

Analytical and Bioanalytical Chemistry

Electronic Supplementary Material

Optimization of a sequential extraction procedure for trace elements in Arctic PM₁₀

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Table S1 Operating conditions applied for the instrumental analysis

ICP-OES			HR-ICP-MS		
Analyte	λ (nm)	Torch position	Analyte	Isotopes	Resolution
Al	396.2	Axial - Radial	As	75	Medium
Ca	317.9	Radial	Ba	135-137	Medium
Fe	238.2	Axial - Radial	Cd	111-112-114	Low - Medium
K	766.5	Axial - Radial	Co	59	Medium
Mg	285.2	Axial - Radial	Cr	52-53	Medium
Na	589.6	Axial	Cu	63-65	Medium
Pb	220.4	Axial - Radial	Fe	56-57	Medium
Si	251.6	Axial - Radial	Mn	55	Medium
Ti	334.9	Axial	Ni	60-61-62	Medium
Zn	206.2	Axial - Radial	Pb	206-207-208	Medium
			Sb	121-123	Medium
			Ti	47-49	Medium
			V	51	Medium

Table S2 Crustal (CEF) and marine (MEF) enrichment factors calculated for the CRM NIST 1648a

	CEF	MEF	
Al	1.00	8490000	
As	130	95300	
Ca	4.48	362	
Cd	1630	1660000	
Co	3.49	444000	
Cr	25.9	19900000	
Cu	96.3	504000	
Fe	2.87	9710000	
K	0.832	68.8	
Mg	1.36	14.9	
Mn	3.38	978000	
Na	0.373	1.00	
Ni	9.84	100000	
Pb	870	541000000	
Sb	331	225000	
Si	0.952	106000	
Ti	2.91	9960000	
V	5.41	157000	
Zn	208	1190000	

$$CEF_i = \frac{C_{iPM}/C_{rPM}}{C_{i crust}^*/C_{r crust}^*}$$

$$MEF_i = \frac{C_{iPM}/C_{rPM}}{C_{i sea}^+/C_{r sea}^+}$$

* Wedepohl (1995)

+ Goldberg (1965)

Table S3 Recovery percentages obtained for the CRM NIST 1648a with the ten tested procedures

	HPW - Stir	Buffer - Stir	CH ₃ COOH - Stir	HCl - Stir	HNO ₃ - Stir	HPW - US	Buffer - US	CH ₃ COOH - US	HCl - US	HNO ₃ - US
Al	55 ± 3	61 ± 3	56 ± 7	56 ± 5	62 ± 3	59 ± 2	57 ± 2	51 ± 4	53 ± 3	48 ± 4
As	109 ± 3	107 ± 8	108 ± 3	105 ± 3	105 ± 4	112 ± 6	105 ± 2	99 ± 3	95 ± 6	100 ± 2
Ba	77 ± 1	83 ± 6	78 ± 3	82 ± 3	78 ± 3	80.7 ± 0.5	78 ± 2	71 ± 2	69 ± 2	69 ± 3
Ca	108 ± 2	106 ± 4	102 ± 2	106 ± 2	105 ± 2	109 ± 2	102 ± 2	105 ± 3	104 ± 5	103 ± 2
Cd	101 ± 5	103 ± 3	100 ± 1	105 ± 3	101 ± 4	103 ± 5	100 ± 4	97 ± 1	96 ± 4	100 ± 7
Co	76 ± 3	81 ± 2	78 ± 4	81 ± 2	81 ± 3	84 ± 4	76 ± 3	74.4 ± 0.5	70 ± 2	74 ± 4
Cr	32 ± 3	36 ± 3	32 ± 4	34 ± 2	35 ± 3	34 ± 2	35 ± 1	31 ± 1	30 ± 2	31 ± 3
Cu	84 ± 3	91 ± 4	89 ± 2	95 ± 4	97 ± 2	88 ± 5	84.5 ± 0.7	85 ± 3	88 ± 4	91 ± 5
Fe	83 ± 1	92 ± 7	83 ± 4	84 ± 3	112 ± 6	90 ± 1	80 ± 3	78 ± 4	98 ± 3	71 ± 2
K	56 ± 2	57 ± 3	54 ± 6	63 ± 4	70 ± 6	57 ± 2	54 ± 2	50 ± 4	57 ± 3	56 ± 5
Mg	87.1 ± 0.7	90 ± 3	86 ± 3	88 ± 1	89 ± 2	91 ± 2	84 ± 2	83 ± 3	83 ± 2	80.6 ± 0.9
Mn	92 ± 1	95 ± 5	93.3 ± 0.6	96 ± 2	101 ± 2	95 ± 2	94 ± 2	86 ± 2	87 ± 5	91 ± 2
Na	64 ± 1	64 ± 2	69 ± 4	57.0 ± 0.8	59 ± 1	64.8 ± 0.8	69 ± 3	63 ± 1	59 ± 2	57 ± 3
Ni	93 ± 2	98 ± 3	93 ± 4	95 ± 4	97 ± 1	101 ± 3	92 ± 2	86 ± 3	92 ± 3	90 ± 3
Pb	97 ± 2	100 ± 5	96 ± 4	102 ± 1	102 ± 4	104 ± 4	94 ± 2	92 ± 2	96 ± 1	97 ± 1
Sb	65 ± 2	64 ± 3	67 ± 2	63 ± 2	64 ± 2	66 ± 2	62 ± 1	58.0 ± 0.1	57 ± 2	54 ± 1
Si	13 ± 3	14 ± 4	13 ± 5	13 ± 3	17 ± 4	14 ± 5	14 ± 2	12 ± 3	14 ± 4	11 ± 3
Ti	29.5 ± 0.7	32.6 ± 0.5	31 ± 3	33 ± 2	37 ± 1	30 ± 2	32 ± 1	27 ± 1	31 ± 1	28 ± 2
V	86 ± 1	90 ± 5	84 ± 4	88.1 ± 0.8	91 ± 1	90 ± 3	84 ± 1	81 ± 3	80 ± 2	84 ± 4
Zn	96 ± 2	99 ± 4	97 ± 2	99 ± 2	102 ± 1	101 ± 3	98 ± 3	93 ± 2	96 ± 3	94 ± 3

Stir = 16 hours stirring; US = 15 min ultrasounds; Buffer = CH₃COOH/CH₃COONH₄ buffer.

Table S4 Extraction percentages obtained for the CRM BCR 701 with the five tested procedures: a) fraction I; b) fraction II

a)	FRACTION I				
	HPW - Stir	Buffer - Stir	CH ₃ COOH - Stir	HCl - Stir	HNO ₃ - Stir
Cd	1.03 ± 0.06	56 ± 2	80 ± 2	83 ± 2	86.6 ± 0.7
Cr	0.42 ± 0.04	0.75 ± 0.01	4.36 ± 0.03	10.6 ± 0.2	14.1 ± 0.5
Cu	2.3 ± 0.2	14 ± 1	49.4 ± 0.9	60.8 ± 0.4	64 ± 3
Ni	5 ± 1	15 ± 1	23.5 ± 0.6	33 ± 3	33 ± 1
Pb	0.32 ± 0.03	0.76 ± 0.08	28.6 ± 0.3	71 ± 5	77 ± 7
Zn	16 ± 5	41.6 ± 0.4	70 ± 10	66 ± 3	62.0 ± 0.5

b)	FRACTION II				
	HPW - Stir	Buffer - Stir	CH ₃ COOH - Stir	HCl - Stir	HNO ₃ - Stir
Cd	94 ± 5	42.8 ± 0.3	15 ± 1	8.0 ± 0.4	8.1 ± 0.3
Cr	104 ± 3	105 ± 3	98 ± 3	90 ± 4	89 ± 1
Cu	80 ± 4	73 ± 2	42 ± 2	29.0 ± 0.2	27.3 ± 0.3
Ni	88 ± 4	82.0 ± 0.1	74 ± 3	65 ± 4	60 ± 2
Pb	75 ± 4	73 ± 1	49 ± 1	22 ± 3	18 ± 2
Zn	98 ± 5	72 ± 5	56 ± 4	49 ± 3	44 ± 2

Stir = 16 hours stirring; Buffer = CH₃COOH/CH₃COONH₄ buffer.

Table S5 Extraction percentages (fraction I) calculated for the ten PM₁₀ samples collected in Ny-Ålesund in 2010 and 2012

	23Mar10	27Mar10	17Apr12	25Apr12	29Apr12	26Jun10	9Jul10	18Jul12	22Jul12	26Jul12
Al	6.9 ± 0.3	5.7 ± 0.3	n.a.	22.5 ± 0.5	23.4 ± 0.6	5.1 ± 0.2	3.21 ± 0.01	7.7 ± 0.4	9.60 ± 0.02	6.5 ± 0.2
As	79 ± 3	57 ± 1	95 ± 3	94 ± 4	95 ± 6	47 ± 2	69 ± 4	79 ± 5	95 ± 2	88 ± 5
Ba	46 ± 2	33 ± 1	72 ± 2	64 ± 3	74 ± 3	22 ± 1	20 ± 1	26 ± 1	45 ± 3	38 ± 2
Ca	100 ± 2	94 ± 2	100 ± 4	78.3 ± 0.4	100 ± 4	65.0 ± 0.9	60 ± 3	64 ± 2	97 ± 4	100 ± 2
Cd	95 ± 5	32 ± 1	93 ± 6	79 ± 4	89 ± 4	100 ± 7	< PB	< PB	77 ± 8	76 ± 4
Co	67 ± 2	57 ± 4	65 ± 3	64 ± 5	78 ± 3	57 ± 1	62 ± 7	59 ± 2	83 ± 4	68 ± 3
Cr	15.1 ± 0.6	8.5 ± 0.2	19.8 ± 0.8	20.4 ± 0.5	22.2 ± 0.4	20.1 ± 0.6	11.6 ± 0.5	9.0 ± 0.4	52 ± 2	9.0 ± 0.4
Cu	81 ± 2	46 ± 2	91 ± 2	63 ± 2	84 ± 2	57 ± 2	85 ± 2	60 ± 2	56 ± 1	93 ± 2
Fe	15.8 ± 0.5	10.9 ± 0.5	33.8 ± 0.5	33.7 ± 0.6	41.8 ± 0.5	11.7 ± 0.5	9.5 ± 0.2	16.6 ± 0.6	47 ± 2	17.5 ± 0.3
K	77 ± 2	63 ± 3	84 ± 2	86 ± 2	93 ± 3	79 ± 3	52 ± 1	64 ± 4	92 ± 2	57 ± 1
Mg	29.4 ± 0.5	23.3 ± 0.2	97 ± 4	95 ± 2	98 ± 3	16.9 ± 0.5	12.0 ± 0.2	85 ± 4	97 ± 1	91 ± 2
Mn	51 ± 2	36.7 ± 0.9	81 ± 1	76.6 ± 0.3	82 ± 3	19.0 ± 0.4	24 ± 2	50 ± 2	78 ± 2	68 ± 1
Na	67 ± 1	69.9 ± 0.6	99 ± 2	98 ± 4	99 ± 2	80.0 ± 0.7	85 ± 1	97 ± 3	100 ± 3	98 ± 3
Ni	61 ± 3	78 ± 5	84 ± 1	58 ± 1	91 ± 2	41 ± 1	98 ± 2	36.5 ± 0.8	86 ± 2	75 ± 2
Pb	97 ± 3	92 ± 4	99 ± 3	77 ± 2	91 ± 4	57 ± 3	53 ± 2	63 ± 2	70 ± 3	78 ± 3
Sb	66 ± 2	15.6 ± 0.8	74 ± 4	67 ± 4	62 ± 3	< PB	< PB	34 ± 2	46 ± 1	30 ± 2
Si	< PB	< PB	12.5 ± 0.5	18.7 ± 0.6	19.5 ± 0.7	< PB	72 ± 4	11.1 ± 0.8	24.9 ± 0.3	16.2 ± 0.4
Ti	4.8 ± 0.1	2.1 ± 0.1	11.3 ± 0.5	29 ± 2	39 ± 1	3.6 ± 0.2	2.8 ± 0.1	3.3 ± 0.2	10.1 ± 0.8	2.3 ± 0.1
V	80 ± 5	60 ± 2	68 ± 2	77 ± 4	71 ± 2	73 ± 3	90 ± 5	71 ± 3	97.3 ± 0.6	89 ± 3
Zn	100 ± 1	79.8 ± 0.7	95 ± 2	< PB	< PB	100.0 ± 0.8	100 ± 1	< PB	89 ± 2	72 ± 1

PB = procedural blank

Table S6 Enrichment factors calculated for the Arctic PM₁₀ samples: a) crustal (CEF); b) marine (MEF)

a)	23Mar10	27Mar10	17Apr12	25Apr12	29Apr12	26Jun10	9Jul10	18Jul12	22Jul12	26Jul12
Al	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
As	973	204	193	143	138	16.1	184	58.4	76.6	63.4
Ba	2.17	1.85	1.25	1.41	1.64	0.863	1.33	0.87	1.34	1.38
Ca	8.80	5.66	5.76	7.08	10.34	6.16	9.69	6.56	9.47	7.30
Cd	4960	1770	406	386	375	756	752	24.6	202	110
Co	3.31	4.35	2.20	1.28	2.12	3.47	-	10.3	8.21	5.49
Cu	58	8.95	59.6	36.7	59.9	7.47	0.447	34.8	68.7	147
Fe	4.32	3.00	2.26	2.47	2.27	2.63	3.40	2.67	2.46	2.59
K	4.67	2.74	3.55	4.97	7.57	3.68	3.04	3.27	5.11	2.17
Mg	-	-	23.0	31.5	52.5	-	-	20.5	34.9	13.8
Mn	7.88	4.77	3.53	3.65	3.78	2.33	3.30	3.03	2.92	3.00
Na	47.0	37.1	65.5	103	162	67.3	113	71.1	135	34.1
Ni	60.7	47.9	33.1	25.7	29.2	41.1	175	242	187	51.2
Pb	550	167	79.4	76.1	67.1	5.87	15.1	1.92	-	-
Ti	0.975	0.855	0.962	1.08	0.939	1.15	1.18	1.19	0.905	0.909
V	13.4	6.00	5.21	5.96	5.45	16.1	82.3	17.2	155	36.6
Zn	390	116	86.5	70.7	62.6	49.4	216	54.3	42.3	72.8

b)	23Mar10	27Mar10	17Apr12	25Apr12	29Apr12	26Jun10	9Jul10	18Jul12	22Jul12	26Jul12
Al	67400	85400	48300	30800	19600	47100	28100	44500	23500	92800
As	5640	1500	804	379	232	65.0	444	224	155	507
Ba	420	455	174	125	92.4	117	107	111	90.2	368
Ca	5.64	4.60	2.65	2.07	1.93	2.76	2.59	2.78	2.11	6.44
Cd	40000	18100	2350	1420	881	4260	2530	131	566	1220
Co	3350	5560	1590	590	622	2450	-	6880	2890	7640
Cu	2420	471	1780	695	723	216	7.72	953	993	8390
Fe	116000	102000	43600	30300	17800	49400	38100	47400	23000	95800
K	3.06	2.27	1.67	1.49	1.45	1.69	0.831	1.42	1.17	1.96
Mg	-	-	1.44	1.25	1.33	-	-	1.18	1.06	1.66
Mn	18100	13900	5800	3820	2520	3730	3160	4590	2330	9470
Na	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ni	4910	4910	1920	950	686	2320	5910	12900	5260	5710
Pb	2710000	1040000	281000	171000	96200	20200	30900	6250	-	-
Ti	26500	29400	18700	13300	7410	21900	13400	21300	8550	34000
V	3090	1750	862	628	365	2590	7910	2620	12400	11600
Zn	17600	6660	2810	1460	824	1560	4070	1620	667	4540

Table S7 Total concentrations obtained by direct digestion for the ten PM₁₀ samples collected in Ny-Ålesund in 2010 and 2012 (Bazzano et al., 2016, Conca et al., 2019)

	23Mar10	27Mar10	17Apr12	25Apr12	29Apr12	26Jun10	9Jul10	18Jul12	22Jul12	26Jul12
Al (ng/m³)	5.26 ± 0.05	11.9 ± 0.2	9.6 ± 0.3	6.4 ± 0.2	7.4 ± 0.4	9.43 ± 0.09	3.87 ± 0.04	6.8 ± 0.1	5.5 ± 0.1	7.1 ± 0.3
As (pg/m³)	132 ± 1	62.8 ± 0.6	48 ± 3	24 ± 2	26 ± 3	3.91 ± 0.04	18.3 ± 0.2	10.3 ± 0.9	10.9 ± 0.9	11.6 ± 0.5
Ba (pg/m³)	98 ± 1	190 ± 2	104 ± 4	78 ± 3	105 ± 4	70.2 ± 0.7	44.3 ± 0.4	51 ± 1	64 ± 2	84 ± 2
Ca (ng/m³)	17.6 ± 0.2	25.7 ± 0.3	21.1 ± 0.2	17.3 ± 0.1	29.2 ± 0.2	22.1 ± 0.2	14.2 ± 0.1	17.0 ± 0.2	19.9 ± 0.4	19.6 ± 0.3
Cd (pg/m³)	34.4 ± 0.3	27.8 ± 0.3	5.1 ± 0.8	3.3 ± 0.7	3.7 ± 0.4	9.39 ± 0.09	3.83 ± 0.04	0.22 ± 0.04	1.5 ± 0.2	1.0 ± 0.4
Co (pg/m³)	2.61 ± 0.03	7.75 ± 0.08	3.2 ± 0.2	1.23 ± 0.02	2.36 ± 0.08	4.90 ± 0.05	< 0.052	10.5 ± 0.4	6.8 ± 0.3	5.8 ± 0.3
Cu (pg/m³)	56.6 ± 0.6	19.7 ± 0.2	106 ± 2	43 ± 2	82 ± 2	13.0 ± 0.1	0.32 ± 0.01	44 ± 1	70 ± 2	192 ± 3
Fe (ng/m³)	9.06 ± 0.09	14.3 ± 0.1	8.7 ± 0.2	6.32 ± 0.08	6.74 ± 0.07	9.90 ± 0.09	5.25 ± 0.05	7.3 ± 0.2	5.4 ± 0.2	7.29 ± 0.08
K (ng/m³)	9.08 ± 0.09	12.1 ± 0.1	12.6 ± 0.1	11.79 ± 0.03	20.8 ± 0.2	12.9 ± 0.1	4.35 ± 0.04	8.25 ± 0.07	10.4 ± 0.1	5.7 ± 0.1
Mg (ng/m³)	n.a.	n.a.	38 ± 1	35.2 ± 0.3	68.1 ± 0.9	n.a.	n.a.	24.4 ± 0.5	33.6 ± 0.7	17.0 ± 0.4
Mn (pg/m³)	282 ± 3	387 ± 4	231 ± 5	159 ± 5	191 ± 8	149 ± 1	86.9 ± 0.9	141 ± 2	110 ± 2	144 ± 1
Na (ng/m³)	82.0 ± 0.8	146 ± 1	210 ± 20	220 ± 10	398 ± 5	210 ± 2	145 ± 1	161 ± 4	250 ± 20	80 ± 4
Ni (pg/m³)	76.7 ± 0.8	137 ± 1	77 ± 3	40 ± 3	52 ± 2	93.0 ± 0.9	163 ± 2	396 ± 7	247 ± 9	87 ± 3
Pb (pg/m³)	635 ± 6	437 ± 4	168 ± 6	107 ± 2	109 ± 3	12.1 ± 0.1	12.8 ± 0.1	2.87 ± 0.06	< 0.032	< 0.032
Ti (pg/m³)	207 ± 2	410 ± 4	370 ± 10	278 ± 8	280 ± 10	438 ± 4	184 ± 2	327 ± 5	200 ± 10	259 ± 9
V (pg/m³)	48.2 ± 0.5	48.9 ± 0.5	34 ± 2	26.2 ± 0.8	28 ± 1	104 ± 1	218 ± 2	80.3 ± 0.5	580 ± 20	177 ± 9
Zn (pg/m³)	1380 ± 10	929 ± 9	560 ± 20	300 ± 20	310 ± 10	313 ± 3	561 ± 6	250 ± 10	157 ± 9	350 ± 20

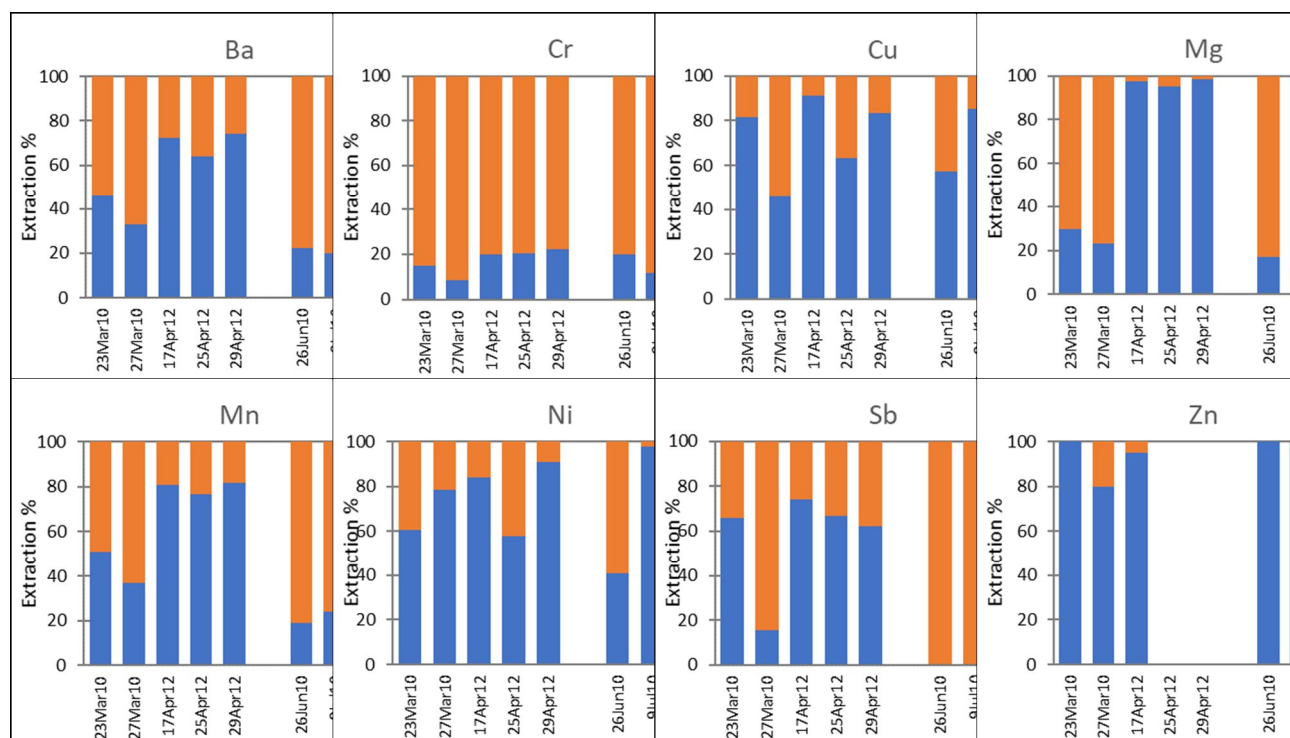


Fig. S1 Extraction percentages obtained for the ten Arctic PM₁₀ samples

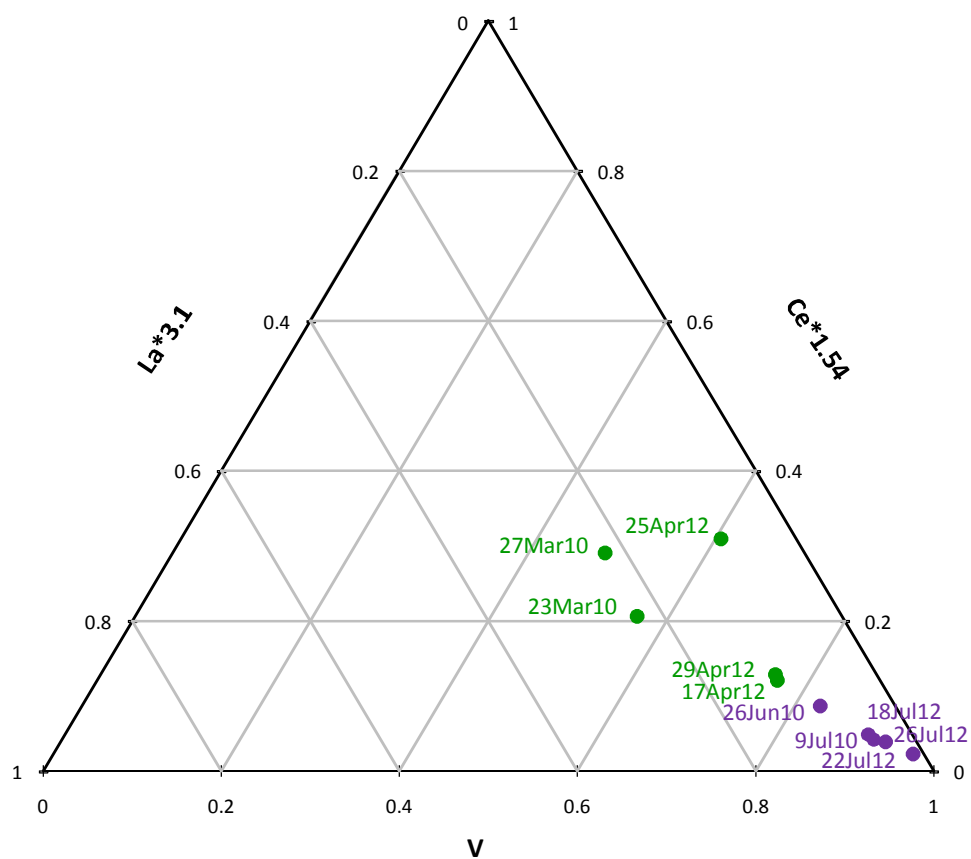


Fig. S2 Ce-La-V ternary diagram for the investigated 2010 and 2012 Arctic PM₁₀ samples

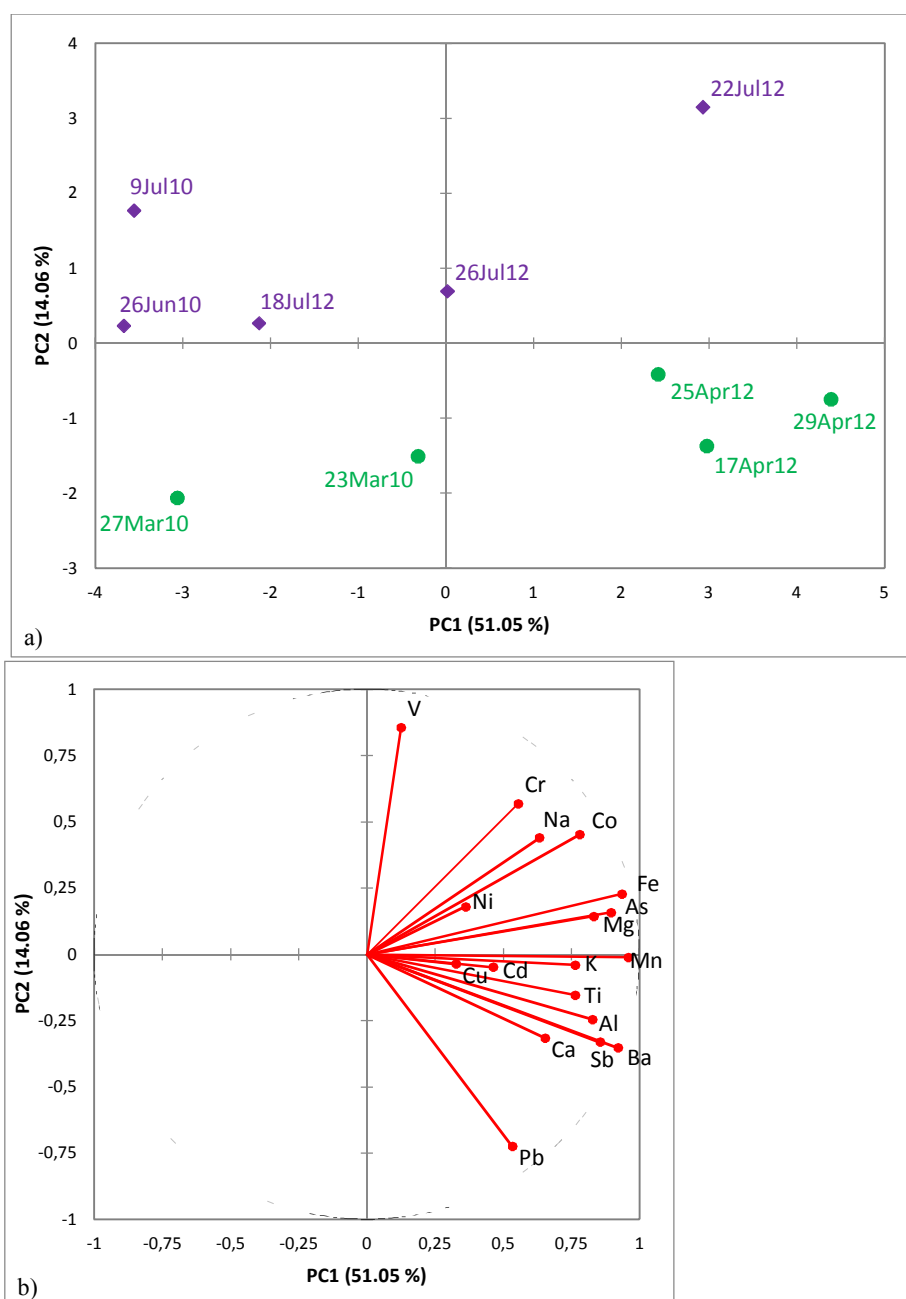


Fig. S3 Principal Component Analysis (PC1 vs. PC2) for the results of the sequential extraction procedure (fraction I) performed on ten PM₁₀ samples collected in Ny-Ålesund in 2010 and 2012: a) score plot; b) loading plot