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Concentration–discharge relationships vary among hydrological events, reflecting differences in event characteristics

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S1 Technical details on ICP-MS analysis

Samples collected for ICP-MS analysis were analyzed batch-wise (typically one or several weeks of samples together, one week of samples is considered a batch) at the laboratory of the Institute of Terrestrial Ecosystems at ETH Zurich. Within a single batch, all streamwater samples were analyzed first, followed by all precipitation samples.

The ICP-MS was re-calibrated before the analysis of each batch using six different calibration standards in order of low to high concentrations; for this different dilutions of ICP multi-element standard solution Y for surface water testing (Merck KGaA, Darmstadt, Germany) with ultrapure water were generated. These calibration standards were followed by three laboratory blanks (ultrapure water), two quality control standards (MULTI-ELEMENT Standard solution for ICP supplied by CPAchem, Bulgaria, and a quality control containing 10 mg L^{-1} of calcium, magnesium, sodium, and potassium), and three further laboratory blanks (ultrapure water).

After every 20 samples, another blank (ultrapure water) and a quality control standard (MULTI-ELEMENT Standard solution for ICP supplied by CPAchem, Bulgaria) were analyzed, followed by a blank to avoid carry over from the quality control standard to the next samples.

Holmium, lutetium, indium, and scandium were used as internal standards in the ICP-MS analysis.

S2 Comparison of two-year and event-scale cQ slopes and intercepts

Figure 1 (main text) visualizes the two-year cQ behavior determined from the 2-year time series, and compares it to the variability in cQ relationships observed on the event scale. The two-year slopes and intercepts, as well as ranges and averages of event slopes and event intercepts are displayed in Table S1.

Table S1: Two-year and event-scale concentration-discharge (cQ) slopes and intercepts (± 1 standard error). In the analysis of two-year data, slopes and intercepts are broadly similar if the cQ relationships are fitted to the whole time series, or to recession samples only (first two columns). For event-scale cQ relationships, the smallest, largest and the average of all event slopes and intercepts are provided.

Solute	two-year (all data)	two-year (recession only)	min. event value	max. event value	mean event value
Slope:					
EC	-0.14 ± 0.0002	-0.14 ± 0.0002	-0.24 ± 0.002	-0.03 ± 0.002	-0.16 ± 0.0006
Ca	-0.14 ± 0.001	-0.15 ± 0.001	-0.29 ± 0.02	-0.05 ± 0.006	-0.17 ± 0.002
Mg	-0.18 ± 0.001	-0.19 ± 0.001	-0.35 ± 0.02	-0.06 ± 0.008	-0.20 ± 0.003
Na	-0.29 ± 0.001	-0.31 ± 0.002	-0.39 ± 0.02	-0.06 ± 0.009	-0.25 ± 0.003
Sr	-0.18 ± 0.003	-0.20 ± 0.003	-0.35 ± 0.05	-0.09 ± 0.01	-0.22 ± 0.008
Ba	-0.21 ± 0.005	-0.24 ± 0.009	-0.31 ± 0.10	-0.06 ± 0.02	-0.18 ± 0.01
B	-0.21 ± 0.003	-0.23 ± 0.005	-0.24 ± 0.04	-0.03 ± 0.009	-0.14 ± 0.01
SO4	-0.35 ± 0.003	-0.35 ± 0.003	-0.40 ± 0.03	-0.09 ± 0.01	-0.22 ± 0.003
K	-0.13 ± 0.001	-0.14 ± 0.002	-0.17 ± 0.02	0.20 ± 0.04	-0.03 ± 0.004
Cl	-0.25 ± 0.004	-0.26 ± 0.005	-0.26 ± 0.03	0.46 ± 0.04	0.14 ± 0.007
NO3	-0.21 ± 0.005	-0.31 ± 0.005	-0.69 ± 0.07	0.49 ± 0.04	0.17 ± 0.007
Fe	0.62 ± 0.007	0.67 ± 0.01	0.32 ± 0.08	1.15 ± 0.07	0.67 ± 0.02
Mn	0.54 ± 0.01	0.60 ± 0.02	0.82 ± 0.10	2.24 ± 0.4	1.43 ± 0.09
Cr	0.24 ± 0.004	0.26 ± 0.006	0.15 ± 0.02	0.61 ± 0.04	0.32 ± 0.02
Cu	-0.02 ± 0.003	-0.02 ± 0.005	-0.08 ± 0.03	0.30 ± 0.03	0.11 ± 0.04
Intercept:					
EC	2.32 ± 0.0002	2.32 ± 0.0002	2.28 ± 0.002	2.38 ± 0.0006	2.32 ± 0.0002
Ca	4.59 ± 0.001	4.59 ± 0.001	4.54 ± 0.005	4.69 ± 0.01	4.60 ± 0.001
Mg	3.37 ± 0.001	3.38 ± 0.001	3.29 ± 0.007	3.48 ± 0.01	3.38 ± 0.002
Na	3.21 ± 0.001	3.20 ± 0.001	3.05 ± 0.008	3.44 ± 0.003	3.22 ± 0.001
Sr	2.35 ± 0.003	2.35 ± 0.002	2.25 ± 0.03	2.44 ± 0.03	2.36 ± 0.004
Ba	1.52 ± 0.004	1.50 ± 0.006	1.40 ± 0.06	1.70 ± 0.008	1.55 ± 0.006
B	0.81 ± 0.003	0.80 ± 0.003	0.70 ± 0.02	1.02 ± 0.007	0.84 ± 0.005
SO4	3.80 ± 0.002	3.78 ± 0.002	3.63 ± 0.01	4.31 ± 0.003	3.81 ± 0.001
K	2.82 ± 0.001	2.81 ± 0.001	2.64 ± 0.006	2.97 ± 0.003	2.82 ± 0.002
Cl	2.29 ± 0.003	2.27 ± 0.003	1.88 ± 0.01	2.87 ± 0.001	2.34 ± 0.004
NO3	2.64 ± 0.003	2.57 ± 0.003	2.23 ± 0.02	3.13 ± 0.005	2.60 ± 0.003
Fe	1.05 ± 0.006	1.10 ± 0.007	0.99 ± 0.02	1.95 ± 0.02	1.30 ± 0.007
Mn	-0.27 ± 0.01	-0.31 ± 0.01	-1.29 ± 0.1	0.73 ± 0.2	-0.42 ± 0.04
Cr	-1.17 ± 0.004	-1.13 ± 0.004	-1.32 ± 0.04	-0.78 ± 0.007	-1.06 ± 0.009
Cu	0.07 ± 0.003	0.08 ± 0.003	-0.07 ± 0.01	0.28 ± 0.01	0.12 ± 0.02

S3 Comparison of event-scale cQ slopes and intercepts

The uncertainty in the slopes and intercepts in Fig. 4 is mostly smaller than the variability among events, indicating that the observed inter-event variability in slopes and intercepts reflects real-world behavior rather than sampling and measurement noise. This statement still holds true if we include slopes and event of all events, even those excluded due to high relative standard errors in slope and/or intercept values as shown in Figure S1.

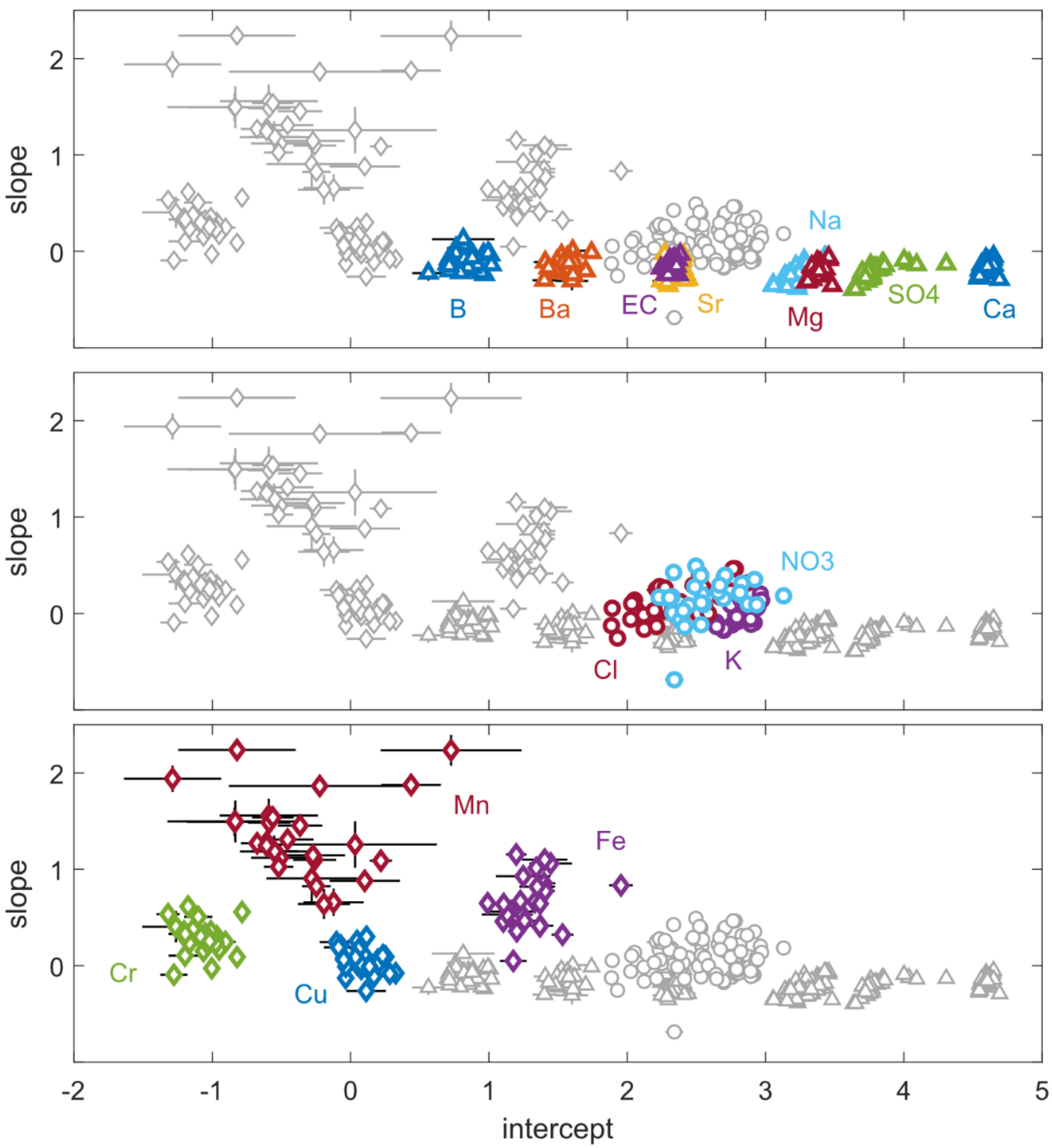

Figure S1: Scatter plots of event cQ slopes and intercepts of the 14 different solutes and EC (error bars indicate one standard error). Conversely to Fig. 4 (main text), this version of the figure also includes all cQ slopes and intercepts from events excluded from further analysis due to high relative standard errors in slopes and/or intercepts.

S3 Dependence of event-scale cQ slopes on environmental controls

We used weighted rank correlation coefficients to assess how variations in cQ slopes and intercepts from event to event are related to seasonality indicators, relative input concentrations, antecedent catchment conditions, event characteristics, and event-water contributions. Individual examples of these relationships are shown in Fig. S2 for different solutes and drivers. A heatmap (Fig. 5, main manuscript) illustrates how event-scale cQ slopes and intercepts depend on these different environmental controls.

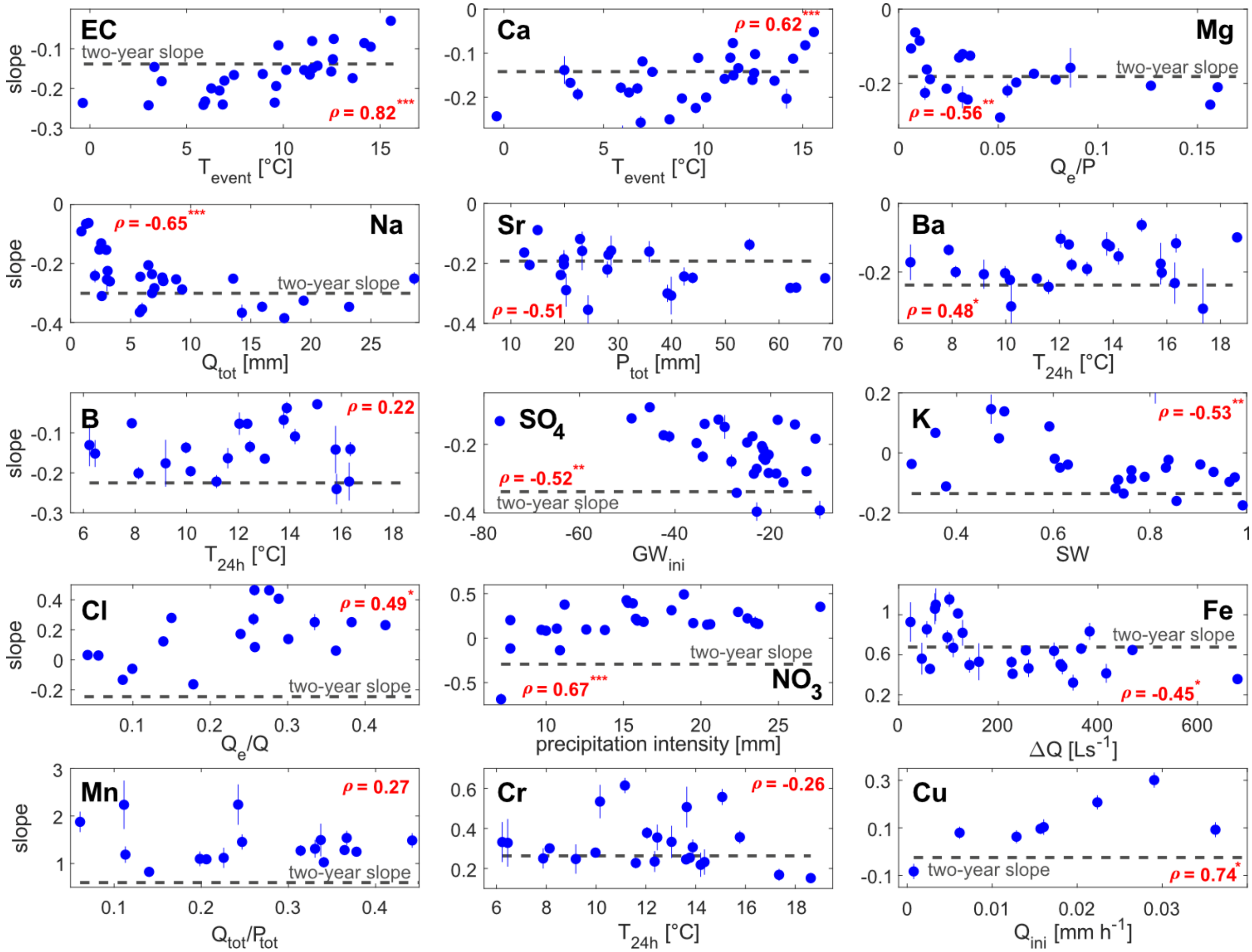

Figure S2: Scatter plots illustrating relationships between event cQ slopes and environmental controls (blue circles, error bars indicate ± 1 standard error). Gray dashed lines indicate two-year cQ slopes. Rank correlation coefficients are shown in red, with their statistical significance indicated by asterisks (*, **, and * indicate p<0.05, p<0.01, and p<0.001, respectively). This figure only displays the relationship between the event-slopes of each solute and one selected controlling variable (either a randomly selected environmental control with a correlation coefficient <0.40, or the environmental control with the highest correlation coefficient). An overview of all correlations is provided in Fig. 5. Event slopes deviate substantially from two-year slopes for several solutes (e.g. chloride, sulfate, and nitrate).**