Disentangling Scatter in Long-Term Concentration-Discharge Relationships: the Role of Event Types

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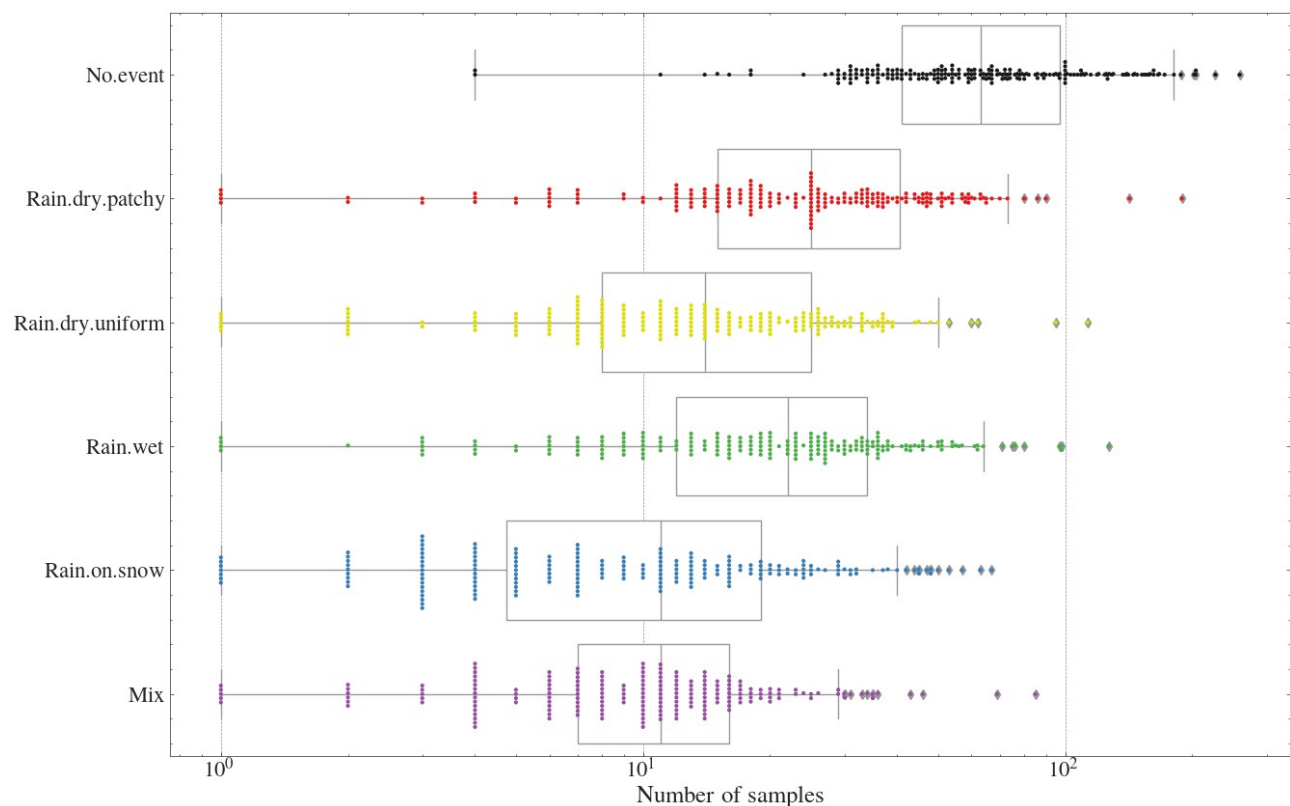
Supplementary Information

Figure S1. Number of samples in all 184 catchments attributed to each event type. Vertical lines show medians, 5th and 95th percentiles of boxplots.
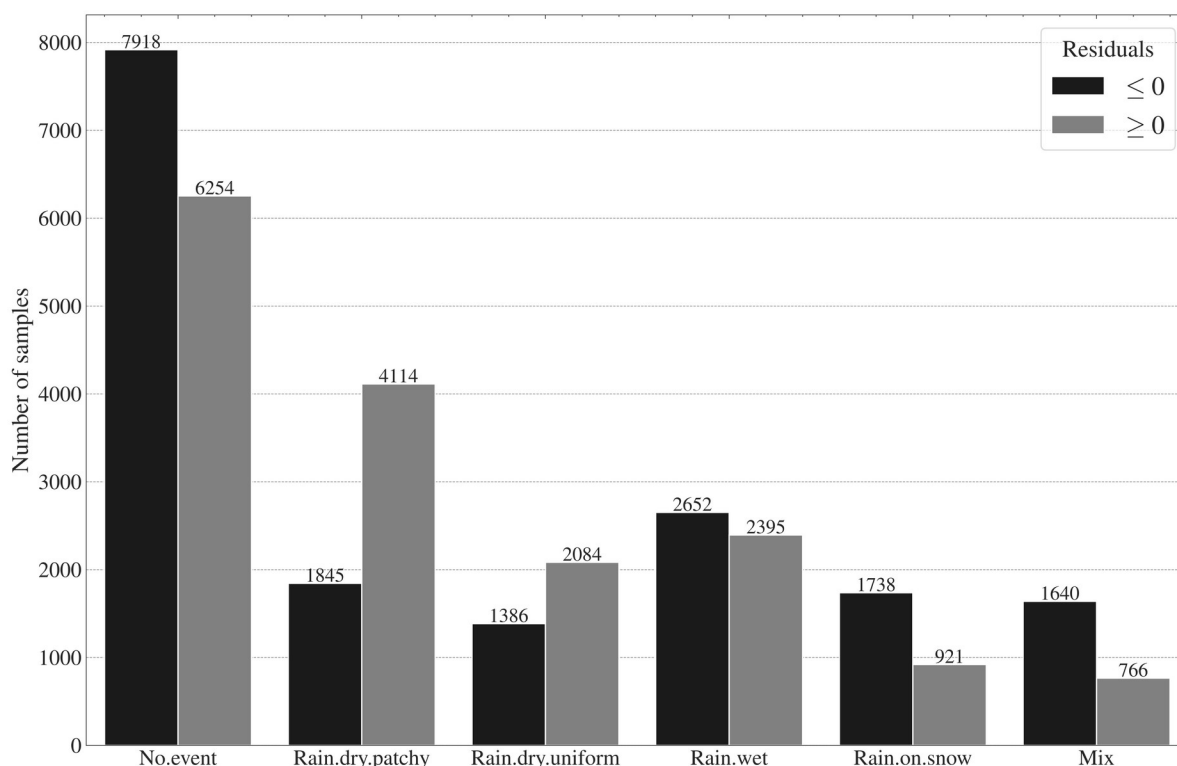
Figure S2: Number of nitrate samples from all catchments with positive and negative residuals for each event type.
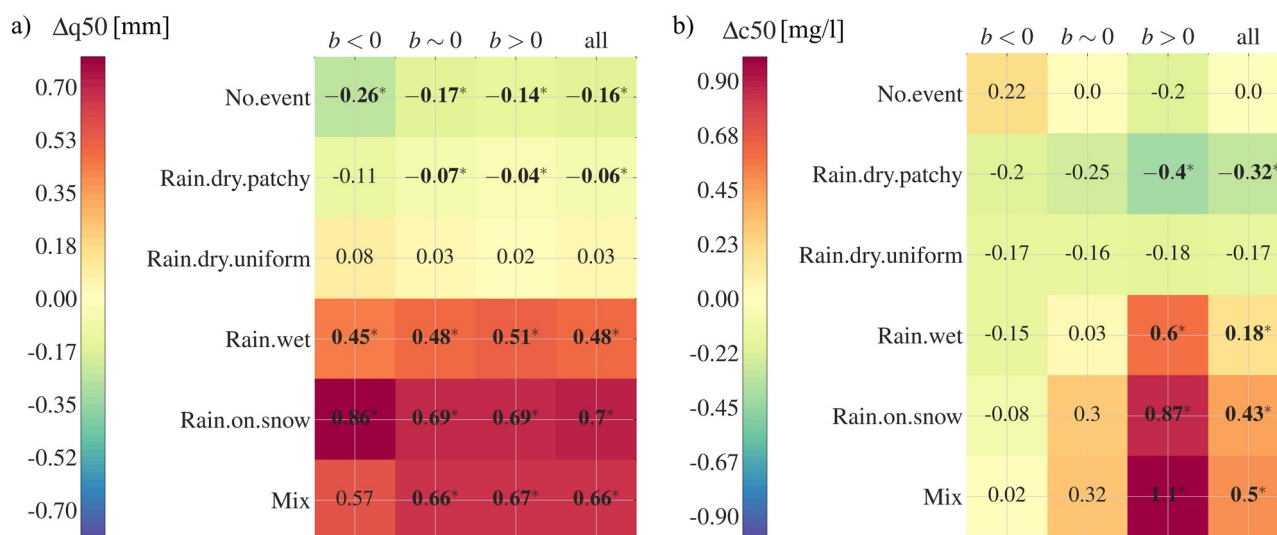

Figure S3. Heatmaps of differences between samples taken during different event types or No.event and all samples (analogous to Figure 5) for a) discharge and b) concentration of nitrate, averaged across different groups of catchments, considering all nitrate data for each event type and No.event. The three first columns of the heatmap correspond to one of the long-term export patterns (i.e., dilution (slope b<0), neutral (slope b~0) and enrichment (slope b>0)) and the fourth column corresponds to all study catchments. Bold font and * indicates significant differences (Kruskal-Wallis test, p<0.05).
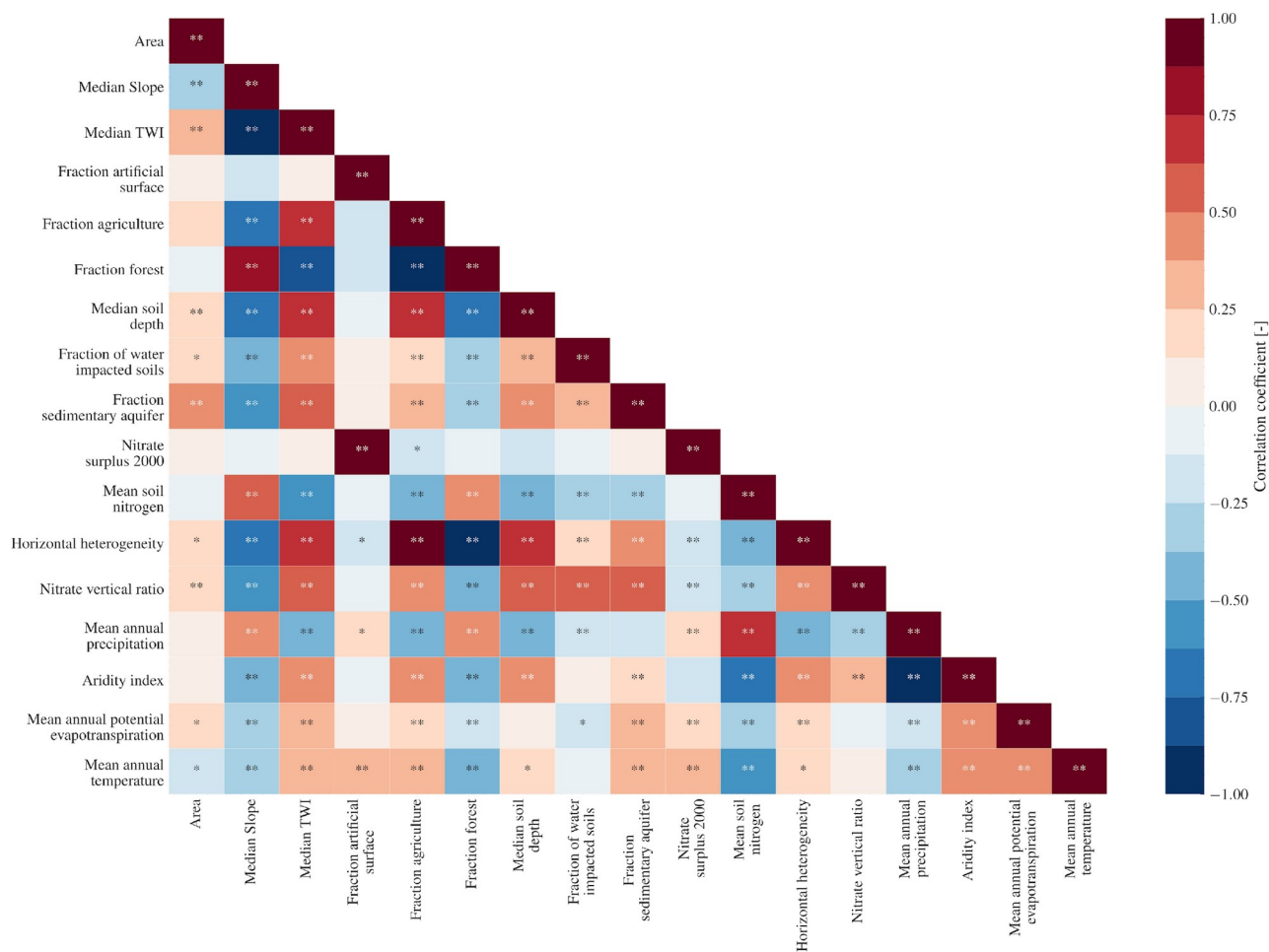
Figure S4. Spearman rank correlation coefficient between catchment descriptors. Significant correlations are indicated as * for p<0.05 and ** for p<0.01.

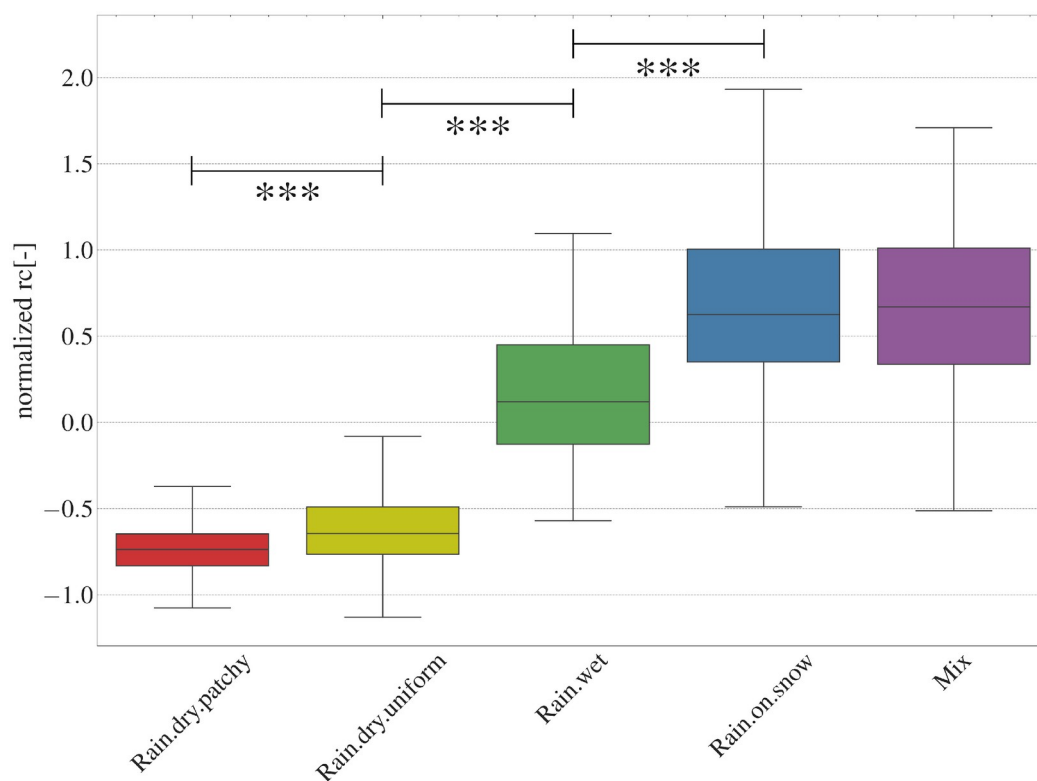**Figure S5. Median normalized event runoff coefficients for each catchment and each event type. Normalization of nitrate samples was computed for each catchment subtracting the mean value and dividing by the standard deviation. Significant differences between medians of adjacent boxplots was estimated using Kruskal-Wallis test (displayed as *** for p<0.001, * *for p<0.01 and * for p<0.05))**

Table S1: Thresholds and variables used for classification of runoff events (modified from Tarasova et al., 2020).

Layer	Selected indicator	Expression	Thresholds	Performed Split
a) Inducing event	Ratio of event rainfall volume and total event precipitation volume	$\dfrac{R_{x,y,t}}{P_{x,y,t}}$	0.95	Rainfall vs. Mix or Rain.on.snow
	Normalized spatial covariance of event-averaged snow cover and rainfall	$\dfrac{\mathrm{cov}_{x,y}(SWE_t, R_t)}{SWE_{x,y,t} \times R_{x,y,t}}$	0	Rain.on.snow vs. Mix
b) Wetness state	Catchment-averaged antecedent soil moisture	$SM_{x,y}(t_0)$	$max(\kappa)$	Wet vs Dry
c) Spatial distribution of mositure	Spatial coefficient of variation of antecedent soil moisture	$\dfrac{\sqrt{\mathrm{var}_{x,y}(SM_{t_0})}}{SM_{x,y,t}}$	Q_2	Uniform vs Patchy

Note: Input data is grid-based, for each cell (x,y) and time step t during an event the following variables are provided: event rainfall rate $R(x,y,t)$ [mm]; total event precipitation rate $P(x,y,t)$ [mm/day] and snow water equivalent $SWE(x,y,t)$ [mm]. At the beginning of each event (t_0) antecedent soil moisture $SM(x,y,t_0)$ [-] is provided. Q_2 correspond to median value and κ is the curvature of a nonlinear function that describes the relation between event runoff coefficients and simulated soil moisture (Tarasova et al., 2018). Rainfall data was obtained from REGNIE data set (Rauthe et al., 2013). Snow water equivalent and soil moisture were simulated by the mHM model (Samaniego et al 2010; Kumar et al 2013) and provided in Zink et al. (2017).

Table S2: Catchment descriptors used for correlation analysis. (according to Ebeling et al., 2021).

Category	Variable	Unit	Description
Topography	Area	km^2	Catchment area
	Median Slope	°	Mean topographic slope of catchment
	Median TWI	-	Mean topographic wetness index
Land Cover	Fraction of agriculture	-	Fraction of agricultural land cover
	Fraction of forest	-	Fraction of forested land cover
Soil & Aquifer	Median soil depth	cm	Median depth to bedrock in the catchment
	Fraction of sedimentary aquifer	-	Fraction of sedimentary aquifer
Nutrient source	Nitrate surplus 2000	kgN ha^{-1}y^{-1}	Mean nitrogen surplus per catchment during sampling period (2000–2015) including N surplus on agricultural land and atmospheric deposition on non-agricultural areas
	Horizontal heterogeneity	-	Slope of relative frequency of source areas in classes of flow distances to stream as a proxy for horizontal source heterogeneity
	Nitrate vertical ratio	-	Mean ratio between potential seepage and groundwater NO3-N concentrations as proxy for vertical concentration heterogeneity
Hydrometeorology	Mean annual precipitation	mm y^{-1}	Mean annual precipitation for the period 1986–2015
	Mean annual potential evapotranspiration	mm y^{-1}	Mean annual potential evapotranspiration for the period 1986–2015
	Aridity index	-	Fraction of mean annual potential evapotranspiration and mean annual precipitation
	Mean annual temperature	°C	Mean annual air temperature for the period 1986–2015