Electronic Supplementary Information

A new rapid treatment of human scalp hair for elemental determination by inductively coupled mass spectrometry

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Table S1 - Summary of the characteristics of the hair analytical methods used in the present study and comparison with previous methods.

Reference	Decomposition procedure	Total sample digestion time	Analyte and remarks	LOD[a]	ULOQ or LOQ[b]	Linearity range (log)
This study	20 mg of hair + 0.5 mL HNO3 and 0.25 mL H2O2 in open-vessel heated in a water bath to 95 °C (OD*95°C) for 20 min -> volume completed to 10 mL with deionized water	About 40 min for 120 samples (time of digestion, 20 min; and cooling, 20 min)	40 elements; the ICP-MS instrument was operated in CRI mode for As, Ca, Cr, Fe, Mn, Se and V; In, Sc, Rh, Th and Y as internal standards; method validation using hair certified material and in-field hair samples and analyte recovery tests were carried out	0.02 µg kg^{-1} (U) to 30 mg kg^{-1} (K)	0.3 mg kg^{-1} (Al, As, Ba, Be, Bi, Cd, Cr, Cs, Cu, Ga, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Te, Ti, Tl, U, V, W and Zr) to 250 mg kg^{-1} (Ca)	1.3 to 2
	200 mg of hair certified material + 1 mL HNO3 and 0.5 mL H2O2 in open-vessel heated in a water bath to 95 °C (OD95°C) for 20 min -> volume completed to 20 mL with deionised water	About 40 min for 120 samples (time of digestion, 20 min; and cooling, 20 min)		0.01 µg kg^{-1} (Tl) to 10 mg kg^{-1} (Ca)	0.05 mg kg^{-1} (Al, As, Ba, Be, Bi, Cd, Cr, Cs, Cu, Ga, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Te, Ti, Tl, U, V, W and Zr) to 50 mg kg^{-1} (Ca)	1.2 to 2
	200 mg of hair certified material + 1 mL HNO3 and 0.5 mL H2O2 in open-vessel at room temperature (ODRT) for 24 h -> volume completed to 20 mL with deionised water	About 24 h for >120 samples (time of digestion, 24 h)		0.02 µg kg^{-1} (Be, Tl and U) to 10 mg kg^{-1} (Ca)		
	200 mg of hair certified material + 1 mL HNO3 and 0.5 mL H2O2 + 1.5 mL deionised water in closed-vessel heated to 180 °C with microwave energy (CD180°C) for 40 min -> volume completed to 10 mL with deionised water	About 100 min for 20 samples (closing and opening of the 20 quartz vessels, 10 min; time of digestion, 40 min; cooling, 20 min; washing vessels 20 min; and transfer of digests into the polypropylene tubes, 10 min)		0.01 µg kg^{-1} (U) to 4 mg kg^{-1} (K)		
	200 mg of hair certified material + 1 mL HCl and 3 mL HNO3 in closed-vessel heated to 180 °C with microwave energy (CD*180°C) for 40 min -> volume completed to 10 mL with deionised water	About 75 min for six samples (closing and opening of the six PTFE vessels, 5 min; time of digestion, 40 min; cooling, 20 min; washing vessels 5 min; and transfer of digests into the polypropylene tubes, 5 min)	41 elements using ICP-OES; Y as internal standard	0.01 mg kg^{-1} (Be and Pb) to 300 mg kg^{-1} (S)	0.1 mg kg^{-1} (Be, Cd, La, Mn) to 1000 mg kg^{-1} (C)	0.5 to 2
	200 mg of hair certified material + 1 mL HF, 1 mL HCl and 3 mL HNO3 in closed-vessel heated to 180 °C with microwave energy (CD**180°C) for 40 min -> volume completed to 10 mL with deionised water	About 75 min for six samples (closing and opening of the six PTFE vessels, 5 min; time of digestion, 40 min; cooling, 20 min; washing vessels 5 min; and transfer of digests into the polypropylene tubes, 5 min)	41 elements using ICP-OES; Y as internal standard	0.02 mg kg^{-1} (Pb) to 300 mg kg^{-1} (S)		
Ballesteros et al.[1]	10 - 20 mg hair + 1 mL Triton X-100 + 1 mL HNO3 left in contact for 16 h at 80 °C	-	Al, As, Ag, Ba, Bi, Cd, Cr, Co, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sr, Tl and Zn; Ge and Rh as internal	0.001 µg kg^{-1} (Tl) to 0.9 mg kg^{-1} (Fe)	-	-

			standards			
Grassin-Delile et al.[2]	10 mg hair + 10 µL internal standard solution (10 µg mL^{-1} gallium and iridium, and 100 µg mL^{-1} In and Sc) + 200 µL HNO3 and 200 µL H2O2 in microwave reaction chamber at 1500 W (220 °C) and 110 bar for 25 min -> volume completed to 6 mL with deionised water	-	38 elements; the ICP-SFMS instrument was operated in low-, medium- or high resolution mode, depending on interferences and sensitivity; method validation using commercial reference standards and in-house quality control samples	-	0.0001nM (Hf) to 10 µM (Al)	1.3 to 7
Luo et al.[3]	20 mg of hair + 0.8 mL HNO3 and 0.2 mL H2O2 in an electric heating block at 90 °C for 3h -> volume completed to 10 mL with deionised water	-	33 elements; Ge, In, Li, Tb and Y as internal standards; method validation analyzing a certified reference material	0.1 µg kg^{-1} (Cs and Th) to 10.9 mg kg^{-1} (Ca)	0.5 µg kg^{-1} (Cs, Mo,Th, Tl and U) to 25 mg kg^{-1} (Ca)	2 to 5.3
Raposo et al.[4]	200 mg of hair + 10 mL 5% (v/v) HNO_3 in microwave oven -> volume completed to 50 mL	-	22 elements; Sc, Y, Rh and Ho as internal standards; the spray chamber was cooled (2 °C) to reduce MO^+ formation in the ICP; Ca, K, Mg and Sr determined by ICP OES	0.007 mg kg^{-1} (As) to 1.5 mg kg^{-1} (Ca, Na and K)	-	-
Varrica et al.[5]	150 mg of hair + 3 mL HNO3 in contact for 24 h at room temperature -> addition of 0.5 mL H2O2 -> standing for more 24 h -> volume elevated to 25 mL with water	-	21 elements; Re, Sc and Y as internal standards; the ICP-MS instrument was operated in DRC mode for As, Cr, Fe, Se and V; standard addition calibration and analyte recovery tests were carried out	0.6 µg kg^{-1} (Sb) to 0.063 mg kg^{-1} (Fe)	-	-

[a] LOD, limit of detection (mg kg^{-1}).
[b] LLOQ or LOQ, lower limit of quantification or limit of quantification (mg kg^{-1}).

Table S2 - Method blanks [n = 10; mean (μg kg^{-1}) and relative standard deviation percent (RSD%)] for each element obtained by inductively coupled plasma mass spectroscopy.

	ODRT[a]		OD95°C[a]		OD*95°C[a]		CD180°C[a]	
Element	mean	RSD%	mean	RSD%	mean	RSD%	mean	RSD%
Al	78	3.8	105	17	852	4.1	145	15
As	3.8	76	3.9	50	15	38	2.0	17
B	72	27	46	38	527	8.0	63	30
Ba	93	29	313	5.8	2049	5.9	239	63
Be	0.11	10	0.14	30	0.68	21	0.13	11
Bi	0.18	39	0.30	31	2.4	31	0.41	31
Ca	44000	36	81000	11	270000	2.8	76000	1.5
Cd	0.20	34	0.27	109	1.8	24	0.35	34
Ce	0.43	26	4.4	30	2.8	18	0.6	16
Co	0.27	18	3.0	74	2.5	10	0.5	42
Cr	10	16	20	46	67	22	13	29
Cs	0.073	42	0.10	42	0.50	46	0.14	28
Cu	42	22	45	26	229	7.9	30	33
Fe	142	32	134	42	884	10	226	28
Ga	0.020	50	0.060	71	0.13	78	0.023	66
K	2600	11	3300	5.4	15000	14	2400	14
La	0.25	23	0.19	60	1.4	15	0.30	29
Li	0.38	25	0.28	39	2.2	20	0.77	29
Mg	1100	23	1000	49	5300	9.1	3500	26
Mn	12	29	10	23	63	23	25	28
Mo	9.1	5.1	4.3	7.0	28	27	3.9	6.4
Na	6200	29	7600	13	43000	20	12000	1.1
Nb	0.42	44	0.15	63	0.90	40	0.14	28
Ni	29	17	35	4.9	150	2.2	30	5.7
P	4600	3.3	4000	4.2	20000	5.8	4500	7.5
Pb	10	15	9.3	3.0	57	9.4	10	24
Rb	1.8	46	1.0	33	8.2	11	1.6	16
Sb	0.53	36	0.35	51	1.8	18	0.69	22
Se	3.1	63	0.29	88	30	33	1.1	73
Si	5800	6.5	5200	4.8	27000	1.6	9500	2.5
Sn	0.45	11	0.48	28	3.6	6.4	0.94	7.5
Sr	71	27	53	28	300	5.6	200	32
Te	0.27	43	0.31	60	1.9	44	0.26	45
Ti	9.1	2.8	12	4.5	70	10	13	7.9
Tl	0.040	50	0.65	21	0.15	33	0.023	65
U	0.037	57	0.21	61	0.23	12	0.057	37
V	0.54	66	0.31	18	10	61	0.48	88
W	2.5	38	1.1	15	9.4	20	1.1	19
Zn	230	20	390	65	2500	5.1	460	9.3
Zr	1.0	14	0.63	3.4	3.9	21	1.0	16

[a] The method blanks were obtained using different acid digestion treatments [room temperature open-vessel digestion (OD_{RT}), open-vessel digestion heated to 95°C ($OD_{95°C}$ or $OD*_{95°C}$), and closed-vessel microwave-assisted digestion ($CD_{180°C}$)]. Mass of certified material = 0.2 g for all treatments except for OD*95°C (0.02 g).

Table S3 - Method blanks [n = 10; mean and relative standard deviation percentage (RSD%); mg kg^{-1}], background equivalent concentration (BEC; mg kg^{-1}), limit of detection (LOD; mg kg^{-1}), lower and upper limit of quantification (LLOQ and ULOQ; mg kg^{-1}) for each element obtained by inductively coupled plasma-optical emission spectroscopy.

Element	CD*[a]				CD**[a]				CD* and CD**		
	Mean	RSD%	BEC	LOD	Mean	RSD%	BEC	LOD	LLOQ	ULOQ	Linearity range (log)
Al	0.11	12	1	0.4	0.093	6	1	0.2	1	5	0.7
As	1.8	5.4	0.5	0.1	1.8	2.2	0.6	0.04	3	10	0.5
B	4.5	22	14	9	4.1	39	6	7	20	300	1.2
Ba	0.98	21	0.5	0.3	0.95	22	0.5	0.3	1	5	0.7
Be	0.0019	11	0.04	0.01	0.0025	51	0.04	0.07	0.1	5	1.7
Bi	0.15	10	0.5	0.1	0.16	61	0.3	0.5	1	5	0.7
C	760	2.5	500	40	740	3.6	500	50	1000	10000	1.0
Ca	7.8	73	100	200	3.0	108	60	200	250	5000	1.3
Cd	0.0056	28	0.05	0.04	0.0031	18	0.05	0.03	0.1	5	1.7
Ce	0.036	13	0.4	0.2	0.098	22	0.5	0.3	1	25	1.4
Co	0.036	31	0.1	0.1	0.037	38	0.1	0.1	0.3	25	1.9
Cr	0.040	16	0.2	0.1	0.042	27	0.2	0.1	0.3	5	1.2
Cs[b]	-	-	-	-	-	-	-	-	-	-	-
Cu	0.15	16	0.4	0.2	0.18	25	0.5	0.4	1	5	0.7
Fe	0.20	8	0.5	0.1	0.21	22	0.5	0.3	1	50	1.7
Ga	0.19	10	0.9	0.3	0.11	15	1.0	0.4	1	5	0.7
K	0.19	70	100	200	0.23	80	100	200	250	2500	1.0
La	0.020	40	0.05	0.06	0.018	37	0.04	0.04	0.1	5	1.7
Li	0.15	12	0.1	0.05	0.15	15	0.1	0.06	0.5	5	1.0
Mg	1.1	27	7	6	0.95	40	6	8	25	2500	2.0
Mn	0.0037	33	0.05	0.05	0.0075	43	0.05	0.06	0.1	5	1.7
Mo	0.019	62	0.05	0.09	0.018	48	0.09	0.1	0.5	5	1.0
Na	8.1	31	10	10	8.2	35	10	11	25	2500	2.0
Nb	0.15	30	0.6	0.6	0.11	36	0.6	0.7	1	5	0.7
Ni	0.012	40	0.4	0.4	0.014	44	0.3	0.4	0.5	5	1.0
P	0.43	39	13	16	0.20	60	11	20	25	250	1.0
Pb	2.1	1.8	0.2	0.01	2.1	1.1	0.5	0.02	3	10	0.5
Rb	0.85	5.5	3	0.6	1.0	13	4	2	3	10	0.5
S	7.4	56	200	300	7.4	54	200	300	500	10000	1.3
Sb	0.17	34	0.6	0.6	0.29	36	0.7	0.8	1	5	0.7
Se	1.3	4.1	4	1	1.4	9.4	2	1	3	10	0.5
Si	1.9	78	6	20	4.0	76	8	20	25	250	1.0
Sn	0.12	62	0.1	0.2	0.068	42	0.05	0.06	1	5	0.7
Sr	0.036	27	0.2	0.2	0.022	32	0.2	0.2	1	300	2.5
Te	0.46	47	1	1	0.42	44	2	2	3	10	0.5
Ti	0.020	40	0.2	0.2	0.051	30	0.3	0.2	0.3	5	1.2
Tl	0.26	52.8	1	2	0.29	52	2	2	3	10	0.5
U	0.83	8.5	2	1	0.77	6.4	1	0.2	3	10	0.5
V	0.028	29	0.2	0.2	0.012	28	0.1	0.1	0.3	5	1.2
W	0.19	29	2	2	0.19	27	2	2	3	10	0.5
Zn	0.37	20	2	1	0.20	45	2	2	3	50	1.2
Zr	0.12	10	0.2	0.05	0.12	5	0.2	0.03	0.5	5	1.0

[a] The method blanks were obtained using closed-vessel microwave-assisted digestion (CD) with different reagents (CD*: HNO3/HCl; CD**: HNO3/HCl/HF; sample mass 0.2 g).

[b] Cs could not be analysed because axial view ICP-OES is strongly affected by ionisation interference when elements with low ionisation potentials coexist in the sample.

Table S4 - Background equivalent concentration (BEC; mg kg^{-1}), limit of detection (LOD; mg kg^{-1}), lower and upper limit of quantification (LLOQ and ULOQ; mg kg^{-1}) for each element obtained by inductively coupled plasma mass spectroscopy.

Element	BEC	ODRT	OD95°C	CD180°C	All		
		LOD	LOD	LOD	LLOQ	ULOQ	Linearity range (log)
Al	0.1	0.01	0.1	0.1	0.05	2	1.6
As	0.003	0.007	0.004	0.001	0.05	2	1.6
B	1	1	1	1	3	300	2.0
Ba	0.5	0.4	0.1	0.9	0.05	5	2.0
Be	0.0001	0.00002	0.00005	0.00002	0.05	5	2.0
Bi	0.0001	0.0001	0.00005	0.00005	0.05	2	1.6
Ca	30	30	10	1	50	5000	2.0
Cd	0.0000	0.00003	0.0001	0.00003	0.05	2	1.6
Ce	0.0002	0.0002	0.0002	0.0001	0.3	30	2.0
Co	0.001	0.001	0.002	0.001	0.3	10	1.5
Cr	0.002	0.001	0.003	0.002	0.05	5	2.0
Cs	0.0001	0.0001	0.0001	0.0001	0.05	5	2.0
Cu	0.01	0.004	0.01	0.01	0.05	5	2.0
Fe	0.05	0.05	0.06	0.04	0.5	50	2.0
Ga	0.0001	0.0001	0.0001	0.0001	0.05	5	2.0
K	10	3	2	4	30	2500	1.9
La	0.0001	0.0001	0.0002	0.0001	0.05	2	1.6
Li	0.001	0.001	0.001	0.001	0.05	5	2.0
Mg	2	2	4	2	30	2500	1.9
Mn	0.004	0.003	0.003	0.003	0.05	5	2.0
Mo	0.0004	0.0001	0.0001	0.0001	0.05	5	2.0
Na	1	1	1	0.05	30	2500	1.9
Nb	0.00002	0.00003	0.00004	0.00002	0.05	5	2.0
Ni	0.009	0.005	0.001	0.001	0.05	5	2.0
P	4	0.4	1	1	3	50	1.2
Pb	0.004	0.002	0.0003	0.003	0.05	5	2.0
Rb	0.001	0.001	0.001	0.0005	0.05	5	2.0
Sb	0.0003	0.0003	0.0004	0.0002	0.05	5	2.0
Se	0.01	0.02	0.03	0.02	0.05	1	1.3
Si	20	4	3	2	3	250	1.9
Sn	0.0003	0.0001	0.0003	0.0001	0.05	5	2.0
Sr	0.04	0.03	0.03	0.04	3	300	2.0
Te	0.0004	0.0005	0.0006	0.0006	0.05	2	1.6
Ti	0.01	0.001	0.001	0.003	0.05	5	2.0
Tl	0.00001	0.00002	0.00001	0.00002	0.05	2	1.6
U	0.00001	0.00002	0.00002	0.00001	0.05	2	1.6
V	0.0005	0.001	0.0003	0.001	0.05	5	2.0
W	0.0003	0.0003	0.0001	0.0002	0.05	5	2.0
Zn	0.3	0.2	0.5	0.1	0.5	20	1.6
Zr	0.0002	0.0001	0.00002	0.0001	0.05	2	1.6

[a] The method blanks were obtained using different sample treatments [room temperature open-vessel digestion (OD_{RT}), open-vessel digestion heated to 95°C ($OD_{95°C}$), and closed-vessel microwave-assisted digestion ($CD_{180°C}$); sample amount 0.2 g].

Table S5 - Limit of detection (LOD; mg kg^{-1}) and quantification (LOQ; mg kg^{-1}) for each element obtained using the residuals of the slope by inductively coupled plasma mass spectroscopy.

Element	OD*95°C[a]	
	LOD	LOQ
Al	0.5	0.6
As	0.5	1
B	10	20
Ba	10	20
Be	0.1	0.3
Bi	0.3	0.7
Ca	1500	3000
Cd	0.2	0.5
Ce	0.5	1
Co	0.4	0.8
Cr	0.6	1
Cs	0.3	0.6
Cu	0.3	0.6
Fe	5	10
Ga	0.3	0.5
K	200	500
La	0.2	0.5
Li	0.2	0.3
Mg	100	200
Mn	2	4
Mo	0.2	0.4
Na	300	600
Nb	0.2	0.5
Ni	0.3	0.7
P	30	40
Pb	0.3	0.7
Rb	0.3	0.8
Sb	0.2	0.5
Se	0.8	2
Si	100	200
Sn	0.3	0.6
Sr	30	70
Te	0.4	0.7
Ti	0.3	0.4
Tl	0.4	0.8
U	0.4	0.7
V	0.6	1
W	0.5	1
Zn	4	7
Zr	0.2	0.4

[a] Open-vessel digestion heated to 95°C (OD*95°C) and sample amount of 0.02 g.

Table S6.a - Concentrations of the certified material (ERM DB001; n=6) obtained for each element by inductively coupled plasma-mass spectrometry.

Element	Unit	Informative concentration	Sample treatment[a]																				
			OD_{RT}							$OD_{95°C}$							$OD^*_{95°C}$						
			%N <LOD	AM	ASD	GM	GSD	median	IQR	%N <LOD	AM	ASD	GM	GSD	median	IQR	%N <LOD	AM	ASD	GM	GSD	median	IQR
Al	mg kg^{-1}	18.1	0	14.9	1.1	14.9	1.08	14.6	1.1	0	16.9	0.7	16.9	1.04	16.9	0.7	0	17.0	0.4	17.0	1.02	17.0	0.3
B	mg kg^{-1}	3.1	0	3.13	0.54	3.10	1.18	2.87	0.49	0	3.26	0.22	3.26	1.07	3.26	0.22	0	2.82	0.12	2.82	1.04	2.82	0.12
Ba	mg kg^{-1}	0.90	0	0.498	0.022	0.497	1.04	0.485	0.019	0	0.524	0.001	0.524	1.00	0.524	0.001	0	1.00	0.10	1.00	1.11	1.01	0.10
Be	µg kg^{-1}	2.9	0	2.21	0.04	2.21	1.02	2.21	0.04	0	2.35	0.01	2.35	1.00	2.35	0.01	0	2.84	0.32	2.83	1.12	2.77	0.32
Bi	µg kg^{-1}	9.0	0	10.1	1.1	10.0	1.12	10.1	1.1	0	9.7	1.0	9.7	1.11	9.7	1.0	0	10.4	0.5	10.4	1.05	10.4	0.5
Ca	mg kg^{-1}	1028	0	1040	17	1040	1.02	1040	17	0	946	12	946	1.01	946	12	0	956	4	956	1.00	956	4
Ce	µg kg^{-1}	-	0	178	7	178	1.04	174	6	0	180	6	180	1.04	180	6	0	225	9	225	1.04	225	9
Co	µg kg^{-1}	106	0	94.7	2.4	94.7	1.03	94.7	2.4	0	94.1	1.6	94.1	1.02	94.1	1.6	0	101	1	101	1.00	101	1
Cr	µg kg^{-1}	500	0	201	22	200	1.11	191	20	0	215	20	214	1.09	207	18	0	325	10	325	1.03	325	10
Cs	µg kg^{-1}	1.2	0	0.48	0.11	0.47	1.24	0.42	0.10	0	0.56	0.02	0.56	1.04	0.57	0.02	0	1.23	0.08	1.23	1.06	1.23	0.08
Fe	mg kg^{-1}	22.6	0	10.5	0.8	10.4	1.08	10.6	0.8	0	12.9	0.2	12.9	1.02	12.9	0.2	0	17.5	0.6	17.5	1.04	17.5	0.6
Ga	µg kg^{-1}	-	0	4.86	0.21	4.86	1.04	4.80	0.21	0	5.11	0.02	5.11	1.00	5.11	0.02	0	5.90	0.40	5.89	1.07	5.87	0.40
K	mg kg^{-1}	-	100	<3	-	<3	-	<3	-	100	<2	-	<2	-	<2	-	100	<30	-	<30	-	<30	-
La	µg kg^{-1}	-	0	95.8	4.2	95.7	1.04	94.3	4.0	0	89.9	1.3	89.9	1.02	89.9	1.3	0	110	6	110	1.05	110	6
Li	µg kg^{-1}	48	0	13.7	2.2	13.6	1.17	12.5	2.0	0	21.1	1.1	21.0	1.06	21.6	1.1	0	44.8	2.5	44.8	1.06	44.9	2.5
Mg	mg kg^{-1}	63.5	0	57.4	3.2	57.4	1.06	56.0	3.0	0	55.8	0.3	55.8	1.00	55.8	0.3	0	64.9	1.9	64.9	1.03	65.0	1.9
Mn	µg kg^{-1}	442	0	452	4	452	1.01	452	4	0	436	8	436	1.02	436	8	0	445	25	444	1.06	445	25
Mo	µg kg^{-1}	200	0	164	40	161	1.28	164	40	0	165	30	163	1.22	180	27	0	188	7	187	1.04	191	7
Na	mg kg^{-1}	-	0	11.9	1.2	11.9	1.11	12.2	1.2	0	10.2	2.6	10.0	1.31	10.7	2.6	0	13.2	1.0	13.2	1.08	13.2	1.0
Nb	µg kg^{-1}	-	0	2.01	0.17	2.01	1.09	2.01	0.17	0	1.61	0.04	1.61	1.03	1.61	0.04	0	2.55	0.15	2.55	1.06	2.55	0.15
Ni	µg kg^{-1}	780	0	640	9	640	1.01	640	9	0	670	6	670	1.01	670	6	0	821	6	821	1.01	821	6
P	mg kg^{-1}	142.2	0	131	9	130	1.07	127	9	0	129	1	129	1.01	129	1	0	144	6	144	1.04	143	6
Rb	µg kg^{-1}	-	0	4.44	0.57	4.42	1.13	4.17	0.53	0	6.67	0.13	6.67	1.02	6.67	0.12	0	16.7	2.2	16.6	1.14	16.4	2.2
Sb	µg kg^{-1}	128	0	87.7	1.3	87.7	1.01	87.7	1.3	0	87.2	6.9	87.0	1.08	83.4	6.1	0	113	13	112	1.13	112	13
Si	mg kg^{-1}	-	0	93.6	3.1	93.6	1.03	93.6	3.1	0	91.5	0.9	91.5	1.01	91.5	0.9	0	89.8	0.4	89.8	1.00	89.8	0.4
Sn	µg kg^{-1}	440	0	430	51	428	1.13	429	51	0	424	11	424	1.03	424	11	0	417	41	415	1.10	410	40
Sr	mg kg^{-1}	-	0	1.56	0.16	1.56	1.10	1.48	0.14	0	2.22	0.22	2.21	1.10	2.18	0.22	0	2.23	0.06	2.23	1.03	2.23	0.06
Te	µg kg^{-1}	-	100	<0.5	-	<0.5	-	<0.5	-	100	<0.6	-	<0.6	-	<0.6	-	100	<2	-	<2	-	<2	-
Ti	mg kg^{-1}	109	0	78.3	5.9	78.1	1.08	75.4	5.3	0	75.3	3.5	75.2	1.08	75.3	3.5	0	78.9	5.5	78.8	1.03	78.9	5.5
Tl	µg kg^{-1}	0.48	0	0.343	0.035	0.342	1.11	0.340	0.035	0	0.373	0.025	0.373	1.07	0.370	0.025	0	0.443	0.040	0.442	1.10	0.450	0.040
U	µg kg^{-1}	10.1	0	8.61	0.46	8.61	1.05	8.37	0.40	0	8.72	0.20	8.72	1.02	8.72	0.20	0	10.8	0.8	10.8	1.08	11.2	0.7
V	µg kg^{-1}	49.3	0	57.3	8.8	56.9	1.17	57.0	8.8	0	50.0	2.3	49.9	1.05	50.0	2.3	0	49.1	2.5	49.1	1.05	49.0	2.5
W	µg kg^{-1}	15.2	0	10.6	0.1	10.6	1.01	10.6	0.1	0	10.0	0.2	10.0	1.02	10.1	0.2	0	13.0	2.8	12.8	1.23	12.2	2.7
Zr	µg kg^{-1}	64	0	34.5	3.2	34.4	1.10	34.1	3.1	0	35.8	4.2	35.6	1.13	36.7	4.1	0	56.8	3.6	56.7	1.07	56.8	3.6

[a] Mass of the certified material = 0.2 g for room temperature open-vessel digestion (ODRT), and open-vessel digestion heated to 95°C (OD95°C), and 0.02 g for OD*95°C . %N <LOD, percentage of samples below the limit of detection; AM, arithmetic mean; ASD, arithmetic standard deviation; GM, geometric mean; GSD, geometric standard deviation; IQR, interquartile range.

Table S6.b - Concentrations of the certified material (ERM DB001; n=6) obtained for each element by inductively coupled plasma-mass or -optical emission spectrometry.

Element	Unit	Sample treatment[a]						
		CD$_{180°C}$[a]						
		%N <LOD	AM	ASD	GM	GSD	median	IQR
Al	mg kg^{-1}	0	18.0	1.0	18.0	1.06	18.0	1.0
B	mg kg^{-1}	0	3.33	0.22	3.32	1.07	3.33	0.22
Ba	mg kg^{-1}	0	0.929	0.084	0.927	1.09	0.883	0.074
Be	µg kg^{-1}	0	2.70	0.08	2.70	1.03	2.71	0.08
Bi	µg kg^{-1}	0	9.94	0.32	9.9	1.03	9.78	0.29
Ca	mg kg^{-1}	0	973	14	973	1.01	973	14
Ce	µg kg^{-1}	0	190	4	190	1.02	190	4
Co	µg kg^{-1}	0	96.9	1.2	96.9	1.01	96.9	1.2
Cr	µg kg^{-1}	0	515	12	515	1.02	519	11
Cs	µg kg^{-1}	0	1.17	0.08	1.16	1.07	1.12	0.07
Fe	mg kg^{-1}	0	18.6	0.3	18.6	1.02	18.6	0.3
Ga	µg kg^{-1}	0	6.25	0.22	6.25	1.04	6.20	0.22
K	mg kg^{-1}	100	<4		<4		<4	
La	µg kg^{-1}	0	101	2	100.6	1.02	101	2
Li	µg kg^{-1}	0	34.7	1.0	34.7	1.03	34.3	0.9
Mg	mg kg^{-1}	0	64.1	1.8	64.0	1.03	65.0	1.6
Mn	µg kg^{-1}	0	479	39	478	1.08	479	39
Mo	µg kg^{-1}	0	217	6	217	1.03	216	6
Na	mg kg^{-1}	0	14.7	2.1	14.6	1.15	14.0	2.0
Nb	µg kg^{-1}	0	3.19	0.18	3.19	1.06	3.22	0.18
Ni	µg kg^{-1}	0	828	29	827	1.04	825	29
P	mg kg^{-1}	0	140	4	140	1.03	141	4
Rb	µg kg^{-1}	0	18.7	0.2	18.75	1.01	18.7	0.2
Sb	µg kg^{-1}	0	91.8	1.9	91.8	1.02	92.0	1.9
Si	mg kg^{-1}	0	110	1	110.3	1.01	110	1
Sn	µg kg^{-1}	0	423	26	423	1.06	409	23
Sr	mg kg^{-1}	0	1.95	0.12	1.94	1.06	1.88	0.11
Te	µg kg^{-1}	100	<0.6	-	<0.6		<0.6	-
Ti	mg kg^{-1}	0	86.0	2.2	86.0	1.03	87.1	1.9
Tl	µg kg^{-1}	0	0.500	0.020	0.500	1.04	0.500	0.020
U	µg kg^{-1}	0	9.83	0.25	9.83	1.03	9.95	0.23
V	µg kg^{-1}	0	54.2	2.1	54.2	1.04	54.6	2.1
W	µg kg^{-1}	0	10.1	0.7	10.1	1.08	10.4	0.7
Zr	µg kg^{-1}	0	61.9	0.2	61.9	1.00	61.8	0.2

[a] Mass of certified material = 0.2 g. %N <LOD, percentage of samples below the limit of detection; AM, arithmetic mean; ASD, arithmetic standard deviation; GM, geometric mean; GSD, geometric standard deviation; IQR, interquartile range.

Table S7 - Concentrations of the certified material (ERM DB001; n=6) obtained for each element by inductively coupled plasma optical emission spectrometry.

Element	Unit	Sample treatment[a]					
		CD*[a]			CD**[a]		
		%N <LOD	AM	ASD	%N <LOD	AM	ASD
Al	mg kg^{-1}	0	16.6	0.9	0	17.6	1.0
B	mg kg^{-1}	100	<9		100	<7	
Ba	mg kg^{-1}	0	1.07	0.12	0	1.06	0.15
Be	µg kg^{-1}	100	<10		100	<70	
Bi	µg kg^{-1}	100	<100		100	<500	
Ca	mg kg^{-1}	0	976	9	0	910	14
Ce	µg kg^{-1}	100	<200		100	<300	
Co	µg kg^{-1}	0	116	100	0	<100	
Cr	µg kg^{-1}	0	512	15	0	519	3
Cs	µg kg^{-1}	-	nd[b]		-	nd[b]	
Fe	mg kg^{-1}	0	22.5	0.7	0	21.5	0.7
Ga	µg kg^{-1}	100	<300		100	<400	
K	mg kg^{-1}	100	<200		100	<200	
La	µg kg^{-1}	0	102	100	0	<40	
Li	µg kg^{-1}	100	<50		100	<60	
Mg	mg kg^{-1}	0	59.3	1.0	0	56.6	3.0
Mn	µg kg^{-1}	0	446	33	0	450	42
Mo	µg kg^{-1}	100	<90		0	112	42
Na	mg kg^{-1}	100	<10		100	<11	
Nb	µg kg^{-1}	100	<600		100	<700	
Ni	µg kg^{-1}	0	839	72	0	779	40
P	mg kg^{-1}	0	139	7	0	136	6
Rb	µg kg^{-1}	100	<600		100	<2000	
Sb	µg kg^{-1}	100	<600		100	<800	
Si	mg kg^{-1}	0	95.9	5.8	0	106	13
Sn	µg kg^{-1}	0	476	84	0	373	100
Sr	mg kg^{-1}	0	2.07	0.01	0	2.03	0.07
Te	µg kg^{-1}	100	<1000		100	<2000	
Ti	mg kg^{-1}	0	110	4	0	107	7
Tl	µg kg^{-1}	100	<2000		100	<2000	
U	µg kg^{-1}	100	<1000		100	<200	
V	µg kg^{-1}	100	<200		100	<100	
W	µg kg^{-1}	100	<2000		100	<2000	
Zr	µg kg^{-1}	0	62.5	7.8	0	63	20

[a] Mass of certified material = 0.2 g for closed-vessel microwave-assisted digestion (CD) with different reagents (CD*: HNO3/HCl; CD**: HNO3/HCl/HF).

[b] Not determined (nd) = Cs could not be analysed because axial view ICP-OES is strongly affected by ionisation interference when elements with low ionisation potentials coexist in the sample.

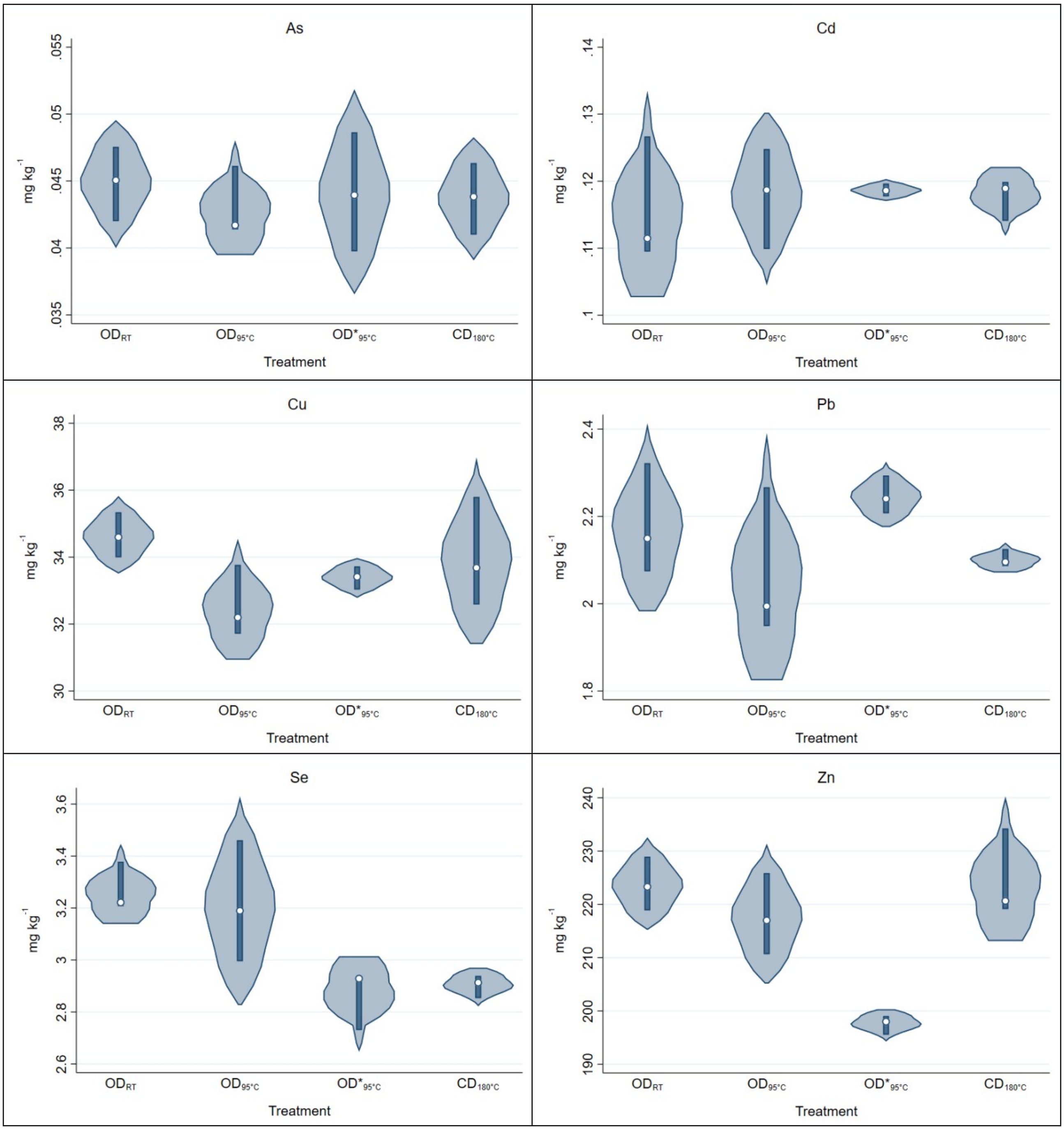


Figure S1. Violin plots of the certified elements (As, Cd, Cu, Pb, Se, and Zn) in ERM DB001 obtained by different acid digestion treatments [open-vessel digestion (ODRT, OD95°C and OD*95°C), and closed-vessel microwave-assisted digestion (CD180°C)]. The determination on elemental contents was performed using an inductively coupled plasma mass spectrometer.

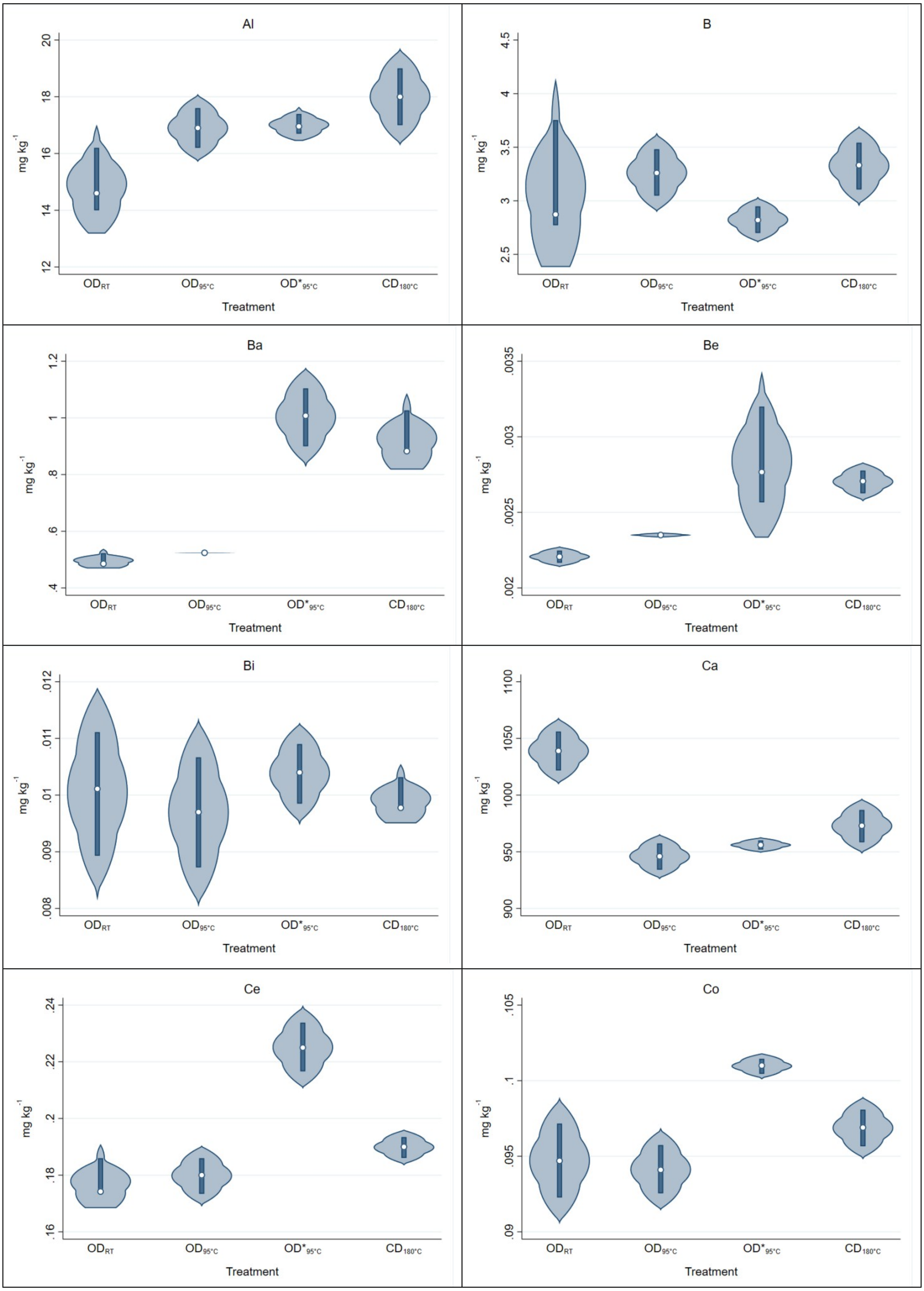


Figure S2.a. Violin plots of the non-certified elements (Al, B, Ba, Be, Bi, Ca, Ce, Co) in ERM DB001 obtained by different acid digestion treatments [open-vessel digestion (ODRT, OD95°C and OD*95°C), and closed-vessel microwave-assisted digestion (CD180°C)]. The determination on elemental contents was performed using an inductively coupled plasma mass spectrometer.

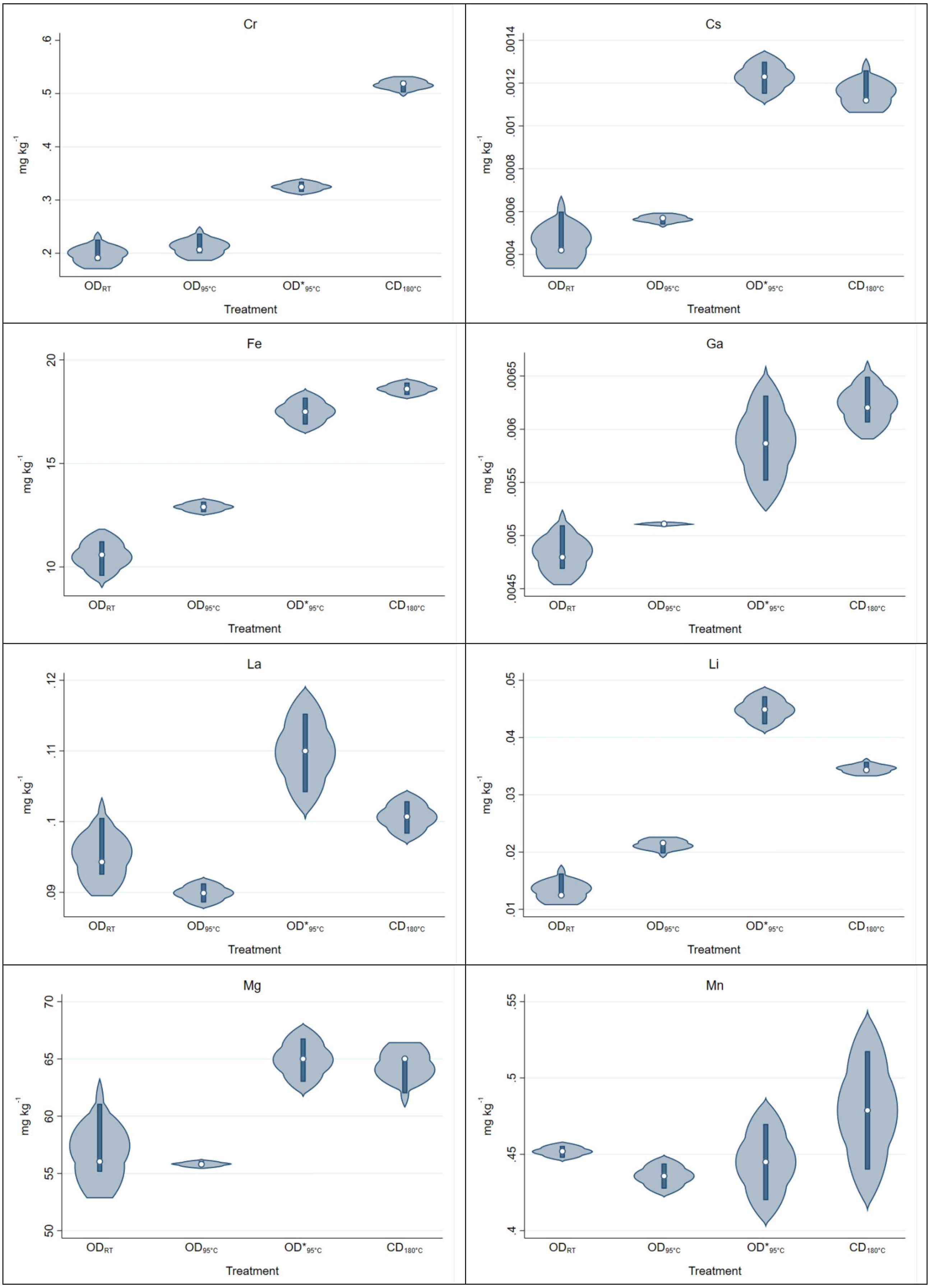


Figure S2.b. Violin plots of the non-certified elements (Cr, Cs, Fe, Ga, La, Li, Mg, and Mn) in ERM DB001 obtained by different acid digestion treatments [open-vessel digestion (ODRT, OD95°C and OD*95°C), and closed-vessel microwave-assisted digestion (CD180°C)]. The determination on elemental contents was performed using an inductively coupled plasma mass spectrometer.

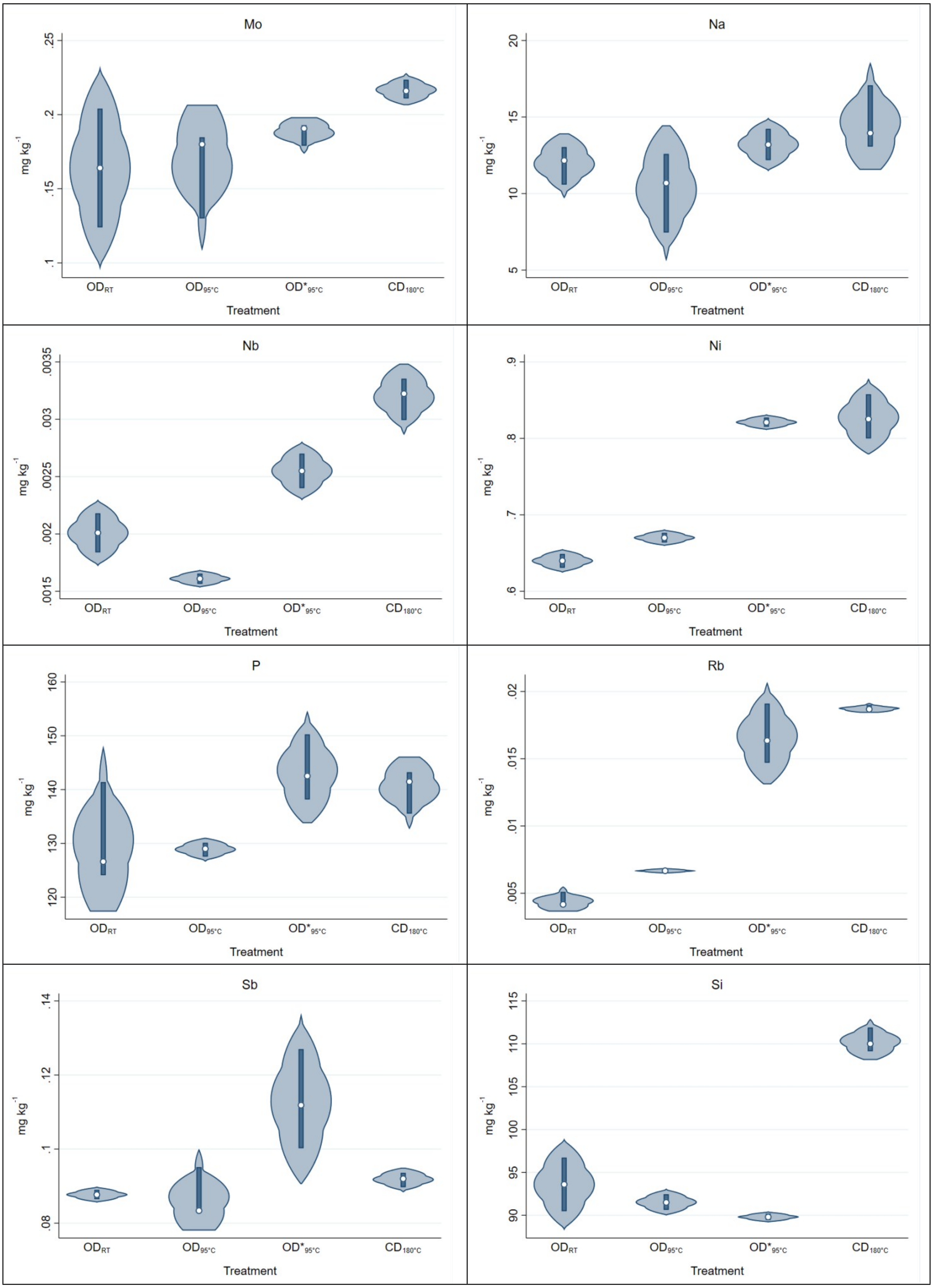


Figure S2.c. Violin plots of the non-certified elements (Mo, Na, Nb, Ni, P, Rb, Sb, and Si) in ERM DB001 obtained by different acid digestion treatments [open-vessel digestion (ODRT, OD95°C and OD*95°C), and closed-vessel microwave-assisted digestion (CD180°C)]. The determination on elemental contents was performed using an inductively coupled plasma mass spectrometer.

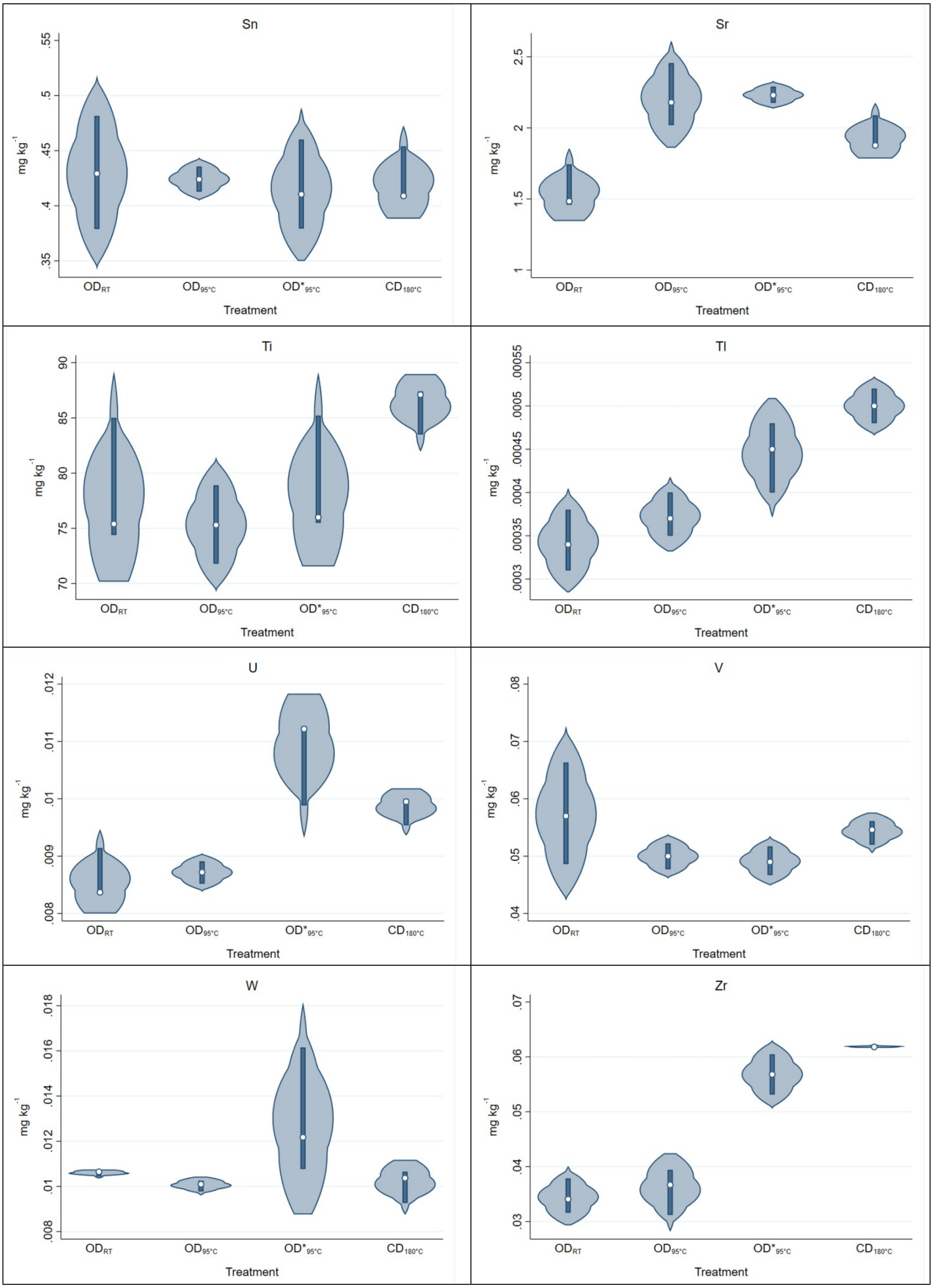


Figure S2.d. Violin plots of the non-certified elements (Sn, Sr, Ti, Tl, U, V, W and Zr) in ERM DB001 obtained by different acid digestion treatments [open-vessel digestion (ODRT, OD95°C and OD*95°C), and closed-vessel microwave-assisted digestion (CD180°C)]. The determination on elemental contents was performed using an inductively coupled plasma mass spectrometer.

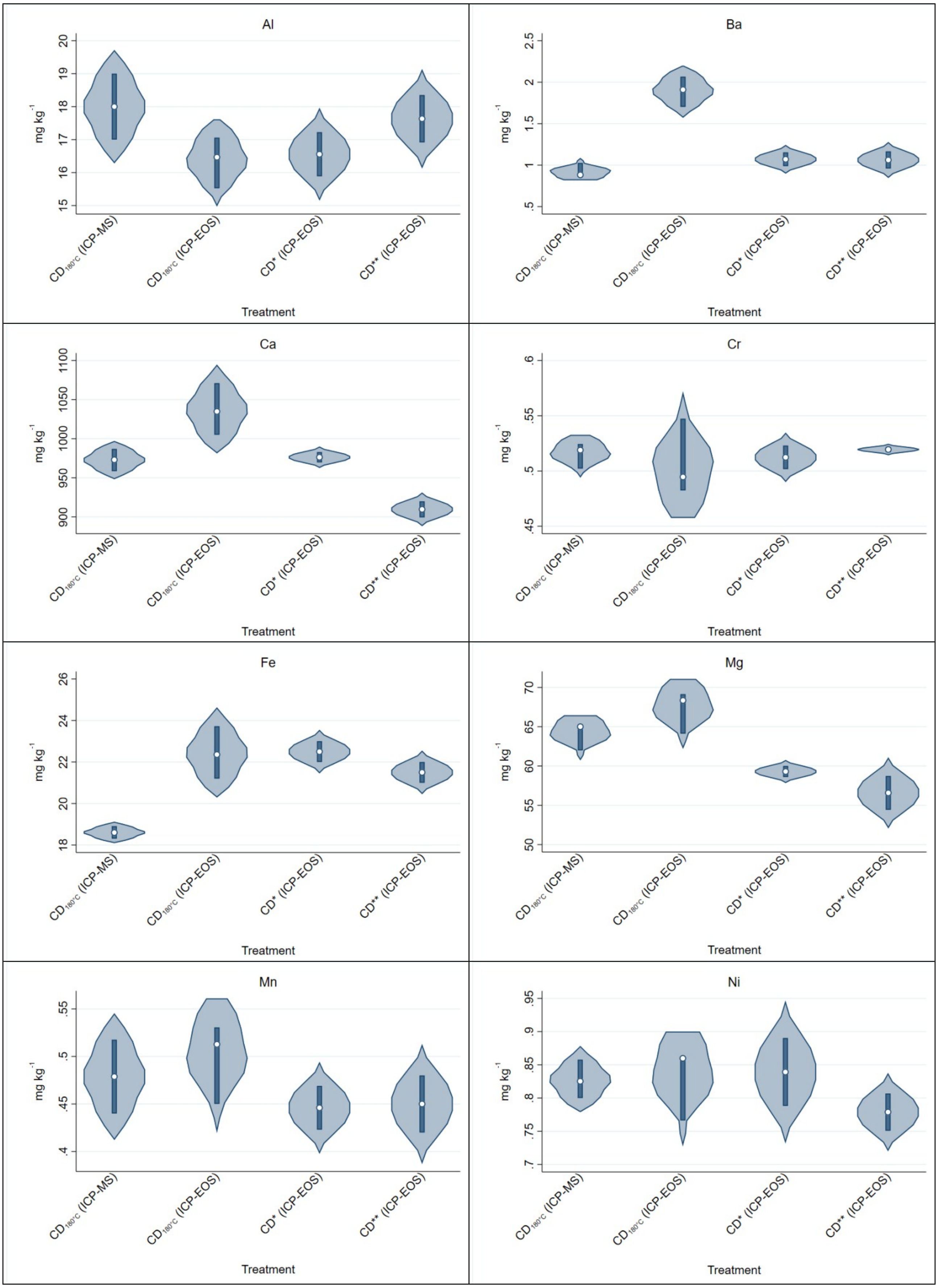


Figure S3.a. Violin plots of some non-certified elements (Al, Ba, Ca, Cr, Fe, Mg, Mn, and Ni) in ERM DB001 obtained by different acid digestion treatments [closed-vessel microwave-assisted digestion with HNO_3/H_2O_2 (CD180°C), HCl/HNO_3 (CD*) and $HF/HCl/HNO_3$ (CD**)]. The determination on elemental contents was performed using an inductively coupled plasma –mass or optical emission spectrometer (ICP-MS or ICP-OES).

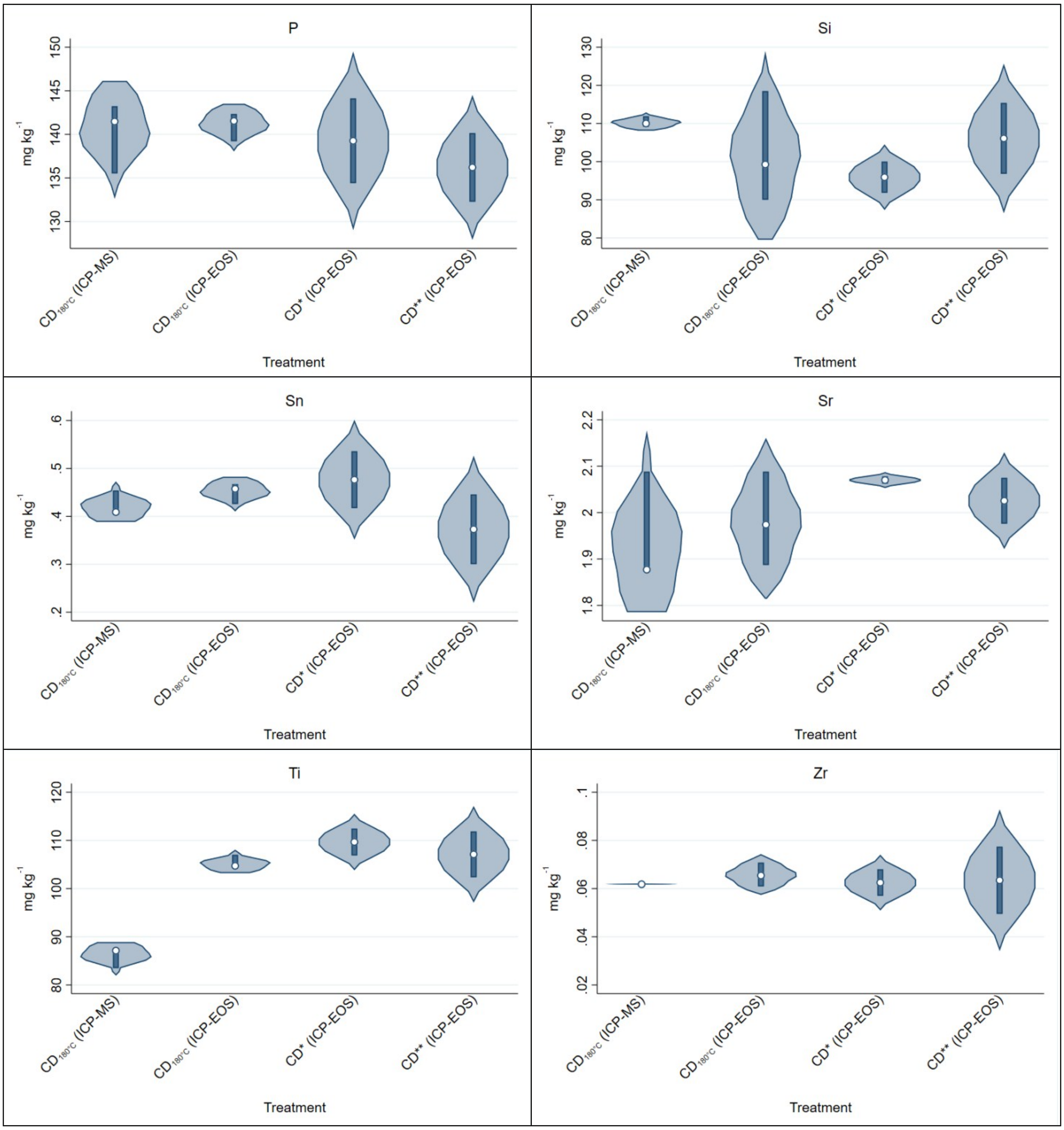


Figure S3.b. Violin plots of some non-certified elements (P, Si, Sn, Sr, Tl and Zr) in ERM DB001 obtained by different acid digestion treatments [closed-vessel microwave-assisted digestion with HNO_3/H_2O_2 (CD180°C), HCl/HNO_3 (CD*) and $HF/HCl/HNO_3$ (CD**)]. The determination on elemental contents was performed using an inductively coupled plasma –mass or optical emission spectrometer (ICP-MS or ICP-OES).

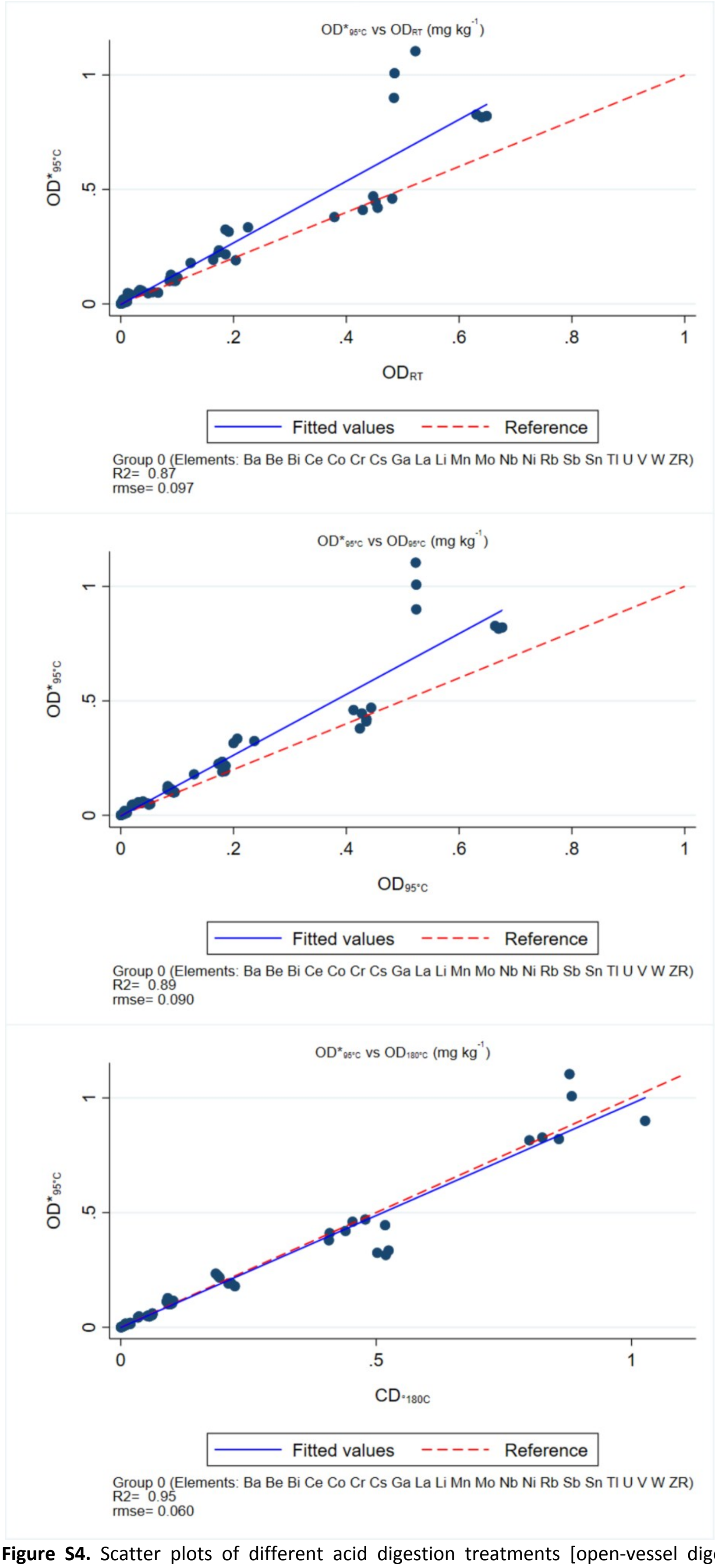
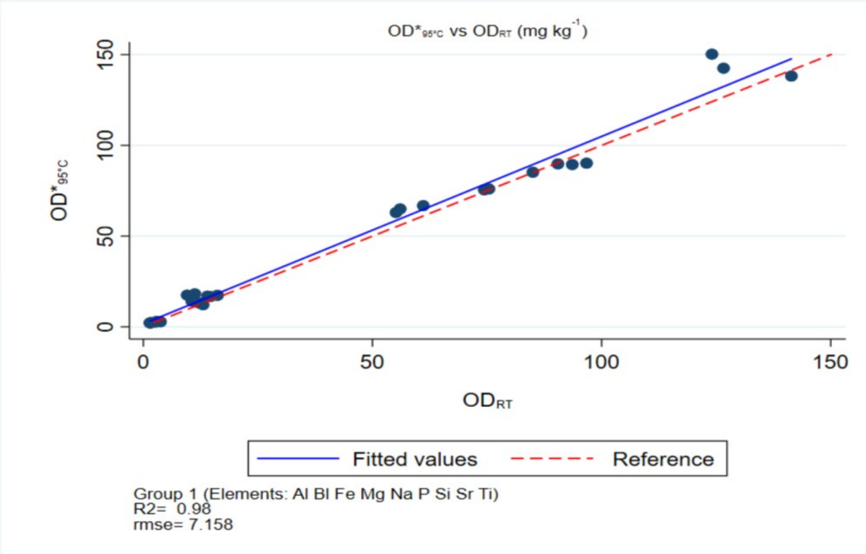
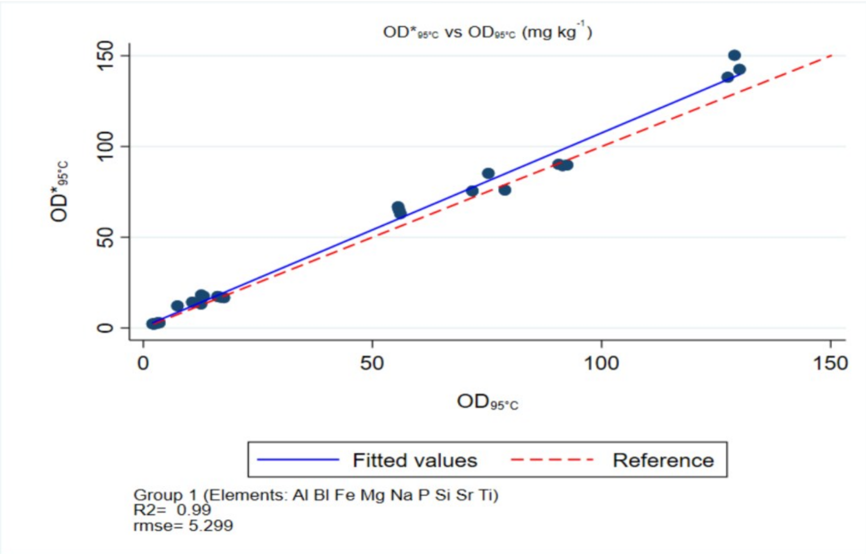


Figure S4. Scatter plots of different acid digestion treatments [open-vessel digestion (ODRT, and OD95°C), and closed-vessel microwave-assisted digestion (CD180°C) versus open-vessel digestion heated to 95 °C (OD*95°C) for the non-certified elements with yields <2 mg kg^{-1}. Fitted values lines represents the predicted values of the linear regression model (OD*95°C as the dependent variable). The reference line represent the 1:1 line (perfect concordance). Rmse: root mean standard error.





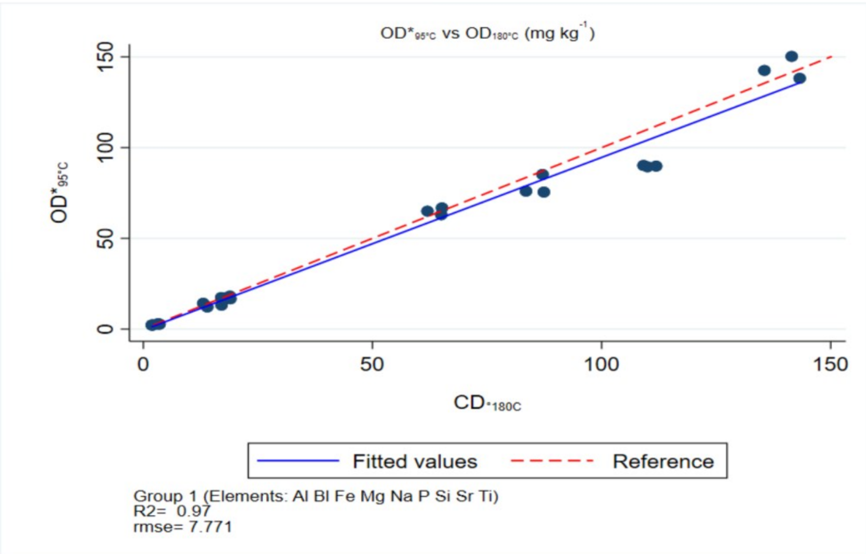


Figure S5. Scatter plots of different acid digestion treatments [open-vessel digestion (ODRT, and OD95°C), and closed-vessel microwave-assisted digestion (CD180°C) versus open-vessel digestion heated to 95 °C (OD*95°C) for the non-certified elements with yields >2 mg kg^{-1}. Fitted values lines represents the predicted values of the linear regression model (OD*95°C as the dependent variable). The reference line represent the 1:1 line (perfect concordance). Rmse: root mean standard error.

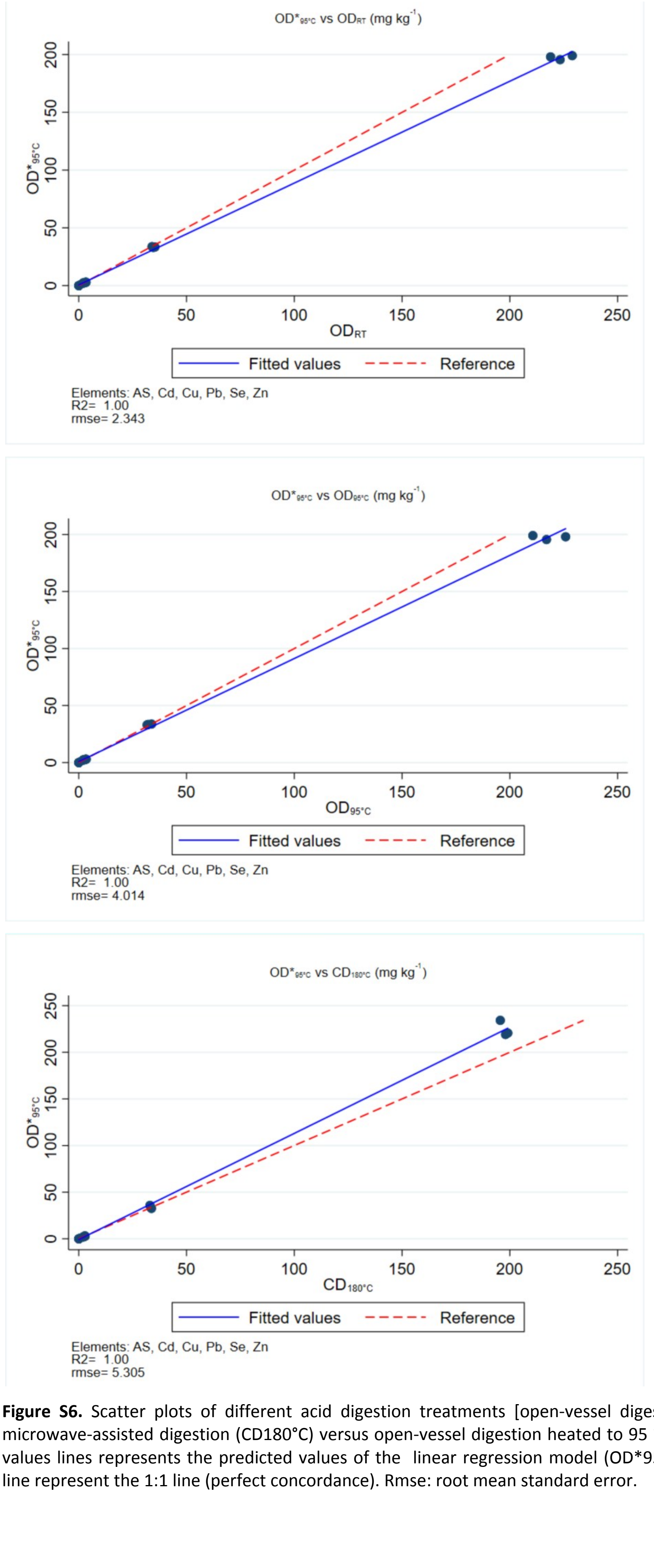


Figure S6. Scatter plots of different acid digestion treatments [open-vessel digestion (ODRT, and OD95°C), and closed-vessel microwave-assisted digestion (CD180°C) versus open-vessel digestion heated to 95 °C (OD*95°C) for the certified elements. Fitted values lines represents the predicted values of the linear regression model (OD*95°C as the dependent variable). The reference line represent the 1:1 line (perfect concordance). Rmse: root mean standard error.

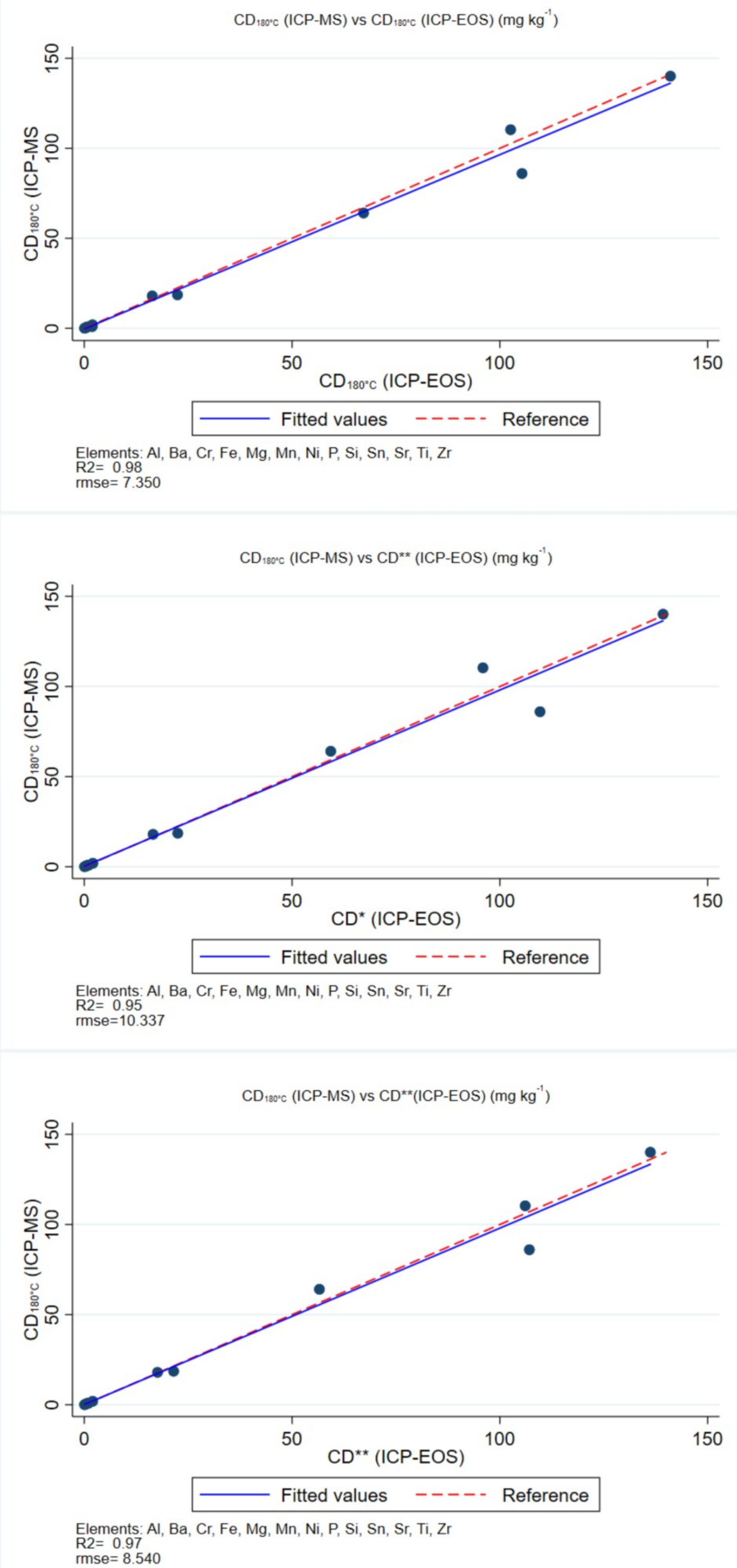


Figure S7. Scatter plots of [closed-vessel microwave-assisted digestion with HNO_3/H_2O_2 (CD180°C), HCl/HNO_3 (CD*) and $HF/HCl/HNO_3$ (CD**) by inductively coupled plasma optical emission spectroscopy (ICP-OES) versus CD180°C by inductively coupled plasma mass spectroscopy (ICP-MS). Fitted values line represent the predicted values of the linear regression model (CD180°C by ICP-MS as the dependent variable). The reference line represent the 1:1 line (perfect concordance). Rmse: root mean standard error.

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