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Hydrologic connectivity and source heterogeneity control concentration–discharge relationships

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Abstract

Changes in streamwater chemistry have frequently been used to understand the storage and release of water and solutes at the catchment scale. Streamwater chemistry typically varies in space and time, depending on sources, mobilization mechanisms, and pathways of water and solutes. However, less is known about the role of lateral hydrologic connectivity and how it may influence streamwater chemistry and solute export patterns under different wetness conditions. This study analyses long-term low-frequency data from four UK catchments using antecedent catchment wetness as proxy for lateral hydrologic connectivity. We demonstrate that solute mobilization mechanisms can vary depending on catchment wetness, as different catchment areas become hydrologically connected to or disconnected from streams. We show that flow and streamwater chemistry are mostly decoupled under dry conditions, leading to stronger impacts of the heterogeneity in solute sources on mobilization patterns during dry conditions compared to wet conditions. Our results demonstrate that the lateral and vertical distributions of solutes need to be integrated and considered together with the temporally variable hydrologic connectivity of these lateral areas to the stream when assessing streamwater chemistry. This combined analysis thus enables inferences regarding the lateral distribution of solutes throughout the catchment; it also indicates that a better understanding of the relationship between lateral hydrologic connectivity and the lateral and vertical distributions of solute concentrations can help to identify particularly vulnerable points in the catchment and their potential polluting effects on streams.

KEYWORDS
antecedent wetness, concentration–discharge relationships, hydrologic connectivity, solute mobilization, spatial heterogeneity, vertical solute profiles

1 | INTRODUCTION

How catchments store and release water has substantial implications for the transport of solutes and contaminants through the landscape. Understanding the sources, mobilization mechanisms, and pathways of natural and anthropogenic solutes in the landscape is essential to predict and manage their impact on water quality. To contribute to streamflow, landscape elements have to be hydrologically connected to the stream, meaning water has to be able to pass from these source areas to the stream channel (Bracken & Croke, 2007). Numerous studies have investigated the impact of hydrologic catchment connectivity on streamflow generation (e.g., Detty & McGuire, 2010; Rinderer et al., 2019), but its impact on streamwater chemistry is less understood.

Many studies have examined streamwater chemistry variation with discharge, typically interpreting discharge-dependent concentration variations based on assumptions of vertical or lateral heterogeneity of solute distributions in catchments. On the one hand, variations in solute concentrations with discharge are assumed to be largely controlled by the vertical distribution of the solutes in catchments. Concentrations of solutes found predominantly in bedrock typically decrease with discharge, as the relative contribution of groundwater to streamflow becomes smaller with increasing streamflow (Neal et al., 1990; Stewart et al., 2022; Zhi et al., 2019). Conversely, the concentration of solutes enriched in litter and top soil layers increases with flow, because these layers increasingly contribute to streamflow at high-flow conditions (Herndon et al., 2015; Neal et al., 2012). These patterns of decreasing and increasing concentration variations with discharge are typically termed 'dilution' and 'flushing' behaviour, respectively. The importance of vertical solute distributions in determining streamwater chemistry patterns has also been confirmed through various modelling studies. Seibert et al. (2009) presented the 'Riparian Flow-Concentration Integration Model' using vertical profiles of water fluxes and solute concentrations (i.e., vertical changes in water contributions and solute concentrations in the soil column) in the riparian zone to explain temporal variability in streamwater chemistry. More recently, Zhi et al. (2019) showed that vertical differences in solute source can recreate observed concentrations of various solutes at high and low flows using a simple, spatially-implicit model. Botter et al. (2020) and Zhi and Li (2020) demonstrated that the depth of solute generation controls concentration–discharge (cQ) patterns during storm events.

At the same time, the importance of the lateral source distribution for solute export patterns has also been widely recognized, with the lateral distribution of sources and their topographic position controling streamflow concentrations of dissolved organic carbon (DOC; Boyer et al., 1997) and nitrate (Vidon & Hill, 2004). Additionally, redox conditions are often spatially heterogeneous and patchy, due to water table fluctuations and catchment topography, thus further influencing solute mobilization. Source heterogeneity has previously been investigated by comparing the coefficients of variation of concentrations (CV_c) and flow (CV_q), with a higher value of CV_c/CV_q indicating a greater decoupling of flow and concentrations and thus a chemodynamic regime (Musolff et al., 2017; Zhi et al., 2019). Similarly, Thompson et al. (2011) argue that 'the decline in CV_c/CV_q arises if the internal mass store is distributed homogeneously in space'. Dupas et al. (2016) observed a transition from a chemodynamic to an increasingly chemostatic regime for nitrate over a duration of 30 years, and interpreted it as a source 'homogenisation' over time resulting from decades of anthropogenic nitrate inputs. Additionally, spatial source variability in the direction parallel to the river (i.e., from the headwaters to the outlet) likely also plays a role in stream water responses, and is known to cause hysteresis in cQ relationships during storm events (Evans & Davies, 1998; Inamdar et al., 2006).

cQ relationships have often been observed to not conform to a single power-law relationship across the full discharge range, but show different behaviour at low and high discharge (e.g., Minaudo et al., 2019; Moatar et al., 2017). For example, steeper cQ slopes of nitrate at low flows have been linked to higher chlorophyll-a concentrations and thus increased microbial activity (Moatar et al., 2017), or an increase in reactive streambed area (Dehaspe et al., 2021). Similarly, cQ relationships may differ across seasons (Bastviken et al., 2007; Gorski & Zimmer, 2021; Shaw et al., 2020; Shogren et al., 2020), possibly indicating different reactions among seasons. It is conceivable that these non-continuous relationships describe different mechanisms at different times (or discharge). These mechanisms may be partly related to discharge-dependent reaction processes, for example, with in-stream reaction processes becoming more relevant when flow is low (and temperatures are high). One can, however, also entertain additional influencing factors that are not directly related to discharge, but rather reflect changes in catchment connectivity. Results from high-frequency data analysed on the scale of individual rainstorms showed substantial variability in cQ slopes among storm events (Knapp et al., 2020; Musolff et al., 2021; Rose et al., 2018; Winter et al., 2022). These findings suggest that delivery mechanisms vary as function of catchment conditions and event characteristics, which, in turn, affect stream discharge (Wen et al., 2020; Xiao et al., 2019). Similarly, hysteresis in storm-event cQ relationships is often attributed to the activation of different regions within the catchment and thus changing water sources throughout the event (e.g., Evans & Davies, 1998; Inamdar et al., 2006). The fact that clockwise and anticlockwise hysteresis patterns can occur at different times within the same catchment illustrates the dependence of solute activation on catchment conditions and event characteristics, rather than on discharge per se. For a source area to contribute to streamflow, it needs to be hydrologically connected to the stream, which highly depends on catchment wetness and soil moisture. Consequently, it stands to reason that lateral catchment connectivity and catchment conditions like antecedent wetness significantly influence differences in solute mobilization, rather than discharge itself. As such, discharge rate and varying solute export patterns can be considered a 'symptom', whereas their underlying causes and first-order controls are more likely catchment conditions, storm event characteristics, and hydrologic connectivity.

Catchment connectivity has been included in modelling of streamwater chemistry explicitly (e.g., Smethurst et al., 2009) and implicitly (by quantifying time-varying contributions from different end-members to streamflow, e.g., Ali et al., 2010; Kiewiet et al., 2020). Here we assess lateral hydrologic connectivity using antecedent precipitation as indicator of catchment wetness. We argue that connectivity likely matters most in catchments with a heterogeneous lateral distribution of solutes, and affects contributions from the shallow zone more strongly than contributions from the deeper subsurface including groundwater. Taking these aspects into account, we illustrate why a purely vertical differentiation of solute concentrations may be insufficient to re-create the highly variable patterns in streamwater chemistry observed over time. Instead, we show that the vertical distribution needs to be considered together with the horizontal distribution of solutes, and paired with changes in catchment conditions and lateral hydrologic connectivity, to understand changes in streamwater chemistry.

Here we ask the question how solute export changes as a function of antecedent wetness—and thus hydrologic connectivity. To do this, we quantify and compare cQ slopes and concentration–discharge variability using weekly data from four catchments in the United Kingdom. We investigate whether we can use this information to infer more precisely the relationships among vertical concentration profiles and their spatial changes, source heterogeneity, and hydrologic connectivity across the catchment. We illustrate findings using a simple model approach inspired by Seibert et al. (2009). We hypothesize that cQ slopes and CV_c/CV_q will differ depending on antecedent wetness, reflecting varying connectivity of riparian areas and hillslopes to the stream. We also hypothesize that cQ slopes and CV_c/CV_q will vary substantially between wetness states for solutes enriched in the shallower subsurface, because of large lateral and vertical variations in the solute distribution in the shallow soil zones, but substantially less for solutes enriched in groundwater. We also anticipate lower CV_c/CV_q ratios during wet conditions, as an increased wetness will result in a more homogeneous activation of the catchment.

2 | MATERIALS AND METHODS

2.1 | Site information

We compare changes in cQ behaviour as function of antecedent wetness at four sites in the United Kingdom, described in the following from North to South with some general characteristics detailed in Table 1.

Birnie Burn is an upland catchment in Scotland (0.8 km^2, altitude ranging from 220 to 435 m a.s.l.), located 35 miles south-west of Aberdeen, within the Glensaugh monitoring site. Soil type and vegetation vary with altitude, with steeper slopes of freely draining humus-iron podzols on thin glacial tills in the lower sections covered by heather and European blueberries, and hill peats on gentle slopes with sphagnum moss and cotton grass in the upper areas (Cooper et al., 2007). The stream is narrow (<1 m wide), draining an incised valley in an area of rounded hilltops (Demars, 2019) typical for previously glaciated regions. The combination of steep slopes and thin soils results in fast runoff responses (Cooper et al., 2007). Catchment usage and land management consists mostly of hill farming with mixed grazing of cattle and sheep, and regular heather burning. Average annual precipitation is 1090 mm (1996–2003) with substantial snowfall in winter. Mean annual runoff is 819 mm (1994–2003; Cooper et al., 2007), resulting in an average annual evapotranspiration of around 25% of total precipitation.

Trout Beck is a headwater catchment located in the North Pennines in the Moor House National Nature Reserve (11.4 km^2, 535–848 m a.s.l.). Large areas of the catchment are covered with blanket peats, with some skeletal soils toward the hill tops, on top of alternating strata of limestone, sandstone and shales. Heather, cotton grass, and sphagnum moss are the dominant vegetation. Mean annual precipitation in the years 1993–2013 amounted to 1931 mm (Moody et al., 2016), with a significant portion falling as snow in winter. Average streamflow between 1957–2020 was 1553 mm (NRFA, 2021), meaning annual evapotranspiration was around 20% of total precipitation.

The Plynlimon catchments are situated in central Wales, approximately 20 km from the coast. The bedrock consists of Lower Palaeozoic grits, mudstones, and shales. We analysed data from two

TABLE 1 Characteristics of the four catchments calculated from the data

	Birnie Burn	Trout Beck	Hafren	Hore
Catchment area (km^2)	0.8	11.4	3.6	3.2
Mean annual temperature (°C)	7.51 ± 5.05	5.85 ± 5.41	6.49 ± 5.30	6.49 ± 5.30
Mean annual precipitation (mm)	1090[a]	1931[b]	2513[c]	2533[d]
Maximum P4d (mm)	146	193	258	229
R^2 of $\ln(Q)$ versus P4d	0.24	0.37	0.58	0.58
Mean air temperature in summer[e] (°C)	12.57 ± 3.38	11.19 ± 3.77	11.80 ± 3.56	11.80 ± 3.56
Mean air temperature in winter[e] (°C)	2.83 ± 3.05	1.06 ± 3.53	1.70 ± 3.61	1.70 ± 3.61
Mean daily precipitation in summer[e] (mm)	3.23	4.16	5.62	5.62
Mean daily precipitation in winter[e] (mm)	2.86	7.70	9.07	9.07
Mean P4d in summer[e] (mm)	12.94 ± 14.74	16.62 ± 18.15	22.26 ± 22.75	22.26 ± 22.75
Mean P4d in winter[e] (mm)	11.64 ± 14.39	31.17 ± 38.51	36.43 ± 39.87	36.43 ± 39.87

Note: Uncertainties in mean air temperature and P4d are given as one standard deviation. Catchments are ordered from North to South.

[a] 1996–2003, Cooper et al. (2007).

[b] 1993–2013, Moody et al. (2016).

[c] 1961–1990, NRFA (2022a).

[d] 1961–1990, NRFA (2022b).

[e] These numbers are the same at Hafren and Hore, because they are calculated from the same AWS at Carreg Wen.

adjacent headwater catchments of the River Severn. The Hore catchment (3.17 km^2, 338–736 m a.s.l.) is mostly covered by plantation forests of Sitka spruce with some semi-natural moorland headwaters. Soils are thin (typically <1 m in thickness) and dominated by podzols and gleys. Large parts of the upper Hafren catchment (3.58 km^2, 352–690 m a.s.l.) consist of semi-natural moorland with organic-rich peat soils. Land-use and soils in the lower part of the Hafren are similar to the Hore catchment, and water-logged gley soils dominate the riparian areas (Kirby et al., 1991). Phased felling and subsequent replanting have been carried out in the plantation forests of both catchments over the years, and soils were ploughed prior to first plantation, creating drainage networks. These result in flashy hydrograph responses to rainfall (Kirby et al., 1991; Leeks & Marks, 1997) and short travel times of water (Knapp et al., 2019). The bedrock is highly fractured, supporting fast flow and dominant pathways through the catchment (Shand et al., 2007), but flow in the peat-dominated parts of the catchment is typically lateral rather than vertical (Shand et al., 2009). Mean annual rainfall in the years 1961–1990 was 2513 and 2533 mm at Hafren and Hore, respectively, while average annual runoff was 2096 and 2059 mm (NRFA, 2022a, 2022b), yielding annual evapotranspiration of around 17% and 19%, respectively.

2.2 | Water quality and hydrometric data

Both Birnie Burn and Trout Beck are part of the UK Environmental Change Network (ECN). We used stream water samples collected as weekly grab samples between March 1995 and December 2015 at Birnie Burn, and between January 1993 and December 2015 at Trout Beck (Rennie et al., 2017b). Details of the measurements, sampling and analyses procedures are specified elsewhere (Rennie et al., 2020; Sykes & Lane, 1996). At these two sites, discharge is supplied as 15 min averages calculated from 10 s stage height readings (Rennie et al., 2015). We used the 15-min discharge value closest in time to the chemistry sampling time. If the sampling time was not specified (which was the case for 3.7% and 2.2% of all samples collected at Birnie Burn and Trout Beck, respectively), we excluded the chemistry sample from analysis as it could not be matched to a discharge value. Hourly precipitation data were obtained from automatic weather stations (AWS) located at the two ECN sites. Two different AWS operated at Glensaugh during the period analysed here, with an overlap in 2005. We used data from station 1 between March 1995 and end of 2005, and data from station 2 thereafter. Some short gaps in precipitation data affecting less than 6% of the data set exist; all samples collected during these sampling times are excluded from analysis.

At the two Plynlimon sites, Hafren and Hore, we used streamwater chemistry data published by Neal et al. (2013). Streamwater samples were collected as approximately weekly grab samples between May 1983 and June 2011, and details on the sampling and analysis procedures are provided by Neal et al. (2011, 2013). Fifteen minutes discharge measurements at the outlets of both catchments, as well as hourly precipitation data measured at Carreg Wen AWS were obtained from the UK Centre for Ecology and Hydrology for the relevant period.

A range of solutes were used in the analysis: calcium, sodium, chloride, sulphate, nitrate, DOC, iron, aluminium, manganese, and pH. These solutes were available from all four sites, except manganese, which was only measured at Hafren and Hore.

2.3 | Quantification of catchment conditions

We used antecedent wetness as proxy for lateral hydrologic connectivity, based on the assumption that wetter conditions result in an expanding lateral connectivity away from the stream. We quantified antecedent catchment wetness as the total volume of precipitation that fell in the previous 4 days up until and including the hour the streamwater sample was taken (denoted as P4d in the following). P4d was chosen rather than P7d (precipitation of the previous 7 days), since previous research showed the strongest relationship between P4d and catchment connectivity (Zuecco et al., 2019). However, summing precipitation over any duration of 4–7 days resulted in similar results in this study.

The calculated antecedent wetness conditions (P4d) varied from 0 to 258 mm of rain in the 4 days prior to streamwater sampling. To assess solute mobilization at different wetness conditions, we split the concentration time series according to ranges of antecedent wetness (based on percentiles of P4d, with P4d in the 0–34th, the 34–66th, and 66–100th percentile ranges defined as low, medium and high antecedent wetness, respectively) and calculated cQ slopes and CV_c/CV_q values separately for the resulting subsets of data.

To assess the possible confounding effect of P4d in split concentration–discharge analyses, we calculated the coefficient of determination (R^2) between discharge at the sampling times and corresponding catchment wetness (Table 1). At Birnie Burn and Trout Beck, antecedent wetness explains around 25% and 37% of the variability in discharge, respectively. At the Plynlimon catchments, antecedent wetness explains more than 50% of the discharge variability. At all sites, discharge is positively related to antecedent catchment wetness (see also Figures S1 and S2).

Mean daily air temperature was substantially higher in summer than winter at all sites (Table 1). At three of the four catchments, catchment wetness was lower in summer than in winter due to less precipitation; at Birnie Burn, antecedent wetness was similar in both summer and winter (Table 1).

2.4 | Statistical metrics: Concentration–discharge relationships and coefficients of variation

Solute concentration c and discharge Q are assumed to relate through a power-law relationship

$$c = aQ^b, \tag{1}$$

with the constant a and the exponent b. In double-logarithmic space, b becomes the slope of the linear cQ relationship and $\log_{10}(a)$ its intercept.

We also calculated ratios of the coefficients of variation of concentration and discharge, CV_c/CV_q (Basu et al., 2011; Musolff et al., 2015). A coefficient of variation quantifies the relative dispersion of data points around the mean, and consequently, the ratio describes the relative variability of concentration and discharge. If $CV_c/CV_q < < 1$, the relative variability of discharge, CV_q, is substantially greater than the variability of solute concentrations, CV_c, and the regime is termed chemostatic. Conversely, if the relative concentration variability is high relative to the variability of discharge (with $CV_c/CV_q \geq 0.5$), the regime is considered chemodynamic. Combining the direction of the cQ relationship (dilution/neutral/flushing) with dynamics of variations (chemodynamic to chemostatic) improves the classification of solute-generating mechanisms and helps to understand mobilization behaviour (Ebeling et al., 2021; Musolff et al., 2015).

The coefficient of variation is typically calculated as

$$CV = \frac{\sigma}{\mu}, \tag{2}$$

with the standard deviation and mean of the data, σ and μ, respectively. In case of a log-normal distribution of the data, a more robust way of calculating a coefficient of variation is given by:

$$CV = \frac{\sigma}{\mu} = \frac{\exp\left(m_{\ln} + 0.5 s_{\ln}^2\right)}{\exp\left(2m_{\ln} + s_{\ln}^2\right)\left(\exp\left(s_{\ln}^2\right) - 1\right)} = \sqrt{\exp\left(s_{\ln}^2\right) - 1}, \tag{3}$$

where, $m_{\ln}$ and $s_{\ln}$ are the mean and standard deviation of the log-transformed data, respectively (Koopmans et al., 1964).

An Anderson-Darling test showed that concentrations and discharge rates neither follow strictly a normal nor a log-normal distribution, but the data are much closer to a log-normal distribution. A careful comparison demonstrated that CV_c values were typically similar when calculated with Equations (2) or (3). However, subsets of discharge frequently included one or two large discharge values (see also Figure S2), which artificially inflate the standard deviation of the untransformed data much more severely than the one of the lognormally transformed discharge data, resulting in large CV_q values and unrealistically small CV_c/CV_q values. For this reason, we used Equation (3) instead of the standard approach (Equation 2) for the calculation of CV_c and CV_q.

3 | RESULTS AND DISCUSSION

3.1 | Concentration–discharge relationships as functions of catchment wetness

Concentration–discharge (cQ) relationships vary substantially among solutes and catchments, with some solute concentrations following a very clearly defined pattern with discharge, while other solutes have much more scattered variations with discharge (Figure 1). Changing cQ slopes for different wetness conditions result in bending cQ relationships observed for, for example, manganese, aluminium, and pH at Hafren, with flatter slopes at higher flows. However, even solutes featuring relatively straight (but scattered) relationships across all data, like sulphate and nitrate, exhibit varying slopes under different wetness conditions. This indicates that a lack of direct relationships between concentrations and discharge may be responsible for the scattered cQ clouds of some solutes, which in turn could imply changes in solute mobilization caused by wetness-mediated changes in catchment connectivity. If concentrations are assessed directly as functions of discharge only, these changes in processes may be overlooked.

Slopes of cQ relationships vary across sites, solutes, and wetness states (Figure 2a, values of b and CV_c/CV_q are in Tables S1 and S2). For most solutes and sites, we observe approximately neutral behaviour ($b \approx 0$) under wet antecedent conditions, and stronger deviations from neutral behaviour toward solute flushing (frequently) or dilution (sometimes) when the catchment is dry (Figure 2a).

3.1.1 | High variability in mobilization behaviour with wetness for shallow-zone solutes

The shallow and deep subsurface often carry different water chemistry due to distinct surface hydro-biogeochemical conditions. Groundwater from deeper zones is typically more enriched in base cations than shallow water (Anderson et al., 1997); in contrast, organic materials rich in carbon-, nitrogen-, and iron-containing solutes are often more abundant in the shallow soils (Lidman et al., 2017; Tittel et al., 2022; Zhi & Li, 2020). Although no detailed and consistent information on the sources of solutes is available from the four study catchments, collated soil and groundwater chemistry at Plynlimon (Neal et al., 2004; Shand et al., 2005; Stewart et al., 2022) and soil water data at the ECN sites (Rennie et al., 2017a) supports these vertical sources. We therefore group solutes such as DOC, nitrate, iron, and aluminium as more from shallow subsurface, and cations from groundwater.

We observed the largest changes in cQ slopes with wetness for nutrients and metals, like nitrate, aluminium, manganese, iron, and DOC (Figure 2a). These solutes are typically more abundant in the shallower subsurface (or mobilized more readily from these parts), and thus likely more strongly affected by wetness-mediated changes in lateral connectivity (Musolff et al., 2021; Tittel et al., 2022). Conversely, slopes of solutes derived from bedrock and thus dominant in groundwater, including calcium, sodium, chloride, and sulphate (Anderson et al., 1997; Godsey et al., 2009; Stewart et al., 2022), are relatively invariant across wetness states, indicating that their mobilization is less affected by changes in hydrologic connectivity, because the deeper, groundwater-dominated zones contribute to streamflow much more independently of catchment wetness. These findings support our hypothesis regarding the importance of both catchment

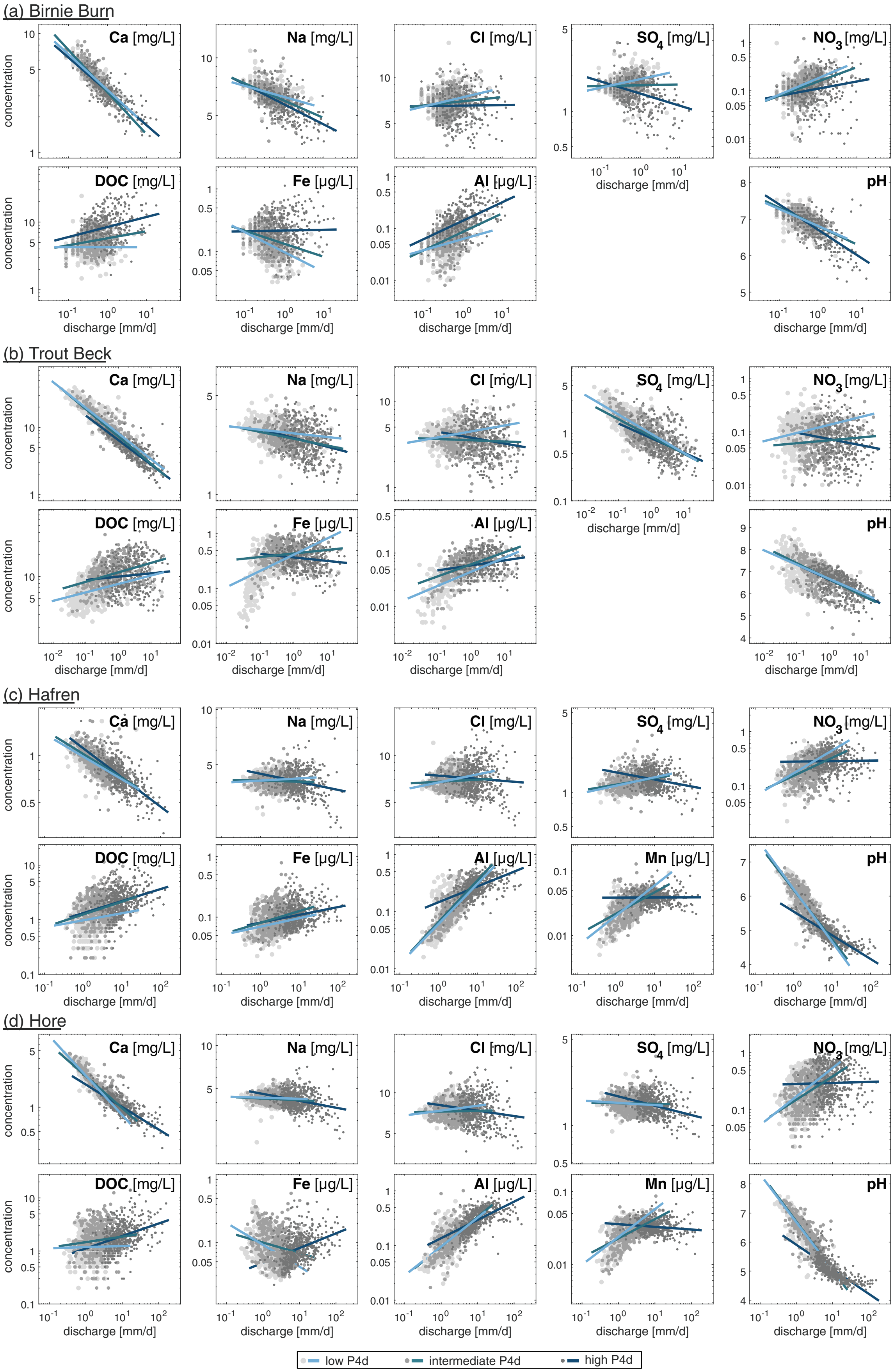

FIGURE 1 Concentration versus discharge at (a) Birnie Burn, (b) Trout Beck, (c) Hafren, and (d) Hore. Lighter points show concentration and discharge values associated with low antecedent wetness values, and darker points represent wetter conditions. The blue lines show the power-law relationship associated with different ranges of antecedent wetness conditions.

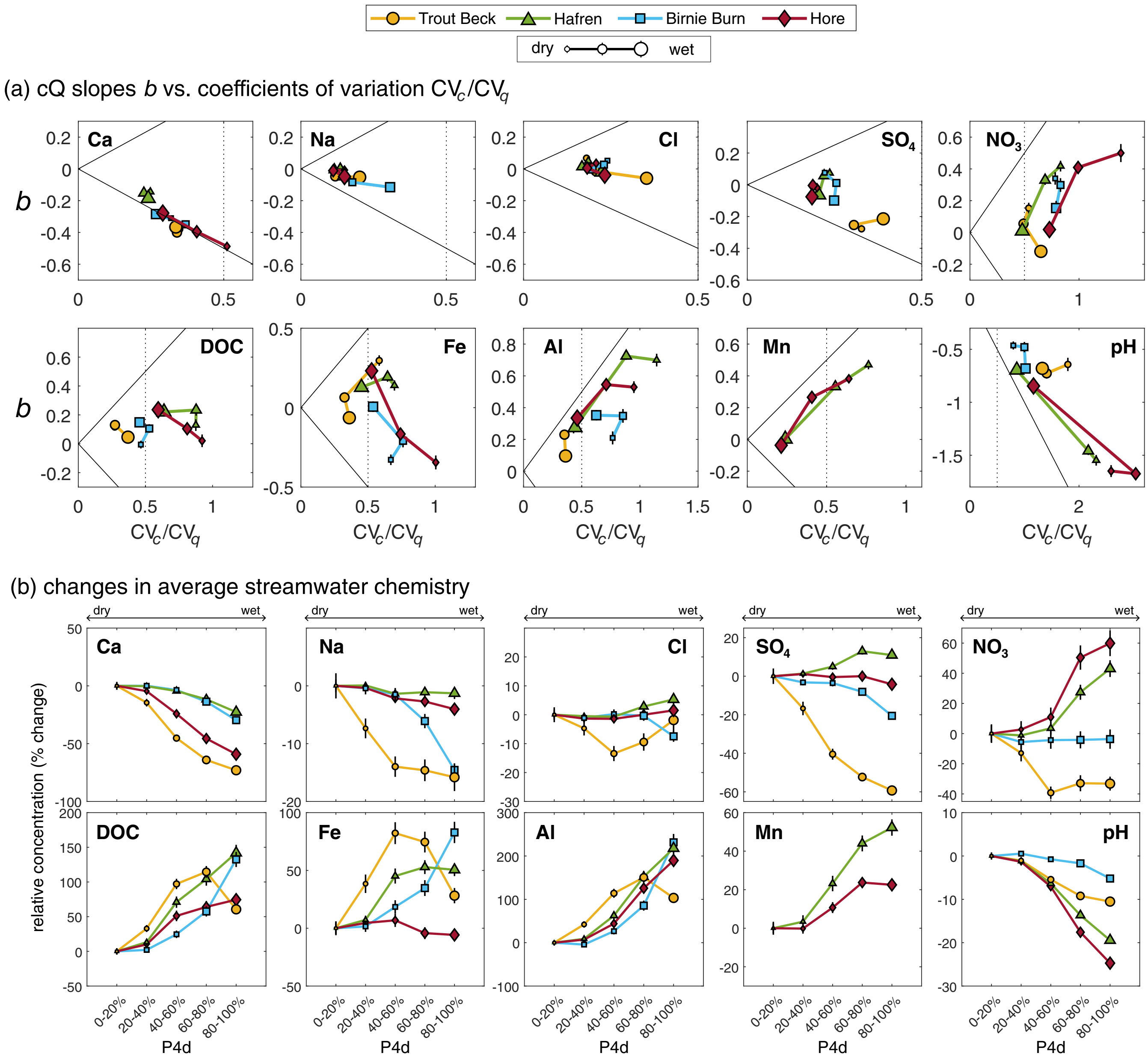

FIGURE 2 (a) cQ slopes and coefficients of variation as function of antecedent wetness. Smaller symbols indicate drier conditions (P4d). For easier visual comparison of slope variability, we have set identical scales of y-scales of one unit for all subplots except the last one (pH), where the range includes 1.5 units. Vertical dashed lines at $CV_c/CV_q = 0.5$ identify the transition from chemostatic to chemodynamic (Musolff et al., 2017). For pH, cQ slopes and CV_c/CV_q are calculated from untransformed data. Negative slopes for pH actually indicate a flushing behaviour (rather than dilution), because $\mathrm{pH} = -\log_{10}(\mathrm{H}^+)$. (b) Relative concentration changes for different antecedent wetness ranges (average concentrations of each wetness category relative to the average concentration at the lowest P4d range). Error bars show one standard error; smaller and larger symbols indicate drier and wetter conditions, respectively. Manganese is not measured at Trout Beck or Birnie Burn, hence no concentrations are shown for those sites.

connectivity together with the lateral and vertical solute distributions for solute mobilization (see also Figure 3a).

Patterns of CV_c/CV_q values reinforce these observations from the cQ slope values. Groundwater-derived solutes (calcium, sodium, chloride, and sulphate) show little variability in both cQ slopes b and CV_c/CV_q ratios. Of these solutes, sodium, chloride and sulphate have slopes close to zero at all wetness states, indicating neutral behaviour (in line with findings, e.g., by Godsey et al., 2009), whereas cQ slopes of calcium are always negative. Furthermore, both b and CV_c/CV_q values of the groundwater-derived solutes either hardly change between dry and wet conditions, or move along the $b - CV_c/CV_q$ bounds, and observed changes in CV_c/CV_q are thus fully explained by changes in b (Musolff et al., 2015).

Conversely, for nutrients and metals, the ratios of CV_c/CV_q are highly variable, similar to the cQ slope values. The CV_c/CV_q ratios are mostly greater during dry conditions than wet conditions, indicating

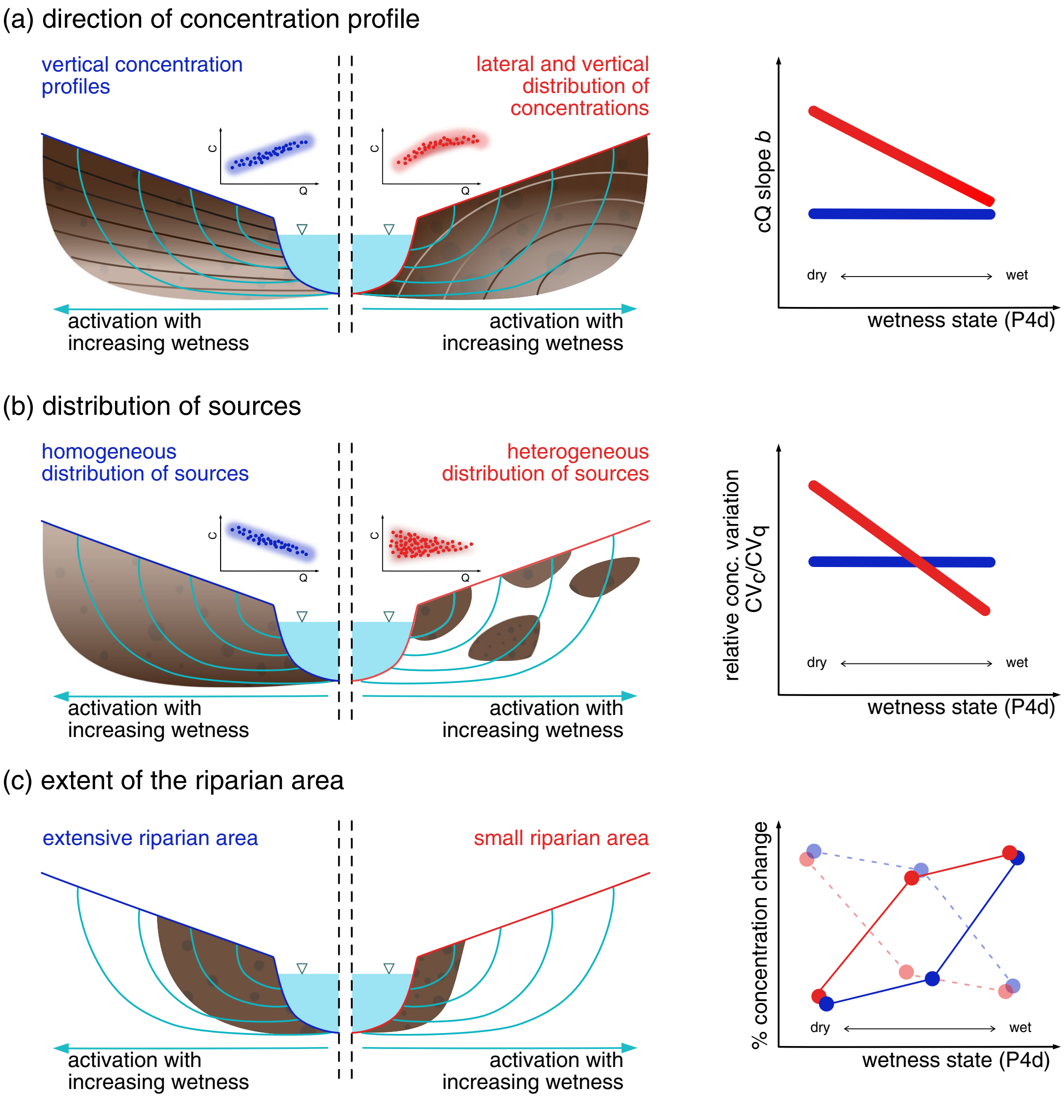

FIGURE 3 A conceptual illustration of the effect of vertical and horizontal concentration profiles on streamwater chemistry as function of wetness and connectivity. (a) The direction and type of the concentration profiles (brown shading and lines) can regulate whether the cQ slope *b* will be constant across wetness conditions (left) or vary across wetness states (right). With a purely vertical layering of concentrations (blue, left), cQ slopes will be constant and linear across wetness conditions (in double-logarithmic space). To obtain bending cQ relationships with wetness-dependent cQ slopes, however, both a lateral and vertical change in concentrations is needed (red, right). The example illustrates a solute with higher concentrations in both the riparian zone and the shallow subsurface, reflecting expected behaviour and distributions of DOC or aluminium. (b) The heterogeneity of the solute distribution substantially affects CV_c/CV_q. With a homogeneous lateral distribution (blue, left) (i.e., a bottom-to-top gradient), increasing wetness and connectivity does not substantially affect CV_c/CV_q values. With a heterogeneous lateral distribution of sources (red, right), the CV_c/CV_q value is highest at dry conditions, as hydrologic connectivity connects different parts of the catchment to the stream, and these may or may not act as sources of the solute. (c) The extent of the riparian area influences the shape of the change in average solute concentration with increasing wetness. With an extensive riparian area (blue, left), average streamwater chemistry remains relatively constant across gradients of antecedent precipitation (dry to intermediate P4d). With a small riparian area (red, right), the hydrologically connected area extends beyond the riparian area as wetness increases, resulting in substantial changes in average streamwater chemistry. The illustrated patterns of concentration change versus P4d can occur if the concentration in the riparian area is lower than in the rest of the catchment. If concentrations are higher in the riparian area, a pattern similar to the dashed, lighter pattern is likely.

that heterogeneity in solute sources and activation has a stronger effect under dry conditions, as only selected parts of the catchment are hydrologically connected to the stream, thus confirming our initial hypothesis. This is further supported by the shift toward chemodynamic behaviour indicated by greater CV_c/CV_q values during drier conditions, demonstrating that concentration variability becomes more strongly decoupled from discharge variations as the catchment dries out. These results highlight that variations in streamwater chemistry are affected by both the heterogeneous distribution of solute sources across the catchment, and their heterogeneous activation (see Figure 3b).

The larger variations in cQ slopes with wetness for solutes predominantly found in the shallow subsurface, compared to those of groundwater-derived solutes, are similar to findings from event-scale studies (Knapp et al., 2020; Winter et al., 2022). In their event-scale analysis, Knapp et al. (2020) observed a strong dependence of event-scale cQ slopes on antecedent conditions in case of solutes mobilized from the shallow subsurface, whereas cQ slopes of groundwater solutes were mostly dependent on event size with stronger dilution observed for larger events. Our findings confirm the importance of changes in hydrologic connectivity for mobilization of compounds located in these shallower layers, which are typically more heterogeneously distributed. Shallower parts of the catchment thus provide varying contributions to streamflow as function of hydrologic connectivity, due to spatial heterogeneity in vertical concentration profiles resulting from changes in, for example, soil structure, distance from the stream, and topography (Blackburn et al., 2017; Grabs et al., 2012; Tetzlaff et al., 2014). Conversely, the streamwater composition of groundwater solutes is mostly affected by mixing of water from different depths (independent of which lateral areas of the catchment the water comes from).

For nutrients and metals, the magnitude and direction in the variability in cQ slopes and CV_c/CV_q ratios are mostly similar across sites. In all catchments, nitrate, aluminium, and manganese show approximately neutral behaviour when the catchment is wet and strongly positive slopes during dry conditions. Iron and DOC, however, exhibit inconsistent behaviour with wetness across sites. At Birnie Burn and Hore, cQ slopes of iron are negative during dry antecedent conditions ($b < -0.3$) and increase with increasing wetness, reaching neutral (Birnie Burn) and positive (Hore) slopes at the wettest conditions. Conversely, at Trout Beck, cQ slopes of iron decrease with increasing wetness, starting off at positive values during dry conditions ($b \approx 0.3$) and moving toward neutral conditions with increasing wetness. At Hafren, cQ slopes of iron hardly change with wetness, and remain slightly positive throughout all wetness states. This varied behaviour may possibly be linked to differences in the spatial distribution of iron at the four sites (see also Figure 3). Because iron is typically more easily mobilized from the shallower layers of the catchment rich in organic carbon (Adhikari et al., 2017; Fuss et al., 2011; Neal et al., 2008; Tittel et al., 2022), its behaviour is likely to be affected more strongly by land use than bedrock geology. Additionally, iron is sensitive to changing redox conditions. If iron is dominantly mobilized in the reduced from, it is likely to be oxidized again when leaving the soil and entering the stream. Consequently, a part of it will be retained at redox interfaces or in streams, with the exact processes depending on pH, temperature, and in-stream travel time, resulting in highly site-specific mobilization behaviour. Additionally, iron and DOC mobilization have been found to be strongly related (Knorr, 2013; Tittel et al., 2022), which could explain the similar direction of patterns observed for the two compounds.

3.1.2 | cQ slope changes with wetness provide insight into the lateral solute distribution

Rather than only considering the general direction of the cQ slope change with wetness, we can also look more closely at the rate of the change in cQ slopes with different wetness states, to draw more detailed inferences regarding the distribution of solutes throughout the catchment. At Hafren and Hore, aluminium has similar slope values during intermediate and dry conditions, while the cQ slopes of manganese continuously change from wet through intermediate to dry conditions. This negligible change in slope values for aluminium between low and intermediate wetness may indicate that the distribution of aluminium is relatively homogeneous throughout all areas of the catchment except the hillslopes which become connected only at the wettest conditions (or that the riparian zone is more extensive here than at the other sites). Conversely, the continued change in cQ slope values of manganese with wetness indicates that the vertical profiles of manganese concentrations differ throughout the catchment, resulting in changing manganese contributions to the stream as the wetness sphere of influence expands.

In conclusion, we can interpret changing cQ slopes with wetness (Figure 2a) as changes in solute mobilization behaviour in response to changes in catchment connectivity. During dry conditions, only the riparian area is hydrologically connected to the stream, and groundwater is the dominant stream water source. As the catchment wets up (i.e., when antecedent wetness increases), the extent of the hydrologically connected area increases and the hillslopes start to contribute to streamflow. These connections are initially patchy and hydrochemically variable, whereas under wet conditions, there is little opportunity to further increase connectivity in an already well-connected catchment, resulting in mostly neutral cQ slope values. On the other hand, we assume that the groundwater table is closely related to stream discharge (Seibert et al., 2009). Discharge thus regulates which vertical sections of the concentration profiles in the hydrologically connected areas contribute to streamflow and thus streamwater chemistry, with low flow resulting only in the activation of the deeper sections of the soil profile, while high discharge activates the whole vertical profile.

Consequently, these changing patterns of cQ slopes with catchment wetness allow drawing certain inferences regarding solute distributions across and within the catchment, as different parts of the catchment become hydrologically connected to the stream with increasing wetness. This is in line with findings, for example, by Tetzlaff et al. (2014), who observed that the water table in the riparian zone is relatively constant, but increasingly variable as the distance from the stream increases. This indicates—similar to findings by Wen et al. (2020)—that riparian areas are likely always connected to the stream at these sites, whereas more distant areas only become connected episodically.

3.1.3 | Effect of season and reactivity is smaller than the effect of hydrologic connectivity

Antecedent conditions are confounded by season and thus temperature and reactivity, because summers in the UK are typically drier than winters (see also Table 1). To verify that the observed patterns are indeed due to changes in wetness, rather than merely a consequence of season and changed reaction processes, we repeated the above analysis for concentration subsets by season. Indeed, we observed more similar cQ slope values during summer and dry conditions, and during winter and wet conditions (Figure S3). However, both cQ slopes and CV_c/CV_q values were significantly less variable between seasons than among wetness conditions. This was the case at all four sites, including at Birnie Burn where wetness in summer and winter is comparable (Table 1). Thus, we can conclude that solute mobilization appears to be more strongly influenced by changes in hydrologic connectivity than by changes in reaction processes, at least for the solutes at these sites. At the same time, reaction processes likely modulate the observed patterns and strongly influence their variability across wetness conditions, as similarly illustrated by Winterdahl et al. (2011) for DOC. Additionally, catchment wetness itself is known to affect reactivity, because drier spells often coincide with warmer temperatures that can enhance microbial activities (Davidson & Janssens, 2006).

We observe few changes with both wetness (Figure 2a) and season (Figure S3a) for geogenic solutes like calcium, sodium, and chloride, while solutes with significant redox behaviour like nitrate, iron, and manganese vary substantially. This might indicate the importance of redox conditions including denitrification and iron reduction (but not sulphate reduction), in addition to the difference in their vertical distribution discussed above. Additionally, changes in pH may be indicative of greater contributions from acidic soils such as peat and are coupled to redox reactions. The mobility of aluminium in turn changes with pH, potentially explaining the substantial variability in cQ slopes and CV_c/CV_q ratios of aluminium and pH. This illustrates how the mobilization of redox-sensitive species may be linked to changes in catchment wetness and temperature. These results suggest once more that we cannot consider hydrology separately from biogeochemistry (Li et al., 2021). Due to changes in temperature, season can serve as simplified proxy for reactivity and microbial activity, but more in-depth investigations are necessary to understand how exactly changes in reactivity and catchment connectivity interact to shape the observed cQ patterns. Furthermore, it should be pointed out that temperature, rather than season, may serve as better proxy for reactivity. This might also circumvent potential confounding effects arising from precipitation falling as snow during the winter months, potentially obscuring the relationship between precipitation, catchment wetness, and discharge.

3.2 | Changes in average streamwater chemistry as function of catchment wetness

In addition to solute mobilization, we also explore the dependence of average streamwater chemistry on antecedent wetness, which may provide further insights into changes in source activation with changing catchment conditions. Average streamwater solute concentrations may increase or decrease with antecedent wetness for different elements, relative to concentrations measured during the driest conditions (Figure 2b). Some solutes behave similarly at all sites (e.g., calcium showing a decrease in concentration with increasing wetness at all four sites). Others exhibit varied behaviour across sites, likely owing to different bedrock geology and land use. The two Plynlimon catchments exhibit similar behaviour for most solutes, likely because of their close proximity, and thus similar geology and slight differences in land cover.

At Trout Beck, the largest changes in concentrations typically occur at lower wetness ranges and level off once P4d has reached about 50% of its maximum. At other sites, changes in concentrations are relatively small and gradual at drier conditions but increase as the catchments reach greater wetness. This is particularly obvious when comparing sodium concentration changes with wetness at Birnie Burn and Trout Beck (Figure 2b). Assuming that increasing wetness expands the hydrologically connected area from the riparian area out to the hillslope, we can use these patterns to draw inferences regarding the average concentrations of different vertical profiles. Consequently, these varied patterns across sites indicate that the riparian area may be smaller at Trout Beck and more expansive at other sites—either in actual spatial extent or water holding capacity (see Figure 3c). Additionally, the riparian zone will be particularly sensitive to even small water table changes, and the vertical solute distribution may vary substantially here, because redox and concentration gradients are often steep in the riparian area. At the same time, microtopography within the riparian zone creates both lateral and vertical heterogeneity in concentrations (Werner et al., 2021).

3.3 | Reconciling cQ slopes and concentration changes

The interaction of patterns in cQ slopes and solute concentrations can be illustrated using specific solutes as examples. All sites show a relatively strong increase in average DOC concentrations with increasing wetness (Figure 2b), while the mobilization mechanisms (i.e., the cQ slopes, Figure 2a) are less affected by catchment wetness. In case of manganese and aluminium, concentrations increase quite substantially with wetness (Figure 2b), while cQ slope values decrease as the catchment wets up (Figure 2a).

Average streamwater chemistry and cQ slopes provide distinct but complementary pieces of information that can help to disentangle the spatial heterogeneity in vertical solute distributions across the catchment as well as their mobilization from the land to the water. Average solute concentrations represent the average flux-weighted concentrations from the hydrologically connected sections of the catchment, integrating both lateral heterogeneity and vertical concentration profiles. As the catchment wets up, the hydrologically connected area expands laterally outward from the riparian zone. In addition, the water level rises with increasing runoff, and the resulting streamwater integrates solute distributions in both lateral and vertical directions. The vertical concentration profiles in the connected areas may differ in space, and the observed chemistry is thus the flux-weighted concentration of multiple vertical profiles from the hydrologically connected areas. cQ slopes, on the other hand, quantify concentration changes with discharge and thus changes in mobilization behaviour. A more positive cQ slope indicates a stronger mobilization mechanism (i.e., a progressively stronger increase in concentrations with discharge), but does not necessarily result in higher solute concentrations at a given wetness range. If we assume that discharge is directly related to water level (Seibert et al., 2009), then the cQ slope indicates the vertical solute distribution within the hydrologically connected catchment area and its change from deeper sections activated at low discharge to shallower sections activated as discharge increases. Consequently, in a simplified view, cQ slope values reflect the concentration changes *within* activated concentration profiles from bottom to top by expressing changes in response to changing runoff and water levels (e.g., Zhi et al., 2020). Average streamwater chemistry, on the other hand, compares flux-weighted concentration profiles *among* subsets, that is, integrating from the bottom to the top of the concentration profiles. Consequently, different levels of P4d and different levels of discharge sample the subsurface in different ways.

3.3.1 | Model illustration of the effect of hydrologic connectivity

In the real world, the effects of catchment wetness and discharge rates are intertwined and the distinction is much less clear-cut. However, this simplified view presented here, where an increasing hydrologic connectivity determines a defined mixing of different profiles through wetness and runoff changes, results in distinct changes of cQ slopes and streamwater chemistry that can be tested through numeric modelling. We built a simple model to illustrate and synthesize these differences in discharge and wetness, and to re-create cQ patterns and average chemistry from our data analysis. The model assumes that increasing antecedent wetness results in a lateral expansion of the hydrologically connected area from the channel and riparian zone to the hillslope area (Figure 4a). The observed discharge in the stream, on the other hand, is assumed to be directly related to the vertical water level, and discharge thus controls the part of the vertical concentration profile that contributes to streamflow. The model also assumes that the contribution of the water flux q decreases exponentially with depth z, to accommodate decreasing porosity and hydraulic conductivity with depth (e.g., Seibert et al., 2009; Figure 4a):

$$q(z) = a\left(e^{-b_q z} - e^{-b_q z_{\max}}\right),$$

with coefficients b_q and a. To ensure that the flux at the greatest depth is zero, we scale by the flux at maximum depth $z_{\max}$. a was chosen such that the highest observed discharge Q resulted in a groundwater level at the land surface, by summing up the flux contributions from the greatest depth to the groundwater level:

$$Q = \int_{z_{\max}}^{z} q(z).$$

We further defined different exemplified vertical concentration profiles to represent simplified real-life concentration patterns with depth in the riparian zone and in the hillslope area, $c_{rp}(z)$ and $c_{hs}(z)$, respectively. In the applied model, these are defined by four arbitrary concentration values with depth, between which a piecewise cubic interpolation was applied to obtain a continuous profile. The shifting contribution from the two concentration profiles in the riparian zone, f_{rp}, and the hillslope area, f_{hs}, depend on the antecedent wetness values. At the driest conditions (P4d $= 0$ mm), only the riparian zone is assumed to contribute ($f_{rp} = 1$); at the wettest conditions (P4d$_{\max}$), 90% of the contribution comes from the hillslope and only 10% from the riparian zone (and consequently $f_{hs}(\text{P4d}_{\max}) = 0.9, f_{rp}(\text{P4d}_{\max}) = 0.1$, see Figure S5). In between, we assume an exponential transition as a function of antecedent wetness (a linear function yields very similar results):

$$f_{rp} = \exp\left(\frac{\ln(0.1)}{\text{P4d}_{\max}}\text{P4d}\right),$$

$$f_{hs} = 1 - f_{rp}.$$

We use measured streamflow and antecedent wetness from Trout Beck to determine the groundwater level and the extent of riparian and hillslope mixing, respectively, at each sampling time. We then tested the effect of different concentration profiles (see Figure 4b–e) on resulting streamwater chemistry, and calculated cQ slope values separately for subsets of antecedent wetness, similar to the analysis of the real-world time series data.

The model outcomes show that different combinations of vertical concentration profiles in the riparian area and hillslope can result in changing cQ relationships and streamwater chemistry as functions of antecedent wetness (Figure 4b–e). The interplay between the vertical variation in concentration and average concentration of the vertical profile jointly modulates the cQ and streamwater chemistry response, while the changing contributions from riparian and hillslope areas with wetness make up the final picture. To achieve more positive slopes during dry conditions as observed for nitrate, manganese, and aluminium (Figure 2a), the riparian area needs to have the strongest concentration increase toward the top layers (Figure 4b,c). This is in line with observations regarding nitrate concentrations in a small forested catchment by Blackburn et al. (2017), where fluctuations of the near-stream water table increased the rate of nitrate mineralisation. The interplay of higher and lower concentrations in the riparian zone and hillslopes thus modulates the change in average streamwater chemistry with wetness (e.g., compare Figure 4b,c, which feature similar profile shapes, but different average concentrations of the vertical profiles). The effect of unstructured, patchy heterogeneity (Musolff et al., 2017, Figure 3b) has also been incorporated into the model (Figure 4e) by randomly selecting one of the two hillslope profiles in each time step of the analysis. This results in a more scattered cQ relationship than when considering only structured heterogeneity (right hand side of Figure 3b).

The model is a simplified representation of nature; it cannot capture processes like overland and shallow subsurface flow, and thus cannot include the frequently observed faster routing of precipitation to streamflow during wet conditions (Knapp et al., 2019; Tetzlaff

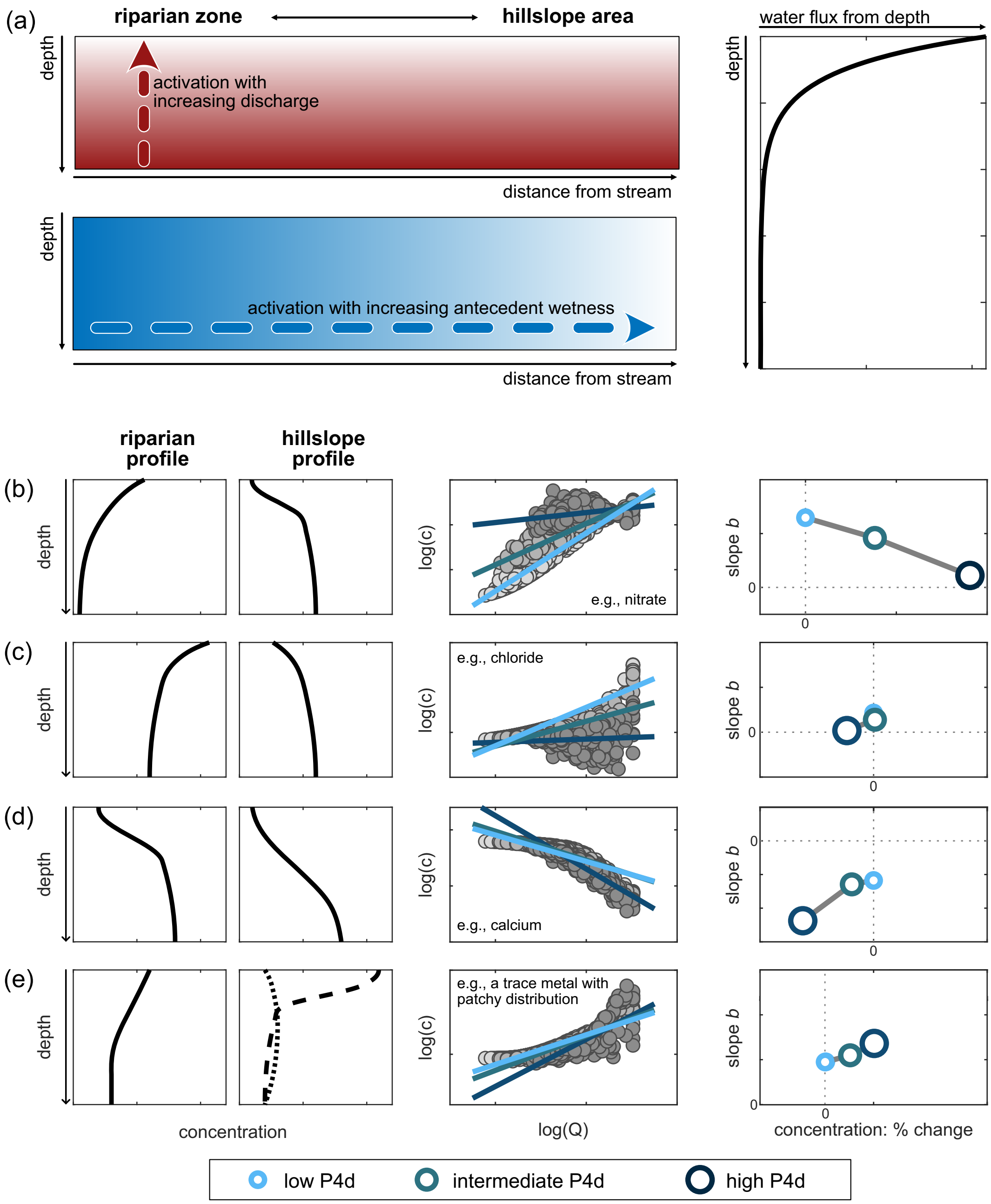

FIGURE 4 Results from the explorative model approach to the interaction of solute source heterogeneity and connectivity. (a) As discharge increases, the subsurface water level rises, activating the vertical profile from bottom to top. Increasing antecedent wetness, conversely, expands the sphere of influence from the riparian zone to the hillslope area. The water flux is assumed to decrease with depth. (b–e) Vertical concentration profiles and average concentrations in the riparian and hillslope areas may differ (with four examples shown in (b–e), which can represent nitrate (b), chloride (c), calcium (d) and a trace metal with patchy distribution in hillslope (e), resulting in changing concentration–discharge relationships as function of antecedent wetness. How antecedent wetness may thus affect cQ slopes and concentration changes is illustrated in the rightmost column.

et al., 2014). Furthermore, it is conceivable that various combinations of vertical profiles may result in similar cQ relationships and average concentration changes. It is thus difficult to conclusively identify soil profiles from cQ slopes and streamwater chemistry. Nevertheless, as Figure 4 shows, the model can capture different cQ patterns and changes in average streamwater chemistry by combining only two vertical profiles modulated by antecedent wetness. Note that artificial noise was neither added to the soil concentration profiles, nor to the discharge or wetness time series. Instead, all scatter observed in the cQ plots of Figure 4 results from the combined influences of connectivity and the spatial heterogeneity in vertical concentration profiles.

In conclusion, we can combine different subsets of cQ relationships at various antecedent conditions to make up an average cQ plot across all data. At the same time, the cQ relationships of the subsets may differ substantially from the result of the overall dataset as shown for nitrate or manganese in Figure 1, due to lateral heterogeneity in vertical concentration profiles. Consequently, the overall, average behaviour is not necessarily suitable to conclude on the actual processes occurring at different points in time. Varying connectivity could thus explain bending long-term cQ relationships observed in previous studies (e.g., Dehaspe et al., 2021; Moatar et al., 2017) and general scatter in cQ relationships. When analysing cQ relationships, discharge is typically used as independent variable to infer solute mobilization, maybe at least in part owing to the ease with which it can be measured. However, it stands to reason that the dependence of concentrations on discharge is at best an indirect one, with discharge summarizing different variations in catchment conditions and seasonal characteristics that likely affect solute mobilization in a more direct manner. Albeit the most straightforward approach, relating concentrations to discharge probably only describes a symptom, rather than a cause. It is the spatial heterogeneity of vertical solute distributions, together with changes in catchment wetness and lateral connectivity, as well as biogeochemistry and redox conditions that modulate solute mobilization, and in turn, the patterns of cQ relationships.

4 | CONCLUSION

This study explored how lateral hydrologic connectivity, approximated by antecedent catchment wetness, affects solute mobilization by quantifying slopes of cQ relationships. As expected, cQ slopes indicate changes in the mixing of groundwater and soil waters, and thus changes in solute mobilization. At low discharge, streamwater is dominated by groundwater, but soil water contributions increase as runoff increases. Contributing soil water originating from different catchment areas with different vertical concentration profiles results in different cQ slopes under different antecedent conditions, as these areas become hydrologically connected to or disconnected from the stream. By knowing which parts of the catchment are connected to the stream, we can improve our understanding of spatial variability in solute distributions and biogeochemical processes. This information can also be used to identify particularly vulnerable points in catchments, and their potential for transmitting contaminants to streams.

To better constrain spatial variations in vertical solute concentration profiles, we need more information on which catchment areas are hydrologically connected to streams under which conditions, and how the concentration profiles of these areas may differ. Past research has shown that the topographic wetness index (TWI; Beven & Kirkby, 1979) can be useful to simulate groundwater levels (Rinderer et al., 2014) and provide information on catchment areas that are connected to streams. In a similar vein, Jencso et al. (2009) showed that the upslope accumulated area—one of the two variables considered in the calculation of TWI—is strongly related to the connectivity of the hillslope and riparian area. While TWI has been helpful in establishing hydrologic connectivity, it needs to integrate with information on spatial distributions of solutes to assess the combined effects of hydrology, source distribution, and biogeochemistry.

Here we considered data from four catchments in the UK with limited rainfall seasonality and only small differences between the 'dry' and 'wet' endmembers. In spite of these relatively limited differences between dry and wet conditions, we do see substantial changes in solute mobilization as catchment connectivity changes. We expect that these changes are even more substantial in other climate regions, for example, the Mediterranean where streams may dry out completely during dry summers, or become stronger if the UK summers become hotter and drier in the future.

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DATA AVAILABILITY STATEMENT

All data used in this study is publicly accessible online or available on request from the relevant agencies. Two of the catchments (Trout Beck and Birnie Burn) are part of the UK Environmental Change Network (http://data.ecn.ac.uk), and hydrometric data and streamwater chemistry were published by Rennie et al. (2015) and Rennie et al. (2017a, 2017b), respectively. Solute date from the Plynlimon catchments Hafren and Hore were published by Neal et al. (2013) through the NERC Environmental Information Data Centre (https://catalogue.ceh.ac.uk), and precipitation data from Carreg Wen AWS and discharge data from Hafren and Hore at Plynlimon have kindly been provided by the UK Centre for Ecology & Hydrology.

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SUPPORTING INFORMATION

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