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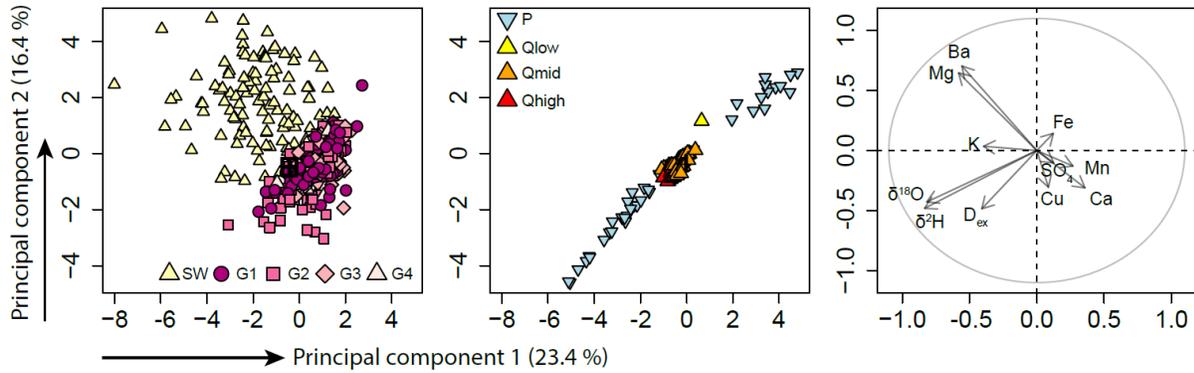
Supplement of

Do stream water solute concentrations reflect when connectivity occurs in a small, pre-Alpine headwater catchment?

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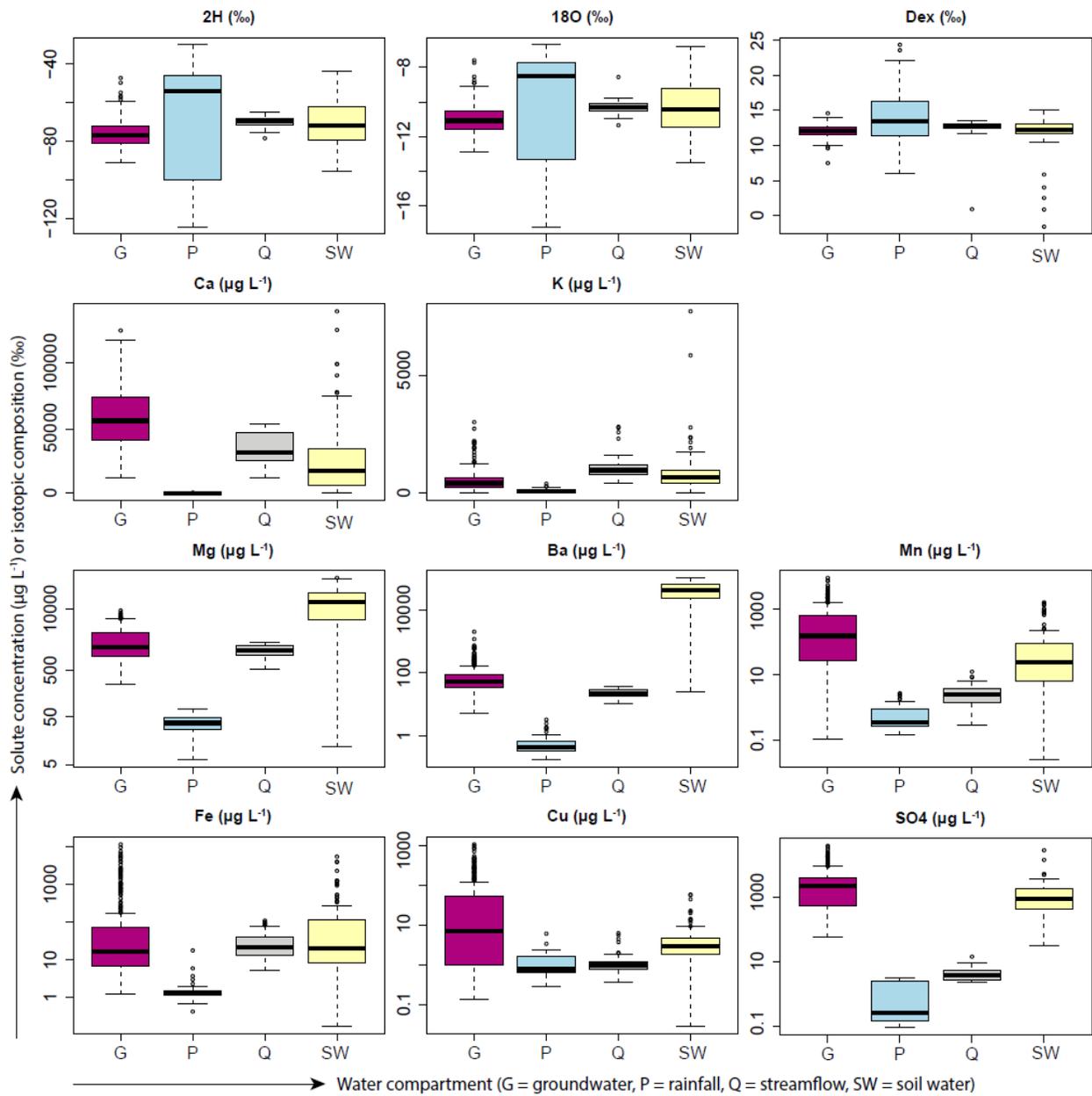
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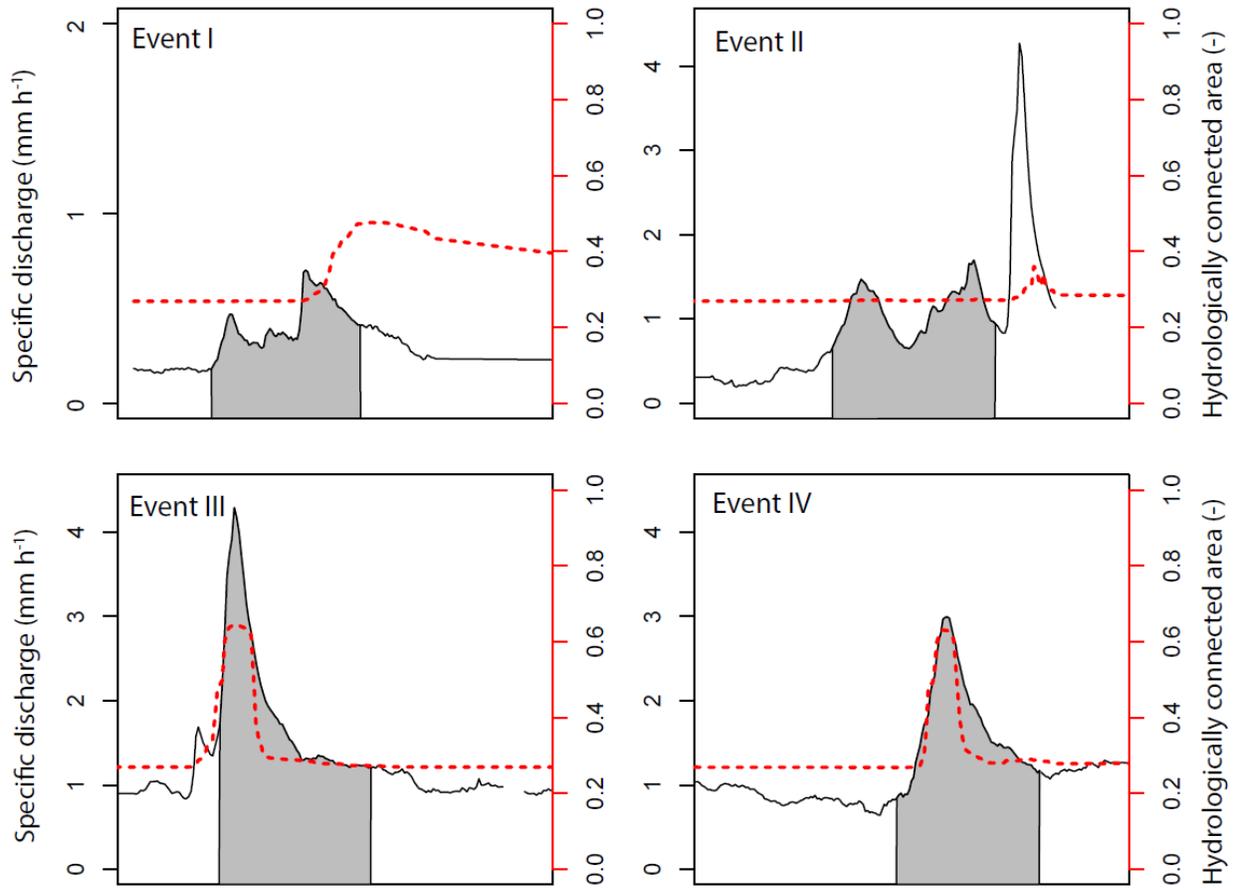
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S1: PCA results for all groundwater (n=335) and soil water samples (n=116) taken during the nine baseflow snapshot campaigns (Kiewiet et al., 2019), and all streamwater (n=100) and rainfall (n=47) samples taken during the four events used in this study. The left panel shows the individual soil water samples (left-hand panel, yellow triangles) and groundwater samples (left-hand panel, purple circles, pink squares, light pink diamonds and rose triangles, representing groundwater types 1-4 based on Kiewiet et al., 2019) for the first two principal components. The middle panel shows the rainfall samples (light blue reversed triangles) and streamwater samples taken during low flow (Qlow, one baseflow sample) in yellow, during high flow (Qhigh) in red and during all other flow conditions in orange (Qmid). In the biplot (right panel) the length of the arrow represents the explanatory power for the solutes. The explanatory power of the first two principal components (PC1 and PC2) was 23.4 and 16.4%, respectively.



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 13 **S2: Boxplots of the tracer concentrations for the different water types: groundwater (G), rainfall (P), streamflow (Q) and**
 14 **soil water (S). Each boxplot contains all streamflow or rainfall samples taken during the four events presented in this**
 15 **study, or all soil water or groundwater samples taken during the two snapshot campaigns used in the study. Isotopic**
 16 **tracers are shown in ‰, values for chemical tracers in $\mu\text{g L}^{-1}$. Please note that y-axes differ for each panel, and that the y-**
 17 **axes of the panels on the bottom two rows are logarithmic.**

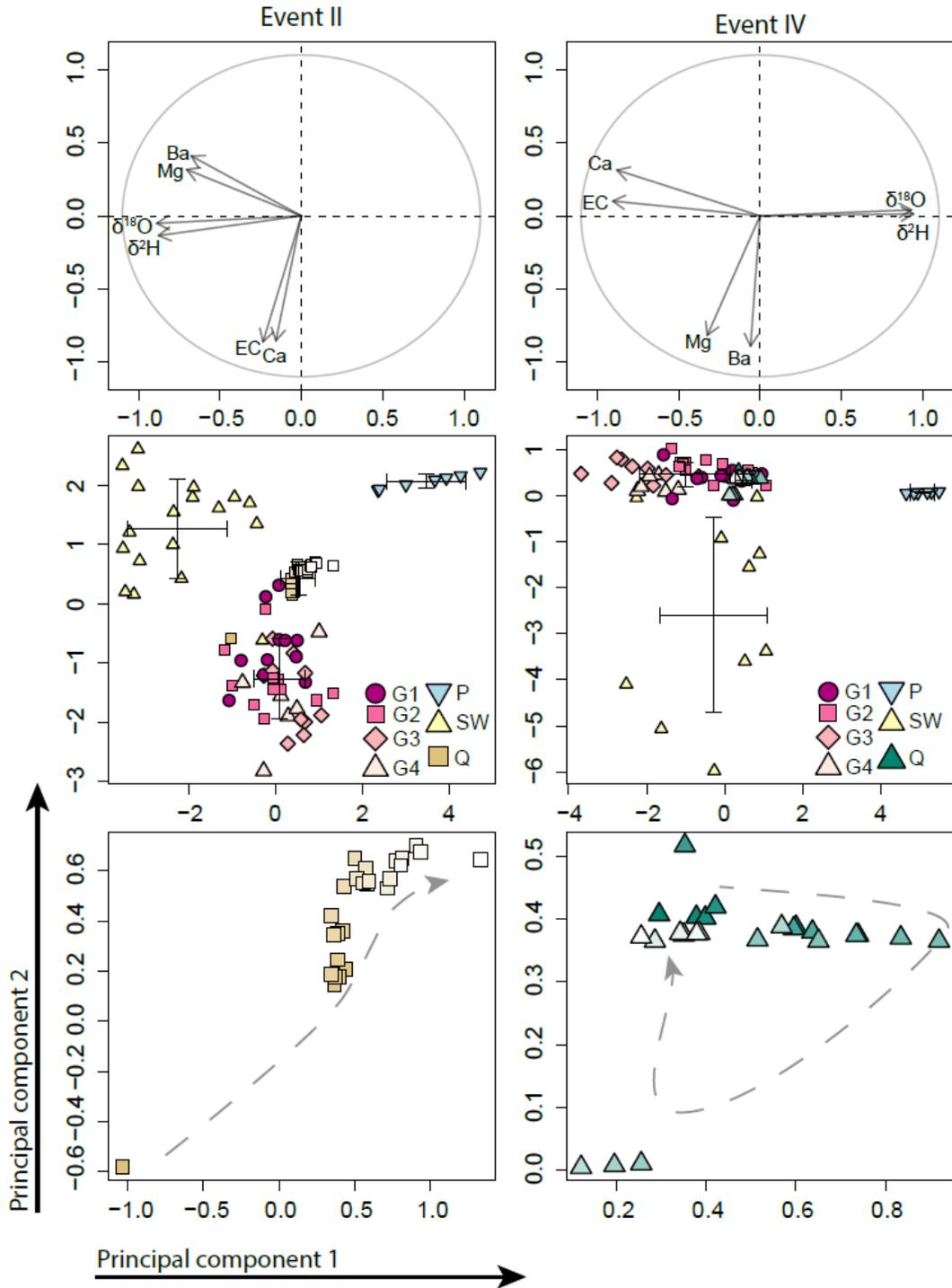


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19 **S3: Time series of specific discharge (solid black line), fraction of the catchment area that was hydrologically connected**
 20 **(red dashed lines), and the time during which stormflow samples were collected (grey area) for events I to IV.**

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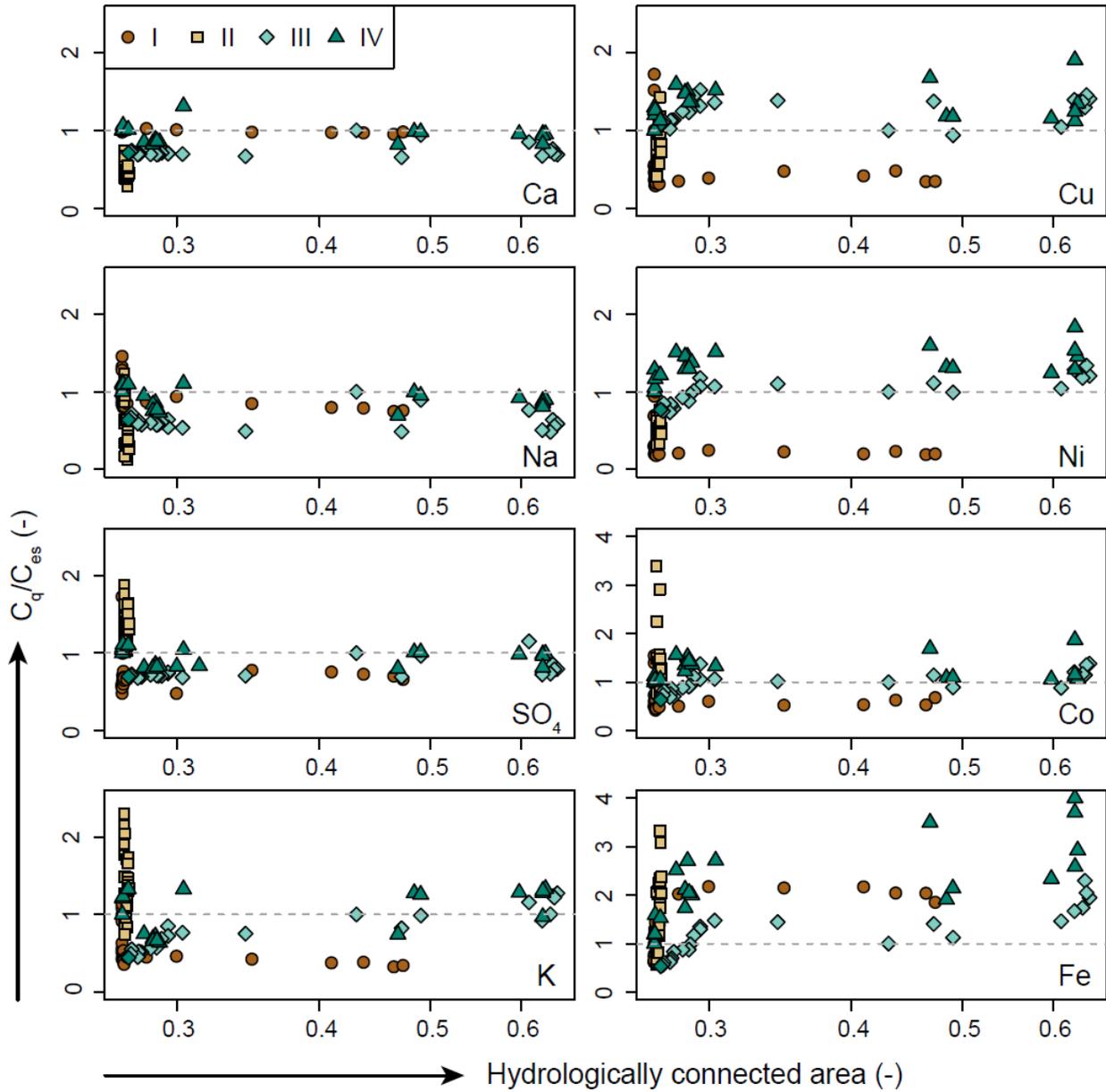
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24 S4. PCA results and mixing diagrams for event II and IV. In the biplots (top row), the length of the arrow represents the
 25 explanatory power. The mixing diagrams are based on the first two principle components (middle row) show the
 26 individual rainfall (light blue reversed triangles), soil water (yellow triangles), and groundwater samples (purple circles,
 27 pink squares, light pink diamonds and rose triangles, representing groundwater types 1-4 based on Kiewiet et al., 2019),
 28 the streamflow samples (Q), as well as the average and standard deviation for each component (error bars). The third row
 29 shows a zoom in of the streamflow samples and highlights the evolution of the streamwater composition (colors fade to
 30 white towards the end of the event) and the general direction of change indicated with a grey arrow and dashed lines. For
 31 the results for events I and II, see Figure 7.

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 34 **S5: Ratio of measured (C_q) and estimated stormflow concentrations (C_{es} ; Eq. 3) for calcium, sodium, sulfate, potassium,**
 35 **cobalt, copper, nickel and iron as a function of the simulated fraction of the catchment that was hydrologically connected**
 36 **to the stream from the data driven model. The dashed grey line indicates that C_q and C_{es} are equal; the different symbols**
 37 **reflect the different events (I-IV). Note the difference in scale for cobalt and iron.**

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