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Competition for electron donors (ED) and electron acceptors (EA)

ED_i primary electron donor

oED_i oxidized electron donor

Oxidation

Reduction

EA_j terminal electron acceptor

rEA_j reduced electron acceptor
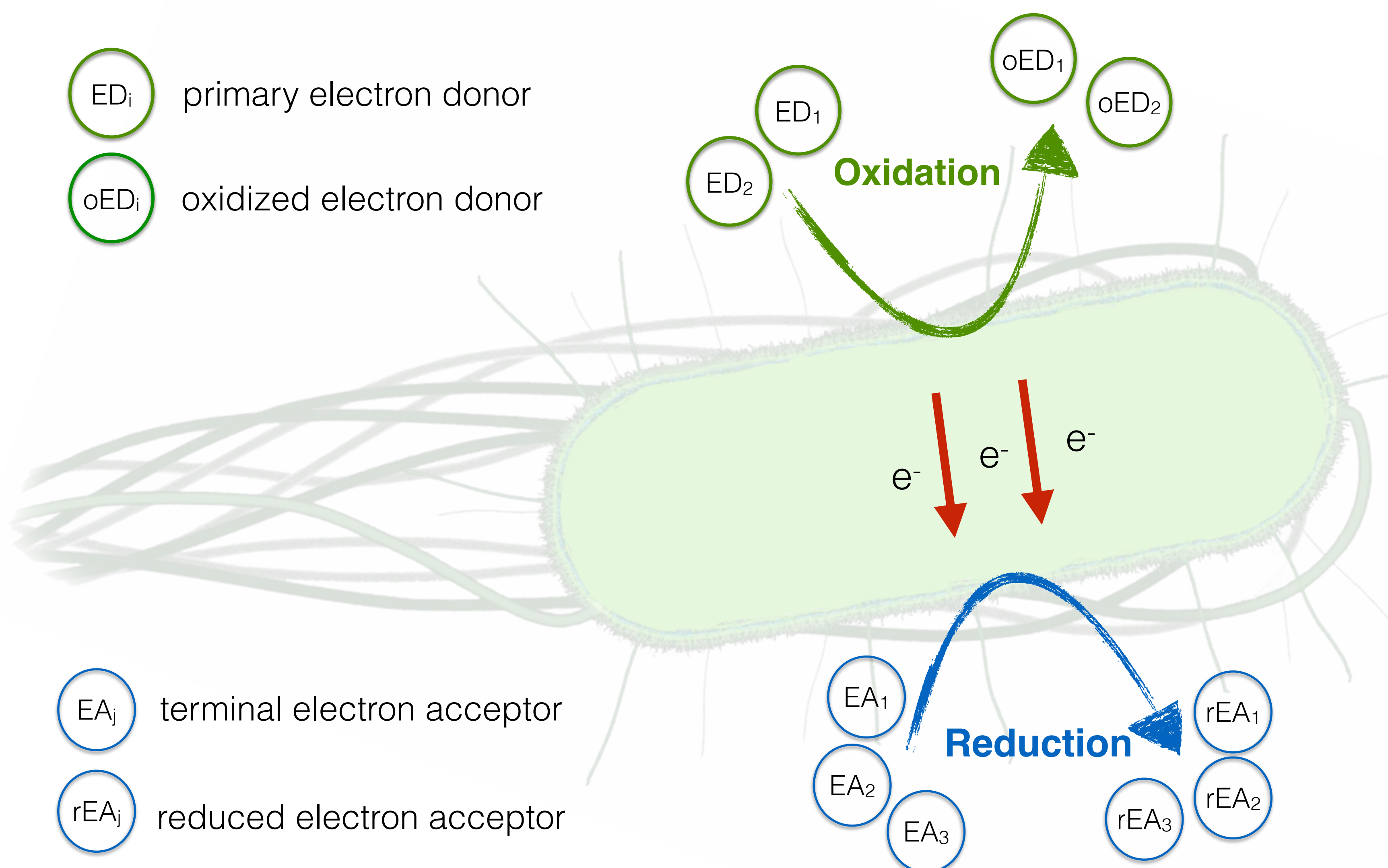
$$R_i = k_i \cdot X \cdot \left[\frac{C_{ED}}{K_{ED}^m + C_{ED}}\right]_i \cdot \left[\frac{C_{EA}}{K_{EA}^m + C_{EA}}\right]_i \cdot F_T^i \cdot F_X^i$$

R_i - rate of oxidation of a ith ED by the reduction of ith EA
k_i - reaction rate constant per unit biomass
X - microbial biomass
C_{ED} - concentration of the electron donor
C_{EA} - concentration of the electron acceptor
K^m - half-saturation constant
F_T^i - thermodynamic term (LaRowe and Van Cappellen, 2011)
F_X^i - "inhibition" term

Common practice

The most widely used expression to simulate the succession of electron acceptor utilization during the microbial degradation of organic matter is that of Humphrey (1972):

$$F_X^i = \prod_{i=1}^{N} \frac{K_I^{i-1}}{K_I^{i-1} + C_{EA}^{i-1}}$$

C_{EA}^{i-1} - concentrations of all oxidants stronger than the ith EA
K_I^{i-1} - inhibition constant

Drawbacks

1. Inhibition model requires the **a priori assignment of the order** of EA utilization.

2. Inhibition constants are specific to a particular set of environmental or experimental conditions and, hence, **lack general applicability.**

3. The inhibition model cannot respond to variations in **dynamic conditions** that may reshuffle the order of EA or ED utilization (e.g., causing sulfate to be used before ferric iron oxyhydroxides – see Jakobsen R. & Postma D, 1999).

Alternative approach

In energy-limited environments (e.g., the subsurface), microbial communities compete for energy substrates. We propose to represent this competition by taking into account the **power** (P_i) of catabolic reactions:
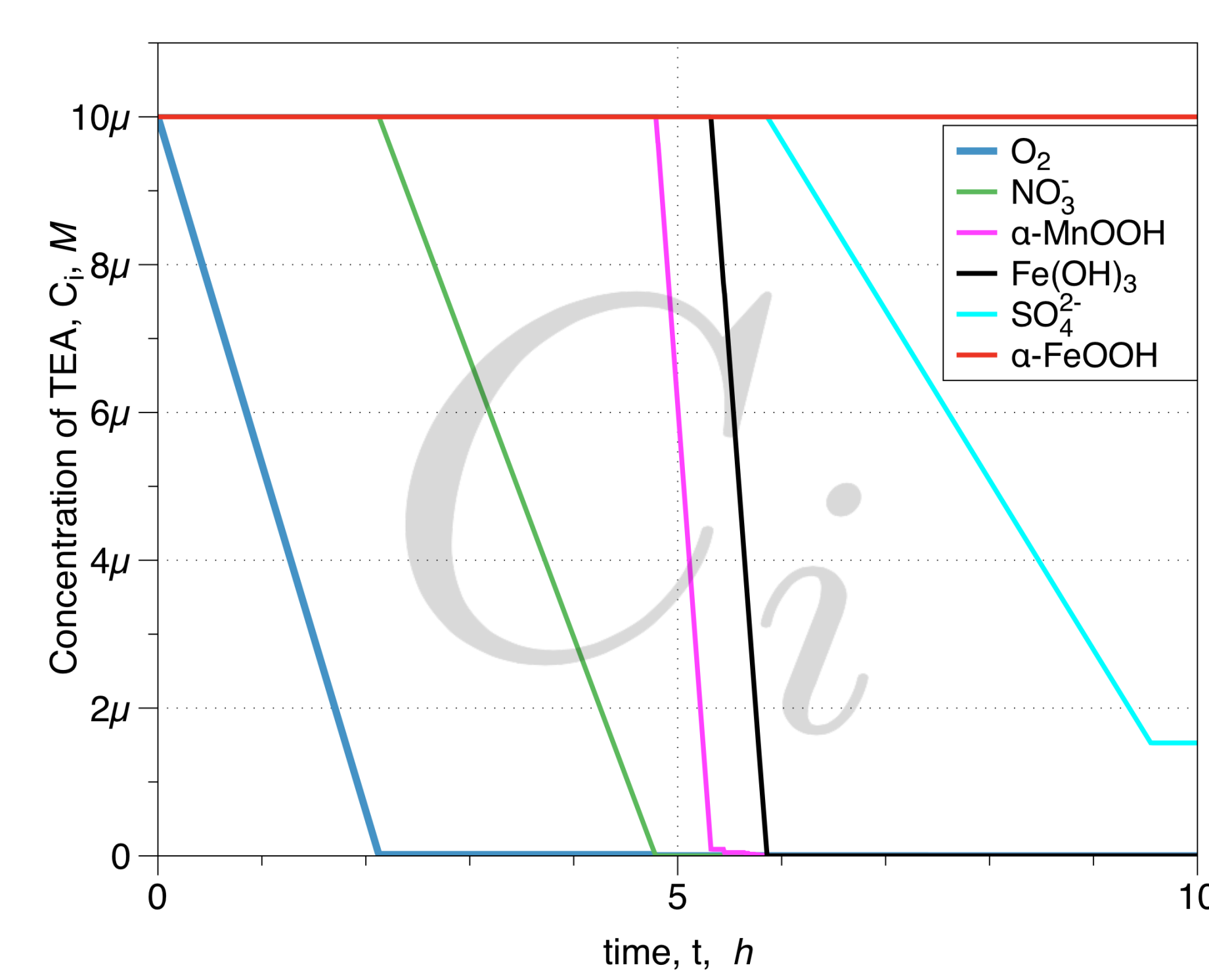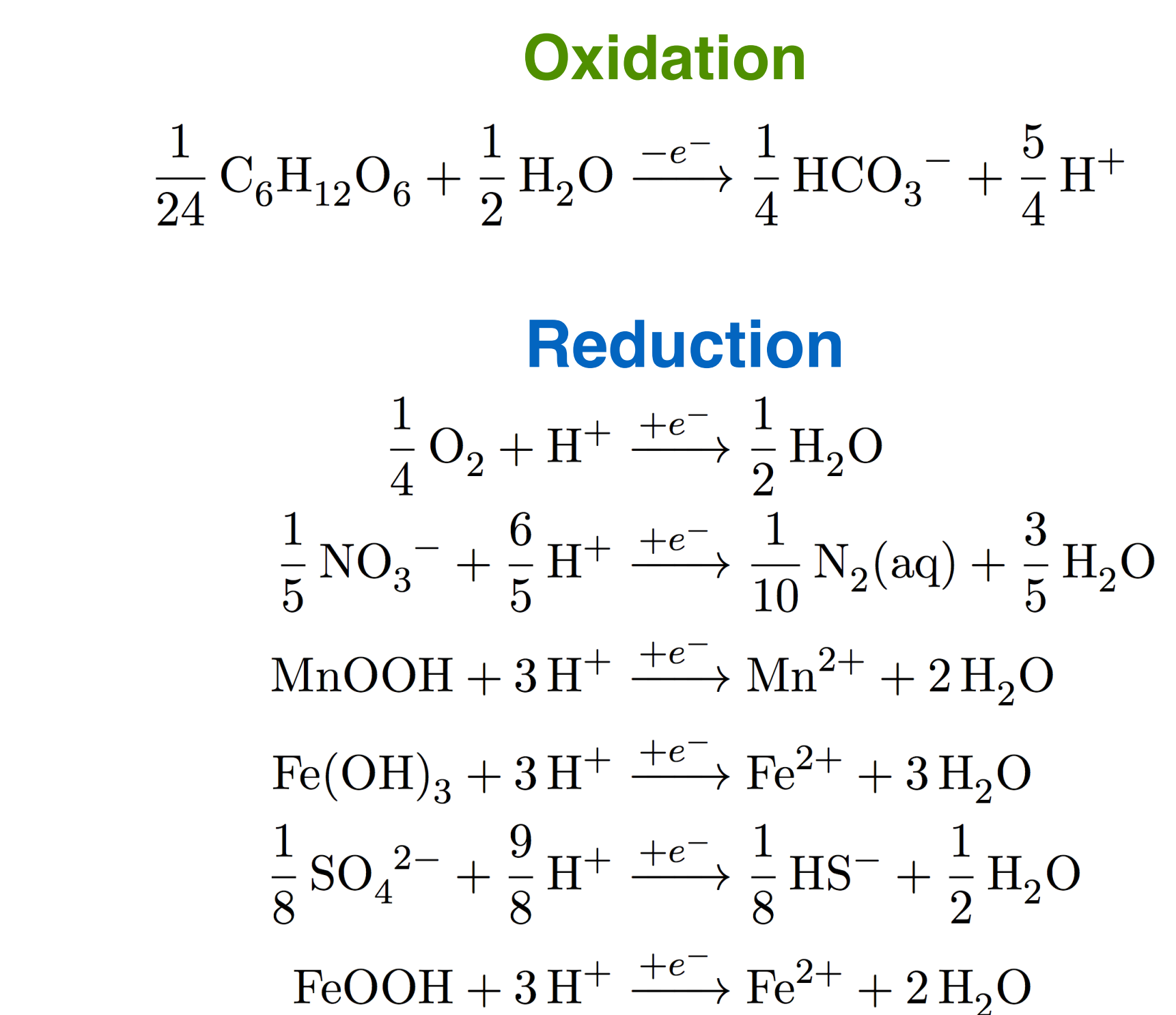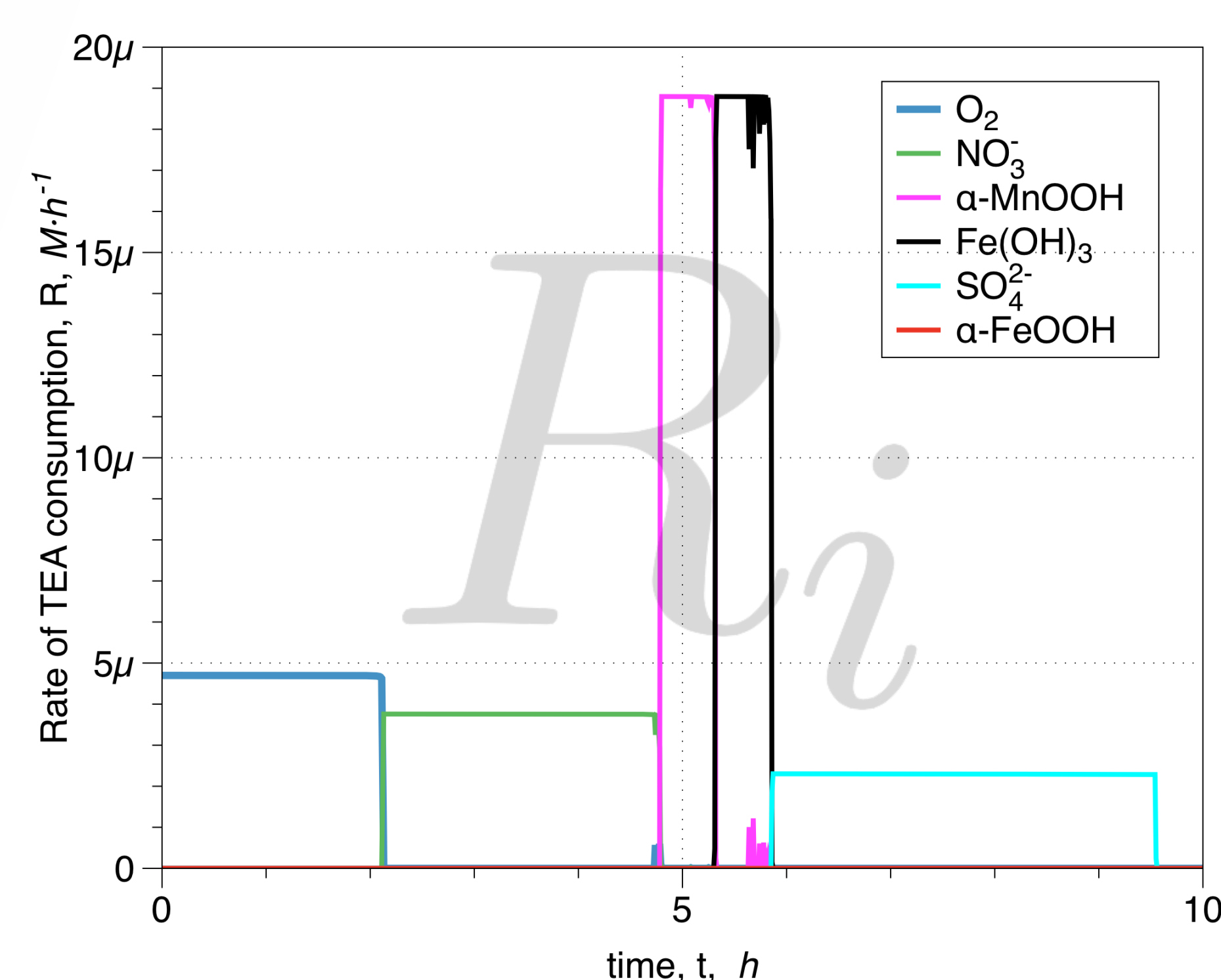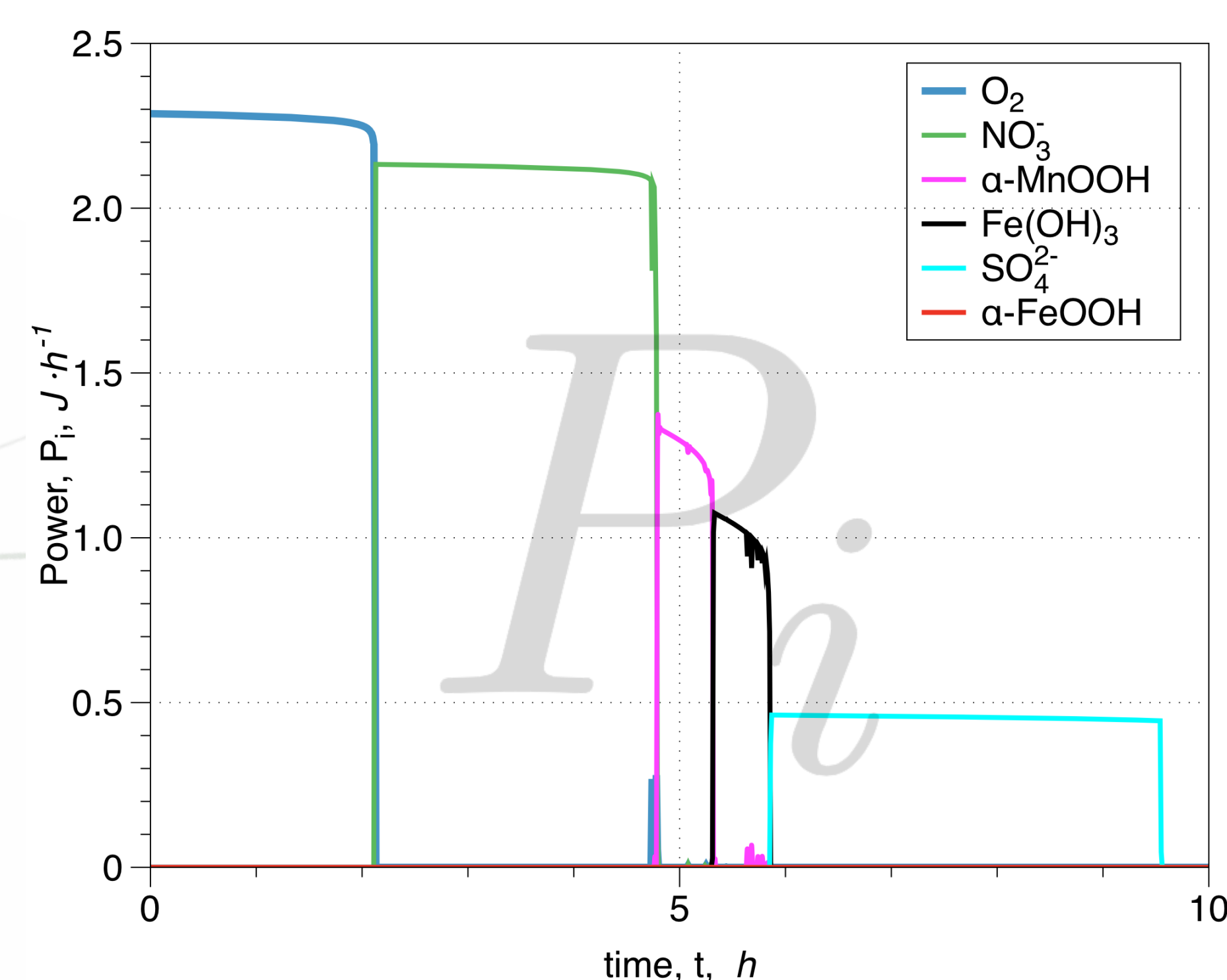
$$P_i = -\Delta G_i^e \cdot R_i^e$$

The sequence of redox reactions is now determined by the power that can be harvested by the microbial populations.

$$\begin{cases} \max\left\{-\sum_{i=1}^{N} \Delta G_i^e \cdot R_i^e \cdot F_X^i\right\} \\ \sum_{i=1}^{N} F_X^i = 1 \\ F_X^i \geq 0 \end{cases}$$

Optimize power generation!

P_i - power produced by i^{th} redox reaction
ΔG_i^e - Gibbs energy of the reaction per electron equivalent
R_i^e - rate of the reaction per electron equivalent
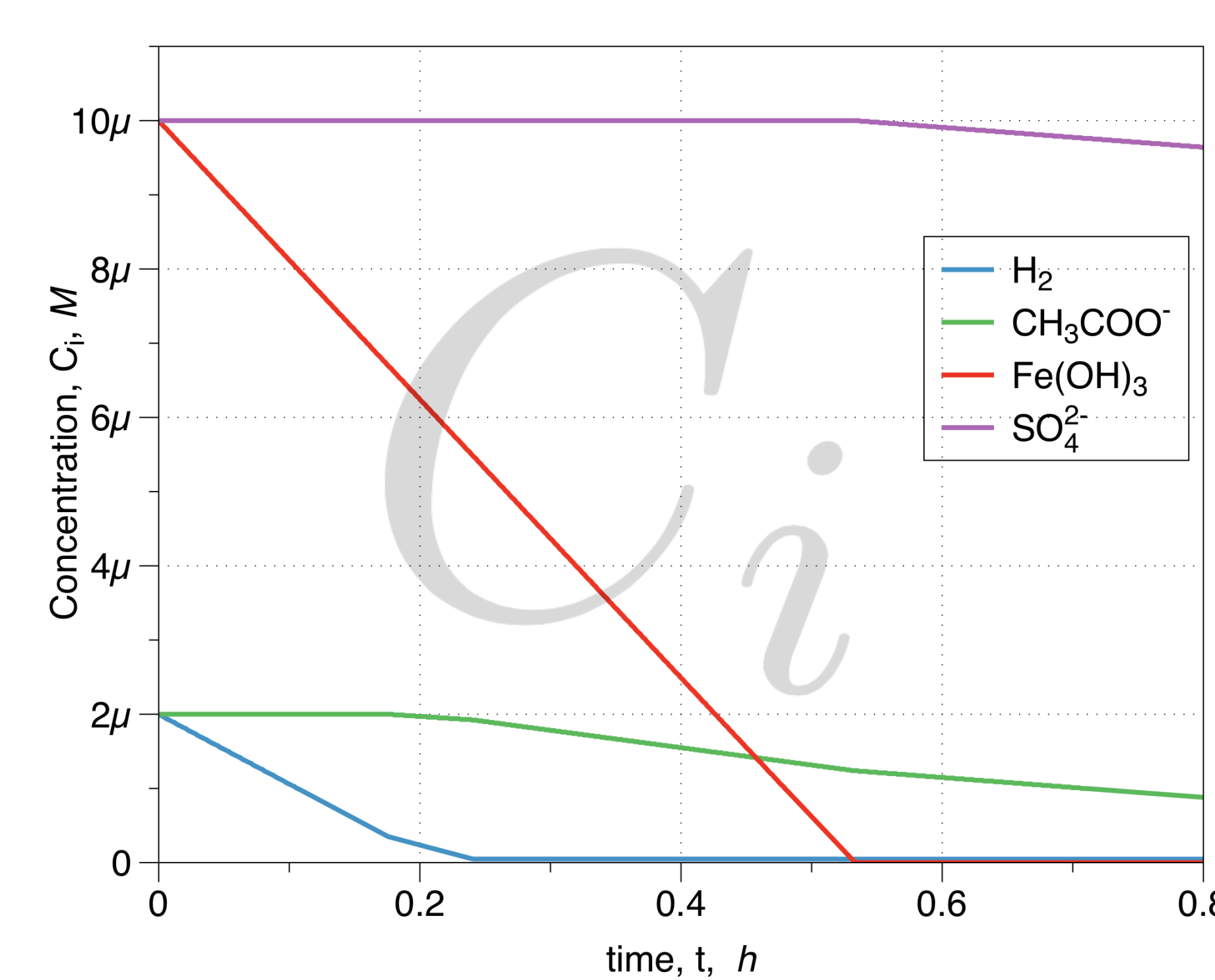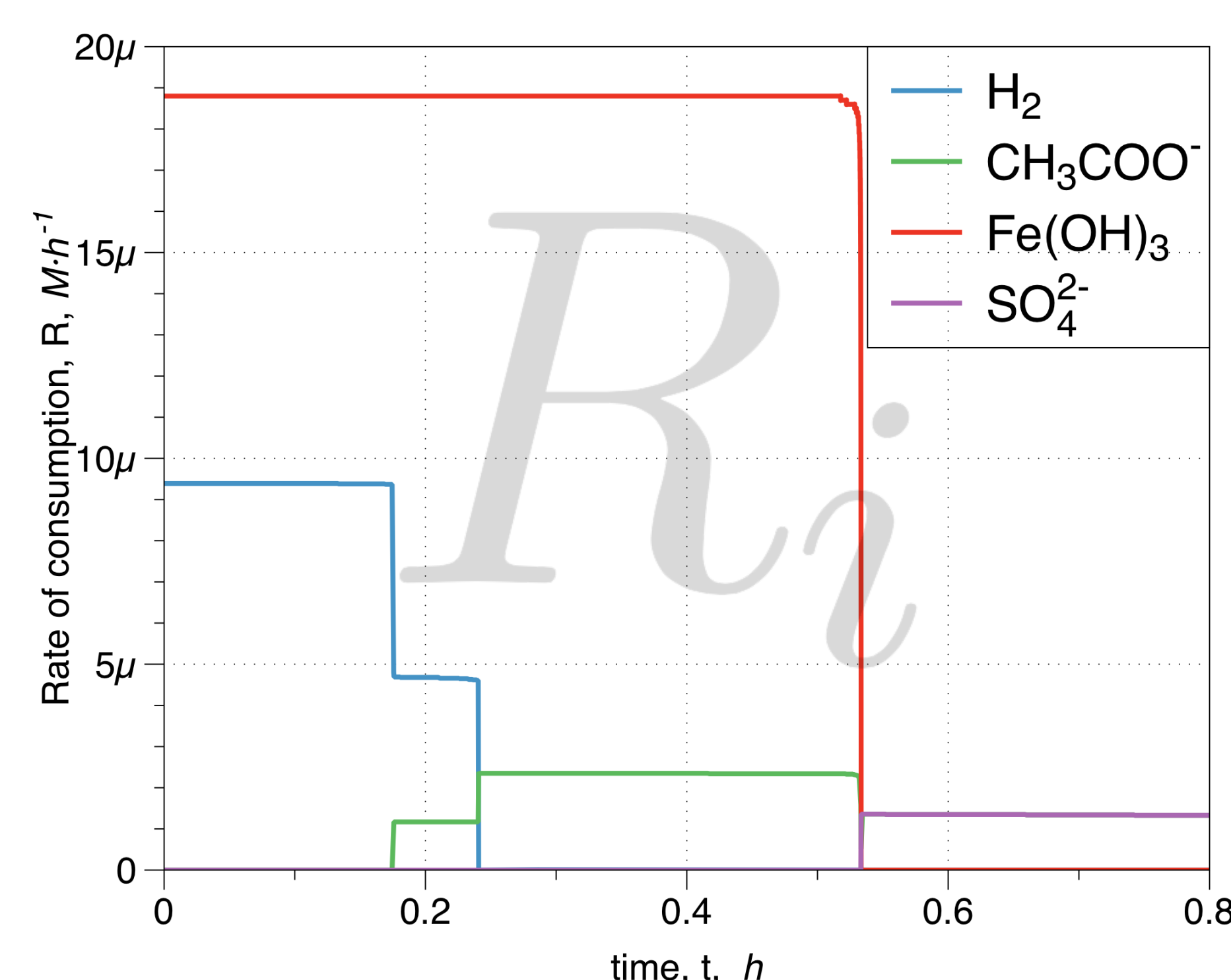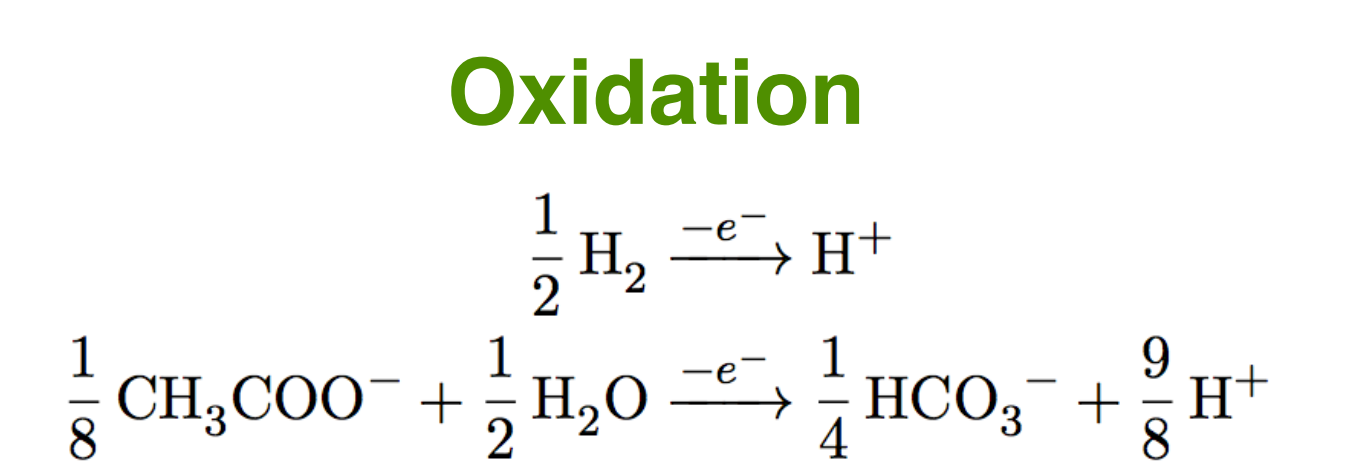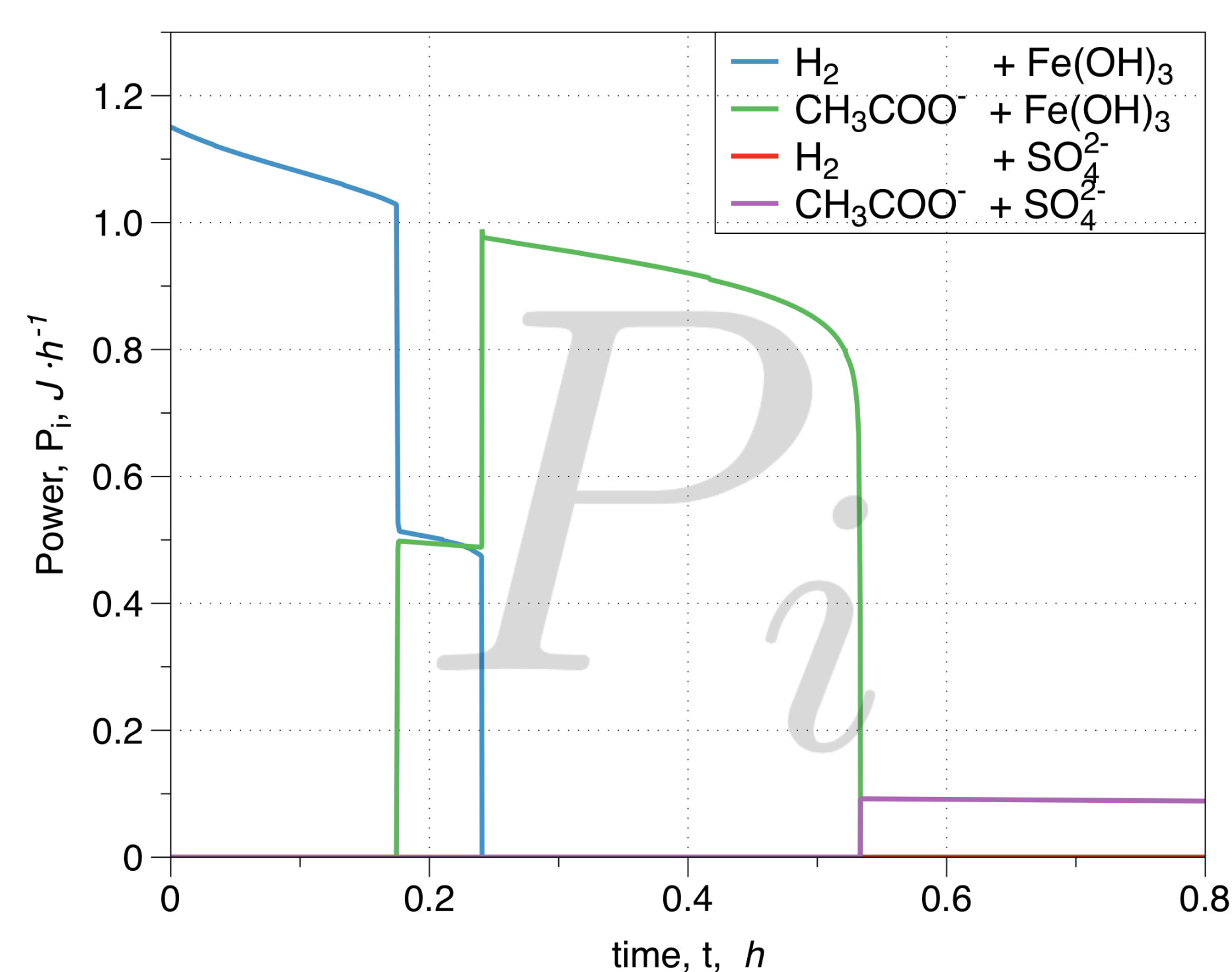F_X^i - the **unknown.** The part of bacteria which utilize i^{th} reaction

Example: 1 ED and 6 EA

$$\mathbf{P}[O_2] > \mathbf{P}[NO_3^-] > \mathbf{P}[\alpha\text{-}MnOOH] > \mathbf{P}[Fe(OH)_3] > \mathbf{P}[SO_4^{2-}] > \mathbf{P}[\alpha\text{-}FeOOH]$$

Oxidation

$$\frac{1}{24}C_6H_{12}O_6 + \frac{1}{2}H_2O \xrightarrow{-e^-} \frac{1}{4}HCO_3^- + \frac{5}{4}H^+$$

Reduction

$$\frac{1}{4}O_2 + H^+ \xrightarrow{+e^-} \frac{1}{2}H_2O$$

$$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ \xrightarrow{+e^-} \frac{1}{10}N_2(aq) + \frac{3}{5}H_2O$$

$$MnOOH + 3H^+ \xrightarrow{+e^-} Mn^{2+} + 2H_2O$$

$$Fe(OH)_3 + 3H^+ \xrightarrow{+e^-} Fe^{2+} + 3H_2O$$

$$\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ \xrightarrow{+e^-} \frac{1}{8}HS^- + \frac{1}{2}H_2O$$

$$FeOOH + 3H^+ \xrightarrow{+e^-} Fe^{2+} + 2H_2O$$

Example: 2 ED and 2 EA

$$\mathbf{P}[H_2 + Fe(OH)_3] > \mathbf{P}[CH_3COO^- + Fe(OH)_3] > \mathbf{P}[CH_3COO^- + SO_4^{2-}] > \mathbf{P}[H_2 + SO_4^{2-}]$$

Oxidation

$$\frac{1}{2}H_2 \xrightarrow{-e^-} H^+$$

$$\frac{1}{8}CH_3COO^- + \frac{1}{2}H_2O \xrightarrow{-e^-} \frac{1}{4}HCO_3^- + \frac{9}{8}H^+$$

Reduction

$$Fe(OH)_3 + 3H^+ \xrightarrow{+e^-} Fe^{2+} + 3H_2O$$

$$\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ \xrightarrow{+e^-} \frac{1}{8}HS^- + \frac{1}{2}H_2O$$

Geochemical implications

Using an approach based on the **optimization of the power** generated by catabolic processes allows one to account for **dynamic** environmental conditions (e.g., variability of temperature, pH, ionic strength, activities of redox active species). The method can be applied to simulate the redox stratification observed in **early diagenesis** and other **energy-limited environments**, such as oligotrophic aquifers, where energy substrates are in low abundance.

References

Humphrey A. E. (1972). Adv. Chem, p. 630-650
Jakobsen R. & Postma D. (1999). Geochim. Cosmochim. Acta, p. 137-151
LaRowe D. E. & Van Cappellen P. (2011). Geochim. Cosmochim. Acta, p. 2030-2042