Reply to the comments

We thank the reviewers and the editor for their constructive feedback, which has substantially improved our manuscript. All changes are clearly marked in the revised version. Reviewer comments are addressed in the following sections. First, we respond to the comments of Reviewer 1, followed by those of Reviewer 2, in chronological order. Reviewer comments are repeated in italics, answers are given with normal letters. For clarity, the responses are numbered.

Detailed Response to Reviewer 1

1. Major comments (Reviewer 1)

1.1 Attribution to climate change

As indicated in the title, the goal of the manuscript is to identify the impact of climate change on solute export. However, I am not convinced that this objective is achieved. The authors compare two time periods (before and after 2012), with an unspecified duration for the respective time series, in terms of concentration-discharge (CQ) relationships . Differences in the CQ relationship between these two periods are attributed to climate change. While I agree that climate change might be a crucial driver for solute export patterns, I find the attribution of the observed effects to climate change unconvincing. In particular, I noted a lack of information on how periods 1 and 2 differ specifically in terms of climatic conditions, as well as how these differences vary among catchments. It remains unclear whether the observed effects are a result of the drought that began in 2018, more intensive rain events, increased temperatures, etc. Although comparing two periods is acceptable (albeit climate change is inherently a gradual process), I strongly recommend conducting an analysis of hydro-climatic anomalies between these periods, accounting for spatial variation, and then attributing these anomalies to the observed changes in CQ relationships rather than to climate change per se. Furthermore, care should be taken in attributing every temporal change to climate change since, for example, Erhardt et al. (2019) demonstrate that CQ relationships can shift over time due to past changes in solute input. Additionally, it should be noted that the period before 2012 is not "unaffected" by climate change, as stated in the caption of Figure 1.

Statement Author to Section 1. Introduction (L. 73/ 74) and Section 2.2 Data Selection and Data Structure (L. 159-173):

To address the concerns raised regarding the attribution of observed changes to climate change, we now provide detailed climatic data comparing period 1 and period 2 in the material and method section, as follows: "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 (see Figure 2). 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."

In addition, we have added a passage to the Introduction highlighting that comparing periods 1 and 2 reveals a segment of this gradual trend (L. 73/74).

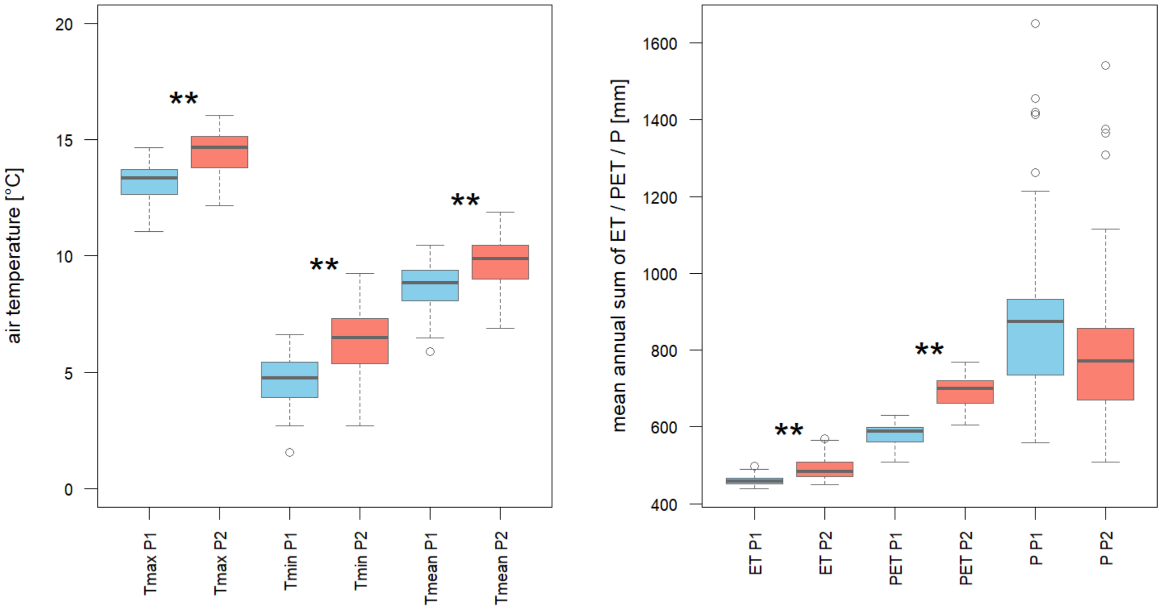


Figure 2: Changes in air temperature (left) and mean annual sums of evapotranspiration (ET), potential evapotranspiration (PET), and precipitation (P, mm; right) between period 1 (P1) and period 2 (P2). Tmax = maximum air temperature (°C), Tmin = minimum air temperature (°C), Tmean = mean annual air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

1.2 Catchment characteristics

From my perspective, the manuscript lacks a table summarizing the catchment characteristics, particularly concerning the variables listed in Table 1. Including such a table would help readers understand the variability across catchments and how these variables may relate to changes in solute export patterns.

Statement Author to Section Supplement:

We have now included a detailed table (see below) in the supplementary materials that clearly presents the characteristics of the catchments and the underlying data used to infer the variables applied in this study, helping readers to better understand how the variables relate to changes in solute export patterns. Furthermore, in Chapter 2.1 Study Site, we have added a reference to these tables to guide readers accordingly (L.99/100).

Table S1: Overview about catchment characteristics including the categories Hydrological (Q_{mean}, Q_{median}, log(Q_{mean}), q – discharge per unit catchment area), Topography (altitude, A – catchment area), Land use (forest, pastures, arable land, urban area), and Geology and soil (soil moisture, sediments, loess sediments, crystalline rock, sandstone, clay rock). Soil moisture is calculated for Period 1 (P1), Period 2 (P2) and the whole observation period (all).

stream	Q_{median} [m^3 s $^{-1}$]	Q_{mean} [m^3 s^{-1}]	log(Q_{mean}) [m^3 s^{-1}]	A [km^2]	q [L s^{-1} km^{-2}]	altitude [m.a.s.l.]	soil moisture [% nFK]			carbonate rock [%]	sediments [%]	loess sedi-ments [%]	crystalline rock [%]	sandstone [%]	clay rock [%]	forest [%]	pastures [%]	arable land [%]	urban area [%]
							P1	P2	all										
Aisch	3.7	5.8	0.6	991	5.8	268	1014	914	980	0	0	2	0	45	53	21	26	48	4
Kammel	2.2	2.7	0.4	251	10.6	548	1124	1063	1103	0	4	92	0	0	0	34	32	28	6
Loisach	18.9	21.6	1.3	638	4.2	827	1234	1214	1227	78	1	0	0	0	7	50	18	0	4
Naab	35.6	49.7	1.6	5434	9.0	449	1099	1027	1075	15	4	4	40	33	5	45	18	30	5
Schwarzach	6.1	8.5	0.8	820	10.2	553	1125	1063	1104	0	0	0	100	0	0	40	29	28	3
Tiroler Achen	27.9	35.8	1.5	945	37.8	613	1202	1171	1191	91	9	0	0	0	0	69	17	0	3
Vils	7.4	11.0	1.0	1440	7.1	357	1103	1040	1081	0	0	100	0	0	0	18	0	80	2
Alf	4.0	1.3	0.1	138	45.5	433	1090	1034	1071	0	0	0	0	0	100	18	56	22	4
Alsenz	2.3	1.7	0.1	316	9.4	351	1079	1003	1053	0	0	0	10	90	0	9	51	34	5
Appelbach	10.7	0.5	-0.2	170	84.2	148	1017	926	985	0	1	50	12	37	0	3	28	63	6
Erlenbach	19.4	0.5	-0.2	97	240.5	173	1034	938	1001	0	23	51	0	26	0	25	15	51	9
Glan	19.3	10.1	0.8	1088	21.2	335	1065	985	1037	0	0	0	8	86	2	14	54	20	11
Hornbach	18.2	4.5	0.6	425	50.7	290	1066	982	1037	3	0	0	0	10	87	3	50	34	13
Nahe	20.1	29.8	1.3	4039	7.2	363	1082	1009	1057	0	0	6	9	53	30	14	49	28	8
Nette	38.0	2.0	0.2	369	147.2	441	1098	1038	1077	0	0	1	58	0	40	14	34	39	12
Pfrimm	32.5	0.8	-0.1	226	198.9	395	1070	992	1043	23	10	20	0	47	0	4	25	63	8
Queich	37.6	1.1	0.0	268	189.0	187	1040	948	1009	0	19	12	0	68	0	46	33	12	9
Ruwer	36.5	2.7	0.2	222	222.7	412	1092	1035	1072	0	0	0	0	1	99	34	49	13	4
Selz	5.8	0.5	-0.3	363	27.5	226	1039	952	1009	0	0	98	0	2	0	0	2	89	9
Simmerbach	6.9	2.3	0.1	362	25.1	422	1078	1007	1053	0	0	0	0	14	86	22	38	36	4
Speyerbach	6.3	1.8	0.2	312	29.3	293	1063	979	1034	0	3	0	0	97	0	77	20	0	3
Wiesbach	27.5	0.4	-0.2	197	177.6	187	1021	931	990	0	0	64	10	26	0	2	21	70	7
Hahnenbach	27.3	1.7	0.1	255	144.8	345	1073	1002	1048	0	0	0	0	0	100	25	40	30	5
Aar	27.9	1.4	0.0	243	144.1	254	1043	960	1014	0	0	0	0	0	100	7	56	33	4
Doersbach	28.7	0.7	-0.1	113	324.9	343	1060	984	1034	0	0	0	0	0	100	10	49	38	3
Enz	6.7	1.2	0.1	101	115.4	525	1103	1068	1091	0	0	0	0	4	96	14	58	26	2
Schwarzbach	8.1	4.6	0.6	530	20.2	460	1095	1018	1068	0	0	0	0	65	35	32	46	14	8
Brigach	8.3	1.9	0.1	101	115.1	835	1192	1135	1172	0	0	8	59	33	0	54	32	0	13
Donau	1.6	9.0	0.7	827	4.6	827	1194	1135	1174	29	0	5	28	14	24	42	34	15	8
Eger	0.8	1.0	0.0	107	12.8	514	1104	1033	1080	23	0	5	0	1	71	16	25	52	7
Erms	0.4	3.2	0.4	159	3.4	393	1098	1022	1072	2	98	0	0	0	0	0	41	40	19
Jagst	0.5	9.6	0.7	1030	2.7	508	1098	1024	1072	39	0	31	0	0	31	15	37	43	5
Neckar	3.8	4.9	0.5	452	15.5	743	1170	1107	1149	25	0	21	0	16	38	34	32	20	13
Rems	7.0	6.7	0.7	569	31.9	339	1065	982	1036	50	0	3	0	0	46	20	38	26	16
Schutter	1.0	0.6	-0.2	49	28.5	327	1104	1022	1076	0	0	0	72	28	0	56	43	1	0
Tauber	0.6	8.9	0.8	1584	0.5	318	1045	954	1014	66	0	24	0	2	8	8	28	84	5
Fils	0.8	9.4	0.8	696	2.0	457	1110	1039	1085	59	0	0	0	0	41	6	55	28	12
Kocher	0.8	22.3	1.2	1932	0.9	442	1092	1015	1065	40	0	27	0	0	33	23	36	34	7
Wolfegger Ach	0.5	3.0	0.4	164	3.6	632	1170	1116	1151	0	100	0	0	0	0	27	60	6	4
Breg	0.8	5.6	0.5	291	6.8	827	1194	1135	1174	12	0	2	59	20	8	63	25	7	4

Table S2: Overview about catchment climatic characteristics including precipitation (P), evapotranspiration (ET), potential evapotranspiration (PET), evaporative index (ET/P), and aridity index (PET/P) calculated for Period 1 (P1), Period 2 (P2) and the whole observation period (all).

stream	P [mm]			ET [mm]			PET [mm]			ET/P [-]			PET/P [-]			dMI [mm °C^{-1}]		
	P1	P2	all	P1	P2	all	P2	P1	all	P1	P2	all	P1	P2	all	P1	P2	all
Aisch	679.0	597.6	657.2	450.3	462.0	454.3	724.6	602.4	644.4	0.7	0.8	0.7	0.9	1.2	1.0	34.1	26.6	32.1
Kammel	915.8	849.9	898.2	483.3	523.9	497.3	688.3	583.5	619.5	0.5	0.6	0.6	0.6	0.8	0.7	46.7	40.0	44.9
Loisach	1371.9	1297.6	1352.0	498.7	572.0	523.9	625.4	534.5	565.7	0.4	0.4	0.4	0.4	0.5	0.4	84.5	73.4	81.5
Naab	833.3	706.9	799.4	456.3	485.6	466.4	669.5	564.6	600.7	0.6	0.7	0.6	0.7	1.0	0.8	49.3	35.7	45.6
Schwarzach	901.2	798.5	873.7	450.1	484.7	462.0	644.9	544.5	579.0	0.5	0.6	0.5	0.6	0.8	0.7	57.3	43.0	53.4
TirolerAchen	1623.6	1521.1	1596.1	498.6	568.9	522.8	662.5	558.7	594.4	0.3	0.4	0.3	0.3	0.4	0.4	101.1	87.3	97.4
Vils	889.4	792.6	863.4	484.1	525.5	498.3	701.6	599.6	634.6	0.5	0.7	0.6	0.7	0.9	0.7	50.2	38.8	47.2
Alf	903.0	786.2	871.6	440.0	452.7	444.4	657.7	560.7	594.1	0.5	0.6	0.5	0.6	0.8	0.7	52.0	40.3	48.8
Alsenz	739.1	714.6	732.5	450.0	472.4	457.7	695.2	578.5	618.6	0.6	0.7	0.6	0.8	1.0	0.9	37.8	33.1	36.5
Appelbach	543.3	483.2	527.1	459.1	475.2	464.6	759.2	625.1	671.2	0.9	1.0	0.9	1.2	1.6	1.3	22.5	17.7	21.2
Erlenbach	783.8	731.7	769.8	472.8	497.1	481.2	772.4	632.7	680.7	0.6	0.7	0.6	0.8	1.1	0.9	37.3	31.2	35.7
Glan	847.7	784.8	830.8	461.1	482.2	468.3	723.7	600.4	642.8	0.5	0.6	0.6	0.7	0.9	0.8	44.1	37.3	42.3
Hornbach	905.3	809.1	879.5	469.4	493.7	477.7	737.9	609.9	653.9	0.5	0.6	0.5	0.7	0.9	0.7	47.9	37.9	45.2
Nahe	851.9	794.2	836.4	450.2	470.3	457.1	691.1	577.8	616.7	0.5	0.6	0.6	0.7	0.9	0.7	46.3	39.3	44.4
Nette	852.5	765.1	829.0	433.4	445.9	437.7	642.7	548.7	581.0	0.5	0.6	0.5	0.7	0.9	0.7	47.7	39.1	45.4
Pfrimm	705.8	666.0	695.1	448.4	470.0	455.8	700.2	581.6	622.4	0.7	0.8	0.7	0.9	1.2	1.0	37.0	31.3	35.5
Queich	803.9	795.2	801.6	469.9	493.7	478.1	760.3	624.3	671.1	0.6	0.6	0.6	0.8	1.0	0.8	39.3	35.9	38.4
Ruwer	996.3	910.0	973.2	454.1	471.8	460.2	681.6	576.7	612.7	0.5	0.5	0.5	0.6	0.8	0.6	55.5	47.5	53.4
Selz	636.6	576.1	620.4	450.1	468.4	456.4	729.1	601.7	645.5	0.7	0.8	0.7	1.0	1.3	1.0	29.8	24.2	28.3
Simmerbach	697.2	613.1	674.6	442.6	459.3	448.3	681.0	571.7	609.3	0.6	0.8	0.7	0.8	1.1	0.9	35.2	27.8	33.2
Speyerbach	815.5	718.6	789.5	459.7	483.1	467.7	725.0	599.1	642.4	0.6	0.7	0.6	0.7	1.0	0.8	41.7	33.1	39.4
Wiesbach	540.0	491.5	527.0	455.7	471.9	461.3	750.9	618.6	664.1	0.9	1.0	0.9	1.2	1.5	1.3	22.7	18.8	21.7
Hahnenbach	768.2	655.8	738.0	446.2	462.6	451.8	691.2	578.8	617.5	0.6	0.7	0.6	0.8	1.1	0.8	40.3	30.5	37.7
Aar	645.3	554.9	621.1	441.7	457.3	447.1	709.6	589.9	631.0	0.7	0.8	0.7	0.9	1.3	1.0	31.0	23.6	29.0
Doersbach	739.1	640.9	712.7	439.4	455.1	444.8	690.5	577.4	616.3	0.6	0.7	0.6	0.8	1.1	0.9	37.8	29.4	35.5
Enz	930.8	767.8	887.1	442.0	451.4	445.2	635.8	553.3	581.7	0.5	0.6	0.5	0.6	0.8	0.7	54.0	38.9	49.9
Schwarzbach	958.8	866.7	934.1	457.7	484.2	466.8	694.5	578.7	618.5	0.5	0.6	0.5	0.6	0.8	0.7	54.4	44.1	51.7
Brigach	1454.8	1364.7	1430.6	457.9	509.5	475.6	623.6	518.1	554.4	0.3	0.4	0.3	0.4	0.5	0.4	99.8	86.6	96.2
Donau	1229.6	1169.6	1213.5	463.6	518.5	482.4	631.6	521.6	559.4	0.4	0.5	0.4	0.5	0.6	0.5	83.6	75.1	81.3
Eger	872.4	764.8	843.5	461.0	492.7	471.9	677.1	569.9	606.7	0.5	0.6	0.6	0.7	0.9	0.7	49.2	37.6	46.1
Erms	903.0	807.1	877.3	472.3	508.6	484.8	708.9	591.1	631.6	0.5	0.6	0.6	0.7	0.9	0.7	44.9	35.7	42.4
Jagst	878.1	770.7	849.3	459.0	489.4	469.5	681.1	571.4	609.1	0.5	0.6	0.6	0.7	0.9	0.7	49.3	38.5	46.4
Neckar	972.5	897.6	952.4	465.9	516.6	483.4	651.9	540.4	578.7	0.5	0.6	0.5	0.6	0.7	0.6	59.3	49.2	56.6
Rems	929.4	870.6	913.6	471.9	500.0	481.6	728.2	606.9	648.6	0.5	0.6	0.5	0.7	0.8	0.7	47.2	40.9	45.5
Schutter	1213.3	1114.9	1186.9	481.3	526.0	496.7	739.7	601.6	649.1	0.4	0.5	0.4	0.5	0.7	0.6	62.1	54.7	60.1
Tauber	721.8	636.3	698.9	452.5	473.8	459.8	717.3	592.7	635.5	0.6	0.8	0.7	0.8	1.1	0.9	36.7	28.5	34.5
Fils	1052.3	931.1	1019.8	466.7	502.0	478.9	687.1	576.4	614.5	0.5	0.6	0.5	0.6	0.8	0.6	58.0	47.9	55.2
Kocher	929.6	831.6	903.3	460.4	490.3	470.7	690.8	578.0	616.8	0.5	0.6	0.5	0.6	0.8	0.7	51.5	42.2	49.0
Wolfegger Ach	1242.0	1052.6	1191.2	490.8	547.5	510.3	673.9	566.3	603.3	0.4	0.5	0.4	0.5	0.6	0.5	71.1	54.1	66.5
Breg	1229.6	1169.6	1213.5	463.6	518.5	482.4	631.6	521.6	559.4	0.4	0.5	0.4	0.5	0.6	0.5	83.6	75.1	81.3

1.3 Characterization and grouping of solutes

I am not entirely convinced by the classification of solutes into different groups. The terminology used raises some concerns: while it is evident that nitrogen (N) and phosphorus (P) are major nutrients, also carbon (C) can be conceived as a nutrient (see Wachholz et al. 2023), as well as to magnesium (Mg) and calcium (Ca), which are secondary nutrients rather than primary ones. When comparatively describing these solutes, greater care should be taken not to mix up their functional roles (e.g., nutrition) with their origins (e.g., geogenic sources).

Additionally, the grouping of shallow-sourced & biogeochemically affected, shallow-sourced & discharge-driven, and discharge-driven groundwater-sourced solutes appears unconvincing. Firstly, it *is inconsistent with what is illustrated in Figure 5, where nitrate is represented across all layers. Secondly, I would recommend avoiding the term "discharge-driven," as discharge results from various factors, including catchment wetness and hydrological connectivity. Thus, solute export patterns may be influenced by hydrological processes but not necessarily by discharge as such. Furthermore, the definition of "biogeochemically affected" lacks precision. For instance, while nitrate may not be as volatile as ammonium (NH4), it is still subject to various biogeochemical processes, such as uptake and denitrification. Referring to Figure 5 again, total phosphorus (TP) is only depicted in the surface layer, while soluble reactive phosphorus (SRP) is depicted in the subsurface layer as well. It is unclear how SRP could be present in the absence of TP. Overall, I find the reasoning behind the grouping of solutes to be unclear, as well as the justification for its generalizability across the observed catchments.*

Statement Author to Section 4.2 Changes in SEM associated with Seasonality, Humidity Level and Climate Change (L. 478-482):

We follow the reasoning of the reviewer in several points, and the respective revisions have been incorporated into the manuscript. Whilst the grouping of solutes will remain in its original form as a meaningful basis for analysis, it is acknowledged that the current interpretative labels, such as "shallow-sourced biogeochemically affected solutes", "shallow-sourced discharge-driven solutes", or "discharge-driven groundwater-sourced solutes", may be ambiguous and potentially misleading.. The grouping of the solutes has been based on descriptive data analysis with regard to temporal changes in the respective c-Q relationship, which will be explained in the revised manuscript in detail. The group of “temporal-dynamic solutes” shows seasonal variability in their c–Q relationships (slope b), while “long-term dynamic” and” long-term stable” solute c-Q relationships do not change between seasons. Both, ”temporal-dynamic” and “long-term dynamic” solutes exhibit significant changes in slope b between periods 1 and 2, indicating shifts in solute export mechanisms. In contrast, “long-term stable” solutes display no significant changes in slope b either seasonally or over time, suggesting temporally consistent export patterns. In line with the reviewer’s suggestion, the term “discharge-driven” will no longer be used.

This reframing emphasizes temporal characteristics of the data rather than mechanistic/biogeochemical interpretations, offering a clearer and more objective basis for discussion. The group labels will be revised to reflect observed temporal behaviour, specifically regarding intraannual and interannual variability. The three groups will be renamed as follows:

(a) temporal-dynamic solutes,

(b) long-term dynamic solutes, and

(c) long-term stable solutes.

In the revised Discussion, the categories were introduced as follows: “Changes in slope b over time reveal shifts in solute mobilization, transportation, and transformation processes, depending on seasonality, humidity levels, and responses to climate change. SEM cluster into three groups: (1) temporal-dynamic solutes, (2) long-term dynamic solutes, and (3) long-term stable solutes (Fig. 3).”

Furthermore, following the reviewers’ suggestions, total organic carbon (TOC) will be incorporated within the nutrient category rather than being listed separately. To maintain a clear distinction from primary nutrients, calcium (Ca^{2+}) and magnesium (Mg^{2+}) will continue to be referred to as "geogenic minerals." It should be noted that, when comparing the water quality parameters, the functional roles (e.g., nutritional relevance) and origins (e.g., geogenic sources) will no longer be used simultaneously or in combination. This adaptation was implemented throughout the entire manuscript.

1.4 Grammar and manuscript length

The writing quality is generally good. However, the manuscript requires a careful check for grammar, word choice, and consistency, and it should be shortened, particularly in the discussion section. While I appreciate that the manuscript is grounded in a thorough literature review, the discussion would benefit from being streamlined to emphasize the main message. In addition to these three major points, you will find my minor comments below. Please note that I may not have grasped all the details of the discussion, as it is quite lengthy, making it sometimes difficult to extract the main message.

Statement Author to Section 4 Discussion:

Since it is our intention to convey the main message as clearly as possible to our readers, we have made a concerted effort to shorten the manuscript, particularly the discussion section, to improve clarity and focus.

2. Minor comments (Reviewer 1)

2.1 Title

The term “major nutrients” is misleading, as explained in major comment 3.

Statement Author to Title:

We follow the reviewer concerns and change the wording of the title by removing the parts in question. The new title will be called: “Exploring Controls on Solute Export Mechanisms in Anthropogenically Impacted Catchments in Southern Germany under Climate Change”

2.2 Abstract

L. 9: When I first read "SEM," I initially thought the reviewers were referring to structural equation models, which is a common interpretation of this abbreviation. To avoid confusion, I suggest not using the abbreviation and instead writing it out in full throughout the manuscript.

Statement Author to Abstract (L. 9):

As the reviewer, some readers might find the term 'SEM' misleading. However, after careful consideration, we have decided to keep the abbreviation throughout the manuscript. Including the full term every time would result in excessive wording, and given the high frequency of its appearance, spelling it out each time would make the manuscript less convenient to read.

L14: One example of why a grammar check is necessary: “solutes exhibit slightly increase in diluting export mechanisms” should be revised to “solutes exhibit a slight increase in dilution patterns.” (Please note that "dilution" is a pattern resulting from a mechanism, rather than a mechanism itself.) There are more instances requiring correction, which I will not all mention here. Please refer to my general advice above for a thorough grammar check.

Statement Author to Abstract (L. 15):

In accordance with the reviewer's comment, we described "dilution" exclusively as a pattern and no longer as a mechanism. We also followed the reviewer's broader recommendation and performed a comprehensive grammar check of the manuscript. This has been implemented as follows: "Our results indicate an increase in enrichment behaviour for nutrients, while geogenic solutes exhibit a slight but insignificant increase in dilution pattern."

2.3 Introduction

L55-56: Here and in other sections, these citations serve as examples of studies that have found similar results. I believe their number could be reduced, and it should be clarified that there are even more examples by adding "e.g."

Statement Author to section 1 Introduction and subsequent sections (e.g. L. 57/58):

We have taken the reviewer's suggestion into consideration and carefully reviewed the cited literature. Where appropriate, we have reduced the number of citations and eliminated unnecessary duplications.

L60: Here and in other sections, please ensure that CV_C and CV_Q are consistently written with subscripts "C" and "Q."

Statement Author:

To maintain clarity and consistency, CV_C and CV_Q have been consistently formatted with subscripts 'C' and 'Q' throughout the manuscript.

2.4 Material and Methods

L91-93: There is some redundancy in mentioning the state agencies. This could be one option to shorten the manuscript.

Statement Author to section 2.1 Study site (L. 94-98):

To make the Materials and Methods section more concise, overlapping information about the state agencies was removed, as illustrated by the following example: "The present study comprises quality-controlled discharge and water quality data from 40 stations in South and Southwest Germany. Discharge QQ (m^3 s^{-1}) and water quality data CC (mg L^{-1}) are delivered by various federal agencies, covering catchments located in Rhineland-Palatinate (RLP), Baden-Württemberg (BW), and Bavaria (BY; LfU Bayern, 2022; LfU RLP, 2022; LUBW, 2022)."

L155: I appreciate that b=0 is not automatically attributed to chemostatic patterns; however, I struggle to understand the second part of the sentence, as well as the following paragraph. This may be a wording issue.

Statement Author to section 2.3.3 Assessment of Chemostatic and Chemodynamic Behaviour (L. 203-213):

We acknowledge the readers' concerns and will improve the wording of the paragraph as follows: "Further, a slope close to zero ($b \approx 0$) suggests that solute concentrations are largely independent of discharge magnitude. However, this does not necessarily imply low variability in solute concentrations (Musolff et al., 2015). In fact, high concentration variability can still occur despite the absence of correlation with discharge. To avoid misinterpreting such near-zero b slopes as indication of chemostatic behavior, we additionally used the CV_C/CV_Q ratio as proposed by Thompson et al. (2011)."

2.5 Results

L203-204: This sentence does not convey a clear message. I suggest either expanding it or deleting it entirely and starting with section 3.1.

Statement Author to section 3 Results (L.286):

As recommended by the reviewer, the entire paragraph has been deleted and the revised manuscript starts now with section 3.1 directly.

L205-212: I did not observe any trend analysis, and I find it difficult to refer to the differences between the two periods as a "trend."

Statement Author to section 3.1 Assessment of Solute Mean Concentration (L. 291-293):

The trend analysis has been conducted using linear regression over the entire observation period; however, this was not properly documented in the original Materials and Methods section. In the revised manuscript, we have now document this analysis in a dedicated subsection titled 2.3.1 Trend Analysis of Solute Concentration (L. 182). This section documented trend analysis in mean solute concentration for each catchment using linear regression, with statistical significance tested by ANOVA F-tests corrected for multiple testing (Benjamini–Hochberg procedure; $p<0.05$), and classifies trends as increasing, decreasing, or non-significant (see also Table 2). In the Results section (3.1), we additionally include the following statement: "Trend analysis across the full observation period of each catchment revealed significant decreases in mean concentrations in 57.5% (NH_4-N), 72.5% (NO_3-N), 60.5% (TP), and 67.5% (SRP) of catchments, as confirmed by ANCOVA ($p < 0.05$)."

L269-270: Or could it be something entirely different?

Statement Author to section 3.2 Predominant SEM affected by temporal circumstances (L. 368-371):

We acknowledge the reviewer's comment and recognise that legacy effects or changes in land use and/or land management could be an additional factor influencing changes in SEM. Although, to our knowledge, there have been no major changes in fertilizer regulation in recent years, local legacy effects may occur in individual catchments. We have included the additional information in the manuscript as follows: "Additionally, no SEM changes were observed in response to variations between wet and dry years, suggesting that climate-driven shifts in SEM are primarily linked to processes induced by climate change effects (Fig. 4). 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."

L283: What are "surface factors"?

Statement Author to section 3.3 Controls of SEM and their Changing Influence along Time (L. 398/399):

We follow the reviewer and redefine the term "surface factors" by naming the factors directly as follows: "Shallow-sourced nutrients are primarily influenced by near-surface environmental conditions, 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 such as Ca^{2+} and Mg^{2+} are predominantly controlled by geological weathering processes."

2.6 Discussion

L330: What are fertile sources?

Statement Author to section 4.1 Assessment of Solute Mean Concentration (L 462-464):

We follow the reviewer's suggestion and have redefined the term 'fertile sources' as follows: "TOC, is less reactive and more persistent, with carbon-rich landscape types (e.g. wetlands or riparian zones) serving as sources, visible in higher and more variable mean concentrations."

L333: High compared to what? I am unclear about what is meant by "consistent with" in this context. Does this indicate that the concentrations are in a similar range?

Statement Author to section 4.1 Assessment of Solute Mean Concentration (L. 466-469):

We acknowledge the reviewer's concerns about the wording. Thus, the sentence has been revised as follows: "The mean concentrations of geogenic solutes (Ca^{2+} and Mg^{2+}) are consistent with previous reports, and their spatial variability reflect the heterogeneous geology of the catchment regions (Musolff et al., 2015)."

L354-356: I disagree with the assertion that shallow sources can lead to both enrichment and dilution patterns. In my understanding, these concepts contradict one another. If a solute has higher concentrations from shallow layers that become connected during high flow, this would cause an enrichment pattern. Conversely, if the source becomes depleted (indicating a limited supply in the shallow layers), this would result in a clockwise hysteresis, with concentrations decreasing even as discharge (Q) is still rising. A dilution pattern would imply that concentrations are higher during base flow (i.e., derived from groundwater or point sources).

Statement Author to section 4.2.1 SEM of temporal-dynamic, long-term dynamic and long-term stable solutes (L. 489-496):

We concur with the reviewer's interpretation and acknowledge that our initial explanation of the export processes may have been too unclear. In order to enhance clarity, the paragraph will be revised providing a more precise and detailed description of the implicated mechanisms: “However, in intensively managed catchments, homogeneous solute sources might mask biogeochemical effects and can lead to a chemostatic behaviour proportional to discharge, accordingly (Ali et al., 2017; Basu et al., 2011). Temporal-dynamic solutes show chemodynamic enrichment behaviour when unevenly mobilized at higher discharges, while a dilution pattern occurs when deeper sources dominate during low flow (Basu et al., 2011; Ebeling et al., 2021).”

L358: Why only mimicking? There might also be real point sources.

Statement Author to section 4.2.1 SEM of temporal-dynamic, long-term dynamic and long-term stable solutes (L. 496-498):

We used the term 'mimicking' deliberately to distinguish between temporally variable biogeochemical processes, such as the biological release of SRP during periods of low flow in summer, and persistent point sources, such as effluents from wastewater treatment plants (WWTPs). To clarify this distinction, we will rephrase the sentence as follows: “Dilution dynamics can also result from the release of biological SRP during periods of low flow, acting as temporal point sources in sediments and riparian zones (Dupas et al., 2018; Ebeling et al., 2021; Smolders et al., 2017).”

L390: I assume you are referring to Winter et al. (2022) here? This fits well and should definitely be cited here, but the year is missing, and the reference is not included in the reference section.

Statement Author to section 4.2.2 Alteration in SEM due to Seasonal and Humidity Variation (L. 536):

We agree with the reviewers' suggestion and have corrected the citation to properly refer to Winter et al. (2022), including the full reference in the reference section (see also in references of the revised manuscript).

L506: How can wet conditions be explained by a high drought index?

Statement Author to section 3.3 Controls of SEM and their Changing Influence along Time (L. 416/417):

We understand that this might be confusing. As explained in the Materials and Methods section, higher dMI values indicate more humidity, while lower values indicate dry conditions. To avoid confusion, we will change the term "high drought index" to "humidity inferring drought index values" in this text.

L507: How do arable land and evapotranspiration create internal sources and transport limitations?

Statement Author to section 4.3 Controls on SEM Influenced by Climate Change (L. 692-698):

We acknowledge that the correlation between arable land, evapotranspiration, and their role in generating internal sources and transport limitations may not have been sufficiently clear. To address this issue, the paragraph has been rephrased providing a more comprehensive explanation of the relevant mechanisms, thus assisting readers in comprehending the argumentation more easily. The following corrections have been applied to the paragraph: "In contrast, arable land and high evapotranspiration rates seem to promote enrichment behaviour. Fertilizer use on arable land accumulates nitrogen in the soil creating diffuse sources. Meanwhile, 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 typically create dilution behaviour due to steady contributions from point sources (Aubert et al., 2013; Basu et al., 2010; Dupas et al., 2018; Musolff et al., 2015)."

L545: I do not see this as a consequence. A solute concentration driven by hydrological and biogeochemical processes does not mean that its (anthropogenic) input is no longer relevant. These processes are not mutually exclusive.

Statement Author to section 5 Conclusion (L. 742-747):

We are in agreement with the reviewers' evaluation that hydrological and biogeochemical processes influencing solute concentrations do not exclude the relevance of anthropogenic inputs. To reflect this more accurately in the manuscript, a revision of the paragraph has been necessary. The following updated text elucidates that export mechanisms are shaped by natural processes, while human influence remains important for all water quality parameters: "Under prevailing fertilizer application and land manage strategies, the export mechanisms of nutrients are shaped by a combination of biogeochemical processes and hydrological connectivity, except for NO_3-N. NO_3-N is typically buffered by large and persistent sources, which become active during catchment saturation/increased winter discharges and limit changes in solute export due to global warming, 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."

2.7 Figures and Tables

Figure 1: This appears to be a strangely skewed projection of Germany. This should be checked, and the projection type should be indicated on the map or in the figure caption.

Statement Author to section 1 Introduction (L. 116-121):

We agree with the reviewer´s observation and have applied a more commonly used map projection. The projection type is also indicated in the figure caption for clarity. Due to space constraints, the figure order (a, b, c) has been changed.

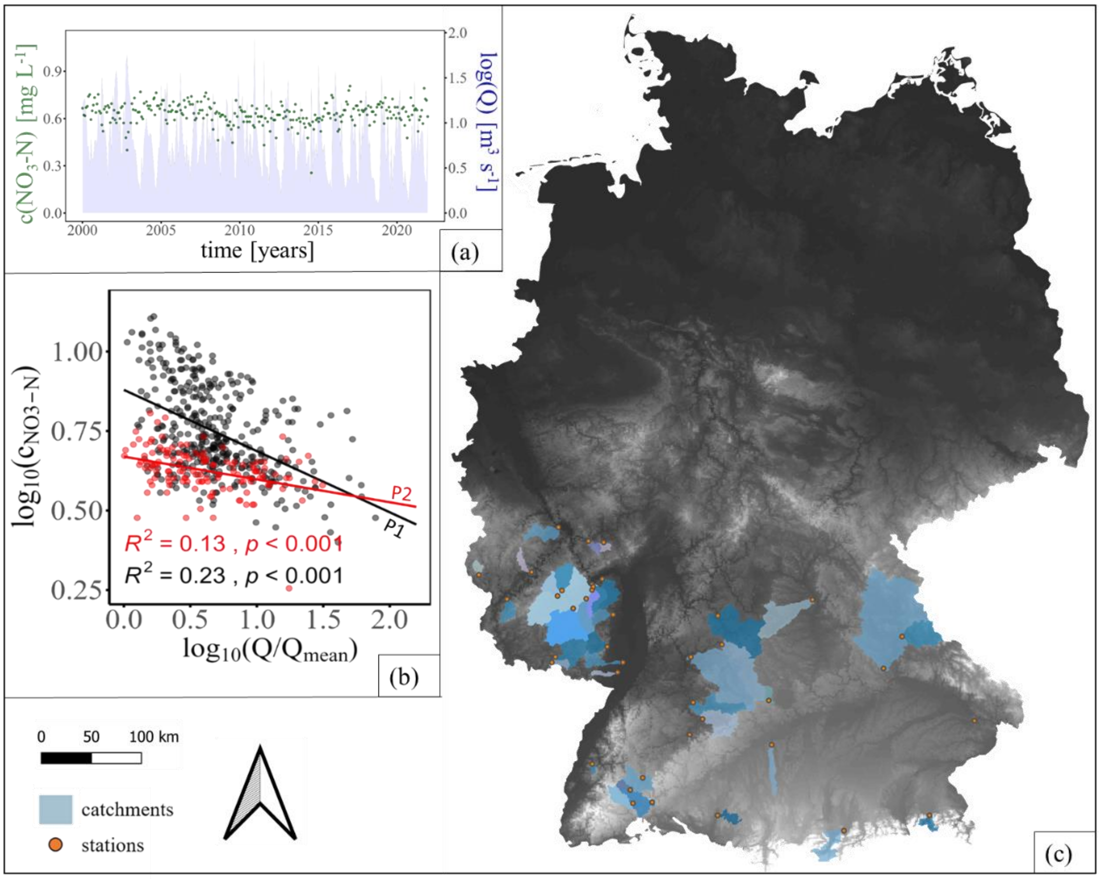


Figure 1: (a) Time series of discharge and nitrate (NO_3-N) in the Fils catchment. (b) cQ-relationships for NO_3-N in the Fils catchment, showing for period 1(black, P1) and period 2 (red, P2 – heightened presence of climate change effects). Differences between P1 and P2 were tested by ANCOVA ($p<0.05$) 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).

Figure 2: My concerns regarding the grouping definitions have been noted above. Furthermore, I recommend adding labels (a-c) to the panels and ensuring consistent axis limits across all plots to make the differences clearer. Additionally, incorporating areas (e.g., boxes) to indicate chemodynamic and chemostatic patterns, as well as enrichment and dilution, similar to Musolff et al. (2015), might help convey the message more effectively.

To avoid what I consider arbitrary grouping, I suggest either plotting all solutes in one graph, displaying each solute individually (with consistent axis limits), or grouping them into categories that require less interpretation, such as N-based (NO3 and NH4), P-based (TP and SRP), TOC, and geogenic sources (Ca and Mg), for example.

Statement Author to section 3.2 Predominant SEM affected by temporal circumstances (L.325-331):

Regarding the grouping definitions, we provided a detailed explanation of our rationale for maintaining the current grouping approach earlier in the response (Major comments: 1.3 Characterization and grouping of solutes). To clarify here as well, this reframing emphasizes the temporal characteristics of the data rather than mechanistic or biogeochemical interpretations, thereby offering a clearer and more objective basis for discussion. The group labels have been revised to reflect observed temporal behaviour, specifically with respect to intraannual and interannual variability, and are now named as follows: (a) temporal-dynamic solutes, (b) long-term dynamic solutes, and (c) long-term stable solutes. We believe that this clustering is meaningful and justified by the underlying data patterns as well as the objectives of the study.

Regarding the visualization of export behaviour (e.g., enrichment, dilution, chemostatic, and chemodynamic patterns), these are indicated by the vertical and horizontal reference lines in the figure. To enhance clarity and intuitiveness, this is now addressed in the figure caption (see below. Furthermore, error bars are now included.

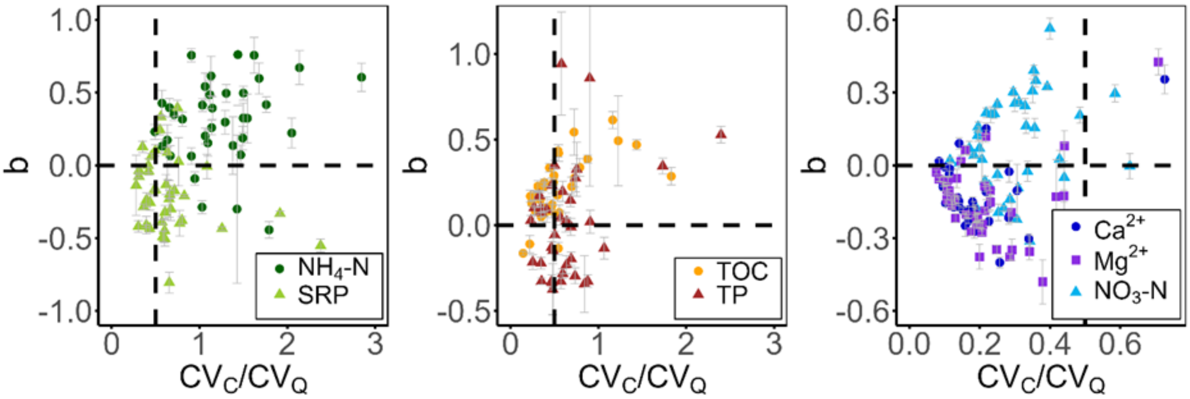


Figure 3: Illustration of the SEM for ▲ SRP, ● NH4-N, ▲ TP, ● TOC, ▲ NO3-N, ● Ca2+ and ■ Mg2+ clusters, with error bars representing ±1 standard error. Clusters represent temporal-dynamic solutes (green, left), short-term stable solutes (yellow/brown, middle), and long-term stable solutes (blue/violet, right). The vertical line separates chemostatic (left) from chemodynamic behaviour (right), while the horizontal line distinguishes enrichment (top) from dilution (bottom) patterns.

Figure 3: The y-axis label is not clearly attributed, and the text is relatively small. Consider rotating the figure for better visibility.

Statement Author to section 3.2 Predominant SEM affected by temporal circumstances (L. 374-381):

In order to enhance the clarity of the figure, the font size has been increased. Furthermore, the meaning of the y-axis label in the figure caption has been addressed as follows: "b = solute export mechanisms (b < 0: dilution; b > 0: enrichment behaviour). Regarding the suggestion to rotate the figure, this modification has not be implemented, as the quality of the figure in the final manuscript will be significantly higher than the version used during the review process. We therefore consider rotation unnecessary. Revised caption and figure is visualized as follows:

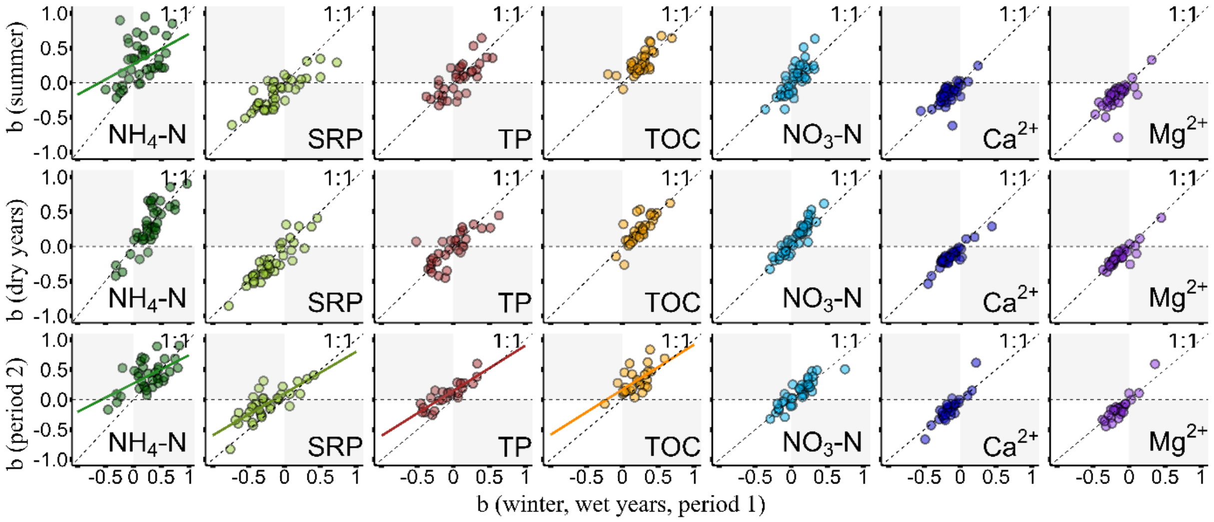


Figure 4: Differences in solute export mechanisms for NO$_3$-N, NH$_4$-N, SRP, TP, TOC, Ca, and Mg in response to temporal changes. Differences in solute export mechanisms between (top) summer and winter, (middle) between dry years and wet years and (bottom) between period 2 (climate change-affected 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: I suggest testing if these changes are significant. Because if not, the changes should be depicted as equally sized arrows (i.e., indicating no change in pattern) in Figure 5, which may be applicable for Ca and Mg.

Statement Author to section 4.2.3 Alteration in SEM due to Global Warming (L. 626-630):

We think we are in line with the reviewer's perspective. In the figure (see below), only statistically significant changes will beare now represented, as opposed to displaying tendencies. The significance of the data had previously been tested using the Kruskal-Wallis test, and the results of this test are also documented in the supplementary figures. This adjustment is intended to ensure that the figure exclusively highlights robust patterns of change, thereby addressing the reviewer's concerns regarding elements such as NO3-N, Ca and Mg.

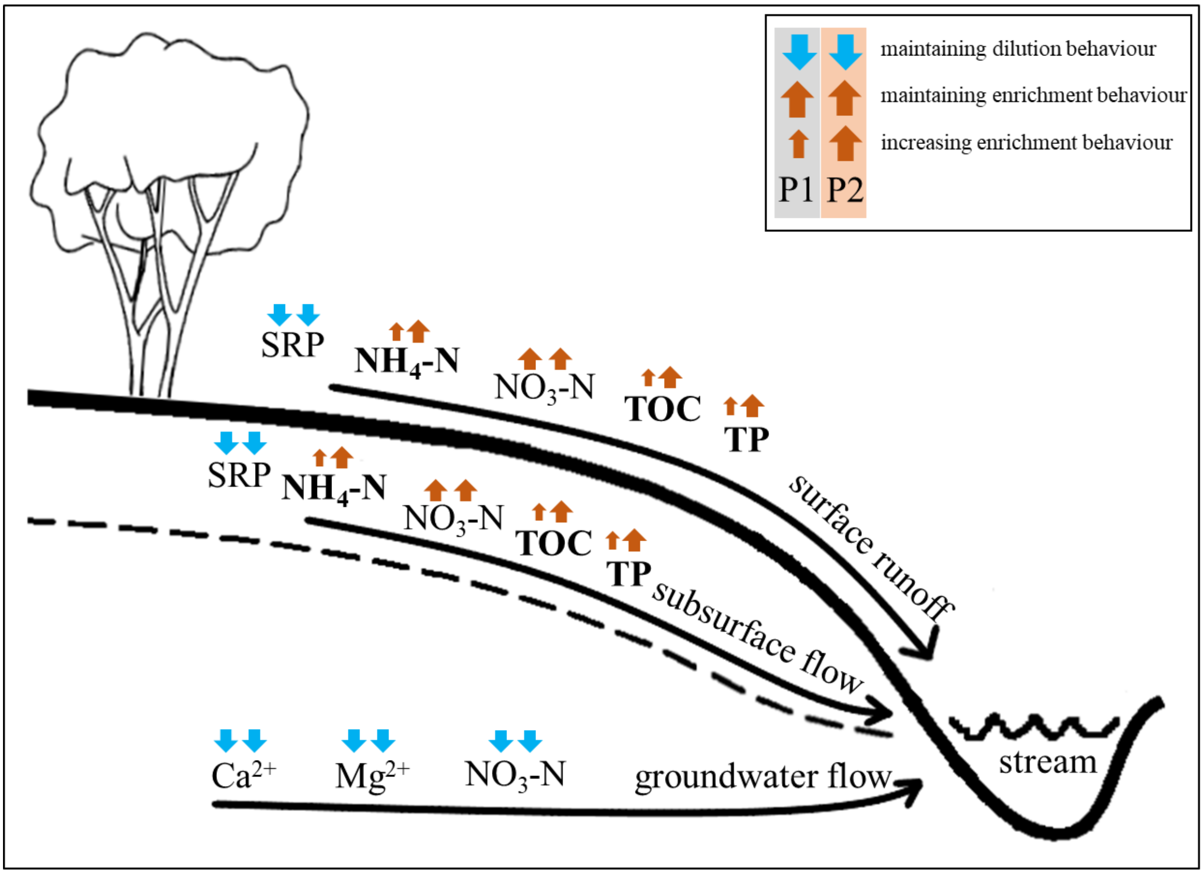


Figure 6: Illustration of mobilization and transportation pathways for nutrients and geogenic minerals. Change in SEM based on climate change illustrated by direction and size of the arrows. P1 – period 1 (onwards 1st Jan. 2012) less affected by climate change. P2 – period 2 (after 1st Jan 2012) more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

Figure S1: Mg is missing

Statement Author to section Supplement:

Due to the very similar behaviour of Mg2^{+} compared to Ca^{2+} and initial space constraints, Mg^{2+} was originally not included in the figure. However, since space limitations are less critical in the supplementary material, Mg^{2+} will now be added as an additional plot in Figure S1 (see below).

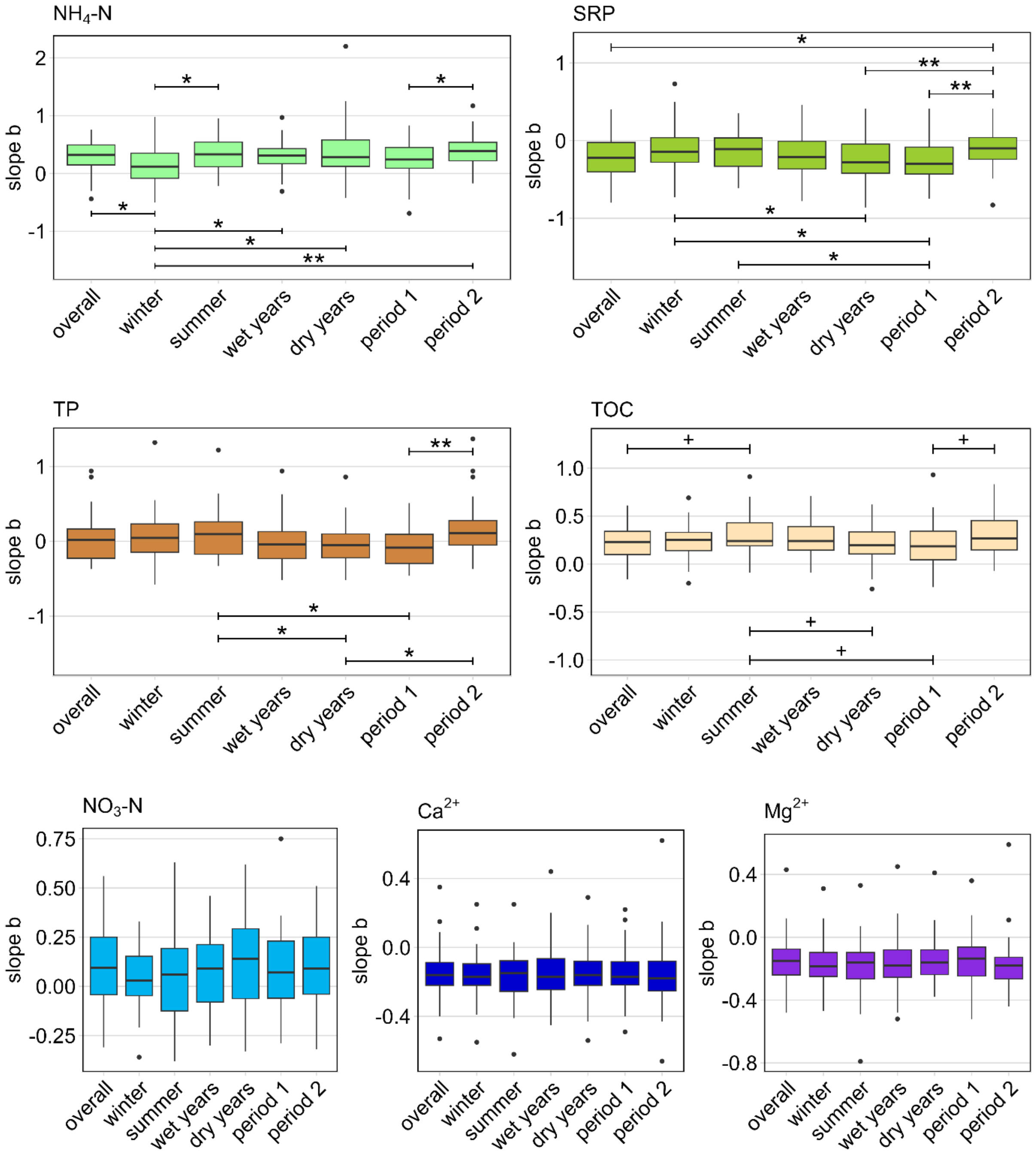


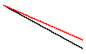
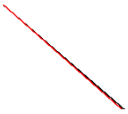
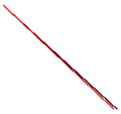
Figure S1: Boxplots of slope b for NH_4-N, SRP, TP, TOC, NO_3-N and Ca^{2+} (Ca) across different periods (overall, winter, summer, wet years, dry years, period 1, period 2). Significant differences were tested using the Kruskal-Wallis test and corrected by Bonferroni correction ($^{+}$<0.1, *<0.05, **<0.01).

Table 4: This table conveys a wealth of interesting information. However, I do not see the triangles mentioned in the caption. Additionally, I suggest adding asterisks to indicate where slopes are significantly different and including the respective number of catchments for each change class (a-c). Alternatively, categories a-c might be combined into a more general message (optional suggestion!). For example, ammonium (NH4) shows a variety of slopes for the black line but comparable red lines, all indicating a higher slope. For soluble reactive phosphorus (SRP), categories a) and b) appear very similar and could be presented as one image. Total phosphorus (TP) consistently shows a higher red slope, while TOC and category c are also quite similar. Nitrogen (NO3-N) and geogenic minerals show virtually no change in red and black slopes.

Statement Author to section 4.3 Controls on SEM Influenced by Climate Change (L.648-653):

The impacts of controls (triangles) have been added behind the control labels in the table to improve clarity. We have also reviewed the significance of the slopes and indicate them now, accordingly. Regarding the grouping, we would like to keep the division into overall catchments, pre-enrichment catchments, and pre-dilution catchments, as this structure effectively highlights differences in export behaviour among catchments in period 1 and their subsequent changes. Additionally, we will include the number of catchments considered in each analysis to provide further transparency (see below).

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

2.8 Acknowledgements

“Further, the data that support the findings of this study are available from the corresponding author upon reasonable request.” – I would prefer to see this information in the supplement. Additionally, I would like a supplementary section that contains detailed information on the catchments, their

characteristics (particularly concerning the variables mentioned in Table 1), and the differences between periods 1 and 2.

Statement Author to section Acknowledgments (L. 784-787):

Upon reconnection with the relevant state agencies, we have confirmed that the data used in this study cannot be freely distributed by the authors. The datasets are available through the responsible authorities and can be accessed upon a justified request. We will clarify this in the manuscript and refer to the appropriate data sources. Additionally, we will include a supplementary section with detailed information on the catchments and their characteristics.

Detailed Response to Reviewer 2

3. Major comments (Reviewer 2)

3.1 Methodological Issues

The choice of January 1, 2012 as the temporal division point lacks strong scientific justification, as the authors cite KLIWA (2021) climate data but fail to demonstrate that this specific date represents a meaningful threshold for biogeochemical changes. A more robust approach would employ change-point analysis or demonstrate statistical significance of the 2012 breakpoint rather than relying on an arbitrary division. Additionally, the manuscript suffers from inadequate statistical rigor, lacking confidence intervals for cQ slopes, statistical tests for differences between periods, assessment of temporal autocorrelation, and power analysis for detecting changes.

Statement Author to section 2 Material and Methods and 3 Results:

The reasoning about the choice of the temporal division point has been given above (Major comments RC1: Chapter 1.1).To strengthen the statistical rigor of the analysis, standard errors for all calculated cQ slopes have been added, and error bars are now included in Figure 3 (2.7 Figures and Tables). This enhances a clearer representation of the variability in concentration–discharge (c–Q) relationships within individual catchments.

Differences in cQ slopes between the two periods are now formally assessed using analysis of covariance (ANCOVA), allowing for the statistical comparison of regression slopes between period 1 (before 2012) and period 2 (since 2012). In the revised visualizations of figure 5, significant differences between periods are highlighted through increased symbol size to aid interpretation (see figure 5 below). Methods are documented the section 2.3.3 as follows: "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 slopes 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."

The influence of catchment descriptors (explanatory controls) on cQ slopes has been evaluated using Pearson correlation tests. To account for multiple comparisons across 23 variables, p-values have been adjusted using the Benjamini–Hochberg correction. In addition, analysis of covariance (ANCOVA) has been conducted to test for significant differences in the relationships between explanatory controls and slope b across the two time periods, and to examine whether the influence of explanatory controls has shifted over time. Updated results are presented in table 3 (see Minor comments RC2: Chapter: 4.2). Further, the table description was revised to include detailed statistical information, such as significance thresholds and adjustment methods, in order to enhance clarity and transparency in the interpretation of results.

These methodological refinements provide a more rigorous foundation for interpreting differences between time periods and for evaluating the role of potential drivers of change. All statistical corrections, including the use of adjusted p-values (Benjamini–Hochberg procedure), the application of ANCOVA for slope comparisons, and the inclusion of standard errors for cQ-slopes, are now addressed in the newly revised material and method section. Thus following chapters were created to improve the structure of the manuscript: 2.3.1 Trend Analysis of Solute Concentration, 2.3.2 Assessment of cQ-Relationship, 2.3.3 Assessment of Chemostatic and Chemodynamic Behaviour and 2.3.4 Linking Catchment Characteristics to slope b.

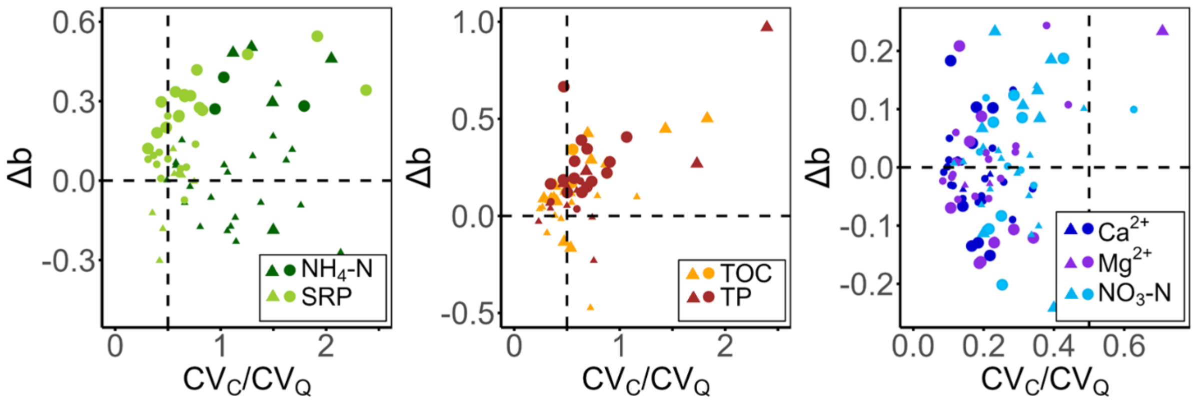


Figure 5: Change in cQ-relationships (Δb) for SRP, NH4-N, TP, TOC, NO3-N, Mg^{2+}, and Ca^{2+} explained by climate change. Positive Δb values indicate an increasing enrichment behaviour. ▲ represent catchments exhibiting enrichment behaviour in period 1, while ● indicate catchments with dilution behaviour in period 1. Significant differences in slope b between period 1 and period 2 are highlighted by larger symbol sizes.

3.2 Data Quality and Sampling Issues

The authors acknowledge that their monthly to biweekly sampling frequency may miss critical high-flow events where nutrients are preferentially transported, potentially underestimating loads and fundamentally undermining their conclusions about changing export mechanisms (Lines 325-329). While 40 catchments provide reasonable coverage, the selection criteria (Lines 119-132) may introduce bias toward certain catchment types, limiting the broader representativeness of the findings.

Statement Author to section 2.2 Data Selection and Data Structure (L. 145-147) to section to 4.1 Assessment of Solute Mean Concentration (L. 454-462) and to section 4.2.2 Alteration in SEM due to Seasonal and Humidity Variation (L.):

We acknowledge the concern regarding the lower sampling frequency (monthly to biweekly), which may potentially miss critical high-flow events that can significantly contribute to nutrient export. However, large-scale monitoring networks seldomly maintain higher frequencies, so our analysis necessarily relies on existing monthly to biweekly records. Thus, we optimized our analysis to extract the most reliable insights from the available datasets.

This sampling frequency allows us to capture seasonal variability in solute transport, with presumably higher flows in winter and lower flows in summer. However, we acknowledge that event-based transport processes, such as those described by Knapp et al. 2020 and Winter et al. 2022, cannot be resolved at this resolution.

We are convinced that hydroclimatic events, especially prolonged droughts, are associated with climate change and play an important role in our study. These might have caused more frequently samples being taken during low-flow conditions. Crucially, the sampling interval remained unchanged between the two periods, preserving comparability. Nevertheless, we have considered the potential effects of missing high-flow events in our analysis in the revised manuscript. Thus, we have mentioned the relevance of event-based processes as a promising avenue for further investigation.

The paragraph was revised as follows: “In contrast, intense high-flow events increase nutrient export, but biweekly to monthly sampling likely misses these peaks, and hence, leads to a potential underestimation of total nutrient loads. Nevertheless, the sampling frequency remained unchanged across both study periods and hence, observed changes in SEM are better explained by hydroclimatic shift linked to global warming rather than by sampling limitations. Still, further high-resolution monitoring would be valuable 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)."

In order to provide a clearer picture of the study's sampling resolution in the context of long-term SEM, the following paragraph has been added to section 4.2.2 of the manuscript, 'Alteration in SEM due to Seasonal and Humidity Variation: "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 Figure 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 Figure 4, middle panel) show no differences in SEM. Hence, mean annual discharge levels alone have minor effect on the SEM of nutrients. 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 mean annual discharge humidity alone are insufficient to explain SEM alterations. Broader climatic processes driven by global warming contribute to these shifts."

Further, the selection criteria may introduce bias towards certain catchment types. However, these criteria are essential to ensure that concentration (c) and discharge (Q) measurements are directly coupled, which presents a significant challenge in Germany, where c and Q are typically monitored at different locations (by different public entities). Enforcing these coupling rules optimises the use of the public databases while preserving the integrity of the analysis. Nevertheless, the selected catchments still represent a diverse range of characteristics, including variations in size, altitude and geology, ensuring that the findings remain broadly informative. However, in the revised manuscript, the possibility of introduced bias is mentioned as follows: "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."

3.3 Climate Attribution Problems

The study fails to adequately separate climate change effects from other confounding factors, including changing agricultural practices, policy interventions such as EU Water Framework Directive implementation around 2000-2015, and other environmental changes that could influence nutrient export patterns. The manuscript relies heavily on KLIWA (2021) for climate characterization but doesn't provide detailed climate trend analysis for their specific study period and locations, weakening the attribution of observed changes to climate drivers.

Statement Author to section 5 Conclusion (L. 739-748):

Although agricultural practices, policy measures (e.g., the EU Water Framework Directive), and additional environmental changes can influence nutrient export, our results indicate that land-use effects on SEM remained stable across both periods. While the influence of EU policies cannot be entirely excluded, the SEM analysis revealed significant correlations primarily with climatic, soil, and geological variables, whereas anthropogenically impacted landscape factors like arable land showed limited influence and no change between the observed periods (see table 3 in chapter: 4.2). Accordingly, agricultural factors are considered to play a smaller role in this context. Nonetheless, their potential effects are now addressed more thoroughly in the revised discussion section as follows: “Time series data reveal declining mean solute concentrations of 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 improved fertilizer management in in agricultural landscapes in southern Germany. Under prevailing fertilizer application and land manage strategies, the export mechanisms of nutrients would be shaped by a combination of biogeochemical processes and hydrological connectivity, except for NO_3-N. NO_3-N can be buffered by large and persistent sources, which might limit future changes in solute export due to global warming, 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.”

Furthermore, for each observation period, mean climatic descriptors were calculated individually for each catchment. Specifically, we used the periods 1982/1991–2011 and 2012–2022 to derive mean climatic variables for each catchment, allowing us to account for long-term trends and differences in local climate conditions. This approach strengthens the attribution of observed changes to climate drivers by explicitly considering catchment-specific climate developments alongside land-use and landscape controls (see newly created table S1 and S2).

3.4 Conceptual and Analytical Issues

While the authors propose mechanisms for observed changes (Lines 430-443), many explanations remain speculative without supporting process-level data such as soil moisture or plant uptake measurements to validate their hypotheses. The study examines catchment-scale responses but infers field-scale biogeochemical processes without adequate mechanistic support, creating a problematic scale mismatch between observations and interpretations.

Statement Author:

This study used extensive databases, which included data provided by governmental authorities as well as publicly available datasets. The focus of our analysis was to evaluate these existing data, which also included variables such as soil moisture, and to identify differences and relationships through advanced data analysis approaches. We relied on comprehensive, spatially resolved datasets from the German Weather Service (DWD), which provided high-quality, area-wide coverage. Soil moisture, for instance, was calculated for each catchment as the percentage of plant-available water (% nFK), assuming a sandy-loam texture with a field capacity of 37 vol%. These reliable datasets ensured robust and consistent input for all analyses.

Further, the study was based entirely on extensive database analysis and did not include new field measurements, which would have been impractical on a regional scale due to resource constraints. Instead, we applied well-established biogeochemical interpretations from the literature to our datasets. We acknowledged the reviewer’s criticism, and in the revised discussion we highlighted more clearly that our biogeochemical interpretations were grounded in previously published findings. Many of these studies had employed comparable methods and similarly structured datasets. By aligning our interpretations with these established studies, we ensured a robust contextual foundation for assessing biogeochemical processes and for extending them to evaluate the influence of climate change.

4. Minor comments (Reviewer 2)

4.1 Specific line items

Lines 64-67: Run-on sentence needs restructuring for clarity.

Statement Author to section 1 Introduction (L. 65-68):

We have rewritten the sentences as follows to improve clarity: “The combined approach of cQ-relationship and CV_C/CV_Q exhibits temporal variability in solute concentrations and can identify flow conditions with elevated solute levels. High solute concentrations are linked to eutrophication processes that harm aquatic ecosystems and pose risks to drinking water quality (Radach et al., 2010; van der Velde et al., 2010; Winter et al., 2020).”

Lines 154-157: The definition of chemostatic vs. chemodynamic behavior using $CV_C/CV_Q > 0.5$ threshold needs better justification. This threshold appears arbitrary.

Statement Author to section 2.3.3 Assessment of Chemostatic and Chemodynamic Behaviour (L. 224-234):

We acknowledge the reviewer's concern regarding the choice of the $CV_C/CV_Q > 0.5$ threshold to distinguish chemostatic from chemodynamic behavior. Thompson et al. (2011) demonstrated that the CV_C/CV_Q ratio for a conservative tracer was consistently around 0.5, with variability in concentration mainly driven by stochastic inputs in the recharge. We use this literature based value as a benchmark to clearly identify chemostatic conditions representative of conservative cQ behavior. This approach is also supported by Musolff et al. (2021), who applied the same threshold to analyze spatial and temporal variability in concentration-discharge relationships.

We acknowledge that threshold values in the literature vary (e.g. 0.5 or 1). In our study, a value of 0.5 aligns with the behaviour of the solute groups, enabling a clearer distinction between chemostatic and chemodynamic patterns. This threshold is used solely as a structural element to categorise and distinguish the solute groups. A higher threshold (e.g. 1) would be less appropriate for our data and impair the distinction between the solute groups. The choice of 0.5 as a threshold is explained in the revised manuscript as follows: "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."

Lines 208-212: The reported concentration decreases (60-73% of catchments) are substantial but lack statistical significance testing.

Statement Author to section 3.1 Assessment of Solute Mean Concentration (L. 298-304):

The trend was tested using linear regression, and significance was evaluated using the F-test from ANOVA and additionally corrected by Benjamini-Hochberg correction ($p<0.05$). Results are presented in Table 2 and described in the table caption (see below). Further methodological details are provided in the Materials and Methods section (subsection 2.3.1).

Table 2: Descriptive statistics of mean solute concentrations (C_{mean}, mg L^{-1}) and associated standard deviations ($C_{mean \pm SD}$) 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=6188)
$C_{mean + sd}$ (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	2.6	15.2	2.5	15.0	12.5
	$C_{decrease}$ (%)	57.5	67.5	60.5	6.1	72.5	5.0	2.5
	NC (%)	40.0	32.5	36.8	78.8	25.0	80.0	85.0

Lines 223-228: Repetitive description of solute behavior.

Statement Author to section 3.2 Predominant SEM affected by temporal circumstances (L. 306-322):

To address this comment and improve the manuscript's readability, we have shortened the paragraph to maintain only necessary information. The whole paragraph is revised as follows: "Long-term slope b and CV_C/CV_Q metrics in southern Germany revealed explicit solute export mechanisms (SEM) for nutrients and geogenic solutes, reflecting differences in mobilization, transport, and transformation processes influenced by seasonality, humidity, and climate change. Nutrients such as NH_4-N, SRP, and TP exhibited more pronounced chemodynamic behaviour than conservative solutes like Ca^{2+} and Mg^{2+} (Fig. 3). When exhibiting chemodynamic behaviour, 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 under conditions of high enrichment, suggesting discharge-decoupled processes. In contrast, Ca^{2+} and Mg^{2+} typically displayed dilution dynamics, while NO_3-N combined dilution and enrichment pattern but retained an overall chemostatic signature."

Lines 285-297: The correlation analysis between catchment characteristics and cQ slopes needs correction for multiple testing and should report effect sizes, not just significance.

Statement Author to section 2.3.4 Linking Catchment Characteristics to slope b (L. 278-284):

To ensure a more robust assessment of statistical significance, the Benjamini-Hochberg correction has been applied considering 23 variables. In addition, Pearson's r has been included to provide a measure of effect size (Chapter: 4.2).

Lines 477-482: The mechanistic explanation for NH_4-N behavior is overly simplistic and doesn't account for complex nitrogen cycling processes.

Statement Author to section 4.3 Controls on SEM Influenced by Climate Change (L. 655-661):

The aim of this study is not to explore detailed biogeochemical processes in depth. Instead, it simplifies these processes and focuses on identifying the sources and transport pathways of NH_4-N with regard to hydrological connectivity. Our findings align closely with literature documenting biogeochemical processes, and have been simplified for interpretation on a large scale. Thus, the paragraph was changed solely for improved wording and only includes significant changes in the explanatory controls, resulting in the following shortened version: "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, drought reduces hydrological connectivity and limits solute transport particularly during prolonged heatwaves, enhancing accumulation, and intensifying enrichment dynamics. Climate change amplifies the effects of drought (increasing impact of dMI on SEM), explained by extended transport limitations while increasing solute accumulation, ultimately intensifying enrichment dynamics."

4.2 Tables and Figures (Reviewer 2)

Table 2: Standard deviations should include sample sizes.

Statement Author to section 3.1 Assessment of Solute Mean Concentration (L. 298-304):

Sample sizes is now included to improve statistical transparency for each parameter (see table 2: Chapter 4.1 Specific line items).

Table 3: Correlation symbols are inconsistent and poorly explained.

Statement Author to section 3.3 Controls of SEM and their Changing Influence along Time (L. 403-416 and L. 426-434):

Information about the explanatory variables and related variables has been added to the description to improve clarity and understanding (see below). Correlation symbols in the text are adjusted for greater consistency.

Table 3: Pearson correlation test between catchment descriptors of different categories and slope b showing influence of catchment characteristics on 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			+ / △				
	crystalline rock							
	clay rock		- / △	- / ▽				
	sediments							
	loess sediments							
	soil moisture	- / △		++ / △				

Figure 1c: The cQ-relationship comparison is visually compelling but lacks statistical analysis of differences between periods.

Statement Author to section 1 Introduction (L. 116-121):

We appreciate the reviewer's observation regarding the lack of statistical evaluation accompanying the visual comparison of cQ relationships. To address this, statistical differences between period 1 and period 2 have been assessed using analysis of covariance (ANCOVA). For example, in Figure 1b, the difference between periods in the Fils catchment is statistically significant ($p < 0.001$), as determined by ANCOVA. This information will be incorporated into the figure description to provide greater analytical clarity and support for the visual interpretation. Due to space constraints, the figure order (a, b, c) has been changed. Figure 1c is now Figure 1b (Minor comments RC1: Chapter 2.7).

Figure 3: The scatter plots showing temporal differences would benefit from regression lines and confidence intervals.

Statement Author to section 3.2 Predominant SEM affected by temporal circumstances (L. 374-381):

Regression lines were initially omitted because temporal differences for overall, dilution, and enrichment catchments are already evaluated in table 4. However, to improve clarity, regression lines are added to figure 4 (see Minor comments RC1: Chapter 2.7 Figures and Tables) where significant temporal differences occur. To maintain visual clarity, we refrain from adding confidence intervals, but the regression lines clearly deviate from the 1:1 line, underscoring relevant shifts between the two periods.

Figure 5: The conceptual diagram oversimplifies complex biogeochemical processes and transport pathways.

The aim of this study is not to explore biogeochemical processes in detail. Instead, the conceptual diagram illustrates dominant transport pathways at the catchment scale and provides a general overview of how these pathways may change in response to climate change. As we explain in the discussion, the diagram is a necessary simplification that highlights general patterns and dominant processes. Due to the resolution of the underlying data, event-based dynamics and fine-scale biogeochemical mechanisms cannot be captured in detail (see Knapp et al., 2020; Winter et al., 2022; Chapter: 3.2 Data Quality and Sampling Issues). Nevertheless, interpretation is guided by well-established findings from the existing literature. Accordingly, the focus remains on illustrating broad-scale transport behaviour rather than event-scale processes, providing a general overview of how these pathways may shift in response to climate change. Only significant changes in SEM are visualized, using different arrow sizes in the legend and graph (Minor comments RC1: Chapter 2.7 Figures and Tables).

4.3 Throughout the manuscript

Results lack uncertainty quantification.

We appreciated the reviewer's concern and agreed that adding the above-mentioned uncertainty quantification improved the clarity and statistical rigour of our results. In this context, we conducted different statistical tests and presented, as well as described, the tests we had already performed more clearly in the revised manuscript.

5. References

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