# Response to referee #1

**We thank referee #1 for once again for the helpful advise and hope that we have satisfactorily address all concerns.**

**Recommendation to the editor**

**Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)**

This is my second review of this paper. The authors have properly addressed most of my original concerns. My only major comment is to better organize the section on interpreting the clusters, preferably with a visualization. I think this would help with the interpretability of the hypothesized controls of the clusters and would make a powerful contribution.
**A figure (Figure 7) was added that leads through the interpretation of clusters in the discussion section.**
Other minor comments are below.

Line 28: End the abstract with a broad conclusion statement.
**Done (l. 19-20)**
Line 145: How did the water authority measure discharge? At least list the method.
**Done (l. 92)**
Line 287: It still isn't clear to me where the 95% CI come from. A model (time-series, regression, etc.) must have been used to get these values, and I don't see anything about a model in the methods.
**The intervals show the spread of the original data. No model is involved. In order to avoid misunderstanding, we decided to show the individual recordings instead of shaded areas in a modified version of figure 2.**
Line 325/ Figure 4: This is still challenging to interpret. If the points were close to the shaded area does that mean that transport dictated the difference in NO3 between sites. In other words, when the values are less than the shaded area, differences in NO3 between sites are caused by in-stream processes. Please add a line in the caption that describes the main conclusion to take away from this graph.
**D We added the sentence** *"Points falling below the shaded areas indicate in-stream control on diel NO3- patterns, whereas points within the range of travel time estimates suggest transport control"* **to the figure caption.**
Also, the authors have not addressed my comment about how its possible to have a negative travel time.
**Travel times cannot not be negative, but time lags produced by cross-correlation can. We removed the misleading axis label and added information to the figure caption.**
Line 563: Yes, if GW N inputs are constant, they shouldn't affect the signal (shape of the diel curve). Although, GW N inputs would mess with your interpretation of transport vs. in-stream processes. I would talk about that here.
**We understand diffuse groundwater inputs as features of a longer stream reach (as opposed to point sources). In our differentiation between in-stream and transport control, we consider them as in-stream condition. We clarified this in the introduction (l 53-55.):**

*"In this sense, we use the term 'in-stream' to refer to average properties of a reasonably long stream reach and its immediate surroundings including biochemical conditions in the stream and in the hyporheic zone as well as diffuse groundwater interaction."*

Line 564: What does longitudinally stable mean? It implies stability over space, say between sensors, but that doesn't fit with the context of this sentence. Do you mean stabile in time, e.g., a similar pattern over multiple days? Please describe.

**The concept of longitudinal stability is introduced in the methods section (l. 116-118). We further clarified the sentence in question. It now reads:** *"Yet, the influence on patterns in the main stream must have been small as the patterns were usually longitudinally stable, i.e. the same upstream (S1) and downstream (S2) of the tributary."* **(l.259-260)**

Line 585-589: I would remove this reference. If there is no riparian vegetation in your stream this is irrelevant.

**Done**

Line 603: How would diel temperature variation affect denitrification and not nitrification? This correlation should be described more fully.

**We reworked our interpretation of clusters C to E including our hypothetical explanations for the clusters. The section now reads:**

*" Patterns with a midday maximum such as those observed in cluster C are hard to explain by photoautotrophic assimilation 315 alone in systems without intense seasonal shading by riparian vegetation (as opposed to e.g. Rusjan and Mikoš (2010)). Figure 7 (a, b, c, f) shows that $NO_3^-$ peak time gradually shifts towards midday when photoautotrophic assimilation decreases and the relative importance of a $NO_3^-$ depleting process negatively related with temperature increases. This suggests that either denitrification or heterotrophic assimilation or both are promoted by stream temperature and drive the shape of the signal. Diel variability has been observed both in denitrification (Christensen et al., 1990; Harrison et al., 2005; Cohen et al., 2012) and 320 heterotrophic respiration (Hotchkiss and Hall, JR., 2014) which is closely linked to heterotrophic $NO_3^-$ assimilation. However, peak $NO_3^-$ depletion occurs in the afternoon, when oxygen levels are expected to be elevated and unfavorable for anaerobe denitrification (Rysgaard et al., 1994). In addition, it is not clear how denitrification in the lower anoxic sediments could be promoted by temperature without simultaneously increasing nitrification in the upper sediment layers. However, it seems possible that the driving force of cluster C was not temperature but another process with similar diel pattern. Exudation of 325 algal photosynthate rich in labile organic carbon (Kaplan and Bott, 1982) may have a similar diel course and stimulate assimilation and denitrification by heterotrophs but not nitrification by autotrophs. Under such conditions, heterotrophic assimilation or denitrification or both may drive diel $NO_3^-$ fluctuation in cluster C.*

*In literature, diel patterns with a $NO_3^-$ peak in the afternoon (cluster D) have been attributed to intense evapotranspiration (Aubert and Breuer, 2016; Flewelling et al., 2014; Lupon et al., 2016a). In the present study, evapotranspiration was not 330 measured, however, it did not produce systematic diel fluctuations in water level and the latter were not correlated with diel $NO_3^-$ signals. Such patterns could also not be reproduced by overlaying rates of light-dependent and temperature-dependent processes (Fig. 7). An explanation for cluster D is therefore still warranted.*

*Diel patterns with a midday low (cluster E) could be the result of low photoautotrophic assimilation and a temperature-dependent $NO_3^-$ producing processes like nitrification (Fig. 7g). Diel variability in nitrification is well documented (Warwick, 335 1986; Laursen and Seitzinger, 2004; Dunn et al., 2012) and it seems principally plausible that temperature promotes*

*nitrification without influencing denitrification in deeper anoxic sediment layers. Another reason for independence of nitrification and denitrification may be limitation of heterotrophic denitrification in absence of an organic carbon source. " (l.315-338)*

Also, what about the possibility of diel changes in heterotrophic respiration (see: Hotchkiss and Hall 2014, https://doi.org/10.4319/lo.2014.59.3.0798) . How might that describe some of the clusters?

**Thank your for this hint. Heterotrophic respiration is now part of our hypotheses and is considered to potentially explain cluster C. S. above**

Line 608-609: But above you seem definitive that diel changes in lateral inputs are negligible. Which one is it?

**Based on water level measurements, potential diel variability in hydraulic gradient between groundwater and stream water was minimal. This is now stated in lines 329-333:**
*" In literature, diel patterns with a $NO_3^-$ peak in the afternoon (cluster D) have been attributed to intense evapotranspiration (Aubert and Breuer, 2016; Flewelling et al., 2014; Lupon et al., 2016a). In the present study, evapotranspiration was not measured, however, it did not produce systematic diel fluctuations in water level and the latter were not correlated with diel $NO_3^-$ signals. Such patterns could also not be reproduced by overlaying rates of light-dependent and temperature-dependent processes (Fig. 7). A satisfactory explanation for cluster D is therefore still needed."*

Lines 585-615: Thank you for toning down the language about the causes of the diel patterns. However, this section seems to have lost its teeth. You are definitely on the right track in using nitrification and denitrification to explain the clusters that aren't closely related with autotrophic based assimilation, but the current explanation is disjointed and could use some organization.
I suggest creating a conceptual diagram/figure with hypotheses about the controls on each cluster, and using this figure to write about each cluster in this section. Frame it as hypotheses that readers can use in their research to pursue controls on diel trends that they see. I think this would be very powerful and useful for folks that use diel data. You are on the right track, I just think a little organization and a visualization would make what you are describing more obvious and insightful.

**A corresponding figure and introductory text was added (l. 281-295):**
*" In the following, we therefore aim to interpret our findings based on in-stream processes. In terms of biochemical processes, diel $NO_3^-$ variability depends on the time-varying balance of $NO_3^-$ removal (via assimilation by both heterotrophs and autotrophs as well as denitrification) and $NO_3^-$ production (via mineralization and subsequent nitrification). We do not regard our interpretations on the controls of the observed patterns complete but as hypotheses for further research on diel dolute patterns to build upon. Considering the idea of multiple superposed biochemical processes as a starting point, some assumptions can be made on the diel course of the processes mentioned above. Photoautotrophic assimilation depends on the light availability and can be conceptualized as a function of solar irradiance. In contrast, the degree of diel variability in nitrification, denitrification, and heterotrophic assimilation is less clear. However, we generally assume that the rate of microbial metabolism (besides other influences) increases with temperature. Figure 7 schematically illustrates the diel concentration signals resulting from overlaying the diel courses of light-dependent photoautotrophic ($r_{aa}$) assimilation and a complementary temperature-dependent processing rate ($r_{comp}$). The latter represents the combined net effect of heterotrophic assimilation, nitrification and denitrification. Particularly,*

*we consider different levels of light intensity (columns in Fig. 7) and different types of relationship with temperature (rows in Fig. 7), including positive and negative correlation with temperature as well as constant $r_{comp}$. The shapes of $r_{aa}$ and $r_{comp}$ reflect means over all measurements of global irradiance and water temperature, respectively, during the course of the present study. ”*

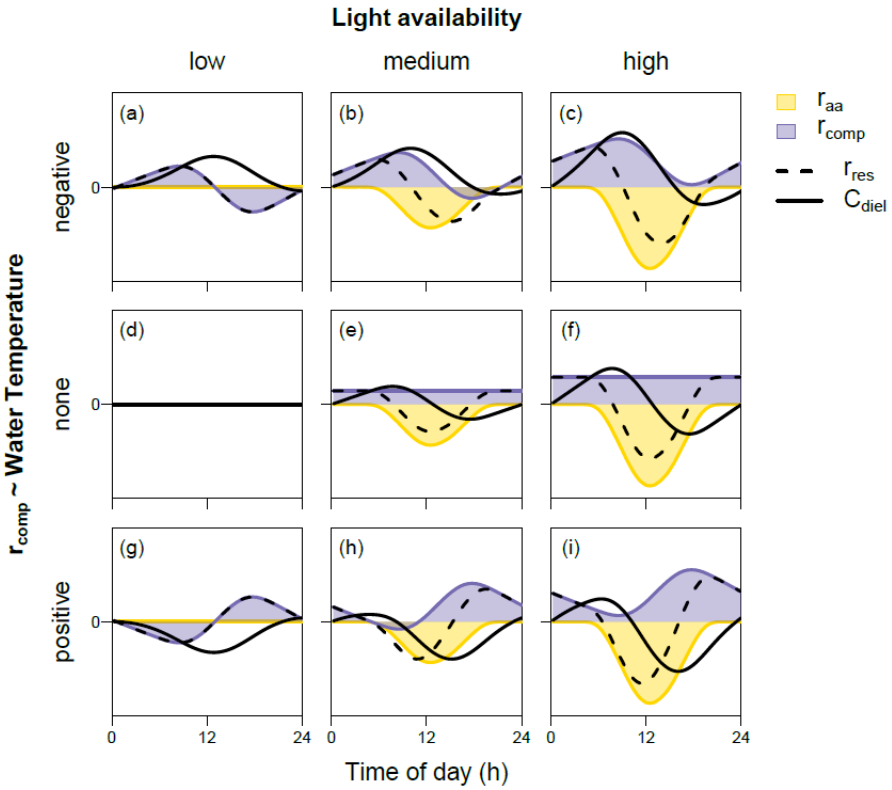


*Figure 1: Schematic representation of diel courses of assimilation rate ($r_{aa}$) and a complementary processing rate ($r_{comp}$) required to produce equilibrium conditions. Black lines show the resulting change rate ($r_{res}$) and concentration (C). While $r_{aa}$ is considered a function of global irradiance (columns represent different levels of irradiation intensity), $r_{comp}$ is conceptualized as a function of stream temperature (rows represent a negative (a-c), no relationship (d-f) and a positive relationship (g-i)).*

# Response to referee #2

**We thank referee #2 once again for the helpful advise and hope that we have satisfactorily address all concerns.**

**Recommendation to the editor**

**Suggestions for revision or reasons for rejection (will be published if the paper is accepted for final publication)**

I very much enjoyed reading this revised manuscript. The authors did an excellent job of responding to reviewer questions and concerns, and I find the paper much improved.

I still have some (very) minor comments and technical notes that I am sure the authors can easily solve.

Minor comments

1. I suggest a small **reordering in the methods and results**. In section 2.3.1., I would begin with seasonal patterns of stream nitrate concentrations and then move to diel patterns. (i.e. move lines 109-113 earlier in this section). Same in the results (i.e. move lines 167-176 at the beginning of section 3.1).
**The section have been reordered accordingly.**

2. Looking at Fig. 5, I wonder if it is possible to add **some test (i.e. ANOVA)** that support your results. This shouldn't be difficult to do, and it might support your rational.
**An ANOVA and post hoc Tukey HSD test were performed on the cluster data. Corresponding changes were made in the methods section (l. 144-146):**
*" Differences between clusters were statistically assessed using analysis of variance (ANOVA) and Tukey honestly significant difference (HSD) tests as implemented in the 'stats' R-package (R Core Team, 2019)."*
**, the results (l. 215-226),**
*" We found clear differences in the distribution of daily means of environmental parameters among clusters (Fig. 5). The following characterization of the clusters refers to significant differences ($p<0.05$) according to Tukey HSD test applied to an ANOVA on the cluster data. Cluster A presented overall lowest $NO_3^-$ concentrations (median 4.36 mg $L^{-1}$) which differed from those during cluster B (median 4.87 mg $L^{-1}$) and C (median 4.88 mg $L^{-1}$). Cluster A also showed the lowest water temperature (median 14.1 °C) and elevated water levels (median 41.9 cm) compared to cluster B and C. Cluster B was characterized by the highest global irradiance (median 825.0 W/m²), highest water temperature (21.7 °C) and lowest water levels (median 21.2 cm). Disregarding cluster F with only 3 data points, the difference in water temperature was significant for all remaining clusters. Global irradiance in cluster B differed from all clusters but C. Water level differed with all clusters but C and E. Cluster C occurred during very similar conditions as cluster B and only differed from cluster B in terms of water temperature (median 16.4 °C). The two clusters D and E were characterized by lower global irradiance than cluster*

*B and C and did not differ from one another. Cluster F consisted of only 3 days, but all of these represented water levels (median 77.2 cm) hardly ever observed in the remaining clusters."*
**and in figure 2:**

*"*

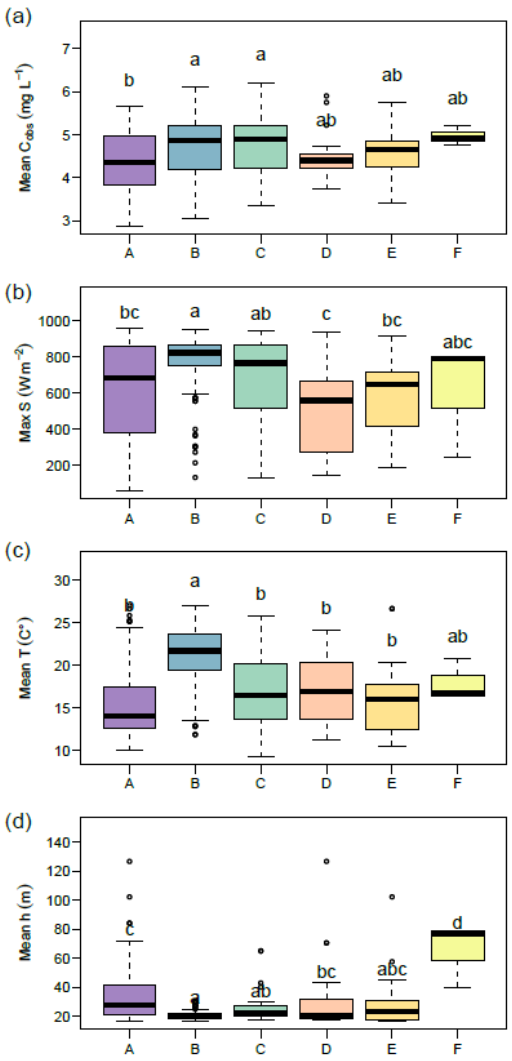


*Figure 2: Environmental conditions during occurrence of clusters. The panels show daily average $NO_3^-$ concentration (a), daily maximum of global irradiance (b), daily average water temperature (c), and daily average water level (d). Lowercase letters above boxplots were assigned to groups that do not differ significantly according to analyses of variance (ANOVA) and Tukey tests."*

3. Finally, I still have some minor concerns about the discussion.

First, **the section "lateral inputs" is not needed**. The first paragraph of this section can easily go to "General patterns", as the authors talk about how lateral inputs affect longitudinal patterns of stream nitrate concentrations at seasonal scale.
**The first paragraph was moved to the "general patterns" section (l.255-268)**

Similarly, the second paragraph links nicely to line 308, where the authors say that cluster D might be caused by intense evapotranspiration.

**The second paragraph was partly deleted due to redundancy with the interpretation of cluster D.**

Similarly, I think the section "in-stream vs transport" can easily fit in "interpretation of diel patterns".

**The section on "in-stream vs transport" now forms the first paragraph of the "interpretation of diel patterns" section (l. 270-280).**

The rational on how evapotranspiration influences diel patterns is confusing. The authors said that **intense evapotranspiration** can cause cluster D. However, the authors also said that there were no diel patterns of water level, which goes against the previous hypothesis. Please, clarify it.

**It is true that diel changes in water level were very minimal. We revised the paragraph on cluster D. We now refer to cases where similar observations were explained by evapotranspiration, but make clear that this was very unlikely in our study (l. 329-333):**

*" In literature, diel patterns with a $NO_3^-$ peak in the afternoon (cluster D) have been attributed to intense evapotranspiration (Aubert and Breuer, 2016; Flewelling et al., 2014; Lupon et al., 2016a). In the present study, evapotranspiration was not measured, however, it did not produce systematic diel fluctuations in water level and the latter were not correlated with diel $NO_3^-$ signals. Such patterns could also not be reproduced by overlaying rates of light-dependent and temperature-dependent processes (Fig. 7). A satisfactory explanation for cluster D is therefore still needed. "*

I did not follow **why the relation between Cdiel and water temperature suggest that nitrification denitrification may be the underlying processes.** Please, can you develop a little bit more this rational?

**We added a figure (Fig. 7) to illustrate how we imagine the superposition of different processes (as requested by referee 1) and revised the interpretation of the individual clusters (l. 303-338):**

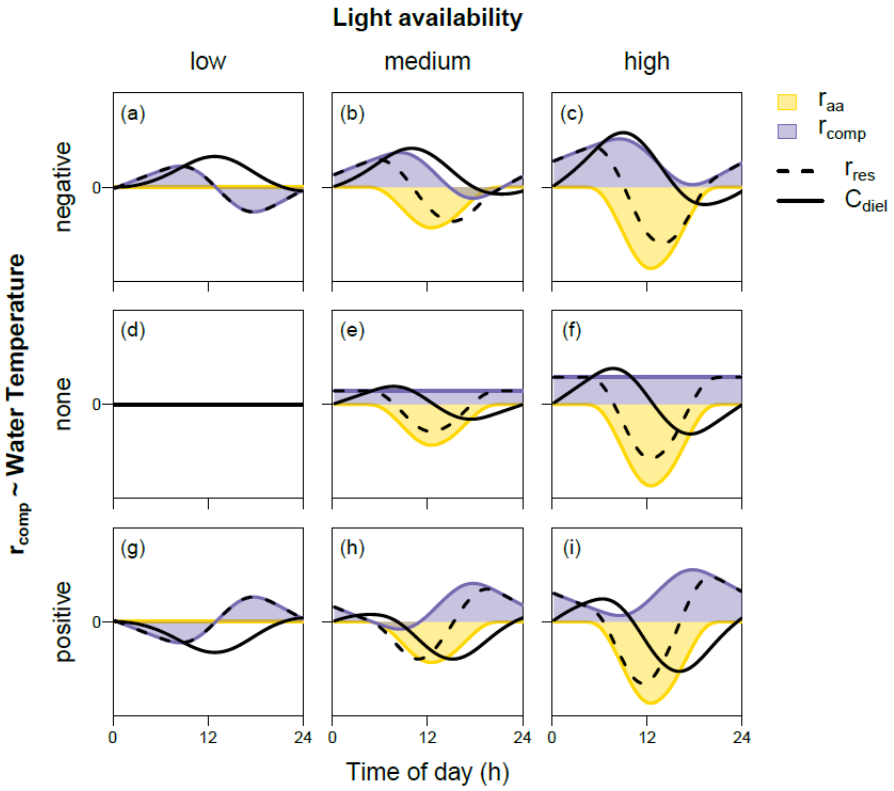


*Figure 3: Schematic representation of diel courses of assimilation rate ($r_{aa.}$) and a complementary processing rate ($r_{comp}$) required to produce equilibrium conditions. Black lines show the resulting change rate ($r_{res}$) and concentration (C). While $r_{aa}$ is considered a function of global irradiance (columns represent different levels of irradiation intensity), $r_{comp.}$ is conceptualized as a function of stream temperature (rows represent a negative (a-c), no relationship (d-f) and a positive relationship (g-i)).*

**Technical notes**

Title: "stream nitrate concentration"?

**Done**

Ln 9. This sentence is quite long. I suggest to start a new one on "We performed a k-means cluster analyses to ....".

**Done**

Ln 15. Perhaps add "Results from cluster analyses show that at least 70% …"

**Done**

Ln 16: "or physical (lateral inputs) processes"

**Done**

Ln 2. This sentence seems quite off here. I suggest to either move it at the beginning of the introduction or to delete it and simply say "Among the different nutrients, nitrate is of special interest …"

**Done**

Ln 42. Add here also the hypothesis that diel signals might also be due to diel variations in groundwater NO3- inputs due to evapotranspiration.

**Done**

Ln 50. Move the ref at the end of the sentence.

**Done**

Ln 61. “Al our site, “

**Done**

Ln 66. “gravel bed,”

**Done**

Ln 88. “in the latter dilution measurement,”

**Done**

Ln 92. Perhaps is better to indicate which patterns of NO3- concentrations you are referring to. I suggest to change the heading to “Identification of diel patterns in stream NO3- concentration”

**Done**

Ln 99. Remove “e.g.”

**Done**

Ln 100. You did a great job here; this reads much clearer now! However, I would perhaps clarify that “diel portion of the solute concentration signal” means “Residuals concentrations”, i.e. add residuals concentrations in parenthesis after “concentration signal”.

**Instead we replaced “Residual” with “diel” in the following sentence to overall avoid the term “residual” which had been suggested in the first revision cycle.**

Ln 124. Clarify that you did this exercise for both reaches and all clusters. Also, can you add the number of days for each reach separately? If you do so, data would match perfectly with Fig 4.

**Done**

Lnn138, “Particularly, we assessed daily means of nitrate concentration, water level and water temperature”

**Done**

Ln 155. Add a comma after “(n=119)”

**Done**

Lm 166. “stream nitrate concentration”

**Done**

Ln 172. This rho is negative. So either the symbol is wrong, or the relation between water temperature and daily average nitrate concentration is negative.

**Typo corrected**

Ln 183. “differed between stream reaches and among clusters”

**Done**

Ln 194. “In both reaches, the time lags roughly ranged between zero and travel time estimates”

**Done**

Fig 4. Nitpicking, but perhaps it is better to show first the upper reach.

**Done**

Ln 232: “In our data, we found patterns in stream nitrate concentration”

**Done**

Ln 238. “On diel scale, “

**Done**

Fig 6. Nitpicking, but can you highlight the zero line to make it easier for the reader?

**Done**

Ln 270-274. This rational does not make sense in the current version of the discussion. I suggest deletion.

**Done**

Ln 281. “, when cluster B prevailed”

**Done**

Ln 319. “Germany,”

**Done**