Oxidation-Reduction (Redox) Reactions and Potentials

Oxidation-reduction reactions are very important in natural water systems. In fact, all aquatic organisms obtain their energy for metabolic processes from redox reactions. Photosynthetic organisms catalytically reduce carbon dioxide to reduced organic matter by trapping light energy, while nonphotosynthetic organisms catalytically decompose the organic products of photosynthesis through energy-yielding redox reactions. Nitrogen, which is one of the major elements in the terrestrial and aquatic environments, circulates by many microbially catalyzed redox reactions. In fact, the only non-redox process in the entire nitrogen cycle is ammonia integration with and liberation from nitrogen-containing organic matter. The movements of many other elements also involve redox reactions, such as carbon, iron, and sulfur (Snoeyink, 1996).

Redox potentials (E), like free energy (G), are not absolute. The former are measured with reference to the reduction of hydrogen ions to hydrogen gas at standard state conditions: 25 degrees Celsius (°C), 1 atmospheric pressure, and one unit activity for all species. The potential of this reaction, by convention, is taken as zero. Furthermore, redox potentials are comprised of two parts: the oxidation potential, and the reduction potential. The potential of the overall reaction at the standard state can be shown by the following equation (Snoeyink, 1996):

$$E^o = E^o_{ox} + E^o_{red} \qquad \text{Eq. 2-1}$$

where E^o_{ox} and E^o_{red} are oxidation half reaction and reduction half reaction, respectively. For nonstandard states, the redox potential (E) may be related to standard potential by the Nernst equation (Snoeyink, 1996):

$$E = E^o - RT/nF \ln Q \qquad \text{Eq. 2-2}$$

where R = gas constant
T = absolute temperature, ^oK
n = number of electrons involved in the reaction
F = the Faraday number
Q = the reaction quotient

The redox potential is sometimes called the electrochemical version of Gibbs free Energy, ΔG. E and E^o may be related to ΔG and ΔG^o, respectively, by (Snoeyink, 1996):

$$\Delta G^o = -nFE^o \qquad \text{Eq. 2-3}$$

or

$$\Delta G = -nFE \qquad \text{Eq. 2-4}$$

Sequence of Redox Reactions

Redox potentials were important in this study because only certain redox reactions occur at a given redox level. If redox reactions occurred in the order of their thermodynamic possibility, reductants (*e.g.,* organic material—say CH_2O) would transfer electrons to the lowest unoccupied electron level, which is oxygen (O_2). When the number of electrons are greater than the number of unoccupied electron levels of oxygen, the higher unoccupied electron level will be filled up, namely, NO_3^-, NO_2^-, $MnO_{2(s)}$, and so on (Stumm and Morgan, 1996). The sequence of microbially mediated redox processes may be seen in the schematic shown in Figure 2-2 reproduced from Sigg (2000). The oxidant with the highest redox potential will be utilized first, followed by the one with the next lower potential.

This sequence has been prominently observed in the vertical distribution of components in a nutrient-enriched (eutrophied) lake and also in closed systems containing excess organic matter, such as batch digesters (anaerobic fermentation unit) (Stumm and Morgan, 1996). Most of the reactions are microbially mediated (except for the reduction of MnO_2 and $FeOOH_{(s)}$), and they are, therefore, paralleled by an ecological succession of microorganisms: aerobic heterotrophs, denitrifiers, fermenters, sulfate reducers, and methane bacteria. It has also been observed that higher energy-yielding reactions take precedence over lower energy-yielding processes (Stumm and Morgan, 1996). As shown in Table 2-1, the aerobic oxidation of CH_2O yields the highest energy (125 kJ per equivalent), followed by the CH_2O oxidation with nitrate (119 kJ per equivalent), and so on.

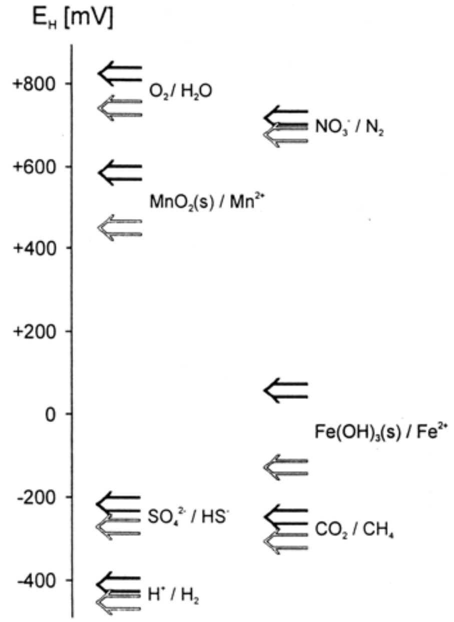


Figure 2-2. Redox potential of some important redox couples in natural water at pH 7 (dark arrows) and pH 8 (light arrows). The redox potential is calculated for activities {Red} = 1 and {OX} = 1; in the case of Mn and Fe, $\{Mn^{2+}\} = 1x10^{-6}$ M and $\{Fe^{2+}\} = 1x10^{-6}$ M are assumed. (Taken from Sigg, 2000)

Overview of Redox Potentials in Natural Systems and Interactions Between Sediment and Water

Redox potentials in natural waters range from about –400 mV to +800 mV at pH 7 to 8. They are bounded in the negative range by the reduction of H_2O to hydrogen gas ($H_{2(g)}$) and in the positive range by the oxidation of H_2O to $O_{2(g)}$ (Sigg, 2000). Figure 2-3, reproduced from Stumm and Morgan (1966), shows four representative ranges of redox potentials in water and sediment. Water saturated with oxygen may have a redox potential within the first range (710 to 800 mV at pH 7 to 8). In systems where some oxygen has been consumed, the redox potentials may range between –100 to 710 mV (Range 2) at pH 7 to 8 (Stumm and Morgan, 1996). The potential is not, however, sensitive to oxygen concentrations and has been observed to remain nearly constant down to values of 0.1% O_2 saturation (Greatz et al, 1973). Within the second range, solid iron three (Fe(III)), and manganese three and four (Mn(III,IV) are reduced to soluble iron two (Fe(II)) and manganese two (Mn(II)) when organic matter is mineralized. Phosphorus, which is initially bound to Fe(III) hydroxides, is released to the overlying water as a result of the reduction of Fe(III) solid phases. Under even more reduced conditions (Range 3, -240 to –100 mV at pH 7 to 8), the concentration of Fe(II) and Mn(II)

Table 2-1. Reduction and Oxidation Reactions that May Be Combined to Result in Biologically Mediated Exergonic Processes at pH = 7 (taken from Stumm and Morgan, 1996)

Reduction	$p\varepsilon^\circ(W) = \log K(W)$	Oxidation	$p\varepsilon^\circ(W) = -\log K(W)$
(A) $\frac{1}{4}O_2(g) + H^+(W) + e^- = \frac{1}{2}H_2O$	+13.75	(L) $\frac{1}{4}CH_2O + \frac{1}{4}H_2O = \frac{1}{4}CO_2(g) + H^+(W) + e^-$	-8.20^a
(B) $\frac{1}{5}NO_3^- + \frac{6}{5}H^+(W) + e^- = \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	+12.65	(L-1) $\frac{1}{2}HCOO^- = \frac{1}{2}CO_2(g) + \frac{1}{2}H^+(W) + e^-$	−8.73
(C) $\frac{1}{2}MnO_2(s) + \frac{1}{2}HCO_3^-\ (10^{-3}) + \frac{3}{2}H^+(W) + e^- = \frac{1}{2}MnCO_3(s) + H_2O$	+8.9	(L-2) $\frac{1}{2}CH_2O + \frac{1}{2}H_2O = \frac{1}{2}HCOO^- + \frac{3}{2}H^+(W) + e^-$	−7.68
(D) $\frac{1}{8}NO_3^- + \frac{5}{4}H^+(W) + e^- = \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	+6.15	(L-3) $\frac{1}{2}CH_3OH = \frac{1}{2}CH_2O + H^+(W) + e^-$	−3.01
(E) $FeOOH(s) + HCO_3^-\ (10^{-3}) + 2H^+(W) + e^- = FeCO_3(s) + 2H_2O$	−0.8	(L-4) $\frac{1}{2}CH_4(g) + \frac{1}{2}H_2O = \frac{1}{2}CH_3OH + H^+(W) + e^-$	+2.88
(F) $\frac{1}{2}CH_2O + H^+(W) + e^- = \frac{1}{2}CH_3OH$	−3.01	(M) $\frac{1}{8}HS^- + \frac{1}{2}H_2O = \frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+(W) + e^-$	−3.75
(G) $\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+(W) + e^- = \frac{1}{8}HS^- + \frac{1}{2}H_2O$	−3.75	(N) $FeCO_3(s) + 2H_2O = FeOOH(s) + HCO_3^-\ (10^{-3}) + 2H^+(W) + e^-$	−0.8
(H) $\frac{1}{8}CO_2(g) + H^+(W) + e^- = \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O$	−4.13	(O) $\frac{1}{8}NH_4^+ + \frac{3}{8}H_2O = \frac{1}{8}NO_3^- + \frac{5}{4}H^+(W) + e^-$	+6.15
(J) $\frac{1}{6}N_2 + \frac{4}{3}H^+(W) + e^- = \frac{1}{3}NH_4^+$	−4.68	(P) $\frac{1}{2}MnCO_3(s) + H_2O = \frac{1}{2}MnO_2(s) + \frac{1}{2}HCO_3^-\ (10^{-3}) + \frac{3}{2}H^+(W) + e^-$	8.9

Examples	*Combinations*	$\Delta G^\circ(W)$ pH = 7 (kJ eq^{-1})
Aerobic respiration	A + L	−125
Denitrification	B + L	−119
Nitrate reduction	D + L	−82
Fermentation	F + L	−27
Sulfate reduction	G + L	−25
Methane fermentation	H + L	−23
N fixation	J + L	−20
Sulfide oxidation	A + M	−100
Nitrification	A + O	−43
Ferrous oxidation	A + N	−88
Mn(II) oxidation	A + P	−30

[a] CH_2O is used as a formula for an "average" organic substance. The free energy change involved with different specific organic substances may differ from that given for CH_2O. The difference may be large, especially in anoxic processes with substrates whose carbon has a different oxidation state than that in CH_2O.

rises further; SO_4^{2-} begins to be reduced, accompanied by the precipitation of Manganous Sulfide (MnS) and Ferrous Sulfide (FeS), and the formation of pyrite.

At oxic-anoxic interfaces, which could be in the deeper parts of a lake, at the sediment-water interfaces, or within sediments, Fe and Mn may transform between the dissolved and solid forms. Fe and Mn may be observed to go through a sequence of upward diffusional transport of their reduced forms, oxidation to the insoluble forms, and subsequent settling and reduction back their soluble forms as shown in Figure 2-4. This sequence normally occurs within a relatively narrow redox cline (Stumm and Morgan, 1996).

Many researchers have studied the relationships between oxidation-reduction potential and the physical, chemical, and biological processes in soil-water systems. One of the pioneers in this field was Mortimer (1941, 1942). Mortimer studied the factors which control the rate of nutrient supply to phytoplankton in systems of lake water and sediment deposits. He also

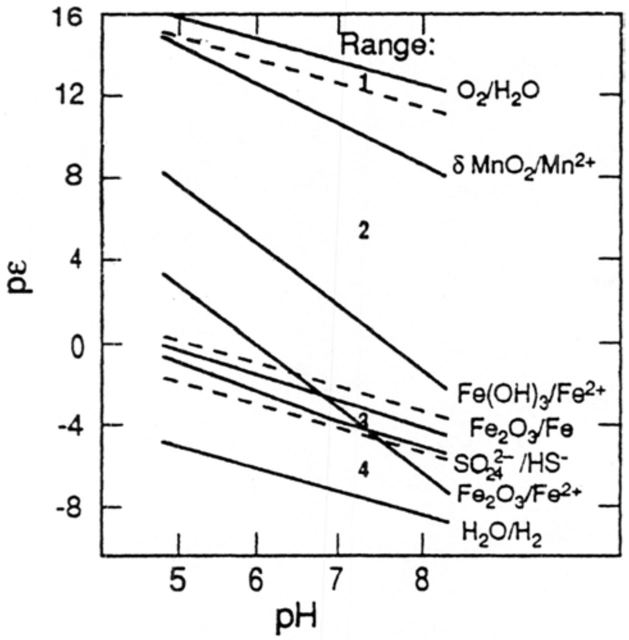


Figure 2-3. Representative ranges of redox intensity in soil and water. Range 1 is for oxygen-bearing waters. Range 2 is representative of many ground and soil waters where O_2 has been consumed (by degradation of organic matter), but SO_4^{2-} is not yet reduced. In this range soluble Fe(II) and Mn(II) are present; their concentration is redox-buffered because of the presence of solid Fe(III) and Mn(III,IV) oxides. Range 3 is characterized by SO_4^{2-}/HS or SO_4^{2-}/FeS_2 redox equilibria. Range 4 occurs in anaerobic sediments and sludges. Note: $p\varepsilon = 16.9E^o$. (Taken from Stumm and Morgan, 1996)

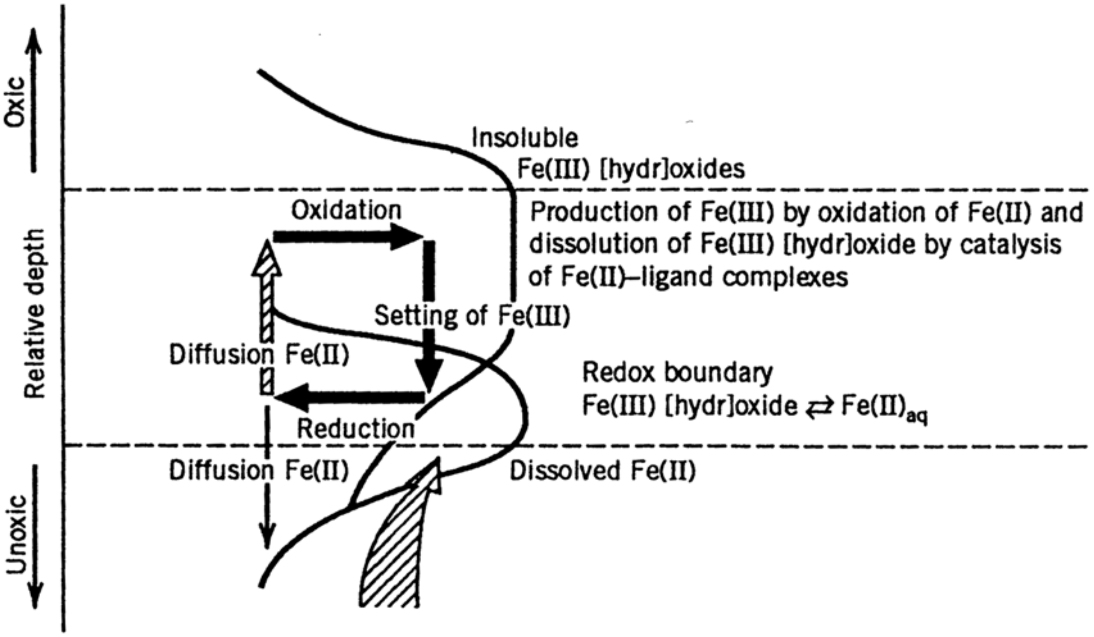


Figure 2-4. Transformation of Fe(II, III) at an oxic-anoxic boundary in a water or sediment column. Note: The Fe(III) peak lays on top of Fe(II) peak. (Taken from Stumm and Morgan, 1996)

investigated the seasonal changes in hypolimnetic waters and the bottom muds. He captured the pattern of events in Lake Esthwaite after the onset of thermal stratification as follows: Stage I, hypolimnetic oxygen depleted at a constant rate until the concentration reached 2 mg/l. Then the rate retarded. The oxidation-reduction potential was relatively constant. Slight increases of alkalinity, conductivity, color and iron were observed. A rapid decrease of oxygen concentrations and oxidation-reduction potential to 0.5 mg/l and 0.25 mV, respectively, characterized Stage II. After the decrease, the alkalinity, conductivity, Fe, Si, P, color, and turbidity increased rapidly, while nitrate concentrations decreased, accompanied with the appearance of a relatively large amount of nitrite. The rate of ammonia production was higher than the rate of nitrate reduction, which had been completely reduced at low levels close to the sediment. This indicated that the sediments were the main source of ammonia.

In stage III, the solute concentrations continued to increase, but at slower rates. Finally, the fall overturn reversed the reduction changes listed above. The oxygen concentration rapidly increased, followed by decreases of alkalinity, conductivity, Fe, Si, P, and ammonia. The color decreased less rapidly and nitrate was detected several weeks after the overturn. Mortimer conducted further laboratory experiments to confirm his findings, and he was able to observe practically similar results. The laboratory experiment enabled him to more completely investigate the role of the oxidized mud layer. Mortimer established that the oxidized and reduced mud layers were separated at an ORP of 240 mV. When the 240 mV isovolt line rose into the water column, the oxidized, light-brown mud surface disappeared, and the concentration of solutes increased.

He described the following ranges of oxidation-reduction potential (E_7) where a particular reaction was active, and where the lower potential is the potential below which none of the oxidized phase could be detected:

- NO_3^{2-} to NO_2^{2-}, 0.45 - 0.40 v
- NO_2^{2-} to NH_4^{2+}, 0.40-0.35 v
- ferric complex to Fe_2^+, 0.30 - 0.20 v
- SO_4^{2-} to S_2^-, 0.10 - 0.06 v

The oxygen concentrations associated with each range were 4, 0.4, 0.1 and 0 mg/l, respectively.

Mortimer continued with similar investigations on other lakes, including oligotrophic Lake Windermere. Comparison of the results led him to conclude that the occurrence or non-occurrence of the pattern observed in Lake Esthwaite depended on the reducing power of the mud and the amount of oxygen supplied to the mud. Thus, the release of solutes from the muds could be the result of an increase in the reducing power brought about by natural or cultural changes, and could result in higher lake productivity.

Song and Muller (1999) conducted an extensive set of studies on sediment-water interactions to determine the relationships between mineralization of organic matter and the mobility of heavy metals and nutrients in the heavily polluted sediments of major German rivers, including the Rhine, Neckar, Main, Weser, and Elbe. The study determined the distribution of Fe, Mn, Cd, Zn, Pb, Cu, Cr, and Co in the pore waters and sediments, and NO_3^-, SO_4^{2-}, NH_4^+, PO_4^{3-}, Ca^{2+}, Mg^{2+}, Br^-, alkalinity, and pH in the pore waters. It was found that NO_3^- and SO_4^- decreased with depth into the sediments, while the concentrations of Fe and Mn increased. This was attributed to the mineralization of organic matter where NO_3^-, SO_4^{2-}, Fe^{3+}, and Mn^{4+} served as electron acceptors, which suggested highly anoxic conditions in the sediments. A more complete discussion of the reduction of NO_3^- is given later in the "Denitrification" section.

Song and Muller, citing Matsunaga *et al.* (1993), stated that the concentrations of Fe^{2+} and Mn^{2+} are influenced not only by redox reactions, but also by the precipitation and dissolution of Fe and Mn minerals. The authors observed that the soluble Fe and Mn (Fe^{2+} and Mn^{2+}) concentrations in porewaters were supersaturated with respect to rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$), and the ions seemed to precipitate as and dissolve from these compounds. Song and Muller also found that soluble Fe^{2+} and Mn^{2+} diffused upward due to concentration gradients, and precipitated in the oxic surface sediment layer. In contrast to observations by Mortimer (1941 and 1942), however, they did not observe accumulations of oxidized Fe and Mn on the sediment surface. They thought this to be the result of high geogenic Fe and Mn concentrations already existing in the sediments or sediment mixing from bioturbation and/or scouring.

In addition, it was found that products of organic matter mineralization, such as NH_4^+, Br^-, and alkalinity increased with depth. Despite the high concentration of phosphate and NH_4^+ in the porewaters, the fluxes of phosphate and NH_4^+ to the overlying waters were observed to be low. This was attributed to the existence of an oxic surface layer where diffusing phosphate was adsorbed to freshly formed Fe oxides. This zone was also thought to promote the oxidation of NH_4^+ to nitrate.

Due to the serious problems associated with eutrophication and the frequent finding of phosphorus as the main limiting nutrient in impounded waters, the adsorption and release of phosphorus to and from lake and reservoir sediments has received a great deal of attention. Numerous researchers have investigated the phenomenon.

Syers *et al.* (1973), citing Gastuche *et al.* (1963); Muljadi *et al.* (1966); and Hingston *et al.* (1969) stated that inorganic phosphorus is retained in sediments by adsorption to oxides and hydrous oxides of Fe and Al. Hsu (1965) postulated that the phosphate adsorption in soil is chemical in nature, and that physical adsorption should not be considered to be of any significance in the fixation process. He said that precipitation and adsorption result from the same chemical force. In other words, the adsorption force that holds the molecule or ion at the surface of another phase is exactly the same as that occurring between bound atoms in a molecule or between molecules in a compound. Furthermore, Hsu postulated that the factor that determines whether adsorption or precipitation occurs is the form of iron or aluminum present at the moment of reaction. At normal soil pH, adsorption occurs because surface-reactive iron oxides and amorphous aluminum hydroxides dominate the process of phosphate fixation rather than Al_3^+ or Fe_3^+.

Syers *et al.* (1973) stated that the mobility of phosphate depends on the nature of the sorbing surface. The authors postulated that the importance of Fe as a phosphate-containing component indicates that the mobility of phosphorus should highly depend on redox potential. Holdren and Armstrong (1980) found that lowering ambient oxygen concentrations increased the phosphorus release rate, particularly from calcareous sediments. Patrick and Kjalid (1974) found that soils suspended in solutions low in soluble phosphate tended to release more phosphorus under anaerobic conditions than under aerobic conditions. In solutions high in phosphate, they observed a tendency to adsorb more phosphorus under anaerobic conditions than under aerobic conditions. The authors explained this apparent contradiction by noting that, under reduced conditions, ferric oxyhydroxides convert to the more soluble and highly dispersed ferrous forms, and release the phosphorus sorbed to them. The ferrous forms of iron, although less capable of binding orthophosphate ions, have more surface area, thereby they can adsorb more phosphorus in solutions high in phosphate.

Studying the phosphorus release from the Occoquan Reservoir sediment, To (1974) found that the rate of phosphorus release could be enhanced by anaerobic conditions and also by the amount of phosphorus in the sediment. He said that under aerobic conditions, the sediment would act as either a sink or source of phosphorus, depending on the phosphorus concentration in the overlying water. If the concentration in the water were below a critical concentration, which To called the "availability critical concentration" (ACC), the sediment would serve as source. Otherwise, it could be expected to serve as a sink. This condition would be upset by the onset of anaerobic conditions. According to To, the phosphorus release rate under anaerobic conditions could be several magnitudes higher than the rate under aerobic conditions (0.054 microgram per square centimeter per week (μg/sq. cm/w) under aerobic conditions versus 15.63 μg/sq. cm/w under anaerobic conditions).

Bonanni *et al.* (1992) studied the sediments, interstitial waters, and release of nutrients from the sediments in the Orbetello lagoon, Italy. They observed that the concentrations of phosphorus decreased with increased depth in the sediments. Explanations for this observation include: (1) the water body becoming more eutrophic over time, thereby the newer depositing sediment had higher phosphorus content, or (2) reprecipitation of dissolved phosphorus with iron and manganese oxides in the oxidized zone. Furthermore, they found that phosphorus was the second species (following NH_4^+) released from the sediments after the onset of anoxic conditions in the sediments. They believed that phosphorus release under anoxic conditions is dominated by diffusion and that organic matter mineralization, as suggested by Syers *et al.* (1973) and Song and Muller (1999), was a minor source.

Jensen *et al.* (1992) showed that the capability of aerobic sediments to buffer phosphate concentrations in 15 representative Danish lakes correlated well with the Fe:P ratio in the sediments, while the maximum adsorption capacity correlated with the total iron content. Their results showed that, for sediments with Fe:P ratios greater than 15 (by weight), it is possible to control internal P loading by keeping the surface sediment well oxidized.

There are many other interesting studies on oxidation-reduction potential in sediment-water systems. A few works with results similar to this study are presented here. Hargrave (1972) measured oxidation-reduction potentials with permanent and temporarily-placed 1-mm white platinum electrodes in undisturbed sediment cores and in resettled mud cores from Lake Esrom, Denmark. He found that seasonal variations in redox potential occured in the upper 1-cm layer on the surface of sediment. By adding formalin as a bacteriocide, he found that at depths into the sediments greater than 1 cm, there were only chemical redox processes because oxygen consumption below 1 cm was barely affected by the formalin. In the upper 1-cm layer, however, the oxygen consumption was reduced by an average of 80 percent. The upper layer corresponded to the same zone of marked decrease in E_h. Moreover, when E_h dropped below 100 mV, he could detect no dissolved oxygen in the water over the sediment.

Hargrave concluded that, although there are many difficulties associated with the quantitative interpretation of E_h values, the measurements could be productively used as an operational method to differentiate oxidized and reduced sediments. Furthermore, although Hargrave observed that the E_h values where oxygen was absent were low, it does not follow that oxygen controls the E_h potentials. He concluded that it is more likely that reducing substances responsible for lowering E_h do not exist in the presence of oxygen. He also suggested other uses of E_h values, such as quantifying the degree of stagnation in sediments or approximating the thickness of the oxidized surface layer.

Greatz *et al.* (1973) studied E_h values with respect to nitrogen transformations in artificial sediment-water systems. The authors made redox measurements with permanently placed white and black platinum electrodes and found that both types of electrodes yielded similar results. The permanently placed electrodes in both water and sediment did not show signs of electrode *poisoning* as discussed below. They found that even when the overlying water was oxygenated, only a thin oxidized sediment layer existed on the sediment surface. E_h values of the sediments were reported to decline rapidly to between –150 and –250 mV after the start of the experiments, and to stay at similar values regardless of the dissolved oxygen concentrations in the overlying water.

They noted, however, that the rates of the E_h decrease varied among sediments. Sediments with high iron content appeared to be more resilient to redox potential changes. The authors also noted that the range of E_h values observed corresponded to the region where CO_2-CH_4 and H^+-H_2 couples dominate the system. This idea was confirmed by the detection of CH_4 in the system headspace. Unfortunately, the evolution of H_2 was not measured. E_h values in the overlying water exhibited a slight initial increase in all experiments, which the authors attributed to reduced species in the sediment being stirred up during the experiment setup. With direct applicability to the work described herein, the presence of nitrate nitrogen was found to stabilize E_h values at 180 to 200 mV until the nitrate was nearly depleted. Lastly, Greatz *et al.* found that E_h values began to drop rapidly again only after all nitrate was depleted from the system.

Some researchers have observed a rapid drop of sediment E_h values after the depletion of dissolved oxygen, followed by a slight increase. Yamane and Sato (1968) found that when air-dried soils were flooded, the E_h values dropped rapidly and went up again within 24 hours as shown in Figure 2-5, which is a plot of their experimental results. They attributed the decrease to the production of hydrogen gas, which they detected in all of their experiments. Supporting this conclusion, some of the lowest values observed were in the vicinity of -420

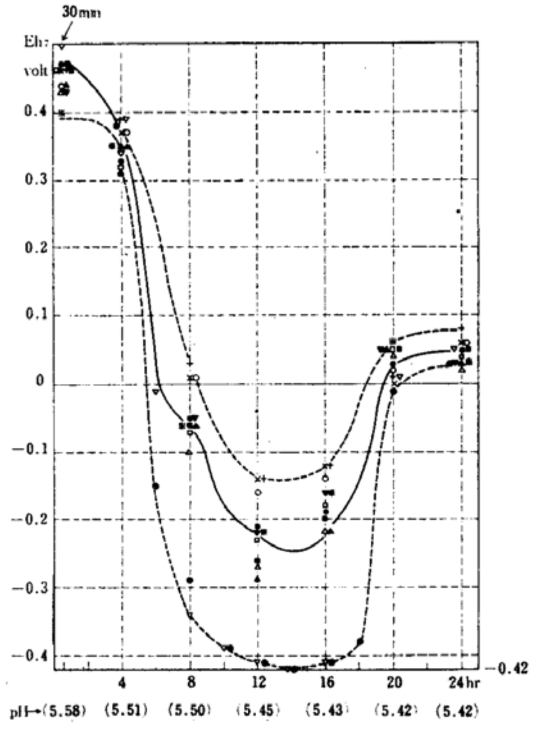


Figure 2-5. Time series plot of average E_h values and their confidence interval from twelve duplicated experiments with Kashimadai soil. (Taken from Yamane and Sato, 1968)

mV, which is in the region where H_2 production controls the redox potentials (Stumm and Morgan, 1996 and Sigg, 2000). Yamane and Sato also found that the pre-incubation of soils seemed to increase the magnitude of the decrease in E_h.

When Yamane and Sato added nitrate and/or cyanide to the soils, it was found that the decrease was suppressed and the degree of suppression increased with increasing concentration of the chemical added. They further recognized that the magnitude of the decrease correlated with the amount of organic carbon available in the soils. This correlation reflected the fact that hydrogen gas is a product of heterotrophic decomposition of an organic carbon source. This was confirmed by Bell (1969), who observed the rapid E_h decrease and slight recovery only in an experiment amended with glucose, as may be seen in Figure 2-6, which is a time series plot of Bell's results. Yamane and Sato also tested the possibility that the addition of sulfate could prevent the rapid drop in E_h, but they found little or no effect.

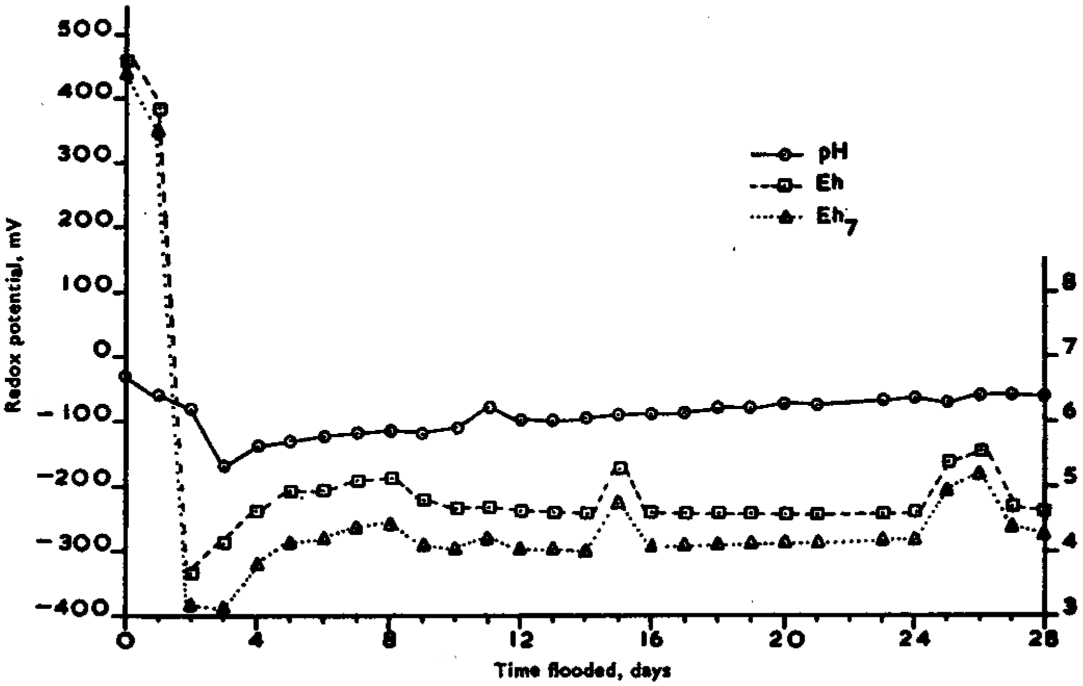


Figure 2-6. E_h and pH of flooded soils amended with glucose. (Taken from Bell, 1969)

Bell (1969) also concluded that the rapid drop and recovery of E_h values after oxygen depletion was caused by the production of hydrogen gas from organic matter (glucose) decomposition. However, Bell also identified two stable E_h regimes: one at +200 mV and the other at values less than -250 mV. The former was accompanied by active denitrification and the latter corresponded with the evolution of CH_4. He concluded that, "A characteristic pattern of gas evolution was produced during the decomposition of the added substrates. These patterns of gas evolution reflect the interaction between the changing reduction state and availability of substrate occurring within each system."

Measurement of Oxidation Reduction Potential

Although the redox potential (E^o) of a system may be easily obtained by an electrometric measurement of the potential difference between an inert indicator electrode and the standard hydrogen electrode in solution, it should not be equated to E_h. In order to equate E^o to E_h, a discussion of redox potential measurement in *Standard Methods for the Examination of Water and Wastewater* (APHA, 1998) concluded that the following conditions must be met: the chemical equilibrium must be reversible, kinetics of the reactions at the electrodes must be rapid, and there must be no interfering reactions at the electrode surface. As may be expected, these conditions are rarely found in natural systems. Other operational problems, such as chemical poisoning of the electrode(s); the presence of multiple redox couples; a very small exchange current; and inert redox couple(s), may be expected to further complicate the measurement. In order to obtain a quantitative estimate of E_h, an alternative procedure would be to analyze all the redox couple constituents in the sample of interest, and calculate the redox potential from them. Even so, it was noted that some researchers have shown that the measured E_h corresponded poorly with the calculated potential. Nevertheless, redox potential measurements, when carried out and interpreted properly, can provide a more thorough understanding of water chemistry (APHA, 1998).

Electrochemical Measurement

Electrochemical measurement appears to be a very promising method because it allows *in situ* measurements, and also makes it possible to obtain continuous space- and time-resolved data. Nevertheless, the theoretical and practical difficulties associated with this method have not yet been sufficiently concluded, even though they have been debated for many years (Sigg, 2000). Redox potential measurement is normally made and/or reported in reference to the H_2 redox couple, which is found by combining the oxidation half reaction of $H_{2(g)}$ shown in Equation 2-5 with the reduction half reaction shown in Equation 2-6. The overall reaction is shown in Equation 2-7. The redox potential under standard condition may then be defined as shown in Equation 2-8:

$$\tfrac{1}{2}H_{2(g)} \rightarrow H^+ + e^- \qquad \text{Eq. 2-5}$$

$$Ox + ne^- \rightarrow Red \qquad \text{Eq. 2-6}$$

$$Ox + \tfrac{n}{2}H_{2(g)} \rightarrow Red + nH^+ \qquad \text{Eq. 2-7}$$

$$E_h{}^o = 2.3\frac{RT}{nF}\log K \qquad \text{Eq. 2-8}$$

where Ox = Oxidant
Red = Reductant
$E_h{}^0$ = Redox potential [V] (in relation to a normal hydrogen electrode) under standard conditions (all activities = 1, pH2 = 1 atm, $\{H^+\}$ = 1 M)
n = Number of exchanged electrons

K = Thermodynamic constant of the overall reaction, $\{Red\}\{H^+\}/\{Ox\}(p_{H2})^{n/2}$
F = 1 faraday (96490 $C \cdot mol^{-1}$)
R = Gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$)
T = Temperature in Kelvin

For general conditions, E_h may be calculated using Nernst's equation, which is shown in Equation 2-9 and shows the relationship between the redox potential and the respective activities of the oxidized and reduced species. It is critical to recognize that redox potentials stem from the principles of equilibrium thermodynamics, and may therefore only be adequately measured at equilibrium (Sigg, 2000).

$$E_h = E_h^o + 2.3 \frac{RT}{nF} \log \frac{\{Ox\}}{\{Red\}} \qquad \text{Eq. 2-9}$$

The oxidation of organic matter and the corresponding reduction reactions, including the reduction of oxygen to water and nitrate to nitrogen gas are the most essential redox reactions in natural water. As discussed earlier, the sequence of reduction of the oxidants is well known and it follows that the measurement of redox potential in a natural system should match with the potential range of predominant redox reaction under a given set of conditions (Sigg, 2000).

In principle, the redox potential may be measured with an electrochemical cell in a so-called potentiometric measurement, which is a determination of the potential difference between an inert electrode (usually made of platinum) and a reference electrode, both of which are submerged in the solution or connected with a salt bridge. A schematic of a simple measurement system is shown in Figure 2-7. In practice, the standard hydrogen electrode is usually replaced with other reference electrodes, because the former is fragile and impractical for routine laboratory and field uses. The silver:silver-chloride and calomel reference electrodes are commonly employed in ORP measurements, and the indicated potential is corrected to E_h (APHA, 1998).

Stumm and Morgan have summarized voltage corrections for both of the commonly used reference electrodes, as shown in Table 2-2. In addition to correcting for the reference electrode potential, the ORP measurement must be performed in the absence of a net reaction over the cell; that is, the net current over the cell must be zero. For this condition, the current of oxidation (i_{ox}) and reduction (i_{red}) reactions, which flows in opposite directions as shown in Equations 2-10 and 2-11, is equal. In order to obtain an indication with the measuring

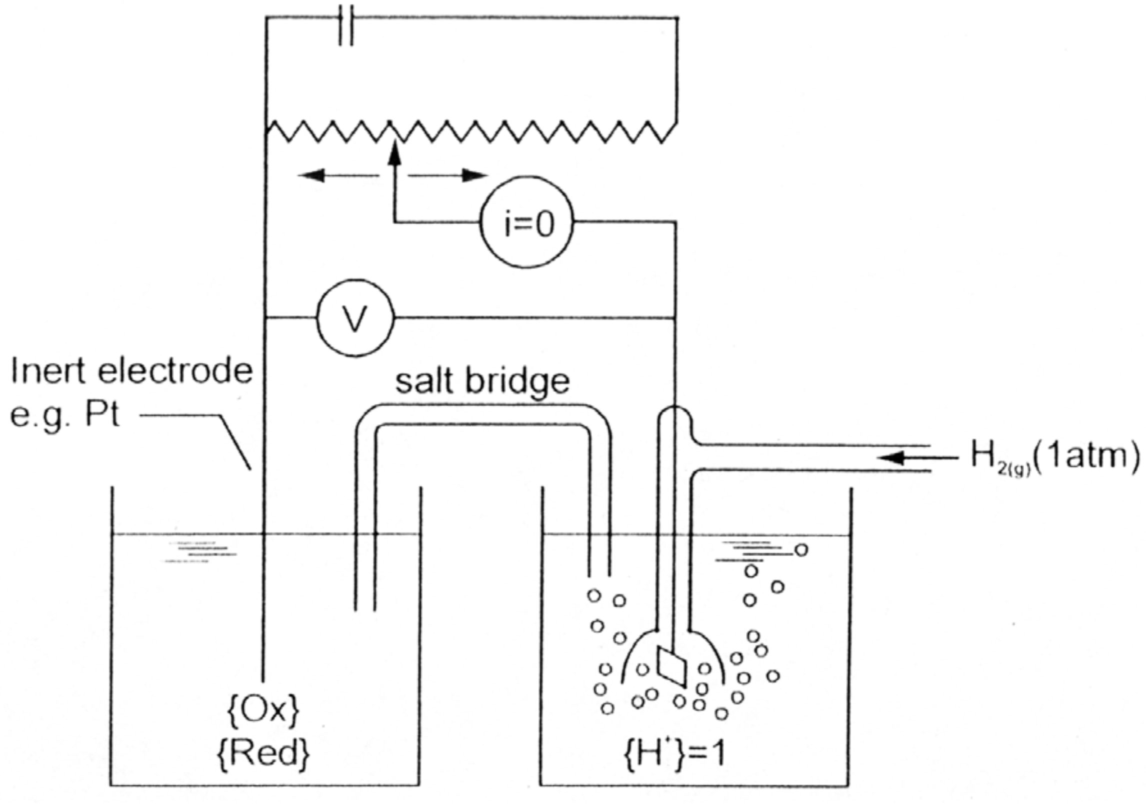


Figure 2-7. Schematic diagram of an electrochemical cell for the measurement of redox potential E_h. The potential defference is measured between an inert electrode (usually Pt) in contact with a solution containing the oxidized {Ox} and reduced {Red} species, and a reference electrode (here a standard reference hydrogen electrode, Pt in contact with $H_{2(g)}$ at 1 atm and $\{H^+\} = 1$ (at 25 °C)). The potential Eh must be measured in the absence of a net reaction over the cell, namely i = 0. (Taken from Sigg, 2000)

$$\mathrm{Ox} + ne^- \xleftrightarrow{i_{red},\, i_{ox}} \mathrm{Red} \qquad \text{Eq. 2-10}$$

$$i_{red} = i_{ox} = i_o;\ i_o = \text{exchange current} \qquad \text{Eq. 2-11}$$

instrument, however, the net exchange current between the electrodes cannot be zero. The potential must be slightly shifted from its equilibrium value to cause a finite current to pass through the cell. Even though this will cause the half-reactions to shift away from an equilibrium condition, maintaining a high concentration of reactants allows the measurement to take place approximately at an equilibrium state.

Table 2-2. Potentials of Reference Electrodes[a] (taken from Stumm and Morgan, 1996)

Temperature	Calomel		AgCl/Ag	
(°C)	0.1 M KCl	Saturated	0.1 M	Saturated
12	0.3362	0.2528	-	-
20	0.3360	0.2508	-	-
25	0.3356	0.2444	0.2900	0.1988

[a]The values listed (V) included the liquid junction potential. Cell: Pt, H_2/H^+ (a = 1) $\|$ reference electrode.

In addition, electrodes with large surface areas are also desirable; however, larger areas tend to magnify the effects of trace impurities or other reactions on the electrode surfaces. Such adsorption of surface-active materials may lead to a decrease in the electron-exchange rate or in the effective area. Modern measuring instruments have low current drain; therefore, the shift does not need to be great. If the exchange current is greater than 10^{-7} ampere (A), a consistent measurement may be made (Stumm and Morgan, 1996).

When applying the principles of electrometric measurement, Sigg (2000) suggested that two major problems might be generally encountered in field and laboratory situations:

- The important redox reactions in natural waters are very slow, and proceed only by microbial catalysis. Several electron exchanges and other complex mechanisms are involved. Moreover, exchange current of these reactions at an electrode is, by and large, inadequate to establish a stable potential.

- Not only is equilibrium at the electrode required for consistent measurement, but also equilibrium among the various redox couples in solutions. This condition is also rarely met because of the slow kinetics of most redox reactions in natural waters and their strict dependence on bacterial catalysis.

Furthermore, Stumm and Morgan (1996) suggested that the apparent redox potential obtained when the redox couples are not at equilibrium is difficult to quantitatively interpret. An apparent equilibrium may be obtained where the anodic and cathodic currents are balanced.

The overall system, however, is not at equilibrium because the net current results from a summation of electron exchange rates of a variety of redox couples that also are not at equilibrium. Figure 2-8, which is an example taken from Stumm and Morgan (1996), is an Fe^{2+}/Fe^{3+} system with some trace of dissolved oxygen. The measured potential (E_m) in this system is at the point where the rate of oxygen reduction equals the rate of Fe^{2+} oxidation while the potential of having equal rates of iron reduction and oxidation is E_{eq}. Such so-called "mixed" potentials generally exhibit a slow drift as the overall system tends toward equilibrium. Citing Grenthe *et al.* (1992), Stumm and Morgan stated that long periods of time (up to 20 days) might be required for quantitative measurements.

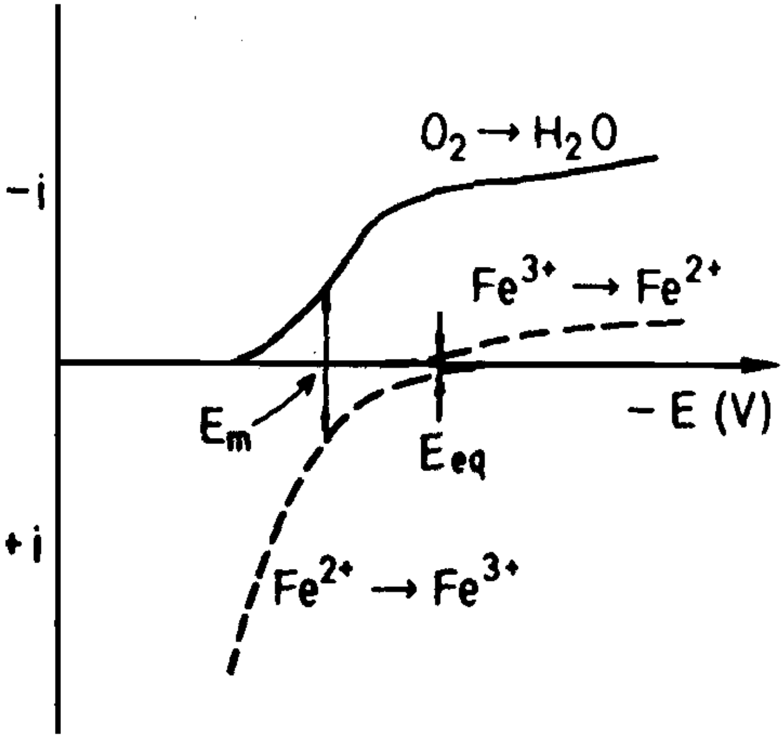


Figure 2-8. Electrode polarization curves for oxygen-containing solutions in the presence (nonequilibrium) of some Fe^{2+}. Curves are schematic but in accord with available data at significant points. (Taken from Stumm and Morgan, 1996)

ORP should be measured *in situ*, or as soon as possible after sample retrieval, because any sample removed from the environment may exhibit unknown changes due to contact with the atmosphere and the interior surfaces of the sample container. *In situ* measurement is preferred, and one should consider making measurement in a closed flow-through cell, such as a 500-mL, airtight bottle with sleeve connectors for the electrodes and a thermometer (Galster H., 2000). APHA (1998) also recommends measuring in a closed-flow cell.

E_h as An Operational Parameter

As noted above, quantitative interpretation of the E_h values has been impractical due to the problems associated with the electrochemical E_h measurement. Many studies, however, have shown that E_h measurements provide valuable information when used as a qualitative or operational parameter (Hargrave, 1972; Greatz *et al.*, 1973; Yamane and Sato, 1968; and Bell, 1969). An example may be found in an estuarine study by Whitefield (1969). He found that E_h has the following important characteristics, which make it particularly suitable for characterizing sediments:

- It ranges widely, and thereby provides a high measurement resolution
- It is relatively easy to measure
- It may be linked to important chemical and biological processes controlling sediments. In other words, one should be able to generally characterize the oxidation-reduction state of a sediment-water system from generally high or low values of E_h.
- The link is reasonably stable enough for obtaining coherent and intelligible results.

Whitefield (1969) concluded that, although the quantitative measurement of ORP is difficult due to measurement problems, inert electrode performance, and the thermodynamic of the system, it is still useful for providing an indication of a specific system's degree of stagnation. In the study cited, he successfully mapped areas of stagnation (poorly mixed, reduced zone) using ORP. He further suggested this type of study as a pilot survey to plan detailed studies of the distribution of benthic fauna or of the effects of sediment-water interaction on the chemistry of the estuary.

Inert Electrodes

Inert electrodes play an important role in the electrochemical measurement of redox potential. While, in theory, any electron-conducting material is usable as an electron-selective electrode, Galster (2000) stated that (1) the inert electrode is neither permitted to react with parts of the solution nor to catalyze the reactions and that (2) only when the standard potential of a metal is at least 100 mV greater than the redox potential of the sample may it be considered inert. For these reasons, the noble metals—particularly gold and platinum—have proven to be useful. Most other metals react with chlorides as well, which are often present in natural waters. Galster also stated that higher relative exchange current (calculated by current/voltage functions) of metals is preferred because it may reduce the response time of a measurement. Table 2-3 shows that platinum has a relative higher exchange current; therefore, it is preferred over gold. He noted that one might only obtain reasonable response times in diluted solutions with platinum. Furthermore, Galster stated that platinum has the desirable characteristic of being fusible in glass, thereby it allows simple manufacture of robust electrodes with common laboratory materials.

Galster (2000) noted that the only difficulty with platinum is that it reacts with oxygen. He stated that although oxygen atoms only form a monolayer on the surface, the binding mechanisms range from adsorption type processes to the formation of a range of platinum oxides. Table 2-4, reproduced from Galster (2000), shows the standard voltages of some identified Pt-oxides at pH = 0. At moderate values of pH, the electrode potentials would be expected to be lower. Platinum electrodes may also be observed to form oxides on the surface when exposed to air during storage. Although platinum oxides are good conductors of electrons, they do tend to increase the time it takes to reach equilibrium between the electrode

Table 2-3. Comparison of Gold and Platinum Electrodes (taken from Galster, 2000)

Properties	Gold	Platinum
standard voltage (V)	1.42	1.2
forming oxides	no	yes
catalytic activity	rare	possible
rel. exchange current	0.3 mA/cm^2	10 mA/cm^2
melts with glass	no	yes

Table 2-4. Standard Potentials [V] of different platinum oxides (taken from Galster, 2000)

Electrode	Standard Potential	Electrode	Standard Potential
Pt/Pt-O	0.88	$Pt/PtO_2 \cdot 4H_2O$	1.06
Pt/PtO	0.9	Pt/PtO_3	1.5
$Pt/Pt(OH)_2$	0.98	Pt/PtO_2	>1.6
$Pt/PtO \cdot 2H_2O$	1.04	Pt/Pt_3O_4	1.11
$Pt/PtO_2 \cdot 2H_2O$	0.96	$Pt(OH)_2/PtO_2$	1.1
$Pt/PtO_2 \cdot 3H_2O$	0.98	O_2	1.23

and solution, and are generally observed to result in higher ORP measurements (Galster, 2000).

Electrodes having oxidized surfaces may be expected to return to the pure metallic state when placed in a reducing environment, shown, for example, in Equations 2-12 - 2-14:

$$PtO_2 + PtO(H_2O) \rightarrow 2PtO(OH) \qquad \text{Eq. 2-12}$$

$$PtO(OH) + H^+ + e^- \rightarrow PtO(H_2O) \qquad \text{Eq. 2-13}$$

$$PtO(H_2O) + 2H^+ + 2e^- \rightarrow Pt + 2H_2O \qquad \text{Eq. 2-14}$$

The first step occurs on the platinum surface and the second and last steps require one and two electrons from the solution, respectively. On the other hand, if the measurement takes place in a solution with higher redox potential than the existing Pt-oxides, the Pt-oxides may be oxidized to higher states (Galster, 2000).

Platinum Electrode Design

The design of platinum electrodes should take into account the demands of the principal application, including microcosm systems. Classically, such electrodes have been designed with a wire or small sheet of platinum as the sensing element, but these have been generally found to be susceptible to bending and breakage (Mortimer, 1941 and 1942). There are many more modern variations, which integrate the platinum surface into a glass tube, and in some cases, also integrate the reference electrode into the same structure. The tubing imparts better stability to the electrode. One such design consists of a small platinum ring, which is fused into the end of a small diameter glass tube. The ring provides a mechanically stable structure, and one can polish it without the danger of it breaking (Galster, 2000).

In practice, Galster noted that the need for a large electrode surface area (in order to provide good contact with the medium in which ORP is to be sensed) must be balanced against the need for a small enough area to avoid undue adsorption of oxygen. In some cases, the use of small-diameter wire electodes cannot be avoided because they allow measurement of E_h within sediment layers only a few millimeter thick, thereby making it possible to measure depth gradients of ORP (Hargrave, 1972).

Electrode Poisoning

Electrode poisoning may be a confounding factor in ORP measurements, particularly in the case of platinum electrodes kept in place for long-term experiments, such as those undertaken by the author for this project. Bailey and Beauchamp (1971) obtained similar saturated soil ORP measurements using temporarily and permanently placed white platinum electrodes except for the case where measurements were made in anaerobic soils. The ORP measurements with permanently placed electrodes in anaerobic soil were found to be poised at –200 mV.

Bailey and Beauchamp attributed the poising to the poisoning of the platinum electrodes caused by lower electrical conductivity or responsiveness, and possibly due to the the following reactions:

- Platinum may combine with sulfur under reducing conditions.

  $x(H_2S) + Pt_x \rightarrow PtS_x$, where x = valence state of platinum

  This reaction occurs when platinum remains in contact with H_2S for a prolonged period of time. Platinum sulfide has a very low standard potential.

- Platinum metal may adsorb hydrogen gas, resulting in reductions of electrical conductivity and magnetic susceptibility of the metal. In this case, the measured value would not reflect the actual reactions occurring at the platinum surface. Although the standard potential of the H^+-H_2 system is well below -300 mV, higher values could be observed due to mixed potentials.

- Platinum may also form complexes with carbon compounds, which are very stable and kinetically inert. Bailey and Beachamp (1971) gave $[(CH_3)_3\ Pt\ (O_2C_5H_7)]_2$ as a well-known example of such a platinum-carbon complex. Because the Pt-C bond is stronger than the Pt-O bond, the authors postulated that, at low redox potentials, Pt-CHx may form a thin film over the platinum surface, thereby decreasing the responsiveness of the permanently inserted electrode, and possibly explaining the poising at low redox values.

Hargrave (1972) also observed irreversible decreases of E_h in black, highly reduced, subsurface sediments from Lake Esrom. He attributed this to precipitation of sulphides (*sic*) on the platinum electrode surface, and concluded that only a freshly cleaned electrode would measure the true potential in such conditions.

Pre-Treatment of Platinum Electrode

Galster (2000) recommended removal of all contaminants and precipitates on the electrode surface before making any measurements. He suggested using hydrochloric acid as a cleaning agent, because both nitric acid and chromic acids caused the formation of an oxide layer, which must later be removed, on the platinum surface.He also suggested fine mechanical polishing of the platinum, because a rough open surface would stimulate catalytic activity. The polishing medium should be chemically inert and adequately fine, such as 1000-grit corundum paper, to produce a smooth platinum surface. Galster concluded that polishing the platinum electrodes was essential after long-term use.

Galster (2000) also suggested a convenient method for cleaning and testing platinum electrodes by pre-treatment with chinhydrone in a buffer solution with pH = 4.01. Because the cleaning solution has a standard redox potential of E_h = 225 mV one may simultaneously clean and test the measuring cell. Galster discouraged heating of the platinum for cleaning, because, although organic contaminants would be removed, metal oxides would not. In fact, he concluded that metals could be reduced and form alloys with the platinum. Galster also discouraged the chemical reduction of Pt-oxides with sodium sulfite, sodium hydrogensulfite, or ascorbic acid; or cathodic reduction with an applied voltage because the reduction may form a fine platinum powder, and repeated application could increase the catalytic activity.

APHA (1998) recommended treating platinum electrodes by immersion in warm (70 °C) aqua regia (1:3 v/v nitric acid: hydrochloric acid) for 1 to 2 minutes, or 5 minutes in boiling 6N HNO_3, or 5 minutes in chromic acid at room temperature followed by 6N HCl and rinse with water.

Hargrave (1972) suggested that different cleaning methods might be responsible for problems of variation in replicate measurements. He discouraged cleaning with acid solutions, because of the risk of altering the platinum surface. By contrast, he encouraged polishing of the metal surface, which was reported to improve the reproducibility of ORP measurements in his study.

Reference Electrode

The reference electrode for the measurement of oxidation-reduction potential is the same as that used in pH measurement (Galster, 2000). Because of its fragility, the standard hydrogen electrode is not a practical choice for use in microcosms, or *in situ*. Typical reference electrode choices were previously shown in Table 2-2. The AgCl/Ag electrode is comprised of a silver electrode coated with AgCl, and immersed in a solution of high chloride content. The dissolution or precipitation of AgCl keeps the potential of the electrode constant. Measurements may be made if even a small current passing through the half-cell. This characteristic makes it very convenient in practice (Stumm and Morgan, 1996).

Calomel electrodes, which are similar to AgCL/Ag electrodes, are another popular laboratory-reference electrode. The calomel electrode is comprised of a platinum wire set in a paste that is a mixture of elemental mercury, mercurous chloride (calomel, $Hg_2Cl_{2(s)}$), and potassium chloride (KCl). The paste is submerged in a saturated KCl and $Hg_2Cl_{2(s)}$ solutions. The potential of the saturated calomel electrode is controlled by the dissolution and precipitation of the mercurous chloride (Snoeyink, 1996). When a reference electrode is combined with an indicating electrode, thereby forming an electrochemical cell, the electromotive force of the cell can be given by (Stumm and Morgan, 1996):

$$E_{cell} = E_{H(ox\text{-}red)} - E_{ref} \qquad \text{Eq. 2-15}$$

There are some practical considerations that one should take into account when selecting a reference electrode. When measuring ORP in a solution with poor salt content and low conductivity, one should use reference electrodes or electrolyte bridges with large diameter liquid junctions, or preferably, a ground glass sleeve. Furthermore, unlike inert electrodes, reference electrodes have limited lifetimes. The deviation from their correct potential should be routinely checked with standard solutions (Galster, 2000).

Redox Measurement with Analytical Information

In addition to potentiometric measurement, redox potentials may be calculated from a combination of free energy data or from equilibrium constants. This is sometimes called the *indirect* evaluation of redox potentials. The method requires the determination of the concentrations of the members of one of the redox couples in the system, followed by the application of the electrochemical relation in reverse to get the redox potential, providing that the system is at equilibrium. Because the method is only useful when the system is in equilibrium or a sufficiently constant metastable state, it has limited utility in making field measurements. An example where it might be considered, however, is where the relative inertness of processes involving N_2 may allow them to be ignored while considering the equilibrium achieved by other species When appropriately applied, Stumm and Morgan (1996) reported that the analytical determination of ORP may yield results accurate within 5 - 20 mV.

Using a large number of groundwater samples, Lindburg and Runnells (1984) compared E_h values measured electrometrically to those determined by the analytical method described above. As shown in Figure 2-9 they found no consistent correlation between the measured and calculated E_h values. The authors suggested that this was because the redox reactions were not at equilibrium at the electrode.

Sigg (2000) concluded that it is common to find natural systems that are not at equilibrium. Thus, the analytical determination of redox potential for each redox couple in the systems gives more detailed and accurate information about the redox processes and the actual state in a given system. This may be taken in contrast to the potentiometric method, in which the redox couples controlling the measured value at the electrode may not be the same as the predominant redox couples in the solution.

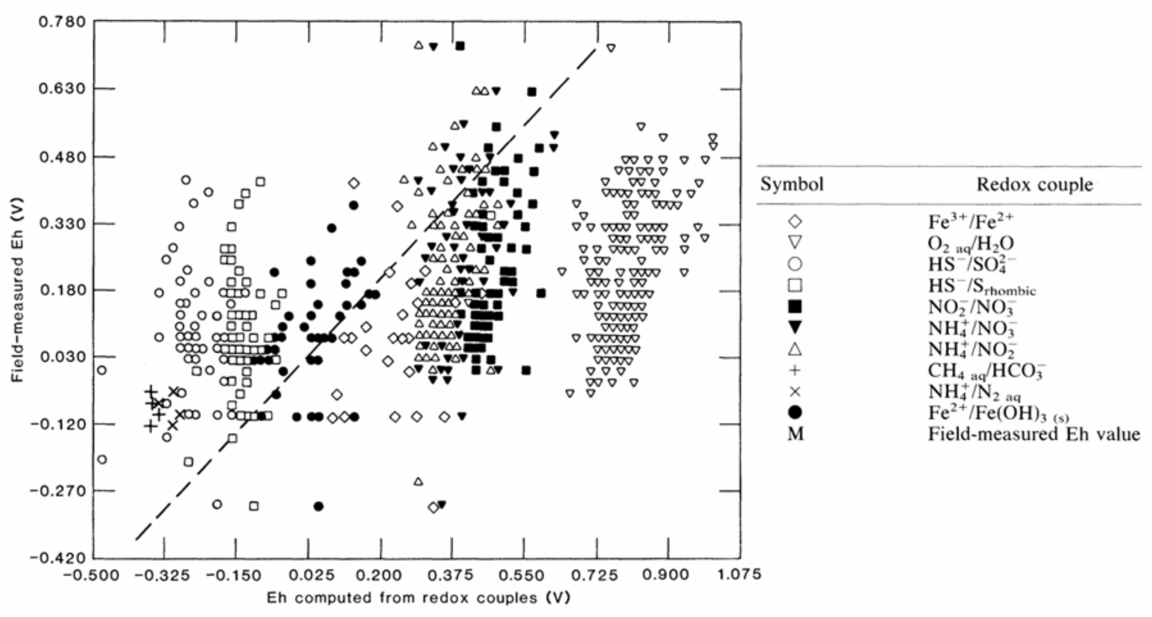


Figure 2-9. Diagram showing ten computed Nernstian Eh values versus field-measurement Eh values for the same samples measured with a platinum electrode. (Modified from Lindburg and Runnells, 1984)

Oxidative Capacity

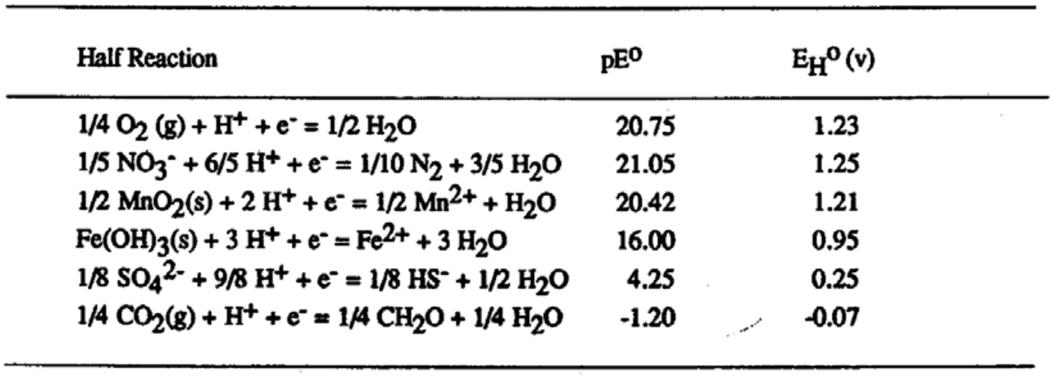
The use of intensity factors, such as E_h and pε, often results in poorly characterized redox systems, which are generally not at equilibrium as a result of kinetically slow redox reactions. For this reason, recent research has concluded that another qualitative guide is required. A conservative quantity, called the oxidative capacity (OXC) has been proposed by Scott and Morgan (1990). OXC incorporates the entire chemical analysis of redox couples of an aqueous system into a single descriptive parameter. While intensity factors reflect activities of free species, oxidative capacity, on the other hand, reflects the total concentration of all relevant species. The total concentration of each component in the system is an important controlling factor in determining the redox status. For example, systems that are open to the large reservoir of oxygen in the atmosphere are well buffered against oxygen depletion, and therefore, their redox status is very stable. The need for a complete analysis of all couples is, nevertheless, the main limitation in the use of oxidative capacity (Scott and Morgan, 1990).

In practice, the oxidation capacity (OXC) can be defined as the equivalent sum of all reducible oxidants to a selected equivalent point. In the same manner, the reduction capacity (RDC) can be defined as the equivalent sum of all oxidizable reductants to a preselected equivalent point. Thus the measurement is reduced to an ordinary titration. The equivalent point is an electron reference level (ERL). It is arbitrary and normally chosen as a matter of convenience. The relationship between OXC and RDC may be shown as:

$$\mathrm{OXC} = \Sigma n_i[\mathrm{Ox}]_i - \Sigma n_i[\mathrm{Red}]_i = -\mathrm{RDC} \qquad \text{Eq. 2-16}$$

where $[\mathrm{Ox}]_I$ and $[\mathrm{Red}]_i$ represent the molal concentrations of the individual oxidants and reductants of the system, and n_i is the number of equivalent electrons that are transferred. System oxidants or reductants are determined by a redox ladder such as that shown in Table 2-5, which places oxidant species on the left above the selected ERL, and reductant species on the right below the ERL. For example, if one selects H_20 as an ERL, OXC = $4[O_2]$ and RDC = $5[NO_3^-] + 2[MnO_2] + [Fe(OH)_3] + 8[SO_4^{2-}] + 4[CH_2O]$. If OXC is greater than RDC, one may say that the system will be oxic when it has reached equilibrium (Scott and Morgan, 1990).

Table 2-5. Selected Important Half Reactions in a Groundwater System (taken from Scott and Morgan, 1990)



Half Reaction	**pE°**	**E_H^o (v)**
$1/4\ O_2\ (g) + H^+ + e^- = 1/2\ H_2O$	20.75	1.23
$1/5\ NO_3^- + 6/5\ H^+ + e^- = 1/10\ N_2 + 3/5\ H_2O$	21.05	1.25
$1/2\ MnO_2(s) + 2\ H^+ + e^- = 1/2\ Mn^{2+} + H_2O$	20.42	1.21
$Fe(OH)_3(s) + 3\ H^+ + e^- = Fe^{2+} + 3\ H_2O$	16.00	0.95
$1/8\ SO_4^{2-} + 9/8\ H^+ + e^- = 1/8\ HS^- + 1/2\ H_2O$	4.25	0.25
$1/4\ CO_2(g) + H^+ + e^- = 1/4\ CH_2O + 1/4\ H_2O$	-1.20	-0.07