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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, 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 increase in diluting export mechanisms. 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 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

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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 dissolved substances, such as nutrients and minerals, are mobilized and transported from terrestrial systems to downstream water bodies. Catchments, characterized by different size 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; 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 (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 (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 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 (CVC/CVQ). Chemostatic regimes characterise 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 CVC/CVQ exhibits temporal variability in solute concentration, where elevated nutrient concentrations are linked to eutrophication processes that harm water bodies 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, 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 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), covering catchments located in Rhineland Palatinate, Baden-Württemberg, and Bavaria (LfU Bayern, 2022; LfU RLP, 2022; LUBW, 2022). Subsequently, the catchments include different regions with contrasting climate and catchment characteristics. The study focuses on mid-mountain catchments in Eifel,

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Hunsrück, Palatinate Mountains, Black Forest, Swabian Alb, and Upper Palatinate Forest. Additionally, catchments are also located in Upper Rhine Lowlands, wurttembergisches Unterland, and Franconia (Fig. 1).

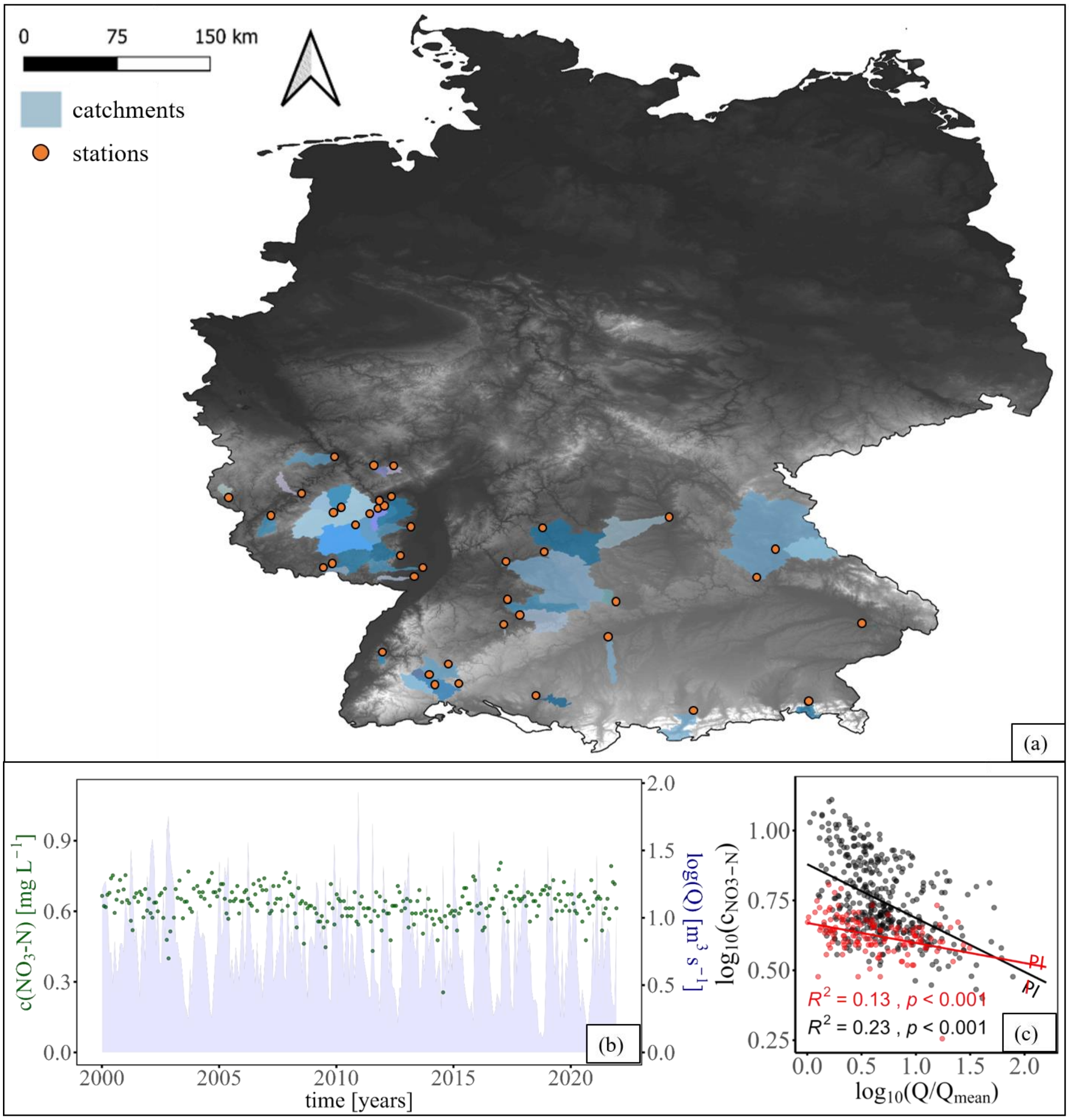

Figure 1: Study area in Southwest Germany with 40 catchments. (a) Map of catchments with measuring stations (orange), with a black-white gradient indicating elevation (BKG, 2013). (b) Time series of discharge and nitrate (NO_3-N) in the Fils catchment. (c) cQ-relationships for NO_3-N in the Fils catchment, 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

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Köppen und Geiger climate classification, the climate is humid continental (Dfb) in Bavaria and most parts of Baden-Wurttemberg (Beck et a., 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 three orders of magnitude and varies from 0.41 $m^3 s^{-1}$ to 49.73 $m^3 s^{-1}$.

The regional geology is heterogenous with crystalline rocks in the Palatinate Mountains and Black Forest. Formations of carbonate rocks are located in Swabian Albs, 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 km^2), which account for over 80% of all catchments (Fig. 1). 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 1 and 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.

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, which are relatively stronger affected by climate change.

2.3 Data Treatment and Analysis

Trends in solute mean concentration C along the whole observation period were determined by using linear regression ($p<0.05$) for each catchment. cQ-relationships for each of the parameters and each catchment were calculated based on the the power-law relation of concentration *C* and discharge *Q* (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}.

$$c = a * Q^b \qquad (1)$$

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

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.

A positive slope ($b>0$) represents an enriching behaviour when solute concentration increases with rising discharge. Meanwhile, a negative slope ($b<0$) displays a diluting behaviour when solute concentration decreases with increasing discharge. Further, a slope close to zero ($b\approx0$) indicates a solute concentration largely independent of discharge magnitude, but there is no evidence of small concentration variability (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 high concentration variability compared to discharge variability were classified as chemodynamic behaviour. Solutes with low concentration variability compared to discharge variability were assigned to chemostatic solutes. The CV_C/CV_Q ratio deals 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).

$$\frac{CV_C}{CV_Q} = \frac{\mu Q * \sigma c}{\mu c * \sigma Q} \qquad (3)$$

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

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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.

2.4 Catchment characteristics

Additionally, SEM are potentially controlled by various catchment characteristics quantified by analysis of spatial and temporal data delivered from multiple institutions (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 mean discharge Q_{mean}, median of discharge Q_{median}, logarithmized mean discharge $log(Q_{mean})$, and discharge per unit catchment area q (Eq. 4) are calculated for each catchment. 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 $l s^{-1}$.

$$q = \frac{Q*1000}{A} \quad (4)$$

Considered controls of topography are mean altitude and catchment area A, whereas climate controls comprising average precipitation P, average evapotranspiration ET, average potential evapotranspiration PET, and de Martonne drought index (dMI, Eq. 5). The dMI was applied to categorize dry regions with low values and wet regions with high values. The index describes also the gradual transition from arid to humid, the limit 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.

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

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

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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	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.

3.1 Assessment of Solute Mean Concentration

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

Table 2: Descriptive statistics of solute mean concentrations (mg L^{-1}) and standard deviations ($C_{mean \pm SD}$) for each solute. 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).

		NH_4-N	SRP	TP	TOC	NO_3-N	Ca^{2+}	Mg^{2+}
$C_{mean + sd}$ (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	18.2	2.5	20.0	17.5
	$C_{decrease}$ (%)	60.0	70.0	63.2	12.1	72.5	5.0	2.5
	NC (%)	37.5	30.0	36.8	69.7	25.0	75.0	80.0

3.2 Predominant SEM affected by temporal circumstances

Long-term cQ-slopes and CV_C/CV_Q metrics in southern Germany reveal explicit solute export mechanisms (SEM) for major nutrients, TOC, and geogenic solutes, highlighting variations in mobilization, transport, and transformation processes influenced by seasonality, humidity, and climate change. Predominant SEM were analysed using slope b and CV_C/CV_Q metrics, indicating both spatial and temporal variations in solute behaviour.

Major nutrients, such as NH_4-N, SRP, and TP, exhibited more pronounced chemodynamic behaviour compared to inert minerals like Ca^{2+} and Mg^{2+} (Fig. 2). Reactive 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 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 enrichment displayed chemodynamic behaviour, indicating 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). NO$_3$-N follows dilution and enrichment pattern while maintaining a chemostatic signature.

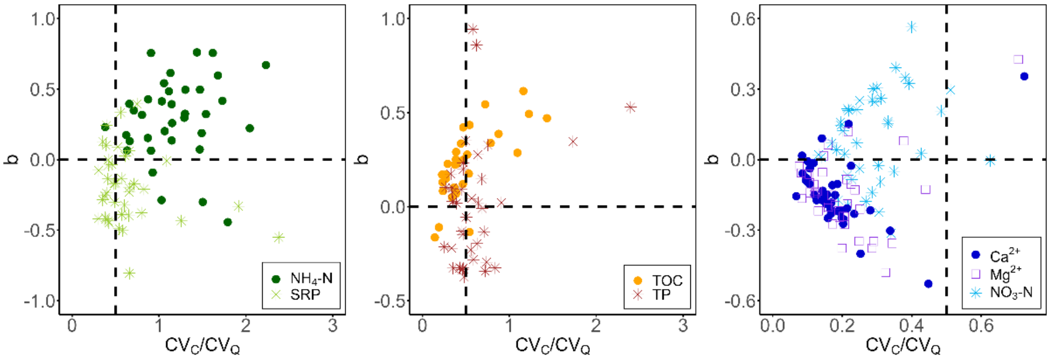

Figure 2: Illustration of the SEM of ✳ SRP, ● NH4-N, ✳ TP, ● TOC, ✳ NO3-N, ● Ca2+ and □ Mg2+ as cluster. Cluster represent shallow-sourced solutes affected by biogeochemical processes (green, left), discharge-driven shallow-sourced solutes (yellow/ brown, middle) and discharge-driven groundwater-sourced solutes (blue/ violet, right).

Temporal analyses revealed significant changes in SEM for NH$_4$-N, SRP, TP, and TOC, driven by seasonal and climatic factors. Among these, NH4-N exhibited the highest seasonal variability in SEM, with pronounced enrichment during summer and reduced enrichment dynamics in winter. In contrast, SRP tended to follow a dilution pattern in summer and showed enrichment mechanisms in winter (Fig. 3). Reactive nutrients such as NH$_4$-N and SRP displayed higher 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 the recent decade, dilution processes have weakened, as indicated by a positive Δb, particularly in catchments that exhibited dilution SEM in prior decades (Fig. 4). Further, for 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 less temporal variability in SEM, as no significant seasonal changes in export dynamics were observed. However, during the more recent period (Period 2), characterized by warmer, drier summers with sporadic but intense one-day precipitation events (KLIWA, 2021; Payne et al., 2020), TP and TOC showed an increasing tendency toward enrichment, highlighting the influence of long-term climatic trends (Fig. 3). TP exhibit increasing slope b (Δb), especially in catchments that had displayed 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, catchments with chemodynamic behaviour predominantly exhibit an increase in enrichment behaviour.

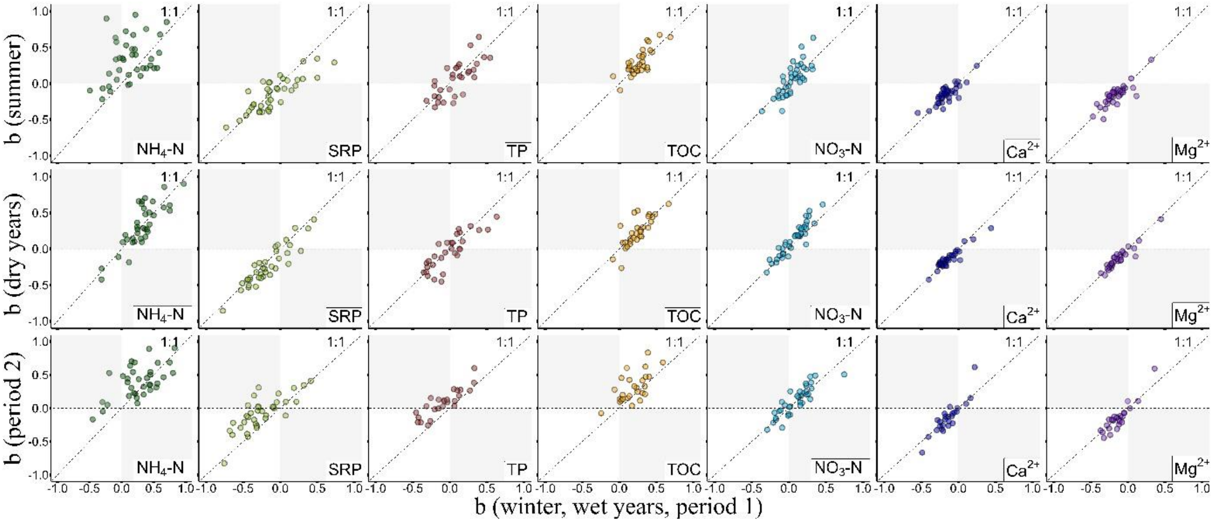

Figure 3: Differences in SEM for NO_3-N, NH_4-N, SRP, TP, TOC, Ca, and Mg due to temporal impacts. Differences in SEM between summer and winter (upper row), between dry years and wet years (middle row), and between the climate-change-affected decade (Period 2: from 2012 onward) and the unaffected decade (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 to seasonal variations, humidity levels, or climate change (Fig. 3). These solutes exhibited minimal changes in Δb (ranging from -0.25 to 0.25), with no clear trend (Fig. 4). Mean slope b calculations suggested a slight, but not significant, increase in enrichment for NO_3-N, while Ca^{2+} and Mg^{2+} showed a slight, non-significant trend toward increasing dilution behaviour in recent decades (Table 4).

Solutes with chemostatic patterns, such as NO_3-N, Ca^{2+}, and Mg^{2+}, exhibited lower 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, suggesting that climate-driven shifts in SEM are linked to processes beyond humidity variations (Fig. 3).

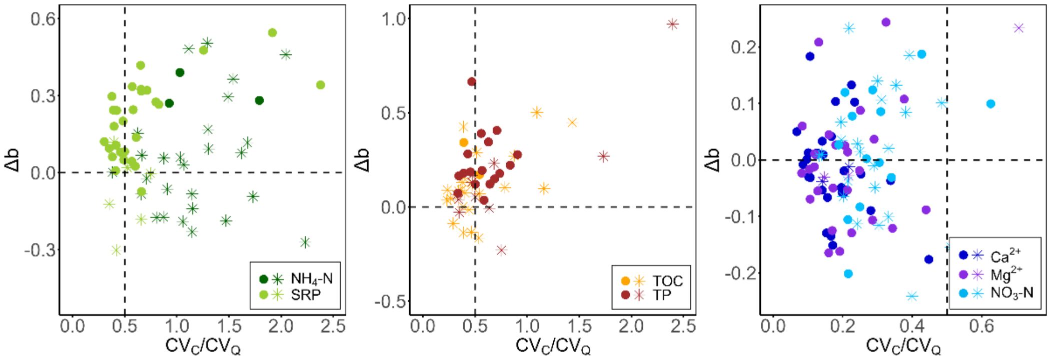

Figure 4: Change in cQ-relationships (Δb) for SRP, NH_4-N, TP, TOC, NO_3-N, Mg^{2+} and Ca^{2+} explained by climate change. Positive (Δb) indicating increasing enrichment behaviour. ✳ Catchments with enrichment behaviour in Period 1, ● catchments with dilution behaviour in Period 1.

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, $p < 0.05$) were used to assess these relationships between SEM (slope b) and explanatory control for the decade before and after January 1, 2012. 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 surface factors, particularly climatic conditions, whereas geogenic solutes like Ca^{2+} and Mg^{2+} are predominantly 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.

For NH_4-N, precipitation (-), drought index (-), and soil moisture (-) show negative correlations with slope b, indicating dilution behaviour in wet catchments and enrichment behaviour in dry catchments. During Period 2, the impact of these controls intensified, leading to a stronger regulation of cQ relationships by explanatory factors. 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 and soil moisture has increased, hydrological indices and further geological controls have become less influencing in regulating cQ relationships. TOC, which is primarily governed by surface processes, is exclusively influenced by evapotranspiration (+), with its higher impact during 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 drought index) are more likely to exhibit dilution SEM. Over time, the influence of land use on SEM has diminished, whereas the impact of climatic conditions and soil moisture has increased. As expected, geogenic solutes, such as Ca^{2+} and Mg^{2+}, are primarily controlled by geological factors, with sandstone proportion correlating positively with SEM. However, in the recent period the small effect of sandstone proportions in catchments on SEM has diminished.

Table 3: Explanatory controls of different categories influencing SEM Results based on Pearson Correlation. Significance level $p<0.05$. Description: highly significant positive correlation (++), significant positive correlation (+), significant negative correlation (-), highly significant negative correlation (--), increased impact of control due to climate change (△), decreased impact of control due to climate change (▽), no change (O).

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

4 Discussion

Solute concentration and SEM varied due to temporal and spatial factors, influencing solute mobilization, transportation, storage, and transformation processes. The analysis reveals 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, geogenic solutes, and TOC 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 concentrations of NH_4-N can be attributed to 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 contrast, NO_3-N concentrations averaged 4.04 mgL^{-1}, reflecting agricultural influences. Persistent NO_3-N levels are closely linked to fertilization practices (Reynolds et al., 1997; Aubert et al., 2013). Between 1979 and 2000, nutrient concentrations in Germany were elevated, leading to substantial nutrient storage, particularly for nitrate. A decline in nutrient concentrations observed in later decades (1990–2000) coincided with reductions in fertilizer application. While NH_4-N, TP, and SRP concentrations decreased, NO_3-N levels remained high due to legacy effects, resulting in a slower overall decline (Basu et al., 2010). The continued decline in NH_4-N, TP, and SRP concentrations can also be attributed to prolonged drought periods driven by climate change. Extended dry conditions, particularly in summer, 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 events are associated with increased nutrient transport. Since sampling occurs biweekly to monthly, it is more likely to capture low-water-level conditions, potentially underestimating overall 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.

TOC is less reactive and more persistent, with high emissions from fertile sources, resulting in higher mean concentrations with wider variability. TOC showed a slight tendency toward increasing concentrations, though interannual variability was less dominant compared to major nutrients, suggesting less influence from anthropogenic actions. Geogenic solutes like Ca^{2+} and Mg^{2+} exhibited high mean concentrations, consistent with findings by Musolff et al. (2015). The heterogeneous geology of southern Germany induces variation in solute source, leading to high spatial variability in Ca^{2+} and Mg^{2+} concentrations. These solutes, primarily influenced by geological processes, showed only slight increases in mean concentration in a moderate fraction of overall catchments ($Ca2^{+}$: 20 %, Mg^{2+} 12.5 %) The persistence of the lithosphere and weathering processes contributed to low interannual variability. However, climate change, induce warmer temperatures and lower groundwater levels, promoting higher residence times and enhanced weathering rates. These conditions may explain the slight increase in concentrations. Ca^{2+}-rich rocks are particularly affected, as they are more vulnerable to weathering processes (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 shifts in 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 into distinct groups, namely: (1) shallow-sourced solutes affected by

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biogeochemical processes, (2) primarily discharge-driven shallow-sourced solutes, and (3) groundwater-sourced solutes (Fig. 2).

4.2.1 SEM of Shallow-Sourced and Groundwater-Sourced Solutes

Shallow-sourced solutes influenced by biogeochemical processes dominantly exhibit chemodynamic behaviour (Fig. 2, left). Variability in solute concentration exceeding discharge variability reflects additional biogeochemical processes decoupled from discharge (Musolff et al., 2015). Highly reactive nutrients such as NH_4-N, SRP, and TP demonstrate rapid uptake and turnover rates (Birgand et al., 2007; Marti and Sabater, 1996), making their variability dominated by biogeochemical processes rather than discharge. However, in intensively managed catchments, homogeneously and largely distributed solute e.g., SRP- and TP- sources mask biogeochemical effects, resulting in chemostatic behaviour where solute mobilization is proportional to discharge (Ali et al., 2017; Basu et al., 2011; Thompson et al., 2011). Enrichment as well as dilution behaviour characterize shallow-sourced solutes. Enrichment 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 (Basu et al., 2011; Pohle et al., 2021; Rose et al., 2018). Dilution dynamics can also result from biological SRP release during low flow periods, mimicking point sources in sediments and riparian zones (Dupas et al., 2018; 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 solutes, including TOC, TP and partly NO_3-N, show a strong correlation with discharge 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, middle). TOC and particulate-bound TP generally exhibit enrichment behaviour, as increased discharge activates surficial pathways, assisting hydrological connectivity that leads to elevated instream solute concentrations (Huntington and Wieczorek, 2021). However, variability in TOC and TP concentrations can exceed discharge variability due to heterogeneous vertical and horizontal TOC source distribution in riparian zone or SRP related biogeochemical processes, promoting chemodynamic tendencies (Basu et al., 2011; Ebeling et al., 2021; Pohle et al., 2021; Rose et al., 2018; Thompson et al., 2011). 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 biogeochemical variability. In contrast, natural systems without human impact exhibit chemodynamic NO_3-N behaviour, a phenomenon, which is not observed in the anthropogenic 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 chemostatic enrichment dynamics, while groundwater-derived sources typically result in chemostatic dilution behavior (Basu et al., 2011; Moatar et al., 2017; Pohle et al., 2021).

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

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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

Biogeochemical processes vary significantly over time, influenced by seasons, humidity levels, and climate change. Consequently, shallow-sourced nutrients especially NH_4-N and SRP exhibit substantial temporal fluctuations in SEM, with pronounced differences between summer and winter seasons (Fig. 2). Seasonal effects, particularly temperature variations, play a critical role in nutrient production and depletion rates due to rapid biogeochemical turnover (Basu et al., 2010; Ebeling et al., 2021; Greaver et al., 2016; Hellwig et al., 2017; Pohle et al., 2021).

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

Seasonal influences significantly NH_4-N and SRP SEM. NH_4-N show stronger enrichment behaviour in summer due to low hydrological connectivity and high NH_4-N accumulation, while SRP shows higher slope b in winter. Warm summer temperatures enhance biological activity, promoting dilution behaviour due to instream SRP point sources and depletion of terrestrial diffuse sources by e.g. plant uptake. In winter, colder temperatures suppress these processes (Bieroza et al., 2014; Dupas et al., 2018; Marti 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 particle-bound phase, contributing to lower susceptibility to biogeochemical processes. This phase supports discharge-driven mobilization, particularly during increased discharge, resulting in enrichment behaviour (Bieroza et al., 2024; Thompson et al., 2011; Marti and Sabater, 1996). In summer, when hydrological connectivity is low and TP accumulation is exceptionally high, enrichment behaviour becomes more pronounced triggered by 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.

Discharge-driven solutes such as NO_3-N, TOC, and the solid phase of TP experience limited temporal variation due to their relatively reduced sensitivity to biogeochemical processes. Temporal fluctuations in SEM for these solutes are mainly tied to

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seasonal discharge changes, with higher rates in wet winters and lower rates in dry summers, explained by hydrological connectivity (Winter et al., 2020). NO_3-N shows minimal temporal variability because of its widespread presence and reliance on 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 temporal effects, with not significant seasonal variations solely driven by residence time and a consistent solute source. Solutes influenced by biogeochemical processes (NH_4-N, SRP) are most affected by seasonal factors, followed by shallow discharge-driven solutes (TP, TOC) and groundwater discharge-driven solutes (NO_3-N, Ca^{2+}, Mg^{2+}).

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 sporadic intense one-day precipitation events have significantly influenced shallow-sourced solutes (KLIWA, 2021; Payne et al., 2020). While underground weathering processes seem to remain largely unaffected, shallow-sourced solutes, except NO_3-N, have become increasingly sensitive to global warming by changing subsurface processes. Shallow-sourced solutes exhibit enhanced enrichment and reduced dilution behaviour in Period 2, regardless of whether their SEMs are influenced by biogeochemical or discharge-driven processes (Fig. 3 and 4). This trend reflects changes in solute source distribution and mobilization processes.

Prolonged drought and excessive heat amplify the production of decomposable organic material, increasing the availability of nitrogen and phosphorus. 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 nutrient accumulation in upper soil layer (Huntington and Wieczorek, 2021; Kukal and Irmak, 2018). At the same time, drought conditions reduce plant-based nutrient uptake, as terrestrial vegetation becomes limited, leading to greater accumulation of major nutrients. Oxygenation of previously waterlogged soil further suppresses nitrogen removal through denitrification, promoting nutrient accumulation additionally (Bieroza et al., 2024; Gomez et al., 2011). These factors contribute to increased internal sources of TOC (including DOC), TP, SRP, NH_4-N, and NO_3-N in shallow soil layers compared to previous decades. Global warming further degrades soil structure and reduces soil moisture, diminishing the retention capacity for key nutrients, particularly SRP and TP (Lucas et al., 2023). This reduction in retention capacity promotes leaching processes. Consequently, the combination of increased internal sources, drier antecedent conditions, transport limitations, and sporadic high-intensity precipitation events intensifies nutrient leaching and amplifies pulsed nutrient delivery (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 nutrients accumulate in the pedosphere and are later transported through subsurface flow during autumn and winter, when rising water tables and increased discharge enhance hydrological connectivity (Fig. 5; Bieroza et al., 2024). Both transport pathways via surface runoff and subsurface flow lead to increased enrichment behaviour for all shallow-sourced solutes, 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 processes driven by climate change (as observed in Period 2).

NO_3-N exhibits contrasting behaviour due to the extensive anthropogenic legacy stores, which outweigh the effects of climate change and counteract enrichment trends, thus maintaining a dilution-dominated SEM in multiple catchments. While warmer conditions increase substrate availability and biological activity, their impact remains minimal compared to the human-applied NO_3-N in prior decades. As a result, in some catchments, NO_3-N shows only a slight, non-significant decrease in dilution and increase in enrichment behaviour, setting it apart from other nutrients.

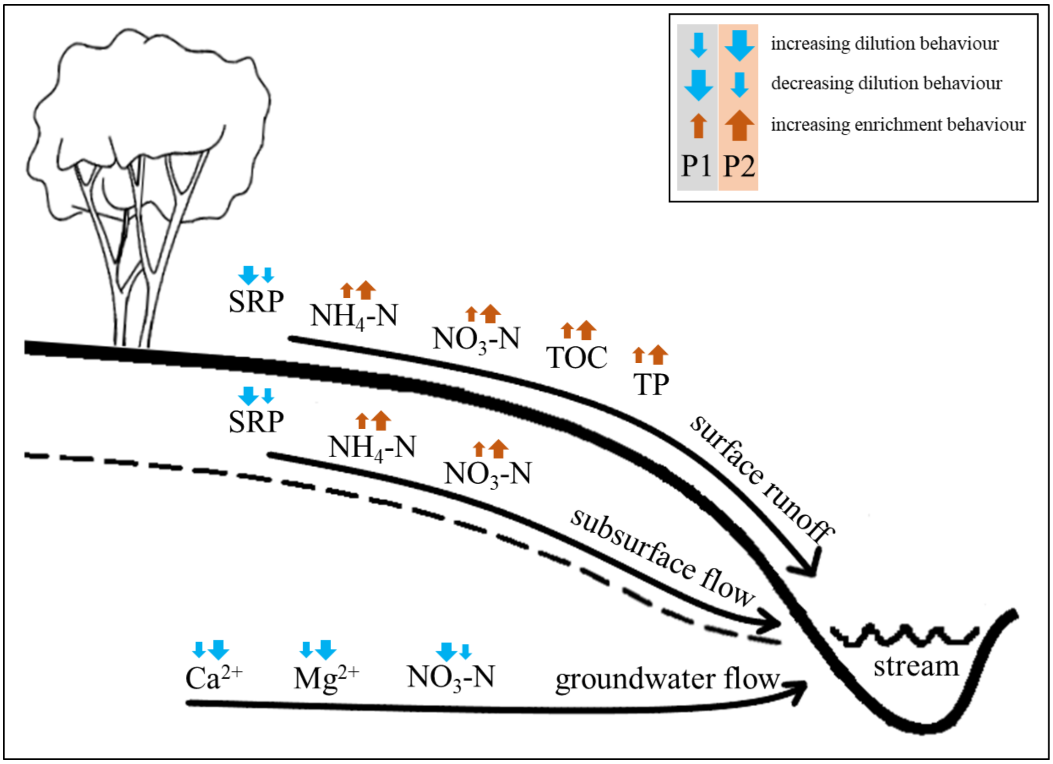

Figure 5: Illustration of mobilization and transportation pathways for shallow-sourced major nutrients, TOC and geogenic minerals. Change in SEM based on climate change illustrated by direction and size of the arrows. P1 – Period 1 (onwards 1st Jan. 2012) less affected by climate change. P2 – Period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

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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 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.

For NH_4-N, surface controls shape SEM. Soil moisture, along with climatic factors such as precipitation and drought indices, drives 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 hydrological connectivity create transport limitations, leading to accumulation patterns, particularly during prolonged heatwaves, which result in larger NH_4-N sources. Climate change amplifies the effects of drought (e.g., soil moisture, drought index) and sporadic precipitation events, explained by extended transport limitations while increasing solute accumulation, ultimately intensifying enrichment dynamics. For SRP, evapotranspiration and clay-rich soils play key roles. In addition to in-stream point sources, low evapotranspiration helps keep pathways active in shallow soils. This connectivity links terrestrial SRP sources to streams, promoting dilution patterns through 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 2, this buffering effect has intensified, highlighting rapid SRP leaching in areas lacking clay minerals, especially under climate change conditions. The impact of evapotranspiration has also increased in recent years due to climate change. Higher evapotranspiration leads to extended SRP accumulation and reduced hydrological connectivity, ultimately diminishing dilution behaviour.

TP SEM reflects the interplay between discharge-driven and biogeochemical processes due to its presence in both solid and soluble phosphorus phases. Increased discharge activates preferential pathways, enhancing enrichment behaviour through sediment mobilization. This process is driven 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, precipitation, evapotranspiration, soil moisture, clay rock, and carbonate rock. Carbonate rock formations facilitate preferential pathways,

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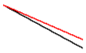
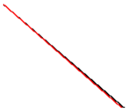
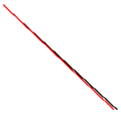
amplifying enrichment behavior. In contrast, clay materials mitigate this effect by slowing phosphorus mobilization (Basu et al., 2011; Thompson et al., 2011). However, climate change expands TP sources and transport limitation (control: evapotranspiration, soil moisture, drought index), intensifying mobilization during sporadic summer rainfall and rising winter water tables (control: precipitation). This leads to pulsed delivery events and weakens dilution patterns. As climate controls and soil moisture become more influential, the impact of hydrological indices and geology 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).

NO_3-N displays subsurface controls but maintains a distinctive chemostatic behaviour representing a more or less temporal invariable solute. Wet conditions, explained by high precipitation, high drought index, and high soil moisture content, enhance dilution dynamics. In contrast, arable land and evapotranspiration promote enrichment behaviour by creating internal sources and transport limitations. Urban areas contribute to dilution behaviour as 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 of land cover, specifically arable land and urban areas, has diminished. This suggests a lower disturbance in SEM from anthropogenic activities, such as reduced emissions from wastewater treatment plants and decreased fertilizer application. Minor changes, including lower hydrological connectivity and increased NO_3-N generation during prolonged heatwaves, slightly amplify enrichment behaviour and weakened dilution SEM. However, 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.

Climate change significantly alters the impact of controls on shallow-sourced solute export mechanisms. Climatic controls and soil moisture gain influence, driving 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 may increase solute concentration peaks, posing risks to ecosystems and human health by exceeding water quality benchmarks (Outram et al., 2016; Radach et al., 2010; Winter et al., 2020). To counteract these enrichment trends, effective catchment management strategies are essential. For groundwater-sourced solutes, the impact of climate change remains minor. However, slight increases in dilution dynamics are assumed due to prolonged residence times.

Table 4: 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. Symbols indicate increasing (△) or decreasing (▽) control impact. Panels: (a)

all catchments, (b) catchments with enrichment behaviour in Period 1 (n≥10), (c) catchments with dilution behaviour in Period 1 (n≥10). Trends are based on mean calculations.

		Changing SEM			Controls
Biological impacted shallow sourced solutes	NH$_4$-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
	NO$_3$-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 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 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 findings confirm enhanced enrichment behaviour for shallow-sourced 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.

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 as intensive land management in southern Germany. Consequently, the export mechanisms of major nutrients are primarily driven by biogeochemical processes and hydrological connectivity, except for NO_3-N. Large NO_3-N sources still persist, buffering seasonal variations and limiting alterations in SEM due to global warming.

Shallow-sourced 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-driven solutes such as TP and TOC are less affected by temporal changes, showing no clear seasonal patterns but rather inter-annual variations in response to climate change. Shallow-sourced solutes 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 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 periods and to rising water levels in winter, leading to intensified pulse delivery. 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 alterations. Consequently, geogenic solutes experience minimal influence from reduced discharge and show only a slight, non-significant increase in dilution behaviour. The SEM of shallow-sourced solutes 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 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 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 and Schuetz conceptualized the study. Further, Frietsch collected and analysed the solute data. Both Frietsch and Schuetz contributed to the final version of the manuscript, while Schuetz supervised the project.

Competing interests

The authors declare that they have no conflict of interest.

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