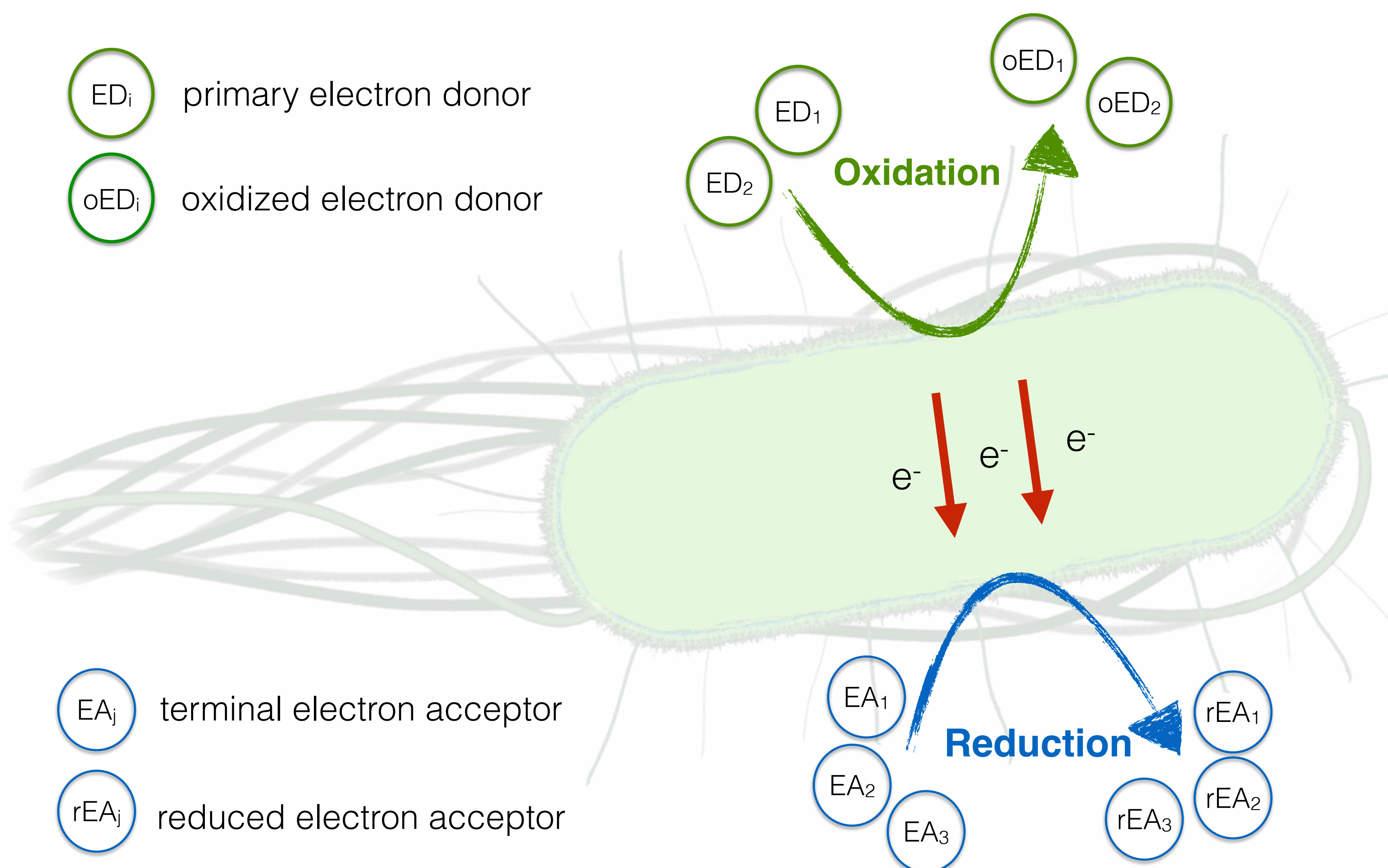


Competition for electron donors (ED) and electron acceptors (EA)



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

- R_i - rate of oxidation of a i^{th} ED by the reduction of i^{th} 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):

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

- C_{EA}^{i-1} - concentrations of all oxidants stronger than the i^{th} 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:

$$P_i = -\Delta G_i^e \cdot R_i^e$$

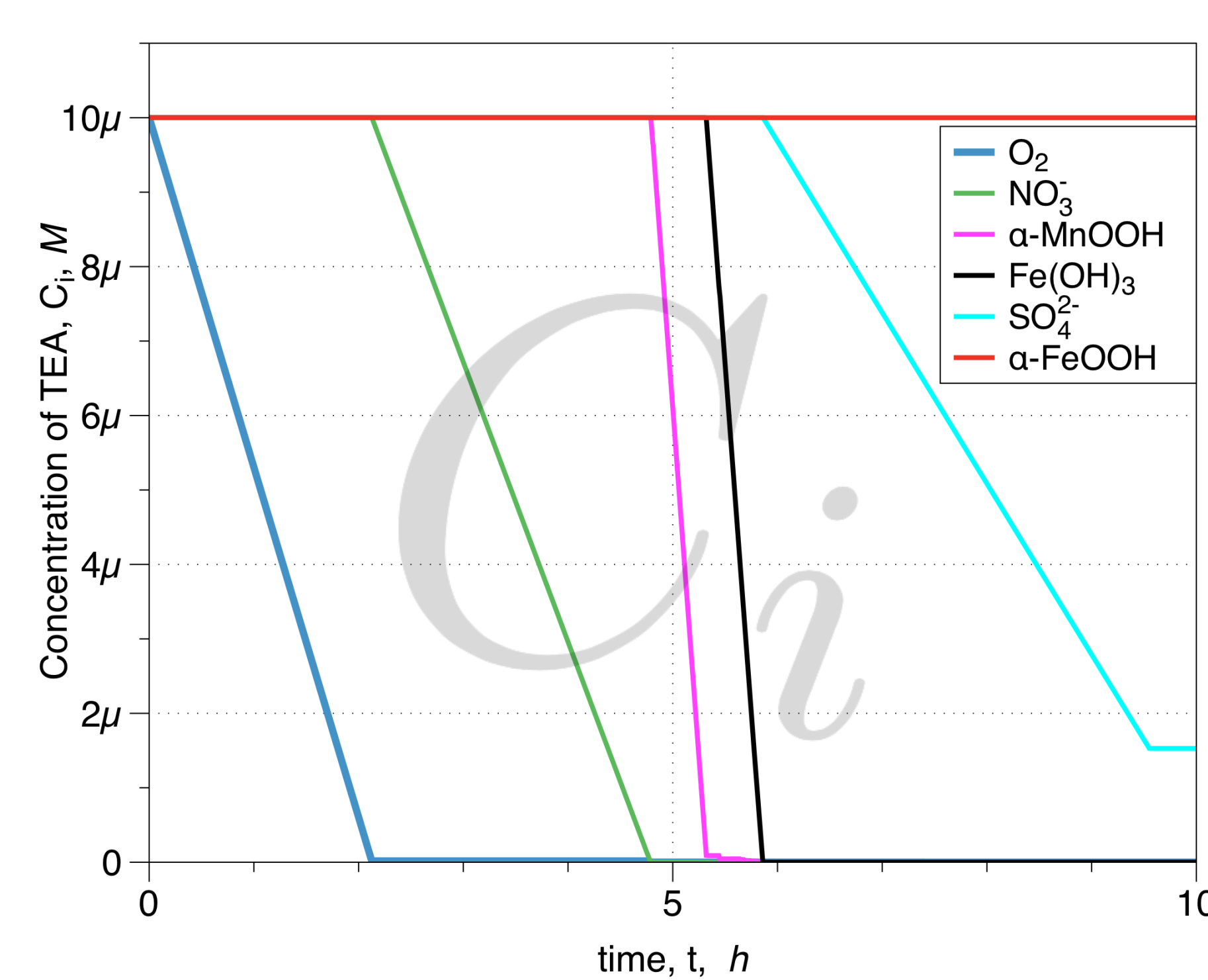
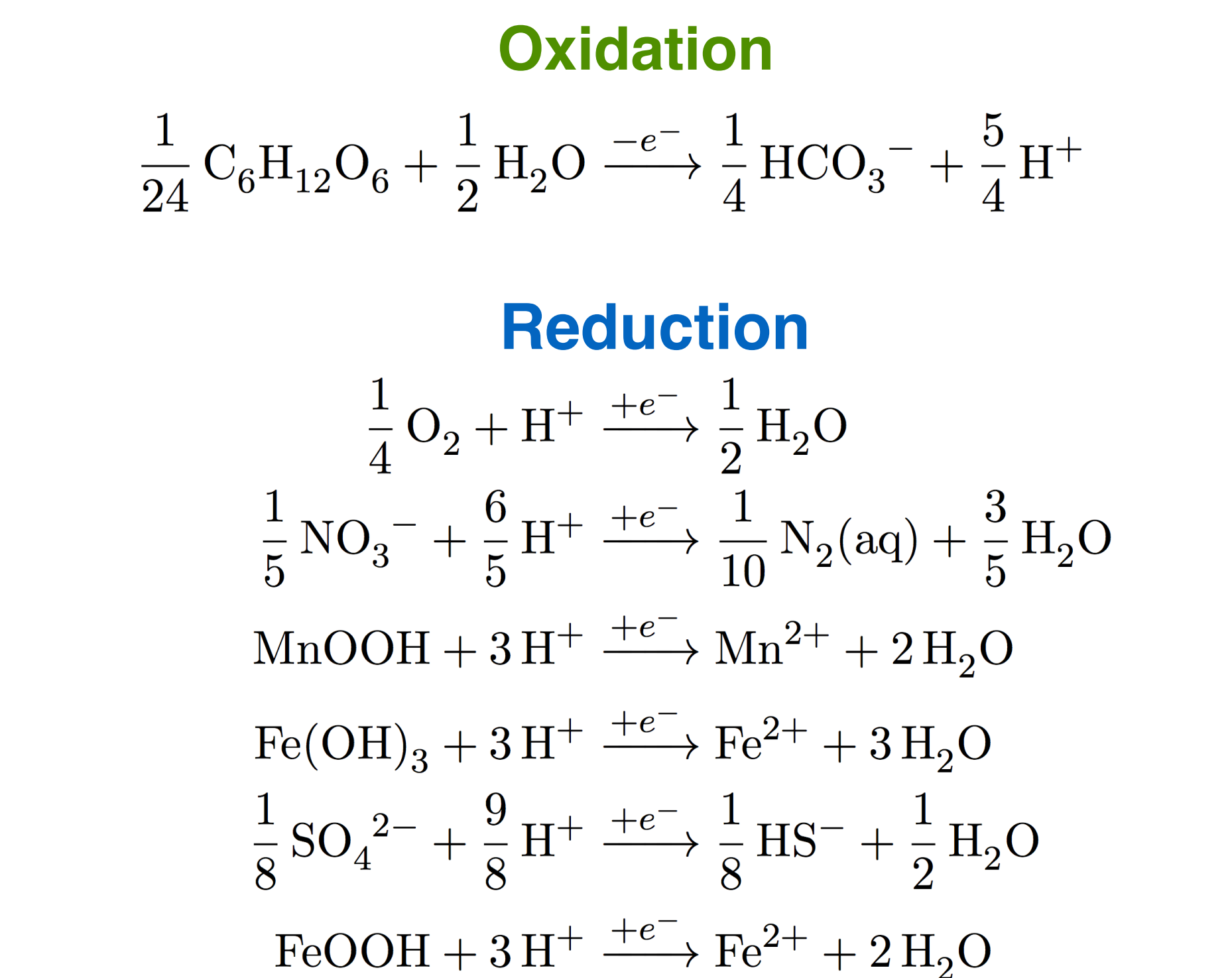
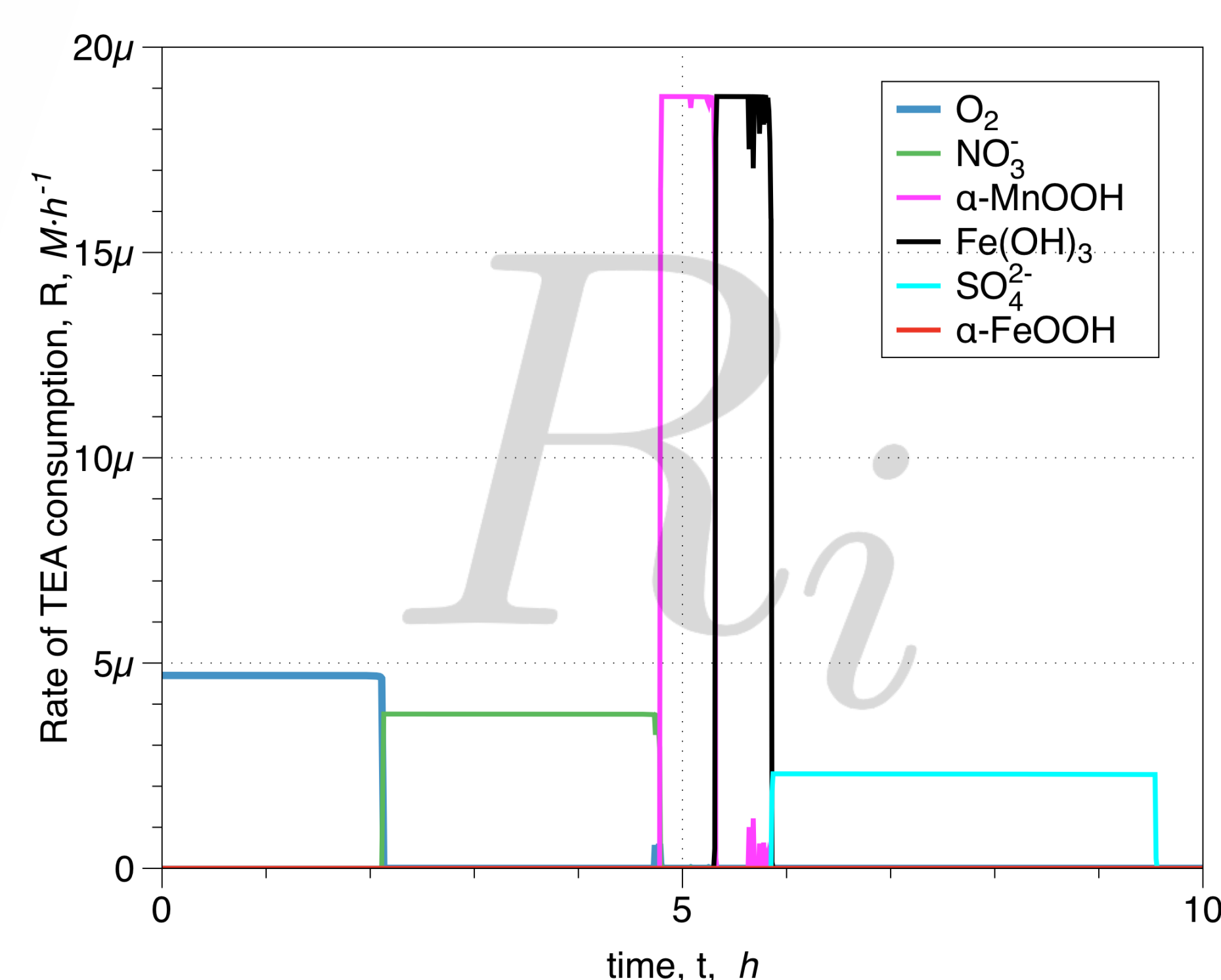
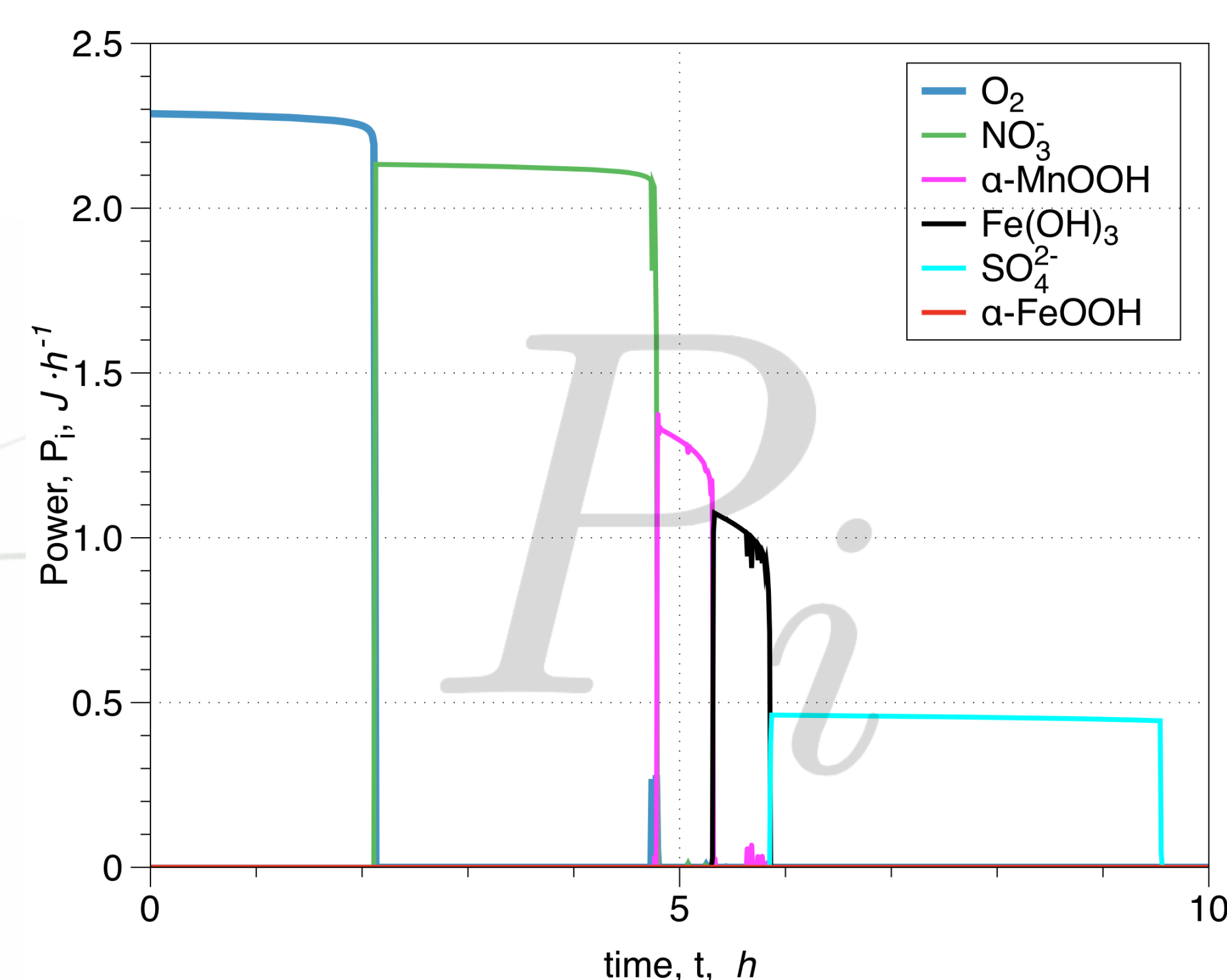
The sequence of redox reactions is now determined by the power that can be harvested by the microbial populations.

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

- 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 respire i^{th} reaction

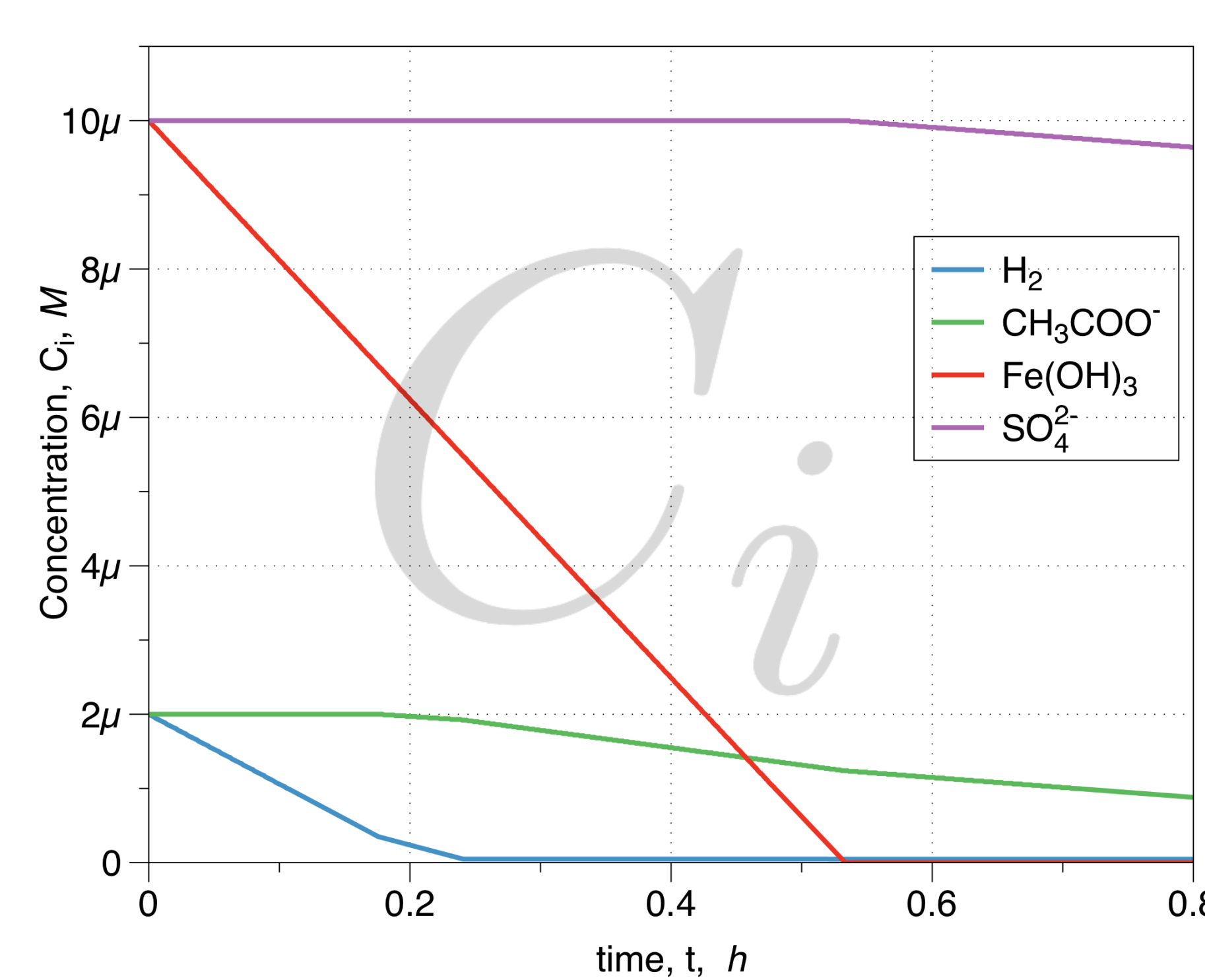
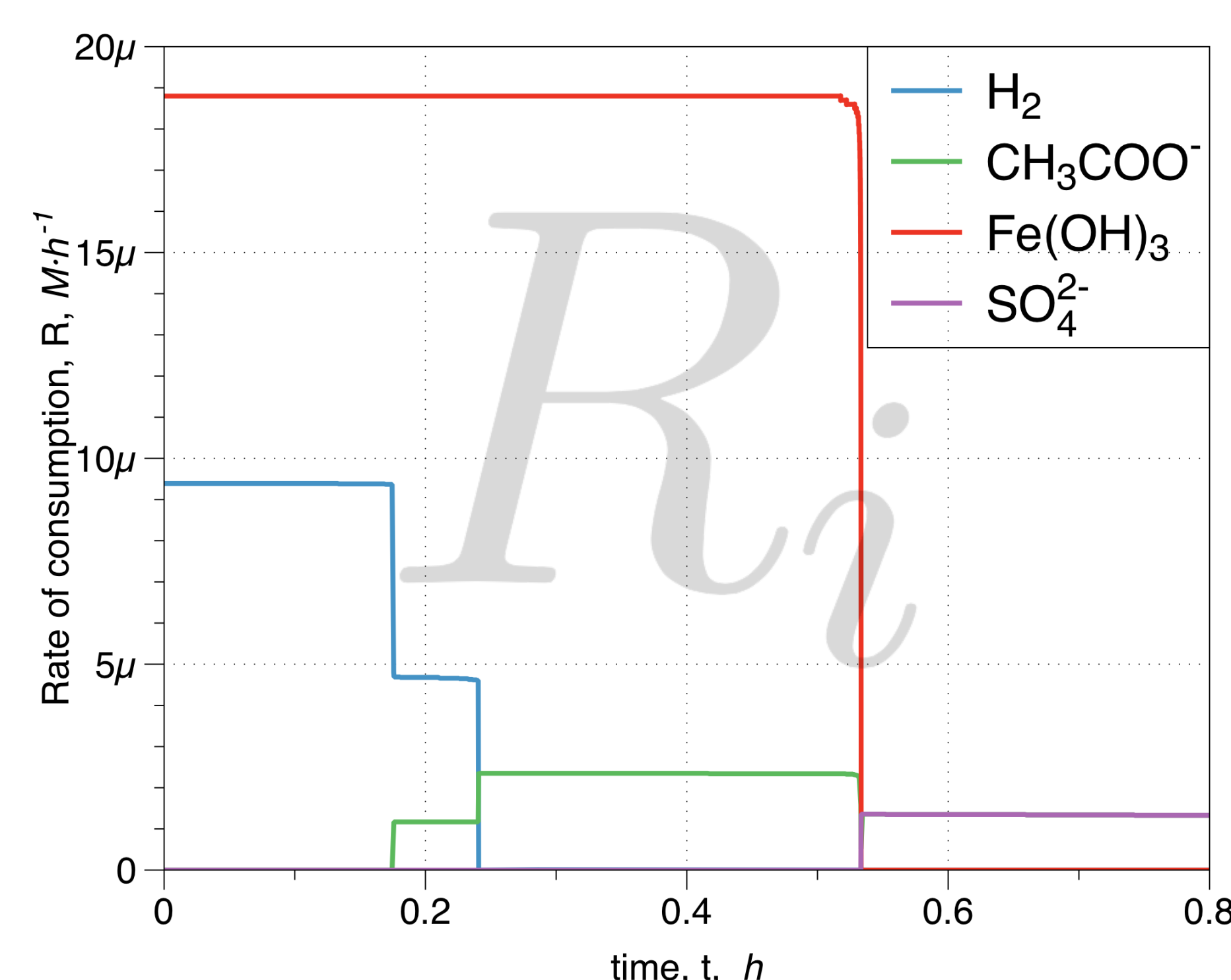
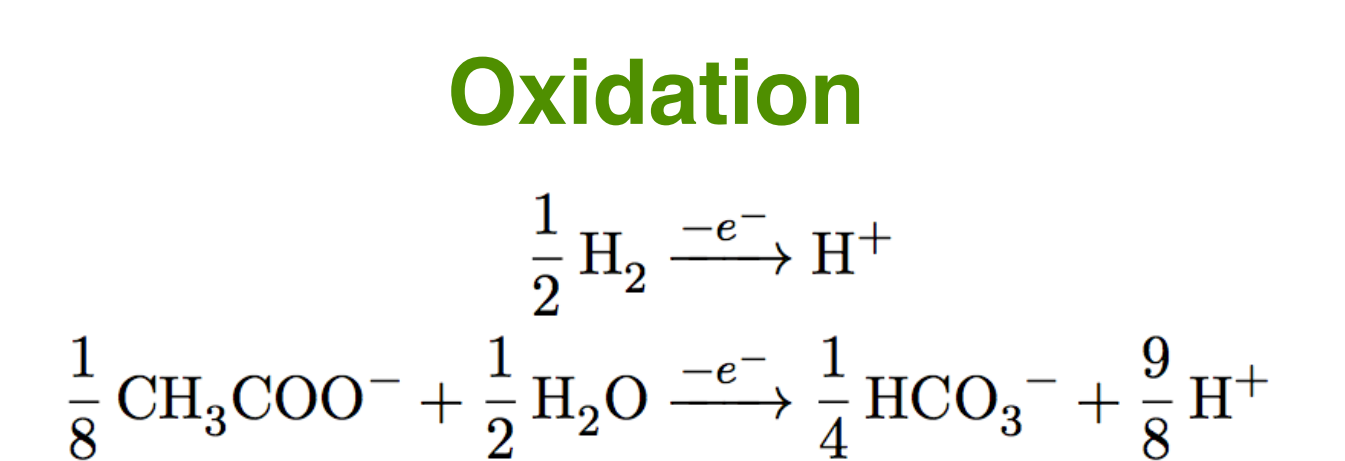
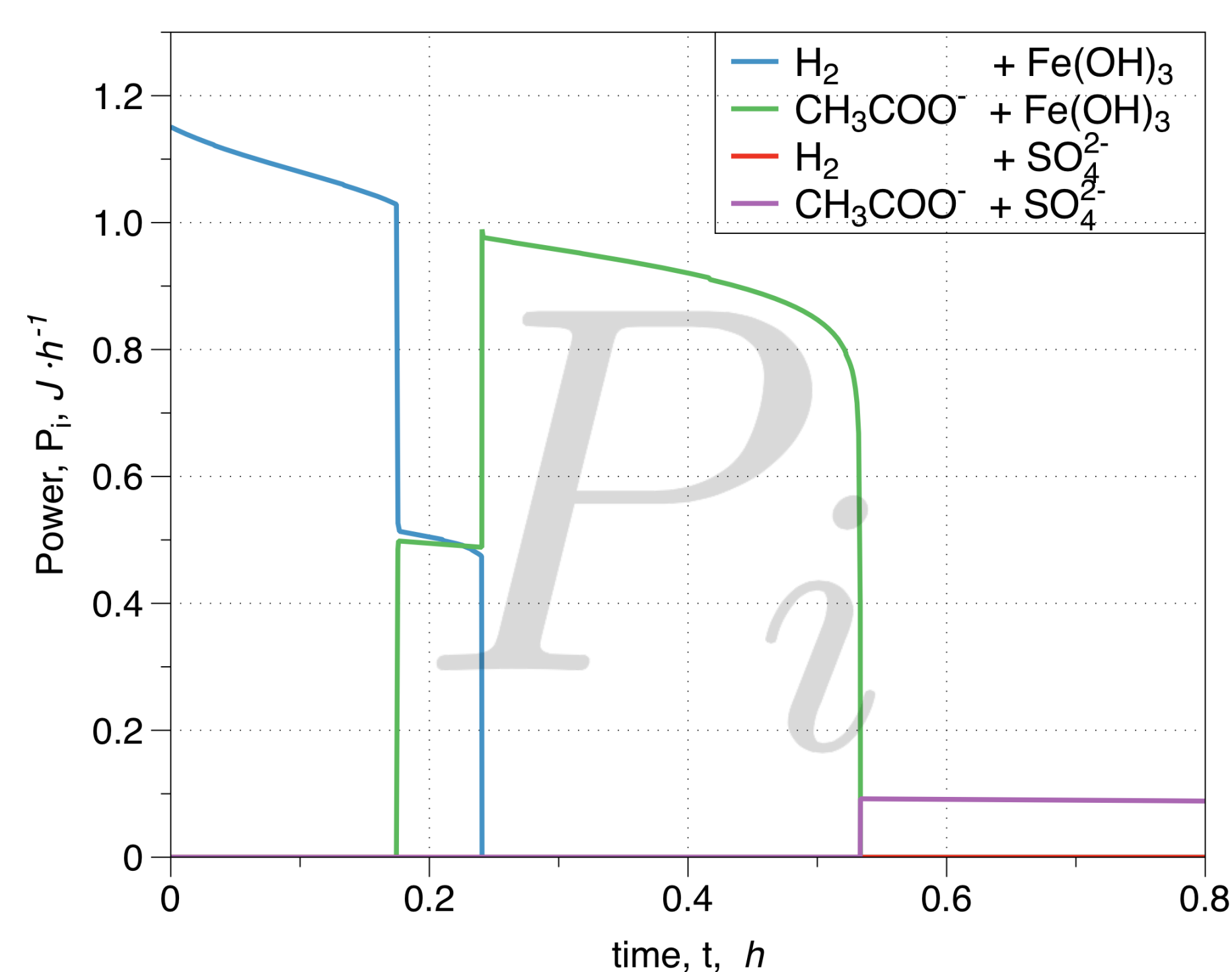
Example: 1 ED and 6 EA

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



Example: 2 ED and 2 EA

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



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

