Referee comment on the manuscript egusphere-2026-1048

The manuscript **“Redox-network reconfiguration inferred from the ln[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[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 long-term 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 $\partial Eh/\partial \ln x$ 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.

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.
2. Oxygen often plays a leading role in controlling Eh, and the authors propose the ln[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 redox-active components, such as iron or manganese cycling.
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.
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.

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.

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.