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Key Points:

- Solute fluxes from benthic lake sediments varied in response to temperature, with oxygen fluxes responding most strongly
- Temperature effects on the magnitude of benthic fluxes were stronger under anoxic than oxic conditions
- Direct temperature effects on reservoir water quality will be small compared to indirect effects through anoxia facilitation

Supporting Information:

Supporting Information may be found in the online version of this article.

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Oxygen Dependent Temperature Regulation of Benthic Fluxes in Reservoirs

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Abstract Temperature and dissolved oxygen concentration are critical factors affecting the exchange of solutes between sediment and water; both factors will be affected by warming of lakes and thereby influence water quality. Temperature and oxygen responses of single solute fluxes are well known; however, not much is known about the interaction of temperature and oxygen in regulating the balance of different fluxes in the benthic environment. We analyzed benthic flux (mobilization and immobilization) data of various solutes (dissolved organic carbon (DOC), CH₄, NO₃⁻-N, NH₄⁺-N, SRP, SO₄⁻, Fe, Mn, and O₂) collected from laboratory incubations of 142 sediment cores from 5 different reservoirs incubated under varying in situ temperature and oxygen conditions. Oxygen was the primary driver of benthic fluxes, while temperature and total organic content were secondary. Temperature effects on benthic fluxes were stronger under anoxic conditions which imply that warming will substantially increase the benthic fluxes if the sediment surface becomes anoxic. The varying temperature response of processes underlying the studied fluxes will result in a shift of their relative importance in the benthic environment, especially in shallow lakes that are more vulnerable to warming. For example, more anoxic conditions will shift the equilibrium between net sulfate reduction and methane release toward the latter. We also predict that physical effects of warming leading to hypolimnetic oxygen depletion, that is, stronger stratification and longer hypolimnetic confinement will increase the benthic mobilization of phosphorus, DOC, and methane into water and immobilization of sulfate by the sediments even in deep lakes.

Plain Language Summary Temperature and dissolved oxygen concentration control the release of undesirable components buried in lake or reservoir sediments, that is, nutrients, metals, and organic matter, which can cause water quality problems. We investigated the effects of rising temperature and levels of oxygen on the release of undesirable components by performing experiments using sediments and water from five different reservoirs. The sediments with a layer of water on top were incubated under different in situ temperature (low and high) and oxygen conditions (with and without). Our results show that the absence of oxygen was the main cause of the release of nutrients and metals. When there was no oxygen in the sediment and water, nutrients and metals were released from the sediment into the water and this effect increased when temperature was high. There is higher possibility that phosphorus, dissolved organic carbon, and methane will be released from sediments in some reservoirs as a result of global warming.

1. Introduction

Temperature and oxygen regulate biogeochemical processes in aquatic ecosystems (Wetzel, 2001) and thereby influence water quality. Increasing hypolimnetic temperatures in some lakes and reservoirs have been reported (Jankowski et al., 2006; Kraemer et al., 2017; Verburg & Hecky, 2009; Woolway, Sharma, et al., 2021). Rising temperature directly affects both oxygen consumption and solubility in water, that is, decreasing solubility of oxygen with increasing temperature. Higher surface temperature in lakes and reservoirs leads to stronger stratification which depletes oxygen in the hypolimnion and at the sediment surface (Boehrer & Schultze, 2008) and reduces heat transfer to deep water (Bartosiewicz et al., 2019; Niedrist et al., 2018). It is expected that many lakes and reservoirs will experience longer periods of high temperature and absence of oxygen in deep layers (Woolway et al., 2022). This will likely have some impacts on the interaction between the sediment and water in lakes and reservoirs, for example, increase in solute exchange at the sediment water-interface (Deemer & Harrison, 2019; Harrison et al., 2017; Perrin et al., 2000). Solute exchange in reservoirs is important given the wide ranging water withdrawal regimes, which together with extreme events (e.g., drought) can create a large decrease in

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water levels and impact water quality (Furey et al., 2004; Keller et al., 2021; Weber et al., 2017). In reservoirs, the sediment surface exposed to higher temperatures and anoxia is therefore highly dynamic and hence an ideal location to study the effects of temperature and oxygen on the exchange of solutes at the sediment water interface. Moreover, within a certain water depth range, one can also avoid bottom warming (by epilimnetic withdrawal) or bottom water anoxia (by hypolimnetic withdrawal).

The exchange of solutes between sediment and water is a major determinant of water quality in water bodies (Søndergaard et al., 2003). It can be quantified as a flux that is regulated by mobilization/production, immobilization/consumption and transport processes; mobilization and immobilization are mostly chemical and biological, while the transport processes are mostly physical (Orihel et al., 2017). The mobilization/production processes include hydrolysis or mineralization, desorption, dissociation, dissolution, exudation; immobilization/consumption processes include assimilation, adsorption, complexation, precipitation; the transport processes include, diffusion, advection, sedimentation and resuspension (Orihel et al., 2017). The mobilization and immobilization of carbon, nitrogen, phosphorus, iron, and sulfur from/into the sediments is well documented in the literature (Dadi et al., 2016; Einsele et al., 1936; Katsev et al., 2006; Kristensen & Holmer, 2001; Lovley & Phillips, 1986; Mortimer, 1942; Orihel et al., 2017; Roden & Edmonds, 1997). These processes are controlled by temperature and oxygen concentrations (Holdren & Armstrong, 1980; Jensen & Andersen, 1992; Liikanen et al., 2002), albeit differently.

Temperature effects on biotic processes have been known for more than a century; rates of biological processes increase exponentially with temperature (Arrhenius, 1889; Boltzmann, 1970). The temperature response of different biogeochemical processes can be compared by looking at their activation energy (E_a) derived from Arrhenius type equations (Arrhenius, 1889). This relationship is confined to the temperature range of normal activity that is, 0–40°C (Brown et al., 2004). Although in general, temperature dependence follows an optimum curve, lake sediment studies only consider the rising side of the temperature response curve because temperatures above 30°C rarely occur in most lake sediments (Brown et al., 2004). Biological processes in sediments are predominantly microbial (Jones et al., 1985). The increase of various microbially mediated processes with increasing temperatures (below 30°C) is well established, that is, organic carbon mineralization (Gudasz et al., 2010), methane emission (Yvon-Durocher et al., 2014), sulfate reduction (Meier et al., 2005), nutrient fluxes (Liikanen et al., 2002), nitrification (Thamdrup et al., 1998), and bioturbation (Roskosch et al., 2012). By combining nonlinear temperature response data of different processes with long-term temperature data from numerous lakes, it has been shown that increases in metabolic rates due to lake warming are stronger in warmer regions and in the surface water (Kraemer et al., 2017). Temperature also affects abiotic processes however differently in comparison to biotic processes; for example sorption of organic pollutants can increase, decrease or show no effect with/temperature (Ten Hulscher & Cornelissen, 1996; Huang et al., 2011). Physical processes such as adsorption may also be temperature-insensitive, as shown for ammonium (Mackin & Aller, 1984), but the influence of oxygen level was not studied. Given the differences in the temperature dependency of different processes, we hypothesize that temperature rise will result in shifts in the relative importance of benthic mobilization and immobilization processes of solutes, as has been shown for pelagic carbon cycling (Yvon-Durocher et al., 2010, 2014). These studies revealed a shift in the metabolic balance of the experimentally warmed ecosystems since ecosystem respiration increased more than primary production.

Anoxia effects on solute fluxes have been known for a long time. Anoxia at the sediment-water interface occurs when the uptake rate of oxygen is higher than the rate of oxygen supply; even under oxic conditions the oxidized surface layer of the sediment is restricted to a few millimeters (Jensen & Andersen, 1992). However, even this small oxidized layer has a profound influence on sediment water exchange. It is well established that in some sediments the benthic flux of dissolved P is regulated by adsorption to ferric minerals (Einsele et al., 1936; Mortimer, 1942), organic matter deposition, and the ratios of Fe, P, and S (Gachter & Muller, 2003; Hupfer & Lewandowski, 2008). Since the speciation and solubility of iron strongly depends on redox conditions (Davison, 1993), the benthic fluxes of associated solutes, dissolved P (Einsele et al., 1936; Mortimer, 1942), and dissolved organic carbon (DOC) (Dadi et al., 2016; Peter et al., 2016) are strongly affected by redox conditions in the uppermost layer of sediments rich in redox sensitive iron bound P and DOC. Under oxic conditions, Fe:P ratio >2 (Gachter & Muller, 2003), and low sulfate concentration (Caraco et al., 1993), the sorption capacity of the sediment surface can control the flux of SRP (Liikanen et al., 2002) and DOC (Dadi et al., 2016). The oxic sediment is also a site of intensive microbial oxidation of upward diffusing reduced substances. It is well known that most of the CH_4 (Frenzel et al., 1990) and H_2S (Holmer & Storkholm, 2001) produced in sediments is oxidized during passage

through oxic surface sediments. Given the higher solute fluxes occurring under anoxic conditions, we expect temperature change effects to be stronger under anoxia.

The effects of temperature and oxygen on benthic solutes release are well understood for single solutes such as phosphorus and iron (Bergström et al., 2010; Hupfer & Lewandowski, 2008; Jensen & Andersen, 1992; Katsev et al., 2006; Søndergaard et al., 2003). Benthic oxygen conditions and temperature are not independent from each other. Temperature affects many processes that can influence the exchange of solutes; microbial and macrofauna activity (Glud et al., 2003; Kristensen & Holmer, 2001), particle sedimentation (Laufkötter et al., 2017), and hypolimnetic oxygen depletion (Foley et al., 2012). While there exists considerable knowledge about the effect of oxygen conditions or temperature on single processes (Duc et al., 2010; Gudasz et al., 2010), there are few studies investigating the combined effect of both factors on the benthic fluxes of different solutes simultaneously (Delsontro et al., 2016; Kelderman, 1984; Liikanen et al., 2002). The existing studies are based on sediment cores from single location and at different laboratory conditions; our approach was to incubate sediment cores sampled from many different reservoirs at in situ conditions, at different times of the year to mimic the natural changes of oxygen and temperature in the reservoirs. This approach enables us to determine the combined effects of temperature and oxygen in the highly dynamic reservoirs.

We used laboratory sediment incubation experiments to disentangle the temperature and oxygen effects and to understand the effect of their interaction on benthic fluxes of solutes relevant for water quality evaluation since most reservoirs are used for drinking water or bathing purposes. We hypothesize that (a) the interaction of temperature and oxygen will affect the magnitude of solute fluxes differently by altering the relative importance of benthic mobilization and immobilization processes of solutes; and (b) the dependence of benthic fluxes to temperature is steeper under anoxic conditions than under oxygenated conditions. We quantified the temperature effect on the flux of soluble reactive phosphorus (SRP), oxygen (O_2), DOC, nitrate (NO_3^- -N) ammonium (NH_4^+ -N), sulfate (SO_4^{2-}), iron (Fe), and manganese (Mn) under oxic versus anoxic conditions. This was done by incubation of 142 intact sediment cores from seven sites in five reservoirs exhibiting (at different seasons) a large range of bottom temperatures and oxygen conditions.

2. Materials and Methods

2.1. Study Sites

We sampled five reservoirs in Germany and Spain, which differed in hypolimnetic oxygen conditions and temperature (Table 1, Figure 1). Oxygen conditions were categorized into the presence or absence ($O_2 < 5\%$ saturation, reduced) of molecular oxygen. In Sau Reservoir, Hassel and Rappbode predams we sampled two sites, one at the deepest point and one in the intermediate section of the reservoir (Table 1, Figure 1); the intermediate section points were mostly oxic however at Sau Reservoir it was anoxic at the time of sampling (Table 1, Figure 1).

Rappbode Reservoir (51.7306°N, 10.8772°E) is the largest drinking water reservoir in Germany (Rinke et al., 2013). The mesotrophic reservoir maintains a completely oxic water body throughout the year and the hypolimnion temperature never exceeds 6°C. The reservoir was sampled once in September 2015.

Rappbode (51.70917°N, 10.79766°E) and Hassel (51.70932°N, 10.83195°E) predams are predams of Rappbode Reservoir. Both predams develop an anoxic hypolimnion during summer stratification (Wendt-Potthoff et al., 2014). Sampling sites were at the deepest point of the reservoir, where the bottom water was mostly anoxic except in winter and a shallow site halfway to the inflow with permanently oxic conditions at the bottom (Dadi et al., 2016). During the year, bottom temperatures fluctuated between 4 and 17.5°C at the shallow sites and between 4°C and 6°C at the deep sites respectively. Hassel predam was sampled 6 times in 2013, Rappbode predam was sampled 6 times in 2014 (Table 1, Figure 1).

The shallow eutrophic Bautzen Reservoir (51.218°N, 14.466°E) is used for the low water elevation of the river Spree (Germany). The reservoir usually develops an anoxic hypolimnion during summer but in some years high winds can trigger polymixis (Kerimoglu & Rinke, 2013). Hypolimnion temperatures varied seasonally between 4 and 20°C. Bautzen reservoir was sampled in May 2014 when bottom temperature was 13.8°C (Figure 1).

Sau Reservoir (41.9717°N, 2.3888°E) is an intensively studied eutrophic reservoir providing drinking water for the city of Barcelona, Spain (Marcé et al., 2010). The reservoir was chosen because in contrast to the German reservoirs, it develops an anoxic but warm (4–12°C) hypolimnion during summer (Figure 1). Sau was sampled in October 2015 at the deepest point as well as in the intermediate zone of the reservoir.

Table 1
Reservoirs and Sampling Site Characteristics

	Hassel PD	Rappbode PD	Sau	Rappbode	Bautzen
Volume (10 ³ m ³)	1,448	1,146	168,200	113,100	39,200
Mean depth (m)	5.0	5.3	29	28.6	7.4
Max depth (m)	14	17	65	89	13.5
Surface area (km ²)	0.288	0.218	5.8	3.95	5.33
Residence time (d)	18	26	113	344	164
Catchment area (km ²)	44.6	47.6	1680	274	310
Alkalinity (meq L ⁻¹)	0.6–1.5	0.3–1.1	2–3	NA	1.27
pH	7.1–8.2 (6.8–7.0)	6.8–7.3 (6.5–7.2)	7.7 (7.6)	(7.15–8.5)	(7.2–7.7)
Oxygen (mg L ⁻¹)	6.9–10.4 (0–6)	0–10.8 (0–11)	0 (0)	(7.4–10.4)	(8.4–8.9)
Temperature (°C)	4–17.5 (4–5.2)	5–15 (5–6)	12 (7)	(4.9–20.3)	(12.9–13.9)
DOC (mmol L ⁻¹)	0.4–0.6 (0.3–0.6)	0.2–0.5 (0.2–0.5)	0.17–0.52 ^{SC}	(0.28–0.32)	(0.25–0.32)
TN (μmol L ⁻¹)	60–310 (10–380)	20–70 (62–113)	73–2582 ^{SC}	(96–129)	NA
TP (μmol L ⁻¹)	0.3–0.5 (0.3–5.5)	0.2–0.5 (0.1–0.4)	0.4–11 ^{HD}	< DL (0.32)	(1.71–1.90)
TFe (μmol L ⁻¹)	10–20 (1–130)	3–9< (1–150)	0.22–2.0 ^{SC}	(0.18–0.25)	(0.482–0.607)
TC (g C kg ⁻¹ dw)	65.3 ± 1.0 (108 ± 9.8)	72.8 ± 1.1 (88.8 ± 2.8)	52.5 ± 7.5 (58.8 ± 21.1)	56 ± 7	78.90*
TFe (g kg ⁻¹ dw)	48.9 ± 0.6 (68 ± 5)	49.5 ± 0.8 (74 ± 8)	35 (36)	35.3 ± 3	34.2*
Sediment sampling dates	29 April, 26 June, 23 July, 17 September, 15 October and 12 November 2013	18 March, 23 April, 11 June, 23 July, 02 September, and 28 October 2014	13 October 2015	14 September 2015	14 May 2014
Sampling points—water depth	Inflow—3.5 m Dam—13 m	Inflow—4 m Dam—16 m	Inflow—26 m Dam—65 m	Inflow—17 m	Dam—12 m

Note. Values in brackets refer to deep sites. DOC, TN, TP, TFe data (with the exception of Sau) refer to hypolimnetic water samples taken at the time of sediment sampling. For Sau, DOC, TN, and TFe data refer to the initial sampling from the overlying water in the sediment cores (SC) and TP is from historical data (HD). Physical data for Hassel predam and Rappbode predam are from (Wouters, 2011) and (Friese et al., 2014). Physical data for Rappbode are from Rinke et al. (2013). Bautzen physical data are from Deppe et al. (2004) and Rinke et al. (2007); chemical data were measured on 14.5.2014. PD = predam, NA = no data, DL = detection limit. Sedimentary content of TC and TFe is data collected from this study, * refers to data from Bautzen (09.03.2017) published in Dadi et al. (2020).

2.2. Sediment Core Incubations

Undisturbed sediment cores were taken with a gravity sampler (Uwitec, Mondsee, Austria). Cores were immediately capped with a custom-designed gas tight stirring head and transported in an insulation box to keep in situ temperature (Dadi et al., 2015). The cores had a mean water height of 22.9 ± 4.4 cm ($n = 142$, mean \pm standard deviation), ranging from 13 to 32 cm, which translates to a water volume of 0.8–1.9 L. In the laboratory, cores were incubated in climate chambers under in situ temperature and oxygen conditions for 1–3 weeks; exact durations for each individual experiment are shown in Tables S3a–S3d in Supporting Information S1. We kept the incubation period short to minimize the uncertainty with regards to sedimentation effects, which normally occur in lakes but were absent in our set-up, as well as to minimize substrate depletion during incubations. Sediment cores were wrapped with aluminum foil to exclude light. Oxygen content in the cores was checked prior to the start of the experiments using O₂ optodes (Pyro Science, Aachen, Germany). Anoxic cores were kept anoxic by sparging with a mixture of nitrogen and carbon dioxide (99.96% N₂/0.04% CO₂). This was done periodically; prior to the start of the incubations and immediately after sampling to exclude any oxygen contamination. Oxidic cores were kept oxidic by gently sparging continuously with air using aquarium pumps; this was really necessary above 10°C because oxygen consumption was higher. Oxygen consumption rates in oxidic cores were determined during the first hours of incubation using O₂ optodes (Pyro Science, Aachen, Germany). To correct for changes related to processes occurring in the water, bottles with hypolimnetic water from each sampling point were incubated at the same temperature and oxygen conditions. Sediment incubation was performed with 4 replicate cores, with the exception of Rappbode Reservoir which had 3 replicates. About 30 mL of the overlying water was

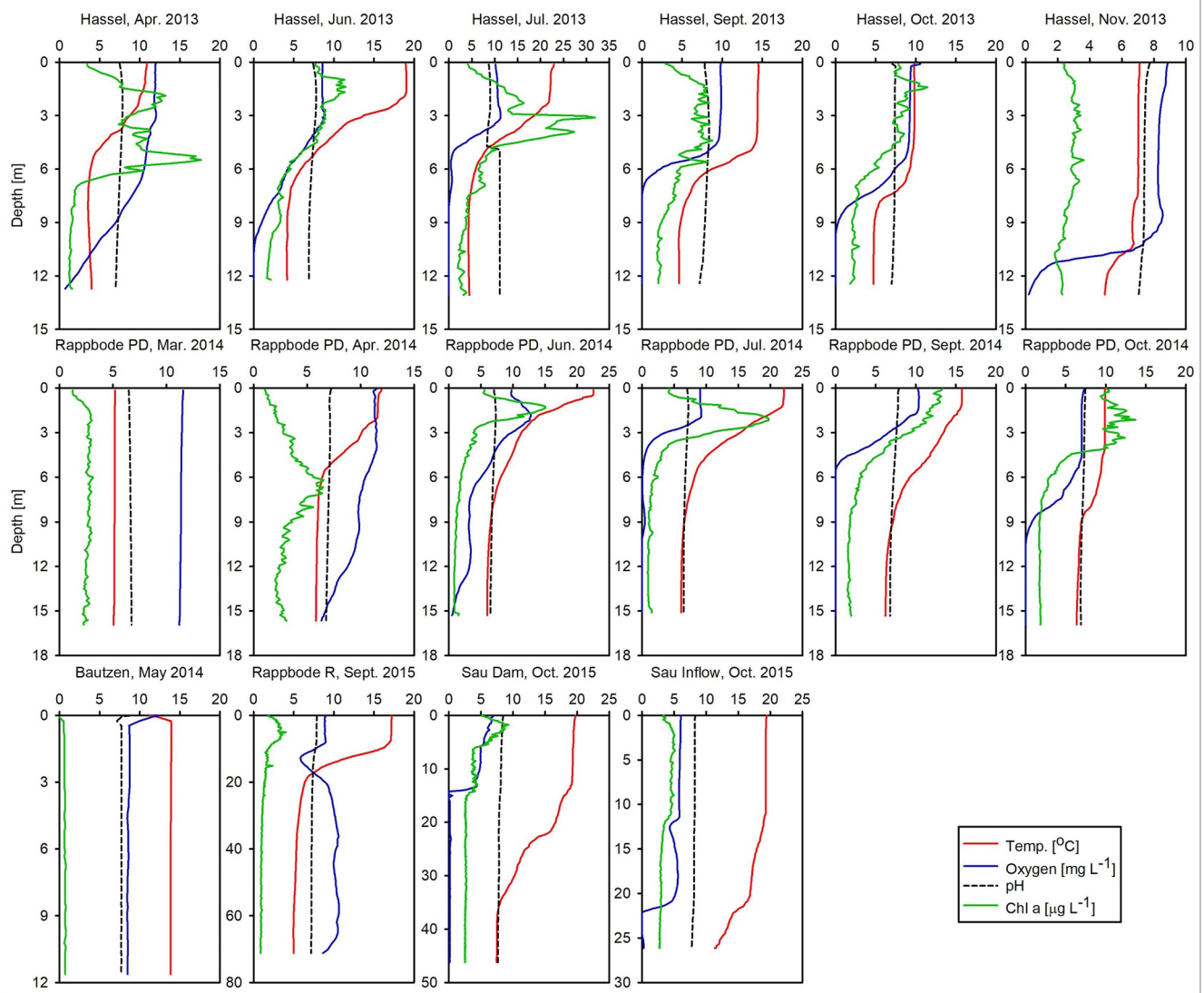


Figure 1. Temperature, oxygen, pH and chlorophyll a profiles at the time of sediment sampling. Please note that PD and R refer to predam and reservoir, respectively.

sampled consecutively four to seven times during the 14–21 days with subsequent analysis of DOC, CH₄, SRP, SO₄²⁻, NO₃⁻-N, NH₄⁺-N, Fe, and Mn. The sampled water volume was replaced by hypolimnion water from each sampling point, which was kept in storage bottles at in situ temperature and oxygen conditions. Details of the incubation procedure are given in Dadi et al. (2015). All incubations were carried out under in situ oxygen and temperature conditions except for (a) Sau, where replicates were also incubated at an additional elevated temperature of 20°C, and the experiments were conducted in 2 phases, that is, phase 1, in situ conditions (anoxic) and phase 2, oxic conditions and (b) Bautzen, where replicates were incubated at 8 and 20°C. After the end of incubation, sediment porewater was extracted from the upper 5 cm by centrifugation and analyzed for aforementioned solutes.

2.3. Analytics

Samples for DOC were filtered into precombusted (550°C) brown glass vials through precombusted (450°C) GFF filters. Dissolved organic carbon samples were analyzed by a total organic carbon (TOC) analyzer (DIMATOC 2000, DIMATEC Analysentechnik GmbH, Germany). Methane samples were prepared by adding 200 µL 1 M hydrochloric acid (Merck suprapure®) into 10 mL glass vials, which were closed with a rubber septum and aluminium crimp, and flushed with argon/nitrogen gas for 5 min. One mL sample was added to the prepared glass

vials. Headspace gas samples were withdrawn from the vials for analysis by a gas chromatograph (SRI, U.S.A.). Ammonium was measured by an ammonium ion selective electrode with a separate lithium acetate reference electrode (ELIT 8051 & ELIT 003n, Nico2000 Ltd, UK). Samples for NH_4^+ -N, NO_3^- -N, SO_4^{2-} , Fe, and Mn were filtered using a 0.2 μm syringe filter (Sartorius, Germany). SRP, NO_3^- -N and NH_4^+ -N were analyzed photometrically (Skalar, The Netherlands). The syringe filters were rinsed with 2 mL of sample. To prevent oxidation of redox sensitive elements in the anoxic samples, the syringe filter was flushed by a mixture of nitrogen and carbon dioxide (99.96% N_2 /0.04% CO_2) prior to rinsing with sample. Sulfate was analyzed by ion chromatography (ICS-3000, Dionex, Idstein, Germany). Fe and Mn were determined by ICP-OES (Perkin Elmer, Überlingen, Germany) after acidification with nitric acid (Merck suprapure®). Soluble reactive phosphorus (SRP) samples for the Sau Reservoir were analyzed photometrically (Cary 60 UV/Vis spectrophotometer; Agilent, Malaysia) based on the method of Laskov et al. (2007). The pH was measured using a conventional pH meter and glass electrode (WTW, Weilheim, Germany). The limits of quantification for the solutes are as follows: DOC (29 $\mu\text{mol L}^{-1}$), CH_4 (0.02 $\mu\text{mol L}^{-1}$), SRP (0.1 $\mu\text{mol L}^{-1}$), SO_4^{2-} (8 $\mu\text{mol L}^{-1}$), NO_3^- -N (3 $\mu\text{mol L}^{-1}$), NH_4^+ -N (0.7 $\mu\text{mol L}^{-1}$), Fe (0.18 $\mu\text{mol L}^{-1}$), and Mn (0.13 $\mu\text{mol L}^{-1}$) and O_2 (0.31 $\mu\text{mol L}^{-1}$).

Sediment water content was determined gravimetrically after drying at 105 °C. Sediment organic matter content was analyzed using the loss on ignition (LOI) method. Total carbon (TC), TOC and total nitrogen (TN) were measured with a CN-elemental analyzer after combustion of the sample material in a high-temperature combustion unit flushed with helium and jet injection of oxygen directly to the sample at temperatures of 1150°C (vario EL cube; Elementar Analysensysteme Hanau). Subsamples for TOC were acidified before measuring by adding sulfuric acid to eliminate inorganic carbon if present. Total inorganic carbon (TIC) was calculated as the difference between TC and TOC (TIC = TC—TOC in weight-%). An aliquot of the powdered sample was diluted with $\text{Li}_2\text{B}_4\text{O}_7$ to prepare glass discs to analyze total iron by wavelength dispersive X-ray fluorescence spectrometry (S4 Pioneer; Bruker-AXS). The relative repeatability precision of the measurements was better than 1% (Morgenstern et al., 2001). Data on sediment composition can be found in the Supporting Information S1 (Table S1).

2.4. Calculations

Sediment-water fluxes (J in $\text{mmol m}^{-2} \text{d}^{-1}$) were calculated from the linear concentration change of the different solutes during the incubation. No changes were observed in the control bottles, so no corrections for the calculated fluxes were necessary. The flux of reduced solutes (F_{red}) expressed as the total O_2 required per area to oxidize all reduced compounds released by the sediment was calculated according to Steinsberger et al. (2017):

$$F_{\text{red}} = 2 \times J_{\text{CH}_4} + 2 \times J_{\text{NH}_4} + 0.5 \times J_{\text{Mn}} + 0.25 \times J_{\text{Fe}} \quad (1)$$

Each core was treated separately in the data analysis, resulting in 142 datasets containing various fluxes as well as porewater concentrations. Fluxes of NO_3^- -N, NH_4^+ -N, SRP, SO_4^{2-} , Fe, and Mn were not measured in every core, resulting in a reduced data set of 118 fluxes for these parameters. For sediment analysis (porewater and sediment), replicate core samples were pooled before analysis. The resulting mean sediment matrix data were then applied to each core from the respective replicate incubation.

The contribution of different respiratory processes to sediment metabolism was calculated by multiplying the respective fluxes with compound specific electron transfer coefficients (5 for NO_3^- -N, 8 for SO_4^{2-} , 4 for CH_4 , 2 for Mn, and 1 for Fe (Wendt-Potthoff et al., 2014)).

Different models have been applied to describe the temperature dependence of biogeochemical processes (Ahlgren, 1987; Lloyd & Taylor, 1994). The temperature dependence of biological processes is usually described by the exponential Boltzmann-Arrhenius model (Dell et al., 2011):

$$V = b_0 \times e^{\frac{-E_a}{k \times T}} \quad (2)$$

Where v is a process rate, b_0 a normalization constant, E_a the activation energy [eV], k the Boltzmann constant ($8.617 \times 10^{-5} \text{ eV K}^{-1}$), and T is the temperature [K]. This equation originates from metabolism theory and it is a matter of debate under which conditions it can be applied to biogeochemical processes (Montagnes et al., 2003). To compare the temperature response of different processes, process specific E_a values have been used (Dell et al., 2011). We calculated E_a from the slope of Arrhenius plots ($\ln v$ vs. $1/kT$, Figure S1 in Supporting Information S1). The often applied Q_{10} values, which are based on this exponential Arrhenius type relationship, are

problematic. Mathematically, fitting an exponential equation to linear data automatically results in Q_{10} values between 1.7 and 3.2 (Montagnes et al., 2003), which would explain that most studies report Q_{10} values in the range between 2 and 3. Since we have a narrow temperature range between 4 and 20°C and considerable scatter of the data, we did not know a priori whether our data better fit to a linear or exponential model. Thus, we evaluated both models to describe the temperature dependence of the different benthic fluxes.

2.5. Statistical Analyses

The significance of the slope of linear relationships between constituent fluxes, temperature and activation energy was tested by *F*-tests. Linear slopes were compared by *t*-tests after checking for normality of the residuals and homogeneity of variance (QQ plot).

We performed a Principal Component Regression analysis using fluxes as individual dependent variables and the whole environmental data set (porewater and sediment analyses and temperature and oxygen conditions of incubations) as the explanatory matrix in order to further describe the dependency of benthic fluxes on temperature and oxygen conditions in the presence of other potential explanatory variables. The analysis (see Data Set S1) showed high collinearity between the explanatory variables, particularly among variables measured in the sediment related to organic carbon content (TC, TOC, TN, LOI, and total iron—TFe), and porewater analyses (see also Figure 3). Moreover, porewater variables showed low influence on the predictive power of the analysis. Therefore, we decided to explore the dependence of fluxes on temperature and oxygen conditions by only keeping TOC as an additional explanatory variable. We used mixed-effects linear modeling including TOC, incubation temperature, and oxygen conditions (categorical variable with two levels, oxic/anoxic) as fixed factors, and a composite categorical variable that combined reservoir and site (location, for a total of 11 levels, see Table S2 in Supporting Information S1) as a random factor accounting for location effects. We tested the effects of the different fixed factors (including interactions) using the *lmer* function of the R package *lme4* (Bates et al., 2015). *P*-values for the significance of the fixed effects were calculated by Type-II Wald *F* tests as implemented in the *Anova* function of the R package *car* (Fox & Weisberg, 2019). We also calculated the R^2 value of the linear regression between the mixed-effects model results and the observations as a simple and intuitive approach to model fit. Statistical analyses were performed using R (R-Core-Team, 2018), Microcal (Origin 9, 2012) and the XLSTAT 2018.2 macro for Microsoft EXCEL (Microsoft Corporation, 2018). Figures were prepared using Origin 9 (2012); R; Python (Kluyver et al., 2016) and (SigmaPlot Version 12.3, 2014).

3. Results

3.1. Sediment Incubation Conditions and Benthic Fluxes

Experimental conditions covered a temperature range from 4°C to 20°C and oxygen levels between 0.1% and 100% (Tables S3a–S3d in Supporting Information S1). For most of the anoxic experiments NO_3^- -N was depleted before the end of the experiment (Table S3 in Supporting Information S1), which might have affected the magnitude of the fluxes. As a result, we did not use the anoxic nitrate data in subsequent analysis. The pH value remained constant in circum-neutral range except for Sau Reservoir which had a pH around 8. We were able to keep near natural conditions including anoxia during the incubations.

Benthic fluxes of different solutes spanned four orders of magnitude and they were either positive that is, from sediment to water or negative that is, from water to sediment (Figure 2). Thus, depending on conditions the sediment could be either a source or sink of the particular solutes. On average, sediments were a sink for SO_4^{2-} , NO_3^- -N and O_2 but a source of DOC, NH_4^+ -N, CH_4 , and metals (Figure 2). The flux of SRP was low compared to the other fluxes, most probably because background SRP concentration was lower in comparison to other solutes (Figure 2). F_{red} (Equation 1) summarizes the fluxes of reduced species expressed as oxygen equivalents. Our F_{red} fluxes ($2.7 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$, Figure 2) were quite low compared to previous estimates (8.75 – $10.63 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$) in Swiss lakes (Müller et al., 2012; Steinsberger et al., 2017) and were, similar to previous studies, dominated by CH_4 (59%) and NH_4^+ -N (34%).

3.2. Overall Effects of Temperature and Oxygen Conditions

When analyzing all data together, there were several significant correlations between fluxes and porewater concentrations or sediment matrix composition (Figure 3). Most measured parameters were weakly correlated

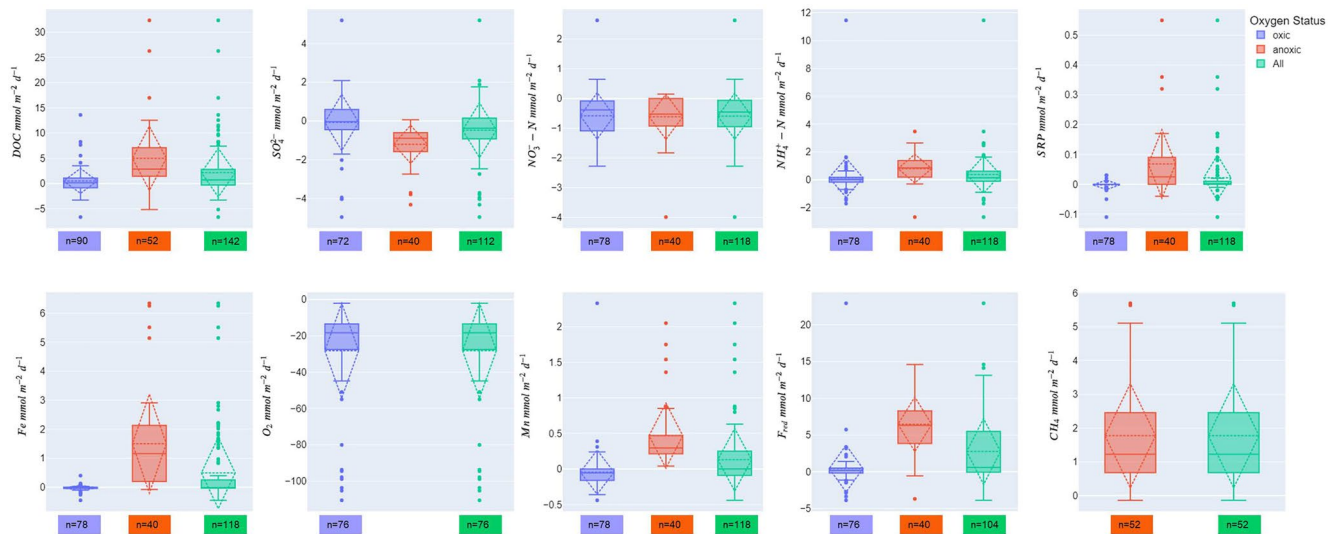


Figure 2. Boxplots showing the range, mean and standard deviation of benthic fluxes [$\text{mmol m}^{-2} \text{d}^{-1}$] of different solutes under oxic and anoxic conditions. Positive fluxes are directed from the sediment into the water. The dotted diamonds center line shows the means, and the upper and lower tips show the standard deviation. Oxic and anoxic fluxes for dissolved organic carbon, SRP, O_2 , SO_4^{2-} , Fe, Mn, F_{red} , CH_4 were significantly different (t -test, $p < 0.001$) and also for NH_4^+ . (t -test, $p < 0.01$).

with temperature (Figure 3). The fluxes of DOC, Fe and Mn, and O_2 were weakly correlated with sediment composition (Figure 3). The flux of DOC was correlated with the fluxes of SRP and SO_4^{2-} , and there was a strong correlation ($R^2 = 0.76$) between the fluxes of the two metals Fe and Mn (Figure 3).

The mixed-effects linear models showed a significant effect of oxygen conditions on all fluxes measured (Table 2). In contrast, temperature and TOC effects were only significant in a few cases. Interestingly, the joint interaction of temperature and oxygen conditions was significant for more solutes than the effect of temperature alone (5 for temperature and oxygen vs. 3 for temperature alone), suggesting a dependency of temperature effects on oxygen conditions for DOC, SRP, SO_4^{2-} , O_2 , and F_{red} (Table 2). Taken together, these results show that the dominant driver of benthic fluxes was oxygen conditions, followed by temperature and TOC, and that the interaction between temperature and oxygen conditions is relevant for fluxes of DOC, SRP, SO_4^{2-} , and O_2 .

3.3. Effect of Bottom Water Oxygen Conditions on Benthic Fluxes

To make differences between reduced and oxidized conditions visible, we divided our data set into situations with and without oxygen in the overlying water. In coherence with the mixed-effects models, systematic differences between reduced and oxidized conditions became apparent (Figure 2). Under anoxic conditions the fluxes of all investigated species except O_2 were typically about 10 times higher compared to oxic conditions (Figure 4) that is, oxic versus anoxic fluxes in $\text{mmol m}^{-2} \text{d}^{-1}$; DOC (0.5 ± 2.5 vs. 5.0 ± 6.4), $\text{NH}_4^+\text{-N}$ (0.15 ± 1.4 vs. 0.8 ± 1.0), SRP (-0.07 ± 1.46 vs. 0.07 ± 0.12), NO_3^- (-0.58 ± 0.79 vs. -0.62 ± 0.77), SO_4^{2-} (-0.1 ± 1.5 vs. -1.2 ± 1.0), Fe (-0.02 ± 0.09 vs. 1.5 ± 1.7), Mn (-0.04 ± 0.31 vs. 0.47 ± 0.46), F_{red} (0.4 ± 3.2 vs. 6.5 ± 3.8), CH_4 (0.02 ± 0.26 vs. 1.8 ± 1.6). This effect was most pronounced for SRP and Fe (Figure 4).

3.4. Temperature Response of Benthic Fluxes

The temperature response of benthic fluxes differed between solutes and oxygen conditions (Figure 4). Clear-cut temperature responses both at oxic and anoxic conditions were observed for DOC and SO_4^{2-} (Figure 4). In the case of DOC and sulfate at oxic conditions, temperature change did not only change the magnitude but also the direction of the flux: the sediment was a sink for DOC at low temperature (below 8°C) that is, $-0.5 \pm 1.0 \text{ mmol m}^{-2} \text{d}^{-1}$ but a source at temperatures above 8°C that is, $1.65 \pm 3.0 \text{ mmol m}^{-2} \text{d}^{-1}$ (Figure 4). Temperature stimulation of sulfate reduction in the anoxic part of the sediment turned the sediment into a sulfate sink above 10°C that is, $0.52 \pm 1.46 \text{ mmol m}^{-2} \text{d}^{-1}$ (Figure 4).

The slopes of the linear temperature response curves were quite different for different fluxes (Table 3). The oxygen flux showed by far the strongest temperature response (Table 3). Dissolved organic carbon, SO_4^{2-} , and

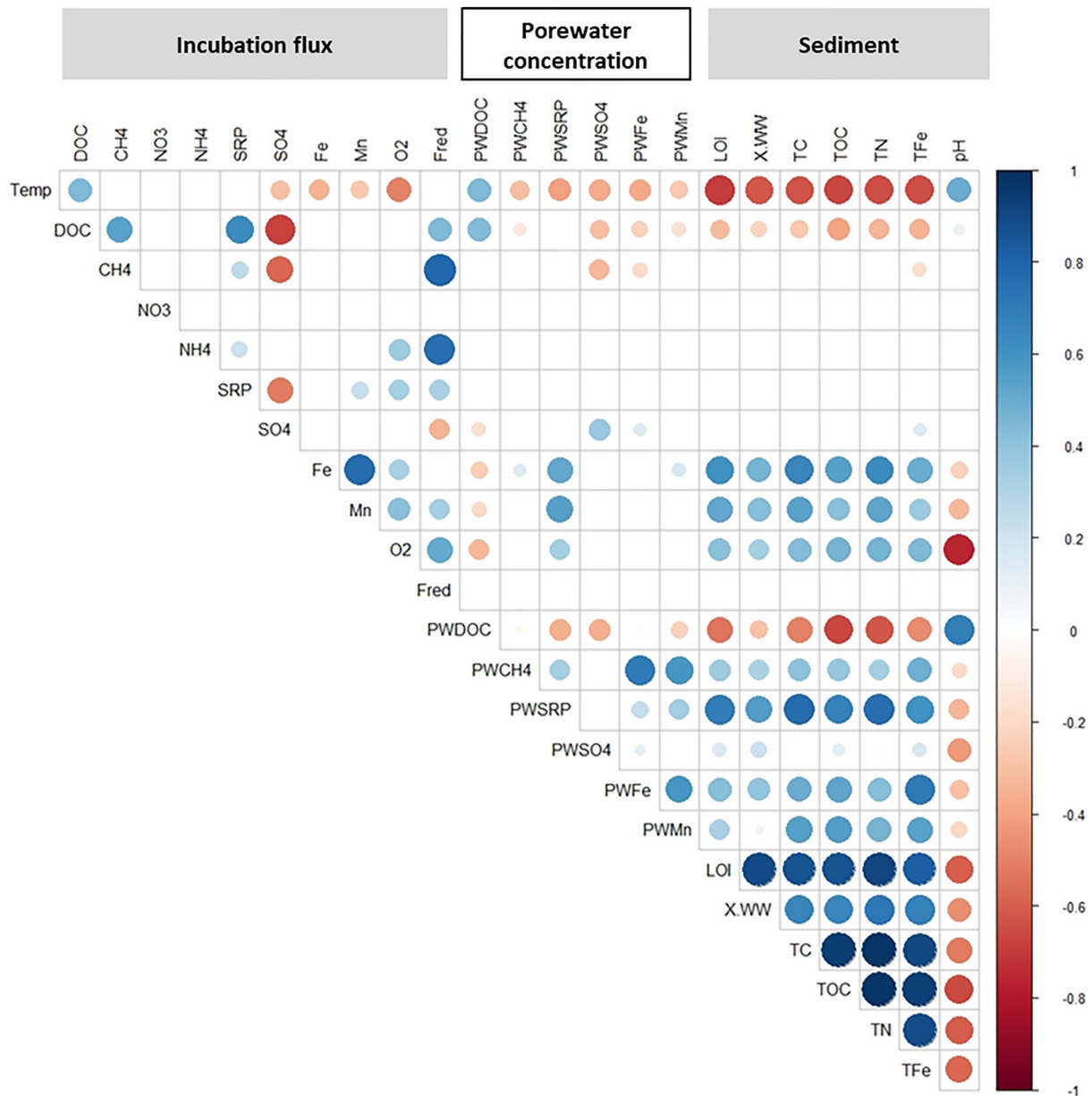


Figure 3. Correlation matrix. Color and size of the dots visualize R^2 . Only significant linear correlations (Spearman, $p < 0.01$) are shown (LOI = loss on ignition, PW = porewater, X.WW = water content, Temp = temperature).

Fe showed intermediate temperature response while the temperature response of the nutrient fluxes $\text{NH}_4^+\text{-N}$ and SRP as well as of the Mn flux was quite low (Table 3).

Comparing the slopes of the temperature response curves shows the effect of oxygen conditions on the temperature dependence of different fluxes (Table 3). Slopes were generally higher under anoxic conditions, with significant differences for DOC, Fe, and F_{red} , which includes CH_4 , $\text{NH}_4^+\text{-N}$, Fe, and Mn (Table 3). For these fluxes, increasing temperature had a significantly higher effect at anoxic conditions compared to oxic conditions (Table 3). For sulfate and SRP fluxes, the temperature effect, if any, was weakly dependent on oxygen state (Table 3).

Activation energies were mostly at the lower end of the range typical for biological processes (Table 3). The E_a of O_2 and DOC flux at anoxic conditions were around 0.5 eV, which is a typical value for metabolic processes (Dell et al., 2011). The E_a and thus the temperature response of the other fluxes was either low or even zero in the case of SRP and Mn flux (Table 3). These fluxes were probably controlled by other sediment properties. Q_{10}

Table 2
The Significance of the Fixed Effects Included in the Mixed-Effects Linear Models for the Different Fluxes Measured

Flux	n	r ²	Oxygen conditions	Temperature	TOC	Temp* oxygen	TOC* oxygen
DOC	134	0.58	<0.0001	0.0003	0.1990	0.0004	0.4711
CH ₄	134	0.74	<0.0001	0.8348	0.0099	0.5516	0.0043
NH ₄ ⁺ -N	110	0.17	0.0382	0.4982	0.3623	0.0658	0.4134
SRP	110	0.42	<0.0001	0.0736	0.1407	0.0001	0.0907
SO ₄ ²⁻	104	0.63	<0.0001	0.0003	0.7695	0.0350	0.3754
Fe	110	0.59	<0.0001	0.8856	0.0355	0.5752	0.0004
Mn	110	0.36	<0.0001	0.2469	0.0818	0.5758	0.1883
O ₂	128	0.88	<0.0001	<0.0001	0.0011	<0.0001	<0.0001
F _{red}	104	0.59	<0.0001	0.5054	0.4564	0.0220	0.1275

Note. P-values below 0.05 are in bold. See Table S2 in Supporting Information S1 for the complete parameterization of the models.

values calculated for the temperature range 4–20°C were 4.2, 2.6, and 1.2 for the anoxic fluxes of DOC, SO₄²⁻, and F_{red}, respectively, while the Q₁₀ of the O₂ flux was 3.7. These values are in a similar range as in a previous study (Liikanen et al., 2002).

4. Discussion

We hypothesized that the interaction of temperature and oxygen alters the magnitude of solute fluxes (from or into the sediments) differently; and the dependence of benthic fluxes to temperature is steeper under anoxic conditions than under oxygenated conditions. Our results indeed show that the interaction of temperature and

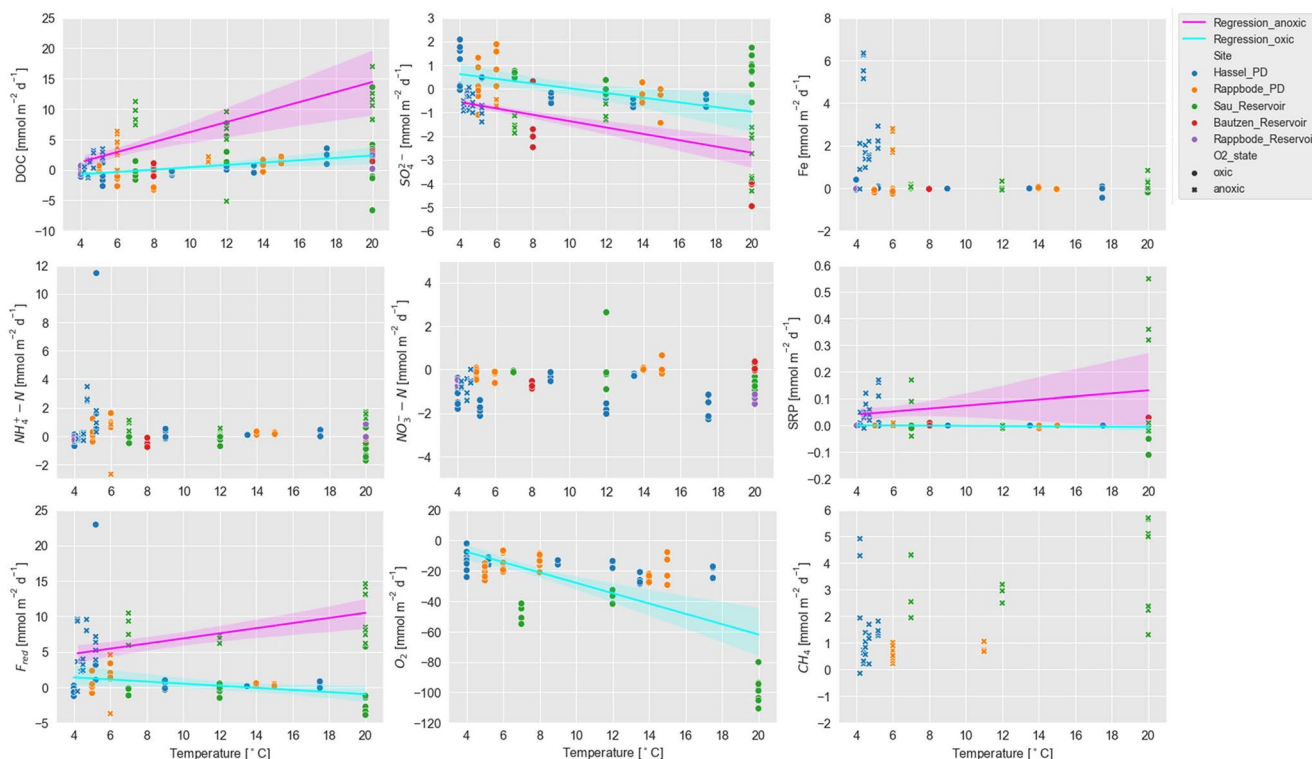


Figure 4. Temperature dependence of benthic fluxes under oxic (open symbols) and anoxic (closed symbols) conditions. Linear fits with 95% confidence limits are shown only for fluxes which had significant temperature-oxygen interaction.

Table 3
Temperature Dependence of Different Benthic Fluxes

	Slope (mmol m ² d ⁻¹ °C ⁻¹)		p	E _a [eV]	
	Oxic	Anoxic		Oxic	Anoxic
DOC	0.19 ± 0.5***	0.82 ± 0.12***	0.00195**	0.24 ± 0.04***	0.46 ± 0.06***
NH ₄ ⁺ -N	-0.055 ± 0.027*	0.049 ± 0.026	0.0141*	-0.16 ± 0.05**	0.13 ± 0.05*
SRP	-0.0004 ± 0.0003	0.006 ± 0.003	0.015*	-0.02 ± 0.01	0.07 ± 0.07
O ₂	-3.40 ± 0.43***	–	–	0.63 ± 0.09***	–
NO ₃ ⁻ -N	0.01 ± 0.02	–	0.55	0.11 ± 0.10	–
SO ₄ ²⁻	-0.10 ± 0.03***	-0.13 ± 0.02***	0.37	0.31 ± 0.12**	0.25 ± 0.03***
Fe	-0.0003 ± 0.0017	-0.14 ± 0.04**	3 × 10 ⁻⁷ ***	0.003 ± 0.01	-0.39 ± 0.1***
Mn	0.0036 ± 0.0061	-0.020 ± 0.012	0.15	0.002 ± 0.017	-0.05 ± 0.03
CH ₄	–	0.14 ± 0.07	–	–	-0.58 ± 1.38***
F _{red}	-0.15 ± 0.07*	0.36 ± 0.08***	8 × 10 ⁻⁶ ***	-0.22 ± 0.66***	0.23 ± 0.08**

Note. Slope of linear regression (mean ± SE) as well as activation energy calculated from Arrhenius plots (Figure S1 in Supporting Information S1). p indicates whether oxic and anoxic slopes were significantly different (*t*-test, data were log transformed if residuals were not normal distributed, asterisks indicate significance: **p* < 0.05, ***p* < 0.01, ****p* < 0.001).

oxygen impacts differently the solute fluxes and that temperature dependence of some solutes, for example, DOC, are indeed higher under anoxic conditions.

4.1. Temperature Response of Benthic Fluxes

Most of the measured fluxes exhibited temperature dependence either under oxic and/or anoxic conditions. For DOC, SO₄²⁻, O₂, SRP, and F_{red}, we observed significant temperature responses or interactions between temperature and oxygen conditions. Activation energies (E_a) for the fluxes of DOC, O₂, and SO₄²⁻ (Table 3) were within the range reported for various ecological processes (median 0.54 eV in Kraemer et al. (2017)). If we convert our O₂ fluxes to OC mineralization rates and plot the logarithm of those rates versus temperature, the slope of a linear regression is 0.04 which is exactly the same value as in a compilation of sediment carbon mineralization rates from 966 lakes around the world (Cardoso et al., 2014) and also of carbon burial rates in 388 lakes and reservoirs (Mendonça et al., 2017). Thus, we think that our data set allows general conclusions. The surprising similarity of the E_a values across all kinds of biologically mediated environmental processes supports our view that metabolic kinetics is the principal determinant of benthic biogeochemical exchange in some lentic systems.

Activation energies for the SRP, NH₄⁺-N, NO₃⁻-N, Fe, and Mn fluxes were low in comparison to other studies (Table 4). Low E_a for SRP, Fe and Mn might be due to a mixture of biotic and abiotic release and immobilization processes. This combination of processes might have dampened the temperature effects. Similarly, NH₄⁺-N adsorption is known to be insensitive to temperature (Mackin & Aller, 1984); this interaction with the sediment matrix might have contributed to the low E_a.

The E_a values for NO₃⁻-N from the compilation of literature are highly variable; 0.12–1.86 eV (Palacin-Lizarbe et al., 2018); however, our E_a (0.11 ± 0.1 eV) is on the lower end of the range. Lower nitrate concentration but similar E_a values have been observed in another study (Cameron & Schipper, 2010) and have been attributed to carbon limitation (Palacin-Lizarbe et al., 2018). Most studies on E_a of nitrate removal are designed with nitrate and carbon enrichment (Palacin-Lizarbe et al., 2018) and studies without C enrichment tend to have lower E_a values. In the case of sulfate, higher sulfate reduction at higher temperature is probably compensated by higher sulfide oxidation rates, as observed in other studies (Al-Raei et al., 2009; Thamdrup et al., 1994), which results in a dampened temperature response of the sulfate flux under oxic conditions.

4.2. Oxygen Conditions More Important Than Temperature

As expected, the absence of oxygen in the bottom water generally increased benthic solute fluxes; this has been demonstrated in several studies (Dadi et al., 2016; Einsele et al., 1936; Mortimer, 1942; Skoog & Arias-Esquivel, 2009) and is linked to the reductive dissolution of iron oxyhydroxides (Davison, 1993).

Table 4
Activation Energy of Solutes Mobilization and Immobilization Processes

Solute	Temp (°C)	Oxygen status	Incubation system	E_a (kJ mol ⁻¹) (E_a [eV])	Reference
SRP release	4–20	Oxic	Undisturbed sediment cores, 7–21 days	-2 ± 1 (-0.02 ± 0.01)	This study
		Anoxic		7 ± 7 (0.07 ± 0.07)	
SRP release	14–21	Oxic	Undisturbed sediment cores, 21 days	$88-135^*$ ($0.91-1.4$) [*]	Jensen and Andersen (1992)
SRP release	10–20	Anoxic	Sediment slurry, 8 days	$13-71^*$ ($0.13-0.74$) [*]	Kelton and Chow-Fraser (2005)
	15–25	Anoxic		$2-52^*$ ($0.021-0.54$) [*]	
SRP release	4–32	Anoxic	Sediment slurry enriched with 2 g dry cyanobacteria biomass, 41 days	$12-33^*$ ($0.12-0.34$) [*]	Chen et al. (2014)
SRP release	5–18	Anoxic	Sediment slurry mesocosm, 200 days	76 (0.79)	Matisoff et al. (1981)
TP release	6–23	Oxic	Undisturbed sediment cores, Flow though, 7 days	73^* (0.76) [*]	Liikanen et al. (2002)
		Anoxic		44^* (0.46) [*]	
NH ₄ ⁺ -N release	4–20	Oxic	Undisturbed sediment cores, 7–21 days	-15 ± 5 (-0.16 ± 0.05)	This study
		Anoxic		13 ± 5 (0.13 ± 0.05)	
NH ₄ ⁺ -N anaerobic ammonium oxidation	1–35	Anoxic	Sediment slurry, 2 hr	Summer: 41.2 ± 15.9 (0.43 ± 0.16) Winter: 58.1 ± 10.4 (0.6 ± 0.11)	Tan et al. (2020)
NH ₄ ⁺ -N release	6–23	Anoxic	Undisturbed sediment cores, Flow though, 7 days	60^* (0.62) [*]	Liikanen et al. (2002)
NH ₄ ⁺ -N release	5–18	Anoxic	Sediment slurry mesocosm, 200 days	74.5 (0.77)	Matisoff et al. (1981)
NO ₃ ⁻ -N release	4–20	Oxic	Undisturbed sediment cores, 7–21 days	11 ± 10 (0.11 ± 0.1)	This study
NO ₃ ⁻ -N denitrification	5–15	Anoxic	Undisturbed sediment cores, 3 days	46 ± 7 (0.48 ± 0.07)	Palacin-Lizarbe et al. (2018)
NO ₃ ⁻ -N denitrification	1–35	Anoxic	Sediment slurry, 2 hr	Summer: 73.7 ± 9.8 (0.76 ± 0.1) Winter: 74.0 ± 10.7 (0.77 ± 0.11)	Tan et al. (2020)
O ₂ uptake	4–20	Oxic	Undisturbed sediment cores, 7–21 days	61 ± 9 (0.63 ± 0.09)	This study
O ₂ uptake	–1–22	Oxic	Sediment slurry	$50-70$ (0.52 ± 0.73)	Thamdrup et al. (1998)
O ₂ uptake	14–21	Oxic	Undisturbed sediment cores, 21 days	$35-71^*$ ($0.36-0.74$) [*]	Jensen and Andersen (1992)
O ₂ uptake	6–23	Oxic	Undisturbed sediment cores, Flow though, 7 days	28^* (0.29) [*]	Liikanen et al. (2002)
CH ₄ production	4–20	Anoxic	Undisturbed sediment cores, 7–21 days	-56 ± 133 (-0.58 ± 1.38)	This study
Organic carbon mineralization (CO ₂ + CH ₄ release)	1–21	Oxic	Semidisturbed sediment cores, 150 Days	Svarttjärn: $47-64$ (0.49 ± 0.66) Vallentunasjön: $45-54$ (0.47 ± 0.56)	Gudasz et al. (2015)
CO ₂ production	6–23	Oxic	Undisturbed sediment cores, Flow though, 7 days	80^* (0.83) [*]	Liikanen et al. (2002)
		Anoxic		57^* (0.59) [*]	
CH ₄ production	6–23	Anoxic		57^* (0.59) [*]	
Organic carbon mineralization (CO ₂ + CH ₄ release)	6–23	Oxic		57^* (0.59) [*]	
		Anoxic		76^* (0.79) [*]	
SO ₄ ²⁻ reduction	4–20	Oxic	Undisturbed sediment cores, 7–21 days	30 ± 12 (0.31 ± 0.12)	This study
		Anoxic		24 ± 3 (0.25 ± 0.03)	
SO ₄ ²⁻ reduction	4–28	Anoxic	Undisturbed sediment cores, 4 hr	53.1 ± 4.5 (0.55 ± 0.05)	Meier et al. (2005)
SO ₄ ²⁻ reduction	5–15	Anoxic	Sediment slurry, 1 hr	54.1 (0.56)	Bak and Pfennig (1991)
SO ₄ ²⁻ reduction	4–30	Anoxic	Sediment slurry, 40 hr	67^* (0.69) [*]	Urban et al. (1994)
SO ₄ ²⁻ reduction	4–32	Anoxic	Sediment slurry enriched with 2 g dry cyanobacteria biomass, 41 days	$22-26^*$ ($0.23-0.27$) [*]	Chen et al. (2014)

Table 4
Continued

Solute	Temp (°C)	Oxygen status	Incubation system	E_a (kJ mol ⁻¹) (E_a [eV])	Reference
Fe release	4–20	Oxic	Undisturbed sediment cores, 7–21 days	0.3 ± 1 (0.003 ± 0.12)	This study
		Anoxic		–38 ± 10 (–0.39 ± 0.1)	
Fe reduction	4–28	Anoxic	Sediment slurry, 25 days	45.5 ± 11.6 (0.47 ± 0.12)	Meier et al. (2005)
Fe reduction	4–32	Anoxic	Sediment slurry enriched with 2 g dry cyanobacteria biomass, 41 days	12–89* (0.12–0.92)*	Chen et al. (2014)
Fe release	5–18	Anoxic	Sediment slurry mesocosm, 200 days	28.2 (0.29)	Matisoff et al. (1981)
Mn release	4–20	Oxic	Undisturbed sediment cores, 7–21 days	0.2 ± 1.6 (0.002 ± 0.017)	This study
		Anoxic		–5 ± 3 (–0.05 ± 0.03)	
Mn oxidation	12–20	Oxic	Sediment slurry, 26 hr	45*(0.47)*	Kepkay (1985)
Mn oxidation	25–35	Oxic	Seawater	53*(0.55)*	Sunda and Huntsman (1987)
Mn release	5–18	Anoxic	Sediment slurry mesocosm, 200 days	41 (0.42)	Matisoff et al. (1981)
F_{red}	4–20	Oxic	Undisturbed sediment cores, 7–21 days	–21 ± 64 (–0.22 ± 0.66)	This study
		Anoxic		22 ± 8 (0.23 ± 0.08)	

Note. *Denotes values calculated from the data from the Q_{10} values and temperature in the publication, using the Arrhenius equation.

Mechanistically, the difference between oxic and anoxic fluxes should be caused by the oxic surface layer of the sediment, which is typically only a few millimeters thick (Glud et al., 2003; Horppila et al., 2015). This thin layer, when present, acts as a reactive barrier that is, oxidizes solutes diffusing upwards from the anoxic sediments, which results in lower fluxes of solutes from the sediment to the surface water. In Hassel Predam this layer ranges between 1.4 and 3.4 mm (Kloss, 2013). The effect of this thin oxidized layer is long known for Fe and Mn (Davison, 1993), H₂S (Kuhl et al., 1998), SRP (Mortimer, 1942), and CH₄ (Frenzel et al., 1990). In the case of H₂S, NH₄⁺-N, and CH₄, the filtering mechanism of the oxic surface sediment is primarily not caused by sorption but by microbial oxidation (Kortelainen et al., 2000; Liikanen & Martikainen, 2003). In case of P, organic matter deposition and the ratios of Fe, P, and S dominantly control the flux, on longer timescales (Gachter & Muller, 2003; Hupfer & Lewandowski, 2008). Fe regulation of solutes, for example, P only works if the molar stoichiometric Fe:P ratio is greater than 2 and low sulfate concentration since hydrogen sulfides can permanently immobilize Fe through the formation of iron-sulphides (Gachter & Muller, 2003). The molar stoichiometric ratio of SRP and dissolved Fe in the investigated reservoirs was much greater than 2 at the end of the incubations (see porewater concentrations Table S4 in Supporting Information S1), so P immobilization was limited by Fe.

Although oxygen consumption was high under oxic conditions (indicating high mineralization of organic matter), fluxes of solutes were mostly lower under oxic conditions despite the higher concentration of solutes in the porewater compared to the overlying water (Figure 5). This implies that there was an equally effective process which counteracted the release of solutes by mineralization. For SRP, this could be adsorption, accumulation in bacterial biomass as polyphosphate, and immobilization through DNA formation (Boström et al., 1988; De Sena et al., 2022; Hupfer et al., 1995). An interesting case is the sulfate flux, which is a measure of net sulfate reduction in the sediment; it is not clear why there was only a small difference between oxic and anoxic conditions. It could be that H₂S was immobilized by the formation of iron sulfides (Rothe et al., 2015) or that oxidation of H₂S in the oxic sediment layer and/or adsorption of SO₄²⁻ to ferric minerals was either not very efficient or did not result in the production of sulfate but elemental sulfur (Holmer & Storkholm, 2001). In addition, sulfate reduction is more temperature-dependent than sulfate diffusion (Urban et al., 1994). This contrasts with CH₄, which was more or less completely oxidized under oxic conditions. The different behavior of SO₄²⁻ and CH₄ could be expected because H₂S, as the end product of sulfate reduction, is immobilized by Fe even at anoxic conditions, while CH₄, as the end product of methanogenesis, is not. This means that more anoxic conditions at the sediment water interface will shift the equilibrium between net sulfate reduction and methane release toward methane release.

Despite this, organic matter mineralization under anoxic conditions was not dominated by methanogenesis. Taking into account the electron budget of the respective processes, sulfate reduction contributed 43% to mean organic

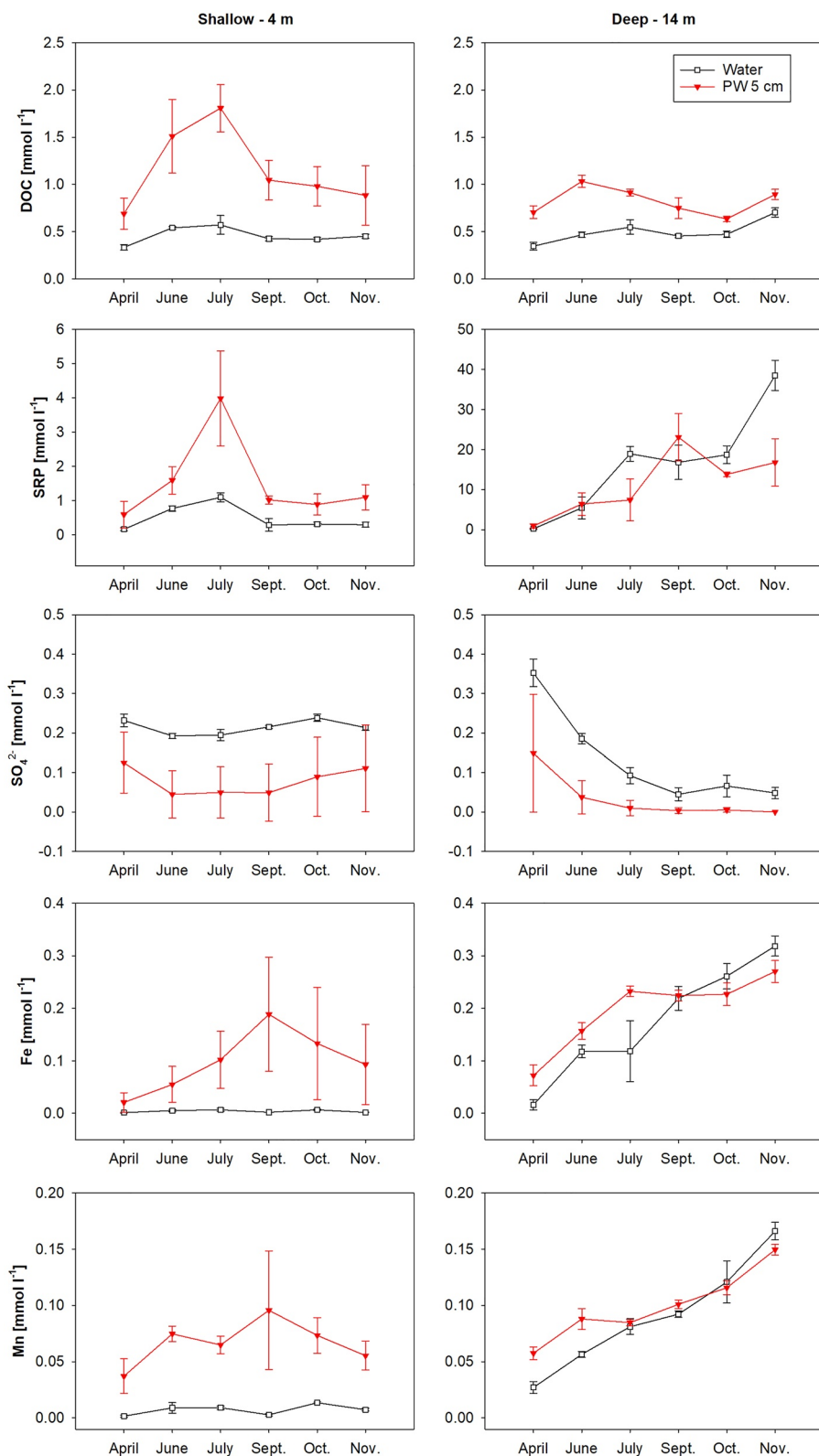


Figure 5. Mean porewater (PW; upper 5 cm) and water solutes concentration data for Hassel predam at the end of the incubation. Error bars indicate standard deviation, $n = 4$ sediment cores.

matter mineralization under anoxic conditions, while methanogenesis, nitrate consumption, Fe, and Mn reduction contributed 32%, 14%, 7%, and 4%, respectively. Thus, even under anoxic conditions, most of the organic carbon was mineralized to CO_2 (and not to CH_4). This agrees with results from previous studies (Kristensen & Holmer, 2001; Liikanen et al., 2002) which showed similar organic matter mineralization rates under oxic and anoxic conditions. It also highlights the relevance of fermentation, sulfate reduction, and other nonmethanogenic anaerobic processes. The role of nitrate as an electron acceptor cannot be ascertained in our study since nitrate was depleted in most of the cores prior to the end of the incubation. The contribution of denitrification to the electron budget in freshwater systems with higher nitrate concentrations can therefore be expected to be higher, as found in other studies (David et al., 2006; Mccarthy et al., 2016).

4.3. Experimental Approach

Our approach of using data from several sites and dates offers a wider perspective of sediment solute fluxes compared to studies analyzing sediment cores from a single location at different laboratory conditions (Kelderman, 1984; Liikanen et al., 2002). Furthermore, the incubations were for a short-time to minimize the lack of sedimentation effects which cause elevated and unnaturally high P binding capacity in the uppermost sediments (Hietanen & Lukkari, 2007; Hupfer & Lewandowski, 2008). We kept the oxygen status close to in situ conditions as laboratory experiments with manipulation of oxygen status have the disadvantage that oxygen switches result in nonsteady state conditions. Another advantage of our approach is that we were able to detect those fluxes which were mostly regulated by temperature. The scatter of the data does not allow a decision about the most appropriate temperature function to describe this temperature dependence. The fits of our data to a linear and Arrhenius model were equally good (Table 3, Figure 4, Figure S1 in Supporting Information S1). For simplicity, we used the linear model. It is clear that our conclusions are only valid for the investigated temperature range and cannot be projected above 20°C.

4.4. Implications for Reservoir Warming Scenarios

In shallow lakes, global warming is generally expected to increase both temperature and the occurrence of anoxic conditions in the hypolimnion (Woolway et al., 2022). For example, a recent study (Woolway, Jennings, et al., 2021) showed that heat waves lasted longer but were less intense in deep lakes compared to shallow lakes. Here we show that a change of benthic oxygen conditions stimulates benthic solute fluxes more than temperature rise. At 10°C, a switch to anoxic conditions would for example, increase the flux of DOC and SO_4^{2-} consumption by 5.8 and 1.3 $\text{mmol m}^{-2} \text{d}^{-1}$, respectively. To get the same flux change under constant oxic conditions, an unrealistic temperature rise to 40 and 36°C would be necessary.

The dependence of benthic fluxes on temperature was higher under anoxic than under oxic conditions. If we assume that organic matter mineralization is similar under oxic and anoxic conditions in the short-term (Bastviken et al., 2004), then this implies that there is a mechanism responsible for the observed differences in fluxes. The likely mechanism controlling solute fluxes at short timescales is the oxic sediment surface layer, as shown in the conceptual model in Figure 6. The main basis of this model is the classical redox dependent iron oxidation and reduction (Einsle et al., 1936; Mortimer, 1942) and the luxury storage of polyphosphates under oxic conditions (Hupfer et al., 1995). Under anoxic conditions, microbial mineralization of organic matter and benthic solute fluxes are closely linked. The oxic sediment surface layer uncouples those two, leading to a higher conversion of adsorbable and oxidizable species in the sediment. By decreasing the relative occurrence of oxic sediment zones, global warming might promote a closer coupling between sediment and water and between the biogeochemical cycles of different elements. This means that there is a domino like effect on benthic processes that is triggered by temperature. Increasing temperature leads to intensive mineralization. The temperature-dependent mineralization increases the oxygen consumption until the rate of oxygen consumption outpaces the rate of oxygen replenishment in the sediment, eventually leading to oxygen depletion. This reduces and eventually eliminates the trapping of solutes by the oxic sediment layer. Once this layer is eliminated and the water becomes anoxic, the rate of solute accumulation/depletion in the water column will increase and further temperature increase will increase the solute mobilization until the optimum temperature for each solute mobilization process is reached. The trapping of solutes is important especially in drinking water reservoirs where changes in water quality have immediate impacts on drinking water treatment plants.

The effects discussed here are likely to influence shallow systems since temperature in some deep lakes might not change (Woolway, Jennings, et al., 2021) and in some cases it might even decrease (Magee & Wu, 2017). In this

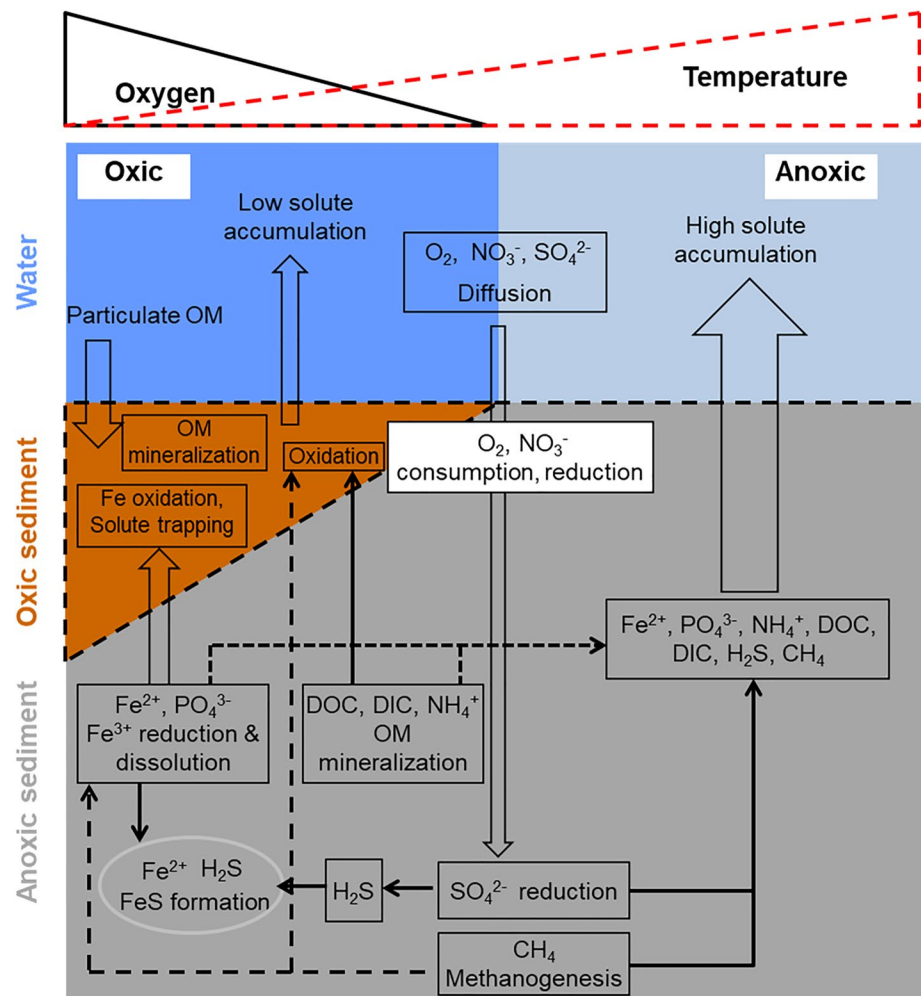


Figure 6. Conceptual model of the trapping mechanism controlling solute fluxes at the sediment water interface. Adsorption of solutes to Fe minerals and luxury uptake of P in the oxic sediment layer balance solute immobilization and mobilization processes under oxic conditions. However during the transition from oxic to anoxic conditions, when the oxic sediment layer decreases, the mobilization and immobilization processes become imbalanced. Under anoxic conditions, this imbalance becomes more prominent, resulting in higher fluxes across the sediment. Please note, this mechanism only applies to reservoirs with adequate free Fe for the adsorption of solutes (Gachter & Muller, 2003).

study, we did not investigate the interaction of pelagic and benthic warming on benthic metabolism. Ecosystem wide studies on the temperature response of various processes in different compartments are necessary to understand the effect of temperature rise on aquatic biogeochemical cycles.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data presented in this manuscript is archived PANGAEA (Dadi et al., 2021; <https://doi.pangaea.de/10.1594/PANGAEA.928570>).

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