

New thermodynamic approach to represent the redox sequence of oxidant utilization during organic matter decomposition.

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Inhibition terms are often used to reproduce the well-known sequential of consumption of terminal electron acceptors (TEA) during microbial degradation of organic matter [1,2]. Using these terms implies a non-competitive inhibition of reactions. However, this approach does not take into account the dynamic nature of environmental systems, such as changes in pH, temperature, or redox state, which affect the thermodynamic driving force of energy-yielding reactions. Moreover, the parameters of the inhibiting terms usually are site or experiment specific and, thus, lack general validity.

We propose a new approach that is based on the optimization of the energy yield of catabolic processes. The new approach accounts for the Gibbs energy of reaction of the potential redox processes and simulates TEA consumption based on the actual conditions in the system. That is, energetically less favorable oxidants are outcompeted by more favorable ones. The approach does not require any additional parameters to be calibrated and can be applied in environments with time and space variable conditions.

The method is applied to the redox stratification observed in early diagenesis, including the following TEAs: O_2 , NO_3^- , MnO_2 , $Fe(OH)_3$ and SO_4^{2-} . The results of the simulations are in agreement with experimental data.

[1] Blanch, H.W., (1981) *Chemical Engineering Communications*, **8(4-6)**, 181–211; [2] Wang, Y. & Van Cappellen, P (1996) *Geochimica et Cosmochimica Acta* **60**, 2993–3014;