	35

Table S2 Conditions used during the optimization of LA213 ablation. The optimal set of parameters is underlined

Fluence optimization		
Fluence (J cm^{-2})		**Laser output (%)**
0.86		5
<u>1.71</u>		<u>10</u>
3.43		20
5.14		30
8.57		50
Dosage optimization		
Dosage	**Scan speed (µm s^{-1})**	**Repetition Rate (Hz)**
2	250	4
5	250	10
8	250	16
<u>10</u>	<u>250</u>	<u>20</u>
12	125	12
15	125	15
18	125	18
20	125	20

Table S3 List of samples with calculated airborne PM_{10} concentrations corresponding to PM mass loadings

Date of sampling	Sampled volume (m^3)	PM_{10} mass concentration ($\mu g\ m^{-3}$)	Test
2.5.2015	710.845	8.7	sample for comparison
5.5.2015	716.742	38	sample for comparison
28.6.2015	713.934	11	sample for comparison
14.8.2015	725.993	38	sample for comparison
7.12.2015	682.110	43	sample for comparison
27.1.2016	691.893	49	sample for comparison
4.2.2016	694.125	16	sample for comparison
16.4.2016	709.669	18	sample for comparison
21.7.2015	721.826	26	LA213 parameter optimization
25.7.2015	718.459	14	LA213 parameter optimization
30.1.2016	694.147	48	LA213 parameter optimization
5.2.2016	691.178	21	LA213 parameter optimization

Table S4 Parameters used for the ablation of NIST 610 and 612 glass reference material

Parameters	LA193*	LA213
Laser beam size	56 µm (square mask)	125 µm (square mask)
Scan speed	112 µm s^{-1}	250 µm s^{-1}
Acquisition time	0.5 s	0.5 s
Dosage	10	10
Repetition rate	20 Hz	20 Hz
Fluence	3.5 J cm^{-2} (with 10x demagnification)	10.28 J cm^{-2}

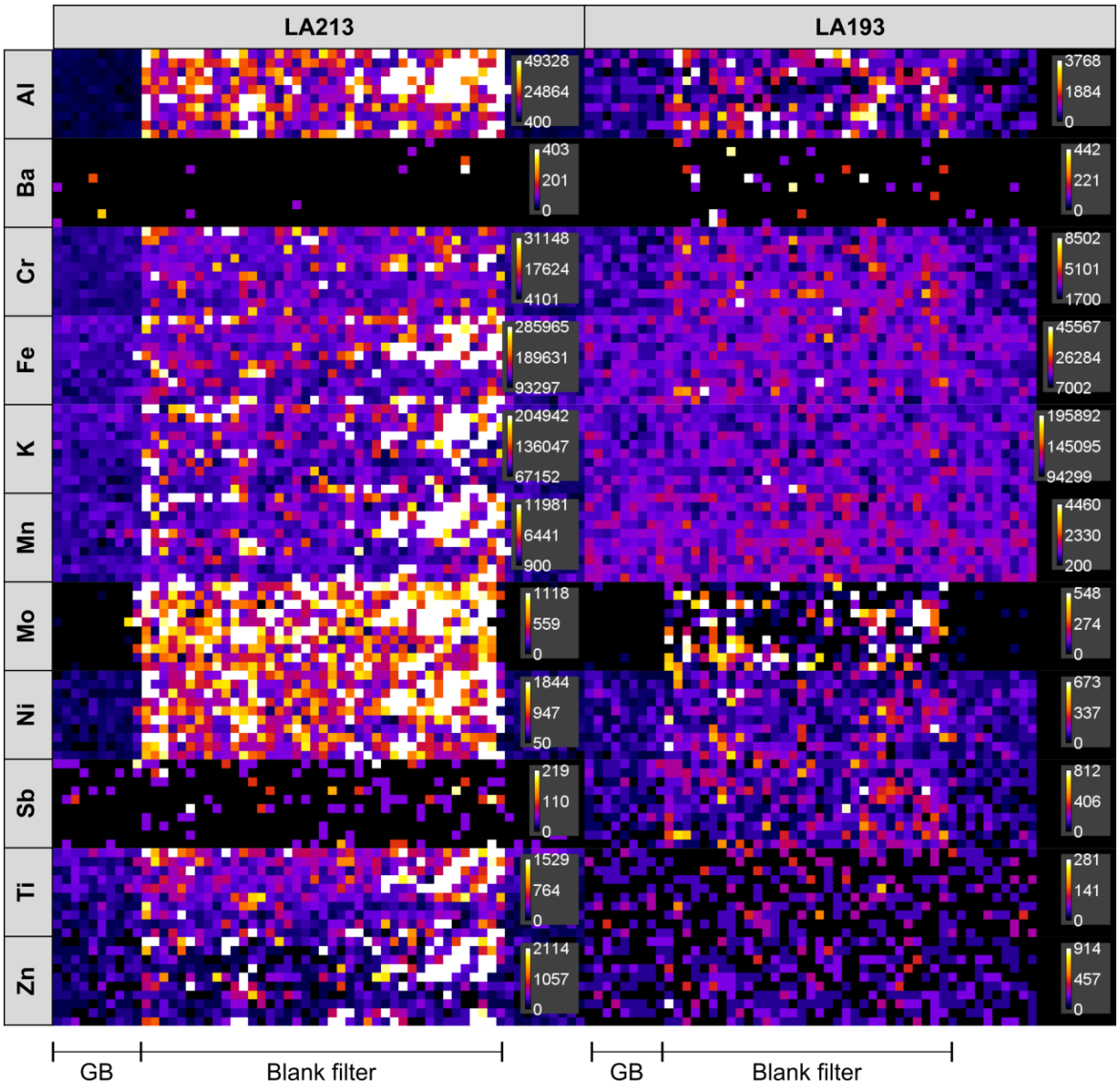

Fig. S1 Comparison of gas blank (GB) and blank filter ablation with the optimal parameters by LA213 and LA193 systems in counts per pixel

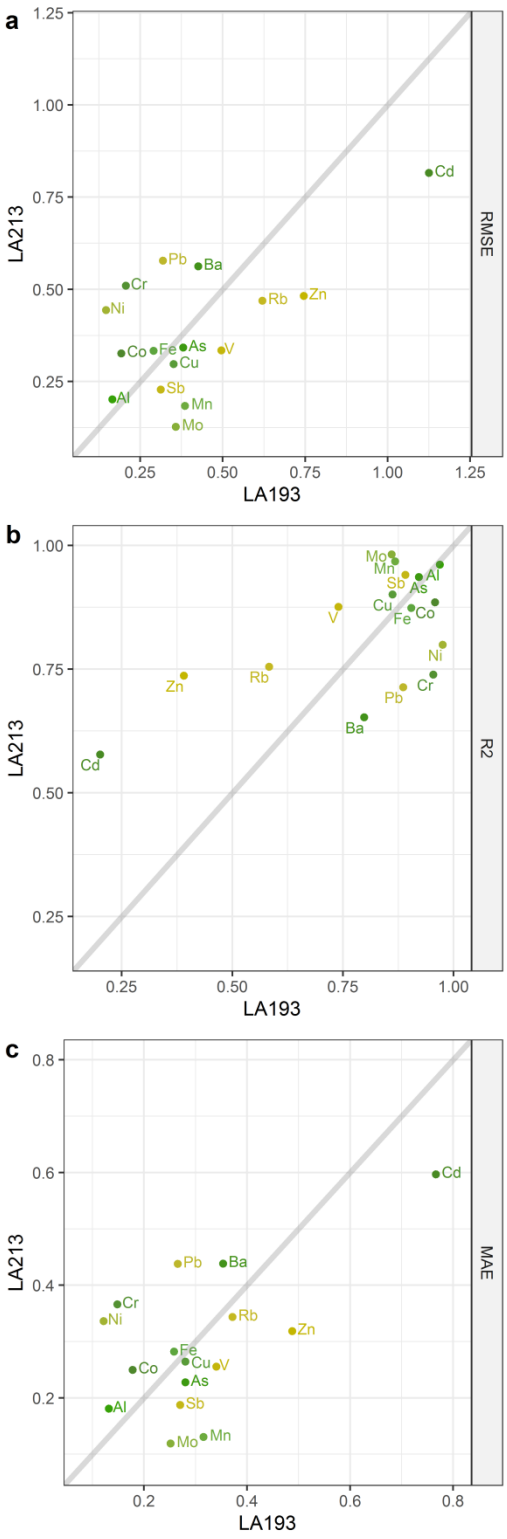

Fig. S2 Graphical comparison of LOOCV statistics of LA193 and LA213; (a) root mean squared error (RMSE), (b) R-squared, and (c) mean absolute error (MAE). The statistics is calculated on normalized data to eliminate differences in different scales of the two instruments

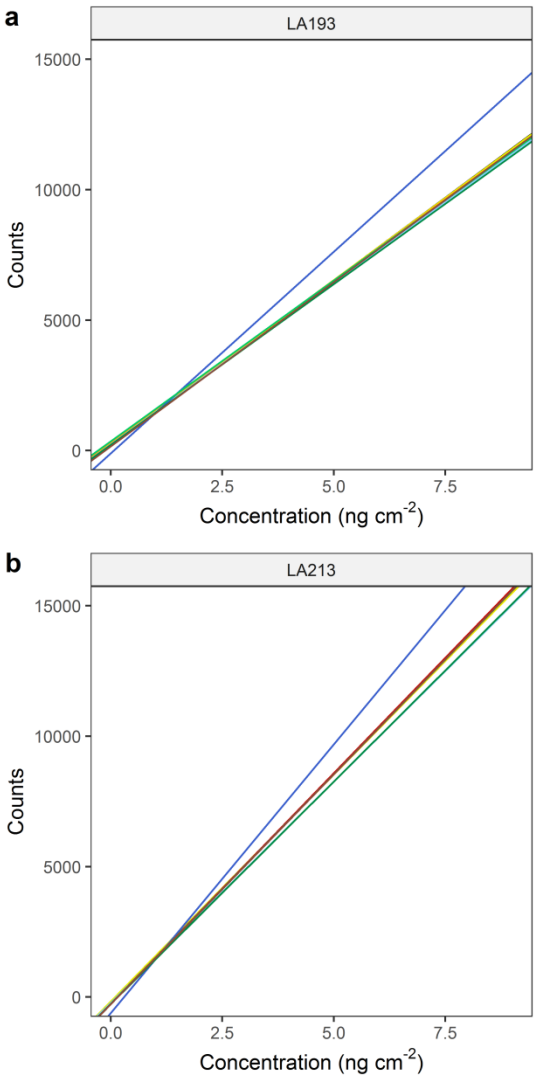

Fig. S3 Calibration curves constructed during the leave-one-out cross validation procedure for (a) LA193 and (b) LA213: example for As. Different colors represent calibration curves with different leave-out samples. The blue curve is always the variation with the highest concentration omitted, consequently deviating significantly from the other curves

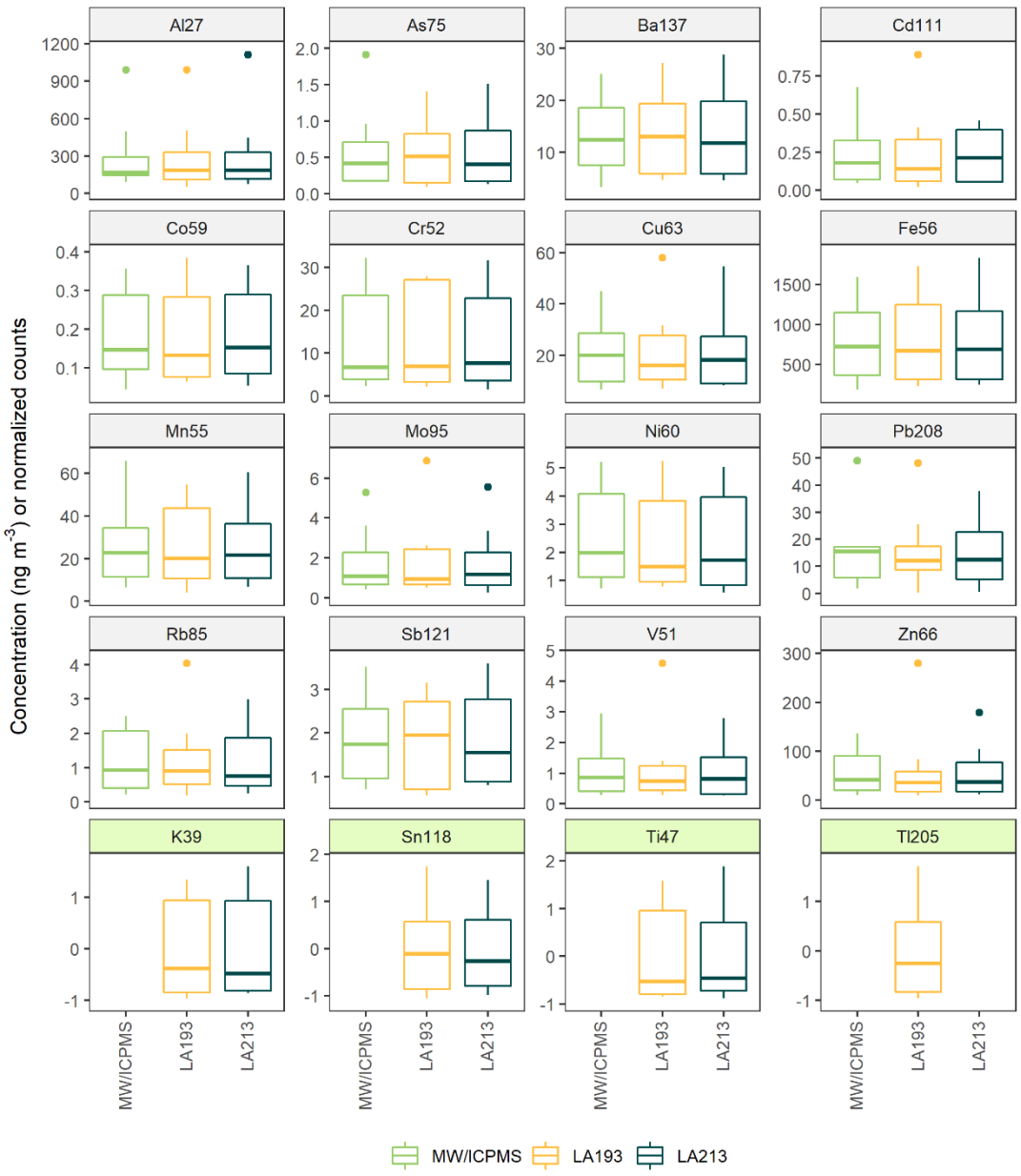

Fig. S4 Boxplots for LA193, LA213, and MW/ICPMS including all 8 ambient PM samples; outliers are depicted with dots. Raw data for K, Sn, Ti, and Tl were normalized to adjust for the different scales, since they were not measured with MW/ICPMS, and Tl could not be determined with LA213

Table S5 Statistics from comparison of MW/ICPMS, LA193, and LA213

		Repeated measures ANOVA[a,b]					Friedman rank sum test[b,c]				
Element	Shapiro-Wilk test	DFn[a]	DFd[b]	F	p	ges	n	statistic	DF	p	Effect size
Al27	**	2	14	0.243	0.788	4.0E-04 (small)	8	1.75	2	0.417	0.109 (small)
As75	*	1.22	8.57	0.130	0.776	5.8E-04 (small)	8	0.75	2	0.687	0.047 (small)
Ba137		1.11	7.76	0.023	0.903	2.0E-04 (small)	8	0.25	2	0.882	0.016 (small)
Cd111	*	2	14	0.045	0.956	2.0E-03 (small)	8	1	2	0.607	0.063 (small)
Co59		2	14	0.029	0.972	1.3E-04 (small)	8	0.25	2	0.882	0.016 (small)
Cr52	**	1.06	7.39	0.002	0.974	9.0E-06 (small)	8	0.75	2	0.687	0.047 (small)
Cu63		2	14	0.129	0.880	5.8E-04 (small)	8	0.25	2	0.882	0.016 (small)
Fe56		2	14	0.041	0.960	1.8E-04 (small)	8	0	2	1	0.000 (small)
Mn55		1.22	8.55	0.012	0.948	4.6E-05 (small)	8	0.25	2	0.882	0.016 (small)
Mo95	**	1.13	7.94	0.246	0.663	1.0E-03 (small)	8	0.25	2	0.882	0.016 (small)
Ni60	*	2	12	0.008	0.992	5.4E-05 (small)	7	0.29	2	0.867	0.020 (small)
Pb208	*	2	14	0.002	0.998	2.5E-05 (small)	8	0.75	2	0.687	0.047 (small)
Rb85		2	14	0.049	0.952	6.3E-04 (small)	8	0	2	1	0.000 (small)
Sb121		2	14	0.035	0.966	1.4E-04 (small)	8	0.75	2	0.687	0.047 (small)
V51	***	2	14	0.200	0.821	3.0E-03 (small)	8	0.25	2	0.882	0.016 (small)
Zn66	***	1.14	8	0.239	0.669	5.0E-03 (small)	8	1.75	2	0.417	0.109 (small)

*normality assumption was not met at least in one group, $\alpha = 0.05$; *$p < 0.05$, **$p \leq 0.01$, ***$p \leq 0.001$. Where normality could be assumed, parametric test (repeated measures ANOVA) was used and where normality assumption was not met, nonparametric alternative (Friedman rank sum test) was used for comparisons.

[a]reported statistics are: degrees of freedom in the numerator (DFn), degrees of freedom in the denominator (DFd), F-statistics value (F), p-value (p), and generalized effect size (generalized eta squared; ges)

[b]when Holm method was used for adjusting p-value for multiple comparisons problem, all adjusted p-values were 1

[c]reported statistic are: number of samples (n), Friedman chi-squared statistic value (statistic), degrees of freedom (DF), p-value (p), and Effect size (Friedmans test effect size was assessed with Kendall's W value)

Table S6 Statistics (p-values) from comparison of LA systems

Element	Shapiro-Wilk test[a]	t-test[b,c]	Wilcoxon test[c,d]
Al27	0.123	0.496	-
As75	0.205	0.768	-
Ba137	0.266	0.910	-
Cd111	0.003**	-	0.461
Co59	0.149	0.901	-
Cr52	0.188	0.948	-
Cu63	0.667	0.814	-
Fe56	0.972	0.965	-
Mn55	0.493	0.940	-
Mo95	0.762	0.623	-
Ni60	0.292	0.843	-
Pb208	0.797	0.971	-
Rb85	0.257	0.863	-
Sb121	0.442	0.802	-
V51	0.017*	-	1
Zn66	0.0014**	-	0.742

*significant differences detected, $\alpha = 0.05$; *$p < 0.05$, **$p \leq 0.01$

[a]testing the assumption of normality; when $p < 0.05$ the normality assumption was not met

[b]parametric t-test for paired comparisons (n = 8), used when normality assumption was met

[c]when Holm method was used for adjusting p-value for multiple comparisons problem, all adjusted p-values were 1

[d]nonparametric alternative for paired comparisons (n = 8), used when normality assumption was not met

Table S7 Airborne concentrations of all measured elements in ng m^{-3}

Sample	Method	Al27	As75	Ba137	Cd111	Co59	Cr52	Cu63	Fe56	Mn55	Mo95	Ni60	Pb208	Rb85	Sb121	V51	Zn66
MB0205	MW/ICPMS	91	0.17	6.5	0.046	0.066	2.2	8.2	280	6.7	0.44	<LOD	17	0.22	0.70	0.41	10
	LA193	110	0.16	6.1	0.047	0.076	2.1	11	300	8.4	0.68	0.82	11	0.22	0.73	0.47	17
	LA213	96	0.13	5.4	0.050	0.053	1.4	8.9	250	7.1	0.27	0.60	5.8	0.24	0.82	0.28	12
MB0402	MW/ICPMS	180	0.18	11	0.095	0.11	4.1	15	540	13	0.72	0.87	3.1	0.73	1.1	0.38	22
	LA193	110	0.13	7.9	0.065	0.089	3.2	11	330	11	0.65	1.0	2.3	0.71	0.60	0.30	18
	LA213	120	0.17	8.4	0.077	0.092	3.4	12	340	12	0.91	0.93	2.9	0.59	0.89	0.33	18
MB0505	MW/ICPMS	500	0.50	23	0.32	0.36	32	30	1300	34	1.8	5.2	49	1.1	2.5	3.0	140
	LA193	500	0.60	18	0.89	0.39	28	32	1200	44	2.4	5.3	48	1.1	2.4	4.6	280
	LA213	450	0.48	15	0.43	0.28	20	27	1000	34	1.9	3.8	38	0.92	2.0	2.8	180
MB0712	MW/ICPMS	120	0.96	14	0.68	0.19	22	25	910	30	3.6	3.8	17	2.4	2.4	0.60	90
	LA193	160	1.0	21	0.31	0.17	27	26	1200	21	2.6	3.5	11	1.4	2.6	0.65	31
	LA213	170	1.1	23	0.39	0.21	32	29	1200	27	3.4	4.5	19	1.6	2.7	0.81	42
MB1408	MW/ICPMS	990	1.9	17	0.27	0.28	8.7	28	1100	66	1.2	2.0	17	2.0	2.8	1.7	54
	LA193	990	1.4	19	0.19	0.26	9.4	21	1000	55	1.1	1.8	26	2.0	3.1	1.4	49
	LA213	1100	1.5	19	0.35	0.31	11	25	1200	60	1.4	2.3	34	2.8	3.0	2.3	68
MB1604	MW/ICPMS	150	0.16	7.9	0.072	0.11	4.5	10	400	7.6	0.54	1.4	1.8	0.41	0.86	1.4	14
	LA193	53	0.094	4.7	0.024	0.075	3.2	7.1	230	4.2	0.50	1.2	0.30	0.19	0.56	0.83	9.7
	LA213	75	0.16	6.0	0.050	0.096	4.0	8.4	310	6.8	0.62	1.2	0.57	0.34	0.79	0.81	14
MB2701	MW/ICPMS	220	0.62	25	0.36	0.31	29	45	1600	37	5.3	4.3	14	2.5	3.5	1.1	93
	LA193	270	0.75	27	0.41	0.36	28	58	1700	44	6.9	5.0	15	4.0	3.2	1.2	84
	LA213	290	0.78	29	0.46	0.37	30	55	1800	44	5.6	5.0	18	3.0	3.6	1.3	100
MB2806	MW/ICPMS	150	0.33	3.4	0.067	0.043	3.1	6.7	190	16	0.97	0.72	6.8	0.39	0.98	0.28	29
	LA193	210	0.43	5.3	0.091	0.064	4.3	9.0	330	19	0.85	0.79	13	0.61	1.5	0.39	41
	LA213	190	0.32	4.6	0.059	0.060	3.5	9.2	330	17	0.64	0.58	7.1	0.52	1.1	0.32	31

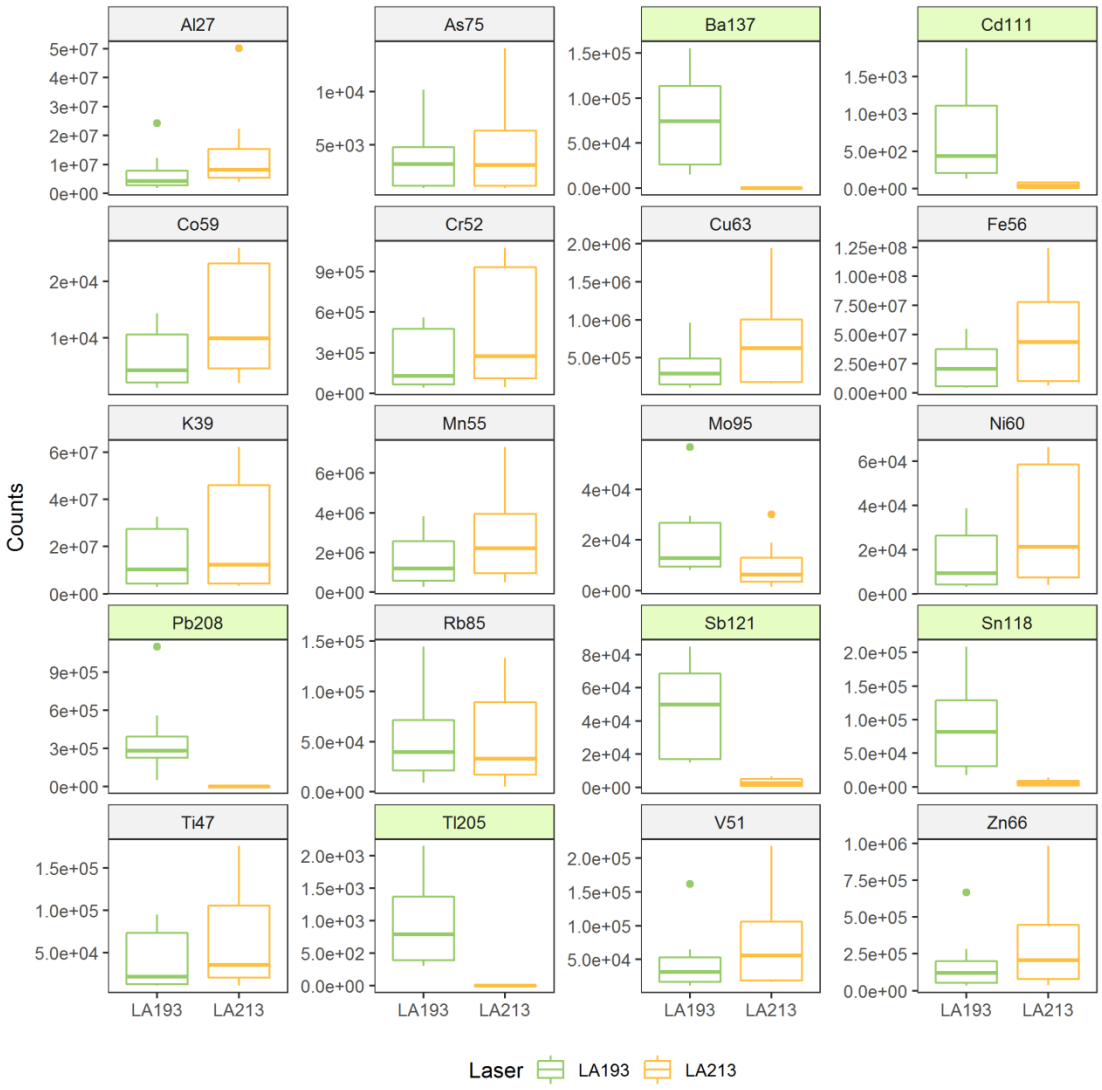

Fig. S5 Boxplots for LA193 and LA213 including all 8 ambient PM samples; outliers are depicted with dots. Intensities (counts) are given after the subtraction of gas blank

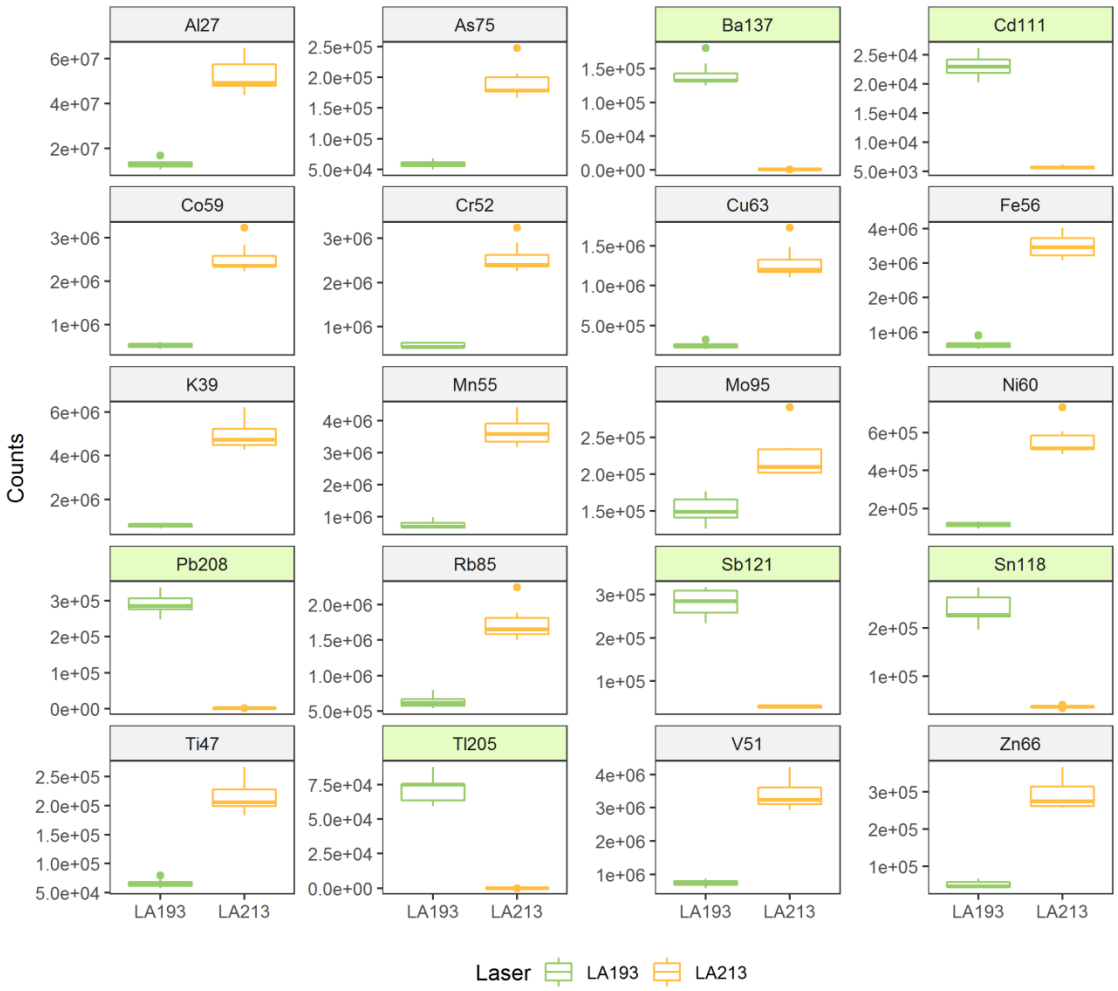

Fig. S6 Boxplots for LA193 and LA213 measurement of NIST 610 (n=9); outliers are depicted with dots. Intensities (counts) are given after the subtraction of gas blank

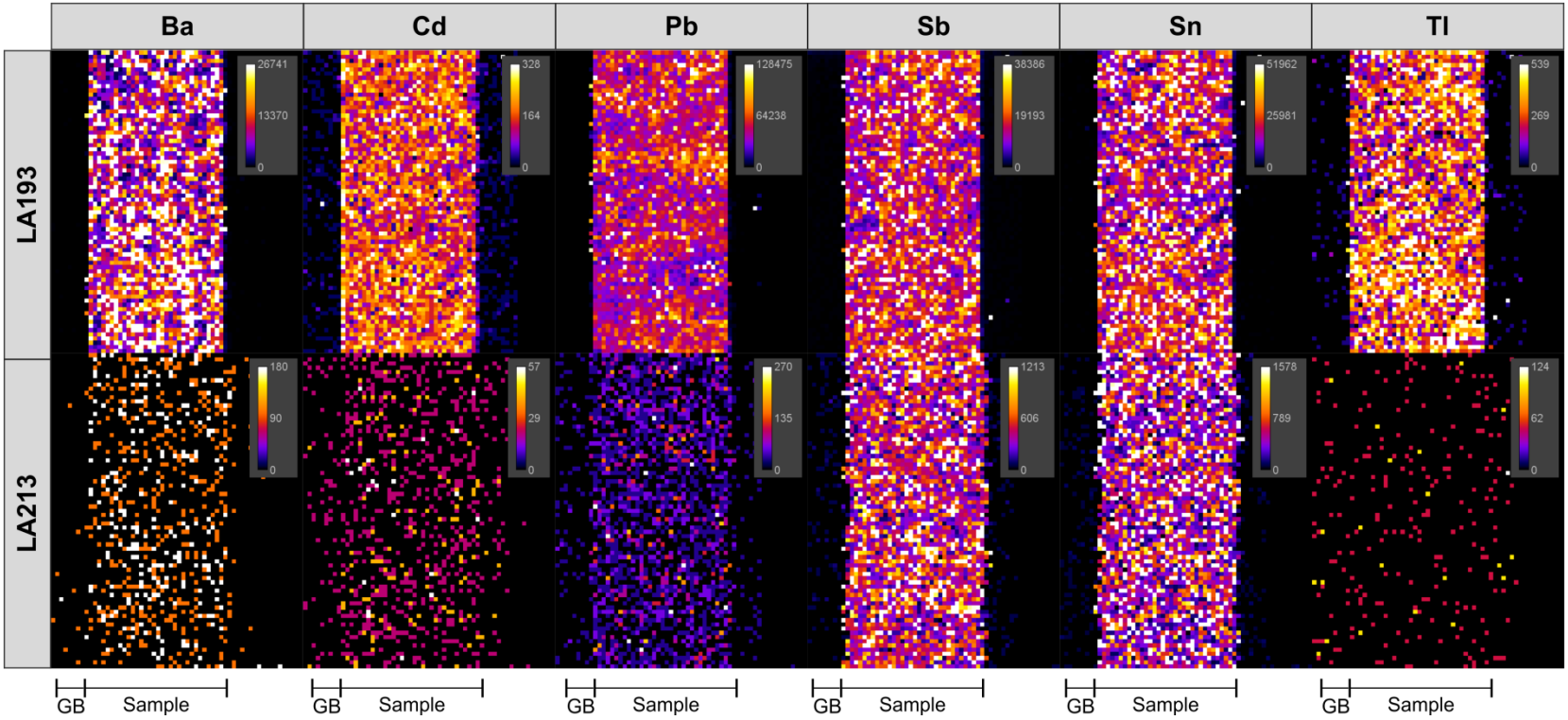

Fig. S7 Comparison of gas blank (GB) and a sample with the lowest concentration of particular element. Ablation by LA213 and LA193 was performed with the optimal parameters for each system

Table S8 Ratios between LA193 and LA213 counts for every element, for NIST glass standards

Element	NIST 610 LA193/LA213	NIST 612 LA193/LA213
Al27	0.25	0.40
As75	0.31	0.41
Ba137	157	376
Cd111	4.0	11
Co59	0.21	0.32
Cr52	0.22	0.34
Cu63	0.19	0.26
Fe56	0.19	0.32
K39	0.16	0.67
Mn55	0.21	0.31
Mo95	0.69	1.2
Ni60	0.20	0.28
Pb208	590	3500
Rb85	0.37	0.56
Sb121	6.8	18
Sn118	6.5	20
Ti47	0.30	0.45
Tl205	1900	2600
V51	0.22	0.37
Zn66	0.18	0.09

Since different volumes of NIST glass standards were ablated with LA193 and LA213 (dependent on the beam size, wavelength, and fluence, which are specific for the LA systems), the comparison was made by calculating the ratio of LA193 to LA213 counts to find anomalies, which could point to different fractionation between the LA systems. For most elements, the ratio was around 0.2 for NIST 610 and 0.3 for NIST 612, however, for Ba, Cd, Pb, Sb, Sn, and Tl the ratios differed substantially from the other elements, which is also seen in Fig. S6. This implies different fractionation effects in those elements and consequentely contributes to different sensitivity of the LA systems.