REDOX POTENTIAL SOP

Excerpt from Bruce A. Pruitt. 2001. Hydrologic and soil conditions across hydrogeomorphic settings. Dissertation. University of Georgia, Athens, GA.

Redox Chemistry. Pankow (1991) described the negative logarithm of the electron activity (pe) as the master variable for describing the equilibrium position for all redox pairs in a given system:

$$pe \equiv -\log \{e\} \qquad (1)$$

According to Faulkner et al. (1989) oxidation-reduction potential (redox) is a quantitative measure of electron availability and is indicative of the intensity of oxidation or reduction in both chemical and biological systems. When based on a hydrogen scale, redox potential (E_H) is derived from the Nernst Equation (Stumm and Morgan 1981):

$$E_H = E_H^o + 2.3 \times (R \times T)/nF \times \log (\Pi_i \{ox\}^{ni}/\Pi_j \{red\}^{nj}) \quad (2)$$

where

E_H^o = potential of reference, mV

R = gas constant = 81.987 cal deg^{-1} $mole^{-1}$

T = temperature, ^oK

n = number of moles of electrons transferred

F = Faraday constant = 23.061 cal/mole-mv

{ox} and {red} = activity of the oxidants and reductants, respectively

At standard conditions, pe can be estimated from E_H by:

$$pe = E_H / 0.05916 \quad (3)$$

Sulfates are transformed to sulfides at an approximate E_H range of -0.075 to -0.150 V (Mitsch and Gosselink 1993, Stumm and Morgan 1981). Similar to sulfide emissions, variability in E_H can be attributed to spatial heterogeneity in texture, structure, organic matter, aeration, and moisture (Megonigal et al. 1993).

Typically, redox potential is reported in millivolts (mV) as referenced to a **H**ydrogen probe, hence $E_{\mathbf{H}}$. A saturated calomel electrode (E_{SCE}) is used in the following example. Silver chloride reference probes (E_{AgCl}) would have a different correction factor. *In situ* redox potential (E_{sce}) needs to be corrected in the following steps:

1) corrected to calibration curves specific to the electrode:

$$\text{Corrected } E_{sce} = 24.05 + 1.207 \ (\text{Observed } E_{sce}) \quad (4)$$

2) normalized to a predetermined soil pH (e.g., pH 5) for comparison between sample populations:

$$E_{sce,\ pH5} = \text{Corrected } E_{sce} + 59.16\ (\text{Field pH} - 5) \quad (5)$$

3) corrected to a hydrogen probe using the Nernst Equation and accounting for a calomel reference electrode and soil temperature (Pankow 1991):

$$E_H = E_{sce,\ pH5} + 0.268 - (2.303 \times RT)/2F \ \log (\{Hg_{(l)}\}^2 \{Cl^-\}^2)/\{Hg_2Cl_{2(s)}\}) \quad (6)$$

In general, the correction from a E_{SCE} and E_{AgCl} is +244 mV and +222 mV, respectively.

Application. Several applications of redox potential have been identified below:

1. "Red Flag": conditions are too reduced to use Clarke-type D.O. probes without spoiling the silver anode. In general, anaerobic conditions occur at a redox potential of approximately +320 mV (pH-dependent and adjusted to hydrogen reference electrode). When redox drops below this level, D.O. readings are highly suspect since the membrane does not discriminate between partial O_2 and sulfides. In other words, *you may be reading sulfides and not oxygen*.
2. Redox potential could be viewed as an extension of the oxygen scale. In other words, the D.O. probe spans the aerobic scale and the redox probe extends that scale to measure anaerobic conditions. Inferences to geochemistry and chemical speciation can be made from the oxidative state of the system. Application to metal sequestration, metal-iron, -sulfide, -methane complexation, and the subsequent bioaccumulation potential is possible;
3. Redox potential can be used to identify anaerobiosis at or near the water column and sediment interface in streams, lakes, and estuaries; In addition, based on the partial pressure of oxygen, a relationship can be developed between redox potential and the consumption of oxygen by anaerobic and even highly reducing sediments (anaerobic metabolism) in lakes, rivers, and estuaries;
4. Based on a redox potential, a pe vs. pH stability diagram can be developed to aid in nutrient exchange studies including the timing, release, and partitioning of important water and sediment quality pollutants such as nitrogen and phosphorus. Most importantly, redox potential can be used to address error associated with chamber-effect during closed chamber measurements of the water-sediment interface;
5. As indicated above, redox potential is critical in establishing water and sediment

quality standards applicable to wetlands; and

6. Redox potential can be used to develop technical standards across wetland hydrogeomorphic gradients (Personal Communication with Wade Hurt, NRCS-NTCHS, August 2000 and Pruitt 2001).

Construction. Soil redox potential probes were constructed using a 7 to 8 mm long, 18-gage platinum tip soldered (silver solder) to 10-gage, solid copper wire. The platinum was cut using a new, stainless steel wire cutter, bathed in a 1:1 solution of concentrated HCl and HNO_3, rinsed with deionized water, and air dried before construction. The connection between the platinum and the copper was sealed with epoxy and heat shrink wrap. The completed probe was wired to a Campbell™ CR-10 and multiplexer AM-16 with –gage, shielded wire. The connection between the probe and the shielded wire was water-proofed by using epoxy, shrink wrap, tygon tubing, and silicon caulking.

Calibration. Redox potential probes were calibrated to quinhydrone ($C_6H_{10}OH_2$). Quinhydrone is poisonous if ingested, but does not affect pH buffers and is easily prepared fresh prior to meter calibration. Thus, it must be prepared "fresh" prior to calibration. However, field preparation is as simple as adding pH buffered standards to a pre-weighed aliquot of quinhydrone and mixing thoroughly as follows:

1. Three standards were made by mixing 250 mg of quinhydrone with 250 ml each of pH buffered standards of 4, 7, and 10 resulting in redox standards +218.4, +41, and -36.5 mV, respectively;
2. The standard is thoroughly mixed to reach saturation;
3. The resulting saturated solution is decanted into a suitable container and the redox potential probe and the reference probe is placed in the solution;

4. A pre-calibration of each redox probe was conducted to ensure proper probe construction;
5. A final calibration, on the probes that passed the pre-calibration step, was conducted following complete wiring through the Campbell™ CR-10 to account for resistance and equipment effects;
6. Once the reading was stable, the values of each of the three standards were recorded; and
7. A three-point, calibration curve for each probe is developed.

3.0 BIBLIOGRAPHY

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