Oxidation-Reduction Reactions (Redox Reactions)

Significant redox reactions in natural waters

Topics of concern

- What is a redox reaction?
- A list of the important redox reactions in natural waters
- The role of organisms
- Where redox reactions occur
- Some important biogeochemical cycles and redox
- Summary-(or putting it all together)

The quick answers!

- Redox reactions involve the transfer of electrons (e^-)
- The most important reactions involve C, N, Fe, S
- Organisms: (*prokaryotes*)
  - Catalyze (speed up) the reactions
  - Organisms benefit by harvesting energy
- The reactions occur:
  - Somewhere in the water column or in the sediment
  - Or, *where chemical conditions dictate*

Sample oxidation-reduction reactions.

- **Oxidation** of iron:
  - $Fe^{+2} \rightarrow Fe^{+3} + e^-$
    - (*Useful mnemonic: SOIL = Substance Oxidized Increases in valence and Loses electrons*)

- **Reduction** of oxygen:
  - $O_2 + 2\ H_2O\ + 4\ e^- \rightarrow 4\ OH^-$
- Notes:
  - Stoichiometry: everything balances (Fe, H, O, charges, etc.)
  - As written, these are "*half-reactions*". (But electrons cannot just float around!)

Oxidation and reduction occur together (to account for electrons)

- **Oxidation** of iron:
  - $Fe^{+2} \rightarrow Fe^{+3} + e^{-}$
- **Reduction** of oxygen:
  - $O_2 + 2\ H_2O\ + 4\ e^{-} \rightarrow 4\ OH^{-}$
- Add the two reactions to account for electrons
  - $(4\ Fe^{+2} \mathbf{=} 4\ Fe^{+3} + 4\ e^{-+})$
  - $+\ (O_2 + 2\ H_2O\ + 4\ e^{-} \mathbf{=} 4\ OH^{-+})$
  - ________________________________
  - $4\ Fe^{+2} + O_2 + 2\ H_2O \mathbf{=} 4\ Fe^{+3} + 4\ OH^{-}$

REDOX reaction: electron has been transferred (*but we don't see it in the balanced equation!*)

- $4\ Fe^{+2} + O_2 + 2\ H_2O \rightarrow 4\ Fe^{+3} + 4\ OH^-$
  - Note that all atoms and charges *balance*
  - Note also that in addition to e^-, *H^+* can also be involved in redox reactions
- This reaction will occur where there is an excess of Fe^{+2} and O_2 at the same time
- O_2 is the "*oxidizing agent*" and Fe^{+2} is the "*reducing agent*".

Some questions for this particular reaction. (oxidation of ferrous iron)

- Is it important? -Sometimes
- What is the role of organisms?
  - Iron oxidizing bacteria catalyze the reaction. They harvest energy and speed the reaction. (Sample genera are: *Leptothrix, Gallionella, Ferrobacillus ferrooxidans*.)
- Where does the reaction occur?
  - Where water with somewhat reducing conditions encounters the air, e.g. ground water comes to the surface, or at the sediment/water interface

Iron and the phosphorus cycle

- In oligotrophic lakes, the surface sediment is oxidized. Fe^{+3} traps dissolved PO_4^{-3} in the sediment
- When the hypolimnion becomes anoxic, the surface layer of sediment is reduced. Fe^{+2} is much more soluble and diffuses into the overlying water.
- PO_4^{-3} is released from the sediment.
- Lakes may become “self-fertilizing”.

Summary so far:

- Oxidation and reduction reactions are paired together, hence *Redox* reactions
- Redox reactions involve the transfer of electrons, e-
- Reactions are balanced for atoms and charge (both e^- and H^+)
- Reactions occur where participating species are present in excess

What reactions are important?
An *<u>idealized</u>* oxidation-reduction system

Surplus Organic Matter Heterotrophic organisms	**Kcal per mole of CH2O** **ΔG**	**Surplus Oxygen** Autotrophic organisms	Kcal per mole of O2 **ΔG**
$CH_2O + O_2 \rightarrow CO_2 + H_2O$ *(aerobic respiration)*	-121.89	$CO_2 + H_2O \rightarrow CH_2O + O_2$ *(photosynthesis)*	+121.89
$2\ CH_2O + NO_3^- + 2\ H^+ \rightarrow$ $2\ CO_2 + NH_4^+ + H_2O$	-85.88	$NH_4^+ + 2\ O_2 \rightarrow$ $NO_3^- + 2\ H^+ + H_2O$	-36.01
$CH_2O + 4\ Fe^{+3} \rightarrow$ $CO_2 + Fe^{+2} + 4\ H^+$	-75.68	$4\ Fe^{+2} + 4\ H^+ + O_2 \rightarrow$ $4\ Fe^{+3} + 2\ H_2O$	-46.21
$2\ CH_2O + SO_4^{-2} + 2\ H^+ \rightarrow$ $2\ CO^2 + H_2S + H_2O$	-32.54	$H_2S + 2\ O_2 \rightarrow SO_4^{-2} + 2\ H^+$	-89.35
$CH_20 + CH_2O \rightarrow$ $CO_2 + CH_4$	-19.24	$CH_4 + 2\ H_2O \rightarrow$ $CO_2 + 2\ H_2O$	-102.65
$CH_2O + H_2O \rightarrow$ $CO_2 + 2\ H_2$	+3.90	$2\ H_2 + O_2 \rightarrow 2\ H_2O$	-125.79

An alternate view of the important reactions and where they occur

- pH = -log$_{10}$ (H$^+$)
  - Thus, *low pH* means high H$^+$ potential (concentration) and very acid conditions
- pE = -log$_{10}$ (e$^-$)
  - Thus, *low pE* means high e$^-$ potential (i.e. lots of e$^-$ to reduce any available species)
- Note: pE and Eh are alternative scales for presenting electron density.

- Fi

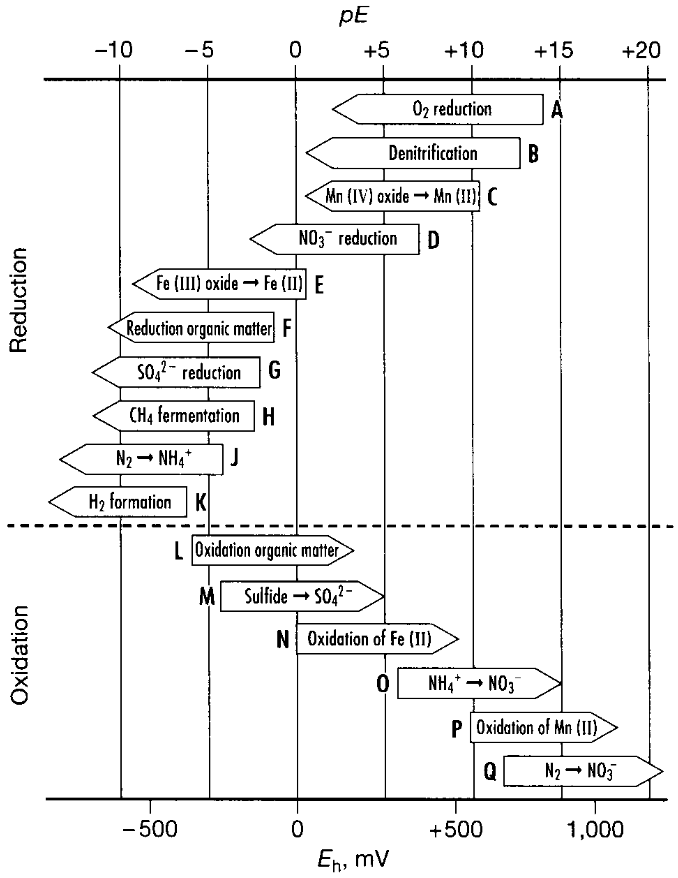


Figure 16–2 Biologically mediated redox processes (calculated for pH = 7) in the oxidation of organic matter (A–K, and L), nitrogen fixation (J and L), and the oxidation of reduced elements in the presence of oxygen (M–Q), which yields energy for the reduction of CO_2 in chemosynthetic processes. Overlapping E_h or *pE* ranges indicate that several redox systems operate at the same time. *(After Stumm and Baccini 1978.)*

- *Phase diagrams*: Another version of where reactions take place.
- Strongly reducing conditions are at the bottom of the diagram.

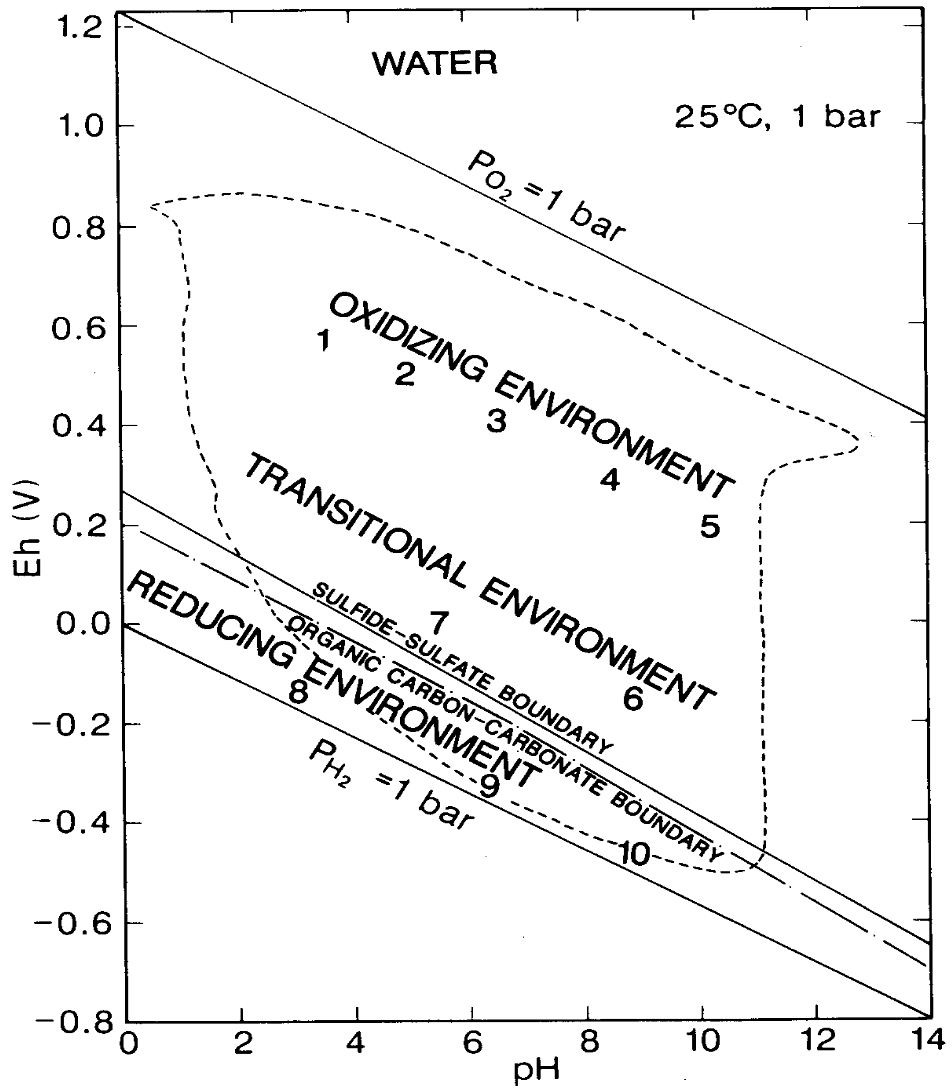


Fig. 1. Generic Eh-pH diagram for water showing several features. The upper and lower stability limits of water are given where P_{O_2} and P_{H_2} = 1 bar, r tively. The *dotted line* represents the range of natural Eh-pH water measurements rep by Baas Becking et al. (1960). The *solid line* marked sulfide-sulfate boundary separat idizing, sulfate-bearing waters above this boundary to reducing, sulfide (as H HS^-)-bearing waters below. The *dash-dot* boundary separates organic carbon (boundary) from carbonate species (above boundary). Oxidizing, transitional, and red environments are indicated. Specific environments are (*numbers on figure*): *1* mine w *2* rain; *3* streams; *4* normal ocean water; *5* aerated saline water residues; *6* ground w *7* bog waters; *8* water-logged soils; *9* euxenic marine waters; *10* organic-rich, saline w See text for discussion

Phase diagram for iron

- This diagram indicates chemical conditions each iron species could be expected to dominate.
- Note that Fe^{+3} is the dominant species where conditions are more oxidizing, and Fe^{+2} is dominant where conditions are more reducing.

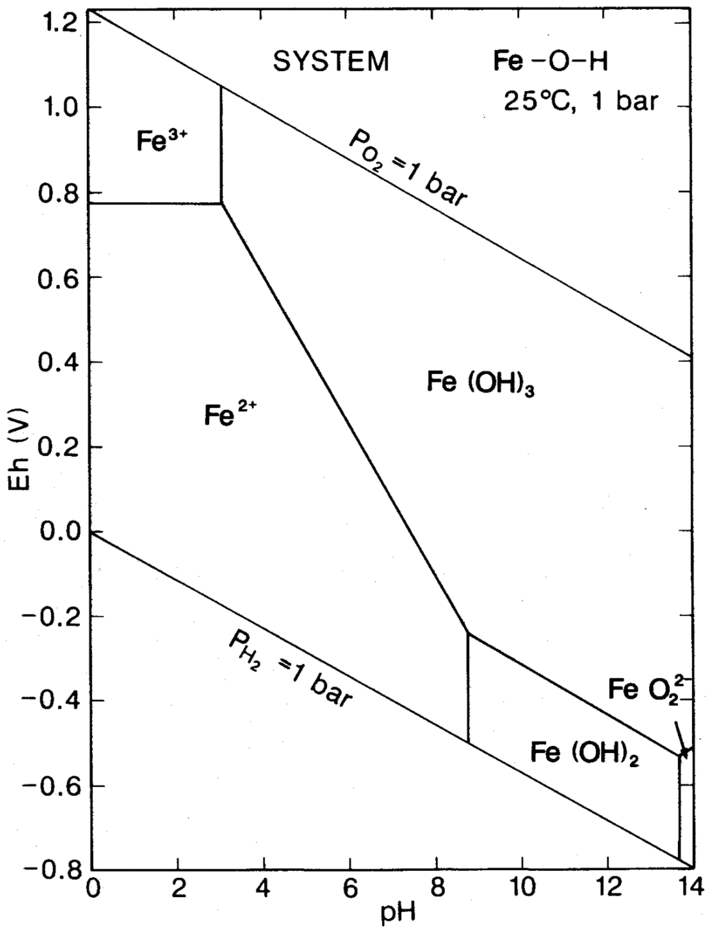


Fig. 36. Eh-pH diagram for part of the system Fe-O-H assuming $Fe(OH)_3$ as stable Fe(III) phase. Assumed activity of dissolved Fe = 10^{-6}. See text for discussion

What is the role of organisms?

- Organisms (mostly bacteria) catalyze all the important redox reactions.
- The bacteria involved are specialized: iron bacteria catalyze iron reactions, sulfur bacteria sulfur reactions, etc.
- Their names are sometimes a give-away:
  - Oxidation of NO_2^- by *Nitrobacter*
  - Sulfate reduction by *Desulfovibrio* (and others)

Some useful vocabulary

- *Assimilatory* metabolism: organisms accumulate an element for biosynthesis
- *Dissimilatory* metabolism: organisms catalyze a reaction to harvest energy (they don’t retain the element).

Three biogeochemical cycles

- Nitrogen cycle
  - Reducing conditions: NH_4^+ is more stable
  - Oxidizing conditions: NO_3^- is more stable
- Sulfur cycle
  - Reducing conditions: S^- is more stable
  - Oxidizing conditions: SO_4^{-2} is more stable
- Carbon cycle
  - Reducing conditions: methane (CH_4) may appear
  - Oxidizing conditions: CO_2 is the most oxidized species

Nitrogen is an important plant nutrient

- Plants *assimilate* nitrogen to use in metabolism.
- Plants assimilate either NH_4^+ or NO_3^-
  - (often with a preference for ammonia)
- This nitrogen is deployed into proteins, DNA, etc.

Nitrogen cycle: nitrate *reduction*

- Where there is excess organic matter but no oxygen, NO_3^- can substitute for oxygen as an oxidizing agent (*dissimilatory metabolism*).
  - $C_6H_{12}O_6 + 12\ NO_3^- \rightarrow 12\ NO_2^- + 6\ CO_2 + 6\ H_2O$
  - $C_6H_{12}O_6 + 8\ NO_2^- \rightarrow 4\ N_2 + CO_2 + 6\ H_2O$
- Net effect: loss of fixed N from the ecosystem, hence the process is called "denitrification". Organisms are "facultative anaerobes".

Nitrogen cycle: ammonia *oxidation*

- Where O_2 and NH_4^+ are both present, bacteria catalyze the oxidation of the ammonia.
  - $NH_4^+ + 3/2\ O_2 \rightarrow 2\ H^+ + NO_2^- + H_2O$
    - *Nitrosomonas*
  - $NO_2^- + 1/2\ O_2 \rightarrow NO_3^-$
    - *Nitrobacter*
- The overall reaction is called "*nitrification*"
  - $NH_4^+ + 2\ O_2 \rightarrow NO_3^- + H_2O + 2\ H^+$

Nitrogen cycle

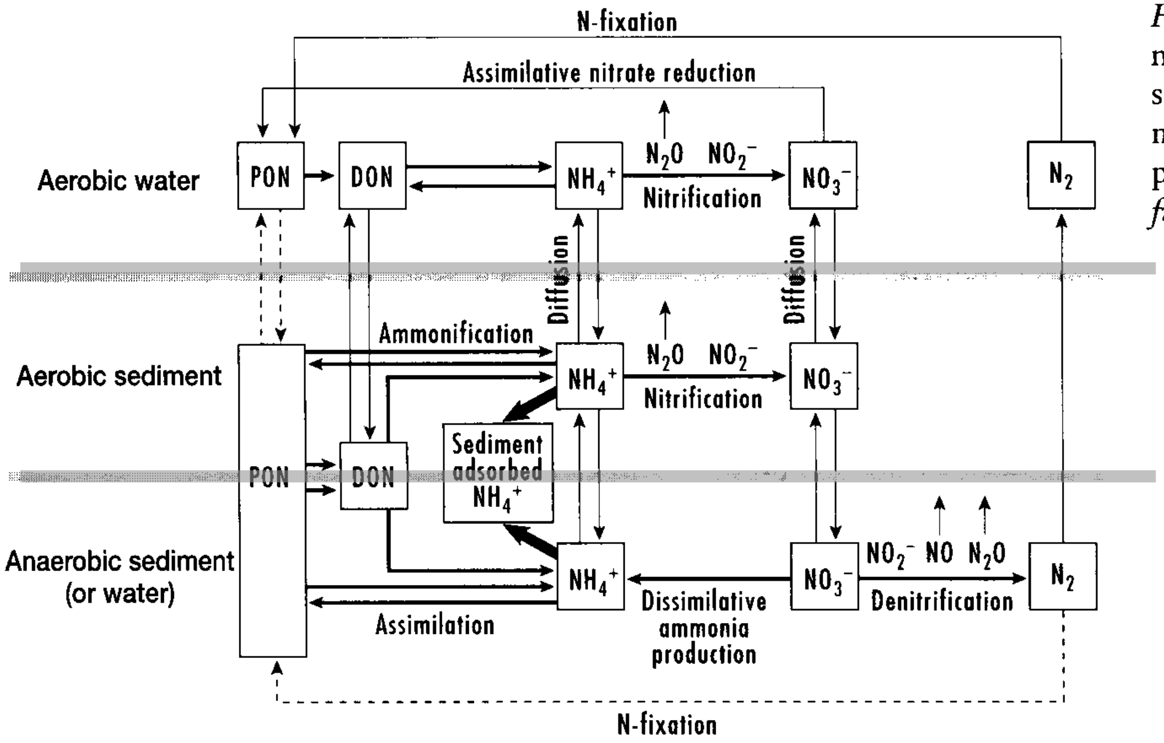


Figure 18–2 Nitrogen transformations near the sediment–water interface. Not shown are inputs from the land and atmosphere or stream outflows. Minor pathways are also not shown. *(Modified from Kamp-Nielson and Anderson 1977.)*

Something new under the sun (i.e. recently discovered)

- A recent discovery is the “*anammox*” reaction.
  - For (**an**aerobic **amm**onia **ox**idation)
  - $NH_4^+ + NO_2^- \rightarrow N_2 + 2\ H_2O$
- Reaction has been observed in the Black Sea and the Golfo Dulce in Costa Rica (partially anaerobic marine seas). The reaction may be important because of the shortage of fixed N in the sea. It has also been reported from Lake Tanganyika.

Nitrogen species in stratified lakes.

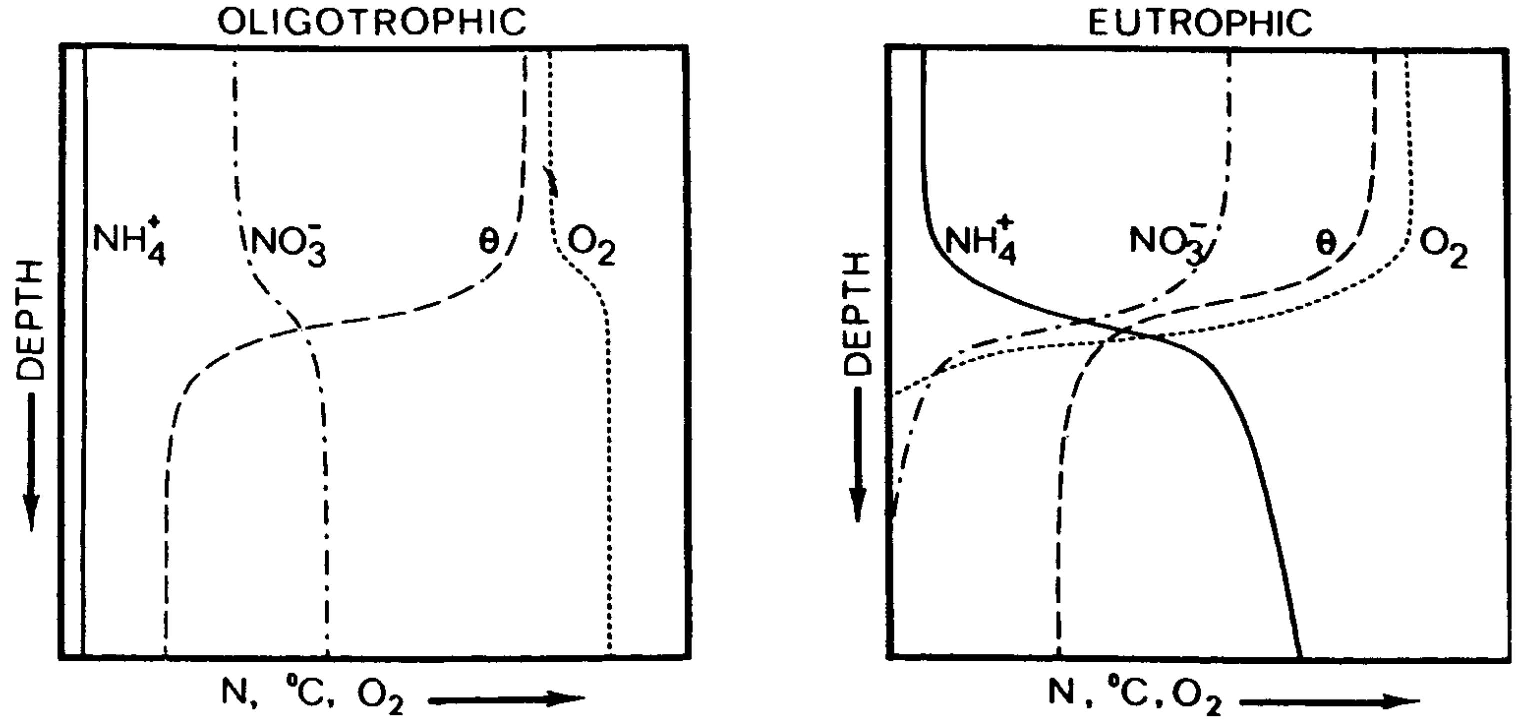


FIGURE 12-4 Generalized vertical distribution of ammonia and nitrate nitrogen in stratified lakes of very low and high productivity.

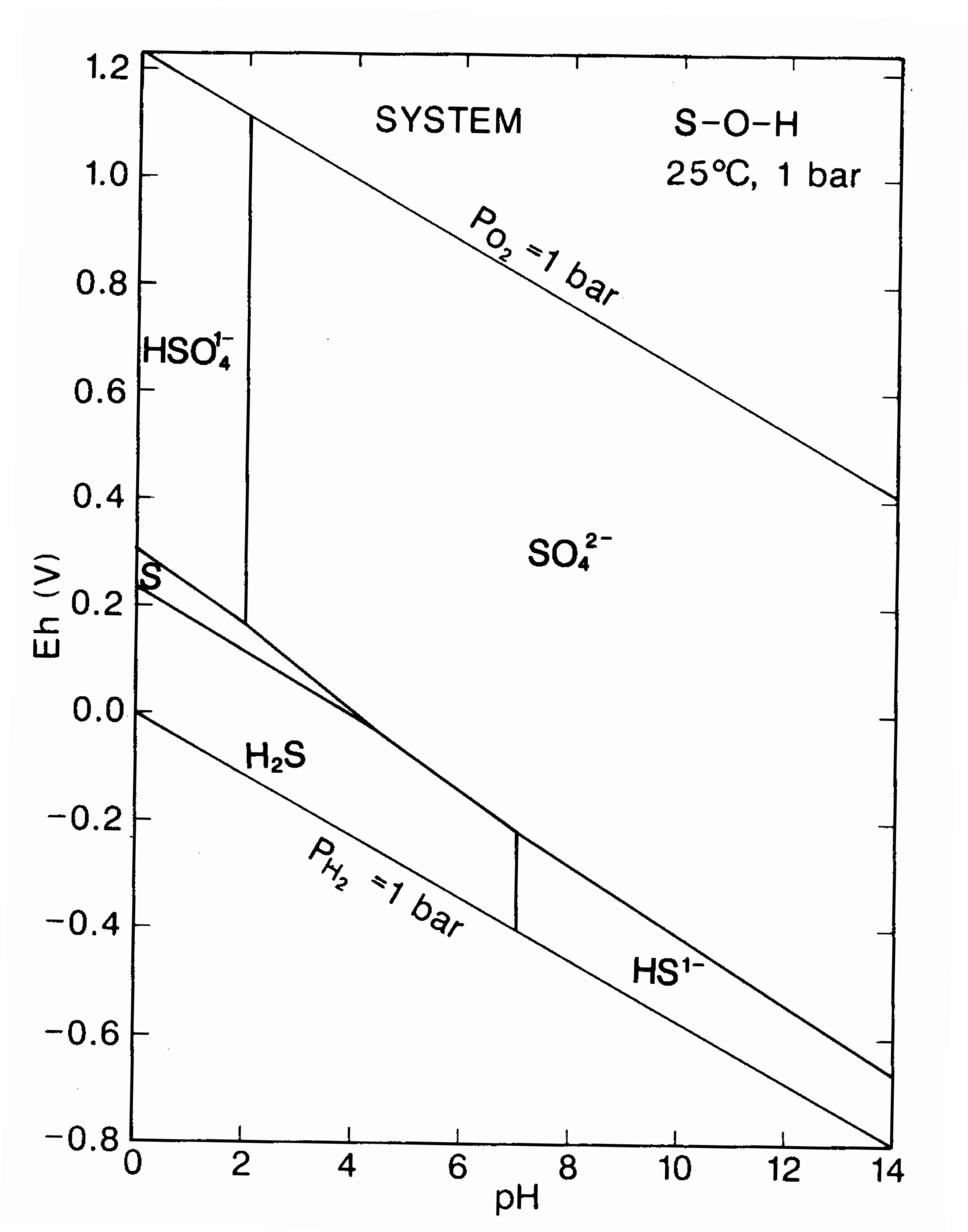
The sulfur cycle: Sulfate reduction

- Where conditions are strongly reducing (no remaining O_2 or NO_3^-), sulfate may serve as the oxidizing agent for anaerobic respiration.
  - $3\ SO_4^{-2} + C_6H_{12}O_6 \rightarrow 6\ CO_2 + 6\ H_2O + 3\ S^{-2}$
  - Some of the bacteria that catalyze this and similar reactions are: *Desulfovibrio* and *Desulfotomaculum.* These bacteria are *obligate anaerobes.*

Sulfur cycle: sulfide oxidation

- In an environment containing O_2, any S^- (sulfide) will be quickly oxidized.
  - $H_2S + 1/2\ O_2 \rightarrow S + H_2O$
  - $S + 3/2\ O_2 + H_2O \rightarrow H_2SO_4$
    - *Thiobacillus thiooxidans, Thiothrix, Beggiatoa,*

- Sulfur oxidation and reduction reactions cluster along the interface between SO_4^{-2} and S^{-2}
- No oxygen is present where S^{-2} is the stable species.



Various cycles may have *cross-links*.

- Sulfur and nitrogen cycles:
  - – $5 S + 2 H_2O + 6 NO_3^- \rightarrow 5 SO_4^- + 4 H^+ + N_2$
    - *Thiobacillus denitrificans*
- Iron and sulfur cycles:
  - – $FeS_2 + 7/2 O_2 + H_2O \rightarrow Fe^{+2} + 2 SO_4^{-2} + 2 H^+$
  - – $Fe^{+2} + 1/4 O_2 + H^+ \rightarrow Fe^{+3} + 1/2 H_2O$
    - *Thiobacillus thiooxidans*
  - – This reaction, the oxidation of pyrite, occurs in abandoned mines and produces very strong acid.

Sulfide and phosphorus

- When the iron in the surface of the sediment is reduced to Fe^{+2}, PO_4^{-3} is released.
- With fall turnover, Fe^{+2} is oxidized to Fe^{+3} and PO_4^{-3} is returned to the sediment
- However, if S^{-2} has precipitated some of the Fe^{+2}, PO_4^{-3} may remain in the water column
- With strongly reducing conditions, the sediment ceases to be an efficient phosphorus trap.

The carbon cycle

- The big story: CO_2 reduction to produce reduced carbon species. I.e. photosynthesis
  - $CO_2 + H_2O \rightarrow CH_2O + O_2$
  - Most of the organic matter on earth is ultimately produced by this reaction. Almost all the primary production is via photosynthesis. (A minor exception: chemosynthesis around deep sea vents, etc.)

Carbon cycle: carbon oxidation

- The organic matter produced by photosynthesis is mostly oxidized by aerobic respiration:
  - $CH_2O + O_2 \rightarrow CO_2 + H_2O$
- Only where O_2 is missing will anaerobic respiration occur with NO_3^- or SO_4^{-2} acting as oxidizing agents

- Methane is fermented where there is ample organic matter and conditions are strongly reducing (high density of electrons).

Native C = C in organic compounds

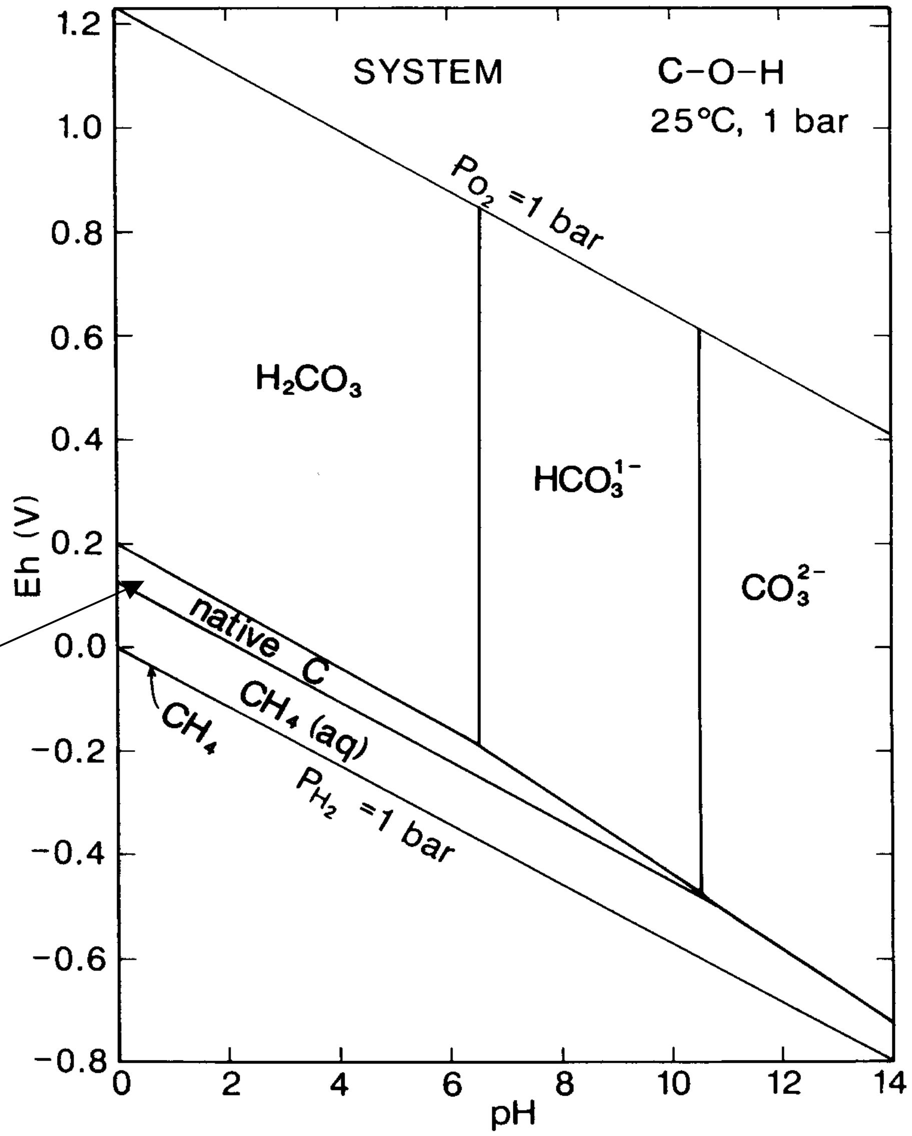


Fig. 13. Eh-pH diagram for part of the system C-O-H. The assumed activity of dissolved C = 10^{-3}. See text for discussion

Carbon cycle: methane production

- Where conditions are extremely reducing (very high e^- potential, very low pE) and no suitable oxidizing agent remains (no O2, NO_3^- or SO_4^{-2}), *methane fermentation* may occur.
  - $CH_3COOH \rightarrow CH_4 + CO_2$
  - $CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$
    - *Methanobacterium, Methanobacillus, Methanococcus*

Carbon cycle: methane consumption

- Where methane and oxygen (only a little!) occur together, methanotrophs will oxidize methane.
  - $5\ CH_4 + 8\ O_2 \rightarrow 2\ CH_2O + 3\ CO_2 + 8\ H_2O$
    - *Methanomonas methanica, Methanomonas methanooxidans*

Review

- Redox reactions involve the transfer of electrons (e^-)
- The most important reactions involve C, N, Fe, S
- Organisms: (*prokaryotes*)
  - Catalyze (speed up) the reactions
  - Organisms benefit by harvesting energy
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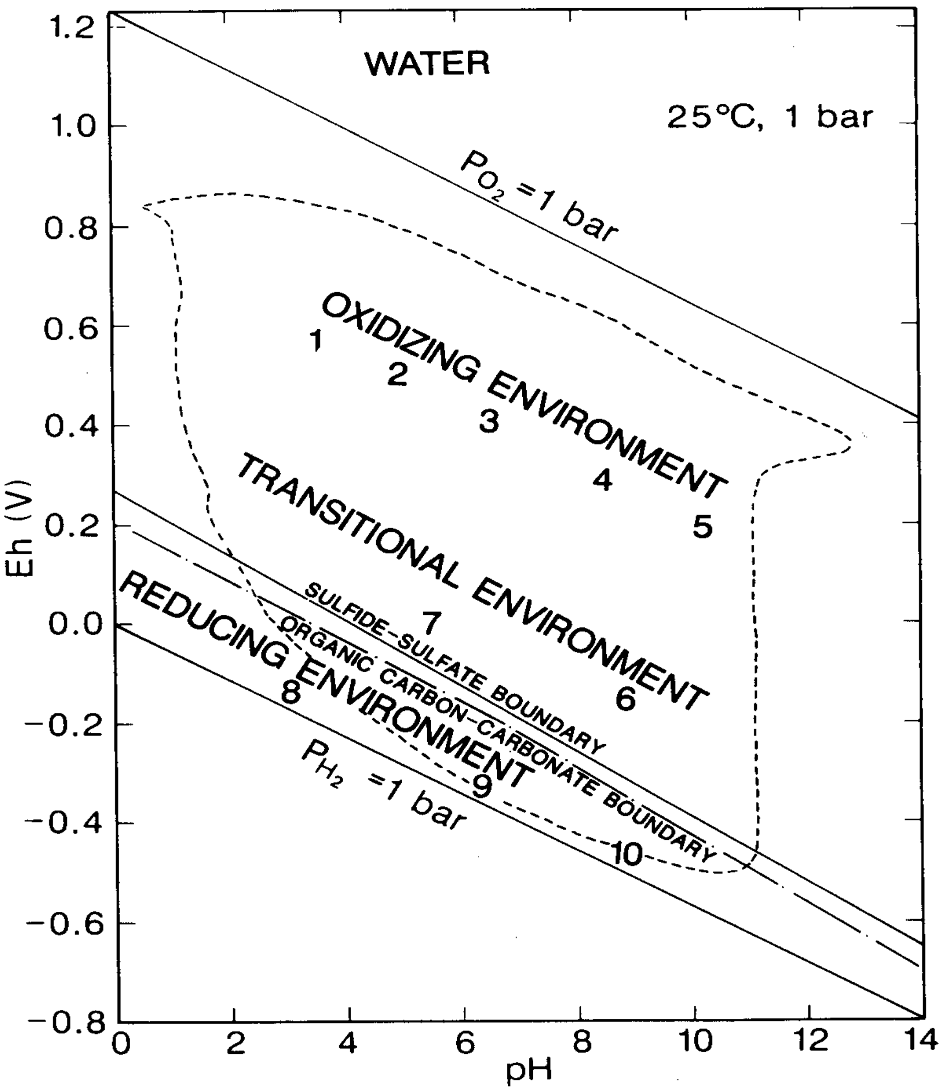

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Lake type and redox

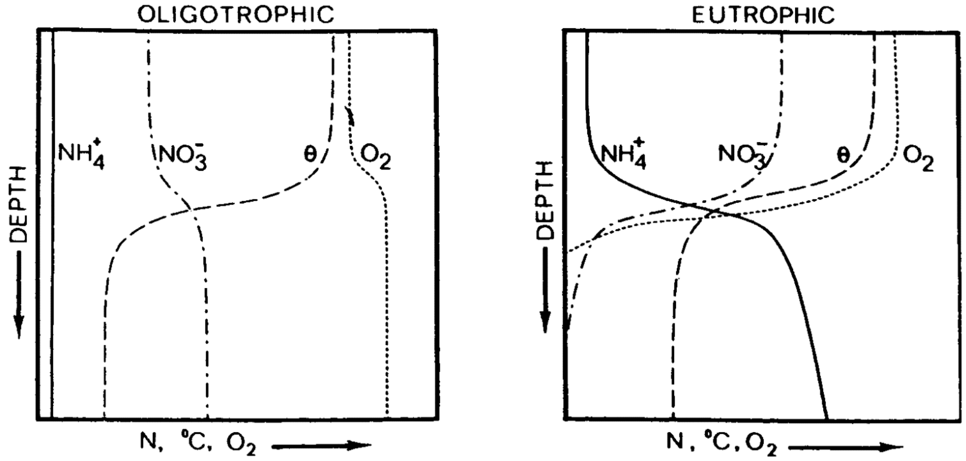

FIGURE 12-4 Generalized vertical distribution of ammonia and nitrate nitrogen in stratified lakes of very low and high productivity.

- Oligotrophic Lakes: oxygen present throughout the year at all depths.
- Eutrophic Lakes: Excess organic matter leads to oxygen loss in hypolimnion during summer stratification

Meromictic lakes: extreme redox conditions

- Meromictic lakes have permanent stratification because of high salt content in the lower layer (monimolimnion).
- Isolation from the atmosphere leads to complete anoxia.
- S^{-2} and methane may accumulate to high concentrations

Oligomictic lakes

- Lakes in the tropics sometimes mix only once every several year (oligomictic lakes)
- Redox conditions are likely to be intermediate between eutrophic and meromictic lakes.
- Famous example of a dangerous lake:
  - Lake Nyos in West Africa

Degassing of Lake Nyos

<http://perso.orange.fr/mhalb/nyos/index.htm
>

Summary: how it all works.

Surplus Organic Matter Heterotrophic organisms	Kcal per mole of CH2O **ΔG**	**Surplus Oxygen** Autotrophic organisms	Kcal per mole of O2 **ΔG**
$CH_2O + O_2 \rightarrow CO_2 + H_2O$ *(aerobic respiration)*	-121.89	$CO_2 + H_2O \rightarrow CH_2O + O_2$ *(photosynthesis)*	+121.89
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