

Response to comments from referee 1

> **[R1-1]** *The manuscript “Redox-network reconfiguration inferred from the $\ln[\text{O}_2]$ –Eh relationship under mixed-potential conditions in a shallow pond time series” presents a conceptually interesting attempt to reinterpret field measurements of redox potential (Eh) within a mixed-potential framework. The idea of considering Eh not as a proxy for individual redox couples but as an emergent property of a complex redox reaction network is timely and relevant. The proposed use of the $\ln[\text{O}_2]$ –Eh relationship as a simplified indicator of redox-network stability and, under appropriate conditions, may provide a useful tool for interpreting complex natural systems.*

> *The authors correctly emphasize that Eh in natural waters reflects a mixed potential formed by multiple concurrent redox reactions involving a range of potential-determining couples, including dissolved oxygen, iron and manganese species, sulfur in different oxidation states, and organic matter, particularly humic substances. The overall redox state of a water body results from the combined action of these systems, although their contributions are not equivalent and depend on the prevailing physicochemical conditions.*

> *The present work is clearly written, and the combination of theoretical development with longterm field observations is a strong aspect of the study. The dataset, collected over nearly two years in a small artificial water body, is valuable. Measurements were carried out weekly at four sites and at two depths, and included pH, Eh, dissolved oxygen, electrical conductivity, as well as water temperature and depth.*

> *The theoretical framework presented in the manuscript is well structured and offers a useful formalization of mixed-potential behavior. In particular, the decomposition of $\partial\text{Eh}/\partial\ln x$ into Nernstian and kinetic contributions provides a clear conceptual basis for the analysis. Building on the evident strengths of the manuscript, a more in-depth discussion of selected aspects would help to further reinforce the study’s conclusions.*

[Response to R1-1]

We sincerely thank the referee for the positive and constructive assessment of our manuscript. We are grateful that the referee found the mixed-potential interpretation and the combination of theoretical development with field observations valuable. In response to the comments, we have revised the manuscript to clarify the assumptions underlying the framework, better delimit the role of oxygen, acknowledge alternative explanations for the disturbance response, and frame the proposed $\ln[\text{O}_2]$ –Eh approach as an indicative, screening-level tool rather than a definitive method for identifying dominant redox pathways.

> **[R1-2]** *1. The proposed framework relies on assumptions (e.g., near-equilibrium conditions and stable conductance weights) that may not hold in dynamic natural systems. Expanding the discussion of these limitations would strengthen the analysis.*

[Response to R1-2]

We thank the referee for this important comment. We agree that natural aquatic systems are dynamic and that one should not assume environmental steady state or geochemical equilibrium at the system scale. To avoid possible ambiguity, we have clarified that the near-equilibrium/near-linear assumption in our formulation applies to the interfacial electrode reactions used in the mixed-potential description, not to the pond environment or to the redox reaction network as a whole.

Specifically, the linearization assumes that the partial current-potential response of the interfacial

reactions contributing appreciably to the open-circuit potential can be approximated locally around their equilibrium potentials. Likewise, the assumption of relatively stable conductance weights refers to the relative contributions of those interfacial partial reactions over the range of variation considered. It does not require that concentrations, microbial processes, hydrological conditions, or the environmental redox network remain stationary. If environmental variability changes the effective equilibrium potentials, polarization conductances, or their relative weights, such changes would appear as departures from a stable $\ln[\text{O}_2]$ -Eh relationship.

We have revised the manuscript to make this distinction clearer. We now define G_k explicitly as the local polarization conductance of partial reaction k, i.e., the slope of the partial current-potential curve near E_k , and we clarify that the conductance-weighted expression for E_{mix} follows under a small-overpotential, near-linear polarization approximation. We also revised the text to emphasize that departures from a stable $\ln[\text{O}_2]$ -Eh relationship should be interpreted as changes in the effective mixed-potential response, rather than as a direct inversion of individual environmental redox pathways.

[Changes in manuscript]

We revised Sect. 3.1 and Appendix A to clarify that the linearization is an interfacial electrode-reaction approximation, not an assumption of environmental steady state. In Sect. 3.1, G_k is now defined as:

where $G_k \equiv (\partial i_k / \partial E)_{E=E_k}$ is the local polarization conductance of partial reaction k, defined as the slope of the partial current-potential curve near E_k ; equivalently, G_k is the reciprocal of the local polarization resistance.

We also added the following clarification in Sect. 3.1:

We emphasize that this near-linear approximation concerns the interfacial current-potential response at the electrode surface and does not imply environmental steady state or geochemical equilibrium of the pond as a whole. Environmental variability is instead represented in this formulation through changes in the effective equilibrium potentials E_k , conductances G_k , and their relative weights.

We further revised Appendix A to state that the conductance-weighted expression for E_{mix} is obtained for the subset of partial reactions that contribute appreciably to the mixed potential, under a small-overpotential, near-linear polarization approximation.

> **[R1-3]** 2. Oxygen often plays a leading role in controlling Eh, and the authors propose the $\ln[\text{O}_2]$ -Eh
> relationship as an indicator of redox-network stability. However, its dominance is not universal and

> depends on environmental conditions. Under oxygen-limited settings, other redox systems (e.g., Fe, Mn, sulfur, and eventually methanogenesis) may become dominant. In this context, it would be useful to more clearly define the conditions under which oxygen controls Eh and to acknowledge that the proposed indicator may not be universally applicable. It would also be helpful to clarify how sensitive the $\ln[\text{O}_2]$ –Eh relationship is to other redoxactive components, such as iron or manganese cycling.

[Response to R1-3]

We thank the referee for this important comment. We agree that dissolved oxygen does not universally control Eh, and that the proposed $\ln[\text{O}_2]$ -Eh relationship should not be interpreted as a generally applicable indicator in all redox settings. Our intention was not to assume oxygen dominance, but to examine whether the relationship between a routinely measured redox-active variable, DO, and the measured mixed potential can provide a site-specific diagnostic of changes in the effective mixed-potential response.

We also agree that in oxygen-depleted or strongly reducing environments, other redox-active systems may dominate the mixed potential. Because redox-sensitive solutes such as Fe, Mn, nitrogen, and sulfur species were not measured in the present study, we cannot identify the dominant redox couples or resolve the underlying redox processes from the DO-Eh relationship alone. We have therefore revised the manuscript to state more explicitly that the proposed approach is a screening-level, site-specific tool whose applicability is limited to settings where oxygen is present and variable enough for a DO-Eh relationship to be evaluated.

[Changes in manuscript]

We revised Sect. 4.3 to clarify the role of oxygen and the interpretive limits of the proposed DO-Eh approach. In particular, we added the following clarification:

At the same time, the mixed-potential nature of Eh imposes clear limits on interpretation. Because multiple combinations of interfacial pathways can yield the same electrode potential, co-monitoring DO and Eh cannot identify the dominant redox couple(s), resolve aqueous speciation, or quantify individual reaction fluxes without complementary measurements of redox-active species. Furthermore, the proposed DO-Eh approach is not intended to imply that dissolved oxygen universally controls Eh. Its applicability is limited to settings where oxygen is present and variable enough for a DO-Eh relationship to be evaluated. In oxygen-depleted or strongly reducing environments, other redox-active systems may dominate the mixed potential, and complementary measurements of redox-active species would be needed to identify the underlying processes.

We also revised the concluding statement of Sect. 4.3 to frame DO-Eh co-monitoring as a screening-level approach rather than a substitute for comprehensive geochemical characterization:

DO-Eh co-monitoring is therefore best viewed not as a substitute for comprehensive geochemical characterization, but as a low-cost screening-level approach for detecting departures from a site-specific DO-Eh baseline that may indicate changes in effective redox conditions or in the relative contributions of redox-active processes.

> [R1-4] 3. *The interpretation of disturbance effects based on electrical conductivity (EC) is reasonable, and the use of change-point detection is appropriate. However, the link between the EC anomaly and redox-network reconfiguration remains indirect. Considering alternative drivers (e.g., hydrological variability, temperature, or organic matter inputs) would strengthen the analysis.*

[Response to R1-4]

We thank the referee for this important comment. We agree that the link between the EC anomaly and redox-network reconfiguration is indirect. In the present field setting, the number of repeatedly measured variables was limited by logistical constraints. Among the measured variables, EC provided the clearest and most physically interpretable response to the excavation-related disturbance, because sediment mobilization and the exposure of freshly disturbed material can produce detectable changes in ionic composition. We therefore used EC as an operational proxy for defining the timing of the physical disturbance, rather than as a direct measure of redox-network reconfiguration.

We also agree that other disturbance-related drivers, including hydrological variability, turbidity or suspended sediments, organic-matter inputs, temperature-dependent biological activity, and biofilm-associated oxygen production and consumption, may have contributed to the observed DO and Eh dynamics. Because the present study did not include direct measurements of redox-sensitive species or the full set of physical disturbance indicators, the specific mechanisms linking the EC anomaly to subsequent changes in the $\ln[\text{O}_2]$ -Eh relationship remain uncertain. We have therefore revised the manuscript to clarify the operational role of EC and to frame the inferred link as indicative rather than definitive.

[Changes in manuscript]

We revised Sect. 3.2 to clarify that EC was used as an operational basis for defining the pre- and post-disturbance regimes, rather than as a direct measure of redox-network reconfiguration. The revised text states:

We used electrical conductivity (EC) as a proxy for the excavation-related physical disturbance because sediment mobilization and the exposure of fresh mineral surfaces can enhance ion release via accelerated weathering, producing detectable EC anomalies. The EC anomaly was therefore used as an operational basis for defining pre- and post-disturbance regimes against which changes in the $\ln[\text{O}_2]$ -Eh relationship were evaluated.

> [R1-5] 4. Another limitation is the absence of water chemistry data needed to independently constrain dominant redox processes. Without measurements of key redox-sensitive species (e.g., Fe, Mn, nitrogen, sulfur), it remains uncertain whether variations in the $\ln[O_2]$ -Eh relationship reflect genuine shifts in redox pathways. In its current form, the analysis is therefore better interpreted as indicative rather than definitive, and the conclusions could be framed more cautiously.

[Response to R1-5]

We thank the referee for this important comment. We agree that the absence of concurrent water-chemistry data is a key limitation of the present study. Because redox-sensitive solutes such as Fe, Mn, nitrogen, and sulfur species were not measured, we cannot independently identify the dominant redox processes or assign the observed changes in the $\ln[O_2]$ -Eh relationship to specific redox pathways.

Our intention was therefore not to present the DO-Eh relationship as definitive evidence for particular biogeochemical pathways, but rather as an indicative, screening-level signal of departures from a site-specific mixed-potential baseline. In response to the referee's comment, we have revised the manuscript to make this limitation more explicit and to frame the conclusions more cautiously.

[Changes in manuscript]

We revised Sect. 4.3 to clarify that DO-Eh co-monitoring cannot identify dominant redox couples or resolve aqueous speciation without complementary measurements of redox-active species. The revised text states:

At the same time, the mixed-potential nature of Eh imposes clear limits on interpretation. Because multiple combinations of interfacial pathways can yield the same electrode potential, co-monitoring DO and Eh cannot identify the dominant redox couple(s), resolve aqueous speciation, or quantify individual reaction fluxes without complementary measurements of redox-active species.

We also revised the final statement of Sect. 4.3 and the Conclusions to frame the approach as a screening-level indicator of departures from a site-specific baseline, rather than as definitive evidence for specific redox pathways. In the Conclusions, we now state:

These departures are consistent with disturbance-driven changes in effective redox conditions, although complementary measurements of redox-active species would be needed to resolve the underlying redox processes and dominant redox couples.

> [R1-6] 5. The study is based on a small artificial pond, which may limit the generalizability of the results. A clearer discussion of the applicability of the approach to more complex systems (e.g., lakes, rivers, reservoirs) would be desirable.

[Response to R1-6]

We thank the referee for this helpful comment. We agree that the present study, conducted in a small constructed pond, should not be generalized directly to larger and more complex aquatic systems without caution. In lakes, rivers, and reservoirs, processes such as stratification, advective transport, sediment-water exchange, lateral inputs, and spatial heterogeneity may produce multiple DO-Eh regimes within the same system.

We have therefore revised Sect. 4.3 to clarify that application of the proposed approach to more complex systems would require site-specific baseline characterization, careful spatial design of co-located DO and Eh measurements, and, where possible, complementary measurements of redox-active species.

[Changes in manuscript]

We added the following clarification to Sect. 4.3:

Because the present study was conducted in a small constructed pond, generalization to larger and more complex aquatic systems should be made cautiously. In lakes, rivers, and reservoirs, stratification, advective transport, sediment--water exchange, lateral inputs, and spatial heterogeneity may produce multiple DO-Eh regimes within the same system. Application of the proposed approach to such environments would require site-specific baseline characterization, careful spatial design of co-located DO and Eh measurements, and, where possible, complementary measurements of redox-active species.

> **[R1-7]** *In conclusion, the manuscript presents an original and potentially valuable approach to interpreting Eh in natural waters within a mixed-potential framework. With a more explicit discussion of the underlying assumptions, clearer constraints on the role of oxygen, and a more careful consideration of alternative explanations, could make a meaningful contribution to the understanding of redox processes in aquatic systems; however. I would recommend some revision prior to publication.*

[Response to R1-7]

We sincerely thank the referee for the positive assessment and constructive recommendation. We appreciate the recognition that the manuscript presents an original and potentially valuable approach to interpreting field-measured Eh within a mixed-potential framework. In the revised manuscript, we have addressed the referee's main suggestions by clarifying the assumptions underlying the linearized mixed-potential formulation, delimiting the role and applicability of oxygen in the DO-Eh approach, acknowledging the indirect nature of the EC-based disturbance interpretation, and framing the conclusions more cautiously as indicative and screening-level rather than definitive. We hope that these revisions have strengthened the manuscript and clarified the scope of the proposed approach.

Response to comments from referee 2

- > **[R2-1]** *This paper presents a very interesting approach to a common problem when interpreting field measurements of redox potential. What do they actually mean in the chemical world out there? The authors have put thorough work in modelling the interactions in their system and present an explanatory model that is of great inspiration to the readers. They actually use another research question, in which they want to identify the effects of a single disturbance of the system in time, but they do come back to the focus in the title of the paper. Interpreting redox potentials from field sites is not easy and I want to thank the authors for the big effort in it. This paper contributes well to the scientific knowledge in this field. I highly recommend publishing, but I would also like to challenge the authors to improve and/or clarify some parts of the manuscript. This mostly refers to the documentation of the field work and disturbance.*

[Response to R2-1]

We sincerely thank the referee for the positive and encouraging assessment of our manuscript. We are grateful that the referee found the mixed-potential interpretation and explanatory model interesting and potentially useful for interpreting field measurements of redox potential. We also appreciate the constructive suggestions to improve the documentation of the field setting and disturbance. In response, we have revised the manuscript to clarify the site description, channel-construction history, pumping conditions, leaf-litter treatment, and the interpretation of the disturbance-related EC, DO, and Eh dynamics.

- > **[R2-2]** *Fig 2: It appears from the text that a side channel was dug. This is not clear from the image (a). Can you please clarify which part of the water system was dug out when? Also, please add an arrow/indicator of point of view of the photographs (b, c). Is/was the lower channel a closed system/pipe, or an open side channel? The pumping was intermittent. What was the frequency? Was the pumping slow, thus not disturbing the water visibly, or was this on such a scale that the water became turbid again, with sediments like in photo c (which might influence the vertical profile). The subscript to Fig 2 mentions the leaf litter in the system. This litter is a large input of organic matter and thus microbial activity, influencing the Eh. Was this litter removed at any stage? Or was it left to decompose?*

[Response to R2-2]

We thank the referee for these helpful comments. We agree that the original Fig. 2 and its caption did not make the channel configuration, excavation history, and photograph viewpoints sufficiently clear. In the revised manuscript, we clarified that the lower channel was an open peripheral side channel, not a closed pipe, and that the channel-construction works were conducted in two stages: an initial manual excavation in August 2022, followed by a larger-scale mechanical excavation in May--June 2023.

We also added viewpoint markers to Fig. 2a to indicate the approximate viewing directions of the photographs shown in Fig. 2b and 2c.

Regarding pumping, we clarified that water was pumped intermittently during daytime using a solar-powered system. The available pumping-volume measurements indicate variable daily pumping, with a mean of 499 L day^{-1} during 26 August - 14 September 2022 and a range of $124 - 1300 \text{ L day}^{-1}$. The short-term on/off frequency of the pump was not continuously logged. We also clarified that the visibly sediment-laden inflow shown in Fig. 2c was observed after the June 2023 excavation and was associated with freshly disturbed soils.

Regarding leaf litter, we clarified that leaf litter was not actively removed during the monitoring period and was left to decompose within and around the pond. We agree that this organic-matter input may influence microbial activity and Eh, and this point is now stated explicitly in the site description.

[Changes in manuscript]

We revised Sect. 2.1 to clarify the treatment of leaf litter, the open-channel configuration, the timing of the excavation works, and the intermittent nature of pumping. The revised text now states:

Leaf litter was not actively removed during the monitoring period and was left to decompose within and around the pond.

and:

To promote water circulation, the open peripheral side channel shown in Fig. 2a was constructed in two stages: an initial manual excavation in August 2022, followed by a larger-scale mechanical excavation in May--June 2023. After channel construction, water was pumped intermittently (daytime only) using a solar-powered system. Pumping volumes measured during 26 August - 14 September 2022 averaged 499 L day^{-1} (range: $124\text{--}1300 \text{ L day}^{-1}$). The short-term on/off frequency of the pump was not continuously logged. Following the June 2023 excavation, sediment-laden inflow from freshly disturbed soils was observed to enter the pond.

We also revised Fig. 2a by adding viewpoint markers for photographs (b) and (c), and revised the Fig. 2 caption to clarify that the channel was an open peripheral side channel and that the markers indicate the approximate viewing directions of the photographs.

> **[R2-3]** Line 80. Possibly out of scope, but have the authors found any consistency in the length
> required for the reading and the disturbance/stability of the water flow?

[Response to R2-3]

We thank the referee for this comment. We agree that the time required for the readings to stabilize could potentially provide useful information about local flow stability or disturbance intensity. However, stabilization time was not recorded systematically during the monitoring period, and we therefore cannot quantitatively evaluate its relationship with water-flow stability or disturbance conditions.

> **[R2-4]** Line 102. Please explain and/or add reference to "partial polarization conductance". This
> term is not a common term. line 135. Another explanation lies in the leaf litter on site that is being
> degraded in the water, releasing particles contributing the EC.

[Response to R2-4]

We thank the referee for pointing this out. We agree that “partial polarization conductance” is not a common standalone term and should be defined more explicitly. In the revised manuscript, we define G_k as the local polarization conductance of partial reaction k , i.e., the slope of the partial current--potential curve near the equilibrium potential E_k . We also clarify that this quantity is equivalent to the reciprocal of the local polarization resistance for that partial reaction. The word “partial” refers to the partial current associated with each interfacial reaction in the mixed-potential formulation.

In addition, we revised the corresponding derivation in Appendix A to use the same terminology consistently and to clarify the small-overpotential, near-linear polarization approximation under which the conductance-weighted expression for E_{mix} is obtained. We also revised the description of the second term in Eq. (5) from a “kinetic reweighting contribution” to a more general “reweighting contribution”, because changes in the relative polarization conductances may reflect changes in the relative contributions of the partial reactions.

[Changes in manuscript]

We revised the definition following Eq. (3) as follows:

where $G_k \equiv (\partial i_k / \partial E)_{E=E_k}$ is the local polarization conductance of partial reaction k , defined as the slope of the partial current--potential curve near E_k ; equivalently, G_k is the reciprocal of the local polarization resistance.

We also revised Appendix A to define G_k consistently as the local polarization conductance of partial reaction k , and to state explicitly that the mixed-potential expression is obtained by evaluating the linearized current balance at $E = E_{mix}$ and imposing the zero-current condition under the small-overpotential approximation.

Finally, we revised the explanation of Eq. (5) as follows:

Equation (5) decomposes the sensitivity into (i) a weighted sum of Nernst contributions, through $\partial E_k / \partial x$, and (ii) a reweighting contribution that arises when the relative polarization conductances, and hence the relative contributions of the partial reactions, change with x .

The referee also noted that degraded leaf litter may have contributed to EC. We agree that leaf-litter decomposition can contribute to background ionic and organic inputs and may influence microbial activity and Eh. We have clarified in Sect. 2.1 that leaf litter was not actively removed and was left to decompose within and around the pond. At the same time, the EC anomaly discussed in Sect. 3.2 was a synchronous, pronounced increase across sites following the May-June 2023 mechanical excavation, and we therefore used it as an operational proxy for the excavation-related physical disturbance rather than as a direct or exclusive measure of redox-network reconfiguration.

> [R2-5] Fig 3. It seems the authors assume EC to be stable throughout the year ("Baseline Level").
> That would however be exceptional. In any system outside there are variations caused by the
> season. Is the "baseline mean" (line 136-137) the average, or the seasonal trend? "pooled"
> assumed that all values were taken to calculate an averaged mean. The figure also indicate the
> trend line. Please explain how that was calculated.

[Response to R2-5]

We thank the referee for pointing out this ambiguity. We agree that EC in outdoor systems can show seasonal variability, and we did not intend to assume that EC remains stable throughout the year. In the original manuscript, "baseline" referred to a descriptive pre-disturbance reference range rather than a fitted seasonal trend. To clarify this point, we revised the text to specify that the reference range was calculated from all EC observations at all sites before completion of the excavation works. We also revised the Fig. 3 caption to state explicitly that the horizontal solid

lines and shaded bands represent the pooled pre-disturbance mean and mean $\pm$ 1.96 SD range, respectively.

[Changes in manuscript]

We revised the relevant sentence in Sect. 3.2 as follows:

Nevertheless, EC during June--August 2023 clearly exceeded the pre-disturbance reference range: values were above the pooled pre-disturbance mean and outside the mean $\pm$ 1.96 SD range calculated from all EC observations at all sites before the completion of the excavation works (7 July 2022 - 7 June 2023).

We also revised the Fig. 3 caption as follows:

Horizontal solid lines and shaded bands indicate the pooled pre-disturbance mean and mean $\pm$ 1.96 SD range, respectively, calculated from all observations at all sites before completion of the excavation works (7 July 2022--7 June 2023).

> **[R2-6]** *Fig 3. Please consider adding the year to the date (x-axis).*

[Response to R2-6]

We thank the referee for the suggestion. We have added the year to the x-axis labels in Fig. 3 to improve clarity.

> **[R2-7]** *Line 138. A1 is at the same distance of the inlet as A0 (see fig 2). This line however states > something else. Please explain. Also, please consider depth, and water flow. Were those different > between the two points?*

[Response to R2-7]

We thank the referee for pointing this out. We agree that the original wording was ambiguous. Our intention was not to state that Site A1 was closer than Site A0 in terms of simple geometric distance from the inlet. Rather, we intended to indicate that A1 was more directly exposed to the main circulation pathway and sediment-laden inflow, whereas A0 was located in a more hydrodynamically sheltered part of the pond geometry.

The water depths at A1 and A0 were broadly similar, typically approximately 40-45 cm, although they varied seasonally during dry periods. Therefore, we do not interpret

the stronger EC response at A1 as primarily reflecting a difference in depth, but rather as reflecting differences in hydrodynamic exposure associated with the pond geometry. We have revised the text to clarify this point.

[Changes in manuscript]

We revised the sentence in Sect. 3.2 as follows:

The largest increase was observed at Site A1, which was more directly exposed to the circulation pathway and sediment-laden inflow than Site A0, whereas the response at Site A0 was less pronounced, consistent with partial hydrodynamic shielding by the pond geometry rather than a difference in water depth (Fig. 2a).

> **[R2-8]** *Line 149. Please add reference to Wolfram here.*

[Response to R2-8]

We thank the referee for this suggestion. We have clarified the software environment used for the peak detection by adding the Mathematica version and Wolfram Research information in the relevant sentence.

[Changes in manuscript]

We revised the sentence in Sect. 3.2 as follows:

Local maxima in the likelihood profile were identified using the FindPeaks function in Wolfram Language (Mathematica 12.0; Wolfram Research, Champaign, IL, USA).

> **[R2-9]** *Line 156: If O2 increases due to water flow, the water flow must have been very turbid.
> This seems unlikely. A more common explanation is O2 production (and consumption) in the
> water. The authors state that there was no plants growing, but it can be assumed a biofilm was
> present during the experiment as the water was filled with leaf litter and the photos indicate a
> living environment.*

[Response to R2-9]

We thank the referee for this helpful comment. We agree that the original wording attributed the DO increase too narrowly to inflow-related mixing. Our intention was not to imply that the DO increase necessarily required strong turbidity or sediment resuspension. In a shallow pond, inflow and pumping events may enhance air-water gas

exchange and vertical exchange, but we agree that biological oxygen production and consumption, including processes associated with biofilms and organic matter, may also contribute to the observed DO dynamics. We have revised the text to avoid attributing the DO increase to a single mechanism. The revised wording now acknowledges both physical and biological contributions as possible explanations.

[Changes in manuscript]

We revised the sentence in Sect. 3.2 as follows:

Dissolved oxygen (DO) tended to increase during the latter part of the post-disturbance regime relative to the same season in the previous year (Fig. 3c). This pattern may reflect multiple processes, including enhanced air--water gas exchange and vertical exchange associated with inflow/pumping events, as well as biological oxygen production and consumption. Over the same period, Eh exhibited an overall upward shift following the disturbance (Fig. 3d).

> **[R2-10]** *Line 160: Temperature is a great predictor for bio activity. Please consider moving the appendix to the main text.*

[Response to R2-10]

We thank the referee for this helpful suggestion. We agree that temperature is an important environmental variable because it can influence oxygen solubility and biological activity. We considered moving the temperature and pH time series to the main text. However, because the temperature record mainly provides seasonal context rather than an independent disturbance marker, we retained the figure in the Supplementary Information to keep the main figures focused on the EC, DO, and Eh dynamics. To address the referee's point, we revised the final sentence of Sect. 3.2 to explicitly acknowledge the relevance of temperature.

[Changes in manuscript]

We revised the final sentence of Sect. 3.2 as follows:

Temperature, which can influence oxygen solubility and biological activity, showed typical seasonal cycles and vertical structure over the observation period, while pH ranged from 5.79 to 7.35 (mean 6.60) (Supplementary Fig. A1).

> **[R2-11]** Line 257: Do these metrics come from the current paper, or from literature. Please
> add to the sentence to clarify. Also, please consider naming this 2 year period a two-
> year period. "Long-term" is an interpretation which will depend on the reader's
> perspective. Line 273 uses '21-month" as a good descriptor.

[Response to R2-11]

We thank the referee for this helpful suggestion. We agree that “long-term” is subjective and that the duration of the dataset should be stated explicitly. We also agree that the origin of the two metrics should be clarified. These metrics are proposed and applied in the present study, rather than adopted from previous literature. We have therefore revised the sentence to explicitly state that the metrics are based on the co-located 21-month DO and Eh measurements in this study.

[Changes in manuscript]

We revised the sentence in Sect. 4.3 from:

Two complementary metrics emerge from co-located, long-term measurements.

to:

In this study, we propose two complementary metrics based on the co-located 21-month DO and Eh measurements.

> **[R2-12]** Line 266-7: The conclusion in this last line has a self reference in it. DO will always only
> measure O₂. Eh is the value for a wide range of redox active species, as explained in the lines
> before. Probably the text can end without this line. Or please rephrase your conclusion. For
> reference: see the standard works of the relationship between redox potential values and
> dominant pairs and hence the dominant idea that O₂ can only be present in an active state at
> higher Eh.

[Response to R2-12]

We thank the referee for this helpful comment. We agree that DO measures only O₂, whereas Eh integrates contributions from multiple redox-active species as a mixed potential. Our intention was not to imply that DO–Eh co-monitoring can identify dominant redox couples or directly resolve redox pathways. Rather, we intended to describe it as a screening-level approach for detecting departures from a site-specific DO–Eh baseline.

To avoid overstatement, we have rephrased the final sentence of Sect. 4.3 and the corresponding statement in the Conclusions. The revised text now emphasizes that DO–

Eh co-monitoring can indicate changes in effective redox conditions or in the relative contributions of redox-active processes, but that complementary measurements of redox-active species would be needed to resolve the underlying redox processes and dominant redox couples.

[Changes in manuscript]

We revised the final sentence of Sect. 4.3 as follows:

DO-Eh co-monitoring is therefore best viewed not as a substitute for comprehensive geochemical characterization, but as a low-cost screening-level approach for detecting departures from a site-specific DO-Eh baseline that may indicate changes in effective redox conditions or in the relative contributions of redox-active processes.

We also revised the corresponding statement in the Conclusions as follows:

Together, these results support the use of the $\ln[\text{O}_2]$ -Eh slope and baseline residuals as practical, screening-level indicators of departures from a site-specific redox baseline derived from co-located sensor measurements. These departures are consistent with disturbance-driven changes in effective redox conditions, although complementary measurements of redox-active species would be needed to resolve the underlying redox processes and dominant redox couples.

Response to comments from referee 3

> **[R3-1]** *This paper proposes an innovative way for the mechanistic interpretation of Eh measurements under mixed-potential conditions in aquatic environments. Using time-series data from field experiments over a period of almost two years from a shallow artificial pond the authors identified changes in the $\ln[\text{O}_2]$ –Eh relationship and interpreted these as evidence for redox-network reconfiguration. This is a valuable manuscript, with thoughtful considerations on modelling interactions among the factors that affect system dynamics, and it is potentially valuable for researchers using Eh measurements in aquatic systems. The conceptual novelty, addressing the interpretation of field-measured Eh values under mixed-potential conditions, and the combination of theory and field observations are clear strengths of this work. I strongly recommend its publication, but would recommend the authors to consider some considerations for improvement:*

[Response to R3-1]

We sincerely thank the referee for the positive and encouraging assessment of our manuscript. We are grateful that the referee found the mixed-potential interpretation, conceptual novelty, and combination of theoretical development with field observations valuable. In response to the comments, we have clarified the pond configuration, the field conditions, the treatment and possible influence of leaf litter, and the role of seasonal temperature variation in the interpretation of the $\ln[\text{O}_2]$ –Eh relationship.

> **[R3-2]** *Figure 2: Could this figure show with more clarity the design of the pond and the conditions of the experiment? E.g., flow direction, segments of the channel that were modified, relationships in the spatial location and photo directions.*

[Response to R3-2]

We thank the referee for this helpful suggestion. We agree that the original Fig. 2 did not sufficiently clarify the pond configuration, the modified channel, flow direction, and photograph viewpoints. In the revised manuscript, we have revised Fig. 2a to show the monitoring sites, open peripheral side channel, pumping location, flow direction, and approximate viewing directions of the photographs. We have also revised the caption to clarify that the channel was an open peripheral side channel and that the arrows indicate the direction of water flow driven by intermittent pumping.

> **[R3-3]** *The authors mention a leaf litter system. Can the authors elaborate on how it affected the measurements? Are any assumptions made regarding the changes in the chemistry of the pond due to the presence of leaves?*

[Response to R3-3]

We thank the referee for this important comment. The pond is surrounded by trees and receives substantial inputs of leaf litter, especially in autumn. In the revised

manuscript, we have clarified that leaf litter was not actively removed during the monitoring period and was left to decompose within and around the pond. We agree that leaf-litter decomposition can influence microbial activity, oxygen production and consumption, organic-matter inputs, and potentially the measured Eh and EC. At the same time, we did not make a quantitative chemical assumption about the changes in pond chemistry caused specifically by leaf litter, because redox-sensitive solutes and dissolved/particulate organic matter were not measured in this study. We therefore treat leaf litter as a plausible background source of organic matter and microbial activity, rather than as a separately quantified driver. The EC anomaly used to define the disturbance regimes was interpreted operationally as a response to the May–June 2023 excavation-related physical disturbance, not as a direct or exclusive measure of redox-network reconfiguration.

[Changes in manuscript]

We revised Sect. 2.1 to state that leaf litter was not actively removed and was left to decompose within and around the pond. The revised text now states:

Leaf litter was not actively removed during the monitoring period and was left to decompose within and around the pond.

We also revised Sect. 3.2 to acknowledge that biological oxygen production and consumption, including processes associated with organic matter and biofilms, may have contributed to the observed DO and Eh dynamics:

Dissolved oxygen (DO) tended to increase during the latter part of the post-disturbance regime relative to the same season in the previous year (Fig. 3c). This pattern may reflect multiple processes, including enhanced air--water gas exchange and vertical exchange associated with inflow/pumping events, as well as biological oxygen production and consumption. Over the same period, Eh exhibited an overall upward shift following the disturbance (Fig. 3d).

> [R3-4] *Consider including supplementary analyses showing seasonal variations or temperature normalization.*

[Response to R3-4]

We thank the referee for this helpful suggestion. Seasonal variation is shown in Supplementary Fig. A1, which presents the pH and water-temperature time series over

the monitoring period. In the revised manuscript, we also explicitly state that temperature can influence oxygen solubility and biological activity and that it showed typical seasonal cycles and vertical structure during the observation period.

We considered adding an additional temperature-normalized analysis. However, we decided not to apply a single empirical temperature normalization to the $\ln[\text{O}_2]$ –Eh relationship because temperature can affect several processes simultaneously, including oxygen solubility, microbial activity, transport, and interfacial reaction kinetics. Under mixed-potential conditions, these effects need not act through a single correction factor and a simple normalization could therefore obscure rather than clarify the interpretation. In addition, the reported Eh values were already converted to SHE-referenced values using the manufacturer-recommended temperature correction for the Ag/AgCl reference electrode. We therefore used the temperature record as seasonal context rather than as an independent normalization variable.

[Changes in manuscript]

We retained Supplementary Fig. A1 as the seasonal-context figure and revised Sect. 3.2 to explicitly acknowledge the relevance of temperature. The revised text states:

Temperature, which can influence oxygen solubility and biological activity, showed typical seasonal cycles and vertical structure over the observation period, while pH ranged from 5.79 to 7.35 (mean 6.60) (Supplementary Fig. A1).