

REDOX POTENTIAL

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Introduction

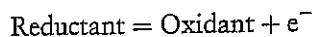
Geochemists, soil scientists, and limnologists have used redox potential (E_h) measurements to characterize oxidation–reduction status of surface environments. The redox potential of soil, water, and marine systems is a measure of electrochemical potential or electron availability within these systems. Electrons are essential to all inorganic and organic chemical reactions. Redox potential measurements allow for rapid characterization of the degree of reduction and for predicting stability of various compounds that regulate nutrients and metal availability in soil and sediment. Redox potential is diagnostic for determining whether an area is functioning as wetland or nonwetland.

Oxidation and reduction reactions regulate many of the biogeochemical reactions in surface environments. Redox potential (E_h) is determined from the concentration of oxidants and reductants in the environment. The inorganic oxidants include oxygen, nitrate, nitrite, manganese, iron, sulfate, and CO_2 , while the reductants include various organic substrates and reduced inorganic compounds.

Theoretical Relationships

Oxidation and reduction reactions involve transfer of electrons from one compound to another and play a major role in regulating many reactions in biological systems. Oxidation–reduction reactions are coupled reactions.

Oxidation is defined as removal of electrons from a compound. Such a compound is usually referred to as ‘electron donor’ or ‘reductant.’ During this process it is oxidized and increases its oxidation number:



Reduction is defined as the addition of electrons to a compound.

A compound that accepts electrons is usually referred to as ‘electron acceptor’ or ‘oxidant.’ During this process the compound is reduced and its oxidation number is decreased:



The tendency of compounds to accept or donate electrons is expressed as ‘reduction potential’ or ‘redox potential.’ The redox potential of a substance depends upon:

- Affinity of molecules for electrons;
- Concentration of reductants and oxidants (referred to as redox pair);

Reductants (electron donors) in wetland soils are:

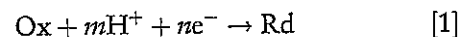
- Organic matter and various organic compounds;
- Reduced inorganic compounds such as NH_4^+ , Fe^{2+} , Mn^{2+} , S^{2-} , CH_4 , and H_2 .

Oxidants (electron acceptors) are inorganic compounds such as O_2 , NO_3^- , MnO_2 , FeOOH , SO_4^{2-} , and HCO_3^- .

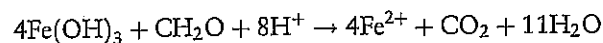
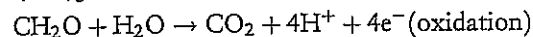
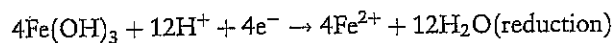
Anaerobic environments such as wetland soils are usually limited by electron acceptors and have an abundant supply of electron donors. Aerated soils are usually limited by electron donors and have an abundant supply of electron acceptors (primarily O_2).

Redox–pH Relationships

Redox reaction in surface environments can be represented by the following half-cell reduction equation:



where Ox is the oxidized component or electron acceptor, Rd is the reduced component or electron donor, m is the number of hydrogen ions involved in the reaction, and n is the number of electrons involved in the reaction. The electrons used in eqn [1] must be supplied by an accompanying half-cell oxidation reaction. In soils, organic matter (CH_2O) is the primary source of electrons. The oxidation reaction balances the reduction reaction. This is illustrated below with the reduction of $\text{Fe}(\text{OH})_3$:



The reduction reaction can be defined quantitatively through the change in Gibbs free energy (ΔG):

$$\Delta G = \Delta G^0 + RT \ln \left(\frac{\text{Rd}}{(\text{Ox})(\text{H}^+)^m} \right) \quad [2]$$

where ΔG^0 is the standard free energy change, R is the gas constant, and T is absolute temperature. The Nernst equation expresses the reduction reaction in terms of electrochemical energy (millivolts) using the relationship $\Delta G = -nEF$.

$$E_h = E^0 - \frac{RT}{nF} \ln \left(\frac{(\text{Rd})}{(\text{Ox})} \right) - \frac{mRT}{nF} \ln(\text{H}^+) \quad [3]$$

where E_h is the electrode potential, E^0 is the standard half-cell potential, F is the Faraday constant, n is the number of electrons exchanged in the half-cell reaction, m is the number of protons exchanged, and the activities of the various oxidized and reduced components are shown in parentheses. Substituting values of $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ for R , $9.65 \times 10^4 \text{ C mol}^{-1}$ for F , and 298 K for T , and using the relationship $\ln(x) = 2.303 \log(x)$, eqn [3] simplifies to:

$$E_h(\text{mV}) = E^0 - \frac{59}{n} \log \left(\frac{(\text{Rd})}{(\text{Ox})} \right) + 59 \frac{m}{n} \text{pH} \quad [4]$$

Inspection of eqns [3] and [4] reveals that redox potential (E_h) increases with increasing activity of the oxidized component, decreases with increasing activity of the reduced component, and increases with an increase in H^+ activity (or a decrease in pH).

Equation 4 shows the importance of pH in redox reactions. When the ratio of protons to electrons (m/n) is equal, there is a predicted 59 mV change in E_h per pH unit. The E_h/pH slope can vary depending on the oxidants and reductants involved.

The E_h/pH slope predicted from the Nernst equation assumes that the redox couple controls the pH of the system. This is only true for pure chemical solutions. Measured slopes in natural systems due to mixed potential or various redox couples deviate from the predicted values. Applying the 59 mV correction factor cannot be used under those conditions.

The reduction reaction in eqn [1] can also be defined by an equilibrium constant:

$$K = \frac{(\text{Rd})}{(\text{Ox})(e^-)^n(\text{H}^+)^m} \quad [5]$$

which can be rewritten in log form:

$$\log K = \log(\text{Rd}) - \log(\text{Ox}) - n \log(e^-) - m \log(\text{H}^+) \quad [6]$$

The $-\log(e^-)$ term in eqn [6] can be defined as pE (relative electron activity) in the same way pH is defined as $-\log(\text{H}^+)$. Rearranging eqn [5] yields:

$$\text{pE} + \text{pH} = \log K - \log(\text{Rd}) + \log(\text{Ox}) \quad [7]$$

Equation [7] can be used for plotting equilibrium solubility diagrams, because the pE + pH sum can be used

as one axis and species activity as the other axis. E_h is the more-common expression of soil redox potential, since it is readily determined with a platinum electrode. Soil pE can be calculated from E_h using eqn [8]:

$$\text{pE} = \frac{E_h(\text{mV})}{59} \quad [8]$$

Normal Limits of pH and Redox Potential (E_h) in the Environment

Carbon dioxide from the atmosphere and organic acids formed by decaying organic matter are the two sources of acidity in most near-surface environments, resulting in acid pHs in the range 5–6. Lower pHs are found in acid sulfate soils, where values as low as 4.0 are sometimes recorded. As a result, a pH of 4 can be selected as the usual lower limit of pHs in natural environments (Figure 1).

The upper end of the pH limits is associated with CO_2 -free water in contact with carbonate rocks and can acquire a pH of 10 and, in contact with some silicates, a pH up to nearly 11. But since most surface waters emit CO_2 to the atmosphere, such alkalinities are not attained. A reasonable upper limit of pH in most near-surface environments is near 9.0.

Oxygen is the strongest oxidizing agent commonly found in nature. Stronger agents than this cannot persist, because they react with water to liberate oxygen. Thus the upper limit of redox potentials is defined by the reaction:

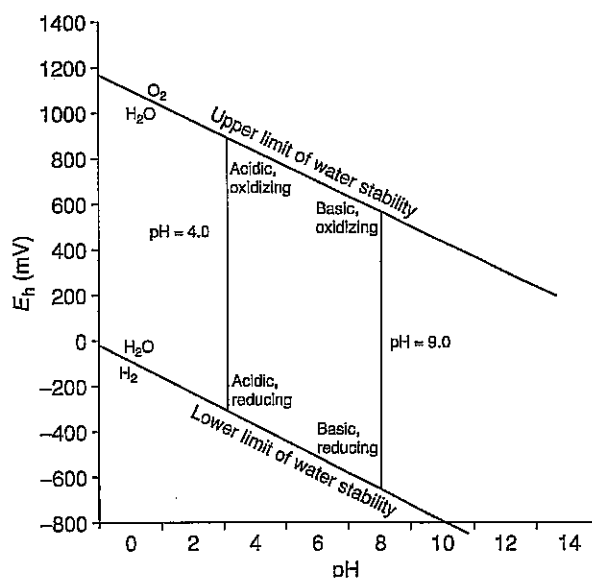
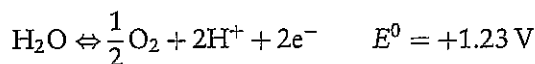
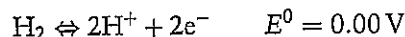


Figure 1 The E_h -pH range found in soil surface environments. Adapted from Krauskopf KB (1967) *Introduction to Geochemistry*. New York, NY: McGraw Hill.

The potential of this half-reaction, which reflects the upper limitations of water stability, clearly depends on the pH, as shown by the equation:

$$E = +1.23 + 0.03 \log[\text{O}_2]^{1/2} [\text{H}^+]^2$$

The lower limit of redox potential is that of the hydrogen reaction,



For which

$$\begin{aligned} E &= 0.00 + 0.03 \log[\text{H}^+]^2 - 0.03 \log[\text{H}_2] \\ &= -0.059 \text{ pH} - 0.03 \log[\text{H}_2] \end{aligned}$$

Since the pressure of hydrogen in surface environments could not exceed 101 kPa, the maximum possible reducing potential in the presence of water would be:

$$E_h = -0.059 \text{ pH} - 0.03 \log(1) = -0.059 \text{ pH}$$

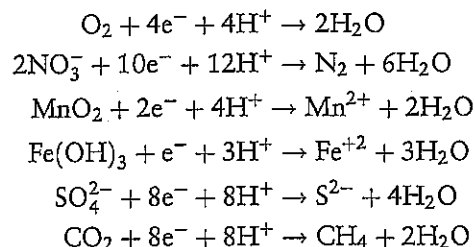
Aerobic and/or Anaerobic Redox Potential Range in the Environment

The E_h scale used to quantify reduction intensity (or oxidation intensity) in chemical and biological systems is shown in Figure 2. The scale is in electromotive force units or volts (or millivolts) and can be divided into zones ranging from oxidized (where the aerobes function) to highly reduced (where the methane producers and sulfate reducers function).

Typically in wetland soils, E_h values range from -300 to 700 mV, with a total range of approximately 1000 mV. In aerobic soils where the $\text{O}_2/\text{H}_2\text{O}$ redox couple functions, the E_h range is between 300 and 700 mV.

Redox Couples in Wetlands

Although several redox couples function in wetlands soils, the following are the most common reduction reactions involving a specific redox couple:



The various inorganic redox systems found in soil and sediment become unstable at critical redox potentials (Figure 3). Sequentially following flooding, oxygen is reduced first, followed by nitrate and oxidized manganese compounds, and then ferric iron compounds. After the reduction of ferric iron, the next redox compound to become unstable is sulfate, followed by the reduction of carbon dioxide to methane.

Soil redox potential represents an indication of the oxidation-reduction status of the various redox couples. For example, a redox potential of 0 mV indicates that oxygen and nitrate are not likely to be present and that the bioreducible iron and manganese compounds are in a reduced state. At this same potential, however, sulfate is stable in the soil with no production of sulfide, which is toxic to plants. A redox potential of +400 mV indicates that oxygen may be present even though there may be excess water.

Redox potential measurements in pure systems can be used to predict the ionic distribution between chemical species which may interact with the transfer of electrons, such as ferrous and ferric iron or nitrite and nitrate nitrogen. However, in natural systems, there are many redox couples present, and not all redox couples are chemically interactive with others. Unless the concentration of a given redox couple is relatively high, inert electrodes (generally platinum) used for redox measurements are not specific for a specific redox couple. The redox electrode responds to the collective electrochemical potentials of all redox couples present.

The measured redox potential in soil is generally a mixed potential which reflects a weighted average of the potentials contributed by each of the redox couples present. As a result of the continuous

Anaerobic					Aerobic	Sediment condition
Highly reduced	Reduced	Moderately reduced			Oxidized	Redox condition
CO_2	SO_4^{2-}	Fe^{3+}	Mn^{4+}	NO_3^-	O_2	Electron acceptor
Anaerobic					Microbial metabolism	
Facultative						
-300	-200	-100	0	+100 +200 +300	+400 +500 +600 +700	

Figure 2 Redox potential range in soil and sediment, showing the microbial metabolism process and electron acceptor.

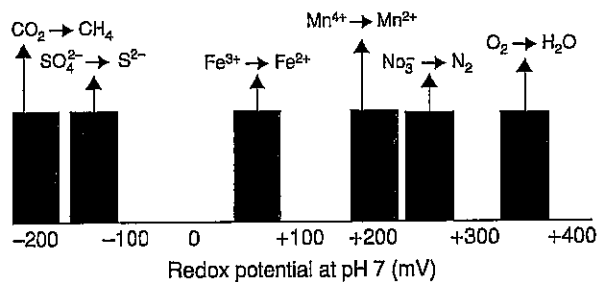


Figure 3 Critical redox potential for the transformation of redox couples.

addition of organic matter, which oxidizes and serves as an electron donor, a redox equilibrium is almost never attained in a natural system.

With the theoretical limitations involved in the use of redox potentials to quantitatively describe a specific ionic distribution in a mixed system, redox measurements can be successfully applied to characterize the oxidation-reduction transformations of many elements, including heavy metals and plant nutrients in soil.

Predicting Mineral Stability

E_h and pH can also be used for plotting stability fields for specific minerals. For example, the E_h -pH stability field for iron in Figure 4 can be interpreted that hematite (Fe_2O_3) is a stable iron mineral under oxidizing environments. Under reducing environments, a stable mineral may be pyrite. If dissolved sulfur is low, siderite (FeCO_3) may be the predominant mineral under reducing conditions.

Intensity and Capacity of Reduction

Redox potential measurement is only one measure of intensity of reduction in soils and sediment, as described below.

Intensity

The ease of reduction is represented by the free energy of reduction or equivalent electromotive forces of the reaction (oxidation-reduction potential or redox potential).

The reduction processes that take place in a soil as a result of the oxidation of organic matter utilizing alternate electron acceptors of nitrate, manganic manganese, ferric iron, sulfate, and carbon dioxide do not proceed together. As indicated previously, nitrate is utilized first after oxygen disappears, followed by manganic manganese, ferric iron, sulfate, and finally carbon dioxide. For this reason the soil must be considerably more reduced for sulfate to be

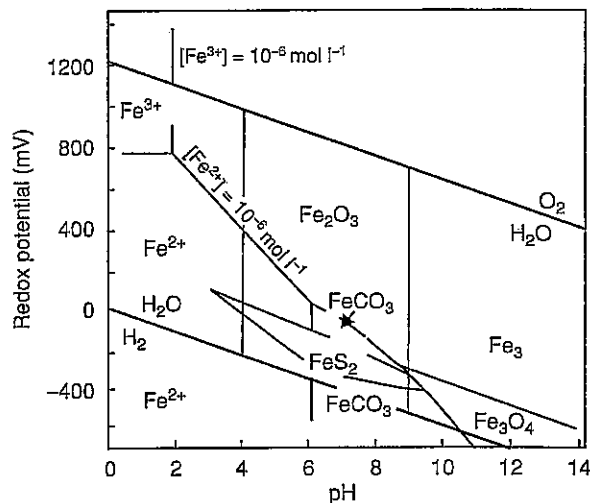


Figure 4 Redox-pH effect on stability of iron minerals. Adapted from Krauskopf KB (1967) *Introduction to Geochemistry*. New York, NY: McGraw Hill.

reduced than for nitrate to be reduced. If nitrate and sulfate and a suitable organic substrate are all present in a flooded, oxygen-deficient soil at the same time, the denitrifiers will reduce all of the nitrate before any of the sulfate is reduced by the sulfate reducers. The intensity of reduction is different for the two reduction processes. The soil is not very reduced (low reduction intensity or low electron pressure) for the reduction of nitrate, while it is very reduced during the reduction of sulfate (high reduction intensity or high electron pressure).

This intensity of reduction can be thought of in terms of the pressure of the electrons that the microorganisms need to dispense with as they carry out oxidation of the energy source. It does not require much electron pressure for the nitrate to accept electrons (and even less electron pressure for oxygen, if it is present, to accept electrons). This is why a large energy yield can be obtained from the oxidation of the energy source, since not so much of the possible energy from the oxidation process is utilized in forcing the electron acceptor to accept the electrons from the organic matter oxidation.

Electron acceptors that are difficult to reduce require more electron pressure to force the electrons to move to the electron acceptor. For example, sulfate reducers in soil and sediment can oxidize organic substrates, but a great deal of the energy derived from the oxidation is required to force the sulfate ion to accept the electrons and be converted to sulfide. This leaves less energy than the microorganism derives from the reaction that it can use for its energy needs. A great intensity of reduction is required for

sulfate to accept the electrons produced during the oxidation of the energy source.

This approach to determine the intensity of reduction is called the oxidation-reduction or redox potential of the soil. Measurement of redox potential is conducted by placing a platinum electrode in the soil, connecting it to a suitable circuit that balances and measures the electron pressure from the reduction processes.

Reduction capacity described below differs from intensity of reduction.

Capacity

The total amount of electrons accepted by oxidants or number and redox system undergoing reduction is the 'capacity.' The capacity can be best described in terms of its O_2 equivalent (not redox potential measurement).

The capacity factor of the various redox systems varies from one soil to another. The amount of oxygen present in the soil at the time of flooding is usually low. The amount of NO_3^- present in the soil is dependent on soil organic matter and can be variable. Biologically reducible Mn can be present in soils at varying levels (less than 100 to 1000 mg kg⁻¹), while reducible Fe can be in the range of 500–3000 mg kg⁻¹ of soil.

Although the critical redox potential at which the inorganic redox systems become unstable provides valuable information, it does not provide any indication of the total capacity of the system to accept electrons or support microbial respiration. Capacity factor is equivalent to the total amount of electrons accepted by the oxidants in support of microbial respiratory activity. The redox couple present in lowest quantity has the smallest capacity for supporting microbial respiration. In mineral-flooded soils, reducible Mn and Fe primarily support the organic matter decomposition. In estuarine areas that receive sea water containing large amounts of SO_4^{2-} , the reduction of SO_4^{2-} to S^{2-} supports the microbial respiratory activities.

Redox Condition and Metal/Metalloid Chemistry

Redox conditions of soil and sediment deposits also govern heavy metal chemistry (Figure 5). For example, chromium can exist in several oxidation states from Cr(0), the metallic form, to Cr⁶⁺. The most stable oxidation states of chromium in the environment are Cr³⁺ and Cr⁶⁺. Besides the elemental metallic form, which is extensively used in alloys,

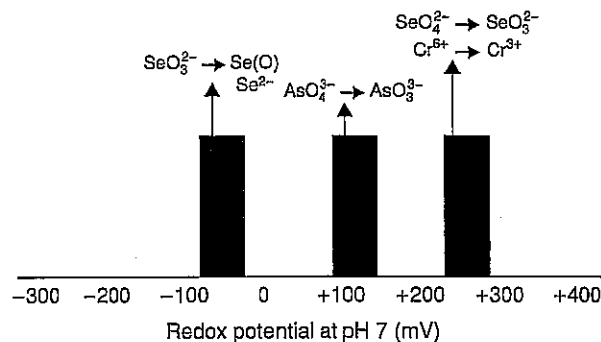


Figure 5 Redox potential as related to metal and/or metalloid chemistry or transformation.

chromium has three important valence forms: Cr²⁺, Cr³⁺, and Cr⁶⁺.

The trivalent chromic Cr³⁺ and the tetravalent dichromate Cr⁶⁺ are the most important forms in the environmental chemistry of waters and sediments. The presence of chromium Cr⁶⁺ is of particular importance, because in this oxidation state Cr is water-soluble and extremely toxic. They are also the only forms that undergo valence changes in the E_h -pH ranges encountered in natural systems. The solubility and potential toxicity of the chromium that enters into aquatic or sediment columns are governed to a large extent by oxidation-reduction reactions. Cr⁶⁺ reduces to Cr³⁺ at approximately +300 mV (Figure 5).

Oxidation-reduction processes also play a role in arsenic (As) and selenium (Se) chemistry (Figure 5). For the pH and redox conditions in most soils and sediments, As exists as an oxyanion in the arsenate ($H_2AsO_4^-$ and $HAsO_4^{2-}$, As⁵⁺) or arsenite [H_3AsO_3 ; As³⁺] form. Monomethylarsenic acid (MMAA) and dimethylarsenic acid (DMAA) are important organoarsenic chemical species. Se occurs as selenate (SeO_4^{2-} , Se⁶⁺), selenite ($HSeO_3^-$ and SeO_3^{2-} ; Se⁴⁺), and elemental selenium (Se(0)), but selenide (DMS₂Se) is the most important. At higher soil redox levels (+200 to +500 mV), As⁵⁺ is the predominant As species present. The reduction of As⁵⁺ to As³⁺ occurs at redox levels corresponding within the nitrate-reducing zone of soils characterized by a soil redox level of approximately +300 mV. When Fe reduction starts and soil redox levels drop below +50 mV, selenite is reduced to elemental Se or metal selenides. Reoxidation of reduced As and Se species occurs at similar soil redox levels to those identified for reduction reactions. Both microbial-mediated and chemical-oxidation processes are thought to be involved in the oxidation of reduced As and Se species.

Measurement of Redox Potential

Inert metal electrodes (usually platinum) are widely used to measure the oxidation-reduction potentials of chemical systems. The inert metal electrode is used in conjunction with a reference electrode to form a complete cell. The most widely used reference electrodes for redox potential measurement are the calomel (mercury-mercurous chloride) and the silver/chloride electrode. The redox potential (E_h) is obtained from the potential of the cell (E) by adding the appropriate value for the reference electrode potential corrected for liquid junction effects. The potential measured with the platinum electrode and the secondary reference electrode must be corrected to give true E_h or redox potential.

The platinum electrode referenced to a saturated calomel electrode will give E_h or millivolt readings, provided corrections are made for the potential of the calomel electrode.

Performance of the platinum electrodes is checked by immersing the platinum electrode along with the reference calomel electrode in pH 4.00 and pH 7.00 buffer to which a small amount of quinhydrone has been added. The reading on the E_h meter in millivolts should agree with that shown in Table 1. The meter reading is corrected relative to hydrogen by adding the calomel potential (Table 1). This value is the quinhydrone E_h in millivolts relative to hydrogen. For example, a meter reading of 218 mV at 25°C for quinhydrone in pH 4.00 buffer gives an E_h of 462.3 mV:

$$E_h = \text{meter reading} + \text{calomel potential}$$

$$E_h = 218.0 + 244.3 = 462.3 \text{ mV}$$

An electrode is considered satisfactory if it does not deviate from the above values by more than 5 mV.

When making soil E_h measurements, the calomel potential must be added to the meter reading (millivolts). The procedure is as follows:

The potential is measured by inserting the electrodes in the substance to be measured and reading the millivolt scale on the pH meter. Since the calomel

Table 1 Effect of temperature on the standard potential of a calomel half-cell and platinum electrode

Temperature (°C)	Calomel potential (mV)	Meter reading ^a	
		pH 4 (mV)	pH 7 (mV)
5	257.0	236.0	66.5
10	253.9	231.6	60.1
15	250.8	227.3	53.7
20	247.3	222.7	47.3
25	244.3	218.0	40.8
30	240.9	213.4	34.3
35	237.5	208.5	27.7
40	234.1	203.5	21.0
45	230.6	198.4	14.2

^aMeter reading with platinum and calomel electrode immersed in buffer saturated with quinhydrone.

electrode is used as a reference, +244.3 mV is added to the recorded potential for reference to the hydrogen electrode.

Further Reading

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