Carbon and nutrient export regimes from headwater catchments to downstream reaches

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Abstract: Excessive amounts of nutrients and dissolved organic matter in freshwater bodies affect aquatic ecosystems. In this study, the spatial and temporal variability in nitrate (NO_3), dissolved organic carbon (DOC) and soluble reactive phosphorus (SRP) was analyzed in the Selke (Germany) river continuum from headwaters draining $1 - 3$ km² catchments to downstream reaches representing spatially integrated signals from $184 - 456$ km² catchments. Three headwater catchments were selected as archetypes of the main landscape units (land use x lithology) present in the Selke catchment. Export regimes in headwater catchments were interpreted in terms of NO_3, DOC and SRP land-to-stream transfer processes. Headwater signals were subtracted from downstream signals, with the differences interpreted in terms of in-stream processes and contribution of point-source emissions. The seasonal dynamics for NO_3 were opposite those of DOC and SRP in all three headwater catchments, and spatial differences also showed NO_3 contrasting with DOC and SRP. These dynamics were interpreted as the result of the interplay of hydrological and biogeochemical processes, for which riparian zones were hypothesized to play a determining role. In the two downstream reaches, NO_3 was transported almost conservatively, whereas DOC was consumed and produced in the upper and lower river sections, respectively. The natural export regime of SRP in the three headwater catchments mimicked a point-source signal, which may lead to overestimation of domestic contributions in the downstream reaches. Monitoring the river continuum from headwaters to downstream reaches proved effective to investigate jointly land-to-stream and in-stream transport and transformation processes.

1.   Introduction

Riverine exports are a key component in the global biogeochemical cycles of carbon (C), nitrogen (N) and phosphorus (P) (Beusen et al., 2016). River export regimes of their dominant soluble forms, dissolved organic C (DOC), nitrate-N (NO_3) and soluble reactive P (SRP), result from the interplay of land-to-stream diffuse transfer processes and in-stream transformations, and can be altered by point-source contributions (Seitzinger et al., 2010). Excess delivery of DOC, NO_3 and SRP into sensitive water-bodies affects ecosystems structure and functions, and elemental stoichiometric ratios have been shown to be of major importance (Sardans et al., 2012). Therefore, detailed knowledge of the catchment processes controlling the spatial and temporal variability in the delivery of DOC, NO_3, SRP and stoichiometric ratios at relevant management scales, e.g., the European Union Water Framework Directive (CEC, 2000) water-bodies, is a prerequisite for designing effective water pollutions mitigation programs (Wall et al., 2011).

Water-quality assessment programs performed by environmental agencies typically focus on relatively large (> 100 m²) catchments, to increase spatial coverage within a given hydrographic basin or administrative unit, while reducing the density of monitoring stations and thus the cost (Bouraoui and Grizzetti, 2011; Dupas et al., 2015a). However, large catchments include both diffuse and point-source emissions and possibly various landscape units. Thus, the water quality signal measured at the outlet integrates several transfer mechanisms contributing to emissions to the river network, as well as in-stream processes (Grathwohl et al., 2013). Therefore, it is difficult to decipher the diffuse contributions of different landscape units from point-source contributions and in-stream transformations. In contrast to environmental agency monitoring programs, scientific programs often focus on headwater catchments free of point-sources and with relatively homogeneous landscape types (Fealy et al., 2010; McGonigle et al., 2014), and where in-stream processes are often considered to be minimal (Salmon-Monviola et al., 2013). Comparison of export regimes in contrasting catchments representing different landscape types can be performed to investigate the effect of, for example, contrasting dominant land use, dominant flow paths or climate (Outram et al., 2014; Dupas et al., 2015d). In headwater catchments, several studies have highlighted the important role of landscape heterogeneity within hillslopes, notably the crucial role of reactive zones such as riparian wetlands (Dick et al., 2015; Pinay et al., 2015; Tiwari et al., 2017), in controlling solute export regimes.

To upscale headwater signals to downstream reaches, previous landscape mixing models, i.e., "models mixing headwater signals in proportion to their patch coverage" (Tiwari et al., 2017) often lack consideration of temporal variability in headwaters signals and explicit consideration of in-stream transformations (e.g., Laudon et al. (2011), Agren et al. (2014)). Few opportunities exist to study the export regimes of several headwater catchments representing "archetypes" of the main landscape units in a larger catchment, for multiple solutes and at different time scales, and to compare headwater export regimes to the integral signal measured in downstream reaches. The Bode catchment (3,300 km²) is part of the hydrological Harz/Central German Lowland Observatory, in the Helmholtz Association Terrestrial Environmental Observatories (TERENO) network (Zacharias et al., 2011). The Bode catchment covers large gradients in topography, climate, geology, soil, and land use, and all combinations of these landscape features are represented in the 456 km² catchment of the Selke tributary (Wollschlager et al., 2016), taken as a case study in this paper. The Harz/Central German Lowland Observatory also includes monitoring of 1-3 km² headwater catchments representing the dominant combinations of land-use x lithology, termed here landscape units, in the Selke and Bode catchments. In this paper we

hypothesized that the land use and lithology characteristics of the landscape units identified control export regimes in headwaters, and that in-stream processes and point-source contributions alter export regimes in downstream reaches. We also hypothesized that spatial and temporal variability in solute concentrations could lead to variability in N and P limitation in streams and rivers. Keck and Lepori (2012) have reviewed 382 nutrient-enrichment experiments to examine which factors promote limitation of micro-phytobenthos biomass by N or P. They found that prediction of N or P limitation was highly uncertain, except at extreme N:P molar ratios <1 : 1 and >100 : 1. Other studies have considered a narrower range of N:P molar ratios to assess possible co-limitation: for example McDowell et al. (2009) considered that N − P co-limitation could take place for N:P molar ratios between 16:1 and 32:1.

The main objective of this paper, therefore, was to characterize the spatial and temporal variability in NO_3, DOC and SRP export regimes from archetypal headwater catchments to downstream reaches, and to analyze the resulting nutrient stoichiometric ratios. Export regimes in headwater catchments are used for interpretation of land-to-stream C, N, P transfer processes and compared with those in downstream reaches to infer in-stream processes and point-source contributions. The potential ecological impacts of the observed export regimes at different spatial scales are discussed in terms of nutrient stoichiometric ratios. In this study, we considered both the large interval of Keck and Lepori (2012) and the narrower interval of McDowell et al. (2009) to evaluate possible N-P co-limitation; hence both thresholds 100:1 and 32:1 were considered.

2. Material and methods

2.1. Study area

The Bode catchment (3,300 km²) is located in the German part of the Elbe river basin (144,055 km²) (Zacharias et al., 2011). The Bode catchment stretches from the Harz Mountains, a low mountain range in central Germany (altitude max 1,142 m above sea level), to the Central German Lowlands, a flat and fertile area dedicated to arable agriculture (altitude around 100 m above sea level). This topographic gradient coincides with gradients of climate, geology, soil, and land use pressures (Wollschlager et al., 2016). Long-term mean annual (1951-2011) precipitation and temperature in the Bode catchment ranges from 1700 mm and 5°C in the Harz Mountains to 500 mm and 9.5°C in the lowland area, with the lowest and highest temperatures in January and July (Wollschlager et al., 2016). The Selke tributary catchment (456 km²) was selected for study here as it encompasses the different combinations of land use and lithology present in the Bode catchment and it has been intensively monitored since 2010. Other varying environmental factors, such as soil types, climate and dominant farming systems, coincide with the topographic gradient reflected in the differentiation according to lithology.

[Insert Figure 1 here]

The 456-km² Selke catchment (Fig. 1) comprises upper and lower portions. The upper Selke (184km²), monitored at Meisdorf station (MEIS), is located in the Harz Mountains (209-595 m above sea level). The dominant soil type is Cambisol overlaying impervious schist and claystone, resulting in a dominance of shallow flow pathways (Jiang et al., 2014b). These shallow groundwater systems favor the development of hydromorphic riparian soils (periodically waterlogged soils near the streams, delineated in this study according to a soil map), representing 10% of the surface area. The land use is dominated by 71% forest (including broad-leaved,

coniferous and mixed forest) followed by 26% agriculture (mainly arable crops: winter cereals, rapeseed and maize). Artificial surfaces cover the remaining 3%. The upper Selke catchment also includes three wastewater treatment plants with 9,300 equivalent inhabitants. The lowland area of the lower Selke (272 km²) is a fertile plain (62-209 m above sea level) dominated by Chernozems overlaying non-metamorphic sedimentary rocks

110 partly covered by loess. The downstream monitoring station at Hausneindorf (HAUS) integrates the combined influence of the upper and lower Selke. Hydrology in the lowland area is dominated by deeper groundwater flows (Jiang et al., 2014b); soils classified as hydromorphic represent only 3% of the surface area. The land use is dominated by 81% agriculture (mainly arable crops: winter cereals, rapeseed, maize and sugar beet) followed by 10% forest. The remaining 9% comprises artificial surfaces and small lakes. The lowland area includes two

115 wastewater treatment plants with 10,600 equivalent inhabitants. More than 95% of the population in the Selke catchment is connected to a wastewater treatment plant (Rode et al., 2016a).

In addition to these two stations located on the main river, three first-order headwater catchments (Fig. 1) representing the main landscape units (i.e. combinations of land use x lithology) in the Selke catchment were monitored. The Schäfertal (1.44 km²) is representative of an agricultural catchment in the upper Selke. Its

120 elevation ranges between 379 m and 466 m above sea level, 19% of the surface area consists of hydromorphic riparian soils and 98% of the land use is arable agriculture (only 2% forest). The upper Rappbode (2.58 km²) is representative of a forested catchment in the upper Selke. Its elevation ranges between 542 and 619 m above sea level, 19% of the surface area consists of hydromorphic riparian soils and 100% of the land use is forest. The Sauerbach (1.37 km²) is representative of an agricultural catchment in the lower Selke. Its elevation ranges

125 between 144 and 200 m above sea level, 100% of the surface area consists of well-drained soils and 98% of the land use is arable agriculture (only 2% forest).

In this study the three headwater catchments are considered as "archetypes" of the different landscape units (land use x lithology) in the Selke catchment. Schäfertal and upper Rappbode represent respectively agricultural and forested areas in the Harz Mountains, i.e. the fraction of the Selke catchment upstream of the MEIS station.

130 Schäfertal and upper Rappbode are termed thereafter "US-Agr" and "US-For" for "Upper Selke – Agriculture" and "– Forest", respectively. Sauerbach represents agricultural land use in the lowland part of the catchment, i.e. the dominant landscape between the MEIS and HAUS stations. Sauerbach is termed thereafter "LS-Agr" for "Lower Selke – Agriculture". Minor landscape types (e.g. forest in lowland area) are neglected. All three headwater catchments are located in the 3,300 km² Bode catchment of the TERENO Harz/Central German

135 Lowland Observatory, but only US-Agr is a sub-catchment of the Selke; US-For and LS-Agr are nearby sub-catchments of the Bode (distance from the Selke catchment: 13 km and 20 km, respectively) and are considered representative of headwater catchments in the Selke catchment.

2.2. Monitoring strategy

Discharge and water quality were monitored comparably at the outlet of the two large catchments (MEIS and

140 HAUS) and three headwater catchments (US-Agr, US-For and LS-Agr). At MEIS and HAUS, discharge data were measured by the hydrological state authority of Saxony-Anhalt (*Landesbetrieb für Hochwasserschutz und Wasserwirtschaft*) at 15 min interval. Water quality was sampled as part of the TERENO program biweekly from June 2010 to September 2013 and monthly from October 2013 to December 2015, complemented by high

frequency sampling during 8 storm events at MEIS and 7 storm events at HAUS (2 to 4 hours interval, ISCO 6700 autosampler).

In US-Agr, discharge was measured every 15 minutes at a gauging station with a water level sensor upstream of a V-notch weir. Manual grab samples were collected biweekly to monthly from March 1999 to September 2010, complemented by high frequency sampling during 8 storm events (20 min to 1 hour interval, ISCO 6700 autosampler). In US-For, discharge was measured every 10 minutes using a Solinst LTC data logger and external barometric measurements. Manual grab samples were collected biweekly from March 2013 to October 2015 and no high frequency monitoring of storm events has been performed in this catchment. In LS-Agr, discharge was measured every 10 minutes at a gauging station with a pressure logger (ecoTech PDL) upstream of a triangular weir (V-notch weir). Manual grab samples were collected biweekly to monthly from June 2010 to December 2015, complemented by high frequency sampling during 4 storm events (20 min to 1 hour interval, ISCO 6700 autosampler).

All samples were filtered in the field using 0.45 μm cellulose acetate filters and kept cool until analysis within 2 days. Nitrate concentration was determined by ion chromatography (ICS-2000, Dionex), DOC was determined with a carbon analyzer (TOC 5050, Shimadzu) and SRP was determined colorimetrically by reaction with ammonium molybdate. Samples from all five catchments were analyzed following the same protocol and in the same laboratory at UFZ Magdeburg. An exception to this standardized protocol was measurement of total phosphorus (TP) in US-For; to convert TP into SRP and allow comparison with the other catchments, the mean SRP/TP ratio of 0.42, established in 55 forested catchments throughout Germany (Musolff et al., 2016b), was used (standard deviation of the SRP/TP ratio was 0.19, reflecting relatively small variability).

2.3.   Data analysis

Export regimes for DOC, NO_3 and SRP where characterized on an intra-annual basis (seasonal variability) and for discrete storm events. The reference study period in this analysis was June 2010 - December 2015, i.e., the period when data was available in the two stations situated in the main Selke river (MEIS and HAUS) and in LS-Agr. The US-Agr catchment was monitored prior to the establishment of the TERENO observatory (March 1999 - September 2010). The US-For catchment was not part of the permanent TERENO monitoring, so this catchment was monitored for 20 months for this study (March 2013 – October 2014). The different monitoring periods in two of the headwater catchments were assumed to have minimal effect on mean annual concentration and seasonal variability, due to the well-documented biogeochemical stationarity in catchments (Basu et al., 2010; Humbert et al., 2015; Godsey et al., 2009) resulting in consistent annual pattern in solutes concentration despite potentially large interannual variability in the hydroclimate. This biogeochemical stationarity can be verified with the 10-year record in the US-Agr catchment (Supplementary material) and in the comparison of discharge and solute variability (Sect. 3.1). The same assumption cannot be made for discharge due to interannual climate variability.

2.3.1.   Discharge and concentration variability

First, river flow regimes were characterized in all five study catchments after aggregation of discharge data on a monthly basis. Second, to quantify the overall variability of discharge and concentration data (grab sampling),

the coefficients of variation (CV) for both discharge and concentrations were calculated for each study catchment and for each year using daily data. The coefficient of variation, defined as the ratio of the standard deviation to the mean of a variable, has been used for the same purpose in previous water quantity (Botter et al., 2013) and water quality studies (Dupas et al., 2016; Musolff et al., 2015; Thompson et al., 2011). Finally, correlation coefficients were calculated between solute concentrations and discharge and between pairs of solute concentrations. The Spearman rank correlation coefficient was used because relations between pairs of variables are not necessarily linear (Thomas et al., 2016).

2.3.2. Seasonal variability in concentrations and stoichiometric ratio

Grab sampling data were used to fit a periodic equation to the data in all five study catchments:

$$Concentration = a + b * cos (2\pi / i + c) \quad (1)$$

In Eq. (1), "a" is an estimate of the mean concentration, "b" is an estimate of the seasonal amplitude, "c" is a phase coefficient to identify seasonal maximum and "i" is the Julian day. In addition, the coefficient of determination R^2 was calculated to quantify the percentage of the variance explained by a periodic signal (i.e., the seasonal variation) and the "b/a" ratio was calculated as an estimate of the relative amplitude of the seasonal variation. The periodic equation was not fitted to the discharge data because: i) daily discharge data does not exhibit a clear cosine shape (due to storm events) and ii) interannual climate variability results in varying seasonal amplitudes from year to year (data not shown).

In this study, the influence of in-stream processes and point-source emissions was inferred by the difference between the observed export regimes in downstream reaches and the export regimes that would have been expected if the integral downstream signal consisted of a "conservative mixing" of the export regimes observed in the archetypal headwater catchments. The "conservative mixing" method to simulate the export regime for MEIS consisted in a surface area weighted averaging of US-Agr and US-For export regimes; we chose not to use observed discharge as a weighting factor because both headwater catchments have been monitored during different periods. The "conservative mixing" method to simulate the export regime for HAUS consisted in a weighted averaging of MEIS and LS-Agr export regime, with a weighting factor being the discharge measured at MEIS and the difference between discharges measured in HAUS and MEIS (assuming that this difference represented the contribution of the lowland area, with a concentration export regime represented by LS-Agr). For HAUS, we used discharge as a weighting factor because both MEIS and HAUS have been monitored during the same period.

2.3.3. Storm event response

High-frequency autosampler data were used to calculate the linear slope of the concentration – discharge (C-Q) relations during discrete storm events. A *p value* of 0.05 was used as a threshold for each event to have a significant positive slope (accretion pattern) and negative slope (dilution pattern). This metric was calculated for all storm events in the MEIS, HAUS, US-Agr and LS-Agr catchments; because the US-For catchment was not part of the permanent TERENO monitoring, no high-frequency autosampler data were available in this catchment. The mixing model was not applied to storm event export regimes because rainfall could be very localized in the study area, hence a mixing model applied to storm events would require precise knowledge of

the spatial distribution of rainfall over the different landscape archetypes for each event, which is beyond the scope of this paper.

3. Results

3.1. Discharge and concentration variability

Seasonal variability in discharge exhibited high-flow periods both during the spring and the autumn-winter period, which is characteristic of a nivo-pluvial river regime (Fig. 2). In the headwater catchments (Fig. 2a), a higher seasonal variability in discharge was observed in the two catchments located in the Harz Mountains, representing the upper Selke (US-Agr and US-For), compared to the catchment located in the lowland area (LS-Agr). This difference in seasonal discharge can be explained both by the climate gradient, with higher snowfall in the Harz Mountains compared to the lowland area, and by the different lithology, which results in a flashier river regime in the upper Selke compared to the lower Selke (Jiang et al., 2014b). The same conclusions hold when observing seasonal discharge variability at the downstream stations MEIS and HAUS (Fig. 2b), namely with a higher variability in the upper Selke than in the lower Selke. The coefficient of variation of daily discharge CV_Q (Table 1) was also higher in catchments representing the upper Selke (on average 2.32, 1.25 and 1.23 in US-Agr, US-For and MEIS, respectively) than in the lower Selke (on average 0.22 and 0.99 in LS-Agr and HAUS, respectively).

[Insert Figure 2 here]

[Insert Table 1 here]

In a large majority of situations (all three solutes in US-Agr, US-For, MEIS and HAUS, and NO_3 in LS-Agr), $CV_C < CV_Q$ (Table 1), which reveals a biogeochemical stationarity termed "chemostasis" in previous catchments studies (Basu et al., 2010; Musolff et al., 2015; Godsey et al., 2009). Only SRP and DOC in the LS-Agr catchment exhibited a higher coefficient of variation than discharge (Table 1).

3.2. Seasonal variability in concentrations and stoichiometric ratio

The mean concentration observed in the three headwater catchments (quantified by the "a" parameter in Table 2) was in the order US-For < US-Agr < LS-Agr for NO_3, and LS-Agr < US-Agr ≈ US-For for DOC and SRP (Fig. 3a). The seasonal amplitude of the periodic function (quantified by its absolute value "b" or relative value "b/a" in Table 2) was higher in US-Agr and US-For than in LS-Agr for all three solutes. Consistent with the higher seasonal amplitude in US-Agr and US-For compared to LS-Agr, the percentage of the variation explained by the cosine function (quantified by the R^2 parameter in Table 2) was higher in US-Agr and US-For than in LS-Agr, ranging from 0.16 - 0.67 in US-Agr, 0.09 - 0.69 in US-For and 0.03 - 0.15 in LS-Agr. Despite differences in mean concentration values and seasonal amplitudes, the three catchments were in phase (cf. "seasonal maximum" in Table 2) for each solute. Nitrate reached its annual maximum between Julian days 23 – 66, i.e., during a period of high flow and low temperature, whereas DOC and SRP reached their annual maxima between Julian days 236 – 282 and 248 – 258, respectively, i.e., during a period of low flow and high temperature. Nitrate was positively and significantly correlated with discharge in all three catchments (r = 0.63 – 0.81, Table 3). DOC and SRP were negatively and significantly correlated with discharge only in the US-Agr catchment (r = -0.51

and r = -0.65, respectively), whereas the negative correlations and positive correlations in US-For and LS-Agr, respectively, were not significant (Table 3).

[Insert Figure 3 here]

[Insert Table 2 here]

In terms of comparing the solute export regimes, DOC and SRP exhibited similar behavior, with: i) higher concentration in US-Agr and US-For compared to LS-Agr and ii) a seasonal maximum in the late summer, during a period of low flow and high temperature. The export behavior of NO_3 was opposite, with: i) higher concentration in LS-Agr compared to US-Agr and US-For and ii) a seasonal maximum in the winter-early spring season, during a period of high flow and low temperature. The similar behavior of DOC and SRP, and their opposite dynamics to NO_3, was confirmed by the generally negative coefficients of correlation calculated between pairs of solutes (Table 3).

[Insert Table 3 here]

In the downstream reaches, the observed export regimes approximately matched those expected from conservative mixing of headwater signals for NO_3 (MEIS and HAUS) and SRP at MEIS, but not for DOC (MEIS and HAUS) and SRP at HAUS (Fig. 3). For NO_3, the difference between observed concentrations and concentrations simulated through "conservative mixing" was on average < 1 mg N l^{-1} in both MEIS and HAUS. In MEIS, the relative seasonal amplitude for NO_3 was 72%, i.e., similar to the 68% and 73% observed in US-Agr and US-For, and the seasonal maximum was reached on Julian day 27, i.e., similar to Julian days 41 and 23 observed in US-Agr and US-For. In HAUS, the relative seasonal amplitude for NO_3 was small ("b/a" = 8% and R^2 = 0.05) but the chemostatic export regime at this location could be predicted by the "conservative mixing" of the MEIS export regime (which exhibited a large seasonal amplitude) and the LS-Agr export regime (which exhibited a small seasonal amplitude) (Fig. 3b). For DOC, difference between observed concentrations and concentrations simulated through "conservative mixing" was considerable (up to 3 mg DOC l^{-1}) in both MEIS and HAUS. In both MEIS and HAUS, the large relative seasonal amplitude that would have been expected from "conservative mixing" was not observed ("b/a" was 12% in MEIS and 7% in HAUS, and R^2 was only 0.09 in MEIS and 0.07 in HAUS). Conservative mixing of DOC export regimes resulted in an overestimation of the observed concentrations at MEIS, and an underestimation of DOC at HAUS. For SRP, difference between observed concentrations and concentrations simulated through "conservative mixing" was < 0.01 mg SRP l^{-1} in MEIS and ranged from < 0.01 mg SRP l^{-1} in winter to up to 0.04 mg SRP l^{-1} in summer in HAUS. In MEIS, the relative seasonal amplitude for SRP was 62%, i.e., similar to the 79% and 77% observed in US-Agr and US-For, and the seasonal maximum was reached on Julian day 235, i.e., similar to Julian days 248 and 258 observed in US-Agr and US-For. In HAUS, the relative seasonal amplitude for SRP was 65%, i.e., slightly higher than would have been expected from the "conservative mixing" of MEIS and LS-Agr (Fig. 3c), but the seasonal maximum was reached at a date comparable to MEIS and LS-Agr (Julian day 223, versus 235 and 257 in MEIS and LS-Agr, respectively). In HAUS, the underestimation of the relative seasonal amplitude was mainly due to underestimation of summer concentration (up to 0.04 mg SRP l^{-1}, Fig. 3b and 3c).

290   Results show that the N:P ratio was more variable than NO_3 and SRP concentrations in US-Agr, US-For, MEIS and HAUS, and was more variable than NO_3 but not SRP in LS-Agr (Table 2). The higher variability of the N:P ratio compared to NO_3 and SRP in a large majority of situations is a direct consequence of the opposite seasonal dynamics of NO_3 and SRP in all the catchments, except LS-Agr where NO_3 and SRP seasonal amplitudes were small. In all the catchments, the N:P ratio remained above the two thresholds defined to assess possible N-P co-

295   limitation for a majority of the time. However, in two of the headwater catchments (US-Agr and US-For) and in the two downstream reaches (MEIS and HAUS), the thresholds defined to assess possible N-P co-limitation were crossed during the late summer low-flow season (Fig. 4). Considering the threshold defined by Keck and Lepori (2012), N-P co-limitation occurred 4% of the time in US-Agr, 14% in US-For, 36% in MEIS and 3% in HAUS. Considering the threshold defined by McDowell et al. (2009), N-P co-limitation occurred 17% of the

300   time in US-Agr, 47% in US-For, 57% in MEIS and 28% in HAUS.

[Insert Figure 4 here]

3.3. Storm event responses

Among the three headwater catchments, high frequency monitoring data during storm events was available in US-Agr (n=8) and LS-Agr (n=4) (Fig. 5a). Similar to seasonal dynamics, DOC and SRP storm dynamics

305   exhibited similar behavior with each other but opposite to NO_3 in a majority of situations. However, DOC and SRP exhibited a majority of accretion patterns during storm events (whereas SRP and DOC was generally negatively related to discharge on a seasonal basis) and NO_3 exhibited a majority of dilution patterns during storm events (whereas NO_3 was generally positively related to discharge on a seasonal basis) (Table 4). In addition, NO_3 storm dynamics appeared to be more complex in US-Agr with the occurrence of one accretion

310   pattern and two non-significant slopes but apparent accretion patterns. It should be noted that the slopes of the C-Q relationships did not always reflect the amplitude of solute concentration responses or the absolute concentrations, and slopes were generally larger in LS-Agr than in US-Agr because the former had smaller variations in discharge due to the more groundwater dominated flow regime: in general, concentration values in LS-Agr remained higher for NO_3 and lower for DOC and SRP than in US-Agr, similar to concentrations from

315   the grab sampling. In the two downstream reaches, high frequency monitoring data during storm events was available in both MEIS (n=8) and HAUS (n=8) (Fig. 5b). For these two stations, accretion patterns appeared to be dominant for NO_3, DOC and SRP when significant slopes were detected. One significant dilution pattern was observed for NO_3 in HAUS, similar to the dominant storm pattern in LS-Agr. However, non-significant slopes were dominant in a majority of events for SRP in MEIS and for all three solutes in HAUS, and among the non-

320   significant slopes, apparent dilution patterns were observed for SRP in the two downstream reaches (Fig. 5b).

[Insert Figure 5 here]

[Insert Table 4 here]

4.   Discussion

Solutes export regimes were interpreted in terms of land-to-stream transfer and in-stream processes. Archetypal

325   headwater catchments were selected without point sources and in-stream processes were deemed to have

minimal effect due to the small catchment size; hence they are suitable spatial units to study NO_3, DOC and SRP land-to-stream transfer processes in relatively homogeneous landscape units. The two downstream reaches were influenced by point-source emissions and potentially in-stream processes; hence the difference between export regimes observed in headwater and downstream reaches can be interpreted in terms of point-source and in-stream influences.

4.1. Land-to-stream transfer

The three archetypal headwater catchments had synchronous seasonal export regimes for each solute. Yet, the mean concentrations and the seasonal periodic amplitudes differed between catchments and solutes. We thus conclude that the same controlling factors influenced NO_3, DOC and SRP export in the three catchments, but that the respective influence of these controlling factors differed according to landscape. Seasonal concentration variability is traditionally explained by the varying contribution of several conceptual compartments (end-members) with distinct chemical signatures (Aubert et al., 2013), the contribution of theses compartments to stream discharge being controlled by changing hydroclimatic conditions on a seasonal basis. In addition, biogeochemical processes controlled by temperature and by the convergence of reactants in reactive hotspots such as the riparian zone (Pinay et al., 2015; Tiwari et al., 2017; Dick et al., 2015) could lead to temporal variability in the concentrations within different conceptual compartments. Thus the interplay of hydrological and biogeochemical processes controls stream NO_3, DOC and SRP concentrations (Thomas et al., 2016).

Considering catchment compartments with distinct chemical signatures, the seasonal variability of NO_3, DOC and SRP concentrations in headwater catchments can result from the mixing of i) a riparian compartment with low NO_3 concentration (because of no fertilizer application in the riparian zone in agricultural catchments, and because of high denitrification potential due to hydromorphic soils in both agricultural and forested catchments (Anderson et al., 2014)) and high DOC and SRP concentration (because of the shallow groundwater interacting with the organic soil horizons), and ii) an upslope compartment with higher NO_3 concentration (because of fertilization in agricultural catchments, and because of low denitrification potential in well-drained soils) and lower DOC and SRP (because of the deeper groundwater level hindering interaction with organic soil layers (Dupas et al., 2015b)). During the dry season, the contribution of the riparian compartment dominates, leading to low NO_3 and high DOC and SRP concentrations, whereas during the wet season, the contribution of the upslope compartment dominates, leading to high NO_3 and low DOC and SRP concentrations (Fig. 6). In addition to this lateral differentiation of NO_3, DOC and SRP sources, a vertical distribution has previously been observed (e.g., Musolff et al., 2016a)) or hypothesized (e.g., Dupas et al. (2016)) for NO_3, with higher NO_3 concentrations in the uppermost soil layers compare to deeper soil layers, leading to higher NO_3 concentrations in the stream during the wet season due to activation of shallow flow pathways. The hypothesis of a vertical differentiation of concentrations controlling seasonal variations in concentrations cannot apply to DOC and SRP, because these two elements are also expected to be present in higher concentrations in the uppermost soil layers and this should therefore lead to seasonal DOC and SRP variations similar to NO_3. Furthermore, biogeochemical processes take place in the riparian and upslope compartments, which may lead to additional seasonal variability linked to mobilization and/or retention of C, N and P sources. Biogeochemical processes are temperature-dependent, and they are also influenced by residence time (Hrachowitz et al., 2016) and by the presence/absence of reactants in biogeochemical hotspots such as the riparian zone (Pinay et al., 2015; Tiwari et al., 2017; Dick et al., 2015). In

this respect, high temperature and low flow velocity during the summer season (leading to high residence time in the riparian zone) provide favorable conditions for riparian denitrification and DOC and SRP mobilization. Finally, C, N and P also interact with each other, and several mechanisms can take place: for example increased DOC mobilization during the summer period represents a source of electron donors which can enhance denitrification (Taylor and Townsend, 2010), and DOC and SRP can be mobilized via redox processes for which NO_3 can act as a buffer (Musolff et al., 2016b; Dupas et al., 2015c).

Considering these hydrological and biogeochemical mechanisms, one can explain the different mean NO_3, DOC and SRP concentrations in the three headwater catchments with i) higher NO_3 concentrations in LS-Agr due to high N source in agricultural land and low denitrification potential because of the absence of riparian hydromorphic soils; intermediate NO_3 concentration in US-Agr due to high N source in agricultural land but high denitrification potential because of the presence of riparian hydromorphic soils; low NO_3 concentration in US-For due to low N source in agricultural land but high denitrification potential because of the presence of riparian hydromorphic soils; ii) lower DOC and SRP concentrations in LS-Agr due to the deep groundwater level, inhibiting hydrological connectivity between soil C and P sources and the stream; higher DOC and SRP concentrations in US-Agr and US-For due to soil-groundwater interactions in the riparian zone, leading to hydrological connectivity between soil C and P sources and the stream. One can also explain the larger seasonal amplitudes in US-Agr and US-For compared to LS-Agr, linked to the presence of riparian hydromorphic soils with different hydrological and biogeochemical properties than upslope soils (Fig. 6).

[Insert Figure 6 here]

Whereas the seasonal concentration-discharge variability appeared clearly in the three headwater catchments, with high NO_3 during high flow and high DOC and SRP during low flow, these relationships seemed to be more complex during storm events. Storm events pattern (accretion or dilution) provide insight into the NO_3, DOC and SRP concentrations in the flow pathways activated during storms, i.e. overland flow and shallow sub-surface flow, relative to the baseflow concentration (Dupas et al., 2016; Buda and DeWalle, 2009; Jiang et al., 2014a). In both US-Agr and LS-Agr, DOC and SRP storm event dynamics exhibited a majority of accretion patterns, suggesting high C and P source in the uppermost soil layers compared to deeper soil layers (Dupas et al., 2015d; Outram et al., 2014; Bieroza and Heathwaite, 2015). Therefore we conclude that, whereas lateral differentiation of C and P sources could explain the seasonal variability in DOC and SRP, vertical gradients of sources could explain the storm event responses. In contrast to DOC and SRP, NO_3 storm dynamics exhibited a majority of dilution patterns in LS-Agr and a combination of dilution and accretion pattern in US-Agr. This suggests that soil NO_3 concentrations in LS-Agr were lower than in the subsoil, due to plant uptake in the soil and presence of legacy NO_3 in the subsoil of LS-Agr (Outram et al., 2016), whereas soil NO_3 concentrations in US-Agr could be lower or higher than in the subsoil according to seasonal variability in soil NO_3 availability and possibility lateral difference between non-cultivated riparian soils and cultivated upslope soils (Dupas et al., 2016). Therefore, both lateral and vertical gradients of N sources can explain variability in NO_3 storm responses.

4.2. In-stream processes and point-source contributions

In the downstream reaches, the observed export regimes approximately matched the export regimes expected from conservative mixing of headwater signals for NO_3 (MEIS and HAUS) and SRP at MEIS, but not for DOC

(MEIS and HAUS) and SRP at HAUS. This means that in-stream processes and point-source contributions affect NO_3 export regimes to a lesser degree than DOC and SRP export regimes.

405 For NO_3, the difference between observed concentrations and concentrations estimated through "conservative mixing" model was on average < 1 mg N l^{-1} in both MEIS and HAUS, which was considered as a low absolute difference given the potentially high uncertainty in input estimation (see Sect. 4.4). However, this low absolute difference represents a large relative difference in MEIS (39% on an annual basis and up to 73% in summer) and a moderately large difference in HAUS (18% on an annual basis and up to 63% in summer). In a previous study

410 analyzing gross primary production and NO_3 assimilatory uptake in the MEIS and HAUS catchments, Rode et al. (2016a) estimated that annual in-stream NO_3 uptake represented 5% of NO_3 input in MEIS, with summer daily maxima up to 41%, and 13% of NO_3 input in HAUS, with summer daily maxima up to 47%. Whereas in HAUS the same orders of magnitude of relative NO_3 uptake were obtained with the balance calculation used in this study, the large relative difference in MEIS was arguably due to overestimation of NO_3 inputs (in relative

415 terms) because NO_3 concentrations were low in this forest dominated catchment. Point-source contributions were not likely to explain the overestimation of inputs at MEIS because inputs were overestimated the most during the winter period (Fig. 3b) whereas point-source contributions to load would be expected to be highest during the summer low flow period. To summarize, the mean concentration and the seasonal patterns observed for NO_3 at MEIS and HAUS were close to the expected result of conservative mixing of headwater export

420 regimes, despite relative errors exceeding 50% when NO_3 concentration were low; interestingly, conservative mixing of NO_3 can lead to large seasonal amplitudes (72% in MEIS, R^2 = 0.47) or to small seasonal amplitudes (8% in HAUS, R^2 = 0.05), depending on the seasonal export regimes of the different contributing landscape units. During storm events, the large variability in the patterns observed at MEIS and HAUS can be explained by the contribution of different landscape units, therefore no conclusion can be drawn about effects of in-stream

425 processes and point-source contributions on NO_3 storm dynamics.

For DOC, the difference between observed concentrations and those estimated through "conservative mixing" model was large (up to 3 mg DOC l^{-1}) in both MEIS and HAUS, and the large seasonal amplitudes observed in US-Agr and US-For were not observed in MEIS. In MEIS, conservative mixing of DOC resulted in an overestimation of the observed concentration, whereas in HAUS, DOC concentrations were underestimated. This

430 suggests an in-stream consumption of DOC in the upper part of the Selke river (with low nutrient and low light availability due to forest shading, (Rode et al., 2016a)), and an in-stream production of DOC in the lower part of the Selke river (with high nutrient and high light availability due absence of riparian shading, (Rode et al., 2016a)). The attenuation of seasonal amplitudes, increase of low DOC concentrations and decrease of high DOC concentrations suggests that the Selke river acts as a "chemostat" (Creed et al., 2015), transforming

435 chemodynamic headwater signals into chemostatic export regimes in downstream reaches. Within two independent forested catchments (~ 40 km²) of the TERENO Harz/Central German Lowland Observatory, Kamjunke et al. (2016) observed that heterotrophic bacteria respiration could consume up to 90% of the DOC during low flow periods. From a national scale analysis of DOC concentration and chemical composition in the USA, Creed et al. (2015) found that, in low order rivers, labile dissolved organic matter of terrestrial origin was

440 rapidly removed, while in higher order rivers, more aliphatic autochthonous DOC could be produced. These findings are compatible with observations in the Selke river, where an apparent DOC consumption was observed

in the upstream part, close to the sources of terrestrial DOC, and an apparent DOC production was observed in the downstream part, where all labile DOC from the upstream was likely to have been consumed, but where autochthonous DOC production was made possible by higher light and nutrient availability (Rode et al., 2016a). During storm events, DOC dynamics exhibited a majority of accretion patterns, as expected from DOC dynamics in headwater catchments, suggesting limited in-stream or point-source influences during storm events.

For SRP, the seasonal fluctuations observed at MEIS and HAUS corresponded to observations in headwater catchments free of point-sources, namely with annual SRP maxima during the late summer low-flow period. High phosphorus concentrations during low flow are commonly interpreted as resulting from un-diluted point-sources (Withers et al., 2014; Bowes et al., 2014, 2015), and this may lead catchment managers to target point-sources in priority in order to reduce eutrophication risk during the summer low flow period. However in the present study, high SRP during low flow was also observed in headwater catchments free of point-source emissions, and this phenomenon was more prominent in the headwater catchments with presence of riparian hydromorphic soils (US-Agr and US-For). In independent (mostly forested) catchments located in low Mountain areas in Germany, Musolff et al. (2016b) have observed that summer SRP release was associated with iron release, suggesting that iron colloids could be a vector of SRP. Musolff et al. (2016b) also showed that DOC was closely associated with SRP transfer, similar to observations in US-Agr and US-For. Hence, a biogeochemical process taking place in the riparian zone could release SRP during the summer low flow in headwater catchments, mimicking a point-source signal in downstream reaches. In the MEIS catchment, which included three waste water treatment plants, the signal from the headwater catchments represented 88% of SRP during the late summer. In the lowland area, which included two waste water treatment plants, the signal from the headwater catchments represented 57% of SRP during the late summer. Therefore, attributing all summer SRP load to point-source emissions would lead to an overestimation of their contribution to phosphorus load. For a quantitative assessment of this overestimation, it would be necessary to consider in-stream exchange of SRP with particulate P and unreactive soluble P. During storm events, SRP accretions patterns in MEIS and HAUS were less dominant than in the headwater catchments, with a majority of non-significant concentration-discharge slopes and even occurrence of apparent dilution patterns; this reflects the contrasting effect of point sources dilution and diffuse transfer activation during storm events.

4.3. Implications for monitoring and management

Monitoring of the Selke river continuum from headwater catchments to downstream reaches showed that NO_3, DOC and SRP concentration variability, characterized by export regime metrics, was influenced both by land-to-stream transfer processes, and downstream processes such as in-stream transformations and point-source contributions. Thus, monitoring headwater catchments was necessary to disentangle both types of processes, as observed downstream export regimes may not describe well the dynamics of land-to-stream emissions (Worrall et al., 2012). Furthermore, both upstream processes (e.g., summer SRP release) and downstream emissions (e.g., point-source SRP emission during summer) may lead to the same export regime (e.g., high SRP during low flow); this phenomenon creates epistemic uncertainty, which may lead to equifinality problems when calibrating catchment models to the data (Beven, 2013). This epistemic uncertainty can be effectively reduced by integrating headwater and downstream reaches in monitoring and modeling studies, as proposed by Jiang et al. (2014b). In this respect, authority monitoring programs, which typically focus on catchments > 100 km², are suitable for

water quality assessment but this data alone may not be enough to interpret land-to-stream transfer processes, as the signal from land emission might be altered by downstream processes.

The results of this study also have implications for management, to improve the ecological status of rivers. First, the export regimes observed exhibit large temporal and spatial variability in C, N, P emission: i) the opposite seasonal dynamics of NO_3 and SRP concentrations can lead to a switch from P limitation to N-P co-limitation during the summer growing season; ii) emissions from different landscape units vary in space and time. This knowledge of temporal and spatial variability is necessary for prioritizing management effort towards N or P according to a water quality target (for which N:P ratio should be considered) and towards the landscape units most responsible for not attaining the water quality targets (Doody et al., 2016). Second, comparison of seasonal export regimes in headwater and downstream reaches showed that attributing the seasonal SRP maximum during low flow only to point-source contribution could lead to ineffective management decision if the wrong source is targeted. Finally, in-stream transformations of C, N, P are typically given less consideration in management programs than the reduction of land-to-stream emissions. Management approaches in which landscape units would be relocated geographically in order to maximize in-stream retention could provide a viable addition to conventional management schemes.

4.4. Limits and perspectives

This study considers archetypal headwater catchments as representative of the main landscape units present in larger catchments. Although this assumption corresponds to the expert knowledge in the study area, and it has led to satisfying results in previous modeling studies (e.g., Jiang et al. (2014b)), variability within landscape units (for example agricultural management practices) may exist and further research would be necessary to quantify it. This could be undertaken by considering a larger number of headwater catchments and developing empirical models such the landscape model of Tiwari et al. (2014) combined with a stream network model. Without a quantification of uncertainty, it is difficult to assess quantitatively the effect of the different processes evidenced qualitatively in this study. For example, the small absolute difference between modeled and observed NO_3 at MEIS should not be interpreted in relative terms to infer in-stream NO_3 retention, as the concentrations involved were small compared to the uncertainty in the inputs. Another limit in this study, which prevents a quantitative assessment of processes from mass balance calculations, is the consideration of only one N and P form, and DOC as a bulk, whereas the chemical composition of C, N, P compounds may be more diverse (Yates and Johnes, 2013). For example, the finding that previous P load apportionment studies may overestimate point-source contribution cannot be made qualitatively when only SRP data is available; a quantitative assessment would require consideration of particulate P and soluble unreactive P, and exchange-transformation with SRP.

This top-down analysis study also led to new hypotheses that should be further explored via process-based studies in geochemical hotspots such as the riparian and hyporheic zones. For example, SRP release during the summer low-flow period has rarely been documented to our knowledge (see however Smolders et al. (2017)). Finally, this study focused mainly on manual grab sampling data, with a limited number of high frequency sampling of storm events; however, the storm events monitored exhibited different export regimes from seasonal variations, with for example NO_3 and SRP exhibiting alternatively synchronous and opposite dynamics, whereas NO_3 and SRP consistently had opposite dynamics on a seasonal basis. These short terms variations have

implication of N:P load ratios and further research involving high frequency sensors will allow their quantitative evaluation (Rode et al., 2016b), including seasonal variability of storm event patterns (Dupas et al., 2015d).

5.   Conclusions

The C, N, P export regimes observed at the outlet of large catchments (> 100 km²) result from the combined effects of land-to-stream transfer processes, in-stream transformations, and point-source contributions. In this study, monitoring the river continuum from headwaters to downstream reaches allowed:

- Identifying land-to-stream transfer processes for different solutes and for the main landscape units present in the study area. A seasonal export regime for NO_3 opposite to those of DOC and SRP was evidenced in the three landscape types investigated. Presence/absence of riparian hydromorphic soils appeared to play a crucial role in C, N, P export intensity and seasonal variability.
- Identifying in-stream transformation processes and point-source contributions, highlighting that downstream signals could be strongly altered by in-stream processes (e.g., for DOC) and that natural SRP release during summer and point-source contributions could lead to similar export regimes.

Thus, this study highlights the benefit of complementary monitoring of downstream reaches and headwaters representing archetypical of landscape units, in order to improve understanding of processes throughout the continuum from soils to large rivers. This study also calls for a seasonal strategy to achieve water quality targets, and a landscape approach designed to maximize land and in-stream retention is advocated.

Data availability

The data is available upon request

Supplementary material

The manuscript has additional graphs as supplementary material

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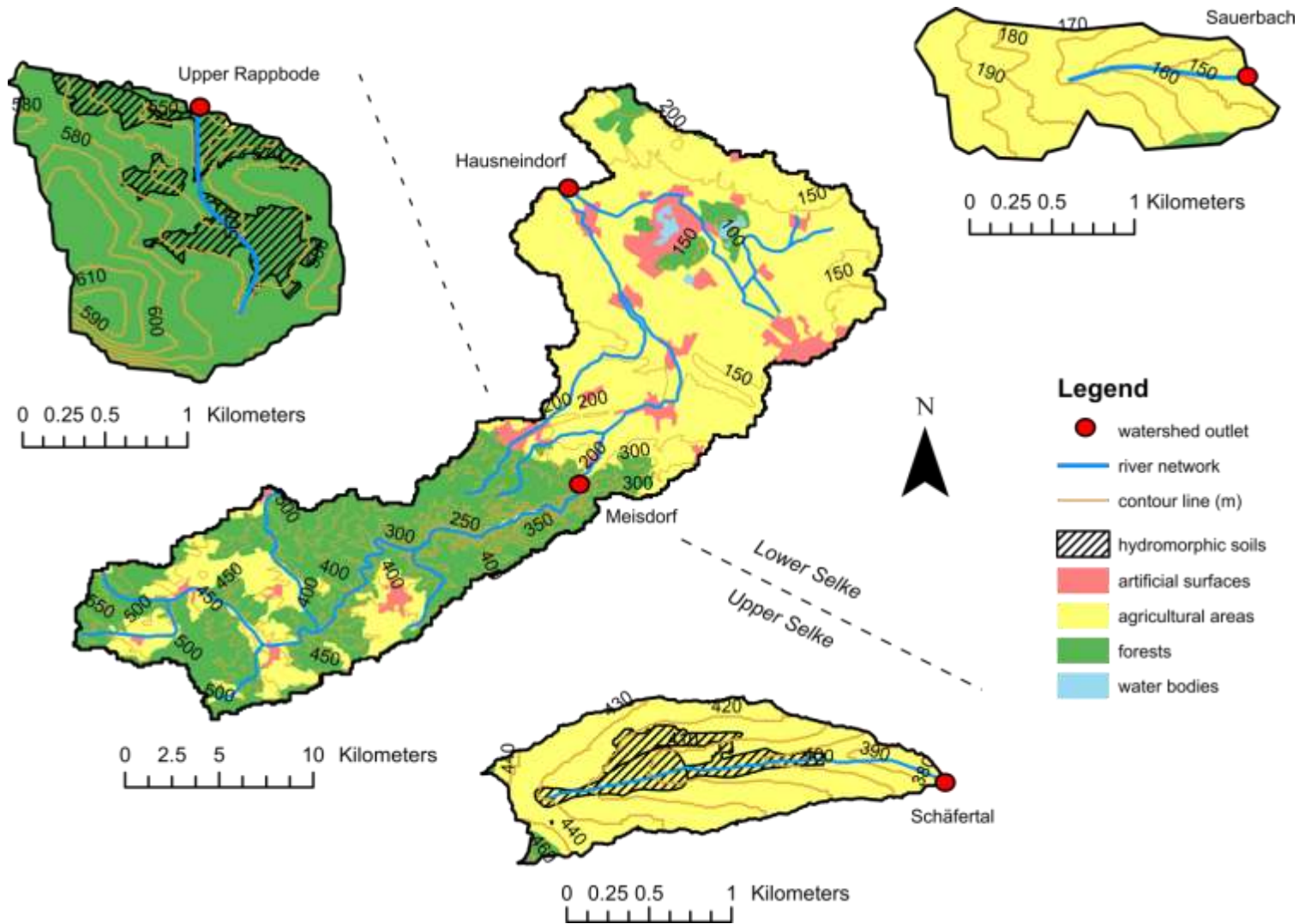


Fig. 1: Landscape types in the Selke catchment and location of monitoring sites.

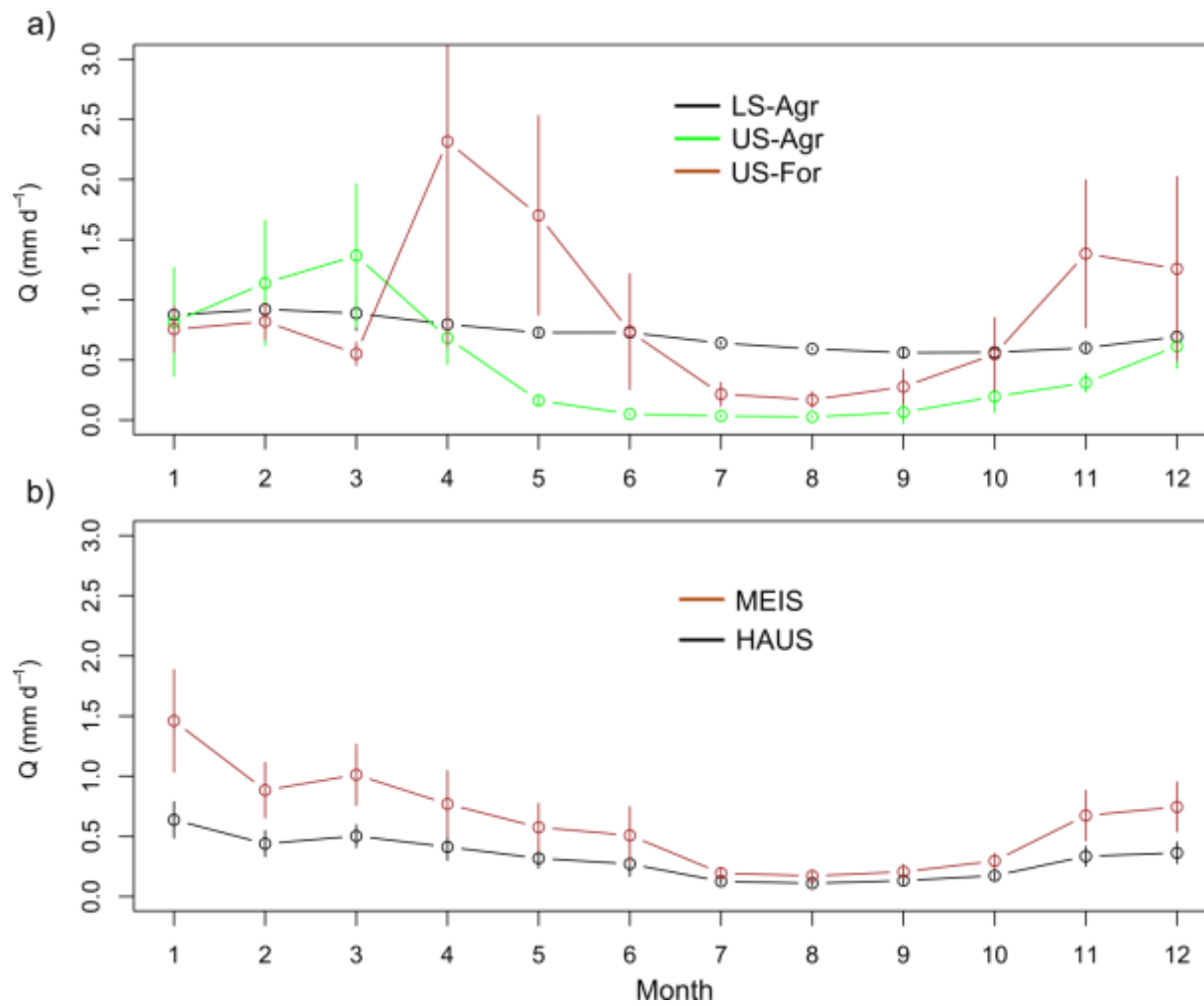



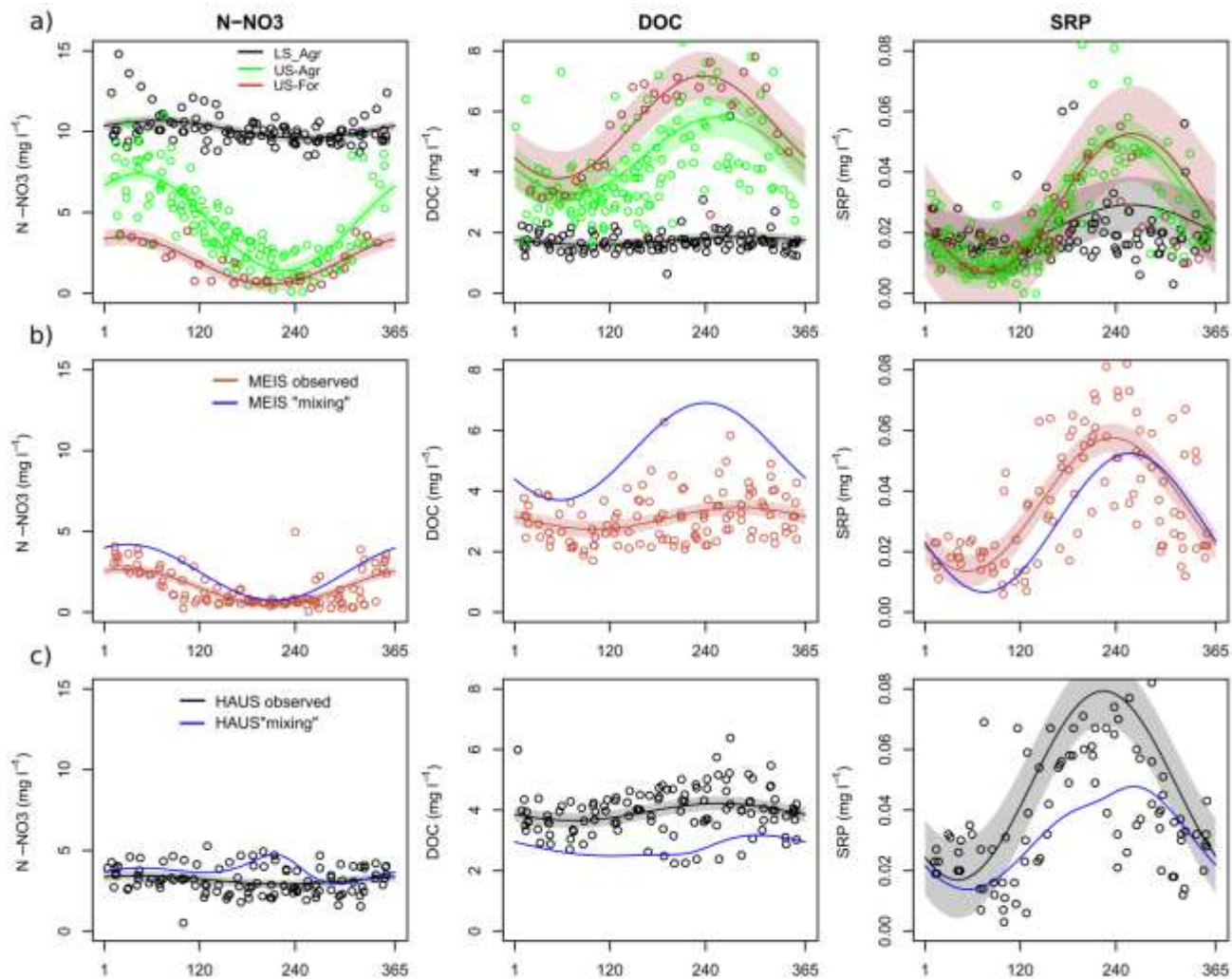
Fig. 2: Monthly discharge in headwater catchments (a) and downstream catchments (b). Error bar represent standard deviation (n = 2 – 10 years).

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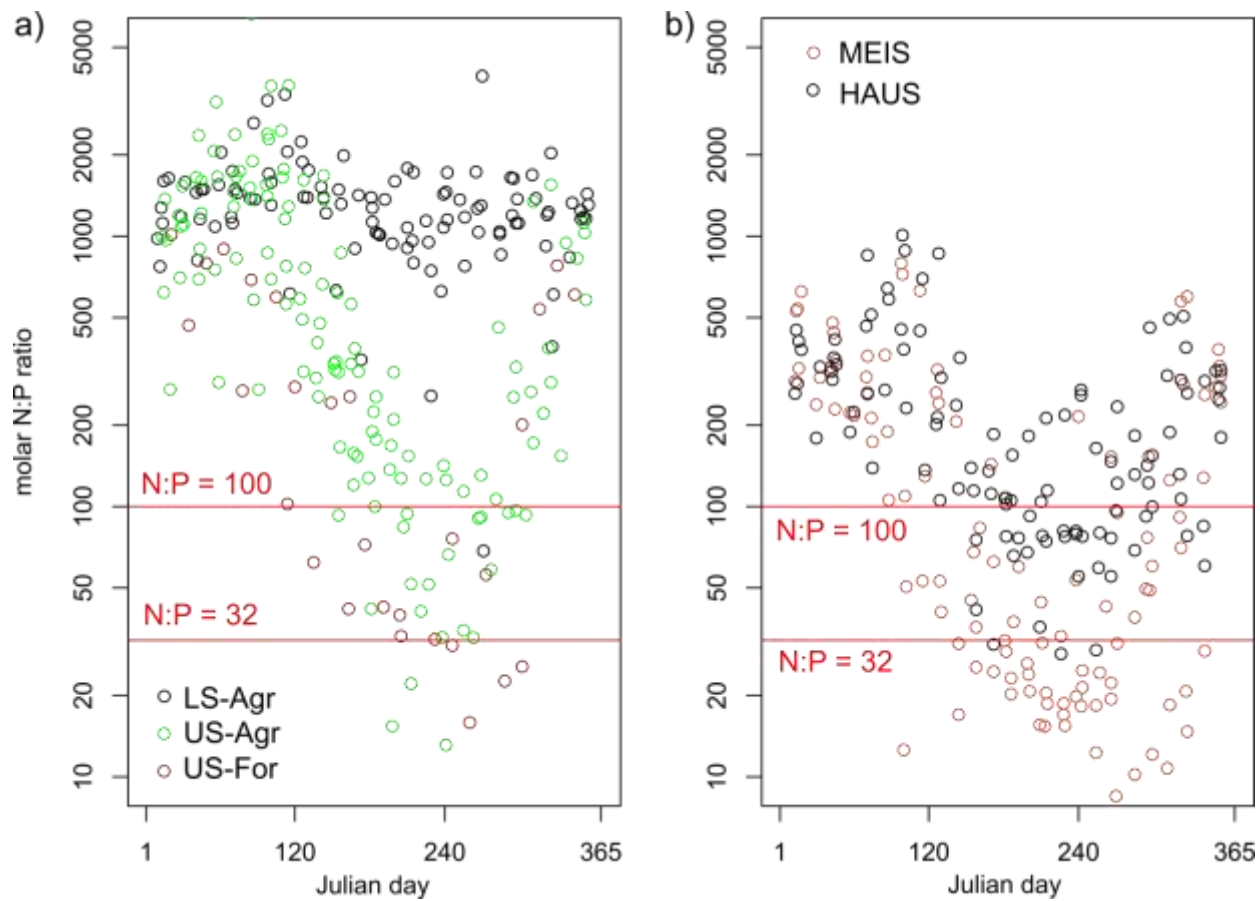
Fig. 3: Infra-annual variability of nitrate (N-NO3), Dissolved Organic Carbon (DOC) and Soluble Reactive Phosphorus (SRP) in headwater catchments (a) and in the downstream catchments Meisdorf (b) and Hausneindorf (c). Circles represent observation data, lines represent cosine fitting and shaded areas represent 95% confidence intervals.

725 **Fig. 4: Infra-annual variability of the molar N:P ratio calculated with grab sampling data in headwater catchments (a) and downstream reaches (b). The two thresholds represent N:P = 32 mol:mol and N:P = 100 mol:mol.**

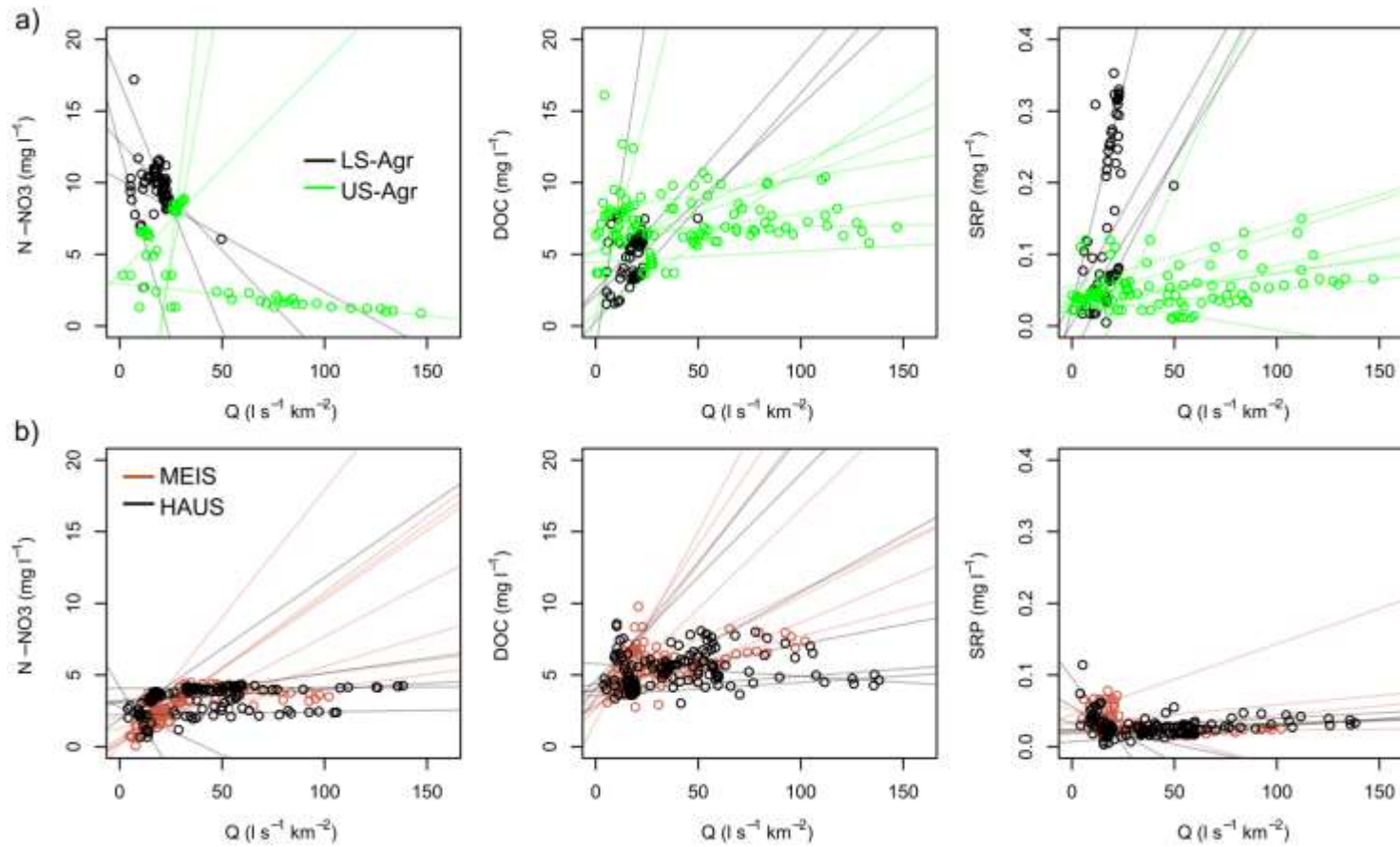



Fig. 5: Concentration-discharge relationships during storm events in (a) two headwater catchments (LS-Agr n=4, US-Agr n=8) and in (b) two downstream reaches (MEIS n= 8, HAUS n=8) for three solutes: nitrate-N, Dissolved Organic Carbon (DOC) and Soluble Reactive Phosphorus (SR... ear regression models were fitted to each event to quantify the proportion of events with a dilution (negative slope) or an accretion pattern (positive slope).

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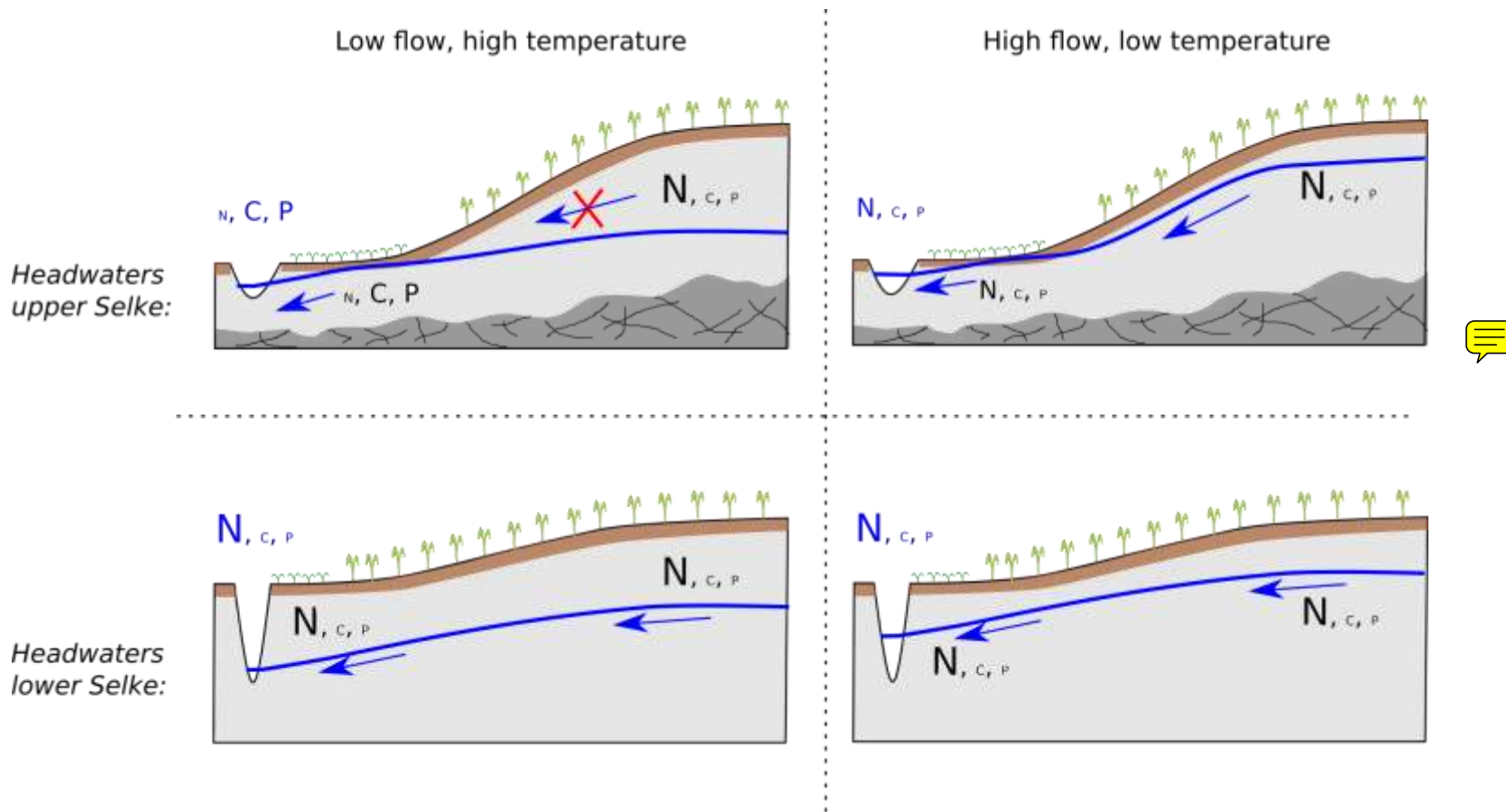
Figure 6: Conceptual model of C, N, P intra-annual variability in headwater catchments in the upper Selke (archetypes US-Agr and US-For) and in the lower Selke (archetype LS-Agr). Letter size refers to the intensity of the mass flux for each solute.

Table 1: Coefficient of variation (mean ± standard deviation, n = 2-10 years) of daily discharge, concentrations N:P ratio.

	CV_Q	CV_{NO3}	CV_{DOC}	CV_{SRP}	$CV_{N:P}$
LS-Agr	0.22 ± 0.15	0.06 ± 0.03	0.24 ± 0.18	0.55 ± 0.47	0.42 ± 0.23
US-Agr	2.32 ± 0.72	0.56 ± 0.18	0.45 ± 0.15	0.73 ± 0.24	1.04 ± 0.44
US-For	1.25 ± 0.96	0.60 ± 0.12	0.30 ± 0.07	0.74 ± 0.20	1.05 ± 0.37
MEIS	1.23 ± 0.39	0.73 ± 0.12	0.25 ± 0.07	0.48 ± 0.22	0.98 ± 0.27
HAUS	0.99 ± 0.29	0.22 ± 0.08	0.19 ± 0.10	0.65 ± 0.27	0.70 ± 0.24

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Table 2: Coefficient of the cosine equation fitting to grab sampling concentration data.

		LS-Agr	US-Agr	US-For	MEIS	HAUS
N-NO3	a (mg l^{-1})	10.14	4.39	2.01	1.55	3.18
	b (mg l-1)	0.54	3.00	1.46	1.12	0.26
	b/a (%)	5.33	68.33	72.59	72.20	8.27
	seasonal maximum (Julian day)	66	42	24	27	42
	R²	0.15	0.67	0.69	0.47	0.05
DOC	a (mg l^{-1})	1.73	4.55	5.48	3.10	3.94
	b (mg l-1)	0.13	1.27	1.69	0.36	0.28
	b/a (%)	7.75	27.96	30.91	11.61	7.12
	seasonal maximum (Julian day)	282	254	237	284	256
	R²	0.03	0.16	0.51	0.09	0.07
SRP	a (mg l^{-1})	0.02	0.03	0.03	0.04	0.05
	b (mg l-1)	0.01	0.02	0.02	0.02	0.03
	b/a (%)	33.33	79.46	77.27	61.92	64.73
	seasonal maximum (Julian day)	258	249	259	235	224
	R²	0.03	0.49	0.33	0.51	0.28

Table 3: Spearman's rank correlations for discharge and concentration parameters. Significant correlations (p < 0.05, Holm-corrected) are in bold.

LS-Agr	Q	NO3	SRP
NO3	**0.63**		
SRP	0.11	0.06	
DOC	0.08	0.05	0.20

US-Agr	Q	NO3	SRP
NO3	**0.81**		
SRP	**-0.65**	**-0.78**	
DOC	**-0.51**	**-0.63**	**0.62**

LS-For	Q	NO3	SRP
NO3	**0.70**		
SRP	-0.53	**-0.72**	
DOC	-0.16	-0.44	0.64

MEIS	Q	NO3	SRP
NO3	**0.79**		
SRP	**-0.67**	**-0.66**	
DOC	**0.46**	0.19	0.01

HAUS	Q	NO3	SRP
NO3	0.18		
SRP	**-0.47**	-0.03	
DOC	-0.02	**-0.39**	0.07

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Table 4: Counting of accretion and dilution patterns during storm events derived from the slope of concentration-discharge relationships (p < 0.05).

		dilution	accretion	non-significant slope
LS-Agr	N-NO3	3/4	0/4	1/4
	DOC	0/4	4/4	0/4
	SRP	0/4	4/4	0/4
US-Agr	N-NO3	1/4	1/4	2/4
	DOC	0/8	3/8	5/8
	SRP	0/8	5/8	3/8
MEIS	N-NO3	0/8	6/8	2/8
	DOC	0/8	7/8	1/8
	SRP	0/5	1/5	4/5
HAUS	N-NO3	1/8	2/8	5/8
	DOC	0/7	3/7	4/7
	SRP	0/7	2/7	5/7

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