

“Chemical and Biological Characteristics of Surface Waters”

Module 2: Surface Waters, Lecture 5

Chemical Fate and Transport in the Environment, 2nd edition. H.F. Hemond and E.J. Fechner-Levy. Academic Press. London. 2000.

2.4.1 Acid-Base Chemistry

pH often called a “master” variable in natural water chemistry and the equilibrium of reactions that produce or consume H⁺ is of special interest.

Strong acids (such as HCl, HNO₃, and H₂SO₄) and strong bases (NaOH) ionize completely in water under normal environmental conditions.

Alkalinity is defined as the concentration of strong bases minus the concentration of strong acids: $Alk = C_B - C_A$

Surface waters contain dissolved CO₂, an acid, that reacts in water to form three carbonate system species H₂CO₃* (concentration of dissolved CO₂ and its reaction product with water), HCO₃⁻, and CO₃²⁻

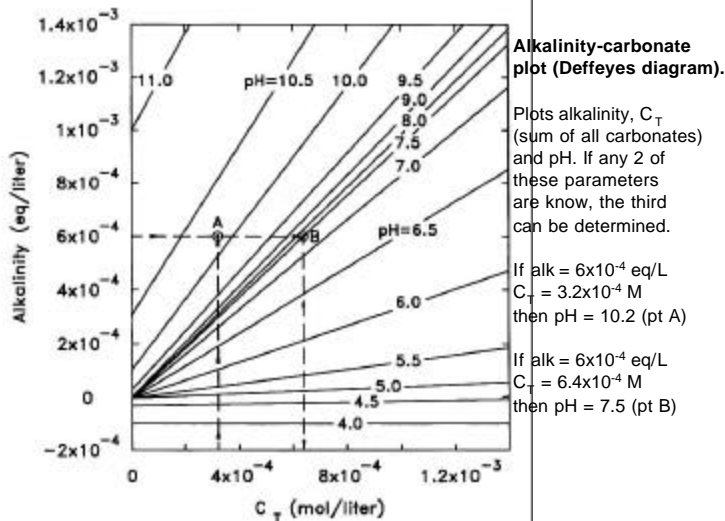
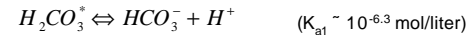
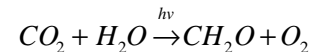


Fig 2-15 Hemond and Fechner-Levy 2000

2.4.2 Aquatic Ecosystems – Energy Flow

A general chemical representation of the photosynthesis process is:



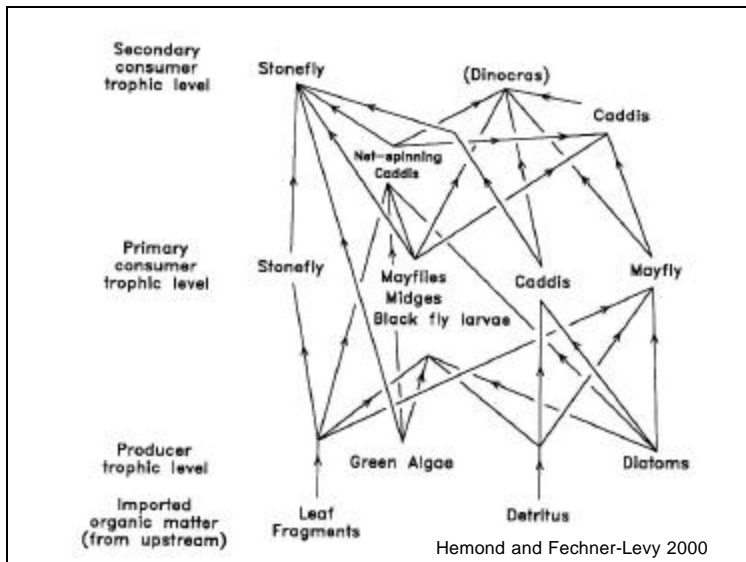
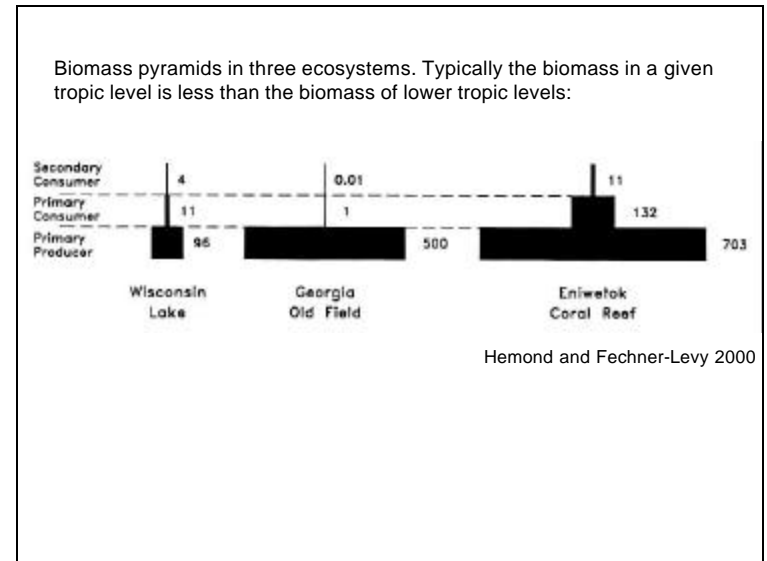
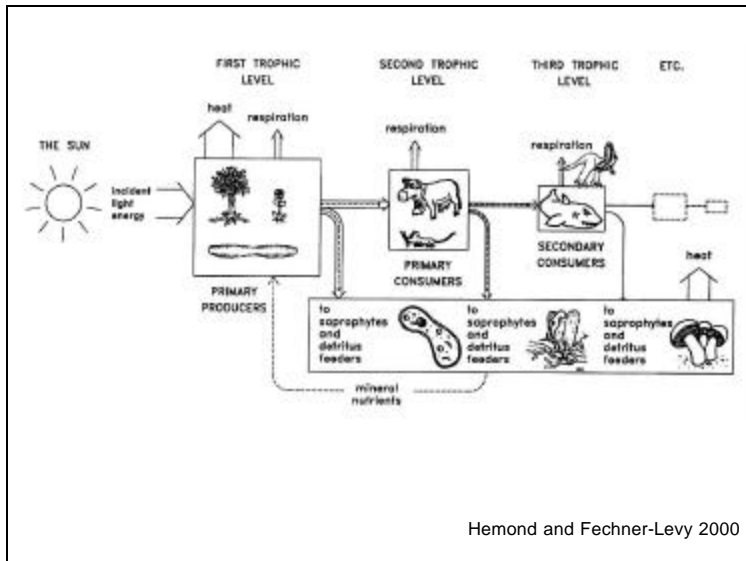
The reverse of this reaction is respiration (consumes oxygen when dark, producing CO₂).

Energy is transferred from photosynthetic organisms to nonphotosynthetic organisms via a food chain/web.

Primary consumers (herbivores) eat the photosynthetic plants (primary producers).

Secondary consumers obtain organic carbon by eating primary consumers.

Etc.



The "Redfield" ratio describes the relative components of major elements in free-living photosynthetic algae in surface waters:
 $C_{106}H_{263}O_{110}N_{16}P_1$

The simplified photosynthetic reaction can be expanded to include the major nutrients (N and P). The following equation assumes that NO_3^- is the predominant N source:

$$106CO_2 + 16NO_3^- + H_2PO_4^- + 122H_2O + 17H^+ \rightarrow C_{106}H_{263}O_{110}N_{16}P + 138O_2$$

Concept of limiting nutrients (usually N vs. P, others in abundance) and eutrophication if nutrients in excess.

2.4.3 Reduction-Oxidation Chemistry (the power for ecosystems)

- Electrons are transferred from one atom to another in reduction-oxidation reactions.
- Photosynthetic reactions are examples of redox reactions.
- Other examples are fuel combustion for heating, cooking, and transportation.
- Reduction is the gain of electrons and oxidation is the loss of electrons.
- Tables show the equilibrium constant and the standard free energy change for redox half reactions.
- Any complete redox reaction is a combination of half reactions (can't have free electrons as they are too unstable to persist for long as isolated species in water).
- When two half reactions are combined into one reaction, the free energies are added and used to calculate the equilibrium constant (as previously described in chapter 1).

Common Environmental Redox Half-Reactions

Half-reaction	log K, (ΔG° , kcal/mol)
$\frac{1}{4}\text{O}_2(\text{g}) + \text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2\text{O}$	20.75 (-28.22)
$\frac{1}{2}\text{NO}_3^- + \frac{1}{2}\text{H}^+ + e^- \rightarrow \frac{1}{10}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2\text{O}$	21.05 (-28.63)
$\frac{1}{2}\text{MnO}_2(\text{s}) + 2\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{Mn}^{2+} + \text{H}_2\text{O}$	21.00 (-28.56)
$\text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ + e^- \rightarrow \text{Fe}^{2+} + 3\text{H}_2\text{O}$	16.5 (-22.44)
$\frac{1}{8}\text{SO}_4^{2-} + \frac{1}{2}\text{H}^+ + e^- \rightarrow \frac{1}{8}\text{H}_2\text{S}(\text{g}) + \frac{1}{2}\text{H}_2\text{O}$	5.25 (-7.14)
$\frac{1}{8}\text{SO}_4^{2-} + \frac{1}{2}\text{H}^+ + e^- \rightarrow \frac{1}{8}\text{HS}^- + \frac{1}{2}\text{H}_2\text{O}$	4.25 (-5.78)
$\frac{1}{2}\text{CO}_2(\text{g}) + \text{H}^+ + e^- \rightarrow \frac{1}{2}\text{CH}_4(\text{g}) + \frac{1}{2}\text{H}_2\text{O}$	2.87 (-3.90)
$\frac{1}{2}\text{CH}_2\text{O} + \frac{1}{2}\text{H}_2\text{O} \rightarrow e^- + \text{H}^+ + \frac{1}{4}\text{CO}_2(\text{g})$	1.2 (-1.63)

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Redox Scale

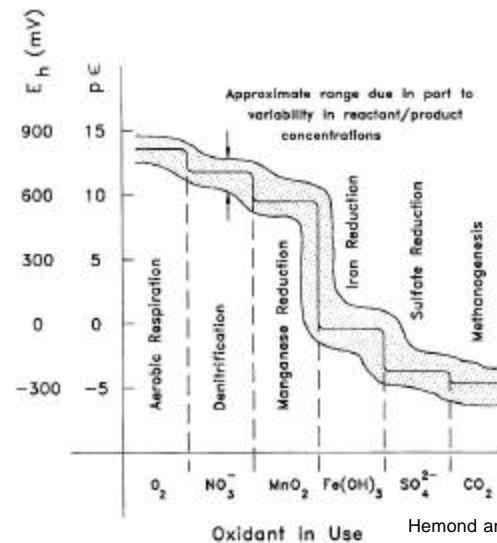
A sequence of redox reactions is consistently observed in the environment. The redox scale indicates the predominant redox reactions occurring. The pE can be used to predict the predominate reactions. pE is a measure of the electron activity:

$$pe = -\log\{e^-\}$$

Usually measured by Eh and a redox (ORP) probe:

$$E_h = \frac{2.3RT}{F} \cdot pe$$

$$E_h = 0.059 \cdot pe$$



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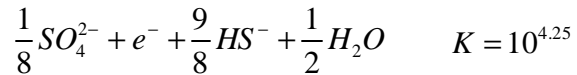
Example Problem 2-13

HS⁻ at 0.1 mg/L, as S in a sediment pore water whose sulfate concentration is 10⁻⁶M. What is the theoretical pE and Eh if these species are in equilibrium?

Convert the HS⁻ concentration to molar units:

$$\frac{0.1 \text{ mg}}{\text{L}} \cdot 10^{-3} \frac{\text{g}}{\text{mg}} \cdot \frac{1 \text{ mol HS}^-}{33 \text{ g}} = 3.0 \times 10^{-6} \frac{\text{mol HS}^-}{\text{L}}$$

From the table of redox half reactions:



Combining and re-arranging the equations results in:

$$\frac{[\text{HS}^-]^{1/8}}{[\text{SO}_4^{2-}]^{1/8} \{e^-\} \{H^+\}^{9/8}} = 10^{4.25}$$

$$\{e^-\} = \frac{(3.0 \times 10^{-6})^{1/8}}{(10^{-6})^{1/8} (10^{-7.3})^{9/8} (10^{4.25})} = 1.1 \times 10^{-4}$$

$$pe = -\log\{e^-\} = -\log(1.1 \times 10^{-4}) = -3.96$$

$$E_h = 0.059 \cdot pe = -0.23 \text{ V}$$

Example Problem 2-14

An ORP electrode is inserted 0.3 cm below the sediment-water interface of a stratified lake in late August. A reading of 0.25 V is obtained. ORP is commonly used to estimate Eh. What reactions are most likely occurring in the sediment where this value was measured?

$$ORP \approx pe = \frac{0.25 \text{ V}}{0.059} = 4.2$$

As shown on the ecological redox sequence figure, iron oxides and manganese oxides are most likely the chemical species being used as oxidants in the degradation of organic matter at this pE value.