Figure S1 : Land use map of the Rapel catchment (central Chile) showing major land cover classes, river network, and sampling locations

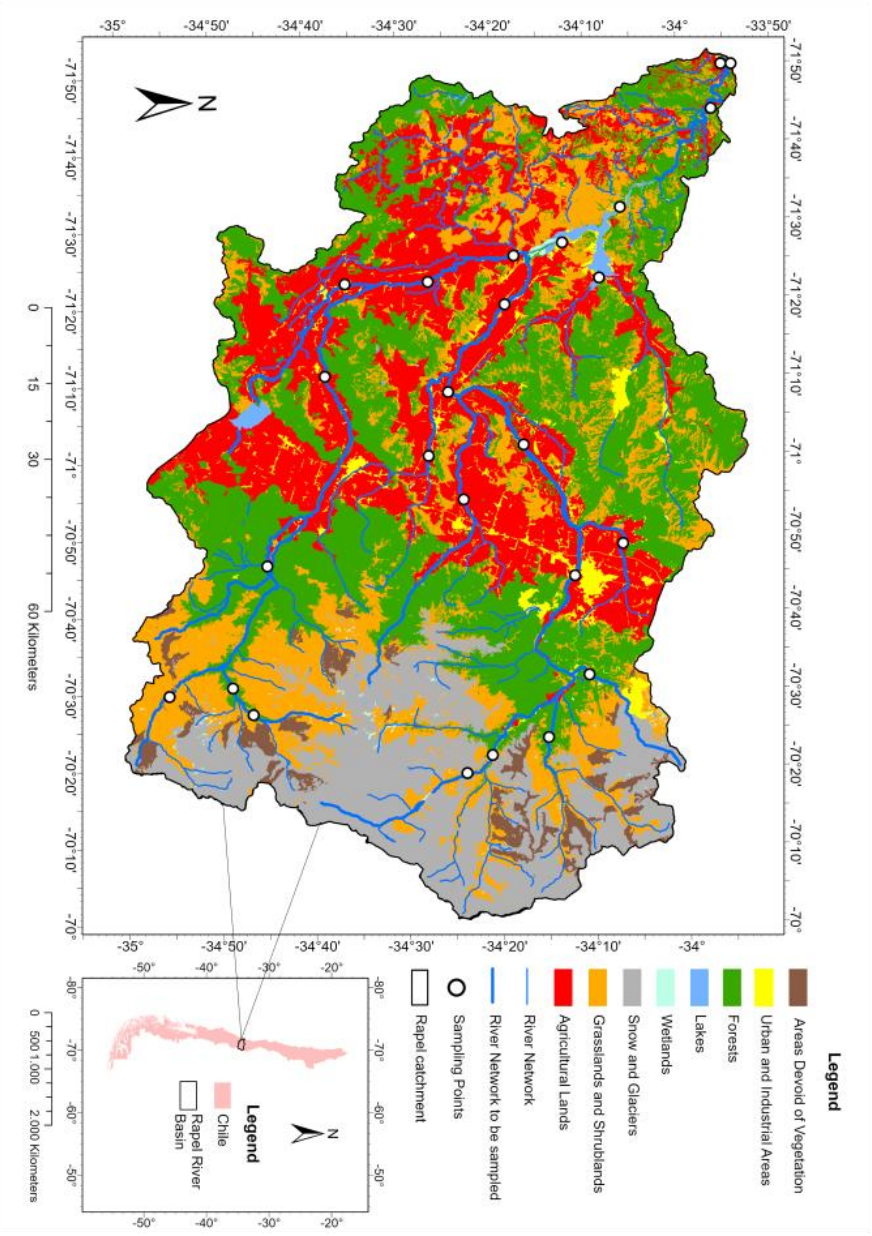


Figure S2: Loadings of the 4 components validated by the PARAFAC analysis of the EEMs

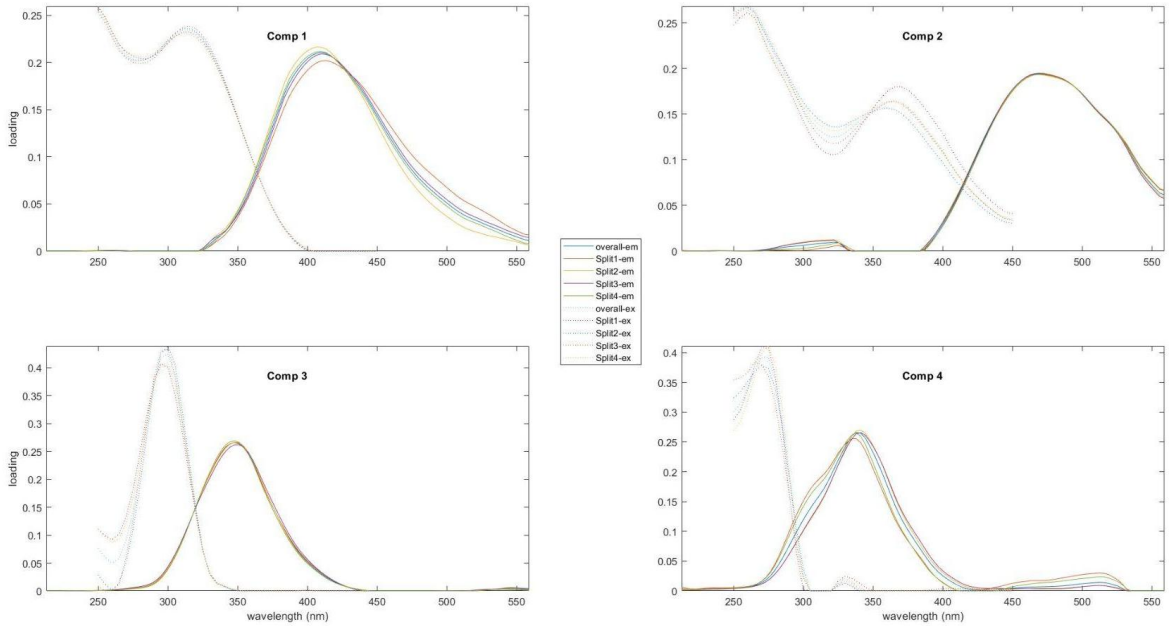


Fig. S3 – Spearman Correlations between the distance from glacier base, the elevation, the EC, the temperature and pH with physicochemical parameters, organic matter characteristics and metal concentrations. The number and the color indicate the ρ coefficient. Note that only the significant ($P < 0.05$) correlations are shown, empty cells mean no significant correlation.

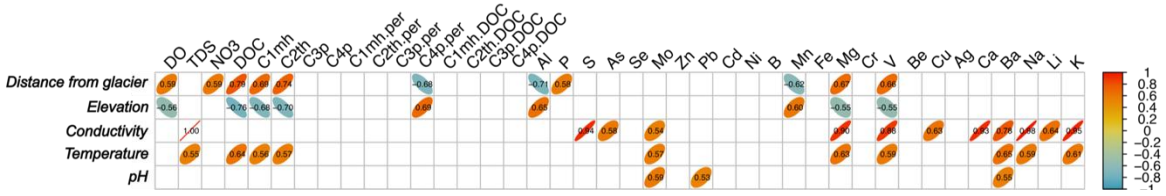


Fig. S4 - PCoA ordination based on Bray–Curtis distances showing the spatial and seasonal structuring of microbial communities across subcatchments and altitudinal zones. Each point represents a sample replicate.

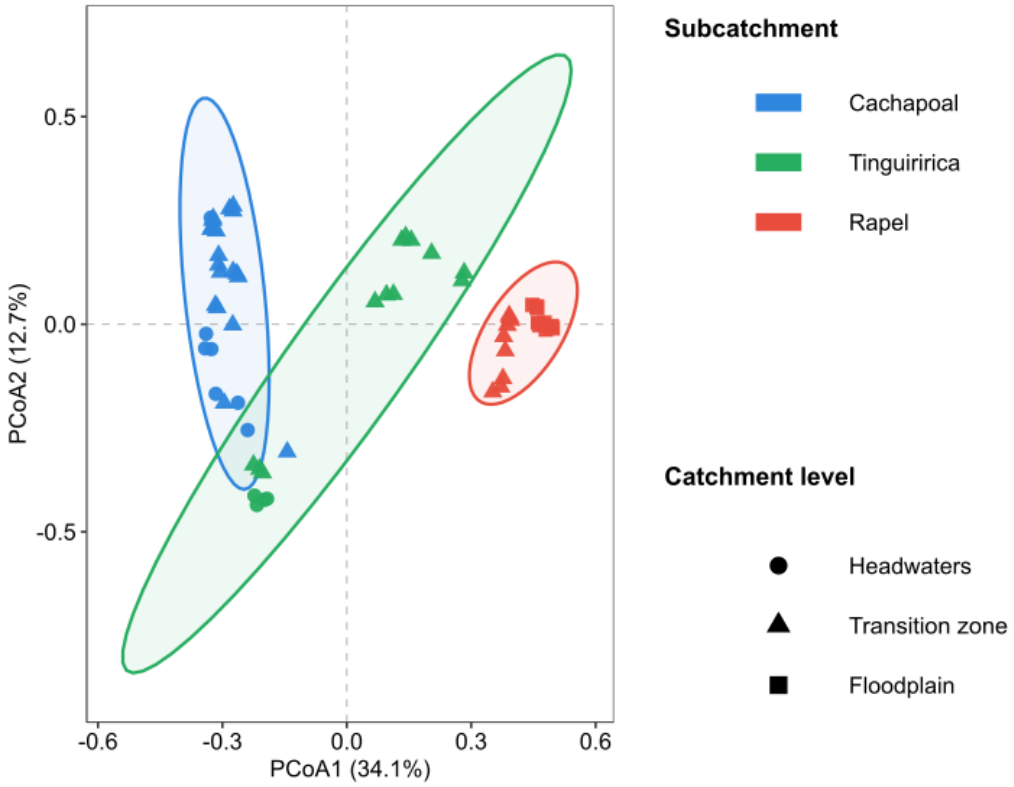


Table S1: Excitation and Emission maxima of the 4 FDOM components validated by PARAFAC analysis of the EEMs, their attribution to specific groups of fluorophores, and references to some examples of similar components within the Openfluor Database (TCC>0.97).

Component	λex max	λem max	Attribution	Similar components within Openfluor
C1mh	315	409	"Microbial" humic-like	**C2** in Logozzo et al. (2023) **C1** in Borisover et al. (2009) **C2** in Wampler et al. (2024) **C1** in Yan et al. (2020)27-10-2026 11:33:00
C2th	260 (365)	469	Terrestrial humic-like	**C2** in Yan et al. (2020) **C1** in Chen et al. (2019) **C1** in Menendez and Tzortziou (2024) **C2** in Borisover et al. (2009)
C3p	300	348	Protein-like	**C3** in Maurischat et al. (2022) **C6** in Eder et al. (2022) **C1** in Chen et al. (2018)
C4p	275	338	Protein-like	**C6** in Lapierre and del Giorgio, (2014) **C7** in Lambert et al. (2017) **C7** in Eder et al. (2022) **C3** in Nimptsch et al. (2015)

References

Borisover, M., Laor, Y., Parparov, A., Bukhanovsky, N., and Lado, M.: Spatial and seasonal patterns of fluorescent organic matter in Lake Kinneret (Sea of Galilee) and its catchment basin, Water Research, 43, 3104–3116, https://doi.org/10.1016/j.watres.2009.04.039, 2009.

Chen, M., Jung, J., Lee, Y. K., and Hur, J.: Surface accumulation of low molecular weight dissolved organic matter in surface waters and horizontal off-shelf spreading of nutrients and humic-like fluorescence in the Chukchi Sea of the Arctic Ocean, Science of The Total Environment, 639, 624–632, https://doi.org/10.1016/j.scitotenv.2018.05.205, 2018.

Chen, S., Lu, Y., Dash, P., Das, P., Li, J., Capps, K., Majidzadeh, H., and Elliott, M.: Hurricane pulses: Small watershed exports of dissolved nutrients and organic matter during large storms in the Southeastern USA, Science of The Total Environment, 689, 232–244, https://doi.org/10.1016/j.scitotenv.2019.06.351, 2019.

Eder, A., Weigelhofer, G., Pucher, M., Tiefenbacher, A., Strauss, P., Brandl, M., and Blöschl, G.: Pathways and composition of dissolved organic carbon in a small agricultural

77 catchment during base flow conditions, Ecohydrology & Hydrobiology, 22, 96–112,
78 https://doi.org/10.1016/j.ecohyd.2021.07.012, 2022.

79 Lambert, T., Bouillon, S., Darchambeau, F., Morana, C., Roland, F. A. E., Descy, J.-P., and
80 Borges, A. V.: Effects of human land use on the terrestrial and aquatic sources of fluvial
81 organic matter in a temperate river basin (The Meuse River, Belgium), Biogeochemistry,
82 https://doi.org/10.1007/s10533-017-0387-9, 2017.

83 Lapierre, J. F. and del Giorgio, P. A.: Partial coupling and differential regulation of
84 biologically and photochemically labile dissolved organic carbon across boreal aquatic
85 networks, Biogeosciences, 11, 5969–5985, https://doi.org/10.5194/bg-11-5969-2014, 2014.

86 Logozzo, L. A., Hosen, J. D., McArthur, J., and Raymond, P. A.: Distinct drivers of two
87 size fractions of operationally dissolved iron in a temperate river, Limnology and
88 Oceanography, 68, 1185–1200, https://doi.org/10.1002/lno.12338, 2023.

89 Maurischat, P., Lehnert, L., Zerres, V. H. D., Tran, T. V., Kalbitz, K., Rinnan, Å., Li, X.
90 G., Dorji, T., and Guggenberger, G.: The glacial–terrestrial–fluvial pathway: A
91 multiparametrical analysis of spatiotemporal dissolved organic matter variation in three
92 catchments of Lake Nam Co, Tibetan Plateau, Science of The Total Environment, 838,
93 156542, https://doi.org/10.1016/j.scitotenv.2022.156542, 2022.

94 Menendez, A. and Tzortziou, M.: Driving factors of colored dissolved organic matter
95 dynamics across a complex urbanized estuary, Science of The Total Environment, 921,
96 171083, https://doi.org/10.1016/j.scitotenv.2024.171083, 2024.

97 Nimptsch, J., Woelfl, S., Osorio, S., Valenzuela, J., Ebersbach, P., von Tuempling, W.,
98 Palma, R., Encina, F., Figueroa, D., Kamjunke, N., and Graeber, D.: Tracing dissolved
99 organic matter (DOM) from land-based aquaculture systems in North Patagonian streams,
100 Science of the Total Environment, 537, 129–138,
101 https://doi.org/https://doi.org/10.1016/j.scitotenv.2015.07.160, 2015.

102 Wampler, K. A., Bladon, K. D., Myers-Pigg, A., and Jr., J. A. R.: Spatial and temporal
103 shifts in dissolved organic matter composition across a burned stream network, ESS Open
104 Archive, https://doi.org/10.22541/essoar.173524605.50324304/v1, 2024.

105 Yan, C., Sheng, Y., Ju, M., Ding, C., Li, Q., Luo, Z., Ding, M., and Nie, M.: Relationship
106 between the characterization of natural colloids and metal elements in surface waters,
107 Environ Sci Pollut Res, 27, 31872–31883, https://doi.org/10.1007/s11356-020-09500-x,
108 2020.

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Table S2: Physical and chemical in-situ parameters, percentage of fluorescence components, and elements concentration in water samples of the Rapel catchment. Metals and metalloids concentration below the detection limit of the instrument are indicated as <DL.

	Cachapoal subcatchment										
	C-C1	**C-C2**	**C-C3**	**C-C4**	**C-C5**	**C-Ca**	**C-Cl**	**C-Cor**	**C-Coy**	**C-P**	**C-Z**
pH	8.04	7.68	8.09	8.01	8.06	7.36	7.39	7.90	5.97	7.95	7.55
EC (µS cm^{-1})	635	386	435	610	542	596	377	269	746	307	451
Salinity	0.32	0.19	0.21	0.30	0.26	0.29	0.18	0.13	0.37	0.15	0.22
Temp (°C)	13.14	16.70	21.55	15.80	17.45	19.30	15.22	11.90	21.22	16.12	16.88
DO (mg L^{-1})	6.33	5.73	9.30	9.90	9.10	4.46	7.49	8.38	6.10	5.70	9.11
TDS (mg L^{-1})	320	194	218	305	271	300	189	135	376	143	225
NO_3^- (µM)	10.3	14.5	35.7	193.3	127.8	84.9	142.7	10.5	52.9	14.6	274.7
C1mh (%)	4.9	12.0	12.7	26.4	6.4	26.8	14.1	19.8	10.1	18.2	37.5
C2th (%)	0.1	8.8	9.7	21.2	5.0	14.4	12.9	15.5	3.5	13.1	30.7
C3p (%)	61.0	59.6	57.3	36.9	71.0	36.2	54.9	37.4	61.0	50.3	15.6
C4p (%)	34.0	19.7	20.3	15.6	17.7	22.7	18.1	27.3	25.4	18.4	16.3
Ag (ppm)	0.022	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Al (ppm)	0.043	0.065	0.042	0.006	0.015	0.017	0.005	0.002	0.021	0.075	<DL
As (ppm)	0.016	0.004	0.009	0.007	0.009	0.006	0.004	0.000	0.002	0.010	0.000
B (ppm)	0.126	<DL	0.015	0.003	0.011	0.017	<DL	<DL	<DL	<DL	<DL
Ba (ppm)	0.014	0.011	0.013	0.015	0.016	0.016	0.007	0.008	0.018	0.015	0.007
Be (ppm)	0.001	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.002	<DL
Ca (ppm)	23.204	21.067	21.866	24.261	23.670	21.763	21.269	20.457	24.331	19.719	22.232
Cd (ppm)	0.001	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.005	0.002	<DL
Cr (ppm)	0.007	0.001	0.002	0.002	0.001	0.004	0.001	0.001	0.002	0.004	<DL
Cu (ppm)	0.005	0.017	0.005	0.004	0.006	0.027	0.006	0.000	4.710	0.003	<DL
Fe (ppm)	0.028	0.020	0.008	0.010	0.006	0.028	0.009	0.006	0.016	0.007	<DL
K (ppm)	3.056	1.876	2.310	2.413	2.548	5.073	1.222	0.756	2.507	0.971	2.113
Li (ppm)	0.089	0.043	0.047	0.026	0.033	0.048	0.009	0.002	0.011	0.026	0.005
Mg (ppm)	5.268	4.478	5.038	8.899	7.665	6.313	6.159	2.328	12.066	4.331	9.705
Mn (ppm)	0.049	0.083	0.020	0.015	0.016	0.017	0.005	0.003	2.168	0.013	0.018
Mo (ppm)	0.003	0.001	0.002	0.000	0.001	0.000	<DL	0.001	0.013	0.003	<DL

Na (ppm)	17.400	12.024	13.705	15.940	15.563	20.552	10.042	3.452	22.218	7.085	14.393
Ni (ppm)	0.006	0.002	0.001	0.001	0.001	0.002	0.001	0.001	0.023	0.004	<DL
P (ppm)	0.004	0.003	0.020	0.019	0.024	0.384	0.019	0.006	<DL	0.006	0.115
Pb (ppm)	0.004	0.001	0.001	0.002	0.002	<DL	0.000	<DL	0.001	0.006	0.001
S (ppm)	38.206	28.386	29.606	38.132	34.680	30.613	20.516	25.474	99.744	20.969	26.097
Se (ppm)	0.002	0.001	0.001	<DL	0.002	0.001	0.000	0.002	0.003	0.006	<DL
V (ppm)	0.007	0.004	0.004	0.012	0.010	0.007	0.007	0.002	0.017	0.006	0.016
Zn (ppm)	0.003	0.001	<DL	<DL	0.000	0.007	0.000	<DL	0.796	0.002	<DL

Tinguiririca subcatchment

	T-T1	**T-T2**	**T-T3**	**T-T4**	**T-A**	**T-Ch**	**T-Cl**	**T-P**
pH	7.62	7.30	7.68	7.73	7.45	7.54	7.41	7.38
EC ($\mu S\ cm^{-1}$)	284	170	254	288	188	319	39	125
Salinity	0.14	0.08	0.12	0.14	0.09	0.15	0.02	0.06
Temp (°C)	8.60	14.13	15.79	18.01	15.39	16.34	17.05	12.46
DO ($mg\ L^{-1}$)	8.37	9.20	9.10	8.98	7.48	8.43	9.03	8.43
TDS ($mg\ L^{-1}$)	141	85	127	142	94	159	19	62
NO_3^- (µM)	11.5	11.8	28.4	36.0	6.5	38.7	4.0	9.4
C1mh (%)	26.1	5.6	23.9	42.1	3.9	22.1	5.6	23.0
C2th (%)	12.3	0.7	19.0	33.7	0.0	17.1	0.9	14.7
C3p (%)	22.4	60.4	41.5	11.3	62.4	43.8	60.4	35.2
C4p (%)	39.2	33.3	15.7	12.9	33.8	17.0	33.0	27.2
Ag (ppm)	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Al (ppm)	0.044	0.036	0.017	0.014	0.063	0.006	0.016	0.055
As (ppm)	0.004	0.002	0.000	0.002	0.002	0.000	<DL	<DL
B (ppm)	<DL	<DL	<DL	<DL	0.034	<DL	<DL	<DL
Ba (ppm)	0.008	0.004	0.005	0.008	0.004	0.009	0.000	0.003
Be (ppm)	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Ca (ppm)	18.778	14.627	17.056	18.045	13.569	18.781	5.164	12.403
Cd (ppm)	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL

Cr (ppm)	0.004	0.001	0.001	0.001	0.001	0.000	0.001	0.001
Cu (ppm)	0.002	0.001	0.001	0.001	0.000	0.000	0.001	0.000
Fe (ppm)	0.027	0.009	0.007	0.009	0.008	0.014	0.014	0.010
K (ppm)	1.044	0.722	1.182	1.423	1.570	1.728	0.132	0.344
Li (ppm)	0.033	0.006	0.007	0.007	0.004	0.008	<DL	0.002
Mg (ppm)	2.961	2.477	4.110	4.799	4.249	5.054	0.649	1.914
Mn (ppm)	0.080	0.032	0.009	0.005	0.090	0.030	0.001	0.043
Mo (ppm)	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Na (ppm)	8.881	4.923	8.358	9.390	6.543	11.674	1.368	3.041
Ni (ppm)	0.003	0.001	0.001	0.000	0.001	0.000	0.001	0.001
P (ppm)	<DL	0.001	0.002	0.010	<DL	0.009	0.006	<DL
Pb (ppm)	0.002	0.001	0.001	0.002	0.001	0.001	0.000	0.000
S (ppm)	25.025	11.626	16.601	17.793	17.567	19.740	<DL	10.006
Se (ppm)	0.002	0.005	0.003	0.002	0.001	<DL	<DL	0.003
V (ppm)	0.002	0.000	0.004	0.005	0.002	0.005	<DL	<DL
Zn (ppm)	0.000	0.000	<DL	<DL	<DL	<DL	0.001	<DL

Rapel subcatchment						
	R-R1	**R-R2**	**R-R3**	**R-R4**	**R-R5**	**R-S**
pH	8.02	8.90	8.77	8.06	7.80	7.88
EC ($\mu S\ cm^{-1}$)	462	581	432	410	409	2513
Salinity	0.22	0.28	0.21	0.20	0.20	1.28
Temp (°C)	20.04	23.05	23.12	19.88	18.72	18.74
DO ($mg\ L^{-1}$)	6.20	11.50	10.30	10.35	9.31	8.96
TDS ($mg\ L^{-1}$)	230	292	216	205	204	1264
NO_3^- (µM)	19.8	5.4	54.9	66.1	65.4	54.4
C1mh (%)	35.3	18.6	23.1	35.4	17.5	3.8
C2th (%)	26.2	13.6	16.2	24.6	12.5	3.1
C3p (%)	19.6	48.4	41.8	22.4	52.5	74.3
C4p (%)	18.8	19.3	18.9	17.6	17.5	18.9
Ag (ppm)	<DL	<DL	<DL	<DL	<DL	<DL

Al (ppm)	0.002	0.005	0.013	0.011	0.003	<DL
As (ppm)	0.005	0.002	0.004	0.004	0.006	0.006
B (ppm)	<DL	<DL	<DL	<DL	<DL	0.028
Ba (ppm)	0.024	0.028	0.016	0.013	0.014	0.011
Be (ppm)	<DL	<DL	<DL	<DL	<DL	<DL
Ca (ppm)	22.288	23.393	21.308	20.943	21.211	21.667
Cd (ppm)	<DL	<DL	<DL	<DL	<DL	<DL
Cr (ppm)	0.002	0.002	0.001	0.004	0.002	0.001
Cu (ppm)	0.004	0.003	0.003	0.005	0.004	0.002
Fe (ppm)	0.012	0.016	0.010	0.020	0.011	0.006
K (ppm)	2.383	4.421	2.272	1.954	2.085	13.890
Li (ppm)	0.025	0.019	0.020	0.019	0.019	0.021
Mg (ppm)	7.137	9.257	6.486	6.013	6.239	22.378
Mn (ppm)	0.001	0.004	0.003	0.006	0.003	0.003
Mo (ppm)	0.001	0.041	0.006	0.002	0.004	0.003
Na (ppm)	14.513	17.987	13.280	11.950	12.690	79.169
Ni (ppm)	0.001	0.001	0.001	0.003	0.002	0.001
P (ppm)	0.008	0.006	0.000	0.021	0.019	0.023
Pb (ppm)	0.002	0.002	0.002	0.000	0.002	0.001
S (ppm)	28.162	51.145	27.202	24.364	25.917	49.829
Se (ppm)	0.003	0.002	0.002	0.001	0.000	<DL
V (ppm)	0.009	0.015	0.008	0.008	0.007	0.055
Zn (ppm)	<DL	<DL	<DL	0.000	0.000	<DL

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Table S3: Summary of the PERMANOVA revealing the effect of the subcatchment on metal concentrations.

	Df	Sum of squares	R^2	F	Pr(>F)
Model	2	101.32	0.1759	2.3478	0.002 **
Residual	22	474.68	0.8241		
Total	24	576	1		

Signif. codes: *** < 0.001 ; ** < 0.01; * < 0.05

Table S4: Pairwise comparison associated to the PERMANOVA revealing the effect of the subcatchment on metal concentrations

	Df	Sum of squares	F Model	R^2	P	P adjusted
Cachapoal vs Tinguiririca	1	59.7987	2.6831	0.14	0.007	0.0105 *
Cachapoal vs Rapel	1	28.7692	0.9987	0.06	0.437	0.437
Tinguiririca vs Rapel	1	64.8323	5.6212	0.32	0.002	0.006 **

Signif. codes: *** < 0.001 ; ** < 0.01; * < 0.05