Authors response to Reviewer 1 & 2

Reviewer 1

General Response:

We would like to thank the reviewer for their careful reading and valuable comments, which helped to improve the clarity and quality of our manuscript. Below, we address each point raised in detail.

1. *“Section 2.2.2: The description of how to calculate the h-index is not clear. It may be beneficial to add a schematic diagram.”*

Response:

Thank you for this suggestion. We have revised the description in Section 2.2.2 to improve clarity and we will have a schematic diagram illustrating the calculation steps of the h-index following Zuecco et al. (2016). The diagram will show the rising and falling limbs of a sample hysteresis loop, normalized variables, and how the area differences are computed. We believe this will help readers understand the calculation more intuitively.

2. *“What are the valence states of iron and manganese measured in this study? How can the concentrations of these ions and DOC be used to determine changes in redox conditions? Why was dissolved oxygen (DO) concentration not measured?”*

Response:

In this study, total dissolved iron and manganese were measured using atomic absorption spectroscopy (AAS) after filtration, without speciation of individual oxidation states. Therefore, both Fe(II)/Fe(III) and Mn(II)/Mn(IV) may be present, but due to their solubility characteristics, we interpret the dissolved fractions to largely represent the reduced forms: Fe^{2+} and Mn^{2+}.

We used the presence and relative concentrations of DOC, $NO3^{-}$ Fe, and Mn as indirect indicators of redox conditions, following the redox ladder in oxygen-depleted environments, microbial respiration first consumes oxygen, then nitrate, followed by manganese and iron oxides (Zehnder & Stumm, 1988). Hence, the co-occurrence of elevated DOC and dissolved Fe^{2+}/Mn^{2+} in riparian groundwater, especially during low-flow summer conditions, suggests partly reducing environments with potentially high microbial activity.

DO was not measured due to field limitations and the focus on solute-based proxies. We acknowledge that including DO data would have strengthened the redox interpretation and have now added this as a limitation in the discussion.

Revised: “This sequence is influenced by factors such as redox potential, pH, electron acceptor availability, and the presence of bioavailable organic matter. While our study lacks direct measurements of dissolved oxygen (DO) and pH, which would have strengthened the interpretation of redox processes, we infer redox conditions based on observed concentrations of DOC, Fe^{2+}, and Mn^{2+}. Although the significance tests indicate that DOC concentrations are comparable across the sampling sites and that Fe^{2+} and Mn^{2+} do not differ significantly between the groundwater wells, we interpret that, during summer and under counterclockwise hysteresis conditions, microbial activity is increased. Thus, during summer and under counterclockwise hysteresis conditions the increased microbial activity and oxygen depletion is based on the co-occurrence of high DOC concentrations, elevated Fe^{2+} and Mn^{2+} in GW1 during losing conditions and counterclockwise hysteresis, likely driven by enhanced inflow of labile organic carbon from the stream into near-stream sediments (Smith & Arah, 1986)."

3. *"The hydraulic gradient is used to determine losing and gaining conditions, and these results should be compared with the analysis of the h-index."*

Response:

We agree with the reviewer that this connection strengthens the interpretation. We revised the Discussion to clarify the comparison of hydraulic gradients with h-index values. We emphasize that steep negative gradients correlate with counterclockwise hysteresis (losing conditions), while positive or flat gradients often coincide with clockwise hysteresis (gaining conditions).

Revised: "A distinct seasonal pattern emerges, steeper hydraulic gradients during summer events correspond with counterclockwise hysteresis, while gentler gradients in autumn and winter are associated with clockwise hysteresis (Figure 7). This relationship is reflected in our results, where counterclockwise hysteresis (negative h-index) predominantly occurs under steep negative hydraulic gradients, indicating losing conditions, whereas positive or near-zero gradients are typically associated with clockwise hysteresis and gaining conditions (Figure 7 and corresponding h-index values in Section 3.2)."

Additionally, we will add a short paragraph/sentence in the discussion section relating to the non-exclusive co-occurrence of H-Index and gaining and losing conditions to literature:

"Additionally, our results show that gaining and losing conditions are not exclusively associated with one hysteresis direction. Similar observations were reported by Gelmini et al. (2022), who found that hysteresis behavior—captured by the h-index—can vary depending on antecedent conditions and event timing, rather than being strictly determined by the direction of exchange."

4. *"Before the section '3.1 Hysteresis Index in relation to HT,' please add a results section heading. Change 3.1 to 3.2."*

Response:

Thank you for pointing this out. We have added the missing section heading as "3 Results" before the previous subsection 3.1, which is now correctly labeled as 3.2 Hysteresis behaviour. We changed all the following section titles.

5: *“In Figure 3, for panel c, should the y-axis label ‘Field Capacity’ be ‘Ratio of soil moisture to field capacity’?”*

Response:

Yes, the reviewer is correct. The label was imprecise. We updated the y-axis label now in Figure 4c to: **“Soil moisture as ratio to field capacity (–)”** to clarify that the values are normalized.

6: *“In Figure 4, panel f is difficult to interpret. Please provide additional explanation. What do the vertical line and cyan filled circle represent?”*

Response:

We agree that this panel needed clarification. The vertical line indicates the transition point between summer and winter periods. The cyan filled circle marks the streamflow net change over the observed stream section. We have revised the figure captions:

“(f) Hydrological turnover (HT) in %/m point measurements (n= 28) during the observation period. Grey bars indicating net losses and gains, cyan dots net changes”

7: *“Lines 271–272: This sentence is difficult to understand; please elaborate to make it more convincing.”*

“The redox sensitive species were observed in all samples in varying concentrations, with the highest concentrations in the near stream groundwater.”

Response:

We revised the sentence for clarity as follows:

Revised:

“We detected redox-sensitive species (Fe, Mn, $NO3^-$) in all samples, with the highest concentrations of iron and manganese consistently observed in near-stream groundwater wells. This suggests heterogeny redox conditions in the riparian groundwater compared to the stream.”

8: *“Lines 277–279: Please check for logical inconsistencies in these two sentences.”*

“During summer and the corresponding system states GW1 exceeds the GW2 concentration median showing increased redox potential/activity directly in the riparian zone of the stream. During summer, losing conditions and with counterclockwise hysteresis manganese and iron concentrations are highest at GW1.”

Response:

We understand the confusion and revised these sentences for clarity and internal consistency:

Revised:

“During summer, manganese and iron concentrations were higher at GW1 compared to GW2, suggesting increased redox activity closer to the stream. These conditions coincided with losing hydraulic gradients and counterclockwise hysteresis, indicating stream-derived import may stimulate microbial activity in the near-stream sediments.”

9: *“Lines 337–339: Please elaborate to make this statement more convincing.”*

“This promotes biogeochemical activity, as fluctuating water stages create alternating oxic and anoxic conditions, evident by the ions present during such conditions, especially at GW1 (Figure 8).”

Response:

We have elaborated this point to be more specific and evidence based. We introduced the hydrological framework of redox-active compounds in aquatic systems by Peiffer et al., (2021) and the inherent redox variability of wetlands shown by Frei et al., (2012) as micro-topographic hot-spots together with Knorr et al., (2009), to show that heterogeneity in redox environment at the riparian zone impacting biochemical activity:

Revised:

“Short-time alternating water level gradients during and after stream flow events create oxic-anoxic transition zones within the riparian zone that could promote microbial processes (Knorr et al., 2009). These redox hot spots are variable in time and space across the riparian zone and facilitate biogeochemical processes (Frei et al., 2012). This is supported by elevated concentrations of DOC, Fe^{2+}, and Mn^{2+} at GW1 during summer losing conditions, fitting with the concept of the hydrological framework of redox-active compounds in aquatic systems (Peiffer et al., 2021) explaining the simultaneous occurrence of ions along the redox ladder. Thus, enhanced biogeochemical activity is likely to be driven by the observed redox fluctuations (Figure 9).”

10: *“Lines 344–346: Please provide the data or evidence to support this statement.”*

“We observed increased microbial activity and oxygen depletion within the riparian zone, likely driven by enhanced inflow of labile organic carbon from the stream into near stream sediments.”

Response:

We recognize the need for clearer support. We revised the statement according to the changes in the Discussion.

Revised:

"During summer and under counterclockwise hysteresis conditions, we interpret increased microbial activity and oxygen depletion based on the co-occurrence of DOC concentrations, elevated Fe^{2+} and Mn^{2+} in GW1 during losing conditions, likely driven by enhanced inflow of labile organic carbon from the stream into near-stream sediments (Smith & Arah, 1986). This is evidenced by elevated DOC concentrations and redox-sensitive solutes at GW1 (Figure 9)."

We added relevant citations at the Conclusion (Peiffer et al., 2021; Frei et al., 2012 and Knorr et al., 2009).

Additional Literature:

Peiffer, S., Kappler, A., Haderlein, S. B., Schmidt, C., Byrne, J. M., Kleindienst, S., ... & Planer-Friedrich, B. (2021). A biogeochemical–hydrological framework for the role of redox-active compounds in aquatic systems. Nature Geoscience, 14(5), 264-272.

Frei, S., K. H. Knorr, S. Peiffer, and J. H. Fleckenstein (2012), Surface micro-topography causes hot spots of biogeochemical activity in wetland systems: A virtual modeling experiment, J. Geophys. Res., 117, G00N12,doi:10.1029/2012JG002012.

*Knorr, K. H., Lischeid, G. & Blodau, C. Dynamics of redox processes in a minerotrophic fen exposed to a water table manipulation. Geoderma **153**, 379–392 (2009).*

Zehnder, A. J. B., & Stumm, W. (1988). Geochemistry and biogeochemistry of anaerobic habitats. In Biology of anaerobic microorganisms, 1-38.

Reviewer 2

General Response:

We would like to thank Reviewer 2 for the constructive and detailed comments, which helped us to further improve the clarity and robustness of our manuscript.

General comments

1. *"...very limited number of groundwater wells, which may not be representative... such limitation should be discussed..."*

Response:

We acknowledge the reviewer's concern regarding the limited number of groundwater wells and agree that this represents a potential limitation. However, at the studied catchment there are no groundwater wells other than the near stream monitoring wells utilized in this study. Geological conditions of that catchment do not provide a continuous, near surface groundwater aquifer. Hence, in this catchment with fissured schist bedrock and comparably shallow soils, alluvial groundwater wells are most likely suitable to capture stream–groundwater connectivity. Hence, we relate to the soil moisture model as an alternative proxy for catchment saturation conditions, since larger scale groundwater monitoring is absent.

Our analysis is based on one stream section and two groundwater wells, which we will now explicitly acknowledge in the discussion. We clarify that the findings reflect local hydrogeological conditions and should not be considered directly transferable to other parts of the catchment. At the same time, we emphasize that the conceptual framework developed (h-index/HT relationships) is intended as a process-based example illustrating hydrological connectivity, rather than a catchment-wide quantification. We added the following sentence to the discussion chapter of the manuscript:

> *"This study is relying on two available groundwater wells located in the close vicinity of the stream reach under study. While these wells provide valuable process-based insights into GW–SW exchange and redox dynamics, they cannot capture spatial heterogeneity across the catchment. The geological setting with fissured schists as the near surface bedrock does not provide a contiguous shallow aquifer, and thus no groundwater monitoring network at the catchment-scale. Therefore, larger-scale GW monitoring is absent. We instead utilize the standardized soil moisture model provided by the public weather service for each weather station (DWD) as an alternative proxy for subsurface storage dynamics. Consequently, the conceptual framework we propose (h-index/HT relationships) should be understood as locally constrained and hypothesis-generating, rather than directly representative of larger scales."*

2. *"...a characterization of the runoff events is currently missing..."*

Response:

We acknowledge the reviewer's suggestion. Precipitation characteristics and corresponding streamflow responses are already included in Figures 3 and 4, where rainfall is shown as bar plots alongside discharge. We will clarify this in the caption and Methods section to make it easier for the reader to connect runoff dynamics with our event analysis. While descriptive statistics (rainfall amounts, intensities, duration, peak discharge, antecedent wetness) are useful context, our classification of events is based on hysteresis behaviour and hydrological turnover, rather than on event magnitude or precipitation metrics. We added a short descriptive summary of event characteristics in the Methods text but maintain the focus of our framework on hysteresis-based classification.

> *"During the observation period (2021–2023), we monitored 68 runoff events with precipitation totals ranging up to 60 mm. Corresponding streamflow responses showed peak discharges between 20 and 700 L s $^{-1}$. Antecedent soil moisture conditions varied from dry at summer drought events to near saturation at winter events (Fig.3). While these event descriptions provide hydrological context, the classification of events in this study is based on hysteresis behaviour and hydrological turnover rather than on precipitation or discharge metrics."*

3. *"...specific objectives should be clarified at the end of the introduction, and results/discussion should be organized based on these objectives."*

Response:

As suggested by Commentator 1 and Reviewer 1, we now explicitly state our objectives and hypotheses at the end of the Introduction.

> *"The objective of this study is to explore how seasonal changes in hydraulic conditions influence groundwater–surface water interactions in a headwater stream. We hypothesize that (1) the direction and magnitude of hysteresis between groundwater and stream water levels are indicative of seasonal hydrological states, and (2) consequently, the direction and magnitude of the hysteresis is related to hydrological turnover. thus facilitating (3) redox fluctuations creating oxic-anoxic transition in the riparian zone, shaping redox hot spots."*

We revise our Results and Discussion sections to be restructured accordingly, to better align with these objectives and hypotheses.

Specific comments:

1. *Line 12: Please explain which variables are used for hysteresis analysis.*

Response:

Clarified in Methods: hysteresis analysis was performed using stream stage and groundwater levels (GW1, GW2), normalized to facilitate comparison across events.

We clarified the sentence accordingly:

> *"This study examines the relationship between hydrological turnover (HT) and stream-stage-groundwater-level hysteresis patterns under various system states in a third-order tributary of the River Mosel in Trier, Germany, using high-resolution stream-stage and groundwater-level data (GW1, GW2) together with complementary chemical observations collected over two years."*

2. *Introduction: The specific objectives of this study are not clearly presented. Furthermore, the authors should consider reporting their research hypotheses, which are later mentioned at Line 306 (Discussion).*

Response:

Addressed as above; hypotheses are now clearly stated at the end of the Introduction (see also responses to Reviewers 1 & Commentator 1).

3. *Materials and methods: details about the selected events… rainfall amounts, intensities, etc.*

Response:

We agree that event details are beneficial to the study. We added a table presenting the suggested details for rainfall events and streamflow response prior to HT estimation experiments. After the presented events, one or multiple HT experiments were conducted. The complete list of all monitored events can be provided as supplementary material.

Table 1. *Characteristics of events occurring prior to one or multiple tracer experiments. Duration of the Hydrograph response; Precipitation of the event; Mean discharge; Runoff volume and Runoff coefficient (Precipitation/Runoff volume).*

Date	Duration [h]	Precipitation [mm]	Mean Q [L/s]	Runoff vol. [m^3]	Runoff coeff. [–]
03-08-2020	70	3.8	13.5	3387	0.111
17-08-2020	24	8.3	14.5	1259	0.019
18-08-2020	48	2.2	0.1	10	0.001
02-09-2020	26	3.0	13	1240	0.596
24-09-2020	33	8.0	29.9	3529	0.056
06-10-2020	24	16.3	47.6	4110	0.031
09-10-2020	289	22.6	25.6	26684	0.148
23-10-2020	50	8.2	13.9	2524	0.039
08-02-2021	84	19.5	165.5	49981	0.321
13-03-2021	29	18.2	61.2	6336	0.044
19-03-2021	337	30.9	42.8	51882	0.210
11-04-2021	588	42.1	36.5	77294	0.229
26-05-2021	116	15.3	14.8	6171	0.050
04-06-2021	71	19.8	18.6	4777	0.030
29-06-2021	122	7.0	4.9	2159	0.039
05-07-2021	51	18.1	38.7	7114	0.049
27-07-2021	150	28.2	80.1	43289	0.192
08-08-2021	31	4.2	16.7	1861	0.056
26-11-2021	85	15.4	17.6	5376	0.044
07-12-2021	557	29.4	95.3	190892	0.813

4. *Lines 114–123: belong elsewhere.*

Response:

This section is now moved to the Experimental setup subsection.

5. *Lines 139–141: provide NaCl injection details.*

Response:

We added several sentences and provided additional information about the monitored stream section, the multiple injection points, distances from wells, and timing.

We revised the section as follows:

> *"Instantaneous NaCl tracer injections were performed for HT estimation, during recession, utilizing salt dilution gauging (Day, 1976; Covino et al., 2011; Mallard et al., 2014). At the monitored stream section (~250 m) two independent discharge measurements were conducted, at the upstream and downstream ends of the stream reach. Injection distance for the measurement devices was approximately 30m*

(Bäthke & Schuetz, 2024). The Q_{loss} estimation is based on an additional tracer injection injected at the upstream site and measured at the downstream site, following the instructions of Payn et al. (2009). The wells are located in 1.5 m and 3 m lateral distance from the upstream measurement point. Electrical conductivity during tracer injections…"

6. *Lines 155–156: When were samples taken?*

Response:

We will add sentences and provide additional information about the timing of water sampling. We revised the sentence as follows:

> *"Groundwater and stream samples were collected during stream flow recession towards baseflow conditions, immediately prior to the dilution gauging experiments (n = 48, table xx) and not during rainfall events. Laboratory analyses were carried out after filtration through a 0.45 µm glass fiber filter (Macherey & Nagel). Nitrate was determined by ion chromatography (±2%), potassium (±5%) and silica (±8%) by ion chromatography, iron and manganese (±5%) by atomic absorption spectroscopy (AAS, contrAA 300), and dissolved organic carbon (DOC) by combustion followed by IR detection (TOC analyzer, ±2%)."*

7. *Lines 157–159: What do ± values indicate?*
   Response:

We added clarification about the meaning of the ± values.

"The reported ± values represent the standard deviation of replicate analyses."

8. *Equation 3: How is Q_{gain} determined?*

Response:
Q_{gain} is calculated by combining discharge and conservative solute mass balances along the reach. Starting with determination of Q at the start and the end of the stream section. Upstream and downstream discharge measurements are used to determine the net discharge change (ΔQ), while the separate tracer measurement along the total stream-section allows for the determination of gross losses to the subsurface. The tracer-marked stream water losses are replaced by unmarked groundwater inflow. Balancing ΔQ and Q_{loss} allows Q_{gain} calculation We added an explanatory sentence to the Methods section accordingly.

> *"The absolute differences in Q (ΔQ, eq. 3) between upstream and downstream discharge measurement sites in combination with Q_{Loss} (eq. 2) results in Q_{gain} as the residual, i.e. the part of ΔQ which is not explained by Q_{loss} (eq. 2)."*

9. *Lines 191–195: A scheme with hysteretic loops would be helpful.*

Response:

As also suggested by Reviewer 1, we created a schematic, illustrating clockwise and counterclockwise hysteresis loops and their interpretation.

10. *Results should be structured according to objectives.*

Response:

Revised structure: Results now will follow the three stated objectives (Hysteresis behaviour → Hydrological turnover → Solute/redox dynamics) according to suggestions of Commentator 1 and Reviewer 1.

11. *Section 3.3: Expand link between hysteresis and solutes.*

Response**:**

We expanded this section leading to the discussion on tracer behaviour (Reviewer 1), event-specific differences, and rationale for grouping tracers into mixing vs. redox-sensitive groups (linking to revised hypotheses).

> *"We grouped the tracers into a conservative mixing set (geogenic silica, Potassium) and a redox-related set to reflect the hypotheses 1&2 as well as 3, respectively: mixing tracers diagnose hydrological turnover and its seasonal variability in groundwater-surface water exchange. This separation allows redox tracers (DOC, NO_3^-, Fe, Mn) to specifically indicate the biogeochemical response to that exchange. Redox tracers can track redox dynamics as conceptualized by biogeochemical hydrological coupling (Peiffer et al., 2021) and the classical redox sequence in oxygen-limited environments (Zehnder & Stumm, 1988). We emphasize that event metrics are used as hydrological context, while event classification itself is based on hysteresis behaviour."*

12. *Figure 8: Are differences significant?*

Response:

We will add significance indicators within the Graphics of Figure 9.

13. *Line 306: Hypotheses should be reported earlier.*

Response:

Is stated in the introduction.

14. *Discussion: lacks structure, does not address limitations.*

Response:

We added several sentences to the Discussion to improve clarity and structure. The revised Discussion explicitly addresses both limitations (e.g., limited number of wells and hydrological turnover events) and broader implications.

"This study relies on two available groundwater wells located in the close vicinity of the stream reach under study. While these wells provide valuable process-based insights into GW–SW exchange and redox dynamics, they cannot capture spatial heterogeneity across the catchment. The geological setting with fissured schists as the near surface bedrock does….."

"Consequently, the conceptual framework we propose (h-index/HT relationships) should be understood as locally constrained and hypothesis-generating, rather than directly representative of larger scales."

*"*While our study lacks direct measurements of dissolved oxygen (DO) and pH, which would have strengthened the interpretation of redox processes, we infer redox conditions based on observed concentrations of DOC, Fe^{2+}, and Mn^{2+}. Although the significance tests indicate that DOC concentrations are comparable across the sampling sites and that Fe^{2+} and Mn^{2+} do not differ significantly between the groundwater wells, we interpret that, during summer and under counterclockwise hysteresis conditions, microbial activity is increased. Thus, during summer and under counterclockwise hysteresis conditions the increased microbial activity and oxygen depletion is based on the co-occurrence of high DOC concentrations, elevated Fe^{2+} and Mn^{2+} in GW1 during losing conditions and counterclockwise hysteresis, likely driven by enhanced inflow of labile organic carbon from the stream into near-stream sediments (Smith & Arah, 1986). This is evidenced by elevated DOC concentrations and redox-sensitive solutes at GW1 (Figure 9). However, our observations revealed the co-occurrence of nitrate, manganese, and iron in groundwater and stream samples. This simultaneous presence of multiple electron acceptors suggests that the redox sequence is not strictly adhered to under field conditions a finding consistent with Alewell et al. (2008) and others. Such deviations from idealized zonation likely result from heterogeneous flow paths, dynamic hydraulic gradients (Peiffer et al., 2021; Frei et al., 2012 and Knorr et al., 2009), and continuous mixing at the GW-SW interface (Gu et al., 2012).*"*

The discussion is now organized into the following sections: addressing hysteresis direction and magnitude as indicators of seasonal hydraulic states, hydrological turnover, and solute and redox dynamics.

We thank the reviewer for reminding us of such technical oversights. We changed all according to the reviewer's suggestions in the manuscript:

- Lines 77–78: Rephrased for clarity.
- Line 105: "mouth" replaced by "outlet".
- Figure 3 caption: explained "mQ".
- Figure 5: number of samples added; caption revised to "violin plots".
- Line 241: comma inserted.
- Line 253: corrected "deivided" → "divided".
- Figure 8: added number of samples per boxplot.
- Line 267: inserted missing "for".
- Line 330: inserted missing "with".