**The following document contains the responses to the reviewers, the manuscript with tracked changes and the revised manuscript with comments connecting the changed parts to the points raised by the reviewers**

**Response to anonymous Referee #1**
General response: We thank the referee for the valuable inputs and remarks. We address all comments below and hope to clarify the questions raised. In the manuscript with tracked changes notation on the responses can be found.

**1. How is error propagated? The authors often report four significant figures, but do not report standard deviation, confidence intervals, or some other estimate of uncertainty. Given the compound assumptions of the input chronicle models and the hydrological components, a sensitivity analysis or some kind of quantification of uncertainty seems warranted.**

R1: Right, an uncertainty analysis was missing so far and will for sure improve the analysis. We derived the confidence band of flow normalized concentration and fluxes based on a bootstrap method for WRTDS proposed by Hirsch et al. (2015) and available in the egretCI package in the R environment. We estimated 5$^{th}$ and 95$^{th}$ percentiles of flow normalized concentration and fluxes for each year of measurements in a conservative best case/ worst case analysis in the input-output budgeting and in the estimation of travel times. We added a section in the methodology, describing this and changed table 3, and 4 and figures 3, and 4 respectively. For the input of nitrogen (nitrogen surplus) we stated the methodological error provided by Bach & Frede (1998) in the method section as well.

**2. The idea of comparing biogeochemical and hydrological legacies is very compelling but it remains unclear to me how these parameters were estimated and compared. Structuring the methods around the research questions or overarching hypotheses and carrying this through the manuscript would make this flow clearer would make the results/discussion more impactful.**

R2: That is a very helpful comment. We revisited the introduction and the research questions and made them more clear especially on where we see the potential of using the C-Q relationships to better disentangle the biogeochemical and hydrological legacies. Moreover, we wrote introductory sentences for the different method parts to better integrate research questions with the method steps. Finally we made the discussion on this topic more explicit in the discussion part as well. Based on the results of our analyses, we improved upon the discussion part raising new hypothesis on dominant legacy types. Since our study is based on a data-driven analysis, we can’t test such new hypothesis – but certainly we feel it is worth raising them from the data evidence so that a future initative could start looking into those new aspects.

**3. I think the discussion would be more engaging if the authors focused on the applicability of this approach to catchments generally, rather than explaining specific observations from their study. They do this effectively several times (e.g. starting on page 22 starting around line 20), but there is also quite a bit of retreatment of the results, which are specific to these sites.**

R3: We carefully reviewed and revised the sections that are specific to our catchments - shortening them without losing the main message. Here and in the conclusions we more explicitly indicated where we discuss and draw conclusions for the studied catchment and where we can generalize our findings. We also see a greater potential of applying this local analysis to a wide range of catchments where we can more easily draw general conclusions (Page 29 Line 30 ff.).

**4. The authors present an interesting puzzle of massive nitrogen retention/removal that cannot be attributed to typical pathways (e.g. denitrification, uptake, mineral association). The authors then conclude that N storage (the biogeochemical and hydrological legacies) account for the disconnect. However, the dismissal of denitrification seems to be based on a few studies from this area, which are not described in detail (e.g. Page 23, line 15). If these other studies are definitive and reliable, more description of their methods should be given. Another explanation is associated with point 1 - could the N removal be much lower when uncertainty in inputs and outputs are included?**

R4: Yes – as mentioned above in R1 we addressed the uncertainty of the regression approach and the N input from agricultural areas. We would like to note here a recent paper published in November 2018 giving an overview on denitrification potential in the federal state this catchment is part of (Hannappel et al., 2018). It connects hydrochemical analysis of groundwater nitrate, oxygen and redox potential to the hydrogeological units in this region and states a general weak potential for denitrification for the study site. We included this study with methodological details to strengthen our argumentation on the denitrification part. We already included the study by Müller et al. (2018) within the same study area that provided strong evidence on the lack of denitrification based on their assessment on isotopic signatures in the integrated nitrate signal in the surface water. We put more emphasis on discussing this study as well to better argue our case.

**5. Line edits Page 2 Line 5: (Elser et al. 2007)**

R5: We added this reference here.

**6. Line 6: It seems odd to say these changes were strictly terrestrial. It seems they influenced both.**

R6: We dropped the word “terrestrial” at the specified location.

**7. Line 10: Do the authors mean the natural rate of reactive N fixation has been doubled (e.g. (Vitousek et al. 1997))?**

R7: Yes, Vitousek et al. (1997) and Smil (1999) refer to the same: Human activities are mainly responsible for doubling the amount of reactive/ biological active N that enters the element’s cycle from the unreactive atmospheric pool of $N_2$. We added this reference and adjusted the sentence, accordingly.

**8. Page 3 Line 2: management interventions (instead of “measures”)?**

R8: Thanks – we changed that.

**9. Line 2: Recent study from similar agricultural and climatic context that found decadal hydrologic (Kolbe et al. 2016; Marçais et al. 2018)**

R9: Thanks for the suggestion. We, refer to time lags of nitrate in response to interventions in the catchment here. The suggested studies address water travel time without making the connection to time lags in nitrate are therefore not eligible here but are used later on in the manuscript.

**10. Line 16: I actually think there are quite a few studies, especially recently (Dupas et al. n.d.; Howden et al. 2010; Burt et al. 2011; Minaudo et al. 2015; Meter & Basu 2017; Abbott et al. 2018; Coble et al. 2018; Garnier et al. 2018; Marcé et al. 2018; Pinay et al. 2018; Fanelli et al. 2019)**

R10: Thanks for the input. We adjusted the sentences adding four of the suggested studies.

**11. Line 20: How do these analyses compare with soil-surface N balance approaches that include a crop and livestock removal component (Poisvert et al. 2017; Abbott et al. 2018)?**

R11: Both, Jawitz and Mitchell (2011) as well as Musolff et al. (2015) are not based on N balances but on an interpretation of the temporal dynamic (or lack of temporal dynamic) in the observed nitrate concentrations. We added that to this sentence. Our paper aims at a combination of both approaches – N balancing (since the N-input takes crops and livestock into account) and C-Q assessment. Both, Poisvert and Abbott refer to a comparable data basis for N-surplus as we do.

**12. Line 30: Recent paper on concentration-discharge responses to catchment saturation (Moatar et al. 2017)**

R12: Moatar et al. (2017) do not state what we wanted to say here for nitrate – an increase of "chemostasis" with increasing intensification of agriculture. We therefore did not include this citation at this point in the manuscript.

**13. Page 5 Line 18: In what dimensions is this catchment especially vulnerable to climate change?**

R13: A recent study by Wollschläger et al (2017) states a high vulnerability due to low water availability and a pronounced risk of summer droughts that is likely to be exacerbated by decreasing summer precipitation and increasing temperature/ potential evapotranspiration. One new reference stating that were included here as well (Samaniego et al. 2018). We added this information in the revised manuscript.

**14. Page 8 Line 13-20: Interesting that the primary datasets do not include non-agricultural land for N deposition. Why did the authors not use one of the products that provided a consistent N deposition rate across land-use types? Perhaps this is a small portion of the overall N budget, but it would be worthwhile to specify.**

R14: We combined two products for N input to agricultural and non-agricultural land as there is no consistent product available in Germany, covering both with the required spatial and temporal resolutions. We added this information to the text.

**15. Page 9**
**Figure 2: The dissimilarity in the NO3 concentration time series is striking as are the drops to zero mg/L even at the lowest site. Consider combining Figures 2 and 3 to allow visual comparison of discharge and concentration.**

R15: The "drops to zero" are actually the no-data-values that are erroneously displayed as zero (but not considered in the WRTDS regressions). We adjusted the figure to properly reflect the missing information; and also combined Fig. 2 with the discharge in Fig. 3.

**16. Page 10**
**Line 9: the discharge time series were used. . .**

R16: Thanks – we changed this in the revised manuscript.

**17. Page 11**
**Line 8: allows increasing . . .**
R17: Thanks – we changed this in the revised manuscript.

**18. Page 12**
**Line 10: Because our purpose was to balance and compare . . .**
R18: Thanks – we changed this in the revised manuscript.

**19. Line 12: This justification seems unclear. Is it simply claiming that the longer-term trends are accurate, though the daily values are not?**

R19: No, the daily values are accurate but just that they not available at a daily time scale. We thus refer to the robust aggregated annual wastewater flux that much better fits to the flow normalized fluxes provided by the WRTDS regression analysis (see statement P11L31ff). Daily values are used to estimate an average fraction of $NO_3$-N in the wastewater N flux.

**20. Page 14**
**Table 2: These differences in specific discharge are remarkable. Is this typical for this area or is the three-fold difference due to a known environmental or anthropogenic variable?**

R20: Yes this is remarkable but typical, and one of the reasons behind the establishment of the TERENO observatory system (Wollschläger et al. 2017). Wollschläger et al. (2017) state the strong precipitation gradient from 1700 mm/ a down to less than 500 mm/a within a range of 50 km due to the rain shadow of the Harz mountains; and thereby leading to strong spatial differences in the resulting specific discharges. We made this fact more clear in the method section.

**21. Page 15**
**Line 11: Revise sentence for grammar and clarity (with implications for instead of with discussion on?)**

R21: Thanks - we revised the sentence.

**22. Page 16**
**Line 14: It is striking that the retention capacity increases 5-fold with landscape position. Is this because of shifts in soil and subsurface properties or because the retention or removal rates are dependent on substrate concentration?**

R22: Yes, this is quite a strong difference that is stated here as an observed result. Discussion on the reasoning can be found later on in Section 4.1.

**23. Page 22**
**Line 20: Nitrification also results in gaseous N loss via the "leaky pipe" pathway (Hart et al. 1994).**

R23: Right – there can be losses of $N_2O$ leaving the system at the nitrification step. However, in comparison to denitrification it does not appear to be a dominant loss term in N-budgets (Rivett et al. 2008, Galloway et al. 2004). See also comment R4 – the paper by Müller et al. (2018) on the isotope evidence for the lack of N removal in the study catchment.

**24. Line 29: Is this referring to denitrification in the near-surface zone or throughout the whole catchment? With pyrite, sulfur, and other iron ubiquitous in the weathered and fractured zones, aquifer denitrification is likely occurring**

R24: We refer to denitrification in general, taking both autotrophic and heterotrophic denitrification into account. Both need the absence of oxygen independent of whether electron donors are available or not. Also both affect the finally measured isotope signature in the remaining nitrate in the stream. See also our comment R4 with the new study (Hannappel et al. 2018) stating the lack of denitrification evidence that we included in the revised manuscript.

**25. Page 23 Line 18: New methods for constraining aquifer travel time to constrain removal rates using numerical or empirical methods (Kolbe et al. 2016; Marçais et al. 2018).**

R25: Right. Enhanced knowledge on water travel time will improve the estimation of reaction rates. We considered Marcais et al (2018) and the more recent study by Kolbe et al. (2019) in the conclusion of the revised manuscript.

**26. Page 25 Line 1: Similar to these observations, though they are on a much smaller scale (Thomas & Abbott 2018)**

R26: Thanks – we considered this in the revised manuscript.

**27. Page 28 Line 9: were explained**
R27: Thanks – we changed that as suggested.

**28. Line 14: catchment reaction seems like an odd description for transit time.**

R28: That is right. We changed that phrase as suggested.

**Response to anonymous Referee #2**
General response: We thank the referee for the valuable inputs and remarks. We address all comments below and hope to clarify the questions raised. In the manuscript with tracked changes notation on the responses can be found.

**General comments:**
**1. The manuscript addresses the important issue of legacy stores of nutrients, which may prevent mitigation actions that reduce the inputs from having immediate effects on stream water quality. I like the date drive approach to investigate the travel times of nitrate. The paper shows that 85% of the N input is retained within the catchment. The investigation about the fate of this lost N is not very convincing and inconclusive. Based on data on inputs and outputs alone, the authors cannot proof whether the N is retained in the soil, whether it is traveling along long flow paths, or whether it is denitrified. The authors try to give answers based on literature, but this is not very convincing. A weak point of the paper is that the entire soil and groundwater system is addressed as a black box. This is a bit strange given the focus on the paper on N – stores and travel times in soil and groundwater. Including data on e.g. groundwater heads and flow-paths and concentration depth profiles for N could provide more certainty about the fate of the lost N.**

R1: We understand the reviewer remark. With the current datasets at hand and rather invoking any model conceptualization, our study can only hypothesize and argue about travel times (TTs) and legacy, which is unfortunately a common methodological challenge of studies on catchment scale. We treat the entire catchment including soil and groundwater system as a black box and try to understand the inherent processes by looking at the signals produced or altered by this box. By doing a data-driven analysis, our aim is to provide observation-based evidence on the system input-output response behavior, which can then be a starting point for developing either more targeted field-based or model-based "mechanistic" studies. Groundwater measurements and soil profiles would be a great help to support the hypothesis, but those observational records are generally not available. We tried hard to overcome this lack of knowledge by strengthening with the isotopic evidence on a minor role of denitrification, by incorporating a new regional study on denitrification, and by a comprehensive literature review for our studied catchment and comparable study sites (see also response R4 for Referee #1).

**Specific comments:**
**2. Title: Consider to leave out 'decadal'. I don't understand why you would only be looking at decadal trajectories**

R2: Agree, we dropped "decadal" in the title.

**3. Abstract: The abstract is rather long. Especially the description of the results (from "We show: : :"). Consider to start a new paragraph here to make the structure more clear. The conclusion statement is a bit weak. Management should both address longer term and short term N-loads. How does this change water quality management in practice?**

R3: We carefully reviewed the abstract, shortened the result section and put a clear focus on consequences for management practice that results from our analysis.

**4. From P3L4 until P4L22 the introduction reads like a description and a justification of the methods that you apply. It remains unclear what is not yet known from the existing scientific literature, why that is important, and what new science this paper brings.**

R4: We carefully reviewed the Introduction part of the paper to highlight the suggested mentioned aspects: What is known? Why it is important? And what's new in our study? This is also in line with comment 2 of the Reviewer 1. We made the importance and the new scientific messages conveyed from our work clearer in the revised version.

**5. In P4L20 you state that "data-driven studies focused either solely on N-budgeting and legacy estimation or on TTs." What data-driven studies do you mean here? Why is this a problem / what problem do you solve by combining these? The referencing to Van Meter and Basu is quite excessive.**

R5: We refer to the data-driven studies e.g. by Worral et al., 2015 and Dupas et al., 2016. We have adapted the introduction text to further underline the advantage of combining the quantification of legacy and TT in one study (and from the same database) to use the TTs to explain the legacy. In terms of studies cited: See also comment R10 for Referee #1 where we aim at including a greater variety of studies.

**6. P2L11-12: here you state that the agricultural nitrogen input is still high since the 1980's. It did decrease in most EU member states since the '80s as a result of the introduction of manure legislation, didn't it?**

R6: The reviewer is right in pointing this out that N-inputs, also from agricultural sources were reduced (but they are still on a high level). We rewrote the concerned sentence to correct this inaccuracy.

**7. P2L26: "The evaluation of measures: : :" What evaluation of measures. This sentence is a bit hard to follow.**

R7: Thanks - we revised this sentence to make it clear

**8. P5L18: why is the region vulnerable to climate change?**

R8: Yes, we added the explanation on this. For details, see reply R13 to Referee #1

**9. P6L3: it's not clear where the 2 WWTP's are located. Can you add them to your map?**

R9: We added the locations to the map in Fig. 1.

**10. P6L8: how much are agriculture and WWTP's (and other sources) contributing in %?**

R10: Referring to the last 5 years of observations, $NO_3$-N load from wastewater made up 17% of the total observed $NO_3$-N flux at the midstream station (see below) and 11% at the downstream station. We added this information here. Note that this fraction is removed from the exported nitrate in our analysis to focus on the diffuse pathways only (see P11, L29ff).

**11. Figure 1: the stream is not very clear on this map.**
R11: We highlighted the river system**.**

**12. P7L5 :"artificially drained" Do you mean drained by open ditches or by subsurface tube drains? How much has subsurface tube drainage?**

R12: We now differentiate between "open ditches" and "tile drains" in the sentence by adding corresponding percentages. While more than half of the drains in the midstream sub-catchment are tube drains, the downstream sub-catchment is much more dominated by open ditches.

**13. Table 1: The fraction artificially drained (last row) is much lower downstream. I would expect more artificial drainage in the downstream part of the catchment as this is usually the wetter part of the catchment. Is there a reason why there is less artificial drainage needed in the downstream part?**

R13: Thank you for this remark. This is related to the hydro-climatic conditions. The downstream area is significantly warmer and dryer in comparison to the colder and wetter upstream areas (see also response R20 for Referee #1 on this issue). This is also reflected in precipitation and discharge behavior – particularly in the strong drop of discharge contribution is noted from the different sub-catchments as indicated in Table 2.

**14. P8L30 ": : :we do not account for wastewater fluxes at this point: : :" Why is this legitimate? Is the wastewater N flux negligible?**

R14: We focused on diffuse N pathways via soil and groundwater where the legacy accumulation and time lags between input and output can potentially occur. Therefore we discounted the point contribution from both WWTPs from our N-data prior to TT analyses. See also the reply R10 above for the contribution of the WWTPs.

**15. Figure 2 and 3: shouldn't these figures be presented in the results section?**

R15: We understand your remark, but we still favor these figures related to data presentation in this section as it is now in the manuscript (see a similar example in Tetzlaff et al. (2014)). It's a presentation of the measured raw-data, while the results present the derived aggregated concentration and fluxes after using the WRTDS method. We adjusted the concerned section heading to "Data and methods" so to make this clearer.

**16. Figure 2c: It seems like the NO3 concentration is 0 around 2007 and at the end of the graph. Please check this. There also seems to be a regime-shift in this plot just before 2000. What happened?**

R16: You are right, we corrected these data points dropping to zero in Fig. 2 (see comment to that in response R15 of the Referee #1). The visible regime-shift around 2000 is related to the changing C-Q relations at the time where the dilution pattern switches to the enrichment pattern (see also Fig.7 c1 and c2). We address that in section 3.5 and in the discussion.

**17. P11L6: "flow-normalized concentrations" It is not clear here why you need flow normalization. Consider to bring forward the end of the paragraph. Why would you want to take out the impact of variable flow conditions?**

R17: We dropped the wording "flow-normalized" from here as the reasoning and procedure for the normalization is explained later on in this section (P12, L5-8).

**18. P11L9: I don't understand how you interpolate the bi-weekly/monthly data. ": : :using a flexible statistical representation for every day of the discharge record".**

R18: We carefully revised that section to make methods more clear. The interpolation is based on a regression model using discharge (Q) as a predictor, a trend component and a seasonal (sinusoidal) component. This model is fitted for every day separately utilizing a weighted regression approach that weights observation before and after that day differently based on their relevance for that specific day. Details are given in Hirsch et al. (2010). We noted a mistake in the references here, and corrected this in the revised manuscript (the citation Hirsch & DeCicco in the text refers to the R-package while in the reference list the according paper Hirsch et al. is cited).

**19. P13L14: "purple line"!purple dashed line**

R19: Thanks - we changed that in the revised manuscript.

**20. P13L21: "peaked 1980" ! peaked in 1980**
R20: Thanks - we changed that in the revised manuscript.

**20. Table 2: It is hard to connect the numbers for the LFS and HSF contributions in the text (<10%, 33%) with this table. It would be better not to give the cumulative contributions, so for HFS: 21, 69, 10.**

R20: We revised the table to avoid confusion between cumulative and single sub-catchment information.

**21. P15L11: I don't understand ": : :besides the statistical evaluation of the time series"**

R21: Thanks - we revised this sentence to make it clear.

**22: P16L6-15: During the measurement period the catchment will partly export N-inputs from before 1970/76. This could be seen as the legacy of the period before the measurement period. The missing N described here adds to the legacy from before 1970/76.**

R22: Your point is right and we are aware of this discrepancy. We tried to underline this problem by stating: "*overlapping time period of in- and output*". A more appropriate comparison of in- and output would only be possible with the exact knowledge of TTs. In this first view of input-output-differences, we took the corresponding years for a quantitative comparison. Later on in the conclusions (P27, L22-25), we shift the input to the output ("*assuming the temporal offset of peak TTs between in- and output of 12 a*") and quantify the imbalance between both. We added a sentence in the concerned section, to underline this difference in a better way.

**23. P18L6: why are these TTs for all seasons taken together not presented?**

R23: We added these lines in Fig. 5.

**24. Figure7b1: The concentrations seem to drop here, before the input drops. How is this possible?**

R24: Of course input changes cannot affect output earlier on. We think this drop in riverine nitrate concentration around 1985 is rather related to the sharp stop of increasing N-input at the beginning to mid of the 1970s and the following decrease of inputs.

**25. Figuret7c1: The higher concentrations in summer and fall during the peak around 1990 are surprising. This would indicate that the concentrations in deep groundwater with long travel times to surface water are higher than the concentrations in shallow groundwater with short travel times. Is this groundwater N that infiltrated in the midstream catchment and seeps up in the downstream catchment?**

R25: We can understand your reasoning, but as explained in Section 4.2, the higher concentrations downstream in summer and fall are result of different nitrate source contribution during low flow seasons (LFS) and high flow seasons (HFS). HFS-signals downstream are dominated by contributions from the wetter midstream sub-catchment with higher discharge per area and generally lower concentrations (see also Table 2 and similarity of midstream and downstream high flow concentrations shown in Fig. 6), whereas the low flow concentrations are dominated by the groundwater discharging from the downstream sub-catchment with much lower groundwater recharge and likely higher groundwater nitrate concentrations.

**26. Figure 7a2-c2: add a legend.**
R26: We added the color gradient to Fig. 6.

**27. P20L9: refer to figure 7a2.**
R27: We added the suggested reference.

**28.P20L7-P21L17: This text in combination with figure 7 is quite a hard puzzle.**

R28: Thank you for that comment. We carefully revised this section and payed close attention to focus on the information needed for the discussion later on.

**29. P22L1: "was difficult" ! "was impossible"**
R29: Thanks, we revised that sentence.

**30. P22L1-2: Degradation of organic matter may play a role.**

R30: Yes, NO3 may be released from organic matter. However, on the longer term there cannot be more release than input. As the balance indicate more export than import we rather think we either have unaccounted sources or overrestimated the biological N-fixation (underestimation of resulting N surplus). Both arguments are in the text.

**31. P22L17-20: I don't understand why "steeper terrain suggests a deeper infiltration" and "leaching of NO3 from a wider depth range than flat terrains". I would expect the opposite; deeper infiltration and leaching from a wider depth range in flat terrains. Of course, this depends on the geology.**

R31: For this point, we would like to refer the reasoning provided in the recent paper by Jasechko et al. (2016):
*"Conversely, the reduced prevalence of young streamflow in steeper terrain suggests that steeper landscapes tend to favor deeper vertical infiltration rather than shallow lateral flow. A tendency for greater infiltration in mountainous watersheds* ***may seem counterintuitive****, but is consistent with conceptual models of runoff generation and groundwater flow that suggest that topographic roughness drives long groundwater flow pathways that bypass first-order streams*."

**32. P22L26:"to for an" ! "for an"**

R32: Thanks, we changed this as suggested.

**33. P23L9-10: "Hence,: : :output" I think that this conclusion that denitrification is weakly supported by the previous text. Groundwater quality measurements would be very useful here.**

R33: We improved the overall argumentation made here through a support by findings in another study by Hannappel et al. (2018) who analyzed groundwater and an enhanced discussion of the isotope evidence by Müller et al. (2018) – see more information in response R4 for Referee #1.

**34. P23L16: why did Kuhr et al exclude denitrification?**

R34: We dropped this citation at this point and refer to Hannappel et al (2018) – see the previous comment R33.

**35. P24L4-9: from this paragraph and especially the last 2 sentences it seems like it is not important whether the legacy store is growing or the denitrification capacity is used, however on P22L23-25 you stated that this difference is important.**

R35: We changed this paragraph to make the point clearer in the revised text. With the long-term data collection, we can only hypothesize whether the missing N is stored or denitrified, although it would be important for management. Beside management advices, we can show that the catchment N-input is unsustainable high, either due to the ongoing build-up of an even bigger legacy or due to relying on a denitrification capacity which is unlikely to be infinite.

**36. Figure 8: This figure does not make any sense to me.**

R36: We have revised this figure to make our conceptual understanding of N-storages and release in the study catchment more clear.

**37. P25L3-5: I don't think that you can make this assumption; the flow contributions from a certain depth can vary a lot due to interannual variability**

R37: We don't think that there is evidence of a long-term change of flow paths in the catchment. Hydroclimatic conditions did not change; land use, topography and river network are stable over the long observation period. We added these aspects here to better justify our assumption.

**38. P26L3: You can also argue that groundwater seeping up is more important in the downstream catchment. This would mean more discharge of relatively old water.**

R38: The TTs in the downstream part are shorter than those in Midstream, and not the other way round. Our argumentation is based on the greater prevalence of young streamflow in flatter terrain as shown also by Jasechko et al. (2016). See also response R31.

References uses (that are not in the main manuscript)


- Tetzlaff, D., Birkel, C., Dick, J., Geris, J. and Soulsby, C. (2014) Storage dynamics in hydropedological units control hillslope connectivity, runoff generation, and the evolution of catchment transit time distributions. Water Resources Research 50(2), 969-985.

# ~~Decadal~~ T~~t~~rajectories of nitrate input and output in three nested catchments along a land use gradient

Kommentar [SE1]: Ref2, No.2

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**Abstract.** Increased anthropogenic inputs of nitrogen (N) to the biosphere during the last decades have resulted in increased groundwater and surface water concentrations of N (primarily as nitrate) posing a global problem. Although measures have been implemented to reduce N-inputs ~~especially from agricultural sources~~, they have not always led to decreasing riverine nitrate concentrations and loads. This~~e~~ limited response to the measures can either be caused by the accumulation of ~~slowly mineralized~~ organic N in the soils ~~acting as a~~ (biogeochemical legacy) or ~~legacy or~~ by long travel times (TTs) of inorganic N to the streams ~~forming a~~ (hydrological legacy). ~~Both types of legacy are hard to distinguish from the TTs and or the N budgets alone.~~ Here we ~~jointly analyze~~compare atmospheric and agricultural N inputs with long-term observations (1970-2016) of riverine nitrate concentrations and ~~discharge~~ loads in a Central German mesoscale catchment with ~~in Central Germany. For~~ a three nested sub-catchments arrangement ~~with~~ of increasing agricultural land use~~,~~. Based on a data-driven approach, w~~w~~e assess jointly the ~~catchment scale~~ N-budget and~~,~~ the effective TTs of N through the soil and groundwater compartments. In combination with long-term trajectories of the ~~C-Q~~C–Q ~~-~~relationships, we ~~finally~~ evaluate the potential for and the characteristics of an N~~N~~-legacy.

We show that in the 42-year-long observation period, the catchment (282 km$^2$) with 60% of agricultural area have received an N-input of 42 758 tonns~~,~~ ~~of which 97 % derived from agricultural sources. The riverine N export sums up to~~ while it exported 6 ~~592~~ 592 ~~t~~tons; indicating ~~that the catchment retained~~an overall N-retention of 85 % ~~of the N input~~. Removal of N by de-nitrification could not ~~fully~~ sufficiently explain this imbalance. Log-normal travel time distributions (TTDs) ~~for N~~ that link the N-input history to the riverine export differed seasonally, with modes spanning 8–17 years and the mean TTs being systematically higher during the high-flow season as compared to low-flow conditions. ~~. Under low flow conditions, TTs were found to be systematically longer than during high discharges.~~ Systematic shifts in the ~~C-Q~~C–Q relationships were noticed over the time that could be attributed to ~~significant~~ strong changes in N-inputs resulting from agricultural intensification before 1989, ~~and~~ the break-down of the East German agriculture after 1989, and as well to the ~~longer travel times TTs of nitrate during low flows compared to high flows~~seasonal differences in TTs. A chemostatic export regime of nitrate was only found after several years of stabilized N-inputs. ~~We explain these observations by the vertical migration of the N-input and the seasonally changing contribution of subsurface flow paths with differing ages and thus differing N loads.~~

Formatiert: Hochgestellt

The changes in ~~C-Q~~ C–Q relationships suggest a dominance of the hydrological N-legacy ~~rather than a~~over the biogeochemical N-fixation in the soils, ~~which should result in~~as we expected to observe a stronger and even increasing dampening of the riverine N-concentrations after sustained high N-inputs. Our analyses reveal ~~Despite the strong N-legacy,~~ ~~Though a chemostatic nitrate export regime is not necessarily a persistent endpoint of intense agricultural land use, but rather depends on a steady replenishment of the stored mass of N propagating through the catchments subsurface.~~ ~~The~~an imbalance between ~~in~~N-input and ~~-~~outputs ~~imbalance~~, the long time-lags, and the lack of significant denitrification in the catchment; all these suggest ~~let us conclude~~ that catchment management needs to address both, a longer-term reduction of N-inputs and shorter-term mitigation of today's high N-loads. ~~this demands a temporally and quantitatively adjusted fertilizer application to enable depletion instead of a further build-up or stabilization of the legacy. To deal with N losses from current or past N inputs,~~The latter may be covered by interventions ~~to encourage~~triggering denitrification, such as hedgerows around agricultural fields, riparian buffers zones or constructed wetlands~~, , are can be~~. Further joint analyses of N-budgets and TTs ~~of data~~ covering a higher variety of catchment ~~characteristics may~~will provide a ~~more comprehensive picture of~~deeper insight to N-trajectories and their controlling parameters.

## 1 Introduction

In terrestrial, freshwater and marine ecosystems nitrogen (N) species are essential and often limiting nutrients (Webster et al., 2003; Elser et al., 2007). Changes in strength of their different sources like atmospheric deposition, wastewater inputs ~~as well as~~and agricultural activities caused major changes in the ~~terrestrial~~ ~~nitrogen~~N cycle (Webster et al., 2003). Especially two major innovations from the industrial age accelerated anthropogenic inputs of reactive ~~nitrogen~~N species into the environment: artificial ~~nitrogen~~N fixation and the internal combustion engine (Elser, 2011). ~~The~~ By that ~~anthropogenically released~~ the amount of reactive ~~nitrogen~~N that enters into the element's biospheric cycle has been doubled in comparison to the preindustrial era (Smil et al., 1999; Vitousek et al.; 1997). However, the different input sources of ~~nitrogen~~N show diverging ~~trends~~ rates of change over time and space. While the atmospheric emissions of ~~nitrogen~~N oxides and ammonia have strongly declined in Europe since the 1980s (EEA, 2014), the agricultural nitrogen input (N-input) through fertilizers declined but is still at a high level (Federal Ministry for the Environment and Federal Ministry of Food, 2012). ~~Consequently, in~~In the cultural landscape of Western countries, most of the ~~nitrogen~~N emissions in surface and groundwater bodies stem from diffuse agricultural sources (Bouraoui and Grizzetti, 2011; Dupas et al., 2013).

**Kommentar [SE2]:** Ref1, No.5

**Kommentar [SE3]:** Ref1, No.6

**Kommentar [SE4]:** Ref1, No.7

**Kommentar [SE5]:** Ref2, No.6

The widespread consequences of these excessive N-inputs are significantly elevated concentrations of dissolved inorganic nitrogen (DIN) in groundwater and connected surface waters (Altman and Parizek, 1995; Sebilo et al., 2013; Wassenaar, 1995) leading to increased ~~as well as the associated increases in~~ riverine DIN fluxes (Dupas et al., 2016) and causing the ecological degradation of freshwater and marine systems. This degradation is caused by the ability of ~~nitrogen~~N species to increase primary production and to change food web structures (Howarth et al., 1996; Turner & Rabalais, 1991). Especially the coastal marine environments, where nitrate ($NO_3$) is typically the limiting nutrient, are affected by these eutrophication problems (Decrem et al., 2007; Prasuhn and Sieber, 2005).

~~To cope with this problem,~~Several initiatives in forms of ~~–~~international, national and federal regulations have been implemented aiming at an overall reduction of N-inputs into the terrestrial system and its transfer to the aquatic system. In the European Union, guidelines are provided to its member states for national programs of measures and evaluation protocols through the Nitrate Directive (CEC, 1991) and the Water Framework Directive (CEC, 2000).

The evaluation of interventions showed that policy-makers still struggle to set appropriate goals for water quality improvement particularly in heavily human-impacted watersheds. Often, interventions like reduced N-inputs mainly in agricultural land use ~~are~~do not immediately result~~ting~~ in ~~decreasing~~declining riverine $NO_3$-N concentrations (Bouraoui and Grizzetti, 2011) and fluxes.

~~The evaluation of the measures showed that policy-makers struggle to set appropriate goals for water quality improvement in human-impacted watersheds, as the reduced N-inputs mainly in agricultural land use, are often not immediately resulting in decreasing riverine nitrate concentrations (Bouraoui and Grizzetti, 2011) and fluxes.~~ ~~Also i~~In Germany considerable progress has been achieved towards the improvement of water quality, but the diffuse water pollution from agricultural sources continues to be of concern (Wendland et al., 2005). This limited response to mitigation measures can partly be explained by nutrient legacy effects, which stem~~mings~~s from an accumulation of excessive fertilizer inputs over decades creating a ~~time lag~~strongly dampened response between the implementation of measures and water quality improvement (van Meter & Basu, 2015). Furthermore, the multi-year ~~transfer travel time~~travel times (TT) of nitrate through the ~~unsaturated and saturated zones of the catchment itself~~ soil and groundwater compartments causes large time lags (Howden et al., 2010; Melland et al., 2012) that can ~~mask~~ substantially delay the riverine response to applied ~~measures~~management interventions. For a targeted and effective water quality management ~~W~~we therefore need a profound understanding of the processes and controls of time lags of N from the source to groundwater and surface water bodies. ~~Joint analyses that derive TTs and~~Bringing together N balancing and accumulation with estimations of N ~~travel time~~TT from application to riverine exports ~~legacy estimation in one study and hence from the same data,~~ can contribute to this ~~this needed understanding~~lack of knowledge.

~~Calculating~~Estimation of the ~~travel time (TT) of~~ water and ~~-~~/or solutes TTs ~~through the landscape~~ is essential for predicting the retention, mobility and fate of solutes, nutrients and contaminants at catchment-scale (Jasechko et al., 2016). Time series of solute concentrations and loads that cover both, input to the geosphere and the subsequent riverine export, can be used not only to determine ~~travel times~~TTs (~~TTs;~~ van Meter & Basu, 2017), but also to quantify mass losses in the export ~~or the~~ as well as the behaviour of the catchment's retention capacity~~, respectively~~ (Dupas et al., 2015).~~-~~ Knowledge on the TT of N ~~in the catchment~~ would therefore allow understanding on the N-transport behaviour; ~~help to~~ defining~~e~~ the fate of injected N mass into the system and its contribution to rive~~r~~rine N-response~~from previous inputs that is still on its way to the stream~~.

**Kommentar [SE6]:** Ref2, No.7

**Kommentar [SE7]:** Ref1, No.9

**Kommentar [SE8]:** Ref1 No.8

**Kommentar [SE9]:** Ref2, No.4

**Kommentar [AM10]:** Ref1, No.2

The mass of N being transported through the catchment storage can be referred ~~to a~~as hydrological legacy. Data driven or simplified mechanistic approaches have often been used to derive stationary and seasonally variable TT distributions using in- and output signals of conservative tracers or isotopes (Jasechko et al., 2016; Heidbüchel et al., 2012) or chloride concentrations (Kirchner et al., 2000; Bennettin et al., 2015). ~~However, recently~~Recently, van Meter & Basu (2017) estimated the solute TTs for ~~nitrogen~~N transport at several stations across a catchment located in Southern Ontario, Canada, showing decadal time-lags between input and riverine exports. Moreover, systematic seasonal variations in the $NO_3$-N ~~nitrate~~ concentrations have been found, which were explained by seasonal shifts in the ~~nitrogen~~N delivery pathways and connected time lags (van Meter & Basu, 2017). Despite the determination of ~~these~~ such seasonal ~~concentration~~ changes and age dynamics, there are ~~only~~relatively few studies ~~is generally a lack of studies~~ focussing on their long-term trajectory under conditions of changing N-inputs (Dupas et al., 2018; Howden et al., 2010; Minaudo et al., 2015; Abbott et al., 2018). ~~.~~ Seasonally differing time shifts, resulting in changing intra-annual concentration variations, are of importance ~~for~~ to aquatic ecosystems health and their ~~–~~ functionality. Seasonal concentration changes can also be directly connected to changing concentration–discharge (C–Q) relationships – a tool for classifying observed solute responses to changing discharge conditions and for characterizing and understanding anthropogenic impacts on solute input, transport and fate (Jawitz & Mitchell, 2011; Musolff et al. 2015). ~~Especially i~~Investigations of temporal dynamics in the C-Q~~is~~ relationship are a valuable ~~supplement~~addition to approaches based on ~~the~~ N balancing~~e approach~~only (e.g. Abbott et al. 2018), when evaluating the effect of management interventions.

**Kommentar [SE11]:** Ref1, No.10

**Kommentar [SE12]:** Ref1, No.11

The C–Q relationships can be on the one hand classified in terms of their pattern characterized by the slope b of the lnC–lnQ regression (Godsey et al., 2009): with enrichment ($b > 0$), dilution ($b < 0$) or constant ($b \approx 0$) patterns (Musolff et al., 2017). On the other hand, C–Q relationships can be classified according to the ratio between the coefficients of variation of concentration ($CV_C$) and of discharge ($CV_Q$; Thompson et al., 2011). This export regime can be either chemodynamic ($CV_C/CV_Q > 0.5$) or chemostatic, where the variance of the solute load is more ~~strongly~~ dominated by the variance in discharge than the variance in concentration (Musolff et al., 2017). Both, patterns and regimes are dominantly shaped by the spatial distribution of solute sources (Seibert et al., 2009; Basu et al., 2010; Thompson et al., 2011; Musolff et al., 2017). High source heterogeneity and consequently high concentration variability ~~in the discharge~~ is thought to be characteristic for nutrients under pristine conditions (Musolff et al., 2017, Basu et al., 2010). It was shown that catchments under intensive agricultural use evolve from chemodynamic to more chemostatic ~~behavior~~behaviour regarding nitrate export (Thompson et al., 2011; Dupas et al., 2016). Several decades of human N-inputs seem to dampen the discharge-dependent concentration variability, resulting in chemostatic ~~behavior~~behaviour where concentrations are largely independent of discharge variations (Dupas et al., 2016). Also Thompson et al. (2011) stated observational and model-based evidence of an increasing chemostatic response of nitrate with increasing agricultural intensity. ~~It has been argued that this~~This shift in the export regimes is caused by a long-term homogenisation of the nitrate sources in space and/~~-~~or in depth within soils and aquifers (Dupas et al., 2016; Musolff et al., 2017). Long-term N inputs lead to a loading of all flow paths in the catchment ~~are~~ with mobile fractions of N and by that the formation of a hydrological N-legacy (van Meter ~~et al.~~& Basu, 2015) and chemostatic riverine N exports. On the other hand, excessive fertilizer input is linked to the above-mentioned build-up of legacy ~~nitrogen~~N stores in the catchment, changing the export regime from a supply- to a transport-limited chemostatic one (Basu et al., 2010). This legacy is manifested as a biogeochemical legacy in form of increased, less mobile, organic N content within the soil (Worral et al., 2015; van Meter ~~et al.~~& Basu, 2015; van Meter et al., 2017a). This type of legacy buffers biogeochemical variations, so that management measures can only show their effect if the build-up source gets substantially depleted (Basu et al., 2010).

Kommentar [RK13]: Which above one – may be better that we can spell out here --

Depending on the catchment configuration, both forms of legacy – hydrological and biogeochemical – can exist with different shares of the total ~~nitrogen~~N stored in a catchment (van Meter et al., 2017a). However, biogeochemical legacy is hard to distinguish from hydrological legacy when looking at time lags between N-input and output or at catchment scale N-budgets only (van Meter & Basu~~et al.~~, 2015). ~~Here,~~One way to better disentangle the N-legacy types is applying the framework of ~~C-Q~~C–Q relationships as defined ~~in~~ by Jawitz & Mitchell (2011), Musolff et al. (2015) and Musolff et al. (2017)~~. can help to better disentangle N~~N~~ legacy types:~~ In case of a hydrological legacy, strong changes of fertilizer inputs (such as increasing inputs in the initial phase of intensification and decreasing inputs as a consequence of measures) will temporarily increase spatial concentration heterogeneity (e.g. comparing young and old water fractions in the catchment storage), and therefore also shift the export regime to more chemodynamic conditions. On the other hand, a dominant biogeochemical legacy will lead to ~~a~~ sustained concentration homogeneity in the N source zone in the soils and to an insensitivity of the riverine N export regime to fast changes in inputs.

Common approaches to quantify catchment scale N-~~nitrogen~~ budgets ~~(N-budgets)~~ and to characterize legacy or to derive TTs are either based on data-driven ~~top-down approaches~~ (Worral et al., 2015; Dupas et al., 2016) or on ~~on~~ forward modeling (van Meter ~~et al.~~& Basu, 2015; van Meter et al., 2017a) approaches. So far, ~~the~~ data-driven studies focused either solely on N-budgeting and legacy estimation or on TTs. Here we ~~aim at~~conducted a joint~~, unique~~ data-driven assessment of catchment scale N-budget, the potential and characteristics of an ~~nitrogen legacy (~~N-legacy~~)~~ and on the estimation of ~~effective~~ TTs of the riverine exported ~~nitrogen~~N. ~~More specifically, we estimate N-budgets and effective nitrogen TT of a catchment from the same data base.~~ ~~This combination supports the differentiation between biogeochemical and hydrological legacy, both reasons for missed targets in water quality improvement.~~ ~~Furthermore, w~~We utilize the trajectory of agricultural catchments in terms of C–Q relationships, their changes over longer time scales and their potential evolution to a chemostatic export regime ~~to better disentangle the two legacy types~~. ~~This~~The novel combination of the long-term N-budgeting, TT estimation and ~~C-Q~~C–Q trajectory ~~supports~~will help understanding the differentiation between biogeochemical and hydrological legacy, both reasons for missed targets in water quality ~~improvement~~management. ~~With these objectives, we aim to provide a better understanding of nitrogen retention capacity and transport mechanisms as a basis for a discussion of more effective catchment management.~~ This study will address the following research questions:

Kommentar [AM14]: Ref2, No.5

1. How high is the retention potential for N of the studied mesoscale catchment and what are the consequences in terms of a potential build-up of an N-legacy?

2. What are the characteristics of the TT distribution for ~~nitrogen~~N that links change in the diffuse anthropogenic N-inputs to the geosphere and their observable effect in riverine $NO_3$-N ~~nitrate~~ concentrations?
3. What are the characteristics of a long-term trajectory of C–Q relationships? Is there an evolution to a chemostatic export regime that can be linked to a~~n~~ ~~evolving~~ ~~evolution~~ ~~biogeochemical or hydrological N legacies~~~~of a~~ biogeochemical or hydrological N-legacy?

To answer these questions, we used time series of water quality data over four decades, available from a mesoscale German catchment, as well as estimated N-input to the geosphere. We link the N-in~~–~~put and output on annual and intra-annual time scales ~~by~~ through consideration of N-budgeting and the use of ~~effective~~ TT distributions~~ and likewise N-budgeting~~. This input-output assessment uses time series of the Holtemme catchment (~~282~~ 270 km²) with its three nested sub-catchments along a land use gradient from pristine mountainous headwaters to a lower basin with intensive agriculture and associated increases of fertilizer applications. This catchment with its pronounced increase in anthropogenic impacts from up- to downstream is quite typical for many mesoscale catchments in Germany and elsewhere. Moreover, this catchment offers a unique ~~chance~~ possibility to ~~utilize~~ analyze the system response to strong changes in fertilizer usage in East-Germany before and after reunification. Thereby we anticipate that our improved understanding gained through this study in these catchment settings is transferable to ~~other~~ (similar) regions. In comparison to spatially and temporally integrated water quality signals stemming solely from the catchment outlet, the higher spatial resolution with three stations and the unique length of the monitoring period (1970-2016) allow for a more detailed ~~information~~ investigation about the fate of ~~nitrogen~~N ~~in the catchment~~, and consequently findings may ~~favors a more~~provide~~s~~ guidance for an effective ~~river~~ water quality management.

## 2 ~~Material~~ Data and Methods

Kommentar [SE15]: Ref2 No.15

### 2.1 Study area

The Holtemme catchment (~~282~~ 270 km²) is a sub-catchment of the Bode River basin, which is part of the TERENO Harz/Central German Lowland Observatory (Fig. 1). The catchment ~~was selected~~ as part of the TERENO (**TER**restrial **EN**vironmental **O**bservatories) project ~~because of its~~exhibits strong gradients in topography, climate, geology, soils, water quality, land use and level of urbanization (Wollschläger et al., 2017). ~~Furthermore, the region is ranked as highly vulnerable to climate change (Schröter et al., 2005)~~ D~~,~~ue to the low water availability and the risk of summer droughts that might be further exacerbated by a decrease in summer precipitation and increased evaporation with rising temperatures, the region is ranked as highly vulnerable to climate change (Schröter et al., 2005; Samaniego et al., 2018). With these conditions, the catchment is representative for other German and central European regions showing similar vulnerability (Zacharias et al., 2011). The observatory is one of the meteorologically and hydrologically best-instrumented catchments in Germany (Zacharias et al., 2011; Wollschläger et al., 2017), and provides long-term data for many environmental variables including water quantity (e.g. precipitation, discharge) and water quality at various locations.

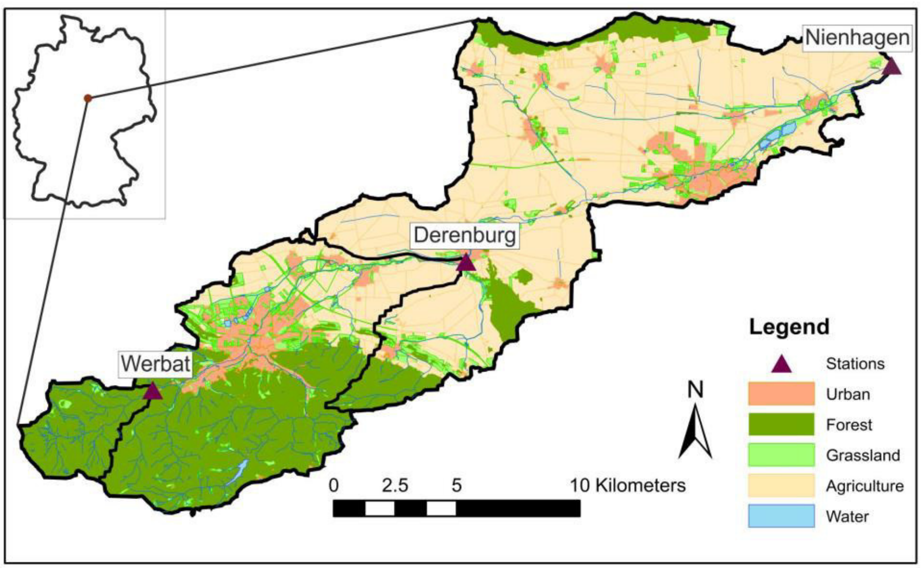
Kommentar [SE16]: Ref1, No.13 & Ref2, No.8

The Holtemme catchment has its spring at 862 m a.s.l. in the Harz Mountains and extends to the Northeast to the Central German Lowlands with an outlet at 85 m a.s.l.. The long-term annual mean precipitation (1951–2015) shows a remarkable decrease from colder and humid climate in the Harz Mountains (1262 mm) down to the warmer and dryer climate of the Central German Lowlands on the leeward side of the mountains (614 mm; Rauthe et al., 2013; Frick et al., 2014). Discharge time series, provided by the State Office of Flood Protection and Water Management (LHW) Saxony-Anhalt show a mean annual discharge at the outlet in Nienhagen of 1.5 m³ $s^{-1}$ (1976–2016) referring to 172 mm $a^{-1}$.

The geology of the catchment is dominated by late Paleozoic rocks in the mountainous upstream part that are largely covered by Mesozoic rocks as well as Tertiary and Quaternary sediments in the lowlands (Frühauf & Schwab, 2008; Schuberth, 2008). Land use of the catchment changes from forests in the pristine, mountainous headwaters to intensive agricultural use in the downstream lowlands (EEA, 2012). According to Corine Land Cover (CLC) from different years (1990, 2000, 2006, 2012), the land use change over the investigated period is negligible. Overall 60 % of the catchment is used by agriculture, while 30 % is covered by forest (EEA, 2012). Urban land use occupies 8 % of the total catchment area (EEA, 2012) with two major towns (Wernigerode, Halberstadt) and several smal~~ler~~l villages. Two wastewater treatment plants (WWTPs) discharge into the river. The town of Wernigerode had its WWTP within its city boundaries until 1995, when a new WWTP was put into operation about 9.1 km downstream in a smaller village, called Silstedt, replacing the old WWTP. The other WWTP in Halberstadt was not relocated but renovated in 2000. Nowadays, the total nitrogen load (TNb) in cleaned water is approximately 67.95 kg $d^{-1}$ (WWTP Silstedt: $NO_3$-N load 55 kg $d^{-1}$~~; 24 % of daily load~~) and 35.09 kg $d^{-1}$ (WWTP Halberstadt: $NO_3$-N load 6.7 kg $d^{-1}$; mean daily loads 2014; ~~13.7 % of daily load;~~ Müller et al., 2018). Referring to the last 5 years of observations, $NO_3$-N load from wastewater made up 17% of the total observed $NO_3$-N flux at the midstream station (see below) and 11% at the downstream station. Despite this point source N-input, major nitrate contribution ~~in recent years was~~is mainly ~~related to~~due to inputs from agricultural land use (Müller et al., 2018), which is predominant in the mid- and downstream part of the catchment (~~Müller et al., 2018~~Fig. 1).

**Kommentar [AM17]:** Ref1, No.20

**Kommentar [AM18]:** Ref2, No.10



Nienhagen
Derenburg
Werbat
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Stations
Urban
Forest
Grassland
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2.5
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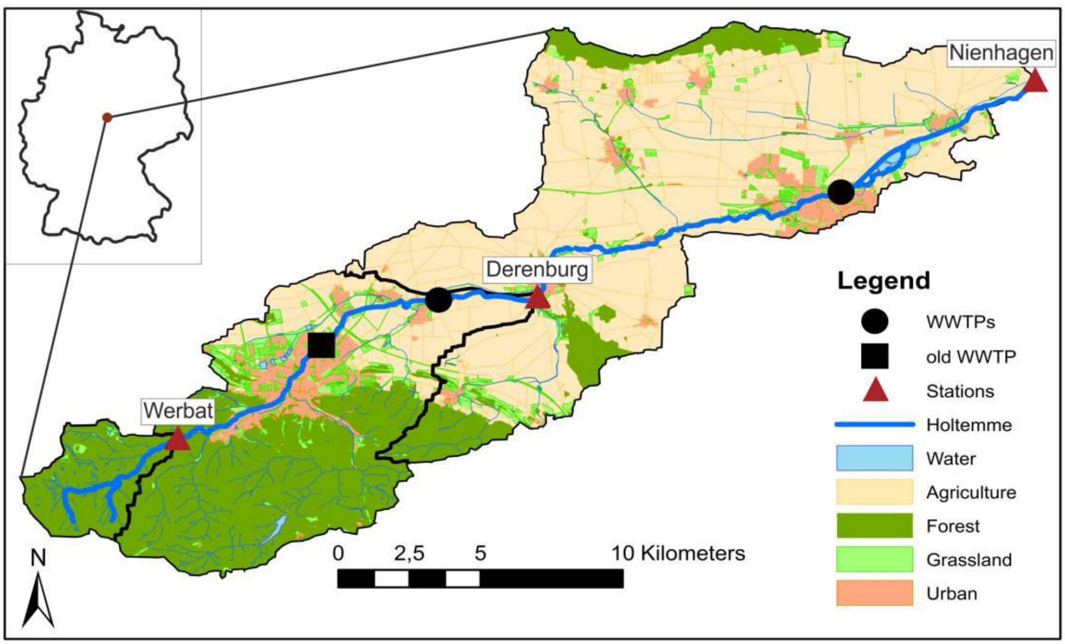



**Figure 1~~11~~: Map of the Holtemme catchment with the selected sampling locations.**

The Holtemme River has a length of 47 km. Along the river, the LHW Saxony-Anhalt maintains long-term monitoring stations, providing the ~~to provide~~ daily mean discharge and the biweekly to monthly water quality measurements covering roughly the last four decades (1970–2016). Three of the water quality stations along the river were selected to represent the characteristic land use and topographic gradient in the catchment. From up- to downstream, the stations are named Werbat, Derenburg and Nienhagen (~~Fig. 1~~Figure 1~~Fig. 1Figure 1~~); and in the following referred to as Upstream, Midstream and Downstream. The pristine headwaters upstream represent the smallest (6~~-~~% of total catchment area) and ~~at~~ the ~~same time~~ steepest area ~~of~~ among the three selected ~~subcatchment~~sub-catchments ~~as it has~~with about a three times higher mean topographic slope than the downstream parts (DGM25; Table1). According to the latest ~~CLC~~ Corine landcover dataset (CLC ~~from~~ 2012; EEA 2012), the land use is characterized by forest only. The larger midstream ~~subcatchment~~sub-catchment that represents one third of the total area is still dominated by forests, but with growing anthropogenic impact due to increasing agricultural land use and the town of Wernigerode. ~~In this subcatchment~~sub-catchment ~~m~~More than half of the agricultural land in the midstream ~~subcatchment~~sub-catchment is artificially drained with open ditches (Midstream: 38 %; Downstream: 82 %) and tube drains (Midstream: 62 %, Downstream: 18 %; LHW, 2011; Table 1; S1.1). The largest ~~subcatchment~~sub-

**Kommentar [SE19]:** Ref2, No.12

catchment (61-%) ~~constituting~~ constitutes the downstream ~~part, is located in the~~ lowlands areas~~. This Central German lowlands a~~, which are predominantly covered by Chernozems (Schuberth, 2008), ~~which are the~~and represents one of the most fertile soils within Germany (Schmidt, 1995). Hence, the agricultural land use in this ~~subcatchment~~sub-catchment is the highest (81%) in comparison to the two upstream ~~subcatchment~~sub-catchments ~~and makes up 81 %~~ (EEA, 2012). ~~Also the second town, Halberstadt, increases the anthropogenic impact to the Holtemme River.~~

~~The time series of the three gauging stations along the Holtemme River cover roughly the last four decades (1970–2016) and represent the N-output of the input-output assessment.~~

**Table 1~~1~~: General information on study area including input/ output datasets. ~~Subcatchment information.~~ n – number of observations, Q - discharge.**

| | Upstream | Midstream | Downstream |
|---|---|---|---|
| n Q | 16 132 | - | 12 114 |
| n nitrate-N ($NO_3$-N) | 646 | 631 | 770 |
| Period of $NO_3$-N time series | 1972–2014 | 1970–2011 | 1976–2016 |
| | | | |
| ~~Subcatchment~~Sub-catchment area (km²) | 15.06 | 88.50 | 165.22 |
| Cumulative catchment area (km²) | 15.06 | 103.60 | 268.80 |
| Stream length (km) | 1.5 | 19.3 | 24.4 |
| Mean topographic slope (°) | 9.82 | 7.52 | 2.55 |
| Mean topo. s~~S~~lope in~~:~~ non-forested area (°) | - | 3.2 | 1.9 |
| | | | |
| Land use (Corine land cover; ~~(~~EEA, 2012) | | | |
| Forest land use (%) | 100 | 56 | 11 |
| Urban land use (%) | - | 17 | 8 |
| Agricultural land use (%) | - | 27 | 81 |
| Fraction of agricultural area artificially drained (%) | ~~-~~- | 59.1 | 20.5 |

### 2.2 Nitrogen input

The main N-sources ~~had to be~~ was quantified over time for ~~the~~ assisting the data-based input-output assessment to ~~answer~~address the three research questions ~~covering~~regarding the ~~retention potential~~N-budgeting, effective TTs and C–Q relationships in the catchment. ~~For Germany there is no consistent data set for N input available that covers different land use types and is sufficiently resolved in time and space. Therefore, we needed to combine a data set solely of agricultural N~~

~~input that already included atmospheric deposition with another dataset containing N deposition rates for the remaining non-agricultural land.~~

~~.~~A recent investigation in the study catchment by Müller et al. (2018) showed that the major nitrate contribution stems from agricultural land use and the associated application of fertilizers. The quantification of this contribution is the N-surplus (also referred to as agricultural surplus) that reflects N-inputs that are in excess of crop and forage needs. ~~.~~For Germany there is no consistent data set available for the N-~~-input~~surplus ~~available~~ that covers all land use types and is sufficiently resolved in time and space. Therefore, we combined ~~a data set for~~the available agricultural N ~~input~~input (including atmospheric deposition) dataset with another dataset ~~stating~~of atmospheric N deposition rates for the non-agricultural land.

Kommentar [SE20]: Ref1, No.14

Kommentar [SE21]: Ref1, No.2

Kommentar [SE22]: Ref1, No.14

The annual agricultural N-input for the Holtemme catchment was calculated using two different data sets of agricultural N-surplus across Germany provided by the University of Gießen (Bach & Frede, 1998; Bach et al., 2011). Surplus data [kg N ha$^{-1}$ a$^{-1}$] were available on the federal state level for 1950–2015 and on the county level for 1995–~~2015~~2015; with an accuracy level of 5% (see Bach & Frede,~~;~~ 1998 for more details). ~~.~~ We used the data from the overlapping time period (1995–2015) to downscale the state level data (state: Saxony-Anhalt) to the county level (county: Harzkreis). Both (the state level and the aggregated county to state level) data sets show high correspondence with a correlation ($R^2$) of 0.85, but they slightly differ in their absolute values (by 6~~-~~% of the mean annual values). The mean offset of 3.85 kg N ha$^{-1}$ a$^{-1}$ was subtracted from the federal state level data to yield the surplus in the county before 1995. ~~Bach & Frede (1998) state an accuracy of the N-surplus estimation of XXX5 %.~~

Kommentar [AM23]: Ref1, No. 1

Both of the above datasets account for the atmospheric deposition, but only on agricultural areas. For other non-agricultural areas (forest and urban landscapes), the N-source stemming from atmospheric deposition was quantified based on datasets from the Meteorological Synthesizing Centre - West (MSC-W) of the European Monitoring and Evaluation Programme (EMEP). The underlying dataset consists of gridded fields of EU-wide wet and dry atmospheric N-depositions from a chemical transport model that assimilates different ~~sources of EU wide~~ observational ~~datasets~~ records on ~~different~~ atmospheric chemicals (e.g. Bartnicki & Benedictow, 2017; Bartnicki & Fagerli, 2006). This dataset is available at annual time-steps since 1995, and at every 5 ~~a~~ years between 1980 and 1995. Data between the 5-~~-a~~years~~-dataset~~ time steps were linearly interpolated to obtain annual estimates of N-deposition between 1980 and 1995. For years prior to 1980, we made use of global gridded estimates of atmospheric N-deposition from the three-dimensional chemistry-transport model (TM3) for the year 1860 (Dentener, 2006; Galloway et al., 2004). In absence of any other information, we performed a linear interpolation of the N-deposition estimates between 1860 and 1980.

To quantify the net N-fluxes to the soil via atmospheric deposition, the terrestrial biological N-fixation had to be subtracted for different non-agricultural land use types. Based on a global inventory of terrestrial biological N-fixation in natural ecosystems, Cleveland et al. (1999) estimated the mean uptake for temperate (mixed, coniferous or deciduous) forests and (tall/medium or short) grassland as 16.04 kg N ha$^{-1}$ a$^{-1}$, and 2.7 kg N ha$^{-1}$ a$^{-1}$, respectively. The remaining atmospheric deposition, after accounting for the above prescribed biological fixation~~, calculated~~ for the different land uses~~-amounts in~~

~~each subcatchment~~, was added to the agricultural N-surplus to achieve the total N-input per area~~ and subcatchment~~. In contrast to the widely applied term net anthropogenic nitrogen input (NANI), we do not account for wastewater fluxes ~~at this point~~in the N-input but rather focus on the diffuse ~~atmospheric deposition, biological N fixation and agricultural input, N pathways~~N-input and connected flow paths where legacy accumulation and time lags between in- and output potentially occur.

### 2.3 Nitrogen output

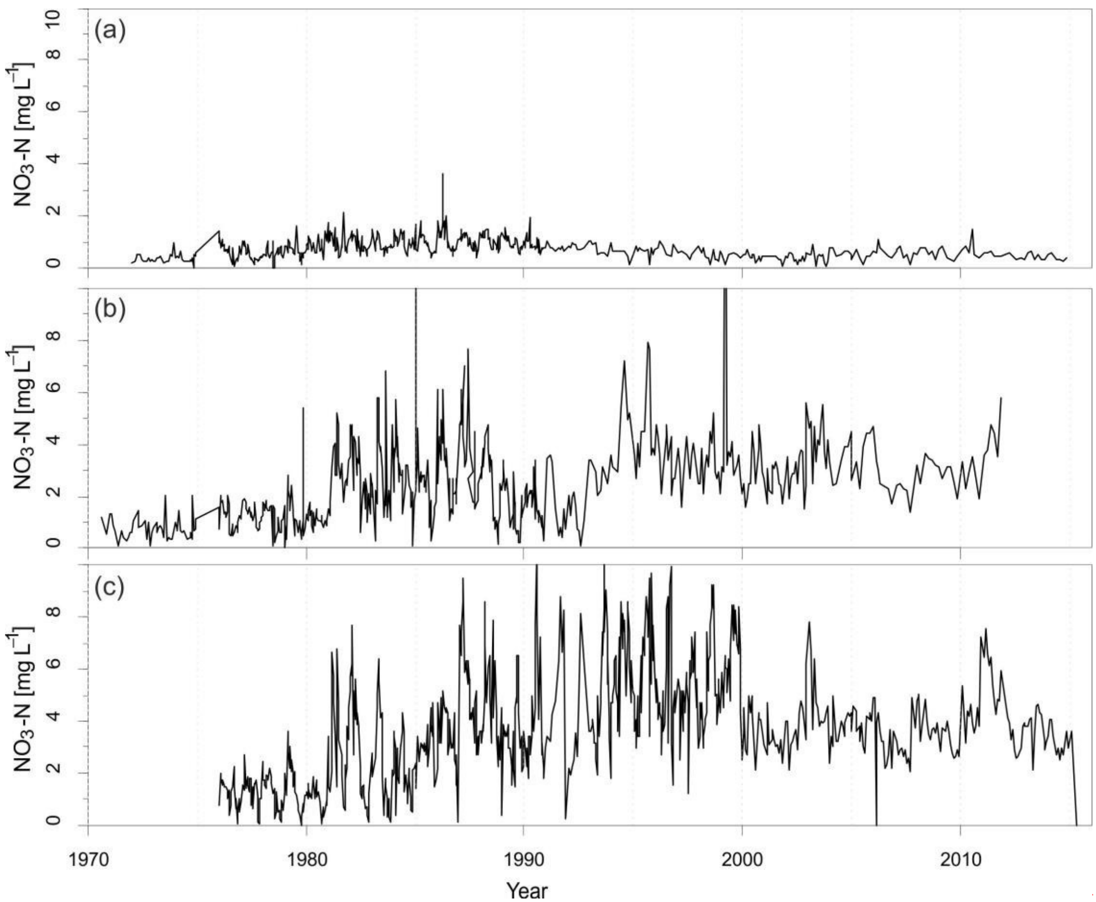
#### 2.3.1 Discharge and water quality time series

Discharge and water quality observations were used to quantify the N load and to characterize the trajectory of $NO_3$-N ~~nitrate~~ concentrations and the ~~C-Q~~C–Q trajectories in the three sub-catchments.

**Kommentar [AM24]:** Ref1 No. 2

The data for water quality (biweekly to monthly) and discharge (daily) from 1970 to 2016 were provided by the LHW, Saxony-Anhalt.

The biweekly to monthly sampling was done at gauging stations defining the three ~~subcatchment~~sub-catchments~~ ($NO_3$-N: Fig. 2; $NH_4$-N: S1.2.1; $NO_2$-N: S1.2.2)~~. The data sets cover a wide range of in-stream chemical constituents including major ions, alkalinity, nutrients and in-situ parameters. As this study only focuses on N-species, we restricted the selection of parameters to nitrate ($NO_3$~~)~~; Fig. 2), nitrite ($NO_2$; ~~)~~ supplement S1.2.2) and ammonium ($NH_4$; ~~)~~ supplement S1.2.1).



(a)
(b)
(c)
NO3-N [mg L-1]
0
2
4
6
8
10
1970
1980
1990
2000
2010
Year

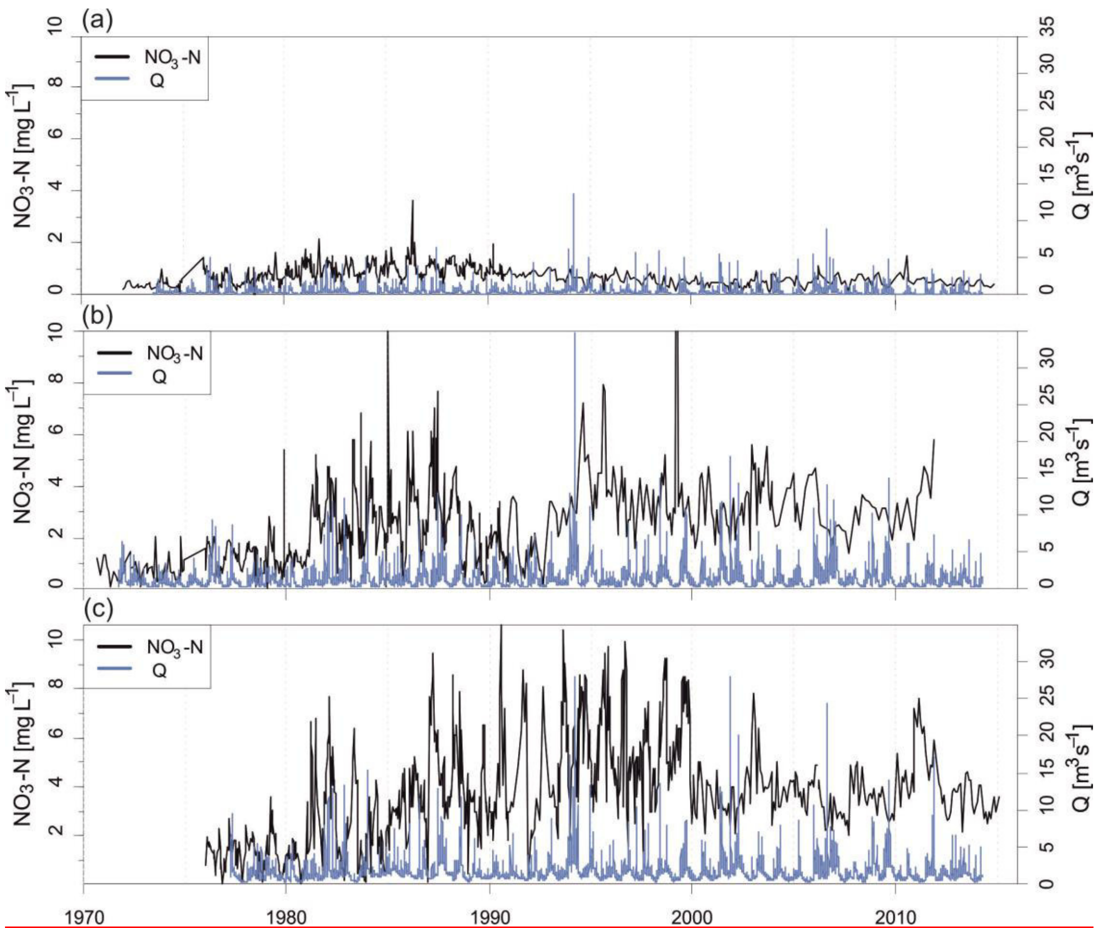
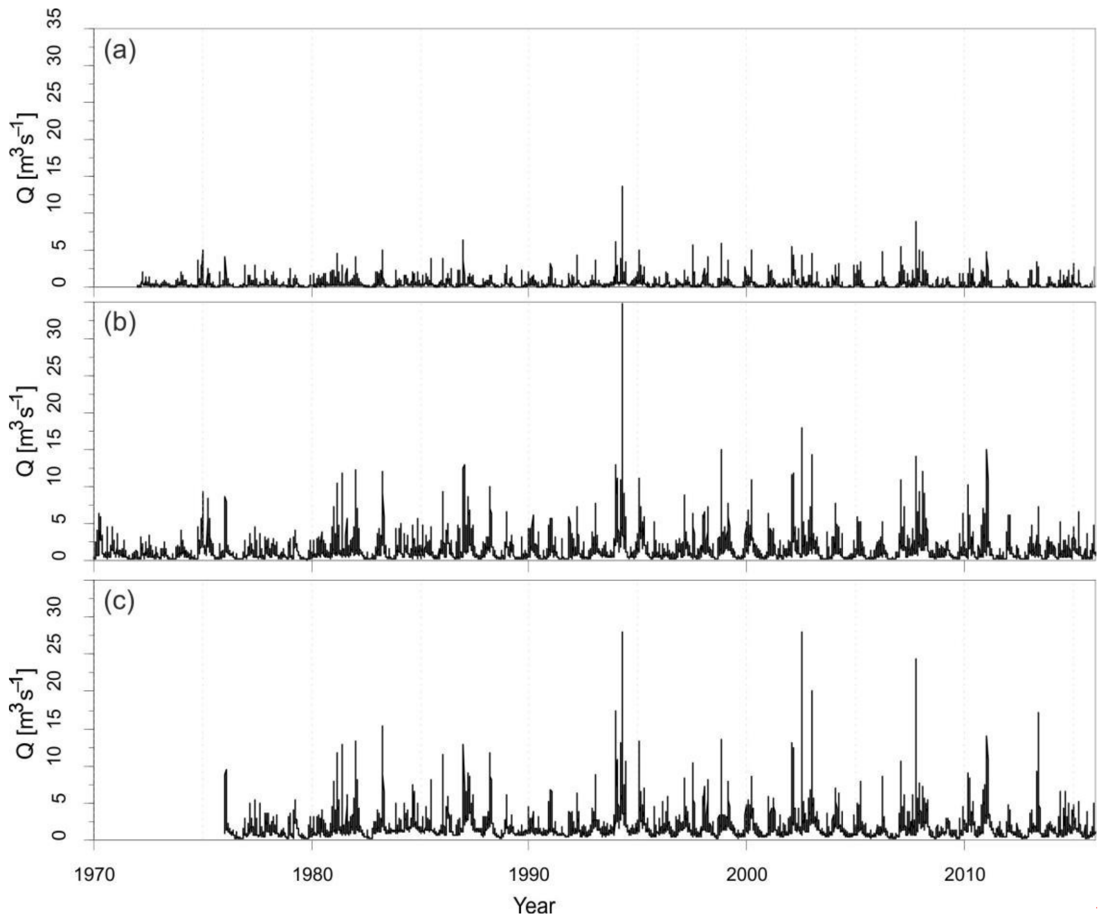



**Figure 2~~2~~2: $NO_3$-N concentration and discharge (Q) time series: Upstream (a), Midstream (b) and Downstream (c).**

Discharge time ~~-~~series at daily time scales were measured at two of the water quality stations (Upstream, Downstream; Fig~~.~~. 2~~3~~). Continuous daily discharge series are required to calculate flow-normalized concentrations (~~S~~see the following ~~S~~section 2.3.2 for more details). To derive the discharge data for the midstream station and to fill measurement gaps at the other stations (2~~-~~% Upstream, 3~~-~~% Downstream), we used simulations from a grid-based distributed mesoscale hydrological model~~,~~ ~~called~~ mHM (Samaniego et al., 2010; Kumar et al., 2013). Daily mean discharge was simulated for the same time frame as the available measured data. We used a model set-up similar to Müller et al. (2016) with robust results capturing the observed variability of discharge in the studied, near-by catchments. We note that the discharge time series ~~is~~ were used as weighting factors in the later analysis of flow-normalized concentrations. Consequently it is more important to capture the temporal dynamics than the absolute values. Nonetheless, we performed a simple bias correction method by applying the regression equation of simulated and measured values to reduce the simulated bias of modelled discharge. After this revision, the simulated discharges could be used to fill the gaps of measured data. The midstream station (Derenburg) for the water quality data is 5.6 km upstream of the next gauging station. Therefore, the nearest station (Mahndorf) with simulated and measured discharge data was used to derive ~~a~~ the bias correction equation that was subsequently applied to correct the simulated discharge data at the Midstream station, assuming the same bias between ~~model~~modelled and ~~measurement~~ observed discharges ~~in~~ at both near-by gauging stations.

**Kommentar [SE25]:** Ref1 Nr.16




~~Figure : Discharge time series: Upstream (a), Midstream (b) and Downstream (c).~~

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### 2.3.2 Weighted regression on time, discharge and season (WRTDS) and waste water correction

The software package "Exploration and Graphics for RivEr Trends" (EGRET) in the R ~~software~~ environment by Hirsch and De~~-~~Cicco~~et al.~~ (201~~0~~9) was used to ~~derive~~estimate daily ~~flow normalized~~ concentrations of $NO_3$-N~~. This tool enables an analysis, based on the long term changes in water quality and streamflow, using the water quality method~~utilizing a "Weighted Regressions on Time, Discharge, and Season" (WRTDS~~; Hirsch & De Cicco, 2010Hirsch et al. 2010~~). The WRTDS method allows the interpolation of irregularly sampled ~~-to increasinge the temporal resolution of~~ concentration

**Kommentar [SE26]:** Ref2 No. 17

**Kommentar [SE27]:** Ref1 No. 17

~~measurements~~ to ~~the~~ a regular series at a daily time-scale using a flexible statistical representation for every day of the discharge record. In brief, a regression model based on the predictors discharge and time (to represent long-term trend and seasonal component) is fitted for each day of the flow record with a flexible weighting of observations based on their time-, seasonal- and discharge “distance” (Hirsch et al., 2010~~Hirsch & De Cicco, 2010~~). ~~Both data sets on a daily resolution (discharge, concentration) were subsequently used to calculate two different time series:~~Results are ~~1. Daily~~daily concentrations and fluxes as well as~~,~~ daily flow-normalized concentrations~~, and 2. Daily, flow-normalized~~ and fluxes. Flow-normalization uses the probability distribution of discharge of the specific day of the year from the entire discharge time series. More specifically, the flow-normalized concentration is the average of the same regression model for a specific day applied to all measured discharge values of the corresponding day of the year. While the non-flow-normalized concentrations are strongly dependent on the discharge, the flow-normalized estimations provide a more unbiased, robust estimate of the concentrations with a focus on changes in concentration and fluxes independent of inter-annual discharge variability (Hirsch et al., 2010~~Hirsch & De Cicco, 2010~~). To account for uncertainty in the regression analysis of annual and seasonal flow-~~-~~normalized concentration (and fluxes), we used the block bootstrap method introduced by Hirsch et al. (2015). We derived the 5th and 95th percentile of annual flow~~-~~-normalized concentration and flux estimates with a block length of 200 days and 10 replicates. The results are utilized to communicate uncertainty in both, the ~~nitrogen~~N- budgeting and the resulting ~~travel time~~TTs estimation.

The study of Müller et al. (2018) indicated ~~a~~ the dominance of ~~nitrogen~~ N from diffuse sources in the Holtemme catchment, but also stressed an impact of wastewater-borne ~~$NO_3$~~ nitrate during low flow periods. ~~Since~~ Because our purpose was to balance and compare~~we aim at balancing and comparing~~ N-input and outputs from diffuse sources only, the provided annual flux of total N from the two WWTPs was therefore used to correct flow-normalized fluxes and concentrations derived from the WRTDS assessment. We argue that the annual wastewater N-flux is robust to correct the flow-normalized concentrations, but it does not allow for the correction of ~~actually~~ measured concentration data at a specific day. Both treatment plants provided snapshot samples of both, $NO_3$-N and total N-fluxes, to derive the fraction of N that is discharged as $NO_3$-N into the stream. This fraction is 19% f~~F~~or the WWTP Halberstadt (384 measurements between January 2014 to July 2016)~~ this fraction is 19 %~~, and 81% for Silstedt (eight measurements from February 2007 to December 2017)~~ 81 %.~~ . We argue that the fraction of N leaving as $NH_4$, $NO_2$ and $N_{org}$ does not interfere with the $NO_3$-N flux in the river due to the limited length and therefore nitrification potential of the Holtemme River impacted by wastewater (see also supplement S 1.2.3). We related the wastewater-borne $NO_3$-N flux to the flow-normalized daily flux of $NO_3$-N from the WRTDS method to get a daily fraction of wastewater $NO_3$-N in the river that we used to correct the flow-normalized concentrations. Note that this correction was applied to the midstream station from 1996 on when the Silstedt treatment plant was taken to operation. In the downstream station, we additionally applied the correction from the Halberstadt treatment plant, renovated in the year 2000. Before that, we assume that waste water-borne N dominantly leaves the treatment plants as $NH_4$-N (see also supplement S1.2.1).

**Kommentar [AM28]:** Ref 1 No. 18

**Kommentar [AM29]:** Ref1 No. 1

**Kommentar [SE30]:** Ref1 No. 18

Based on the daily resolved flow-normalized and wastewater-corrected concentration and flux data, descriptive statistical metrics were calculated on an annual time scale. Seasonal statistics of each year were also calculated for winter (December, January, February), spring (March, April, May), summer (June, July, August) and fall (September, October, November). Note that ~~winter~~ the statistics for the winter season incorporate December values from the calendar year before. Following Musolff et al. (2015, 2017), the ratio of $CV_C/CV_Q$ and the slope (b) of the linear relationship between ln~~-~~(C) and ln(~~-~~Q) ~~-~~were used to characterize the export pattern and the export regimes of $NO_3$-N along the three study catchments. ~~These calculations show the long term trajectory of C-Q relationships and indicate an evolution to a chemostatic export regime linked to evolving biogeochemical or hydrological legacies.~~

### 2.4 Input-output assessment: N-budgeting and effective ~~travel times~~~~TT~~travel times

The input-output assessment is needed to estimate the retention potential for N in the catchment as well as to link the temporal changes in the diffuse anthropogenic N-inputs ~~to the geosphere~~ to ~~their observable effects~~the observed changes in the riverine $NO_3$-N concentrations. The stream concentration of a given solute, e.g. as shown by Kirchner et al. (2000), is assumed at any time as the convolution of the travel time distribution (TTD) and the rainfall concentration throughout the past. This study applies the same principle for the N-input as incoming time series that, when convolved with the TTD, yields the stream concentration time series. We selected a log-normal distribution function (with two parameters,~~;~~ μ and σ) as a convolution transfer function,~~;~~ based on a recent study by Musolff et al. (2017) who successfully applied this form of a transfer function to represent TTs. The two free parameters were obtained through optimization based on minimizing the sum of squared errors between observed and simulated N-exports. The form of selected transfer function is in line with Kirchner et al. (2000) stating that exponential TTDs are unlikely at catchment scale but rather a skewed, long tailed distribution. Note that we used the log-normal distribution as a transfer function between the temporal patterns of input (N-load per area) and flow-normalized concentrations on an annual ~~base~~ time scale only and not as a flux-conservative transfer function. TTDs w~~h~~ere ~~derived~~inferred based on median annual and median seasonal flow-~~-~~normalized concentrations and the corresponding N-input estimates. To account for the uncertainties in the flow -normalized concentration input, we additionally derive TTDs for the confidence bands of the concentrations (5th and 95th percentile) ~~from~~estimated through the bootstrap method (see s~~S~~ection 2.3.2 for more details). Here, we assumed that the width of the confidence bands provided for the annual concentrations also applies ~~for~~to the seasonal concentrations of the same year.

Kommentar [SE31]: Ref.1, No.2

Kommentar [AM32]: Ref. 1, No. 1

## 3 Results

### 3.1 Input assessment

In the period from 1950 to 2015, the Holtemme catchment received a cumulative diffuse N-input of 62,~~.~~335 t~~. From this sum,~~ with ~~-~~the majority of this being ~~part (97 %) can be~~ associated with agriculture related N-applications (97%). Within the period when~~re~~ water quality data were available, the total sum is 51,~~.~~091 t (1970–2015), as well with 97~~-~~% agricultural contribution. The N-input showed a remarkable temporal variability (see Fig. 6~~7~~; purple, dashed line). From 1950 to 1976, the input was characterized by a strong increase (slope of linear increase = 4.2 kg N ha$^{-1}$ a$^{-1}$ per year) with a maximum annual, agricultural input of 132.05 kg N ha$^{-1}$ a$^{-1}$ (1976), which is twenty times the agricultural input ~~from~~ in 1950. After more than 10 ~~a~~ years of high but more stable inputs, the N-surplus dropped dramatically ~~with~~ after the ~~peaceful~~ reunification of Germany and the collapse of the established agricultural structures in East Germany (1989/1990; Gross, 1996). In the time period afterwards (1990–1995), the N-surplus was only one-sixth (20 kg N ha$^{-1}$ a$^{-1}$) of the previous input. After another 8 ~~a~~ years of increased agricultural inputs (1995–2003) of around 50 kg N ha$^{-1}$ a$^{-1}$, the input slowly decreased with a mean slope of -1.3 kg N ha$^{-1}$ a$^{-1}$ per year, but showed distinctive changes in the input between the years.

**Kommentar [SE33]:** Ref2 No.19

The input into the forested catchment upstream with ~~(~~only atmospheric deposition~~)~~ peaked in 1980 and decreased afterwards. ~~All of~~ T~~t~~he annual N-inputs were always below 12 kg N ha$^{-1}$ a$^{-1}$ over the entire period, which is less than one-fifth of the mean agricultural input (60 kg N ha$^{-1}$ a$^{-1}$). Hence, the input to the upstream area was only minor in comparison to the ones further downstream that are dominated by agriculture.

**Kommentar [SE34]:** Ref2 No.20

### 3.2 Output assessment

#### 3.2.1 Discharge time series and WRTDS results on decadal statistics

Discharge was characterized by a strong seasonality throughout the entire data record, which divided the year into a High-Flow-Season (HFS) during winter and spring, accounting for two-thirds of the annual discharge and a Low-Flow-Season (LFS) during summer and fall. ~~Besides this gradient over time, the discharge time series also~~Average discharge in the sub-catchments ~~-~~ ~~reflects the~~is mainly a reflection of a ~~-~~strong spatial precipitation gradient across the study area ~~-~~being on the leeward side of the Harz Mountains ~~(Wollschläger et al., 2017).~~ The upstream ~~subcatchment~~sub-catchment contributed 21 % of the median discharge measured at the downstream station (Table 2). The midstream station, representing the cumulated discharge signal from the up- and midstream ~~subcatchment~~sub-catchments, accounted for 82 % of the median annual discharge at the outlet. Although the upstream ~~subcatchment~~sub-catchment had the highest specific discharge, the major fraction of total discharge (61%) was generated in the midstream ~~subcatchment~~sub-catchment. Also the seasonality in discharge was dominated by this major midstream contribution, especially during high flow conditions. Vice versa, especially during HFSs, the median downstream contribution was ~~<~~less than 10 %, while during low flow periods, the downstream contribution accounted for up to 33 % (summer).

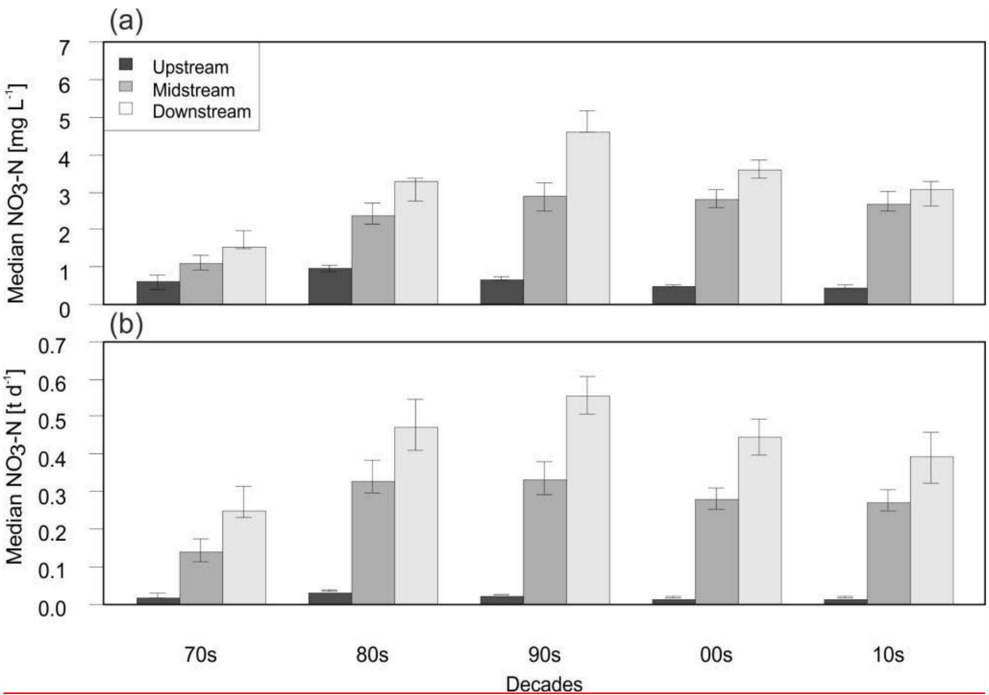
**Table 2~~22~~: Descriptive statistics on discharge at the three observation points. LFS – low flow season (June–November), HFS – high flow season (December–May).**

| | Upstream | Midstream | Downstream |
|---|---|---|---|
| Median discharge (m³ s$^{-1}$) | 0.23 | 0.9 | 1.1 |
| Mean specific discharge (mm a$^{-1}$) | 768 | 411 | 178 |

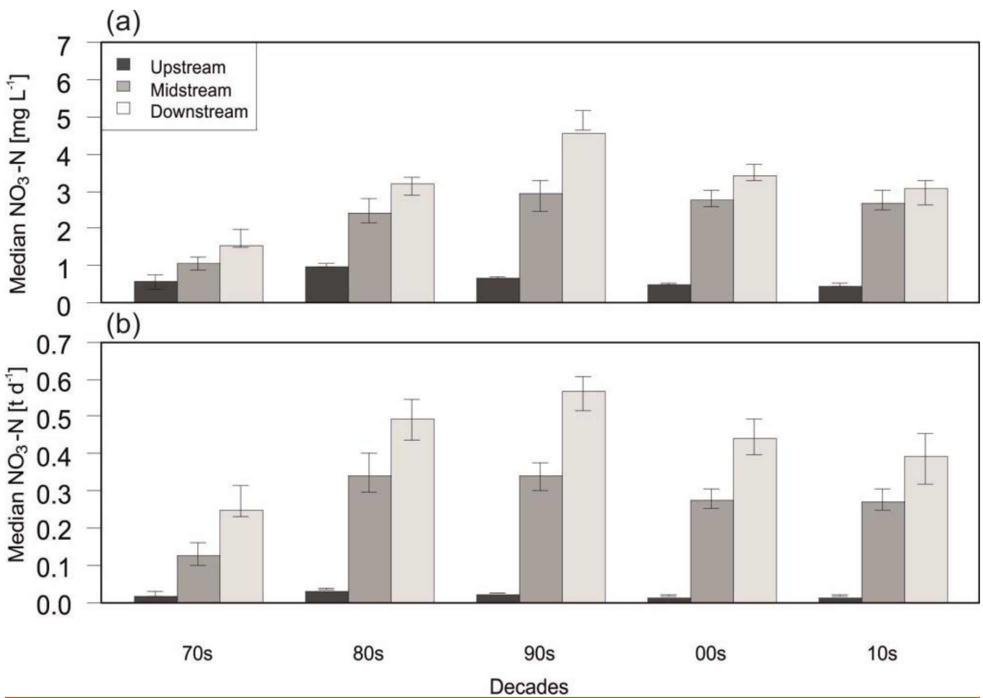
| | | | |
|---|---|---|---|
| LFS ~~subcatchment~~sub-catchment contribution (%) | 17 | 53~~70~~ | ~~100~~30 |
| HFS ~~subcatchment~~sub-catchment contribution (%) | 21 | 69~~90~~ | 10~~0~~ |

Kommentar [SE35]: Ref2, No.20

The flow-normalized $NO_3$-N concentrations in each ~~subcatchment~~sub-catchment showed strong differences in their ~~general~~ overall levels and temporal patterns over the four decades (Fig. 3~~4~~a, see also Fig. 2). The lowest decadal concentration changes and the earliest decrease in concentrations were found in the pristine catchment. Median upstream concentrations were highest in the 80s (1987), with a reduction of the concentrations to about one half in the latter decades~~ afterwards~~. Over the entire period, the median upstream concentrations were smaller than 1 mg $L^{-1}$, so that the described changes are small compared to the $NO_3$-N dynamics of the more downstream stations. High changes over time were observed in the two downstream stations with a tripling of concentrations between the 1970s and 1990s, when maximum concentrations were reached. While median concentrations downstream decreased slightly after this peak (1995/1996), the ones midstream (peak: 1998) stayed constantly high. At the end of the observation period, at the outlet (Downstream), the median annual concentrations did not decrease below 3 mg $L^{-1}$ $NO_3$-N, a level that was exceeded after the 1970s. The differences in $NO_3$-N concentrations between the pristine upstream and the downstream station evolved from an increase by a factor of 3 in the 1970s to a factor of 7 after the 1980s.



(a)
Median NO3-N [mg L-1]
Upstream
Midstream
Downstream
(b)
Median NO3-N [t d-1]
70s
80s
90s
00s
10s
Decades


(a)
Upstream
Midstream
Downstream
Median $NO_3$-N [mg $L^{-1}$]
(b)
Median $NO_3$-N [t $d^{-1}$]
70s
80s
90s
00s
10s
Decades

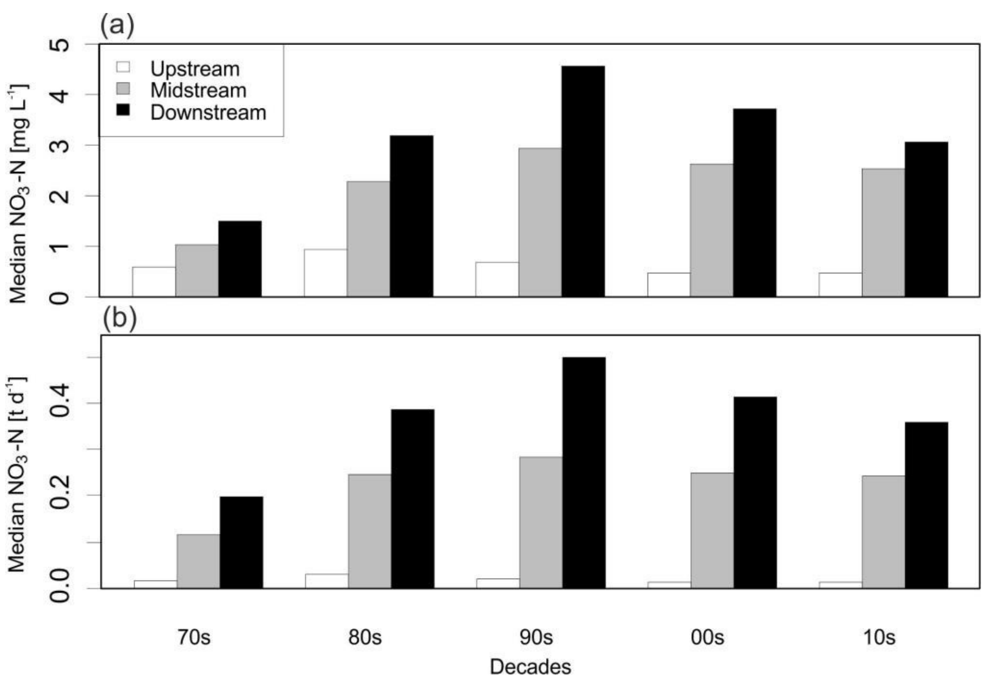



**Figure 3~~34~~: Flow-normalized median $NO_3$-N concentration (a) and $NO_3$-N loads (b) for each decade of the time series and the three stations. Whiskers refer to the $5^{th}$ and $95^{th}$ percentiles of ~~in~~ the WRTDS estimations.**

Kommentar [AM36]: Ref. 1, No. 1

Calculated loads (Fig. 3~~4~~b) also showed a drastic change between the beginning and the end of the time-~~-~~series. The daily upstream load contribution was below 10~~-~~% of the total annual export at the downstream station in all decades and then the estimates decreased from 9~~-~~% (1970s) to 4~~-~~% (2010s). The median daily load between 1970s and 1990s tripled midstream (0.1 t d$^{-1}$ to 0.3 t d$^{-1}$) and more than doubled downstream (0.2 t d$^{-1}$ to 0.5 t d$^{-1}$). In the 1990s, the Holtemme River exported on average more than 0.5 t d$^{-1}$ of $NO_3$-N, which, related to the agricultural area in the catchment, translates into more than 3.1 kg N d$^{-1}$ km$^{-2}$ (maximum of ~~,~~13.4 kg N ha$^{-1}$ a$^{-1}$ in~~,~~ 1995).

### 3.3 Input-Output-balance: N-budget

~~Besides the statistical evaluation of the time series itself, the~~We jointly evaluated the estimated N-inputs ~~were associatedwith~~and the exported $NO_3$-N loads to enable an input-output-~~assessment~~balance. ~~The estimated N-inputs were associated with the exported loads of the subcatchment~~sub-catchment ~~besides the statistical evaluation of the time series.~~ This ~~connection~~ comparison on the one hand allowed for an estimation of the catchment's retention potential~~ with a discussion on potentially accumulated biogeochemical and hydrological legacy~~, and on the other hand ~~it~~ enabled us to ~~predict~~ estimate future exportable loads.

Kommentar [SE37]: Ref.2, No.21

Kommentar [SE38]: Ref1, No.21

**Table 3: ~~Overview about derived n~~Nitrogen retention potentials derived for the midstream and downstream ~~subcatchment~~sub-catchment based on flow-normalized fluxes. Numbers in brackets refer to the $5^{th}$ and $95^{th}$ percentiles of the WRTDS flux estimation.**

| | Midstream | Downstream |
|---|---|---|
| Retention cumulative (%) | 46 (38–53)<br>(Up + Midstream) | 85 (82–86)<br>(Up + Mid + Downstream) |
| Retention ~~subcatchment~~sub-catchment (%) | 48 (39–54) | 94 (93–94) |
| Retention/Year (N kg $a^{-1}$) | 86 282 (70 462–98 513) | 910 349 (90 6629–91 8200) |
| Retention/Area (N kg $a^{-1}$ $ha^{-1}$) | 9.75 (7.96–11.10) | 55.10 (54.87–55.57) |

The load stemming from the most upstream, pristine catchment accounted for less than ~~<~~10 % of the exported load at the outlet. To focus on the anthropogenic impacts ~~on catchments~~, the data from the upstream station are not discussed on its own in the following. At the midstream station, a total sum of input of 7 653 t, compared to 4 109 t of exported $NO_3$-N, for the overlapping time period of in- and output was analyzed (1970–2011). ~~Hence, t~~The midstream catchment hence received 48 % (Table 3) more N mass than it exported at the same time. Note that the exported N is not necessarily the N applied in the same period due to the temporal offset as discussed later in detail. With the assumption that 97 % of the diffuse input resulted from agriculture, the catchment exported 1 545 kg N $ha^{-1}$ (1 350–1 771 kg N $ha^{-1}$) from agricultural areas. The cumulated N-input from the entire catchment (measured downstream) from 1976 to 2015 (overlapping time of in- and output) was 42 758 t, while the riverine export in the same time was only 15 % (6 kg N $ha^{-1}$ $a^{-1}$; 14–18 %) implying an agricultural export of 397 kg N $ha^{-1}$ (353–454 kg N $ha^{-1}$; Fig. 4). This mass discrepancy between in- and output translates into a retention rate in the entire Holtemme catchment of 85 % (82–86 %). ~~The missing N is either removed via denitrification or is still being stored within the terrestrial system in the soil as biogeochemical legacy, or in soil water and groundwater as hydrological legacy.~~ In relation to the entire ~~subcatchment~~sub-catchment area (not only agricultural land use), the median annual retention rate of $NO_3$-N was around 10 kg N $ha^{-1}$ $a^{-1}$ (8–11 kg N $ha^{-1}$ $a^{-1}$) in the midstream ~~subcatchment~~sub-catchment and 55 kg N $ha^{-1}$ $a^{-1}$ (55–56 kg N $ha^{-1}$ $a^{-1}$) in the flatter and more intensively cultivated downstream ~~subcatchment~~sub-catchment.

**Kommentar [AM39]:** Ref2, No. 22

~~**Table : Overview about derived nitrogen** retention potentials derived for the midstream and downstream subcatchment~~sub-catchment ~~based on flow normalized fluxes. Numbers in brackets refer to the $5^{th}$ and $95^{th}$ percentiles of the WRTDS flux estimation.~~

| | ~~Midstream~~ | ~~Downstream~~ |
|---|---|---|
| ~~Retention cumulative (%)~~ | ~~46 (38-53)~~<br>~~(Up + Midstream)~~ | ~~85 (82-86)~~<br>~~(Up + Mid + Downstream)~~ |

| | | |
|---|---|---|
| ~~Retention subcatchment~~sub-catchment ~~(%)~~ | ~~48 (39-54)~~ | ~~94 (93-94)~~ |
| ~~Retention/Year (N kg a$^{-1}$)~~ | ~~86,282 (70462-98513)~~ | ~~910,349 (906629-918200)~~ |
| ~~Retention/Area (N kg a$^{-1}$ ha$^{-2}$)~~ | ~~9.75 (7.96-11.10)~~ | ~~55.10 (54.87-55.57)~~ |

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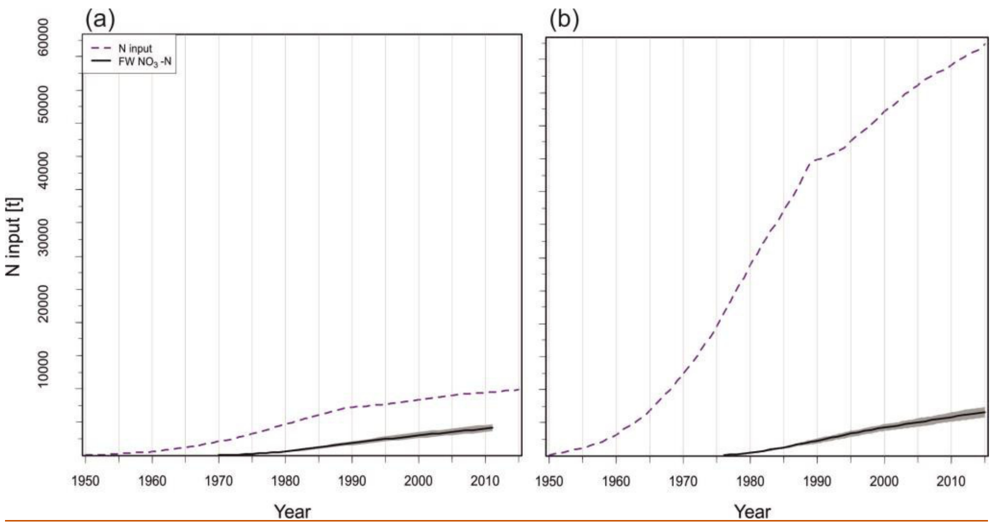
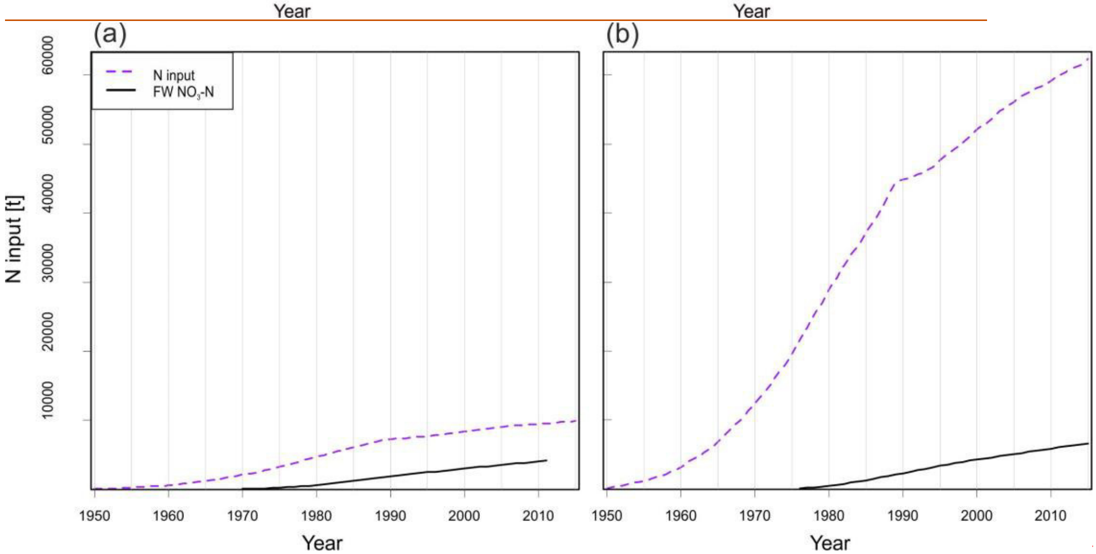
~~The load stemming from the most upstream, pristine catchment accounted for <10 % of the exported load at the outlet. To focus on the anthropogenic impacts on catchments, the data from the upstream station are not discussed on its own in the following. At the midstream station, a total sum of input of 7 653 t resulted compared toin 4 109 t of exported NO$_3$-N for the overlapping time period of in- and output (1970–2011). at the same time. Note thatexportednecessarily the N in the same perioddiscussed later.Hence, 46 % (Table 3) of the applied N was exported in this period by the Holtemme River. With the assumption that 97 % of the diffuse input resulted from agriculture, the catchment exported 1 545 kg N ha$^{-1}$ from agricultural areas. The cumulated N input from the entire catchment (measured downstream) from 1976 to 2015 (overlapping in- and output) was 42 758 t, while the riverine export in the same time was only 15 % implying an agricultural export of 397 kg N ha$^{-1}$ (Fig. 5). This mass discrepancy between in- and output translates into a retention rate in the entire Holtemme catchment of 85 %. The missing N is either removed via denitrification or is still being stored within the terrestrial system in the soil as biogeochemical legacy, or in soil water and groundwater as hydrological legacy. In relation to the entire subcatchment~~sub-catchment ~~area (not only agricultural land use), the average annual retention rate of NO$_3$-N was 10 kg N ha$^{-1}$ a$^{-1}$ in the midstream subcatchment~~sub-catchment ~~and 55 kg N ha$^{-1}$ a$^{-1}$ in the flatter and more intensively cultivated downstream subcatchment~~sub-catchment~~.~~


(a)
(b)
N input
FW $NO_3$-N
N input [t]
Year
10000
20000
30000
40000
50000
60000
1950
1960
1970
1980
1990
2000
2010


(a)
(b)
N input
FW $NO_3$-N
N input [t]
Year
10000
20000
30000
40000
50000
60000
1950
1960
1970
1980
1990
2000
2010

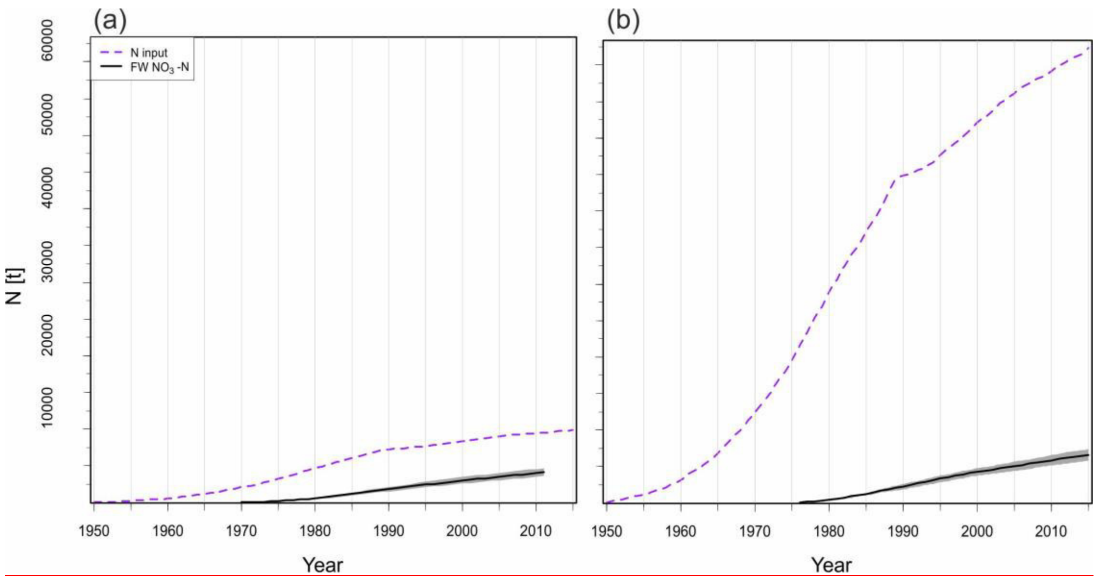


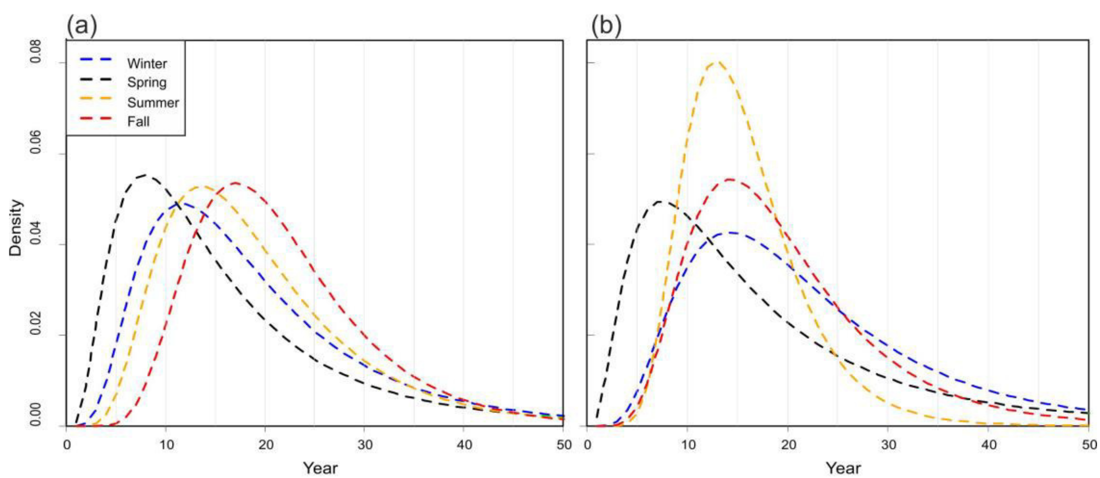

**Figure 44~~5~~: Cumulative annual diffuse N-inputs to the catchment and measured cumulative $NO_3$-N exported load over time for Midstream (a) and Downstream (b). Shaded grey confidence band refer to the 5$^{th}$ and 95$^{th}$ percentile of the WRTDS flux estimation.**

### 3.4 Effective ~~travel times~~TTs of N

We approximated the effective TTs for all seasonal $NO_3$-N concentration trajectories at the midstream and downstream stations by fitting the log-normal TTDs ~~With the fitted log-normal distribution for all seasonal concentration trajectories at the midstream and downstream stations, we were able to approximate the effective TTDs of $NO_3$-N through the catchments~~ (Fig. 5~~6~~; Table 4). Note that the upstream station was not used ~~for this approach~~here ~~as no sufficiently~~due to the lack of a temporally resolved input ~~signal~~ data on the atmospheric N deposition ~~(linear input increase between 1950 and 1979) was available~~(estimated ~~a~~ linear input increase between 1950 and 1979). In general, the optimized distributions were able to sufficiently capture the time lag and smoothing between the input and output concentrations ($R^2 \geq 0.$~~83~~77; see also S2.1~~;~~ S2.2). Systematic differences between stations and seasons can be observed, best represented by the mode of the distributions (peak TT). The average deviation ~~of~~between the best and worst case estimation of the fitted TTDs from their respective average value was only 6~~.0~~ % with respect to the mode of the distributions (Table 4).

**Table 444: Best fit parameters of the log-normal ~~effective~~ ~~travel time distribution~~TTDs ~~of~~ for the N-input and output responses.~~N~~. Parameters in brackets are derived by using the $5^{th}$ and $95^{th}$ percentiles of the ~~WRTDS~~bootstrapped flow ~~weighted~~normalized concentration ~~estimation~~estimates.**

| | Parameter | All seasons | Winter | Spring | Summer | Fall |
|---|---|---|---|---|---|---|
| Midstream | μ | 2.8 (2.8–2.9) | 2.8 (2.8–2.8) | 2.6 (2.6–2.6) | 2.8 (2.8–2.9) | 3.0 (3.0–3.1) |
| | σ | 0.5 (0.5–0.6) | 0.6 (0.6–0.6) | 0.7 (0.7–0.8) | 0.5 (0.5–0.5) | 0.4 (0.4–0.5) |
| | Mode [a] | 12.5 (11.7–13.2) | 11.6 (11.0–12.1) | 7.7 (7.3–7.6) | 13.6 (12.4–14.6) | 17.1 (15.4–18.9) |
| | $R^2$ | 0.91 (0.86–0.90) | 0.86 (0.77–0.84) | 0.87 (0.78–0.85) | 0.93 (0.90–0.92) | 0.86 (0.84–0.84) |
| Downstream | μ | 2.8 (2.8–2.9) | 3.0 (3.0–3.0) | 2.6 (2.7–2.7) | 2.7 (2.7–2.7) | 2.9 (2.9–2.9) |
| | σ | 0.6 (0.6–0.6) | 0.6 (0.5–0.6) | 0.8 (0.7–0.8) | 0.4 (0.3–0.4) | 0.5 (0.5–0.5) |
| | Mode [a] | 11.8 (11.8–12.7) | 14.3 (14.0–15.6) | 7.4 (8.0–8.4) | 12.7 (12.4–13.3) | 14.2 (13.8–14.7) |
| | $R^2$ | 0.96 (0.92–0.95) | 0.90 (0.81–0.90) | 0.83 (0.83–0.92) | 0.93 (0.88–0.91) | 0.86 (0.78–0.82) |

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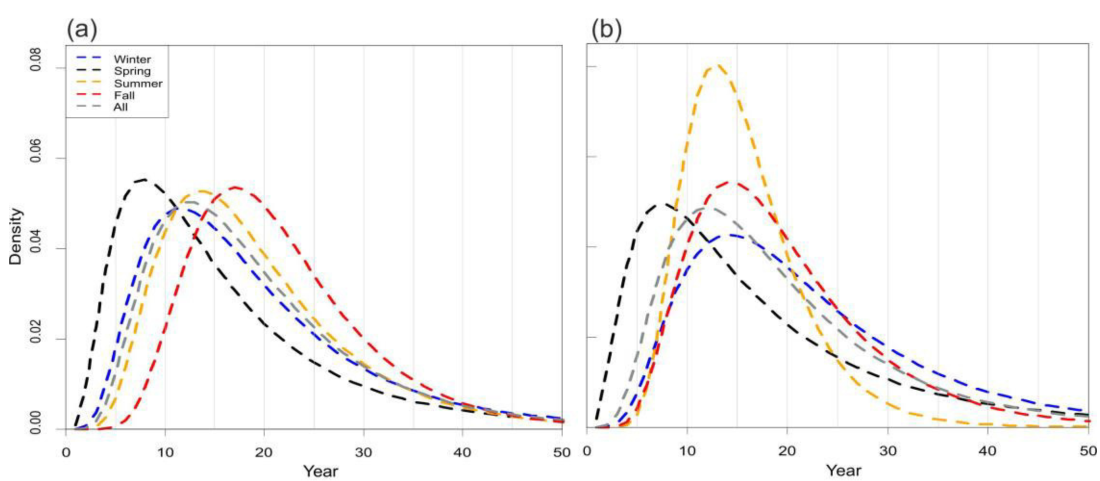


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**Figure ~~5~~56: Seasonal variation in the f~~F~~itted log-normal distributions of effective ~~travel times~~TTs ~~of N~~travel times between N-input and output ~~behaviour~~responses for Midstream (a) and Downstream (b).**

The TTs for all seasons taken together were almost identical for the mid- and downstream stations. However, the comparison of the TTD modes for the different seasons Midstream showed distinctly differing peak TTs between 8 years~~a~~ (spring) and 17 ~~a~~ years (fall), which represented more than a doubling of the peak TT. Fastest times appeared in the HFSs while modes of the TTDs appeared longer in the LFSs. Note that the shape factor σ of the effective TTs also changed systematically: The

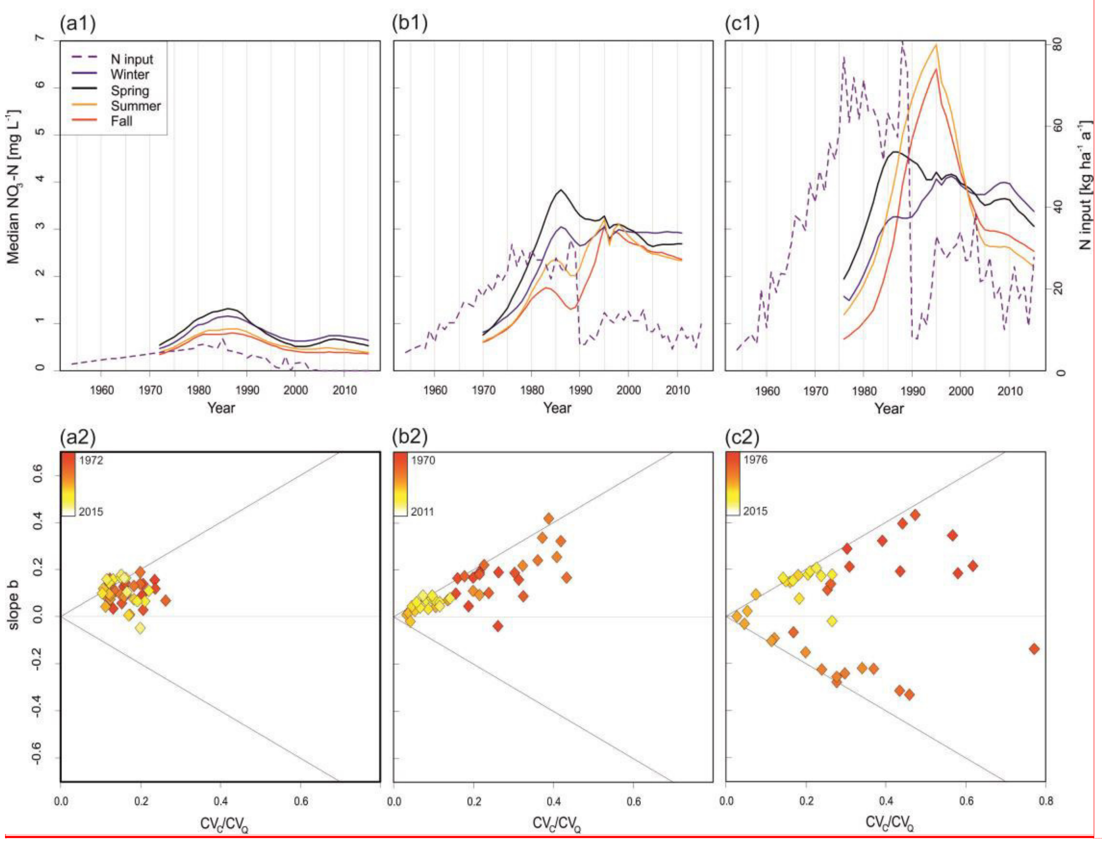
HFs spring and winter exhibited generally higher shape factors than those of the LFSs. This refers to a change in the ~~Midstream~~ coefficient of variation of the distributions in Midstream from 0.8 in spring to 0.4 in fall.

The modes of the fitted functions for the ~~-~~d~~D~~ownstream station during the HFSs (8 ~~a~~ years in spring, 14 years~~a~~ in winter) were almost identical to the ones at the midstream station. Conversely, fall exhibited shorter TTs for the downstream station than for the midstream station. The mode of the TTs ranged between 8 years~~a~~ (spring) and 14 ~~a~~ years (winter, fall). ~~Also~~ T~~t~~he shape factors ~~downstream~~ of the fitted TTDs also ranged between 0.8 (spring) and 0.4 (summer) for the downstream ~~region~~station. In summary, HFSs in both ~~subcatchment~~sub-catchments had quite similar TTDs, whereas the LFSs showed distinct differences in their peak time.

### 3.5 Seasonal $NO_3$-N ~~nitrate~~ concentrations and C–Q relationships over time

As described above, the Holtemme catchment showed a pronounced seasonality in discharge conditions, producing ~~a~~ the HFS in December–May (winter + spring) and the LFS in June–November (summer + fall). Therefore, changes in the seasonal concentrations of $NO_3$-N ~~can also be associated with changes in the annual~~will also reflect in the annual C–Q relationship.~~–~~Analyzing changing seasonal dynamics will provide a deeper insight into N-trajectories in the Holtemme catchment.

~~In addition to the described changes in the N-output on annual time scales, also changing seasonal dynamics were quite common in the data record and can provide more detailed information about N trajectories in in the Holtemme study subcatchments.~~

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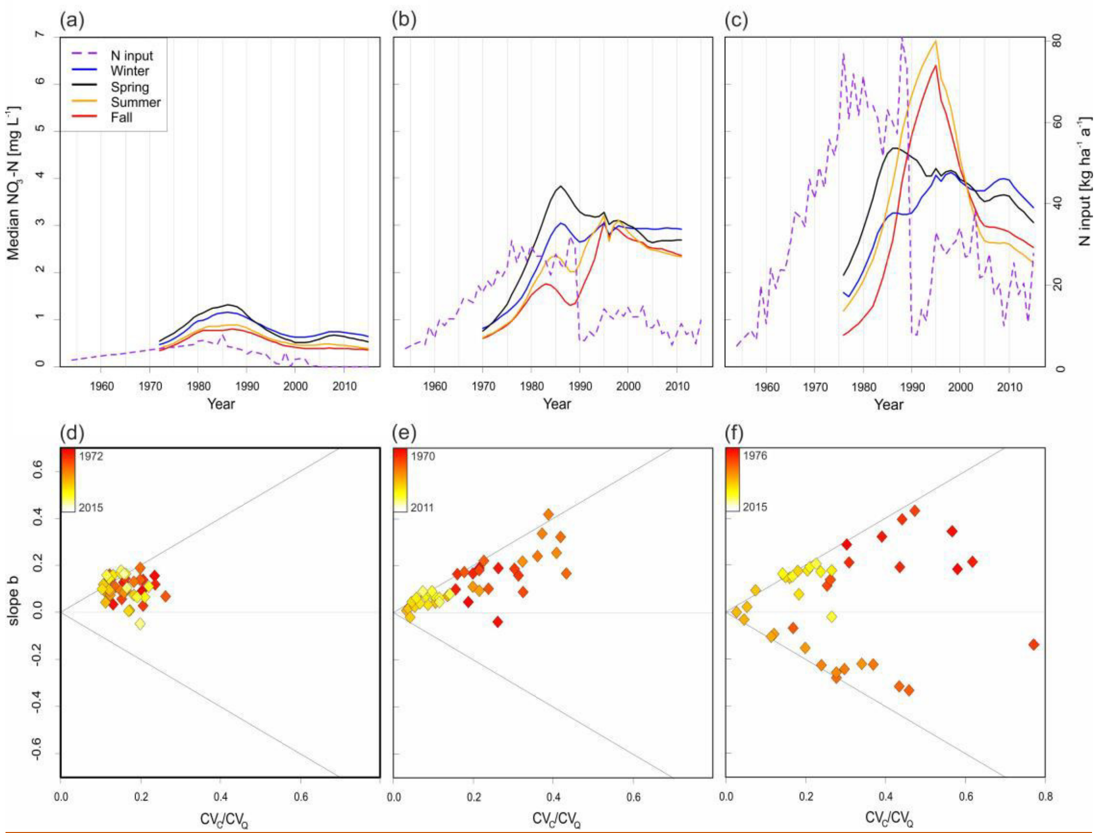


**Figure 66~~7~~: Annual N-input (referred to the whole catchment, 2nd y-axis) to the catchment and measured median $NO_3$-N concentrations in the stream (1st y-axis) over time at three different locations: ~~-~~Upstream (~~a1,a2~~a, d), Midstream (~~b1,b2~~b, e), Downstream (~~c1,c2~~c, f). Lower panels show p~~P~~lots of slope b vs. $CV_C/CV_Q$ for $NO_3$-N for the three ~~subcatchment~~sub-catchments following the classification scheme provided in Musolff et al. (2015). X-axis gives the coefficient of variation of concentrations (C)~~C~~ relative to the coefficient of variation of ~~Q~~discharge (Q). Y-axis gives the slope b of the linear ln (C)–ln (Q) -relationship. Colours indicate the temporal ~~progression~~ evolution from 1970–2016 starting from red to yellow. ~~Upstream (a2), Midstream (b2), Downstream (c2).~~**

In the pristine upstream catchment, no temporal changes in the seasonal differences of riverine $NO_3$-N concentrations could be found (Fig. 6a~~1~~). Also the C–Q relationship (Fig. 6d~~a2~~) showed a steady pattern (moderate accretion~~, all diamonds~~) with highest concentrations in the HFSs i.e. winter and spring. The ratio of $CV_C/CV_Q$ indicates a chemostatic export regime and changed only marginally (amplitude of 0.2) over time.

At the midstream station (Fig. 6b~~1~~), the early 1970s showed ~~the same seasonality~~an export pattern with highest concentration during HFSs ~~as~~similar to the upstream catchment, but with a general increase of ~~all seasonal~~ concentrations from 1970–

1995. During the 1980s, the increase of concentrations in the HFS was ~~steeper/~~faster than in the LFS, which changed the ~~seasonality~~~~C-Q~~ C–Q pattern to a strongly positive ~~pattern~~one ($b_{max}$=0.42, 1987; red to orange ~~diamonds~~symbols in Fig. 6~~7~~e) ~~between C and Q (Fig. b2)~~. This development ~~in the 80s~~ was characterized by a tripling of intra-annual amplitudes ($C_{spring}$ – $C_{fall}$) of up to 2.4 mg L$^{-1}$ (1987)~~, which was a tripling within the years~~. With a lag of around 10 years~~a~~, in the 1990s, also the LFSs ~~showed~~exhibit a strong~~ly~~ increase~~d~~ in concentrations ($c_{max}$= 3.1 mg L$^{-1}$, 1998, Fig. 6b~~1~~). The midstream concentration time series shows bimodality. The C–Q relationships (Fig. 6b2) ~~showed a trisection~~ evolv~~ing~~ed from an intensifying accretion pattern in the 1970s and 1980s (red to orange ~~diamonds~~symbols Fig. 6~~7~~e) to a constant pattern between C and Q in the 1990s and afterwards (yellow ~~diamonds~~symbols). The $CV_C/CV_Q$ increased during the 19~~first decade~~70s and decreased afterwards strongly by 0.4 between 1984 and 1995, showing a trajectory starting from a more chemostatic to a ~~more~~ chemodynamic, and then ~~-~~back to a chemostatic export regime.

At the downstream station (Fig. 6c~~1~~) the concentrations ~~over time~~ in the HFSs ~~proceeded like observed at~~were found to be comparable to the ones observed at the midstream station. As seen at Midstream, the N-concentrations ~~during~~~~of~~ during the LFSs peaked with a delay compared to those noticed ~~for~~of the HFSs. ~~delayed.~~ The resulting intra-annual amplitude ~~in the 80s~~ showed a maximum of 2.4 mg L$^{-1}$ in the 1980s (1983/84), with ~~strongly~~ strongly positive C–Q patterns ($b_{max}$= 0.4, 1985; red ~~diamonds~~symbols in Fig. 6~~c2~~f). ~~As seen Midstream, concentrations during LFSs peaked delayed.~~ ~~Deviating from~~In contrast to the bimodal concentration trends in the mid- and downstream HFSs, the LFSs downstream showed an unimodal pattern peaking ~~in~~around 1995/96 with concentrations above 6 mg L$^{-1}$ $NO_3$-N ($c_{max}$=6.9 mg L$^{-1}$). ~~Such an increase in concentrations in~~In the 1990s, the concentrations in the LFSs ~~above~~were higher than ~~the concentrations~~ those noticed in the HFSs, cause~~d~~ing a switch to a dilution C–Q pattern~~s~~ ~~in the 90s~~ (orange ~~diamonds~~symbols, Fig. 6~~7~~f). ~~This unimodal concentration trajectory in its shape and amplitude in the LFSs is unique at the downstream station and cannot be found in the other stations. Therefore, it can be stated that the seasonality did change with time, but as well as over space.~~ Due to the strong decline of ~~low flow~~LFS concentrations after 1995 (Fig. 6~~7c1~~), the dilution pattern evolved to a constant C–Q pattern (yellow ~~diamonds~~symbols, Fig. 6~~7~~f) from the 2000s onward. After an initial phase with chemostatic conditions (1970s~~??~~), the $CV_C/CV_Q$ strongly increased to a chemodynamic export regime in the 1980s (max. $CV_C/CV_Q$ ~~=~~ = 0.8 in 1984). Later on~~The~~ $CV_C/CV_Q$ declined by 0.7 between 1984 ~~(max. $CV_C/CV_Q$)~~ and 200~~3~~1 (min. $CV_C/CV_Q$ ~~=~~ = 0.03~~) evolving back to a chemostatic~~), which indicated the C-Q trajector~~ie~~y is coming back to a chemostatic~~,~~ export nitrate regime.

~~Despite the differences in concentrations, the trajectory of concentrations between Midstream and Downstream (bimodal vs. unimodal), as well as the overall pattern in the C–Q relationship proceeding from accretion pattern to constant C–Q relationships were the same in both agriculturally used subcatchment~~sub-catchments ~~(Fig. 7b2–c2), while the pristine catchment showed no changes of the intra annual seasonality. However, at the downstream station, an additional dilution pattern (orange diamonds in Fig. 7c2) was observed for several years. In both managed subcatchment~~sub-catchments~~, the temporal concentration trajectory was accompanied by a dominantly decreasing $CV_C/CV_Q$ ratio evolving from chemodynamic to chemostatic behavior.~~

**Kommentar [SE41]:** Ref2 No.27

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~~In the pristine upstream catchment, no changes in the seasonal differences of riverine $NO_3$-N concentrations could be found (Fig. 7a1). The C–Q relationship showed a steady accretion pattern with highest concentrations in the HFSs winter and spring. The ratio of $CV_C/CV_Q$ changed only marginally (amplitude of 0.2) over time.~~

~~At the midstream station (Fig. 7b2), the early 70s showed the same seasonality as in the upstream catchment, but with a general increase of concentrations from 1970-1995. During the 80s, the increase of concentrations in the HFS was steeper/faster than in the LFS, which changed the seasonality to a strongly positive pattern ($b_{max}$=0.42, 1987) between C and Q. This development in the 80s was characterized by intra-annual amplitudes ($C_{spring}$ — $C_{fall}$) of up to 2.4 mg $L^{-1}$ (1987), which was a tripling within the years. With a lag of around 10 years, in the 90s, also the LFSs showed increased concentrations ($c_{max}$= 3.1 mg $L^{-1}$, 1998). These two peaks in the 80s in the HFSs and in the 90s in the LFSs cause bimodality in the concentration time series. The C–Q relationships showed a trisection evolving from an intensifying accretion pattern in the 70s and 80s to a constant pattern between C and Q in the 90s and afterwards. The $CV_C/CV_Q$ increased during the first decade and decreased afterwards strongly by 0.4 between 1984 and 1995, showing a trajectory from a more chemodynamic to a chemostatic regime.~~

~~At the downstream station (Fig. 7c1), the concentrations over time in the HFS proceeded like observed at the midstream station, but with a much more pronounced decrease from 2010 on. The intra-annual amplitude in the 80s showed a maximum of 2.4 mg $L^{-1}$ (1983/84), with strongly positive C–Q patterns ($b_{max}$= 0.4; 1985). Again with a time lag, also concentrations during LFSs peaked. Deviating from the bimodal concentration trends in the mid- and downstream HFSs, the LFSs downstream showed an unimodal pattern peaking in 1995/96 with concentrations above 6 mg $L^{-1}$ $NO_3$-N ($c_{max}$=6.9 mg $L^{-1}$). This increase in concentrations in LFSs above the concentrations in the HFSs caused dilution C-Q patterns in the 90s. This unimodal concentration trajectory in its shape and amplitude in the LFSs is unique at the downstream station and cannot be found in the other stations. Therefore, it can be stated that the seasonality did change with time, but as well as over space. Due to the decline of low flow concentrations after 1995, the dilution pattern evolved to a constant C–Q pattern from the 00s onward. The $CV_C/CV_Q$ declined by 0.7 between 1984 (max. $CV_C/CV_Q$) and 2003 (min. $CV_C/CV_Q$) evolving to chemostatic export.~~

~~Despite the differences in concentrations, the trajectory of concentrations between Midstream and Downstream (bimodal vs. unimodal), the overall pattern in the C–Q relationship proceeding from accretion pattern to constant C–Q relationships were the same in both agriculturally used subcatchment~~sub-catchment~~s (Fig. 7a2–c2), while the pristine catchment showed no changes of the intra-annual seasonality. However, at the downstream station, an additional dilution pattern was observed for several years. In both managed subcatchment~~sub-catchment~~s, the temporal concentration trajectory was accompanied by a dominantly decreasing $CV_C/CV_Q$ ratio evolving from chemodynamic to chemostatic behavior.~~

## 4 Discussion

### 4.1 Catchment scale N-budgeting

Based on the calculated differences between N-inputs and riverine N-outputs ~~(via discharge)~~ for the three ~~subcatchment~~sub-catchments within the Holtemme catchment, we ~~will~~ discuss here differences between the sub-catchments and ~~two~~ potential reasons for the ~~residual~~ missing part in the N-budget: 1) permanent N-removal by denitrification or 2) the build-up of N-legacies.

~~As described above, the~~The N-load stemming from the most upstream, pristine catchment accounted for less than ~~<~~10 % of the exported annual load over the entire study ~~time~~ period. This minor contribution can be attributed to the lack of agricultural and urban land use as dominant sources for N. Consequently, the N-export from the upstream ~~subcatchment~~sub-catchment was ~~assumed to be~~ dominantly controlled by ~~the~~N-inputs from atmospheric deposition ~~of as N input source~~. As the cumulated export over the observation period was higher than the assumed input, the estimation of ~~a retention~~retention potential was ~~difficult~~~~impossible~~not possible in this case. This might be explained by unaccounted N-sources, e.g. stemming from minor anthropogenic activity or an underestimation of N-uptake by terrestrial biological N-fixation ~~This can be explained by unaccounted N sources, e.g. stemming from minor anthropogenic activity.~~. Moreover, the assumed constant biological N-fixation as described by Cleveland et al. (1999), may have le~~a~~d to an underestimation of the ~~real~~ net N-input to the system.

The total input ~~to~~ over the whole catchment area was quantified ~~with~~ as almost 43 000 t N (1976–2015) and compared to the respective output over the same time period yielded export rates of 54 % (47–62 %) ~~46 %~~ at the midstream and 15 % (14–18 %) at the downstream station (Table 3), respectively. There can be several reasons for the difference in export rates between the two ~~subcatchment~~sub-catchments ~~can be various~~. The most likely ones are due to~~,~~ differences in discharge, topography and denitrification capacity among ~~subcatchment~~sub-catchments, which are ~~, will be~~ discussed in the following.

Load export of N from agricultural catchments is assumed to be mainly discharge-controlled (Basu et al., 2010). Many solutes show a lower variance in concentrations compared to the variance in stream flow, which makes the flow variability a strong surrogate for load variability (Jawitz & Mitchell, 2011). This can also be seen in the Holtemme catchment, which evolved to a more chemostatic export regime over time (Fig. 6b~~7~~). Highest N-export and lowest retention were observed in the midstream ~~subcatchment~~sub-catchment, where the overall highest discharge contribution can be found.

Besides discharge-quantity, we argue that the ~~expected~~ midstream ~~flow paths~~sub-catchment, as compared to the downstream, favors ~~a fast~~a more effective ~~leaching~~ export of $NO_3$-N. The higher percentage of artificial drainage by tiles and ditches (59 % vs. 21 %; supplement S1.1) as well as the steeper terrain slopes (3.2° vs. 1.9°) in the non-forested area of the midstream catchment, promote rapid, shallow subsurface flows. These flow paths can more directly connect agricultural N-sources with the stream and in turn cause elevated instream $NO_3$-N concentrations (Yang et al., 2018). ~~Related to surface topography,~~In addition, the steeper ~~terrain~~ surface topography suggests a deeper vertical infiltration (Jasechko et al., 2016) and ~~also a leaching of $NO_3$ from a wider depth range~~by that a wider range of flow paths of different ages than those observed in the

**Kommentar [SE42]:** Ref2 No.29

**Kommentar [AM43]:** Mit deinem Satz müssen wir auch Rivett nicht mehr zitieren oder? Das ist ja jetzt so eine Basic-Aussage, dass es keinen anderen Autor braucht

**Kommentar [SE44]:** Ref2 No. 30

flatter terrain areas~~s~~. Vice versa, fewer drainage installations, a flatter ~~less slope~~terrain and thus in general shallower ~~discharge contribution~~flow paths ~~could~~ may decrease the N export efficiency (increase the retention) potential downstream. The only process able to permanently remove N-input from the catchment is denitrification in soils, aquifers (Seitzinger et al., 2006; Hofstra & Bouwman, 2005), and at the stream-aquifer interface such as in the riparian (Vidon & Hill, 2004; Trauth et al., 2018) and hyporheic zones (Vieweg et al., 2016). As the riverine exports are signals of the catchment or ~~subcatchment~~sub-catchment processes, integrated in time and space, separating a build-up of an N-legacy ~~of $NO_3$~~ from a permanent removal via denitrification is difficult. A clear separation of these two key processes, however, would be important for decision makers as both have different implications for management strategies and different future impacts on water quality. Even if ~~extensive available~~ groundwater quality measurements were available that indicate denitrification, using this type of ~~more local type of~~localized information ~~to~~ for an effective catchment scale estimation of N-removal ~~by~~ via denitrification would be challenging (Green et al., 2016; Otero et al., 2009; Refsgaard et al., 2014). Therefore we discuss the denitrification potential in the soils and ~~in the groundwater~~aquifers of the Holtemme catchment based on a local isotope-study and a literature review of studies in similar settings. A strong argument against a ~~prominent~~dominant role of denitrification ~~is the study by~~is provided by ~~(~~Müller et al.~~,~~ (2018) for the study area~~-~~. On the basis of a monitoring of nitrate isotopic compositions in the Holtemme River and in tributaries, ~~a previous study (~~Müller et al. (~~,~~ 2018) stated that denitrification played no or only a minor role in the catchment. However, we still see the need to carefully check the potential of denitrification to explain the input-output imbalance considering other studies.

If 85 % of the N-input (42 758 t, dominantly agricultural input) to the catchment between 1976 and 2015 (39 ~~a~~years) were denitrified in the soils of the agricultural area (161 km²), it would need a rate of 57.9 kg N ha$^{-1}$ a$^{-1}$. Considering the derived TTs, denitrification of the convolved input would need the same rate (58 kg N ha$^{-1}$ a$^{-1}$, 1976–2015). Denitrification rates in soils for Germany (NLfB, 2005) have been reported to range between 13.5–250 kg N ha$^{-1}$ a$^{-1}$, ~~while~~ with rates larger than 50 kg N ha$^{-1}$ a$^{-1}$ ~~may be~~are found in carbon rich and waterlogged soils in the riparian zones near rivers and in areas with fens and bogs (Kunkel et al., 2008). As water bodies and wetlands make up only 1 % of the study catchment's agricultural land use ~~in our catchment~~ (Fig. 1; EEA, 2012), and consequently the extent of waterlogged soils is negligible, denitrification rates ~~>~~ larger than 50 kg N ha$^{-1}$ a$^{-1}$ ~~can be assumed~~are ~~not likely~~highly unlikely. In a global scale study, ~~This contradicts the necessary rate needed to explain the retention by denitrification in soils only.~~ Seitzinger et al. (2006) assumed a rate of 14 kg N ha$^{-1}$ a$^{-1}$ as denitrification for agricultural soils ~~at a global scale~~. With this rate only ~~This could denitrify~~ 24 % of the retained (85 %) study catchment's N-input can be denitrified. On the basis of a simulation with the modeling framework GROWA-WEKU-MEPhos, Kuhr et al., 2014 estimated very low denitrification rates, of 9–13 kg N ha$^{-1}$ a$^{-1}$, ~~Another study estimates~~ for the soils of the Holtemme catchment ~~very low to low denitrification rates, of 9–13 kg N ha$^{-1}$ a$^{-1}$ on the basis of a simulation with the modeling framework GROWA-WEKU-MEPhos (Kuhr et al., 20104)~~. Based on the~~se~~ above discussion we find for our study catchment, the~~Hence~~, denitrification in the soils, including the riparian zone, may partly explain the retention of $NO_3$-N, but is unlikely to be a single explanation for the observed imbalance between in- and output.

**Kommentar [SE45]:** Ref2 No.32

~~Regarding~~ ~~For~~Regarding the potential of denitrification in groundwater, the literature provides denitrification rate constants of a first order decay process between 0.01–0.56 ~~a~~year$^{-1}$ (van Meter et al., 2017b; van der Velde et al., 2010; Wendland et al., 2005). We derived the denitrification constant by distributing the input according to the fitted log-normal distribution of TTs assuming a first order decay along the flow paths (Kuhr et al., 201~~0~~4; Rode et al., 2009; van der Velde, 2010). The denitrification of the 85~~-~~% of input mass would require a rate constant of 0.12 ~~a~~year$^{-1}$. This constant is in the range of values reported by mentioned modelling studies. However, ~~Based on~~in a ~~spatially discrete sampling approach that evaluates the~~regional evaluation of groundwater ~~quality of the catchment,~~quality,~~–~~ Hannappel et al. (2018) ~~exclude~~provide strong evidence that denitrification in the groundwater of the Holtemme catchment is not a dominant retention process. More specifically, Hannappel et al. (2018) assess denitrification in over 500 wells in the federal state Saxony-Anhalt for nitrate, oxygen, iron concentrations and redox potential and connects the results to the hydrogeological units. Within the hard rock aquifers that are present in our study area, only 0-16% of the wells showed signs of denitrification. ~~However, Kuhr et al. (2004) exclude any denitrification in the upper aquifer for the Holtemme catchment in their modeling framework GROWA-WEKU-MEPhos. The large range of reported denitrification constants in the literature clearly calls for a more rigorous differentiation of denitrification in streams, groundwater and soils in future work.~~ ~~In this present study, however~~Taking together the local evidence from the nitrate isotopic composition (Müller et al., 2018), the regional evidence from groundwater quality (Hannappel et al., 2018) and the rates provided in literature for soils and groundwater, we argue that~~,~~ the role of denitrification in groundwater is unlikely to explain the observed imbalance between N input~~-~~ and output ~~cannot ultimately be quantified~~.

Lastly, assimilatory $NO_3$ uptake in the stream may be a potential contributor to the difference between in- and output. But even with maximal $NO_3$ uptake rates as reported by Mulholland et al. (2004; 0.14 g N m$^{-2}$ d$^{-1}$) or Rode et al. (2016; max. 0.27 g N m$^{-2}$ d$^{-1}$; estimated for a catchment adjacent to the Holtemme), the annual assimilatory uptake in the river would be a minor removal process, estimated to contribute only 3.2–% of the 85–% discrepancy between in- and output. ~~Also denitrification in the stream can be excluded as a dominant removal process.~~ According to the rates reported by Mulholland et al. (2008; max. 0.24 g N m$^{-2}$ d$^{-1}$), the Holtemme River would need a 35-times larger area to be able to denitrify the retained N. ~~Also~~Therefore denitrification in the stream can be excluded as a dominant removal process.

In summary, the precise differentiation between the accumulation of an N-legacy and removal by denitrification ~~is~~ cannot ~~not~~ be fully resolv~~able~~ed on the basis of the available data. Also a mix of both ~~could~~ may account for the missing 85~~-~~% (82–86 %, Downstream) or 46~~54~~% (38–53 %, Midstream) in the N-output. Input-output assessments with time series from different catchments, as presented in van Meter & Basu (2017), covering a larger variety of catchment characteristics, hold promise for an improved understanding of the controlling parameters and dominant retention processes.

**Formatiert:** Hervorheben

**Kommentar [SE46]:** Ref2, No.34; Ref1 No. 4

The fact that current $NO_3$ concentration levels in the Holtemme River still show no clear sign of a significant decrease, calls for a continuation of the $NO_3$ concentration monitoring, best extended by additional monitoring in soils and groundwater. Despite strong reductions in agricultural N-input since the 1990s, the annual N-surplus (e.g. 818 t $a^{-1}$, 2015) is still much higher than the highest measured export ($load_{max}$ = 216 t $a^{-1}$, 1995) from the catchment. Hence, the difference between in- and output is still high ~~and covering a~~with a factor of 4 during the past 10 ~~a~~ years (factor of 5 with the shifted input according to 12 ~~a~~ years of TT). Consequently, either the legacy of N in the catchment keeps growing instead of getting depleted or the system relies on a potentially limited denitrification capacity. Denitrification may irreversibly consume electron donors like pyrite for autolithotrophic denitrification or organic carbon for heterotrophic denitrification (Rivett et al., 2008~~; Kunkel et al., 2008~~).

Based on the ~~guided~~ analyses and literature research, ~~the~~there is evidence but no proof on the fate of missing N ~~could only be hypothesized~~, although a directed water quality management ~~interventions to cope with this problem~~ would need a clearer differentiation between N mass that is stored or denitrified. Though, ~~N~~neither tolerating the growing build-up of legacies nor relying on finite denitrification represents sustainable and adapted agricultural management practice. Hence, also future years will face increased $NO_3$-N concentrations and loads exported from the Holtemme catchment.

**Kommentar [SE47]:** Ref2, No.35

### 4.2 Linking effective TTs, concentrations and C–Q trajectories with N-legacies

Based on our data-driven analyses we propose the following conceptual model (Fig. 7~~8~~) for the N-export from the Holtemme catchment, which is able to plausibly connect and synthesize the available data and findings on TTs, concentration trajectories and ~~C-Q~~ C–Q relationships and, allows for a discussion on the type of N-legacy.

**Kommentar [AM48]:** Ref1 No. 2

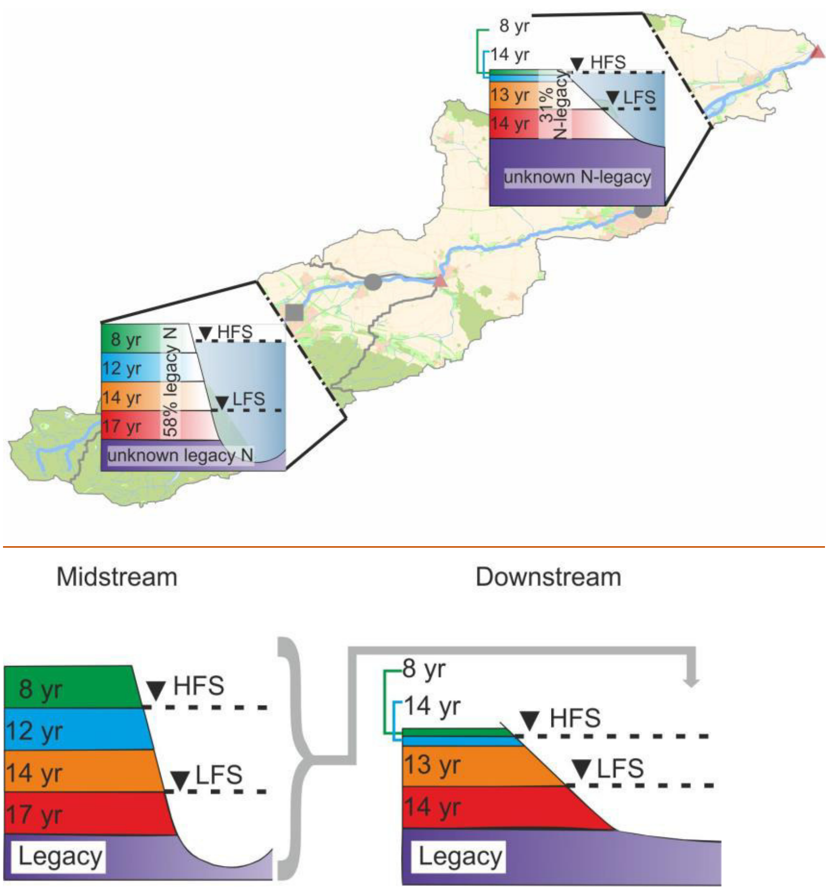


**Figure 7~~78~~: Conceptual model. Hypothetical intra-annual Q contribution (with peak TTs) in different depths and changing water levels (black triangles) during LFS and HFS. The colour of the boxes refers to the seasons as used in Fig. ~~7~~6.**

Over the course of a year, different subsurface flow paths are active, which connect different subsurface N-source zones with different source strength (in terms of concentration and flux) to the streams. These flow paths transfer water and $NO_3$-N to the streams, predominantly from shallower parts of the aquifer when water tables are high during HFSs and exclusively from deeper groundwater during low flows in LFSs (Rozemeijer & Broers, 2007; Dupas et al., 2016; Musolff et al., 2016). This conceptual model allows us to explain the observed intra-annual concentration patterns and the distinct clustering of TTs into low flow and high flow conditions. Furthermore, it can explain the mobilization of nutrients from spatially distributed $NO_3$-N sources by temporally varying flow-generating zones (Basu et al., 2010). Spatial heterogeneity of solute source zones can be a result of downward migration of the dominant $NO_3$-N storage zone in the vertical soil-groundwater profile (Dupas et al., 2016). Moreover, a systematic increase of the water age with depths would, if denitrification in groundwater takes place uniformly, lead to a vertical concentration decrease. Based on the stable hydroclimatic conditions without changes in land use, topography or the river network during the observation period, long-term changes of flow paths in the catchment are unlikely.~~ However,~~ ~~assuming~~ Assuming that flow contributions from the same depths do not change between the years, the observed decadal changes in the seasonal concentrations cannot be explained by a stronger imprint of denitrification with increasing water age. Under such conditions one would expect a more steady seasonality in concentrations and ~~C-Q~~ C–Q patterns over time with $NO_3$-N concentrations that are always similarly high in HFSs and similarly low in LFSs, which we do not see in the data. Additionally, previous findings have indicated no or only a minor role of denitrification in the catchment (Hannappel et al., 2018; Kunkel et al., 2008; Müller et al. 2018). In line with Dupas et al. (2016) ~~W~~we instead argue that the vertical migration of a temporally changing $NO_3$-N input is ~~the key~~one of most likely plausible explanation for our observations with regards to N-budgets, concentrations and C–Q trajectories.

Kommentar [SE49]: Ref2, No.38

~~At the midstream station ~~T~~t~~he faster TTs observed at the midstream station during HFSs are assumed to be dominated by discharge from ~~the shallowest~~ shallow (near-surface) ~~er~~ source zones. This zone is responsible for the fast response of instream $NO_3$-N concentrations to the increasing N-inputs (1970s to mid-1980s). This faster lateral transfer especially in spring (shortest TT) may be also ~~triggered~~ enhanced by the presence of artificial drainage structures such as tiles and ditches. In line with the longer TTs during the LFSs, low flow $NO_3$-N concentrations were less impacted in the 1970s to mid-1980s as deeper ~~source zones~~parts of the aquifer were still less affected by anthropogenic inputs. With ongoing time and a downward migration of the high $NO_3$-N inputs ~~(~~before 1990~~)~~, also those deeper layers and thus longer flow paths delivered increased concentrations to the stream (1990s). In line with the increasing low flow concentrations (in the 1990s) were the decreasing spring concentrations of $NO_3$ caused by a depletion of the shallower $NO_3$-N stocks ~~and a downward migrating peak zone~~ (see also Dupas et al., 2016; Thomas & Abbott, 2018). This depletion of the stock was a consequence of drastically reduced N-input after the German ~~peaceful~~ reunification in 1989. ~~The bimodality in concentrations over time in all four seasons underlined the changing intra-annual dominance of vertically activated zones.~~

Kommentar [SE50]: Ref1, No.26

This conceptual model of N-trajectories is ~~additionally~~ supported by the changing C–Q relationship over time. The seasonal cycle started with increasing $NO_3$-N-maxima during high flows and minima during low flows, since firstly shallow source zones were getting loaded with $NO_3$. Consequently, the accretion pattern was intensified in the first decades. The resulting positive C–Q relationship on a seasonal basis was found in many agricultural catchments worldwide (e.g. Aubert et al., 2013; Martin et al., 2004; Mellander et al., 2014; Rodriguez-Blanco et al., 2015; Musolff et al. 2015). However, after several years of deeper migration of the N-input, the catchment started to exhibit a chemostatic $NO_3$-N export regime (after 1990s), which was manifested in the decreasing $CV_c/CV_Q$ ratio. This stationarity could have been caused by a vertical equilibration of $NO_3$-N concentrations in all seasonally activated depth zones of the soils and aquifers after a more stable long-term N-input after 1995. According to the 50th percentile of the derived TT, after 16 ~~a~~ years only 50 % of the input had been released in Midstream. Therefore without any strong changes in input, the chemostatic conditions caused by the uniform, vertical $NO_3$-

N contamination will remain. At the same time, this chemostatic export regime supports the hypothesis of an accumulated N-legacy rather than denitrification as dominant reason for the imbalance between in- and output.

At the downstream station, the riverine $NO_3$ concentrations during high flows were dominated by inputs from the midstream ~~discharge~~sub-catchment, which explains the similarity with the midstream bimodality in concentrations as well as the comparable TTs. The reason for these dominating midstream flows is the strong precipitation and resulting runoff gradient on the leeward side of the mountains. During low flows, the ~~contribution of the~~ downstream ~~subcatchment~~sub-catchment can contribute much more to discharge and therefore to the overall N-~~nitrate~~ export. ~~For~~ During the LFSs, we observed a higher $NO_3$-N concentration with a unimodal trajectory, and shorter TTs compared to the midstream ~~subcatchment~~sub-catchment. We argue that the lowland ~~subcatchment~~sub-catchment supports higher water levels and thus faster TTs during the low flows. Greater prevalence of young age streamflow in flatter ~~(~~lowland~~)~~ terrain -was also described by Jasechko et al. (2016). But besides the earlier peak time during low flows, the concentration was found to be much higher than midstream. To cause such high intra-annual concentration changes, the downstream $NO_3$-N load contribution, e.g. during the concentration peak 1995/96, had to be high: the summer season was 27 t, which is more than twice the median contribution during summer (11 t). ~~The~~ A more effective export from the downstream catchment happened mainly during LFSs, which is also supported by the narrower TTD (small shape factor σ) in the summer (Fig. 5 ~~6~~). The difference between the 75th and 25th percentiles (7 a) was also the ~~fastest~~ smallest of all seasons in the summer at the downstream station. This could be one reason for the high concentrations in comparison to the midstream catchment and during the HFSs.

In contrast to the midstream catchment, the C–Q trajectory in the downstream catchment evolved from an enrichment pattern, dominated by the high concentration during high flows from Midstream to a dilution pattern, when the high concentrations in the LFS from the downstream ~~subcatchment~~sub-catchment dominated. Although the low flow concentrations were slowly decreasing in the 2000s and 2010s, also the downstream catchment evolved to a chemostatic $NO_3$ export regime as- noticed Midstream (Fig. ~~7~~6).

Our findings support the evolution from chemodynamic to chemostatic ~~behavior~~behaviour in managed catchments, but also emphasize that changing inputs of N into the catchment can lead to fast changing export regimes even in relatively slowly reacting systems. Our findings expand on previous knowledge (Basu et al., 2010; Dupas et al., 2016) as we could show systematic inter-annual C–Q changes that are in line with a changing input and a systematic seasonal differentiation of TTs. Although our study showed chemostatic ~~behavior~~behaviour towards the end of the observation period (Mid- and Downstream; Fig. 6~~7~~), this export regime is not necessarily stable as it depends on a continuous replenishment of the legacy store. Changes in the N-input translate~~d~~ to an increase of spatial heterogeneity in $NO_3$-N concentrations in soil- and groundwater with contrasting water ages. The seasonal changing contribution of different water ages thus results in more chemodynamic $NO_3$-N export regimes. As described in Musolff et al. (2017) both, export regimes and patterns are therefore controlled by the interrelation of ~~travel time~~TT and source concentrations. We argue that a hydrological legacy of $NO_3$-N in the catchment has been established that resulted in a pseudo-chemostatic export ~~behavior~~behaviour we observe nowadays. ~~We furthermore argue that~~This supports for a notion that a ~~a~~ biogeochemical legacy corresponding to the build-up of

**Kommentar [AM51]:** Ref1, No.20

organic N in the root zones of the soil (van Meter et al., 2016) is less probable. If we assume that all of the 84 % of the N-input is accumulating in the soils, we cannot explain the observed shorter-term inter-annual concentration changes and trajectory in the C–Q relationships. We would rather expect a stronger and even growing dampening of the N-input to the subsurface with the build~~t~~-up of a biogeochemical legacy in form of organic ~~nitrogen~~N. However, we cannot fully exclude the accumulation of a protected pool of soil organic matter with very slow mineralization rates as described in van Meter et al. (2017). Our conceptual model assigns the missing N to the long TTs of $NO_3$-N in soil- and groundwater and in turn to a pronounced hydrological legacy. In the midstream ~~subcatchment~~sub-catchment, the estimated TTD explains 58~~-~~% of the retained $NO_3$-N, comparing the convolution of TTD with the N-input time series to the actual riverine export. The remaining 42% cannot be fully explained at the moment and may be assigned to a permanent removal by denitrification (see discussion above), to a fixation due to biogeochemical legacy, or to more complex e.g. longer tailed TTDs, which are not well represented by our assumed log-normal distribution. In the downstream ~~subcatchment~~sub-catchment, our approach explains 31~~-~~% of the observed export. This could in principle be caused by the same processes as described for the midstream ~~subcatchment~~sub-catchment. However, in the downstream ~~subcatchment~~sub-catchment we assume a hydrological legacy store in deeper zones without significant discharge contribution (Fig. ~~8~~7). That mass of N is either bypassing the downstream monitoring station (note that the downstream station is still 3 km upstream of the Holtemme catchment outlet) or is affected by a strong time delay and dampening not captured by our approach. Consequently, future changes in N-inputs will also change the future export patterns and regimes, since this would shift the homogeneous $NO_3$-N distributions in vertical soil and groundwater profiles back to more heterogeneous ones.

## 5 Conclusion

In the present study, we used a unique time series~~-~~ of riverine N concentrations over the last four decades from a mesoscale German catchment as well as estimated N-input ~~and~~ to discuss~~ed~~ the linkage between the two on annual and intra-annual time scales. From the input-output assessment, the build-up of a potential N-legacy was quantified, effective TTs of nitrate were estimated and the temporal evolution to chemostatic $NO_3$-N export was investigated. This study provides four major findings that can be generalized and transferred to other catchments of similar hydroclimatic and landscape ~~as~~settings as well.

First, the retention capacity of the catchment for N is 85 % of the N-input (input and output referring to 1976 to 2015), which can either be stored as a legacy or denitrified in the terrestrial or aquatic system. Although we could not fully quantify denitrification, we argue that this process is not the dominant one in the catchment to explain input-output differences. The observed N-retention can be more plausibly explained by legacy than by denitrification. In consequence, the hydrological N-legacy, i.e. the load of nitrate still on the way to the stream, may have strong effects on future water quality and long-term implications for river water quality management. With a median export rate of 162 t N ~~-~~a$^{-1}$ (1976–2016, downstream, 6 kg N ha$^{-1}$ a$^{-1}$), a depletion of this legacy (< 36 000 t N) via baseflow would maintain elevated riverine concentrations for the next decades. Although N-surplus strongly decreased after the 1980s, during the past 10 ~~a~~ years there still was, an imbalance between agricultural input and riverine export by a mean factor of 5 (assuming the temporal offset of peak TTs between in-and output of 12 years~~a~~). This is a non-sustainable condition, regardless of whether the retained nitrate is stored or denitrified. Export rates as well as retention capacity derived for this catchment were found to be comparable to findings of other studies in Europe (Worrall et al., 2015;~~,~~ Dupas et al., 2015) and North America (van Meter et al., 2016).

**Kommentar [AM52]:** Ref1 No. 3

Secondly, we derived peak time lags between N-input and riverine export between 9–17 ~~a~~ years ~~that~~ with systematic~~ally~~ differences among the different seasons~~ally~~. Catchment managers should be aware of these long time frames when implementing measures and when evaluating them. This study explains the seasonally differing lag times and temporal concentration evolutions with the vertical migration of the nitrate and their changing contribution to discharge by seasonally changing aquifer connection. Hence, inter-annual concentration changes are not dominantly controlled by inter-annually changing discharge conditions, but rather by the seasonal changing activation of subsurface flows with differing ages and thus differing N-loads. As a consequence of this activation-dependent load contribution, an effective, adapted monitoring needs to cover, different discharge conditions when measures shall be assessed for their effectiveness. ~~Thus~~In the light of comparable findings of long time lags (van Meter & Basu, 2017;~~,~~ Howden, 2011), there is a general need for sufficient monitoring length and appropriate methods for data evaluation like the seasonal statistics of time series.

Third, in contrast to a more monotonic change from a chemodynamic to a chemostatic nitrate export regime that was observed previously (Dupas et al., 2016; Basu et al., 2010), this study found a systematic change of the nitrate export regime from accretion over dilution to chemostatic ~~behavior~~behaviour. Here, we can make use of the unique situation in East-German catchments where the collapse of agriculture in the early 90s provided a large scale "experiment" with abruptly reduced N-inputs. While previous studies could not distinguish between biogeochemical and hydrological legacy to cause chemostatic export ~~behavior~~behaviour, our findings support for a hydrological legacy in the study catchment. The systematic inter-annual changes of ~~C–Q~~ C–Q relationships of $NO_3$-N ~~was~~ were explained by the changes in the N input in combination with the seasonally changing effective ~~travel times~~TTs of N. The observed export regime and pattern of $NO_3$-N ~~helped to define the~~suggest a dominance of a hydrological N-legacy over the biogeochemical N-legacy in the upper soils. In turn, observed trajectories in export regimes of other catchments may be an indicator of their state of homogenization and can be helpful to classify results and predict future concentrations. ~~Only on the basis of long term time series these inter-annual systematic changes in C–Q relationships can be detected.~~

**Kommentar [SE53]:** Ref1 No.27

Fourth, although we observed long TTs ~~(slow catchment reaction)~~, significant input changes also showed strong inter-annual changes in the export regime. The c~~C~~hemostatic ~~behavior~~behaviour is therefore not necessarily a persistent endpoint of intense agricultural land use, but depends on steady replenishment of the N-store. Therefore, the export ~~behavior~~behaviour can also be termed pseudo-chemostatic and may further evolve in the future (Musolff et al., 2015) under the assumptions of a changing N-input. Depending on ~~the size of the~~the legacy size, a significant reduction or increase of N-input can cause an evolution back to dilution or enrichment patterns. Simultaneously, input changes affect the homogenized vertical nitrate profile, resulting in larger intra-annual concentration differences and consequently chemodynamic ~~behavior~~behaviour.

**Kommentar [SE54]:** Ref1 No.28

Hence, chemostatic ~~behavior~~behaviour and homogenization are characteristics of managed catchments, but only under constant N-input.

Recommendations for a sustainable management of ~~nitrogen~~N pollution in the studied Holtemme catchment, also transferable to comparable catchments, focus on the ~~three~~ two aspects.

- Our findings could not prove a significant loss of $NO_3$-N by denitrification. To deal with the past inputs and to focus on the depletion of the N-legacy, end-of-pipe measures such as hedgerows around agricultural fields (Thomas & Abbott, 2018), riparian buffers or constructed wetlands may initiate N-removal by denitrification (Messer et al., 2012).
- We could show that there is still an imbalance of N-input and riverine export by a factor of 6~~6~~. A reduced N-input due to better management of fertilizer and the prevention of N-losses from the root zone in present time is indispensable to enable depletion instead of a further build-up or stabilization of the legacy.

The combination of N-budgeting, effective ~~travel times~~TTs with long-term changes in C–Q ~~concentration-discharge~~ characteristics proved to be a helpful tool to discuss the build-up and type of N-legacy at catchment scale. ~~This study strongly benefit~~This study strongly benefits from the availability of long time ~~-~~series in nested catchments with a hydroclimatic and land-use gradient. This wealth of data may not be available everywhere. ~~For future times, we~~However, we see the potential to ~~should~~ ~~utilize~~ transfer this approach to a much wider range of catchments with long-term observations for understanding the spatial and temporal variation and type of legacy build-up, denitrification and TTs as well as their controlling factors. Data-driven analyses of differing catchments covering a higher variety of characteristics may provide a more comprehensive picture of N-trajectories and their controlling parameters. In addition to data-driven approaches emphasis should also be put on robust estimations of water ~~travel time~~TT in catchments to constraint reaction rates. Recent studies present promising approaches to derive ~~travel times~~TTs in groundwater (Marcais et al., 2018;~~,~~ Kolbe et al., 2019) and at catchment scale (Jasechko et al., 2016;~~,~~ Yang et al., 2018)

**Kommentar [AM55]:** Ref1 No. 3

**Data availability**

Discharge data (for all dates) and water quality data (from 1993) can be accessed at the websites of the State Office of Flood Protection and Water Management (LHW) Saxony-Anhalt (http://gldweb.dhi-wasy.com/gld-portal/). Atmospheric deposition data between 1995 and 2015 can be accessed at the website of the Meteorological Synthesizing Centre - West (MSC-W) of the European Monitoring and Evaluation Programme (EMEP) (http://www.emep.int/mscw/index_mscw.html) that is assigned to the Meteorological institute of Norway (MET Norway).

**Author contribution**

~~Sophie Ehrhardt,~~SE carried out the analysis, interpreted the data and wrote the manuscript.

~~Andreas Musolff~~AM designed the study and co-wrote the manuscript.

~~Rohini Kumar~~RK contributed discharge modelling results and atmospheric deposition and co-wrote the manuscript.

~~Jan Fleckenstein and Sabine Attinger~~JHF and SA contributed to the study design and helped finalizing the manuscript.

**Competing interests**

The authors declare no conflict of interest.

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**Revised version with comments referring to the points raised by the reviewers.**

# Trajectories of nitrate input and output in three nested catchments along a land use gradient

Kommentar [AM1]: Ref2, No.2

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**Abstract.** Increased anthropogenic inputs of nitrogen (N) to the biosphere during the last decades have resulted in increased groundwater and surface water concentrations of N (primarily as nitrate) posing a global problem. Although measures have been implemented to reduce N inputs, they have not always led to decreasing riverine nitrate concentrations and loads. This limited response to the measures can either be caused by the accumulation of organic N in the soils (biogeochemical legacy) or by long travel times (TTs) of inorganic N to the streams (hydrological legacy). Here, we compare atmospheric and agricultural N inputs with long-term observations (1970–2016) of riverine nitrate concentrations and loads in a Central German mesoscale catchment with a three nested sub-catchments arrangement of increasing agricultural land use. Based on a data-driven approach, we assess jointly the N budget and the effective TTs of N through the soil and groundwater compartments. In combination with long-term trajectories of the C–Q relationships, we evaluate the potential for and the characteristics of an N legacy.

We show that in the 42-year-long observation period, the catchment (270 $km^2$) with 60 % of agricultural area have received an N input of 42 758 t, while it exported 6 592 t indicating an overall retention of 85 %. Removal of N by denitrification could not sufficiently explain this imbalance. Log-normal travel time distributions (TTDs) that link the N input history to the riverine export differed seasonally, with modes spanning 8–17 years and the mean TTs being systematically higher during the high flow season as compared to low flow conditions. Systematic shifts in the C–Q relationships were noticed over time that could be attributed to strong changes in N inputs resulting from agricultural intensification before 1989, the break-down of the East German agriculture after 1989, and as well to the seasonal differences in TTs. A chemostatic export regime of nitrate was only found after several years of stabilized N inputs. The changes in C–Q relationships suggest a dominance of the hydrological N legacy over the biogeochemical N fixation in the soils, as we expected to observe a stronger and even increasing dampening of the riverine N concentrations after sustained high N inputs. Our analyses reveal an imbalance between N input and output, long time-lags and a lack of significant denitrification in the catchment. All these suggest that catchment management needs to address both, a longer-term reduction of N inputs and shorter-term mitigation of today's high N loads. The latter may be covered by interventions triggering denitrification, such as hedgerows around agricultural fields, riparian buffers zones or constructed wetlands. Further joint analyses of N budgets and TTs covering a higher variety of catchment will provide a deeper insight to N trajectories and their controlling parameters.

## 1 Introduction

In terrestrial, freshwater and marine ecosystems nitrogen (N) species are essential and often limiting nutrients (Webster et al., 2003; Elser et al., 2007). Changes in strength of their different sources like atmospheric deposition, wastewater inputs and agricultural activities caused major changes in the N cycle (Webster et al., 2003). Especially two major innovations from the industrial age accelerated anthropogenic inputs of reactive N species into the environment: artificial N fixation and the internal combustion engine (Elser, 2011). By that the amount of reactive N that enters into the element's biospheric cycle has been doubled in comparison to the preindustrial era (Smil et al., 1999; Vitousek et al.; 1997). However, the different input sources of N show diverging rates of change over time and space. While the atmospheric emissions of N oxides and ammonia have strongly declined in Europe since the 1980s (EEA, 2014), the agricultural N input (N input) through fertilizers declined but is still at a high level (Federal Ministry for the Environment and Federal Ministry of Food, 2012). In the cultural landscape of Western countries, most of the N emissions in surface and groundwater bodies stem from diffuse agricultural sources (Bouraoui and Grizzetti, 2011; Dupas et al., 2013).

**Kommentar [SE2]:** Ref1, No.5

**Kommentar [SE3]:** Ref1, No.7

**Kommentar [SE4]:** Ref2, No.6

The widespread consequences of these excessive N inputs are significantly elevated concentrations of dissolved inorganic nitrogen (DIN) in groundwater and connected surface waters (Altman and Parizek, 1995; Sebilo et al., 2013; Wassenaar, 1995) leading to increased riverine DIN fluxes (Dupas et al., 2016) and causing the ecological degradation of freshwater and marine systems. This degradation is caused by the ability of N species to increase primary production and to change food web structures (Howarth et al., 1996; Turner & Rabalais, 1991). Especially the coastal marine environments, where nitrate ($NO_3$) is typically the limiting nutrient, are affected by these eutrophication problems (Decrem et al., 2007; Prasuhn and Sieber, 2005).

Several initiatives in forms of international, national and federal regulations have been implemented, aiming at an overall reduction of N inputs into the terrestrial system and its transfer to the aquatic system. In the European Union, guidelines are provided to its member states for national programs of measures and evaluation protocols through the Nitrate Directive (CEC, 1991) and the Water Framework Directive (CEC, 2000).

The evaluation of interventions showed that policy-makers still struggle to set appropriate goals for water quality improvement particularly in heavily human-impacted watersheds. Often, interventions like reduced N inputs mainly in agricultural land use do not immediately result in declining riverine $NO_3$-N concentrations (Bouraoui and Grizzetti, 2011) and fluxes.

**Kommentar [SE5]:** Ref2, No.7

In Germany considerable progress has been achieved towards the improvement of water quality, but the diffuse water pollution from agricultural sources continues to be of concern (Wendland et al., 2005). This limited response to mitigation measures can partly be explained by nutrient legacy effects, which stems from an accumulation of excessive fertilizer inputs over decades creating a strongly dampened response between the implementation of measures and water quality improvement (van Meter & Basu, 2015). Furthermore, the multi-year travel times (TTs) of nitrate through the soil and groundwater compartments cause large time lags (Howden et al., 2010; Melland et al., 2012) that can substantially delay the

**Kommentar [SE6]:** Ref1, No.9

riverine response to applied management interventions. For a targeted and effective water quality management, we therefore need a profound understanding of the processes and controls of time lags of N from the source to groundwater and surface water bodies. Bringing together N balancing and accumulation with estimations of N TTs from application to riverine exports can contribute to this lack of knowledge.

**Kommentar [SE7]:** Ref1 No.8

**Kommentar [AM8]:** Ref1, No.2

Estimation of the water and/ or solutes TTs is essential for predicting the retention, mobility and fate of solutes, nutrients and contaminants at catchment-scale (Jasechko et al., 2016). Time series of solute concentrations and loads that cover both, input to the geosphere and the subsequent riverine export, can be used not only to determine TTs (van Meter & Basu, 2017), but also to quantify mass losses in the export as well as the behaviour of the catchment's retention capacity (Dupas et al., 2015). Knowledge on the TT of N would therefore allow understanding on the N transport behaviour; defining the fate of injected N mass into the system and its contribution to riverine N response. The mass of N being transported through the catchment storage can be referred as hydrological legacy. Data driven or simplified mechanistic approaches have often been used to derive stationary and seasonally variable travel time distributions (TTDs) using in- and output signals of conservative tracers or isotopes (Jasechko et al., 2016; Heidbüchel et al., 2012) or chloride concentrations (Kirchner et al., 2000; Bennettin et al., 2015). Recently, van Meter & Basu (2017) estimated the solute TTs for N transport at several stations across a catchment located in Southern Ontario, Canada, showing decadal time-lags between input and riverine exports. Moreover, systematic seasonal variations in the $NO_3$-N concentrations have been found, which were explained by seasonal shifts in the N delivery pathways and connected time lags (van Meter & Basu, 2017). Despite the determination of such seasonal concentration changes and age dynamics, there are relatively few studies focussing on their long-term trajectory under conditions of changing N inputs (Dupas et al., 2018; Howden et al., 2010; Minaudo et al., 2015; Abbott et al., 2018). Seasonally differing time shifts, resulting in changing intra-annual concentration variations are of importance to aquatic ecosystems health and their functionality. Seasonal concentration changes can also be directly connected to changing concentration–discharge (C–Q) relationships – a tool for classifying observed solute responses to changing discharge conditions and for characterizing and understanding anthropogenic impacts on solute input, transport and fate (Jawitz & Mitchell, 2011; Musolff et al. 2015). Investigations of temporal dynamics in the C–Q relationship are a valuable addition to approaches based on N balancing only (e.g. Abbott et al. 2018), when evaluating the effect of management interventions.

**Kommentar [SE9]:** Ref1, No.10

**Kommentar [SE10]:** Ref1, No.11

The C–Q relationships can be on the one hand classified in terms of their pattern, characterized by the slope b of the ln(C)–ln(Q) regression (Godsey et al., 2009): with enrichment ($b>0$), dilution ($b<0$) or constant ($b\approx0$) patterns (Musolff et al., 2017). On the other hand, C–Q relationships can be classified according to the ratio between the coefficients of variation of concentration ($CV_C$) and of discharge ($CV_Q$; Thompson et al., 2011). This export regime can be either chemodynamic ($CV_C/CV_Q > 0.5$) or chemostatic, where the variance of the solute load is more dominated by the variance in discharge than the variance in concentration (Musolff et al., 2017). Both, patterns and regimes are dominantly shaped by the spatial distribution of solute sources (Seibert et al., 2009; Basu et al., 2010; Thompson et al., 2011; Musolff et al., 2017). High source heterogeneity and consequently high concentration variability is thought to be characteristic for nutrients under pristine conditions (Musolff et al., 2017, Basu et al., 2010). It was shown that catchments under intensive agricultural use evolve from chemodynamic to more chemostatic behaviour regarding nitrate export (Thompson et al., 2011; Dupas et al., 2016). Several decades of human N inputs seem to dampen the discharge-dependent concentration variability, resulting in chemostatic behaviour, where concentrations are largely independent of discharge variations (Dupas et al., 2016). Also Thompson et al. (2011) stated observational and model-based evidence of an increasing chemostatic response of nitrate with increasing agricultural intensity. This shift in the export regimes is caused by a long-term homogenisation of the nitrate sources in space and/ or in depth within soils and aquifers (Dupas et al., 2016; Musolff et al., 2017). Long-term N inputs lead to a loading of all flow paths in the catchment with mobile fractions of N and by that the formation of a hydrological N legacy (van Meter & Basu, 2015) and chemostatic riverine N exports. On the other hand, excessive fertilizer input is linked to the above-mentioned build-up of legacy N stores in the catchment, changing the export regime from a supply- to a transport-limited chemostatic one (Basu et al., 2010). This legacy is manifested as a biogeochemical legacy in form of increased, less mobile, organic N content within the soil (Worral et al., 2015; van Meter & Basu, 2015; van Meter et al., 2017a). This type of legacy buffers biogeochemical variations, so that management measures can only show their effect if the build-up source gets substantially depleted (Basu et al., 2010).

Depending on the catchment configuration, both forms of legacy – hydrological and biogeochemical – can exist with different shares of the total N stored in a catchment (van Meter et al., 2017a). However, biogeochemical legacy is hard to distinguish from hydrological legacy when looking at time lags between N input and output or at catchment scale N budgets only (van Meter & Basu, 2015). One way to better disentangle the N legacy types is applying the framework of C–Q relationships as defined by Jawitz & Mitchell (2011), Musolff et al. (2015) and Musolff et al. (2017). In case of a hydrological legacy, strong changes of fertilizer inputs (such as increasing inputs in the initial phase of intensification and decreasing inputs as a consequence of measures) will temporarily increase spatial concentration heterogeneity (e.g. comparing young and old water fractions in the catchment storage), and therefore also shift the export regime to more chemodynamic conditions. On the other hand, a dominant biogeochemical legacy will lead to sustained concentration homogeneity in the N source zone in the soils and to an insensitivity of the riverine N export regime to fast changes in inputs.

Common approaches to quantify catchment scale N budgets and to characterize legacy or to derive TTs are either based on data-driven (Worral et al., 2015; Dupas et al., 2016) or on forward modeling (van Meter & Basu, 2015; van Meter et al., 2017a) approaches. So far, data-driven studies focused either solely on N budgeting and legacy estimation or on TTs. Here, we conducted a joint data-driven assessment of catchment scale N budget, the potential and characteristics of an N legacy and on the estimation of TTs of the riverine exported N. We utilized the trajectory of agricultural catchments in terms of C–Q relationships, their changes over longer time scales and their potential evolution to a chemostatic export regime. The novel combination of the long-term N budgeting, TT estimation and C–Q trajectory will help understanding the differentiation between biogeochemical and hydrological legacy, both reasons for missed targets in water quality management. This study will address the following research questions:

**Kommentar [AM11]:** Ref2, No.5

1. How high is the retention potential for N of the studied mesoscale catchment and what are the consequences in terms of a potential build-up of an N legacy?
2. What are the characteristics of the TTD for N that links change in the diffuse anthropogenic N inputs to the geosphere and their observable effect in riverine $NO_3$-N concentrations?
3. What are the characteristics of a long-term trajectory of C–Q relationships? Is there an evolution to a chemostatic export regime that can be linked to a biogeochemical or hydrological N legacy?

To answer these questions, we used time series of water quality data over four decades, available from a mesoscale German catchment, as well as estimated N input to the geosphere. We linked N input and output on annual and intra-annual time scales through consideration of N budgeting and the use of TTDs. This input-output assessment uses time series of the Holtemme catchment (270 km²) with its three nested sub-catchments along a land use gradient from pristine mountainous headwaters to a lower basin with intensive agriculture and associated increases of fertilizer applications. This catchment with its pronounced increase in anthropogenic impacts from up- to downstream is quite typical for many mesoscale catchments in Germany and elsewhere. Moreover, this catchment offers a unique possibility to analyze the system response to strong changes in fertilizer usage in East-Germany before and after reunification. Thereby, we anticipate that our improved understanding gained through this study in these catchment settings is transferable to similar regions. In comparison to spatially and temporally integrated water quality signals stemming solely from the catchment outlet, the higher spatial resolution with three stations and the unique length of the monitoring period (1970–2016) allow for a more detailed investigation about the fate of N, and consequently findings may provide guidance for an effective water quality management.

**Kommentar [SE12]:** Ref2 No.15

## 2 Data and Methods

### 2.1 Study area

The Holtemme catchment (270 km²) is a sub-catchment of the Bode River basin, which is part of the TERENO Harz/Central German Lowland Observatory (Fig. 1). The catchment as part of the TERENO (**TER**restrial **EN**vironmental **O**bservatories) project exhibits strong gradients in topography, climate, geology, soils, water quality, land use and level of urbanization (Wollschläger et al., 2017). Due to the low water availability and the risk of summer droughts that might be further exacerbated by a decrease in summer precipitation and increased evaporation with rising temperatures, the region is ranked as highly vulnerable to climate change (Schröter et al., 2005; Samaniego et al., 2018). With these conditions, the catchment is representative for other German and central European regions showing similar vulnerability (Zacharias et al., 2011). The observatory is one of the meteorologically and hydrologically best-instrumented catchments in Germany (Zacharias et al., 2011; Wollschläger et al., 2017), and provides long-term data for many environmental variables including water quantity (e.g. precipitation, discharge) and water quality at various locations.

**Kommentar [SE13]:** Ref1, No.13 & Ref2, No.8

The Holtemme catchment has its spring at 862 m a.s.l. in the Harz Mountains and extends to the Northeast to the Central German Lowlands with an outlet at 85 m a.s.l.. The long-term annual mean precipitation (1951–2015) shows a remarkable decrease from colder and humid climate in the Harz Mountains (1262 mm) down to the warmer and dryer climate of the Central German Lowlands on the leeward side of the mountains (614 mm; Rauthe et al., 2013; Frick et al., 2014). Discharge time series, provided by the State Office of Flood Protection and Water Management (LHW) Saxony-Anhalt show a mean annual discharge at the outlet in Nienhagen of 1.5 m³ $s^{-1}$ (1976–2016) referring to 172 mm $a^{-1}$.

The geology of the catchment is dominated by late Paleozoic rocks in the mountainous upstream part that are largely covered by Mesozoic rocks as well as Tertiary and Quaternary sediments in the lowlands (Frühauf & Schwab, 2008; Schuberth, 2008). Land use of the catchment changes from forests in the pristine, mountainous headwaters to intensive agricultural use in the downstream lowlands (EEA, 2012). According to Corine Land Cover (CLC) from different years (1990, 2000, 2006, 2012), the land use change over the investigated period is negligible. Overall 60 % of the catchment is used by agriculture, while 30 % is covered by forest (EEA, 2012). Urban land use occupies 8 % of the total catchment area (EEA, 2012) with two major towns (Wernigerode, Halberstadt) and several small villages. Two wastewater treatment plants (WWTPs) discharge into the river. The town of Wernigerode had its WWTP within its city boundaries until 1995, when a new WWTP was put into operation about 9.1 km downstream in a smaller village, called Silstedt, replacing the old WWTP. The WWTP in Halberstadt was not relocated but renovated in 2000. Nowadays, the total nitrogen load (TNb) in cleaned water is approximately 67.95 kg $d^{-1}$ (WWTP Silstedt: $NO_3$-N load 55 kg $d^{-1}$) and 35.09 kg $d^{-1}$ (WWTP Halberstadt: $NO_3$-N load 6.7 kg $d^{-1}$; mean daily loads 2014; Müller et al., 2018). Referring to the last 5 years of observations, $NO_3$-N load from wastewater made up 17 % of the total observed $NO_3$-N flux at the midstream station (see below) and 11 % at the downstream station. Despite this point source N input, major nitrate contribution is due to inputs from agricultural land use (Müller et al., 2018), which is predominant in the mid- and downstream part of the catchment (Fig. 1).

**Kommentar [AM14]:** Ref1, No.20

**Kommentar [AM15]:** Ref2, No.10

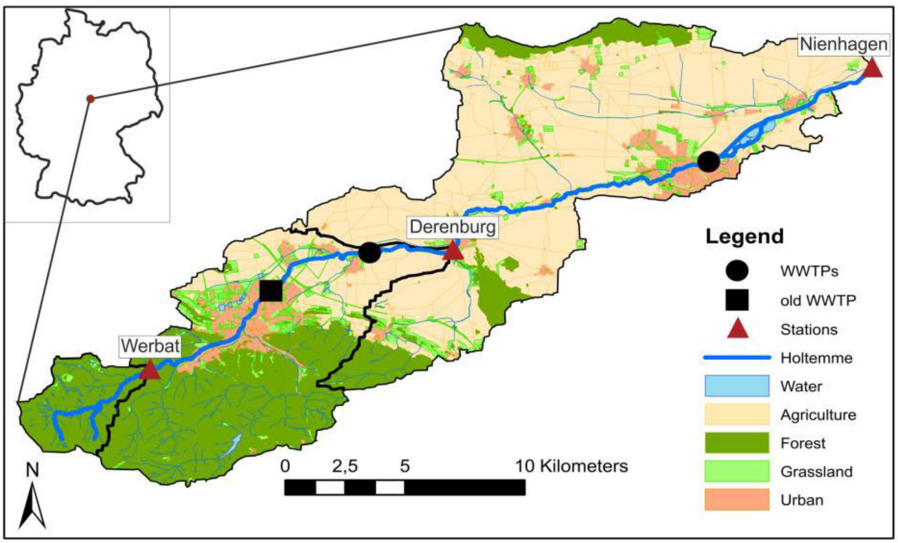


**Figure 1: Map of the Holtemme catchment with the selected sampling locations.**

The Holtemme River has a length of 47 km. Along the river, the LHW Saxony-Anhalt maintains long-term monitoring stations, providing the daily mean discharge and the biweekly to monthly water quality measurements covering roughly the last four decades (1970–2016). Three of the water quality stations along the river were selected to represent the characteristic land use and topographic gradient in the catchment. From up- to downstream, the stations are named Werbat, Derenburg and Nienhagen (Figure 1); and in the following referred to as Upstream, Midstream and Downstream. The pristine headwaters upstream represent the smallest (6 % of total catchment area) and the steepest area among the three selected sub-catchments with about a three times higher mean topographic slope than the downstream parts (DGM25; Table1). According to the latest Corine land cover dataset (CLC 2012; EEA, 2012), the land use is characterized by forest only. The larger midstream sub-catchment that represents one third of the total area is still dominated by forests, but with growing anthropogenic impact due to increasing agricultural land use and the town of Wernigerode. More than half of the agricultural land in this sub-catchment is artificially drained with open ditches (Midstream: 38 %; Downstream: 82 %) and tube drains (Midstream: 62 %, Downstream: 18 %; LHW, 2011; Table 1; S1.1). The largest sub-catchment (61 %) constitutes the downstream lowland areas which are predominantly covered by Chernozems (Schuberth, 2008), representing one of the most fertile soils within Germany (Schmidt, 1995). Hence, the agricultural land use in this sub-catchment is the highest (81 %) in comparison to the two upstream sub-catchments (EEA, 2012).

**Kommentar [SE16]:** Ref2, No.12

**Table 1: General information on study area including input/ output datasets. n – number of observations, Q - discharge.**

| | Upstream | Midstream | Downstream |
|---|---|---|---|
| n Q | 16 132 | - | 12 114 |
| n nitrate-N ($NO_3$-N) | 646 | 631 | 770 |
| Period of $NO_3$-N time series | 1972–2014 | 1970–2011 | 1976–2016 |
| | | | |
| Sub-catchment area (km²) | 15.06 | 88.50 | 165.22 |
| Cumulative catchment area (km²) | 15.06 | 103.60 | 268.80 |
| Stream length (km) | 1.5 | 19.3 | 24.4 |
| Mean topographic slope (°) | 9.82 | 7.52 | 2.55 |
| Mean topo. slope in non-forested area (°) | - | 3.2 | 1.9 |
| | | | |
| Land use (Corine land cover; EEA, 2012) | | | |
| Forest land use (%) | 100 | 56 | 11 |
| Urban land use (%) | - | 17 | 8 |
| Agricultural land use (%) | - | 27 | 81 |
| Fraction of agricultural area artificially drained (%) | - | 59.1 | 20.5 |

**2.2 Nitrogen input**

The main N sources were quantified over time assisting the data-based input-output assessment to address the three research questions regarding the N budgeting, effective TTs and C–Q relationships in the catchment.

**Kommentar [SE17]:** Ref1, No.2

A recent investigation in the study catchment by Müller et al. (2018) showed that the major nitrate contribution stems from agricultural land use and the associated application of fertilizers. The quantification of this contribution is the N-surplus (also referred to as agricultural surplus) that reflects N input that is in excess of crop and forage needs. For Germany there is no consistent data set available for the N-surplus that covers all land use types and is sufficiently resolved in time and space. Therefore, we combined the available agricultural N input (including atmospheric deposition) dataset with another dataset of atmospheric N deposition rates for the non-agricultural land.

**Kommentar [SE18]:** Ref1, No.14

The annual agricultural N input for the Holtemme catchment was calculated using two different data sets of agricultural N-surplus across Germany provided by the University of Gießen (Bach & Frede, 1998; Bach et al., 2011). Surplus data [kg N $ha^{-1}$ $a^{-1}$] were available on the federal state level for 1950–2015 and on the county level for 1995–2015; with an accuracy level of 5 % (see Bach & Frede, 1998 for more details). We used the data from the overlapping time period (1995–2015) to downscale the state level data (state: Saxony-Anhalt) to the county level (county: Harzkreis). Both (the state level and the

**Kommentar [AM19]:** Ref1, No. 1

aggregated county to state level) data sets show high correspondence with a correlation ($R^2$) of 0.85, but they slightly differ in their absolute values (by 6 % of the mean annual values). The mean offset of 3.85 kg N $ha^{-1}$ $a^{-1}$ was subtracted from the federal state level data to yield the surplus in the county before 1995.

Both of the above datasets account for the atmospheric deposition, but only on agricultural areas. For other non-agricultural areas (forest and urban landscapes), the N source stemming from atmospheric deposition was quantified based on datasets from the Meteorological Synthesizing Centre - West (MSC-W) of the European Monitoring and Evaluation Programme (EMEP). The underlying dataset consists of gridded fields of EU-wide wet and dry atmospheric N depositions from a chemical transport model that assimilates different observational records on atmospheric chemicals (e.g. Bartnicki & Benedictow, 2017; Bartnicki & Fagerli, 2006). This dataset is available at annual time-steps since 1995, and at every 5 years between 1980 and 1995. Data between the 5-year time steps were linearly interpolated to obtain annual estimates of N deposition between 1980 and 1995. For years prior to 1980, we made use of global gridded estimates of atmospheric N deposition from the three-dimensional chemistry-transport model (TM3) for the year 1860 (Dentener, 2006; Galloway et al., 2004). In absence of any other information, we performed a linear interpolation of the N deposition estimates between 1860 and 1980.

To quantify the net N fluxes to the soil via atmospheric deposition, the terrestrial biological N fixation had to be subtracted for different non-agricultural land use types. Based on a global inventory of terrestrial biological N fixation in natural ecosystems, Cleveland et al. (1999) estimated the mean uptake for temperate (mixed, coniferous or deciduous) forests and (tall/medium or short) grassland as 16.04 kg N $ha^{-1}$ $a^{-1}$, and 2.7 kg N $ha^{-1}$ $a^{-1}$, respectively. The remaining atmospheric deposition, after accounting for the above prescribed biological fixation for the different land uses, was added to the agricultural N-surplus to achieve the total N input per area. In contrast to the widely applied term net anthropogenic nitrogen input (NANI), we do not account for wastewater fluxes in the N input but rather focus on the diffuse N input and connected flow paths, where legacy accumulation and time lags between in- and output potentially occur.

### 2.3 Nitrogen output

#### 2.3.1 Discharge and water quality time series

Discharge and water quality observations were used to quantify the N load and to characterize the trajectory of $NO_3$-N concentrations and the C–Q trajectories in the three sub-catchments.

**Kommentar [AM20]:** Ref1 No. 2

The data for water quality (biweekly to monthly) and discharge (daily) from 1970 to 2016 were provided by the LHW, Saxony-Anhalt. The biweekly to monthly sampling was done at gauging stations defining the three sub-catchments. The data sets cover a wide range of instream chemical constituents including major ions, alkalinity, nutrients and in situ parameters. As this study only focuses on N species, we restricted the selection of parameters to nitrate ($NO_3$; Fig. 2), nitrite ($NO_2$; supplement, S1.2.2) and ammonium ($NH_4$; supplement, S1.2.1).

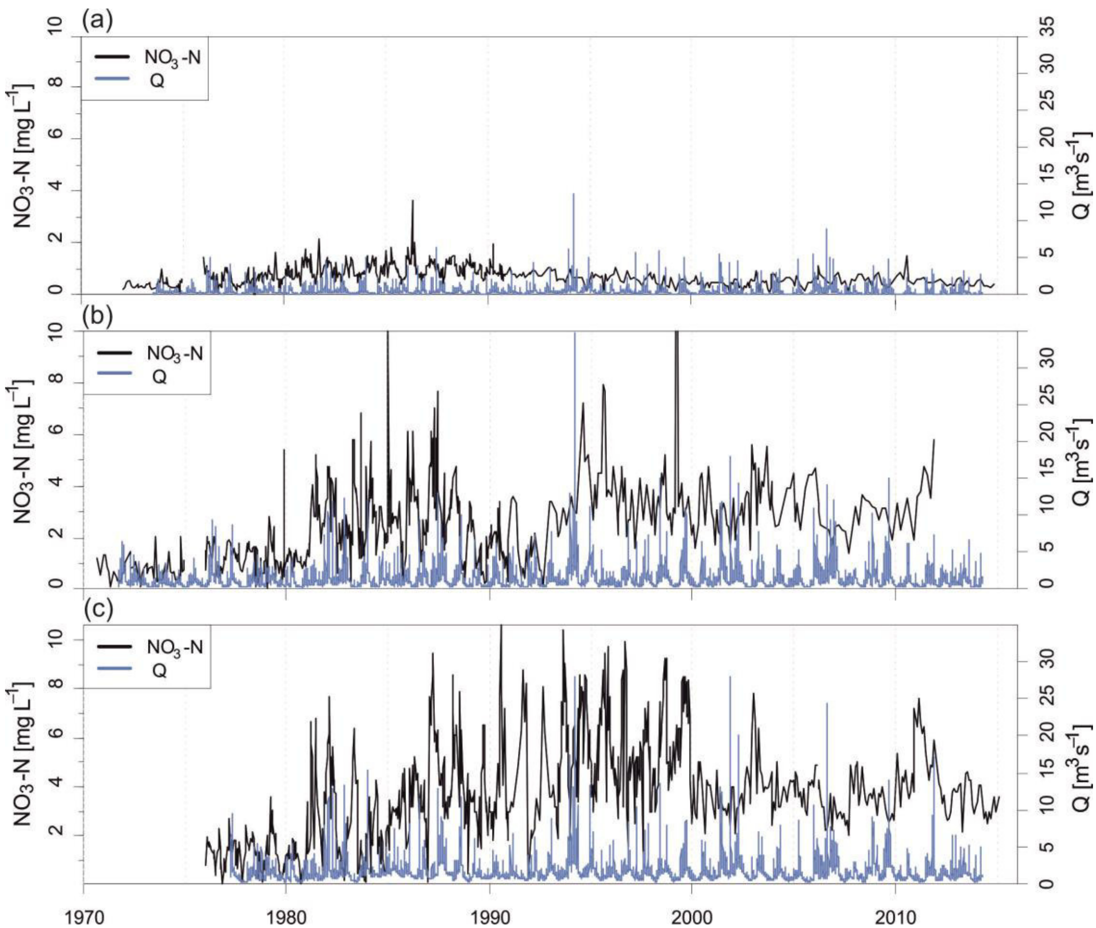

**Figure 2: $NO_3$-N concentration and discharge (Q) time series: Upstream (a), Midstream (b) and Downstream (c).**

Discharge time series at daily time scales were measured at two of the water quality stations (Upstream, Downstream; Fig. 2). Continuous daily discharge series are required to calculate flow-normalized concentrations (see the following section 2.3.2 for more details). To derive the discharge data for the midstream station and to fill measurement gaps at the other stations (2 % Upstream, 3 % Downstream), we used simulations from a grid-based distributed mesoscale hydrological model mHM (Samaniego et al., 2010; Kumar et al., 2013). Daily mean discharge was simulated for the same time frame as the available measured data. We used a model set-up similar to Müller et al. (2016) with robust results capturing the observed variability of discharge in the studied, near-by catchments. We note that the discharge time series were used as weighting factors in the later analysis of flow-normalized concentrations. Consequently it is more important to capture the temporal dynamics than the absolute values. Nonetheless, we performed a simple bias correction method by applying the regression equation of simulated and measured values to reduce the simulated bias of modelled discharge. After this revision, the simulated discharges could be used to fill the gaps of measured data. The midstream station (Derenburg) for the water quality data is 5.6 km upstream of the next gauging station. Therefore, the nearest station (Mahndorf) with simulated and measured discharge data was used to derive the bias correction equation that was subsequently applied to correct the simulated discharge data at the midstream station, assuming the same bias between modelled and observed discharges at both near-by gauging stations.

**Kommentar [SE21]:** Ref1 Nr.16

### 2.3.2 Weighted regression on time, discharge, and season (WRTDS) and waste water correction

The software package "Exploration and Graphics for RivEr Trends" (EGRET) in the R environment by Hirsch and DeCicco (2019) was used to estimate daily concentrations of $NO_3$-N utilizing a "Weighted Regressions on Time, Discharge, and Season" (WRTDS). The WRTDS method allows the interpolation of irregularly sampled concentration to a regular series at a daily time-scale using a flexible statistical representation for every day of the discharge record. In brief, a regression model based on the predictors discharge and time (to represent long-term trend and seasonal component) is fitted for each day of the flow record with a flexible weighting of observations based on their time-, seasonal- and discharge "distance" (Hirsch et al., 2010). Results are daily concentrations and fluxes as well as daily flow-normalized concentrations and fluxes. Flow-normalization uses the probability distribution of discharge of the specific day of the year from the entire discharge time series. More specifically, the flow-normalized concentration is the average of the same regression model for a specific day applied to all measured discharge values of the corresponding day of the year. While the non-flow-normalized concentrations are strongly dependent on the discharge, the flow-normalized estimations provide a more unbiased, robust estimate of the concentrations with a focus on changes in concentration and fluxes independent of inter-annual discharge variability (Hirsch et al., 2010). To account for uncertainty in the regression analysis of annual and seasonal flow-normalized concentration and fluxes, we used the block bootstrap method introduced by Hirsch et al. (2015). We derived the 5$^{th}$ and 95$^{th}$ percentile of annual flow-normalized concentration and flux estimates with a block length of 200 days and 10 replicates. The results are utilized to communicate uncertainty in both, the N budgeting and the resulting TTs estimation.

**Kommentar [SE22]:** Ref2 No. 17

**Kommentar [SE23]:** Ref1 No. 17

**Kommentar [AM24]:** Ref 1 No. 18

**Kommentar [AM25]:** Ref1 No. 1

The study of Müller et al. (2018) indicated the dominance of N from diffuse sources in the Holtemme catchment, but also stressed an impact of wastewater-borne nitrate during low flow periods. Because our purpose was to balance and compare N input and outputs from diffuse sources only, the provided annual flux of total N from the two WWTPs was therefore used to correct flow-normalized fluxes and concentrations derived from the WRTDS assessment. We argue that the annual wastewater N flux is robust to correct the flow-normalized concentrations, but it does not allow for the correction of measured concentration data at a specific day. Both treatment plants provided snapshot samples of both, $NO_3$-N and total N

**Kommentar [SE26]:** Ref1 No. 18

fluxes, to derive the fraction of N that is discharged as $NO_3$-N into the stream. This fraction is 19 % for the WWTP Halberstadt (384 measurements between January 2014 to July 2016), and 81 % for Silstedt (eight measurements from February 2007 to December 2017). We argue that the fraction of N leaving as $NH_4$, $NO_2$ and $N_{org}$ does not interfere with the $NO_3$-N flux in the river due to the limited stream length and therefore nitrification potential of the Holtemme River impacted by wastewater (see also supplement, S1.2.3). We related the wastewater-borne $NO_3$-N flux to the flow-normalized daily flux of $NO_3$-N from the WRTDS method to get a daily fraction of wastewater $NO_3$-N in the river that we used to correct the flow-normalized concentrations. Note that this correction was applied to the midstream station from 1996 on, when the Silstedt treatment plant was taken to operation. In the downstream station, we additionally applied the correction from the Halberstadt treatment plant, renovated in the year 2000. Before that, we assume that waste water-borne N dominantly leaves the treatment plants as $NH_4$-N (see also supplement, S1.2.1).

Based on the daily resolved flow-normalized and wastewater-corrected concentration and flux data, descriptive statistical metrics were calculated on an annual time scale. Seasonal statistics of each year were also calculated for winter (December, January, February), spring (March, April, May), summer (June, July, August) and fall (September, October, November). Note that statistics for the winter season incorporate December values from the calendar year before.

Following Musolff et al. (2015, 2017), the ratio of $CV_C/CV_Q$ and the slope (b) of the linear relationship between ln(C) and ln(Q) were used to characterize the export pattern and the export regimes of $NO_3$-N along the three study catchments.

### 2.4 Input-output assessment: Nitrogen budgeting and effective travel times

The input-output assessment is needed to estimate the retention potential for N in the catchment as well as to link temporal changes in the diffuse anthropogenic N inputs to the observed changes in the riverine $NO_3$-N concentrations. The stream concentration of a given solute, e.g. as shown by Kirchner et al. (2000), is assumed at any time as the convolution of the TTD and the rainfall concentration throughout the past. This study applies the same principle for the N input as incoming time series that, when convolved with the TTD, yields the stream concentration time series. We selected a log-normal distribution function (with two parameters, μ and σ) as a convolution transfer function, based on a recent study by Musolff et al. (2017) who successfully applied this form of a transfer function to represent TTs. The two free parameters were obtained through optimization based on minimizing the sum of squared errors between observed and simulated N exports. The form of selected transfer function is in line with Kirchner et al. (2000) stating that exponential TTDs are unlikely at catchment scale but rather a skewed, long tailed distribution. Note that we used the log-normal distribution as a transfer function between the temporal patterns of input (N load per area) and flow-normalized concentrations on an annual time-scale only and not as a flux-conservative transfer function. TTDs were inferred based on median annual and median seasonal flow-normalized concentrations and the corresponding N input estimates. To account for the uncertainties in the flow-normalized concentration input, we additionally derive TTDs for the confidence bands of the concentrations (5th and 95th percentile)

**Kommentar [SE27]:** Ref.1, No.2

**Kommentar [AM28]:** Ref. 1, No. 1

estimated through the bootstrap method (see section 2.3.2 for more details). Here, we assumed that the width of the confidence bands provided for the annual concentrations also applies to the seasonal concentrations of the same year.

## 3 Results

### 3.1 Input assessment

In the period from 1950 to 2015, the Holtemme catchment received a cumulative diffuse N input of 62 335 t with the majority of this associated with agriculture related N application (97 %). Within the period when water quality data were available, the total sum is 51 091 t (1970–2015), as well with 97 % agricultural contribution. The N input showed a remarkable temporal variability (see Fig. 6; purple, dashed line). From 1950 to 1976, the input was characterized by a strong increase (slope of linear increase = 4.2 kg N $ha^{-1}$ $a^{1}$ per year) with a maximum annual, agricultural input of 132.05 kg N $ha^{-1}$ $a^{-1}$ (1976), which is twenty times the agricultural input in 1950. After more than 10 years of high but more stable inputs, the N-surplus dropped dramatically with the peaceful reunification of Germany and the collapse of the established agricultural structures in East Germany (1989/1990; Gross, 1996). In the time period afterwards (1990–1995), the N-surplus was only one-sixth (20 kg N $ha^{-1}$ $a^{-1}$) of the previous input. After another 8 years of increased agricultural inputs (1995–2003) of around 50 kg N $ha^{-1}$ $a^{-1}$, the input slowly decreased with a mean slope of -1.3 kg N $ha^{-1}$ $a^{-1}$ per year, but showed distinctive changes in the input between the years.

**Kommentar [SE29]:** Ref2 No.19

The input into the forested catchment upstream with only atmospheric deposition peaked in 1980 and decreased afterwards. The annual N inputs were always below 12 kg N $ha^{-1}$ $a^{-1}$ over the entire period, which is less than one-fifth of the mean agricultural input (60 kg N $ha^{-1}$ $a^{-1}$). Hence, the input to the upstream area was only minor in comparison to the ones further downstream that are dominated by agriculture.

**Kommentar [SE30]:** Ref2 No.20

### 3.2 Output assessment

#### 3.2.1 Discharge time series and WRTDS results on decadal statistics

Discharge was characterized by a strong seasonality throughout the entire data record, which divided the year into a high flow season (HFS) during winter and spring, accounting for two-thirds of the annual discharge and a low flow season (LFS) during summer and fall. Average discharge in the sub-catchments is mainly a reflection of the strong spatial precipitation gradient across the study area being on the leeward side of the Harz Mountains. The upstream sub-catchment contributed 21 % of the median discharge measured at the downstream station (Table 2). The midstream station, representing the cumulated discharge signal from the up- and midstream sub-catchments, accounted for 82 % of the median annual discharge at the outlet. Although the upstream sub-catchment had the highest specific discharge, the major fraction of total discharge (61 %) was generated in the midstream sub-catchment. Also the seasonality in discharge was dominated by this major midstream contribution, especially during high flow conditions. Vice versa, especially during HFSs, the median downstream

**Kommentar [SE31]:** Ref1, No.20

contribution was less than 10 %, while during low flow periods, the downstream contribution accounted for up to 33 % (summer).

**Table 2: Descriptive statistics on discharge at the three observation points. LFS – low flow season (June–November), HFS – high flow season (December–May).**

| | Upstream | Midstream | Downstream |
|---|---|---|---|
| Median discharge ($m^3\ s^{-1}$) | 0.23 | 0.9 | 1.1 |
| Mean specific discharge ($mm\ a^{-1}$) | 768 | 411 | 178 |
| LFS sub-catchment contribution (%) | 17 | 53 | 30 |
| HFS sub-catchment contribution (%) | 21 | 69 | 10 |

**Kommentar [SE32]:** Ref2, No.20

The flow-normalized $NO_3$-N concentrations in each sub-catchment showed strong differences in their overall levels and temporal patterns over the four decades (Fig. 3a, see also Fig. 2). The lowest decadal concentration changes and the earliest decrease in concentrations were found in the pristine catchment. Median upstream concentrations were highest in the 80s (1987), with a reduction of the concentrations to about one half in the latter decades. Over the entire period, the median upstream concentrations were smaller than 1 mg $L^{-1}$, so that the described changes are small compared to the $NO_3$-N dynamics of the more downstream stations. High changes over time were observed in the two downstream stations with a tripling of concentrations between the 1970s and 1990s, when maximum concentrations were reached. While median concentrations Downstream decreased slightly after this peak (1995/1996), the ones Midstream (peak: 1998) stayed constantly high. At the end of the observation period, at the outlet (Downstream), the median annual concentrations did not decrease below 3 mg $L^{-1}$ $NO_3$-N, a level that was exceeded after the 1970s. The differences in $NO_3$-N concentrations between the pristine upstream and the downstream station evolved from an increase by a factor of 3 in the 1970s to a factor of 7 after the 1980s.

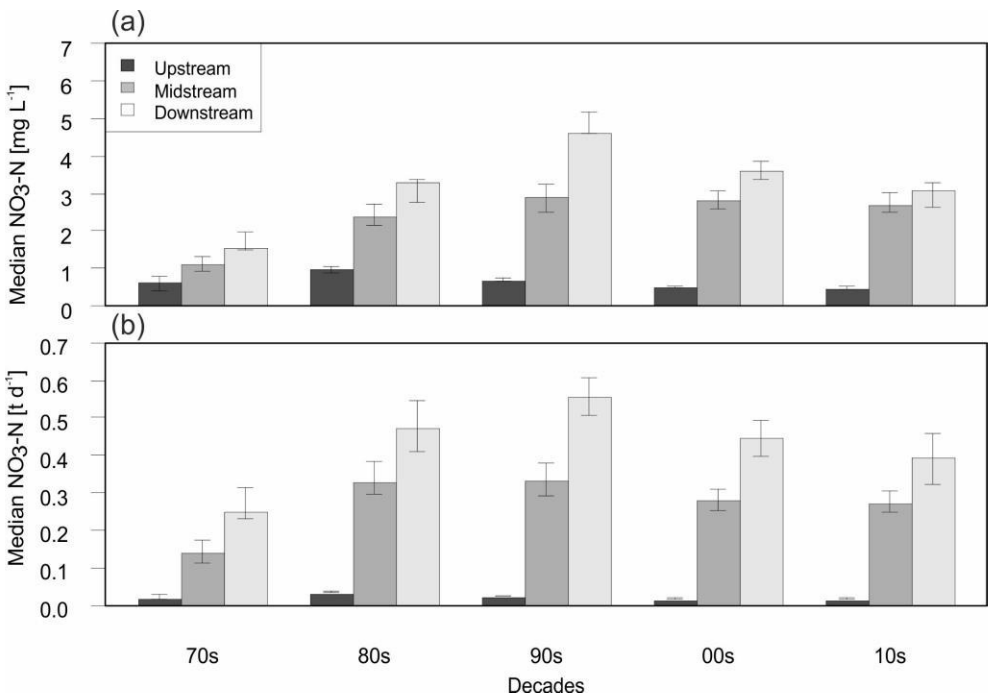


**Figure 3: Flow-normalized median $NO_3$-N concentration (a) and $NO_3$-N loads (b) for each decade of the time series and the three stations. Whiskers refer to the 5th and 95th percentiles of the WRTDS estimations.**

Kommentar [AM33]: Ref. 1, No. 1

Calculated loads (Fig. 3b) also showed a drastic change between the beginning and the end of the time series. The daily upstream load contribution was below 10 % of the total annual export at the downstream station in all decades and then the estimates decreased from 9 % (1970s) to 4 % (2010s). The median daily load between 1970s and 1990s tripled Midstream (0.1 t $d^{-1}$ to 0.3 t $d^{-1}$) and more than doubled Downstream (0.2 t $d^{-1}$ to 0.5 t $d^{-1}$). In the 1990s, the Holtemme River exported on average more than 0.5 t $d^{-1}$ of $NO_3$-N, which, related to the agricultural area in the catchment, translates into more than 3.1 kg N $km^{-2}$ $d^{-1}$ (maximum 13.4 kg N $ha^{-1}$ $a^{-1}$ in 1995).

### 3.3 Input-Output-balance: N budget

We jointly evaluated the estimated N inputs and the exported $NO_3$-N loads to enable an input-output-balance. This comparison on the one hand allowed for an estimation of the catchment's retention potential, and on the other hand enabled us to estimate future exportable loads.

Kommentar [SE34]: Ref.2, No.21

Kommentar [SE35]: Ref1, No.21

**Table 3: Nitrogen retention potentials derived for the midstream and downstream sub-catchment based on flow-normalized fluxes. Numbers in brackets refer to the 5th and 95th percentiles of the WRTDS flux estimation.**

| | Midstream | Downstream |
|---|---|---|
| Retention cumulative (%) | 46 (38–53) | 85 (82–86) |
| | (Up- + Midstream) | (Up- + Mid- + Downstream) |
| Retention sub-catchment (%) | 48 (39–54) | 94 (93–94) |
| Retention/Year (N kg $a^{-1}$) | 86 282 (70 462–98 513) | 910 349 (90 6629–91 8200) |
| Retention/Area (N kg $a^{-1}$ $ha^{-1}$) | 9.75 (7.96–11.10) | 55.10 (54.87–55.57) |

The load stemming from the most upstream, pristine catchment accounted for less than 10 % of the exported load at the outlet. To focus on the anthropogenic impacts, the data from the upstream station are not discussed on its own in the following. At the midstream station, a total sum of input of 7 653 t compared to 4 109 t of exported $NO_3$-N for the overlapping time period of in- and output was analyzed (1970–2011). The midstream catchment received 48 % (Table 3) more N mass than it exported at the same time. Note that the exported N is not necessarily the N applied in the same period due to the temporal offset as discussed later in detail. With the assumption that 97 % of the diffuse input resulted from agriculture, the catchment exported 1 545 kg N $ha^{-1}$ (1 350–1 771 kg N $ha^{-1}$) from agricultural areas. The cumulated N input from the entire catchment (measured Downstream) from 1976 to 2015 (overlapping time of in- and output) was 42 758 t, while the riverine export in the same time was only 15 % (6 kg N $ha^{-1}$ $a^{-1}$; 14–18 %) implying an agricultural export of 397 kg N $ha^{-1}$ (353–454 kg N $ha^{-1}$; Fig. 4). This mass discrepancy between in- and output translates into a retention rate in the entire Holtemme catchment of 85 % (82–86 %). In relation to the entire sub-catchment area (not only agricultural land use), the median annual retention rate of $NO_3$-N was around 10 kg N $ha^{-1}$ $a^{-1}$ (8–11 kg N $ha^{-1}$ $a^{-1}$) in the midstream sub-catchment and 55 kg N $ha^{-1}$ $a^{-1}$ (55–56 kg N $ha^{-1}$ $a^{-1}$) in the flatter and more intensively cultivated downstream sub-catchment.

**Kommentar [AM36]:** Ref2, No. 22

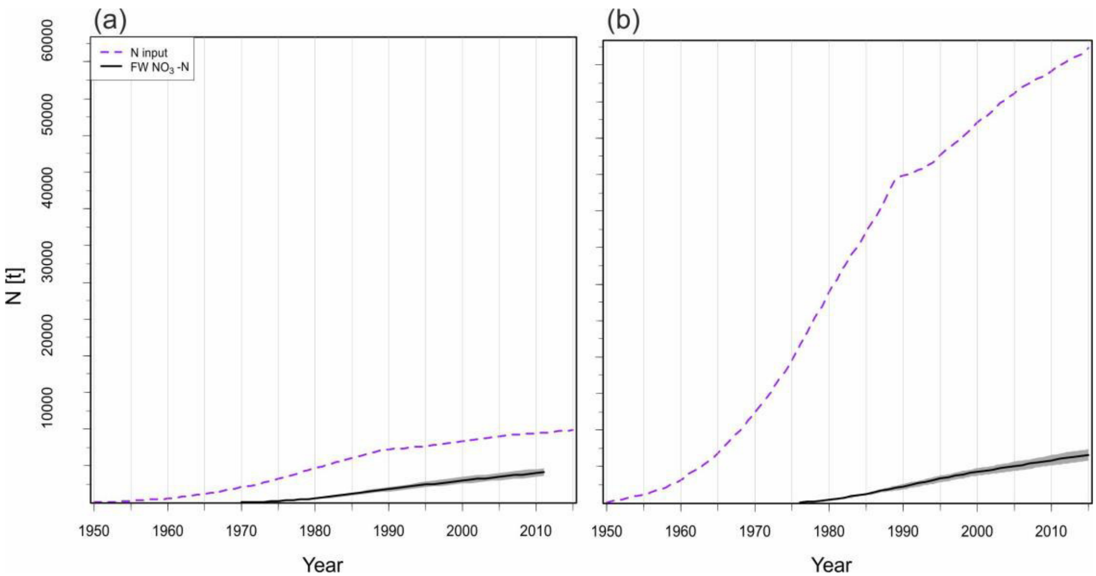


**Figure 4: Cumulative annual diffuse N inputs to the catchment and measured cumulative $NO_3$-N exported load over time for Midstream (a) and Downstream (b). Shaded grey confidence band refer to the 5th and 95th percentile of the WRTDS flux estimation.**

### 3.4 Effective TTs of N

We approximated the effective TTs for all seasonal $NO_3$-N concentration trajectories at the midstream and downstream stations by fitting the log-normal TTDs (Fig. 5; Table 4). Note that the upstream station was not used here due to the lack of temporally resolved input data on the atmospheric N deposition (estimated linear input increase between 1950 and 1979). In general, the optimized distributions were able to sufficiently capture the time lag and smoothing between the input and output concentrations ($R^2 \geq 0.77$; see also supplement, S2.1, S2.2). Systematic differences between stations and seasons can be observed, best represented by the mode of the distributions (peak TTs). The average deviation between the best and worst case estimation of the fitted TTDs from their respective average value was only 6 % with respect to the mode of the distributions (Table 4).

**Table 4: Best fit parameters of the log-normal TTDs for the N input and output responses. Parameters in brackets are derived by using the 5th and 95th percentiles of the bootstrapped flow-normalized concentration estimates.**

| | Parameter | All seasons | Winter | Spring | Summer | Fall |
|---|---|---|---|---|---|---|
| Midstream | μ | 2.8 (2.8-2.9) | 2.8 (2.8-2.8) | 2.6 (2.6-2.6) | 2.8 (2.8-2.9) | 3.0 (3.0-3.1) |
| | σ | 0.5 (0.5-0.6) | 0.6 (0.6-0.6) | 0.7 (0.7-0.8) | 0.5 (0.5-0.5) | 0.4 (0.4-0.5) |
| | Mode [a] | 12.5 (11.7-13.2) | 11.6 (11.0-12.1) | 7.7 (7.3-7.6) | 13.6 (12.4-14.6) | 17.1 (15.4-18.9) |
| | $R^2$ | 0.91 (0.86-0.90) | 0.86 (0.77-0.84) | 0.87 (0.78-0.85) | 0.93 (0.90-0.92) | 0.86 (0.84-0.84) |
| Downstream | μ | 2.8 (2.8-2.9) | 3.0 (3.0-3.0) | 2.6 (2.7-2.7) | 2.7 (2.7-2.7) | 2.9 (2.9-2.9) |
| | σ | 0.6 (0.6-0.6) | 0.6 (0.5-0.6) | 0.8 (0.7-0.8) | 0.4 (0.3-0.4) | 0.5 (0.5-0.5) |
| | Mode [a] | 11.8 (11.8-12.7) | 14.3 (14.0-15.6) | 7.4 (8.0-8.4) | 12.7 (12.4-13.3) | 14.2 (13.8-14.7) |
| | $R^2$ | 0.96 (0.92-0.95) | 0.90 (0.81-0.90) | 0.83 (0.83-0.92) | 0.93 (0.88-0.91) | 0.86 (0.78-0.82) |

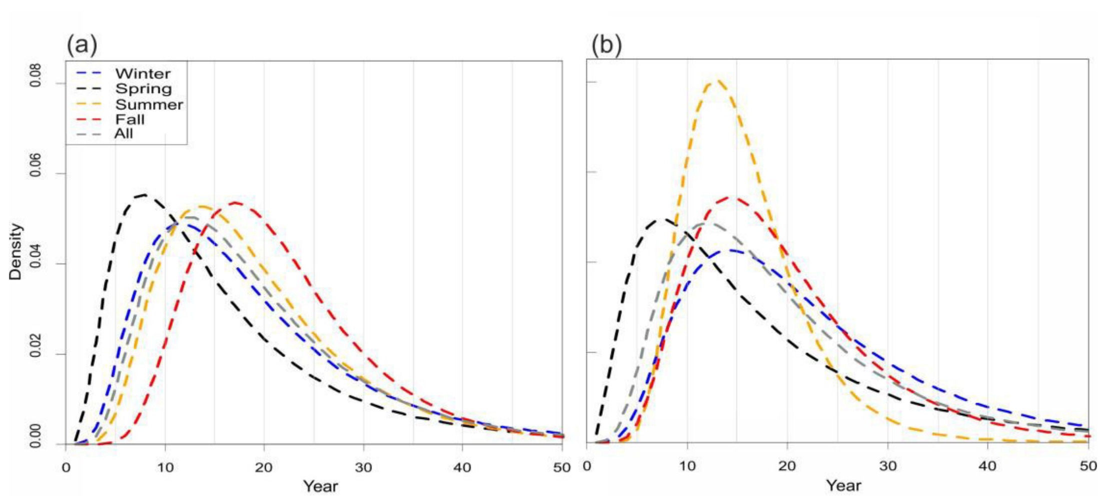


**Figure 5: Seasonal variations in the fitted log-normal distributions of effective travel times between nitrogen input and output responses for Midstream (a) and Downstream (b).**

The TTs for all seasons taken together were almost identical for the mid- and downstream stations. However, the comparison of the TTD modes for the different seasons Midstream showed distinctly differing peak TTs between 8 years (spring) and 17 years (fall), which represented more than a doubling of the peak TT. Fastest times appeared in the HFSs while modes of the TTDs appeared longer in the LFSs. Note that the shape factor σ of the effective TTs also changed systematically: The

HFSs spring and winter exhibited generally higher shape factors than those of the LFSs. This refers to a change in the coefficient of variation of the distributions Midstream from 0.8 in spring to 0.4 in fall.

The modes of the fitted functions for the downstream station during the HFSs (8 years in spring, 14 years in winter) were almost identical to the ones at the midstream station. Conversely, fall exhibited shorter TTs for the downstream station than for the midstream station. The mode of the TTs ranged between 8 years (spring) and 14 years (winter, fall). The shape factors of the fitted TTDs also ranged between 0.8 (spring) and 0.4 (summer) for the downstream station. In summary, HFSs in both sub-catchments had quite similar TTDs, whereas the LFSs showed distinct differences in their peak time.

### 3.5 Seasonal $NO_3$-N concentrations and C–Q relationships over time

As described above, the Holtemme catchment showed a pronounced seasonality in discharge conditions, producing the HFS in December–May (winter + spring) and the LFS in June–November (summer + fall). Therefore, changes in the seasonal concentrations of $NO_3$-N also reflect in the annual C–Q relationship. Analysing the changing seasonal dynamics therefore provide a deeper insight into N trajectories in the Holtemme catchment.

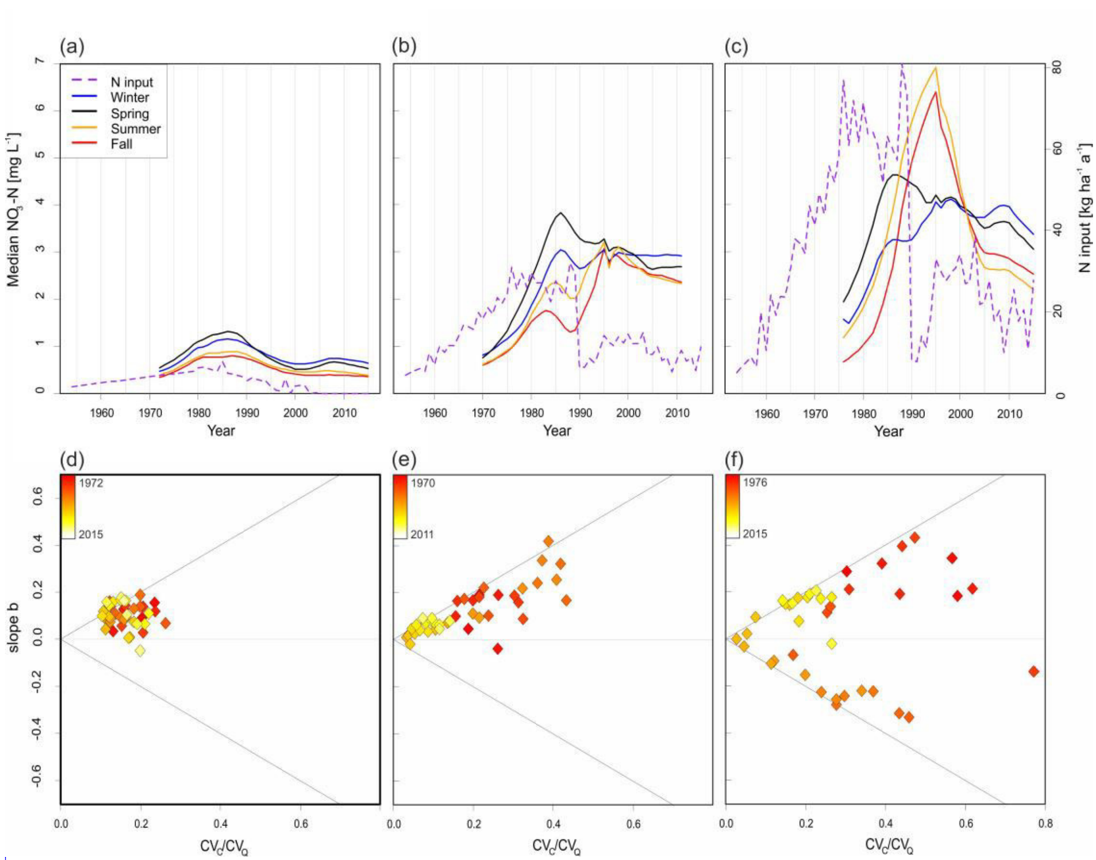


**Figure 6: Annual N input (referred to the whole catchment, 2nd y-axis) to the catchment and measured median $NO_3$-N concentrations in the stream (1st y-axis) over time at three different locations. Upstream (a, d), Midstream (b, e), Downstream (c, f). Lower panels show plots of slope b vs. $CV_C/CV_Q$ for $NO_3$-N for the three sub-catchments following the classification scheme provided in Musolff et al. (2015). X-axis gives the coefficient of variation of concentrations (C) relative to the coefficient of variation of discharge (Q). Y-axis gives the slope b of the linear ln(C)–ln(Q)-relationship. Colours indicate the temporal evolution from 1970–2016 starting from red to yellow.**

**Kommentar [SE37]:** Ref2, No.26

In the pristine upstream catchment, no temporal changes in the seasonal differences of riverine $NO_3$-N concentrations could be found (Fig. 6a). Also the C–Q relationship (Fig. 6d) showed a steady pattern (moderate accretion) with highest concentrations in the HFSs i.e. winter and spring. The ratio of $CV_C/CV_Q$ indicates a chemostatic export regime and changed only marginally (amplitude of 0.2) over time.

At the midstream station (Fig. 6b), the early 1970s showed an export pattern with highest concentration during HFSs similar to the upstream catchment, but with a general increase of concentrations from 1970−1995. During the 1980s, the increase of concentrations in the HFS was faster than in the LFS, which changed the C–Q pattern to a strongly positive one ($b_{max}$=0.42, 1987; red to orange symbols in Fig. 6e). This development was characterized by a tripling of intra-annual amplitudes ($C_{spring} - C_{fall}$) of up to 2.4 mg $L^{-1}$ (1987). With a lag of around 10 years, in the 1990s also the LFSs exhibit a strong increase in concentrations ($C_{max}$= 3.1 mg $L^{-1}$, 1998, Fig. 6b). The midstream concentration time series shows bimodality. The C–Q relationships (Fig. 6e) evolved from an intensifying accretion pattern in the 1970s and 1980s (red to orange symbols in Fig. 6e) to a constant pattern between C and Q in the 1990s and afterwards (yellow symbols). The $CV_C/CV_Q$ increased during the 1970s and decreased afterwards strongly by 0.4 between 1984 and 1995, showing a trajectory starting from a more chemostatic to a chemodynamic, and then back to a chemostatic export regime.

Kommentar [SE38]: Ref2 No.27

At the downstream station (Fig. 6c) the concentrations in the HFSs were found to be comparable to the ones observed at the midstream station. As seen Midstream, the N concentrations during the LFSs peaked with a delay compared to those of the HFSs. The resulting intra-annual amplitude showed a maximum of 2.4 mg $L^{-1}$ in the 1980s (1983/84), with strongly positive C–Q patterns ($b_{max}$= 0.4, 1985; red symbols in Fig. 6f). In contrast to the bimodal concentration trends in the mid- and downstream HFSs, the LFSs Downstream showed an unimodal pattern peaking around 1995/96 with concentrations above 6 mg $L^{-1}$ $NO_3$-N ($C_{max}$=6.9 mg $L^{-1}$). In the 1990s, the concentrations in the LFSs were higher than those noticed in the HFSs causing a switch to a dilution C–Q pattern (orange symbols in Fig. 6f). Due to the strong decline of LFSs concentrations after 1995 (Fig. 6c), the dilution pattern evolved to a constant C–Q pattern (yellow symbols in Fig. 6f) from the 2000s onward. After an initial phase with chemostatic conditions (1970s), the $CV_C/CV_Q$ strongly increased to a chemodynamic export regime in the 1980s (max. $CV_C/CV_Q$=0.8, 1984). Later on $CV_C/CV_Q$ declined by 0.8 between 1984 and 2001 (min. $CV_C/CV_Q$=0.03), which indicate the C–Q trajectory is coming back to a chemostatic export nitrate regime.

## 4 Discussion

### 4.1 Catchment scale N budgeting

Based on the calculated budgets of N inputs and riverine N outputs for the three sub-catchments within the Holtemme catchment, we discuss here differences between the sub-catchments and potential reasons for the missing part in the N budget: 1) permanent N removal by denitrification or 2) the build-up of N legacies.

The N load stemming from the most upstream, pristine catchment accounted for less than 10 % of the exported annual load over the entire study period. This minor contribution can be attributed to the lack of agricultural and urban land use as dominant sources for N. Consequently, the N export from the upstream sub-catchment was dominantly controlled by N inputs from atmospheric deposition. As the cumulated export over the observation period was higher than the assumed input, the estimation of a retention potential was not possible in this case. This might be explained by unaccounted N sources, e.g. stemming from minor anthropogenic activities in the sub-catchment. Moreover, the assumed constant biological N fixation as described by Cleveland et al. (1999), may have led to an underestimation of the net N input into the system.

Kommentar [SE39]: Ref2 No.29

Kommentar [AM40]: Ref2 No. 30

The total input over the whole catchment area was quantified as almost 43 000 t N (1976–2015) and compared to the respective output over the same time period yielded export rates of 54 % (47–62 %) at the midstream and 15 % (14–18 %) at the downstream station (Table 3), respectively. There can be several reasons for the difference in export rates between the two sub-catchments. The most likely ones are due to differences in discharge, topography and denitrification capacity among the sub-catchments, which are discussed in the following.

Load export of N from agricultural catchments is assumed to be mainly discharge-controlled (Basu et al., 2010). Many solutes show a lower variance in concentrations compared to the variance in stream flow, which makes the flow variability a strong surrogate for load variability (Jawitz & Mitchell, 2011). This can also be seen in the Holtemme catchment, which evolved over time to a more chemostatic export regime with high N loads (Fig. 6b). Highest N export and lowest retention were observed in the midstream sub-catchment, where the overall highest discharge contribution can be found.

Besides discharge-quantity, we argue that the midstream sub-catchment favors a more effective export of $NO_3$-N. The higher percentage of artificial drainage by tiles and ditches (59 % vs. 21 %; supplement, S1.1) as well as the steeper terrain slopes (3.2° vs. 1.9°) in the non-forested area of the midstream catchment, promote rapid, shallow subsurface flows. These flow paths can more directly connect agricultural N sources with the stream and in turn cause elevated instream $NO_3$-N concentrations (Yang et al., 2018). In addition, the steeper surface topography suggests a deeper vertical infiltration (Jasechko et al., 2016) and by that a wider range of flow paths of different ages than those observed in the flatter terrain areas. Vice versa, fewer drainage installations, a flatter terrain and thus in general shallower flow paths may decrease the N export efficiency (increase the retention) potential Downstream.

The only process able to permanently remove N input from the catchment is denitrification in soils, aquifers (Seitzinger et al., 2006; Hofstra & Bouwman, 2005), and at the stream-aquifer interface such as in the riparian (Vidon & Hill, 2004; Trauth et al., 2018) and hyporheic zones (Vieweg et al., 2016). As the riverine exports are signals of the catchment or sub-catchment processes, integrated in time and space, separating a build-up of an N legacy from a permanent removal via denitrification is difficult. A clear separation of these two key processes, however, would be important for decision makers as both have different implications for management strategies and different future impacts on water quality. Even if groundwater quality measurements were available that indicate denitrification, using this type of local information for an effective catchment scale estimation of N removal via denitrification would be challenging (Green et al., 2016; Otero et al., 2009; Refsgaard et al., 2014). Therefore, we discuss the denitrification potential in the soils and aquifers of the Holtemme catchment based on a local isotope-study and a literature review of studies in similar settings. A strong argument against a dominant role of denitrification is provided by Müller et al. (2018) for the study area. On the basis of a monitoring of nitrate isotopic compositions in the Holtemme River and in tributaries, Müller et al. (2018) stated that denitrification played no or only a minor role in the catchment. However, we still see the need to carefully check the potential of denitrification to explain the input-output imbalance considering other studies.

If 85 % of the N input (42 758 t, dominantly agricultural input) to the catchment between 1976 and 2015 (39 years) were denitrified in the soils of the agricultural area (161 km²), it would need a rate of 57.9 kg N $ha^{-1}$ $a^{-1}$. Considering the derived TTs, denitrification of the convolved input would need the same rate (58 kg N $ha^{-1}$ $a^{-1}$, 1976–2015). Denitrification rates in soils for Germany (NLfB, 2005) have been reported to range between 13.5–250 kg N $ha^{-1}$ $a^{-1}$, with rates larger than 50 kg N

Kommentar [SE41]: Ref2 No.32

Kommentar [AM42]: Ref1 No. 4

ha$^{-1}$ a$^{-1}$ may be found in carbon rich and waterlogged soils in the riparian zones near rivers and in areas with fens and bogs (Kunkel et al., 2008). As water bodies and wetlands make up only 1 % of the catchment's agricultural land use (Fig. 1; EEA, 2012), and consequently the extent of waterlogged soils is negligible, denitrification rates larger than 50 kg N ha$^{-1}$ a$^{-1}$ are highly unlikely. In a global study, Seitzinger et al. (2006) assumed a rate of 14 kg N ha$^{-1}$ a$^{-1}$ as denitrification for agricultural soils. With this rate only 24 % of the retained (85 %) study catchment's N input can be denitrified. On the basis of a simulation with the modeling framework GROWA-WEKU-MEPhos Kuhr et al. (2014) estimates very low to low denitrification rates, of 9–13 kg N ha$^{-1}$ a$^{-1}$, for the soils of the Holtemme catchment. Based on the above discussion we find for our study catchment, the denitrification in the soils, including the riparian zone, may partly explain the retention of $NO_3$-N, but is unlikely to be a single explanation for the observed imbalance between in- and output.

Regarding the potential for denitrification in groundwater, the literature provides denitrification rate constants of a first order decay process between 0.01–0.56 year$^{-1}$ (van Meter et al., 2017b; van der Velde et al., 2010; Wendland et al., 2005). We derived the denitrification constant by distributing the input according to the fitted log-normal distribution of TTs assuming a first order decay along the flow paths (Kuhr et al., 2014; Rode et al., 2009; van der Velde, 2010). The denitrification of the 85 % of input mass would require a rate constant of 0.12 year$^{-1}$. This constant is in the range of values reported by mentioned modelling studies. However, in a regional evaluation of groundwater quality, Hannappel et al. (2018) provide strong evidence that denitrification in the groundwater of the Holtemme catchment is not a dominant retention process. More specifically, Hannappel et al. (2018) assess denitrification in over 500 wells in the federal state Saxony-Anhalt for nitrate, oxygen, iron concentrations and redox potential and connects the results to the hydrogeological units. Within the hard rock aquifers that are present in our study area, only 0–16 % of the wells showed signs of denitrification. Taking together the local evidence from the nitrate isotopic composition (Müller et al., 2018), the regional evidence from groundwater quality (Hannappel et al., 2018) and the rates provided in literature for soils and groundwater, we argue that the role of denitrification in groundwater is unlikely to explain the observed imbalance between N input and output.

**Kommentar [SE43]:** Ref2, No.34; Ref1 No. 4

Lastly, assimilatory $NO_3$ uptake in the stream may be a potential contributor to the difference between in- and output. But even with maximal $NO_3$ uptake rates as reported by Mulholland et al. (2004; 0.14 g N m$^{-2}$ d$^{-1}$) or Rode et al. (2016; max. 0.27 g N m$^{-2}$ d$^{-1}$; estimated for a catchment adjacent to the Holtemme), the annual assimilatory uptake in the river would be a minor removal process, estimated to contribute only 3.2 % of the 85 % discrepancy between in- and output. According to the rates reported by Mulholland et al. (2008; max. 0.24 g N m$^{-2}$ d$^{-1}$), the Holtemme River would need a 35-times larger area to be able to denitrify the retained N. Therefore denitrification in the stream can be excluded as a dominant removal process.

In summary, the precise differentiation between the accumulation of an N legacy and removal by denitrification cannot be fully resolved on the basis of the available data. Also a mix of both may account for the missing 85 % (82–86 %, Downstream) or 46 % (38–53 %, Midstream) in the N output. Input-output assessments with time series from different catchments, as presented in van Meter & Basu (2017), covering a larger variety of catchment characteristics, hold promise for an improved understanding of the controlling parameters and dominant retention processes.

The fact that current $NO_3$ concentration levels in the Holtemme River still show no clear sign of a significant decrease, calls for a continuation of the $NO_3$ concentration monitoring, best extended by additional monitoring in soils and groundwater. Despite strong reductions in agricultural N input since the 1990s, the annual N-surplus (e.g. 818 t $a^{-1}$, 2015) is still much higher than the highest measured export ($load_{max}$ = 216 t $a^{-1}$, 1995) from the catchment. Hence, the difference between in- and output is still high with a mean factor of 4 during the past 10 years (mean factor of 5 with the shifted input according to 12 years of TT). Consequently, either the legacy of N in the catchment keeps growing instead of getting depleted or the system relies on a potentially limited denitrification capacity. Denitrification may irreversibly consume electron donors like pyrite for autolithotrophic denitrification or organic carbon for heterotrophic denitrification (Rivett et al., 2008).

Based on the analyses and literature research, there is evidence but no proof on the fate of missing N, although a directed water quality management would need a clearer differentiation between N mass that is stored or denitrified. Though, neither tolerating the growing build-up of legacies nor relying on finite denitrification represents sustainable and adapted agricultural management practice. Hence, also future years will face increased $NO_3$-N concentrations and loads exported from the Holtemme catchment.

**Kommentar [SE44]:** Ref2, No.35

### 4.2 Linking effective TTs, concentrations and C–Q trajectories with N legacies

Based on our data-driven analyses, we propose the following conceptual model (Fig. 7) for N export from the Holtemme catchment, which is able to plausibly connect and synthesize the available data and findings on TTs, concentration trajectories and C–Q relationships and, allows for a discussion on the type of N legacy.

**Kommentar [AM45]:** Ref1 No. 2

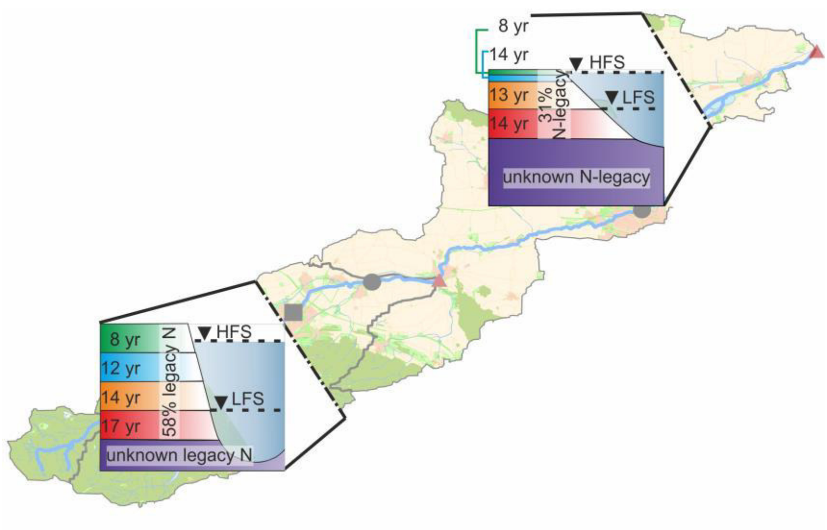


**Figure 7: Conceptual model. Hypothetical intra-annual discharge contribution (numbers indicating peak TTs) in different depths and changing water levels (black triangles) during low flow seasons (LFS) and high flow seasons (HFS). The colour of the boxes refers to the seasons as used in Fig. 6a–c.**

Over the course of a year, different subsurface flow paths are active, which connect different subsurface N source zones with different source strength (in terms of concentration and flux) to streams. These flow paths transfer water and $NO_3$-N to streams, predominantly from shallower parts of the aquifer when water tables are high during HFSs and exclusively from deeper groundwater during low flows in LFSs (Rozemeijer & Broers, 2007; Dupas et al., 2016; Musolff et al., 2016). This conceptual model allows us to explain the observed intra-annual concentration patterns and the distinct clustering of TTs into low flow and high flow conditions. Furthermore, it can explain the mobilization of nutrients from spatially distributed $NO_3$-N sources by temporally varying flow-generating zones (Basu et al., 2010). Spatial heterogeneity of solute source zones can be a result of downward migration of the dominant $NO_3$-N storage zone in the vertical soil-groundwater profile (Dupas et al., 2016). Moreover, a systematic increase of the water age with depths would, if denitrification in groundwater takes place uniformly, lead to a vertical concentration decrease. Based on the stable hydroclimatic conditions without changes in land use, topography or the river network during the observation period, long-term changes of flow paths in the catchment are unlikely. Assuming that flow contributions from the same depths do not change between the years, the observed decadal changes in the seasonal concentrations cannot be explained by a stronger imprint of denitrification with increasing water age. Under such conditions one would expect a more steady seasonality in concentrations and C–Q patterns over time with $NO_3$-N concentrations that are always similarly high in HFSs and similarly low in LFSs, which we do not see in the data. Additionally, previous findings have indicated no or only a minor role of denitrification in the catchment (Hannappel et al., 2018; Kunkel et al., 2008; Müller et al. 2018). In line with Dupas et al. (2016) we instead argue that the vertical migration of

**Kommentar [SE46]:** Ref2, No.38

a temporally changing $NO_3$-N input is one of the most likely plausible explanations for our observations with regards to N budgets, concentrations and C–Q trajectories.

The faster TTs observed at the midstream station during HFSs are assumed to be dominated by discharge from shallow (near-surface) source zones. This zone is responsible for the fast response of instream $NO_3$-N concentrations to the increasing N inputs (1970s to mid-1980s). This faster lateral transfer especially in spring (shortest TT) may be also enhanced by the presence of artificial drainage structures such as tiles and ditches. In line with the longer TTs during the LFSs, low flow $NO_3$-N concentrations were less impacted in the 1970s to mid-1980s as deeper parts of the aquifer were still less affected by anthropogenic inputs. With ongoing time and a downward migration of the high $NO_3$-N inputs before 1990, also those deeper layers and thus longer flow paths delivered increased concentrations to the stream (1990s). In parallel with the increasing low flow concentrations (in the 1990s), the spring concentrations of $NO_3$ decreased caused by a depletion of the shallower $NO_3$-N stocks (see also Dupas et al., 2016; Thomas & Abbott, 2018). This depletion of the stock was a consequence of drastically reduced N input after the German reunification in 1989. This conceptual model of N trajectories is supported by the changing C–Q relationship over time. The seasonal cycle started with increasing $NO_3$-N maxima during high flows and minima during low flows, since firstly shallow source zones were getting loaded with $NO_3$. Consequently, the accretion pattern was intensified in the first decades accompanied by an increase of $CV_C/CV_Q$. The resulting positive C–Q relationship on a seasonal basis was found in many agricultural catchments worldwide (e.g. Aubert et al., 2013; Martin et al., 2004; Mellander et al., 2014; Rodriguez-Blanco et al., 2015; Musolff et al. 2015). However, after several years of deeper migration of the N input, the catchment started to exhibit a chemostatic $NO_3$-N export regime (after 1990s), which was manifested in the decreasing $CV_c/CV_Q$ ratio. This stationarity could have been caused by a vertical equilibration of $NO_3$-N concentrations in all seasonally activated depth zones of the soils and aquifers after a more stable long-term N input after 1995. According to the 50$^{th}$ percentile of the derived TT, after 16 years only 50 % of the input had been released Midstream. Therefore without any strong changes in input, the chemostatic conditions caused by the uniform, vertical $NO_3$-N contamination will remain. At the same time, this chemostatic export regime supports the hypothesis of an accumulated N legacy rather than denitrification as dominant reason for the imbalance between in- and output.

At the downstream station, the riverine $NO_3$ concentrations during high flows were dominated by inputs from the midstream sub-catchment, which explains the similarity with the midstream bimodality in concentrations as well as the comparable TTs. The reason for these dominating midstream flows is the strong precipitation gradient resulting runoff gradient on the leeward side of the mountains. During low flows, the downstream sub-catchment can contribute much more to discharge and therefore to the overall N export. During the LFSs, we observed higher $NO_3$-N concentrations with a unimodal trajectory, and shorter TTs compared to the midstream sub-catchment. We argue that the lowland sub-catchment supports higher water levels and thus faster TTs during the low flows. Greater prevalence of young age streamflow in flatter lowland terrain was also described by Jasechko et al. (2016). But besides the earlier peak time during low flows, the concentration was found to be much higher than Midstream. To cause such high intra-annual concentration changes, the downstream $NO_3$-N load contribution, e.g. during the concentration peak 1995/96, had to be high: the summer season export was 46 t, which is more

**Kommentar [SE47]:** Ref1, No.26

**Kommentar [AM48]:** Ref1, No.20

than twice the median contribution during summer (22 t). A more effective export from the downstream catchment happened mainly during LFSs, which is also supported by the narrower TTD (small shape factor σ) in the summer (Fig. 5b). The difference between the 75$^{th}$ and 25$^{th}$ percentiles (7 years) was also the smallest of all seasons in the summer at the downstream station. This could be one reason for the high concentrations in comparison to the midstream catchment and during the HFSs.

In contrast to the midstream catchment, the C–Q trajectory in the downstream catchment temporarily switched from an enrichment pattern, dominated by the high concentration during high flows from Midstream to a dilution pattern and a chemodynamic regime, when the high concentrations in the LFS from the downstream sub-catchment dominated. Although the low flow concentrations were slowly decreasing in the 2000s and 2010s, also the downstream catchment finally evolved to a chemostatic $NO_3$ export regime as noticed Midstream (Fig. 6f).

Our findings support the evolution from chemodynamic to chemostatic behaviour in managed catchments, but also emphasize that changing inputs of N into the catchment can lead to fast changing export regimes even in relatively slowly reacting systems. Our findings expand on previous knowledge (Basu et al., 2010; Dupas et al., 2016) as we could show systematic inter-annual C–Q changes that are in line with a changing input and a systematic seasonal differentiation of TTs. Although our study showed chemostatic behaviour towards the end of the observation period (Mid- and Downstream; Fig. 6e–f), this export regime is not necessarily stable as it depends on a continuous replenishment of the legacy store. Changes in the N input translate to an increase of spatial heterogeneity in $NO_3$-N concentrations in soil- and groundwater with contrasting water ages. The seasonal changing contribution of different water ages thus results in more chemodynamic $NO_3$-N export regimes. As described in Musolff et al. (2017) both, export regimes and patters are therefore controlled by the interrelation of TT and source concentrations. We argue that a hydrological legacy of $NO_3$-N in the catchment has been established that resulted in a pseudo-chemostatic export behaviour we observe nowadays. This supports for a notion that a biogeochemical legacy corresponding to the build-up of organic N in the root zones of the soil (van Meter et al., 2016) is less probable. If we assume that all of the 84 % of the N input is accumulating in the soils, we cannot explain the observed shorter-term inter-annual concentration changes and trajectory in the C–Q relationships. We would rather expect a stronger and even growing dampening of the N input to the subsurface with the build-up of a biogeochemical legacy in form of organic N. However, we cannot fully exclude the accumulation of a protected pool of soil organic matter with very slow mineralization rates as described in van Meter et al. (2017). Our conceptual model assigns the missing N to the long TTs of $NO_3$-N in soil- and groundwater and in turn to a pronounced hydrological legacy. In the midstream sub-catchment, the estimated TTD explains 58 % of the retained $NO_3$-N, comparing the convolution of TTD with the N input time series to the actual riverine export. The remaining 42 % cannot be fully explained at the moment and may be assigned to a permanent removal by denitrification (see discussion above), to a fixation due to biogeochemical legacy, or to more complex e.g. longer tailed TTDs, which are not well represented by our assumed log-normal distribution. In the downstream sub-catchment, our approach explains 31 % of the observed export. This could in principle be caused by the same processes as described for the midstream sub-catchment. However, in the downstream sub-catchment we assume a hydrological legacy store in deeper zones without significant discharge contribution (Fig. 7). That mass of N is either bypassing the downstream monitoring station (note that the downstream station is still 3 km upstream of the Holtemme catchment outlet) or is affected by a strong time delay and dampening not captured by our approach. Consequently, future changes in N inputs will also change the future export patterns and regimes, since this would shift the homogeneous $NO_3$-N distributions in vertical soil and groundwater profiles back to more heterogeneous ones.

## 5 Conclusion

In the present study we used a unique time series of riverine N concentrations over the last four decades from a mesoscale German catchment as well as estimated N input and to discuss the linkage between the two on annual and intra-annual time scales. From the input-output assessment, the build-up of a potential N legacy was quantified, effective TTs of nitrate were estimated and the temporal evolution to chemostatic $NO_3$-N export was investigated. This study provides four major findings that can be generalized and transferred to other catchments of similar hydroclimatic and landscape settings as well.

First, the retention capacity of the catchment for N is 85 % of the N input (input and output referring to 1976 to 2015), which either can be stored as a legacy or denitrified in the terrestrial or aquatic system. Although we could not fully quantify denitrification, we argue that this process is not the dominant one in the catchment to explain input-output differences. The observed N retention can be more plausibly explained by legacy than by denitrification. In consequence, the hydrological N legacy, i.e. the load of nitrate still on the way to the stream, may have strong effects on future water quality and long-term implications for river water quality management. With a median export rate of 162 t N $a^{-1}$ (1976–2016, downstream station, 6 kg N $ha^{-1}$ $a^{-1}$), a depletion of this legacy (< 36 000 t N) via baseflow would maintain elevated riverine concentrations for the next decades. Although N-surplus strongly decreased after the 1980s, during the past 10 years there still was, an imbalance between agricultural input and riverine export by a mean factor of 5 (assuming the temporal offset of peak TTs between in- and output of 12 years). This is a non-sustainable condition, regardless of whether the retained nitrate is stored or denitrified. Export rates as well as retention capacity derived for this catchment were found to be comparable to findings of other studies in Europe (Worrall et al., 2015; Dupas et al., 2015) and North America (van Meter et al., 2016).

Kommentar [AM49]: Ref1 No. 3

Secondly, we derived peak time lags between N input and riverine export between 9–17 years with systematic differences among the different seasons. Catchment managers should be aware of these long time frames when implementing measures and when evaluating them. This study explains the seasonally differing lag times and temporal concentration evolutions with the vertical migration of the nitrate and their changing contribution to discharge by seasonally changing aquifer connection. Hence, inter-annual concentration changes are not dominantly controlled by inter-annually changing discharge conditions, but rather by the seasonal changing activation of subsurface flows with differing ages and thus differing N loads. As a consequence of this activation-dependent load contribution, an effective, adapted monitoring needs to cover, different discharge conditions when measures shall be assessed for their effectiveness. In the light of comparable findings of long time lags (van Meter & Basu, 2017; Howden, 2011), there is a general need for sufficient monitoring length and appropriate methods for data evaluation like the seasonal statistics of time series.

Third, in contrast to a more monotonic change from a chemodynamic to a chemostatic nitrate export regime that was observed previously (Dupas et al., 2016; Basu et al., 2010), this study found a systematic change of the nitrate export regime from accretion over dilution to chemostatic behavior. Here, we can make use of the unique situation in East-German catchments where the collapse of agriculture in the early 1990s provided a large scale "experiment" with abruptly reduced N inputs. While previous studies could not distinguish between biogeochemical and hydrological legacy to cause chemostatic export behavior, our findings support for a hydrological legacy in the study catchment. The systematic inter-annual changes of C–Q relationships of $NO_3$-N were explained by the changes in the N input in combination with the seasonally changing effective TTs of N. The observed export regime and pattern of $NO_3$-N suggest a dominance of a hydrological N legacy over the biogeochemical N legacy in the upper soils. In turn, observed trajectories in export regimes of other catchments may be an indicator of their state of homogenization and can be helpful to classify results and predict future concentrations.

**Kommentar [SE50]:** Ref1 No.27

Fourth, although we observed long TTs, significant input changes also created strong inter-annual changes in the export regime. The chemostatic behavior is therefore not necessarily a persistent endpoint of intense agricultural land use, but depends on steady replenishment of the N store. Therefore, the export behavior can also be termed pseudo-chemostatic and may further evolve in the future (Musolff et al., 2015) under the assumptions of a changing N input. Depending on the legacy size, a significant reduction or increase of N input can cause an evolution back to more chemodynamic regimes with dilution or enrichment patterns. Simultaneously, input changes affect the homogenized vertical nitrate profile, resulting in larger intra-annual concentration differences and consequently chemodynamic behavior. Hence, chemostatic behavior and homogenization may be characteristics of managed catchments, but only under constant N input.

**Kommentar [SE51]:** Ref1 No.28

Recommendations for a sustainable management of N pollution in the studied Holtemme catchment, also transferable to comparable catchments, focus on the two aspects.

- Our findings could not prove a significant loss of $NO_3$-N by denitrification. To deal with the past inputs and to focus on the depletion of the N legacy, end-of-pipe measures such as hedgerows around agricultural fields (Thomas & Abbott, 2018), riparian buffers or constructed wetlands may initiate N removal by denitrification (Messer et al., 2012).
- We could show that there is still an imbalance of N input and riverine export by a mean factor of 5. A reduced N input due to better management of fertilizer and the prevention of N losses from the root zone in present time is indispensable to enable depletion instead of a further build-up or stabilization of the legacy.

The combination of N budgeting, effective TTs with long-term changes in C–Q characteristics proved to be a helpful tool to discuss the build-up and type of N legacy at catchment scale. This study strongly benefits from the availability of long time series in nested catchments with a hydroclimatic and land-use gradient. This wealth of data may not be available everywhere. However, we see the potential to transfer this approach to a much wider range of catchments with long-term observations for understanding the spatial and temporal variation and type of legacy build-up, denitrification and TTs as well as their

**Kommentar [AM52]:** Ref1 No. 3

controlling factors. Data-driven analyses of differing catchments covering a higher variety of characteristics may provide a more comprehensive picture of N trajectories and their controlling parameters. In addition to data-driven approaches emphasis should also be put on robust estimations of water TT in catchments to constraint reaction rates. Recent studies present promising approaches to derive TTs in groundwater (Marcais et al., 2018; Kolbe et al., 2019) and at catchment scale (Jasechko et al., 2016; Yang et al., 2018)

**Data availability**

Discharge data (for all dates) and water quality data (from 1993) can be accessed at the websites of the State Office of Flood Protection and Water Management (LHW) Saxony-Anhalt (http://gldweb.dhi-wasy.com/gld-portal/). Atmospheric deposition data between 1995 and 2015 can be accessed at the website of the Meteorological Synthesizing Centre - West (MSC-W) of the European Monitoring and Evaluation Programme (EMEP) (http://www.emep.int/mscw/index_mscw.html) that is assigned to the Meteorological institute of Norway (MET Norway).

**Author contribution**

SE carried out the analysis, interpreted the data and wrote the manuscript. AM designed the study and co-wrote the manuscript. RK contributed discharge modelling results and atmospheric deposition and co-wrote the manuscript.
JHF and SA contributed to the study design and helped finalizing the manuscript.

**Competing interests**

The authors declare no conflict of interest.

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