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Hydrological and hydrochemical drought responses across ten solutes in a pre-alpine headwater catchment

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Abstract. There is growing evidence that droughts affect stream water quality in multiple ways, often degrading it and thereby exacerbating water scarcity. However, our understanding of the hydrological and biochemical processes driving these changes is limited, due to a lack of high-frequency measurements across solutes covering pre-drought, drought and post-drought conditions. In this study, we analyzed the hydrological and hydrochemical responses to drought as compared to pre- and post-drought, in a forested pre-alpine catchment in Switzerland using high-frequency concentration data for ten different solutes. During the dry summer of 2018, discharge and groundwater table depth continued to decrease. The decrease in discharge slowed with increasing dryness, and flow never ceased entirely. Compared to normal summer conditions, a smaller fraction of rainfall converted into discharge, further illustrating the depletion of catchment storages. All solute concentrations exhibited significant breakpoints in their relationships with discharge and groundwater table depth. Mostly, they exhibited more chemostatic patterns at lower discharge (i.e., during drought) than during normal summer conditions. Groundwater table depth served as a complementary indicator for the disconnection of the hydrological and hydrochemical drought response. Overall, this observed divergence can be attributed to the fact that old groundwater was the only source of stream water during the drought, while shallower source areas, such as the catchment soils, were hydrologically disconnected from stream discharge. Our results also highlight the role of biochemical processes that alter the overall availability and mobility of different solutes, such as changes in redox conditions and nutrient uptake rates. In summary, our findings confirm the impact of drought on catchment water quality and demonstrate that the catchment's water quality response to drought cannot be explained by discharge dynamics alone. Rather, a detailed assessment of both hydrological and biochemical processes is necessary to identify the underlying drivers.

1 Introduction

With climate change, the occurrence of severe and prolonged droughts is increasing (Hari et al., 2020; IPCC, 2022). While the impact of droughts on water quantity is obvious, the impact of droughts on water quality is less clear and at risk of being overlooked (Hannah et al., 2022; Li et al., 2024). Particularly when water quantity declines, safeguarding its quality and understanding the mechanisms behind potential water quality degradation becomes critical to avoid further aggravation of water scarcity (van Vliet et al., 2021). To date, evidence is accumulating that droughts can significantly alter water quality, sometimes with detrimental impacts for aquatic ecosystems and water supply (e.g., Dupas et al., 2025; Mosley, 2015; Saavedra et al., 2024; van Vliet et al., 2023; Winter et al., 2023).

Mosley (2015) reviewed the impact of droughts on stream water quality, concluding that these hydro-meteorological extremes affect water quality in different ways. For example, in catchments with significant point sources, nutrient concentrations during drought often increased due to a lack of dilution, whereas in catchments without significant point sources, nutrient concentrations often decreased due to reduced hydrological transport and an increased influence internal retention processes. In another recent review, Van Vliet et al. (2023) demonstrated that droughts and heatwaves mostly lead to a degradation in water quality. In a survey of 182 catchments in Germany, Saavedra et al. (2024) reported pronounced seasonal differences in the way droughts can alter stream water nitrate concentrations during or after a drought event. More recently, Dupas et al. (2025) showed that the effects of drought on nitrate, dissolved organic carbon, and soluble reactive phosphorus concentrations can be predicted from the overall concentration-discharge (C-Q) relationship of a catchment, implying that the underlying mechanisms can be generalized if the specific catchment setting and its solute source locations are generally understood.

C-Q relationships, often assessed via the C-Q slope, allow for an integrated analysis of the dynamics of solute concentrations in a catchment under varying discharge and associated catchment wetness conditions (Godsey et al., 2009; Musolff et al., 2017). A continuous increase or decrease in solute concentrations with decreasing discharge enables us to assess whether, as the catchment dries up, a solute source becomes hydrologically disconnected (concentrations decrease with decreasing discharge, leading to a positive C-Q slope often termed an "enrichment" pattern) or whether solute sources remain connected but are less diluted by lower-concentrated waters during drier conditions (concentrations increase with decreasing discharge, leading to a negative C-Q slope often termed a "dilution" pattern). Discharge can be interpreted as an indication of the overall wetness state of the catchment, but other proxies for catchment wetness, such as groundwater table depth, might also reveal similar or additional information on a catchment's hydrochemical response to drought, which, to our knowledge, has not been tested so far.

The commonly used C-Q relationship, which is continuously linear in the log-log space, does not always describe the C-Q relationship adequately. Non-linear C-Q relationships have been observed, for example with a breakpoint around median discharge (Moatar et al., 2017) or a divergence from the long-term nitrate C-Q relationship during a severe drought, resulting from a decrease in plant uptake and denitrification in dry soils (Winter et al., 2023). Similarly, Knapp et al. (2020) and Winter et al. (2024) found that C-Q slopes during individual discharge events can significantly diverge from the long-term relationship, hinting at different mechanisms that dominate at different time scales. Consequently, while the direction of the C-Q relationship, integrated over longer time scales, appears to reflect the overall direction of a catchment's drought response, divergence from the long-term relationship might reveal additional processes that become relevant during intensive dry spells.

In the literature, the mechanisms that shape the integrated signal of water quality at a catchment outlet are often divided into hydrological and biochemical processes (Bieroza et al., 2023). Hydrological processes refer to the movement and distribution of water within a catchment, including the mixing of waters from different source areas that may transport different solutes and solute concentrations. These source areas might become activated or deactivated, depending on the wetness state of a catchment. In contrast, biochemical processes refer to chemical and biological transformations of substances in a catchment, which can lead to an increase or decrease in the source strength and distribution of a particular solute, for example via plant or microbial uptake or a change in redox conditions (Knorr, 2013; Winter et al., 2023). Both hydrological and biochemical processes potentially influence water quality during drought. As these processes might occur at short time scales and differ between solutes, high-frequency (i.e., intra-daily) data across different solutes is needed, covering pre- drought, drought and post-drought conditions. Such data is difficult to measure, which limits our capacity to generate a consistent picture of drought responses and the underlying processes.

One exception is the pre-alpine Erlenbach catchment in Switzerland, which is an intensively monitored research catchment, where hydrological parameters and solute concentrations have been measured at a high temporal resolution (i.e., hourly or half-hourly) for several years, including during the exceptionally dry summer of 2018 (e.g., Bakke et al., 2020; von Freyberg et al., 2017). This unique set-up allows us to compare stream water quality under normal and drought conditions across solutes that stem from different source areas and that are sensitive to different biochemical processes. Therewith, we can finally shed some light on the underlying mechanisms that shape the integrated signal of drought effects on stream water quality at the catchment outlet.

Relying on this wealth of data from the Erlenbach catchment, we ask the following research question: How did the summer drought in 2018 affect stream water quality at the outlet of the Erlenbach catchment as compared to closer-to-average summer periods in 2017, 2019 and 2020? We hypothesize that the extrapolated C-Q slope from normal flow conditions is an approximate predictor of solute concentrations under drought, as similarly reported by Dupas et al. (2025), meaning that under drought, solutes that normally show an enrichment pattern decrease in concentration and solutes that normally show a dilution pattern increase in concentration. We further test the relationship between solute concentrations and groundwater table depth (C-gw) as a complementary indicator for the hydrochemical catchment response to declining catchment wetness. Moreover, while we expect the general direction of the C-Q and C-gw slope to hold true even under drought, we expect that divergences from these C-Q and C-gw relationships occur, for example, in the form of a change in slope, revealing additional insights into the hydrological and biochemical processes shaping water quality under drought.

2 Material and Methods

We analysed the effects of drought on water quality for ten solutes, namely, calcium (Ca), magnesium (Mg), sulfate (SO4), potassium (K), nitrate (NO3), chloride (Cl), iron (Fe), chromium (Cr), manganese (Mn) and strontium (Sr), in the intensively monitored Erlenbach catchment (e.g., von Freyberg et al., 2017, 2018; Knapp et al., 2020, 2024). This pre-alpine headwater catchment is located at 1100-1655 m. a. s. l., with steep terrain and a drainage area of 0.7 km². It is a relatively wet catchment, with a mean annual precipitation of around 2266 mm yr−1 (over the period 1969–2019), with monthly maxima and minima in

June and October, respectively (van Meerveld et al., 2018; Stähli et al., 2021, Figure S1). The dominant geology is flysch, consisting of heterogeneous sandstone and shale layers, resulting in groundwater chemistry dominated by Ca, Mg and hydrogen carbonate (HCO3). Soils are characterized by comparably low permeability due to a high clay content of the flysch geology (von Freyberg et al., 2018). Land use in the Erlenbach catchment is predominantly forest. Around 30% of the catchment area are wet meadows that are prone to saturation and surface discharge, which are widely distributed across the catchment with the highest concentration in the upstream part (von Freyberg et al., 2018). Detailed maps and further information are available in von Freyberg et al. (2018).

The Erlenbach catchment has a long monitoring history and an exceptional wealth of hydro-meteorological and chemical data (von Freyberg et al., 2017; Knapp et al., 2024; Stähli et al., 2021). Here we analyze time series of discharge and precipitation data measured at the catchment outlet and a nearby meteorological station, as well as groundwater table depth below surface at an observation well located in the upstream area of the catchment. We also analyze solute concentrations of Ca, Mg, SO4, K, NO3, Cl, Fe, Cr, Mn and Sr. These concentrations were measured at hourly to half-hourly intervals from 2017 to 2020, so that we restrict all analyses to this specific period. More details on solute concentration data from the Erlenbach catchment are available in Knapp et al. (2020).

2.1 Hydro-meteorological drought characterization

The summer of 2018 was exceptionally dry in the Erlenbach catchment, with lower discharge than the preceding and subsequent years (Figure 1b). To delineate this drought event, we chose a fixed threshold method (Hisdal et al., 2024) using the 10th percentile of the summer discharge (June-August in the years 2012 - 2020) which equated to 0.01 mm h^{-1} at the Erlenbach (Figure 1a). Using this criterion, the drought event started on 26 June 2018 and ended on 13 August 2018. The minimum discharge was 0.001 mm/h on 8 August 2018. Due to a data gap for most solute concentrations at the end of June, and for simplicity reasons, we set the period of the drought to 1 July – 13 August 2018 for all subsequent analyses. The recovery period was defined as starting immediately after the drought event and ending at the end of August, when discharge had returned to 'normal' levels.

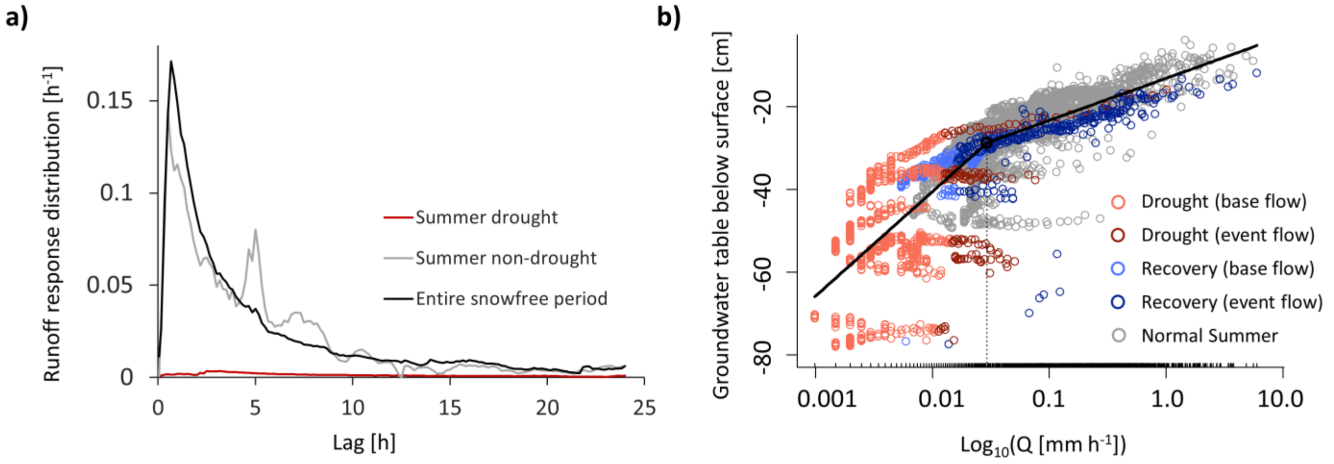

Figure 1: a) Rainfall-discharge behavior during different periods in the Erlenbach catchment, calculated from the Ensemble Rainfall-Discharge Analysis, with the runoff response peaks at a lag time of 0.5 h for summer non-drought, 0.7 h for the entire snow free period, and 3.2 h for the summer drought. Panel b) depicts the relationship between groundwater table depth and log$_{10}$-transformed stream discharge (Q) with a breakpoint between dry and normal-to-wet conditions.

Obviously, there were very few precipitation events during the drought. Nevertheless, we identified five events, which became particularly visible when discharge was plotted on a logarithmic scale, as in Figure 1a. The groundwater table depth reached comparatively low levels (i.e. deeper groundwater table depths), reaching down to -78.2 cm towards the end of the drought period.

2.2 Discharge event identification and characterization

We identified discharge events in the summer period by considering events that started after 30 June and ended before 1 September for the years 2017 - 2020. Events started when discharge increased continuously after a precipitation event and ended when discharge stabilized or when a new event started. We took care to include small events, which are often overlooked in automated event selection because they are more difficult to separate from scatter. Notably, some of these small events occurred during the drought and apparently affected the water quality of the river, so we considered it important to identify these comparably small events during all summer periods. To ensure clear identification and separation, we manually checked all events and corrected their start and end dates where necessary. Overall, we identified 63 events, out of which 6-27 events had no or incomplete concentration measurements, depending on the solute, and were therefore discarded (Table S1).

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2.3 Characterization of the catchment response to drought

To characterize the hydrological response of the catchment to precipitation during drought and normal summer conditions, we calculated the rainfall-discharge behavior using Ensemble Rainfall-Runoff Analysis (ERRA; Kirchner, 2024). ERRA is a data-driven approach based on nonlinear deconvolution that allows us to quantify the rainfall-runoff behavior in a nonlinear, nonstationary, and spatially heterogeneous way, which better reflects real-world behavior than previous approaches (Kirchner, 2024). To compare the hydrological response during the drought with other summer periods, we calculated the rainfall-runoff behavior jointly for the summer periods of 2017, 2019 and 2020, and contrasted it with the behavior during the drought period in 2018. For a broader comparison, we also applied ERRA to the entire snow-free period for the same years.

To compare different metrics for catchment wetness, we evaluated the relationship between $\log_{10}$-transformed discharge, measured at the catchment outlet, and groundwater table depth, measured at an observation well in the upstream area of the catchment. We tested this relationship for a significant breakpoint across all measurements between the years 2017 and 2019 (due to a gap in groundwater table depth data in 2020) using the segmented package in R (Fasola et al., 2018). Breakpoint analysis enables the detection of a statistically significant and abrupt change in slope through the use of moving linear regression analysis.

To characterize the solute concentration responses during drought and normal summer conditions, we calculated the concentration-discharge (C-Q) relationship across summer periods for all 10 solutes, using the commonly applied log-log form of the power-law C-Q relationship (Burns et al., 2019; Godsey et al., 2009; Musolff et al., 2015):

$$Log_{10}(C_i) = a_i + b_i \cdot log_{10}(Q) \qquad (1),$$

Where C is the concentration of solute i, Q is discharge, and a and b are fitted parameters representing the intercept and the C-Q slope, respectively. In particular, the C-Q slope (i.e., parameter b) is commonly used to characterize C-Q relationships, indicating enrichment ($b > 0$), dilution ($b < 0$) or constant patterns ($b \approx 0$) (Musolff et al., 2017).

Similar to groundwater depth and discharge, we analyzed the C-Q relationship across all summer periods, including the drought period, for a significant breakpoint. If a significant breakpoint was identified, we extracted the C-Q slopes above and below the breakpoint, instead of one slope for the entire time series. Additionally we extracted individual C-Q slopes for all discharge events.

As a complementary approach to the C-Q relationship, we analyzed the relationship between solute concentrations and groundwater table depth, which we refer to as the C-gw relationship. We analyzed this relationship in a similar way as the C-Q relationship (e.g., Musolff et al., 2015; Thompson et al., 2011), except that we did not $\log_{10}$-transform groundwater depth values (i.e. assuming exponential rather than power-law behavior):

$$Log_{10}(C) = a_{gw,i} + b_{gw,i} \cdot gw \qquad (2)$$

Where a_{gw} and b_{gw} are fitted parameters representing the intercept and the C-gw slope, respectively.

3 Results

3.1 Hydrological catchment response

Results from ERRA indicate that during normal summer conditions, the fraction of precipitation that converted to discharge was similar to that of the typical snow-free period (compare the black and grey lines in Figure 1a). During the dry period in 2018, the discharge response showed a considerably lower fraction of precipitation that converted to discharge (the red distribution in Figure 1a), meaning the response during the drought period was much weaker than during other times.
Comparing discharge and groundwater table depth reveals a significant breakpoint towards dry conditions, when discharge fell below 0.03 ± 0.02 mm h^{-1} and the groundwater table fell below -29.4 ± 3.6 cm. During normal to wet conditions, discharge and groundwater table depth show a positive relationship, showing a simultaneous increase in discharge and groundwater table with increasing catchment wetness. Precipitation events induce a rapid response in discharge as well as in the groundwater table. In contrast, during dry conditions beyond the breakpoint, the groundwater table gradually declines while discharge levels do not drop much further. Additionally, discharge continues to respond to precipitation events, while the groundwater table lacks such short-term responses and appears to be largely decoupled from the discharge dynamics.

3.2 Water quality response

Time series of solute concentrations in discharge and precipitation for all summer periods show a deviation between drought (i.e., 2018) and normal-to-wet conditions (Figure 2). Several solutes (i.e. NO_3, Cl, K, Ca, Mg, SO_4 and Sr) show significantly higher concentrations during drought compared to non-drought conditions (tested using the Kruskal Wallis test with Bonferroni correction and a significance level of 0.05, see Figure S2), while Fe, Mn and Cr concentrations during drought were significantly lower. In most cases, the main difference is the lack of increasing or decreasing concentrations during discharge peaks, which were obviously rare during drought (Figure 2). However, for NO_3, Cl, SO_4 and partly K, base flow concentrations were also considerably higher than during the other summer periods. Solute concentrations in precipitation were generally below or in the range of the streamflow concentrations.
Streamwater solute concentrations recovered surprisingly quickly during the recovery period. With the first events of the recovery period in the second half of August, the anomalously high concentrations decreased and the anomalously low concentrations increased again, reaching approximately their pre-drought levels, all within only two weeks.

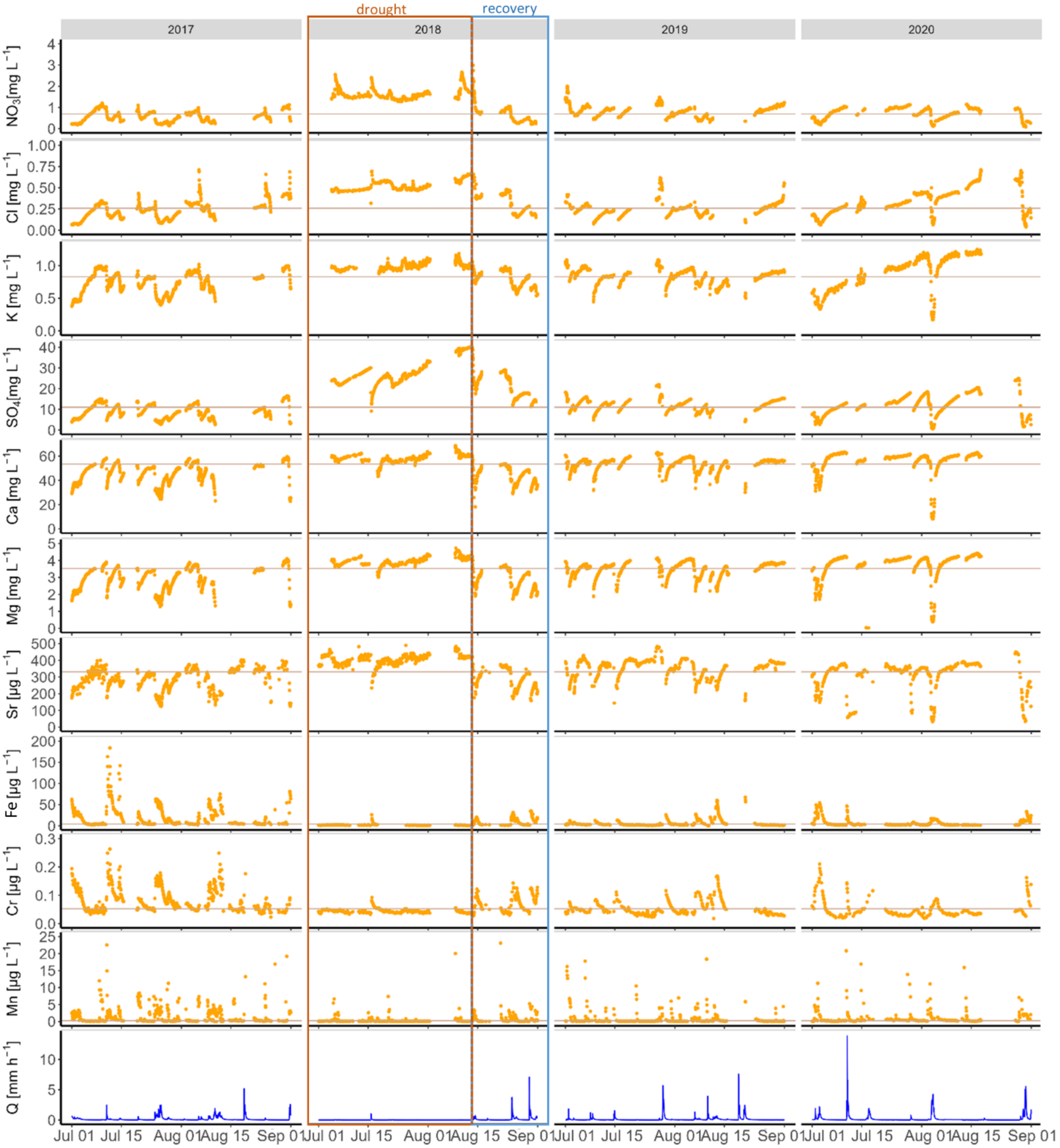

Figure 2: Time series of solute concentrations in stream discharge (orange) and discharge rates (blue) of the summer period (July – August) in the Erlenbach catchment, measured at the catchment outlet. 205

The C-Q relationships show overall negative slopes for NO_3, Cl, K, Ca, Mg, SO_4 and Sr and positive slopes for Fe, Cr and Mn. Moreover, all C-Q relationships showed a significant breakpoint at a discharge value around 0.03 ± 0.02 mm h^{-1} (Table 1), which is a similar breakpoint as the one between stream discharge and groundwater table depth (Figure 3, Figure 1b). Moreover, the discharge value at the breakpoint is close to the arbitrarily chosen threshold 0.01 mm/h for drought identification. At the low-flow side of the breakpoint (i.e., during the drought), the C-Q slopes of all solutes except SO_4, were considerably closer to zero compared to non-drought conditions. For SO_4 the C-Q slope became steeper (i.e., more negative) during low flow. The C-Q relationships for Fe and Mn are the only ones where the low-flow C-Q slopes were clearly above zero (Table 1); however, they were still considerably lower than their respective high-flow C-Q slopes. Particularly Mn concentrations showed high variability, with several peaks during discharge events but also during base flow conditions, which is visible in the time series and also reflected in the residuals of the C-Q and C-gw relationship (Fig. 2 – 4).

Except for SO_4, the C-Q relationships during the recovery period do not differ from the normal behavior during normal conditions at the high-flow site of the breakpoint. For SO_4, concentrations during the recovery period in 2018 appear to be higher than concentrations during similar discharge conditions in the other years (2017, 2019 and 2020).

For NO_3 and Cl, C-Q slopes from individual discharge events diverged from the long-term relationship, with the event-specific slopes ranging around zero (Table 1). Notably, event-specific CQ slopes partly changed their direction from average negative slopes during normal conditions (-0.06 and -0.09, Table 1) to average positive ones during the drought for NO_3 (0.10) and to drought CQ slopes around zero for Cl (0.00). For K, event-specific CQ slopes during the drought did not change direction but were, in average, closer to zero than those during normal conditions (Table 1).

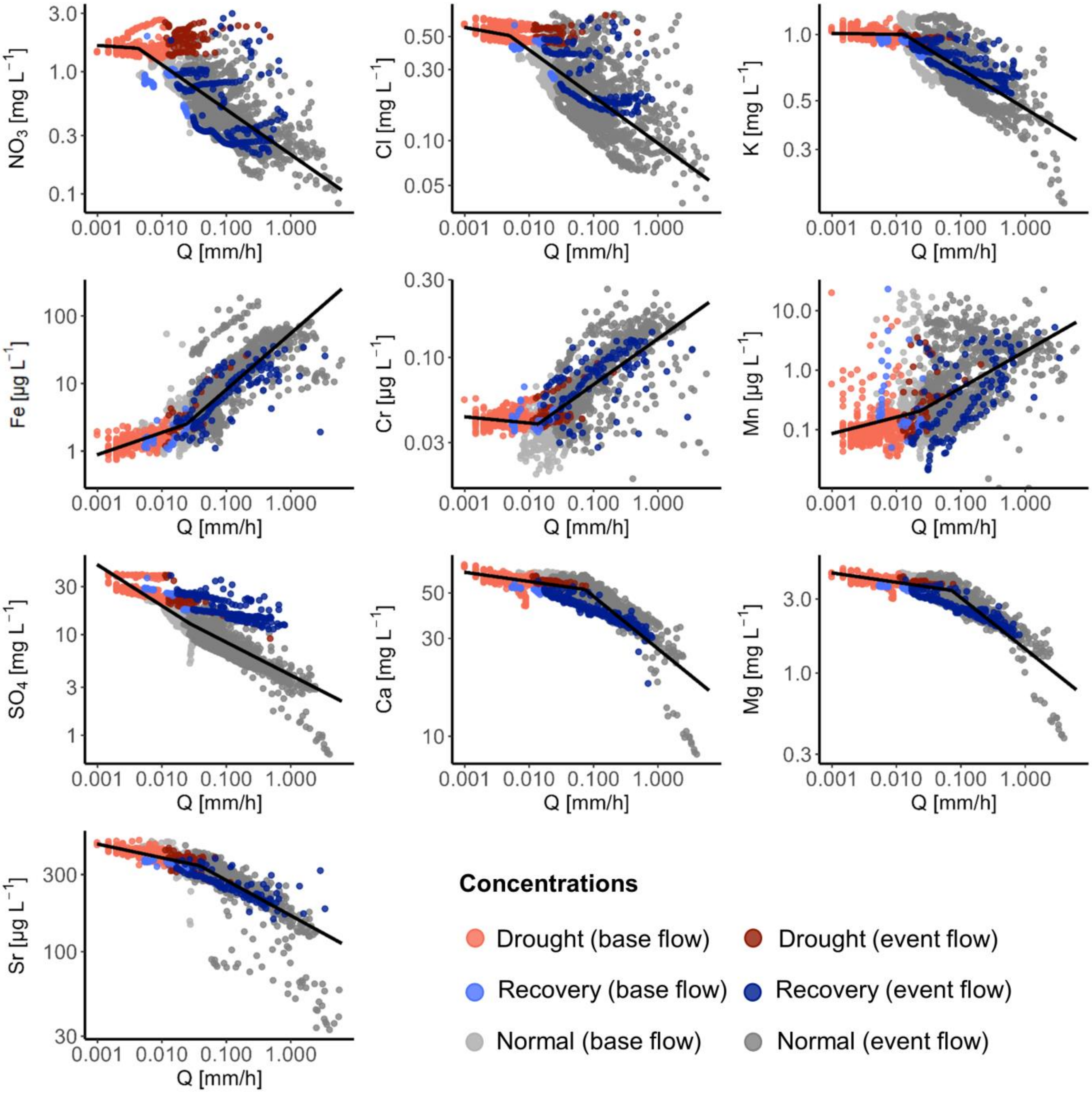

Figure 3: C-Q relationship across all solutes. Colors indicating the flow and hydro-meteorological conditions.

Table 1: Concentration-Discharge (C-Q) relationships in the Erlenbach catchment, including a breakpoint between low and high flow conditions and an additional breakpoint between groundwater table depth (gwd) and solute

concentrations, C-Q slopes with confidence intervals (CI) before and after the breakpoint, and average C-Q slopes across discharge events during different hydro-meteorological conditions, with the number of events (n).

Solute	Breakpoint	CQ slope	CI (95%)		C-Q slope	CI (95%)		Average event slope ± sd					
	Q [mm h^{-1}]	low flow	lower	upper	high flow	upper	lower	Normal	(n)	Drought	(n)	Recovery	(n)
Ca	0.073	-0.04	-0.05	-0.04	-0.26	-0.26	-0.25	-0.09 ± 0.09	(39)	-0.02 ± 0.01	(4)	-0.08 ± 0.06	(3)
Mg	0.072	-0.06	-0.07	-0.05	-0.33	-0.34	-0.32	-0.11 ± 0.12	(39)	-0.02 ± 0.01	(4)	-0.09 ± 0.08	(3)
SO_4	0.028	-0.41	-0.42	-0.39	-0.33	-0.34	-0.31	-0.19 ± 0.17	(57)	-0.07 ± 0.07	(5)	-0.09 ± 0.05	(3)
NO_3	0.004	-0.04	-0.16	0.09	-0.37	-0.38	-0.36	-0.08 ± 0.18	(52)	0.10 ± 0.09	(5)	-0.04 ± 0.02	(2)
Cl	0.005	-0.01	-0.20	0.04	-0.31	-0.33	-0.30	-0.06 ± 0.18	(45)	0.00 ± 0.03	(5)	0.01 ± 0.02	(2)
K	0.013	0.00	-0.02	0.01	-0.18	-0.18	-0.17	-0.07 ± 0.10	(47)	-0.01 ± 0.02	(4)	-0.02 ± 0.02	(2)
Cr	0.014	-0.04	-0.09	0.01	0.28	0.27	0.30	0.20 ± 0.24	(36)	0.07 ± 0.09	(5)	0.11 ± 0.12	(3)
Fe	0.024	0.33	0.28	0.38	0.95	0.90	1.00	0.41 ± 0.40	(41)	0.31 ± 0.26	(4)	0.39 ± 0.26	(3)
Sr	0.039	-0.08	-0.09	-0.08	-0.22	-0.24	-0.20	-0.15 ± 0.15	(40)	-0.05 ± 0.05	(5)	-0.08 ± 0.06	(3)
Mn	0.023	0.28	0.18	0.37	0.62	0.57	0.67	1.45 ± 1.85	(40)	0.62 ± 0.17	(5)	0.67 ± 0.10	(3)

The C-gw relationships showed a very similar pattern to the C-Q relationships (Figure 4), but with a more pronounced change in slope before and breakpoint, resulting from the continuous decrease of the groundwater table even under very dry conditions (Figure 1b). All solute concentrations showed a significant breakpoint around a groundwater table depth of -32.4 cm (± 3.6 cm) (see Table 1). These breakpoints were again in a similar range as the breakpoint between discharge and groundwater table depth at -29.4 ± 0.2 cm.

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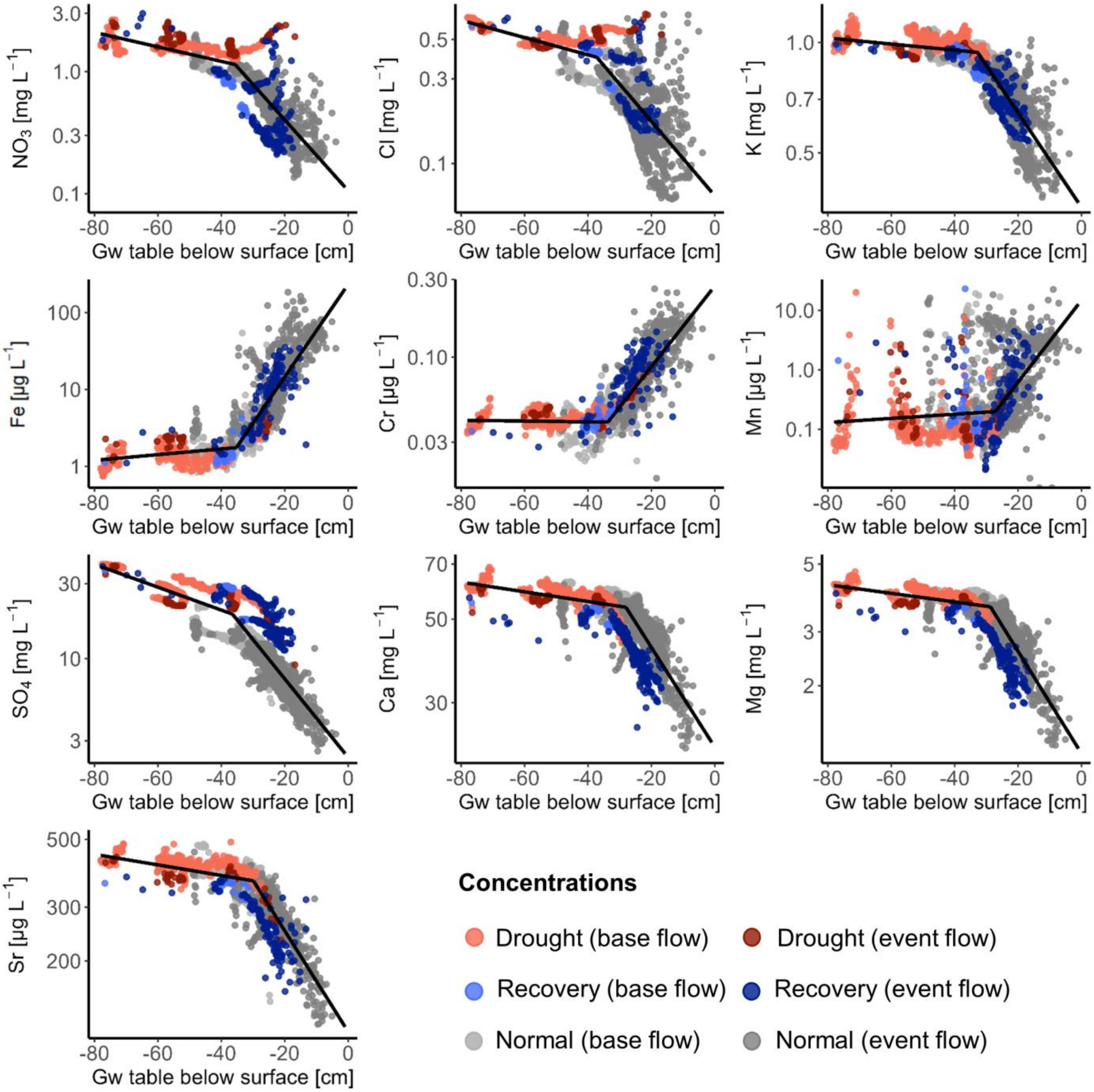

Figure 4: The concentration-groundwater table (C-gw) relationship across all solutes. Colors indicating the flow and 245 **hydro-meteorological conditions.**

3 Discussion

Results from the Erlenbach catchment show how the pronounced summer drought in 2018 affected discharge and in-stream concentrations of all ten solutes measured during both base flow conditions and discharge events. They confirm that droughts not only affect streamflow but also its quality. However, the results also indicate a divergence between the hydrological and hydrochemical catchment response to drought when conditions become very dry, as indicated by the significant breakpoints in the C-Q and C-gw relationships across all solutes. The drought period was followed by a rapid recovery during which solute concentrations - except for SO_4 - recovered to pre-drought concentrations within only a few days. This rapid recovery was likely supported by the steep slopes, shallow soils, and a small catchment size, characteristics that make a catchment particularly responsive to changes in hydro-meteorological conditions (Hrachowitz et al., 2009). These fast responses allowed us to analyze the full drought impact, including the recovery, within a single summer season. In the following, we discuss the divergence between the hydrological and hydrochemical catchment responses and how the interplay of hydrological and solute-specific biochemical processes can explain the observed dynamics of water quality under drought.

4.1 Hydrological catchment response to drought

Results from ERRA revealed that during the drought, a considerably lower fraction of precipitation was converted into discharge, which can be explained by depleted catchment storages from a lack of precipitation, together with continuous evapotranspiration. This storage depletion was also mirrored in the comparably low groundwater table (comp. Figure 1a). A large fraction of precipitation that fell during the drought went into the empty catchment storages so that only a small fraction remained to become stream discharge, at least within the time scale of the drought. However, the small amount of precipitation was apparently not enough to considerably lift the groundwater table. Looking at the relationship between stream discharge and groundwater table depth, we could show that individual precipitation events caused a short-term response in discharge, but – with the exception of the largest drought event – triggered no changes in groundwater table depth. Additionally, towards dry conditions, the groundwater table depth continued to decline, whereas discharge only decreased at a much lower rate than during wetter conditions. This indicates two things: First, discharge in the Erlenbach catchment keeps being sustained by groundwater with only a very slowly declining rate, even when storages in other parts of the catchment continue to dry out. Note here that, while discharge can be considered an integrated signal of the catchment, the groundwater table depth rather represents a point measurement within a heterogeneous landscape. Nevertheless, the groundwater depth can be interpreted as a general indication of catchment storages drying out even when discharge remains constant, yielding additional information to that of discharge, particularly during severe drought. Second, beyond a certain point of catchment dryness, small individual rain events apparently activate shallow catchment layers but are decoupled from deeper layers, while only larger events cause a considerable reactivation of deeper catchment layers. In conclusion, during drought, catchment storages are largely depleted and streamflow mainly consists of old groundwater. Some short-term flushing from very shallow sources occurs during rain events, but there is almost no activation of intermediate catchment layers, such as the soil layer.

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4.2 Hydrochemical catchment response to drought driven by hydrological and biochemical processes

The direction of change in solute concentrations during drought (i.e., increase or decrease) approximately followed the long-term C-Q relationship, as also observed by Dupas et al. (2025) for 126 catchments across Brittany. Specifically, solutes with higher concentrations in the catchments' groundwater than in average streamflow (NO_3, Cl, K, Ca, Mg, SO_4 and Sr; see Table S2) showed increased streamflow concentrations during the drought. From these, NO_3, Cl and K showed different C-Q relationships during discharge events as compared to the long-term relationship, pointing at additional shallow sources within the catchment that become activated during discharge events. By contrast, solutes with lower concentrations in groundwater than in the soil (i.e., Fe, Mn and Cr; see Table S2) were comparably low (comp. Figure 2). This is in line with the hydrological catchment response described above: As discharge during the drought was mainly composed of groundwater, solutes with high concentrations in the groundwater were comparably high and not diluted with water from other sources, while those solutes with higher concentrations in shallower soil layers were comparably low as their main source areas were hydrologically disconnected from the stream network. Besides the described vertical gradient in hydrological connectivity (i.e., shallow versus deep layers), the horizontal contraction of the stream network under drying conditions likely also plays a role in reducing the hydrological connectivity of soils across the catchment (van Meerveld et al., 2019).

The observed breakpoints in the C-Q and C-gw relationships reveal a striking divergence between the hydrological and the hydrochemical catchment response during drought. While both the groundwater table and discharge declined continuously below the breakpoint, solute concentrations leveled off and remained comparably stable (comp. Figure 3, 4 and Table 1). We argue that this change in the relationship between solutes and flow occurs as soon as discharge is fed almost exclusively by deeper groundwater layers and soils are almost entirely disconnected. This assumption is supported by the fact that the breakpoint between discharge and groundwater table depth occurs at the same point as those between solutes and groundwater or discharge. By contrast, at increasing catchment wetness, increasing discharge volumes coincided with an increasing contribution of water from shallower (soil) layers, transporting solutes from these areas and thereby causing chemodynamic patterns (if groundwater and soil water have different concentrations). The drought response thus likely heavily depends on the lateral and vertical distribution of solutes within the catchment (Knapp et al., 2022). In summary, under drought, when shallower sources are disconnected from the stream network, solute concentrations in the stream approach groundwater concentrations without much further variability, even when streamflow declines further. While here we rely on groundwater and soil water concentration data from the neighboring Studibach catchment to confirm our assumptions, spatially distributed measurements from the Erlenbach catchment would have been the desirable choice. We recommend that future studies on the impact of hydro-meteorological extremes on water quality should make sure to sample all these different waters at a reasonable spatial and temporal resolution.

In addition to the hydrological processes of solute transport and mixing from different source areas, as explained above, the drying of a catchment can impact different biochemical processes that influence the availability and mobility of different solutes. The decline in groundwater tables and consequent depletion of catchment storages can cause a change in redox conditions by aerating zones that have been saturated and anaerobic for a long time (e.g., Knorr, 2013; Škerlep et al., 2023). Furthermore, dry conditions can impact plants and microbial communities, thereby reducing their uptake rates (Cramer et al., 2009; RIVM, 2021). However, these biochemical processes are strongly solute-specific. In the following, we explain the hydrologically and biochemically driven solute-specific responses in more detail, with the solutes grouped according to their dominant occurrence either in the groundwater, in the soil water or in different source areas, similar to the categorization made by Knapp et al. (2020).

4.3 Calcium, magnesium and sulfate

4.3.1 Hydrological processes shaping the drought response of calcium, magnesium, strontium and sulfate concentrations

The comparably high concentration in Ca, Mg, Sr and SO_4 during drought can be explained by their geogenic origin, which makes groundwater their main source, in line with the general results in Knapp et al. (2020). Individual precipitation events occurring during the drought period reconnected shallower flow paths and thus caused dilution patterns in all these solute concentrations without exception (comp. Table 1).

4.3.2 Biochemical processes shaping the drought response of sulfate concentrations

From all solutes with a dominantly geogenic origin, concentrations of the redox-sensitive SO_4 stood out as they continued to increase as conditions became drier, unlike concentrations of other solutes, which appeared to level off. In contrast to these other solutes, SO_4 concentrations exhibited a steeper C-Q slope at low flow rates before the breakpoint than at higher flows, and SO_4 concentrations remained high throughout the recovery period. Comparing the redox-sensitive SO_4 to the non-redox-sensitive Mg concentrations revealed a strong concentration-concentration relationship during normal conditions, but a pronounced divergence from that relationship during the drought (SO_4 concentrations were 14.1 ± 5.0 mg L^{-1} higher than expected from the SO_4-Mg relationship, Fig. 5).

Such an increase in SO_4 concentrations during drought could potentially be attributed to higher SO_4 concentrations in deeper groundwater layers (e.g. due to longer weathering or simply a higher availability of SO_4 from the highly heterogeneous flysch layers; Kiewiet et al., 2019). However, this alone would not explain why the recovery of SO_4 concentrations took longer than the hydrological recovery and the recovery of any of the other solutes observed. Instead, Knorr (2013) argues that the change in redox conditions towards oxidizing conditions in a drying subsurface can release SO_4, for example via oxidation of pyrite, which is potentially available in flysch (Kiewiet et al., 2019). The change from anaerobic to aerobic subsurface conditions during drought could increase the overall availability of SO_4 and thus explain the increase in SO_4 concentrations beyond the drought event itself.

Such increases in SO_4 concentrations in response to drought are not restricted to the Erlenbach catchment, but have been found across different catchments (e.g., Devito and Hill, 1997; Knorr, 2013; Mosley, 2015). Besides the oxidation of geogenic S, they can also stem from the (re-)oxidation of organic sulfur in the soil layer (Laudon et al., 2021; Ledesma et al., 2016; Škerlep et al., 2023). Still, the particularly high concentrations during base flow and the dilution pattern during events, when organic soil layers become hydrologically connected, suggest that SO_4 concentrations in the Erlenbach catchment are dominantly of geogenic sources.

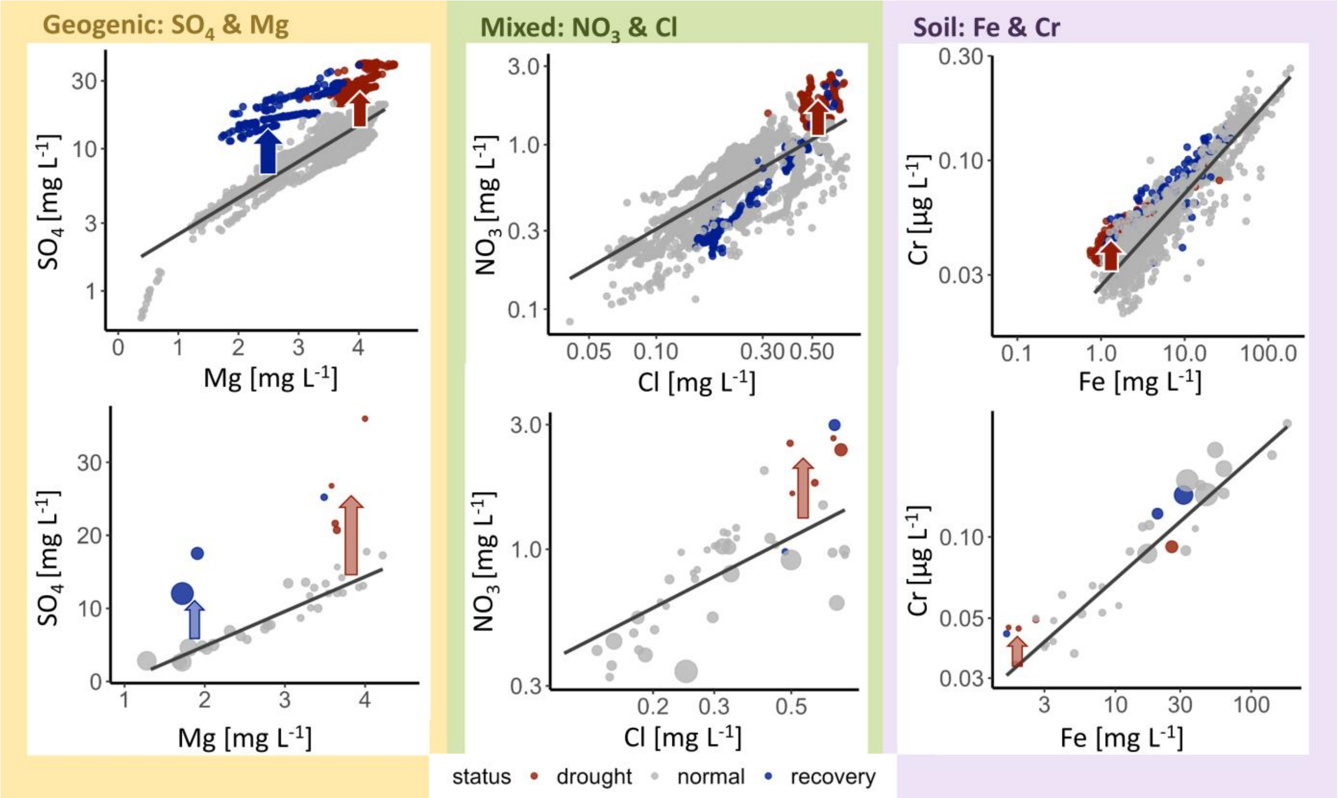

Figure 5: Example concentration-concentration (C-C) relationships with $\log_{10}$-transformed x- and y-axis

4.4 Nitrate, chloride and potassium

4.4.1 Hydrological processes shaping the drought response of nitrate, chloride and potassium concentrations

For NO_3, Cl and to a minor extent also for K, the C-Q relationship was a not as consistent across time scales as for the other solutes: while the long-term C-Q relationship showed a dilution pattern (i.e., negative C-Q slope), individual events showed enrichment patterns or less pronounced dilution (as was the case for K). This divergence in C-Q relationship indicates that there are additional shallow sources that are mobilized during discharge events. Such divergences observed between the long-term and the event-specific C-Q relationships have also been reported, for the entire snow-free period by Knapp et al. (2020) or for NO_3 concentration patterns across 28 catchment in the U.S. by Winter et al. (2023).

As shown in Knapp et al. (2020) and Kiewiet et al. (2019), NO_3, Cl and K concentrations in the groundwater of the region surrounding the Erlenbach catchment are higher than those in soil water or average streamflow (Table S2), which explains their overall increase during dry conditions. Nonetheless, by assessing the output-input-flux index, Knapp et al. (2020) could show that specifically for NO_3 and Cl, atmospheric deposition forms a considerable input to the catchment. This atmospheric deposition can percolate to the groundwater, but it can also accumulate at the catchment surface or in very shallow layers, where it is evapoconcentrated and flushed into the stream during the next precipitation event. Consequently, these atmospheric sources can induce enrichment patterns during individual discharge events that contrast the long-term dilution pattern and make the overall pattern of NO_3 and Cl more variable than those observed for solutes like Ca and Mg that predominantly originate from geogenic sources and show consistent dilution patterns across time scales. Nevertheless, particularly for NO_3, additional biochemical processes might play a role and further explain its more pronounced enrichment patterns, which we discuss in Section 4.4.2.

The export patterns of K fall somewhat in-between those of the dominantly geogenic solutes (Section 4.3) and those of mixed sources (NO_3 and Cl). This can be explained by K stemming mainly from bedrock weathering in the Erlenbach catchment (Knapp et al., 2020), while smaller amounts might also originate from shallow sources, such as decomposed vegetation that had taken up K as a nutrient (Chaudhuri et al., 2007).

4.4.2 Biochemical processes shaping the drought response of nitrate concentrations

NO_3 is redox sensitive and an important nutrient that is taken up by plants and other organisms (Cramer et al., 2009; Haynes, 1986). Consequently, its source strength in a catchment can be affected by different biochemical processes. Under normal conditions, event-specific slopes of both NO_3 and Cl vary around zero, consistent with their similar sources in the catchment (Knapp et al., 2020). During the drought period, event-specific C-Q slopes of Cl remained close to zero, whereas those of Nitrate were more positive, indicating such a change in the source strength and the importance of biochemical processes. The direct comparison to Cl concentrations confirms the general alignment of the two solutes, but also the slightly higher NO_3 concentrations during the drought, which are 0.6 ± 0.2 mg L^{-1} higher than expected from the NO_3-Cl relationship (Figure 5). Similarly, peak concentrations during discharge events during the drought are higher for NO_3 than expected from the general NO_3-Cl relationship (0.8 ± 0.4 mg L^{-1}), as compared to normal residuals around ± 0.3 mg L^{-1}. Winter et al. (2023) demonstrated that a decrease in plant uptake and denitrification rates during drought and a rapid mineralization with rewetting can lead to a higher availability of NO_3 in a catchment and consequently to higher NO_3 concentrations at subsequent high flows, depending on the catchment-specific transit times. Consequently, we argue that such processes could also have occurred in the fast responding Erlenbach catchment, leading to a higher accumulation of shallow NO_3 sources and a rapid transport into the stream network with precipitation. This flushing effect (also described in Mosley 2015) is likely to be even more pronounced in catchments with higher N inputs, as reported for example for agricultural catchments in Germany and France (Saavedra et al., 2023; Dupas et al., 2025).

4.5 Iron, chrome and manganese

4.5.1 Hydrological processes shaping the drought response of iron, chrome and manganese concentrations

In contrast to the solutes discussed above, Fe, Cr and Mn show consistently positive C-Q slopes across all summer periods and for individual events. This pattern was also reported by Knapp et al. (2020) for the entire snow-free period and is related to soils being the main source of these solutes (see Table S2). Kiewiet et al. (2019) and Knapp et al. (2020) showed that their concentrations in the soil water of the neighboring Studibach catchment exceeded the concentrations in precipitation and groundwater by far.

Therefore, we explain the consistently low concentrations during the drought and the chemostatic C-Q slopes by a hydrological disconnection of the catchment's soils during drought, which hinders the mobilization of solutes originating from these areas. Concentrations of the three metals approached values close to zero (comparable to their concentration in the groundwater). With rewetting (i.e., during the recovery period but also during the one larger discharge event during the drought), soils were reconnected and, thus, Fe, Mn and Cr were mobilized and transported to the stream again, resulting in chemodynamic enrichment patterns.

4.5.2 Biochemical processes shaping the drought response of iron, chrome and manganese concentrations

Fe, Cr and Mn are redox-sensitive metals, which means that their mobility can change depending on the wetness state of the catchment soils in which they occur (e.g., Knorr, 2013; Shiller, 1997; Škerlep et al., 2023). Knorr (2013) showed that reductive dissolution, typical for wet conditions, is an important process for Fe mobilization. Škerlep et al. (2023) showed that Fe and Mn concentrations were strongly positively correlated in a boreal catchment and explained this by the fact that Mn has a higher redox potential than Fe and thus, when Fe(III) is reduced to its more mobile form Fe(II), Mn(III,IV) are very likely to be reduced to the more mobile form of Mn(II) as well. By contrast, Cr is less mobile in its reduced form Cr(III), but more mobile in its oxidized form Cr(VI) (Gorny et al., 2016).

Von Freyberg et al. (2018) described wet meadows in the Erlenbach catchment that are patchily distributed and prone to waterlogging (i.e., reducing conditions) so that they mostly contribute to the event water fraction during discharge events. When these areas dry out, conditions change towards conditions that are more favorable for immobile Fe and Mn and mobile Cr. This might explain the slightly higher Cr concentrations during drought as compared to Fe concentrations (Figure 5). However, as the main source areas for Fe, Mn and Cr are mostly hydrologically disconnected during dry periods, concentrations in the stream are still comparably low for all three metals. During rewetting, redox conditions change again towards conditions that are more favorable for mobile Fe and Mn, and immobile Cr. Still, we observed enrichment for all three metals (i.e., their concentrations in the stream were higher at wetter conditions). There are two potential explanations why this is the case for all three metals despite their differences in mobility under reducing conditions: 1) The hydrological processes of mobilization and transport dominate and thus overwrite the biochemical processes; or 2) the waterlogged areas dry out at a regular basis during summer periods in the Erlenbach catchment, so that even more extreme drought conditions would not

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have strong additional effects on the redox conditions in these areas. In either case, redox conditions would still play an important role in determining the overall amount of mobile ions available for hydrological transport during rewetting.

4.6 Transferability of results

The pre-alpine Erlenbach catchment is characterized by a responsive hydrological regime, meaning that precipitation events cause a rapid increase in streamflow and have a relatively short recession (von Freyberg et al., 2018). Therefore, changes in stream water quality caused by hydrological processes occur rapidly and exhibit rapid recovery, as well. In our case, this setting has the advantage that we could study the 2018 drought event and its full recovery. However, it should be noted that catchments characterized by longer transit times may respond much more slowly (Benettin et al., 2022; Ehrhardt et al., 2019). Winter et al. (2023) argued that long hydrological transit times in a mesoscale catchment can lead to a delayed drought response and even create hydrological drought legacies that may take years to decades to become measurable in the stream.

Beside the potentially different timing in the catchment's response to drought, we expect patterns in water quality to be transferable to other catchments in terms of the general impact of sources from groundwater or soil compartments, precipitation, or a mixture from these. However, if solutes have different source areas, as might, for example, be the case for NO_3 in agricultural catchments, the specific drought-induced patterns are also likely to differ from the Erlenbach catchment. In contrast to the Erlenbach catchment, many catchments in the literature show an overall enrichment pattern for NO_3, arguably due to high NO_3 concentrations in zones that are relatively shallow or close to the stream network (e.g., Ebeling et al., 2021; Li et al., 2021; Winter et al., 2024).

Finally, the Erlenbach catchment, as a small headwater catchment, allows for better identification of mechanisms than larger catchments, where many processes can overlap and blur the signal of individual processes, making their disentanglement more difficult (Ehrhardt et al., 2019; Winter et al., 2021)

In summary, we argue that the mechanistic understanding derived from the Erlenbach catchment is generalizable, but predictions about solute-specific behavior or the time scales of the catchment's water quality response to drought will need to take into account specific catchment characteristics.

5 Conclusion

By analyzing the exceptionally dry summer of 2018 in the Erlenbach catchment for diverse solutes from different sources, measured at high temporal resolution, we clearly show that drought affects water quality across a wide range of solutes. The general direction of solute concentration change (increase or decrease) aligns with the general direction of the C-Q and C-gw relationships, which can be explained by changes in the hydrological connectivity within the catchment. However, the breakpoints in these relationships revealed a divergence of the hydrological and hydrochemical catchment response during anomalously dry conditions. Under these conditions, groundwater is the predominant source of stream discharge, so that stream concentrations approximate their contributing groundwater concentration and the variability in solute concentrations deceases even when discharge and groundwater table heads decline further as no further mixing occurs. To detect this breakpoint, the groundwater table depth was a useful addition to discharge, as it continued to decrease as the catchment dried up, even when discharge shifted to a much lower rate of recession. The resulting breakpoint between discharge and groundwater table depth was similar to the breakpoint between discharge or groundwater table depth and solute concentrations, thus serving as an indication for the disconnection of shallower (soil) sources.

Code and data availability

Daily discharge and solute concentration data for the Erlenbach catchment can be obtain from Knapp et al. (2024). The original raw data underlying this work be obtained by the authors upon reasonable request.

Supplement link

The link to the supplement will be included by Copernicus, if applicable.

Author contributions

Data curation (JWK and JLAK), Formal Analysis (CW and JWK), Vizualization (CW), Writing (original draft) (CW), writing (review and editing) (all)

Competing interests

At least one of the (co-)authors is a member of the editorial board of Hydrology and Earth System Sciences. Besides that, the authors have no other competing interests to declare.

Disclaimer

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