

OXIDATION REDUCTION

In soil systems, rapid changes in moisture content strongly affects soil aeration status. In addition to changes in bulk conditions, there are microsites or zone where diffusion of oxygen is restricted, such as small pores filled with water and the interior of aggregates where oxygen consumption is more rapid than oxygen diffusion. In areas where there is better access to soil air and pockets of easily decomposed organics, and intense decomposition can deplete available oxygen and produce a number of redox-active organic compounds.

From a global perspective redox is an important aspect of energy and carbon transfer. Carbon reduction and its subsequent oxidation fuel the biological world. Carbon reduction or gain in electrons is often called photosynthesis by the uninitiated and the reverse oxidation reaction is called respiration when applied to humans and other large animals. Microbial respiration accompanies or is synonymous with mineralization.

Regardless of your perspective, redox reactions are important aspects of soil chemistry. Redox reactions change the speciation and solubility of many elements, create new compounds and alter the biochemistry of soils.

In a complex mixture such as soils the interpretation of redox relationships is difficult. Since the dynamics of soil oxygen which drives the changes in redox potential are rapid, equilibrium may not be attained. From a thermochemistry view point redox is not at equilibrium, because all of the energy yielding compounds by definition contain excess free energy and are unstable with respect to carbon dioxide and water. Processes which reduce oxygen levels and decrease redox potentials are driven by microbial consumption of oxygen. Conditions necessary for lowering redox potentials include, a source of decomposable organic materials (energy source), a population of microbes capable of utilizing this energy source for metabolism, and a restriction on the resupply of oxygen. These requirements are not uniformly distributed in soils and sediments. Thus, redox reactions and redox potentials are not uniform throughout the soil matrix. In fact, redox potentials are highly variable and therefore are best used as an indication or relative status of the soil.

Eh -pH RELATIONSHIPS

Thermochemistry background

The *Gibbs free energy* (G) may be defined in differential form as:

$$dG = - SdT - VdP - w' \quad (1)$$

where w' is defined as the useful work in a chemical system (non-pressure, volume work) in our case this will be the electrical work of the system.

At constant T and P we find:
$$dG = - w' \quad (2)$$

Also remembering that at equilibrium $dG = 0$ and therefore the useful work or electrical work in the system is also zero at equilibrium. In an electro-chemical system the work is derived from the transfer of electrons from one compound to another and is equal to the potential and the charge transferred $w' = EdQ$, where E is the potential and Q is the quantity of charge transferred. In a chemical reaction where n electrons are transferred per mole of reactant, the electrical work is nFE where E is the emf of the system, F is the Faraday constant. Therefore:

$$dG = - nFE \quad (3)$$

and

$$dG^{\circ} = - nFE^{\circ} \quad (4)$$

From thermodynamics it can also be shown (but not here) that:

$$dG = dG^{\circ} + RT \ln Q \quad (5)$$

Q is the reaction quotient.

Equating (3), (4) and (5) we find (6) which is the familiar Nernst Equation

$$E = E^{\circ} - \frac{RT}{nF} \ln Q \quad (6)$$

Other useful relations are derived from (4) and the relationship $dG^{\circ} = -RT \ln K^{\circ}$

to obtain:

$$-nFE^{\circ} = -RT \ln K^{\circ} \quad (7)$$

Rearranging and substituting gives:

$$\log K^{\circ} = 16.9 n E^{\circ} \quad (8)$$

When E is expressed in volts. Solving for E^o evaluating constants and specifying temperature as 298 °K expressing the result in millivolts gives:

$$E^{\circ} = \frac{59.2}{n} \log K^{\circ} \quad (9)$$

The Nernst Equation (6) is the basis for the measurement of redox potential in soils and sediments. Replacing E with E_h and E^o with E_h^o and writing the reaction as a reduction produces the familiar equation used for soil redox potential (E_h) shown in McBride (page 240).

$$E_h = E_h^{\circ} - \frac{0.059}{n} \log \frac{(\text{reduced species})}{(\text{oxidized species}) (H^+)^m} \quad (10)$$

In aqueous systems the bounds of Eh is dictated by the stability of water. In oxidizing systems the oxidation of water to yield oxygen and protons via the following reaction is the upper boundary for Eh. Since the reaction yields protons, the stability is a function of pH.



Using the Nernst Equation evaluated at 25°C gives the following:

$$E_h = E^{\circ} + \frac{0.059}{4} \log \left(\frac{P_{O_2} (H^+)^4}{(H_2O)^2} \right) \quad (12)$$

for conditions where the activity of water is taken to be unity the equation reduces to:

$$E_h = E^{\circ} + \frac{0.059}{4} \log P_{O_2} + 0.059 \log (H^+)$$

$$E_h = E^{\circ} + 0.0148 \log P_{O_2} - 0.059 \text{ pH} \quad (13)$$

$$E_h = 1.229 + 0.0148 \log P_{O_2} - 0.059 \text{ pH}$$

Water oxidation depends on both pH and oxygen pressure. If an arbitrary oxygen pressure is chosen, then the plot of Eh vs pH will have a negative slope of 0.059 V or 59 mV per pH unit and an intercept of E° (1.229 volts). Note that if (H^+) is 1 mole/liter (i.e. pH = 0), and P_{O_2} is 1 atmosphere standard conditions are met and $Eh = E^\circ$, which is the intersection of the line with the vertical axis in Eh-pH plots.

At the other extreme of reducing conditions in aqueous systems, hydrogen ion reduction to hydrogen gas is the lower stability of the system. As written below for as an oxidation potential, the reaction is:



$$E_h = E^\circ + \frac{0.059}{2} \log \left(\frac{(H^+)^2}{P_{H_2}} \right)$$

$$E_h = E^\circ - 0.0295 \log P_{H_2} - 0.059 \text{ pH} \quad (15)$$

but since $E^\circ = 0$ for the Hydrogen half cell,

$$E_h = -0.0295 \log P_{H_2} - 0.059 \text{ pH}$$

At standard conditions where $P_{H_2} = 1$ atmosphere and $\text{pH} = 0$, $E_h = E^\circ = 0$. For a given hydrogen pressure the E_h decreases with a slope of 0.059 volts per pH unit and has an intercept of 0.000.

Thus the stability limits for E_h are bounded by hydrogen and oxygen gas evolution from water. Limits of 1 atmosphere of oxygen and/or hydrogen are not realistic, however they give the bounds for the system. Other values for E_h given oxygen levels of 0.2 atmospheres can easily be calculated and will be parallel to the 1 atmosphere lines. At $\text{pH} = 0$, $0.0148 \log P_{O_2} = -1.229$ is the oxygen pressure required for E_h to equal 0.

In soil and sediment systems reasonable bounds for pH are between about 4 and 9, therefore the Eh - pH relationships of soils are defined in the regions bounded by these values.

Note that in for standard conditions of 1 atmosphere of oxygen and $\text{pH} = 0$, $E^\circ = 1.229$ volts. Since $pe = E_h / 0.059$ or 20.83. The slope of the E_h vs pH line is -0.059 therefore, as pH increases one unit E_h decreases 0.059 volts and $pe + \text{pH} =$ a constant or 20.83. Similarly for the hydrogen water couple, $pe + \text{pH} = 0$.

POURBAIX DIAGRAMS

These diagrams are an extension of the other equilibrium diagrams we have discussed this quarter. In this case the plots are values of E or pE in relation to pH. pH is chosen as the independent variable because oxidation reduction reaction are strongly affected by pH and this is more convenient than partial pressure diagrams involving P_{O_2} , of P_{H_2} . Hydrogen ions or hydroxide ions are often involved in the reactions and are conveniently covered by pH. As an example lets look at the diagram for iron superimposed on the water stability graph discussed in McBride.

The necessary equations are:



The value for $\text{Fe}(\text{OH})_3$ is that for soil ferric hydroxide given in Lindsay (1979).

Since equation (1) is independent of pH, it represents a line parallel to the pH axis.

$$E = E^{\circ} - 0.059 \log \frac{(\text{Fe}^{2+})}{(\text{Fe}^{3+})} \quad (4)$$

Equation (4) contains the activity ratio of Fe^{2+} to Fe^{3+} , Fe concentration is not needed, however the straight line with an intercept at 0.771 volts implies that the activity ratio of the two iron species is always = 1.

Ferric iron level and pH will determine the line separating Fe^{3+} and $\text{Fe}(\text{OH})_3$. Redox reactions are not involved and the line is parallel to the E_h axis. Choosing a Fe^{3+} value will determine the position of line A separating Fe^{3+} and $\text{Fe}(\text{OH})_3$.

$$\text{Fe}^{3+} = \left(\frac{K_{\text{sp}}}{K_w^3} \right) (\text{H}^+)^3 \quad (5)$$

Taking logs of both sides and substituting -3pH for $3 \log(\text{H}^+)$, $10^{-39.294}$ for K_{sp} and 10^{-14} for K_w gives:

$$\log(\text{Fe}^{3+}) = 2.706 - 3\text{pH}; \quad \text{or} \quad \text{pH} = 0.902 - \frac{1}{3} \log(\text{Fe}^{3+}) \quad (6)$$

If Fe^{3+} is taken to be 1 mM, separation between Fe^{3+} and $\text{Fe}(\text{OH})_3$ is drawn at pH 1.902.

At the intersection of the line derived from equation (6) and the redox relation for Fe^{2+} and Fe^{3+} (equation 1), solid phase $\text{Fe}(\text{OH})_3$ can be reduced to Fe^{2+} . The redox equilibrium is derived by summing equations (1) and (2) and adding 3 H^+ ions to each side of equation (2) to give:



This couple has an E° of +0.9306 volts and has the form:

$$E_h = 0.9306 - 0.177 \text{ pH} - 0.059 \log(\text{Fe}^{2+}) \quad (8)$$

If the concentration of Fe^{2+} is taken as 1 mM, then the equation is:

$$E_h = 1.108 - 0.177 \text{ pH} \quad (9)$$

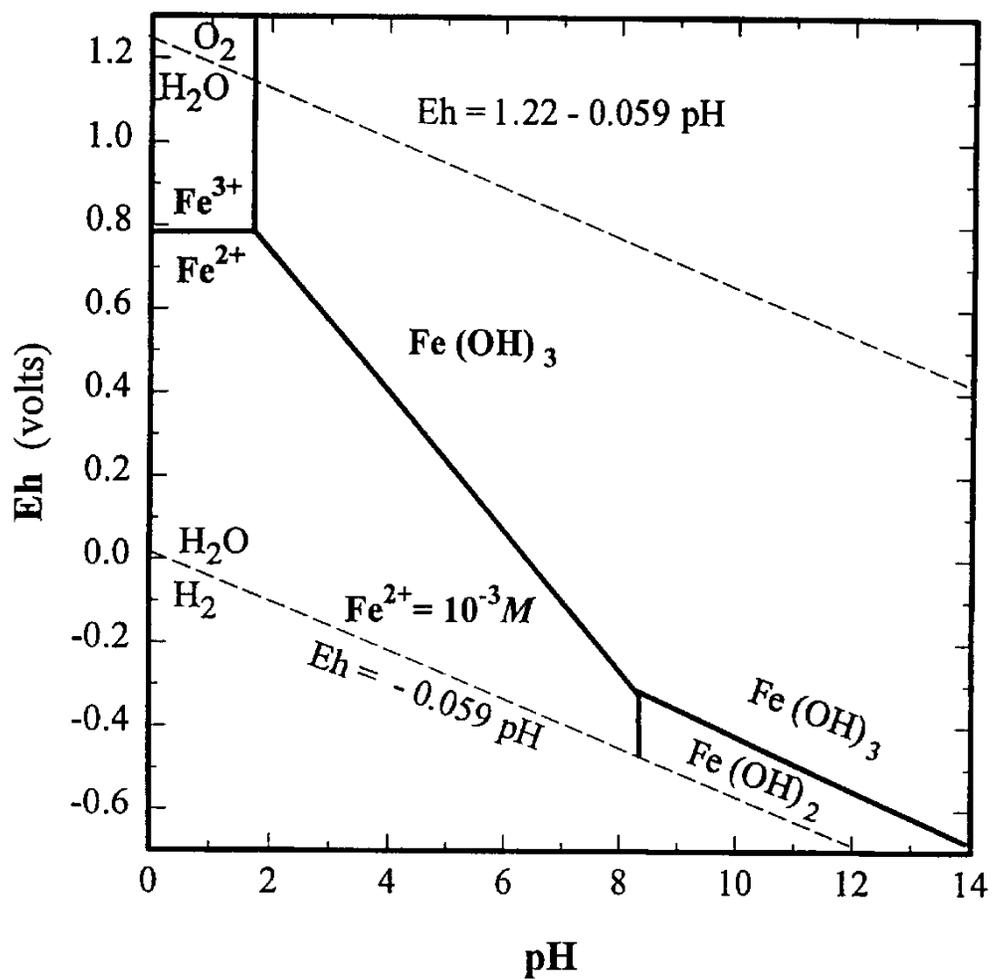
At the pH where our assumed iron concentration will cause precipitation of ferrous hydroxide, the relationship changes to: $\text{Fe}(\text{OH})_3 + \text{H}^+ + e^- \rightleftharpoons \text{Fe}(\text{OH})_2 + \text{H}_2\text{O}$ with an E° of -0.66 volts.

$$E_h = 0.166 - 0.059 \text{ pH} \quad (10)$$

Other phases such as Fe carbonates, Fe sulfides and Fe oxides could be added to this diagram as necessary for the system being considered. Bohn et al. 1985 discuss these diagrams as does McBride, 1994. The more complete discussion is contained in *Solution Minerals and Equilibria* by Garrels and Christ (1965). (Freeman Cooper. San Francisco, CA 94133.) This book is out of print, however if you ever get a chance to pickup a used copy do so!! It is an excellent introduction to geochemistry.

All of the thermodynamic data is based on the information given by Sadiq and Lindsay in Lindsay 1979.

Figure 9.1 Pourbaix diagram for iron in relation to Eh and pH



Review questions

1. Flooded soils may or may not exhibit low redox potentials. What are several reasons for this observation?
2. If sulfides were present in a soil, what might you infer about the nitrate and manganese levels?
3. Why are soils usually not at redox equilibrium?
4. Why do iron and chromium oxidize more readily at higher pH levels? Do they? How would you know?
5. Iron phosphates are considered to be more problematic as sources of P in aquatic systems that are reduced. Why? What other information would be useful to answer this question fully?
6. Why do reduced soils become more alkaline?
7. What conditions cause iron and manganese staining of toilet bowls?
8. Can you determine the chemical reactions taking place from a measurement of soil pH and Eh?
9. What are the bounds for Eh and pH in aqueous systems?
10. What type of work is done in redox cells?
11. Is the Eh of a sterilized soil likely to be high or low?
12. What compounds and/or elements are the electron acceptors and donors in the reduction of nitrate?
13. Why is it said that redox is a coupled reaction?