Supplementary Information

Spatiotemporal variabilities of major, minor and trace elements in the German part of river Rhine

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1. Methods and Materials

Figure S 1: Sampling devices for the short-term temporal variability campaigns (pictures were taken within the project by different project members).

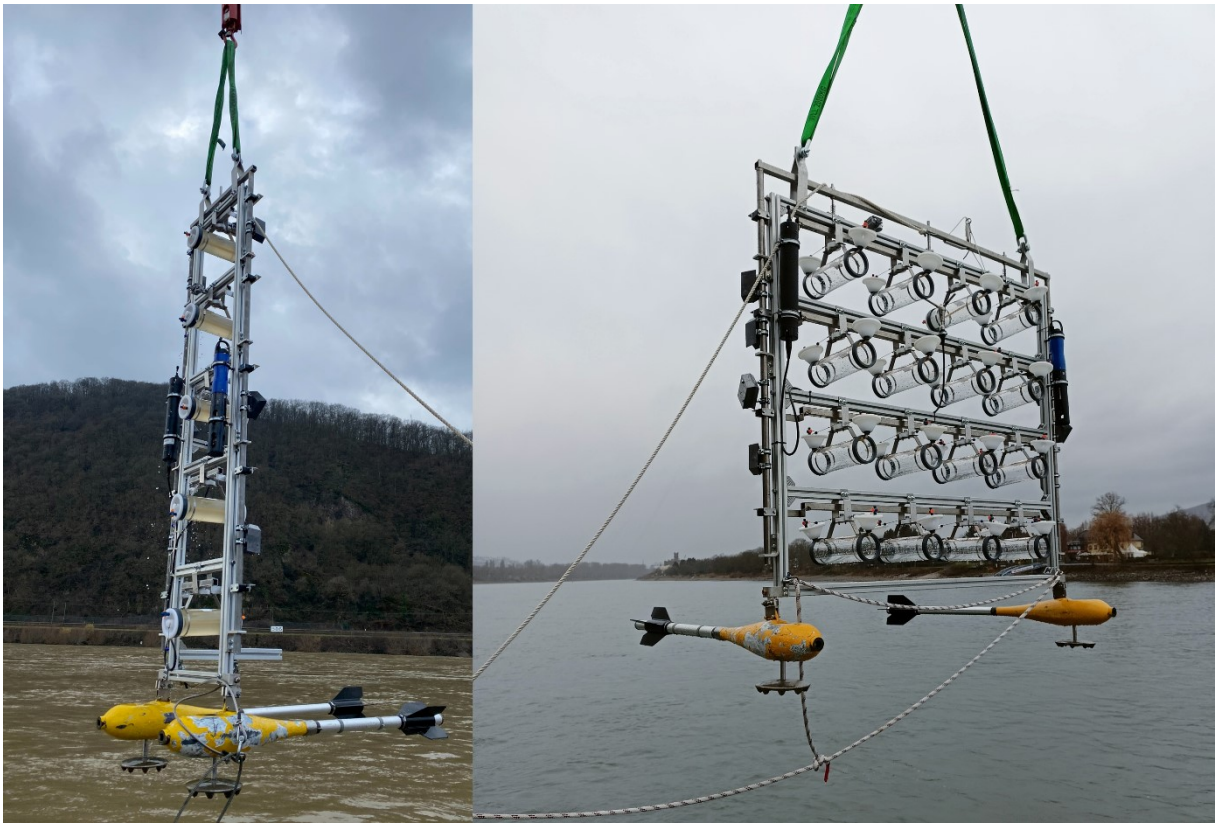


Figure S 2: Sampling devices for the spatial variability campaigns (pictures were taken within the project by different project members).

2. **One-year temporal data Koblenz-Rhine (section 3.1.1 of the manuscript)**

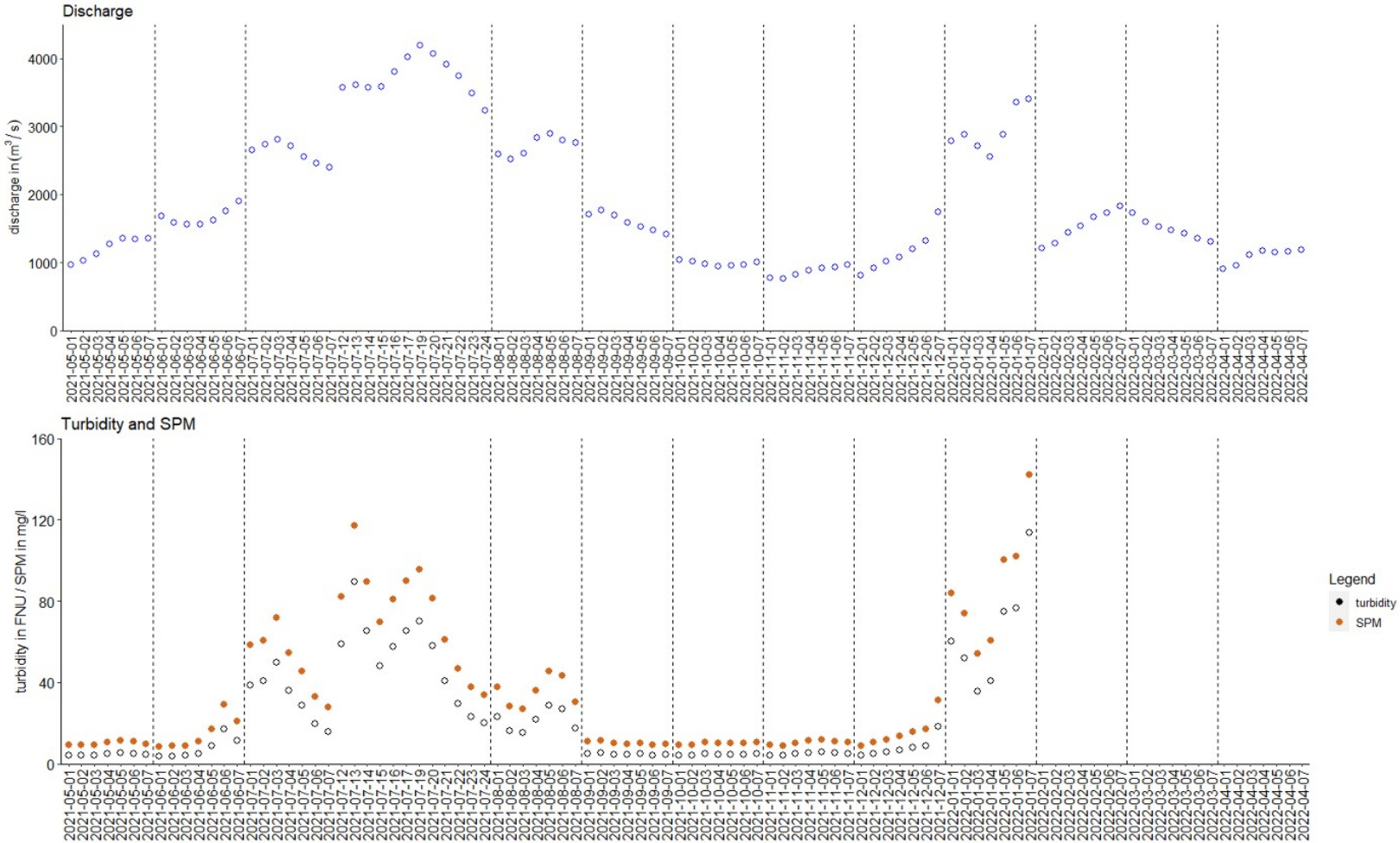


Figure S 3: Discharge (upper panel) as well as turbidity and SPM data (lower panel) for the one-year data between May 2021 and April 2022 of the station Koblenz-Rhine. Turbidity data and the corresponding SPM concentration (calculated from the turbidity data) were not available from February to April 2022.

Table S 1: Pearson correlation coefficients of the one-year temporal data of the whole water samples at the station Koblenz-Rhine.

	Dis-charge	B	P	S	K	Ca	V	Mn	Fe	Co	Ni	Cu	Ga	As	Br	Rb	Sr	Y	Mo	Cs	Ba	La	Ce	Pr	Nd	Sm	Gd	Pb	Th
B	-0.35																												
P	0.47	0.09																											
S	-0.80	0.78	-0.22																										
K	0.005	0.77	0.37	0.41																									
Ca	-0.20	0.66	0.28	0.52	0.60																								
V	0.80	-0.06	0.79	-0.65	0.38	0.10																							
Mn	0.58	-0.10	0.78	-0.51	0.34	0.15	0.90																						
Fe	0.81	-0.14	0.79	-0.66	0.28	0.04	0.99	0.92																					
Co	0.77	-0.12	0.79	-0.62	0.32	0.13	0.98	0.95	0.99																				
Ni	0.78	-0.14	0.78	-0.69	0.24	-0.01	0.99	0.92	0.99	0.99																			
Cu	0.39	-0.27	0.33	-0.44	-0.08	0.02	0.45	0.46	0.47	0.44	0.51																		
Ga	0.81	-0.11	0.79	-0.66	0.38	0.09	0.99	0.90	1.00	0.98	0.99	0.46																	
As	0.60	-0.13	0.84	-0.49	0.29	0.21	0.87	0.82	0.80	0.84	0.81	0.46	0.81																
Br	-0.78	0.55	-0.13	0.75	0.21	0.25	-0.60	-0.54	-0.69	-0.61	-0.68	-0.33	-0.67	-0.35															
Rb	0.74	-0.01	0.81	-0.54	0.39	0.15	0.99	0.90	0.96	0.96	0.97	0.44	0.97	0.90	-0.52														
Sr	-0.56	0.68	0.13	0.80	0.44	0.82	-0.27	-0.17	-0.32	-0.29	-0.37	-0.16	-0.32	-0.10	0.45	-0.21													
Y	0.77	-0.09	0.78	-0.60	0.37	0.12	0.99	0.94	0.98	0.99	0.98	0.46	0.98	0.88	-0.59	0.98	-0.29												
Mo	-0.60	0.30	0.18	0.50	0.16	0.45	-0.10	0.08	-0.18	-0.15	-0.20	0.23	-0.12	0.10	0.20	-0.12	0.64	-0.15											
Cs	0.69	-0.15	0.94	-0.61	0.35	0.12	0.96	0.94	0.96	0.97	0.95	0.47	0.96	0.87	-0.59	0.95	-0.28	0.97	0.03										
Ba	0.32	0.51	0.64	-0.02	0.79	0.60	0.69	0.69	0.66	0.70	0.63	0.18	0.63	0.63	-0.07	0.73	0.25	0.69	0.06	0.70									
La	0.51	-0.12	0.74	-0.48	0.27	0.11	0.83	0.97	0.86	0.89	0.84	0.50	0.83	0.80	-0.43	0.85	-0.18	0.88	0.06	0.92	0.67								
Ce	0.74	-0.19	0.92	-0.67	0.35	0.02	0.98	0.93	0.99	0.98	0.98	0.43	0.98	0.83	-0.68	0.96	-0.39	0.98	-0.20	0.96	0.68	0.88							
Pr	0.73	-0.19	0.88	-0.68	0.34	0.00	0.96	0.91	0.99	0.98	0.98	0.42	0.98	0.77	-0.70	0.93	-0.37	0.97	-0.12	0.94	0.66	0.83	1.00						
Nd	0.74	-0.18	0.74	-0.70	0.31	-0.08	0.98	0.93	0.97	0.98	0.96	0.40	0.97	0.86	-0.63	0.97	-0.49	0.99	-0.29	0.97	0.71	0.90	0.99	0.98					
Sm	0.71	-0.18	0.65	-0.61	0.29	0.04	0.98	0.91	0.97	0.98	0.97	0.38	0.98	0.82	-0.59	0.97	-0.37	0.99	-0.10	0.96	0.64	0.86	0.99	0.98	1.00				
Gd	0.77	-0.14	0.77	-0.66	0.28	0.05	0.98	0.94	0.98	0.99	0.98	0.48	0.98	0.85	-0.61	0.98	-0.38	0.99	-0.16	0.97	0.69	0.90	0.99	0.98	0.99	0.99			
Pb	0.66	-0.16	0.76	-0.65	0.34	0.05	0.97	0.95	0.98	0.99	0.98	0.51	0.98	0.83	-0.69	0.95	-0.41	0.98	-0.12	0.98	0.70	0.92	0.99	0.98	0.98	0.98	0.99		
Th	0.71	-0.19	0.68	-0.68	0.31	-0.07	0.96	0.92	0.96	0.96	0.96	0.51	0.97	0.80	-0.60	0.94	-0.46	0.97	-0.19	0.97	0.66	0.88	0.98	0.98	0.99	0.99	0.98	0.97	
U	-0.43	0.58	0.08	0.62	0.49	0.89	0.25	0.10	0.24	0.25	0.17	0.20	0.18	0.23	0.78	0.35	0.89	0.20	0.51	0.07	0.68	0.14	-0.08	-0.12	-0.27	-0.23	0.10	-0.22	-0.26

Table S 2: p-values of the Pearson correlation coefficients of Table S1. All values with p > 0.05 are marked in bold font and with an underline.

	Dis-charge	B	P	S	K	Ca	V	Mn	Fe	Co	Ni	Cu	Ga	As	Br	Rb
B	1.17E-26															
P	6.02E-26	4.38E-07														
S	1.35E-30	7.72E-33	9.57E-33													
K	6.25E-28	8.62E-59	2.14E-60	6.23E-26												
Ca	5.60E-60	2.72E-59	2.80E-59	8.51E-71	3.39E-58											
V	4.63E-27	5.27E-47	2.62E-11	6.84E-33	5.15E-59	2.64E-59										
Mn	2.21E-26	4.80E-04	3.33E-03	8.41E-33	1.84E-59	2.75E-59	1.13E-11									
Fe	4.54E-05	1.68E-10	1.03E-09	4.69E-33	1.04E-28	1.68E-61	6.95E-11	3.45E-10								
Co	4.25E-27	5.01E-42	1.11E-11	6.76E-33	4.93E-59	2.64E-59	2.14E-10	2.06E-12	6.40E-11							
Ni	4.55E-27	1.01E-44	2.19E-11	6.82E-33	5.11E-59	2.64E-59	**1.90E-01**	7.89E-12	6.83E-11	7.56E-11						
Cu	5.92E-27	1.62E-36	3.27E-10	7.06E-33	5.75E-59	2.66E-59	1.20E-12	1.66E-09	8.80E-11	2.50E-18	4.65E-14					
Ga	4.23E-27	5.42E-42	1.07E-11	6.76E-33	4.92E-59	2.64E-59	6.00E-11	1.92E-12	6.37E-11	**1.80E-01**	1.48E-11	1.55E-18				
As	4.37E-27	1.84E-41	1.46E-11	6.78E-33	5.01E-59	2.64E-59	2.44E-06	3.54E-12	6.57E-11	5.88E-15	1.38E-05	1.13E-16	2.21E-19			
Br	6.73E-03	1.18E-35	1.19E-36	2.60E-30	9.37E-53	6.45E-59	4.68E-36	4.10E-36	4.90E-03	4.31E-36	4.61E-36	5.84E-36	4.30E-36	4.43E-36		
Rb	4.92E-27	3.97E-45	4.90E-11	6.89E-33	5.34E-59	2.65E-59	1.23E-04	3.84E-11	7.37E-11	1.30E-20	5.65E-08	1.47E-08	4.52E-21	1.91E-16	4.98E-36	
Sr	1.72E-22	3.30E-49	1.48E-30	2.55E-32	4.32E-57	3.60E-59	8.08E-51	1.01E-57	8.15E-07	8.09E-51	9.09E-51	2.56E-51	7.97E-51	9.40E-51	1.07E-31	1.15E-50
Y	4.25E-27	4.39E-42	1.12E-11	6.76E-33	4.93E-59	2.64E-59	3.27E-10	2.11E-12	6.40E-11	**7.11E-01**	1.32E-10	2.89E-18	**9.92E-02**	4.40E-13	4.32E-36	1.75E-20
Mo	4.30E-27	1.67E-41	1.25E-11	6.77E-33	4.96E-59	2.64E-59	1.13E-08	2.60E-12	6.47E-11	2.25E-06	1.26E-08	1.33E-17	2.21E-11	1.21E-08	4.37E-36	9.69E-19
Cs	4.25E-27	6.06E-42	1.11E-11	6.76E-33	4.93E-59	2.64E-59	2.15E-10	2.06E-12	6.40E-11	**9.74E-01**	7.64E-11	2.56E-18	**1.40E-01**	6.05E-16	4.31E-36	1.48E-20
Ba	2.18E-26	1.13E-26	2.48E-04	8.37E-33	1.20E-58	2.78E-59	8.07E-52	**5.19E-01**	3.01E-10	2.50E-48	4.84E-50	3.61E-55	2.57E-48	6.20E-48	2.18E-35	1.15E-50
La	4.39E-27	3.09E-43	1.53E-11	6.79E-33	5.02E-59	2.64E-59	3.18E-05	3.86E-12	6.59E-11	6.15E-07	4.40E-04	1.91E-16	3.52E-08	**4.53E-01**	4.45E-36	2.64E-15
Ce	4.41E-27	2.55E-44	1.62E-11	6.79E-33	5.03E-59	2.64E-59	3.82E-04	4.37E-12	6.63E-11	1.90E-06	6.61E-03	4.73E-16	2.43E-07	**1.47E-01**	4.47E-36	1.76E-13
Pr	4.20E-27	5.43E-42	9.93E-12	6.75E-33	4.90E-59	2.64E-59	4.56E-12	1.65E-12	6.33E-11	4.66E-06	5.98E-13	5.66E-19	1.93E-04	2.76E-26	4.26E-36	5.19E-22
Nd	4.29E-27	2.26E-42	1.23E-11	6.77E-33	4.96E-59	2.64E-59	1.09E-08	2.53E-12	6.46E-11	1.03E-02	1.51E-08	9.94E-18	4.26E-04	8.10E-05	4.36E-36	3.59E-19
Sm	4.20E-27	5.49E-42	9.88E-12	6.75E-33	4.90E-59	2.64E-59	3.93E-12	1.63E-12	6.32E-11	1.66E-06	5.01E-13	5.34E-19	6.30E-05	2.32E-26	4.26E-36	4.63E-22
Gd	4.19E-27	5.46E-42	9.75E-12	6.75E-33	4.89E-59	2.64E-59	2.54E-12	1.59E-12	6.32E-11	9.55E-08	2.96E-13	4.49E-19	2.43E-06	9.42E-27	4.26E-36	3.23E-22
Pb	4.40E-27	7.31E-44	1.57E-11	6.79E-33	5.02E-59	2.64E-59	1.07E-04	4.07E-12	6.61E-11	3.10E-06	1.76E-03	2.78E-16	3.52E-07	**2.96E-01**	4.46E-36	2.19E-14
Th	4.21E-27	5.76E-42	1.01E-11	6.75E-33	4.90E-59	2.64E-59	7.82E-12	1.70E-12	6.34E-11	7.50E-05	1.17E-12	7.03E-19	3.19E-03	2.35E-25	4.27E-36	8.50E-22
U	4.27E-27	1.31E-41	1.16E-11	6.76E-33	4.94E-59	2.64E-59	7.62E-10	2.23E-12	6.42E-11	**6.70E-02**	3.96E-10	4.53E-18	6.99E-05	3.52E-15	4.33E-36	7.60E-20

Table S 2 continued.

	Sr	Y	Mo	Cs	Ba	La	Ce	Pr	Nd	Sm	Gd	Pb	Th
Sr													
Y	8.10E-51												
Mo	8.76E-51	6.71E-05											
Cs	8.13E-51	**7.18E-01**	2.81E-07										
Ba	2.40E-48	2.32E-48	5.45E-48	2.80E-48									
La	8.68E-51	1.70E-06	6.35E-04	5.26E-07	5.02E-49								
Ce	8.34E-51	3.89E-06	4.37E-04	1.78E-06	9.97E-50	**4.82E-01**							
Pr	7.71E-51	4.25E-06	1.02E-27	4.25E-07	2.48E-48	9.88E-11	3.48E-09						
Nd	8.32E-51	2.60E-02	**7.07E-01**	8.86E-03	1.61E-48	1.30E-03	6.22E-04	1.01E-07					
Sm	7.69E-51	1.71E-06	1.89E-28	1.20E-07	2.49E-48	6.99E-11	2.70E-09	**7.19E-01**	5.85E-08				
Gd	7.65E-51	1.38E-07	2.87E-31	4.01E-09	2.46E-48	2.63E-11	1.32E-09	**1.18E-01**	1.32E-08	**2.07E-01**			
Pb	8.45E-51	6.63E-06	9.17E-04	2.87E-06	1.96E-49	**7.54E-01**	**7.02E-01**	4.16E-09	1.36E-03	3.21E-09	1.53E-09		
Th	7.77E-51	5.34E-05	3.86E-26	1.14E-05	2.59E-48	3.22E-10	8.30E-09	**2.38E-01**	5.67E-07	**1.14E-01**	4.74E-03	1.03E-08	
U	8.41E-51	**2.36E-01**	6.42E-09	4.37E-02	4.53E-48	4.03E-06	9.33E-06	9.01E-21	**6.52E-02**	4.25E-22	1.99E-32	1.62E-05	5.93E-19

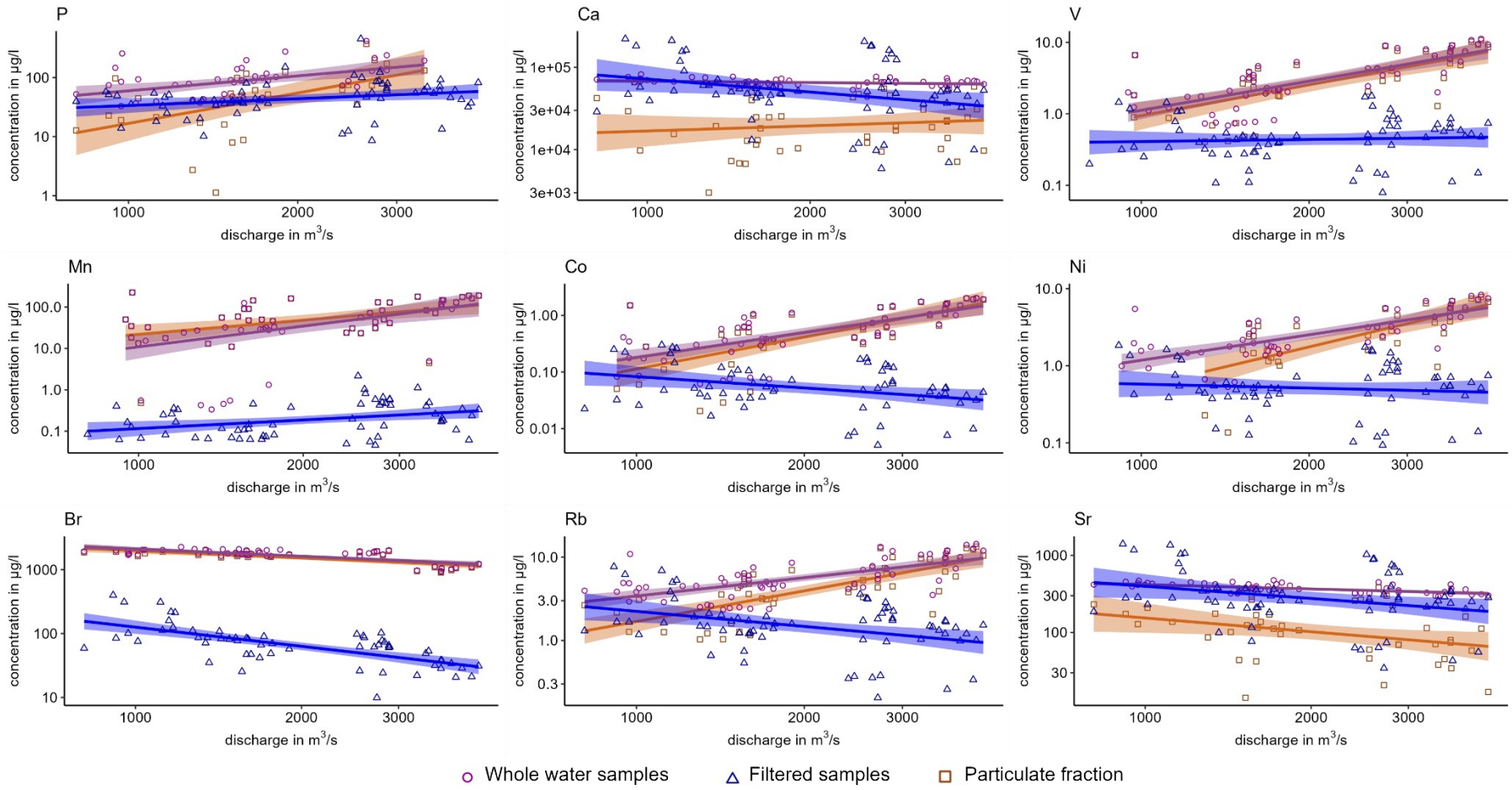


Figure S 4: Concentration-discharge (c-Q) plots (logarithmic scale, base 10) as log-linear regression with a confidence interval of 95% in a lighter shade of the elements P, Ca, V, Mn, Co, Ni, Br, Rb and Sr of the one-year data for water samples from the Koblenz-Rhine station (first seven days of each month between May 2021 and April 2022, n = 84). The particulate fraction was calculated based on the available data for the filtered and whole water fraction.

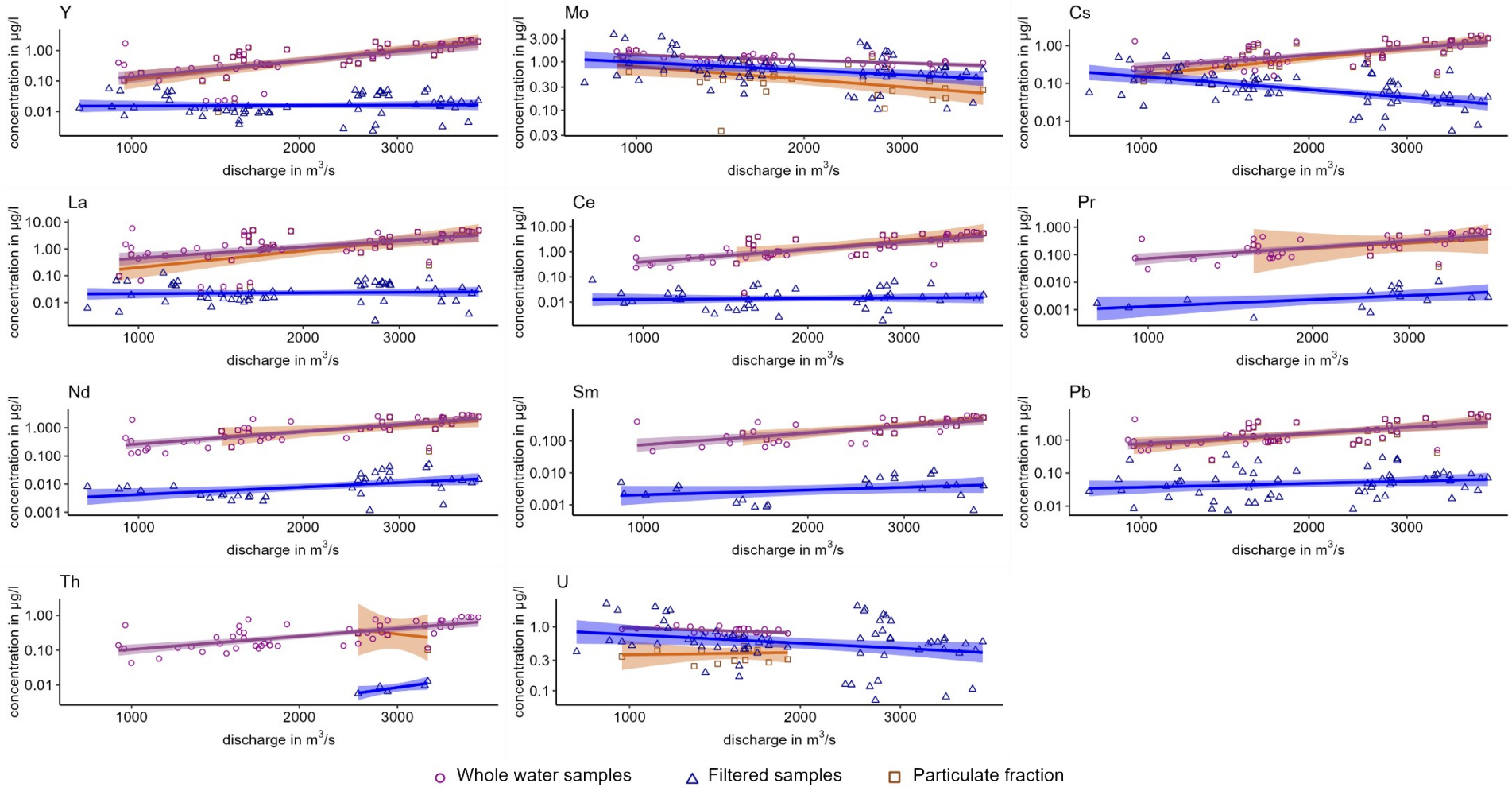


Figure S 5: Concentration-discharge (c-Q) plots (logarithmic scale, base 10) as log-linear regression with a confidence interval of 95% in a lighter shade of the elements Y, Mo, Cs, La, Ce, Pr, Nd, Sm, Pb, Th and U of the one-year data for water samples from the Koblenz-Rhine station (first seven days of each month between May 2021 and April 2022, n = 84). The particulate fraction was calculated based on the available data for the filtered and whole water fraction.

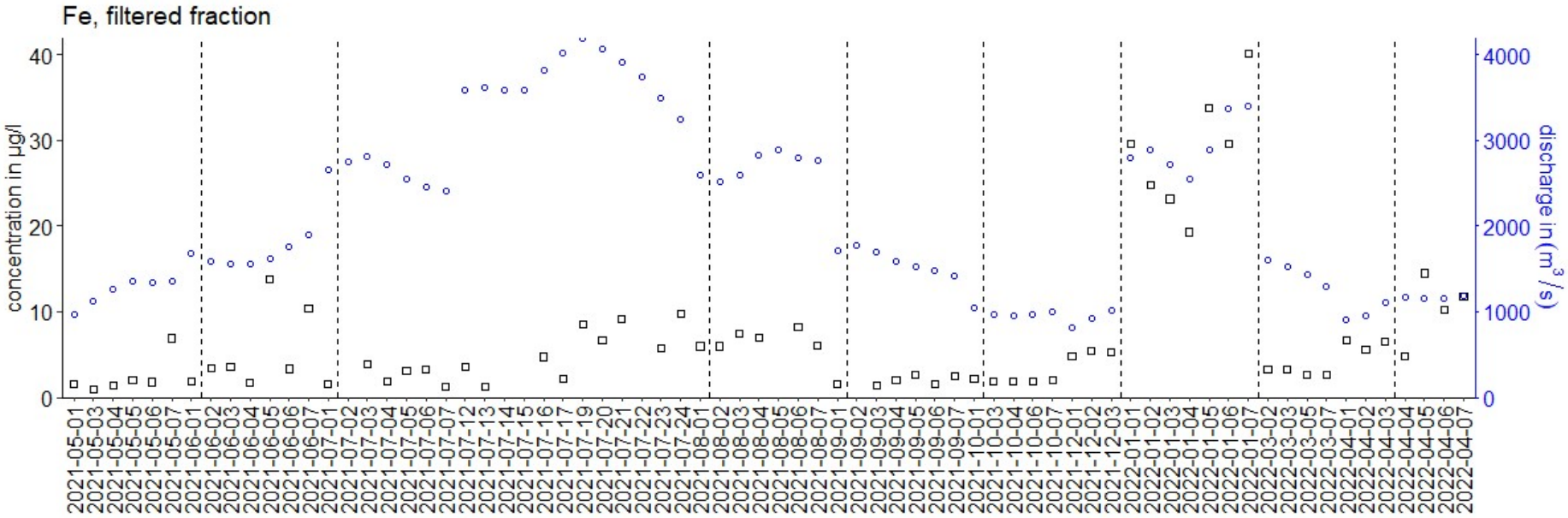
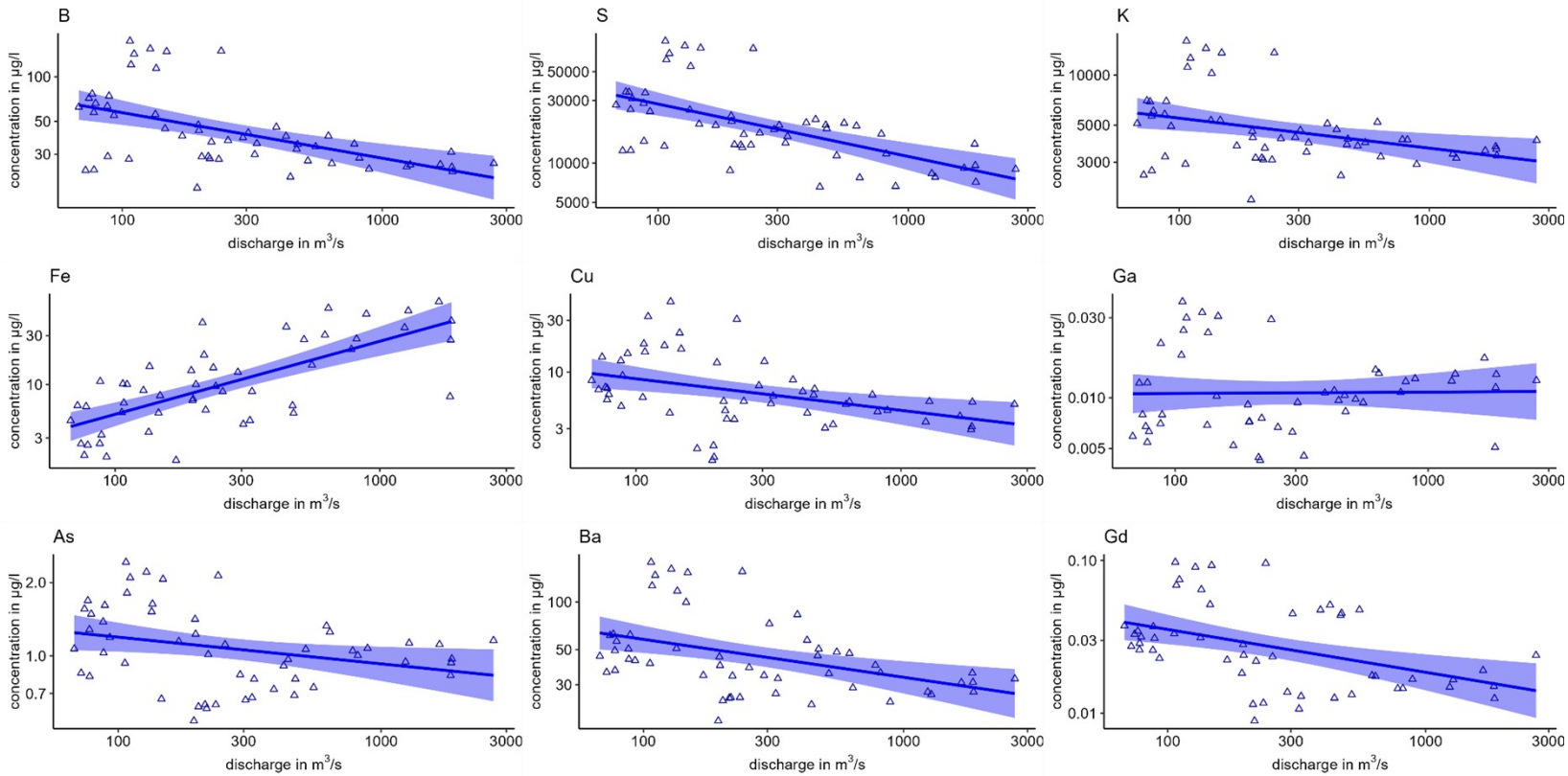


Figure S 6: Fe concentration in µg/l in the filtered fraction (<0.45 µm) as black squares and discharge in m^3/s as blue circles of the one-year temporal data between May 2021 and April 2022 of the station Koblenz-Rhine.

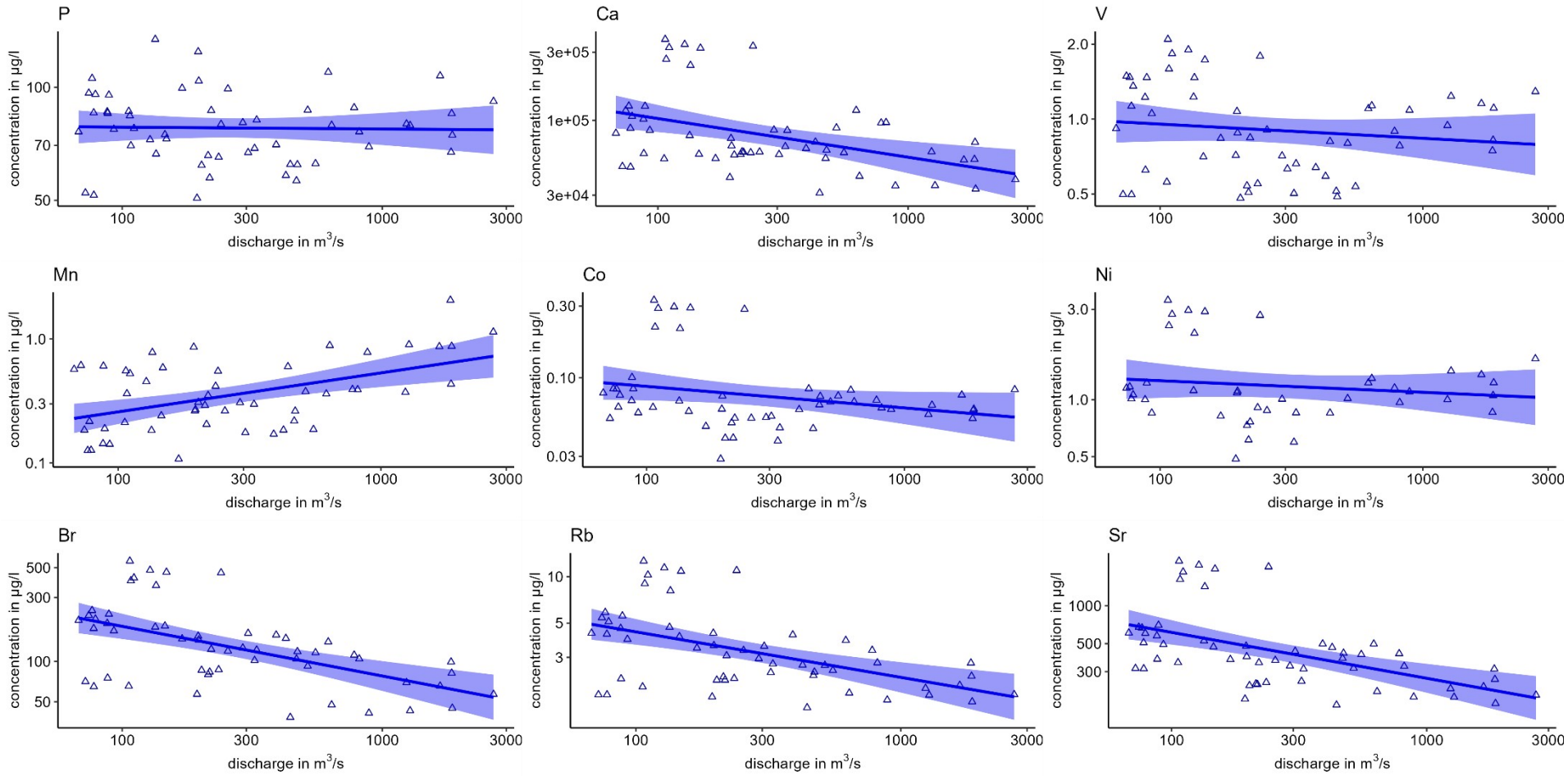
3. One-year temporal data of the filtered fraction for Koblenz-Moselle, Wesel-Rhine and Weil-Rhine (section 3.1.1 of the manuscript)

The figures of this section reflect concentration-discharge (c-Q) plots (logarithmic scale, base 10) as log-linear regression with a confidence interval of 95% in a lighter shade of the one-year data for filtered water samples (<0.45 µm) from the stations Koblenz-Moselle, Wesel-Rhine and Weil-Rhine (first seven days of each month between May 2021 and April 2022, n = 84).

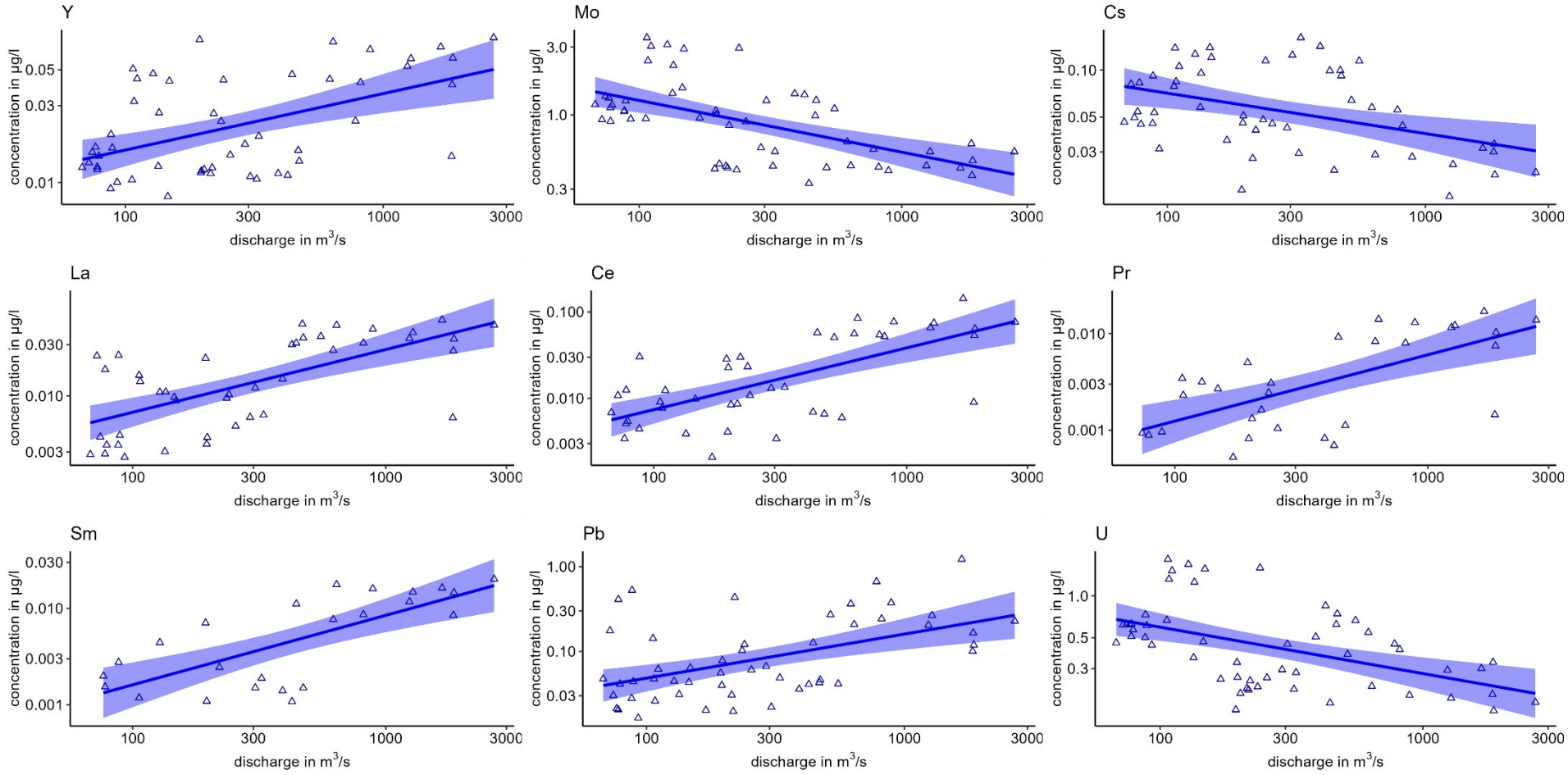
Koblenz-Moselle:



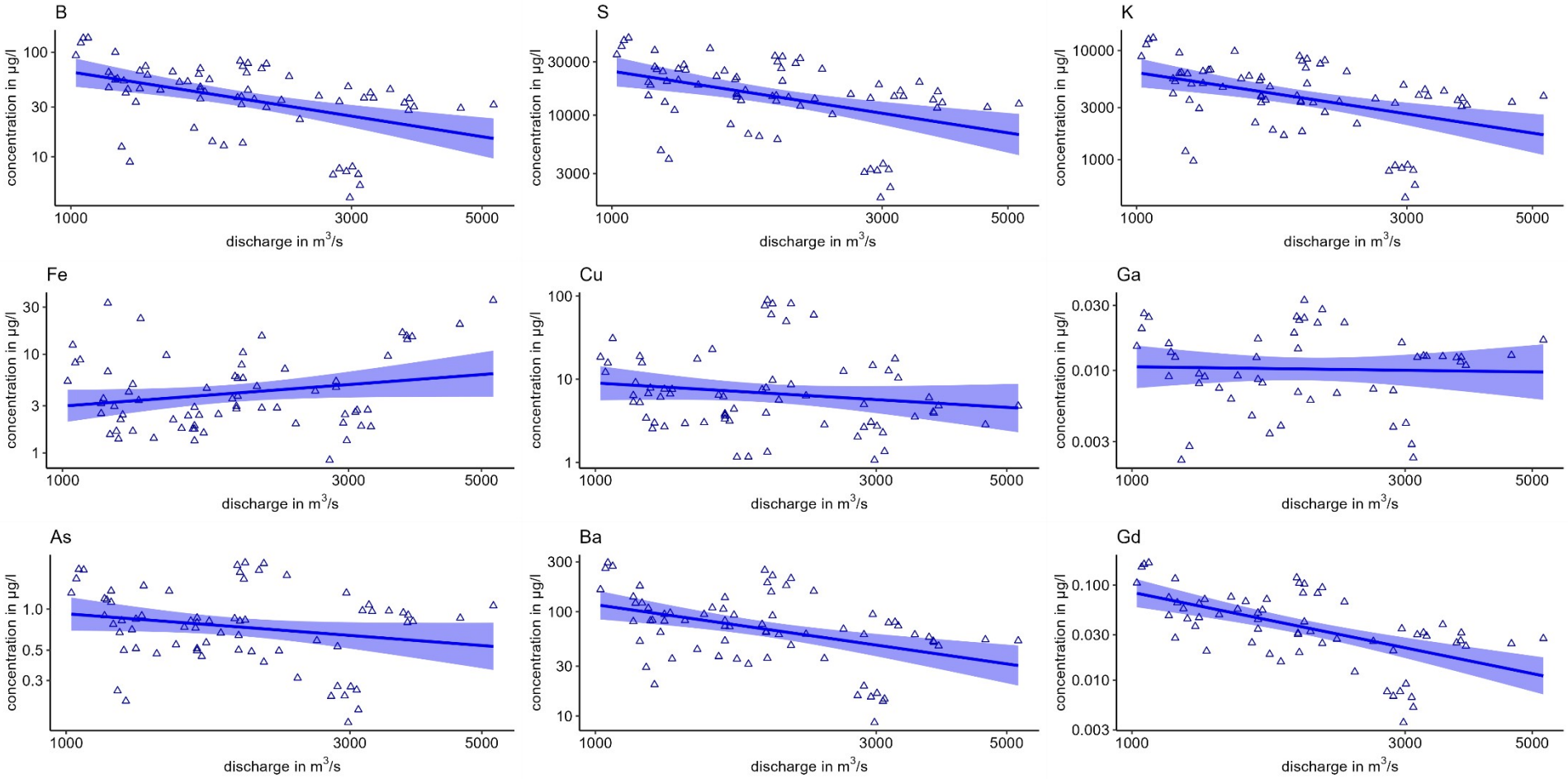
Koblenz-Moselle:



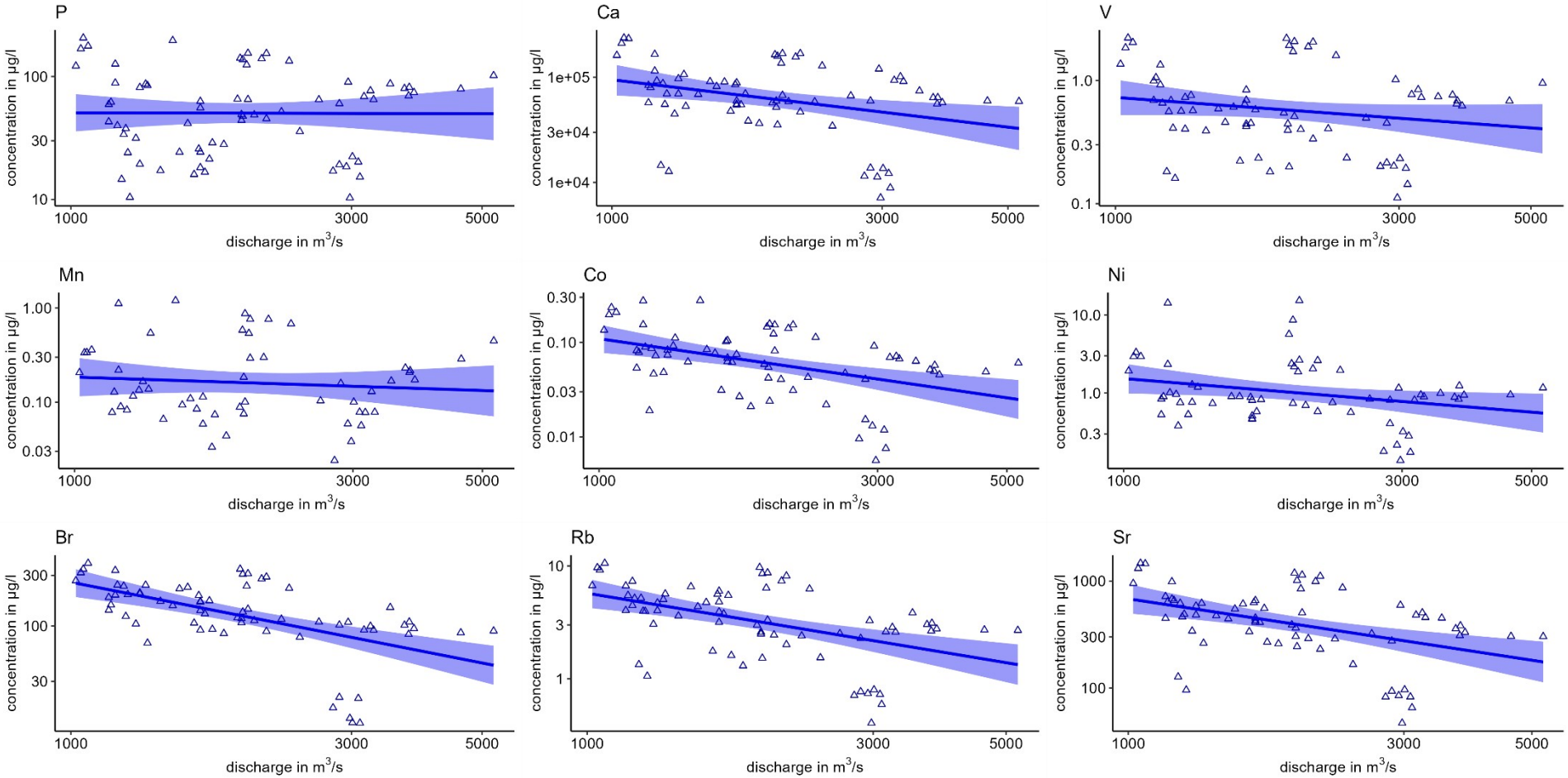
Koblenz-Moselle:



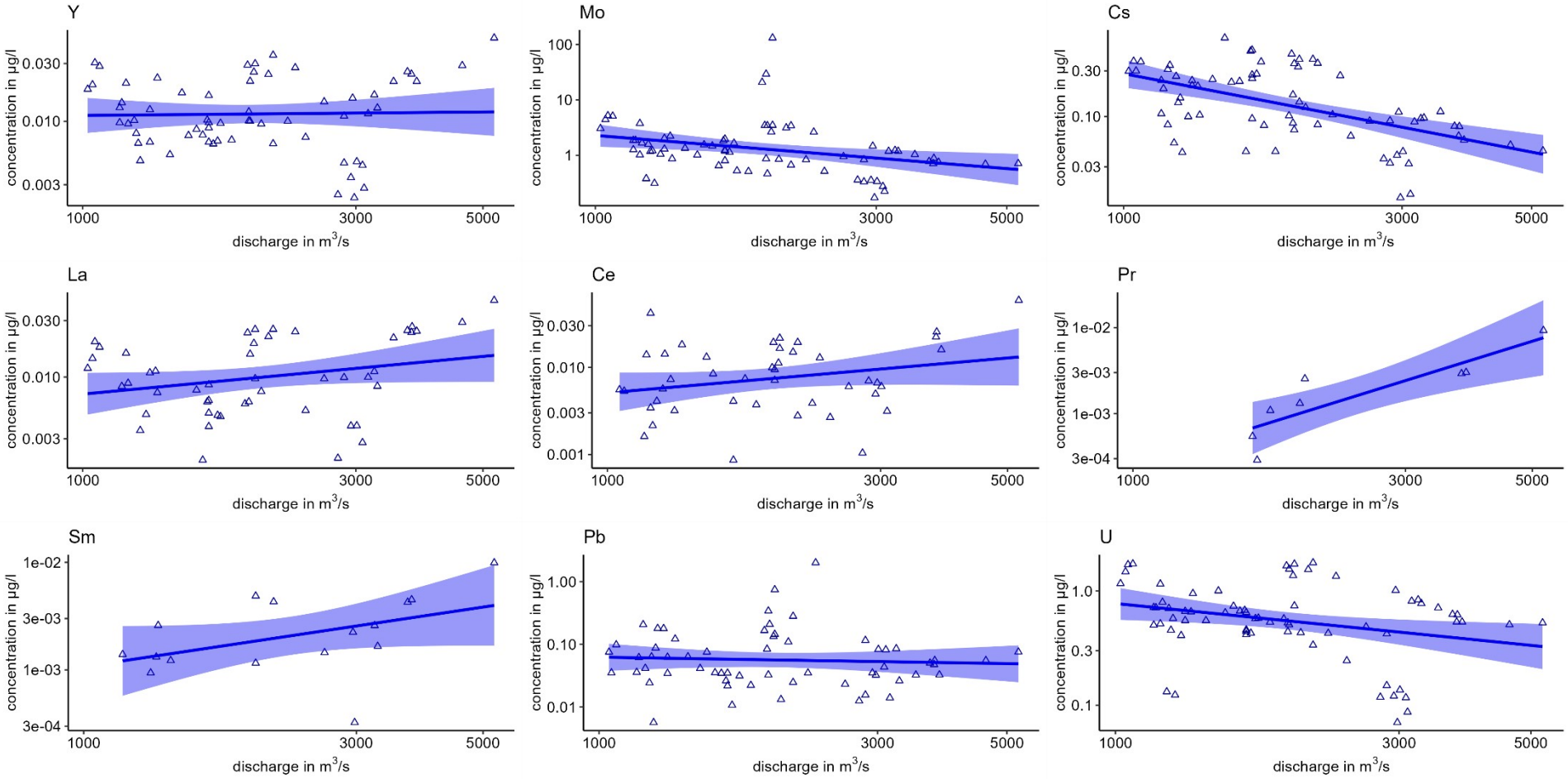
Wesel-Rhine:


B
S
K
Fe
Cu
Ga
As
Ba
Gd
concentration in µg/l
discharge in m³/s
1000
3000
5000

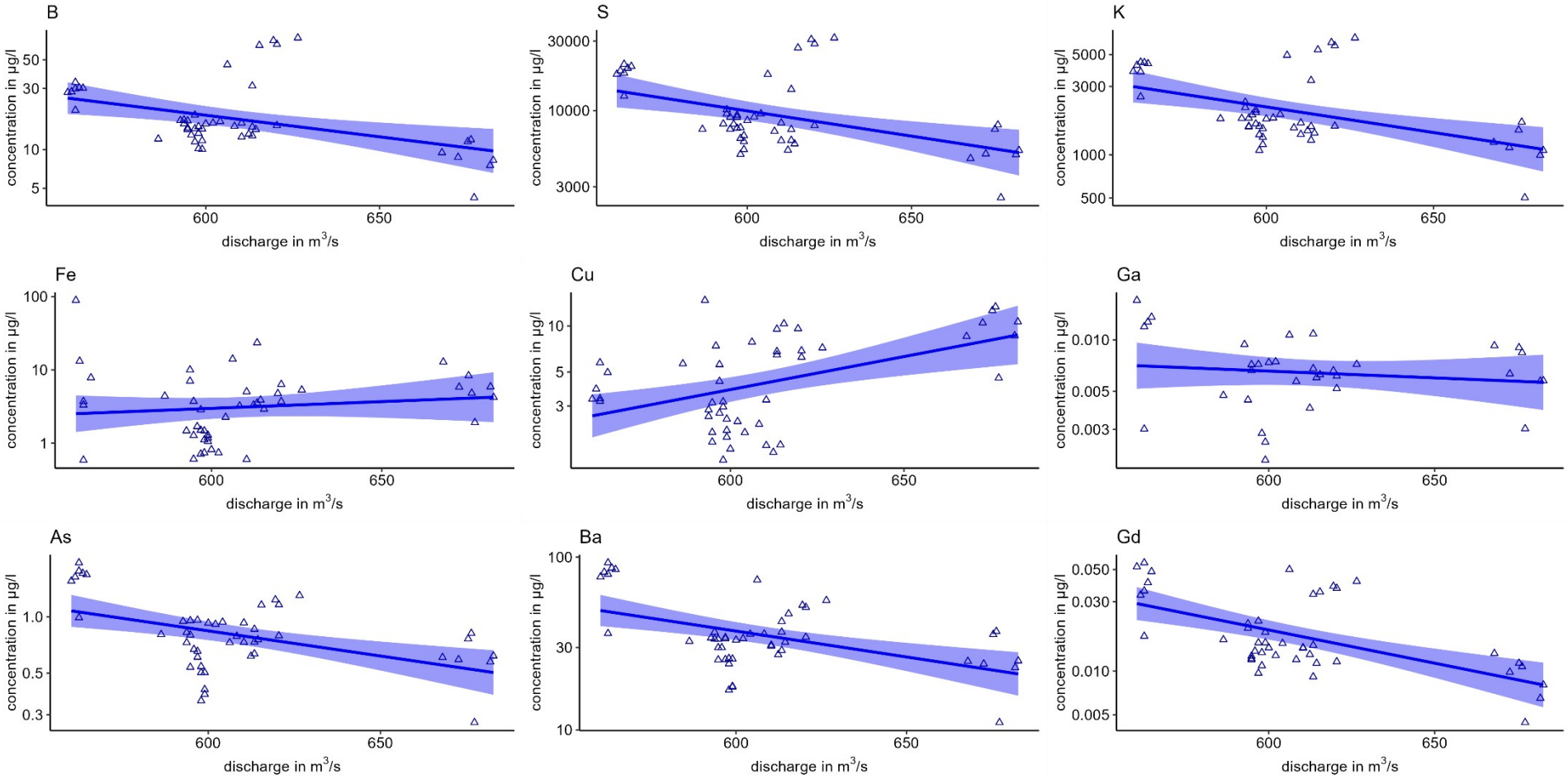
Wesel-Rhine:


P
Ca
V
Mn
Co
Ni
Br
Rb
Sr
concentration in µg/l
discharge in m³/s
1000
3000
5000

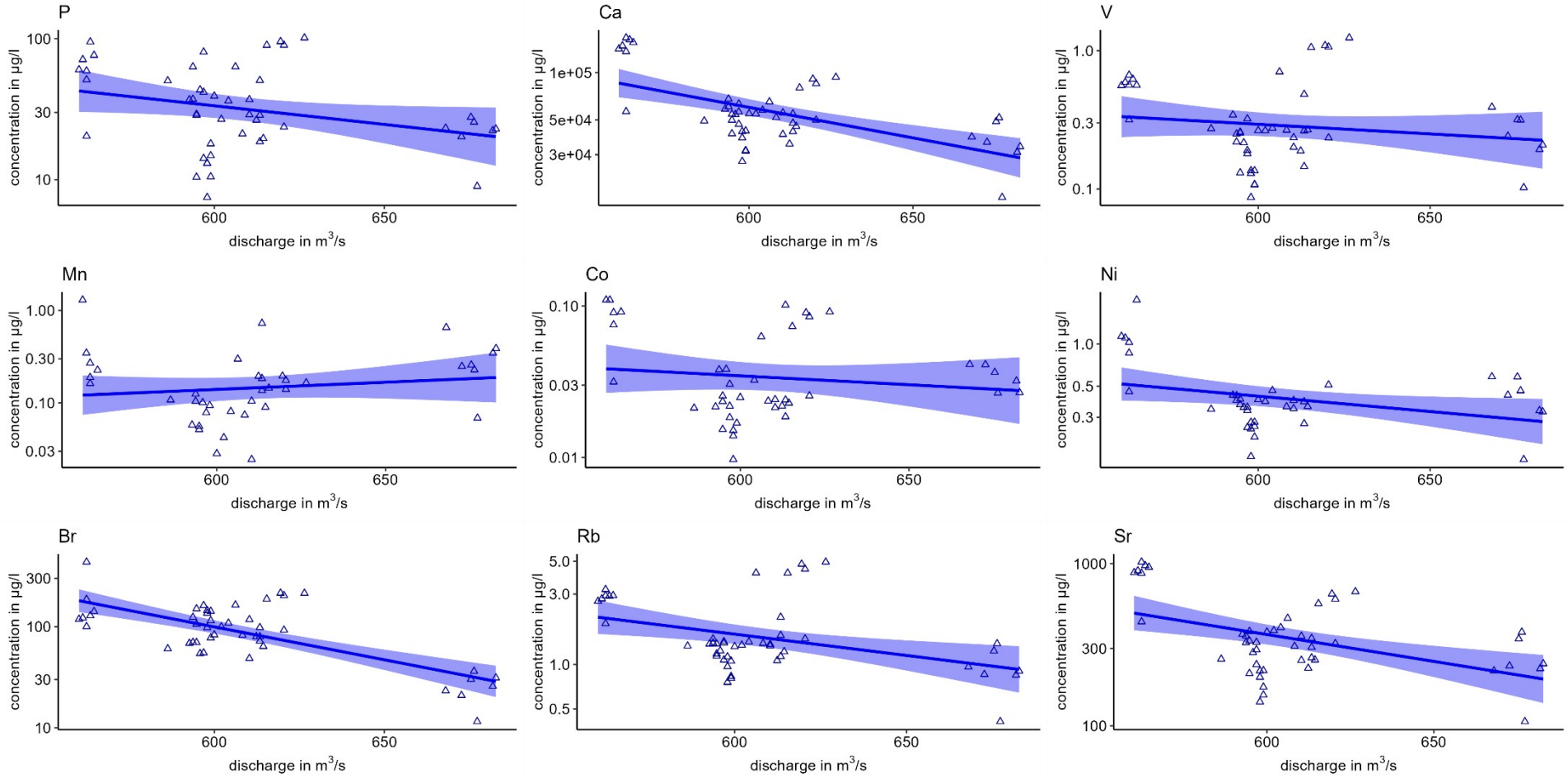
Wesel-Rhine:


Y
Mo
Cs
La
Ce
Pr
Sm
Pb
U
concentration in µg/l
discharge in m3/s
1000
3000
5000

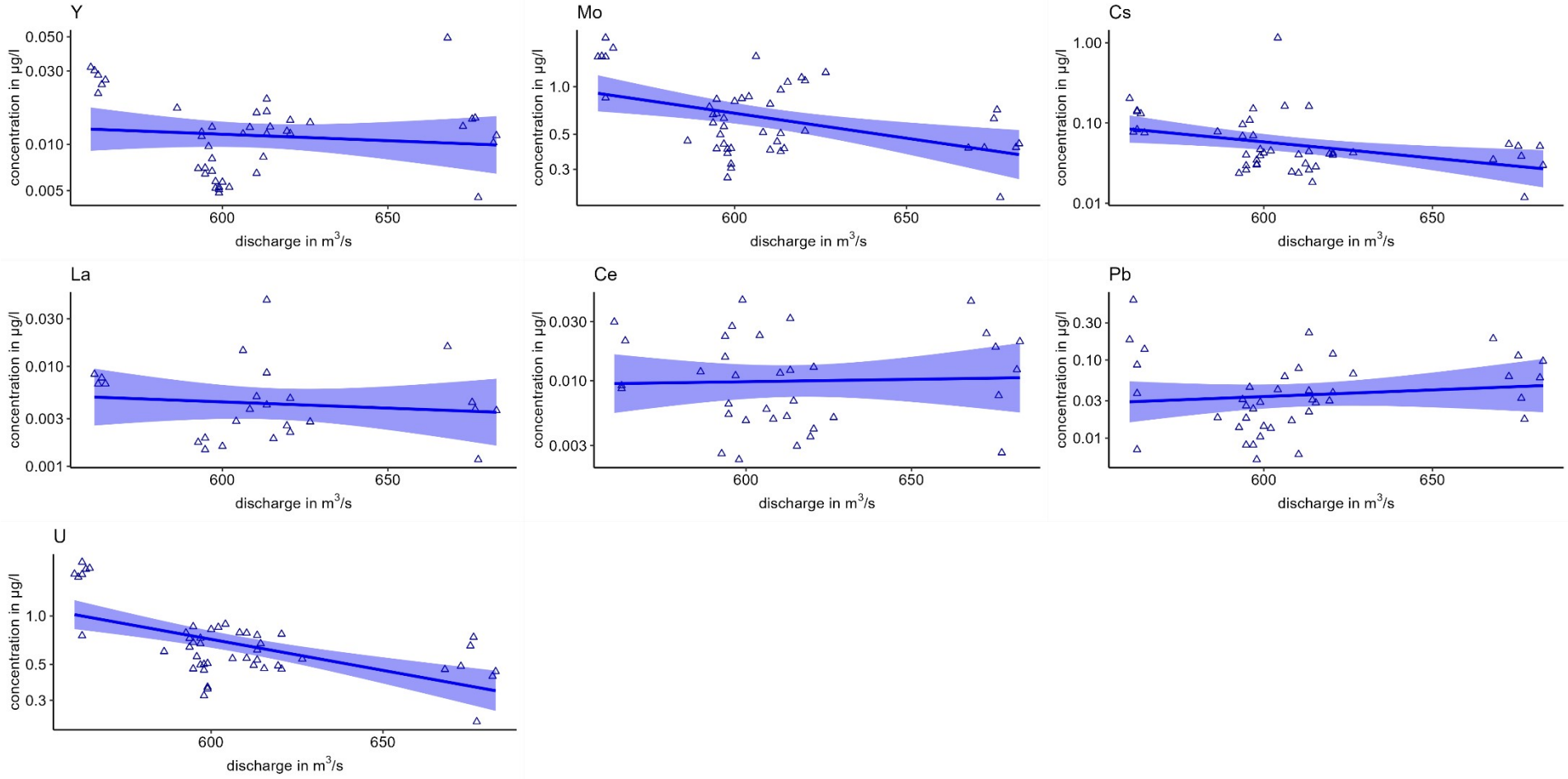
Weil-Rhine:


B
S
K
Fe
Cu
Ga
As
Ba
Gd
concentration in µg/l
discharge in m3/s
600
650

Weil-Rhine:


P
Ca
V
Mn
Co
Ni
Br
Rb
Sr
concentration in µg/l
discharge in m3/s
600
650

Weil-Rhine:


Y
Mo
Cs
La
Ce
Pb
U
concentration in µg/l
discharge in m3/s
600
650

4. Short-term temporal variability data (section 3.1.2 of the manuscript)

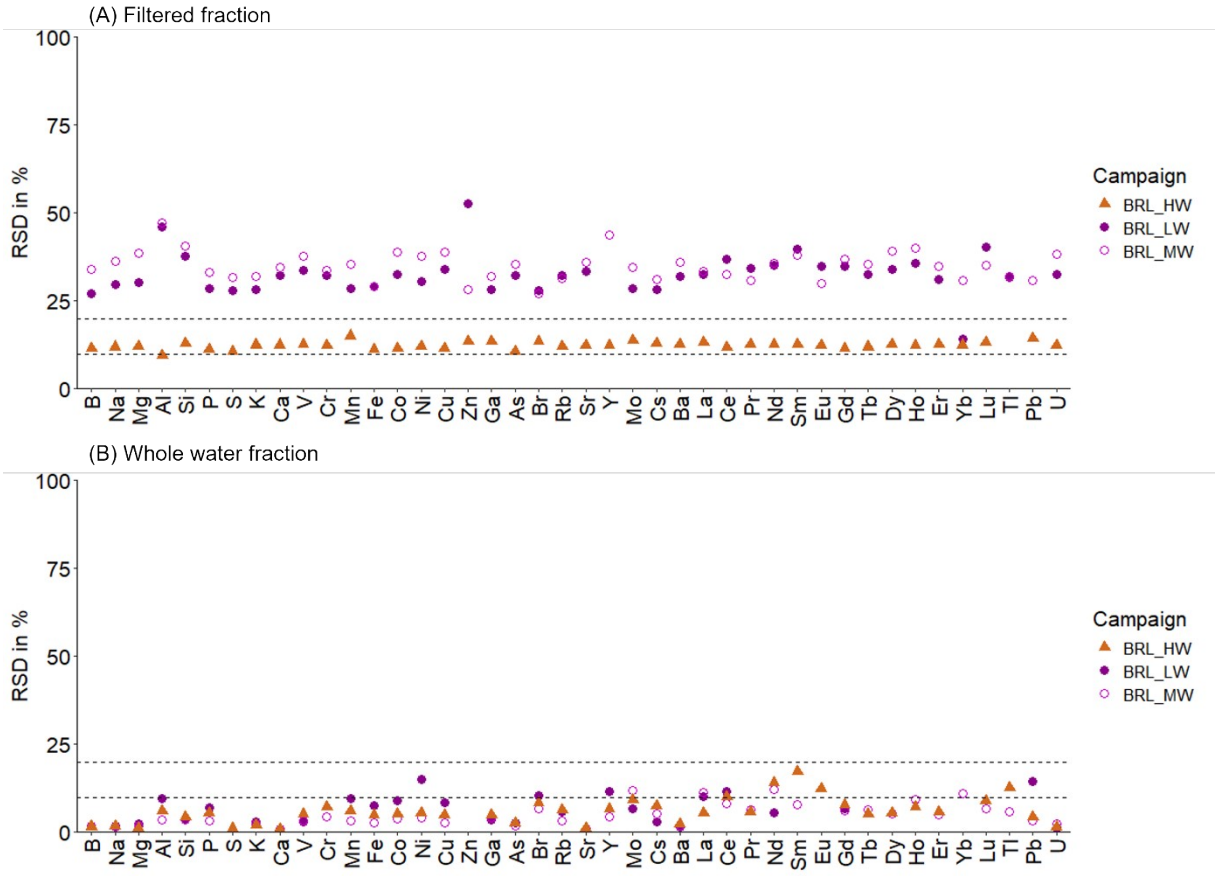


Figure S 7: Relative standard deviation (RSD) in % for the complete dataset of the short-term temporal variability for the station BRL at different discharge levels (LW, MW, HW). Samples were taken in 1-minute intervals for a total time of 10 min (n=10 or n=11). The dashed lines mark RSDs of 10% and 20%, respectively.

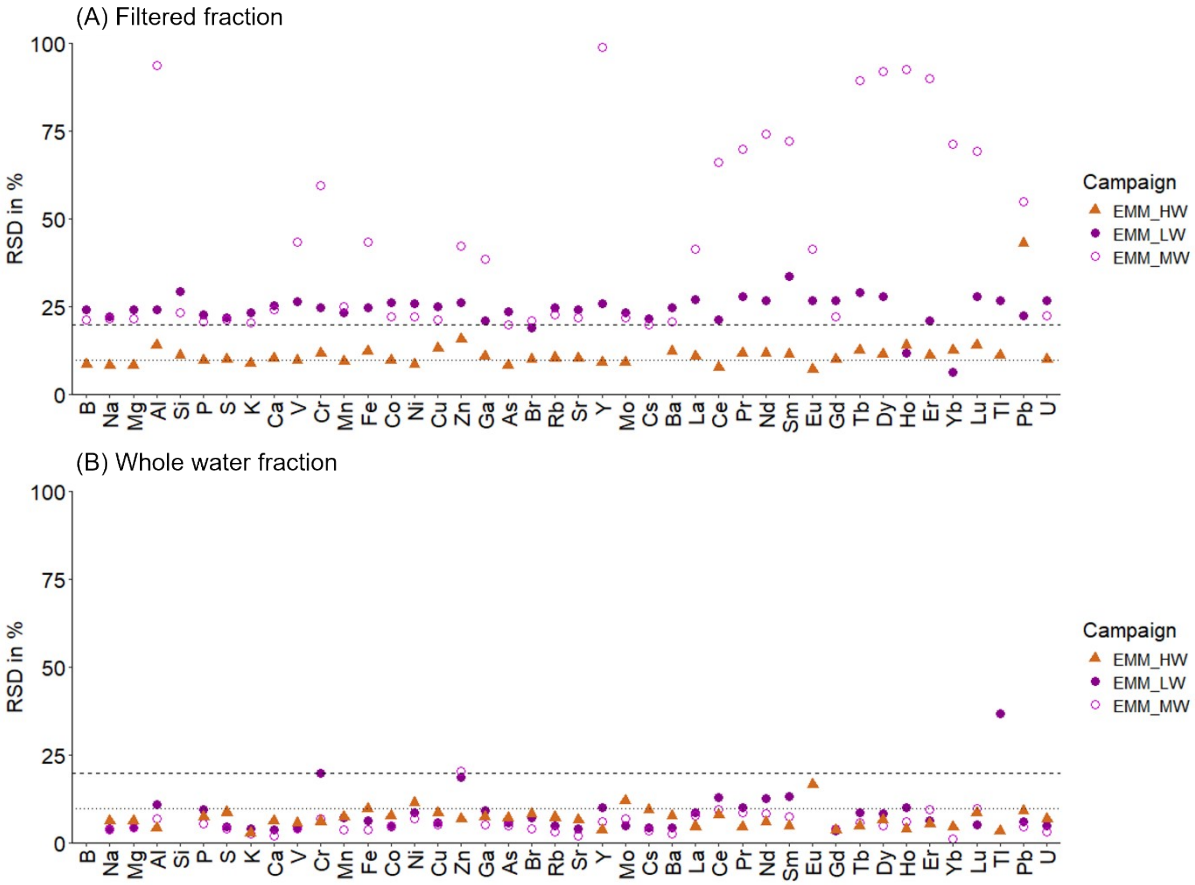


Figure S 8: Relative standard deviation (RSD) in % for the complete dataset of the short-term temporal variability for the station EMM at different discharge levels (LW, MW, HW). Samples were taken in 1-minute intervals for a total time of 10 min (n=10 or n=11). The dashed lines mark RSDs of 10% and 20%, respectively.

Table S 3: Absolute standard deviation in µg/l for all sampling campaigns of the short-term temporal variability of the whole water samples. “NA” (not available) means either not measured, <LOQ or RSDs >10%.

Element	Absolute standard deviation of the whole water in µg/l									
	KAA_LW	KAA_MW	KAA_HW1	KAA_HW2	BRL_LW	BRL_MW	BRL_HW	EMM_LW	EMM_MW	EMM_HW
B	NA	NA	NA	11.3	0.667	0.49	0.362	NA	NA	NA
Na	457	339	365	331	616	842	248	2070	1660	1280
Mg	173	107	188	171	280	194	93.9	489	376	430
Al	27.2	27.2	197	115	18.5	87.4	116	51.3	98	111
Si	50.2	63.9	435	635	64.2	253	263	NA	NA	NA
P	3.46	3.95	7.27	4.82	3.24	4.74	5.5	5.92	6.14	9.99
S	408	457	159	351	60.5	113	111	872	568	816
K	NA	NA	NA	67.2	128	106	58.1	197	111	115
Ca	1890	2510	1320	1030	420	861	423	2340	1360	3090
V	0.0528	0.0632	0.219	0.21	0.0286	0.139	0.178	0.0724	0.128	0.308
Cr	NA	NA	0.168	NA	NA	0.156	0.194	0.285	0.17	0.272
Mn	1.06	0.64	3.43	2.02	1.39	1.95	2.72	2.38	2.08	5.11
Fe	16.2	14.4	109	54.7	10.3	46	64.8	26.4	45.9	204
Co	NA	0.00946	0.0465	0.06	0.0124	0.0246	0.0301	0.0162	0.0287	0.0675
Ni	NA	NA	0.204	0.116	0.121	0.115	0.138	0.137	0.178	0.434
Cu	1.46	0.207	0.203	0.216	0.12	0.0987	0.134	0.164	0.167	0.345
Zn	9.12	5.87	22.2	NA	NA	NA	NA	2.26	4.41	1.52
Ga	0.00497	0.0111	0.0429	0.0366	0.00274	0.0283	0.0261	0.0153	0.0216	0.0587
As	0.038	0.0685	0.0633	0.0558	0.0263	0.0295	0.031	0.0776	0.0648	0.108
Br	63.3	38.7	55.2	43.2	91.5	69.4	84.2	67.9	40	74.9
Rb	0.0837	0.109	0.336	0.237	0.242	0.237	0.319	0.267	0.202	0.54
Sr	7.91	12.7	6.18	7.43	1.54	3.32	2.57	19.2	6.48	15.3

Table S3 continued.

Y	0.0141	0.0129	0.0897	0.0367	0.0085	0.0306	0.037	0.0185	0.0275	0.0287
Mo	0.0165	0.0384	0.0255	0.00347	0.118	0.104	0.0514	0.0903	0.077	0.0781
Cs	0.0355	0.0128	0.0575	0.054	0.0175	0.0489	0.0374	0.0253	0.0277	0.0714
Ba	0.888	0.73	1.57	1.23	0.615	0.885	0.994	3.51	1.63	4.23
La	0.0682	0.0582	0.363	0.167	0.0396	0.142	0.0561	0.0568	0.0788	0.0706
Ce	0.018	0.0804	0.598	0.328	0.0196	0.179	0.181	0.0622	0.135	0.198
Pr	NA	0.0131	0.086	0.0487	NA	0.0166	0.0125	0.00602	0.0149	0.0141
Nd	0.00686	0.0577	0.237	0.159	0.00504	0.137	0.126	0.0295	0.0549	0.0688
Sm	NA	NA	0.0255	0.0319	NA	0.0176	0.0337	0.00665	0.0106	0.0115
Eu	NA	NA	0.0024	0.00869	NA	NA	0.00491	NA	NA	0.00852
Gd	NA	NA	0.0217	3.25E-05	0.00401	0.0128	0.0137	0.0162	0.0126	0.0113
Tb	NA	NA	0.00379	0.00292	NA	0.00165	0.00113	0.000537	0.000948	0.00137
Dy	NA	0.00184	0.0206	0.00498	NA	0.00785	0.00668	0.00292	0.00458	0.0106
Ho	NA	NA	0.00149	0.00202	NA	0.0025	0.00163	0.000584	0.00106	0.00115
Er	NA	0.00469	0.0108	0.00308	NA	0.00387	0.0036	0.00128	0.00434	0.00446
Yb	NA	NA	0.0139	NA	NA	0.00732	NA	NA	0.000574	0.00318
Lu	NA	NA	0.000796	0.00144	NA	0.000645	0.000714	0.000132	0.000493	0.000889
Tl	NA	NA	0.00584	NA	NA	0.00243	0.00346	0.00927	NA	0.0013
Pb	0.0398	0.0553	0.166	0.107	0.062	0.0813	0.0754	0.113	0.105	0.246
U	0.00865	0.0173	0.0101	0.0258	0.0095	0.0143	0.00789	0.0337	0.0169	0.032

5. Spatial variability campaigns

Table S 4: Pearson correlation coefficients of the spatial variability campaign data.

	SPM	B	Mg	S	K	Ca	Br	Sr	Mo	U	Al	Si	P	Ti	V	Mn	Fe	Ni	Cu	Ga	As	Rb	Y	Ba	Cs	La	Ce	Gd	Pb
B	-0.57																												
Mg	-0.20	0.42																											
S	-0.70	0.81	0.56																										
K	0.33	0.41	0.67	0.23																									
Ca	-0.61	0.36	0.59	0.73	0.14																								
Br	0.24	-0.45	0.56	-0.14	0.41	0.23																							
Sr	-0.77	0.43	0.61	0.77	0.10	0.85	0.18																						
Mo	-0.79	0.56	0.61	0.77	0.27	0.73	0.11	0.84																					
U	-0.21	-0.24	0.71	0.18	0.25	0.39	0.69	0.49	0.50																				
Al	0.97	-0.21	-0.11	-0.54	0.50	-0.56	0.13	-0.72	-0.68	-0.26																			
Si	0.98	-0.18	-0.12	-0.56	0.62	-0.61	0.22	-0.65	-0.68	-0.26	0.98																		
P	0.89	0.05	-0.09	-0.33	0.58	-0.51	-0.01	-0.64	-0.54	-0.39	0.93	0.92																	
Ti	0.97	-0.19	-0.12	-0.56	0.55	-0.61	0.22	-0.70	-0.73	-0.29	0.99	0.98	0.95																
V	0.96	-0.12	-0.12	-0.49	0.53	-0.55	0.11	-0.69	-0.66	-0.32	0.99	0.97	0.95	1.00															
Mn	0.89	0.01	-0.24	-0.40	0.45	-0.54	-0.08	-0.70	-0.64	-0.49	0.93	0.90	0.96	0.96	0.96														
Fe	0.97	-0.18	-0.11	-0.52	0.52	-0.54	0.13	-0.70	-0.66	-0.27	1.00	0.98	0.93	0.99	0.99	0.94													
Ni	0.81	-0.09	-0.15	-0.52	0.53	-0.58	0.07	-0.64	-0.56	-0.33	0.86	0.84	0.85	0.83	0.87	0.84	0.86												
Cu	0.06	0.04	-0.30	-0.12	-0.13	-0.36	-0.38	-0.19	-0.28	-0.28	0.13	0.85	0.21	0.29	0.15	0.20	0.14	0.26											
Ga	0.96	-0.22	-0.11	-0.59	0.59	-0.62	0.16	-0.73	-0.71	-0.27	1.00	0.98	0.93	0.99	0.99	0.93	1.00	0.98	0.18										
As	0.88	0.06	0.01	-0.34	0.69	-0.42	0.18	-0.48	-0.43	-0.26	0.90	0.93	0.93	0.93	0.94	0.91	0.92	0.82	0.18	0.93									
Rb	0.95	-0.11	0.02	-0.41	0.63	-0.44	0.21	-0.58	-0.55	-0.19	0.98	0.99	0.92	0.99	0.98	0.91	0.98	0.85	0.10	0.99	0.94								
Y	0.97	-0.19	-0.12	-0.56	0.53	-0.56	0.13	-0.70	-0.68	-0.31	0.99	0.98	0.94	1.00	1.00	0.96	1.00	0.85	0.20	1.00	0.93	0.99							
Ba	0.61	0.09	0.22	-0.05	0.74	-0.03	0.27	-0.12	-0.10	-0.06	0.65	0.74	0.65	0.79	0.69	0.63	0.68	0.64	0.09	0.74	0.82	0.78	0.75						
Cs	0.97	-0.20	-0.09	-0.58	0.60	-0.58	0.22	-0.69	-0.68	-0.27	0.99	0.99	0.92	0.99	0.99	0.93	0.99	0.86	0.26	1.00	0.93	0.99	0.99	0.79					
La	0.93	-0.18	0.04	-0.50	0.63	-0.50	0.27	-0.62	-0.56	-0.10	0.96	0.98	0.90	0.97	0.96	0.88	0.97	0.83	0.10	0.98	0.92	0.97	0.96	0.72	0.98				
Ce	0.97	-0.18	-0.10	-0.55	0.53	-0.57	0.17	-0.70	-0.69	-0.28	0.99	0.98	0.93	1.00	0.99	0.94	1.00	0.85	0.14	1.00	0.93	0.98	1.00	0.72	0.99	0.97			
Gd	0.83	0.03	-0.14	-0.37	0.65	-0.46	0.11	-0.51	-0.51	-0.41	0.85	0.86	0.88	0.90	0.89	0.90	0.88	0.78	0.38	0.91	0.93	0.91	0.91	0.91	0.93	0.86	0.90		
Pb	0.89	-0.16	-0.17	-0.51	0.46	-0.53	0.11	-0.65	-0.63	-0.31	0.89	0.89	0.83	0.91	0.89	0.86	0.90	0.79	0.16	0.89	0.83	0.89	0.90	0.64	0.90	0.86	0.90	0.81	
Th	0.97	-0.53	-0.03	-0.76	0.59	-0.58	0.39	-0.76	-0.78	-0.06	0.99	0.99	0.91	0.99	0.99	0.91	0.99	0.80	-0.04	0.99	0.94	0.99	0.99	0.64	0.99	0.97	1.00	0.82	0.88

Table S 5: p-values of the Pearson correlation coefficients of Table S4. All values with p > 0.05 are marked in bold font and with an underline.

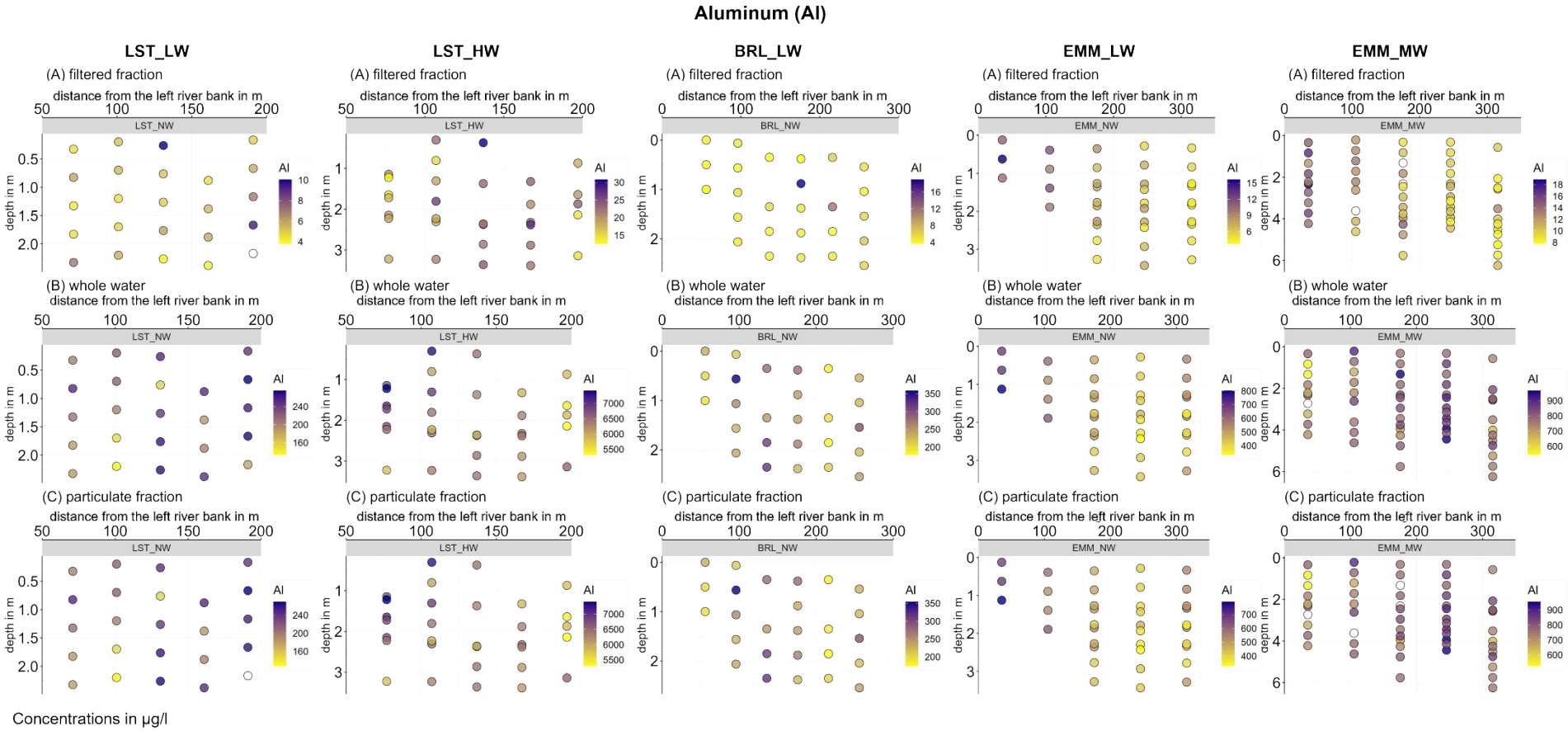
	SPM	B	Mg	S	K	Ca	Br	Sr	Mo	U	Al	Si	P	Ti	V
B	1.68E-09														
Mg	8.40E-229	1.61E-228													
S	2.63E-167	3.28E-167	1.78E-82												
K	5.59E-181	2.41E-180	6.01E-224	1.63E-145											
Ca	2.04E-223	2.17E-223	2.55E-210	7.00E-227	5.85E-219										
Br	4.26E-94	2.57E-93	6.78E-255	1.31E-160	3.32E-131	4.28E-222									
Sr	1.11E-249	5.41E-215	1.54E-225	3.10E-165	8.09E-172	7.36E-223	5.14E-78								
Mo	2.58E-28	2.24E-92	6.70E-229	1.85E-167	2.21E-181	1.86E-223	4.67E-95	2.68E-209							
U	7.30E-29	4.99E-93	6.64E-229	1.84E-167	2.15E-181	1.86E-223	4.49E-95	2.11E-209	4.38E-49						
Al	4.66E-20	1.13E-19	1.75E-228	9.67E-186	1.09E-65	2.20E-233	1.96E-04	1.50E-11	8.63E-21	8.43E-21					
Si	3.55E-32	4.91E-32	1.37E-46	8.44E-115	**1.07E-01**	3.47E-271	2.31E-16	8.03E-29	1.93E-32	1.92E-32	1.43E-19				
P	8.36E-27	4.64E-17	1.12E-228	4.87E-167	2.48E-180	2.40E-223	2.21E-92	1.14E-224	1.83E-56	8.22E-57	8.93E-19	1.05E-31			
Ti	2.55E-02	6.93E-14	5.82E-229	2.35E-167	2.50E-181	1.98E-223	1.66E-94	7.43E-251	2.72E-13	1.12E-13	2.99E-20	3.02E-32	5.24E-31		
V	2.93E-26	2.22E-91	6.91E-229	1.89E-167	2.40E-181	1.87E-223	5.34E-95	2.00E-209	3.68E-15	2.99E-22	9.42E-21	1.99E-32	3.46E-55	7.20E-12	
Mn	**4.09E-01**	1.12E-09	1.03E-228	2.74E-167	8.39E-181	2.06E-223	6.26E-94	3.34E-241	2.03E-46	3.21E-47	5.32E-20	3.73E-32	1.91E-26	1.77E-03	2.09E-43
Fe	2.27E-22	9.78E-22	1.34E-303	7.43E-175	5.56E-133	7.37E-227	3.63E-22	6.65E-09	1.37E-23	1.32E-23	4.89E-03	3.97E-24	3.03E-20	1.09E-22	1.58E-23
Ni	9.12E-27	9.47E-92	6.86E-229	1.88E-167	2.35E-181	1.87E-223	5.17E-95	1.99E-209	6.04E-11	1.28E-17	9.22E-21	1.98E-32	1.66E-55	3.24E-12	**1.23E-01**
Cu	1.39E-23	1.49E-93	7.10E-229	1.93E-167	2.60E-181	1.88E-223	6.22E-95	1.39E-211	6.26E-13	1.53E-15	1.05E-20	2.07E-32	1.20E-53	4.08E-10	1.32E-04
Ga	2.44E-29	1.05E-93	6.59E-229	1.84E-167	2.11E-181	1.85E-223	4.35E-95	1.58E-209	5.40E-42	1.10E-14	8.26E-21	1.90E-32	4.09E-57	5.15E-14	3.02E-28
As	2.59E-28	2.17E-92	6.70E-229	1.85E-167	2.21E-181	1.86E-223	4.67E-95	2.65E-209	**9.66E-01**	1.83E-35	8.64E-21	1.93E-32	1.83E-56	2.73E-13	4.78E-15
Rb	6.81E-23	1.85E-87	7.30E-229	1.95E-167	2.77E-181	1.89E-223	6.72E-95	5.52E-209	1.74E-49	5.66E-56	1.09E-20	2.10E-32	4.98E-53	1.21E-09	7.24E-18
Y	2.17E-29	9.59E-94	6.59E-229	1.83E-167	2.10E-181	1.85E-223	4.33E-95	1.56E-209	6.32E-55	2.49E-21	8.24E-21	1.90E-32	3.79E-57	4.73E-14	4.14E-29
Ba	1.28E-29	1.57E-24	2.42E-228	4.00E-167	6.63E-180	2.29E-223	1.14E-92	5.94E-199	3.84E-188	1.04E-188	2.65E-19	6.72E-32	1.80E-07	3.33E-30	5.93E-198
Cs	2.65E-29	1.27E-93	6.59E-229	1.84E-167	2.11E-181	1.85E-223	4.36E-95	1.65E-209	1.35E-53	1.60E-18	8.27E-21	1.90E-32	4.31E-57	5.46E-14	5.81E-28
La	9.67E-29	5.25E-93	6.66E-229	1.85E-167	2.16E-181	1.86E-223	4.53E-95	2.03E-209	4.34E-09	**6.96E-02**	8.48E-21	1.92E-32	9.77E-57	1.37E-13	6.56E-20
Ce	1.44E-28	3.67E-93	6.67E-229	1.85E-167	2.18E-181	1.86E-223	4.58E-95	1.68E-209	4.78E-02	2.69E-02	8.54E-21	1.92E-32	1.24E-56	1.81E-13	9.67E-16
Gd	1.09E-29	4.86E-94	6.55E-229	1.83E-167	2.08E-181	1.85E-223	4.25E-95	1.43E-209	1.77E-131	2.74E-130	8.14E-21	1.89E-32	2.46E-57	2.89E-14	9.90E-34
Pb	1.57E-27	2.26E-92	6.78E-229	1.87E-167	2.27E-181	1.86E-223	4.91E-95	1.85E-209	5.40E-05	1.38E-11	8.93E-21	1.96E-32	5.53E-56	9.67E-13	4.02E-05
Th	1.63E-29	7.26E-94	6.57E-229	1.83E-167	2.09E-181	1.85E-223	4.30E-95	1.51E-209	3.69E-71	5.69E-35	8.20E-21	1.90E-32	3.17E-57	3.86E-14	4.90E-31

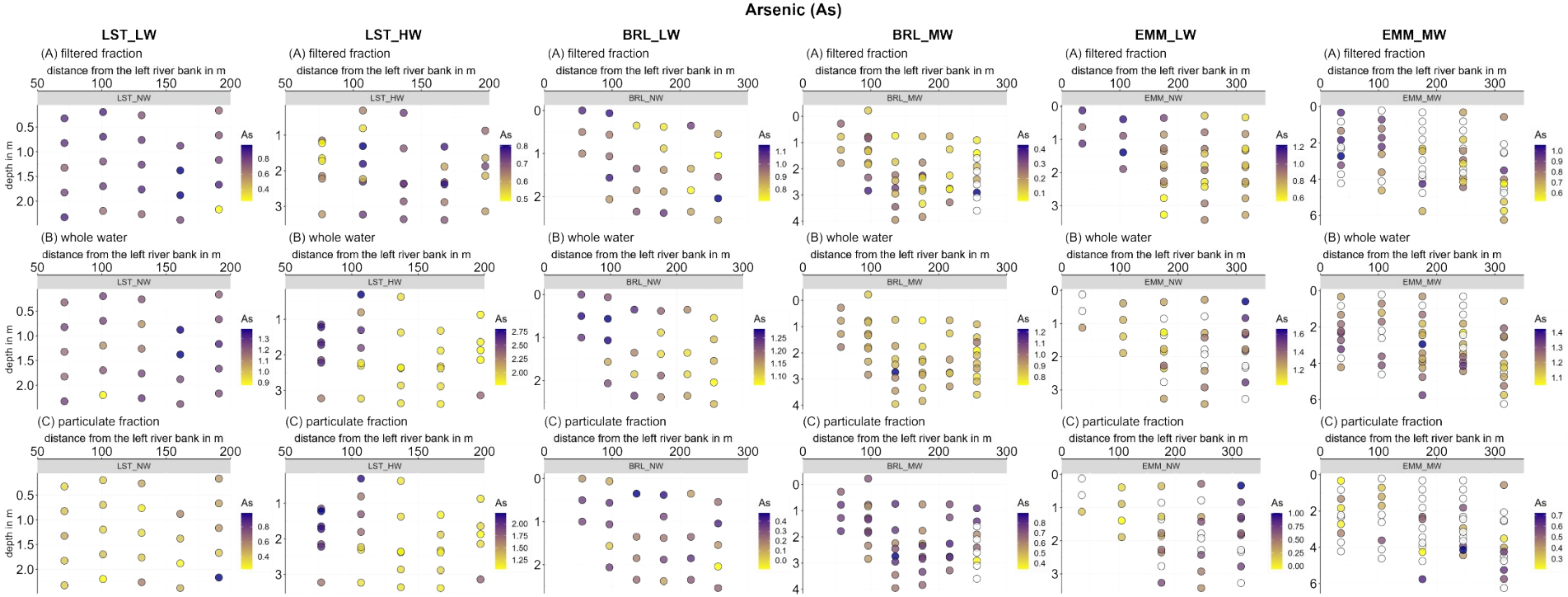
Table S5 continued.

	Mn	Fe	Ni	Cu	Ga	As	Rb	Y	Ba	Cs	La	Ce	Gd	Pb	Th
Fe	2.82E-22														
Ni	3.75E-44	1.53E-23													
Cu	2.45E-39	1.89E-23	3.62E-06												
Ga	6.48E-48	1.27E-23	2.23E-23	7.63E-18											
As	2.05E-46	1.37E-23	7.58E-11	6.59E-13	4.29E-40										
Rb	2.14E-38	2.02E-23	8.91E-24	**1.63E-01**	9.71E-62	1.90E-49									
Y	5.45E-48	1.27E-23	3.50E-24	4.01E-18	**4.93E-01**	2.07E-51	2.62E-62								
Ba	2.29E-38	4.01E-21	2.41E-196	2.09E-228	4.44E-190	2.80E-188	8.60E-198	5.64E-190							
Cs	7.31E-48	1.28E-23	4.42E-23	1.08E-17	**6.13E-01**	1.77E-49	2.98E-61	**1.89E-01**	9.49E-190						
La	4.83E-47	1.33E-23	1.90E-15	7.41E-15	1.45E-11	1.93E-08	1.42E-54	1.89E-14	1.49E-189	5.38E-12					
Ce	8.59E-47	1.34E-23	1.12E-11	9.04E-14	1.02E-07	4.98E-02	4.11E-51	8.82E-09	3.21E-192	1.79E-07	**2.48E-01**				
Gd	2.00E-48	1.24E-23	1.84E-28	1.00E-19	8.41E-09	1.35E-107	1.68E-65	2.31E-08	7.82E-190	1.84E-14	4.19E-34	1.24E-15			
Pb	2.84E-45	1.45E-23	8.39E-03	5.19E-09	5.04E-18	6.39E-05	1.15E-34	4.60E-19	8.91E-195	8.93E-18	3.34E-09	6.36E-06	9.23E-25		
Th	3.60E-48	1.26E-23	5.58E-26	8.75E-19	1.05E-02	2.04E-68	1.17E-63	4.86E-02	6.63E-190	3.80E-04	1.38E-21	2.11E-11	4.00E-05	2.12E-21	

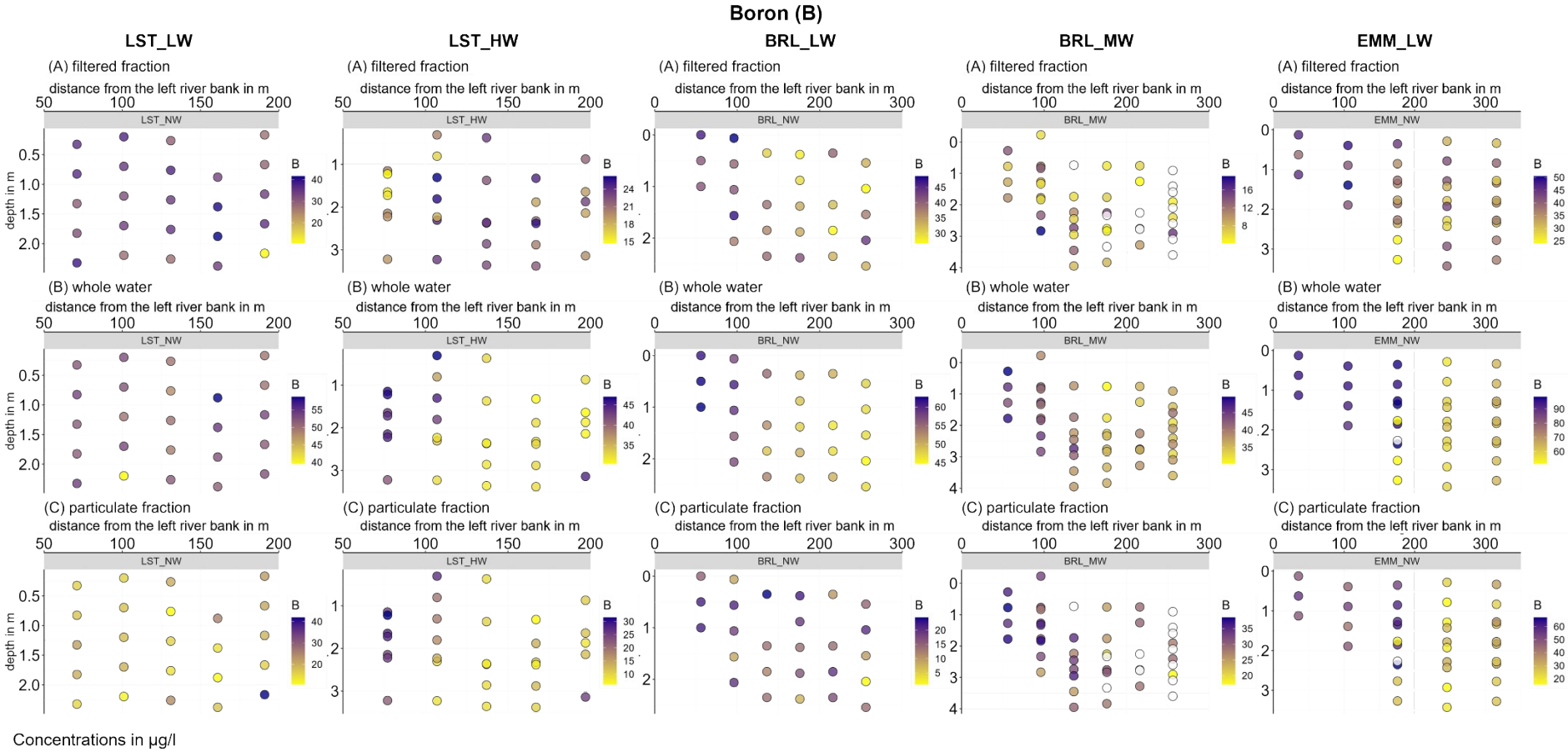
6. Heatmaps of the spatial variability campaigns (section 3.2.1.2 of the manuscript)

Element concentrations in µg/l of all spatial variability sampling campaign in different sampling fractions: filtered fraction (top row), whole water (middle row) and calculated particulate load (bottom row). White circles indicate measurements below LOQ or with an analytical RSD > 10%. The data for LST-MW and EMM-HW are not shown due to the fact that several samples are missing in the cross-profile, thus, a trend is not visible. For EMM-HW (n=13) only one depth-profile could be taken because of the weather conditions during sampling.

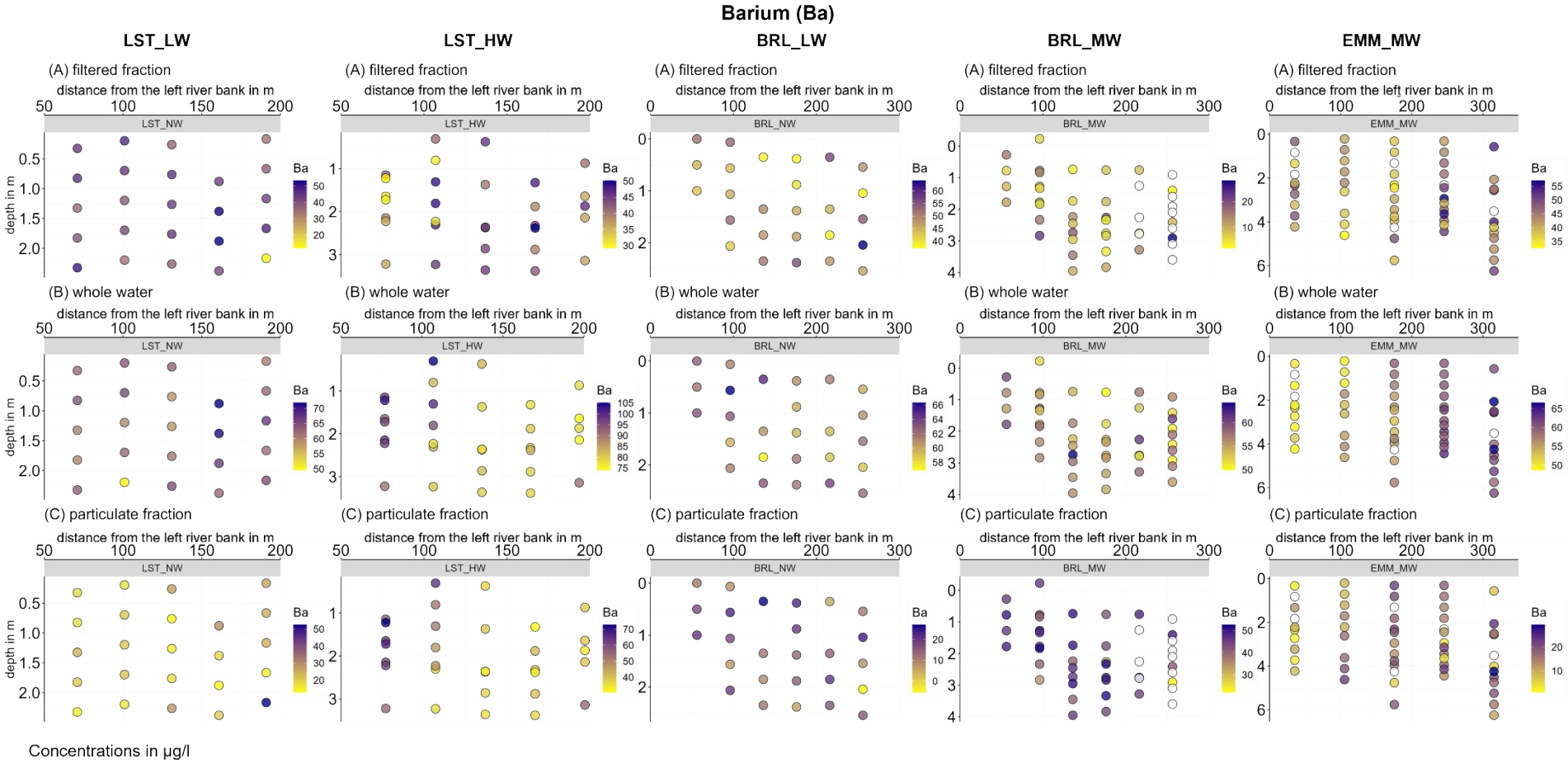




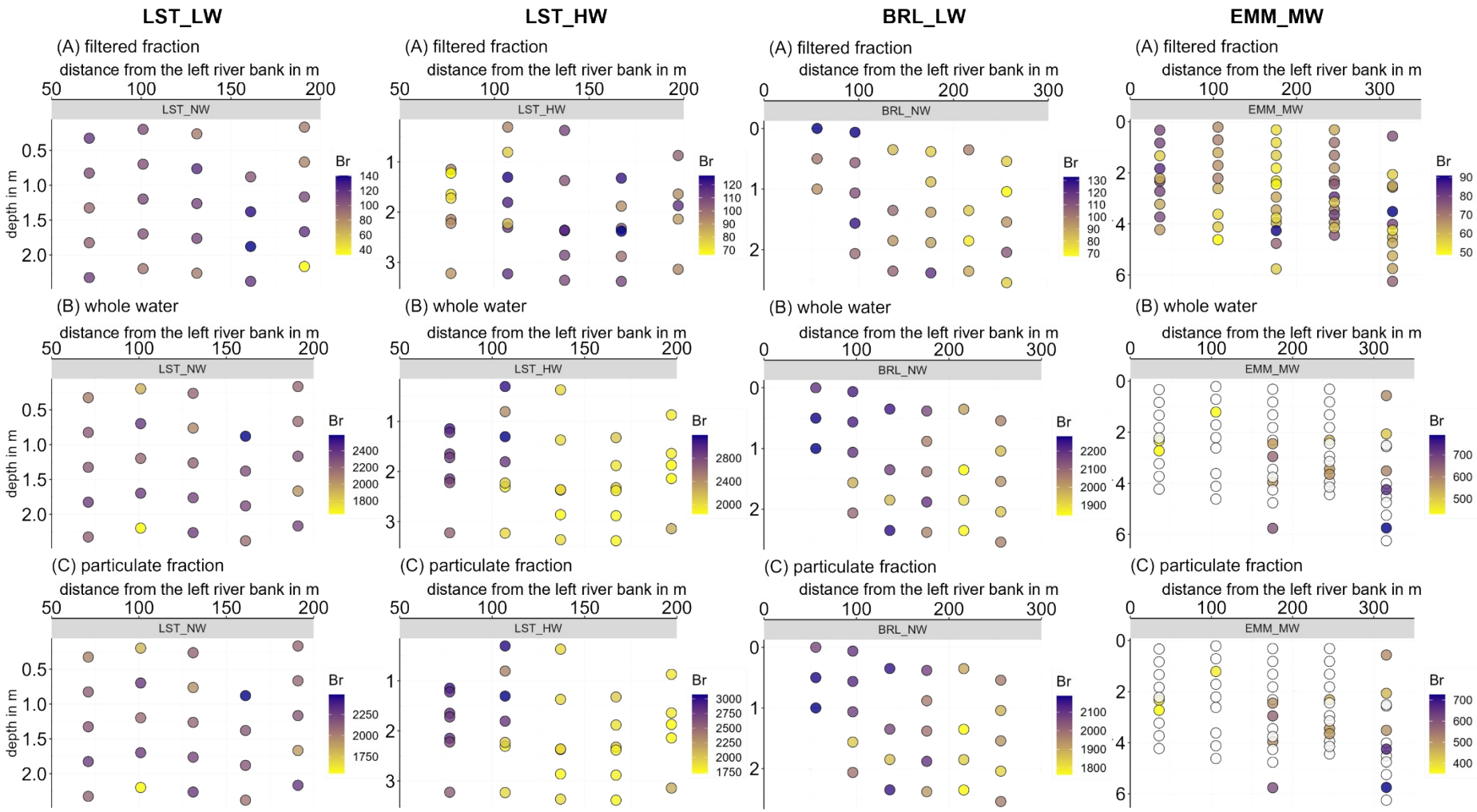
Concentrations in µg/l



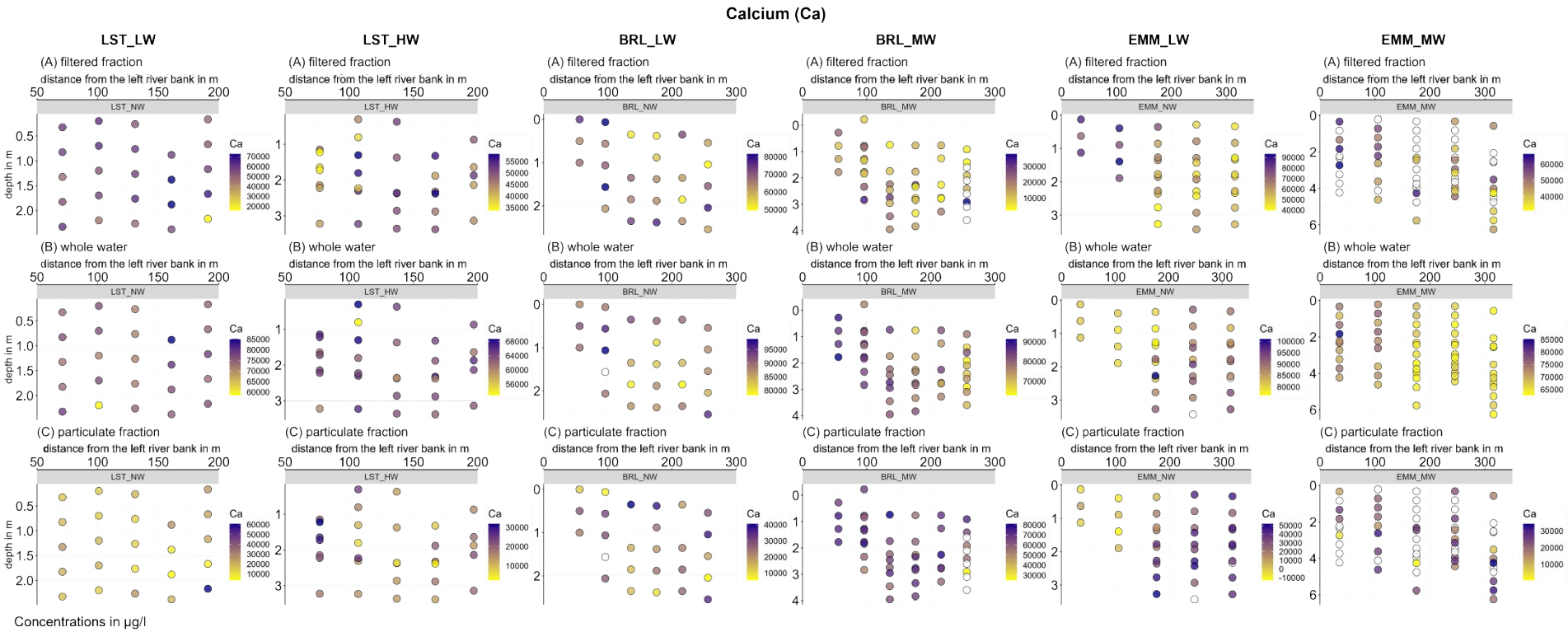
Concentrations in µg/l

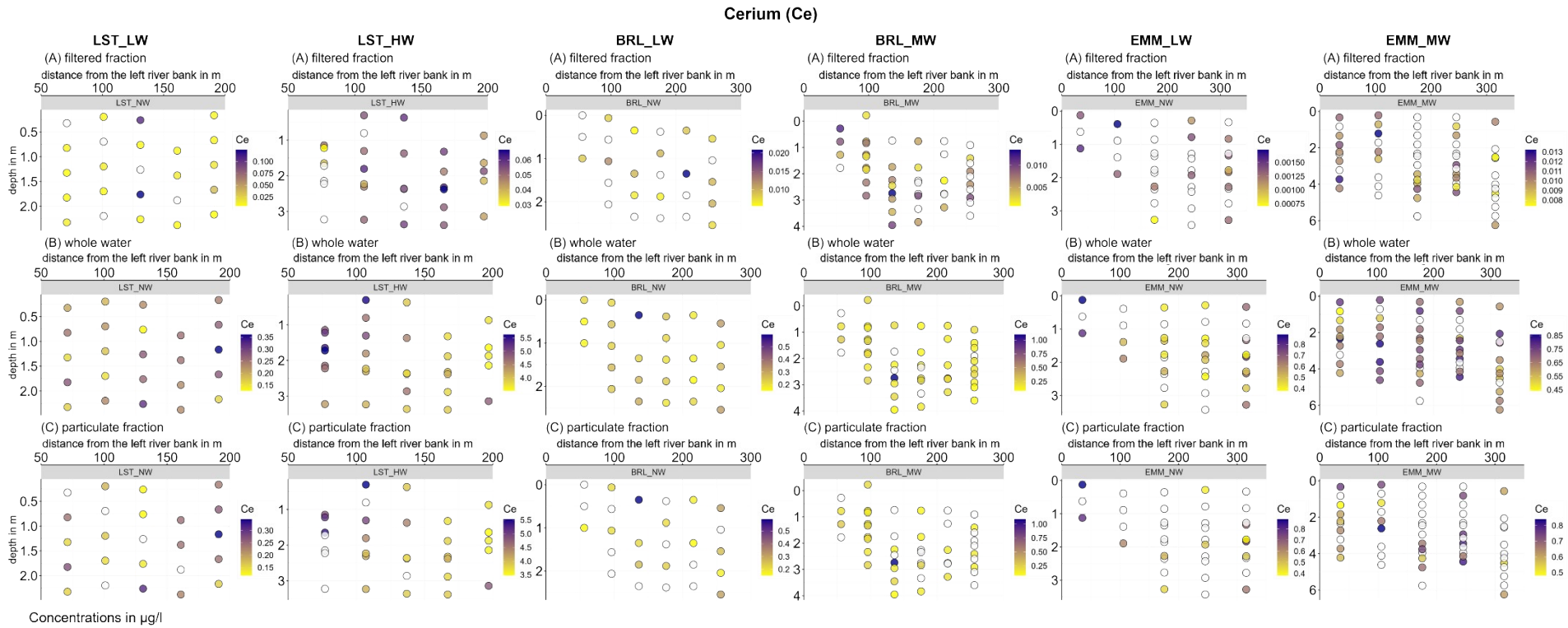

Barium (Ba)
LST_LW
LST_HW
BRL_LW
BRL_MW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
Ba
Concentrations in µg/l

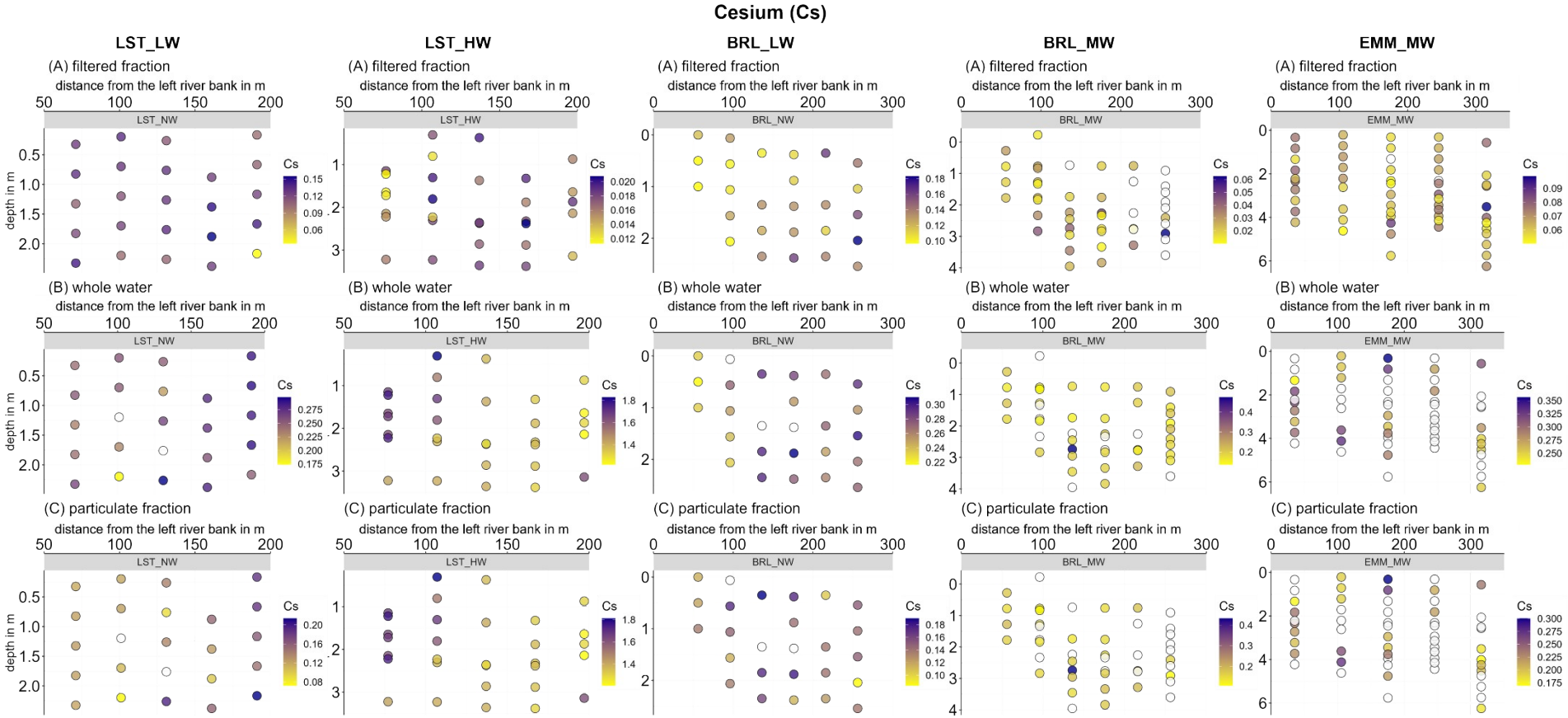
Bromine (Br)



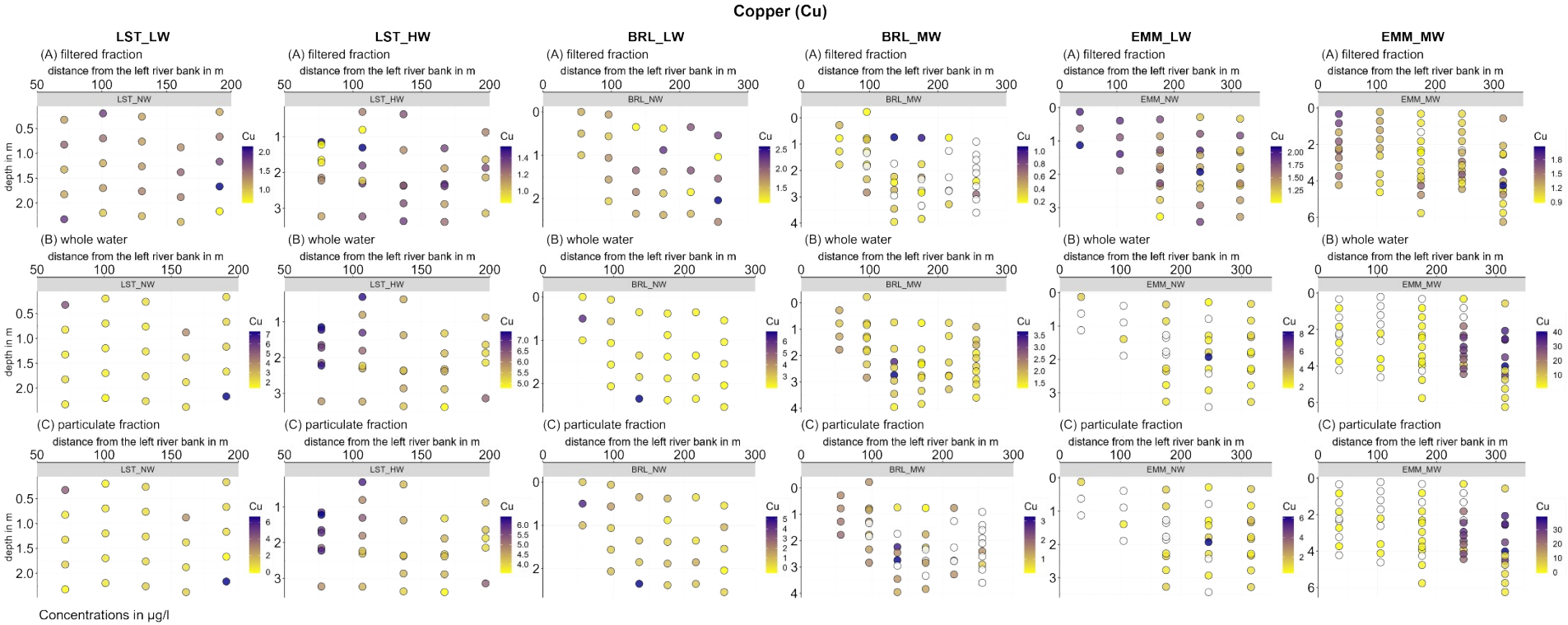
Concentrations in µg/l

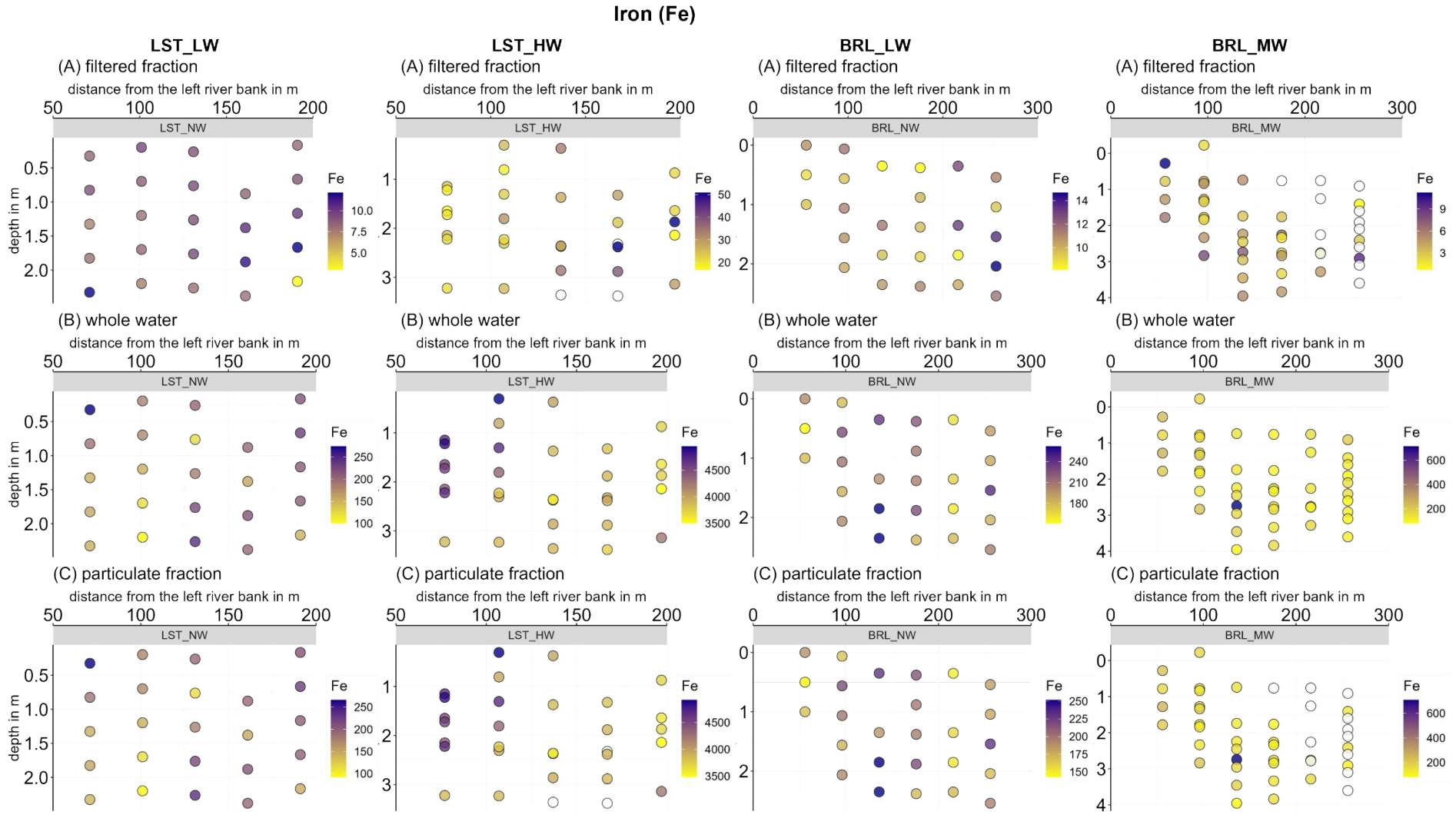

Calcium (Ca)
LST_LW
LST_HW
BRL_LW
BRL_MW
EMM_LW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
Ca
Concentrations in µg/l


Cerium (Ce)
LST_LW
LST_HW
BRL_LW
BRL_MW
EMM_LW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
Ce
Concentrations in µg/l

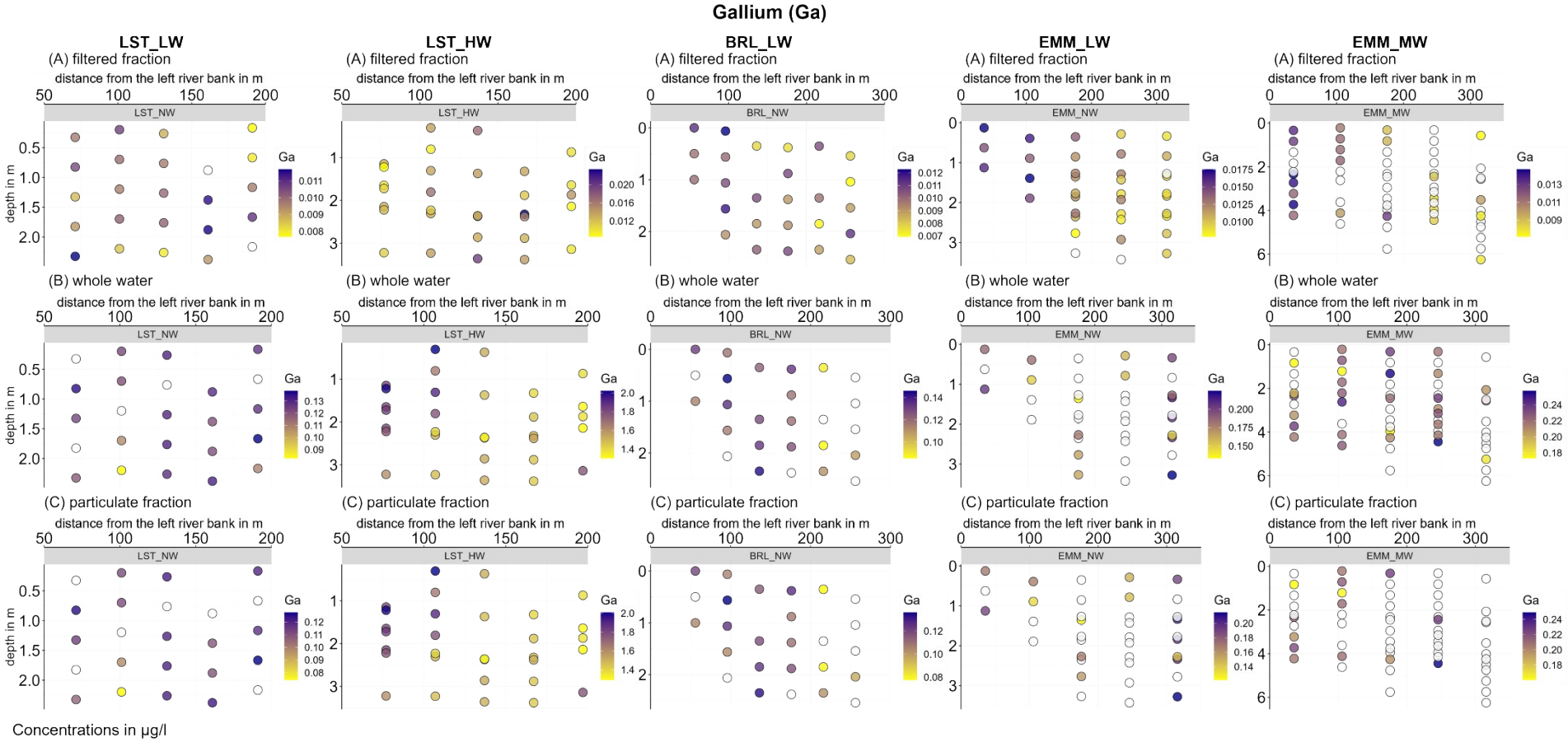


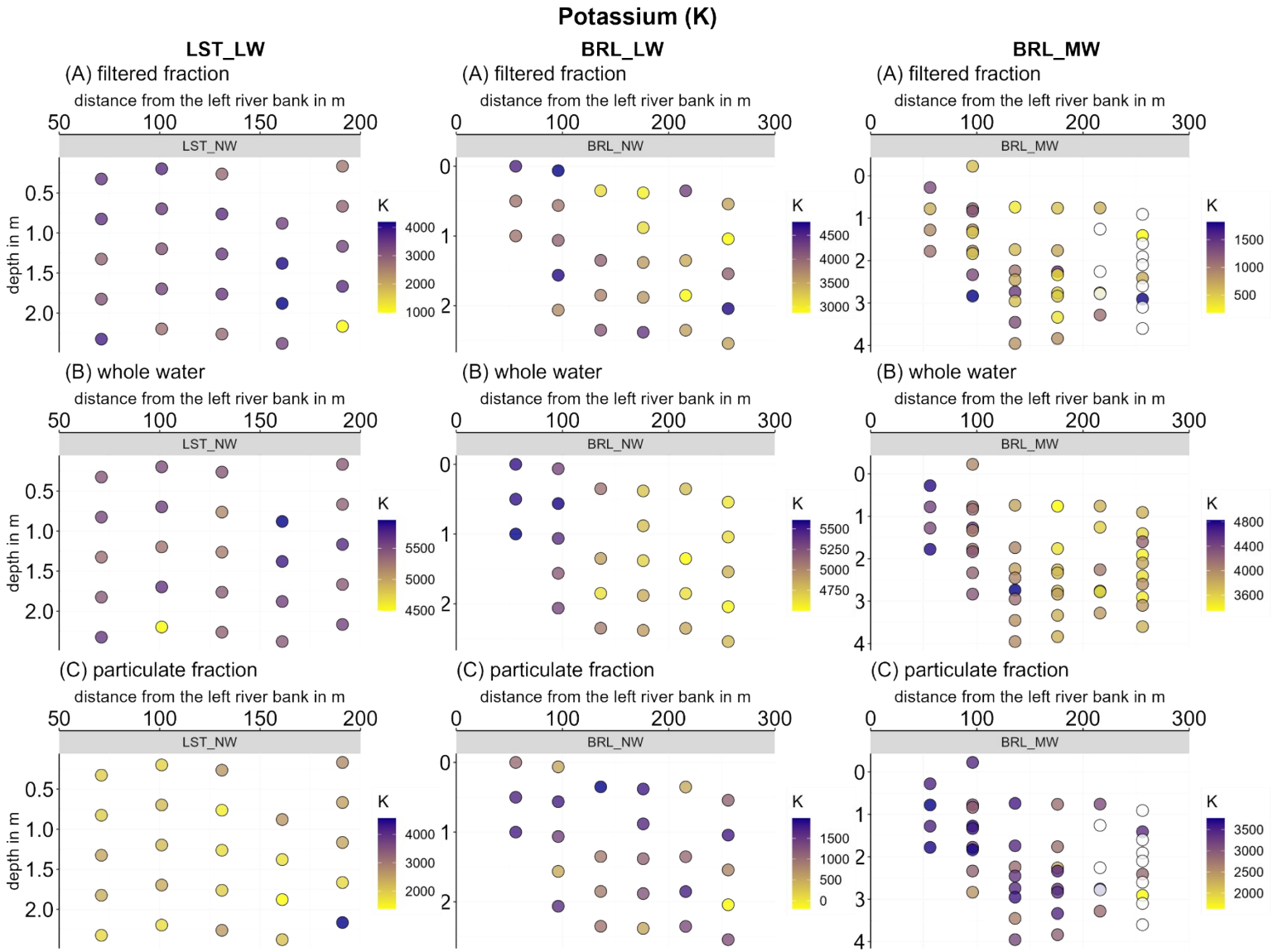
Concentrations in µg/l


Copper (Cu)
LST_LW
LST_HW
BRL_LW
BRL_MW
EMM_LW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
Cu
Concentrations in µg/l



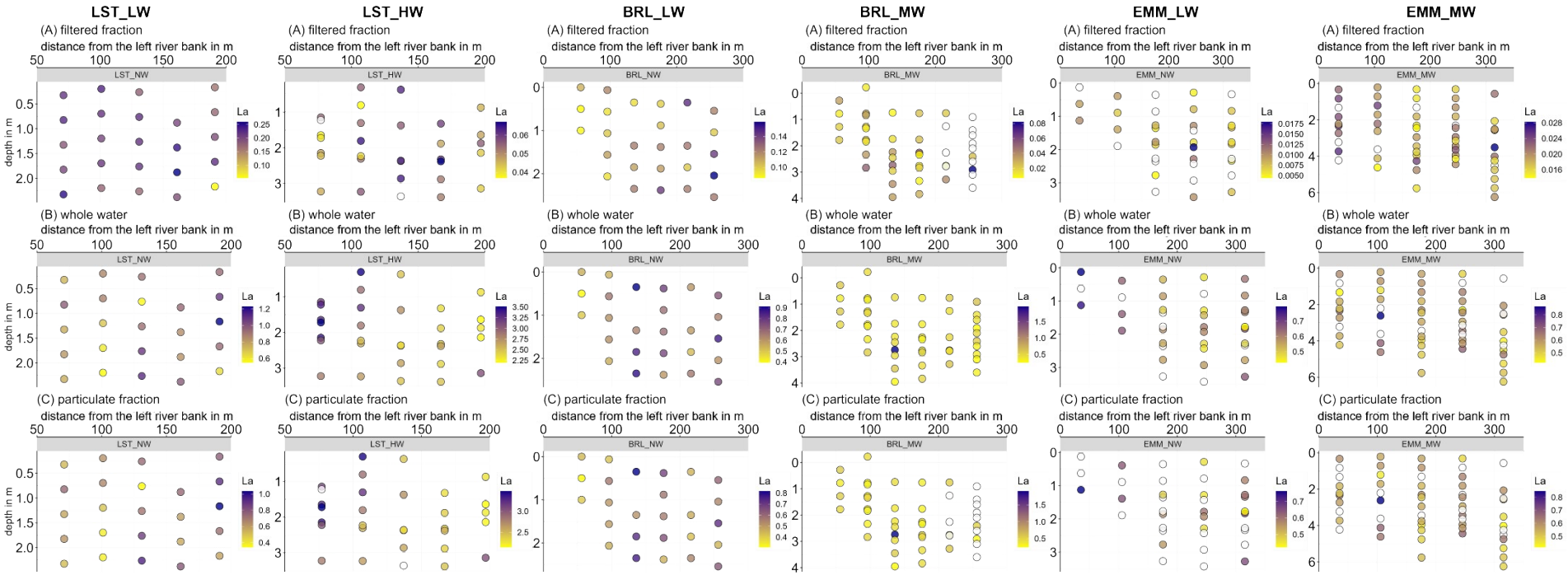
Concentrations in µg/l


Gallium (Ga)
LST_LW
LST_HW
BRL_LW
EMM_LW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
Ga
LST_NW
LST_HW
BRL_NW
EMM_NW
EMM_MW
Concentrations in µg/l

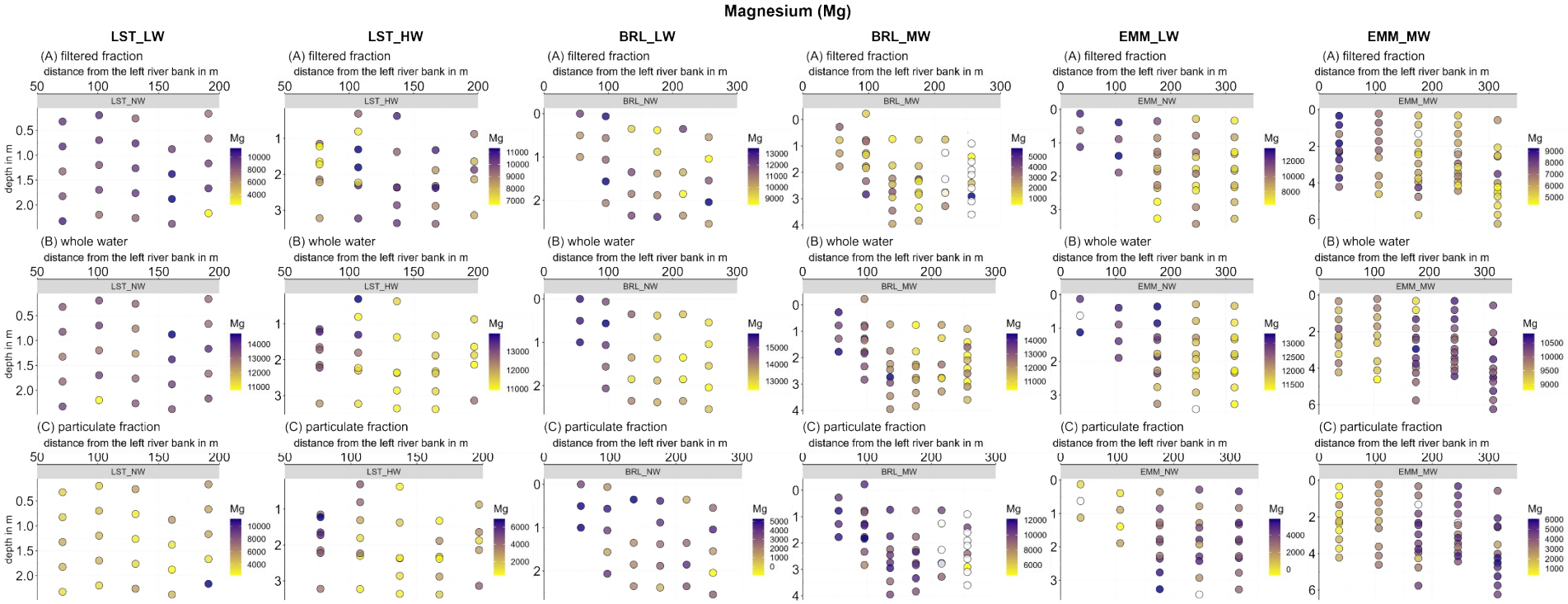


Concentrations in µg/l

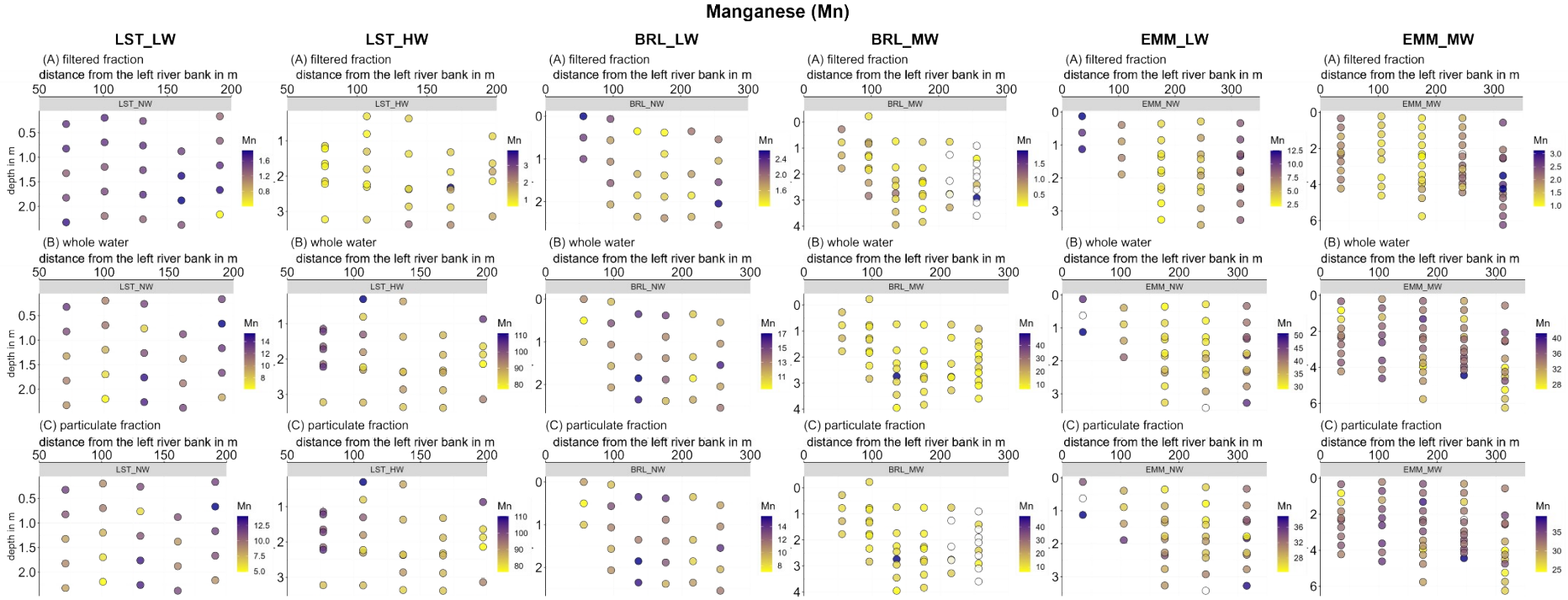
Lanthanum (La)

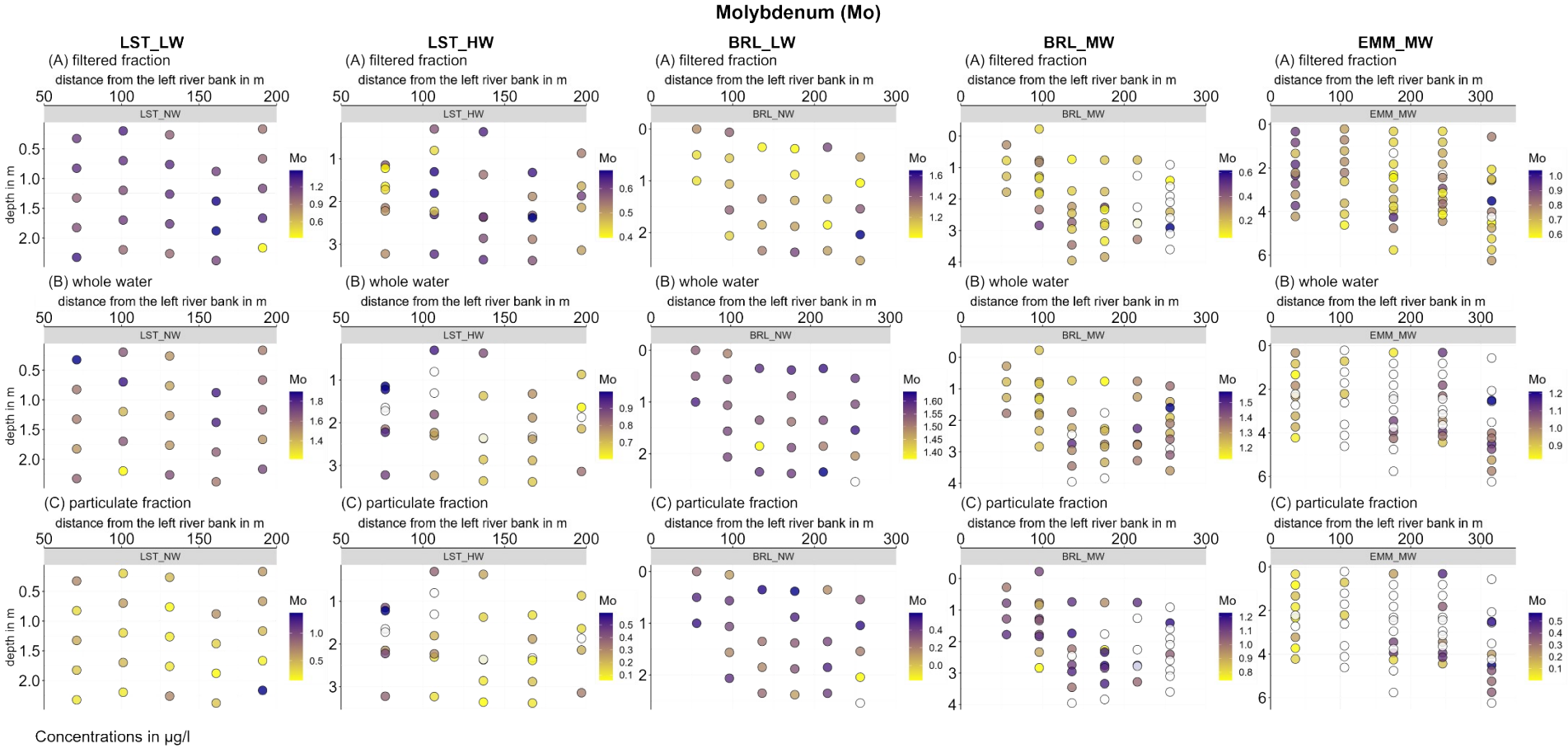


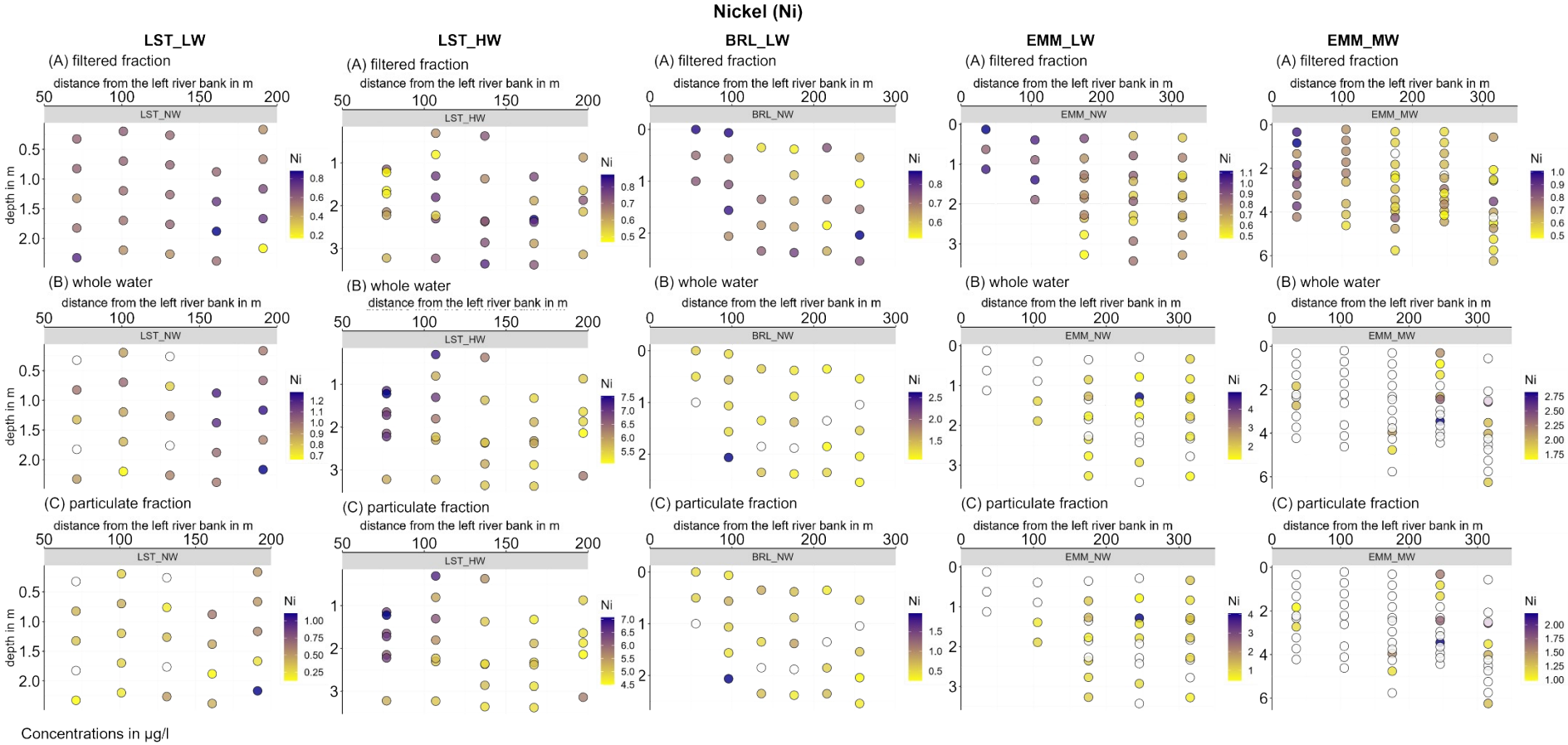
Concentrations in µg/l

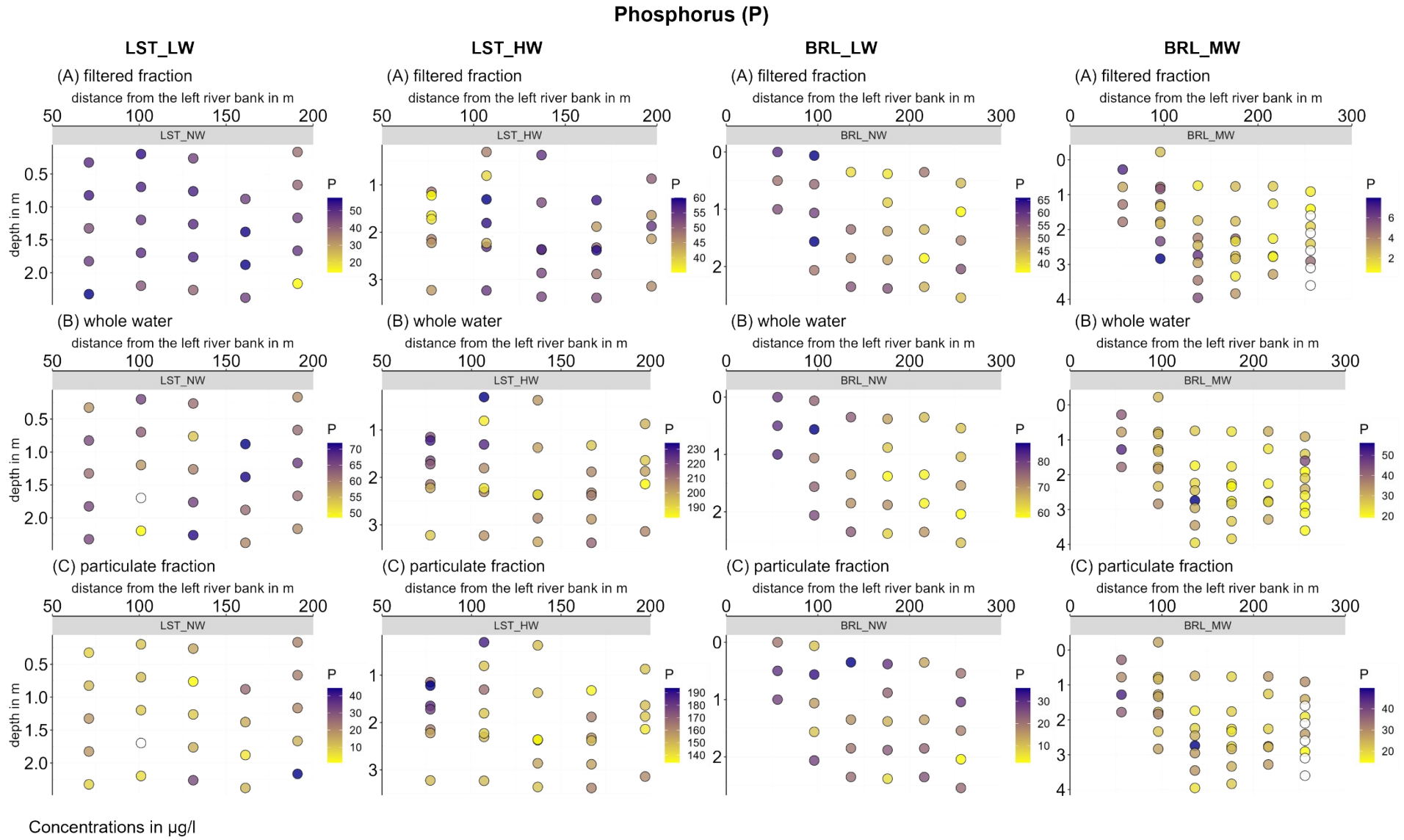


Concentrations in µg/l

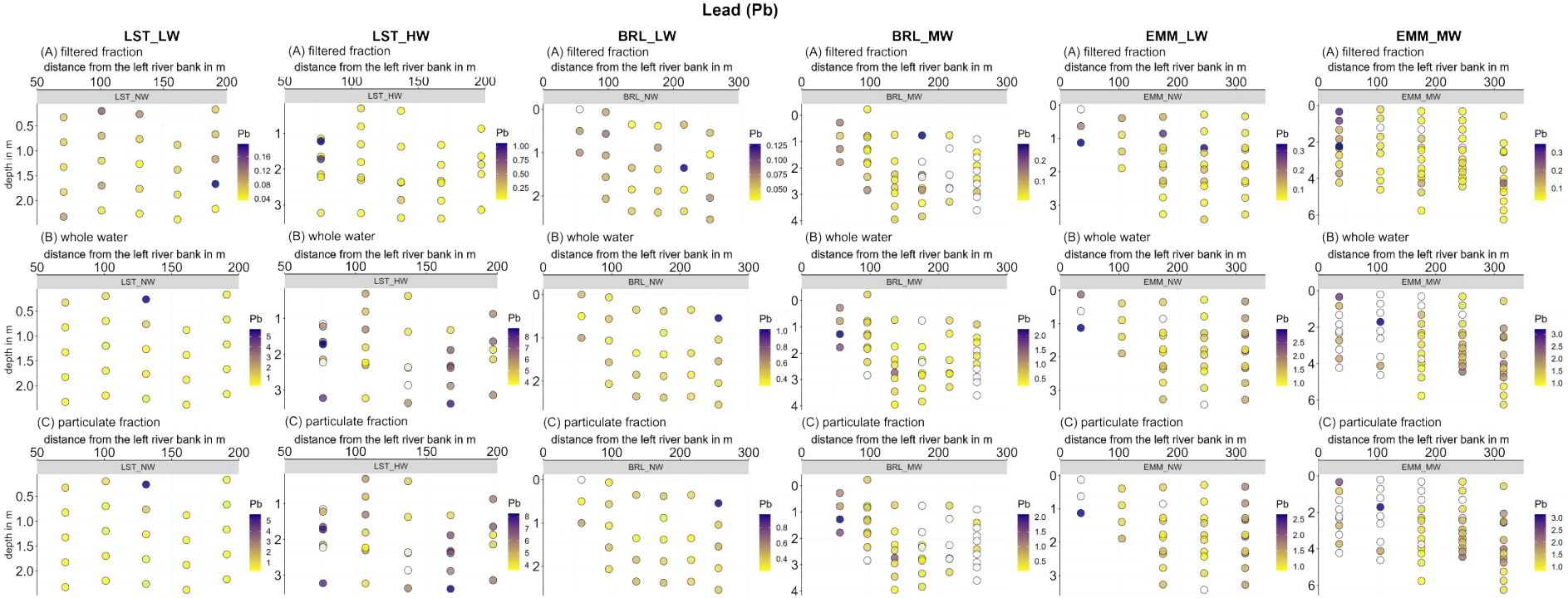

Manganese (Mn)
LST_LW
LST_HW
BRL_LW
BRL_MW
EMM_LW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
Mn
Concentrations in µg/l


Molybdenum (Mo)
LST_LW
LST_HW
BRL_LW
BRL_MW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
Mo
Concentrations in µg/l

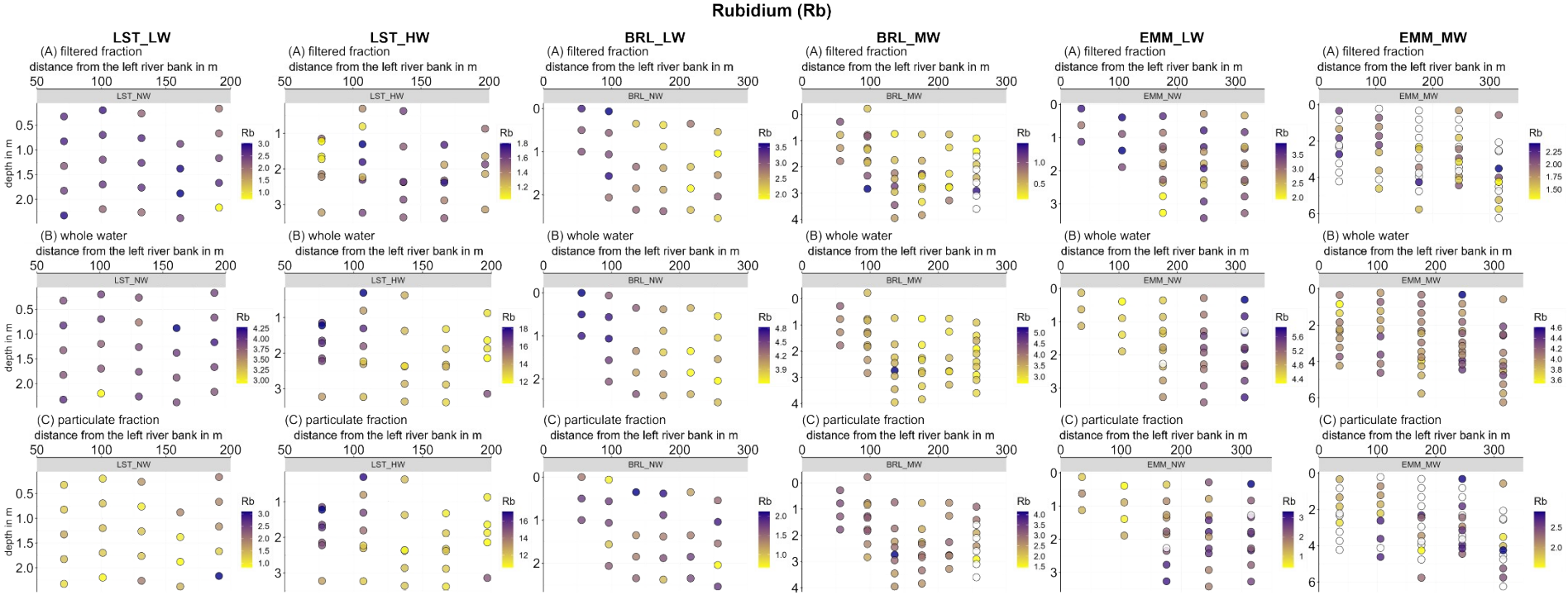

Nickel (Ni)
LST_LW
LST_HW
BRL_LW
EMM_LW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
LST_NW
LST_HW
BRL_NW
EMM_NW
EMM_MW
Ni
Concentrations in µg/l



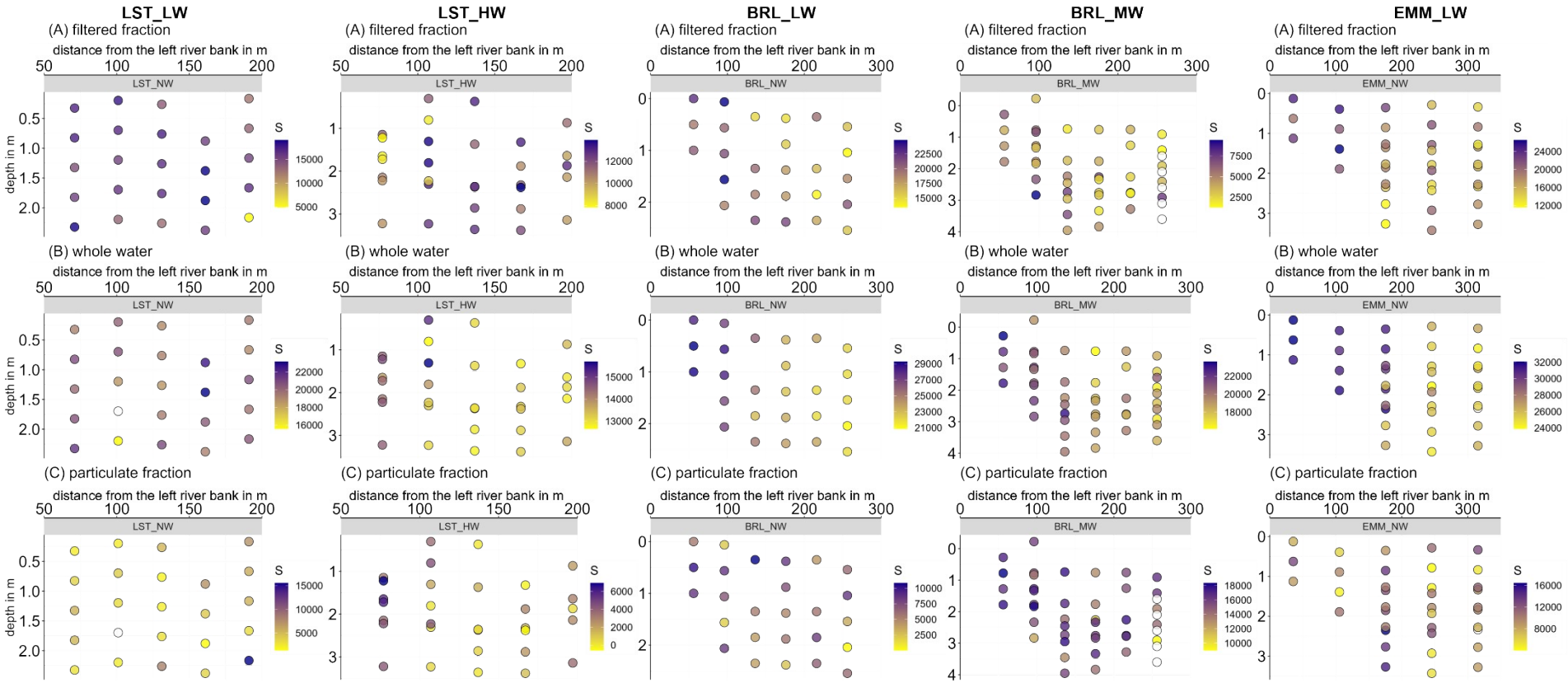
Concentrations in µg/l



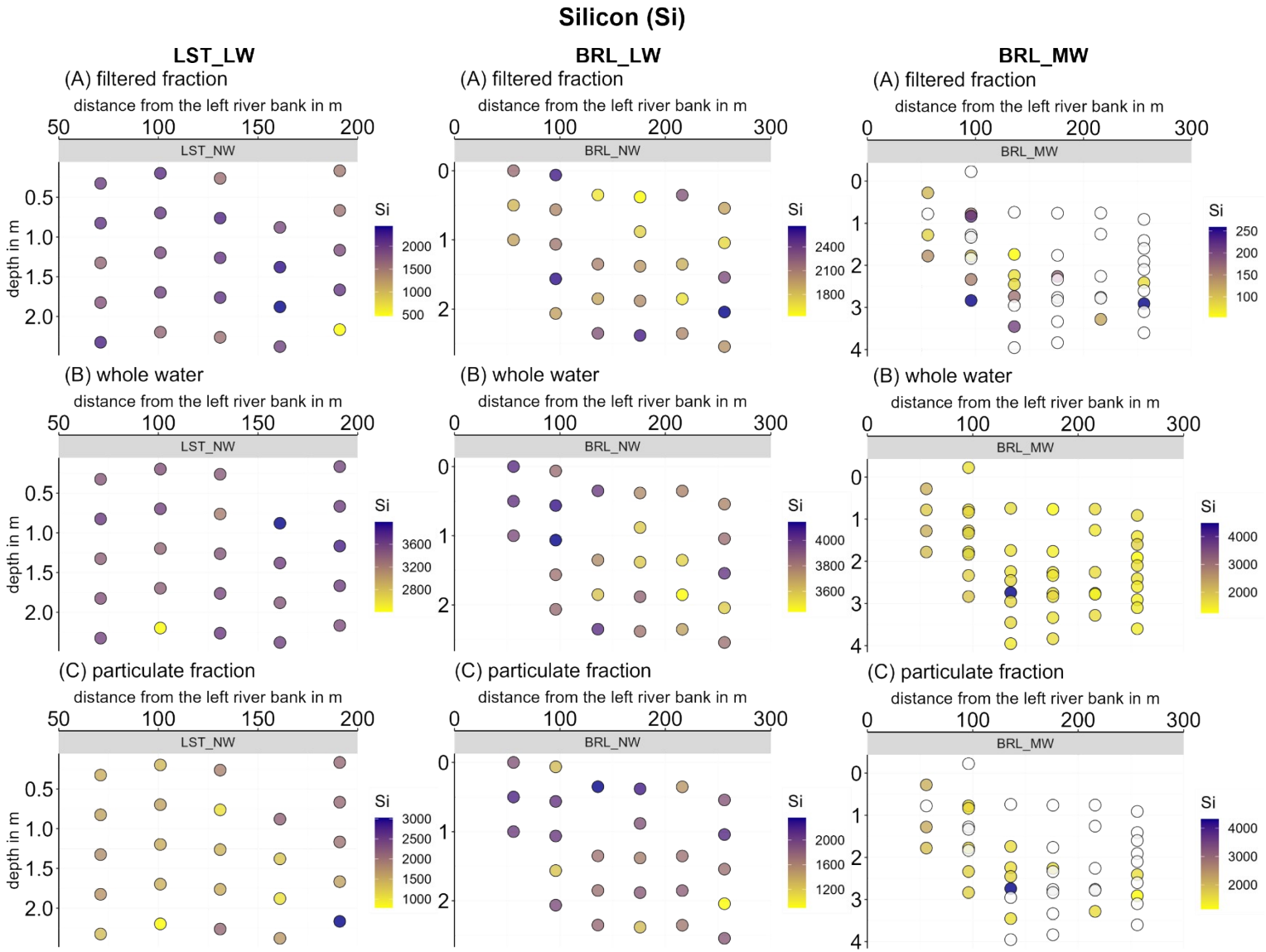
Concentrations in µg/l


Rubidium (Rb)
LST_LW
LST_HW
BRL_LW
BRL_MW
EMM_LW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
Rb
Concentrations in µg/l

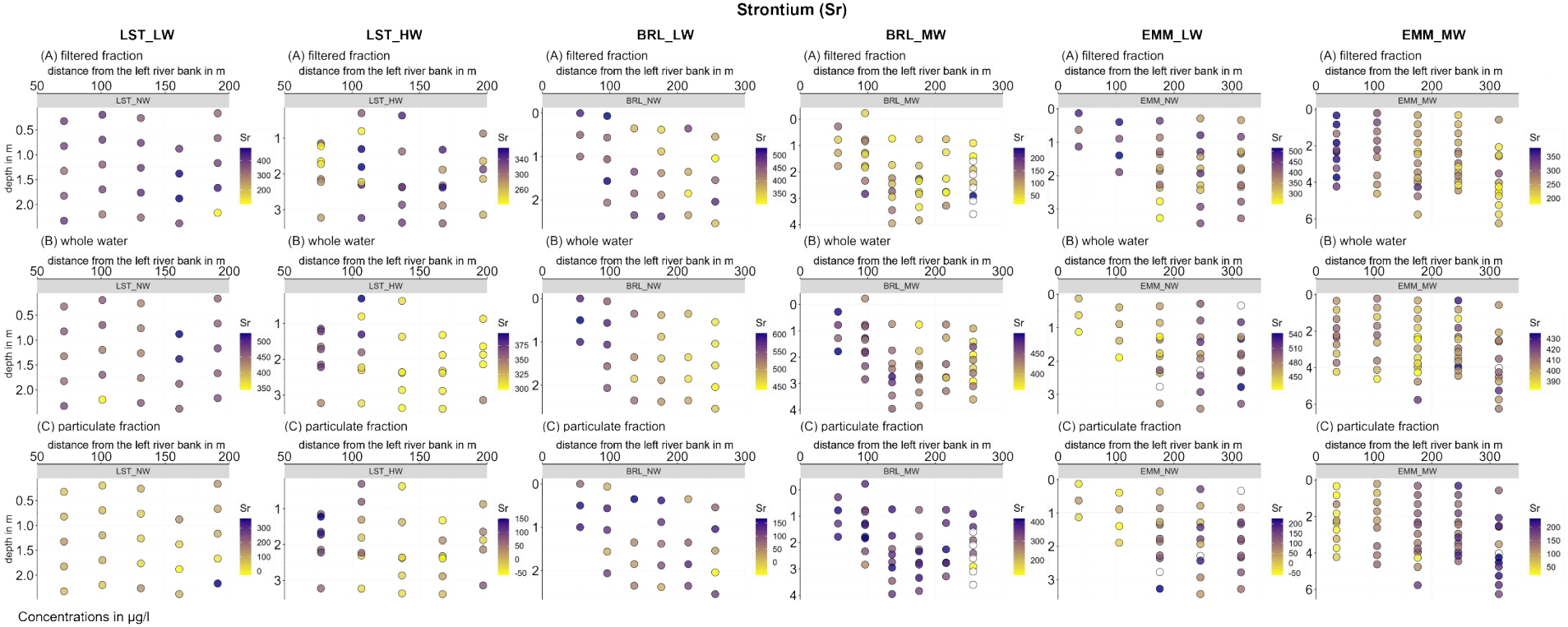
Sulfur (S)



Concentrations in µg/l



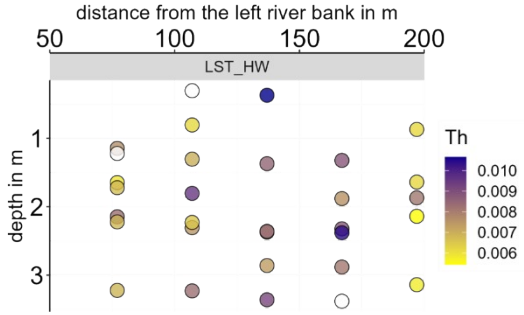
Concentrations in µg/l


Strontium (Sr)
LST_LW
LST_HW
BRL_LW
BRL_MW
EMM_LW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
Sr
LST_NW
LST_HW
BRL_NW
BRL_MW
EMM_NW
EMM_MW
Concentrations in µg/l

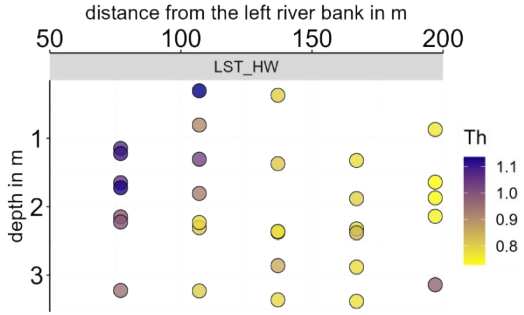
Thorium (Th)

LST_HW

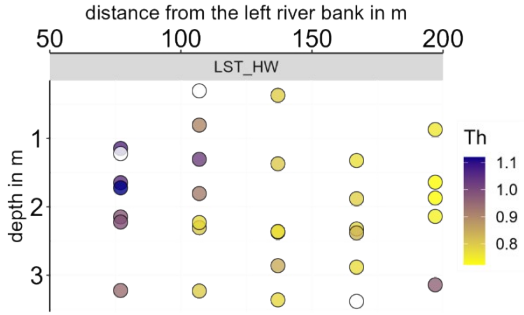
(A) filtered fraction



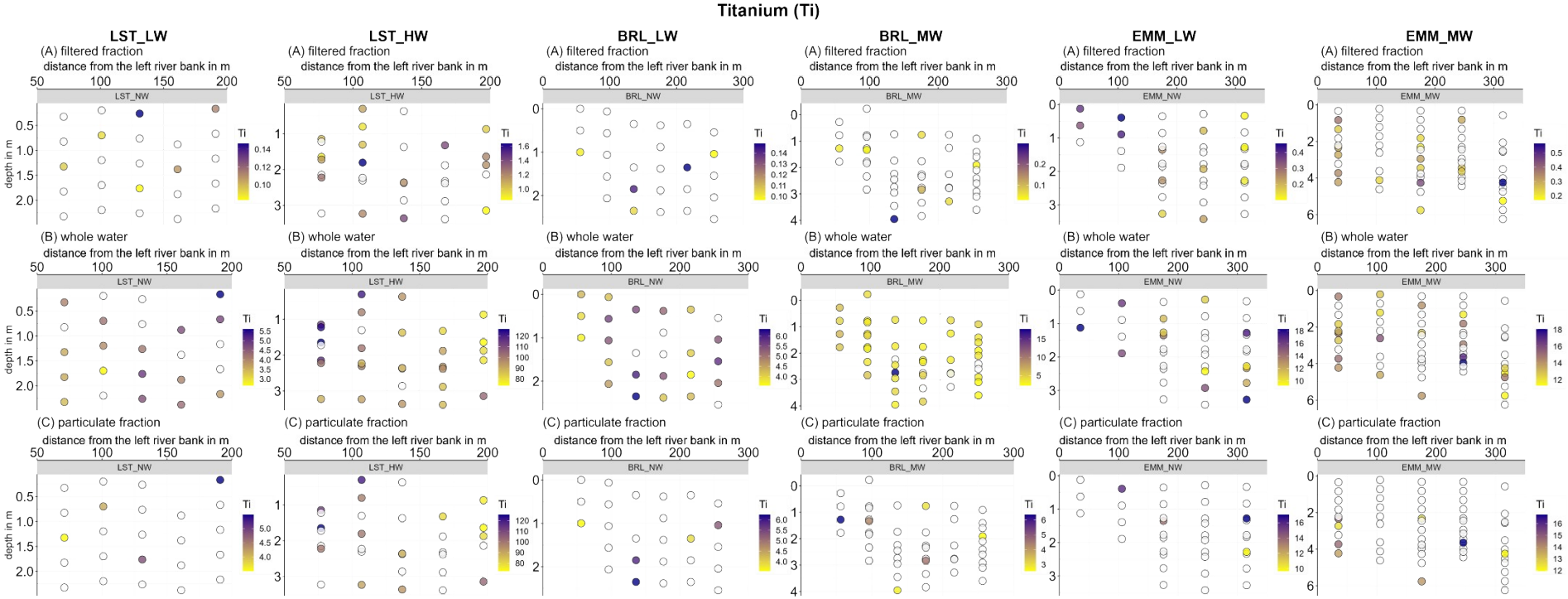
(B) whole water



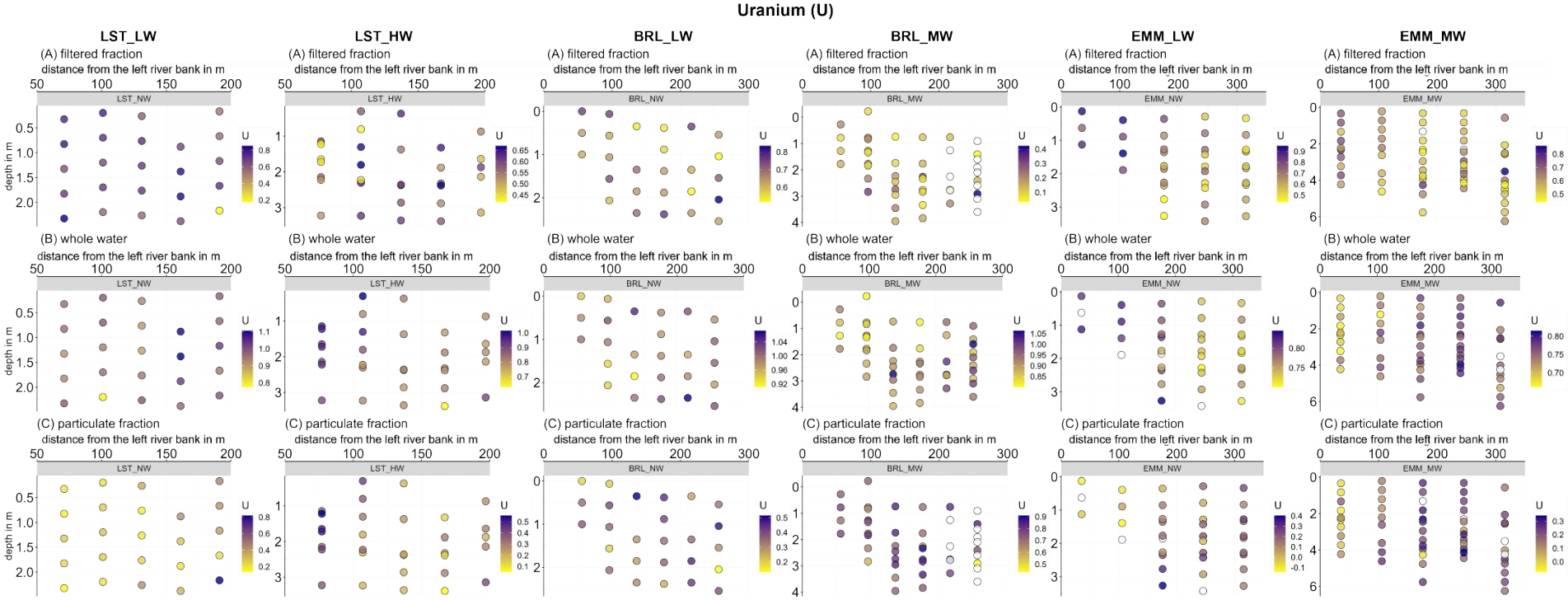
(C) particulate fraction



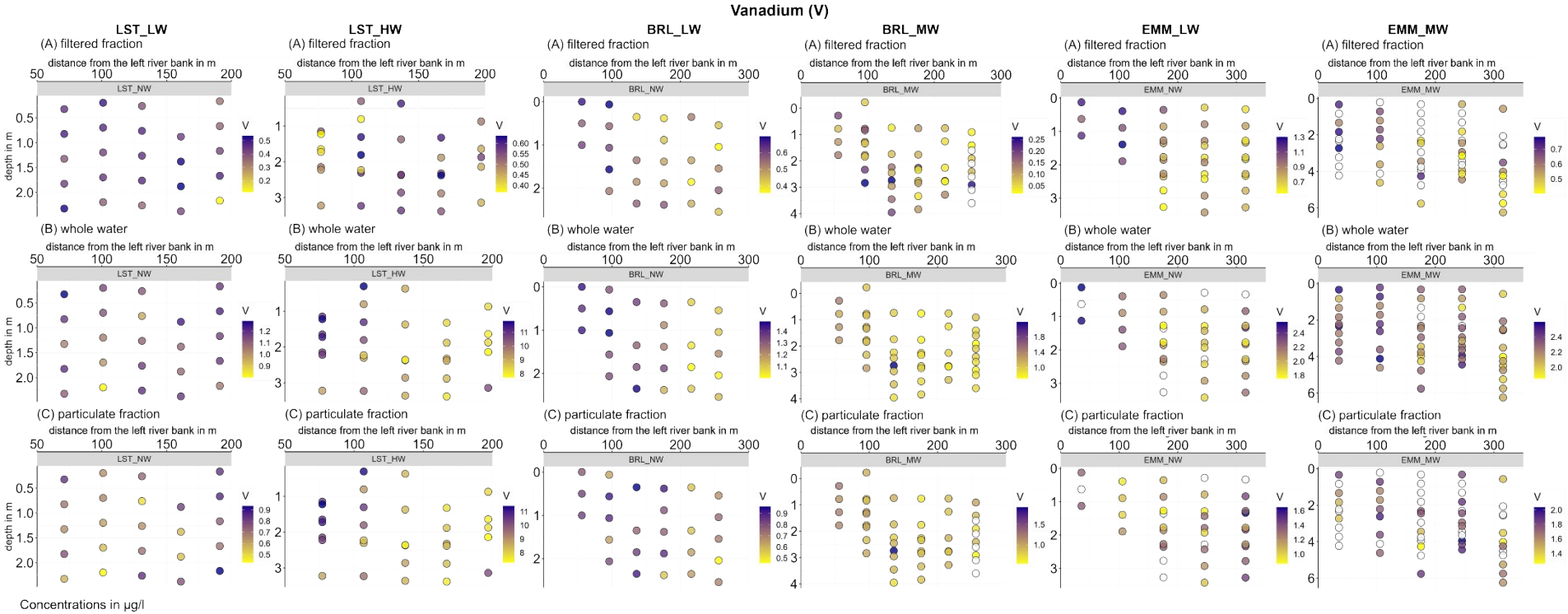
Concentrations in µg/l

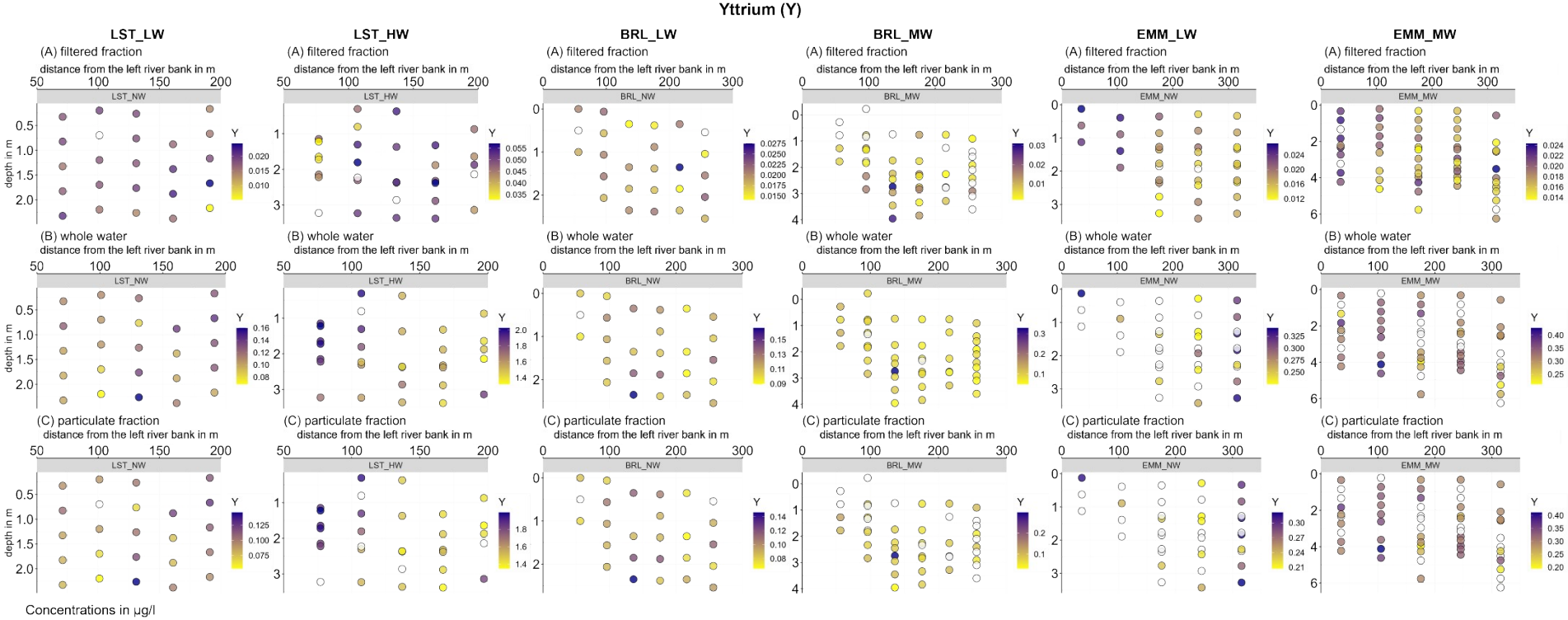


Concentrations in µg/l



Concentrations in µg/l

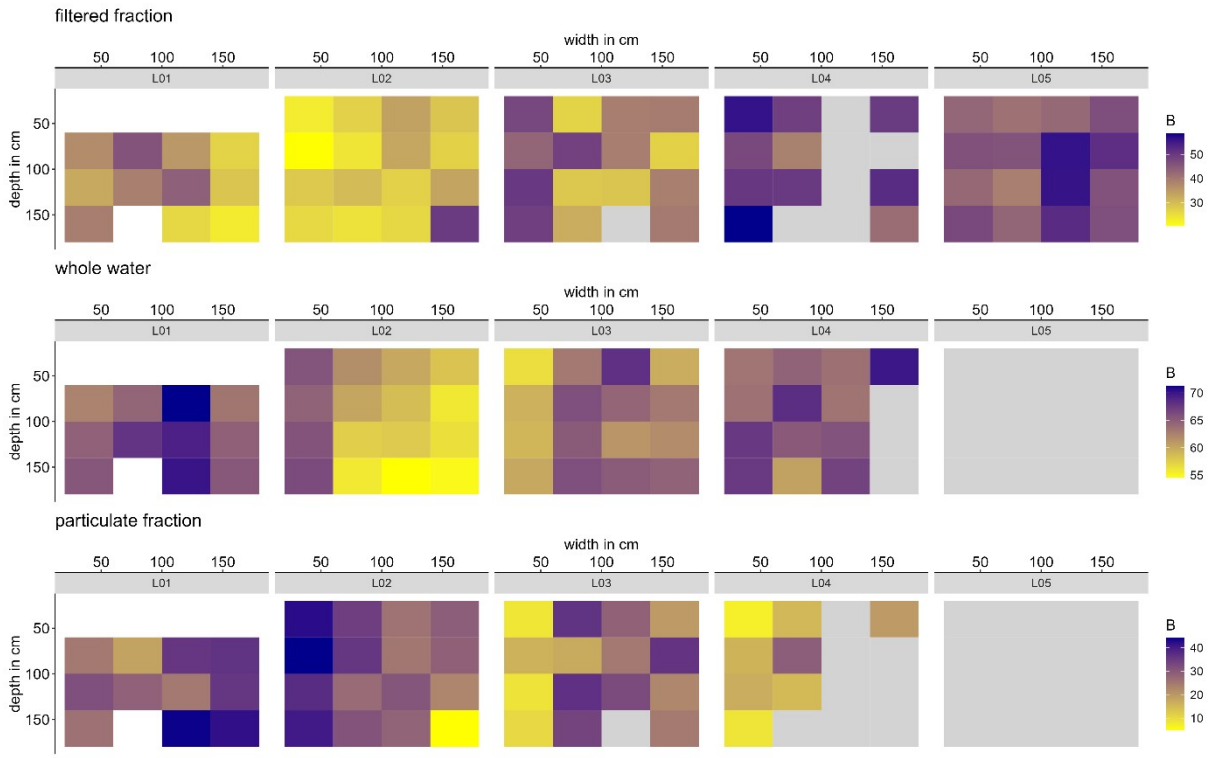

Vanadium (V)
LST_LW
LST_HW
BRL_LW
BRL_MW
EMM_LW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
V
Concentrations in µg/l


Yttrium (Y)
LST_LW
LST_HW
BRL_LW
BRL_MW
EMM_LW
EMM_MW
(A) filtered fraction
(B) whole water
(C) particulate fraction
distance from the left river bank in m
depth in m
Y
Concentrations in µg/l

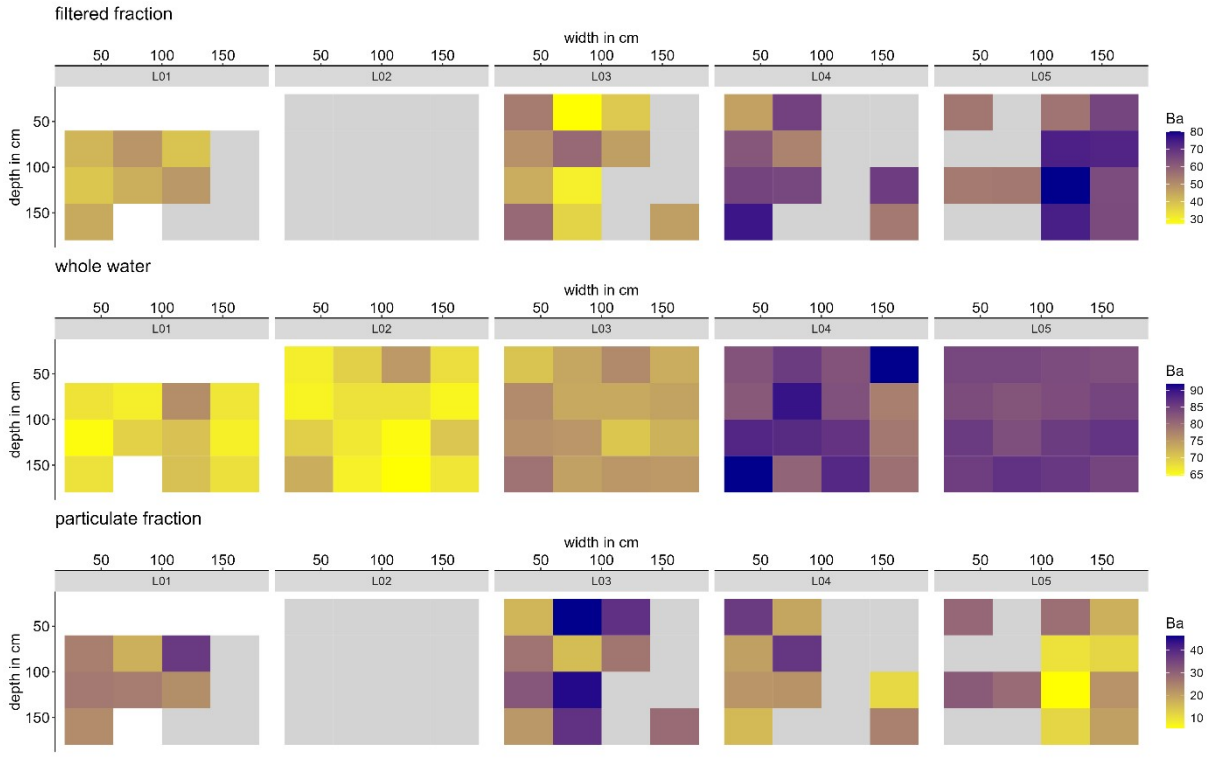
7. Heatmaps of the small-scale spatial variability in EMM (section 3.2.2 of the manuscript)

Element concentrations in µg/l in the small-scale spatial variability sampling campaigns in EMM in different sampling fractions: filtered fraction, whole water and calculated particulate fraction. L01 to L05 indicate one 4x4 sampling grid (16 sampling bottles) at the different sampling locations in the river cross-profile with the following distances from the left riverbank: L01: 35.5 m, L02: 105.5 m, L03: 175.5 m, L04: 245.5 m, L05: 315.5 m. Grey spots indicate measurements below LOQ or with RSDs > 10%. White spots indicate sampling spots which could not be sampled.

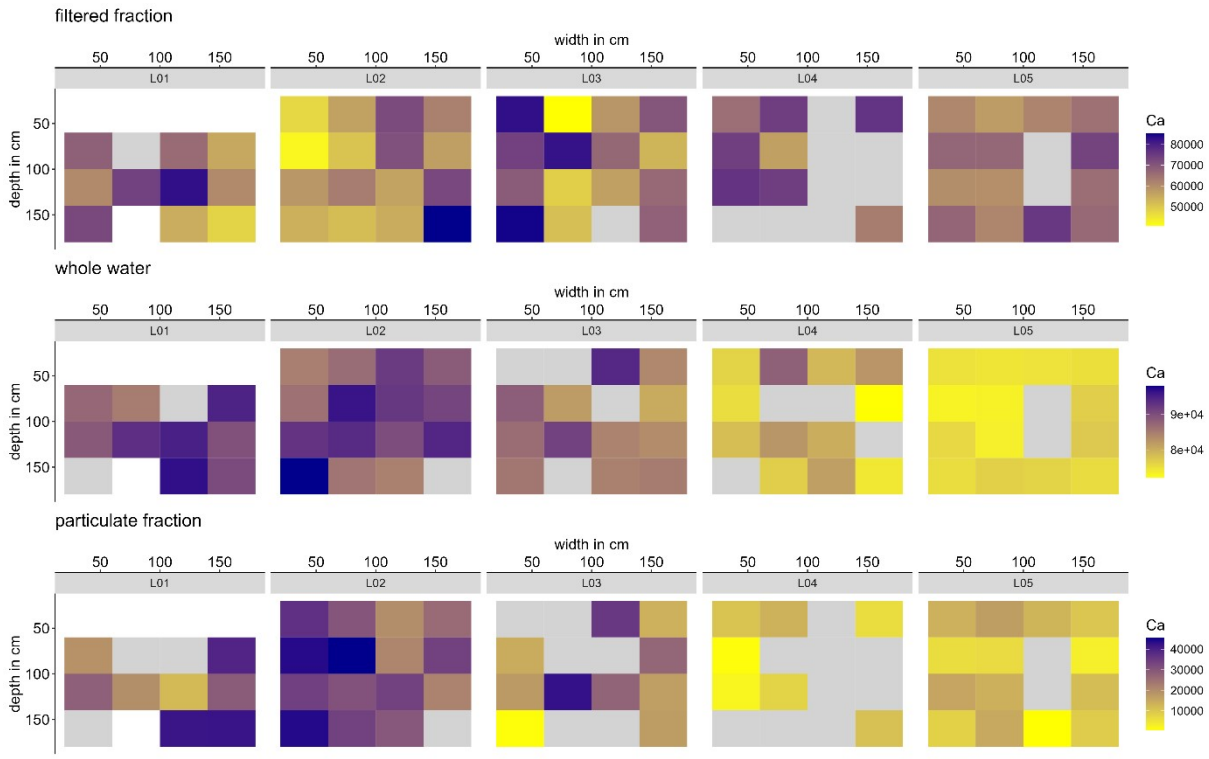
Boron (B)



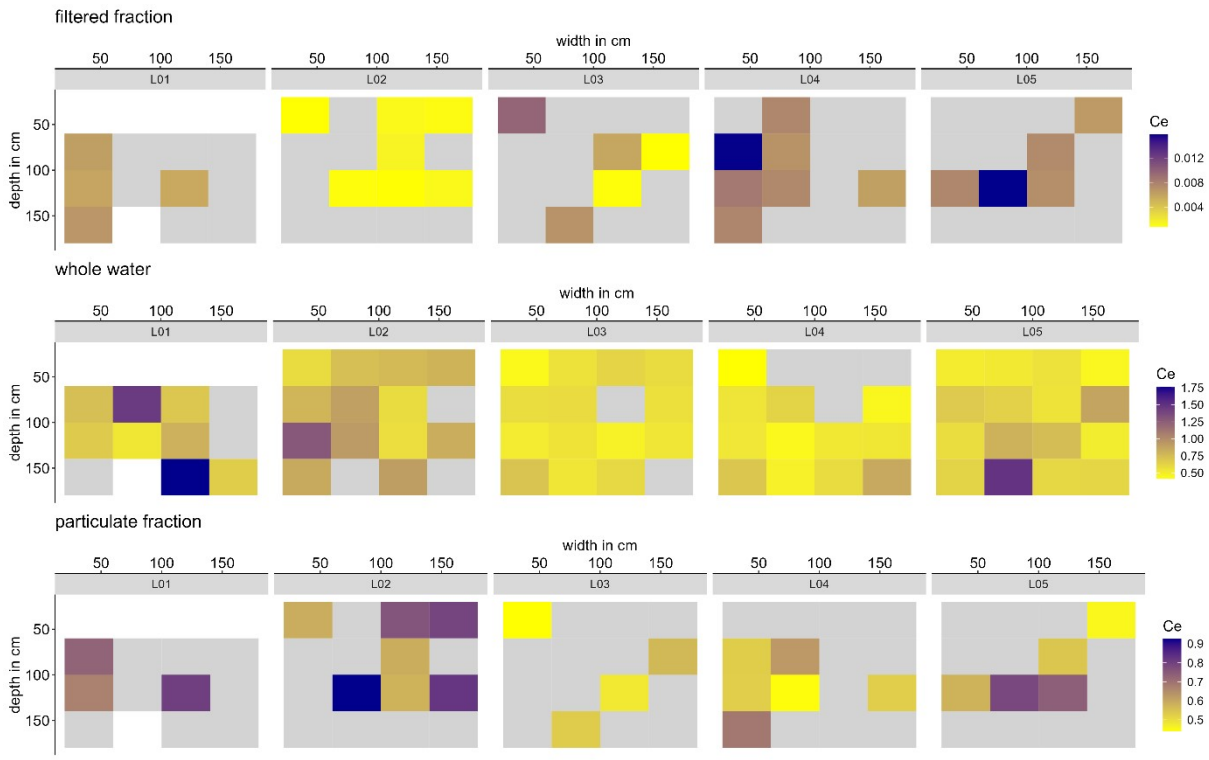
Barium (Ba)



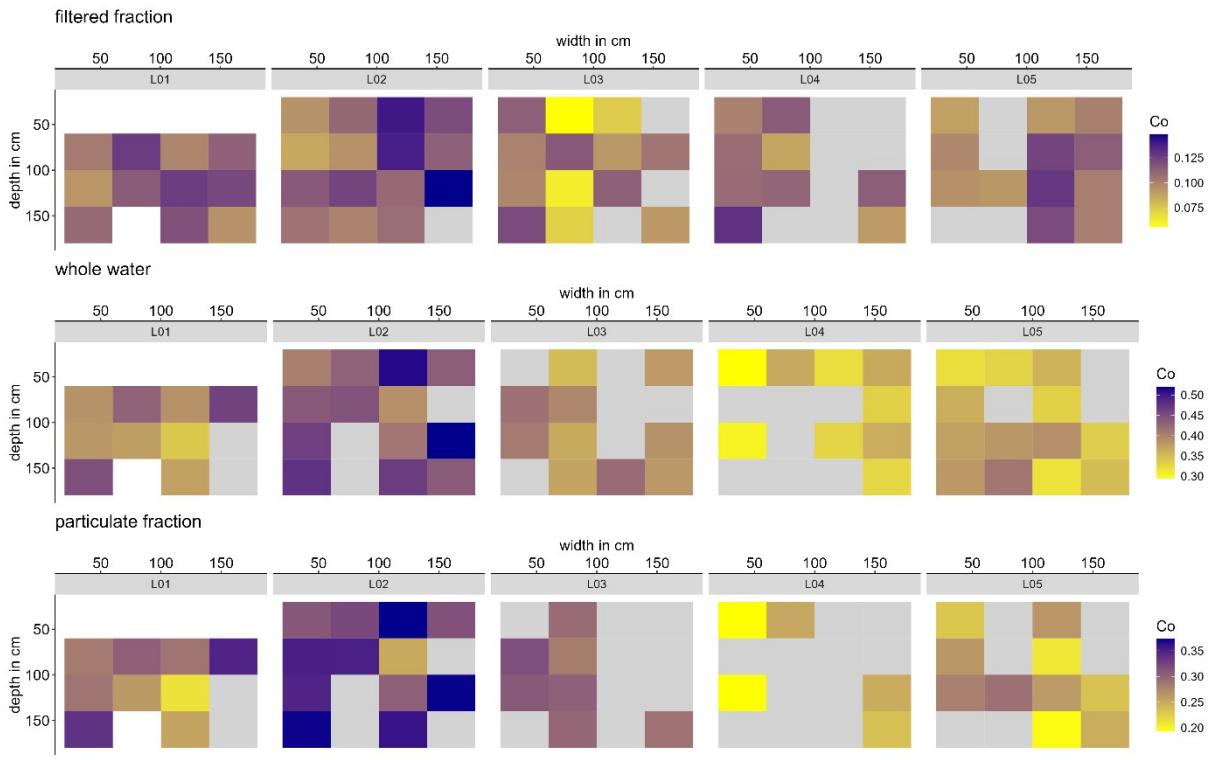
Calcium (Ca)



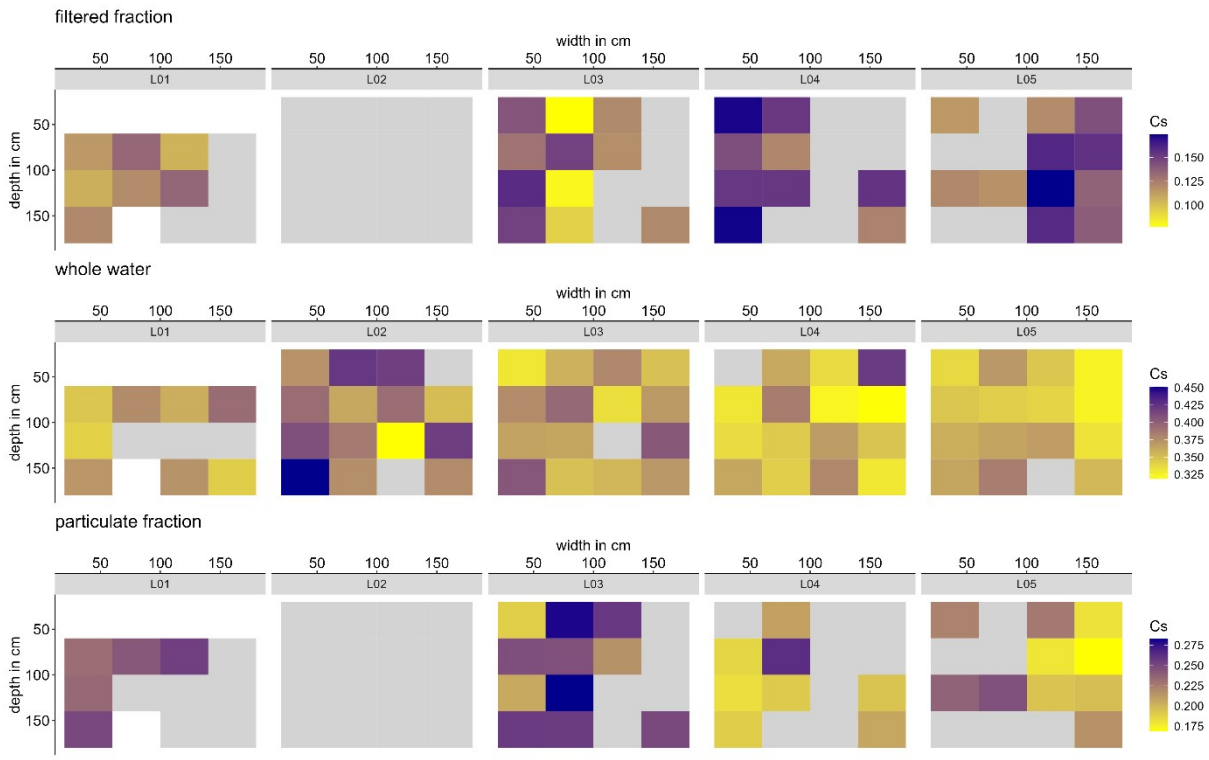
Cerium (Ce)



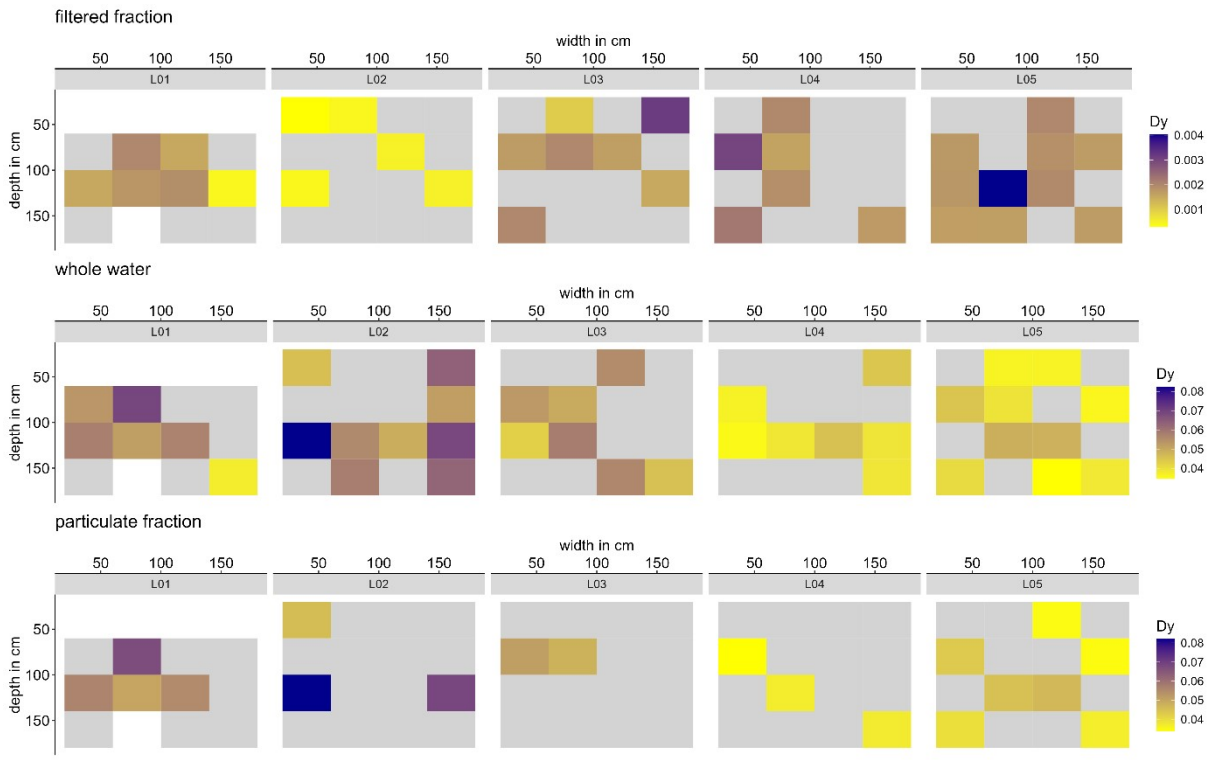
Cobalt (Co)



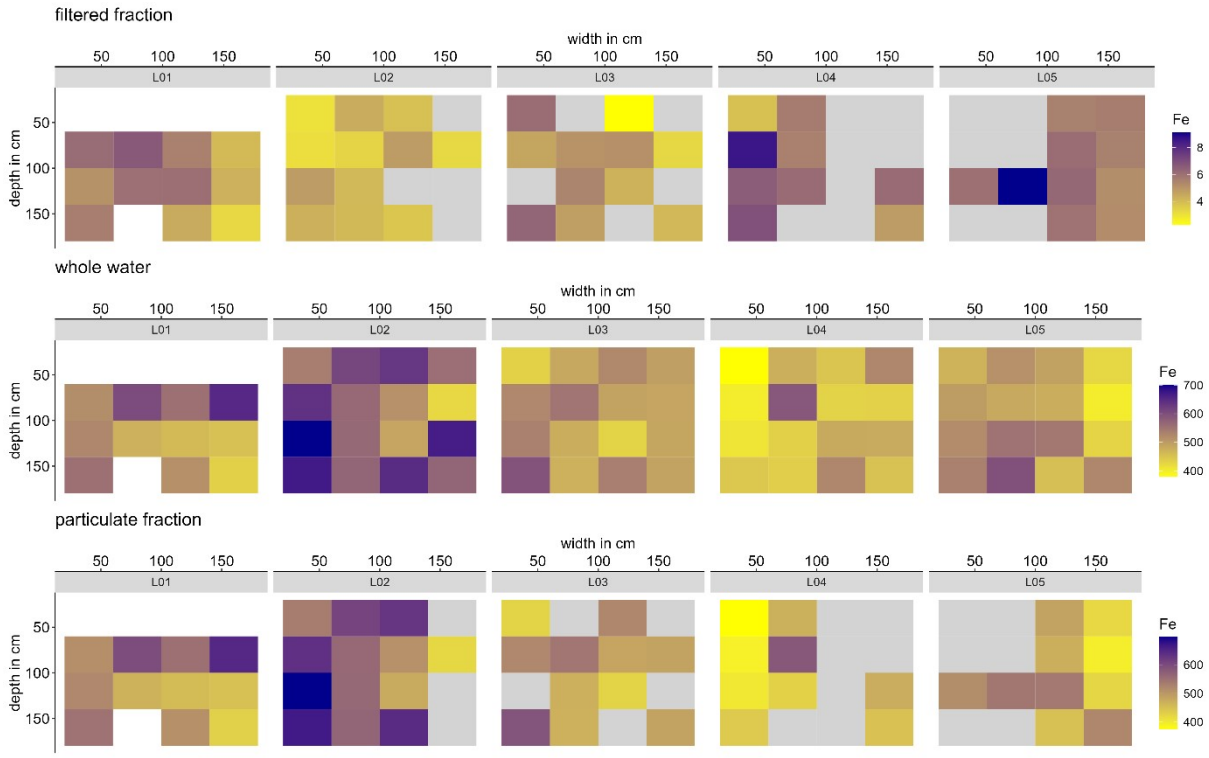
Cesium (Cs)



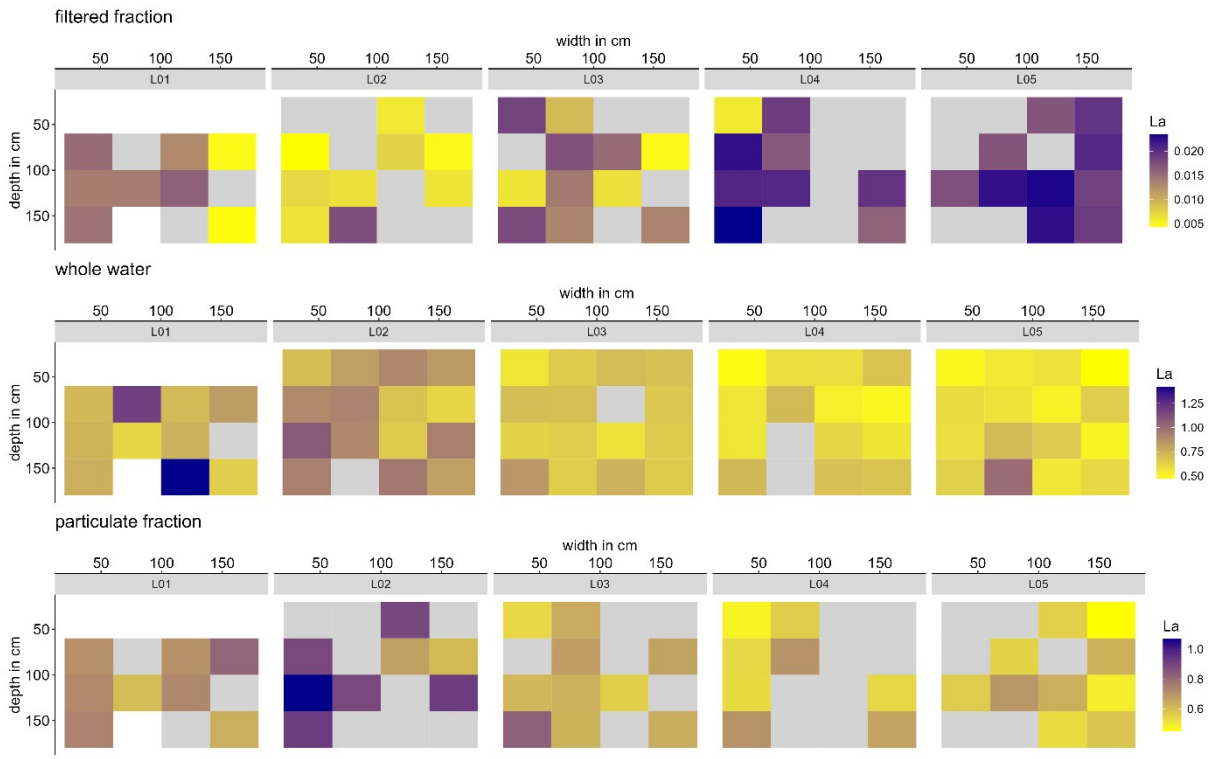
Dysprosium (Dy)



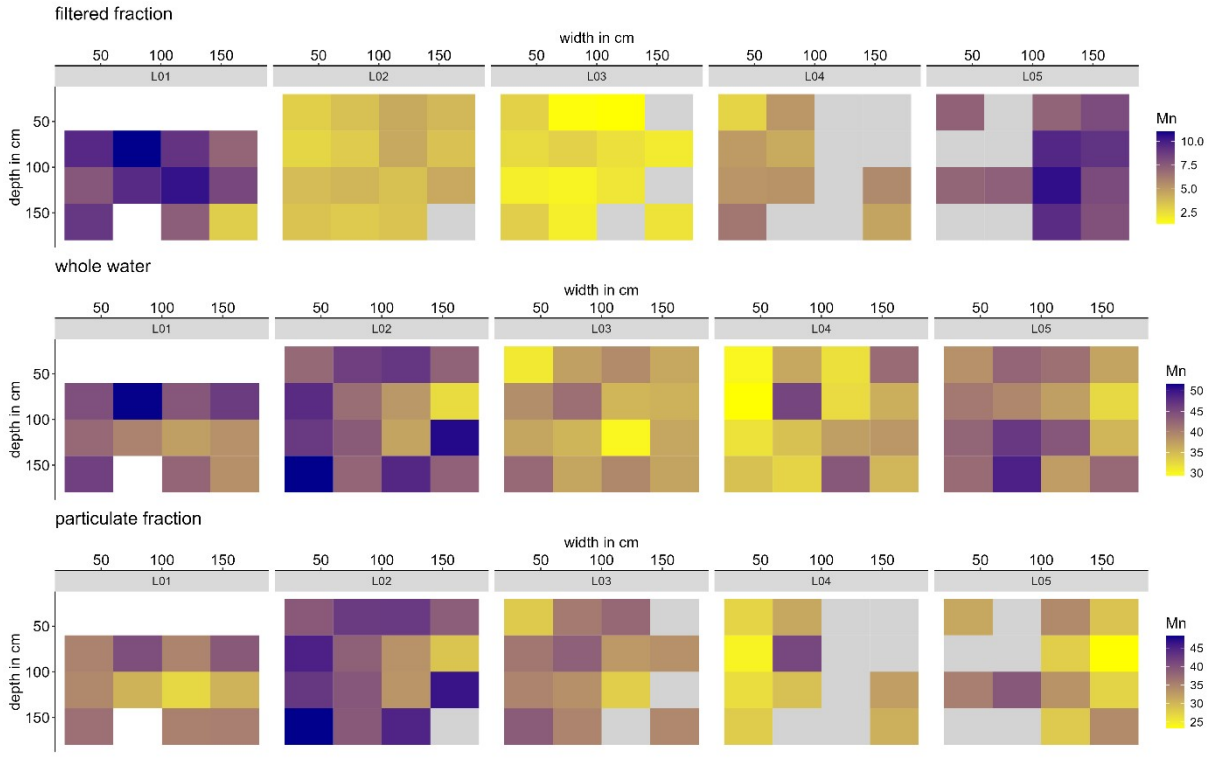
Iron (Fe)



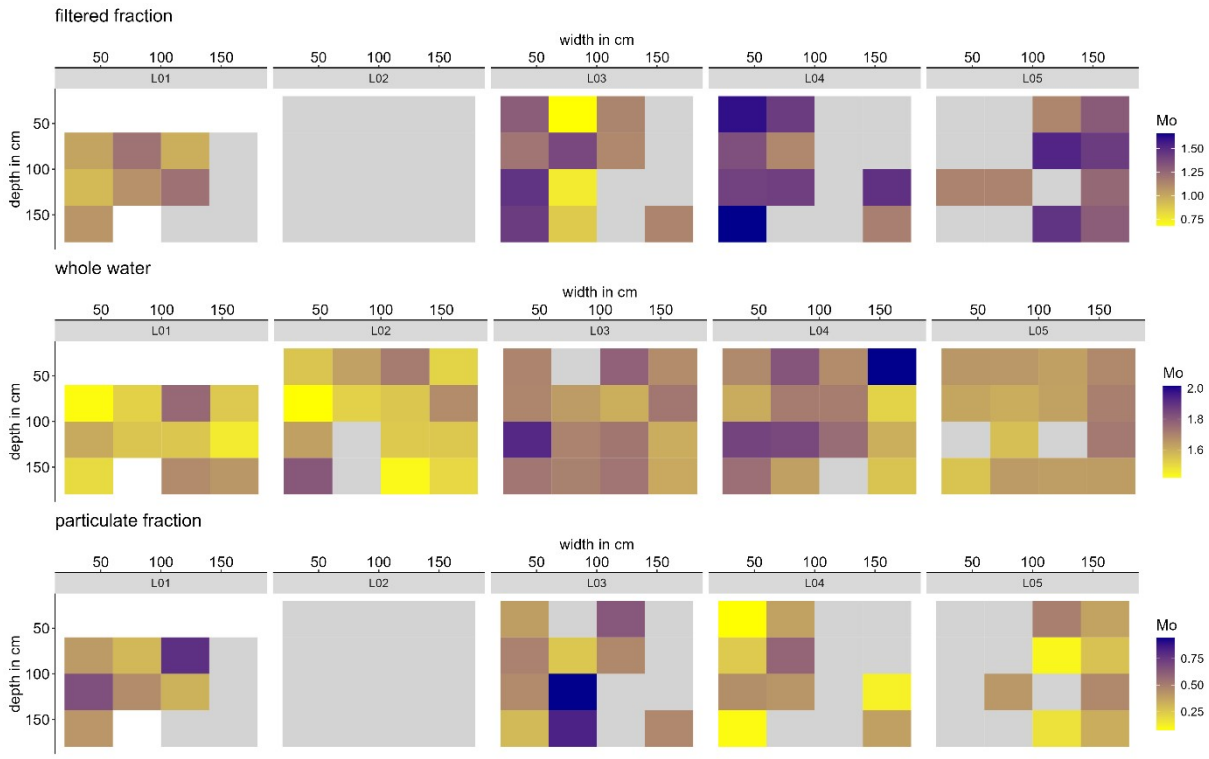
Lanthanum (La)



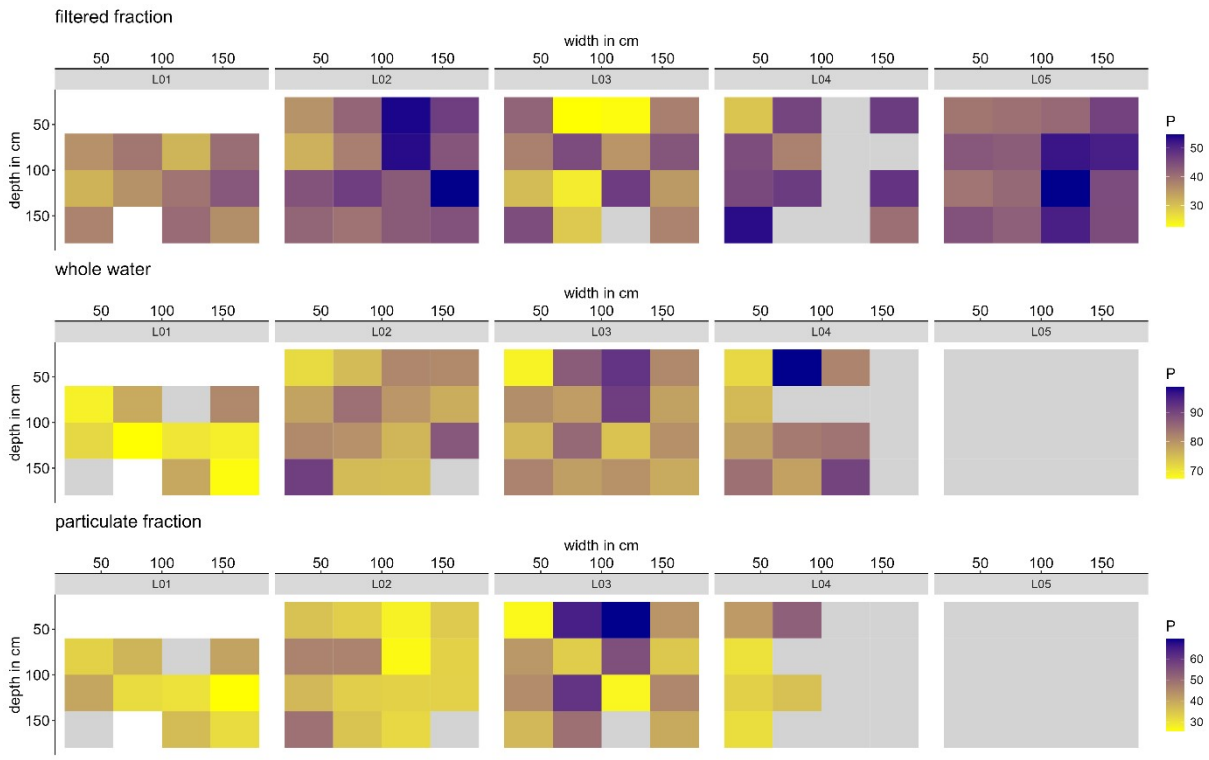
Manganese (Mn)



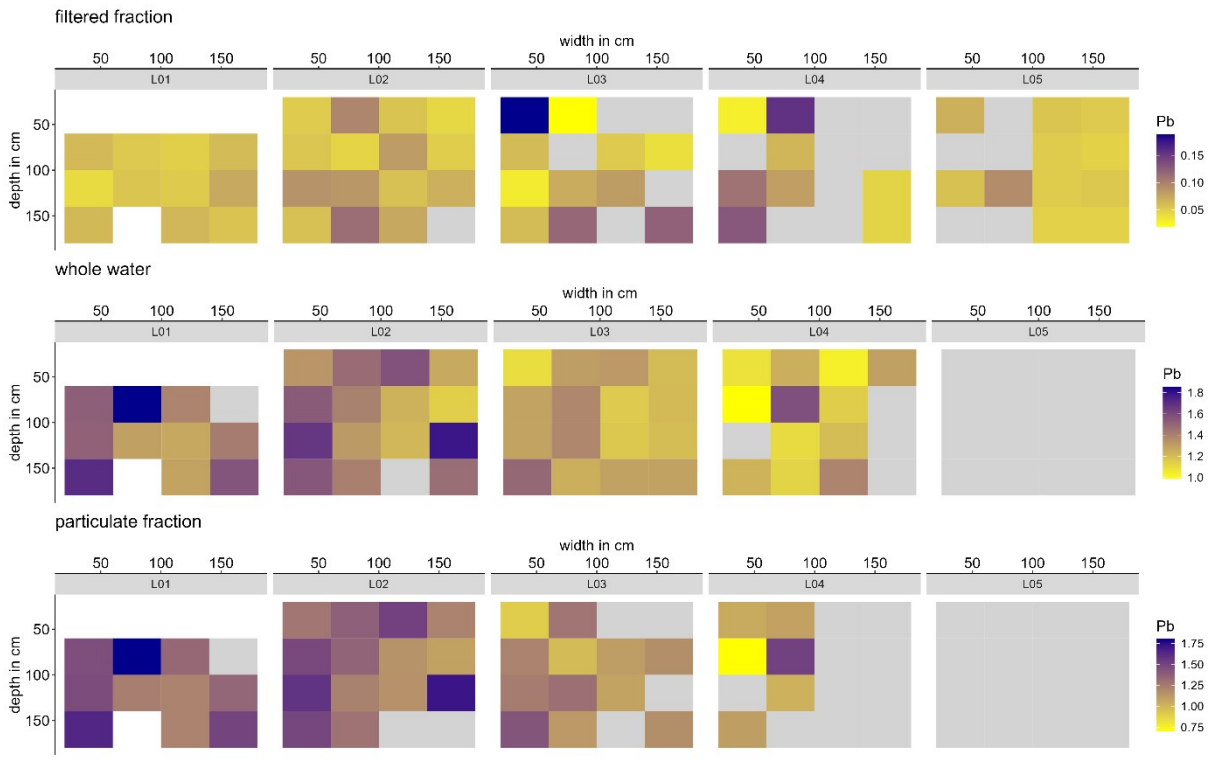
Molybdenum (Mo)



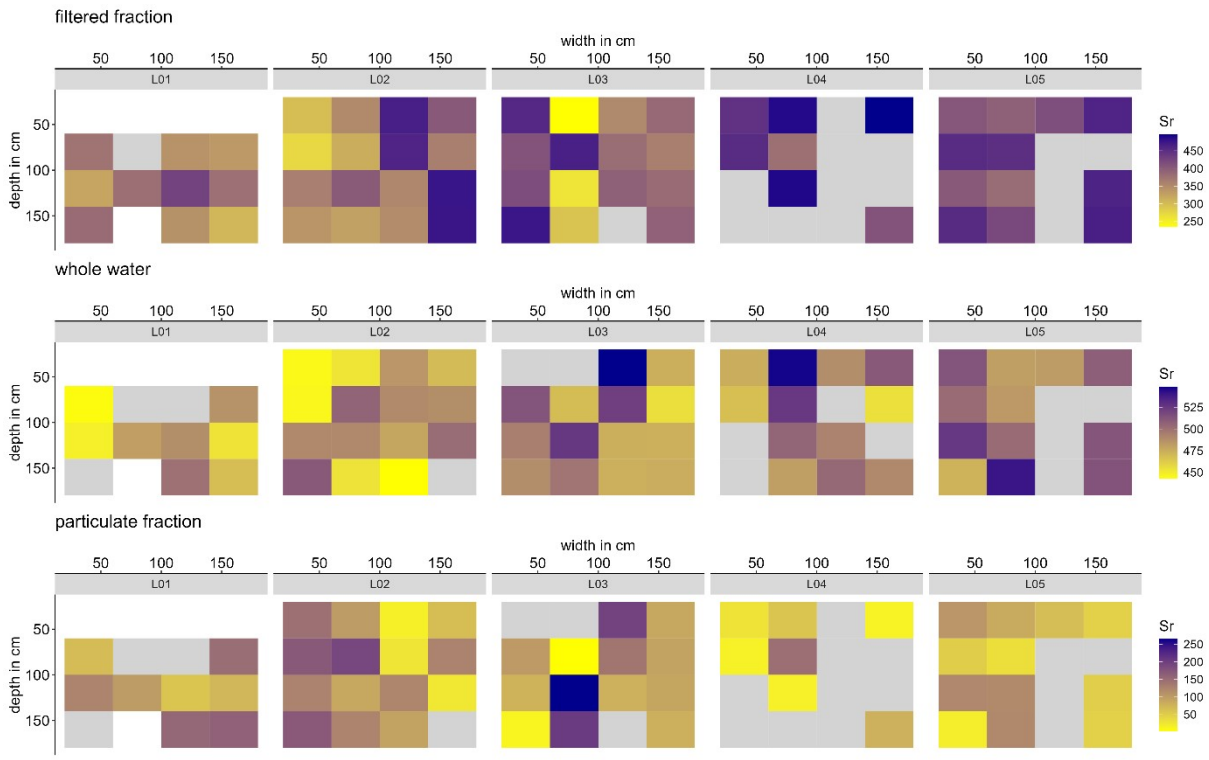
Phosphorus (P)



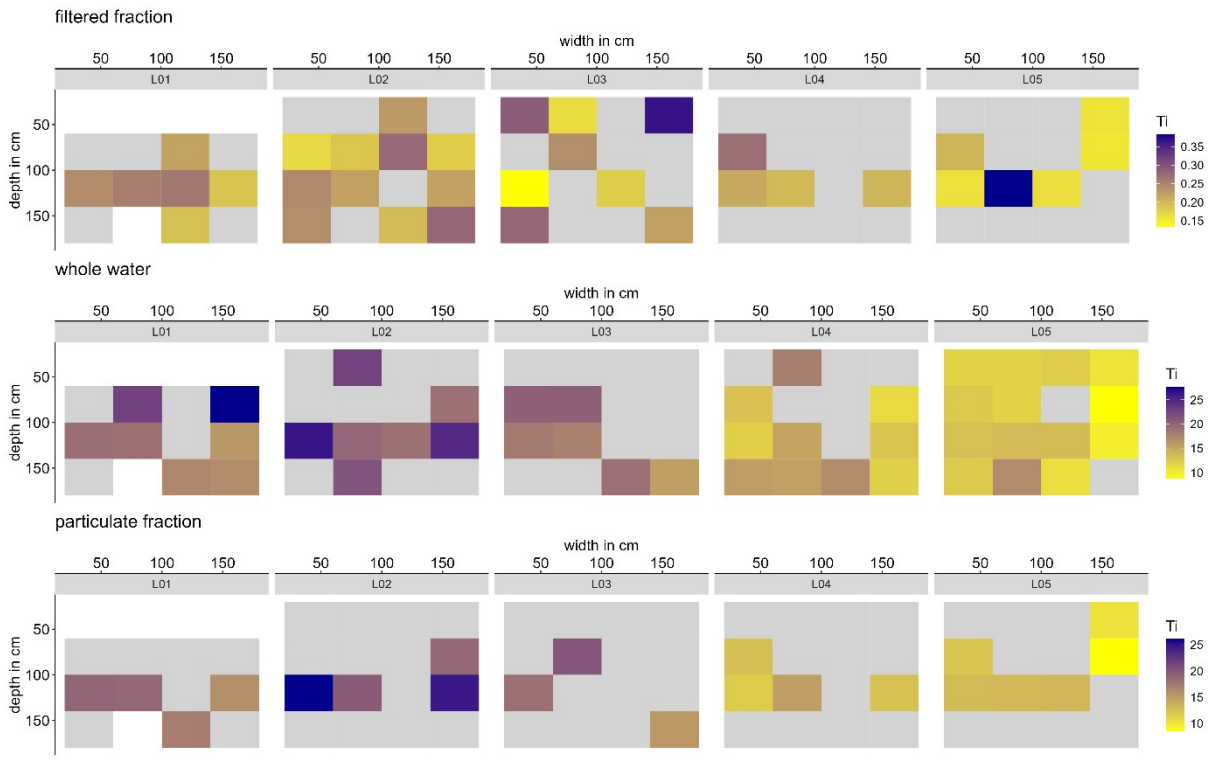
Lead (Pb)



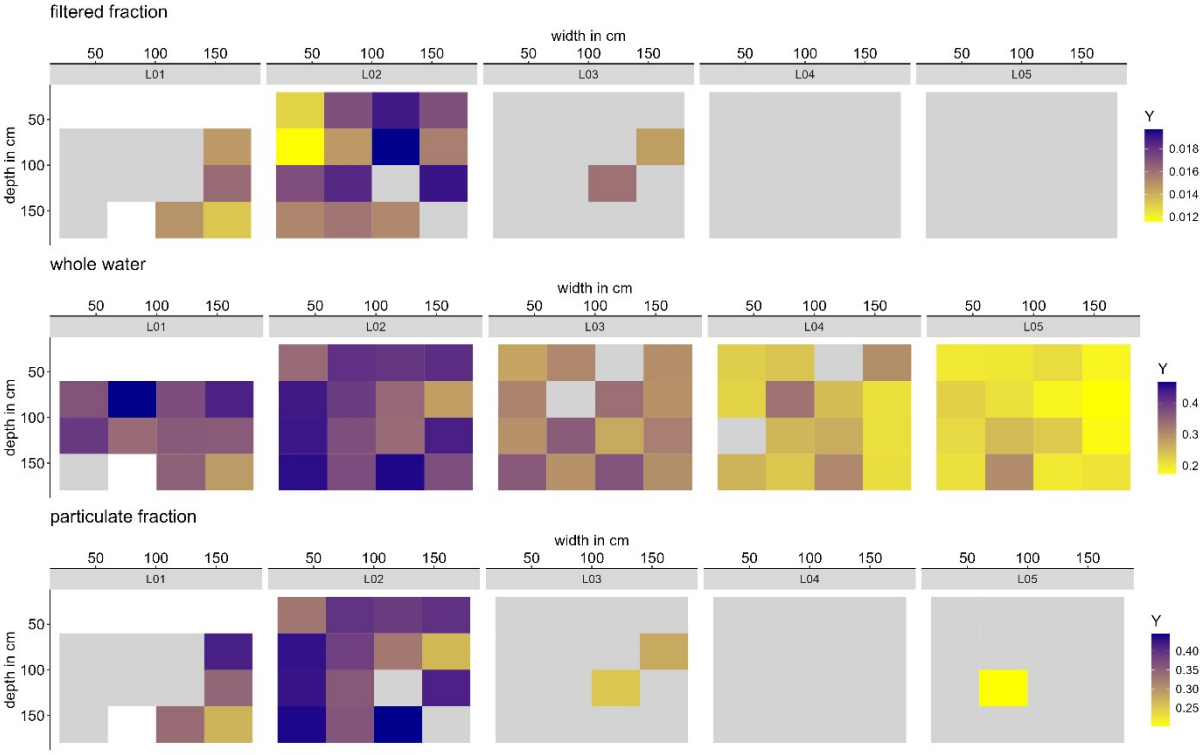
Strontium (Sr)



Titanium (Ti)



Yttrium (Y)


filtered fraction
width in cm
50 100 150
L01
L02
L03
L04
L05
depth in cm
50
100
150
Y
0.018
0.016
0.014
0.012
whole water
0.4
0.3
0.2
particulate fraction
0.40
0.35
0.30
0.25