Redox reactions in the environment

ENV-200 Weeks 5 and 6

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Last lecture-recap

We discussed the importance of redox reactions in technical and natural systems.

We assigned redox numbers, balanced reactions, and used the Nernst equation to assess the feasibility of redox reactions under given conditions.

Today, we will look more closely at redox reactions in natural waters and we will learn how to create pe-pH stability diagrams.

Interpretation of reduction potentials

Combined half reactions are thermodynamically viable if the reduction potential of the electron acceptor is above that of the electron donor

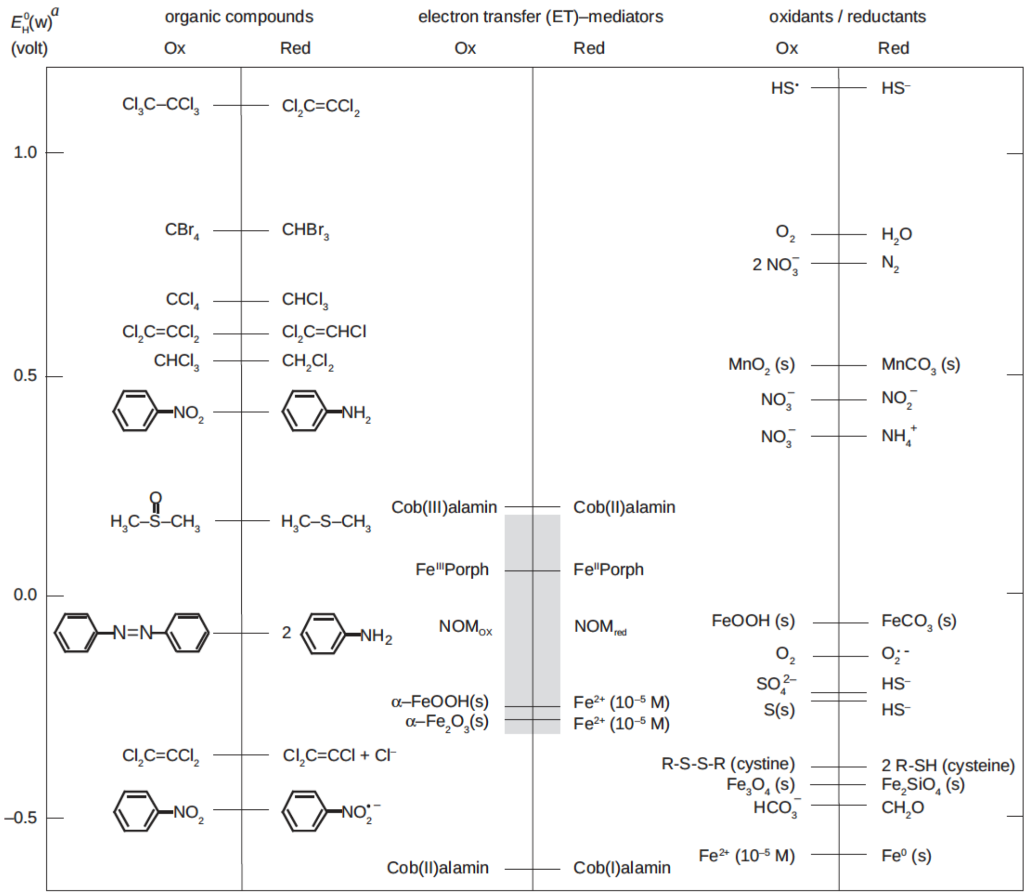

Figure 23.3 in Environmental Organic Chemistry, by Schwarzenbach, Gschwend, Imboden (Edition 3, Wiley).

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Exercise 1: Reduction potentials

1. Can NOM_{red} react with O_2 to form NOM_{ox} and H_2O?
2. Can NOM_{red} react with SO_4^{2-} to form NOM_{ox} and HS^-?

Remember: $\Delta G = -n\ F\ \Delta E$
- $\Delta G > 0$: reaction not feasible
- $\Delta G < 0$: reaction is feasible (but may be kinetically limited)

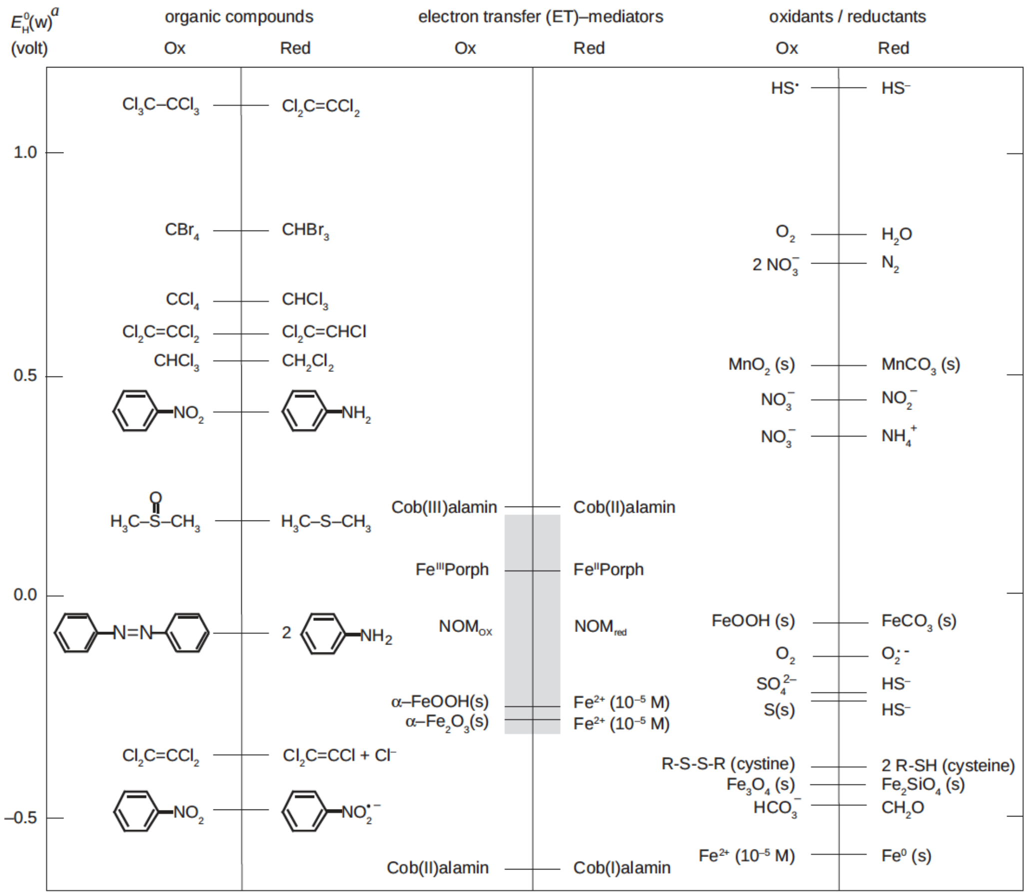

Figure 23.3 in Environmental Organic Chemistry, by Schwarzenbach, Gschwend, Imboden (Edition 3, Wiley).

Interpretation of reduction potentials

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The redox potential of a system is affected by:

1. Availability of electron acceptors
   - In systems with O_2, O_2 is the dominant electron acceptor. In systems without O_2, other terminal electron acceptors become important.
   - If kinetic constraints are not limiting, O_2 will oxidize everything with a lower E value. In other words, while O_2 is available the system has a high redox potential.
2. Microbial activity
   - Microorganisms accelerate redox reactions greatly, and thus are an important factor controlling redox status.
   - They reduce carbon to store energy and oxidize carbon to release energy. These activities rely on O_2 and other electron acceptors. O_2 is the preferred acceptor (provides the greatest energy from respiration).

E_H and pe ranges in natural waters

There is a broad classification for natural waters:

Oxic: pe > 7 $E_H > 400$ mV

Reduction of O_2 or NO_3^-

Suboxic pe 2-7 $100 < E_H < 400$ mV

Reduction of Fe and Mn-oxides

Anoxic pe < 2 $E_H < 100$ mV

Reduction of sulfate or CO_2 (methanogenesis)

Relationship between pe and E_H

Electron activities can be expressed on E_H scale or on pe scales.

pe = -log{e^-} (analogous to pH!)

For Ox + ne^- = Red $\qquad$ $K = \frac{\{Red\}}{\{Ox\}\{e^-\}^n}$

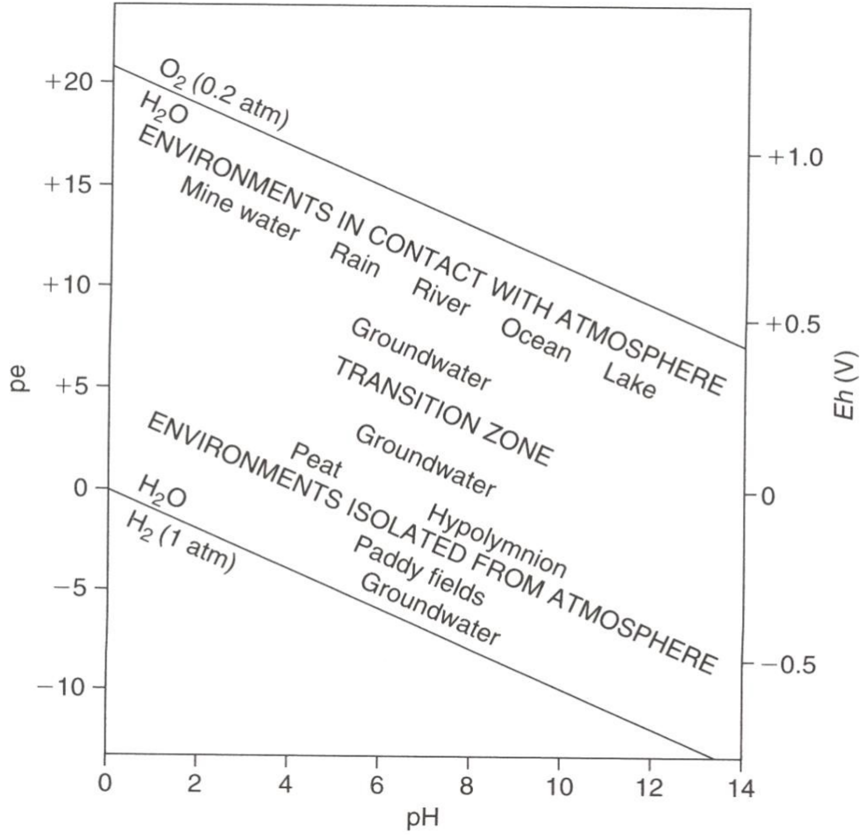
Taking logs: $\qquad$ $\log \frac{\{Red\}}{\{Ox\}} - n \log\{e^-\} = \log K$

$pe = \frac{1}{n} \log K + \frac{1}{n} \log \frac{\{Ox\}}{\{Red\}}$ $\qquad$ at standard conditions: $pe^0 = \frac{1}{n} \log K$

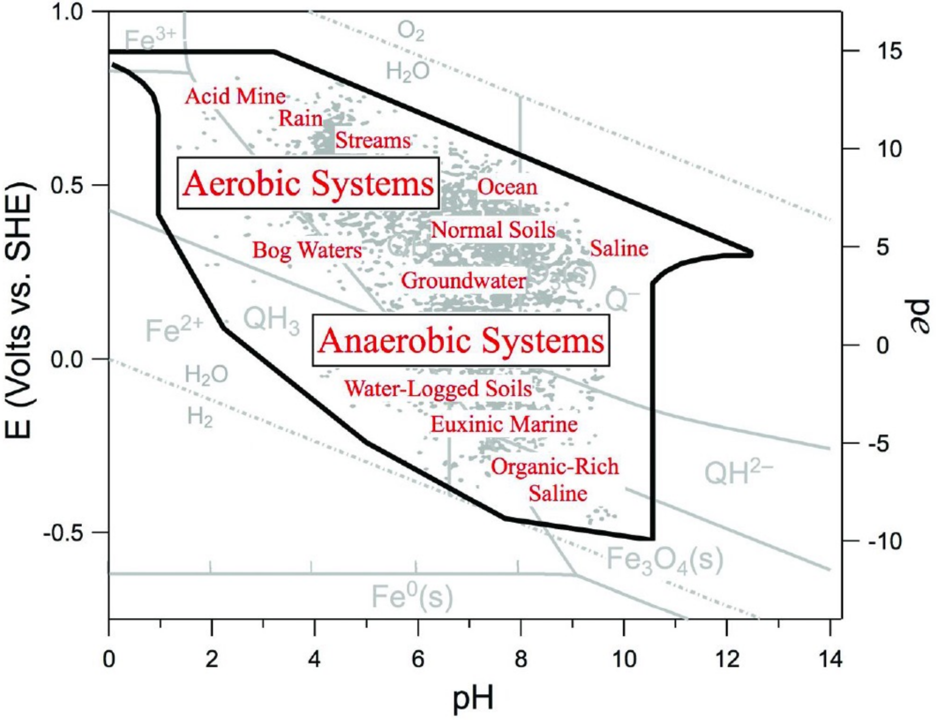
Using $E_H^0 = \frac{2.303\ RT}{nF} \log (K)$ is follows that $E_H^0 = \frac{2.303\ RT}{F} pe^0$

$E_H^0 = 0.059\ pe^0$	at standard conditions (unit activity)
$E_H = 0.059\ pe$	at non-unit activity (at 25°C)

pe/E_H and pH ranges of natural waters



pe/E_H and pH ranges of natural waters



Aquatic Redox Chemistry; Tratnyek, P., et al.; ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Chemistry of oxic and anoxic waters

O_2 present		O_2 absent		
Oxic conditions		Weak anoxia		Strong anoxia
$p\varepsilon >> 0$		$p\varepsilon \sim 0$		$p\varepsilon << 0$
Oxidized solutes and solids:		Reduced solutes		
N	NO_3^-	NO_2^-	NH_4^+	
S	SO_4^{2-}		S^0	H_2S
C	$CO_{2(aq)}$			CH_4
Fe	Fe^{III}; e.g., $FeOOH_{(s)}$		Fe^{2+}	
Mn	Mn^{IV}; e.g., $MnO(OH)_{2(s)}$	Mn^{2+}		

pe-pH diagrams

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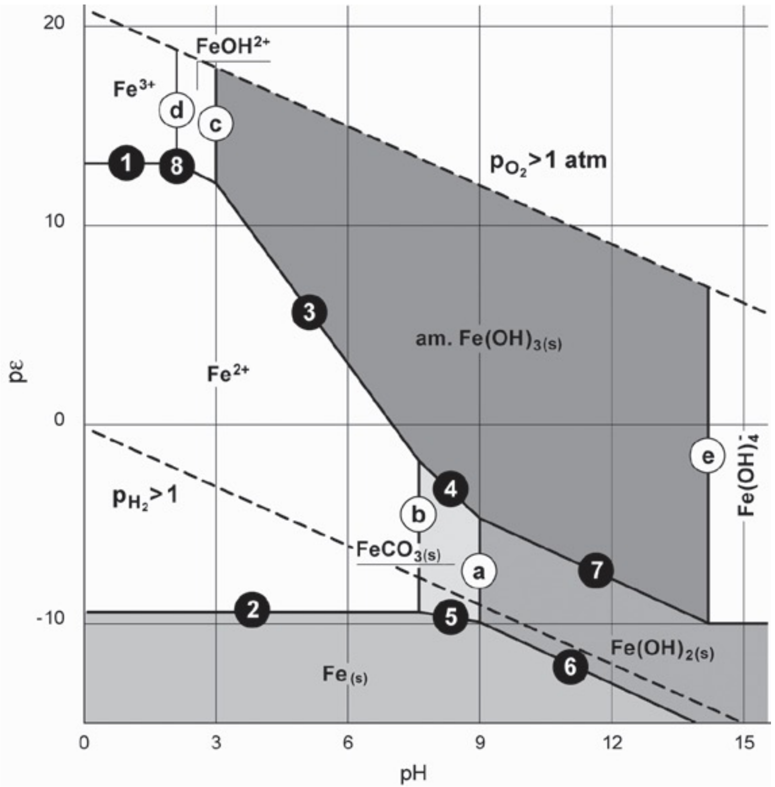
- A stability diagram shows the dominant redox species varying with pH and pe. These zones are not limited to just the dominant species, of course.
- In general, stability diagrams are constructed from thermodynamic (equilibrium) data
- They give a rapid understanding of speciation of redox-sensitive elements
- Field-measured pe (E_H) values are not always compatible with equilibrium conditions
- Stability diagrams are constructed by writing half reactions representing the boundaries between species/phases



pe-pH diagram for water

For water, the range of values of pe and pH are controlled by the atmosphere in contact with it:

- an O_2 atmosphere is completely oxidising (accepts electrons)
- an H_2 atmosphere is completely reducing (gives electrons)

Of course, O_2 and H_2 will be dissolved in water to the extent possible

Redox reactions are:

$$H_2O = 2e^- + 2H^+ + \tfrac{1}{2}\, O_2\,(g) \qquad \text{eq. 1}$$

i.e., O(-2) in water is oxidized to O(0)

$$\tfrac{1}{2}\, H_2\,(g) = H^+ + e^- \qquad \text{eq. 2}$$

i.e., H^+ in water is reduced to H(0)

Any oxidant or reductant in contact with water will be limited by eqs. 1 and 2, so these equations provide limits to natural systems

pe-pH diagram for water

From eq. 1 is follows that

$$-41.55 = \log(K) = \tfrac{1}{2}\log([P_{O2}]) - 2pe - 2pH$$

Since $[P_{O2}] = 0.2$

$$pe = 20.6 - pH$$

For eq. 2

$$0 = \log(K) = -pH - pe - \tfrac{1}{2}\log([P_{H2}])$$

If the maximum $[P_{H2}] = 1$ is considered, then

$$pe = -pH$$

How to draw a line into a pe-pH diagram

General formulation of a straight line:

$$y = mx + c$$

y: value on the y axis (here: pe)

x: value on the x axis (here: pH)

m: slope of the line (i.e., variation in pe per unit variation in pH)

c: y-axis intercept

For O_2/H_2O:

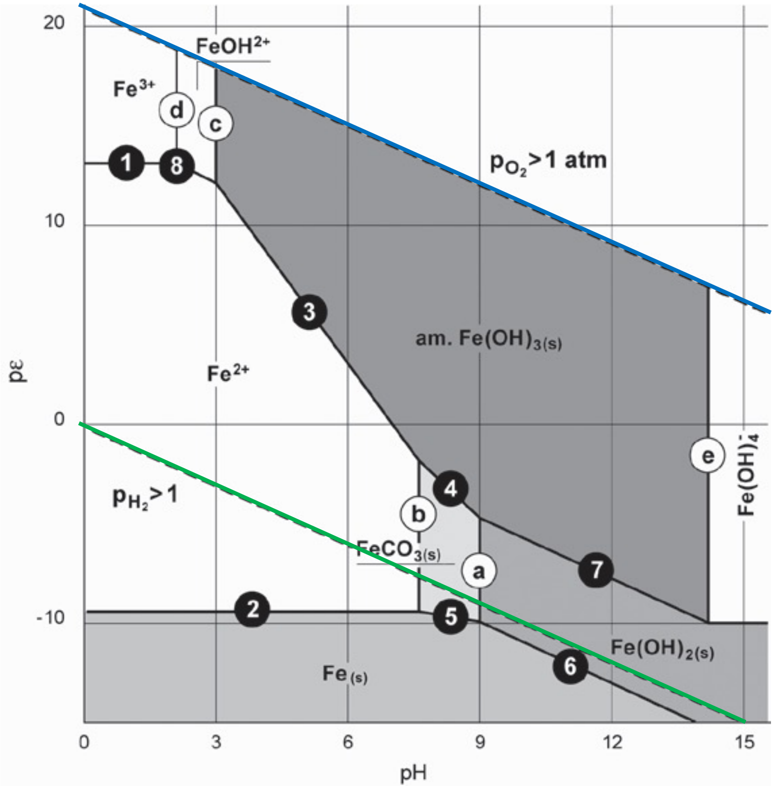
$pe = 20.6 – pH$

$y = pe, x = pH, m = -1, c = 20.6$

For H_2O/H_2:

$pe = -pH$

$y = pe, x = pH, m = -1, c = 0$



Construction of pe-pH diagram for N species

- Nitrogen exists in several stable forms, depending on pe and pH
- Stable nitrogen forms are:
  - Nitrate, NO_3^-
  - Zero-valent nitrogen, i.e., dissolved N_2 gas
  - Ammonia, NH_3,or ammonium ion, NH_4^+, depending on pH
- Nitrite, NO_2^-, does not persist, even though we know that there are organisms in soil and water that liberate nitrite. The reason is that NO_2^- is metastable in water. It exists but will undergo self-oxidation and reduction according to:

$$5NO_2^- + 2H^+ = 3NO_3^- + N_2 + H_2O \qquad \log(K) = 64.23$$

Construction of pe-pH diagram for N species

Redox couple	Reaction	log(K)
N(5) / N(3)	$NO_2^- + H_2O = NO_3^- + 2H^+ + 2e^-$	-28.57
N(5) / N(0)	$N_2 + 6H_2O = 2\ NO_3^- + 12H^+ + 10e^-$	-207.08
N(5) / N(-3)	$NH_4^+ + 3H_2O = NO_3^- + 10H^+ + 8e^-$	-21.14
N(3) / N(0)	$N_2 + 4H_2O = 2NO_2^- + 8H^+ + 6e^-$	-119.077
N(3) / N(-3)	$NH_4^+ + 2H_2O = NO_2^- + 8H^+ + 6e^-$	-149.94
N(0) / N(-3)	$2NH_4^+ = N_2 + 8H^+ + 6e^-$	-31.074
	$NH_4^+ = NH_3 + H^+$	-9.252

This list gives all the possible redox combinations. Grey reactions are (almost) not relevant to the pe-pH stability diagram because (i) NO_2^- is metastable and (ii) NH_4^+ and NO_3^- are separated by N_2 (very stable) on the pe-pH diagram

Exercise 2: Nitrogen redox reactions

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Determine the pe-pH relationship for the two equations below. The final equations should be in the form of pe = x + ypH.

Redox couple	Reaction	log(K)
N(5) / N(3)	$NO_2^- + H_2O = NO_3^- + 2H^+ + 2e^-$	-28.57
N(5) / N(0)	$N_2 + 6H_2O = 2\ NO_3^- + 12H^+ + 10e^-$	-207.08

Construction of pe-pH diagram for N species

We do the same for the remaining equations in the table:

$2NH_4^+ = N_2 + 8H^+ + 6e^-$ $\quad\quad$ $\log(K) = -31.074$

$pe = 5.179 – 1/3 \log([NH_4^+]) – 4/3\ pH + 1/6 \log([P_{N2}])$

and

$NH_4^+ = NH_3 + H^+$ $\quad\quad$ $\log(K) = -9.252$

$pH = 9.252 – \log([NH_4^+]) + \log([NH_3])$

Note that we are ignoring NO_2^- for now as it is metastable.

Exercise 3: Interpreting pe-pH relationships

We now have the following relationships:

N(5)/N(3)

$$pe = 14.285 + \frac{1}{2}\log([NO_3^-]) - \frac{1}{2}\log([NO_2^-]) - pH$$

N(5)/N(0)

$$pe = 20.708 - 6/5pH + 1/5\log([NO_3^-]) - 1/10\log([P_{N2}])$$

N(0)/N(-3)

$$pe = 5.179 - 1/3\log([NH_4^+]) - 4/3pH + 1/6\log([P_{N2}])$$

NH_4^+/NH_3 dissociation

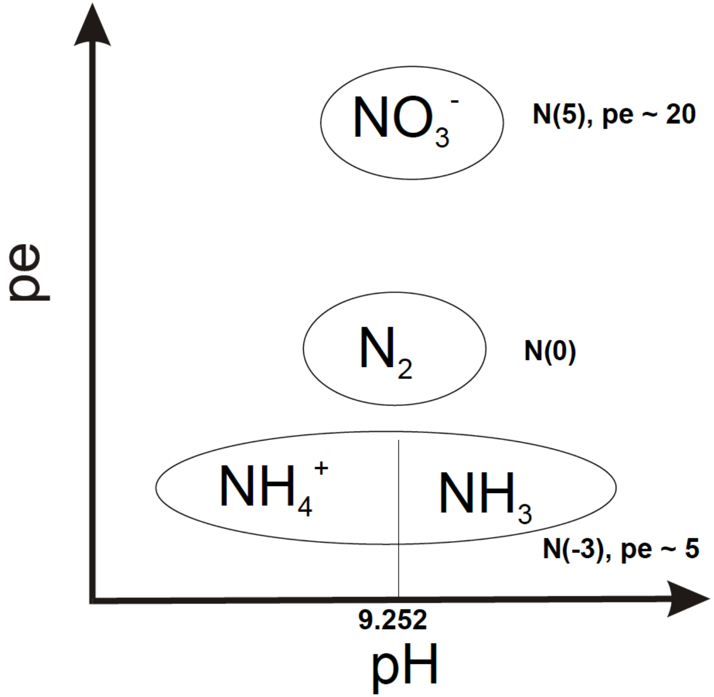
$$pH = 9.252 - \log([NH_4^+]) + \log([NH_3])$$

When plotted on a pe-pH diagram, how will these relationships look?
Assume that all N species have unit activities.

Construction of pe-pH diagram for N species

More oxidized species at high pe

More reduced species at low pe



More protonated species at low pH

Less protonated species at high pH

Construction of pe-pH diagram for N species

Each of the derived pe-pH equations defines a straight line

By choosing appropriate values for the activities of the various species involved, the stability diagram can be completed

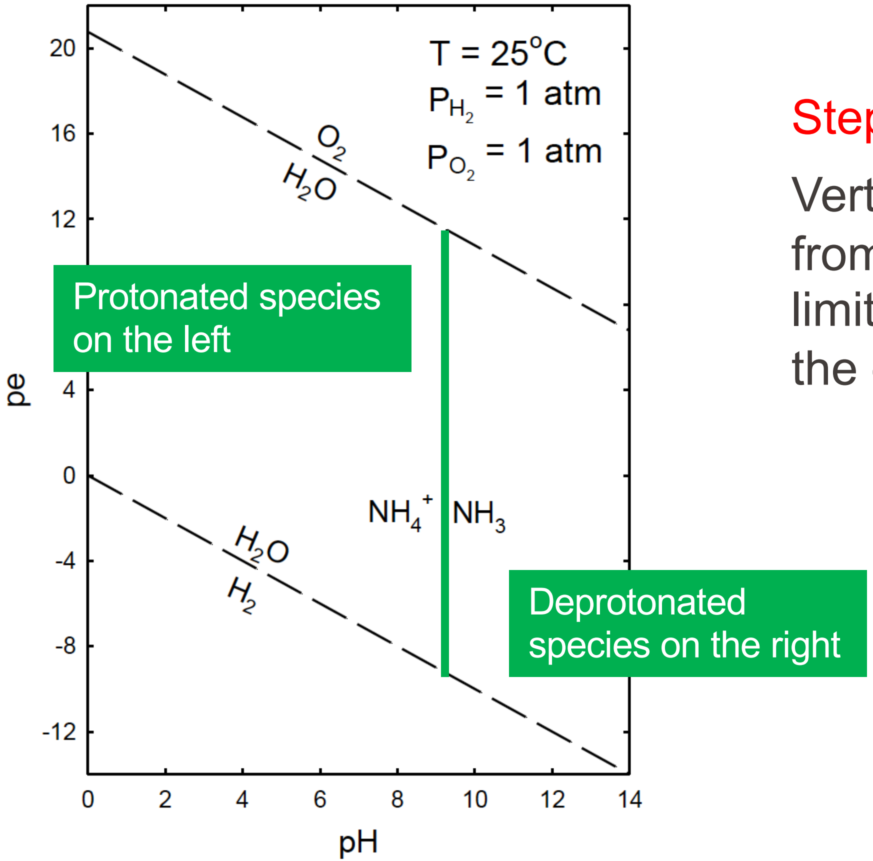
The stability diagram will vary according to the activities selected!

Choose equal activities, unless there are other “typical” values that would be more appropriate

For N: [P_{N2}], [NO_3^-], [NH_4^+] and [NH_3] must be selected

- [P_{N2}] Atmospheric pressure of N_2 is 0.77
- [NO_3^-] Assume polluted groundwater, activity ~10-3
- [NH_4^+] Take same value as [NO_3^-]
- [NH_3] Take same value as [NO_3^-]

Construction of pe-pH diagram for N species



Step 1: add NH_4^+ / NH_3 boundary

Vertical line at pH = 9.25 is plotted from upper to lower water stability limit since it is not yet known where the other lines will intersect it.

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Construction of pe-pH diagram for N species

Step 2: add $N_2(g)$ / NH_4^+ boundary

Recall:

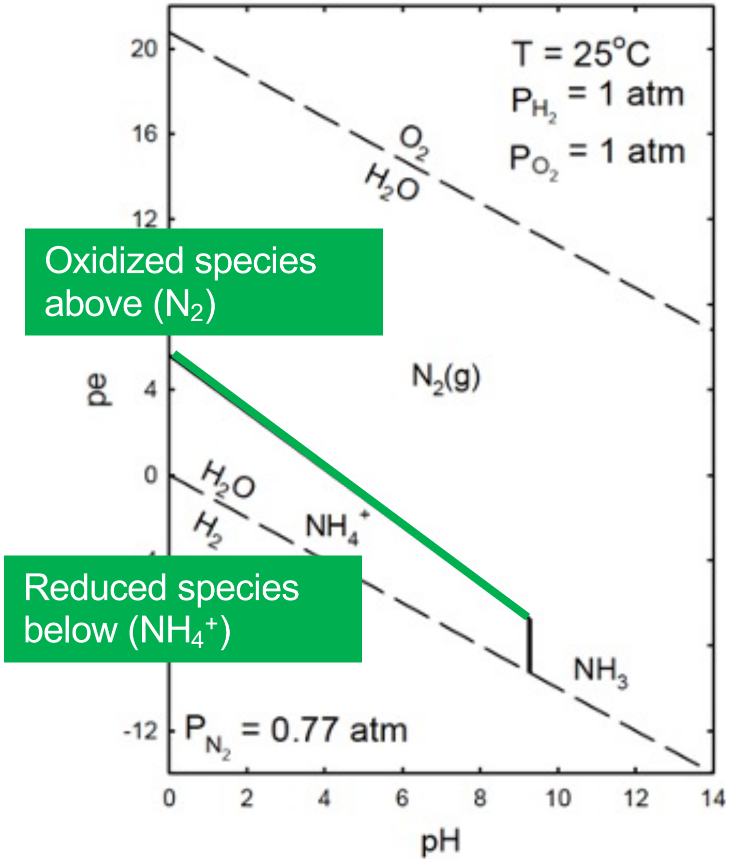
N(0)/N(-3)

$$pe = 5.179 – 1/3\log([NH_4^+]) – 4/3pH + 1/6\log([P_{N2}])$$

with $[NH_4^+] = 10^{-3}$ and $\log([P_{N2}]) = \log(0.77)$:

$$pe = 6.16 – 4/3pH$$

Construction of pe-pH diagram for N species



Step 2: add $N_2(g)$ / NH_4^+ boundary

$$pe = 6.16 – 4/3pH$$

The $N_2(g)$ / NH_4^+ boundary intersects the NH_4^+ / NH_3 boundary at pe = -6.18 and pH = 9.252. The NH_4^+ field is now enclosed.

Construction of pe-pH diagram for N species

Step 3: add $N_2(g)$ / NH_3 boundary

Recall:

N(0)/N(-3)

$$pe = 5.179 – 1/3\log([NH_4^+]) – 4/3pH + 1/6\log([P_{N2}])$$

NH_4^+/NH_3 dissociation

$$pH = 9.252 - \log([NH_4^+]) + \log([NH_3])$$

Eliminate $\log([NH_4^+])$ from the first eq. using the second eq:

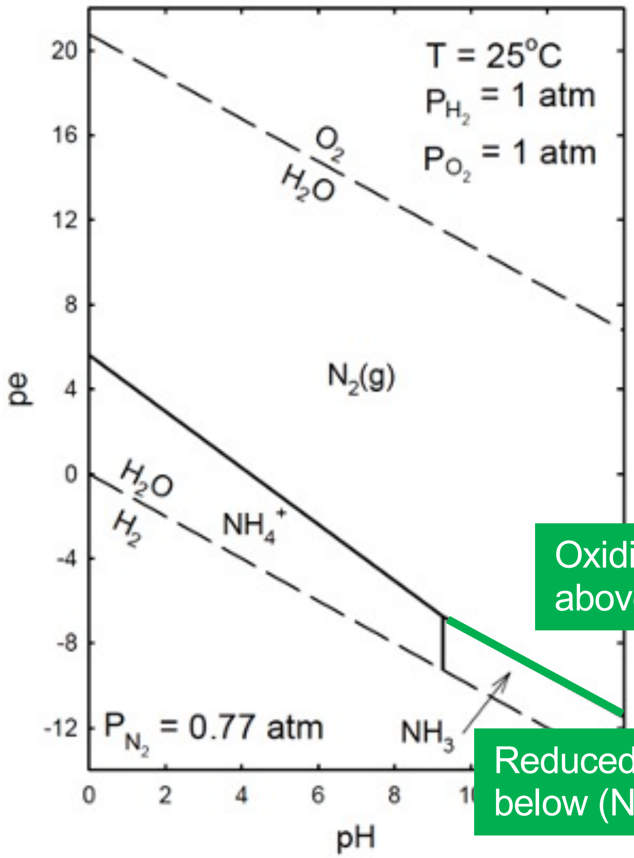
$$pe = 2.095 – 1/3\log([NH_3]) – pH + 1/6\log([P_{N2}])$$

With $[NH_3] = 10^{-3}$ and N_2 partial pressure of 0.77 atm this becomes

$$pe = 3.076 – pH \text{ (valid for pH > 9.252)}$$

Slope with pH changes from -4/3 to -1

Construction of pe-pH diagram for N species



Oxidized species above (N_2)

Reduced species below (NH_3)

Step 3: add $N_2(g)$ / NH_3 boundary

pe = 3.076 – pH

(valid for pH > 9.252)

The NH_3 field is enclosed.

Construction of pe-pH diagram for N species

Step 4: add $N_2(g)$ / NO_3^- boundary

Recall:

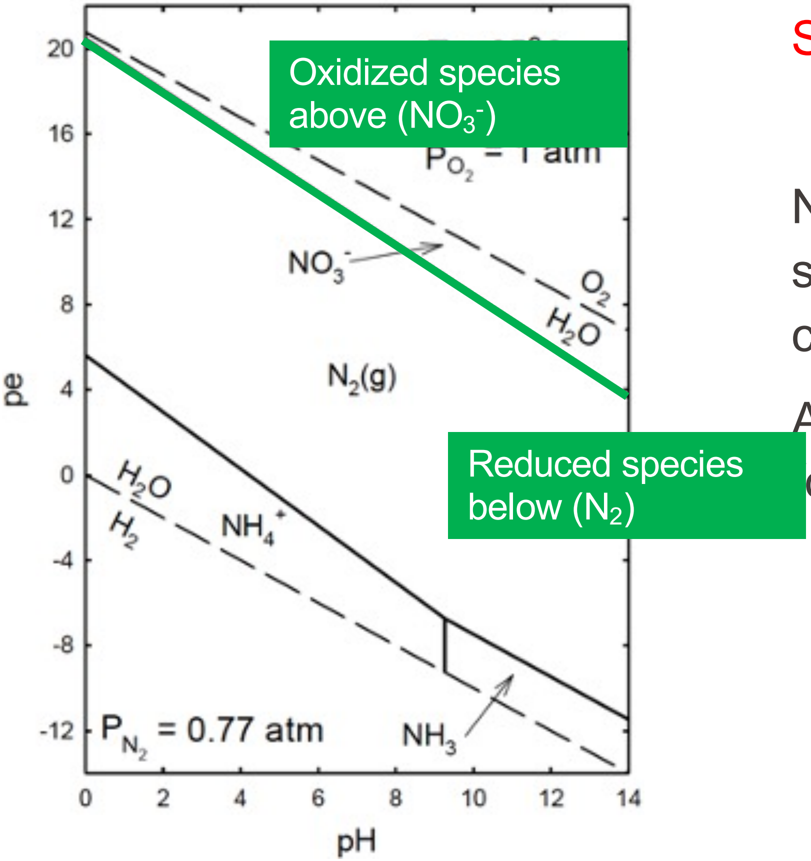
N(5)/N(0)

$$pe = 20.708 - 6/5pH + 1/5\log([NO_3^-]) - 1/10\log([P_{N2}])$$

With $[NH_3] = 10^{-3}$ and N_2 partial pressure of 0.77 atm this becomes

$$pe = 21.32 - 6/5pH$$

Construction of pe-pH diagram for N species



Step 4: add N_2(g) / NO_3^- boundary

$$pe = 21.32 – 6/5pH$$

NO_3^- should be present in significant quantities only in waters containing free oxygen.

Ammonium ions and ammonia are found under reducing conditions.

Role of microorganisms in environmental redox reactions

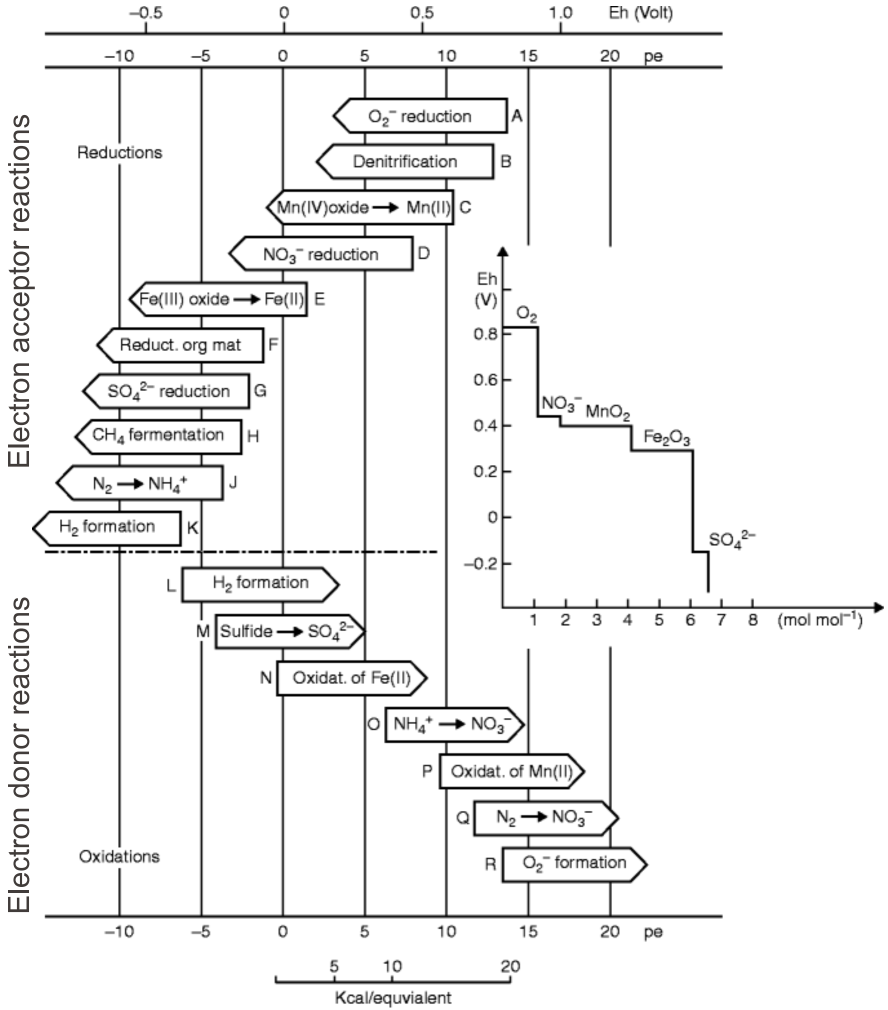
- Microorganisms accelerate redox reactions greatly, and thus are an important factor controlling redox status, especially of soils. They act to:
  - Reduce carbon to store energy
  - Oxidize carbon to release energy
- These activities rely on O_2 and other electron acceptors
- O_2 is the preferred acceptor because it is most easily reduced to water of the available acceptors and provides the greatest energy from respiration
- Without O_2, other redox couples must be used to accept electrons liberated from the oxidation of carbon compounds

Redox ladder

Microbes can use a diversity of redox transformations as part of their overall metabolic pathways. Various reactions (electron acceptor reduction and electron donor oxidation) can be combined to poise the pe value of the environment.

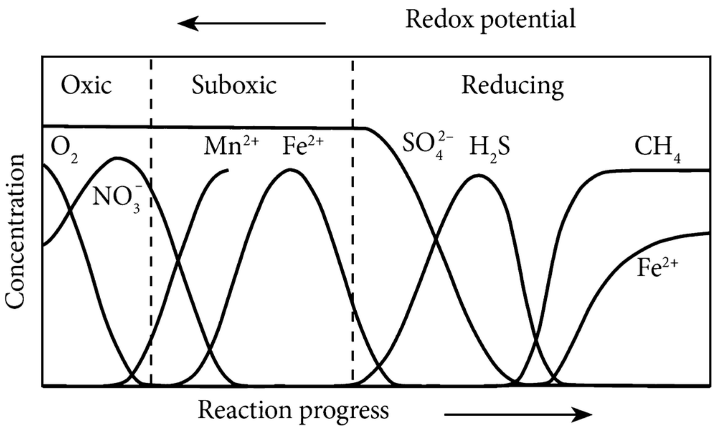
The redox ladder describes the sequence of reduction half reactions that microbes use to oxidize organic matter. In this sequence, the most energetically favorable reactions occur first and reactions that relese less energy follow.

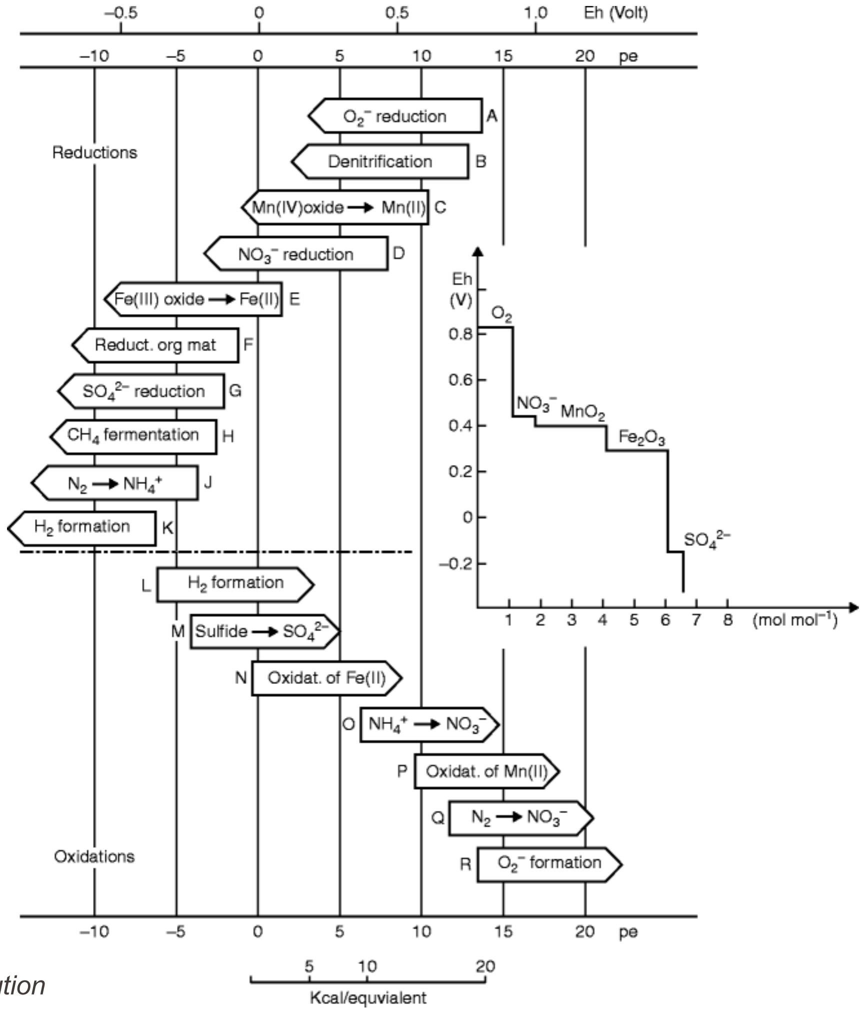
Stumm and Morgan, Aquatic Chemistry.



Redox ladder

Stepwise pe profile is formed: at a particular place or time, pe is fixed until a particular terminal electron acceptor is consumed





Stumm and Morgan, Aquatic Chemistry.
Appelo and Postma, 1996, Geochemistry, Groundwater, and Pollution

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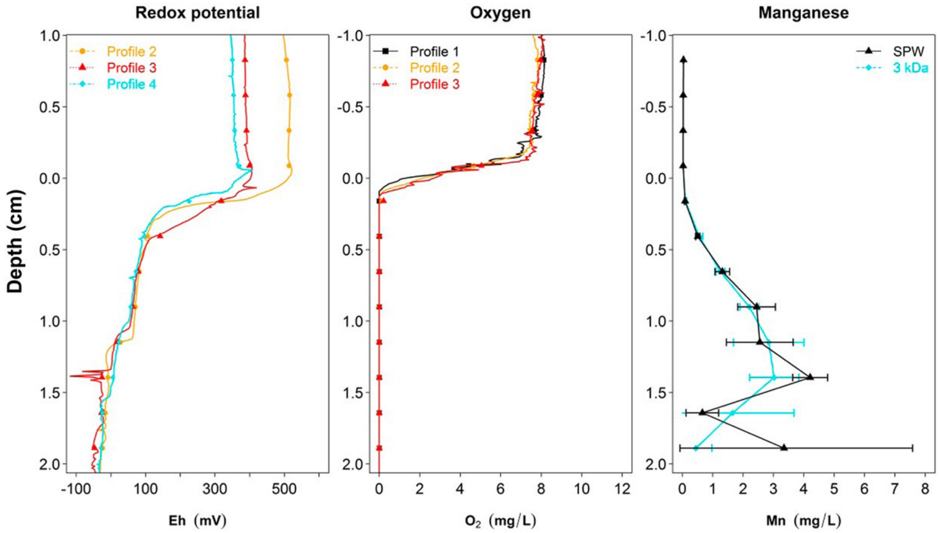
Where do redox ladders occur?

- Soils that are flooded and turn anoxic (right figure)
- Sediment profiles (left figure)
- Contaminated groundwater- remember our environmental engineering challenge?



Fabricius et al., Env Sci Technol, 2016, 50, 17, 9506.

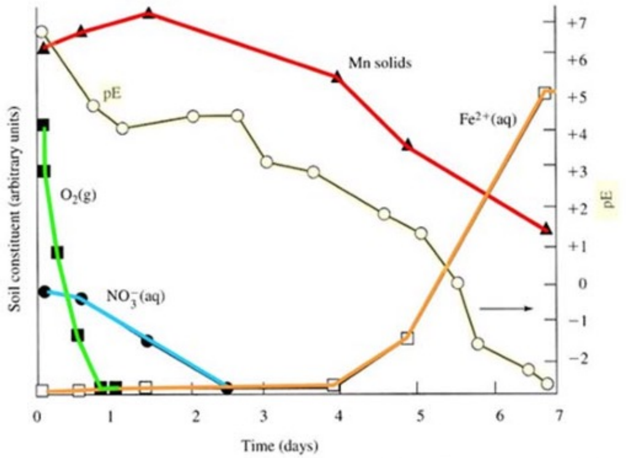


Figure 11.13 Relative changes in O_2, NO_3^-, Mn(IV) solids, Fe^{2+}(aq), and pE of a soil with time after flooding. From G. Sposito, *The chemistry of soils.* Copyright 1989 by Oxford University Press. Used by permission. from Langmuir, "Aqueous Environmental Geochemistry"

Langmuir, Aqueous Environmental Geochemistry

Environmental engineering challenge

A landfill is sitting on top of an aquifer. The landfill is not properly sealed, resulting in the infiltration of water the leaches through the landfill into the underlying aquifer.

- How will the redox conditions in the aquifer be affected by the influx of organic carbon in the form of leachate?
- How does the redox milieu affect groundwater quality in this context?

Environmental engineering challenge

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Assuming that the leachate contains mostly biodegradable organic carbon (we neglect contaminants here), calculate how much biodegradable organic carbon (DOC) can be in the water without formation of anaerobic zones. Assume that the initial water is in equilibrium with atmospheric O_2 concentrations.

Useful information:

- The solubility of O_2 in water can be calculated using $[O_2] = K_H \, pO_2$ where K_H (25 °C) = $1.3 * 10^{-3}$ M atm^{-1}
- Use the chemical formula CH_2O for DOC

Environmental engineering challenge

After oxygen is used up, which electron acceptors will be used next?

For nitrate (eq. 2), Mn oxide (eq. 3), Fe oxide (eq. 6), carbon dioxide (eq. 8b), and sulfate (eq. 9), calculate the Δ E_H^0(W) value using the following table. Use the following reaction for organic carbon:

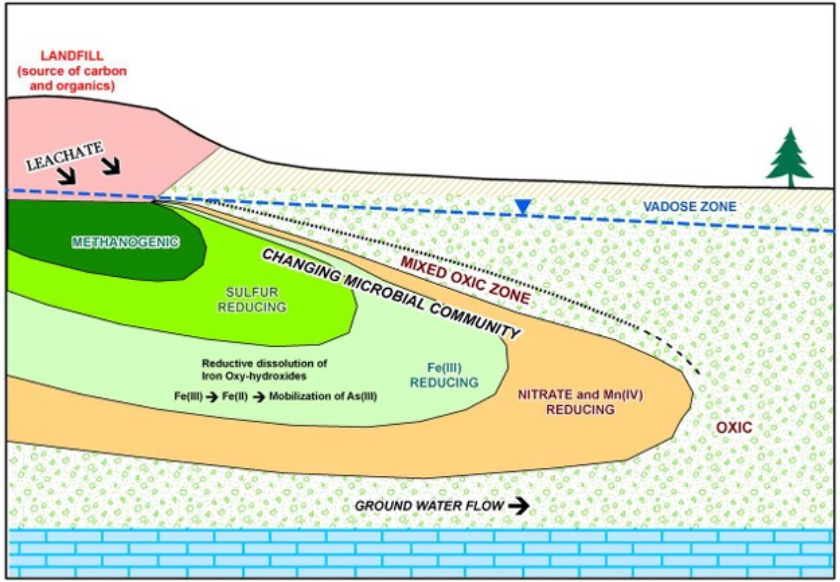
$CO_2 + 4e^- + 4H^+ = CH_2O + H_2O$ $E_H^0(W) = -0.43$ V

Half-reaction				
Oxidized Species	Reduced Species	E_H^0 (V)	E_H^0 (W) (V)	$\Delta_r G^0(W)/n$ [c] (kJ mol–1)
(1a)	$O_2(g) + 4\,H^+ + 4\,e^- = 2\,H_2O$	+1.23	+0.81	−78.3
(1b)	$O_2(aq) + 4\,H^+ + 4\,e^- = 2\,H_2O$	+1.19	+0.77	−74.3
(2)	$2\,NO_3^- + 12\,H^+ + 10\,e^- = N_2(g) + 6\,H_2O$	+1.24	+0.74	−72.1
(3)	$MnO_2(s) + HCO_3^-\,(10^{-3}) + 3\,H^+ + 2\,e^- = MnCO_3(s) + 2\,H_2O$		+0.53 [b]	−50.7 [b]
(4)	$NO_3^- + 2\,H^+ + 2\,e^- = NO_2^- + H_2O$	+0.85	+0.43	−41.6
(5)	$NO_3^- + 10\,H^+ + 8\,e^- = NH_4^+ + 3\,H_2O$	+0.88	+0.36	−35.0
(6)	$FeOOH(s) + HCO_3^-\,(10^{-3}\,M) + 2\,H^+ + e^- = FeCO_3(s) + 2\,H_2O$		−0.05 [b]	+4.8 [b]
(7)	CH_3COCOO^- (pyruvate) $+ 2\,H^+ + 2\,e^- = CH_3CHOHCOO^-$ (lactate)		−0.19	+17.8
(8a)	$HCO_3^- + 9\,H^+ + 8\,e^- = CH_4(aq) + 3\,H_2O$	+0.21	−0.20	+19.3
(8b)	$CO_2(g) + 8\,H^+ + 8\,e^- = CH_4(g) + 2\,H_2O$	+0.17	−0.24	+23.6
(9)	$SO_4^{2-} + 9\,H^+ + 8\,e^- = HS^- + 4\,H_2O$	+0.25	−0.22	+20.9

Environmental engineering challenge

Redox zonation in the aquifer will develop as leachate is coming into the groundwater from the landfill. The leachate plume will be transported with the water. The sequential reduction of different electron acceptors by microbes results in the formation of the following zones, with increasing distance from the landfill: methanogenic zone – sulfur reducing zone - iron reducing zone – nitrate and Mn(IV) reducing zone – oxic zone

The aquatic chemistry in these zones differs markedly!



Summary

- Redox conditions are a dominant control on the chemistry of natural waters.
- pe and E_H are two different scales that both describe electron activity.
- Different environmental systems have characteristic pe and pH ranges.
- pe-pH diagrams give a rapid understanding of the speciation of redox-sensitive elements.
- The sequential use of electron acceptors in microbial respiration gives rise to redox zonation.