Exploring Controls on Solute Export Mechanisms~~ for Major Nutrients~~ in Anthropogenically Impacted Catchments in Southern Germany under Climate Change

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Abstract. Global warming is assumed to impact the mobilization, transport, transformation, and storage of ~~major~~ nutrients, impacting the health and functionality of riverine ecosystems. To enhance future water quality management, it is essential to understand potentially changing solute export mechanisms (SEM) in response to climate change. This study examines SEM for ~~major~~ nutrients (NO_3-N, NH_4-N, ~~SRP~~ soluble reactive phosphorus, total phosphorus, and ~~TP),~~ total organic carbon~~ (TOC),~~) and geogenic minerals (Ca^{2+} and Mg^{2+}) across 40 anthropogenically impacted catchments in southern Germany under global warming conditions. The findings reveal seasonal and climate-driven differences in SEM. We identify explanatory controls impacted by climate change by comparing an earlier time period (Period 1: prior to January 1, 2012) with a more recent one (Period 2: after January 1, 2012). Our results indicate an increase in enrichment behaviour for ~~major~~ nutrients~~ and TOC~~, while geogenic solutes exhibit ~~slightly~~a slight but insignificant increase in ~~diluting export mechanisms~~dilution pattern. Climate change has altered solute source distribution and hydrological connectivity, depending on catchment characteristics such as land cover, climate conditions, ~~hydrological indices,~~ soil properties, and geology. Rising temperatures, prolonged heatwaves, and sporadic but intense one-day precipitation events have led to greater internal nutrient accumulation and decreased hydrological connectivity. Consequently, solute transport is primarily intensified at near-surface pathways that are only active sporadically during summer and ~~with~~during rising groundwater levels in autumn and winter. Further, nutrient dilution mechanisms are increasingly overprinted by enrichment-driven mobilization processes. Looking ahead, solute peak concentrations may more frequently exceed regulatory benchmarks for water quality, posing risks to riverine ecosystems and drinking water supplies. These findings should be integrated into future catchment management strategies to mitigate the intensification of enrichment export mechanisms and safeguard water resources.

1 Introduction

Instream water quality responds to hydrological and biogeochemical processes, which are vulnerable to altering climate and landscape boundary conditions over time and space (Musolff et al., 2015). Under changing climatic conditions, solute source distribution and their hydrological connectivity are likely to shift. These alterations can affect solute mobilization and alter the dominant transport pathways of ~~major~~ nutrients. Climate-change-driven factors, such as prolonged droughts and extreme weather patterns, increase the production of decomposable organic material and weaken the connectivity between solute sources and water bodies (e.g., Bieroza et al., 2024; Winter et al., 2020; Yang et al., 2018). These solutes originate from the decomposition of organic material and the weathering of soil and bedrock, dissolving in water and leaching out (Botter et al., 2020; Ebeling et al., 2021; Musolff et al., 2015). Prolonged droughts allow for an increase in nutrient accumulation at the surface by dead organic materials, increasing the mass stored in shallow solute sources (Ainsworth and Long, 2005; Huntington and Wieczorek, 2021; Kukal and Irmak, 2018; Gomez et al., 2011; Greaver et al., 2016; Meixner and Fenn, 2004). Solutes are mobilized via surface runoff, subsurface flow, or groundwater discharge, depending on the spatial distribution of solute sources and the hydrological connectivity. The term solute export mechanisms (SEM) summarizes the processes ~~how~~by which dissolved substances, such as nutrients and minerals, are mobilized and transported from terrestrial systems to downstream water bodies.

Catchments, characterized by different ~~size~~sizes and diverse land uses, encompass a broad spectrum of hydrological and biogeochemical processes. These processes operate across different temporal scales from individual events to seasonal and intra-annual patterns (~~Basu et al., 2010; Evans et al., 2014; Dupas et al., 2016; ~~e.g. Ebeling et al., 2021; Minaudo et al., 2019; Rose et al., 2018; Westphal et al., 2019). This spatial and temporal variability complicates the understanding of the mechanisms driving solute export across different scales (Ebeling et al., 2021; Schuetz et al., 2016). Despite a principal understanding of these processes, the long-term effects of climate change on solute export mechanisms over decades remains poorly documented (Knapp et al., 2020; Dupas et al., 2024). Monitoring these changes is a crucial tool, as extreme weather patterns induced by climate change significantly affect the mobilization and transport pathways of ecosystem-relevant nutrients (Huntington and Wieczorek, 2021; Knapp et al., 2020; Lucas et al., 2023). To address these challenges long-term water quality observations enable the capturing of key processes, and legacy stores (Bieroza et al., 2014; Ebeling et al., 2021; Knapp et al., 2020; Winter et al., 2020). However, understanding how catchment functions, such as solute mobilization and retention, respond to changing conditions, including land use alterations, remains a significant challenge.

The concentration-discharge (cQ) relationship is a valuable tool for tracking solute mobilization and transportation, identifying shifts in solute source distribution across various temporal and spatial scales (e.g. Basu et al., 2010; Dupas et al., 2016; ~~Evans et al., 2014; Minaudo et al., 2019; ~~Moatar et al., 2020; Rose et al., 2018~~; Westphal et al., 2019~~). Solutes from the surface and upper soil layers are mobilized by surface runoff and rapid interflow, causing increasing solute concentrations with rising discharge. This process, defined as enrichment behaviour, is characterized by a positive concentration-discharge relationship (e.g. Basu et al., 2011; Ebeling et al., 2021; ~~Huntington and Wieczorek, 2021; ~~Musolff et al., 2015~~; Pohle et al., 2021; Rose et al., 2018; Thompson et al., 2011).~~). In contrast, when solute sources become depleted during wet periods, respectively rainfall events, solute concentrations decrease with rising discharge, resulting in a negative concentration-discharge relationship, defined as dilution dynamics (Basu et al., 2011; Dupas et al., 2018; Pohle et al., 2021; Thompson et al., 2011). The degree of dependence between solute concentration and discharge is determined by the coevolving coefficient of variation of solute concentrations and discharges, respectively (CV_C/CV_Q). Chemostatic regimes ~~characterise~~are characterised by lower concentration variability compared to discharge variability, whereas chemodynamic behaviour is characterized by a higher concentration variability compared to discharge variability, showing a decoupled concentration discharge relation (Thompson et al., 2011). The combined approach of cQ-relationship and CV_C/CV_Q exhibits temporal variability in solute ~~concentration, where~~concentrations and can identify flow conditions with elevated ~~nutrient~~solute levels. High solute concentrations are linked to eutrophication processes that harm ~~water bodies~~aquatic ecosystems and pose risks to drinking water quality (~~Halliday et al., 2013; ~~Radach et al., 2010; van der Velde et al~~.;~~., 2010; Winter et al., 2020). Therefore, evaluating changes in solute export mechanisms (SEM) due to climate change might improve our ability to predict solute concentration levels and assess future environmental risks for water bodies.

Recent data from southern Germany (KLIWA, 2021) show a significant increase in temperatures, more frequent heatwaves and widespread soil droughts compared to historical climate data from 1931 to 2000 for this region. ~~Additionally~~Comparing periods 1 and 2 reveals a segment of this gradual trend, as demonstrated by the significant changes in temperature and evaporation data (DWD, 2022). This validates the use of both periods for comparing the effects induced by climate change. Further, trends toward lower groundwater levels, reduced spring discharges, and increase in maximum one-day precipitation have been observed (KLIWA, 2021). Warmer and drier climate lowers the water table and extends residence times in the subsurface, leading to increased concentrations of geogenic minerals in groundwater (Botter et al., 2020; Li et al., 2022; Musolff et al., 2015). Hence, these altering conditions might affect mobilization of ~~major ~~nutrients and geogenic minerals in south-German catchments as well.

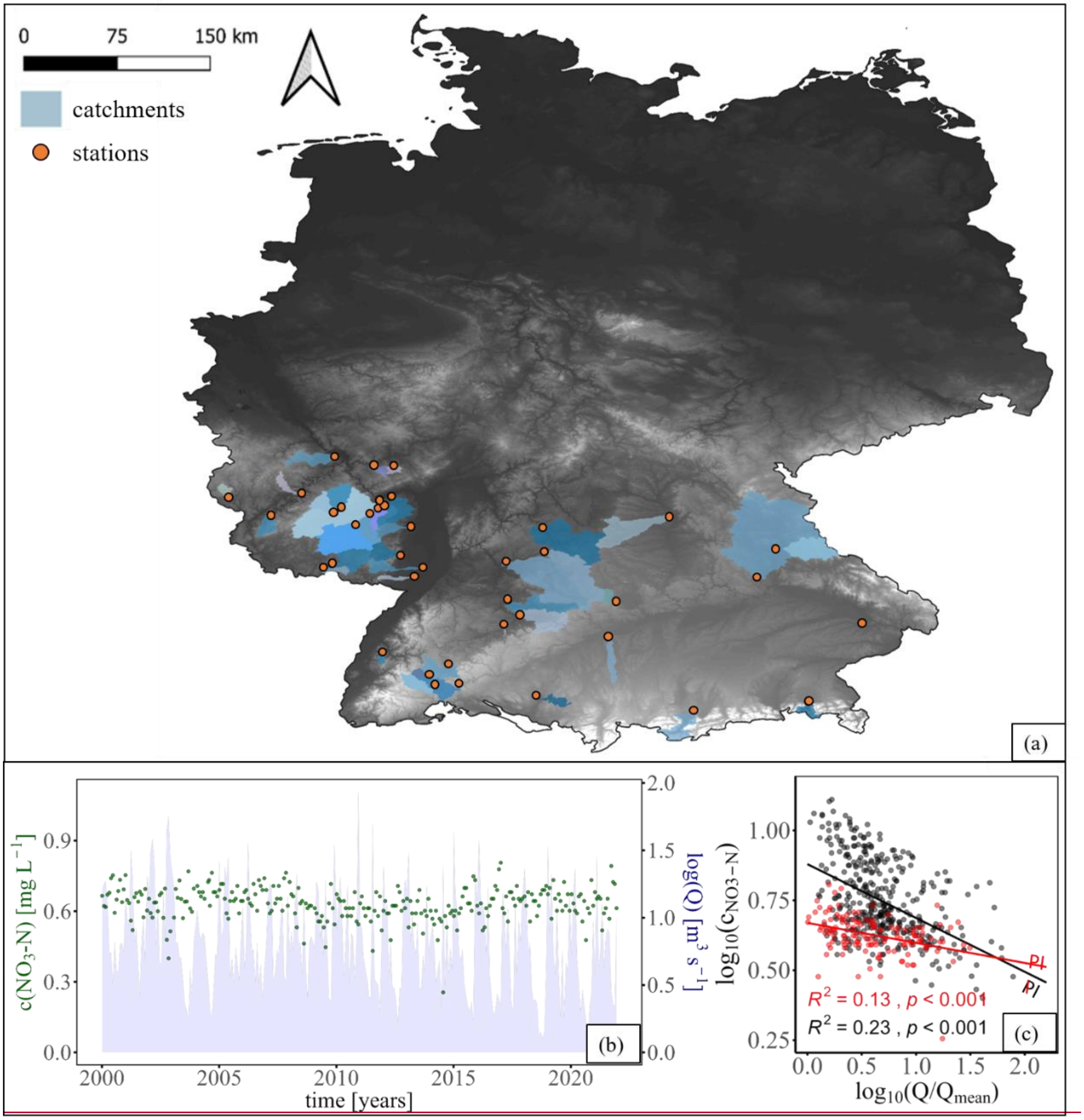
This study examines monthly/biweekly time series (eight to 20 years) of ~~major ~~nutrient and geogenic mineral concentrations and discharges, developing cQ-relationships for 40 catchments in southern Germany considering landscape boundary conditions. These catchments experience varying levels of anthropogenic influence and climate sensitivity, allowing for the assessment of changing export dynamics. We hypothesize that warming temperatures, prolonged heatwaves, and intense one-day precipitation events significantly impact solute mobilization, transport, and retention visible as changes in the cQ relationship of specific solutes. Climate-change-induced SEM anomalies are identified by comparing the current SEMs with those from the past decade (Period 1: prior to January 1, 2012). Seasonal effects (e.g., summer and winter) and variations in humidity levels (e.g., wet and dry years) are compared as well, serving as benchmarks for occurring variation of SEMs. Quantifying changes in SEMs under changing climatic conditions and identifying catchment properties, which favour such changes, will help future decision-making to improve catchment management strategies, counteracting changes in export mechanisms and reducing potential risks to ecosystem health.

2 Material and Methods

2.1 Study Sites

The present study comprises quality~~-~~-controlled discharge and water quality data from 40 stations in South and Southwest Germany ~~provided by the Environmental Agencies of the federal states of Rhineland Palatinate (RLP), Baden-Württemberg (BW), and Bavaria (BY).~~. Discharge Q ($m^3\ s^{-1}$) and water quality data C ($mg\ L^{-1}$) ~~is~~are delivered by ~~the State Environmental~~

~~Agency of Baden Württemberg (LUBW), the State Environmental Agency of Bavaria (LfU Bayern), and the the State Environmental Agency of Rhineland Palatinate (LfU RLP),~~various federal agencies, covering catchments located in Rhineland Palatinate~~,~~ (RLP), Baden-Württemberg~~,~~ (BW), and Bavaria (BY; LfU Bayern, 2022; LfU RLP, 2022; LUBW, 2022). Subsequently, the catchments include different regions with contrasting climate and catchment characteristics~~.~~ (Table S1 and S2). The study focuses on mid-mountain catchments in Eifel, Hunsrück, Palatinate Mountains, Black Forest, Swabian Alb, and Upper Palatinate Forest. Additionally, catchments are also located in Upper Rhine Lowlands, ~~wurttembergisches~~Württembergisches Unterland, and Franconia (Fig. 1).



~~**Figure 1: Study area in Southwest Germany with 40 catchments. (a) Map of catchments with measuring stations (orange), with a black-white gradient indicating elevation (BKG, 2013). (b) Time series of discharge and nitrate (NO$_3$-N) in the Fils catchment. (c) cQ-relationships for NO$_3$-N in the Fils catchment, showing an unaffected period (black, PI – Period 1) and a climate change affected period (red, PII – Period 2).**~~

All regions vary in climate, geology, land cover, and altitude. Catchment altitude varies between 147.5 [m.a.s.l.] and 835 [m.a.s.l.]. Average yearly precipitation ranges from 527 mm per year up to 1596 mm per year (DWD, 2022). According to the Köppen ~~und~~and Geiger climate classification, the climate is humid continental (Dfb) in Bavaria and most parts of Baden-Wurttemberg (Beck et ~~a~~al., 2018). The influence of ocean climate (Cfb) increases in the Northwest of Baden-Wurttemberg and Rhineland Palatinate (Beck et al., 2018). Streams reveal nival and pluvial regimes. The mean discharge ~~spanns~~spans three orders of magnitude and varies from 0.41 $m^3 s^{-1}$ to 49.73 $m^3 s^{-1}$.

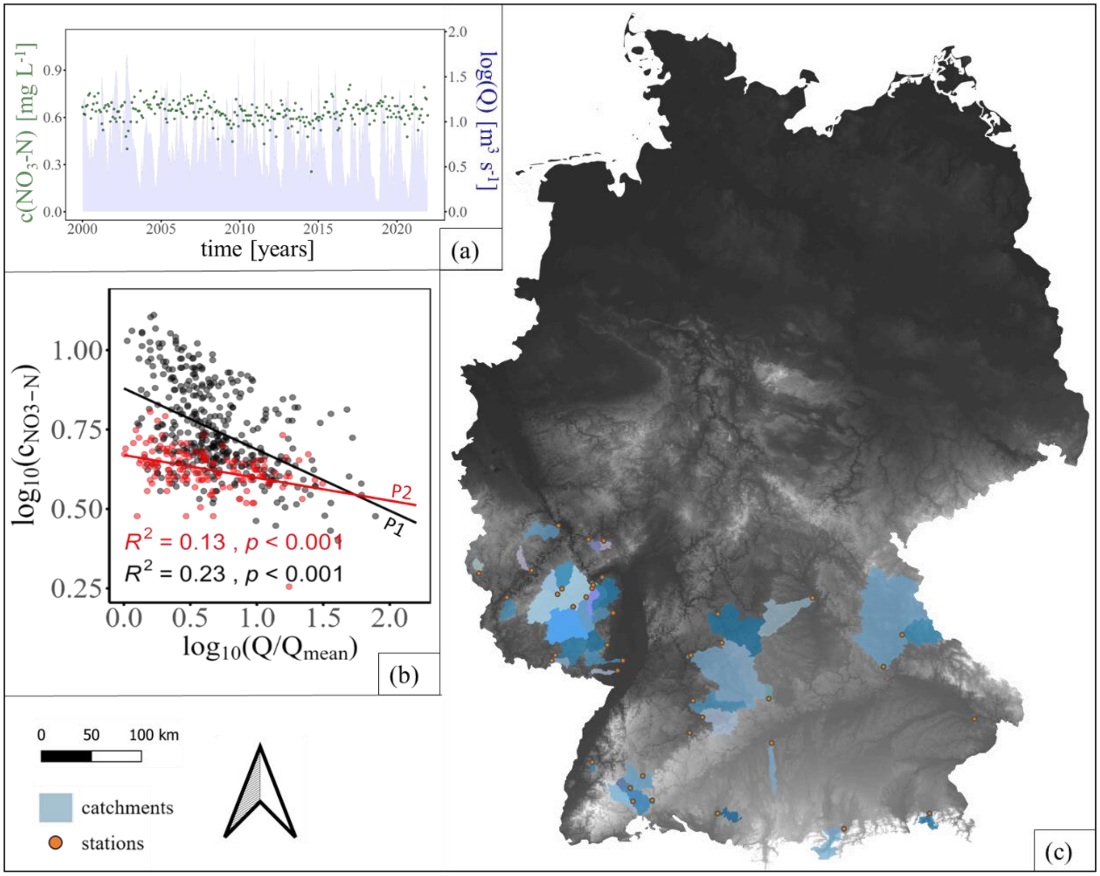


Figure 1: (a) Time series of discharge and nitrate (NO_3-N) in the Fils catchment. (b) cQ-relationships for NO_3-N in the Fils catchment, showing for period 1(black, P1) and period 2 (red, P2 – heightened presence of climate change effects). Differences between P1 and P2 were tested by ANCOVA (p<0.05) for each catchment (illustrated here for catchment Fils, p<0.001). (c) Study area in Southwest Germany with 40 catchments. Map of catchments with measuring stations (orange), with a black-white gradient indicating elevation (BKG, 2013). Map projection: UTM (EPSG: 25832).

The regional geology is ~~heterogenous~~heterogeneous with crystalline rocks in the Palatinate Mountains and Black Forest. Formations of carbonate rocks are located in Swabian ~~Albs~~Alb, Alps and Franconia, respectively. Further rock formations are Hunsrück schist in the Hunsrück, sandstone, and slate in the Eifel (BGR, 2006). Catchment sizes vary between 49 (Schutter) to 5434 km^2 (Naab). However, the focus is on mid-scale catchments (<1,000 km²), which account for over 80% of all catchments (Fig. 1). ~~The~~Arable land, pastures, or forests predominantly cover the majority of these catchments~~ are predominantly covered by arable land, pastures, or forests~~.

2.2 Data Selection and Data Structure

Discharge and water quality samples of public agencies typically are not sampled at the same locations, resulting in data selection criteria (see: below)

a. Assuming that the general behaviour of discharge generation and solute mobilization is not changing abruptly within one catchment, a small distance between the respective gauges was an essential criterion for selecting streams. For that reason, only close stations (max. distance ca. 8 km) of discharge and water quality were accepted as one site in this study.

b. Between the sampling locations for discharge and water quality parameters no neighbouring urban area, inflows from subsidiary streams, or effluent discharges (e.g. wastewater discharge) should be present.

c. The water quality stations should provide data on Nitrate-nitrogene (NO_3-N), Ammonia-nitrogene (NH_4-N), soluble reactive phosphorus (SRP), total phosphorus (TP), total organic carbon (TOC), calcium (Ca^{2+}), and magnesium (Mg^{2+}) for analysis.

d. All water quality parameters were derived from grab samples taken at least monthly to bi-monthly interval.

e. Water quality samples should cover both ~~Period~~period 1 and ~~Period~~period 2 at least partly, while discharge measurements were available as daily averages.

f. The selected streams had to represent the heterogeneous conditions of regions in Southwest Germany.

All applied criteria reduced the number of appropriate measurement stations from 1,004 for discharge and 1,572 for water quality to 40 suitable catchments. Although these strict criteria may introduce bias towards certain catchment types, they were crucial in ensuring reliable c–Q coupling. Nevertheless, the selected catchments still represent a broad range of catchment sizes, altitudes and geological settings, representing large parts of southern Germany.

Further, alteration in SEM caused by varying humidity level, seasonal variation and global warming were determined by splitting the data set into various observation periods:

a. Whole observation period, comprising all measured solute concentrations.

b. Summer, comprising all solute concentrations measured from May to October.

c. Winter, comprising all solute concentrations measured from November to April.

d. Wet years, comprising all solute concentrations measured in years with total discharge [mm] above median.

e. Dry years, comprising all solute concentrations measured in years with total discharge [mm] below median.

f. Period 1, comprising all solute concentrations measured until 31st December 2011, representing previous decades, which were relatively less affected by climate change.

g. Period 2, comprising solute concentration measured since 1st January 2012, representing recent years (2012-2022), which are relatively stronger affected by climate change.

Two intervals (Period 1 and 2) have been selected to represent distinct phases of the gradual climatic change in Southwest Germany. The dividing date of the 1st January in 2012 is arbitrary with regard to the incremental changes in the hydro-climatic system. It has been selected to ensure sufficient sampling coverage (>8 years) for statistical rigor in both periods. The periods under study can be considered as snapshots along a continuous trend of rising temperatures and altered hydroclimatic conditions. Between period 1 and 2, mean annual air temperature increased from 8.68 °C to 9.70 °C, potential evapotranspiration from 578 mm to 693 mm, and actual evapotranspiration from 460 mm to 490 mm, while precipitation declined from 905 mm to 819 mm (not statistically significant; Fig. 2). Period 1 thus is considered being less influenced and serves as a reference for an incremental change, whereas period 2 reflects stronger and more frequent indications of climate change, including exceptionally dry years such as 2018, enabling their use as comparative frameworks for assessing climate-related effects on solute export mechanisms (Table S2). The differences between period 1 and period 2 align with the long-term trend analysis of KLIWA 2021, which show an increase in average air temperature by 1.4°C to 1.8°C per 90 years. Maximum one-day precipitation amounts increased during the hydrological winter half-year (up to +33%) and the summer half-year (up to +28%), although there are regional decreases as well. Due to this variability, the maximum one-day precipitation trends are not statistically significant; however, an overall increase in peak discharge events is evident for southwest Germany.

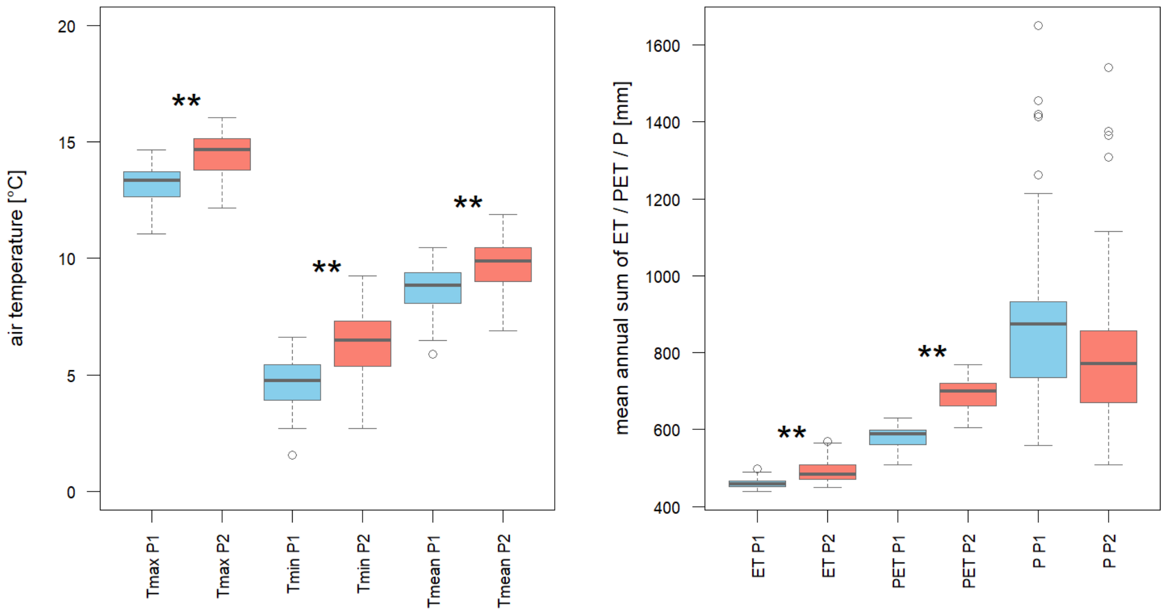


Figure 2: Changes in air temperature (left) and mean annual sums of evapotranspiration (ET), potential evapotranspiration (PET), and precipitation (P, mm; right) between period 1 (P1) and period 2 (P2). Tmax = maximum air temperature (°C), Tmin = minimum air temperature (°C), Tmean = mean annual air temperature (°C). Boxplots represent climatic data from 40 observed catchments. Data obtained from the German Weather Service (DWD, 2022).

2.3 Data Treatment and Analysis

2.3.1 Trend Analysis of Solute Concentration

Trends in mean solute ~~mean~~ concentration (C~~ along the whole observation period~~) were ~~determined by using linear regression ($p<0.05$)~~analyzed separately for each catchment. Linear regression models (concentration vs. time) were applied and statistical significance was evaluated using F-tests from ANOVA, corrected for multiple testing using the Benjamini–Hochberg procedure ($p < 0.05$). Descriptive statistics (C_{mean} ± SD in mg L^{-1}) were calculated for each solute, and interannual trends were classified as increasing ($C_{increase}$), decreasing ($C_{decrease}$), or non-significant (NC) alteration (Table 2).

2.3.2 Assessment of cQ-Relationship

Concentration–discharge (cQ) relationships were quantified for ~~each of the parameters and~~ each solute and catchment ~~were calculated based on the the~~using a power-law ~~relation of concentration *C* and discharge *Q*~~function (Eq~~.~~. 1~~,~~; Musolff et al., 2015~~)~~), which was then transformed into a linear relationship between *C* and *Q* in a double-logarithmic space (Eq. 2), where b defines the slope, whereas $log_{10}(a)$ defines the intercept. ~~To guarantee comparability among the catchments discharge was normalized by the mean discharge Q_{mean}.~~

The slope b was estimated for each solute and catchment with ≥20 samples during each observation period, normalizing the discharge by mean discharge (Q_{mean}) to ensure comparability. Positive slopes ($b>0$) reflect enrichment (increasing concentrations with discharge), while negative slopes ($b<0$) indicate a dilution pattern (decreasing concentrations with discharge).

$$c = a * Q^b \tag{1}$$

$$log_{10}(c) = log_{10}(a) + b * log_{10}(Q) \tag{2}$$

~~The slope b respectively the cQ-slope was calculated for each solute, each catchment, and each kind of observation period with a sampling size ≥20.~~

2.3.3 Assessment of Chemostatic and Chemodynamic Behaviour

Further, a slope close to zero (b~~≈~~ ≈ 0) ~~indicates a~~suggests that solute ~~concentration~~concentrations are largely independent of discharge magnitude~~, but there is no evidence of small concentration~~. However, this does not necessarily imply low variability in solute concentrations (Musolff et al., 2015).

~~Therefore, CV_C/CV_Q was used to avoid misinterpretation of near zero b slopes. Misinterpretation occurs when solute concentration varies extremely but independently from discharge (Thompson et al., 2011). CV_C/CV_Q was calculated for each catchment and each solute (eq. 3). The metrics are described by the ratio between the coefficient of variation of concentration (CV_C) and the coefficient of variation of discharge (CV_Q) to identify chemostatic and chemodynamic behaviour. Solutes with~~In fact, high concentration variability ~~compared to discharge variability were classified~~can still occur despite the absence of correlation with discharge. To avoid misinterpreting such near-zero b slopes as ~~chemodynamic behaviour. Solutes with low concentration variability compared to discharge variability were assigned to chemostatic solutes. The CV_C/CV_Q~~ indication of chemostatic behavior, we additionally used the CV_C/CV_Q ratio as proposed by Thompson et al. (2011). Chemostatic and chemodynamic behaviour was assessed using the ratio ~~deals~~of the coefficient of variation of solute concentration (CV_C) to that of discharge (CV_Q) (Eq. 3; Thompson et al., 2011). This metric was calculated for each catchment and solute, with the statistical descriptor ~~mean (μ) and~~ standard deviation (σ~~). In quantity, $CV_C/CV_Q>0.5$ indicates chemodynamic behaviour, whereas $CV_C/CV_Q\leq0.5$ indicates chemostatic behaviour (Pohle et al., 2021).~~) and mean (μ).

$$\frac{CV_C}{CV_Q} = \frac{\mu Q * \sigma c}{\mu c * \sigma Q} \tag{3}$$

~~The CVC/CVQ metrics and the cQ-relationship applied on the different observation period allows the assessment of SEM in South and Southwest Germany. The differences in SEM shaped by humidity level, season and climate change were identified by graphical comparison and Kruskal-Wallis test (p<0.05). Further, the water quality data was used to examine changes in solute mean concentration along the observation period. Trends in solute concentrations were examined by linear regression (p<0.05) for each catchment.~~

Solutes with $CV_C/CV_Q > 0.5$ were classified as chemodynamic (high concentration variability relative to discharge variability), whereas $CV_C/CV_Q \leq 0.5$ indicated chemostatic behaviour. The threshold of 0.5 for distinguishing chemostatic ($CV_C/CV_Q \leq 0.5$) from chemodynamic behaviour ($CV_C/CV_Q > 0.5$) was chosen following Thompson et al. (2011), who showed that conservative tracers typically yielded values around this level. This benchmark has been adopted in subsequent studies (Ebeling et al., 2021; Musolff et al., 2017) and provides a clear separation of solute groups in our dataset. Although alternative thresholds (e.g. 1) exist in the literature (Musolff et al. 2015), 0.5 was deemed most appropriate for our data structure and applied here as a classification tool. The CV_C/CV_Q metric was applied jointly with cQ-relationships across different observation periods to assess solute export mechanisms (SEM) in South and Southwest Germany. To capture variability, standard errors were calculated for all slope b, with error bars shown in Figure 3. Differences in SEM related to humidity (wet vs. dry), season (winter vs. summer), and climate change (P1 vs. P2) were formally tested using analysis of covariance (ANCOVA, $p < 0.05$), enabling statistical comparison of regression slopes between the two intervals.

2.3.4 Linking Catchment Characteristics to slope b

~~Additionally~~ were analysed to identify potential controls on slope b respectively, SEM ~~are potentially controlled by various catchment~~. Catchment characteristics ~~quantified by analysis of spatial~~were grouped into several categories and ~~temporal data delivered from multiple institutions~~compiled from institutional datasets (Table ~~1). The predictive power of catchment controls was quantified using the Pearson correlation coefficient, determining the strength and the direction of the linkage between catchment characteristics and cQ-slopes. Effects of global warming on explanatory controls and SEM were assessed by linear models (p<0.05) between catchment characteristics and cQ-slopes for the observation periods “Period~~ 1~~” and “Period 2”.~~

~~Therefore, different controls were used including hydrological indices, topography, climate, land use and geology and soil properties (Table 1).~~

). Hydrological ~~controls such as~~ indices included mean discharge Q_{mean}~~,~~ and median ~~of~~ discharge Q_{median}, ~~logarithmized~~ the logarithm of mean discharge $log(Q_{mean})$, and ~~discharge per unit catchment area q (Eq. 4) are calculated for each catchment.~~ specific discharge (*q*; Eq. 4). Specific discharge *q* ~~(mm)~~ is the quotient of discharge *Q* and the catchment area *A*, whereby discharge in m^3 s^{-1} was converted into discharge in l s^{-1}.

$$q = \frac{Q*1000}{A} \tag{4}$$

~~Considered controls of topography are mean~~ Topographic characteristics comprised catchment altitude and ~~catchment~~ area *A*, whereas ~~climate controls comprising average~~climatic characteristics included precipitation *P*, ~~average~~ evapotranspiration *ET*, ~~average~~ potential evapotranspiration *PET*, the evaporative index *ET/P*, aridity index *PET/P*, and the de~~-~~-Martonne ~~drought~~ index (*dMI*~~,~~; Eq~~.~~. 5).

The *dMI* was ~~applied~~used to ~~categorize dry regions with low values and wet regions with high values. The index describes also the gradual transition~~characterize climatic conditions along the gradient from arid to humid~~, the limit~~ and is defined ~~for annual values at dMI=20 (Blüthgen and Weisst, 1980; de Martonne, 1926; DWD, 2022). Evaporative index (*ET*/ *P*) and aridity index (*PET*/ *P*) were derived by calculating the quotient of *ET* and *P*~~ as ~~well as *PET* and *P*.~~

$$dMI = \frac{P}{(T+10)} \tag{5}$$

with low values indicating dry regions and high values indicating wet regions (de Martonne, 1926; Blüthgen & Weisst, 1980; DWD, 2022). Additional categories included land use, geology, and soil properties.

Predominant land uses ~~in each catchment~~ were determined ~~in~~as area ~~percentage by using~~percentages based on simplified ~~land use~~ classes ~~comprising~~ (arable land, ~~pastures~~pasture, forest, urban~~ area~~, and ~~not assignable area~~unclassified), derived from the Corine Land Cover ~~data~~dataset (Copernicus, 2022). ~~Overlaps~~Shares of ~~simplified~~ land ~~use classes with the catchments shape~~uses were ~~determined and computed~~processed in QGIS (QGIS.org, 2022~~). Catchment~~), with catchment shape and size ~~were~~ provided ~~as shapefile and originate from the~~ by GDI RP ~~for~~ (Rhineland~~-~~-Palatinate) and the University of Freiburg for Bavaria and Baden~~-Wurttemberg~~-Württemberg (GDI RP, 2022; Stölzle ~~and~~& Stahl, 2023). Geological ~~controls were determined simultaneously by using simplified geological classes:~~ settings were categorized into sandstone, carbonate~~ rock~~, crystalline~~ rock~~, clay~~ rock~~, sediments, and loess~~ sediments. The~~. As parent ~~rock~~ material ~~influences soil properties, hence geology and soils were summarized into one category. The standardized~~ strongly affects soil properties, geology and soil properties were combined. Soil moisture ~~data is provided by~~was obtained from the German Weather Service ~~and is determined~~(DWD, 2022) as standardized values for a virtual sandy loam soil ~~with a~~(37 % field capacity~~ of 37 % by volume. Soil moisture is then characterized by~~), expressed as percent plant~~-~~-available water ~~(%~~ (% nFK~~) and indicates a comparable degree of soil moisture for each of the catchments (DWD, 2022).~~

Table 1: Catchment descriptors used in the advanced data analysis to assess controls on SEM, associated with a description and data source.

Category	Variable	Unit	Description	Data source
Hydro-logical	Q_{mean}	m^3 s^{-1}	Mean discharge of the streams	LfU Bayern, 2022; LUBW, 2022; LfU RLP, 2022
	Q_{median}	m^3 s^{-1}	Median discharge of the streams	LfU Bayern, 2022; LUBW, 2022; LfU RLP, 2022
	$\log(Q_{mean})$	m^3 s^{-1}	Logarithmized mean discharge of the streams	LfU Bayern, 2022; LUBW, 2022; LfU RLP, 2022
	q	L s^{-1} km^{-2}	Discharge per unit catchment area	LfU Bayern, 2022; LUBW, 2022; LfU RLP, 2022
Topo-graphy	altitude	m.a.s.l.	Average altitude of the catchments determined by using the method of random points (n=2 to n=30) inside each catchment	BKG, 2013
	A	km^2	Catchment area	LfU Bayern, 2022; LUBW, 2022; LfU RLP, 2022
Climate	P	mm	Average precipitation in the catchments for the whole observation time, for winter months, for summer months, for previous decade (1982-2011) and recent years (2012-2022)	DWD, 2022
	ET	mm	Average evapotranspiration in the catchments for the whole observation time, for winter months, for summer months, for previous decade (1991-2011) and recent years (2012-2022)	DWD, 2022
	PET	mm	Average potential evapotranspiration in the catchments for the whole observation time, for winter months, for summer months, for previous decade (1991-2011) and recent years (2012-2022)	DWD, 2022
	dMI	mm~~/~~° °C^{-1}	The de Martonne drought index describes the gradual transition from arid to humid. The index is calculated for the whole observation time, for winter months, for summer months, for previous decade (1982-2011) and recent years (2012-2022~~)~~).	DWD, 2022
	ET/P	-	Average evaporative index derived by the quotient of mean evapotranspiration and precipitation for the whole observation time, for winter months, for summer months, for previous decade (1991-2011) and recent years (2012-2022)	DWD, 2022
	PET/P	-	Average aridity index derived by the quotient of mean potential evapotranspiration and precipitation for the whole observation time, for winter months, for summer months, for previous decade (1991-2011) and recent years (2012-2022)	DWD, 2022
Land use	arable land	%area	Area percentage of arable land in the catchments	Copernicus, 2022
	pastures	%area	Area percentage of pastures in the catchments	Copernicus, 2022
	forest	%area	Area percentage of forest in the catchments	Copernicus, 2022
	urban area	%area	Area percentage of urban area in the catchments	Copernicus, 2022
Geology and soil	sandstone	%area	Area percentage of sandstone in the catchments	BGR, 2006
	carbonate rock	%area	Area percentage of carbonate rock in the catchments	BGR, 2006
	crystalline rock	%area	Area percentage of metamorphic and igneous rock in the catchments	BGR, 2006
	clay rock	%area	Area percentage of clay rock in the catchments	BGR, 2006
	sediments	%area	Area percentage of sediments in the catchments	BGR, 2006
	loess sediments	%area	Area percentage of loess sediments in the catchments	BGR, 2006
	soil moisture	% nFK	~~The soil moisture is a simulation product offered by the German Weather Service and is determined on sandy loam soil with a field capacity of 37% by volume.~~ Soil moisture is characterized by percent plant-available water (% nFK) and is computed for the whole observation time, for winter months, for summer months, for previous decade (1991-2011) and recent years (2012-2022)	DWD, 2022

~~3 Results~~

~~Temporal variability in solute concentration and SEM was observed for major nutrients, geogenic solutes, and TOC, influenced by seasonality, humidity, and global warming.~~

The predictive power of these controls was quantified using Pearson correlation coefficients, providing both the strength and direction of relationships between catchment characteristics and slope b. To ensure robust inference across the 23 tested variables, p-values ($p < 0.05$) were adjusted using the Benjamini–Hochberg correction, and Pearson's r was reported as a measure of effect size (Table 3). Temporal effects induced by climate change were assessed using linear models (Pearson correlation coefficient) relating catchment characteristics to slope b for period 1 (before 2012) and period 2 (since 2012). Differences between the two periods were formally evaluated by analysis of covariance (ANCOVA) to test for significant changes ($p<0.05$) in regression slopes (Table 3).

3. Results

3.1 Assessment of Solute Mean Concentration

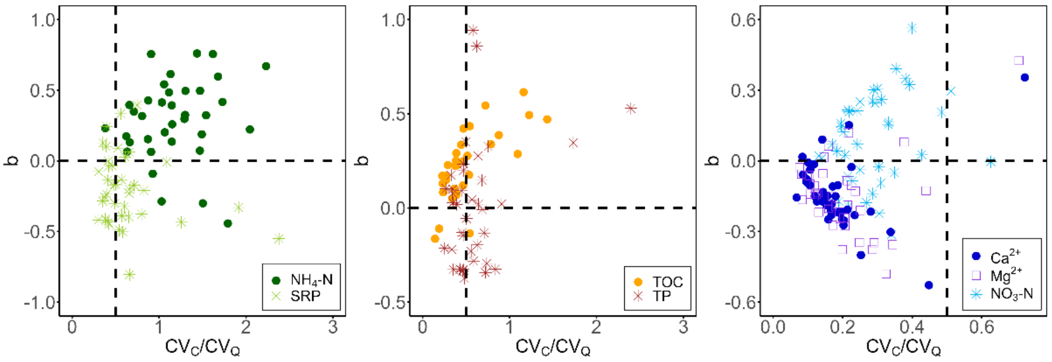
The analysis of in-stream solute concentrations reflects the static ~~signature~~signatures and nutrient stress levels of anthropogenically impacted catchments, ~~revealing~~with trends influenced by human activity and climate change (Table 2). Mean nutrient concentrations ~~of major nutrients varied~~ranged from 0.74~~ to ~~–9.37 mg L~~$^{-1}$~~$^{-1}$ for ~~NO_3-~~NO_3-N~~ concentrations to NH_4-N (~~, 0.04–0.34 mg L~~$^{-1}$), TP (~~$^{-1}$ for NH_4-N, 0.06–0.56 mg L~~$^{-1}$), and SRP (~~$^{-1}$ for TP, 0.02–0.27~~ mg L^{-1}). Over decades,~~ mg L^{-1} for SRP, and 1.9–7.78 mg L^{-1} for TOC. Trend analysis across the full observation period of each catchment revealed significant decreases in mean concentrations ~~decreased significantly in 60 % (NH_4-~~in 57.5% (NH_4-N), ~~73 % (NO_3-~~72.5% (NO_3-N), ~~63 ~~60.5% (TP), and 67.5 % (SRP) of ~~overall ~~catchments, as confirmed by ANCOVA (p~~<~~ < 0.05). ~~TOC ranged from 1.9–7.78 mg L^{-1}, while geogenic~~Geogenic solutes ~~showed~~occurred at higher concentrations (Ca^{2+}: 13–180.9 mg L^{-1}; Mg^{2+}: 2.57–55.12 mg L^{-1}) and showed greater absolute variability~~ (Ca^{2+}: 13–180.9 mg L^{-1}; Mg^{2+}: 2.57–55.12 mg L^{-1}). However, TOC and geogenic solutes exhibited~~, but with lower interannual variation compared to nutrients (Table 2).

Table ~~2:~~2: Descriptive statistics of mean solute ~~mean ~~concentrations (C_{mean}, mg L~~$^{-1}$)~~$^{-1}$) and associated standard deviations (C_{mean}~~±~~ ±SD) ~~for each solute.~~across all catchments. Interannual Trends in interannual solute concentrations are summarized as fraction of catchments (%) showing positive trends ($C_{increase}$), negative trends ($C_{decrease}$), or no significant trends (NC – no change). Trends were assessed using linear regression models (concentration vs. time), with p-values derived from F-tests and adjusted for multiple comparisons within each catchment dataset using the Benjamini–Hochberg procedure ($p < 0.05$). The number of catchments included in the analysis is denoted by n.

		NH_4-N (n=14475)	SRP (n=13996)	TP (n=12644)	TOC (n=11602)	NO_3-N (n=15811)	Ca^{2+} (n=6241)	Mg^{2+} (n=618)
$C_{mean + sd}$ (mg L^{-1})		0.15 ± 0.11	0.11 ± 0.05	0.19 ± 0.09	4.77 ± 1.45	4.04 ± 1.81	66.06 ± 41.48	17.08 ± 12.71
Fraction of catchments	$C_{increase}$ (%)	2.5	0.0	~~0.0~~2.6	~~18~~15.2	2.5	~~20~~15.0	~~17~~12.5
	$C_{decrease}$ (%)	~~60.0~~57.5	~~70.0~~67.5	~~63.2~~60.5	~~12~~6.1	72.5	5.0	2.5
	NC (%)	~~37.5~~40.0	~~30.0~~32.5	36.8	~~69.7~~78.8	25.0	~~75~~80.0	~~80~~85.0

3.2 Predominant SEM affected by temporal circumstances

Long~~-~~-term ~~cQ slopes~~slope b and CV_C/CV_Q metrics in southern Germany ~~reveal~~revealed explicit solute export mechanisms (SEM) for ~~major~~ nutrients~~, TOC,~~ and geogenic solutes, ~~highlighting variations~~reflecting differences in mobilization, transport, and transformation processes influenced by seasonality, humidity, and climate change (Table S3). ~~Predominant SEM were analysed using slope b and CV_C/CV_Q metrics, indicating both spatial and temporal variations in solute behaviour.~~ ~~Major nutrients,~~Nutrients such as ~~NH_4-~~NH_4-N, SRP, and TP~~,~~ exhibited more pronounced chemodynamic behaviour ~~compared to inert minerals like Ca^{2+} and Mg^{2+} (Fig. 2). Reactive~~than conservative solutes~~, particularly SRP and NH_4-N show higher solute concentration variability than discharge variability (CV_C/CV_Q>0.5). NH_4-N dominantly displayed~~ like Ca^{2+} and Mg^{2+} (Fig. 3). When exhibiting chemodynamic behaviour~~ with accretion patterns (b>0), whereas SRP and TP exhibited contrasting trends. SRP predominantly followed a dilution pattern in catchments with chemodynamic signature, while TP exhibited mainly accretion behaviour (b>0.6) in catchments with high CV_C/CV_Q (>1). With few exceptions, TOC generally exhibited chemostatic behaviour in catchments with low accretion, while catchments with high~~, NH_4-N showed dominant enrichment pattern ($b > 0$), SRP tended toward dilution dynamics, and TP displayed strong enrichment behaviour ($b > 0.6$) at elevated CV_C/CV_Q ratios (> 1). TOC was generally chemostatic but shifted toward chemodynamic behaviour~~, indicating~~ under conditions of high enrichment, suggesting discharge~~-~~-decoupled processes. In contrast, ~~groundwater-sourced solutes such as~~ Ca^{2+} and Mg^{2+} ~~display dilution behaviour, closely linked to discharge-driven processes (CV_C/CV_Q <0).~~typically displayed dilution dynamics, while NO~~$_3$-~~$_3$-N ~~follows~~combined dilution and enrichment pattern ~~while maintaining a~~but retained an overall chemostatic signature.



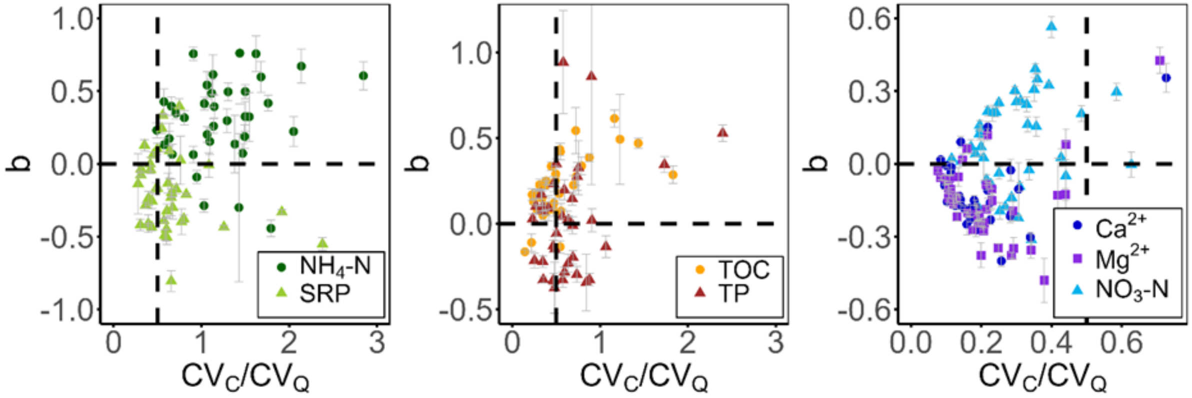
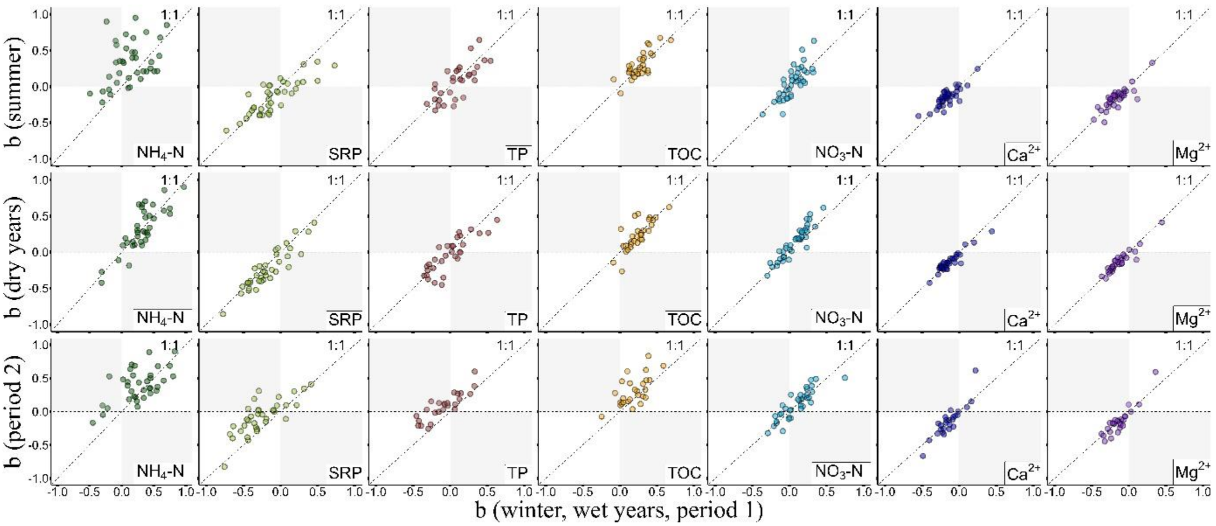


Figure ~~2:~~3: Illustration of the SEM ~~of ✳~~for ▲ SRP, ● NH_4-N, ~~✳~~▲ TP, ● TOC, ~~✳~~▲ NO_3-N, ● Ca^{2+} and ~~□ Mg2+ as cluster. Cluster~~■ Mg^{2+} clusters, with error bars representing ±1 standard error. Clusters represent ~~shallow-sourced~~temporal-dynamic solutes ~~affected by biogeochemical processes~~ (green, left), ~~discharge-driven shallow-~~ long-term dynamic ~~sourced~~ solutes (yellow/~~-~~brown, middle~~) and discharge-driven groundwater-sourced~~), and long-term stable solutes (blue/~~-~~violet, right). The vertical line separates chemostatic (left) from chemodynamic behaviour (right), while the horizontal line distinguishes enrichment (top) from dilution (bottom) patterns.

Temporal analyses revealed significant changes in SEM for ~~NH_4-~~NH_4-N, SRP, TP, and TOC, driven by ~~seasonal~~seasonality and long-term climatic ~~factors. Among these, NH4-~~shifts. NH_4-N exhibited the ~~highest~~strongest seasonal variability~~ in SEM~~, with pronounced enrichment ~~during~~pattern in summer and reduced enrichment dynamics in winter. ~~In contrast,~~ SRP ~~tended to follow~~ atypically tend towards non-significant dilution ~~pattern in~~behaviour during summer and ~~showed~~ enrichment ~~mechanisms~~behaviour in winter~~ (Fig. 3). Reactive nutrients such as NH_4-N and SRP displayed higher~~, highlighting its temporal variability~~, as reflected in changes in SEM across both seasons and decades. Additionally, SRP show dilution SEM in summer, as indicated by a point cloud below the 1:1 line, which corroborates its high temporal variability. (Fig. 3).~~

~~However, in~~ (Fig. 4). Over the recent decade, however, dilution processes ~~have~~ weakened for SRP, as indicated by a positive Δb, particularly in catchments that ~~exhibited~~had displayed dilution SEM in ~~prior~~earlier decades (Fig~~. 4). Further, for~~. 5). For both NH_4-N and SRP,~~ the~~ variability in Δb increased with higher CV_C/CV_Q ratios.

In contrast, ~~discharge-driven solutes like~~ TP and TOC ~~exhibited~~showed less ~~temporal variability in SEM, as no significant~~pronounced seasonal changes~~ in export dynamics were observed.~~. However~~, during the more recent~~ in period ~~(Period~~ 2~~),~~, characterized by warmer, drier summers ~~with~~and sporadic ~~but~~ intense ~~one-day~~ precipitation events (KLIWA, 2021~~; Payne et al., 2020~~), TP and TOC ~~showed an increasing tendency~~shifted toward enrichment~~, highlighting the influence of long-term climatic trends (Fig. 3).~~ pattern indicated by a positive Δb. TP ~~exhibit~~especially exhibited increasing slope b (Δb), ~~especially~~predominantly in catchments ~~that had displayed~~with prior dilution dynamics~~ in prior decade (Fig.~~ . ~~4). For TOC, Δb was predominantly positive, showing an increase in enrichment behaviour (Fig. 4).~~For both ~~TP and TOC~~solutes, catchments with chemodynamic ~~behaviour~~signatures predominantly ~~exhibit an increase in~~shifted toward stronger enrichment behaviour~~.~~ (Fig. 5).



~~**Figure 3: Differences in SEM for NO_3-N, NH_4-N, SRP, TP, TOC, Ca, and Mg due to temporal impacts. Differences in SEM between summer and winter (upper row), between dry years and wet years (middle row), and between the climate-change-affected decade (Period 2: from 2012 onward) and the unaffected decade (Period 1: up to 2011, bottom row). Individual catchments SEMs are represented by the dots in the scatter plots. Positions above the 1:1 line indicate an increase in enrichment or a decrease in diluting SEMs, whereas positions below the 1:1 line indicate a less pronounced enrichment or an increased diluting SEM respectively. The gray areas indicate a directional shift in SEMs.**~~

NO_3-N, Ca^{2+}, and Mg^{2+} showed no significant ~~changes in SEM in response~~responses to seasonal ~~variations~~variability, humidity ~~levels~~, or climate change (Fig. 4). ~~. 3). These solutes exhibited minimal changes~~Changes in Δb ~~(ranging from -~~for these solutes were minor (–0.25 to +0.25), with ~~no clear trend (Fig. 4). Mean slope b calculations suggested a~~only slight, ~~but not~~ non-significant~~, increase in~~ trends toward enrichment for NO_3-N~~, while~~ and dilution for Ca^{2+} and Mg^{2+} ~~showed a slight, non-significant trend toward increasing dilution behaviour in recent decades~~ (Table 4).

~~Solutes~~Overall, solutes with chemostatic ~~patterns, such as~~ signatures (NO_3-N, Ca^{2+}, ~~and~~ Mg^{2+}~~, exhibited lower~~) displayed low temporal variability compared to reactive nutrients ~~like~~ (NH_4-N~~ and~~, SRP~~,~~), which are influenced by biogeochemical processes. Additionally, no SEM changes were observed in response to variations ~~in humidity levels~~between wet and dry years, suggesting that climate-driven shifts in SEM are primarily linked to processes induced by climate change effects (Fig. 4). ~~linked to processes beyond humidity variations (Fig. 3).~~Nonetheless, legacy effects or land-use and management changes may also contribute. While no changes in fertilizer regulation have occurred in recent years, local legacy effects could still influence individual catchments.

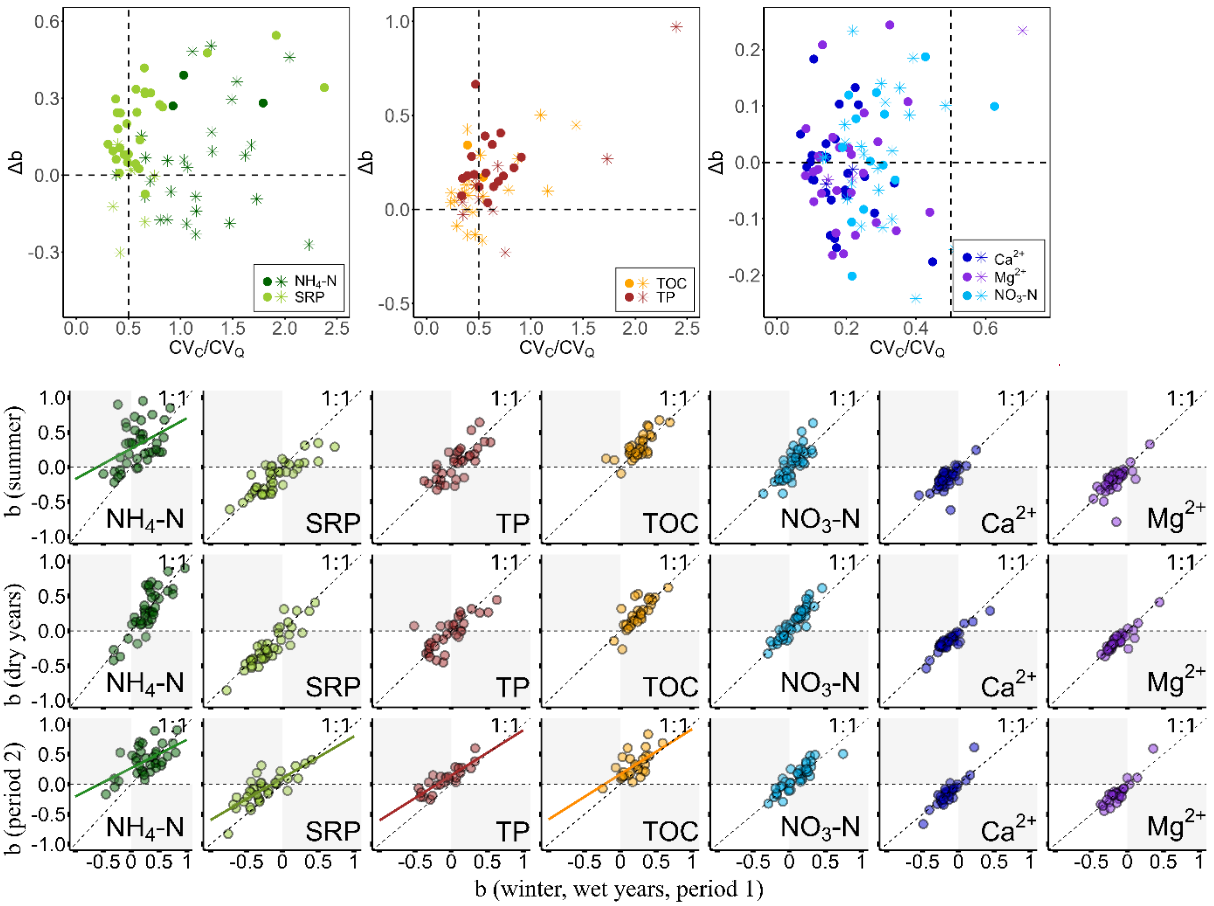


Figure ~~4:~~4: Differences in solute export mechanisms for NO_3-N, NH_4-N, SRP, TP, TOC, Ca^{2+}, and Mg^{2+} in response to temporal changes. Differences in solute export mechanisms between (top) summer and winter, (middle) between dry years and wet years and (bottom) between period 2 (climate change-affected decade) and period 1 (less affected period). Dots represent individual catchments. The b values (y-axis and x-axis) are slopes derived from cQ-relationships, indicating export behavior ($b < 0$: dilution; $b > 0$: enrichment). Points above the 1:1 line indicate an increase in enrichment or a decrease in dilution behaviour, whereas points

below the 1:1 line indicate a less pronounced enrichment or an increased dilution export pattern respectively. The gray areas indicate a directional shift in solute export.

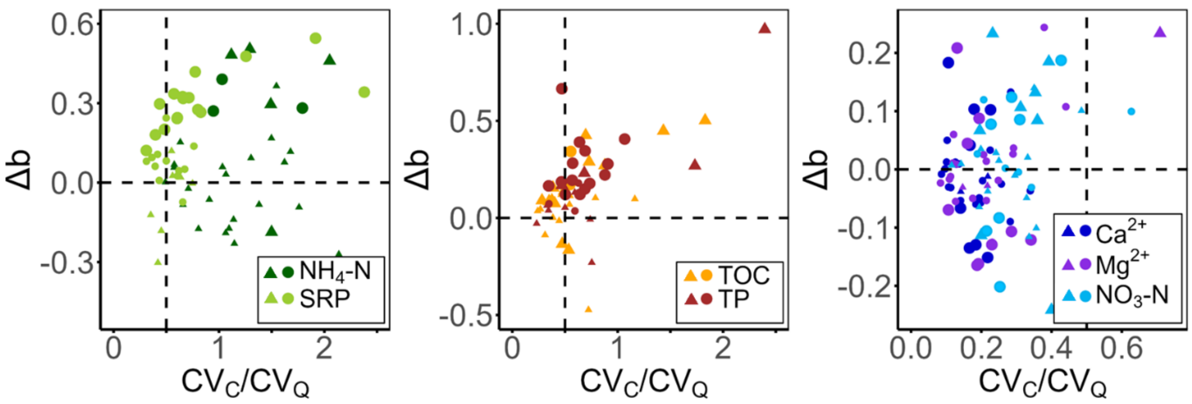


Figure 5: Change in cQ-relationships (Δb) for SRP, NH_4-N, TP, TOC, NO_3-N, ~~Mg^{2+}~~Mg^{2+}, and ~~Ca^{2+}~~Ca^{2+} explained by climate change. Positive ~~(~~Δb~~) indicating~~ values indicate an increasing enrichment behaviour. ~~✳ Catchments with enrichment behaviour in Period 1, ●~~▲ represent catchments ~~with dilution~~exhibiting enrichment behaviour in ~~Period 1~~period 1, while ● indicate catchments with dilution behaviour in period 1. Significant differences in slope b between period 1 and period 2 are highlighted by larger symbol sizes.

3.3 Controls of SEM and their Changing Influence along Time

SEM of ~~major~~ nutrients ~~and TOC~~ are influenced by distinct explanatory controls. The impact of these controls is potentially influenced by climate change. Pearson correlation coefficients (ranging from 0.33 to 0.75, p ~~$<$~~ $\leq$ 0.05 corrected by Benjamini-Hochberg procedure) were used to assess ~~these~~ relationships between SEM (slope b) and explanatory ~~control~~controls for the decade before and after January 1~~,~~ 2012. ~~Obtained~~In addition, statistical differences between correlations for period 1 and period 2 were formally evaluated using analysis of covariance (ANCOVA). The obtained Pearson correlation coefficients indicate both positive and negative correlations (Table 3). Shallow-sourced ~~solutes, such as major~~ nutrients ~~and TOC,~~ are primarily influenced by near-surface ~~factors, particularly climatic~~environmental conditions, ~~whereas~~particularly climate (e.g. temperature and precipitation), as well as soil moisture and the decomposition of organic material on the ground and in the upper soil layers. In contrast, geogenic solutes ~~like~~such as Ca^{2+} and Mg^{2+} are predominantly controlled by geological weathering processes~~controlled by geological factors~~. In addition to climatic influences, ~~shallow-sourced solutes are affected by~~ land cover, ~~hydrological indices,~~ soil moisture conditions and geological characteristics~~.~~ affect shallow-sourced solutes. For NH_4-N, ~~precipitation (-), drought index (-), and~~ soil moisture (-) ~~show~~shows negative correlations with slope b, indicating dilution behaviour in wet catchments and enrichment behaviour in dry catchments. During ~~Period~~period 2, the impact of these controls intensified, leading to a stronger regulation of cQ relationships by ~~explanatory factors.~~soil moisture. SRP is primarily influenced by the climatic factor evapotranspiration ~~(+)~~(++) and the geological factor clay rock (-), with both controls becoming more pronounced in the decade affected by climate change. High evapotranspiration enhances enrichment SEM, while high clay rock proportions in catchments promote dilution behaviour. TP, which includes both particle-bound and soluble reactive phosphorus, is influenced by a broader range of factors, including drought index ~~(+),~~(++), precipitation ~~(+),~~(++), evapotranspiration ~~(+),~~(++), evaporative index (-), aridity index (-), ~~logQmean (+),~~ soil moisture ~~(+),~~(++), carbonate rock (+), and clay rock (-). While the influence of climatic controls (precipitation, evapotranspiration, dMI) and soil moisture has increased, ~~hydrological indices and further~~ geological controls have become less influencing in regulating ~~cQ relationships.~~SEM. Further, TOC, which is primarily governed by surface processes, is exclusively influenced by evapotranspiration ~~(+),~~(++), with its ~~higher~~regulatory impact ~~during Period~~on SEM diminishing in period 2.

Unlike the more reactive solutes, NO_3-N exhibits chemostatic behaviour but remains influenced by multiple controls, including arable land (+), urban area (-), ~~soil moisture (-),~~ drought index ~~(-),~~(--), precipitation (-), and evapotranspiration (-). Arable land, a diffuse source, supports enrichment behaviour, whereas urban areas, acting as potential point sources, promote dilution dynamics. Wet catchments (characterized by high soil moisture, high precipitation, and ~~a high~~humidity inferring drought index values) are more likely to exhibit dilution SEM. Over time, the regulatory influence of ~~land use~~ explanatory controls on ~~SEM~~NO_3-N export dynamics has ~~diminished, whereas~~ remained stable, indicating a robust system. Additionally, the lack of change in land-use impact ~~of climatic conditions~~on SEM further supports that climate change and ~~soil moisture has increased.~~its effects are the dominant drivers of recent shifts in solute export mechanisms. As expected, the SEM of geogenic solutes~~, such as~~ (Ca^{2+} and Mg~~$^{2+}$, are primarily controlled~~$^{2+}$) is largely unaffected by ~~geological factors, with~~external controls. For Mg^{2+} the proportion of sandstone ~~proportion correlating~~correlates positively with ~~SEM. However~~slope b, whereas for Ca^{2+}, no significant regulatory controls on SEM were observed. Notably, in the recent period, the~~ small~~ effect of sandstone ~~proportions in catchments on SEM has diminished~~proportion on Mg^{2+} export dynamics remained unchanged.

Table ~~3: Explanatory controls~~3: Pearson correlation test between catchment descriptors of different categories ~~influencing SEM Results based~~and slope b showing influence of catchment characteristics on ~~Pearson Correlation. Significance level p<0.05. Description~~SEM: highly significant positive correlation ~~(++),~~(++ p<0.01), significant positive correlation ~~(+),~~(+ p<0.05), significant negative correlation ~~(-),~~(- p<0.05), highly significant negative correlation ~~(--),~~(-- p<0.01). Moderate (grey, r>0.3) and strong (dark grey, r>0.5) effect sizes were observed, indicating varying strengths of association. Differences between correlations in period 1 and 2 are determined by using ANCOVA (p<0.05) showing increased impact of control due to climate change (△), decreased impact of control due to climate change (▽), no change (O). Pearson correlation is corrected by Benjamini-Hochberg procedure.

Category	Control	NH_4-N	SRP	TP	TOC	NO_3-N	Ca^{2+}	Mg^{2+}
Hydrology	Qmean							
	Qmedian							
	log(Qmean)			~~+ / ▽~~				
	q							
Topography	altitude							
	A							

Climate	P	~~- / △~~		++ / △		~~-- / △~~- / O		
	ET		++ / △	++ / △	++ / ▽	- / ~~△~~O		
	PET							
	dMI	- / △		++ / △		-- / ~~△~~O		
	ET/P			- / ~~△~~O				
	PET/P			~~-- / △~~- / O				
Land use	arable land					+ / ~~▽~~O		
	pastures							
	forest							
	urban area					- / ~~▽~~O		
Geology and soil	sandstone						~~+ / ▽~~	~~++ / ▽~~+ / O
	carbonate rock			~~++ / O~~+ / △				
	crystalline rock							
	clay rock		- / △	- / ▽				
	sediments							
	loess sediments							
	soil moisture	- / △		++ / △		~~- / △~~		

4 Discussion

Solute concentration and SEM varied ~~due to~~across temporal and spatial ~~factors~~scales, influencing solute mobilization, transportation, storage, and transformation processes. ~~The analysis reveals~~Results show that solute concentration and SEM respond to both global warming and anthropogenic impacts.

4.1 Assessment of Solute Mean Concentration

Significant differences in ~~the~~ mean ~~concentrations of major nutrients,~~nutrient and geogenic solutes~~, and TOC~~ concentrations were observed across catchments. Reactive solutes~~, such as~~ (NH_4-N, SRP, ~~and~~ TP~~,~~) exhibited ~~relatively~~ low mean concentrations~~ with similar magnitudes~~, consistent with previous studies (Ebeling et al., 2021; Musolff et al., 2015). ~~The low~~Low NH_4-N concentrations ~~of NH_4-N can be attributed to~~reflect its rapid turnover~~ rate~~, while phosphoric species are quickly taken up by plants, limiting their availability (Birgand et al., 2007; Martí and Sabater, 1996). ~~In~~By contrast, NO_3-N concentrations averaged 4.04 mgL^{-1}, reflecting agricultural ~~influences. Persistent NO_3-N levels are closely linked to fertilization practices~~inputs and persistent legacy effects (Reynolds et al., 1997; Aubert et al., 2013). ~~Between 1979 and 2000, nutrient~~ Nutrient concentrations in Germany were historically elevated~~, leading to substantial nutrient storage, particularly for nitrate. A decline in nutrient concentrations observed in later decades (1990–2000) coincided with reductions in~~ but have declined since 1990 due to reduced fertilizer ~~application. While NH_4-N, TP, and SRP concentrations decreased, NO_3-N levels remained high due to legacy effects, resulting in~~ use. However, NO_3-N showing a slower ~~overall decline~~ decrease explained by legacy effects compared to NH_4-N, TP, and SRP (Basu et al., 2010). ~~The continued decline~~Declines in NH_4-N, TP, and SRP concentrations can also be attributed to prolonged ~~drought periods driven by~~droughts associated with climate change~~.~~

~~Extended~~, as extended dry ~~conditions, particularly in~~ summer~~,~~ periods lead to lower water levels and reduced mean concentrations (Outram et al., 2016; Van Loon et al., 2019). In contrast, ~~short but~~ intense high~~-water-level~~flow events ~~are associated with increased~~ increase nutrient ~~transport~~export.~~. Since sampling occurs~~, but biweekly to monthly~~, it is more sampling~~ likely ~~to capture low-water-level conditions~~misses these peaks, and hence, leads to potential~~ly~~ underestimation~~ing~~ of ~~overall~~total nutrient loads. ~~Further observations are needed to determine whether the apparent decline in nutrient loads results from sampling resolution limitations or reflects a true reduction. Increasing slope b indicating higher load at high-water events.~~Nevertheless, because the sampling frequency remained unchanged across both study periods and hence observed changes in SEM better explained by hydroclimatic shift linked to global warming rather than by sampling limitations. Still, further high-resolution monitoring would be valuably to better capture event-driven dynamics, as individual events can exhibit slope b values that deviate distinctively from the seasonal behaviour (Knapp et al., 2020).

TOC, is less reactive and more persistent, with ~~high emissions from fertile~~carbon-rich landscape types (e.g. wetlands or riparian zones) serving as sources, ~~resulting~~visible in higher and more variable mean concentrations~~ with wider variability. TOC showed a slight tendency toward increasing concentrations, though~~. However, interannual variability ~~was less dominant compared to major~~in TOC concentrations is less pronounced than for other nutrients, suggesting ~~less~~lower influence from anthropogenic actions. ~~Geogenic~~The mean concentrations of geogenic solutes ~~like Ca^{2+}~~(Ca^{2+} and ~~Mg^{2+} exhibited high mean concentrations,~~ Mg^{2+}) are consistent with ~~findings by Musolff et al. (2015). The~~ previous reports, and their spatial variability reflect the heterogeneous geology of ~~southern Germany induces variation in solute source, leading to high spatial variability in Ca^{2+} and Mg^{2+} concentrations.~~ the catchment regions (Musolff et al., 2015). These solutes, primarily ~~influenced~~governed by geological processes, showed only slight increases in mean concentration ~~in a moderate fraction of overall~~for some catchments (Ca^{2+}: ~~20~~15 %, Mg^{2+} 12.5 ~~%)~~%). The persistence of the lithosphere and weathering processes contributed to low interannual variability. However, ~~climate change, induce~~climatic changes inducing warmer temperatures and lower groundwater levels, ~~promoting~~which could promote higher residence times and enhanced weathering rates. ~~These conditions~~This may ~~explain the~~lead to slight increase in solute concentrations~~. Ca^{2+}-rich rocks are particularly affected, as they are more vulnerable to weathering processes~~, but further confirmation is needed. (Li et al., 2022; Musolff et al., 2015). ~~Nevertheless, these assumptions require further verification.~~

4.2 Changes in SEM associated with Seasonality, Humidity Level and Climate Change

Changes in slope b over time ~~provide valuable new insights into the dynamic~~reveal shifts in solute mobilization, transportation, and transformation processes, depending on seasonality, humidity levels, and responses to climate change. ~~Clusters emerge in the context of~~ SEM~~, enabling the categorization~~ cluster into ~~distinct~~three groups~~, namely~~: (1) ~~shallow-sourced~~temporal-dynamic solutes~~ affected by biogeochemical processes~~, (2) ~~primarily discharge-driven shallow-sourced~~long-term dynamic solutes, and (3) ~~groundwater-sourced~~long-term stable solutes (Fig. ~~2~~3).

4.2.1 SEM of ~~Shallow-Sourced~~Temporal-Dynamic, Long-Term Dynamic ~~-~~and ~~Groundwater-Sourced Solutes~~

~~Shallow-sourced~~LongTterm Stable S~~s~~olutes~~ influenced by biogeochemical processes dominantly~~

Temporal-dynamic solutes: mainly reactive nutrients (NH_4-N, SRP, TP), exhibit chemodynamic behaviour ~~(Fig. 2, left). Variability in~~ with solute ~~concentration~~ variability exceeding discharge variability ~~reflects additional~~due to biogeochemical processes ~~decoupled from discharge~~ (Musolff et al., 2015). ~~Highly reactive nutrients such as NH_4-N, SRP, and TP demonstrate rapid~~Rapid uptake and turnover ~~rates~~ dominate their variability (Birgand et al., 2007; ~~Marti~~Martí and Sabater, 1996~~), making their variability dominated by biogeochemical processes rather than discharge.~~). However, in intensively managed catchments, ~~homogeneously and largely distributed~~homogeneous solute ~~e.g., SRP and TP~~ sources might mask biogeochemical effects~~, resulting in~~ and can lead to a chemostatic behaviour ~~where solute mobilization is~~ proportional to discharge, accordingly (Ali et al., 2017; Basu et al., 2011~~; Thompson et al., 2011). Enrichment as well as dilution~~). Temporal-dynamic solutes show chemodynamic enrichment behaviour ~~characterize shallow-sourced solutes. Enrichment~~when unevenly mobilized at higher discharges, while a dilution pattern occurs when ~~heterogeneous source distribution leads to unsteady nutrient mobilization with rising discharge, while dilution arises from inconsistent source depletion, reducing solute concentrations as discharge increases~~ deeper sources dominate during low flow (Basu et al., 2011; ~~Pohle~~Ebeling et al., 2021~~; Rose et al., 2018).~~). Dilution dynamics can also result from biological SRP release during low flow~~ periods, mimicking~~, acting as temporal point sources in sediments and riparian zones (Dupas et al., 2018; Ebeling et al., 2021; Smolders et al., 2017).~~ Spatial and temporal characteristics defines enrichment respectively dilution behaviour, whereby the amount of mobilizable solute decides about chemostatic or chemodynamic behaviour.~~

~~Discharge-driven shallow-sourced~~ Long-term dynamic ~~-~~solutes~~, including~~: TOC, ~~TP and partly NO_3-N, show a strong correlation~~and particulate-bound TP, strongly correlate with discharge ($CV_C/CV_Q<0.5$) and are less sensitive to transformation processes~~. A CV_C/CV_Q ratio below 0.5 indicates that mobilization and transport are closely tied to discharge (Fig. 2~~ (Fig. 3, middle). TOC and ~~particulate-bound TP generally exhibit~~TP show enrichment behaviour, ~~as~~when increased discharge ~~activates~~and a rising water table activate surficial pathways~~, assisting~~ and enable hydrological connectivity ~~that leads to elevated instream solute concentrations~~ (Huntington and Wieczorek, 2021). ~~However, variability~~Variability in TOC and TP concentrations can exceed discharge variability due to heterogeneous vertical and horizontal TOC ~~source distribution~~sources in riparian zone ~~or~~and SRP~~-~~-related biogeochemical processes, promoting chemodynamic tendencies (~~Basu et al., 2011;~~ Ebeling et al., 2021; ~~Pohle et al., 2021;~~ Rose et al., 2018; Stewart and Li, 2025~~; Thompson et al., 2011~~).

Long-term stable solutes: NO_3-N, Ca^{2+}, and Mg^{2+} primarily display dilution patterns with negative slopes b (Fig. 3, right; Botter et al., 2019; Diamond and Cohen, 2018). NO_3-N typically exhibits chemostatic behaviour, driven by widespread anthropogenic nitrogen inputs in intensively managed catchments, such as those in southern Germany. Historical fertilization has created significant nitrogen stores across soil layers, ~~leading to discharge-driven mobilization that buffers against~~buffering biogeochemical ~~variability~~processes. In contrast, natural systems without human impact exhibit chemodynamic NO_3-N behaviour, a phenomenon, which is not observed in the ~~anthropogenic~~anthropogenically affected southern Germany (Winter et al., 2020). Vertical heterogeneity in NO_3-N sources ~~significantly~~ influences ~~its~~ SEM ~~behaviour~~, with ~~the predominance of~~ shallow sources ~~driving~~causing chemostatic enrichment dynamics~~, while~~ and groundwater-derived sources ~~typically result in~~causing chemostatic dilution ~~behavior~~behaviour (Basu et al., 2011; Moatar et al., 2017~~; Pohle~~). Low temporal concentration variability ($CV_C/CV_Q< 0.5$) and negative slope b for Ca^{2+} and Mg^{2+} indicate chemostatic dilution behaviour, driven by deep chemical weathering and steady groundwater release (Knapp et al., ~~2021).~~2020; Musolff et al., 2015; Botter et al., 2020). ~~Discharge-driven groundwater-sourced solutes, including partly NO_3-N, Ca^{2+}, and Mg^{2+}, primarily display dilution patterns characterized by negative slopes b (Fig. 2, right; Botter et al., 2019; Diamond and Cohen, 2018; Moatar et al., 2017; Wymore et al., 2017). Low variability in Ca^{2+} and Mg^{2+} concentrations and a CV_C/CV_Q ratio below 0.5 indicate chemostatic behavior (Knapp et al., 2020; Musolff et al., 2015; Rose et al., 2018). These solutes are derived from deep-layer chemical weathering processes in the lithosphere and pedosphere, with consistent groundwater release leading to dilution as discharge increases (Botter et al., 2020). The relative inertness of geogenic solutes limits their intraannual and interannual fluctuations, contrasting with more reactive nutrients and TOC.~~

4.2.2 Alteration in SEM due to Seasonal and Humidity Variation

Temporal-dynamic solutes: Biogeochemical processes vary ~~significantly~~ over time, influenced by seasons, humidity (wet and dry years) ~~levels~~, and climate change. ~~Consequently, shallow-sourced~~Temporal-dynamic nutrients, especially NH_4-N ~~and SRP~~ exhibit ~~substantial temporal~~strong seasonal SEM fluctuations ~~in SEM~~, with ~~pronounced differences~~notable shifts between summer and winter ~~seasons~~ (Fig. ~~2~~4; Fig. S1). Seasonal effects, particularly temperature variations~~, play a critical role in~~ influence nutrient production and depletion ~~rates due to~~via rapid biogeochemical turnover ~~(Basu et al., 2010;~~ and rising amount of organic matter (Ebeling et al., 2021; Greaver et al., 2016; Hellwig et al., 2017~~; Pohle et al., 2021).~~

). During ~~long periods of drought in~~extended summer droughts, lower discharge and soil saturation ~~and reduced discharge limit~~ reduce hydrological connectivity~~, diminishing~~ and limit solute transport (~~e.g.,~~ Winter et al., ~~2020 Winter et~~2022; Yang et al., 2018). ~~These~~Under these conditions~~ promote,~~ NH_4-N ~~production through the decomposition of~~accumulates from rising amount of ~~death~~decomposing organic material in shallow soils (Greaver et al., 2016). Sporadic hydrological reconnection ~~leads to~~mobilizes NH_4-N ~~mobilization~~ during rising discharge, ~~intensifying~~leading to intensified enrichment behaviour in summer (Fig. 4). ~~2).~~

~~Seasonal influences significantly NH_4-N and SRP SEM. NH_4-N~~ SRP tends to show ~~stronger enrichment behaviour in summer due to low hydrological connectivity and high NH_4-N accumulation, while SRP shows higher~~ lower slope b in ~~winter~~summer. Warm summer temperatures ~~enhance~~and low flow boost biological activity, promoting SRP dilution ~~behaviour due to~~ through instream ~~SRP~~ point sources in riverbed and ~~depletion of~~through terrestrial ~~diffuse sources by e.g.~~ plant uptake~~.~~ in riparian zones. In winter, colder temperatures suppress these processes (Bieroza et al., 2014; Dupas et al., 2018; ~~Marti~~Martí and Sabater, 1996; Pohle et al., 2021; Smolders et al., 2017).

~~Especially in dry years, instream biological processes release SRP, particularly under low-flow conditions, promoting dilution behaviour. These processes mirroring point-source inputs originating from riverbed sediments and riparian zones (Dupas et~~

~~al., 2018; Marti and Sabater, 1996; Pohle et al., 2021; Smolders et al., 2017). SRP is highly reactive make it especially sensitive to temporal biogeochemical fluctuations compared to the more inert TP (Bieroza et al., 2014; Marti and Sabater, 1996).~~

~~TP includes a less reactive~~ Long-term dynamic solutes: TP's particle-bound phase~~, contributing to lower susceptibility to~~ lowers its biogeochemical ~~processes. This phase~~reactivity but supports ~~discharge-driven~~ mobilization~~, particularly~~ during ~~increased~~rising discharge, ~~resulting in~~causing enrichment behaviour (Bieroza et al., 2024; Thompson et al., 2011; Marti and Sabater, 1996). ~~In summer~~Especially after prolonged dry periods, when hydrological connectivity is ~~low~~limited and TP accumulation is exceptionally high, ~~enrichment behaviour becomes more pronounced triggered by~~ wet periods with precipitation events ~~after prolonged dry periods. The interplay between the solid and soluble phosphorus phases creates a mix of discharge-driven and biogeochemical influences on TP SEM.~~can strongly trigger enrichment behaviour by mobilizing accumulated TP from sediments and soils (Bieroza et al., 2024; Thompson et al., 2011).

~~Discharge-driven~~Long-term dynamic solutes~~ such as NO_3-N, TOC, and the solid phase of TP~~ ~~experience~~show limited temporal variation due to their ~~relatively~~ reduced sensitivity to biogeochemical processes~~. Temporal fluctuations in SEM for these solutes are~~, and mainly ~~tied to seasonal~~tracking discharge~~ changes~~, with higher ~~rates~~flows in wet winters and lower ~~rates~~ in dry summers~~, explained by hydrological connectivity~~ (Winter et al., 2020). ~~NO_3-N shows minimal~~

Long-term stable solutes (NO_3-N, Ca^{2+}, Mg^{2+}) display non-significant temporal effects, driven by residence time and stable solute source. NO_3-N´s variability ~~because of its widespread presence and reliance on~~is buffered by legacy sources and slow biochemical processes (e.g., lower degradation rate~~), making it predominantly discharge-driven (~~; Basu et al., 2011~~,~~; Dupas et al., 2018).

~~Geogenic solutes, such as Ca^{2+} and Mg^{2+}, exhibit even fewer~~

Seasonal influences rank highest for temporal~~ effects, with not significant seasonal variations solely driven by residence time and a consistent solute source. Solutes influenced by biogeochemical processes~~-dynamic solutes (NH_4-N, SRP) ~~are most~~ affected by ~~seasonal factors~~biogeochemical processes, followed by ~~shallow discharge-driven solutes (~~long-term dynamic (TP, TOC~~) and groundwater discharge-driven~~), then long-term stable solutes (NO_3-N, Ca^{2+}, Mg^{2+}). The contrasting SEM patterns of temporal-dynamic, long-term dynamic, and long-term stable solutes highlight the interplay between hydrological drivers, biogeochemical processes, and source distribution in shaping cQ-relationships. While high-frequency monitoring allows these dynamics to be disentangled across temporal scales, low-resolution monitoring provides a complementary perspective. In the context of long-term cQ-relationships, grab samples collected at biweekly to monthly intervals primarily capture seasonal patterns in nutrient export, while short-term event responses are largely missed. For nitrate, this is reflected in high concentrations associated with elevated winter discharge and reduced concentrations during summer low-flow conditions, thereby representing the characteristic positive cQ-relationship. Event-driven dynamics are therefore only incidentally captured and need to be interpreted as deviations from the overarching seasonal signal. Further, long-term and low-resolution records of TOC and TP consistently show higher concentrations during high-flow conditions and lower concentrations during low-flow conditions (positive slope *b*), regardless of season (see Fig. 4, top panel). This indicates that their mobilization is governed by uniform hydrological transport processes throughout the year. In contrast, chemodynamic NH_4-N displays higher concentrations during summer high-flow events compared to winter high-flow events, implying distinct seasonal mobilization and export dynamics.

Besides, years of low-discharge and high-discharge (see Fig. 4, middle panel) show no differences in SEM. Hence, mean annual discharge levels alone have minor effect on the SEM of nutrients.

~~Solely humidity levels affects hardly SEM of major nutrient and TOC. Except for SRP no changes in SEM between dry and wet years were significant.~~ However, long-term variations in SEM over recent decades, influenced by global warming, suggest broader changes in NH_4-N, SRP, TP, and TOC SEM. Therefore, changes in humidity alone are insufficient to explain SEM alterations. Broader climatic processes driven by global warming contribute to these shifts.

4.2.3 Alteration in SEM due to Global Warming

Since 2012, prolonged heatwaves, droughts, and intense sporadic ~~intense~~ one-day precipitation events have significantly influenced ~~shallow-sourced~~temporal-dynamic and long-term dynamic~~-~~solutes (KLIWA, 2021; Payne et al., 2020). While ~~underground~~subsurface weathering processes ~~seem to~~ remain ~~largely unaffected, shallow-sourced solutes,~~mostly stable, most nutrients except NO_3-N~~,~~ have become ~~increasingly~~more sensitive to the effects of global warming~~ by changing subsurface processes. Shallow-sourced~~.

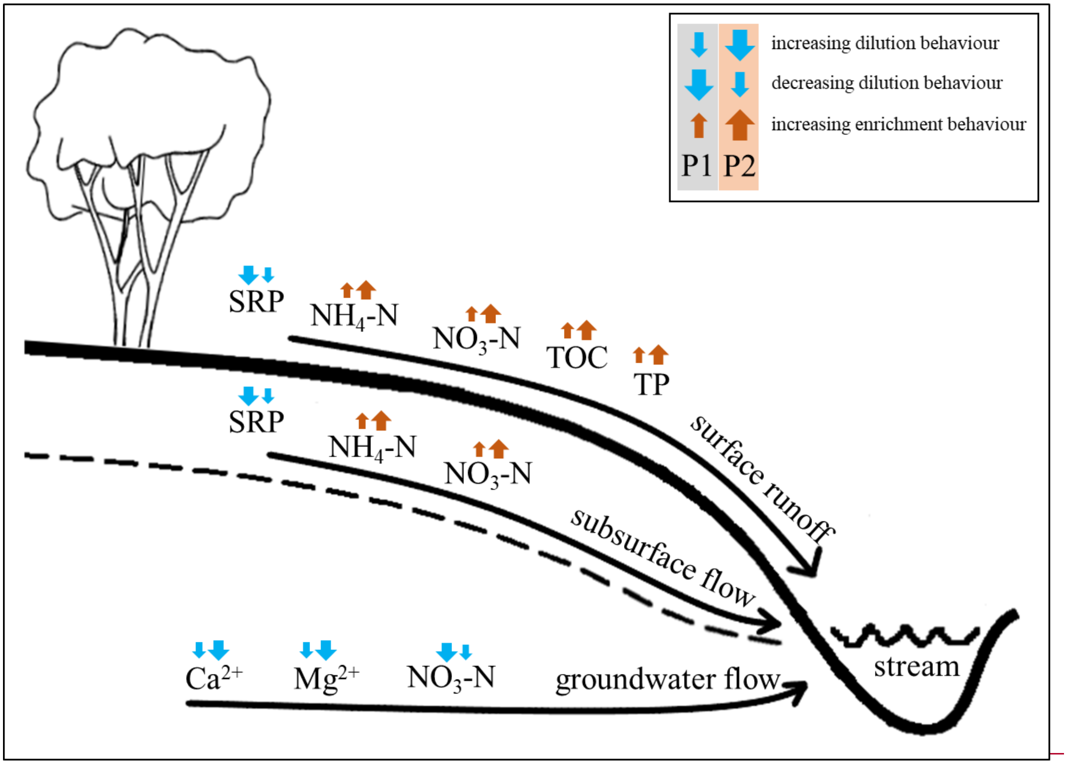
Temporal-dynamic and long-term dynamic~~–~~ solutes exhibit enhanced enrichment and reduced dilution behaviour in ~~Period~~period 2, ~~regardless of whether their SEMs are influenced by biogeochemical or discharge-driven processes (Fig. 3 and~~ reflecting altered~~4). This trend reflects changes in~~ solute source distribution and mobilization ~~processes.~~

(Fig. 4 and 5; Fig. S1). Prolonged heat and drought ~~and excessive heat amplify the production of~~boost decomposable organic ~~material~~matter production, increasing ~~the availability of~~ nitrogen and phosphorus availability. Warmer temperatures stimulate the mineralization of nutrients into inorganic forms by decomposers (Ainsworth and Long, 2005; Freeman et al., 2001; ~~Gomez et al., 2011;~~ Huntington and Wieczorek, 2021). Additionally, elevated CO_2 levels, enhanced plant growth, and fertilizer applications (e.g., manure) ~~contribute to an overall increase in~~raise nutrient accumulation in upper soil ~~layer~~layers (Huntington and Wieczorek, 2021; Kukal and Irmak, 2018, Stewart and Li, 2025). ~~At the same time, drought conditions reduce~~ Drought reduces plant~~-based~~ nutrient uptake, ~~as terrestrial vegetation becomes limited,~~ leading to ~~greater~~further nutrient accumulation ~~of major nutrients. Oxygenation~~. Additionally, oxygenation of previously waterlogged ~~soil further~~soils suppresses nitrogen removal ~~through~~via denitrification, ~~promoting~~enhancing nutrient ~~accumulation additionally~~build-up (Bieroza et al., 2024; Gomez et al., 2011). ~~These factors contribute to increased~~ Together, these effects increase internal sources of TOC~~ (including DOC),~~, TP, SRP, NH_4-N, and NO_3-N in shallow soil layers compared to previous decades. ~~Global~~Subsequently, global warming ~~further~~ degrades soil structure and reduces soil moisture, ~~diminishing the~~lowering nutrient retention capacity (for ~~key nutrients, particularly~~ SRP~~ and~~, TP), thus promoting leaching (Lucas et al., 2023). ~~This reduction in retention capacity promotes leaching processes. Consequently, the combination of increased internal sources,~~Combined with drier antecedent conditions, transport limitations, and sporadic high-intensity precipitation events~~ intensifies~~, these factors intensify nutrient leaching ~~and amplifies pulsed nutrient delivery~~during wet periods (Bieroza et al., 2024; Dupas et al., 2025; Huntington and Wieczorek, 2021; ~~Knapp et al., 2020;~~ Lucas et al., 2023).

~~Pulsed nutrient delivery occurs during intense one-day summer rainfall events, which activate preferential pathways primarily limited to surface and near-surface layers, promoting nutrient transport via surface runoff (Ezzati et al., 2023; Khan et al., 2022; Fig. 5). During this period, patchy soil saturation predominantly affects the upper soil layers (Bieroza et al., 2024; Winter et al., 2020). Unmobilized~~ Accumulated nutrients ~~accumulate in the pedosphere and~~ are ~~later~~ transported ~~through~~ via surface and subsurface flow during wet periods especially in autumn and winter, when rising water tables and increased discharge enhance hydrological connectivity (Fig. ~~5~~6; Bieroza et al., 2024). Both transport pathways ~~via surface runoff and subsurface flow lead to increased~~amplify enrichment behaviour for all ~~shallow-sourced solutes,~~nutrients except NO_3-N. ~~Even SRP dilution SEM, which occurs during low-flow conditions due to in-stream SRP release (as seen in dry years), has been weakened by enrichment~~Enrichment processes driven by climate change (as observed in ~~Period~~period 2~~).~~) have weakened even SRP's usual dilution pattern during low flow.

Long-term stable solutes: NO_3-N, Ca^{2+}, and Mg^{2+} show non-significant changes in SEM. NO_3-N exhibits ~~contrasting behaviour due to the~~stable SEM because extensive anthropogenic legacy stores~~, which outweigh the effects of~~ counterbalance enrichment dynamics forced by climate change ~~and counteract enrichment trends, thus maintaining a dilution-dominated SEM in multiple catchments. While~~effects. Although warmer conditions increase substrate availability and biological activity, their impact remains minimal compared to ~~the~~historic human-applied NO_3-N~~ in prior decades. As a result, in~~. Consequently, some catchments~~, NO_3-N shows only~~ exhibit a slight, non-significant decrease in dilution and increase in enrichment behaviour, ~~setting it apart~~ distinguishing NO_3-N from other temporal-dynamic and long-term dynamic- nutrients.

Ca^{2+} and Mg^{2+} remain resilient due to largely undisturbed lithospheric weathering processes. Warmer temperatures and reduced discharge extend solute residence times, enhancing weathering rates, causing a minor, non-significant rise in dilution dynamics (Fig. 6; Botter et al., 2020; Li et al., 2022; Musolff et al., 2015).


increasing dilution behaviour
decreasing dilution behaviour
increasing enrichment behaviour
P1
P2
SRP
$\mathrm{NH_4}$-N
$\mathrm{NO_3}$-N
TOC
TP
surface runoff
SRP
$\mathrm{NH_4}$-N
$\mathrm{NO_3}$-N
subsurface flow
$\mathrm{Ca^{2+}}$
$\mathrm{Mg^{2+}}$
$\mathrm{NO_3}$-N
groundwater flow
stream

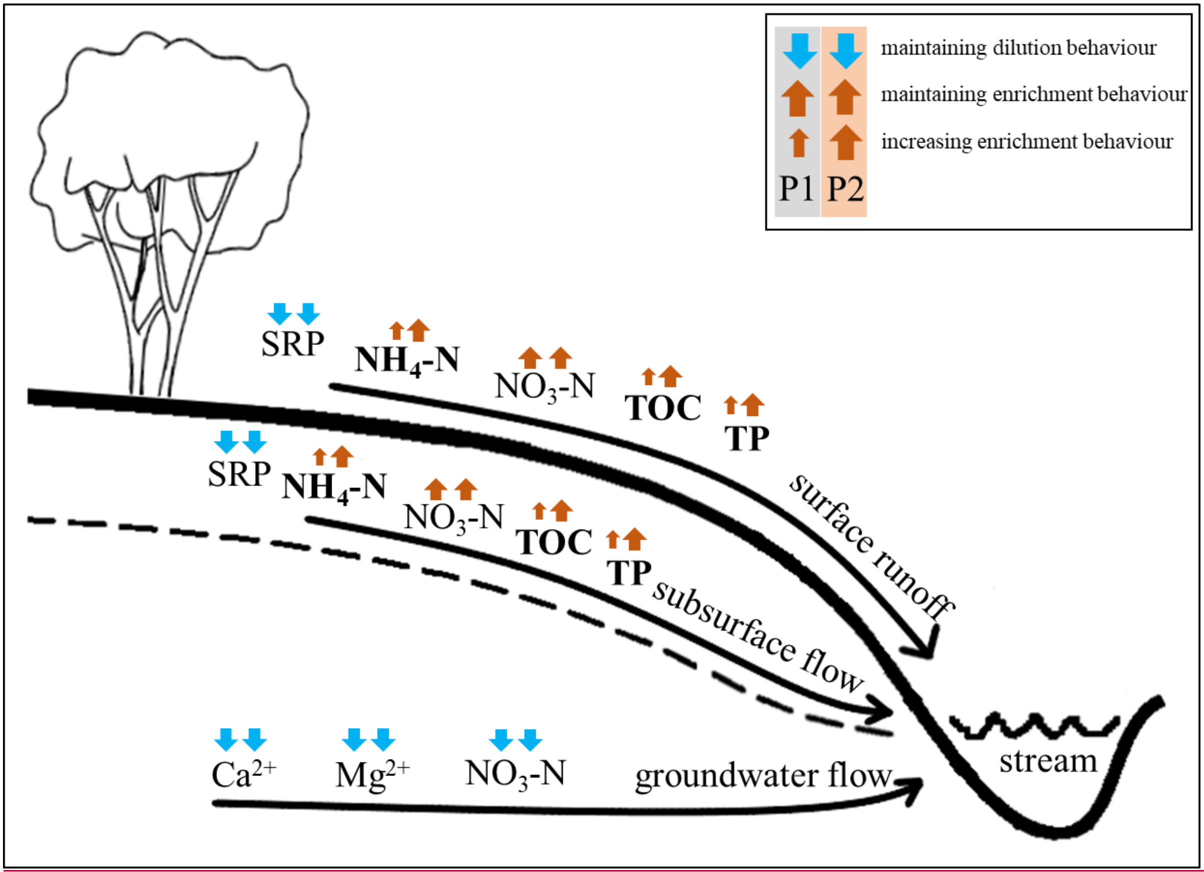


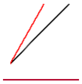
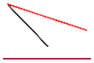
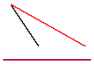
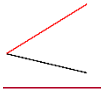
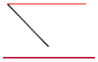
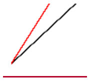
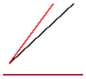
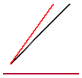
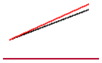
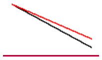
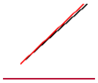
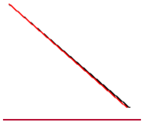
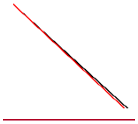
Figure ~~5:~~6: Illustration of mobilization and transportation pathways for ~~shallow-sourced major~~ nutrients~~, TOC~~ and geogenic minerals. Change in SEM based on climate change illustrated by direction and size of the arrows. P1 – ~~Period~~period 1 (onwards 1st Jan. 2012) less affected by climate change. P2 – ~~Period~~period 2 (after 1st Jan 2012) more affected by climate change (modified illustration Jordan et al. 1997).

~~Geogenic solutes such as Ca^{2+} and Mg^{2+} show minimal changes in SEM, with a slight but non-significant trend toward increased dilution in recent years. This resilience is attributed to the largely undisturbed weathering processes in the lithosphere. Warmer temperatures and reduced discharge extend solute residence times. This prolonged residence time, coupled with enhanced weathering rates, leads to increased solute concentrations, which may contribute to a minor rise in dilution dynamics (Botter et al., 2020; Li et al., 2022; Musolff et al., 2015). These trends align with observations from catchments showing increasing geogenic solute mean concentrations over time. However, many catchments exhibit no significant variation in mean concentrations or SEM over the decades.~~

4.3 Controls on SEM Influenced by Climate Change

~~Shallow-sourced~~Temporal-dynamic and long-term dynamic ~~–~~solutes exhibit increased enrichment and reduced dilution dynamics under the influence of climate change. Catchment characteristics, including land cover, geology, pedosphere, ~~hydrological indices, and climate, significantly affect SEM, as identified through Pearson Correlation Coefficients (p<0.05). Correlations between catchment characteristics and slope b were established for the periods before and after January 1st, 2012. However, the influence of these controls varies across solutes, and no single dominant control was identified due to the complexity of SEM.~~and climate, significantly shape SEM in both period 1 and period 2, as confirmed by Pearson correlation coefficients ($p<0.05$).

~~For NH₄-N, surface controls shape SEM. Soil moisture, along with climatic factors such as precipitation and drought indices, drives~~Table 2: Changing SEM across period 1 (black) and period 2 (red – affected by climate change) for SRP, NH_4-N, TP, TPC, NO_3-N, Ca^{2+}, and Mg^{2+}, along with their controlling factors. Significant differences were tested using the Kruskal-Wallis test corrected with Bonferroni correction ($^+$<0.1, *<0.05, **<0.01). Symbols indicate increasing (△),decreasing (▽) or unchanged (O) control impact. Panels: (a) all catchments, (b) catchments with dilution behaviour in period 1 (n≥10), (c) catchments with enrichment behaviour in period 1 (n≥10). Trends are based on mean calculations.

-		Changing SEM			Controls
Biological impacted shallow sourced solutes		(a) n=40	(b)	(c) n=33	Climate, Soil and Geology
	NH_4-N	 strengthened enrichment*		 strengthened enrichment	drought index (△), soil moisture (△)
		(a) n=40	(b) n= 32	(c)	Climate, Soil and Geology
	SRP	 weakened dilution**	 weakened dilution**	-	Evapotranspiration (△), clay rock (△)
Discharge-driven shallow sourced solutes		(a) n=38	(b) n=18	(c) n=20	Climate Soil and Geology
	TP	 shift in export mechanism**	 weakened dilution**	 strengthened enrichment*	Precipitation (△), evapotranspiration (△), drought index (△), evaporative index (O), aridity index (O), soil moisture (△), clay rock (▽), carbonate rock (△)
		(a) n=33	(b)	(c) n=30	Climate
	TOC	 strengthened enrichment$^+$	-	 strengthened enrichment$^+$	evapotranspiration (▽)
		(a) n=40	(b) n=15	(c) n=25	Land Cover, Climate
	NO_3-N	 strengthened enrichment	 weakened dilution	 strengthened enrichment	Precipitation (O), evapotranspiration (O), drought index (O), arable land (O), urban area (O)
Groundwater sourced solutes		(a) Ca^{2+} n=40	(a) Mg^{2+} n=40		Soil and Geology
	geogenic minerals	 slight strengthened dilution	 slight strengthened dilution	-	For Mg^{2+}: sandstone (O)

For temporal-dynamic NH_4-N, humidity conditions expressed by the drought index (dMI) regulate SEM, driving dilution dynamics under wet conditions. Rapid turnover rates (e.g., uptake, transformation) deplete NH_4-N sources as discharge rises and hydrological connectivity increases (Birgand et al., 2007; Marti and Sabater, 1996; Pohle et al., 2021). In drier catchments, ~~reduced precipitation and lower~~drought reduces hydrological connectivity ~~create~~and limits solute transport ~~limitations, leading to accumulation patterns,~~ particularly during prolonged heatwaves, ~~which result in larger NH_4-N sources.~~enhancing accumulation, and intensifying enrichment dynamics. Climate change amplifies the effects of drought (~~e.g., soil moisture, drought index) and sporadic precipitation events,~~increasing impact of dMI on SEM), explained by extended transport limitations while increasing solute accumulation, ultimately intensifying enrichment dynamics.

For SRP, evapotranspiration and clay-rich soils ~~play~~are key ~~roles. In addition to in-stream point sources, low~~controls. Low evapotranspiration ~~helps keep pathways active in shallow soils. This~~sustains hydrological connectivity ~~links~~in shallow soil, linking terrestrial SRP sources to streams~~,~~, and promoting dilution ~~patterns through~~via source depletion. Clay soils act as buffers, hindering SRP mobilization ~~and increasing the potential for source depletion~~ through adsorption-desorption processes (Basu et al., 2011; Thompson et al., 2011). In ~~Period~~period 2, this buffering effect has intensified, highlighting rapid SRP leaching in areas lacking clay minerals~~, especially under climate change conditions. The impact of~~. At the same time, higher evapotranspiration ~~has also increased in recent years due to climate change. Higher evapotranspiration leads to extended~~increasingly drives SRP accumulation and reduced hydrological connectivity~~, ultimately diminishing~~ in period 2, thereby weakening dilution behaviour~~.~~ in response to climate change.

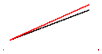
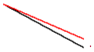
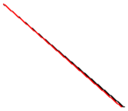
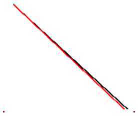
TP SEM reflects ~~the interplay between~~mobilization through discharge~~-driven~~ and biogeochemical processes ~~due to its presence~~since TP occurs in both solid and soluble ~~phosphorus phases~~forms. Increased discharge activates preferential pathways, enhancing enrichment behaviour through sediment mobilization. ~~This process is driven~~TP SEM are influenced by ~~rising stream shear strength, particularly in streams with high logQmean (Bende-Michl et al., 2013; Rose et al., 2018). Several factors influence TP dynamics, including~~ drought index~~,~~ (dMI), precipitation, evapotranspiration, soil moisture, clay rock, and carbonate rock. Carbonate rock ~~formations facilitate~~facilitates preferential ~~pathways~~flow, amplifying enrichment ~~behavior. In contrast,~~behaviour, while clay materials ~~mitigate this effect by slowing~~slow phosphorus mobilization (Basu et al., 2011; Thompson et al., 2011). ~~However, climate~~Climate change expands TP sources and transport limitation (control: evapotranspiration, soil moisture, drought index), intensifying mobilization during ~~sporadic~~ shortened wet periods in summer ~~rainfall~~, as well as in autumn and ~~rising~~ winter when water ~~tables~~table rises (control: precipitation). This ~~leads to pulsed delivery events~~ enhances enrichment dynamics and weakens dilution patterns. ~~As climate~~In period 2, controls ~~and~~of climate, soil moisture and carbonate rock become ~~more influential, the~~stronger, whereas clay's impact ~~of hydrological indices and geology~~on SEM declines~~, enlighten the power of climate change on SEM. The SEM of TOC is entirely discharge-driven, with evapotranspiration playing a dominant role in regulating SEM. High evapotranspiration reduces hydrological connectivity, limiting TOC mobilization to short periods. These dynamics are heightened by climate change. During prolonged drought, large TOC sources are generated and are increasingly mobilized during short-term pulses, amplifying enrichment behaviour (Dupas et al., 2025).~~.

For TOC, prolonged drought (control: evapotranspiration) leads to the accumulation of large TOC sources that are increasingly mobilized during shortened wet periods, thereby amplifying enrichment behaviour (Dupas et al., 2025).

SEM of NO_3-N ~~displays subsurface~~is regulated by several controls but maintains a distinctive chemostatic behaviour representing a ~~more or less temporal invariable~~long-term stable solute. Wet conditions, explained by high precipitation, ~~high~~ and humidity inferred drought index~~, and high soil moisture content~~ values, enhance dilution dynamics. In contrast, arable land and high evapotranspiration rates promote enrichment behaviour~~ by ~~. Fertilizer use on arable land accumulates nitrogen in the soil creating ~~internal~~diffuse sources. Meanwhile,~~ and~~ ~~transport limitations.~~evapotranspiration-induced dryness reduces constant drainage and prevents source depletion. When hydrological connectivity is restored (e.g., during rainfall and rising water table), accumulated nutrients are rapidly mobilized, resulting in pronounced concentration increases. Urban areas ~~contribute to~~ typically create dilution behaviour ~~as~~due to steady contributions from point sources (Aubert et al., 2013; Basu et al., 2010; Dupas et al., 2018; ~~Ebeling et al., 2021;~~ Musolff et al., 2015).~~ ~~In recent years, the ~~impact~~effects of land cover~~, specifically arable land and urban areas, has diminished. This suggests a lower disturbance in~~ on SEM ~~from~~ have lessened, suggesting reduced anthropogenic ~~activities, such as reduced emissions from~~disturbance due to improved wastewater treatment ~~plants~~ and decreased fertilizer ~~application~~use. Minor changes, ~~including~~like lower hydrological connectivity and increased NO_3-N generation during prolonged heatwaves, slightly amplify enrichment behaviour and ~~weakened~~weaken dilution SEM. However, the increase in slope b remains primarily masked by anthropogenic NO_3-N inputs, which continue to dominate SEM. ~~Unlike shallow-sourced solutes, groundwater-sourced solutes such as Ca^{2+} and Mg^{2+} are minimally influenced by subsurface controls. Geological factors, particularly sandstone, primarily dictate SEM. Sandstone generates less soluble Ca^{2+} and Mg^{2+}, producing lower dilution dynamics, while Ca^{2+}- and Mg^{2+}-rich formations promote strengthened dilution behaviour. Climate change increases residence time in the lithosphere, slightly enhancing dilution dynamics (Botter et al., 2020; Li et al., 2022). Despite this, SEM for geogenic solutes remains consistent over the decades with less influence of sandstone on SEM in recent years.~~

Unlike temporal-dynamic and long-term dynamic solutes, Ca^{2+} and Mg^{2+} are mainly governed by geology, particularly sandstone. For Mg^{2+}, sandstone significantly hinders the production of Mg^{2+} ions and weakens dilution dynamics. Climate change extends lithosphere residence time, slightly but not significantly enhancing dilution dynamics (Botter et al., 2020; Li et al., 2022). ~~significantly alters the impact of~~ However, despite climatic changes, Ca^{2+} and Mg^{2+} export dynamics have remained stable over the decades, with regulatory controls maintaining a consistent influence on ~~shallow-sourced solute export mechanisms. Climatic~~Mg^{2+} SEM. Climate change markedly shifts controls on temporal-dynamic and long-term dynamic solutes, strengthening climatic and soil moisture ~~gain influence, driving~~effects that drive enrichment SEM~~. In contrast, other controls, except for clay mineral area proportions in catchments, lose their influence, particularly those associated with dilution dynamics. Heightened pulse delivery~~, while weakening drivers of dilution pattern. This trend may increase solute concentration peaks, ~~posing risks to ecosystems~~risking ecosystem and human health by ~~exceeding~~surpassing water quality ~~benchmarks~~standards (Outram et al., 2016; Radach et al., 2010; Winter et al., ~~2020). To counteract these enrichment trends, effective~~2020). Effective catchment management strategies to counter enrichment behaviour are essential. ~~For groundwater-sourced solutes, the impact of climate change remains~~Climate impacts on long-term stable solutes remain minor~~. However,~~, though slight increases in Ca^{2+} and Mg^{2+} dilution dynamics are assumed due to ~~prolonged~~longer residence times.

~~Table 4: Changing SEM across Period 1 (black) and Period 2 (red~~

	~~NH₄-N~~	~~(a)~~  ~~strengthened enrichment~~	~~(b)~~  ~~shift in export mechanism~~	~~(c)~~  ~~strengthened enrichment~~	~~Climate, Soil and Geology~~ ~~precipitation, drought index, soil moisture~~
	~~SRP~~	~~(a)~~  ~~weakened dilution~~	~~(b)~~  ~~weakened dilution~~	~~(c)~~ -	~~Climate, Soil and Geology~~ ~~evapotranspiration, clay rock~~
~~Discharge-driven shallow sourced solutes~~	~~TP~~	~~(a)~~  ~~shift in export mechanism~~	~~(b)~~  ~~weakened dilution~~	~~(c)~~  ~~strengthened enrichment~~	~~Climate, Hydrology, Soil and Geology~~ ~~precipitation, evapotranspiration, drought index, evaporative index, aridity index, log(Qmean), soil moisture, clay rock, carbonate rock~~
	~~TOC~~	~~(a)~~  ~~strengthened enrichment~~	~~(b)~~ -	~~(c)~~  ~~strengthened enrichment~~	~~Climate~~ ~~evapotranspiration~~
	~~NO₃-N~~	~~(a)~~  ~~strengthened enrichment~~	~~(b)~~  ~~weakened dilution~~	~~(c)~~  ~~strengthened enrichment~~	~~Land Cover, Climate, Soil and Geology~~ ~~precipitation, evapotranspiration, drought index, soil moisture, arable land, urban area~~
~~Groundwater-sourced solutes~~	~~geogenic minerals~~	~~(a) Ca^{2+}~~  ~~slight strengthened dilution~~	~~(a) Mg^{2+}~~  ~~slight strengthened dilution~~	-	~~Soil and Geology~~ ~~sandstone~~

5 Conclusion

To examine alterations in SEM for~~ major~~ nutrient solute concentrations, the ratio of concentration to discharge variability, and cQ relationships were ~~analyzed~~analysed for 40 catchments in southern Germany. Temporal influences on SEM were investigated by comparing slope b across different seasons, humidity levels, and climate change impacts. The study found that temporal effects on SEM vary among ~~shallow-sourced solutes influenced by biogeochemical processes, discharge-driven shallow-sourced solutes, and groundwater-sourced solutes. Shallow-sourced~~temporal-dynamic, long-term dynamic, and long-term stable solutes. Temporal-dynamic solutes, which include fractions mobilized by surface runoff and subsurface flow, show the highest alteration due to seasonal variations and, especially, climate change effects. ~~The~~Further, the findings confirm enhanced enrichment behaviour for ~~shallow-sourced~~temporal-dynamic and long-term dynamic ~~-~~solutes, while geogenic solutes show a slight but non-significant increase in dilution export mechanisms in response to climate change. The influence of controls on SEM during global warming was assessed using the Pearson ~~Correlation Coefficient~~correlation coefficient.

Time series data reveal declining mean solute concentrations of ~~major~~ nutrients. This decline might be attributed to a shift in transported nutrient loads toward short-duration, high water-level events that are not captured by low-resolution grab sampling. A further possible explanation is ~~the shrinking anthropogenic influences such~~ improved fertilizer management ~~as intensive land management~~in agricultural landscapes in southern Germany. ~~Consequently~~Under prevailing fertilizer application and land manage strategies, the export mechanisms of ~~major~~ nutrients ~~are~~would be ~~primarily driven~~shaped by a combination of biogeochemical processes and hydrological connectivity, except for NO_3-N. ~~Large NO_3-N~~NO_3-N is typically buffered by large and persistent sources~~ still persist, buffering~~, which become active during catchment saturation and ~~seasonal variations and limiting alterations~~limit future changes in ~~SEM~~solute export due to global warming~~.~~

~~Shallow-sourced~~, whereas nutrients such as NH_4-N, SRP, and TP exhibit weaker buffering effects. However, the influence of mankind remains present for all water quality parameters. Temporal-dynamic NH_4-N and SRP are strongly influenced by biogeochemical processes and are therefore highly vulnerable to temporal fluctuations, exhibiting distinct seasonal and climate-driven alterations.

In contrast, ~~discharge-~~long-term dynamic ~~driven~~ solutes such as TP and TOC are less affected by temporal changes, showing no clear seasonal patterns but rather ~~inter-annual~~interannual variations in response to climate change. ~~Shallow-sourced solutes~~Nutrients are transported via surface runoff ~~(NH_4-N, SRP, TP, TOC, and NO_3-N)~~ and subsurface flow~~ (NH_4-N, SRP, and NO_3-N).~~. Climate change alters both transport pathways, leading to shifts in SEM. So, since 2012 (~~Period~~period 2), warmer temperatures, prolonged heatwaves, and sporadic but intense precipitation events have led to increased internal source accumulation and reduced hydrological connectivity. As a result, solute mobilization and transport are largely confined to near-surface pathways during ~~short summer~~ shortened wet periods in summer and to rising water levels in winter, leading to intensified ~~pulse delivery.~~enrichment behaviour. Furthermore, enrichment processes have increasingly outweighed dilution mechanisms~~, primarily due to depletion effects and enhanced biological activity~~, particularly in the case of SRP.

In contrast, underground mobilization and transport processes remain largely resilient to ~~subsurface~~climatic alterations. Consequently, ~~geogenic solutes~~Ca^{2+} and Mg^{2+} experience minimal influence from reduced discharge and show only a slight, non-significant increase in dilution behaviour. The SEM of ~~shallow-sourced solutes~~nutrients is primarily shaped by controls related to hydrological connectivity, including climatic factors (precipitation, evapotranspiration, and drought index) and soil properties (soil moisture and clay content). In contrast, ~~groundwater-sourced solutes are more strongly~~long-term stable Mg^{2+} is dominantly influenced by geological controls, such as sandstone formations.

The study highlights the urgent need to focus on ~~major~~ nutrients~~ and TOC~~, as enrichment export mechanisms continue to intensify. The expansion of extreme weather conditions, including heatwaves and droughts, will further amplify these processes. In the future, solute peak concentrations may increasingly exceed water quality benchmarks, posing risks to riverine ecosystems and human health through eutrophication and drinking water contamination (Radach et al., 2010; Winter et al., 2020). These findings should be incorporated into future decision-making to enhance catchment management and mitigate the increasing trend of solute accumulation. Developing efficient strategies to prevent the escalation of enrichment export mechanisms ~~is~~are imperative.

Date Availability Statement

The database used in this study can be requested by the State Environmental Agency of Baden Württemberg (LUBW), the State Environmental Agency of Bavaria (LfU Bayern), and the Ministry for Climate Protection, Environment, Energy and Mobility of Rhineland Palatinate (LfU RLP). ~~Further, the data that support the findings of this study are available from the corresponding author upon reasonable request.~~

Author contributions

~~Frietsch~~SF and ~~Schuetz~~TS conceptualized the study. Further, ~~Frietsch collected~~SF set up the database and ~~analysed~~did the ~~solute~~ data~~.~~ analysis. Both ~~Frietsch~~SF and ~~Schuetz~~TS contributed to the final version of the manuscript, while ~~Schuetz~~TS supervised the project.

Competing interests

The authors declare that they have no conflict of interest.

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