Landscape heterogeneity drives contrasting concentration-discharge relationships in shale headwater catchments

Elizabeth M. Herndon[1,a], Ashlee L. Dere[1,b], Pamela L. Sullivan[1,c], David Norris[2], Brian Reynolds[2], and Susan L. Brantley[1]

Final Response

Comments from editor:

Dear authors,
the paper was reviewed again by one of the reviewers and the reviewer is supporting publication in HESS. I also had a detailed look at the revised paper and would like to ask the authors to correct the following points, before the paper can be accepted for publication in HESS:

1) please change the color codes in the maps on Figure 1 of the two study sites. the two colors are the same, but they represent different properties (swale and planar vs forest and peat). This is misleading.

The shading in Figure 1 has been changed to distinguish between different landform types at Shale Hills and Plynlimon.

2) Table 4 shows that all slopes are statistically different from zero except Na and Fe in Upper Hore. It may help to also highlight the elements which show a chemostatic, dilution and non-chemostatic behavior as shown in Figure 2.

Superscripts have been added to Table 4 to indicate the concentration-discharge pattern that corresponds to each slope.

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Elizabeth M. Herndon[1,a], Ashlee L. Dere[1,b], Pamela L. Sullivan[1,c], David Norris[2], Brian Reynolds[2], and Susan L. Brantley[1]

Author affiliations:

[1] Department of Geosciences, The Pennsylvania State University, University Park, PA 16802

[2] Centre for Ecology and Hydrology, Bangor, Gwynedd LL57 2UW, United Kingdom

Current affiliations

[a] Department of Geology, Kent State University, Kent OH 44242

[b] Department of Geography/Geology, University of Nebraska at Omaha, Omaha NE 68182

[c] Department of Geography, The University of Kansas, Lawrence KS 66045

Corresponding author:

Elizabeth Herndon (eherndo1@kent.edu)

Department of Geology, Kent State University, Kent OH 44242

Abstract

Solute concentrations in stream water vary with discharge in patterns that record complex feedbacks between hydrologic and biogeochemical processes. In a comparison of three shale-underlain headwater catchments located in Pennsylvania, USA (the forested Shale Hills Critical Zone Observatory) and Wales, U.K. (the peatland-dominated Upper Hafren and forest-dominated Upper Hore in the Plynlimon forest), 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 and soil organic matter (SOM). 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 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. Furthermore, concentration-discharge relationships of non-chemostatic solutes changed following tree harvest in the Upper Hore catchment in Plynlimon, while no changes were observed for chemostatic solutes, underscoring the role of vegetation in regulating the concentrations of certain elements in the stream. These results indicate that differences in the hydrologic connectivity of organic-rich soils to the stream drive differences in concentration behavior between catchments. As such, in catchments where SOM is dominantly in lowlands (e.g. Shale Hills), we infer that non-chemostatic elements associated with organic matter are released to the stream early during rainfall events, whereas in catchments where SOM is dominantly in uplands (e.g. Plynlimon), these non-chemostatic elements are released later during rainfall events. The distribution of SOM across the landscape is thus a key component for predictive models of solute transport in headwater catchments.

Keywords

55   Critical Zone, Catchment Hydrology, Concentration-Discharge, Dissolved Organic Carbon, Soil

56   Organic Matter, Chemostasis
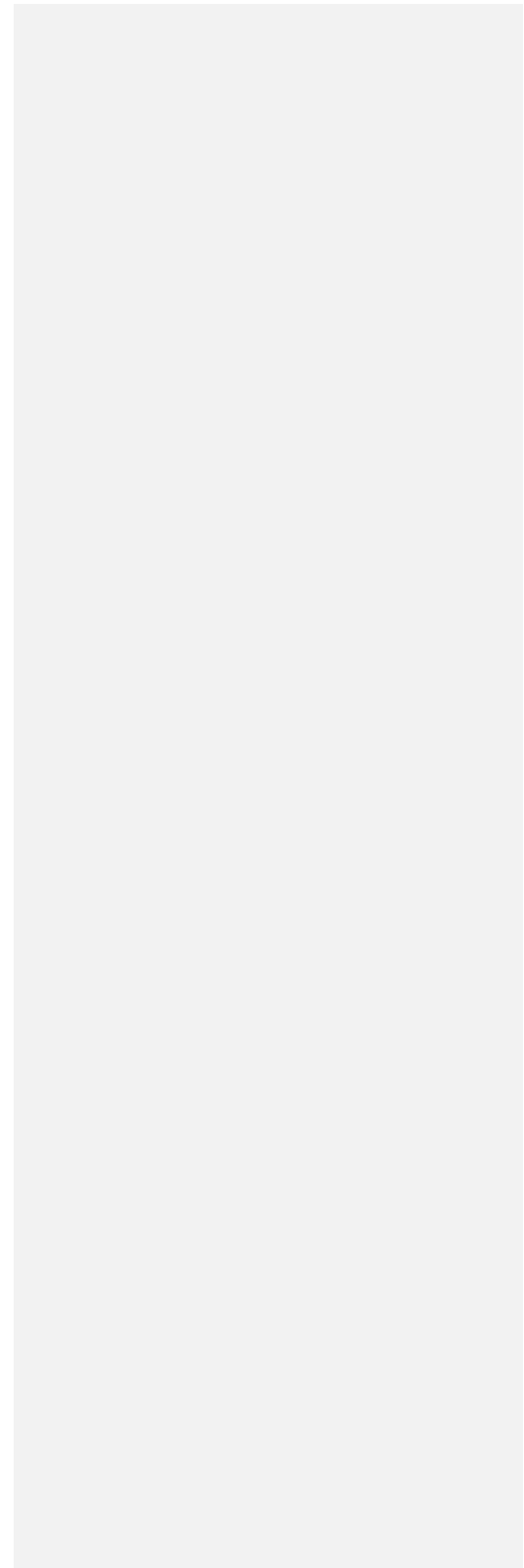
1   Introduction

57
58   Streams are regularly monitored to evaluate watershed geochemistry, ecosystem health, and
59   suitability for human use. However, streams integrate hydrologic and biogeochemical processes
60   over varied spatial and temporal scales, making it difficult to determine both the sources and
61   flow paths of solutes. While many researchers examine short- to long-term element variability in
62   stream water, it has remained difficult to derive generalized models quantifying solute
63   concentration-discharge behavior (Fisher et al. 2004; Sivapalan 2005; Zimmer et al. 2012). Flow
64   paths may dictate stream chemistry by controlling fluid residence times and chemical
65   equilibration of flowing water with soil minerals within catchments (Maher, 2011). Therefore, it
66   is necessary to understand how heterogeneous flow paths through distinct chemical sources
67   within a catchment influence observed solute concentration patterns within streams.
68   When the discharge of a stream (Q) increases, concentrations of solutes (C) can either
69   increase (enrichment behavior), decrease (dilution behavior), or, perhaps most paradoxically,
70   change very little (chemostasis) (Kirchner, 2003; Godsey et al., 2009; Clow and Mast, 2010).
71   Dilution can result during rainfall events as water stored in a catchment is diluted by less
72   concentrated meteoric water. Enrichment can result if a more concentrated source (e.g.
73   groundwater) mixes with stream water during large rainfall events (Johnson et al. 1969). In
74   contrast, chemostasis cannot be explained by the simple mixing of multiple sources and therefore
75   has been attributed to processes such as chemical reactions with the solid-phase along the
76   pathway of water flow (Godsey et al. 2009). Although changing flow paths through soil horizons
77   may explain differences in solute response to discharge along hillslope transects (e.g., Bishop et
78   al., 2004), solutes often show different types of behavior in different streams due to landscape
79   heterogeneity, and a unifying explanation for C-Q behavior has remained elusive.
80   Behavior differences amongst individual solutes in the stream have been linked to variability
81   in solute concentrations within a catchment: in other words, discrete zones of element
82   mobilization within soils and sediments can lead to pulses of solute transport into a stream
83   (McClain et al., 2003; Andrews et al., 2011). This effect is furthermore affected by changes in
84   hydrologic connectivity, defined as the water-mediated transfer of constituents between water
85   sources (Pringle, 2001), within a catchment during rainfall events. Stream chemistry can vary
86   during storm events as dominant water inputs to the stream shift from groundwater and riparian
87   zones during base flow to hillslope runoff at high flow as pore waters stored in upland soils

88   become increasingly connected to the stream (McGlynn and McDonnell, 2003a). Throughout

89   this paper, groundwater is defined as water that is stored in catchment soils and bedrock below

90   the water table, and pore water is defined as water that is present in the pores of unsaturated soil

91   in the vadose zone. Upland soils become hydrologically connected to the stream when soil layers

92   become water-saturated, promoting downslope flow within the unsaturated zone. As a result,

93   concentrations of solutes that are stored preferentially in the riparian zone, e.g. dissolved organic

94   carbon (DOC) released from soil organic matter (SOM), peak in the stream prior to discharge or

95   with rising discharge during storm events (McGlynn and McDonnell, 2003b; Hood et al. 2006).

96   Variability in organic carbon dynamics across different landscape units can subsequently control

97   metal export from headwater catchments and downstream hydrochemistry (Köhler et al., 2014).

98   Many previous studies examine single catchments and/or catchments that were developed on

99   multiple lithologies (e.g., Johnson et al., 1969; Krám et al., 1997; Brown et al., 1999; Likens and

100   Buso, 2006; Godsey et al., 2009), making the interpretation of solute behaviors difficult at best.

101   When mono-lithologic catchments are compared, insights into other factors that influence the

102   response of stream chemistry to discharge (e.g. biota, climatic) can be developed. To elucidate

103   controls on stream chemistry not primarily driven by lithology, we examined C-Q relationships

104   in three shale-underlain headwater streams with extensive hydrogeochemical datasets. Although

105   these catchments are underlain by chemically similar shales, their soils have developed distinct

106   and contrasting distributions of SOM across each landscape; i.e., organic-rich soils are

107   predominantly in low-lands and swales in the Shale Hills Critical Zone Observatory but in

108   upland peat regions of the Upper Hore and Upper Hafren catchments in the Plynlimon forest.

109   Additionally, we investigate how C-Q patterns change following tree harvest in the forested

110   Upper Hore. For these catchments, variations in stream chemistry with flow elucidate non-

111   lithological factors that control solute transport to streams, yielding a paradigm that should help

112   explain other catchments.

113   **2   Methods**

114   Water chemistry was compared for three sites: 1) the Susquehanna Shale Hills Critical Zone

115   Observatory (Shale Hills) in central Pennsylvania, USA and 2) the Upper Hore and 3) Upper

116   Hafren subcatchments in the Plynlimon experimental forest in Wales, UK (Figure 1). The Shale

117   Hills and Plynlimon forests are underlain almost exclusively by Fe-rich, organic-poor, Silurian-

118 aged shale formations that are stratigraphically equivalent. Although these headwater catchments
119 vary by size and location, their similar lithologies and extensive hydrogeochemical
120 characterization (e.g. Kirby et al., 1991; Neal et al., 1997; Shand et al., 2005(a-b); Jin et al.,
121 2010; Neal et al., 2011; Brantley et al., 2013(a-j); Dere et al., 2013; Neal et al., 2013(a-b)) allow
122 development of a unifying theory on factors controlling concentration-discharge behavior.

2.1 Susquehanna Shale Hills Critical Zone Observatory

124   Shale Hills is an 8 ha forested headwater catchment nested within the larger Susquehanna
125 River Basin in Pennsylvania, USA. Shale Hills contains primarily Inceptisol soils developed
126 from shale residuum or colluvium of the Rose Hill Formation, which is dominantly comprised of
127 clay minerals and quartz (Lin et al., 2006; Jin et al., 2010). Small areas of Ultisols are present
128 near the stream (Lin et al., 2006). The regional mean annual temperature (MAT) is 10°C, and
129 precipitation (MAP = 105 ± 17 cm y^{-1}) is acidic (e.g., pH averaged 4.5 ± 0.2 for U.S. National
130 Atmospheric Deposition Program (NADP) sites PA15 & PA42 during 2000-2011). Vegetation is
131 dominated by deciduous oaks and hickories, and the elevation ranges from 256 m at the
132 catchment outlet to 310 m on the ridge. Hillslopes are characterized as either "planar" (mildly
133 convex-upward slopes with shallow soils that grade to concave-upward slopes toward valley
134 floor) or "swale" (concave-upward depressions with deep soils and convergent water flow) (Lin
135 et al., 2006) (Figure 1). Water flows vertically through pores when soils are unsaturated, or
136 downslope along horizon interfaces when rainfall events create transiently perched saturated
137 water zones (Lin, 2006; Jin et al., 2011). Soils in swales are generally wetter than soils on planar
138 hillslopes and remain hydrologically connected to the stream during dry periods, whereas water
139 flow through planar hillslopes is negligible under dry conditions and increases with increasing
140 precipitation (Lin et al., 2006; Qu and Duffy, 2007; Takagi and Lin, 2012). Soils in the swales
141 also store more organic carbon than soils on planar hillslopes and act as sources of DOC
142 transport into streams (Andrews et al., 2011) (Table 1).
143   Water samples from Shale Hills were collected approximately daily from the stream outlet
144 (2008 – 2010) and biweekly from soil lysimeters (2006 – 2011) from March through early
145 December each year (Table 2). Detailed methods and results of chemical analyses, including
146 isotopic variation and concentrations of major ions and DOC, have been reported elsewhere (Jin
147 et al., 2011; Andrews et al., 2011; Brantley et al., 2013(a-j)). Aluminum concentrations in the

148 stream were consistently below detection limits; thus, Al data were not examined for Shale Hills.

149 Daily discharge rates were estimated from continuous discharge measurements integrated over

150 10 min intervals from the stream weir at the catchment's outlet (Duffy, 2012). Soil water was

151 collected from suction lysimeters installed in the soil at 10 cm depth increments from 10 to 50

152 cm depth in the south planar valley floor (SPVF) and from 10 to 90 cm depth in the south swale

153 valley floor (SSVF). The groundwater was sampled from a 2.8 m deep well located 80 m

154 upstream from the weir. Major cation (2000-2011; NADP, 2011) and trace element

155 concentrations (Herndon, 2012) have been reported for precipitation samples collected from

156 NADP sites PA-15 and PA-42. Vegetation chemistry was previously determined for green leaf

157 and leaf litter samples collected throughout summer and fall seasons, respectively, in the Shale

158 Hills catchment (Herndon et al., 2015).

159 **2.2 Plynlimon forest: Upper Hore and Upper Hafren catchments**

160   The Plynlimon forest is a 682 ha watershed located at the headwater of the River Severn, 20

161 km from the west coast of Wales (Reynolds et al., 1997). MAT is 7.2 °C and MAP is 250 ± 78

162 cm with an average pH of 4.98 ± 0.01. Vegetation is predominantly evergreen Sitka spruce

163 (*Picea sitchensis*) with areas of heath, including *Sphagnum* and *Juncus* communities, dominating

164 the uplands. Elevation in the Plynlimon forest ranges from 319 to 738 m.

165   We focus here on two adjacent headwater catchments within the Plynlimon watershed: the

166 Upper Hore and the Upper Hafren (Figure 1). The Upper Hore (162 ha) is predominantly

167 forested with periodically saturated, organic-rich Stagnopodzol soils and uplands that are

168 dominated by grass and saturated Peat soils (Kirby et al., 1991). In contrast, the Upper Hafren

169 (122 ha) is dominated by heath and Peat soils, with waterlogged and organic-rich Peaty gley soils

170 located in riparian areas (Kirby et al., 1991). Generally, the main flow paths in both catchments

171 are approximately orthogonal to the valley direction, with highly fractured shallow bedrock

172 providing an important pathway and storage for water throughout the catchments, especially

173 under base flow conditions (Haria and Shand, 2004; Shand et al., 2005(a-b); Shand et al., 2007).

174 Shallow and deeper groundwater appear to be poorly connected but some mixing does occur

175 (Haria and Shand, 2004; Shand et al., 2005b; Shand et al., 2007). Flow in organic horizons,

176 however, tends to be largely lateral rather than vertical, providing minimal water-rock interaction

177 in peat dominated portions of the catchment and increasing contribution to streams during high

178 flow conditions (Shand et al., 2009).

179   Stream chemistry data for the Upper Hore and Upper Hafren catchments were collected

180 throughout the year for all years between 1983-2005 and 1990-2010, respectively (Neal et al.,

181 2013a and 2013b). Due to extensive tree-cutting in the Upper Hore in 2005, data collected from

182 2005-2010 were evaluated separately to examine the influence of tree removal on C-Q behavior.

183 Stream discharge was measured every 15 min at weirs in both catchments and weekly stream

184 grab samples were analyzed for major and trace ions. Likewise, bulk precipitation was collected

185 weekly at the Carreg Wen meteorological station located between the Upper Hore and Upper

186 Hafren catchments (Reynolds et al., 1997). Precipitation chemistry was influenced by seawater

187 inputs, which varied with wind direction and season (Reynolds et al., 1987). Groundwater

188 chemistry was estimated as average concentrations of solutes in seven shallow (< 3 m) wells

189 located within the Plynlimon forest near the two catchments (Figure 1). Wells were sampled

190 weekly from 1994 – 1999 (Neal et al., 1997) (Table A1). Average solute concentrations (±

191 standard error) were calculated for pore waters sampled from soils classified as Peat,

192 Stagnopodzol, or Peaty Gley throughout Plynlimon (Reynolds et al., 1987; Reynolds et al., 1988;

193 Stevens et al., 1997; Shand et al., 2005b) (Table 3; Table A2).

194 **2.3   Stream flow regimes and concentration-discharge (C-Q) behaviors**

195   To analyze stream chemistry under different flow regimes, stream water discharge (Q, m^3 d^{-1})

196 was categorized as low-flow (lower quartile of Q), moderate-flow (interquartile range), or

197 high-flow (upper quartile) (Figure A1). Perennial stream flow with little seasonal variation in

198 discharge was observed in the Upper Hafren and Upper Hore catchments, and the distributions of

199 Q were positively skewed by intermittent storms. Stream flow at Shale Hills was intermittent and

200 highly seasonal, with extended periods of no- to low-flow during summer months (especially

201 July and August). Solute concentrations for each flow regime at each site were averaged over all

202 collection dates (Tables 2 and 3).

203   Linear regressions were fit to log-transformed C-Q data for each solute j (C_j) for each

204 catchment stream. We included all available data for all years for Shale Hills (2008 – 2010), the

205 Upper Hafren (1990 – 2010), and the pre-harvest Upper Hore (1983 – 2004). The data collected

206 for the Upper Hore following harvest (2005 – 2010) were evaluated separately. The slope of this

207 regression (m_j) was used to identify solute behaviors as "chemostatic" or "non-chemostatic".

208 When m_j showed only minimal effects of dilution by meteoric water, i.e., $-0.1 < m_j < 0$, the

209 solutes were defined as chemostatic (Godsey et al., 2009). In contrast, non-chemostatic elements

210 were defined to exhibit dilution behavior when concentrations decreased with increasing Q ($m_j <$

211 -0.1) or enrichment behavior when concentrations increased with increasing Q ($m_j > 0$). Linear

212 regressions and associated statistical parameters were calculated in Origin.

213   To investigate sources of solutes mobilized to the stream, element ratios in the stream under

214 different flow regimes were compared to element ratios in pore waters, precipitation,

215 groundwater, and leaves (where available). Element ratios have been used in other studies to link

216 river chemistry to end member reservoirs (e.g. Gaillardet et al., 1999). Molar ratios of divalent

217 cations (Ca:Mg) were compared to univalent cations (K:Na) in each reservoir to understand how

218 elements exhibiting non-chemostasis (Ca, K) vary relative to chemostatic elements (Mg, Na). To

219 further explore the association of certain non-chemostatic solutes with organic C, molar ratios of

220 Mn (a non-chemostatic element) to Mg were compared to DOC concentrations. Average DOC

221 concentrations were used to define soil waters as organic-rich or organic-poor, as discussed in

222 section 3.2. In Shale Hills, green leaves were used to represent the most organic-rich end-

223 member since pore waters could not be sampled from the thin O horizon.

224 **3   RESULTS**

225 **3.1 Solute concentration-discharge patterns**

226   Na and Mg behaved near-chemostatically in all catchments (Figure 2; Table 4) while Si and

227 K were only chemostatic at Shale Hills. A subset of non-chemostatic solutes exhibited similar

228 trends to DOC; however, trends were opposite between Shale Hills and Plynlimon. Specifically,

229 when Q increased, concentrations of the non-chemostatic solutes Ca, Mn, Fe and DOC decreased

230 at Shale Hills (i.e. dilution behavior; $m_j < -0.1$) while the non-chemostatic solutes Mn, K, Al,

231 Fe, and DOC increased at Plynlimon (i.e. enrichment behavior; $m_j > 0$) (Figure 2b; Table 4).

232 Note that Fe exhibited enrichment ($m_{Fe} = 0.33 \pm 0.02$) similar to DOC in the Upper Hafren but

233 was more consistent with chemostasis in the Upper Hore ($m_{Fe} = -0.05 \pm 0.02$). Additionally, Si

234 and Ca showed dilution patterns at Plynlimon that contrasted with DOC.

235   In the Shale Hills stream, higher concentrations of stream solutes were observed during the

236   dry summer season (June through September) relative to the wetter spring and autumn (Figure

237   A2). While concentrations of the chemostatic elements increased only slightly (~2X) during the

238   summer, larger increases were observed for Ca (~4X), DOC (~7X), and Mn and Fe (> 100X).

239   Increases in DOC, K, Fe, and Mn in the stream during summer were not consistent with

240   increasing groundwater inputs because groundwater at Shale Hills is depleted in these elements

241   relative to stream water at low flow (Table 2). In the Upper Hafren and Upper Hore streams,

242   chemostatic elements Na and Mg, derived primarily from sea salts, showed no seasonality

243   despite high seasonal variation in inputs from precipitation (Figure A5; Reynolds et al., 1987), as

244   if precipitation-derived solutes were buffered in the catchment soil pore waters before entering

245   the stream (Neal and Kirchner, 2000). In contrast, solutes exhibiting enrichment (K, Al, Mn, Fe,

246   DOC) varied by season (Figures A3 and A4).

247   In the Upper Hore where trees were harvested, solute concentrations and C-Q slopes

248   increased following tree harvest for solutes showing enrichment behavior. Specifically, stream

249   concentrations of DOC, K, Mn, and Fe increased after 2005 (Table 3). Post-harvest C-Q slopes

250   for m_K (= 0.26 ± 0.03) and m_{Mn} (= 0.12 ± 0.02) increased relative to pre-harvest values (0.07 ±

251   0.01 and 0.05 ± 0.01, respectively) (Figure 2; Table 4). No effects of tree harvest on C_j or m_j

252   were observed for chemostatic elements. Additionally, no changes in solute concentrations in the

253   non-harvested Upper Hafren were observed over this time.

254   **3.2   Soil pore waters**

255   We examined the chemical composition of soil pore waters in order to investigate sources of

256   solutes to the stream. Pore waters in each catchment were categorized into distinct chemical

257   pools based on DOC concentrations (Table 2): "organic-rich" waters were defined by average

258   DOC > 1 mM, while all other waters were "organic-poor". At Shale Hills, pore waters collected

259   from the A horizon (10 cm) of the swale (SSVF) were organic-rich (1.28 ± 0.33 mM DOC)

260   while all other pore waters were organic-poor; i.e. the A horizon of SPVF (0.69 ± 0.06 mM

261   DOC) and the B horizons of SSVF and SPVF (> 10 cm; averaged 0.55 ± 0.04 mM DOC) were

262   organic-poor. At Plynlimon, pore waters in organic horizons and Peat soils (1.2 ± 0.2 mM DOC)

263   were organic-rich relative to mineral horizons of Stagnopodzol and Peaty gley soils (0.42 ± 0.07

264   mM DOC) soils.

265   At Shale Hills, concentrations of the non-chemostatic solutes Mn, Fe, and Ca showed

266   evidence of DOC-related behavior. For example, Mn and Fe were positively correlated with

267   DOC across all pore waters ($R^2 > 0.9$) and were highest in the organic-rich waters (6.8 ± 1.9 μM

268   and 1.7 ± 0.3 μM, respectively) (Table 2). Calcium concentrations were enriched in the A

269   horizon (72 ± 11 μM) relative to the B horizon (35 ± 1 μM) in SSVF. Furthermore, Fe and Mn

270   concentrations were spatially variable across pore waters (% RSD = 100% and 140%,

271   respectively). In contrast, chemostatic solutes Mg (33%), Na (19%), and Si (5%) were less

272   variable. Thus, concentrations of non-chemostatic solutes were spatially heterogeneous in soil

273   waters across the landscape while chemostatic solutes were distributed more homogeneously.

274   Like Shale Hills, concentrations of the chemostatic elements Na and Mg were spatially

275   homogeneous in pore waters at Plynlimon amongst the different soils (RSD = 23% and 15%,

276   respectively) (Table 3). Additional solutes chiefly derived from the atmosphere via precipitation

277   (K, Ca) or through carbon fixation (DOC) were enriched in the organic horizons, while elements

278   derived primarily from minerals (Si, Fe, Al, and Mn) were enriched in mineral horizons. In

279   contrast to Shale Hills, many of the non-chemostatic elements at Plynlimon were not correlated

280   with DOC in soil pore waters.

281   Element ratios in stream water under low, moderate, and high flow regimes were compared

282   to element ratios in pore waters, precipitation, and groundwater (Figure 3). At Shale Hills, stream

283   chemistry was most similar to pore waters from organic-rich soils and green leaves at low flow

284   and approached values for pore waters from organic-poor soils at high flow. Ratios of $C_{Ca}:C_{Mg}$

285   and $C_K:C_{Na}$ decreased slightly (< 2X) with increasing discharge (Figure 3a), while $C_{Mn}:C_{Mg}$

286   decreased by 10X (Figure 3b). Stream water was more similar to soil pore waters than

287   groundwater or precipitation under all flow regimes, documenting that flow through shallow

288   soils and bedrock rather than deep groundwater sources dominated inputs to the stream. These

289   trends further indicate a shift from inputs of organic-rich soil water to the stream at low flow to

290   organic-poor soil water at high flow.

291   In contrast to this behavior at Shale Hills, stream chemistries in the Upper Hore and Upper

292   Hafren catchments were most similar to organic-poor sources (precipitation, groundwater) at low

293   flow and organic-rich sources (soil pore waters) at high flow (Figure 3c-f; Figure A7). Values of

294    $C_{Mn}:C_{Mg}$, C_{DOC}, and $C_K:C_{Na}$ increased while $C_{Ca}:C_{Mg}$ decreased and converged towards the

295   most organic-rich end-member in each system, either the peat (Upper Hafren) or peat and

296 organic horizon pore waters (Upper Hore), with increasing discharge. Stream $C_{Ca}:C_{Mg}$ ratios

297 were similar to groundwater at low flow in the Upper Hafren. The limited groundwater data that

298 were available for Plynlimon indicate that groundwater was not chemically similar to stream

299 water under any flow regime in the Upper Hore (Figure 1)..

300 **3.3   Organic influence on concentration-discharge behavior**

301   Finally, we explored how chemical heterogeneity in soil pore waters influenced

302 concentration-discharge relationships in the streams. Specifically, we evaluated solute

303 heterogeneity due to redistribution by vegetation as the ratio of solute concentrations in "organic-

304 rich" to "organic-poor" pore waters. As previously defined, these pore waters were collected

305 from A versus B horizons at Shale Hills, and organic versus mineral soils in the Upper Hafren

306 and Upper Hore. The slope of the concentration-discharge plot (m_j) was used to define the

307 magnitude of non-chemostatic behavior for each solute, i.e. the degree to which an element was

308 diluted or enriched in the stream with increasing discharge.

309   At Shale Hills, elements concentrated in the organic-rich pore waters were diluted rapidly in

310 the stream with increasing discharge, consistent with increasing inputs of water from mineral

311 soils as the planar hillslope soils become saturated during storms (Qu and Duffy, 2007). This

312 trend is documented in Figure 4a where the concentration ratios for organic-rich versus -poor soil

313 waters were negatively correlated with respect to m_j ($R^2 = 0.90$, $p < 0.001$). According to these

314 results, Fe and Mn were most concentrated in organic-rich pore waters and most rapidly diluted

315 in the stream, followed by DOC, Ca, and K. Chemostatic elements Na, Mg, and Si were not

316 concentrated in organic-rich pore waters.

317   No significant correlation ($p > 0.05$) existed between organic to mineral pore water ratios and

318 m_j in the Upper Hore and Upper Hafren subcatchments, likely because organic horizons at

319 Plynlimon have high concentrations of chemostatic solutes due large inputs of sea salts that

320 dominate the chemical signature of near-surface pore waters. Provided this observation, organic-

321 associations in each catchment were evaluated by inspecting the ratio of average solute

322 concentrations in the pore water versus precipitation (Figure 4b,c), i.e., precipitation serves as the

323 most organic-poor pool in the Plynlimon system. For both the Upper Hafren and the Upper Hore,

324 the ratios of concentrations in soil water versus precipitation were positively correlated with m_j

325 ($p < 0.05$). Elements exhibiting enrichment behavior, including DOC, Al, Mn, and K in both

326 catchments plus Fe in the Upper Hafren, were also enriched in pore water relative to
327 precipitation. Chemostatic elements in pore waters were less enriched relative to precipitation. In
328 contrast, the ratios for soil water versus precipitation were not significantly correlated with m_j at
329 Shale Hills (p > 0.05).

4   Discussion

331   Cross-site comparison of the Shale Hills and Plynlimon headwater catchments revealed that
332 the behaviors of non-chemostatic solutes were controlled by the spatial variability of those
333 elements in soil waters and the distribution of DOC. Conversely, chemostatic solutes were
334 homogeneously distributed in pore waters across the catchments. In the following sections, we
335 discuss how the landscape distribution of chemically distinct pools and the connectivity between
336 organic-rich soils and the stream control how concentrations vary with discharge. We contend
337 that the behavior of certain elements are non-chemostatic in these systems due to their
338 association with organic matter. The distribution of soil organic matter across landscapes is in
339 turn influenced by climate (e.g., SOM generally increases with increasing moisture and
340 decreasing temperatures on large geographic scales) and geomorphology (e.g., organic matter
341 accumulates in depressed areas such as swales on small geographic scales).

4.1   Hydrologic connectivity of solute pools across landscapes

343   At first glance, it may appear contradictory that concentrations of non-chemostatic elements
344 in the streams at Shale Hills and Plynlimon trend in opposite directions with increasing
345 discharge; however, the discrepancy can be explained by differences in the distributions of
346 organic-rich source waters in each system. Similar to bioactive elements identified by Stallard
347 and Murphy (2013), we attribute non-chemostatic concentration-discharge behavior to changing
348 water flow through organic-rich soil matrices; however, we also observe that organic-rich
349 sources and flow paths vary between the catchments (Figure 1).
350   At Shale Hills, meteoric water passes through the thin organic horizon and organic-rich A
351 horizon (< 15 cm deep) and is transported along the horizon interfaces to the stream via
352 preferential flow paths (Lin et al. 2006; Jin et al., 2011; Thomas et al., 2013). The stream
353 receives water from organic-rich swales and surface soils during dry periods, and water inputs
354 from organic-poor hillslope soils increase as the catchment saturates (Qu and Duffy, 2007;

355 Andrews et al. 2011). Consequently, we observed that stream water chemistry was similar to
356 organic-rich soil waters at low flow and organic-poor soil waters at high flow (Figure 3). Solutes
357 derived largely from organic-rich soils exhibited greater variability over different flow regimes
358 due to their high spatial variability in soil pore water. Increasingly negative slopes for non-
359 chemostatic elements at high discharge (Figure 2b) may reflect the transition in hydrologic
360 connectivity and hillslope inputs to the stream. Stream chemistry did not reflect inputs from
361 groundwater during dry periods, consistent with a previous finding that the water table drops to >
362 2 m below the stream bed during late summer (Thomas et al., 2013).

363   In the grass-dominated Upper Hafren, which contains peat soils that experience minimal
364 water-rock interaction (Kirby et al., 1991), concentrations of chemostatic elements in the soils
365 never deviated far from an average precipitation signal (Figure 4). In contrast, concentrations of
366 non-chemostatic elements were not driven by precipitation, and we propose that pore water
367 concentrations of these elements are regulated by vegetation. During the drier growing season,
368 certain non-chemostatic elements may be depleted from soil pore water and accumulated in
369 vegetation, leading to lower concentrations in the stream. Indeed, it is well-established that
370 seasonal uptake by vegetation regulates concentrations of nutrient elements in stream water (e.g.,
371 Johnson et al., 1969; Vitousek, 1977; Mulholland, 1992). Warming and drying of the surface
372 peat during this time increases microbial decomposition, thereby increasing mobility of elements
373 that accumulate in vegetation by releasing them from storage in organic matter (Kirby et al.,
374 1991). According to this conceptual model, once transpiration decreases and flow increases
375 through the soil in autumn, concentrations of these elements increase in the stream because 1)
376 transpiration is reduced and the soil water is no longer being depleted; 2) the surface peat is
377 flushed of elements that have accumulated, providing elements in addition to precipitation. As
378 observed at the Upper Hafren and Upper Hore, concentrations of non-chemostatic elements
379 begin to increase in the stream as discharge increases following low-flow in the summer (Figures
380 A3 and A4). This effect may be especially prominent in the peat regions since the grass
381 vegetation decomposes annually with little aboveground storage (i.e. peat is leaky with respect to
382 nutrients), and anoxic conditions limit complete conversion of SOM to CO_2, enhancing release
383 of DOC. Although groundwater can discharge to streams in Plynlimon during summer months
384 (Shand et al., 2005b), the groundwater contains little DOC (Table 3) and therefore cannot
385 explain changes in summer stream chemistry where DOC increases from spring to summer

386   (Figures A3 and A4). At high flow, decreases in Mn concentrations in the stream (Figures 2d and

387   2g) may reflect the low abundance of Mn in the catchment relative to other elements; in other

388   words, the supply of Mn is depleted at high flow and Mn is diluted in the stream.

389   In the spruce-forested Upper Hore, long-term storage of nutrient elements in above-ground

390   biomass is expected to deplete soil pore waters of elements without the flushing effect due to

391   rapid turnover observed in the Upper Hafren (Reynolds et al., 2000). Instead, the positive

392   concentration-discharge slopes in the Upper Hore result from flushing of upland peat soils at

393   high flow conditions (Neal et al., 1990). These effects can be observed by comparing pre- and

394   post-harvest concentration-discharge slopes in the Upper Hore. Tree harvest impacted stream

395   concentrations and C-Q slopes for K, Al, Fe, Mn, and DOC but had no observable effects on

396   chemostatic elements. Specifically, m_K increased from 0.07 to 0.25 following harvest, while the

397   peat-dominated Upper Hafren, which was not harvested, maintained $m_K = 0.15$ during this time.

398   Fe and DOC experienced increases in stream concentrations, but not m_j. Since neither Fe nor

399   DOC is expected to be taken up into the trees in high quantities, increasing C_j may indicate that

400   they were mobilized by increased decomposition of leaf litter debris in the forest region

401   following harvest (Hughes et al., 1990).

402   Values of C_j and m_j for non-chemostatic, organic-associated elements likely increased

403   following harvest because 1) these elements were no longer being taken up and stored in tree

404   biomass (Stevens et al., 1997); 2) the organic debris left after harvest provided a labile pool of

405   organic chelator molecules and organically-complexed elements, and 3) inputs from upland peats

406   to the stream increased due to lack of interception by the forest (Neal et al., 1992; Neal et al.,

407   2004). Such short-term increases in nutrient loss following ecosystem disturbance are well

408   documented, especially for clear-cut systems (e.g., Likens et al., 1970; Vitousek, 1977; Neal et

409   al., 1992). Although non-chemostatic in the Upper Hafren, Fe followed a chemostatic trend in

410   the Upper Hore (Figure 2). This behavior could be due to Fe retention in the forested soils during

411   downslope transport: Stagnopodzols on these slopes have Bs horizons that accumulate

412   sesquioxides and immobilize leached Fe (Reynolds, 1982).

413   Previous studies have hypothesized that hydrologic connectivity within landscapes

414   (McGlynn and McDonnell, 2003a; Hood et al. 2006; Clow and Mast 2010) and/or interactions

415   between soil moisture and mineral reactive surface area (Godsey et al. 2009; Clow and Mast

416   2010) can explain concentration-discharge relationships across multiple catchments. Our results

417   contribute to the understanding of solute behavior by highlighting the importance of hydrologic
418   connectivity across landscapes and at mineral surfaces. At both Shale Hills and Plynlimon, the
419   distribution of soil organic matter and its hydrologic connection to the stream governed non-
420   chemostatic concentration discharge behavior of several solutes (Ca, K, Mn, Fe and Al), a
421   process similarly invoked to explain stream DOC behavior in storm events (McGlynn and
422   McDonnell, 2003b). Our results highlight the need to include or enhance reactive transport
423   components in spatially-distributed watershed-scale hydrologic models such as TOPMODEL
424   (Beven and Kirkby 1979), the Penn State Integrated Hydrologic Model (PIHM; Qu and Duffy
425   2007), and the Regional Hydro-Ecological Simulation System (RHESSys; Brand et al. 1991).
426   Specifically, combining reactive transport modeling with the ability of spatially-distributed
427   models to simulate soil moisture, temperature, and water fluxes at variable depths across
428   geomorphic features (e.g., swales vs. planar slopes) will allow researchers to elucidate specific
429   flow water paths and transit times and better test drivers of chemostasis (cation exchange) and
430   dynamics of mobile vs. immobile water. RT-Flux-PIHM is one model under development (Duffy
431   et al. 2014) that will provide this platform, but it is imperative to cross-compare outputs from
432   various models in order to reach consensus.
433
4.2   Drivers of chemostasis

435   Stream concentrations for most major weathering elements (j = Na, K, Mg, Ca, Si) varied
436   little over a wide range of discharge values (Figure 2): by this definition, most of the major
437   elements were chemostatic, with the exception of Ca at Shale Hills and K at Plynlimon. Note that
438   the standard descriptor "major elements" includes Na and Ca although both are low in abundance
439   in the protolith at Shale Hills and Plynlimon (< 0.7 wt.% and < 0.2 wt.%, respectively), and K is
440   lower at Plynlimon compared to Shale Hills (2.90 wt.% and 3.76 wt.%, respectively) (Jin et al.,
441   2010; Dere et al., 2013). Chemostasis could be expected for elements derived from minerals that
442   are always equilibrated with long residence-time pore waters. However, the fast-dissolving
443   minerals present at Shale Hills and Plynlimon, carbonates and pyrite, do not contain K, Na and
444   Si and are also depleted in the upper protolith (Jin et al., 2010; Neal et al., 1997). Therefore,
445   dissolution of these minerals cannot explain chemostasis of K, Na, Si, Mg and Ca. Godsey et al.
446   (2009) suggested that changes in mineral-water interfacial area during periods of high and low
447   discharge explain chemostasis; however, clay dissolution rates are too slow (Bandstra et al.,

448   2008) to provide a rapidly mobilized source of cations during the short-timescales of

449   precipitation events.

450   The exchangeable cation pool is a likely source of chemostatic elements during rain events

451   (e.g., Clow and Mast, 2010). The cation exchange capacity of soils along the planar hillslope at

452   Shale Hills ranges from 35 to 71 meq kg^{-1} (Jin et al., 2010). At Plynlimon, forest and peat soils

453   have a cation exchange capacity of roughly 77.4 and 300 meq kg^{-1}, respectively (Reynolds et al.,

454   1988; Cuttle, 1983). Elements are displaced from cation exchange sites into solution by H^+ (i.e.

455   protonation of the exchange sites), and we observe that the degree of chemostasis for

456   chemostatic elements was inversely related to the elements' relative strengths of adsorption to

457   cation exchange sites as reported by Evangelou et al. (2005). Furthermore, this explanation can

458   even account for the highly chemostatic, neutrally charged solute $Si(OH)_4^0$, which has also been

459   documented in the exchangeable pool at Shale Hills (Jin et al., 2010). For these catchments

460   where pH is low (pH < 7), Si should be weakly associated to exchange sites due to its neutral

461   charge. The similar concentrations observed for major weathering elements in the planar and

462   swale pore waters at Shale Hills as well as Plynlimon (Tables 2 and 3) are attributed to the quick

463   exchange of protons in rain for cations in the exchange pool throughout the catchment. Thus,

464   chemostasis is explained by increasing connectivity of the exchangeable pool, i.e., cations bound

465   to surfaces of minerals and soil organic matter, to mobile water as soil saturation increases.

4.3   Chemostatic nutrients become non-chemostatic under nutrient-limiting conditions

468   Although geochemically similar to Mg, K, and Na, the concentration-discharge pattern for

469   Ca (Figure 2) is non-chemostatic at Shale Hills. The mixing model (Figure 3a) indicates leaves

470   may be a primary source of Ca to the stream during low discharge. Indeed, these shallow soils

471   are strongly leached of Ca (< 0.16% wt.; Jin et al. 2010), and organic matter may be a relatively

472   large pool of Ca in this system. In contrast to Shale Hills where Ca trends are strongly influenced

473   by organic matter, Ca at Plynlimon may be linked to groundwater, an effect most pronounced in

474   the Upper Hore. Ratios of Ca:Mg trend towards organic-poor sources at low flow, likely due to

475   inputs of Ca-rich groundwater during base flow that is diluted by increasing contribution from

476   soil water at high flow. Although a lack of groundwater data from these two subcatchments

477 limits our ability to directly assess inputs to the stream, groundwater collected from lower

478 elevations in the Plynlimon forest are rich in Ca and Si (Neal et al., 1997).

479   Similar to Ca at Shale Hills, K limitation may drive its increased association with organic

480 matter at Plynlimon. Values of C_K : C_{Na} decrease at Shale Hills and increase at Plynlimon with

481 increasing Q in a manner consistent with changing inputs from organic-rich sources (Figure A7).

482 Although geochemically similar, Na is a nonessential element (Kirkby, 2012) that is readily

483 weathered from soils whereas K is a plant macronutrient that accumulates in leaf tissue (Herndon

484 et al., 2015). From the mixing diagrams and m_K, we infer that K has a stronger organic control at

485 Plynlimon than at Shale Hills. One explanation for this is that net primary productivity (NPP) is

486 higher (896 g C m^{-2} y^{-1}; unpublished data) but bedrock K is lower (2.90 ± 0.13%; Dere et al.,

487 2013) at Plynlimon than at Shale Hills (NPP = 550 g C m^{-2} y^{-1}; Smith, 2013 and K = 3.76 ±

488 0.16%; Jin et al. 2010). These data suggest that K is limiting to vegetation at Plynlimon while Ca

489 is limiting to vegetation at Shale Hills due to high demand and low supply.

490 **5   Conclusions**

491   A comparison of three shale-derived catchments, the Shale Hills CZO in central

492 Pennsylvania, U.S.A. and the Upper Hafren and Upper Hore catchments in the Plynlimon forest,

493 Wales, U.K., reveals that the concentration-discharge behaviors of elements are strongly

494 impacted by the distribution of organic matter in soils and the hydrologic connectivity of these

495 soils to the stream. At Shale Hills, stream water is derived from organic-rich swales at low flow

496 and then from both swale and planar hillslopes with increasing flow. At Plynlimon, stream water

497 is only dominated by water from organic-rich soils at high flow, and contributions from organic-

498 rich upland soils increased following lower elevation tree harvest in the Upper Hore catchment.

499 Solutes that are limiting nutrients or that are strongly retained by vegetation exhibit non-

500 chemostatic behavior in the stream because they are released to the stream along with dissolved

501 organic carbon. This non-chemostatic behavior is opposite between Plynlimon and Shale Hills

502 due to the different landscape distribution of organic-rich soils. Due to minimal redistribution by

503 vegetation, Na, Mg, and Si are equally concentrated in pore fluids for organic-rich and organic-

504 poor soils, and concentrations of these elements in stream water remain relatively constant. From

505 this, we conclude that the transport of elements associated with organic matter, termed

506 previously as organomarker elements (Hausrath et al., 2009), is strongly controlled by the

movement of dissolved organic carbon, leading to a distinct non-chemostatic 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.

Author contributions

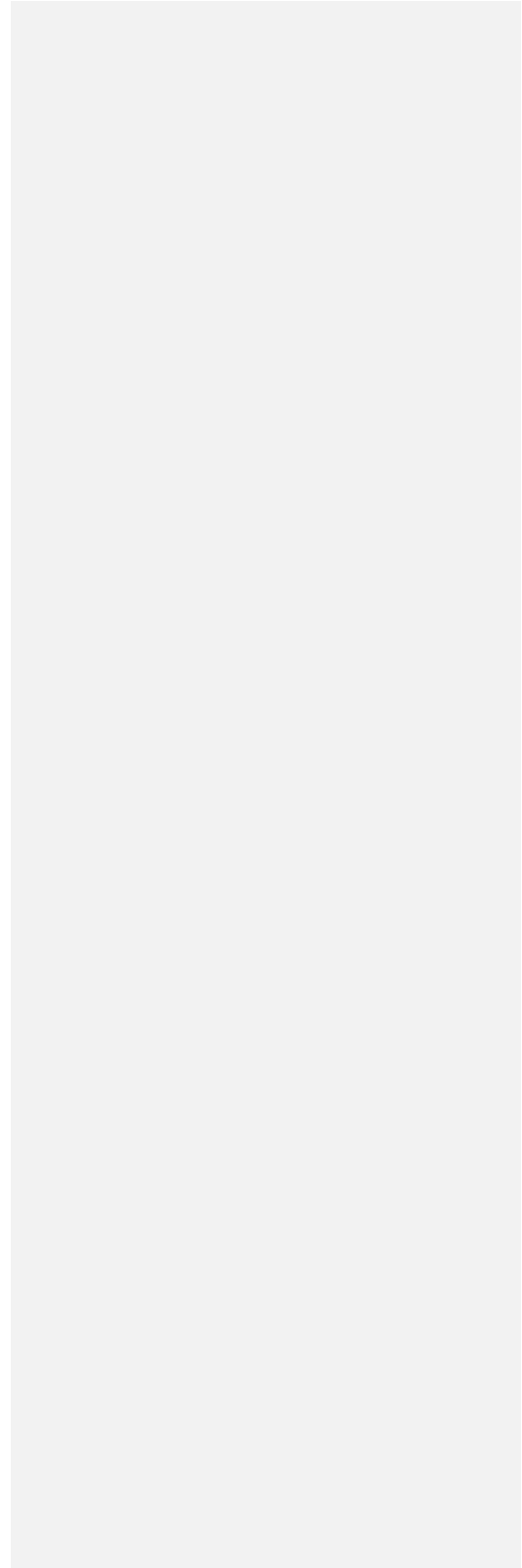EMH, PLS and ALD analyzed the data. EMH prepared the manuscript with contribution from all authors.

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

Site	Category	Horizon	Depth (cm)	DOC (mM)	SOC[b] (% wt.)
Shale Hills[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	--	--
Plynlimon[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	--	--
Stagnopodzol	Organic	O	0-19	1.12	46
	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).

Table 2. Element concentrations (± standard error) in water (precipitation, soil pore water, stream water, groundwater) and vegetation (green leaves, leaf litter) averaged over all available data collected from the Susquehanna Shale Hills Critical Zone Observatory in Pennsylvania, USA between 2006 – 2011

	pH	Na	K	Mg	Ca	Si	Fe	Mn	DOC
					-----------------------------µmol L^{-1}-----------------------------				mmol L^{-1}
Precipitation	4.5	2.1	0.67	0.73	2.65	--	0.24	0.05	0.08[a]
± std. err.	0.2	0.4	0.28	0.16	0.51	--	0.14	0.01	0.02
Soil Pore Water									
SPVF, A horizon	4.5	29	34	62	142	123	0.61	0.38	0.69
± 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
± 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
± 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
± 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
Stream Water									
Low flow	6.3	39	50	162	450	108	14	5.2	0.81
± 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
± 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
± std. err.	0.1	< 1	< 1	2	6	1	0.02	0.03	0.03
Groundwater	--	145	24	404	758	124	0.14	2.9	0.20
± std. err.	--	6	< 1	13	27	1	0.08	0.2	0.05
Vegetation		**Na**	**K**	**Mg**	**Ca**	**Si**	**Fe**	**Mn**	
					-----------------------------µmol g^{-1}-----------------------------				
Leaf litter		n/a	69	59	263	n/a	n/a	49	
± std. err.			6	3	15			3	
Green leaves		1.1	221	69	186		0.99	42	
± std. err.		0.2	15	7	18		0.06	4	

[a]Andrews et al. (2011)

Table 3. Solute concentrations (± standard error) averaged over all available data collected from the Upper Hore (pre-harvest: 1983 – 2005; post-harvest: 2005 – 2010) and Upper Hafren (1990 – 2010) catchments in the Plynlimon forest in Wales, United Kingdom

	pH	Na	K	Mg	Ca	Si	Fe	Mn	Al	DOC
		--------------------------------μmol L^{-1}--------------------------------								mmol L^{-1}
Precipitation	4.98	69.6	2.60	8.52	6.89	2.63	0.19	0.03	0.66	0.045
± std. err.	0.01	3	0.10	0.32	0.59	0.35	0.02	< 0.01	0.05	0.001
Soil Pore Water										
Peat	3.24	143	5.55	27.1	12.6	9.40	2.97	0.16	2.22	1.10
± 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
± 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
± 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
± 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
± std. err.	0.01	< 1	0.04	< 0.1	0.04	0.2	0.02	0.01	0.2	< 0.01
Upper Hore										
Low flow	6.98	177	3.06	36.1	78.3	63.0	2.59	0.32	3.56	0.10
± 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
± 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
± std. err.	0.02	3	0.11	0.5	0.4	0.5	0.07	0.01	0.3	< 0.01
Post-harvest, all flows	5.96	169	8.9	30.2	41.3	45.0	3.33	0.51	7.9	0.31
± std. err.	0.05	1	0.3	0.3	0.7	0.9	0.11	0.01	0.3	0.01
Upper Hafren										
Low flow	6.45	160	2.96	27.8	17.4	67.8	1.21	0.27	2.02	0.08
± 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
± 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
± std. err.	0.02	2	0.15	0.4	0.2	0.8	0.12	0.01	0.22	0.01
Groundwater	5.26	227	8.7	79	94	86	5.9	2.54	1.86	0.032
± std. err.	0.07	8	1.7	11	20	4	1.5	0.33	0.11	0.002

Table 4. Slopes of regression lines fit to C-Q data (log $C = a + m * log Q$) indicate chemostatic[a], non-chemostatic[b], or dilution[c] concentration-discharge patterns

	Na	K	Ca	Mg	Si	Al	Fe	Mn	DOC
Shale Hills (2008 – 2010)									
Slope (*m*)	-0.04[a]	-0.07[a]	-0.12[b]	-0.05[a]	-0.01[a]	-	-0.30[b]	-0.19[b]	-0.11[b]
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
Upper Hafren (1990 – 2010)									
Slope (*m*)	-0.05[a]	0.18[b]	-0.20[c]	-0.08[a]	-0.26[c]	0.58[b]	0.33[b]	0.10[b]	0.42[b]
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
Upper Hore (pre-harvest; 1983 – 2004)									
Slope (*m*)	0.00[a]	0.07[b]	-0.51[c]	-0.12[a]	-0.27[c]	0.52[b]	-0.05[a]	0.05[b]	0.26[b]
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
Upper Hore (post-harvest; 2005 - 2010)									
Slope (*m*)	0.04[a]	0.26[b]	-0.49[c]	-0.11[a]	-0.23[c]	0.42[b]	-0.04[a]	0.12[b]	0.25[b]
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

[1] Calculations exclude data where concentrations fell below the detection limit.

[2] All slopes are statistically different from zero (p < 0.001) except Na (pre-harvest) and Fe (post-harvest) in the Upper Hore

Figure Captions

Figure 1. Map views of the Susquehanna Shale Hill Critical Zone Observatory (Shale Hills, PA, USA; left) and Plynlimon (Wales, UK; right) catchments. Symbols mark locations of precipitation (black square), stream water (red circle), pore water (black triangle), and groundwater (green circle) samplers. ~~Brown and green shading delineate~~Shading delineates major landscape features that are organic-rich or organic-poor in each catchment: swale (brown) versus planar (light green) slopes at Shale Hills or peat (tan) versus forested (dark green) regions at Plynlimon. Notably, the most organic-rich soils are in lowlands in Shale Hills but uplands in Plynlimon; consequently, inputs from organic-rich soils dominate stream flow under low-flow conditions in Shale Hills but high-flow conditions in Plynlimon.
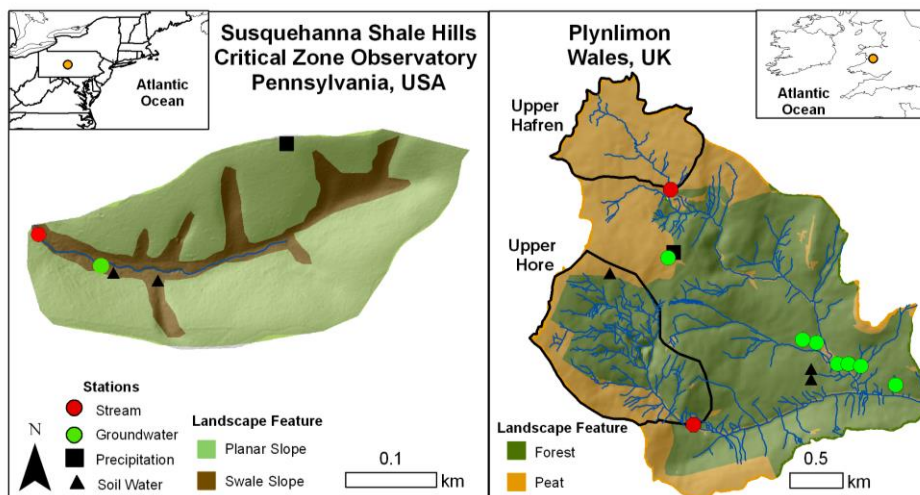
Figure

Figure 2. Log C (solute concentration) versus log Q (discharge) in the Shale Hills catchment (a, b) and two Plynlimon subcatchments, the Upper Hafren (c-e) and Upper Hore (f-h). Data from the post-harvest period (2005 – 2010) in the Upper Hore are plotted in separate panels (i-k). For each catchment, the left panel shows elements that exhibit chemostatic behavior, the middle panel shows non-chemostatic elements that exhibit behavior similar to DOC (e.g. dilution at Shale Hills and enrichment at Plynlimon), and the right panel shows elements that exhibit dilution behavior.
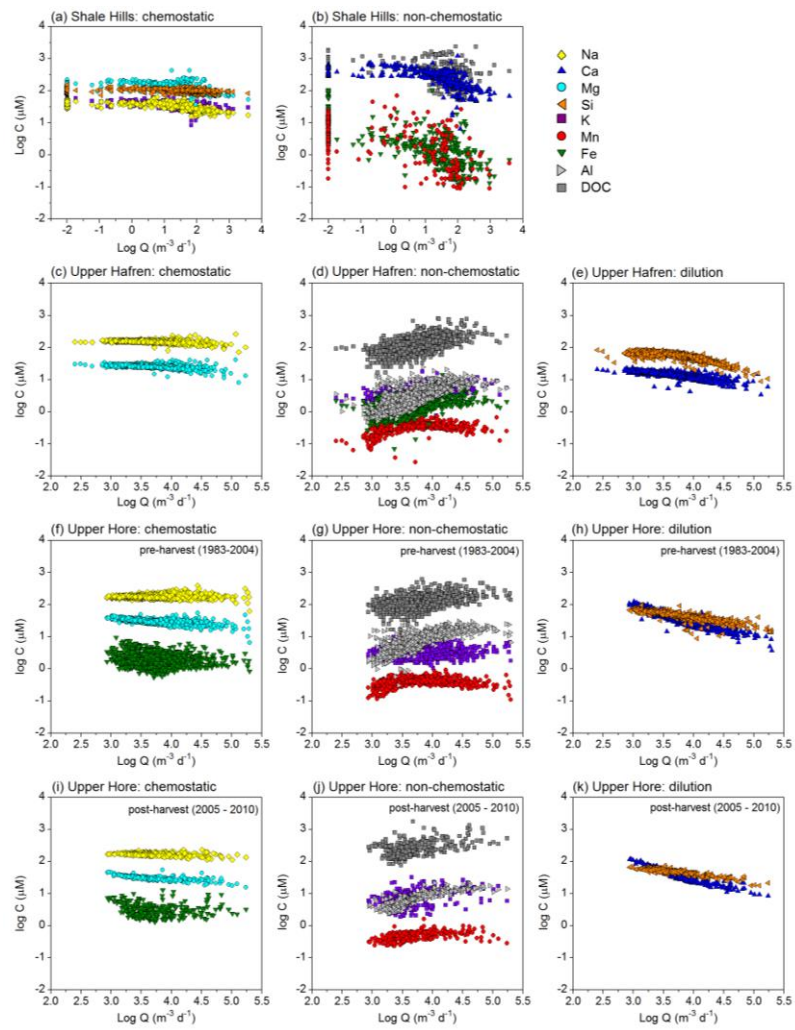
Figure 3. Molar ratios of major divalent (Ca:Mg) versus univalent (K:Na) cations are plotted on the left and the molar ratios of Mn (mmol) to Mg (mol) versus dissolved organic carbon (mmol L^{-1}) are plotted on the right for solute source pools in the forested Shale Hills (a, b), peatland Upper Hafren (c, d), and predominately forested Upper Hore (e, f) catchments. Arrows indicate direction of increasing discharge for average stream chemistries. Values for total C (~ 33 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.
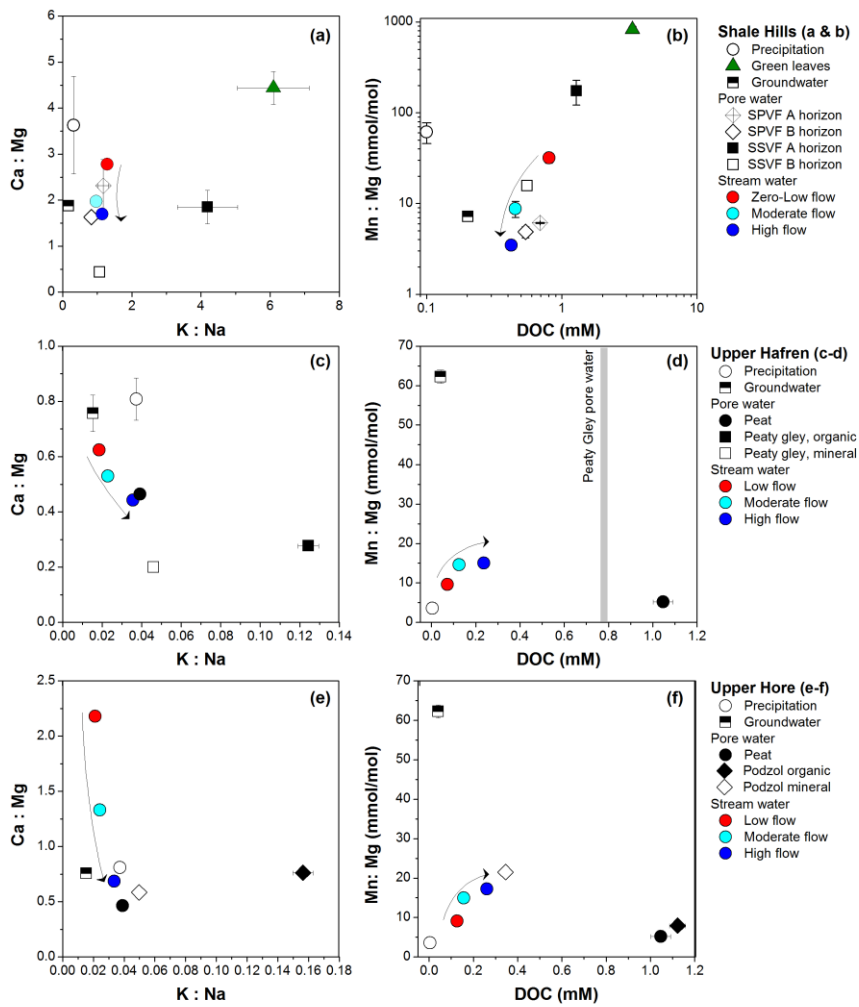
Figure 4. The degree of non-chemostatic behavior for a solute in stream water, denoted by m_j, was correlated with the relative concentration of that solute in organic-rich soil water in each catchment. Specifically, m_j was **(a)** negatively correlated with the ratio of solute concentrations in organic-rich versus 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 versus precipitation in **(b)** the Upper Hafren ($R^2 = 0.48$; $p < 0.05$) and **(c)** the Upper Hore ($R^2 = 0.42$; $p < 0.05$). Error bars represent the standard error of each value and are smaller than the symbol where not visible.