8

REDOX CHEMISTRY OF SOILS

OXIDATION–REDUCTION REACTIONS AND POTENTIALS

Soil chemical reactions involve some combination of proton and electron transfer. Oxidation occurs if there is a loss of electrons in the transfer process while reduction occurs if there is a gain of electrons. The oxidized component or oxidant is the electron acceptor and the reduced component or reductant is the electron donor. Table 8.1 lists oxidants and reductants found in natural environments. The electrons are not free in the soil solution, thus the oxidant must be in close contact with the reductant. Both oxidation and reduction must be considered to completely describe oxidation–reduction (redox) reactions (Bartlett and James, 1993; Patrick *et al.*, 1995).

To determine if a particular reaction will occur (i.e., the Gibbs free energy for the reaction, $\Delta G_r < 0$), one can write reduction and oxidation half-reactions (a half-reaction or half-cell reaction can be referred to as a redox couple) and calculate equilibrium constants for the half-reactions. Redox reactions of soil oxidants can be defined conventionally by the following general half-reduction reaction (Patrick *et al.*, 1995);

$$\text{Ox} + m\text{H}^+ + ne^- \longrightarrow \text{Red}, \tag{8.1}$$

where Ox is the oxidized component or the electron acceptor, Red is the reduced component or electron donor, m is the number of hydrogen ions participating in the reaction, and n is the number of electrons involved in the reaction. The electrons in Eq. (8.1) must be supplied by an accompanying oxidation half-reaction. For example, in soils, soil organic matter is the pri-

TABLE 8.1. Selected Reduction Half-Reactions Pertinent to Soil, Natural Water, Plant, and Microbial Systems[a]

Half-reaction	log $K^{o\,b}$	pe^{c} pH 5	pe^{c} pH 7
Nitrogen species			
$1/2N_2O + e^- + H^+ = 1/2N_2 + 1/2H_2$	29.8	22.9	20.9
$NO + e^- + H^+ = 1/2N_2O + 1/2H_2O$	26.8	19.8	17.8
$1/2NO_2^- + e^- + 3/2H^+ = 1/4N_2O + 3/4H_2O$	23.6	15.1	12.1
$1/5NO_3^- + e^- + 6/5H^+ = 1/10N_2 + 3/5H_2O$	21.1	14.3	11.9
$NO_2^- + e^- + 2H^+ = NO + H_2O$	19.8	9.8	5.8
$1/4NO_3^- + e^- + 5/4H^+ = 1/8N_2O + 5/8H_2O$	18.9	12.1	9.6
$1/6NO_2^- + e^- + 4/3H^+ = 1/6NH_4^+ + 1/3H_2O$	15.1	8.4	5.7
$1/8NO_3^- + e^- + 5/4H^+ = 1/8NH_4^+ + 3/8H_2O$	14.9	8.6	6.1
$1/2NO_3^- + e^- + H^+ = 1/2NO_2^- + 1/2H_2O$	14.1	9.1	7.1
$1/6NO_3^- + e^- + 7/6H^+ = 1/6NH_2OH + 1/3H_2O$	11.3	5.4	3.1
$1/6N_2 + e^- + 4/3H^+ = 1/3NH_4^+$	4.6	−0.7	−3.3
Oxygen species			
$1/2O_3 + e + H^+ = 1/2O_2 + 1/2H_2O$	35.1	28.4	: 26.4
$OH\cdot + e^- = OH^-$	33.6	33.6	33.6
$O_2^- + e^- + 2H^+ = H_2O_2$	32.6	22.6	18.6
$1/2H_2O_2 + e^- + H^+ = H_2O$	30.0	23.0	21.0
$1/4O_2 + e^- + H^+ = 1/2H_2O$	20.8	15.6	13.6
$1/2O_2 + e^- + H^+ = 1/2H_2O_2$	11.6	8.2	6.2
$O_2 + e^- = O_2^-$	−9.5	−6.2	−6.2
Sulfur species			
$1/8SO_4^{2-} + e^- + 5/4H^+ = 1/8H_2S + 1/2H_2O$	5.2	−1.0	−3.5
$1/2SO_4^{2-} + e^- + 2H^+ = 1/2SO_2 + H_2O$	2.9	−7.1	−11.1
Iron and manganese compounds			
$1/2Mn_3O_4 + e^- + 4H^+ = 3/2Mn^{2+} + 2H_2O$	30.7	16.7	8.7
$1/2Mn_2O_3 + e^- + 3H^+ = Mn^{2+} + 3/2H_2O$	25.7	14.7	8.7
$Mn^{3+} + e^- = Mn^{2+}$	25.5	25.5	25.5
$\gamma MnOOH + e^- + 3H^+ = Mn^{2+} + 2H_2O$	25.4	14.4	8.4
$0.62MnO_{1.8} + e^- + 2.2H^+ = 0.62Mn^{2+} + 1.1H_2O$	22.1	13.4	8.9
$1/2Fe_3(OH)_8 + e^- + 4H^+ = 3/2Fe^{2+} + 4H_2O$	21.9	7.9	−0.1
$1/2MnO_2 + e^- + 2H^+ = 1/2Mn^{2+} + H_2O$	20.8	12.8	8.8
$[Mn^{3+}(PO_4)_2]^{3-} + e^- = [Mn^{2+}(PO_4)_2]^{4-}$	20.7	20.7	20.7
$Fe(OH)_2^+ + e^- + 2H^+ = Fe^{2+} + 2H_2O$	20.2	10.2	6.2
$1/2Fe_3O_4 + e^- + 4H^+ = 3/2Fe^{2+} + 2H_2O$	17.8	3.9	−4.1
$MnO_2 + e^- + 4H^+ = Mn^{3+} + 2H_2O$	16.5	0.54	−7.5
$Fe(OH)_3 + e^- + 3H^+ = Fe^{2+} + 3H_2O$	15.8	4.8	−1.2
$Fe(OH)^{2+} + e^- + H^+ = Fe^{2+} + 2H_2O$	15.2	10.2	8.2
$1/2Fe_2O_3 + e^- + 3H^+ = Fe^{2+} + 3/2H_2O$	13.4	2.4	−3.6
$FeOOH + e^- + 3H^+ = Fe^{2+} + 2H_2O$	13.0	2.0	−4.0
$Fe^{3+} + e^- = Fe^{2+}$ phenanthroline	18.0	—[d]	—
$Fe^{3+} + e^- = Fe^{2+}$	13.0	13.0	13.0
$Fe^{3+} + e^- = Fe^{2+}$ acetate	—	5.8	—
$Fe^{3+} + e^- = Fe^{2+}$ malonate	—	4.4 (pH 4)	—
$Fe^{3+} + e^- = Fe^{2+}$ salicylate	—	4.4 (pH 4)	—
$Fe^{3+} + e^- = Fe^{2+}$ hemoglobin	—	—	2.4
$Fe^{3+} + e^- = Fe^{2+}$ cyt b_3 (plants)	—	—	0.68
$Fe^{3+} + e^- = Fe^{2+}$ oxalate	—	—	0.034
$Fe^{3+} + e^- = Fe^{2+}$ pyrophosphate	−2.4	—	—
$Fe^{3+} + e^- = Fe^{2+}$ peroxidase	—	—	−4.6

(Continues)

TABLE 8.1. *(Continued)*

Half-reaction	log K^{ob}	pe^c pH 5	pe^c pH 7
$Fe^{3+} + e^- = Fe^{2+}$ ferredoxin (spinach)	—	—	-7.3
$1/3KFe_3(SO_4)_2(OH)_6 + e^- + 2H^+ = Fe^{2+} + 2H_2O + 2/3SO_4^{2-} + 1/3K^+$	8.9	6.9	2.9
$[Fe(CN)_6]^{3-} + e^- = [Fe(CN)_6]^{4-}$	—	—	6.1
Carbon species			
$1/2CH_3OH + e^- + H^+ = 1/2CH_4 + 1/2H_2O$	9.9	4.9	2.9
$1/2o\text{-quinone} + e^- + H^+ = 1/2diphenol$	—	—	5.9
$1/2p\text{-quinone} + e^- + H^+ = 1/2hydroquinone$	—	—	4.7
$1/12C_6H_{12}O_6 + e^- + H^+ = 1/4C_2H_5OH + 1/4H_2O$	4.4	0.1	-1.9
$Pyruvate + e^- + H^+ = lactate$	—	—	-3.1
$1/8CO_2 + e^- + H^+ = 1/8CH_4 + 1/4H_2O$	2.9	-2.1	-4.1
$1/2CH_2O + e^- + H^+ = 1/2CH_3OH$	2.1	-2.9	-4.9
$1/2HCOOH + e^- + H^+ = 1/2CH_2O + 1/2H_2O$	1.5	-3.5	-5.5
$1/4CO_2 + e^- + H^+ = 1/24C_6H_{12}O_6 + 1/4H_2O$	-0.21	-5.9	-7.9
$1/2deasc + e^- + H^+ = 1/2asc$	1.0	-3.5	-5.5
$1/4CO_2 + e^- + H^+ = 1/4CH_2O + 1/4H_2O$	-1.2	-6.1	-8.1
$1/2CO_2 + e^- + H^+ = 1/2HCOOH$	-1.9	-6.7	-8.7
Pollutant/nutrient group			
$Co^{3+} + e^- = Co^{2+}$	30.6	30.6	30.6
$1/2NiO_2 + e^- + 2H^+ = 1/2Ni^{2+} + H_2O$	29.8	21.8	17.8
$PuO_2^+ + e^- = PuO_2$	26.0	22.0	22.0
$1/2PbO_2 + e^- + 2H^- = 1/2Pb^{2+} + H_2O$	24.8	16.8	12.8
$PuO_2 + e^- + 4H^+ = Pu^{3+} + 2H_2O$	9.9	-6.1	-14.1
$1/3HCrO_4^- + e^- + 4/3H^+ = 1/3Cr(OH)_3 + 1/3H_2O$	18.9	10.9	8.2
$1/2AsO_4^{3-} + e^- + 2H^+ = 1/2AsO_2^- + H_2O$	16.5	6.5	2.5
$Hg^{2+} + e^- = 1/2Hg_2^{2+}$	15.4	13.4	13.4
$1/2MoO_4^{2-} + e^- + 2H^+ = 1/2MoO_2 + H_2O$	15.0	3.0	-1.0
$1/2SeO_4^{2-} + e^- + H^+ = 1/2SeO_3^{2-} + 1/2H_2O$	14.9	9.9	7.9
$1/4SeO_3^{2-} + e^- + 3/2H^+ = 1/4Se + 3/4H_2O$	14.8	6.3	3.3
$1/6SeO_3^{2-} + 4/3H^+ = 1/6H_2Se + 1/2H_2O$	7.62	1.0	-1.7
$1/2VO_2^+ + e^- + 1/2H_3O^+ = 1/2V(OH)_3$	6.9	2.4	1.4
$Cu^{2+} + e^- = Cu^+$	2.6	2.6	2.6
$PuO_2 + e^- + 3H^+ = PuOH^{2+} + H_2O$	2.9	-8.1	-14.1
Analytical couples			
$CeO_2 + e^- + 4H^+ = Ce^{3+} + 2H_2O$	47.6	31.6	23.6
$1/2ClO^- + e^- + H^+ = 1/2Cl^- + 1/2H_2O$	29.0	24.0	22.0
$HClO + e^- = 1/2Cl_2 + H_2O$	27.6	20.6	18.6
$1/2Cl_2 + e^- = Cl^-$	23.0	25.0	25.0
$1/6IO_3^- + e^- + H^+ = 1/6I^- + 1/2H_2O$	18.6	13.6	11.6
$1/2Pt(OH)_2 + e^- + H^+ = 1/2Pt + H_2O$	16.6	11.6	9.6
$1/2I_2 + e^- = I^-$	9.1	11.1	11.1
$1/2Hg_2Cl_2 + e^- = Hg + Cl^-$	4.5	3.9	3.9
$e^- + H^+ = 1/2H_2$	0	-5.0	-7
$1/2PtS + e^- + H^+ = 1/2Pt + 1/2H_2S$	-5.0	-10.0	-12.0

[a] From Bartlett and James (1993), with permission.

[b] Calculated for reaction as written according to Eq. (8.14). Free energy of formation data were taken from Lindsay (1979) as a primary source, and when not available from that source, from Garrels and Christ (1965) and Loach (1976).

[c] Calculated using tabulated log K^o values, reductant and oxidant = $10^{-4} M$ soluble ions and molecules, activities of solid phases = 1; partial pressures for gases that are pertinent to soils: 1.01×10^{-4} MPa for trace gases, 2.12×10^{-2} MPa for O_2, 7.78×10^{-2} MPa for N_2, and 3.23×10^{-5} MPa for CO_2.

[d] Values not listed by Loach (1976).

mary source of electrons. Thus, to completely describe a redox reaction, an oxidation reaction must balance the reduction reaction.

Let us illustrate these concepts for the redox reaction of $Fe(OH)_3$ reduction (Patrick et al., 1995):

$$4Fe(OH)_3 + 12H^+ + 4e^- \longrightarrow 4Fe^{2+} + 12H_2O \text{ (reduction)} \qquad (8.2)$$

$$CH_2O + H_2O \longrightarrow CO_2 + 4H^+ + 4e^- \text{ (oxidation)} \qquad (8.3)$$

$$4 Fe(OH)_3 + CH_2O + 8H^+ \longrightarrow 4Fe^{2+} + CO_2 + 11H_2O \text{ (net reaction)}, \qquad (8.4)$$
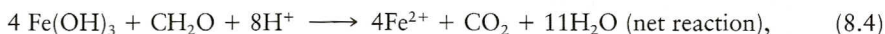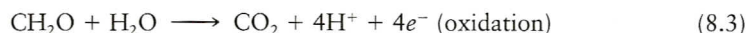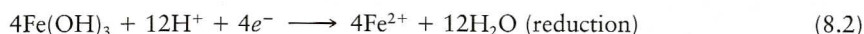
where CH_2O is soil organic matter. Equation (8.2) represents the reduction half-reaction and Eq. (8.3) represents the oxidation half-reaction. The reduction [Eq. (8.2)] reaction can also be described by calculating ΔG_r, the Gibbs free energy for the reaction,

$$\Delta G_r = \Delta G_r^\circ + RT \ln (Red)/(Ox)(H^+)^m, \qquad (8.5)$$

where ΔG_r° is the standard free energy change for the reaction. The Nernst equation can be employed to express the reduction reaction in terms of electrochemical energy (millivolts) using the expression $\Delta G_r = -nFE$ such that (Patrick et al., 1995)

$$Eh = E^\circ - RT/nF \ln(Red)/(Ox) - mRT/nF \ln H^+, \qquad (8.6)$$

where Eh is the electrode potential, or in the case of the reduction half-reaction in Eq. (8.2), a reduction potential, E° is the standard half-reaction reduction potential [with each half-reaction, for example, Eqs. (8.2) and (8.3) there is a standard potential; the standard potential means the activities of all reactants and products are unity], 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 oxidized and reduced species are in parentheses. Determination of Eh will provide quantitative information on electron availability and can be either an oxidation or reduction potential depending on how the reaction is written [see Eqs. (8.2)–(8.3)]. Oxidation potentials are more often used in chemistry, while in soil chemistry reduction potentials are more frequently used to describe soil and other natural systems (Patrick et al., 1995). It should also be pointed out that the Nernst equation is valid for predicting the activity of oxidized and reduced species only if the system is at equilibrium, which is seldom the case for soils and sediments. As noted in Chapter 7, the heterogeneity of soils which promotes transport processes causes many soil chemical reactions to be very slow. Thus, it is difficult to use Eh values to quantitatively measure the activities of oxidized and reduced species for such heterogeneous systems (Bohn, 1968).

Using the values of 8.31 J K^{-1} mol^{-1} for R, 9.65×10^4 C mol^{-1} for F, and 298K for T and the relationship $\ln (x) = 2.303 \log(x)$, Eq. (8.6) becomes

$$Eh(mV) = E^\circ - 59/n \log (Red)/(Ox) + 59 \, m/n \, pH. \qquad (8.7)$$

It is obvious from Eqs. (8.6)–(8.7) that Eh increases as the activity of the oxidized species increases, decreases with increases in the activity of the reduced species, and increases as H^+ activity increases or pH decreases. If the

ratio of protons to electrons is 1 (i.e., $m/n = 1$), one would predict that Eh would change by 59 mV for every unit change in pH. Thus, one could predict the Eh at various pH values by using the 59-mV factor. However, this relationship assumes that redox controls the pH of the system. This assumption is valid for solutions, but in soils pH buffering is affected by soil components such as silicates, carbonates, and oxides, which are not involved in redox reactions. Thus, it may be inappropriate to apply the 59-mV factor (Patrick *et al.,* 1995).

Eh is positive and high in strongly oxidizing systems while it is negative and low in strongly reducing systems. (There is not a neutral point, as one observes with pH.) Eh, like pH, is an intensity factor.

Eh VS pH AND pe VS pH DIAGRAMS

Diagrams of the activities of Eh vs pH can be very useful in delineating the redox status of a system. Figure 8.1 shows such a diagram for soils. The pH range was more narrow in reduced soils (negative Eh) than in oxidized soils (positive Eh). Based on these results, Baas Becking *et al.* (1960) divided the soils into three categories: normal (oxidized), wet (seasonally saturated), and waterlogged (semipermanently saturated) (Fig. 8.1).

The reduction half-reaction given in Eq. (8.1) can also be expressed in terms of an equilibrium constant $K°$ (Patrick *et al.,* 1995)

$$K° = (Red)/(Ox)(e^-)^n(H^+)^m. \qquad (8.8)$$

Expressed in log form Eq. (8.8) becomes

$$\log K° = \log(Red) - \log(Ox) - n\log(e^-) - m\log(H^+). \qquad (8.9)$$

The $-\log(e^-)$ term in Eq. (8.9) is defined as pe in a similar way as pH is expressed as $-\log(H^+)$. The pe is an intensity factor as it is an index of the electron free energy level per mole of electrons (Ponnamperuma, 1972). Thus, pe and pH are master variables of a soil and must be known to completely
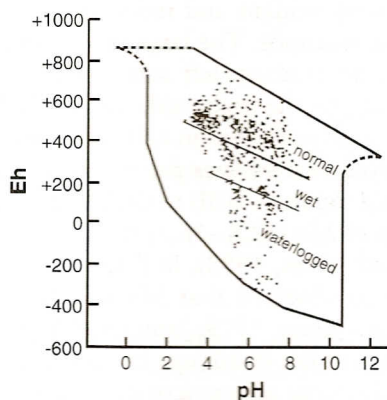

FIGURE 8.1.   Eh–pH characteristics of soils. From Baas Becking *et al.* (1960), with permission.

understand the equilibrium state of a soil. Moreover, to fully determine the redox status of a soil, pe and pH cannot be separated (Bartlett and James, 1993). In strongly oxidizing systems the e^- activity is low and pe is large and positive. In reducing systems pe is small and negative. The pe range of most soils is -6 to $+12$ (Lindsay, 1979). Rearranging Eq. (8.9) one arrives at an expression, given below, that relates pe to pH

$$p e = [(\log K° - \log (\text{Red}) + \log (\text{Ox}))/n] - m/n \text{ pH}. \quad (8.10)$$

Equation (8.10) represents a straight line with a slope of m/n and an intercept given in brackets. The intercept is a function of log $K°$ for the half-reaction and the activities of the oxidized and reduced species. When there is a one-electron transfer (i.e., $n = 1$) and consumption of one proton (i.e., $m = 1$), and when (Red) = (Ox), Eq. (8.10) is simplified to

$$p e + \text{pH} = \log K°. \quad (8.11)$$

At pH = 0,

$$p e = \log K°. \quad (8.12)$$

One can relate log $K°$ to $\Delta G_r°$ using the following equations.

$$\Delta G_r° = -RT \ln K°. \quad (8.13)$$

At 298K and converting to log,

$$-\Delta G_r°/5.71 = \log K°, \quad (8.14)$$

where 5.71 is derived from the product of $(RT)(2.303)$, R is (0.008314 kJ mol^{-1} K^{-1}), and $T = 298.15$K. Therefore, log $K°$ could be estimated by knowing the free energies of formation ($\Delta G_f°$) of H_2O and the Red and Ox species since those for H^+ and e^- are zero by convention (Bartlett and James, 1993).

Information in Box 8.1 shows how one would calculate log $K°$ and pe for a reduction half-reaction at pH 5 and 7 using Eqs. (8.11)–(8.14).

The values of log $K°$ can be used to predict if a reduction and oxidation reaction will combine to effect the transfer of electrons from reductant to oxidant. Table 8.1 lists a number of reduction half-reactions important in natural systems. The log $K°$ values are given in descending order and are pe values at pH 0, when the activities of oxidant and reductant are 1, and are standard reference pe values for the reactions. The larger the values of log $K°$ or pe the greater the tendency for an oxidant (left side of the half-reaction equation) to be reduced (converted to the right side of the half-reaction equation). Therefore, an oxidant in a given reduction half-reaction can oxidize the reductant in another half-reaction with a lower pe, at a particular pH. As an example, Mn(III, IV) oxides could oxidize Cr(III) to Cr(VI) at pH 5 because the range of pe values for reduction of Mn (12.8–16.7) is higher than that for Cr(VI) reduction (10.9) (Bartlett and James, 1993). In field moist soils over a pH range of 4–7 it has indeed been observed that Mn (III, IV) oxides can oxidize Cr(III) to Cr(VI) (Bartlett and James, 1979; James and Bartlett, 1983).

The pe–pH relationship expressed in Eq. (8.10) can be used to determine if an oxidation–reduction reaction can occur spontaneously, i.e., $\Delta G_r < 0$. Figure 8.2 shows pe vs pH stability lines between oxidized and reduced species for several redox couples. If thermodynamic equilibrium is present, the oxidized

BOX 8.1.   Calculation of log $K°$ and pe

The reduction half-reaction below (see Table 8.1) shows the reduction of Fe^{3+} to Fe^{2+},

$$Fe(OH)^{2+} + e^- + H^+ = Fe^{2+} + 2H_2O. \qquad (8.1a)$$
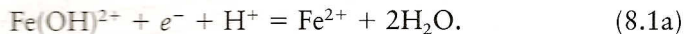
In this reaction there is one electron transfer, i.e., n in Eq. (8.8) is 1 and there is consumption of one proton, i.e., $m = 1$, and $(Fe^{3+}) = (Fe^{2+})$ is an imposed condition. Thus Eq. (8.10) reduces to Eq. (8.11) and at pH 0, Eq. (8.12) results. Relating $\ln K°$ to $\Delta G_r°$, one can employ Eq. (8.13),

$$\Delta G_r° = -RT \ln K°.$$

We know from Eq. (4.7) that

$$\Delta G_r° = \Sigma \Delta G_f° \text{ products} - \Sigma \Delta G_f° \text{ reactants.}$$

Solving $\Delta G_r°$ for Eq. (8.1a) above,

$$\begin{aligned}
\Delta G_r° &= [(-91.342 \text{ kJ mol}^{-1}) + (-237.52 \text{ kJ mol}^-)] \\
&\quad - [(-241.85 \text{ kJ mol}^{-1}) + (0)] \\
&= [-328.86 \text{ kJ mol}^{-1} + 241.85 \text{ kJ mol}^{-1}] \\
&= -87.01 \text{ kJ mol}^{-1}.
\end{aligned} \qquad (8.1b)$$

Using Eq. (8.14),

$$\log K° = \frac{87.01}{5.71} = 15.2. \qquad (8.1c)$$

This value for $\log K°$ is the one shown in Table 8.1 for the reaction in Eq. (8.1a).

To calculate pe at pH 5 and pH 7, one would use Eq. (8.12). For pH 5 and substituting in the value of 15.2 for $\log K°$,

$$pe = \log K° - pH$$

$$pe = 15.2 - 5 = 10.2.$$

For pH 7,

$$pe = 15.2 - 7 = 8.2.$$

These are the pe values shown in Table 8.1 for the reduction half-reaction in Eq. (8.1a).