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Turnover of lake sediments treated with sediment microbial fuel cells: a long-term study in a eutrophic lake

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Abstract

Sediment microbial fuel cells (SMFCs) have previously been successfully used to reduce phosphate release from the sediments of eutrophic lakes. In this study, we investigate the risk that SMFCs stimulate sediment decomposition with the unwanted side effect being the release of legacy pollutants stored in sediments. Electrode pairs (16 m\textsuperscript{2} each) were installed in a eutrophic lake in Denmark and the electricity production was monitored over more than a year at three electrode fields. Equations were derived that allow calculation of the substrate turnover by the SMFCs from the working potential, the open circuit potential, and the external resistance of the SMFCs. The resulting turnover data suggest that the decomposition of the sediment is only slightly expedited by the SMFCs, and that the decomposition process is not significantly stimulated by the type of SMFCs installed in the lake. The measured maximum power density with stainless steel electrodes in the lake sediment was 0.9 mW/m\textsuperscript{2}, which was sufficient to reduce P outflux from sediment. At this power density, the decomposition half-life of the lake sediment (top 5 cm) is calculated to be 277 years, which is only about 10\% of natural lake sediment decomposition half-lives. Higher power densities are not necessary for P fixation but inadvertently increases the risk that legacy pollutants buried in the sediment are released.

Keywords: phosphate; heavy metals; Nernst equation; methane; working potential; decomposition.

Highlights: see separate file

Graphical Abstract

see separate file

Competing interests: the authors have no competing interests to declare.

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1 Introduction

In many eutrophic lakes, a thick layer of sediment has deposited, often over several decades and centuries. Typically, these layers are highly polluted, rich in nutrients and organic matter, and mostly or completely anoxic. Sediments store pollutants such as heavy metals, pesticides, polycyclic hydrocarbons, organochlorine chemicals and other organic micro-pollutants emitted to the environment (US EPA 2004). The National Sediment Quality Survey undertaken by the US EPA revealed that chemicals emitted more than 50 years ago and long since banned, among them organochlorine pesticides (including DDT, chlordane, dieldrin and polychlorinated biphenyls PCB), are still present in high amounts in river and lake sediments, buried in the deeper layers. The same was observed for heavy metals like lead, chromium, nickel, mercury, and for arsenic. Some pollutants, like polycyclic aromatic hydrocarbons (PAHs) and the heavy metal zinc, still show an increasing trend in sediments (US EPA 2004).

The situation in Europe is comparable (Tueros et al. 2009) but in no way better. On the contrary, here pollution events happened over thousands of years and can be dated back to the medieval period or even to the time of the Romans (Brännvall et al. 1999, Cooke and Bindler 2015). On top of this legacy pollution, new and emerging contaminants can be identified in sediments, such as polybrominated flame retardants (Zegers et al. 2003) or, recently, also plastic microparticles (Blettler et al. 2019).

Organochlorine chemicals and pesticides, as well as the other organic substances, survive in the sediments over decades due to their persistence and their low mobility ascribed to their high adsorption to the sediment organic matter (Mackay et al. 1999). Similarly, the distribution coefficients of heavy metals between sediment and water are high, typically in the range of 1,000 L/kg to 100,000 L/kg (Allison and Allison 2005). Thus, even a sediment layer of only a few centimeters contains more organic components, more nutrients and more pollutants than the whole water column of a lake (Avnimelech et al. 1984, Haxthausen et al. 2021a). Unfortunately, many of these chemicals are among the most hazardous compounds to humans and wildlife, due to their comparatively very high ecotoxicity (Johnson et al. 2017). Brief, a release of this toxic legacy accumulated over centuries is a threat to the water quality of these lakes.

Consequently, capping and stabilization of contaminated sediments have been suggested and tested as in situ remediation strategies for contaminated sediments (US EPA 2005), and the continuing burial of this worldwide toxic reminder of a careless past in deeper sediment layers is probably the easiest and cheapest strategy.

Sediment microbial fuel cells (SMFCs) use the naturally occurring difference in redox potential between the anaerobic sediments and the oxic water column for electricity generation, e.g., for remote sensor stations (Tender et al. 2002, Lowy et al. 2006, Donovan et al. 2013). Other uses are enhanced oxidation of organic matter and redox control (De Schamphelaire et al. 2008). Hereby, one electrode is typically placed in the sediment (the anode); the other is placed in the surface water (the cathode). Both electrodes are electrically connected through a resistor or another electricity user. With SMFCs, the electron transfer between the oxidation half-reaction in the sediment and the reduction half-reaction in the surface water is by an electrical current through an external circuit (Logan et al. 2006).

SMFCs stimulate sulfide oxidation (Tender et al. 2002; Touch et al. 2017), thus inhibit Fe-S formation (Ryckelynck et al. 2005) and increase sediment redox potential (Kubota et al. 2019). Moreover, methane emissions can be reduced (Kaur et al. 2014, Friedman et al. 2016, Liu et al.
The average power obtained by SMFCs is approximately 10 to 20 mW/m$^2$ for SMFCs positioned in salty and sulfur-rich marine waters (De Schamphelaire et al. 2008), limited by mass transfer kinetics (Lowy et al. 2006).

Another, novel application was recently uncovered: SMFCs can change the properties of sediments so that phosphate is immobilized. The postulated mechanism is that an anode of a SMFC, placed in or on the top sediment, increases the redox potential and thus inhibits iron sulfide formation, whereupon phosphate adsorbs to iron oxides. Field experiments in a eutrophic lake have shown the feasibility of this application (Haxthausen et al. 2021a).

This application specifically targets eutrophic lakes, and a highly relevant question therefore is whether the sediments are degraded faster with than without SMFC treatment. On the one hand, a rapid decomposition of sediment organic matter might be useful to reduce the amount of sediment material in, for example, harbors, rain retention ponds or aquaria. On the other hand, if applied in eutrophic lakes with high legacy pollution, the stimulation of sediment decomposition would release enormous amounts of nutrients and pollutants, with unpredictable but certainly rather unfavorable consequences for the whole lake ecosystem. Such a release of pollutants is unwanted and bears a considerable risk for the lake ecosystem.

Here, we analyze data obtained in this field study with respect to sediment degradation, in order to estimate the sediment turnover rate and to predict whether there is an increased risk of pollutant release when SMFCs are applied in lake restoration projects. This analysis was done using the in situ measured electrical data, and the sediment decomposition was calculated using the relation between generated energy in a redox reaction and substrate turnover, derived from the change of Gibbs energy and the Nernst equation.

2 Methods

2.1 Turnover of organic matter in sediments

The reactions describing organic matter turnover in sediment are shown for the example substrate acetic acid/acetate, which is a typical substrate of exoelectrogenic microbes (Coates et al. 2001). If no other electron acceptor is present except the organic substrate itself, then it is used as the electron donor and acceptor at the same time, and microorganisms form one mole carbon dioxide and one mole methane as products (Kaur et al. 2014):

$$\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$$

In acetic acid, the carbon has the oxidation state 0, in CH$_4$ -4, in CO$_2$ +4. Thus, 4 electrons are moved in this redox reaction. The Gibbs energy of substrates, products and of the overall reaction are shown in Table 1. Thermodynamically, the reaction gives -27.5 kJ/mol acetic acid and a Nernst potential of 0.07 V. Thus, the reaction is thermodynamically feasible, and the microorganisms can live and grow on the substrate.

If the anode of a SMFC is present as the electron acceptor, then an alternative reaction providing more energy is possible. Exoelectrogens (e.g. Geobacter spp.) at an anode can produce two moles CO$_2$ from one mole acetic acid by taking the oxygen from two water
molecules and releasing 8 (7 if charged acetate) H⁺ into the water, and 8 e⁻ onto the electrode (Kaur et al. 2014):

\[
\text{CH}_3\text{COOH} + 2 \text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8 \text{H}^+ + 8 \text{e}^- 
\]

This redox half reaction moves 8 electrons, gives -207.5 kJ/mol acetic acid and has a Nernst potential of 0.27 V (Table 1).

The cathodic half-reaction is

\[
2 \text{O}_2 + 8 \text{H}^+ + 8 \text{e}^- \rightarrow 4 \text{H}_2\text{O} 
\]

which also moves 8 electrons, releases -629.6 kJ/mol and has a Nernst potential of 0.82 V (Table 1). Cathodic and anodic reaction are added to give the standard potential \(E^0\) of the reaction, together 1.085 V.

**Table 1.** Balanced reactions describing methanogenesis, and the oxidation of acetic acid at the anode and reduction of oxygen at the cathode. The calculations on Gibbs energy of the reaction and corresponding Nernst potentials were done at standard state conditions, except for H⁺ (=10⁻⁷ M). Values for Gibbs energy of formation were taken from Diekert (1997).

| Compound      | Gibbs energy of formation, \(\Delta G^0_f\) (kJ/mol) |
|---------------|-----------------------------------------------|
| Acetate       | -369.4                                       |
| CH₄           | -50.8                                        |
| CO₂           | -386                                         |
| H⁺ (pH = 7)   | -39.9                                        |
| H₂O           | -237.2                                       |
| O₂            | 0                                            |

**Reactions**

**Methanogenesis**

\[
\text{CH}_3\text{COO}^- + \text{H}^+ \rightleftharpoons \text{CH}_4 + \text{CO}_2 
\]

\[
\Delta G^0_r = \Delta G^0_{\text{products}} - \Delta G^0_{\text{educts}}
\]

\[
\Delta G^0_r = [(-50.8) + (-386)] - [(-369.4) + (-39.9)] = -27.5 \text{ kJ/mol}
\]

\[
E^0 = \frac{-\Delta G^0_r}{n F} = \frac{-27.5}{4 \times 96,485.33} \frac{\text{kJ}}{\text{mol} \cdot \text{C/mol}} = 0.071 \text{ V}
\]

**Oxidation of acetic acid in a SMFC**
Anode half-reaction

\[ \text{CH}_3\text{COO}^- + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CO}_2 + 7\text{H}^+ + 8e^- \]

\[ \Delta G_{r,\text{anode}}^0 = [2 \times (-386) + 7 \times (-39.9)] - [(-369.4) + 2 \times (-237.2)] = -207.5 \text{ kJ/mol} \]

\[ E_{\text{anode}}^0 = -\frac{\Delta G_{r,\text{anode}}^0}{n \ F} = -\frac{-207.5 \text{kJ/mol}}{8 \times 96,485.33 \text{ C/mol}} = 0.27 \text{ V} \]

Cathode half-reaction

\[ 2\text{O}_2 + 8\text{H}^+ + 8e^- \rightleftharpoons 4\text{H}_2\text{O} \]

\[ \Delta G_{r,\text{cathode}}^0 = [4 \times (-237.2)] - [2 \times (0) + 8 \times (-39.9)] = -629.6 \text{ kJ/mol} \]

\[ E_{\text{cathode}}^0 = -\frac{\Delta G_{r,\text{cathode}}^0}{n \ F} = -\frac{-629.6 \text{kJ/mol}}{8 \times 96,485.33 \text{ C/mol}} = 0.82 \text{ V} \]

Complete reaction

\[ \text{CH}_3\text{COO}^- + \text{H}^+ + 2\text{C}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O} \]

\[ \Delta G_{r}^0 = [(-369.4) + (-39.9) + 2 \times (0)] - [2 \times (-386) + 2 \times (-237.2)] = -837.1 \text{ kJ/mol} \]

\[ E^0 = -\frac{\Delta G_{r}^0}{n \ F} = -\frac{-837.1 \text{kJ/mol}}{8 \times 96,485.33 \text{ C/mol}} = 1.085 \text{ V} \]

2.2 Theory: calculation of carbon turnover from electrical data

Sediment organic matter (SOM) decomposition in lakes is difficult to determine due to the rather slow turnover rates. Another difficulty is that the produced CH₄ forms bubbles in an erratic way out of the lake water (own observation). The other product is CO₂. It is volatile, exchange with the atmosphere, precipitates with Ca and other minerals as carbonate, and it is rapidly assimilated by algae. The analysis of CH₄ and CO₂ does therefore not give a reliable picture of the sediment decomposition. Moreover, while CH₄ and CO₂ are formed in equal parts during anaerobic (methanogenic) fermentation of organic matter in sediments, the turnover of organic matter in SMFCs forms solely CO₂.

There is another way to determine the turnover of SOM in an SMFC. Substrate turnover by a microbial fuel cell is directly related to the moles of electrons flowing from the anode to the cathode of the SMFC (unit Coulomb or Ampere seconds). Thus, from the measured working potential (WP) at a defined external resistance, the substrate turnover can be calculated if the educts and products of the reaction are known.
The relation between substrate turnover, energy release, and electrical current is described by the Nernst equation. The Gibbs energy change of the reaction \( \Delta G \) (J/mol) is the energy (or work) set free during a redox reaction. Generally, “energy” (unit J) is a synonym for “work”. Thermodynamics states that this energy will always be set free independent of how the reaction was achieved. If 100% of the released energy is collected as electricity, then the Faradaic or Coulombic efficiency is 100% (Logan et al. 2006).

The Nernst equation states (Bosma and Appelo 1998)

1. \[ E^0 = -\frac{\Delta G^0}{nF} \]

where \( E^0 \) is the standard potential (V) or Nernst potential, \( \Delta G^0 \) is the change of Gibbs energy at standard state of the redox reaction (kJ/mol), \( F \) is the Faraday constant (96,485.33 C/mol = A s / mol) and \( n \) is the number of electrons transferred per mol substrate reacting. If this energy is released as electricity, then

2. \[ W = P \times t \cong -\Delta G \times m \]

where \( W \) is the electrical work (J or W s) and \( P \) is the power (V A or W). With

3. \[ P = E \times I = \frac{E^2}{R} \rightarrow W = \frac{E^2t}{R} \]

where \( I \) is the electrical current (A) and \( R \) is resistance (\( \Omega \)), and \( W \) (work, unit J = W s = V A s = V C). Eq. 3 in Eq. 2 gives

4. \[ \frac{E^2t}{R} \cong -\Delta G \times m \]

where \( E \) is the electrical potential (the working potential in V) and \( R \) is the resistance (\( \Omega \)) between anode and cathode. From (1) we also know that

5. \[ m \times n \times F \times E^0 = -\Delta G \times m \]

thus, (4) in (5) gives

6. \[ \frac{E^2t}{R} = m \times n \times F \times E^0 \]

hence,

\[ m = \frac{E^2 \times t}{R} \]

7. \[ m = \frac{R}{n \times F \times E^0} \]

where \( m \) is the mole turnover and is the desired quantity. In experiments with MFCs, the measured open circuit potential (OCP, in unit V) approaches the Nernst potential \( E^0 \) but remains
below due to losses known as “overpotential” (Logan et al. 2006). It is likely that the same losses occur in the closed circuit and affect the measured working potential, and the ratio WP to OCP is the same as the ratio $E$ to $E^0$. Thus, using this assumption, $E$ can be replaced by the WP and $E^0$ by the OCP. Then follows the useful equation

$$m = \frac{WP^2 \times t}{R \times n \times F \times OCP}$$

for the amount of substrate (moles) turned over in time $t$. The substrate flux is $M/T$ (mol/s).

Equation (8) makes it possible (with the given assumptions) to calculate the mole substrate turnover in the SMFC using the measured WP (V), measured OCP (V), time of the experiment $t$ (s), known external resistance $R$ (Ω), number of electrons transferred in the assumed redox reaction, and the Faraday constant.

### 2.3 Lake Søllerød

Lake Søllerød is a highly eutrophic freshwater lake situated in the municipality of Rudersdal in Northern Zealand, Denmark ($55^\circ 48'56.1"$N $12^\circ 29'33.5"$E), 4 km north of the campus of the Technical University of Denmark in Kongens Lyngby. The lake has a surface area of 13 ha and an average depth of 5.6 m (Jensen and Møller 2015). The hydraulic retention time is between 5 and 6 years (Jensen et al. 2009). The lake is hydraulically connected to several downstream lakes (lake Fure, lake Lyngby). Lake Søllerød was chosen as the test site for phosphate immobilization using SMFCs. The project was successful in reducing the P concentration in the bottom water above the electrodes, as described elsewhere (Haxthausen et al. 2021a). The layer of anthropogenically affected sediments in the lake is 1 to 1.5 m thick and has a mass of more than 100 000 tons, with a dry matter content of 11% to 26% (mean 16.8%, std 5.6%, $n = 6$) (Hvidt 2016, SWECO 2017). Between 6 and 10 tons of P and > 100 tons of organic N (Jensen et al. 2009, and own investigations) are stored in this sediment. The heavy metal content is moderate (Pb 91-190 mg/kg; Cd 1.2-2.7 mg/kg; Cu 78-150 mg/kg; Hg 0.6-1.6 mg/kg; Zn 460-890 mg/kg; Sn 29-130 mg/kg, all values dry weight, dw). Oil components (C6 to C35) were measured to be present at 1300-3200 mg/kg dw. It was observed, during sampling of the sediment, that disturbance of the sediment lead to formation of an oil film, which was also visible on the water samples taken. Polycyclic aromatic hydrocarbons (PAH) concentrations measured were benzo[a]pyrene 1.1-2.3 mg/kg dw, sum of 7 PAH 7.2-14 mg/kg dw; the sum of BTEX (benzene, toluene, ethylbenzene, and xylene) was 2-5 mg/kg dw (Sweco 2017). Overall, there is a considerable amount of pollution stored in the sediments.

### 2.4 Sediment microbial fuel cells in Lake Søllerød

In aerated lake sediments, phosphate binds to iron oxides, while in anoxic sediments, sulfide ($S^{2-}$) precipitates iron and makes it unavailable for this binding process (Roden et al. 1997, Haxthausen et al. 2021a). Restoration of the lake water quality can thus be achieved by raising the sediment redox potential to levels at which sulfur reduction to sulfide is inhibited (above -150 mV). Thus, the goal of this SMFC operation was not the oxidation of sediment organic carbon. Contrary, the sediment matrix is required to prevent P release and to bind legacy pollutants, and
oxidation of sediment organic matter is an undesired and detrimental side reaction. Hence, the SMFC in lake Søllerød was not targeting maximum carbon turnover but functioned more as a bioelectrical redox adjustment system.

Three different test fields were investigated in the lake using two SMFCs. The first SMFC was installed in the lake (field 1) in July 2019. Later, in May 2020, the first electrode in field 1 was moved to field 3, where the lake was deeper (Haxthausen et al. 2021a). A second SMFC was installed in June 2020 (field 2). The electrodes were constructed from AISI 316 stainless steel wire spot-welded in 10 mm squares (Filtertek A/S, Denmark). The anode was constructed as a three-layered stacked electrode whereas the cathode consisted of only one layer (Haxthausen et al. 2021a). The electrodes were suspended in 4x4 m square frames made from heavy duty PVC tubing. The anodes were sunk to the bottom of the lake. The frames were allowed to settle a few centimeters into the lake sediment, hence, the layered anode was positioned just at the sediment surface and did not sink into the sediment. The vertical distance between the anode and cathode in field 1 and 3 was fixed at 3 m, in field 2 this could be adjusted and was set to 5.5 m. The anodes were at a depth of 4 m, 7 m, and 7 m in field 1, field 2, and field 3, respectively. The anodes and cathodes were tethered in the four corners and connected to marking buoys at the surface. The electrical circuit was attained using robust electrical wires, which were accessible from a utility box placed on the bank. At the time of writing, the electrodes are still in the lake, though regular electrical recording and chemical sampling was terminated in October 2020.

2.5 Electrical measurements

Robust cables went from anode and cathode to a box on the shore, where the cables were connected through an exchangeable resistor (initially 1000 Ω, later 25 Ω and 10 Ω). WP was measured weekly, later twice a month by measuring the voltage across the external resistor using a hand-held multimeter (Elma 6700, Elma industries). The open circuit potential (with infinite resistance) was initially also measured weekly but was later on only measured rarely to avoid disturbance of the electrogenic biofilm. Despite their robustness, cables were broken twice, possibly due to ice on the lake (Haxthausen et al. 2021b). Only valid results are shown later.

3 Results

3.1 Measured working potentials

The working potentials of the SMFCs in the lake are shown in Figures 1 and 2. Field 2 showed a satisfactory electricity production with a WP around 300 mV (154-480 mV) at 1000 Ω and about 150 mV (135-177 mV) at 25 Ω. The power production was higher with lower resistance, and the peak value was > 1 mW (Fig. 1). Field 3 showed the best electrical results, with > 800 mV at 1000 Ω, a peak power production above 10 mW at 10 Ω resistance (WP = 323 mV) and a working potential up to 450 mV at 25 Ω. Data for field 1 are not shown because the electrode
was poorly placed (sitting on a stone), not deep enough (in 4 m depth), and later also had a broken cable. Therefore, field 1 had low measured working potential, and the lowest electrical power (not shown).

The power production showed seasonal dependency and was lower in autumn and winter and at times of high dissolved oxygen (DO) in the bottom water (Haxthausen et al. 2021a). Reduction of the phosphate concentration in the bottom water could be observed over both field 2 and field 3 from June to October 2020, but was occasionally interrupted by periods with weak P retention efficiency, for example mid-August 2020. This coincides with low electricity production (despite low external resistance) and indicates that a lower threshold of electrical power for P immobilization exists.

**Figure 1.** Measured working potential WP (mV), electrical power (mW) and external resistance for the SMFC in field 2. The anode was positioned 7 m below the surface. The external resistance was changed from 1000 Ω to 25 Ω in September 2020.
Figure 2. Measured working potential WP (mV), electrical power (mW) and external resistance for the SMFC in field 3. The anode was positioned 7 m below the surface. The external resistance was changed from 1000 Ω to 10 Ω in June 2020 and to 25 Ω in September 2020.

3.2 Calculated turnover rates and sediment organic matter half-life

The substrate turnover is coupled to the electrical power production. The maximum power production was achieved in field 3 with 0.323 V at 10 Ω. Except for field 1, the OCP was only initially determined in the field because each interruption of the electrical circuit negatively affects the electro-microbial community. Field 1 had an OCP of initially 0.605 V which quickly declined to 0.1 V, and with minima as low as 0.03 V. As mentioned, field 1 was disturbed and had a damage. Field 2 showed an initial OCP of 0.35 V. The OCP of field 3 was not measured. In laboratory reactors with the same sediment, higher OCP-values of up to 1 V could be obtained (not shown). For calculations, we use the mean value of 0.6 V here. As substrate acetic acid CH₃COOH (\(M = 60.05\) g/mol), is assumed, hence the number of electrons moving is 8 (Table 1). Thus, the substrate turnover \(dm/dt\) (mg/d) within 1 day can be calculated using Eq. (8):

\[
\frac{dm}{dt} = \frac{(0.323 \text{ V})^2 \times 86400 \text{ s}}{10 \text{ Ω} \times 8 \times 96,485.33 \text{ C/mol} \times 0.5 \text{ V}} = 1.95 \text{ mmol/d} = 117 \text{ mg/d}
\]

The result is 1.95 mmol/d or 117 mg acetic acid per day. However, this is the peak value achieved only for a short time between August and September 2020 (Figure 2). Using the same formula, the overall turnover for the whole experimental period, and with actual data for each time point, can be calculated. The upper value is calculated using the lower OCP value measured. Field 2 had 8-11 mmol turnover for the period 17th June to 20th October 2020. Field 3 had, in the period 30th of May to 20th October 2020, a turnover of 63-108 mmol. These values correspond to 3.8-6.5 g of acetic acid in 143 days, or 9.7-16.6 g/year.

The electrical power generation and the substrate turnover refer to a footprint area of 16 m². Assuming that the anode affects the sediment to a depth of 5 cm this corresponds to 0.8 m³ substrate. The sediment had a mean dry matter content of 16.8%. The carbon content in the sediment was measured to be 12.7% C (Haxthausen 2021). This gives 21.3 g C per kg, or (with density of 1 kg/L) 17,069 g C for the electrode-affected sediment.

Thus, the degradation rate of organic carbon in the sediment was \(0.57 \times 10^{-3}\) to \(0.97 \times 10^{-3}\) per year, corresponding to a half-life of 715-1220 years. The peak electricity production was 10.4 mW, or 0.9 mW/m², corresponding to a turnover half-life of 277 years.

4 Discussion

4.1 Half-life of sediment organic carbon
Sediment organic matter (SOM), which is the substrate for the SMFC, consists of long-chain polymeric material mostly composed of the decaying necromass of algae and microbes, with the major fraction composed of amino acids and deaminated peptides (Hardison et al. 2013, Miltner et al. 2012, Abdulla et al. 2018). Decomposition of SOM can be a major source of nutrients in eutrophic lakes. However, the dominant source for the water body is recycling of freshly settled necromass (Hupfer and Lewandowski 2008), while the decomposition of sediment is slow (Avnimelech et al. 1984) and forms refractory organic matter, which is accumulating in buried sediments (Burdige et al. 2016). SOM is thus a recalcitrant, polymeric material, and natural turnover rates are limited by the formation of low-molecular compounds from the long-chain humic materials.

*Geobacter* spp., and their enzymatic capabilities have been intensively studied. *Geobacter* are commonly grown on simple, volatile fatty acids, like acetate or lactate (Coates et al. 2001, Ueki 2021). In anaerobic sediments, the same substrates are utilized for methanogenesis (Nagle and Wolfe 1985). Volatile fatty acids are common intermediates in anaerobic decomposition of organic matter and are easily degradable substrates; their turnover is thus not the limiting step in SOM degradation.

In anoxic sediments, the usual electron acceptors such as oxygen, nitrate, sulfate, Fe(III) and Mn(III) have been exhausted, and the organic matter is both used as electron acceptor and electron donor by the microorganisms (Kaur et al. 2014), leading to large amounts of methane produced and emitted (6-16% of global natural methane emissions, Bastviken et al. 2004). From these considerations, it can be surmised that the installation of an SMFC affects whether methane or CO₂ is produced in the final steps of SOM decomposition, but does not significantly enhance the overall turnover rates.

The calculation of SMFC turnover from electrical power production assumed that the only turnover of organic carbon in the sediment is by electrodes. There are some uncertainties in the calculation of the turnover of the SMFC, however, the range of estimated rates is clearly slower than typical natural decomposition rates of sediments. Avnimelech et al. (1984) found for carbon turnover in 64 North American lake sediments an average half-life of 29 years, with the fastest carbon half-life as low as 8 years. The half-lives calculated from N and P depletion were slower, in average 33 and 139 years, respectively. Thus, natural decomposition half-lives are one to two orders of magnitude lower than the rates determined for the turnover of substrates with the SMFC. The combined half-life resulting from natural decomposition (29 years) and SMFC-stimulated decomposition (277 years) is 26.25 years, only 10% shorter.

Of course, the natural decomposition of lake sediment happens regardless, and the decomposition due to the effect of the SMFC is additional. However, compared to natural decomposition, the decomposition rates obtained with the SMFCs tested in lake Søllerød are negligible. The results therefore suggest that the risk of a sudden pollutant or nutrient pulse into the lake due to rapid lake sediment oxidation due to a SMFC can be considered as very low. Quite the contrary: Hong et al. (2010) found that the reduction of organic carbon in electricity-producing MFCs was not significantly different from controls with OCP (open circuit potential, no electricity generation). Moreover, they showed that MFCs can alter SOM which leads to improved adsorption of hydrophobic organic pollutants and concluded that diagenetic processes were stimulated, leading to solidification of sediments, but not decomposition.
4.2 The optimal design of the SMFC for lake restoration

In a related study, we tested different electrode materials (Haxthausen et al. 2021b). The electrical power produced was not higher when using steel plates or graphite electrodes. It is hence likely that the electrical production of the SMFC is limited by the available substrate, and not by the electrode efficiency (Haxthausen et al. 2021b). It is furthermore questionable whether more efficient electrodes (e.g., with very high surface or with catalytic properties) would be helpful, when the goal of the SMFC treatment is the restoration of eutrophic lakes by immobilization of phosphate (Haxthausen et al. 2021a).

Different from other applications, the goal of the treatment is neither power production nor rapid degradation of the sediment – which would also be counterproductive since the sediment is necessary for phosphate immobilization. Consequently, the design of choice for this purpose differs from other applications, like wastewater and sludge treatment (Aelterman et al. 2006, Zhang et al. 2011), where high power and fast turnover are targeted and achieved. In eutrophic lake restoration, the role of the SMFC is to create a layer with elevated redox potential at the sediment surface, where then phosphate originating from decomposition of organic matter adsorbs to iron oxides. Hence, if the top sediment layer is rapidly decomposed by the SMFC, this goal cannot be achieved (in fact, more P would be released). Thus, the effectiveness of the SMFC must be balanced to achieve the goal but to avoid rapid sediment decomposition. In practice, the electrical power of an SMFC can be regulated by changing the external resistance. In the case of lake Søllerød, a power density of ≤ 1 mW/m² was found efficient for P fixation, but is safe with respect to sediment decomposition and subsequent pollutant release. In future lake restoration projects with SMFCs, the dissolved phosphate at the bottom of the lake should be monitored. The resistance between anode and cathode should be chosen so that P is eliminated, but not lower, to minimize undesired sediment organic matter oxidation.

5 Conclusions

The substrate turnover of microbial fuel cells is proportional to the electrical power generation. Using SMFCs for restoration of eutrophic lakes bears the risk of releasing legacy pollution deposited in the sediments over decades. The SMFC needs to be sufficiently effective to eliminate phosphate release but should not decompose sediment organic matter at a high rate. We investigated the decomposition of sediments by SMFCs by monitoring electrical power production at two large SMFCs installed in a eutrophic lake. A power production below 1 mW/m² was sufficient to reduce P outflux from sediment, corresponding to a sediment decomposition half-life of 277 years (for the top 5 cm layer). It is questionable whether electrodes that are more efficient would be preferable, when the goal of the SMFC treatment is the restoration of eutrophic lakes by fixation of phosphate.

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Graphical abstract
Highlights

- Lake restoration with microbial fuel cells was studied in pilot scale
- Sediment decomposition was negligibly affected by sediment microbial fuel cells
- Risk of release of legacy pollutants is low if the electricity production is low
- Low electricity production is sufficient for phosphate immobilization in sediment