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*Supplement of*

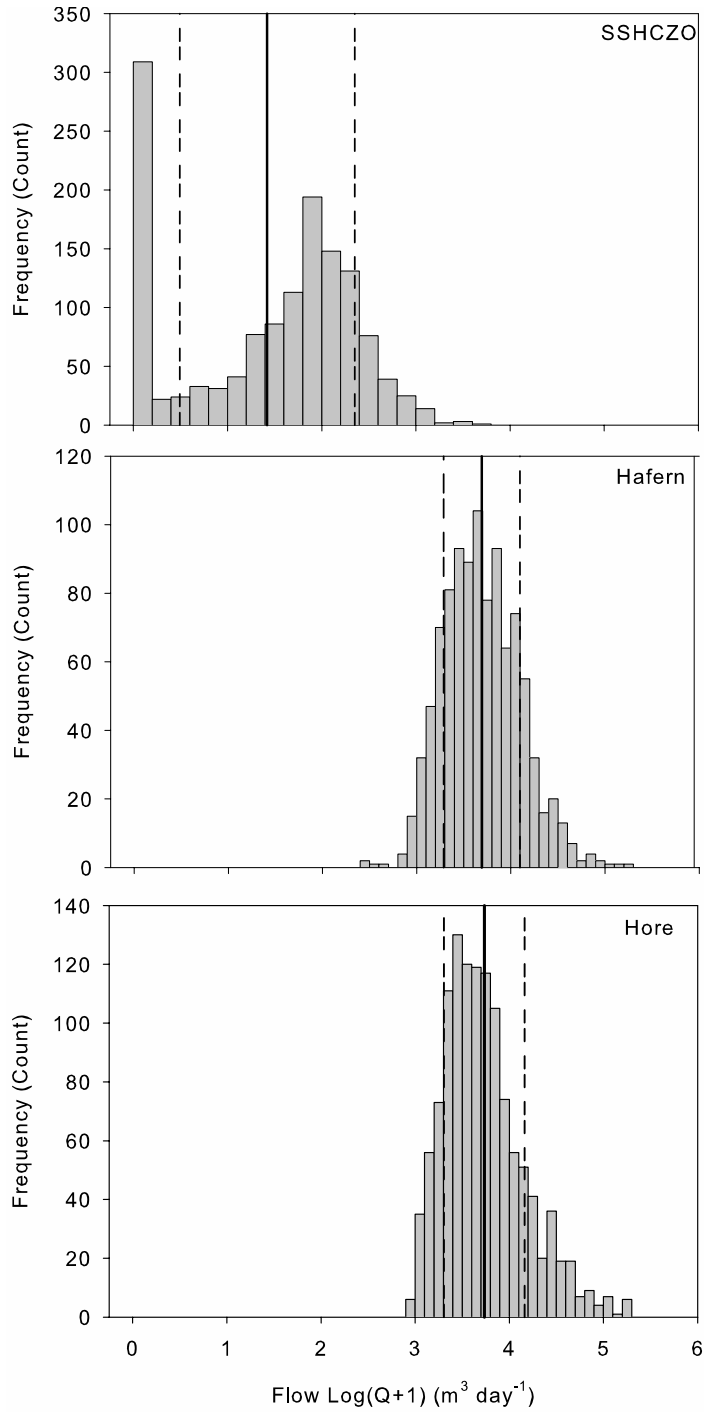
## **Landscape heterogeneity drives contrasting concentration–discharge relationships in shale headwater catchments**

**E. M. Herndon et al.**

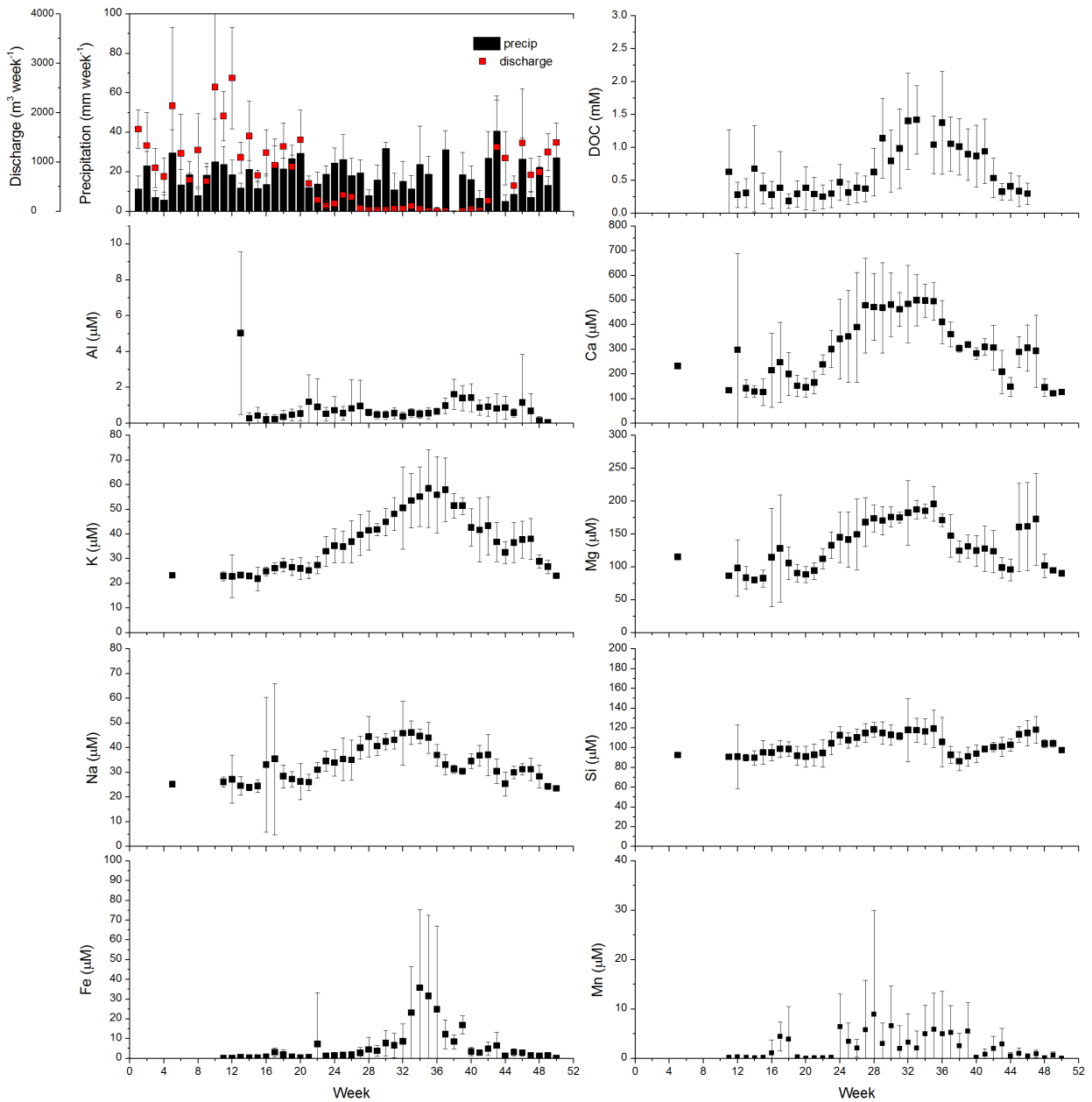
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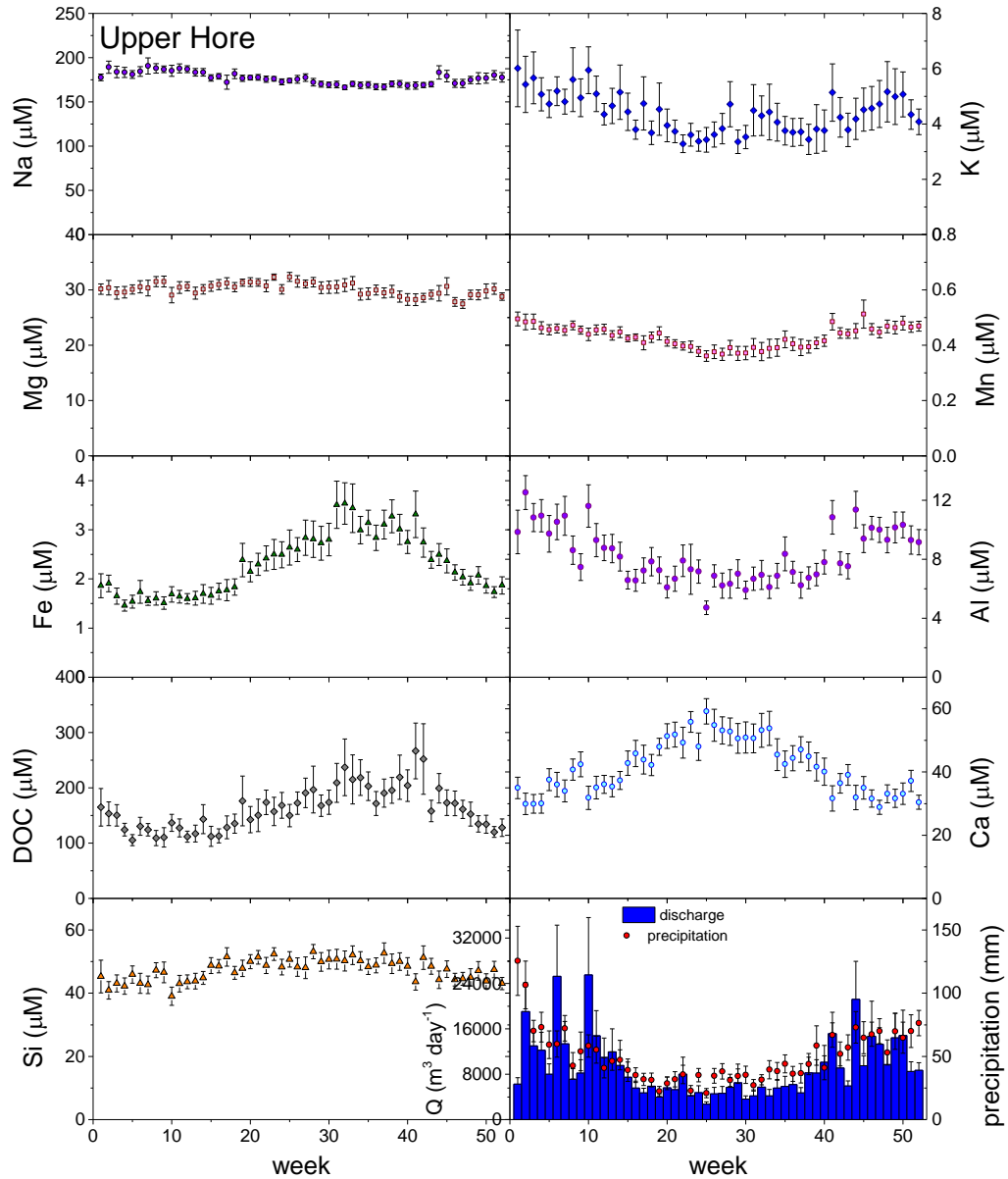
**Figure S1.** Histograms of stream flow used to group stream chemistry into low-flow, moderate-flow, and high-flow bins for Shale Hills ( $< 4.12$ ;  $4.13$  to  $222$ ; and  $> 223 \text{ m}^3 \text{ d}^{-1}$ ), the Upper Hafren ( $< 1,939$ ;  $1,940$  to  $12,469$ ; and  $> 12,470 \text{ m}^3 \text{ d}^{-1}$ ), and the Upper Hore ( $< 2,021$ ;  $2,022$  to  $14,519$ ; and  $> 14,520 \text{ m}^3 \text{ d}^{-1}$ ).



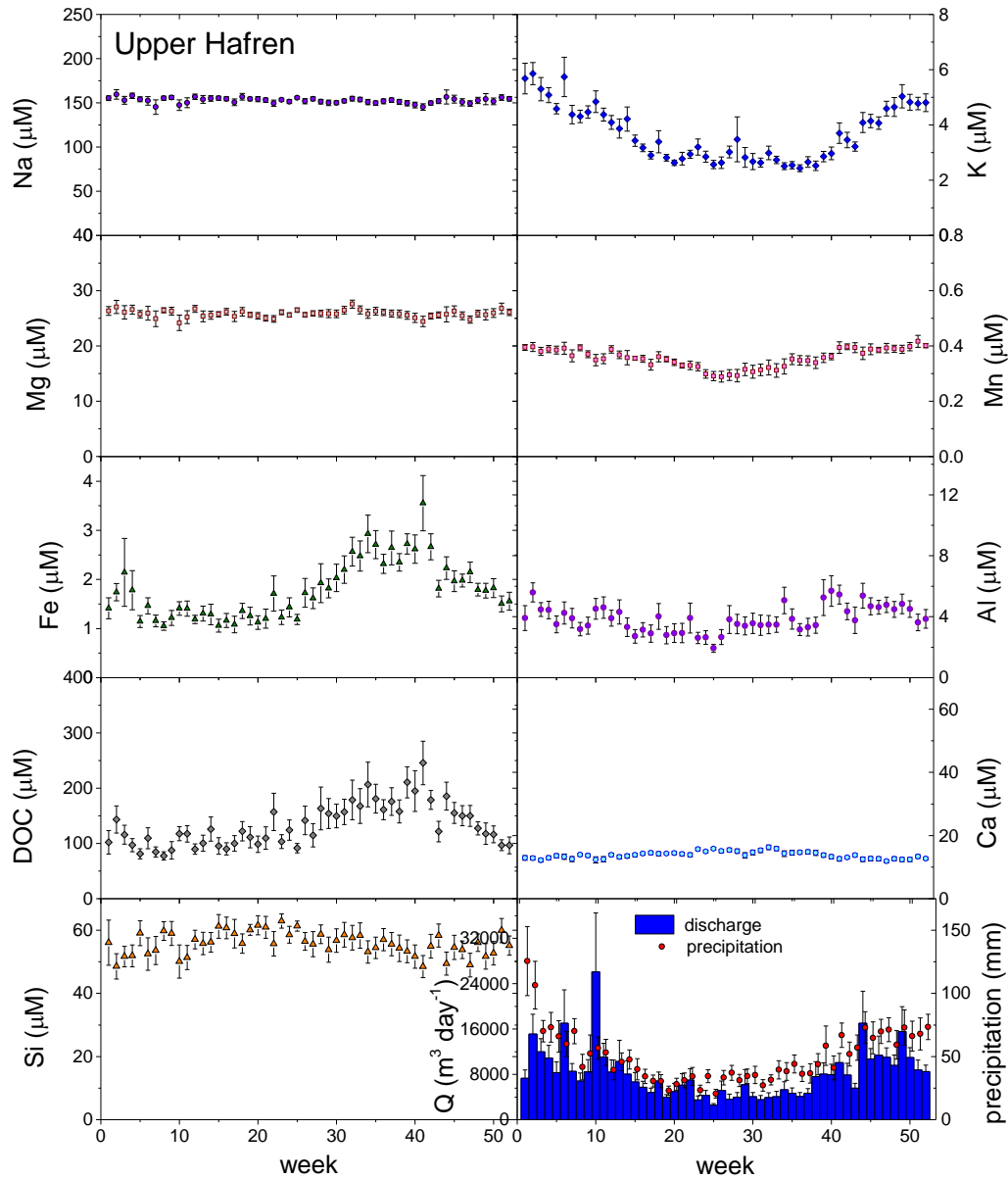
**Figure S2.** Seasonality of precipitation, discharge, and stream chemistry in the Shale Hills catchment. Weekly discharge ( $\text{m}^3 \text{ week}^{-1}$ ), precipitation ( $\text{mm week}^{-1}$ ) and concentrations of solutes ( $\mu\text{M}$ ;  $\text{mM}$  for DOC) averaged over 2006-2010. Error bars represent standard errors.



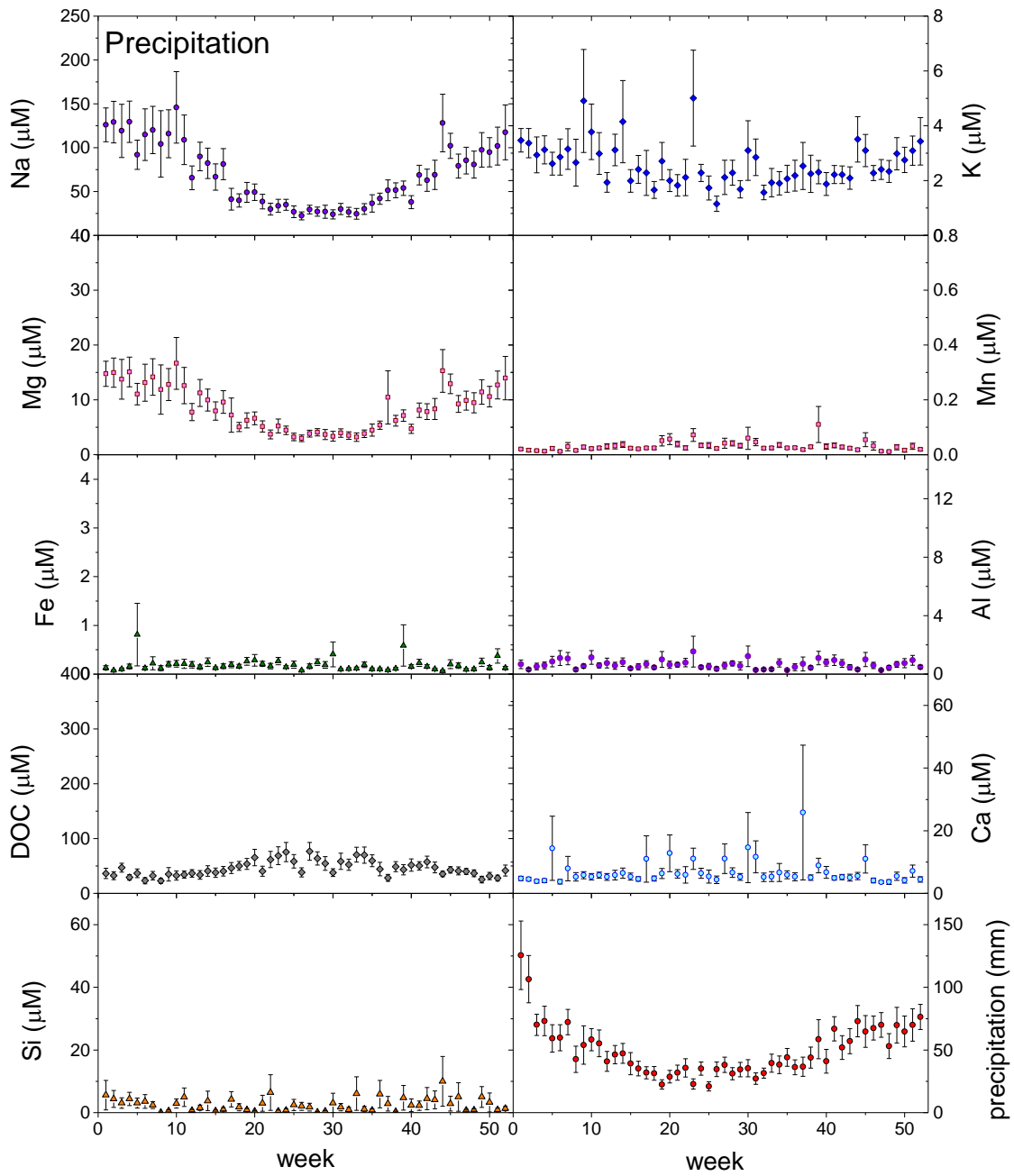
**Figure S3.** Seasonality of precipitation, discharge, and stream chemistry in the Upper Hore catchment. Weekly discharge ( $\text{m}^3 \text{week}^{-1}$ ), precipitation ( $\text{mm week}^{-1}$ ) and concentrations of solutes ( $\mu\text{M}$ ) averaged over 1983-2010. Error bars represent standard errors.



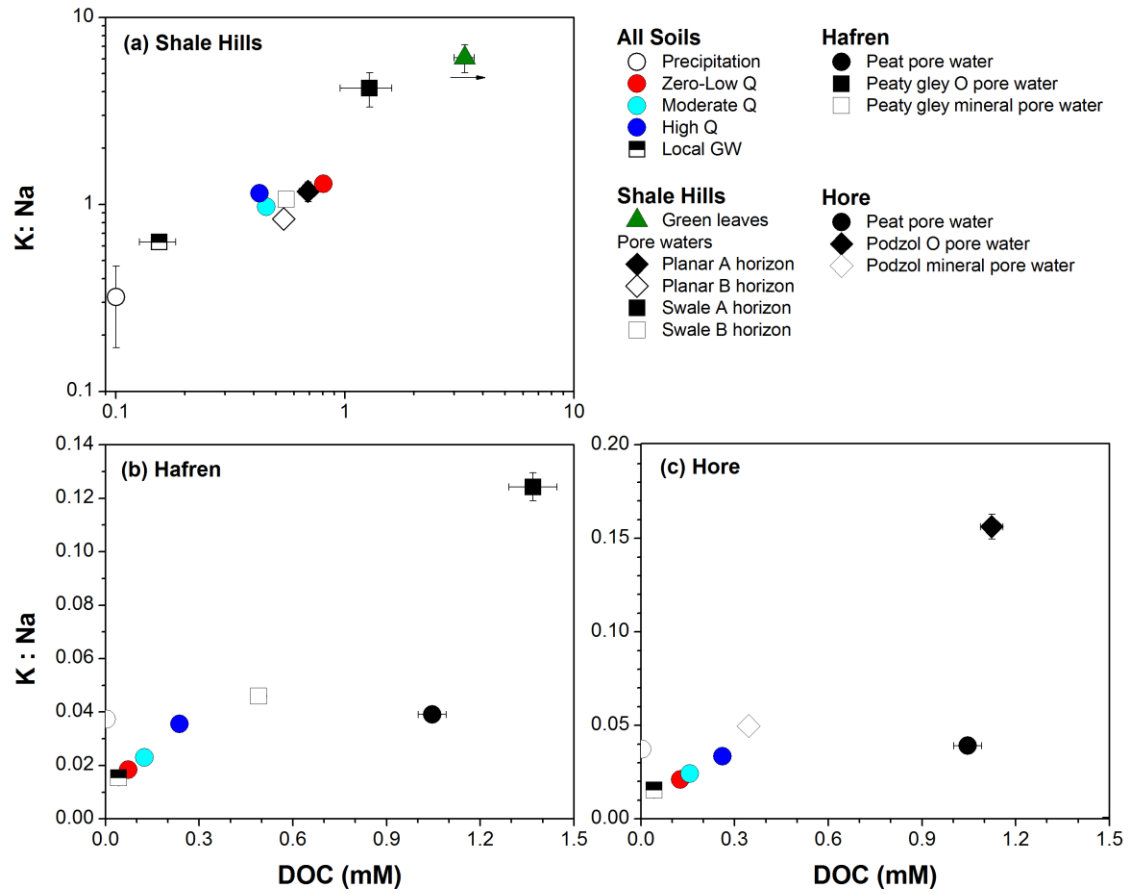
**Figure S4.** Seasonality of precipitation, discharge, and stream chemistry in the Upper Hafren catchment. Weekly discharge ( $\text{m}^3 \text{ week}^{-1}$ ), precipitation ( $\text{mm week}^{-1}$ ) and concentrations of solutes ( $\mu\text{M}$ ) averaged over 1990-2010. Error bars represent standard errors.



**Figure S5.** Seasonality of precipitation chemistry ( $\mu\text{M}$ ) in the Plynlimon forest averaged over 1984-2010. Error bars represent standard errors.



**Figure S6.** Average values for the molar ratios of solutes K:Na versus dissolved organic carbon (DOC,  $\text{mmol L}^{-1}$ ) for various solute sources in the (a) Shale Hills CZO, (b) Upper Hafren, or (c) Upper Hore catchments.



**Table S1.** Groundwater well identification numbers (data access: <http://eidchub.ceh.ac.uk/metadata/44095e17-43b0-45d4-a781-aab4f72da025>)

ID	Latitude	Longitude	Elevation m	Depth m
Upper Slope 1 (UA1)	52.4818	-3.7258	562	1.48
Valley Bottom 1 (VB1)	52.4749	-3.7049	352	1.88
Tannorth (U)	52.4751	-3.7068	363	2.70
Lower Slope 1 (LA1)	52.4732	-3.7004	347	1.62
Lower Slope 2 (LA2)	52.4731	-3.7019	347	1.02
Lower Slope 3 (LA3)	52.4732	-3.7004	347	1.71
SE1 (AC)	52.4730	-3.6987	354	3.37
SE3 (AB)	52.4715	-3.6937	348	2.63



**Table S2.** Plynlimon lysimeter identification numbers, location, horizon and soil type

ID	Latitude	Longitude	Horizon	Soil type
HN0L	52.44253	-3.73820	O	Stagnopodzol
HN0S	52.44253	-3.73820	B	Stagnopodzol
HN1L	52.40979	-3.70163	O	Stagnopodzol
HN1S	52.40979	-3.70163	B	Stagnopodzol
HN2L	52.48035	-3.73380	O	Stagnopodzol
HN2S	52.48035	-3.73380	B	Stagnopodzol
HN3L	52.45077	-3.66494	O	Stagnopodzol
HN3S	52.45077	-3.66494	B	Stagnopodzol
HN4L	52.46105	-3.70066	O	Stagnopodzol
HN4S	52.46105	-3.70066	B	Stagnopodzol
L300	52.47177	-3.70549	O	Stagnopodzol
A301	52.47177	-3.70549	E	Stagnopodzol
A302	52.47177	-3.70549	B	Stagnopodzol
A303	52.47177	-3.70549	C	Stagnopodzol
L200	52.44253	-3.73820	O	Stagnopodzol
L201	52.44253	-3.73820	E	Stagnopodzol
L202	52.44253	-3.73820	B	Stagnopodzol
A201	52.44253	-3.73820	E	Stagnopodzol
A202	52.44253	-3.73820	B	Stagnopodzol
A203	52.44253	-3.73820	C	Stagnopodzol
L7	52.44253	-3.73820	O	Stagnopodzol
L8	52.44253	-3.73820	O	Stagnopodzol
A1	52.44253	-3.73820	E	Stagnopodzol
A2	52.44253	-3.73820	C	Stagnopodzol
A3	52.44253	-3.73820	B	Stagnopodzol
A4	52.44253	-3.73820	E	Stagnopodzol
A5	52.44253	-3.73820	C	Stagnopodzol
A6	52.44253	-3.73820	B	Stagnopodzol
L10	52.44253	-3.73820	O	Stagnopodzol
L12	52.44253	-3.73820	O	Stagnopodzol
L13	52.44253	-3.73820	O	Stagnopodzol
L14	52.44253	-3.73820	E	Stagnopodzol
L15	52.44253	-3.73820	E	Stagnopodzol
L16	52.44253	-3.73820	B	Stagnopodzol
L17	52.44253	-3.73820	E	Stagnopodzol
L18	52.44253	-3.73820	B	Stagnopodzol
A19	52.46050	-3.73891	E	Stagnopodzol
A20	52.46050	-3.73891	B	Stagnopodzol
A21	52.46050	-3.73891	C	Stagnopodzol
L400	52.47267	-3.70552	O	Peaty gley
L401	52.47267	-3.70552	E	Peaty gley
L403	52.47267	-3.70552	C	Peaty gley
A400	52.47267	-3.70552	O	Peaty gley
A401	52.47267	-3.70552	E	Peaty gley
A402	52.47267	-3.70552	B	Peaty gley
A403	52.47267	-3.70552	C	Peaty gley
L2	52.44160	-3.73964	O	Peat
L5	52.44160	-3.73964	O	Peat
L6	52.44160	-3.73964	O	Peat
L11	52.44160	-3.73964	O	Peat