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Supplementary material

Spatiotemporal redox dynamics in a freshwater lake sediment under alternating oxygen availabilities: combined analyses of dissolved and particulate electron acceptors

Maximilian P. Lau,[A,B,D] *Michael Sander,*[C] *Jörg Gelbrecht*[A] *and Michael Hupfer*[A]

[A]Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB), Department of Chemical Analytics and Biogeochemistry, Mueggelseedamm 301, D-12587 Berlin, Germany.

[B]Universität Greifswald, Institut für Biochemie, Felix-Hausdorff-Straße 4, D-17487 Greifswald, Germany.

[C]Swiss Federal Institute of Technology (ETH) Zurich, Department of Environmental Systems Science, Institute of Biogeochemistry and Pollutant Dynamics, Universitaetstrasse 16, CH-8092 Zurich, Switzerland.

[D]Corresponding author. Email: lau@igb-berlin.de

Additional information on methods, mathematical operations and data are presented in the Supplementary material.

Mediated electrochemical reduction (MER) and mediated electrochemical oxidation (MEO)

The setup for MER and MEO was adapted from Aeschbacher et al.[1] In brief, measurements were conducted in electrochemical cells with pH buffered solutions (pH 7.00 ± 0.05) containing 0.1 M $NaClO_4$ as background electrolyte and 0.01 M 4-morpholinepropanesulfonic acid as the buffering species. We used glassy carbon cylinders (volume 9 mL; Sigradur G, HTW Carbon, Tierhaupten, Germany) that served as both the cell reaction vessels and working electrode (WE). The WEs were polarised to reduction potentials of E_h = –0.49 V for MER or +0.61 V for MEO (reported *v*. the standard hydrogen electrode, but experimentally measured *v*. Ag–AgCl reference electrodes). Each electrochemical analysis was initiated by the addition of the dissolved electron transfer mediators 6,7-dihydrodipyrido[1,2-a:2′,1′-c]pyraziniumdibromid monohydrate (99.5 %; $E_h°$ = –0.36 V; Supelco, Bellefonte, PA, USA) (Diquat, DQ) to MER cells and 2,2-azino-bis-(3-ethylbenzthiazoline-6-sulfonic acid) ammonium salt (>98 %; $E_h°$ = +0.7 V; Sigma–Aldrich, St Louis, MO, USA) (ABTS) to MEO cells to final concentrations of 250–350 µM.

Both ABTS and DQ are single-electron transfer mediators: DQ was reduced to the radical species $DQ^{\cdot+}$ in MER and ABTS was oxidised to the $ABTS^{\cdot+}$ radical in MEO. The resulting current responses were peak-shaped with initial high currents followed by a decrease in the currents that ultimately levelled off as the mediators approached E_h equilibria with the E_h applied to the WEs. We subsequently pipette-transferred small volumetric aliquots of 50–200 µL from vigorously stirred sediment suspensions to the MER and MEO cells. In MER, the dissolved $DQ^{\cdot+}$ transferred electrons to electron accepting species in the added sample,

resulting in the formation of DQ^{2+} molecules. The formed DQ^{2+} were subsequently reduced to $DQ^{\cdot+}$ at the WE to re-establish E_h equilibrium in the MER cell. In MEO, $ABTS^{\cdot+}$ radicals were reduced by electron donating species in the added sample, resulting in the formation of ABTS, which was then re-oxidised to $ABTS^{\cdot+}$ at the WE. The addition of redox-active samples to MER and MEO thus resulted in reductive and oxidative current peaks respectively. These peaks were baseline-corrected and integrated to obtain the numbers of electrons, n_e (mmol e^-) transferred to and from the added sample according to:

$$n_e = \int \frac{I}{F} dt$$

where I (A) is the reductive or oxidative current and F (C mol^{-1}) is the Faraday constant. The method detects particulate species that are electroactive in MER/MEO. These species do not include nitrate and sulfate, which we quantified separately.

Sediment porosity

In this work, the concentrations of dissolved and particulate terminal electron acceptors (TEAs) in the sediment suspensions are referenced to the dry mass of the respective sediment sample. We chose this approach to equally account for contributions of dissolved and particulate TEAs to the total TEA pool. The concentrations could have alternatively been referenced to the concentration of the conservative tracer chloride, which showed no variations over time. We verified that the conclusions drawn in the manuscript were unaffected when using chloride concentrations instead of dry sediment masses as a reference.

The sediment porosity (volumetric water content) generally decreases with increasing sediment depths (Fig. S1a). These changes with depth were accounted for when calculating concentration values that integrated over the three separate sediment layers (i.e. 0–7, 7–14 and 14–21 mm) by weighing the averages on the basis of the dry mass of each of the three layers. Porosity was also considered when calculating area-dependent fluxes (as e.g. in Fig. 5).

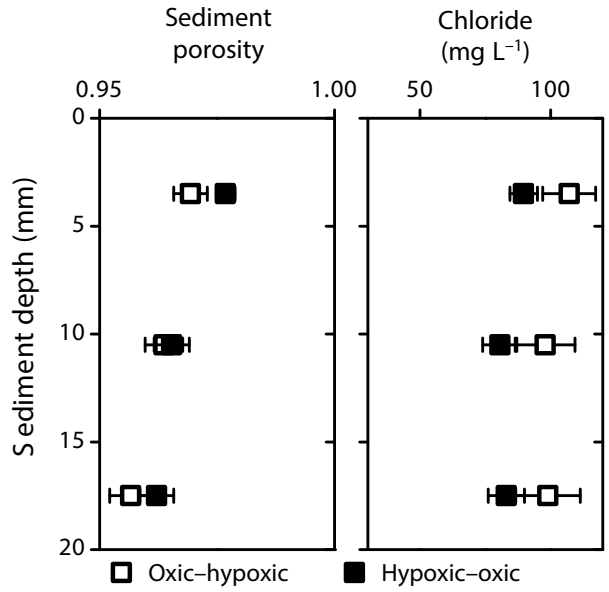

Fig. S1. Sediment porosity (left) and dissolved chloride concentrations in the sediment porewater (right) for each of the three sediment layers analysed (i.e. 0–7, 7–14 and 14–21 mm). Values are averages from all samples analysed over the course of the incubation periods (n = 7 for the oxic–hypoxic mesocosm and n = 5 for the hypoxic–oxic mesocosm experiments). Bars represent standard deviations.

The porosity (ϕ) was calculated from

$$\phi = \left(\frac{\text{water content (mass fraction wet sediment)}}{\text{water density (4 °C)}} \right) \div \left(\frac{\text{water content}}{\text{water density}} + \frac{1 - \text{water content}}{\text{dry mass density}} \right)$$

where the density of the dry mass was assessed with regard to its content of organic (specific density ρ = 1.4 g cm^{-3}) and mineral (ρ = 2.6 g cm^{-3}) constituents.

Reduced TEA species

In this work, the spatiotemporal dynamics of the reduction of nitrate and sulfate were monitored as changes in the concentrations of both the oxidised TEA species and of the reduction end products ammonium and sulfide. The measured sulfide concentrations are presented in Fig. S2. Sulfide concentrations were below the limit of quantitation (LOQ, 30 µg L^{-1}) for most samples. The concentrations of dissolved ammonium in the sediment pore water of the hypoxic–oxic mesocosm are provided in Fig. S3.

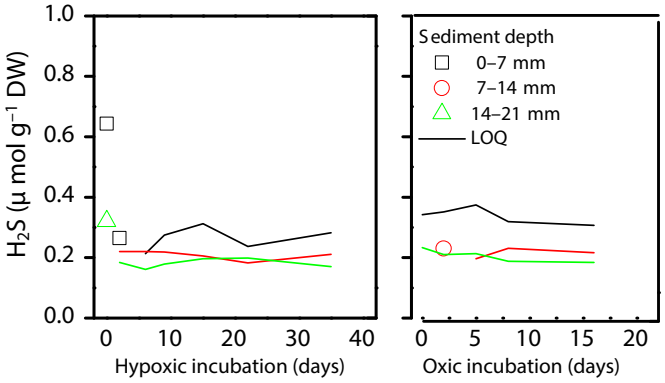

Fig. S2. Hydrogen sulfide (H_2S) concentrations in the wet sediment samples. The oxygen regimes in the water overlying the sediments were changed on day 0 from oxic to hypoxic (left panel) and from hypoxic to oxic (right panel), respectively. Lines indicate the limit of quantitation (LOQ) for the different sediment depths. The symbols represent measurement data where values were above the LOQ.

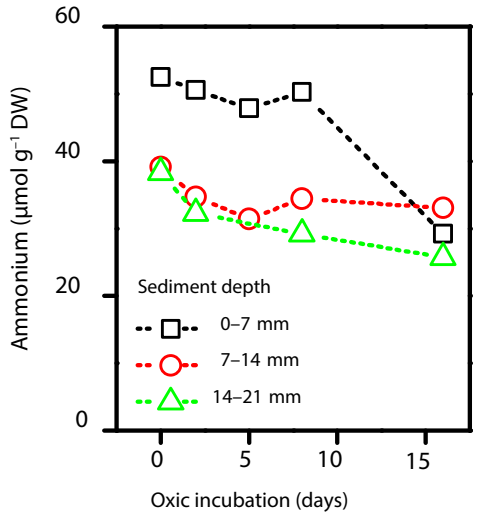

Fig. S3. Ammonium concentrations in the wet sediment samples. The oxygen regime in the water overlying the sediment was changed from hypoxic to oxic on day zero.

Manganese

The total content of manganese in the sediment samples was quantified without determination of the oxidation state of the Mn (i.e. Mn^{II} or Mn^{IV}). The Mn was quantified by inductively coupled plasma atomic emission spectrometry after dissolving the sediment samples in aqua regia. The Mn concentrations in both mesocosms were determined only at the onsets of the incubations. However, in a separate control experiment with six sediment cores from Lake Scharmützelsee that were subjected to similar incubation cycles, no significant changes in Mn concentrations in the uppermost 21 mm of sediment were detected (Fig. S4). Therefore, we assumed that manganese had a constant contribution of EEC_{Mn} of 46 µmol e^- g^{-1} DW to the EEC_{tot}. This value could overestimate the contribution of Mn to the EEC_{tot} if a significant amount of the sediment-associated, aqua-regia extractable Mn is not accessible in electron transfer reactions at milder conditions (as e.g. in situ or during the electrochemical analysis).

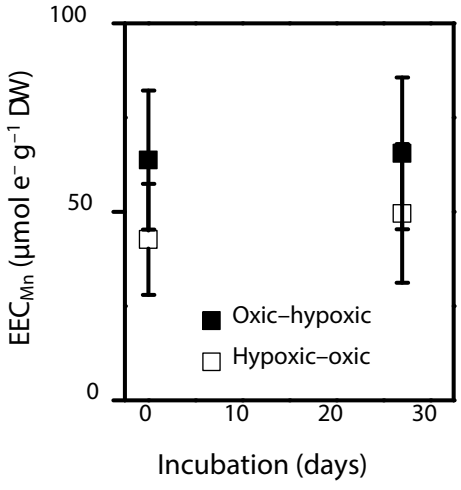

Fig. S4. Manganese content in the lake sediments determined after digestion of the sediment with aqua regia. The contents are expressed as electron exchange capacity (EEC_{Mn}), based on the assumption that each Mn contributed two electrons to the EEC (i.e. assuming that the redox couple Mn^{IV}–Mn^{II} predominated). The oxygen regime in the water overlying the sediment was altered on day 0 from oxic to hypoxic (filled symbols) and from hypoxic to oxic (open symbols). Error bars represent standard deviations between triplicate cores.

TEA consumption during hypoxic incubation

The dynamics of all oxidised TEA species were determined in the oxic–hypoxic mesocosm (Fig. S5) similar to the dynamics of the same species in the hypoxic–oxic mesocosm (Fig. 5a in the manuscript). The resulting reduction rates in the three sediment layers are provided in the results section of the manuscript.

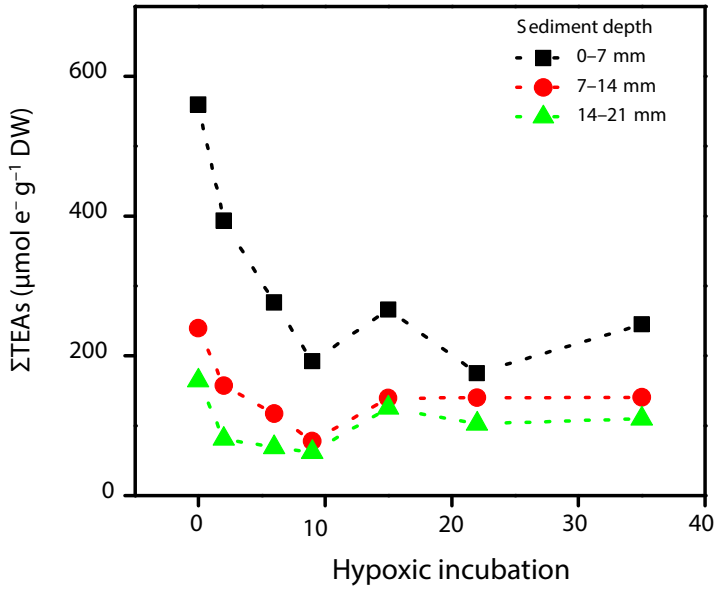

Fig. S5. Dynamics of the dissolved and particulate terminal electron acceptors (TEAs) determined from changes in the concentration of NO^- and SO^{2-} and the changes in the electron accepting capacity (EAC) of the sediments. The incubation conditions were changed from oxic to hypoxic on day 0. Values are expressed in terms of transferred electron (e^-) equivalents.

Calculation of the areal hypolimnetic mineralisation (AHM) from oxygen profiles

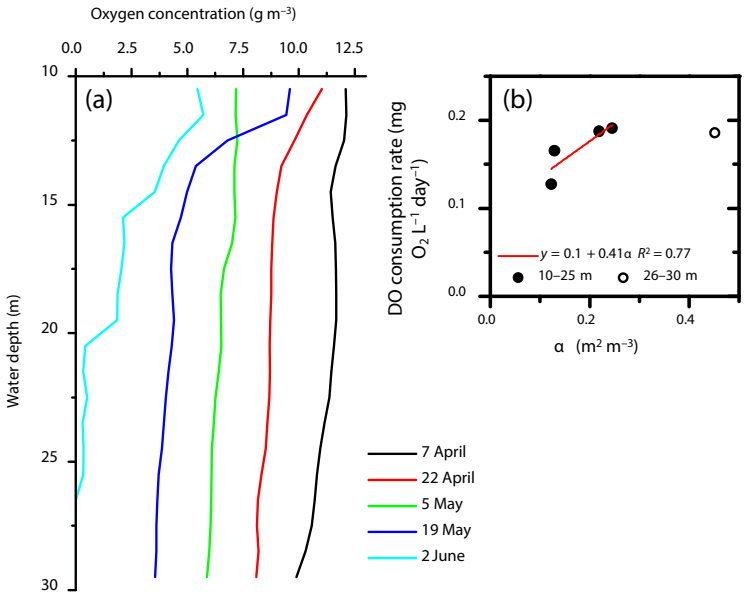

Fig. S6. (a) Dissolved oxygen (DO) concentrations in the hypolimnion of Lake Scharmützelsee as a function of depth, measured at different dates (represented by lines of different colours). (b) DO consumption rate as a function of the ratio of sediment area to water volume, α (circles, calculated for hypolimnion cross-sections of 4-m depth, see methods section). The line is the result of a linear regression fit on the data. The DO consumption rate at α = 0.45 was omitted from the fit: this value corresponds to the hypolimnion cross-section at the depth of 26–30 m (empty circle) and no oxygen was detected in this layer at the end of the measurement period.

In the deepest layer of the hypolimnion (26–30 m), we measured a lower oxygen consumption than what was expected based on its α value (i.e. the sediment area to water volume ratio). These lower-than-average values remain, even when only sampling points were considered when DO was still >0 mg L^{-1}. Hence, we assume that no disproportionate share of fine sediments moved to deeper parts of the lake ('sediment focussing') where this sediment fraction could have additionally accelerated oxygen consumption.

References

[1] M. Aeschbacher, M. Sander, R. P. Schwarzenbach, Novel electrochemical approach to assess the redox properties of humic substances. *Environ. Sci. Technol.* **2010**, *44*, 87. doi:10.1021/es9a02627p