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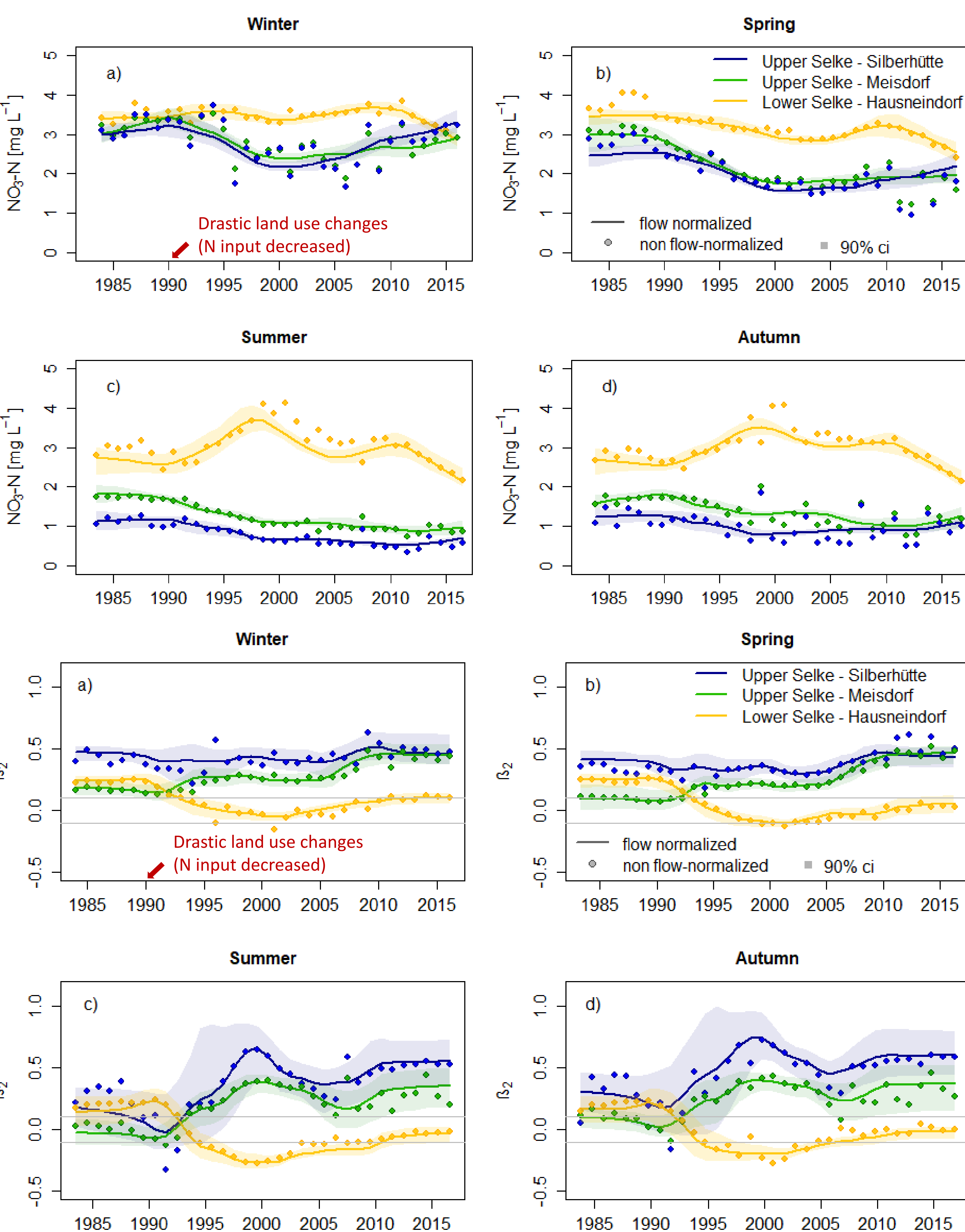
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Disentangling the impact of catchment heterogeneity on nitrate export dynamics across time scales

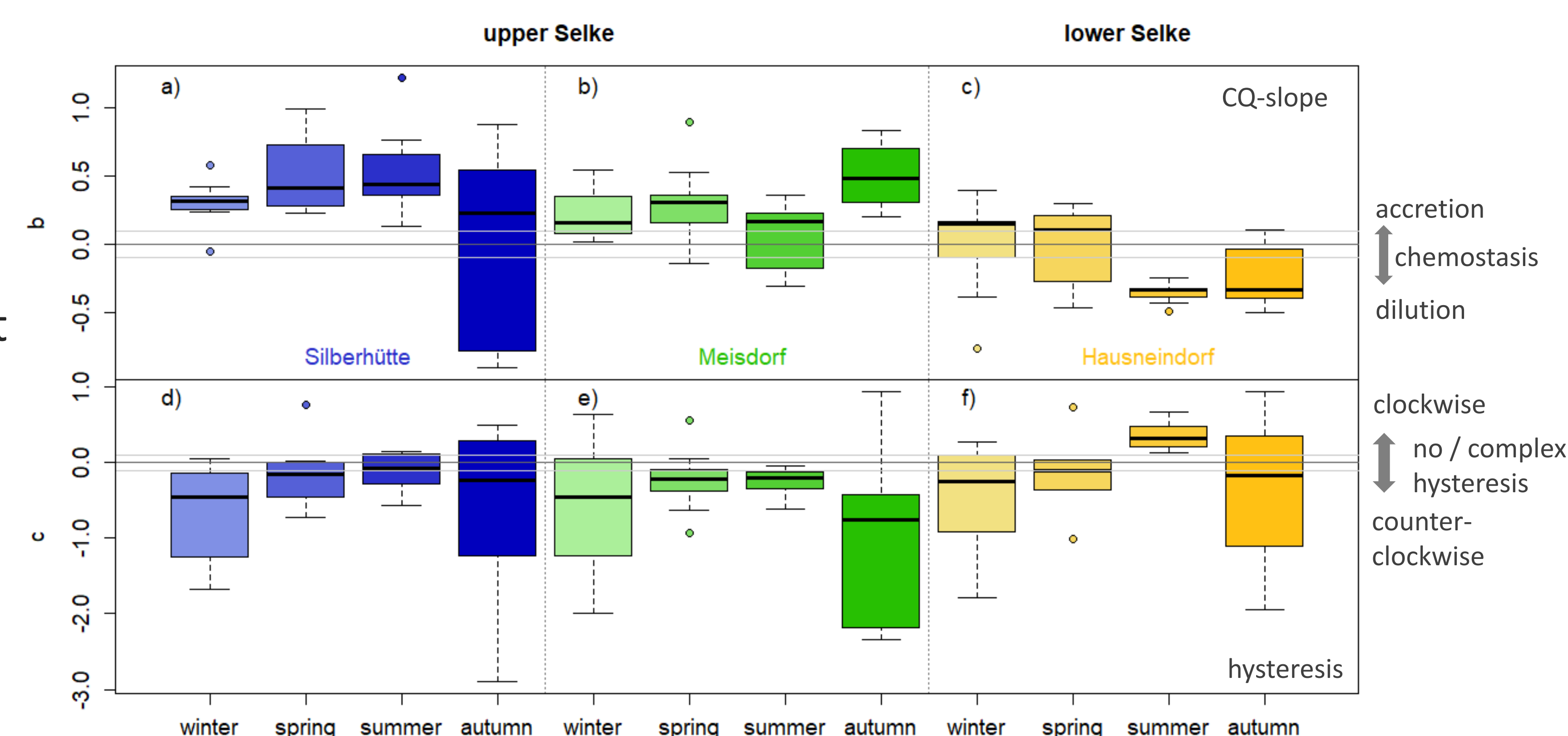
C. Winter¹, S. Lutz¹, A. Musolff¹, M. Weber², J. H. Fleckenstein¹

Background Our aim is to better understand sub-catchment specific contributions to nitrate export and their importance at different time scales in heterogeneous mesoscale catchments. Therefore we analyzed long-term trends, seasonality and event dynamics in three nested catchments in the Selke catchment (456 km²), Germany, which underwent abrupt land use changes in 1990. Both, the forested upstream part (upper Selke) as well as the agriculturally dominated downstream part (lower Selke) considerably contributed to nitrate export, but at very different time scales and flow conditions. This knowledge is crucial for an effective and site-specific management of water quality.

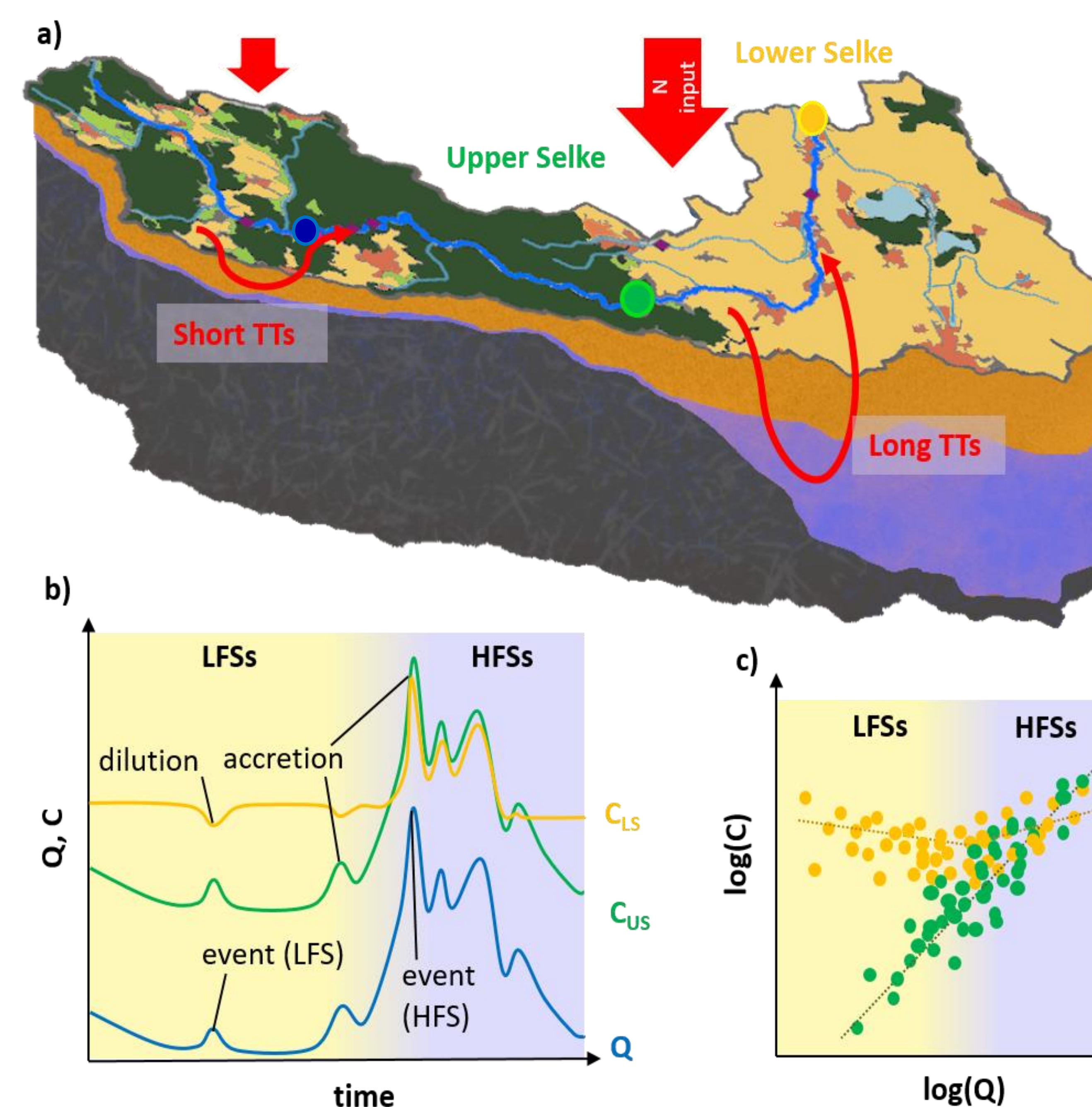


Long-term trends of annual nitrate concentrations show different trajectories in the upper and lower Selke after drastic changes in N input and a more pronounced seasonality in the upper Selke.

Long-term trends of annual CQ-slopes show mainly accretion patterns for the upper Selke and a transition from accretion over dilution towards chemostasis in the lower Selke.



Event dynamics in the lower Selke show accretion patterns, similar to long-term trends, and counterclockwise hysteresis. In the lower Selke, CQ-slopes shift from accretion during winter and spring to dilution during summer and autumn, which can be explained by the impact of upper Selke nitrate concentrations. Hysteresis is counterclockwise except for summer events.



Key findings

- The elevated upstream part of the catchment dominates nitrate export during high flow and disproportionately contributes to nitrate loads.
- The agricultural downstream part of the catchment dominates nitrate export during base flow and poses a long-term threat to water quality due to legacy effects.
- Analyzing the CQ-relationship across time scales allows to disentangle the impact of catchment heterogeneity on nitrate export.

Scroll down for further information on methods, additional results and literature

Supplementary Information for: Disentangling the impact of catchment heterogeneity on nitrate export dynamics across time scales

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Data basis: Long-term nitrate concentration (C) and discharge (Q) data were available between 1983 and 2016, provided by the State Office of Flood Protection and Water Management of Saxony-Anhalt (LHW). High frequency C data (15 min. resolution) were collected by the UFZ as part of the TERENO monitoring program from 2010 to 2016, described in more detail by Rode et al. (2016). High frequency Q data was provided by the LHW.

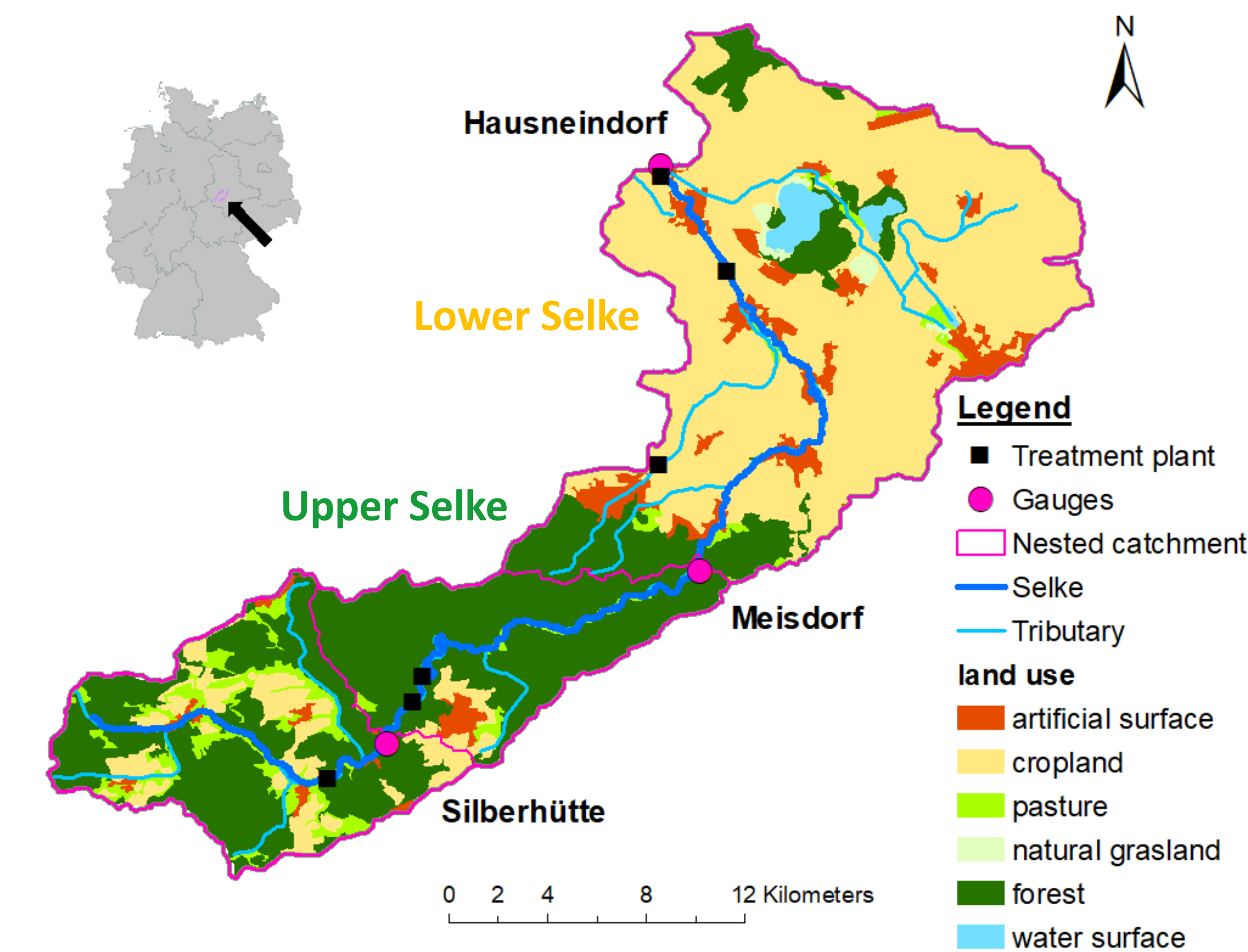
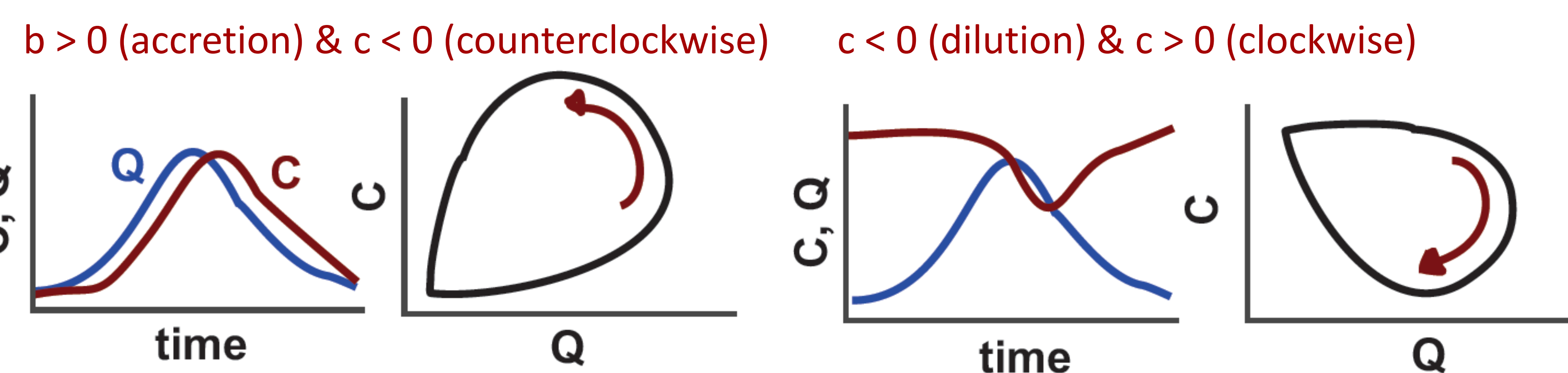
Concentration-discharge relationships (CQ-relationships) were analyzed as the slope between $\log(C)$ and $\log(Q)$, which allows to distinguish between i) chemodynamic export with accretion pattern (positive slope), indicating that C increase with increasing Q, ii) chemodynamic export with dilution patterns (negative slope), indicating that C decreases with increasing Q and iii) chemostasis (CQ-slope \sim zero), which indicates a considerably lower variability of C compared to Q (Musolff et al., 2015).

Long-term trends in nitrate concentrations and CQ-slopes were analyzed using *Weighted Regression on Time Discharge and Season* (WRTDS, Hirsch et al. 2010), implemented in the R-package *Exploration and Graphics for RivEr Trends* (EGRET). We used a modification of the original EGRET codes, developed by Zhang et al. (2016), to extract the daily CQ-slope (fitted parameter β_2).

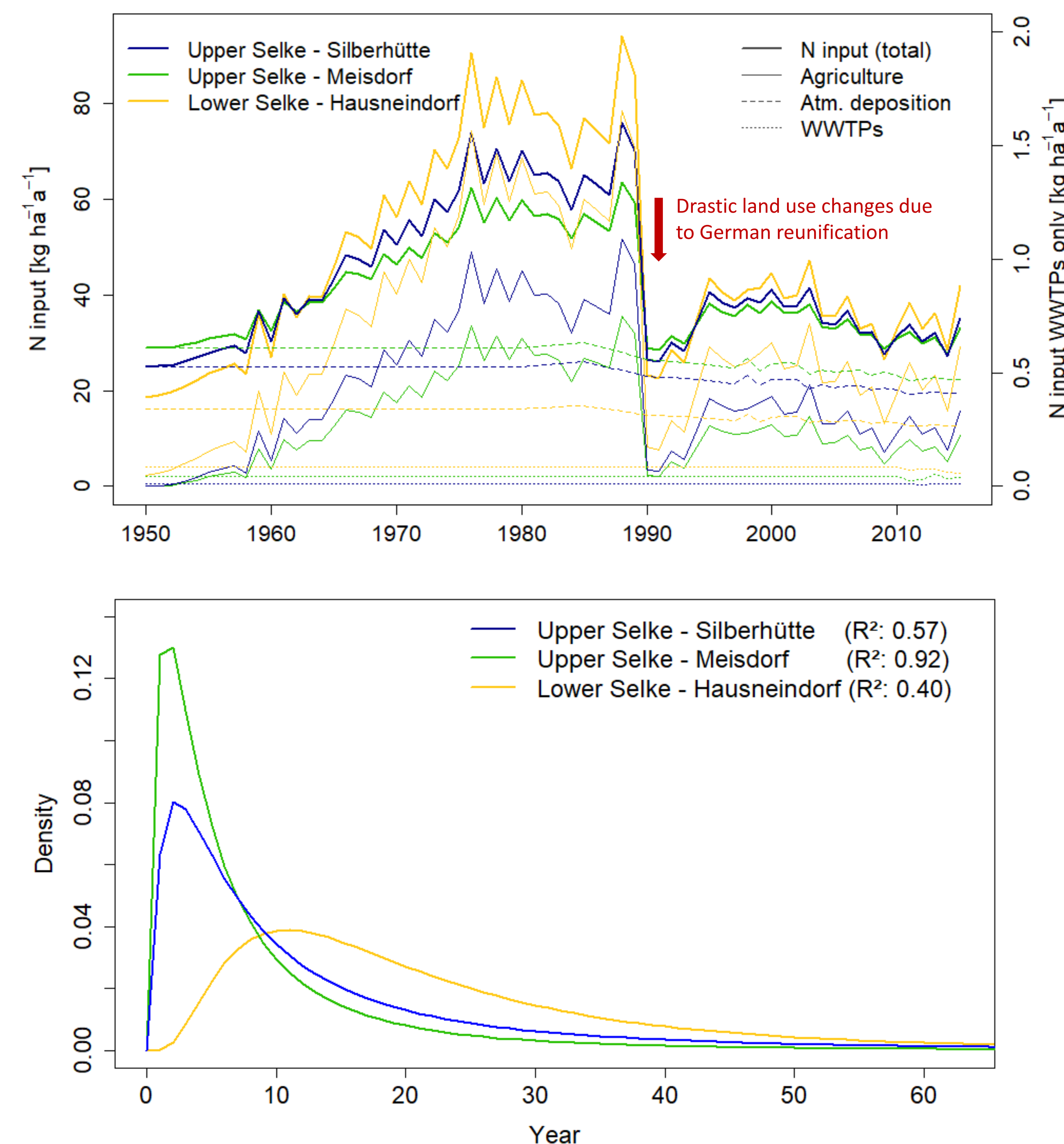
Event dynamics were analyzed, fitting the following equation after Krueger et al. (2009) and Minaudo et al. (2017) to events that were identified from the high frequency data:

$$C = a * Q^b + c * \frac{dq}{dt}$$

where a , b and c were fitted for each event individually. Parameter a gives the event-specific intercept and b the CQ-slope, which is equivalent to the parameter β_2 from the long-term analysis. Consequently, parameter b represents the CQ-slope and parameter c was used to identify the extent and direction of event-specific hysteresis, as depicted below.



Study side is the Selke catchment, an intensive research site located in the Harz Mountains and the Harz foreland and part of the TERrestrial ENvironmental Observatories (TERENO, Wollschläger et al., 2017). Within the Selke catchment, we considered three nested sub-catchments, delineated by the following stations: i) Silberhütte (105 km²), ii) Meisdorf (184 km²) and iii) Hausneindorf (456 km²).



Nitrogen input for all three nested sub-catchments of the Selke catchment, with i) total N input as the sum of ii) N input from agricultural areas, iii) atmospheric deposition and biological fixation on non-agricultural areas, and iv) outflow from wastewater treatment plants (WWTPs).

Effective Transit time distributions for nitrate (TTDs) were calculated according to Musolff et al. (2017) and Ehrhardt et al. (2019), assuming a log-normal distribution that was fitted with scaled flow-normalized nitrate concentrations and scaled N input. The TTDs have their maximum after 3 years in the upper Selke and after 12 years in the lower Selke.

Literature

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