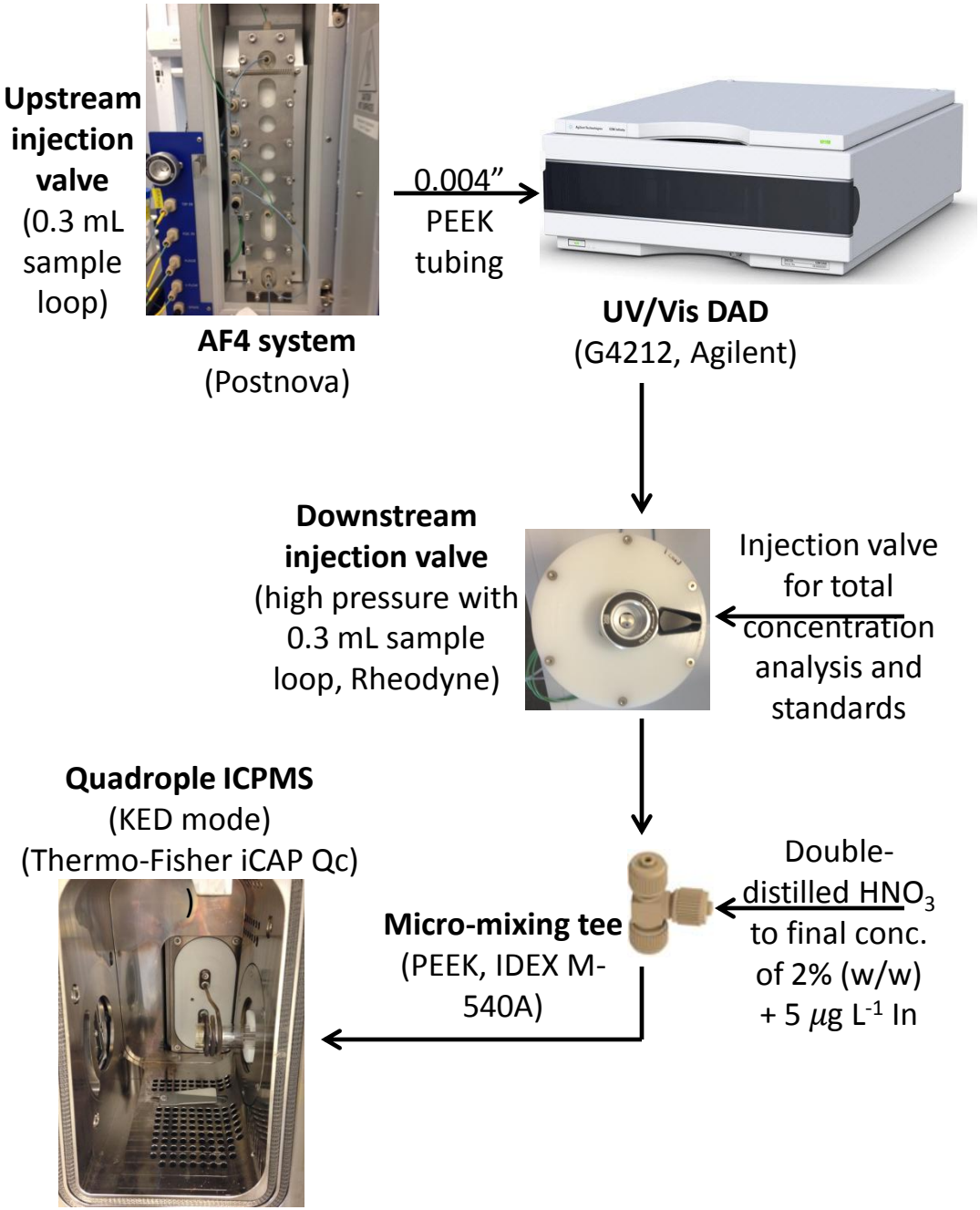

Figure S1- Component schematic for coupling of AF4 to ICPMS.

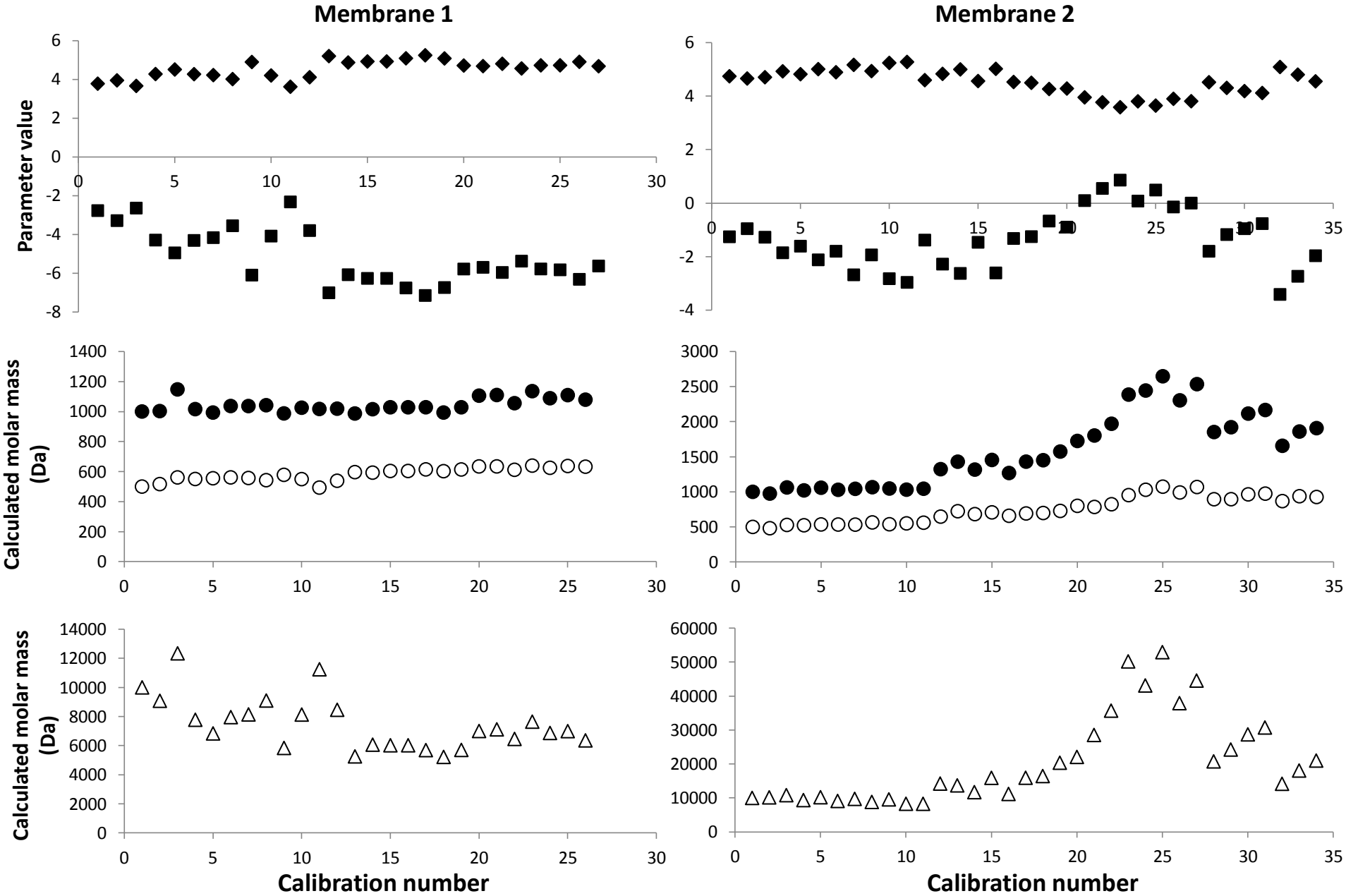

Figure S2- Change in (**upper**) calibration curve parameters (♦ slope, ■ y-intercept) for two 300-Da membranes over time, and (**middle, lower**) corresponding changes in the actual molar mass at fixed retention times. The molar mass calculated for these retention times using the original calibration curve were: (○) 0.50, (●) 1.0, and (△) 10.0 kDa.

Table S1- Measurement accuracy for NIST SRM1640a during over the course of the experiment (n = 4 days). * Element concentration not certified in this standard.

Element	7Li	24Mg	27Al	51V	55Mn	56Fe	59Co	60Ni	63Cu	66Zn	75As	88Sr	89Y	95Mo	137Ba	208Pb	232Th	238U
Measurement accuracy ± 95% CI (%)	97±8	93±2	93±3	96±4	92±2	103±3	96±4	95±4	93±3	90±6	95±3	92±4	*	94±2	89±3	101±2	*	94±4

Table S2- Optimized AF4 flow program and ICPMS settings.

Parameter	Setting
AF4	
Spacer	500 µm PTFE
Sample loop size (mL)	0.3
Injection flow rate (mL min^{-1})	0.2
Crossflow rate (mL min^{-1})	2.1 for 29 min., then linear decrease to 0 over 1 min.
Channel flow rate (mL min^{-1})	0.7
Focussing/elution time (min.)	6/44
ICPMS	
RF power (W)	1550
Nebulizer gas flow rate (L min^{-1})	1.03 (Argon)
Collision cell gas flow (mL min^{-1})	5.0 (Helium)
Cooling gas flow rate (L min^{-1})	14.0
Auxiliary gas flow rate (L min^{-1})	0.8
Spray chamber	Cyclonic, Quartz (Thermo)
Sample and skimmer cone	Ni, with 2.8 mm skimmer insert (Thermo)
Nebulizer	PFA-ST (Elemental Scientific)
Torch	Quartz torch w/ 2.0 mm quartz injector (Thermo)
Dwell time (s)	0.1
Elements/isotopes measured	^{7}Li, ^{24}Mg, ^{27}Al, ^{51}V, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{88}Sr, ^{89}Y, ^{95}Mo, ^{137}Ba, ^{208}Pb, ^{232}Th, ^{238}U
Indium tracer concentration (µg L^{-1})	5

Table S3- $M_p \pm$ 95% CI of size fractions (shaded row, kDa) and associated element distributions (lower row, % of total recovered). The M_p of peaks with t_R < bromophenol blue (M_p = 0.692 kDa) were estimated by extrapolating the linear calibration curve.

Sample	AR15				AR18				SR			
Fraction	1	2	3	4	1	2	3	4	1	2	3	4
DOM	0.95 ± 0.01				0.94 ± 0.03				0.93 ± 0.01			
	48.3 ± 0.3				59.3 ± 6.1				61.9 ± 1.1			
Li	0.39 ± 0.05	-	-	-	0.38 ± 0.08	-	-	-	0.39 ± 0.11	-	-	-
	100	-	-	-	100	-	-	-	100	-	-	-
Mg	0.35 ± 0.02	-	-	-	0.34 ± 0.02	-	-	-	0.46 ± 0.03	-	-	-
	100	-	-	-	100	-	-	-	100	-	-	-
Al	0.45 ± 0.18	-	-	-	0.35 ± 0.01	-	-	-	0.86 ± 0.32	-	-	-
	100	-	-	-	100	-	-	-	100	-	-	-
V	0.33 ± 0.05	-	-	-	0.38 ± 0.03	-	-	-	-	1.24 ± 0.81	-	-
	100	-	-	-	100	-	-	-	-	100	-	-
Mn	0.42 ± 0.01	1.79 ± 0.16	-	-	0.39 ± 0.05	1.82 ± 0.21	-	-	0.76 ± 0.39	2.82 ± 0.79	15.6 ± 2.79	-
	37.0 ± 2.2	57.0 ± 1.5	-	6.0 ± 1.1	37.1 ± 8.2	62.9 ± 8.2	-	-	16.9 ± 9.4	38.6 ± 9.3	40.5 ± 1.6	4.0 ± 0.4
Fe	0.31 ± 0.02	3.20 ± 0.03	-	-	0.24 ± 0.02	3.50 ± 0.12	-	-	0.25 ± 0.01	2.89 ± 0.04	14.7 ± 0.52	-
	5.1 ± 0.3	63.4 ± 0.4	-	31.5 ± 1.2	6.4 ± 1.8	44.7 ± 11.8	-	48.9 ± 13.6	9.6 ± 0.6	26.9 ± 1.8	33.0 ± 1.3	30.5 ± 3.4
Co	0.44 ± 0.04	2.02 ± 0.14	-	-	0.41 ± 0.01	2.25 ± 0.07	-	-	0.33 ± 0.12	2.16 ± 0.10	-	-
	19.4 ± 6.9	80.6 ± 6.9	-	-	12.7 ± 3.2	87.3 ± 3.2	-	-	7.4 ± 9.3	92.6 ± 9.3	-	-
Ni	0.41 ± 0.03	1.51 ± 0.15	-	-	0.40 ± 0.02	2.18 ± 0.12	-	-	0.33 ± 0.06	2.14 ± 0.23	-	-
	10.0 ± 2.1	90.0 ± 2.1	-	-	10.4 ± 1.6	89.6 ± 1.6	-	-	3.4 ± 3.7	96.6 ± 3.7	-	-
Cu	0.37 ± 0.02	2.04 ± 0.03	-	-	0.28 ± 0.01	2.54 ± 0.09	-	-	0.28 ± 0.06	2.11 ± 0.17	-	-
	6.6 ± 1.1	93.4 ± 1.1	-	-	2.7 ±0.6	97.3 ± 0.6	-	-	2.4 ± 2.1	97.6 ± 2.1	-	-
Zn	0.43 ± 0.02	2.28 ± 0.04	-	-	0.38 ± 0.02	2.46 ± 0.15	-	-	0.32 ± 0.02	2.37 ± 0.04	-	-
	11.4 ± 0.6	88.6 ± 0.6	-	-	11.1 ± 1.1	88.9± 1.1	-	-	7.1 ± 1.3	92.9 ± 1.3	-	-
As	0.45 ± 0.14	1.76 ± 0.69	-	-	0.44 ± 0.20	2.49 ± 1.46	-	-	0.38 ± 0.02	1.63 ± 0.06	-	-
	49.9 ± 36.4	50.1 ± 36.4	-	-	41.4 ± 14.8	58.6 ± 14.8	-	-	11.0 ± 16.1	89.0 ± 16.1	-	-
Sr	0.46 ± 0.01	2.10 ± 0.12	-	-	0.45 ± 0.04	2.55 ± 0.55	-	-	0.84 ± 0.01	5.29 ± 0.41	-	-
	68.7 ± 2.2	31.3 ± 2.2	-	-	69.1 ± 0.1	30.9 ± 0.1	-	-	72.8 ± 2.4	27.2 ± 2.4	-	-
Y	0.34 ± 0.03	2.41 ± 0.14	-	-	0.26 ± 0.01	2.96 ± 0.32	-	-	0.33 ± 0.03	2.42 ± 0.18	-	-
	4.2 ± 0.2	93.1 ±0.3	-	2.7 ± 0.1	3.5 ± 1.3	89.7 ± 8.0	-	6.8 ± 9.3	3.4 ± 0.9	94.1 ± 1.1	-	2.5 ± 0.2
Mo	0.39 ± 0.03	2.67 ± 0.28	-	-	0.35 ± 0.05	2.11 ± 0.40	-	-	0.59 ± 0.02	3.03 ± 0.69	-	-
	85.6 ± 2.4	14.4 ± 2.4	-	-	82.1 ± 5.6	17.9 ± 5.6	-	-	68.0 ± 1.4	32.0 ± 1.4	-	-
Ba	0.87 ± 0.04	3.13 ± 0.20	16.0 ± 0.80	-	0.79 ± 0.10	3.26 ± 0.59	19.5 ± 4.76	-	-	2.53 ± 0.26	15.7 ± 0.57	-
	17.2 ± 0.7	33.2 ± 0.6	49.6 ± 0.9	-	17.6 ± 0.2	35.6 ± 1.7	46.7 ± 1.8	-	-	39.5 ± 2.7	60.5 ± 2.7	-
Pb	0.37 ± 0.24	3.41 ± 0.48	-	-	0.24 ± 0.02	3.87 ± 0.26	-	-	0.30 ± 0.05	3.42 ± 0.40	17.0 ± 1.4	-
	4.9 ± 2.2	30.7 ± 3.9	-	64.4 ± 1.7	15.8 ± 9.9	34.2 ± 10.4	-	50.1 ± 20.1	3.3 ± 1.8	9.5 ± 4.1	27.9 ± 0.9	59.3 ± 6.3
Th	0.37 ± 0.02	3.14 ± 0.11	-	-	0.41 ± 0.03	2.95 ± 0.07	-	-	0.42 ± 0.00	3.23 ± 0.16	-	-
	4.3 ± 6.5	81.3 ± 3.9	-	14.3 ± 4.7	12.8 ± 4.7	87.2 ± 4.7	-	-	6.6 ± 13.0	84.0 ± 12.6	-	9.4 ± 0.4
U	0.42 ± 0.02	3.53 ± 0.12	-	-	0.35 ± 0.01	3.72 ± 0.92	-	-	0.93 ± 0.10	2.91 ± 0.70	13.6 ± 3.8	-
	14.2 ± 9.9	85.8 ± 9.9	-	-	18.8 ± 6.8	81.2 ± 6.8	-	-	33.6 ± 6.4	36.8 ± 1.4	29.7 ± 5.3	-

Table S4- Total concentrations and percentage recovered for DOM and trace elements (± 95% CI).

	Sample AR15		Sample AR18		Sample SR	
	Total (μg L^{-1})	**Recovery (%)**	**Total (μg L^{-1})**	**Recovery (%)**	**Total (μg L^{-1})**	**Recovery (%)**
DOM (mg C L^{-1})	4.2 (0.1)	48.3 (0.3)	4.8 (0.1)	59.3 (6.1)	22.0 (0.5)	61.9 (1.1)
Li	4.13 (0.24)	1.6 (0.2)	5.75 (1.32)	1.5 (0.1)	11.9 (0.1)	2.6 (0.3)
Mg	$8.60 \cdot 10^3$ ($0.47 \cdot 10^3$)	3.2 (0.2)	$10.7 \cdot 10^3$ ($1.7 \cdot 10^3$)	2.5 (0.1)	$7.3 \cdot 10^3$ ($0.20 \cdot 10^3$)	6.3 (0.2)
Al	2.91 (0.13)	8.8 (0.2)	3.05 (0.09)	9.4 (10.5)	7.57 (4.56)	19.4 (10.1)
V	0.104 (0.004)	11.3 (1.3)	0.136 (0.017)	15.6 (5.6)	0.230 (0.094)	9.7 (3.4)
Mn	0.922 (0.324)	8.5 (1.9)	0.317 (0.131)	13.3 (9.0)	7.49 (1.82)	14.6 (3.8)
Fe	8.94 (4.97)	36.7 (15.8)	14.5 (1.7)	28.3 (6.3)	435 (65)	20.7 (2.4)
Co	0.048 (0.007)	22.3 (2.8)	0.050 (0.017)	40.2 (20.1)	0.148 (0.039)	50.6 (15.5)
Ni	0.867 (0.089)	45.8 (4.0)	0.938 (0.142)	45.3 (25.0)	4.54 (2.19)	78.0 (53.0)
Cu	0.831 (0.003)	47.0 (0.3)	1.53 (0.10)	37.9 (5.0)	1.214 (0.639)	103.3 (4.5)
Zn	1.48 (0.03)	74.1 (2.8)	8.35 (1.66)	56.3 (54.4)	8.24 (0.23)	128.9 (7.7)
As	0.217 (0.007)	11.2 (2.1)	0.313 (0.008)	8.5 (1.5)	0.530 (0.041)	22.5 (6.9)
Sr	216 (10)	4.2 (0.2)	264 (9)	3.8 (0.4)	88.4 (3.8)	12.1 (0.5)
Y	0.276 (0.014)	101.8 (7.0)	0.070 (0.030)	99.2 (8.3)	3.86 (0.67)	84.0 (11.4)
Mo	0.712 (0.006)	25.3 (0.5)	0.675 (0.036)	21.2 (1.5)	0.541 (0.455)	118.9 (7.8)
Ba	31.9 (1.9)	14.2 (0.6)	44.8 (2.1)	12.1 (1.4)	10.3 (1.1)	58.2 (7.8)
Pb	0.009 (0.003)	37.3 (11.9)	0.107 (0.034)	27.1 (19.8)	0.146 (0.146)	31.6 (21.4)
Th	0.004 (0.001)	33.7 (1.8)	0.012 (0.011)	21.9 (16.2)	0.042 (0.017)	17.9 (5.8)
U	0.344 (0.013)	7.3 (0.3)	0.419 (0.026)	6.9 (2.8)	0.063 (0.006)	50.8 (3.2)

Table S5- LODs ($\mu g\ L^{-1}$) for various elements by analysis day and range of LODs from literature (see discussion in SI for referenced studies).

Day	Li	Mg	Al	V	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Y	Mo	Ba	Pb	Th	U
1	0.069	0.806	1.838	0.038	0.107	2.077	0.039	0.596	1.120	0.294	0.013	0.073	0.135	0.018	0.039	0.166	1.051	0.026
2	0.005	0.443	2.295	0.019	0.221	0.991	0.121	0.333	0.138	3.858	0.022	0.023	0.106	0.015	0.031	0.110	0.984	0.014
3	0.153	1.173	0.705	0.003	0.120	0.694	0.080	0.110	0.073	3.870	0.038	0.083	0.061	0.017	0.162	0.075	0.490	0.102
4	0.037	2.667	0.188	0.010	0.064	0.599	0.017	0.323	0.403	1.009	0.027	0.110	0.042	0.035	0.107	0.103	0.040	0.038
Lit. Max.	0.003	0.4	20	0.003	0.006	300	0.001	0.05	0.6	0.06	0.008	0.01	0.9	0.02	0.04	0.1	0.1	0.07
Lit. Min.	0.003	0.2	0.04	0.003	0.004	0.03	0.0008	0.01	0.005	0.03	0.003	0.0004	0.0001	0.01	0.01	0.002	0.0002	0.0002