

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 $\ln[O_2]$ -
- > 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 $\ln[O_2]$ -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.