



**Biotic controls on
solute distribution
and transport in
headwater
catchments**

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Biotic controls on solute distribution and transport in headwater catchments

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Abstract

Solute concentrations in stream water vary with discharge in patterns that record complex feedbacks between hydrologic and biogeochemical processes. In a comparison of headwater catchments underlain by shale in Pennsylvania, USA (Shale Hills) and Wales, UK (Plynlimon), dissimilar concentration-discharge behaviors are best explained by contrasting landscape distributions of soil solution chemistry – especially dissolved organic carbon (DOC) – that have been established by patterns of vegetation. Specifically, elements that are concentrated in organic-rich soils due to biotic cycling (Mn, Ca, K) or that form strong complexes with DOC (Fe, Al) are spatially heterogeneous in pore waters because organic matter is heterogeneously distributed across the catchments. These solutes exhibit non-chemostatic “bioactive” behavior in the streams, and solute concentrations either decrease (Shale Hills) or increase (Plynlimon) with increasing discharge. In contrast, solutes that are concentrated in soil minerals and form only weak complexes with DOC (Na, Mg, Si) are spatially homogeneous in pore waters across each catchment. These solutes are chemostatic in that their stream concentrations vary little with stream discharge, likely because these solutes are released quickly from exchange sites in the soils during rainfall events. Differences in the hydrologic connectivity of organic-rich soils to the stream drive differences in concentration behavior between catchments. As such, in catchments where soil organic matter (SOM) is dominantly in lowlands (e.g., Shale Hills), bioactive elements are released to the stream early during rainfall events, whereas in catchments where SOM is dominantly in uplands (e.g., Plynlimon), bioactive elements are released later during rainfall events. The distribution of vegetation and SOM across the landscape is thus a key component for predictive models of solute transport in headwater catchments.

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1 Introduction

Streams are regularly monitored to evaluate watershed geochemistry, ecosystem health, and suitability for human use. However, streams integrate hydrologic and biogeochemical processes over varied spatial and temporal scales, making it difficult to determine both the sources and flow paths of solutes. While many researchers examine short- to long-term element variability in stream water, it has remained difficult to derive generalized models quantifying solute concentration-discharge behavior (Fisher et al., 2004; Sivapalan, 2005; Zimmer et al., 2012). Flow paths may dictate stream chemistry by controlling fluid residence times and chemical equilibration of flowing water with soil minerals within catchments (Maher, 2011). Therefore, it is necessary to understand how heterogeneous flow paths through distinct chemical sources within a catchment influence observed solute concentration patterns within streams.

When the discharge of a stream (Q) increases, concentrations of solutes (C) can either increase (enrichment behavior), decrease (dilution behavior), or, perhaps most paradoxically, change very little (chemostasis) (Kirchner, 2003; Godsey et al., 2009; Clow and Mast, 2010). Dilution can result during rainfall events as water stored in a catchment is diluted by less concentrated meteoric water. Enrichment can result if a more concentrated source (e.g., groundwater) mixes with stream water during large rainfall events (Johnson et al., 1969). In contrast, chemostasis cannot be explained by the simple mixing of multiple sources and therefore has been attributed to processes such as chemical reactions with the solid-phase along the pathway of water flow (Godsey et al., 2009). These trends can be explained for an individual solute or single catchment (Bishop et al., 2004), but solutes often show different types of behavior in different catchments, and a unifying explanation for C - Q behavior has remained elusive.

Behavior differences amongst individual solutes have been linked to solute concentration variability within a catchment: discrete zones of element mobilization within soils and sediments can lead to pulses of solute transport into a stream (McClain et al., 2003; Andrews et al., 2011). This effect is furthermore affected by changes in hydrologic con-

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nectivity, defined as the water-mediated transfer of constituents between water sources (Pringle, 2001), within a catchment during rainfall events. Stream chemistry can vary during storm events as flow shifts from groundwater and riparian zones during base flow to upslope soil pore waters at high flow as uplands become increasingly connected to the stream (McGlynn and McDonnell, 2003a). Such connectivity of upland soils can occur if soil layers become water-saturated, promoting downslope flow within the unsaturated zone. As a result, concentrations of solutes that are stored preferentially in the riparian zone, e.g., dissolved organic carbon (DOC) released from soil organic matter (SOM), peak in the stream prior to discharge or with rising discharge during storm events (McGlynn and McDonnell, 2003b; Hood et al., 2006). Variability in organic carbon dynamics across different landscape units can subsequently control metal export from headwater catchments and downstream hydrochemistry (Köhler et al., 2014).

Many previous studies examine catchments that were developed on multiple lithologies, making the interpretation of solute behaviors difficult at best. When monolithologic catchments are compared, insights into other factors that influence C - Q behavior (e.g., biota, climatic) can be developed. To elucidate controls on stream chemistry not primarily driven by lithology, we examined C - Q behaviors in shale-underlain headwater streams with extensive hydrogeochemical datasets. Although these watersheds are underlain by chemically similar shales, their soils have developed distinct distributions of vegetation and SOM across each landscape. For these watersheds, variations in stream chemistry with flow elucidate non-lithological factors that control solute transport to streams, yielding a paradigm that should help explain other catchments.

2 Methods

Water chemistry was compared for three sites: (1) the Susquehanna Shale Hills Critical Zone Observatory (Shale Hills) in central Pennsylvania, USA and (2) the Upper Hore and (3) Upper Hafren subcatchments in the Plynlimon experimental forest in Wales,

UK (Fig. 1). The Shale Hills and Plynlimon forests are underlain almost exclusively by Fe-rich, organic-poor, Silurian-aged shale formations that are stratigraphically equivalent. Although these headwater catchments vary by size and location, their similar lithologies and extensive hydrogeochemical characterization (e.g., Kirby et al., 1991; Neal et al., 1997; Shand et al., 2006; Jin et al., 2010; Neal et al., 2011; Brantley et al., 2013a–j; Dere et al., 2013) allow development of a unifying theory on factors controlling concentration-discharge behavior.

2.1 Susquehanna Shale Hills critical zone observatory

Shale Hills is an 8 ha forested headwater catchment nested within the larger Susquehanna River Basin in Pennsylvania, USA. Shale Hills is underlain by the Rose Hill Formation, which contains dominantly clay minerals and quartz (Jin et al., 2010). The regional mean annual temperature (MAT) is 10 °C, and precipitation (MAP = 105 ± 17 cm yr⁻¹) is acidic (e.g., pH averaged 4.5 ± 0.2 for US National Atmospheric Deposition Program (NADP) sites PA15 and PA42 during 2000–2011). Vegetation is dominated by deciduous oaks and hickories, and the elevation ranges from 256 m at the catchment outlet to 310 m on the ridge. Hillslopes are characterized as either “planar” (mildly convex-upward slopes with shallow soils that grade to concave-upward slopes toward valley floor) or “swale” (concave-upward depressions with deep soils and convergent water flow) (Lin et al., 2006) (Fig. 1). Water flows vertically through pores when soils are unsaturated, or downslope along horizon interfaces when rainfall events create transiently perched saturated water zones (Lin, 2006; Jin et al., 2011). Soils in the swales store more organic carbon than soils on planar hillslopes and act as sources of DOC transport into streams (Andrews et al., 2011) (Table 1).

Water samples from Shale Hills were collected approximately daily from the stream outlet and biweekly from soil lysimeters from 2006–2011. Detailed methods and results of chemical analyses, including isotopic variation and concentrations of major ions and DOC, have been reported elsewhere (Jin et al., 2011; Andrews et al., 2011; Brantley et al., 2013a–j). Aluminum concentrations in the stream were consistently below de-

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tection limits; thus, AI data were not examined for Shale Hills. Average daily discharge rates were estimated from continuous discharge measurements collected at 10 min intervals from the stream weir at the catchment's outlet (Duffy, 2012). Soil water was collected from suction lysimeters installed at 10 cm depth increments in south planar valley floor (SPVF) and south swale valley floor (SSVF) soils. The groundwater was sampled from a 2.8 m deep well located 80 m upstream from the weir. Major cation (2000–2011; NADP, 2011) and trace element concentrations (Herndon, 2012) have been reported for precipitation samples collected from NADP sites PA-15 and PA-42. Vegetation chemistry was previously determined for green leaf and leaf litter samples collected throughout summer and fall seasons, respectively, in the Shale Hills catchment (Herndon et al., 2014).

2.2 Plynlimon forest: Upper Hore and Upper Hafren catchments

The Plynlimon forest is a 682 ha watershed located at the headwater of the River Severn, 20 km from the west coast of Wales (Reynolds et al., 1987). MAT is 7.2 °C and MAP is 250 ± 78 cm with an average pH of 4.98 ± 0.01. Vegetation is predominantly evergreen Sitka spruce (*Picea sitchensis*) with areas of heath, including *Sphagnum* and *Juncus* communities, dominating the uplands. Elevation in the Plynlimon forest ranges from 319 to 738 m.

We focus on two adjacent headwater catchments within the Plynlimon watershed: the Upper Hore and the Upper Hafren (Fig. 1). The Upper Hore (162 ha) is predominantly forested with periodically saturated, organic-rich stagnopodzol soils and uplands that are dominated by grass and saturated peat soils (Kirby et al., 1991). In contrast, the Upper Hafren (122 ha) is dominated by heath and peat soils, with waterlogged and organic-rich peaty gley soils located in riparian areas (Kirby et al., 1991).

Stream chemistry data for the Upper Hore and Upper Hafren catchments were collected between 1983–2005 and 1990–2010, respectively (Neal et al., 2013a, b). Due to extensive tree-cutting in the Upper Hore in 2005, data collected from 2005–2010 were evaluated separately to examine the influence of tree removal on C-Q behav-

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ior. Stream discharge was measured every 15 min at weirs in both catchments and weekly stream grab samples were analyzed for major and trace ions. Likewise, bulk precipitation was collected weekly at the Carreg Wen meteorological station located between the Upper Hore and Upper Hafren catchments (Reynolds et al., 1987). Precipitation chemistry was influenced by seawater inputs, which varied with wind direction and season (Reynolds et al., 1987). Groundwater chemistry was estimated as average concentrations of solutes in shallow (< 3 m) wells located near the weirs. Wells were sampled weekly from 1994–1999 (Neal et al., 1997) (Fig. 1; Table S1 in the Supplement). Average pore water chemistry was calculated for all sampled soils classified as peat, stagnopodzol, or peaty gley throughout Plynlimon (Reynolds et al., 1987, 1988; Stevens et al., 1997; Shand et al., 2005) (Table S2).

2.3 Stream flow regimes and concentration-discharge (C - Q) behaviors

To analyze discharge events, stream water discharge (Q , $\text{m}^3 \text{d}^{-1}$) was categorized as low-flow (lower quartile of Q), moderate-flow (interquartile range), or high-flow (upper quartile) (Fig. S1 in the Supplement). Perennial stream flow with little seasonal variation in discharge was observed in the Upper Hafren and Upper Hore catchments, and the distributions of Q were positively skewed by intermittent storms. Stream flow at Shale Hills was intermittent and highly seasonal, with extended periods of no- to low-flow during summer months (especially July and August).

Linear regressions were fit to log-transformed C - Q data for each solute j (C_j) for each catchment stream. The slope of this regression (m_j) was used to identify solute behaviors as “chemostatic” or “non-chemostatic”. When m_j showed only minimal effects of dilution by meteoric water, i.e., $-0.1 < m_j < 0$, the solutes were defined as chemostatic (Godsey et al., 2009). In contrast, non-chemostatic elements were defined to exhibit dilution behavior when concentrations decreased with increasing Q ($m_j < -0.1$) or enrichment behavior when concentrations increased with increasing Q ($m_j > 0$).

3 Results

3.1 Solute concentration-discharge patterns

Na and Mg behaved chemostatically in all catchments (Fig. 2; Table 4) while Si and K were only chemostatic at Shale Hills. A subset of non-chemostatic solutes exhibited similar trends to DOC; however, trends were opposite between Shale Hills and Plynlimon. Specifically, when Q increased, concentrations of the non-chemostatic solutes Ca, Mn, Fe and DOC decreased at Shale Hills (i.e., dilution behavior; $m_j < -0.1$) while the non-chemostatic solutes Mn, K, Al, Fe, and DOC increased at Plynlimon (i.e., enrichment behavior; $m_j > 0$) (Fig. 2b; Table 4). Note that Fe exhibited enrichment ($m_{Fe} = 0.33 \pm 0.02$) similar to DOC in the Upper Hafren but was more consistent with chemostasis in the Upper Hore ($m_{Fe} = -0.05 \pm 0.02$). Additionally, Si and Ca showed dilution patterns at Plynlimon that contrasted with DOC.

In the Shale Hills stream, higher concentrations of stream solutes were observed during the dry summer season relative to the wetter spring and autumn (Fig. S2). While concentrations of the chemostatic elements increased only slightly ($\sim 2\times$) during the summer, larger increases were observed for Ca ($\sim 4\times$), DOC ($\sim 7\times$), and Mn and Fe ($> 100\times$). Increases in DOC, K, Fe, and Mn in the stream during summer were not consistent with increasing groundwater inputs because groundwater at Shale Hills is depleted in these elements relative to stream water at low flow (Table 2). In the Upper Hafren and Upper Hore streams, chemostatic elements Na and Mg, derived primarily from sea salts, showed no seasonality despite high seasonal variation in inputs from precipitation (Fig. S5; Reynolds et al., 1987), as if precipitation-derived solutes were buffered in the catchment soil pore waters before entering the stream (Neal and Kirchner, 2000). In contrast, solutes exhibiting enrichment varied by season (Figs. S3 and S4). Although groundwater can discharge to streams in Plynlimon during summer months (Shand et al., 2005), the groundwater contains little DOC (Table 3) and therefore cannot explain changes in summer stream chemistry where DOC increases from spring to summer (Figs. S3 and S4).

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In the Upper Hore where trees were harvested, solute concentrations and $C-Q$ slopes increased following tree harvest for solutes showing enrichment behavior. Specifically, stream concentrations of DOC, K, Mn, and Fe increased after 2005 (Table 3). Post-harvest values of m_K ($= 0.26 \pm 0.03$) and m_{Mn} ($= 0.12 \pm 0.02$) increased relative to pre-harvest values (0.07 ± 0.01 and 0.05 ± 0.01 , respectively) (Fig. S6; Table 4). No effects on C_j or m_j were observed for chemostatic elements. Additionally, no changes in solute concentrations in the non-harvested Upper Hafren were observed over this time.

3.2 Soil pore waters

We examined the chemical composition of soil pore waters in order to investigate sources of solutes to the stream. Pore waters in each catchment were categorized into distinct chemical pools based on DOC concentrations (Table 2): “organic-rich” waters were defined by average DOC > 1 mM, while all other waters were “organic-poor”. At Shale Hills, pore waters collected from the A horizon (10 cm) of the swale (SSVF) were organic-rich (1.28 ± 0.33 mM DOC) while all other pore waters were organic-poor; i.e., the A horizon of SPVF (0.69 ± 0.06 mM DOC) and the B horizons of SSVF and SPVF (> 10 cm; averaged 0.55 ± 0.4 mM DOC) were organic-poor. At Plynlimon, pore waters in organic horizons and peat soils (1.2 ± 0.2 mM DOC) were organic-rich relative to mineral horizons of stagnopodzol and peaty gley soils (0.42 ± 0.7 mM DOC) soils.

At Shale Hills, concentrations of the non-chemostatic solutes Mn, Fe, and Ca showed evidence of DOC-related behavior. For example, Mn and Fe were positively correlated with DOC across all pore waters ($R^2 > 0.9$) and were highest in the organic-rich waters (6.8 ± 1.9 μ M and 1.7 ± 0.3 μ M, respectively) (Table 2). Calcium concentrations were enriched in the A horizon (72 ± 11 μ M) relative to the B horizon (35 ± 1 μ M) in SSVF. Furthermore, Fe and Mn concentrations were spatially variable across pore waters (% RSD = 100 and 140%, respectively). In contrast, chemostatic solutes Mg (33%), Na (19%), and Si (5%) were less variable. Thus, concentrations of non-chemostatic

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solutes were spatially heterogeneous in soil waters across the landscape while chemostatic solutes were distributed more homogeneously.

Like Shale Hills, concentrations of the chemostatic elements Na and Mg were spatially homogeneous in pore waters at Plynlimon amongst the different soils (RSD = 23 and 15%, respectively) (Table 3). Additional solutes chiefly derived from the atmosphere via precipitation (K, Ca) or through carbon fixation (DOC) were enriched in the organic horizons, while elements derived primarily from minerals (Si, Fe, Al, and Mn) were enriched in mineral horizons. In contrast to Shale Hills, many of the non-chemostatic elements at Plynlimon were not correlated with DOC in soil pore waters. This is likely due to the fact that organic horizons at Plynlimon receive large inputs of sea salts that dominate the chemical signature of near-surface pore waters.

3.3 Mixing diagrams

To investigate sources of solutes that are mobilized to the stream, element ratios in pore waters, precipitation, groundwater, and leaves (where available) were compared to element ratios in the stream. Element ratios have been used in other studies to link river chemistry to end member reservoirs (e.g., Gaillardet et al., 1999). Molar ratios of divalent cations (Ca : Mg) were compared to univalent cations (K : Na) in each reservoir to understand how elements exhibiting non-chemostasis (Ca, K) vary relative to chemostatic elements (Mg, Na). To further explore the association of certain non-chemostatic solutes with organic C, molar ratios of Mn (a non-chemostatic element) to Mg were compared to DOC concentrations. Average DOC concentrations were used to define soil waters as organic-rich or organic-poor, as discussed in Sect. 3.2. In Shale Hills, green leaves were used to represent the most organic-rich end-member since pore waters could not be sampled from the thin O horizon.

At Shale Hills, stream chemistry was most similar to pore waters from organic-rich soils and green leaves at low flow and approached values for pore waters from organic-poor soils at high flow. Ratios of $C_{Ca} : C_{Mg}$ and $C_K : C_{Na}$ decreased slightly ($< 2\times$) with increasing discharge (Fig. 3a), while $C_{Mn} : C_{Mg}$ decreased by $10\times$ (Fig. 3b). Stream wa-

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ter was more similar to soil pore waters than groundwater or precipitation under all flow regimes, documenting that flow through shallow soils and bedrock rather than deep groundwater sources dominated inputs to the stream. These trends further indicate a shift from inputs of organic-rich soil water to the stream at low flow to organic-poor soil water at high flow.

In contrast to this behavior at Shale Hills, stream chemistries in the Upper Hore and Upper Hafren catchments were most similar to organic-poor sources (precipitation, groundwater) at low flow and organic-rich sources (soil pore waters) at high flow (Figs. 3c–f and A7). Values of $C_{Mn} : C_{Mg}$, C_{DOC} , and $C_K : C_{Na}$ increased while $C_{Ca} : C_{Mg}$ decreased and converged towards the most organic-rich end-member in each system, either the peat (Upper Hafren) or peat and organic horizon pore waters (Upper Hore), with increasing discharge. Stream $C_{Ca} : C_{Mg}$ ratios were similar to groundwater at low flow in the Upper Hafren. Although few data were available to assess the Plynlimon groundwaters, groundwater was not chemically similar to stream water under any flow regime in the Upper Hore (Fig. 3).

3.4 Organic influence on concentration-discharge behavior

Finally, we explored how chemical heterogeneity in soil pore waters influenced concentration-discharge behaviors in the streams. Specifically, we evaluated solute heterogeneity due to redistribution by vegetation as the ratio of solute concentrations in “organic-rich” to “organic-poor” pore waters. As previously defined, these pore waters were collected from A vs. B horizons at Shale Hills, and organic vs. mineral soils in the Upper Hafren and Upper Hore. The slope of the concentration-discharge plot (m_j) was used to define the magnitude of non-chemostatic behavior for each solute, i.e., the degree to which an element was diluted or enriched in the stream with increasing discharge.

At Shale Hills, elements concentrated in the organic-rich pore waters were diluted rapidly in the stream with increasing discharge, consistent with increasing inputs of water from mineral soils as the planar hillslope soils become saturated during storms

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(Qu and Duffy, 2007). This trend is documented in Fig. 4a where the concentration ratios for organic-rich vs. -poor soil waters were negatively correlated with respect to m_j ($R^2 = 0.90$, $p < 0.001$). According to these results, Fe and Mn were most concentrated in organic-rich pore waters and most rapidly diluted in the stream, followed by DOC, Ca, and K. Chemostatic elements Na, Mg, and Si were not concentrated in organic-rich pore waters.

No significant correlation ($p > 0.05$) existed between organic to mineral pore water ratios and m_j in the Upper Hore and Upper Hafren subcatchments, likely because organic horizons at Plynlimon have high concentrations of chemostatic solutes due to atmospheric inputs. Provided this observation, organic-associations in each catchment were evaluated by inspecting the ratio of average solute concentrations in the pore water vs. precipitation (Fig. 4b and c), i.e., precipitation serves as the most organic-poor pool in the Plynlimon system. For both the Upper Hafren and the Upper Hore, the ratios of concentrations in soil water vs. precipitation were positively correlated with m_j ($p < 0.05$). Elements exhibiting enrichment behavior, including DOC, Al, Mn, and K in both catchments plus Fe in the Upper Hafren, were also enriched in pore water relative to precipitation. Chemostatic elements in pore waters were less enriched relative to precipitation. In contrast, the ratios for soil water vs. precipitation were not significantly correlated with m_j at Shale Hills ($p > 0.05$).

4 Discussion

Cross-site comparison of the Shale Hills and Plynlimon headwater catchments revealed that the behaviors of non-chemostatic solutes were controlled by the spatial variability of those elements in soil waters and the distribution of DOC. Conversely, chemostatic solutes were homogeneously distributed in pore waters across the catchments. In the following sections, we discuss how vegetation drives the landscape distribution of chemically distinct pools; subsequently, the connectivity between organic-rich soils and the stream controls how concentrations vary with discharge. We contend that

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the behavior of certain non-chemostatic solutes in these systems should be defined as “bioactive” due to their association with organic matter.

4.1 Hydrologic connectivity of solute pools across landscapes

At first glance, it may appear contradictory that bioactive element concentrations in the streams at Shale Hills and Plynlimon trend in opposite directions with increasing discharge; however, the discrepancy can be explained by differences in the distributions of organic-rich source waters in each system. Similar to Stallard and Murphy (2014), we attribute the concentration-discharge behavior of bioactive solutes to changing water flow through organic-rich soil matrices; however, we also observe that organic-rich sources and flow paths vary between the catchments (Fig. 1).

At Shale Hills, meteoric water passes through the thin organic horizon and organic-rich A horizon (< 15 cm deep) and is transported along the horizon interfaces to the stream via preferential flow paths (Lin et al., 2006; Jin et al., 2011; Thomas et al., 2013). The stream receives water from organic-rich swales and surface soils during dry periods, and water inputs from organic-poor hillslope soils increase as the catchment saturates (Qu and Duffy, 2007; Andrews et al., 2011). Consequently, we observed that stream water chemistry was similar to organic-rich soil waters at low flow and organic-poor soil waters at high flow (Fig. 3). Solute derived largely from organic-rich soils exhibited greater variability over different flow regimes due to their high spatial variability in soil pore water. Stream chemistry did not reflect inputs from groundwater during dry periods, consistent with a previous finding that the water table drops to > 2 m below the stream bed during late summer (Thomas et al., 2013).

In the grass-dominated Upper Hafren, which contains peat soils that experience minimal water-rock interaction (Kirby et al., 1991), concentrations of chemostatic elements in the soils never deviate far from an average precipitation signal (Fig. 4). In contrast, concentrations of bioactive elements are not driven by precipitation, and we propose that pore water concentrations of these elements are attributed to regulation by vegetation. During the drier growing season, bioactive elements are depleted from soil pore

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water and accumulate in vegetation. Drying of the surface peat and higher temperatures during this time increase microbial decomposition, thereby increasing mobility of bioactive elements by releasing them from storage in organic matter (Kirby et al., 1991). According to this conceptual model, once transpiration decreases and flow increases through the soil in autumn, concentrations of bioactive elements increase in the stream because (1) transpiration is reduced and the soil water is no longer being depleted, (2) the surface peat is flushed of elements that have accumulated, providing elements in addition to precipitation. As observed at the Upper Hafren and Upper Hore, concentrations of bioactive elements begin to increase in the stream as discharge increases following low-flow in the summer (Figs. S3 and S4). This effect may be especially prominent in the peat regions since the grass vegetation decomposes annually with little aboveground storage (i.e., peat is leaky with respect to nutrients), and anoxic conditions limit complete conversion of SOM to CO₂, enhancing release of DOC.

In the spruce-forested Upper Hore, long-term storage of nutrient elements in aboveground biomass is expected to deplete soil pore waters of bioactive elements without the flushing effect due to rapid turnover observed in the Upper Hafren (Reynolds et al., 2000). Instead, the positive concentration-discharge slopes in the Upper Hore result from flushing of upland peat soils at high flow conditions (Neal et al., 1990). These effects can be observed by comparing pre- and post-harvest concentration-discharge slopes in the Upper Hore. Tree harvest impacted stream concentrations and C-Q slopes for K, Al, Fe, Mn, and DOC but had no observable effects on chemostatic elements. Specifically, m_K increased from 0.07 to 0.25 following harvest, while the peat-dominated Upper Hafren, which was not harvested, maintained $m_K = 0.15$ during this time. Fe and DOC experienced increases in stream concentrations, but not m_j . Since neither Fe nor DOC is expected to be taken up into the trees in high quantities, increasing C_j may indicate that they were mobilized by increased decomposition of leaf litter debris in the forest region following harvest (Hughes et al., 1990).

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C_j and m_j values for bioactive elements likely increased following harvest because (1) these elements were no longer being taken up and stored in tree biomass (Stevens et al., 1997), (2) the organic debris left after harvest provided a labile pool of organic chelator molecules and bioactive elements, and (3) inputs from upland peats to the stream increased due to lack of interception by the forest (Neal et al., 1992, 2004). Although bioactive in the Upper Hafren, Fe followed a chemostatic trend in the Upper Hore (Fig. 2). This behavior could be due to Fe retention in the forested soils during downslope transport: stagnopodzols on these slopes have Bs horizons that accumulate sesquioxides and immobilize leached Fe (Reynolds, 1982).

4.2 Drivers of chemostasis

Stream concentrations for most major weathering elements ($j = \text{Na, K, Mg, Ca, Si}$) varied little over a wide range of discharge values (Fig. 2): by this definition, most of the major elements were chemostatic, with the exception of Ca at Shale Hills and K at Plynlimon. Note that the standard descriptor “major elements” includes Na and Ca although both are low in abundance in the protolith at Shale Hills and Plynlimon (< 0.7 and < 0.2 w.t. %, respectively), while K is lower at Plynlimon compared to Shale Hills (2.90 and 3.76 w.t. %, respectively) (Jin et al., 2010; Dere et al., 2013). Chemostasis could be expected for elements derived from minerals that are always equilibrated with long residence-time pore waters. However, the fast-dissolving minerals present at Shale Hills and Plynlimon, carbonates and pyrite, do not contain K, Na and Si and are also depleted in the upper protolith (Jin et al., 2010; Neal et al., 1997). Therefore, dissolution of these minerals cannot explain chemostasis of K, Na, Si, Mg and Ca. Godsey et al. (2009) suggested that changes in mineral-water interfacial area during periods of high and low discharge explain chemostasis; however, clay dissolution rates are too slow (Bandstra et al., 2008) to provide a rapidly mobilized source of cations during the short-timescales of precipitation events.

The exchangeable cation pool is a likely source of chemostatic elements during rain events. The cation exchange capacity of soils along the planar hillslope at Shale Hills

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ranges from 35 to 71 meq kg⁻¹ (Jin et al., 2010). At Plynlimon, forest and peat soils have a cation exchange capacity of roughly 77.4 and 300 meq kg⁻¹, respectively (Reynolds et al., 1988; Cuttle, 1983). Elements are displaced from cation exchange sites into solution by H⁺ (i.e., protonation of the exchange sites), and we observe that the degree of chemostasis was inversely related to the elements' relative strengths of adsorption to cation exchange sites (Evangelou and Phillips, 2005). Furthermore, this explanation can even account for the highly chemostatic, neutrally charged solute Si(OH)₄⁰, which has also been documented in the exchangeable pool at Shale Hills (Jin et al., 2010). For these catchments where pH is low (pH < 7), Si should be weakly associated to exchange sites due to its neutral charge. The similar concentrations observed for major weathering elements in the planar and swale pore waters at Shale Hills as well as Plynlimon (Tables 2 and 3) are attributed to the quick exchange of protons in rain for cations in the exchange pool throughout the catchment. Thus, chemostasis is explained by increasing connectivity of the exchangeable cation pool on mineral surfaces to mobile water as soil saturation increases.

4.3 Chemostatic elements become bioactive under nutrient limiting conditions

Although geochemically similar to Mg, K, and Na, the concentration-discharge pattern for Ca (Fig. 2) suggests it exhibits a degree of bioactive behavior at Shale Hills. The mixing model (Fig. 3a) indicates leaves may be a primary source of Ca to the stream during low discharge. Indeed, these shallow soils are strongly leached of Ca (< 0.16 % w.t.; Jin et al., 2010), and organic matter may be a relatively large pool of Ca in this system. In contrast to Shale Hills where Ca trends are strongly influenced by organic matter, Ca at Plynlimon may be linked to groundwater, an effect most pronounced in the Upper Hore. Ca : Mg ratios trend towards organic-poor sources at low flow, likely due to inputs of Ca-rich groundwater during base flow that is diluted by increasing contribution from soil water at high flow. Although a lack of groundwater data from these two subcatchments limits our ability to directly assess inputs to the stream,

groundwater collected from lower elevations in the Plynlimon forest are rich in Ca and Si (Neal et al., 1997).

Similar to Ca at Shale Hills, K limitation may drive its increased association with organic matter at Plynlimon. Values of $C_K : C_{Na}$ decrease at Shale Hills and increase at Plynlimon with increasing Q in a manner consistent with changing inputs from organic-rich sources (Fig. S7). Although geochemically similar, Na is a nonessential element (Kirkby, 2012) that is readily weathered from soils whereas K is a plant macronutrient that accumulates in leaf tissue (Herndon et al., 2014). From the mixing diagrams and m_K , we infer that K has a stronger organic control at Plynlimon than at Shale Hills. One explanation for this is that net primary productivity (NPP) is higher ($896 \text{ gC m}^{-2} \text{ yr}^{-1}$; unpublished data) but bedrock K is lower ($2.90 \pm 0.13 \%$; Dere et al., 2013) at Plynlimon than at Shale Hills (NPP = $550 \text{ gC m}^{-2} \text{ yr}^{-1}$; Smith, 2013 and $K = 3.76 \pm 0.16 \%$; Jin et al., 2010). These data suggest that K is limiting to vegetation at Plynlimon while Ca is limiting to vegetation at Shale Hills due to high demand and low supply.

5 Conclusions

A comparison of two shale-derived watersheds, the Shale Hills CZO in central Pennsylvania, USA and Plynlimon in Wales, UK, reveals that the concentration-discharge behaviors of elements are strongly impacted by the distribution of organic matter in soils and the hydrologic connectivity of these soils to the stream. At Shale Hills, stream water is derived from organic-rich swales at low flow and then from both swale and planar hillslopes with increasing flow. At Plynlimon, stream water is only dominated by water from organic-rich soils at high flow. Solutes that are limiting nutrients or that are strongly retained by vegetation exhibit non-chemostatic behavior in the stream because they are released to the stream along with dissolved organic carbon. This non-chemostatic behavior is opposite between Plynlimon and Shale Hills due to the different landscape distribution of organic-rich soils. Due to minimal redistribution by vegetation, Na, Mg, and Si are equally concentrated in pore fluids for organic-rich and organic-poor soils,

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and concentrations of these elements in stream water remain relatively constant. From this, we conclude that the transport of elements associated with organic matter, termed previously as organomarker elements (Hausrath et al., 2009), is strongly controlled by the movement of dissolved organic carbon, leading to a distinct “bioactive” behavior in stream waters that contrasts with the “chemostatic” behavior of major weathering elements. Stream chemistry in headwater catchments are variable largely because of the chemical heterogeneities in distribution of organic-rich soils in catchments and how those soils connect to the stream.

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Table 1. Soil profile descriptions and associated SOC (% w.t.) and DOC (mM) averages.

Site	Category ^a	Horizon	Depth (cm)	DOC (mM)	SOC ^b (% wt.)
<i>Shale Hills</i> ^c					
Planar, valley	Mineral	A	0–15	0.69	4.7
	Mineral	Bw	15–30	0.54	1.6
		Bt	30–53	–	–
		C	53–147	–	–
Swale, valley	Organic	A	0–11	1.28	2.0
	Mineral	Bw	11–38	0.55	1.2
		BC	38–60	–	–
		C	60–178	–	–
<i>Plynlimon</i> ^d					
Peat	Organic	O	0–100+	1.10	40–50
Peaty gley	Organic	O	0–22	1.37	25
	Mineral	Eag	22–37	0.49	5–6
		Bs	37–86	–	–
		C	86–107	–	–
		O	0–19	1.12	46
Stagnopodzol	Mineral	Eag	19–24	0.35	5
		Bs	24–51	–	–
		C	51–89	–	–

^a Category (organic or mineral) assigned to soil horizons in this paper; Note that reported SOC and DOC values are averaged over all mineral horizons.

^b Shale Hills SOC estimates from Jin et al. (2010) and Andrews (2011).

^c Shale Hills soil descriptions from Lin (2006).

^d Plynlimon soil descriptions from Ruderforth et al. (1984).

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Table 2. Shale Hills average chemical data (\pm standard error).

	pH	Na $\mu\text{mol L}^{-1}$	K $\mu\text{mol L}^{-1}$	Mg $\mu\text{mol L}^{-1}$	Ca $\mu\text{mol L}^{-1}$	Si $\mu\text{mol L}^{-1}$	Fe $\mu\text{mol L}^{-1}$	Mn $\mu\text{mol L}^{-1}$	DOC mmol L^{-1}
<i>Precipitation</i>	4.5	2.1	0.67	0.73	2.65	–	0.24	0.05	0.08 ^a
\pm std. err.	0.2	0.4	0.28	0.16	0.51	–	0.14	0.01	0.02
<i>Soil Pore Water</i>									
SPVF, A horizon	4.5	29	34	62	142	123	0.61	0.38	0.69
\pm std. err.	0.2	3	3	10	26	5	0.15	0.06	0.06
SPVF, B horizon	4.7	34	29	89	146	125	0.25	0.44	0.54
\pm std. err.	< 0.1	2	1	8	15	3	0.02	0.05	0.04
SSVF, A horizon	3.9	21	88	39	72	112	1.7	6.8	1.28
\pm std. err.	0.1	3	14	5	11	11	0.26	1.9	0.33
SSVF, B horizon	4.4	28	29	79	35	126	0.21	1.3	0.55
\pm std. err.	< 0.1	1	1	2	1	2	0.03	0.1	0.03
Average, all soils		28	45	68	99	121	0.69	2.2	0.77
RSD (%), all soils		19	64	33	55	5	100	140	46
<i>Stream Water</i>									
Low flow	6.3	39	50	162	450	108	14	5.2	0.81
\pm std. err.	< 0.1	< 1	1	3	10	1	2	0.7	0.06
Moderate flow	5.7	32	31	122	240	101	1.9	1.1	0.45
\pm std. err.	0.1	1	< 1	3	7	1	0.4	0.2	0.03
High flow	5.9	26	29	96	163	99	0.53	0.33	0.42
\pm std. err.	0.1	< 1	< 1	2	6	1	0.02	0.03	0.03
<i>Groundwater</i>	–	145	24	404	758	124	0.14	2.9	0.20
\pm std. err.	–	6	< 1	13	27	1	0.08	0.2	0.05
<i>Vegetation</i>									
		Na $\mu\text{mol g}^{-1}$	K $\mu\text{mol g}^{-1}$	Mg $\mu\text{mol g}^{-1}$	Ca $\mu\text{mol g}^{-1}$	Si $\mu\text{mol g}^{-1}$	Fe $\mu\text{mol g}^{-1}$	Mn $\mu\text{mol g}^{-1}$	
Green leaves		1.1	221	69	186		0.99	42	
\pm std. err.		0.2	15	7	18		0.06	4	

^a Andrews et al. (2011).

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Table 3. Plynlimon average water concentrations (μmolL^{-1}) (\pm standard error).

	pH	Na μmolL^{-1}	K μmolL^{-1}	Mg μmolL^{-1}	Ca μmolL^{-1}	Si μmolL^{-1}	Fe μmolL^{-1}	Mn μmolL^{-1}	Al μmolL^{-1}	DOC mmolL ⁻¹
<i>Precipitation</i>	4.98	69.6	2.60	8.52	6.89	2.63	0.19	0.03	0.66	0.045
\pm std. err.	0.01	3	0.10	0.32	0.59	0.35	0.02	< 0.01	0.05	0.001
<i>Soil Pore Water</i>										
Peat	3.24	143	5.55	27.1	12.6	9.40	2.97	0.16	2.22	1.10
\pm std. err.	0.10	4	0.54	1.2	0.5	0.38	0.15	0.02	0.20	0.45
Peaty gley organic	3.56	239	29.7	30.0	8.32	47.6	9.29	–	26.6	1.37
\pm std. err.	0.07	6	3.2	1.0	0.41	2.0	0.42	–	1.3	0.77
Peaty gley mineral	4.16	220	10.2	26.7	5.32	57.1	12.2	–	55.9	0.49
\pm std. err.	0.01	1	0.2	0.1	0.02	0.3	0.5	–	0.2	0.09
Stagnopodzol O.	3.82	165	25.7	29.8	22.7	18.9	4.25	0.27	8.00	1.12
\pm std. err.	0.07	5	2.3	1.1	1.4	0.7	0.20	0.04	0.38	0.04
Stagnopodzol min	4.12	159	7.91	19.9	11.7	33.7	0.96	0.47	19.9	0.35
\pm std. err.	0.01	< 1	0.04	< 0.1	0.04	0.2	0.02	0.01	0.2	< 0.01
<i>Upper Hore</i>										
Low flow	6.98	177	3.06	36.1	78.3	63.0	2.59	0.32	3.56	0.10
\pm std. err.	0.02	1	0.06	0.3	1.0	0.9	0.11	0.01	0.40	< 0.01
Moderate flow	6.01	180	3.11	29.8	39.7	48.4	2.02	0.42	7.44	0.12
\pm std. err.	0.02	1	0.05	0.1	0.5	0.3	0.04	< 0.01	0.12	< 0.01
High flow	4.75	184	3.78	25.6	17.5	30.4	2.08	0.40	16.2	0.21
\pm std. err.	0.02	3	0.11	0.5	0.4	0.5	0.07	0.01	0.3	< 0.01
Avg., pre-harvest	5.94	178	3.2	30.1	42.3	47.9	2.03	0.41	8.4	0.13
\pm std. err.	0.03	1	< 0.1	0.2	1.3	0.4	0.04	0.01	0.2	< 0.01
Avg., post-harvest	5.96	169	8.9	30.2	41.3	45.0	3.33	0.51	7.9	0.31
\pm std. err.	0.05	1	0.3	0.3	0.7	0.9	0.11	0.01	0.3	0.01
<i>Upper Hafren</i>										
Low flow	6.45	160	2.96	27.8	17.4	67.8	1.21	0.27	2.02	0.08
\pm std. err.	0.02	1	0.06	0.2	0.1	1.0	0.06	0.01	0.18	< 0.01
Moderate flow	5.79	153	3.52	26.0	13.8	57.7	1.74	0.38	3.51	0.13
\pm std. err.	0.02	< 1	0.06	0.1	0.08	0.5	0.04	< 0.01	0.09	< 0.01
High flow	4.85	142	5.04	22.8	10.1	34.5	2.68	0.34	7.44	0.24
\pm std. err.	0.02	2	0.15	0.4	0.2	0.8	0.12	0.01	0.22	0.01
<i>Groundwater</i>	5.26	227	8.7	79	94	86	5.9	2.54	1.86	0.032
\pm std. err.	0.07	8	1.7	11	20	4	1.5	0.33	0.11	0.002

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Table 4. Slopes of regression lines fit to C - Q data ($\log C = a + m \times \log Q$).

	Na	K	Ca	Mg	Si	Al	Fe	Mn	DOC
<i>Shale Hills</i>									
Slope (m)	-0.04	-0.07	-0.12	-0.05	-0.01	-	-0.30	-0.19	-0.11
Std. Err.	< 0.01	< 0.01	0.01	< 0.01	< 0.01	-	0.01	0.02	0.02
R^2	0.32	0.56	0.43	0.30	0.09	-	0.58	0.24	0.14
<i>Upper Hafren</i>									
Slope (m)	-0.05	0.18	-0.20	-0.08	-0.26	0.58	0.33	0.10	0.42
Std. Err.	0.00	0.01	0.00	0.00	0.01	0.02	0.02	0.01	0.02
R^2	0.20	0.19	0.64	0.27	0.67	0.53	0.26	0.08	0.37
<i>Upper Hore (pre-harvest)</i>									
Slope (m)	0.00	0.07	-0.51	-0.12	-0.27	0.52	-0.05	0.05	0.26
Std. Err.	0.00	0.01	0.01	0.00	0.01	0.01	0.02	0.01	0.02
R^2	0.00	0.04	0.89	0.43	0.75	0.59	0.01	0.04	0.23
<i>Upper Hore (post-harvest)</i>									
Slope (m)	-0.04	0.26	-0.49	-0.11	-0.23	0.42	-0.04	0.12	0.25
Std. Err.	0.00	0.03	0.01	0.01	0.01	0.02	0.03	0.02	0.03
R^2	0.12	0.18	0.90	0.50	0.83	0.68	< 0.01	0.16	0.21

^a Calculations exclude data where concentrations fell below the detection limit.

^b All slopes are statistically different from zero ($p < 0.001$) except Na (pre-harvest) and Fe (post-harvest) in the Upper Hore.

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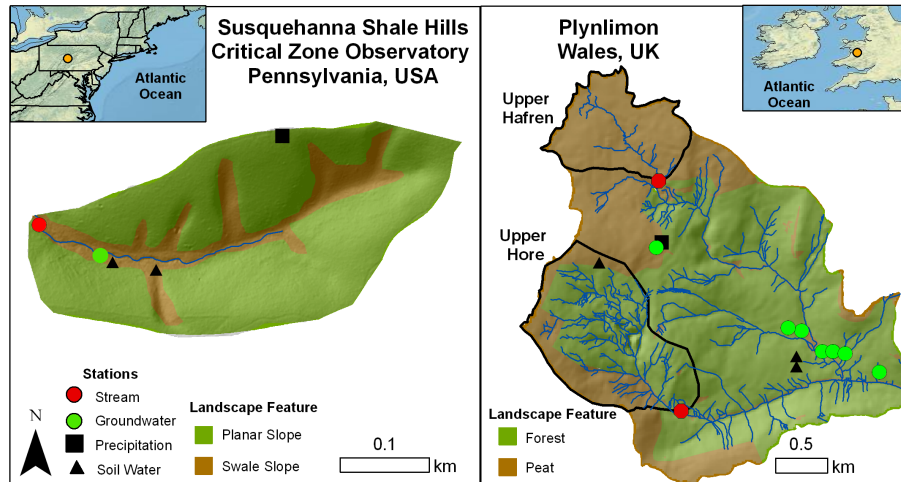


Figure 1. Map views of the Susquehanna Shale Hill Critical Zone Observatory (Shale Hills, PA, USA; left panel) and Plynlimon (Wales, UK; right panel) catchments. Symbols mark location of precipitation (black square), stream water (red circle), pore water (black triangle), and groundwater (green circle) samplers. Brown and green shading delineate major landscape features that are organic-rich or organic-poor in each catchment: swale vs. planar slopes at Shale Hills or peat vs. forested regions at Plynlimon. Notably, the most organic-rich soils are in lowlands in Shale Hills but uplands in Plynlimon.

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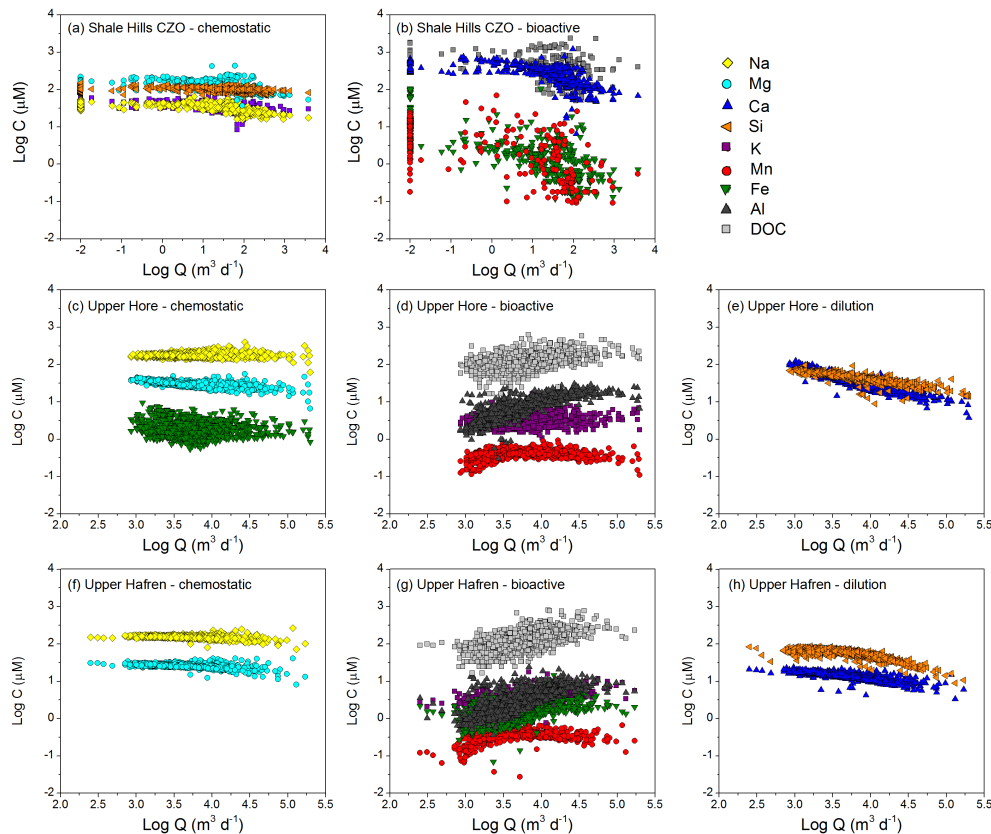


Figure 2. LogC (solute concentration) vs. logQ (discharge) in the Shale Hills catchment (a, b) and two Plynilimon subcatchments, the Upper Hafren (c–e) and Upper Hore (f–h). For each catchment, the left panel shows elements that exhibit chemostatic behavior, the middle panel shows elements that exhibit behavior similar to DOC (e.g., dilution at Shale Hills and enrichment at Plynilimon), and the right panel shows elements that exhibit dilution behavior.

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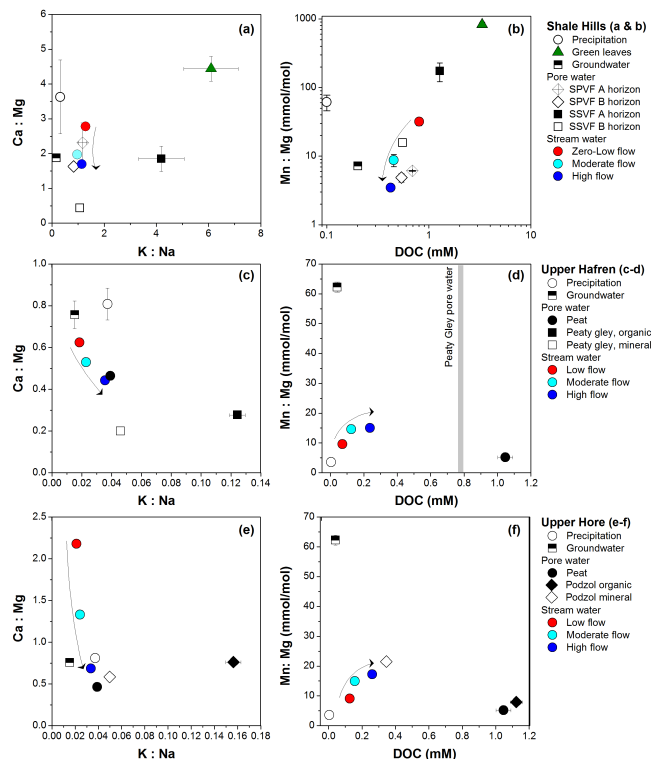


Figure 3. Molar ratios of major divalent (Ca : Mg) vs. univalent (K : Na) cations are plotted on the left and the molar ratios of Mn (mmol) to Mg (mol) vs. dissolved organic carbon (mmol L^{-1}) are plotted on the right for solute source pools in the forested Shale Hills (**a, b**), peatland Upper Hafren (**c, d**), and predominately forested Upper Hore (**e, f**) catchments. Arrows indicate direction of increasing discharge for average stream chemistries. Values for total C. ($\sim 33 \text{ mmol kg}^{-1}$) and K : Na (~ 60) in leaves are divided by 10 to fit on plots (**a**) and (**b**). For soil pore water, filled symbols indicate organic-rich waters and open symbols indicate organic-poor waters.

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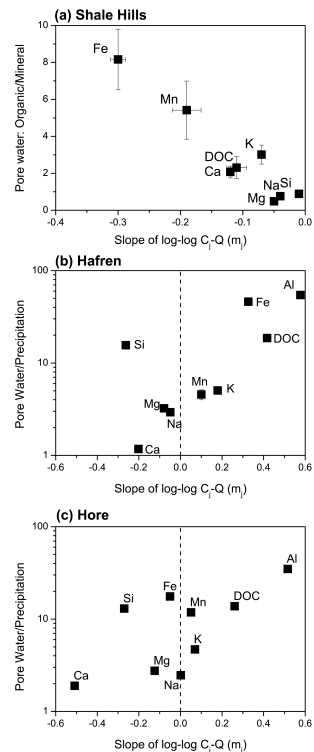


Figure 4. The degree of non-chemostatic behavior for a solute in stream water, denoted by m_j , was correlated with the relative concentration of that solute in organic-rich soil water in each catchment. Specifically, m_j was **(a)** negatively correlated with the ratio of solute concentrations in organic-rich vs. organic-poor soil waters at Shale Hills ($R^2 = 0.90$, $p < 0.001$) and positively correlated with the ratio of solute concentrations in pore waters vs. precipitation in **(b)** the Upper Hafren ($p < 0.05$) and **(c)** the Upper Hore ($p < 0.05$). Error bars represent the standard error of each value and are smaller than the symbol where not visible.