SOIL REDOX POTENTIAL: IMPORTANCE, FIELD MEASUREMENTS, AND OBSERVATIONS

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Reduction and oxidation measurements create important data for analysis of wet soils. These measurements are actually recordings of voltage (EH) over time between a reference electrode and a sensor electrode inserted into

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a soil. The sensor electrodes are usually made of platinum wire (Pt electrode). Hydric soils require a period of reduction, and these measures can provide the length of time that the reduction process is occurring. The voltage results from an exchange of electrons between a redox couple such as ferrous and ferric iron during the process of reduction and oxidation. In soils that have fluctuating wet and dry conditions, wide fluctuations in Eh occur. Micro site differences complicate these measurements in that anaerobes may be active and at 1-cm away they are completely inactive. The ferrous–ferric iron couple usually dominates these measurements but other couple often contributes complicating the measurements and interpretations of the data. Reference electrodes are often fine for laboratory work but are not rugged enough for the field. In this chapter, suggestions for improvement are discussed. Field-measuring equipment and the Pt electrode are also sensitive and subject to problems that often lead to spurious results in the field. These problems are discussed at length. Iron-coated tubes and other methods of establishing redox conditions are relatively recent and are discussed, also.

I. INTRODUCTION

A. Redox and Wetland Issues

Wetland environmental issues have increased in importance in the last three decades. The public became aware of the importance of wetlands after centuries of drainage and other degradation (Mitsch and Gosselink, 1986). In the United States, legal aspects of wetland preservation have increased the need for wetland delineation procedures. Hydric soils are defined as follows: "A hydric soil is formed under conditions of water saturation, flooding, or ponding long enough during the growing season to develop anaerobic conditions in the upper part" (Hurt *et al.*, 2002). There is a need for improved assessment of anaerobic conditions, that is chemical reduction in soils, to identify hydric soils and wetlands. The classic measure of an anaerobic condition is the redox potential (Eh). This chapter is an overview and summary of the measurement of redox potential in soils, including equipment, possible problems, and alternatives.

Hydric soils include soils that developed under sufficiently wet conditions to support the growth and regeneration of hydrophytic vegetation. Soils that are saturated because of artificial measures are included in the concept of hydric soils. Also, soils in which the hydrology has been artificially modified are hydric if the soil was hydric in its unaltered state. Some soil series designated as hydric on hydric soil lists have phases that are not hydric because the water table is deep or because flooding and ponding do not occur. Mottling, nodules, concretions, and other morphological features of soils associated with reduction and oxidation of Fe and Mn are summarized as redoximorphic features (Vepraskas, 1996) and called "paints of the earth" (Fanning and Fanning, 1989).

A hydromorphic soil owes its morphology to water-related processes, because the soils may be submersed below the water table continually, producing gley features or periodically creating redoximorphic features. These soils retain their morphology intact, or the morphology is only partly altered even when the soils are drained. When gleyed soils are drained, for instance, ferrous iron is oxidized to ferric iron on exposure to air (e.g., root channels) and therefore resembles redoximorphic features with the onset of drainage. In the United States, soils that are currently periodically or permanently water saturated are called "wetland soils" even if they are not actually in a "jurisdictional wetland" as defined by the US Army Corps of Engineers Manual (1987). Wetland soils do not differ from hydromorphic soils, except that the hydromorphic soils may or may not be subjected to reduction and wetland soils are definitely reduced.

1. Reduction and Oxidation (Redox) as a Process

Reduction, as a chemical process, occurs when an atom accepts an electron. This process increases the valence of an anion or decreases the valence of a cation. Oxidation is the reverse process and occurs when an atom loses an electron. In wetland soils, a fluctuating water table causes the Fe that coats soil particles to alternate between oxidized and reduced forms over the course of a year. Saturation for periods longer than a couple of weeks is usually sufficient to reduce Fe in the subsoil of many soils (Vepraskas, 2001). Vepraskas *et al.* (1999) created these conditions and observed that redoximorphic features and hydric soil field indicators could be created in less than 3 years with several wetting and drying cycles. Oxidation–reduction (redox) reactions in soils are mainly controlled by microbial activity and the presence of a supply of carbon for the microbes; during respiration, these organisms use organic substances as electron donors (Craft, 2001). Molecular oxygen acts as the preferred electron acceptor as long as there is a sufficient supply of oxygen. If the supply of oxygen is terminated, as is the case under conditions of saturation, the microbial activities switch from aerobic to facultative and eventually to anaerobic respiration. Once oxygen is consumed, alternative electron acceptors are used. The descending sequential order of acceptor preferences is NO_3^-, MnO_2, $Fe(OH)_3$, SO_4^{2-}, and CO_2 (Bartlett, 1981, 1998; Bartlett and James, 1993). Soils containing these elements provide an ecological niche for microbes; the microbes gain energy from the soil organic matter and are able to proliferate (Conrad and Frenzel, 2002). In either temporary or semipermanent water saturation conditions, the diffusion of oxygen into soils is drastically curtailed, at least episodically. The biological and chemical processes are forced to change in an alternating manner with water saturation and then drainage. The soils change from an aerobic to an anaerobic environment and vice versa; soils that remain saturated (gley) are chronically reduced. These gley-weathering zones are quite different morphologically as seen in the field.

2. Redox Potential

The abundance of oxidized and reduced chemical substances can be measured as a potential difference between an inert indicator electrode and a reference cell using a voltmeter or pH meter. The *redox potential* (Eh) is defined as the emf or potential of an electrode consisting of a redoxcouple (e.g., SO_4^{2-}/H_2S) measured in a galvanic cell against the standard hydrogen electrode. Eh in soils generally ranges between -1 and $+1$ V. This variation is due to the buffering effect or poise of water on redox reactions (O_2/H_2O; H_2O/H_2) (Bartlett and James, 1993, 1995). Measured Eh must be regarded as an integrated parameter, which is triggered by the activity of living microbial communities. Thus, changes of external conditions, such as precipitation and water table (as indirect parameters of oxygen supply), temperature, and availability of organic matter, can all lead to changes in Eh values. Consequently, the redox potential can vary by several orders of magnitude both temporally (e.g., minutes, hours, or days) and spatially (e.g., micro sites, horizons, soil types, or landscapes) (Gao *et al.*, 2002; Vepraskas *et al.*, 1999). This enormous range of Eh values, even within a single soil horizon, makes the interpretation of redox data particularly complicated.

According to Reddy *et al.* (2000), microbial aerobic activities reflect oxidizing conditions above an Eh of 300 mV; facultative reducing microbes are active from Eh 300 to -50 mV, or moderately reducing conditions. The preferred electron acceptors are first oxygen followed by NO_3^-, Mn^{4+}, and Fe^{3+}. Obligate-reducing microbes dominate at Eh levels below -50 mV. In these strongly reducing conditions, SO_4^{2-} and CO_2 are the usual electron acceptors. We use the Eh 300 mV as the break between aerobic and anaerobic conditions unless otherwise stated as per Reddy *et al.* (2000).

In his classic paper on redox potential of marine sediments, ZoBell (1946) states, "The redox potential of sediments may be used advantageously in the study and interpretation of the morphology, general nature, and chemical processes in unconsolidated sediments." ZoBell believes that the redox potential has a profound effect on diagenesis of sediments, including conversion of organic matter into petroleum. Organic matter and mineral diagenesis are important redox-related processes in soils. The term "transformation" is preferred as more general rather than diagenesis. As noted by ZoBell (1946), Craft (2001), and Vepraskas (2001), an abundance of readily decomposable organic matter promotes reducing conditions. If organic matter is present in saturated soil, facultative reducing bacteria and perhaps allied organisms create the reducing conditions. The distribution (activity) of methanogenic organisms in anaerobic horizons is governed by fresh organic material. Carbon "hot spots" (Wachinger *et al.*, 2000) are zones in which CH_4 is produced because of very strong redox gradients that are caused by the porous structure of soil, possible colonies of microbes, concentrations of readily usable carbon, and the release of oxygen via the roots (Vepraskas *et al.*, 1999).

Bacteria in saturated soils that are consuming organic matter probably are the principal dynamic agents influencing redox potential. These bacteria produce fatty acids, such as acetic acid, ethanol, and other alcohols. Acetic acid and ethanol inhibit the growth of the bacteria and slow the consumption of organic matter over time. Organic matter undergoes a much slower transformation in anaerobic soils, especially once fermentation starts. As stated by Evans (2002):

> Under anaerobic conditions (lack of oxygen), pyruvic acid produced from glucose in the root cells of higher plants is converted to CO_2 and ethyl alcohol. Ethyl alcohol tends to accumulate within root cells, and if anaerobic conditions persist, may accumulate at concentrations that can become toxic. Anaerobiosis creates an environment that impairs the growth rate of most plants that require oxygen for respiration. Drainage is the practice of removing excess water from land to minimize the occurrence of waterlogging. It has been an important management practice for centuries, and the consequences of poor drainage have been studied extensively over the past century.

Therefore, wetland soils are often characterized by the accumulation of humus. As a result, wetland soils typically have much thicker organic horizons than their aerobic counterparts. The lower efficiency of the decomposition of organic matter under anaerobic conditions leads to an enrichment of water-soluble intermediate metabolites, which are characterized by high aromaticity and complexity of their molecules. In turn, a high level of solute organic reductants can act as an efficient conveyor of redox-sensitive elements (Lovley *et al.*, 1998) and amplify the reducing conditions (Struyk and Sposito, 2001).

B. RELEVANCE OF REDOX MEASUREMENTS IN SOIL SCIENCE

The identification of redox intensities and dominant redox processes in soil under specific field conditions has a long tradition, starting with the pioneering work that was done more than 80 years ago (Bradfield *et al.*, 1934;

Brown, 1934; Clark, 1925; Gillespie, 1920; Pearsall, 1938; Pearsall and Mortimer, 1939; Willis, 1932). Gillespie (1920) used platinum (Pt) electrodes to ascertain redox values, and Brown (1934) recognized that Eh was an intensity measure and introduced poise as a measure of redox capacity. Poise is the resistance to change in Eh when a small amount of oxidant removes electrons from a system or, conversely, a small amount of reductant adds electrons (Rowell, 1981). Poise and Eh are similar to buffer capacity and pH in soils. Poise increases with increasing concentration of oxidant and reductant (Bartlett and James, 1993; Brown, 1934; Rowell, 1981).

Pearsall (1938) and Pearsall and Mortimer (1939) were able to relate various soil chemical properties and marsh vegetation zonation to redox conditions and measurements. Bradfield *et al.* (1934) used Eh measurements to locate suitable planting areas in orchards. After making initial Eh measurements on soil pastes or suspensions, it became apparent that it was only possible to detect oxidation–reduction conditions in soils when the measurements were carried out *in situ* (Bohn, 1968; Quispel, 1947; Willis, 1932). Quispel (1947), with some insight from very few field measures, related Eh (his rH) to water levels, moisture content, soil structure, and the amount of reducible materials. *In situ* measurements of Eh using temporary or permanently installed electrodes have routinely been applied in soil science since the 1960s (Aomine, 1962; Blume, 1968a; Mansfeldt, 2003; McKenzie *et al.*, 1960; Meek *et al.*, 1980; Thompson and Bell, 1996).

Many important redox-sensitive components, in particular trace elements, such as Se(IV)/Se(VI), and Cr(III)/Cr(VI), and associated elements (e.g., P, Mo, Si) undergo redox transformation (Runnells and Lindberg, 1990). Reactivity, mobility, toxicity, and bioavailability of these elements frequently depend on their redox state (Sigg, 2000). Toxic organic materials attenuate biomediation processes and are often activated or deactivated by redox processes (Doong and Wu, 1995).

Furthermore, redox reactions trigger pedogenetic responses. These responses result in the field recognition of hydric soils from nonhydric soils in jurisdictional wetland delineations. In the following sections, brief illustrations are given of field redox measurements showing the importance of the standard procedures.

1. Agriculture and Cultivation

Redox conditions are of basic importance to agriculture. Most of our agriculture systems are based on nonsaturated conditions. Anaerobiosis impairs the growth of most crops (notable exceptions are rice and cranberries). To minimize the negative condition of waterlogging, drainage has been the management tool of choice for many centuries. The consequences of poor drainage have been heavily studied, but the reverse, or restoration of waterlogging, has not been studied as much. Wetland restoration and the use of wetlands for waste disposal and for improving water quality of agricultural runoff and for attenuating chemical contaminants, however, demonstrate the need for research.

2. Plant Nutrients and Vitality

The decrease of the partial pressure of O_2 leads to a decrease in the plants' ability to take up mineral nutrients (Drew *et al.*, 1988), depending on the minerals. For example, the uptake of potassium is hindered to a far larger degree than that of sodium (Drew *et al.*, 1988). The reduced uptake of mineral nutrients and insufficient O_2 supply also impede root growth. Reduced root growth can result in lower production of growth regulators, such as hormones and other metabolites that are produced by roots, which in turn impacts the vitality of the entire plant. It is well recognized that oxygen deficiency inhibits synthesis of indolylacetic acid, gibberellins, and cytokinins by the root and increases the concentration of abscisic acid in the xylem sap (Reid and Bradford, 1984). The increase in free abscisic acid in leaves coincides with decreases in leaf water potential and turgidity (Santiago *et al.*, 2000). Changes in root–shoot chemistry can also interfere with photosynthesis, ion transport (e.g., K^+), and plant growth in general (Kludze and DeLaune, 1996).

In most cases, the absence of oxygen leads to a greater mobility of redox-sensitive elements and hence to the accumulation of Mn^{2+}, Fe^{2+}, or sulfides up to phytotoxic levels (Pezeshki *et al.*, 1988). Redox conditions are known to have a great influence on the transformation of nitrogen and basically determine its loss as N_2O and N_2 or its uptake as NH_4^+ or NO_3^- by plants. Furthermore, pedogenic Fe- and Mn-(hydr-)oxides are the most important adsorbents of micro- and macronutrients such as molybdenum (Gupta, 1997), copper (Cu) (Zhou and Wong, 2001), phosphorus (Frossard *et al.*, 1995), and sulfate (Chao *et al.*, 1962). Under anaerobic conditions, oxides dissolve and thus no longer contribute to nutrient adsorption. In contrast, sulfides are known to be effective sinks for soluble metals in the soil solution by forming inaccessible compounds such as ZnS, CuS, FeS, or FeS_2.

3. Heavy Metals

During petroleum exploration and oil well preparation, drilling mud, crude oil, and saline ground water are spilled onto the surrounding soil near the well and often find their way into surface water (Al-Sawari *et al.*, 1998).

Apart from organic compounds (e.g., polycyclic aromatic hydrocarbons), these fluids contain heavy metals such as vanadium and nickel. Roth (2000) and Roth *et al.* (2000) have studied the vanadium migration at the oil production fields of the *Agua Dulce* District near Tabasco, Mexico. They observed that strong reducing conditions in organic-enriched soils with Eh measurements ranging from 90 to −240 mV enhance the mobility of vanadium. They believe that vanadium can thereby enter into the human food chain.

4. Toxic Organics

The degradation of toxic organics depends on their innate chemical properties and environmental conditions (Reddy *et al.*, 2000). Recently, microbial reductive dechlorination of chlorinated ethane has become an important issue in the context of both natural attenuation and enhanced bioremediation. For example, the frequently observed groundwater contaminants tetrachloroethene (PCE) and trichloroethene (TCE) are dechlorinated under strictly anaerobic conditions by microorganisms (National Research Council, 1994). Dehalogenase enzymes are highly specific enzymes involved in this anaerobic dechlorination process; the highly chlorinated solvents are excellent electron acceptors. In addition, some of these bacteria, for example *Dehalospirillum multivorans* (Scholz-Muramatsu *et al.*, 1995), *Dehalobacter restrictus* (Holliger *et al.*, 1998), and *Dehalococcoides ethenogenes* (Maymó-Gatell *et al.*, 1997), are able to utilize these substances in their energy metabolism.

Reductive dechlorination of PCE is based on the successive replacement of chlorine materials by hydrogen leading to TCE (Cirpka *et al.*, 1999). Less chlorinated aliphatic hydrocarbons, such as *cis*-1,2-dichloroethene (DCE), or vinyl chloride, can be metabolized *aerobically* to CO_2, chloride, and water by methane- and ethane-oxidizing bacteria (Wackett, 1995). Depending on the environmental conditions and the presence of the dechlorinating bacteria, these processes can be utilized for groundwater remediation. In addition, anaerobic conditions are likely to cause an increase of soluble humic substances in wetland soils, which in turn enhances the solubility of toxic organics (Pardue *et al.*, 1993). It is important to have fast, reliable field tests of redox to measure these conditions.

5. Pesticides

There are numerous pesticides for which degradation is favored by anaerobic/reducing conditions (Seybold *et al.*, 2001). We are using only a selected few here. The degradation of such pesticides as 2,4,5-trichlorophenoxyacetic acid (Gibson and Suflita, 1990), pentachlorophenol (Chang *et al.*, 1996), and chloroanilines acid (Kuhn *et al.*, 1990) in soils and aquifers is favored by strong reducing conditions (Eh < 100 mV). Seybold *et al.* (2001) observed rapid degradation of atrazine and metolachlor. Within 25 days in a strongly anaerobic condition, most of the pesticides had degraded to metabolites. The metabolites were not considered hazardous.

6. Radionuclides

Groundwater originating from uranium mine mill-tailing sites is often contaminated with uranium (Abdelouas *et al.*, 1998, 2000; Buck *et al.*, 1996). The behavior of such high-level nuclear water is determined by oxic/anoxic conditions (Casas *et al.*, 1998). The microbially mediated reduction of soluble U^{6+} to insoluble U^{4+} was proposed as a mechanism that removes dissolved uranium from waste streams. The potential of reductive precipitation was demonstrated with anaerobic microbes, such as iron- and sulfate-reducing bacteria (Robinson *et al.*, 1998).

7. Methane

Methane, as part of the greenhouse gas problem, causes a global warming concern. Methane production from wetlands, therefore, needs to be addressed as an important issue. The emission of CH_4 from wetland soils is the result of an interaction between methane production and oxidation. In anaerobic, gray soils (e.g., the Bg horizon in a Histic Humaquept), CH_4 is produced by methanogenic bacteria (Fig. 1). CH_4 can be oxidized by methanotrophic bacteria (consumption) (e.g., the Bg horizon during a dry period in an Aeric Endoaquept) on diffusion through the aerobic zone. Small areas of wet depressions, which are influenced by alluvial and colluvial processes (Endoaquepts), are effective CH_4 emitters (Sommer and Fiedler, 2002). Well-aerated soils can act as effective CH_4 sinks (Smith *et al.*, 2003). Therefore, the spatial arrangement of aerobic and anaerobic soils and of interhorizonal areas in individual soil profiles or even in pedons on landscapes is certainly a key factor for greenhouse gas atmospheric discharges (Fig. 1). The alternations of source and sink of these gases can be observed from the soil morphology itself (Fiedler and Sommer, 2000; Fiedler *et al.*, 2005). An inexpensive assessment of this problem of methane as a greenhouse gas can be made by simply observing soil morphology. Figure 1 illustrates the hydrosequence described by Fiedler and Sommer (2000).

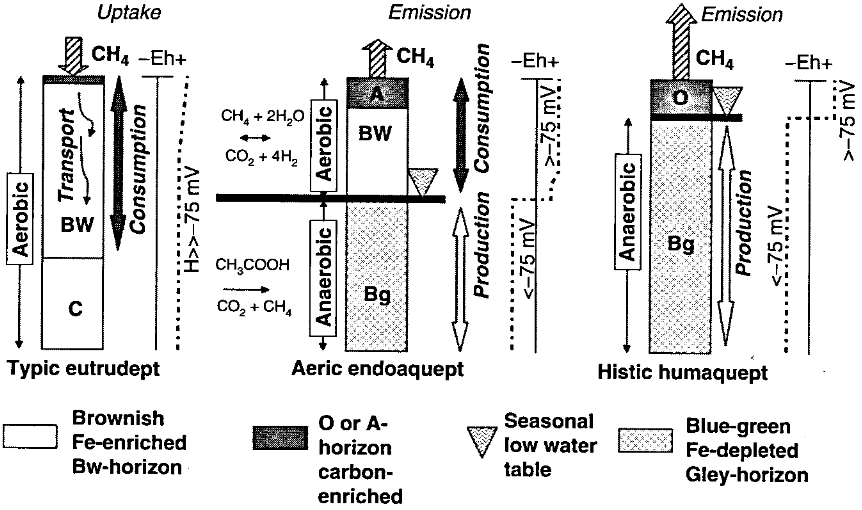

Figure 1 Schematic depiction of the relationship between CH_4 flux, water table, redox conditions, soil morphology, and soil types. (See Color Insert.)

The relationship of the water table to soil morphology, the redox potential, and the production and consumption of organic materials is important.

8. Soil Genesis

Redox processes are regarded as primary mechanisms in the weathering of rocks and minerals (Walker, 1949). Redox conditions determine important properties of clay minerals such as cation-exchange capacity (Stucki and Roth, 1977), surface area, and swelling behavior (Gates *et al.*, 1993; Shen *et al.*, 1992). Of all the elements comprising the crystal structures of minerals, Fe is one of the most interesting because it may be oxidized or reduced *in situ* (Stucki *et al.*, 1987). In general, Fe occurs in its reduced form in primary minerals. Structural Fe^{2+} may be oxidized under aerobic conditions and cause an imbalance in the overall electrostatic charge of the crystal structure (Churchman, 2000). The redox status of Fe in crystal structures ($Fe^{2+} \leftrightarrow Fe^{3+}$) can (1) affect the availability of nutrients (Komadel *et al.*, 1995; Stucki *et al.*, 1984) and (2) initiate clay mineral transformations in the course of pedogenesis following a sequence illite–vermiculite–smectite (Niederbudde and Fischer, 1980; Wilson, 1999). It is well known that this oxidation process leads to ferric Fe oxides (Schwertmann and Taylor, 1989).

Stucki *et al.* (1987) found that octahedral Fe^{3+} in the crystal structures of smectites was reduced to Fe^{2+} by microorganisms indigenous to the soil.

Ernstsen *et al.* (1998) studied microbial reduction of structural Fe in minerals in comparison to chemical reduction. They found that the presence of microbes led to an increase of structural Fe^{2+} from ~10 to 34% of the total Fe content in clay. However, the observed concentrations were lower than those obtained for chemically reduced (Na-dithionite) subsamples (76–79%).

The formation of redoximorphic features, such as Fe/Mn concentrations and nodules, is due to element redistribution (Blume, 1968b,c; Fiedler *et al.*, 2004a; Richardson and Daniels, 1993; Richardson and Hole, 1979; Vepraskas *et al.*, 1999) and has been reviewed by Vepraskas (1996, 2001). The development of depletion and accumulation horizons (Blume and Schlichting, 1985; Dobos *et al.*, 1990; van Schuylenborgh, 1973) and bog iron ores (Blume, 1968b; Dobos *et al.*, 1990; Kaczorek and Sommer, 2003) is also covered by Vepraskas (1996, 2001) and will be discussed later.

The genesis of *acid sulfate* soils is mainly influenced by redox-related processes (Fanning and Fanning, 1989). The exposure of the sulfide in these soils to air by soil disturbance, especially drainage, can lead to the generation of sulfuric acid and a change in carbonate concentration and pH and the formation of either gypsum or jarosite. Under anaerobic conditions, sulfates originating from seawater are reduced and nearly insoluble Fe-sulfides accumulate. On exposure to air, the sulfide oxidizes to sulfuric acid, which "destroys" the carbonates. Often the carbonates neutralize some of the acid and form gypsum. If few or no carbonates are present, the acid sulfate reactions form jarosite. A surplus of sulfuric acid leads to complete decalcification and finally to very strong acidification ($pH < 3$) (Fanning and Fanning, 1989).

II. POTENTIOMETRIC MEASURING TECHNIQUES

The minimum setup for the measurement of Eh requires a working electrode and a reference electrode that are connected to a voltmeter or pH meter (Pearsall and Mortimer, 1939). The potential is transduced by an amplifier (included in the mV or pH meter) and transmitted to a data acquisition unit, such as a data logger (Flessa and Fischer, 1992), personal computer (PC) (Fiedler and Fischer, 1994), or write recorder (Le Brusq *et al.*, 1987), via high-quality, well-protected, and insulated cables. Figure 2 shows a schematic arrangement of a general field measurement circuit using a galvanometer, an amplifier, two known resistances in the instrument, and two electrodes: a reference cell electrode and a working Pt electrode in the soil. This arrangement detects voltage in the soil (Eh) between the electrodes.

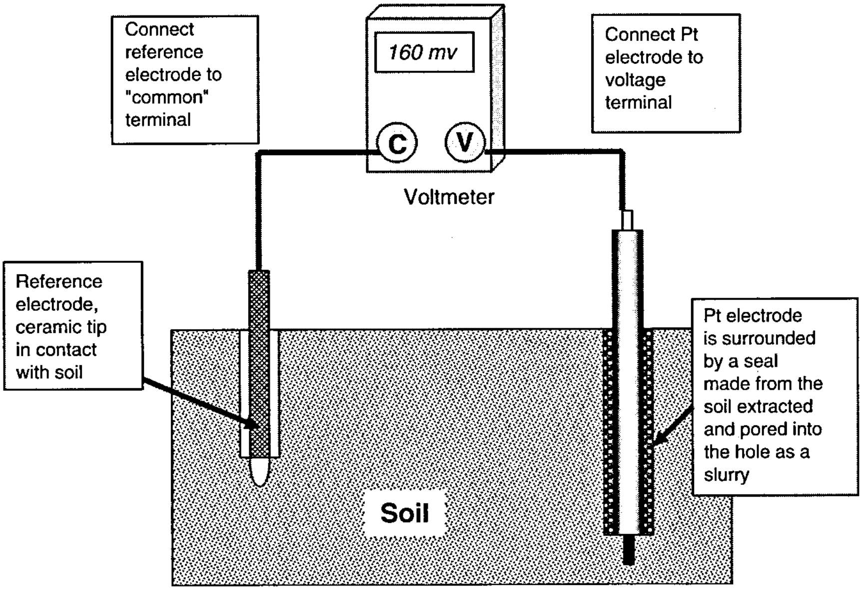

Figure 2 Basic setup for the measurement of soil redox potentials, which is associated with a number of shortcomings (discussed in the text). For simplicity, only one redox electrode is shown, although multiple electrodes should be installed.

Reprocessing the signal impedance by means of an amplifier is essential because the potentials ($\Delta Eh_{max} = 2000$ mV) are loaded with an extremely weak current ($<10^{-7}$ A) (Morris and Stumm, 1967). To prevent voltage deterioration, the amplifier input impedance should be $>10^8\ \Omega$ (preferably $10^{12}\ \Omega$).

Although wetland science and soil science provide abundant opportunity for the application of Eh measurements, currently very few commercial electrodes that solve the voltage deterioration and low wattage problems are available for field use to evaluate soil redox conditions. The high costs of commercial electrodes have driven many researchers to design their own systems and have led to a large number of detailed publications on electrode systems (Blanchar and Marshall, 1981; Fischer and Schaller, 1980; Mann and Stolzy, 1972; Pang and Zhang, 1998; Quispel, 1947; Teasdale *et al.*, 1998; Zhang and Pang, 1999).

A summary of Eh electrode systems that have worked well in field practice for a variety of purposes is included. Technical problems of Eh electrode construction are discussed. A construction "manual" of currently used electrodes will be presented.

A. REFERENCE CELL

Reference cells should be able to provide a defined and constant virtual grounding potential that must be stable against changes in outer electrolyte composition. Ives and Janz (1961) outline most of the diverse variety of reference electrodes and construction.

A common reference cell is the Ag/AgCl single-junction reference electrode. Most commercial versions consist of a glass tube containing 4-M solution of KCl saturated with AgCl. The lower end of the electrode, which is placed in the soil, is sealed with a porous ceramic frit that acts as a diaphragm. The porous ceramic material allows the slow passage of the electrolyte in the electrode to the soil. The electrolyte forms a liquid junction with the soil or soil water. Within the electrode, an Ag wire is coated with a layer of AgCl. This wire dipped in the electrolyte solution is coupled or joined to a low-noise cable, which connects to the pH/Eh meter. Generally, industrial electrodes have very small contact areas, or diaphragms, which may cause problems with the galvanic contact. Frequently, such reference electrodes in the field become erratic during the summer season due to a low moisture content. Also, the glass electrode body is fragile; a sturdier material such as plastic is suggested.

Farrell *et al.* (1991) also noted that the small storage capacity of the KCl electrolyte in the commercial electrodes requires frequent refilling with KCl solution. Such a problem can hinder long-term field use in remote areas and may add to project costs.

Farrell *et al.* (1991) provide instructions for manufacturing reference cells with large diaphragms. Following these instructions with modifications, Fiedler *et al.* (2003) constructed a reference cell with a diaphragm that was ~70 times larger than that of conventional reference cells (Fig. 3). These reference electrodes are able to stand up better in the field than commercial types. These reference cells are conventional Ag/AgCl electrodes designed with tough electrode parts wherever they come in contact with the soil. In contrast to this, however, the diaphragm consisted of a ceramic ring that had been cut from the head of a micro-tensiometer.

The body of the electrode consists of a polyvinyl chloride (PVC) shaft, which is closed by a hollow polyethylene plug at the top. At the bottom, the diaphragm is inserted via waterproof resin into the PVC shaft.

A coiled Ag wire (99.9% Ag, 0.5 mm) was electrolyzed as follows: after the wire was cleaned in ethanol, the Ag wire (anode) and a Pt wire (cathode) were immersed in an HCl solution (1 M) and a potential of 1.7 V was set up for electrolysis. The process was continued for about 5 min. The formation of a gray-brown coating should occur. After the electrolysis process, the Ag wire was cleaned under running water and left in water overnight. Then the

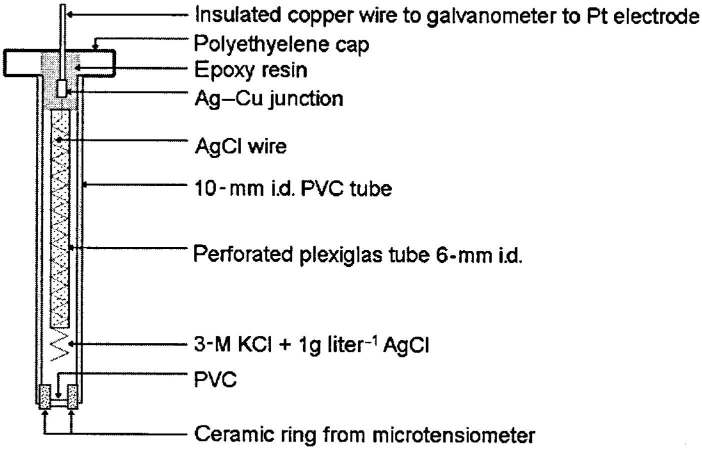

Figure 3 Reference electrode (see text for details). (See Color Insert.)

Ag wire was soldered to the conductance Cu wire at the Ag/Cu junction and suspended into a perforated plexiglass tube (6-mm i.d.), which was inserted into the PVC shaft through the plug. A recess in the interior of the plug contained the soldered joint and a part of the connecting cable to the Eh meter that was sealed with epoxy resin. The reference was filled with 3-M KCl to which 1 g liter^{-1} of AgCl (saturation) was added in order to prevent dissolution of the AgCl wire in the concentrated Cl solution. The electrode potential for this half-cell is 204.6 mV relative to the standard hydrogen electrode at 25°C.

The constructed reference cell showed a current of 2×10^{-5} A, whereas a conventional reference cell exhibited a current of 1×10^{-7} A. It was concluded that the galvanic contact could be maintained for a much longer time when a diaphragm with a larger diameter was used. However, excessive efflux of the electrolyte could be a source of "potassium fertilizer" and might be undesirable in some cases.

Matia *et al.* (1991) tested Calomel (Hg_2Cl_2/Hg) and Ag/AgCl reference electrodes with single, double, ceramic, and sleeve junction types. They demonstrated that the type of junction influenced precision of the measurements. They observed that the highest precision occurred with sleeved junctions on Ag/AgCl electrodes.

Some researchers recommended a KCl salt bridge for rapid and accurate measurements in soils with a low moisture content (Hostettler, 1984; Olness *et al.*, 1989; Veneman and Pickering, 1983) or chemically severe milieu, such as sulfide-enriched environments (Mansfeldt, 2003), or in acid sulfate soils (Charoenchamratcheep *et al.*, 1987). According to Galster as quoted by

Frevert (1984), reactions between internal electrolyte and components of the soil solution can create deviations of up to 60 mV. Strong reducing conditions may liberate H_2S, which then diffuses into the Ag/AgCl reference cell, impairing its function by coating the cell with AgS and hence plugging the diaphragm.

B. Working Redox Electrodes

A working field redox electrode must be chemically inert and must be an excellent electrical conductor. There are two general classes of sensor materials for redox electrodes: (1) metals and (2) semiconductors.

The most important characteristics of such material can be summarized as follows: the electrode should allow an electron transfer between the oxidized and the reduced species of a redox couple through the electrode interface, without any participation or change of the electrode surface in the reaction (Pfeiffer, 2000). Additionally any material used should have no catalytic effect on the equilibrium (Galster, 2000).

1. Metals as Electrode Sensors

No solid material is absolutely chemically inert. Galster (2000) states that a metal can be labeled as "inert" if that metal's standard potential is more than 100 mV higher than the redox potential of the target sample. Frequently, metals from Group VIIIB, including iridium (Ir), platinum (Pt), palladium (Pd), and rhodium (Rh) (Pang and Zhang, 1998), and Group IB, including gold (Cater and Silver, 1961; Grenthe *et al.*, 1992), are applicable in soils with redox potentials between −400 and 850 mV at pH 7. The most commonly used electrode material for Eh measurements is Pt (Biddle *et al.*, 1995; Bohn, 1968, 1969; Galster, 2000; Matia *et al.*, 1991).

Pt offers a high exchange current (10^{-3} mA cm^{-2}) and so can respond to a potential change. Pt also has a high standard potential and is therefore relatively inert: (Eo Pt/Pt^{2+} = 1200 mV at 25°C). Enhanced durability is provided by employing a Pt·10% iridium electrode for added mechanical strength, which ensures a long period of trouble-free service.

In well-drained soils, the Eh depends primarily on the presence of oxygen. The reduction of gaseous O_2 is very slow and cannot be catalyzed by bright Pt. The potentials measured with electrodes of bright Pt are much too low and are poorly reproducible (Quispel, 1947). The electron transfer is enhanced by modifying the surface of the Pt sensor by platinization as recommended by Quispel (1947). We suggest the following as an example of the process.

Briefly, clean the Pt wire with HNO_3 and acetone. Dissolve 3 g of crystallized H_2PtCl_6 and 0.02 g of lead acetate in 100 ml of deionized water. In this solution, submerge two Pt wires. Establish a potential of ~3 V between the wires, and reverse the polarity of the potential every minute for 10 min. A slight production of gas should be observed. At this point, the process of electrolysis should be terminated. Submerge the wires briefly in a dilute solution of H_2SO_4, which has a generated voltage of about 4 or 5 V. The impurities of the Pt solution should be chemically removed with these steps. Finally, wash the Pt sensor in water.

2. Semiconductors as Electrode Sensors

The most common nonmetal semiconductors are wax-impregnated graphite (Biddle *et al.*, 1995; Grundl and MacAlady, 1989) and glassy carbon (Grenthe *et al.*, 1992; Matia *et al.*, 1991; Teasdale *et al.*, 1998). Generally, precision is lower in carbon-fiber electrodes when contrasted to Pt electrodes. Stabilization times are similar, however, to those for Pt electrodes (Matia *et al.*, 1991). Teasdale *et al.* (1998) found that the Pt electrodes were preferred over glassy carbon electrodes for applications in natural waters and soil. The glassy carbon electrodes were preferred for measuring redox potentials involving organic species. These electrodes indicate lower potentials than Pt electrodes in the same environment because carbon-fiber had a differing response to exactly the same redox systems as the Pt electrodes, requiring differing interpretations (Matia *et al.*, 1991). The lower cost graphite electrodes are easily constructed (Biddle *et al.*, 1995) as follows.

> Graphite can be obtained from the anode of carbon batteries and cleaned using *aqua regia* (1:3 conc. HNO_3:conc. HCl). In order to solder an electrical contact lead to the graphite electrode, a Cu plating on a portion of the graphite is needed. This can be achieved by immersing a 1-cm length of graphite in $CuSO_4$ solution and connecting the electrode to a voltage supply with cathode polarity using a length of Cu as the anode. The uniformity of the Cu coating is improved by sanding the graphite with fine corundum paper. The optimum plating condition for a uniform coating of Cu is 1–5 V at 300 mA.

With a 100-fold less exchange current and lower precision, wax-impregnated graphite electrodes are less desirable than Pt electrodes for making Eh measurements, which are erratic even under the best conditions. Biddle *et al.* (1995) pointed out the impracticality of graphite under aerobic conditions. In aerobic conditions, graphite reacted with oxygen ($C_{\text{graphite}} + O_2 \leftrightarrow CO_2 + 4e^-$). As a consequence, accumulation of electrons at the surface of the electrode will cause erroneously lower Eh readings than the actual Eh of the soil.

3. Design and Construction

Schaller and Fischer (1981) examined the question of how much surface area should be exposed from an electrode. They found that surface area exposure was not a factor in their study. Commonly, an effective length of 10 mm is used (Bailey and Beauchamp, 1971; DeLaune *et al.*, 1983), although Yamane and Sato (1970) recommended 15 mm as a minimum. DeLaune *et al.* (1983) state, "Redox potential (Eh) measurements made *in situ* with Pt electrodes constructed by welding 1.5 cm of 1-mm diameter Pt wire to 3-mm diameter solid Cu wire, covering with insulation and sealing with epoxy resin so that only bare Pt was in contact with the sediment. The maximum diameter of the electrode was 5 mm." This is illustrated in Fig. 4.

Loss of current from soil solution to the Pt wire–Cu junction is a common problem with permanently installed electrodes. Usually there are water leaks through the epoxy resin, which result in erroneous and/or erratic measurements. Therefore, watertight or leakproof electrodes are essential if meaningful and reproducible results are to be obtained (Mann and Stolzy, 1972; Mueller *et al.*, 1985). Watertight or leakproof electrodes can provide sufficient isolation of the junctions. Cogger *et al.* (1992) stated that fast-curing epoxies might absorb water from wet soil, leading to deterioration of the epoxy and shorting the electrode. As a result, Eh measures in a soil can drop several months after the electrodes were installed due to connection problems and not field redox conditions. To circumvent the epoxy problems, Fiedler *et al.* (2003) recommended the application of binary silicon resin (Semicosil®, Wacker, Germany), which retains its viscosity after polymerization and does not suffer from capillary ruptures and water absorption (Fig. 4).

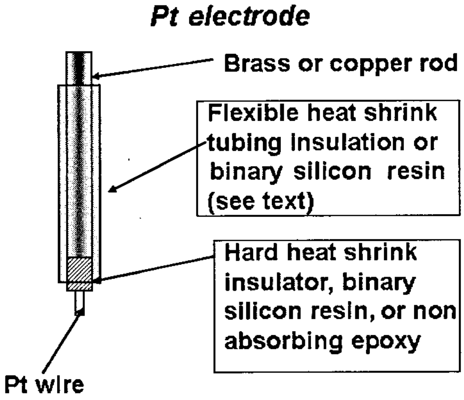

Figure 4 A basic Pt electrode structure with a copper connecting wire attached by heat shrink insulator material or a binary silicon resin. Past history of epoxy resins suggests extreme caution because of water absorption and short life in use.

Heat-shrinkable electrical insulation material has also been used (Mann and Stolzy, 1972; Whisler *et al.*, 1974; Young *et al.*, 1979).

Leak-proof electrodes have also been constructed with dental ceramics (Pfisterer and Gribbohm, 1989), by melting of Pt and glass (Bohn, 1968; Whisler *et al.*, 1974), and by shielding the metal wire with a heat-shrinkable electrical insulation material (Mann and Stolzy, 1972; Young *et al.*, 1979). Because of their fast reaction time, resins are the most frequently applied remedies (Mueller *et al.*, 1985; Whisler *et al.*, 1974).

In some previous investigations, mercury was preferred as linkage between sensor and signal line (Austin and Huddleston, 1999; Bailey and Beauchamp, 1971; Ponnamperuma, 1972). Because of the potential for mercury contamination in the environment, this technique is not recommended. Commonly, the Pt junction is inserted at the end of a tube consisting of several materials such as PVC (Olness *et al.*, 1989), tygon (Mann and Stolzy, 1972), stainless steel (Norrström, 1994), or glass (Mann and Stolzy, 1972).

4. Pretreatment

Contaminants and surface coatings must be removed from electrodes for accurate Eh measurements. Numerous methods have been used for these pretreatments:

Mechanical: Polished with a fine grade of alumina (Al_2O_3), CeO_2, or diamante power (Galster, 2000; Schaller and Fischer, 1981).

Chemical: In most cases, immersion in hydrochloric acid and subsequent washing with distilled water is a suitable cleaning technique (Galster, 2000; Ponnamperuma, 1972).

Thermal: Grundl and MacAlady (1989) and Grundl (1994) recommended soaking the electrode in 6-M HCl and heating in a flame to incandescence. In order to get reproducible values, Yamane and Sato (1970) recommended washing the electrode well with running, deionized water and burning it red with an ethanol or methanol flame. Bailey and Beauchamp (1971) cleaned their electrodes by first heating and cooling, followed by washing in a solution of 10% HCl plus 10% detergent.

5. Testing Procedure

Eh electrodes need to be tested with known redox solutions for electrode reliability before installation. Such test solutions are used to identify gross malfunctions of the electrodes or the electronics used. Abnormalities can happen even with care in construction or from commercial equipment (Table I). Test solutions create a redox equilibrium, which produces a stable, reproducible poised potential. Electrodes that vary substantially from the reference solution need cleaning or need to be reconstructed.

Several of the common solutions used to test the accuracy of newly constructed electrodes are listed in Table I. ZoBell's solution is commonly used for testing Pt electrodes. This solution is well known and generally accepted. Its temperature range is given in Table II.

Test solutions are highly poised by design, which means that they may not perform adequately in low-poise field conditions. Schaller and Fischer (1981) and Teasdale *et al.* (1998) suggest testing in both high- and low-poise test solutions. Teasdale *et al.* (1998) had success with a simple 100:1 dilution of ZoBell's solution.

A suspension of pure quinhydrone in potassium acid phthalate also is commonly used. Quinhydrone solution becomes unstable above 30°C.

Table I
Various Buffer or Poise (Test) Solutions Suggested for Calibration of Working Pt Electrodes

Test solution	Potential versus standard hydrogen electrode (25°C)	References
ZoBells solution 3.3×10^{-3} M $K_4Fe(CN)_6$ + 3.3×10^{-3} M $K_3Fe(CN)_6$ in 0.1-M KCl	+430 mV	Teasdale *et al.* (1998); ZoBell (1946)
Saturated quinhydrone in 0.05-M potassium biphthalate (pH = 4.01)	+462 mV	Austin and Huddleston (1999); Mansfeldt (1993)
Saturated quinhydrone in 0.05-M potassium biphthalate (pH = 7)		Austin and Huddleston (1999)
Ferrous ammonium sulfate-ferric ammonium sulfate solution		Light (1972)
15%Ti(III)Cl_3 in 0.2-M sodium citrate	−480 mV	Zehnder and Wuhrmann[a] (1976)

[a] Zehnder and Wuhrmann (1976) quoted by Teasdale *et al.* (1998).

Table II
Eh of ZoBell's Solution as a Function of Temperature (from Nordstrom and Wilde, 1998)

Temperature (°C)	Eh (mV)	Temperature (°C)	Eh (mV)
10	467	30	418
14	457	34	407
18	448	38	397
22	438	40	393
26	428		

Additionally, the Eh of a quinhydrone solution is pH dependent. Light (1972) suggests that electrodes can also be tested in an Fe(II)–Fe(III) solution, but this solution, like all other standard redox solutions, is so strongly poised that even unsatisfactory electrodes will sometimes give accurate readings (Table I).

C. Problems of Soil Redox Measurements

1. Limit of Eh Measurements

In the case of a reversible chemical reaction involving electrons, the potential (Eh) measured by an inert electrode should reflect the relative concentration of chemical species in the soil (Schüring *et al.*, 2000). The methodology of these measurements is simple in theory. In practice, consideration must be given to many field factors involved with establishing measurements *in situ*, the Pt electrodes themselves, and their connections with the earth and recording apparatus.

The accurate assessment of the redox status using electrodes is still a matter of controversy that is mainly created by the lack of redox equilibrium at the electrode as well as among various redox couples present in a given soil. The problems have been described in numerous publications and will not be repeated here in detail (Grenthe *et al.*, 1992; Grundl, 1994; Pfeiffer, 2000; Sigg, 2000; Stumm and Morgan, 1981; Whitfield, 1969, 1974). In brief, the most common problems can be summarized as follows:

a. Irreversibility. Irreversibility of redox reactions at the Pt surface of the electrode can be caused by any of the following substances that often accumulate on the surface of the Pt: $Pt(OH)_2$, PtS (Hoare, 1962; Rickman *et al.*, 1968; Whitfield, 1969, 1974), organic coatings (Vershinin and Rozanov, 1983), calcium and magnesium carbonates (Rickman *et al.*, 1968), or aluminosilicates (Devitt *et al.*, 1989). When these substances coat the Pt surface, they cause the potential to drift from true values; this is especially true in well-drained soils (Bartlett, 1981) and sulfide-enriched materials (Mansfeldt, 2003; Vershinin and Rozanov, 1983). In spite of these deficiencies, some electrodes perform well for up to 5 years in favorable conditions (Austin and Huddleston, 1999).

b. Slow Reaction Kinetics. Slow reaction kinetics of potential-determining redox couples can prevent a stable potential from developing (von Langen *et al.*, 1997). As Gao *et al.* (2002) reported, Eh can drop rapidly under ponding conditions, such as those in a rice paddy, but the chemical reactions with release of iron and other materials created in the new environment will continue for a substantial time, although they may not be initially observed. This condition is typical of systems that are well poised (Bartlett, 1981; Brown, 1934).

*c. **Mixed Potentials.*** The measured "steady state" potential is given by the redox system with the highest rate of exchange or corresponds to a composite of two or more redox processes (Böttcher and Strebel, 1988; Brümmer, 1974; Chadwick and Chorover, 2001; Stumm, 1984), resulting in the restriction of thermodynamic calculations (Frevert, 1984; Machan and Ott, 1972; Rickman *et al.*, 1968).

2. Technical Problems of Soil Redox Measurements

Additionally, measurements of soil redox potentials associated with technical problems are illustrated in Fig. 5A.

a. Reference Cell. Reference cells are often overlooked in the design of a redox system. According to Galster as quoted by Frevert (1984), reactions between internal electrolyte and components of the soil solution can create deviations of up to 60 mV. Strong reducing conditions may liberate H_2S, which then diffuses into the reference cell, destroying it by coating the cell with AgS and hence plugging the diaphragm (Cammann, 1977). Reference cells with jelly electrolytes, which represent the current state of technology, salt bridges (Veneman and Pickering, 1983), or reference beddings into microbial resistant material in combination with electrolyte reservoirs (e.g., clinical infusion bags) may overcome these problems (Fiedler and Fischer, 1994). The small size of the electrodes as mentioned above may cause a problem with the galvanic contact. The suggested construction avoids these problems (Fig. 3). Fiedler (1994) reported freezing of the electrolyte, which was solved by using a mixture of electrolyte and glycerin. Such solutions do not change the standard potential of the reference cell, but they do alter the temperature coefficient favorably.

b. Working Electrode. Theoretical problems have been described in numerous publications, but technical problems that might occur with the equipment are not usually published. The life span of electrodes depends on the condition of use, for example water saturation, pH conditions, and mineral chemistry. Because the epoxy allows moisture to interfere with the connection between the wires, junction potential, as mentioned previously, is always a potential problem.

Absorptive contamination of the surface of the Pt electrode affects the measured potential (Vershinin and Rozanov, 1983). It is difficult to give precise conditions under which the contamination of electrodes might be prevented because the suggestions of published research are contradictory. Cogger *et al.* (1992) stated that properly constructed and permanently installed soil electrodes were reliable for at least 1 year. Rickman *et al.* (1968) suggested that adverse effects due to contamination can be minimized by removing electrodes after

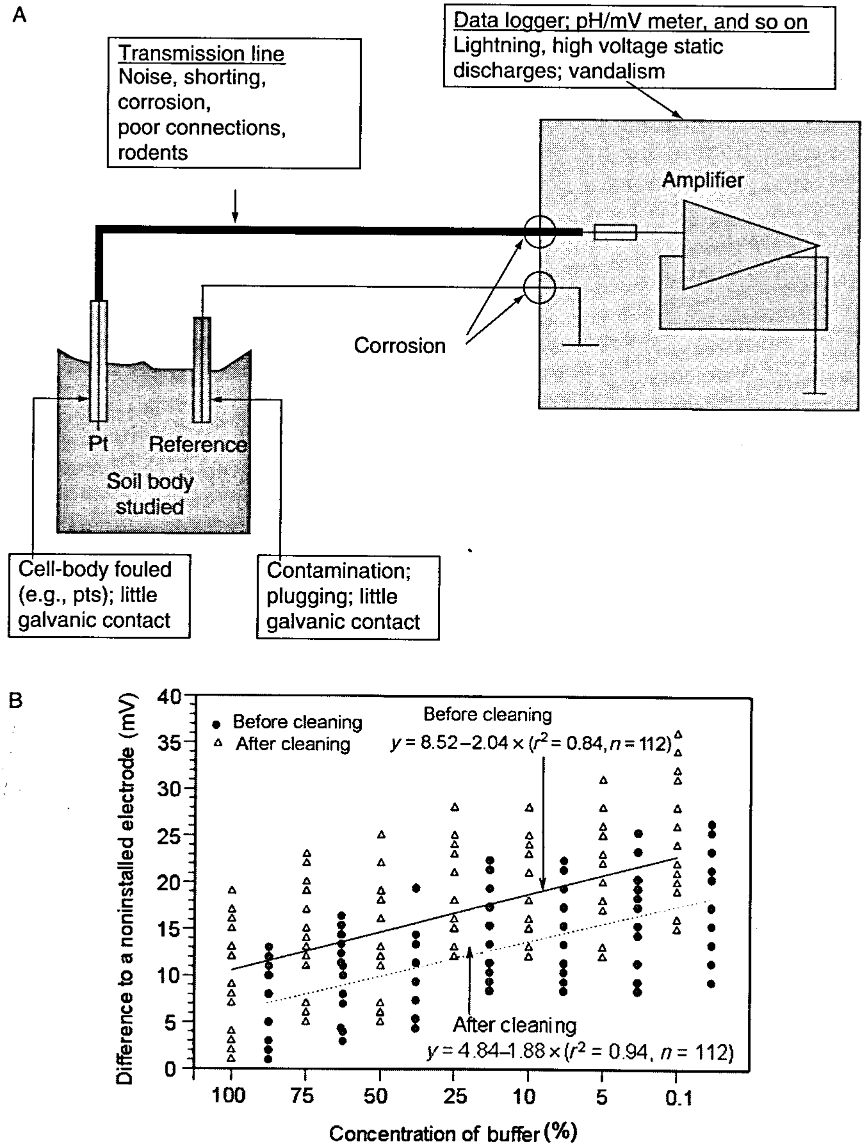

Figure 5 Differences between permanently installed Pt electrodes (18 months) and noninstalled paired electrodes as affected by cleaning and concentration of buffer. (A) Experimental and (B) graphical. (See Color Insert.)

2 months in soil and cleaning the Pt sensor. Bailey and Beauchamp (1971) reported a slow response of electrodes during a 6-month experiment due to sulfide, hydrogen, or organic carbon sorption on the surface of Pt. Whisler *et al.* (1974) reported that PtS would push the redox potential to more negative values and would result in slow electrode response. Recovered permanently installed electrodes can be tested the same way as newly constructed electrodes.

Mansfeldt (1993) found a negligible difference between noninstalled electrodes and electrodes that were installed permanently for over 20 months. Austin and Huddleston (1999) noted that electrode testing in quinhydrone solution after removal from the soil showed that 97% of the electrodes still performed within acceptable limits of accuracy after either 3 or 5 years of continuous use. Fiedler (1997) tested electrodes that were installed over an 18-month period by using different concentrations of test solution (hexacyanoferrate) and found an increasing discrepancy between preinstallation and postremoval testing of electrodes up to 36 mV with a decreasing concentration in paired electrodes (Fig. 5B). These data support statements by Teasdale *et al.* (1998), who reported that a highly concentrated redox solution is much less sensitive to differences between two given electrodes than is the low-poise reference solution.

Whisler *et al.* (1974) speculated that longevity of Pt electrodes might be inferred by the correspondence between the amplitude of oscillations of electrode readings and the intermittent flooding and drying of soil. Seybold *et al.* (2002) and Mansfeldt (2003) stated that if properly constructed and permanently installed Pt electrodes are used, soil Eh can be monitored for extended periods under saturated and reducing soil conditions.

Insufficient galvanic contact and polarization of electrodes with the surrounding soils as reported by Yu (1991) is a problem that all researchers might encounter. Cater and Silver (1961) noted that the use of an amplifier with an input impedance $<10^8\ \Omega$ can polarize electrodes so that they record only half their true equilibrium potential. In contrast, a circuit $>10^8\ \Omega$ was only able to polarize the electrodes by a few millivolts.

c. Transmission Lines. Plastic coatings on cables are subject to rapid deterioration by solar radiation and general field conditions such as rodents. The deterioration results from adsorption of moisture and shorting of the current. The reaction of ambient moisture reacting with inferior quality plugs and junctions creates corrosion. Corroded transmission lines and connections will result in false signal transmission. The direct soldering of the transmission cables to the data handling boards complicates the maintenance of the apparatus. Therefore, it is recommended that clips, screws, or plug junctions be used instead. Sealing with silicone resins provides excellent insulation. Note that resins containing acetate can increase corrosion.

The cables transmitting data to the data loggers are often greater than 10 m and subject to interference (Frevert, 1984). We recommend that the electrode cables be shielded against electrostatic coupling such as human and animal bodies, traffic (cars, railroads), atmospheric loads, and other emitters. It is not the relatively low voltages but the low current that makes the signals suffer from electrostatic interferences. Such currents are randomly generated and complicate the interpretation of the signals. At higher amperages, which result from lower impedance, the signals gain immunity.

Problems such as interferences due to static, capacitive, or inductive coupling of stray fields can be avoided by using an "active" redox electrode, including an amplifier directly incorporated into the electrode body (Fiedler *et al.*, 2003). This setup eliminates the most important sources of errors that often occur with traditional electrode designs by decoupling the sensitive high-impedance primary circuit from all other devices of the signal chain. Similar construction processes were applied for the construction of ion-selective electrodes (Pérez-Olmos *et al.*, 2001).

d. Data-Recording Unit. Commercial or self-made multichannel data loggers are commonly used for recording Eh data. However, these units need to be protected against moisture. In particular, it must be ensured that the printed circuit board (PCB) is equipped with an effective insulation such as spray lacquer (e.g., acetate-free silicone resin). Sometimes, PCBs that are in contact with high-impedance primary signals from a working electrode are regarded as the best (e.g., Teflon within ion-sensitive electrode equipment). However, in the case of Eh, the standard epoxy PCB ($R < 10^{11}\ \Omega\ \mathrm{cm}^{-1}$) is suitable for use with circuits processing soil redox potentials. Lightning, static high-voltage discharges, and voltage spikes are events that may cause permanent damage to electronic devices, especially in complementary metal oxide semiconductor devices (CMOS).

D. TESTING ELECTRODES PRIOR TO INSTALLATION

All electrodes need to be tested for accuracy prior to being used in the field. The testing procedure is necessary to ensure that the electrodes are functioning properly and also to place electrodes into groups that will provide the same range in Eh when placed in the soil in multiple plots. We recommend that testing be done in two phases, with each phase using a different test solution. The first phase uses a solution of known and stable redox potential. The ferrous–ferric buffer solution described by Light (1972) will be used for illustration, but other solutions are available (Owens *et al.*, 2005; Tables I and II).

Before the testing begins, the Pt wire must be cleaned to remove coatings that will impede electron flow. Coatings can be oxides, organic greases, or numerous other problem materials. The coatings frequently cannot be seen with the naked eye. To remove coatings, all electrode tips should be rubbed hard or scratched with steel wool. Once cleaned, the electrode tips are placed in a beaker containing the buffer solution along with a reference electrode. Redox potential is then measured for each electrode using the voltmeter. If the solution by Light (1972) is used, then the redox potential reading taken directly from the voltmeter will be ~+476 mV. Electrodes falling between 496 and 456 mV are acceptable. Other ranges of acceptability can be defined, depending on the objectives of the work. Electrodes falling outside the acceptable range should not be used. In some cases, failure is due to leaks near the electrode tip, which allow the test solution to contact metal in the electrode other than Pt. The electrodes can occasionally be repaired by resealing the area near the electrode tip with epoxy or heat-shrink tubing (Owens *et al.*, 2005). Before repairs are attempted, it is helpful to examine the seal around the Pt wire under a microscope so that cracks and holes in the insulation can be identified.

The ferrous–ferric buffer solution is well poised, but soil solutions generally are not. Electrodes that appear acceptable in buffer solutions may not perform adequately when placed in the soil. Another test is recommended with tap water before electrodes are selected for field use. Examples of test results for 15 electrodes (five sets in triplicate) are shown in Table III. Redox potential was measured both in the Light (1972) solution and in the tap water. Means and ranges are shown at the bottom of the table. The Light (1972) solution produced data with a narrow range of only 38 mV, indicating that all electrodes would be acceptable for use. Two tests were also done with tap water that was flowing out of an open faucet. Results between the two water tests were similar, but the range was approximately five times as large as that found for the buffered solution. While the results with tap water would seem too variable for the electrodes to be considered reliable, it must be remembered that the tap water is poorly buffered or poised. As a result, the redox potential in the water will change during the testing process.

III. DATA INTERPRETATION

A. CORRECTION OF FIELD DATA

1. Correction of Field Data to a Standard Hydrogen Electrode

Generally, redox field data are corrected in order to be relative to the potential of a standard hydrogen electrode by adding a temperature and reference electrode correction to the experimental readings. The temperature correction for various solutions for reference electrodes is given in Table IV. Using an Ag/AgCl reference electrode, for example, the correction factor

Table III
Results of Testing 15 Electrodes in a Well-Poised Redox Buffer Solution, as well as in Flowing Tap Water

Electrode group	Redox potential (uncorrected) (mV)		
		Tap water	
	Buffer solution	Test 1[a]	Test 2
A	481	360	363
A	465	360	364
A	482	367	371
B	478	370	373
B	476	375	386
B	480	383	387
C	482	390	387
C	464	410	413
C	482	410	413
D	481	420	413
D	482	420	431
D	476	440	443
E	482	441	445
E	482	457	461
E	475	461	465
Mean	478	377	409
High	482	461	465
Low	464	360	363
Range	22	101	102

[a] This test was used to sort results from lowest readings to highest reading.
The tap water is not well poised, but may be closer to soil solution than a redox buffer. The Eh measurements in water are much more variable than with the buffer solution, but can be used to group electrodes into categories that would respond similarly in soil. In this example, three plots having five electrodes each were to be instrumented. Each plot would have one electrode from group A, one from group B, and so on. In this way, the redox potential in each plot would be measured with electrodes responding with the same range in poorly poised solutions.

would be ~200 mV for most regions. Note that a 4-M solution is close to saturation, and readings should not be changed appreciably if saturated solutions (4.5 M) are used in the reference electrodes.

2. Correction of Field Data for pH

An inert electrode will not only show a positive potential change in response to a change of Eh, but it also responds inversely to changes in pH; as pH increases, Eh decreases. The value most commonly used by

Table IV
Standard Half-Cell Potentials of Selected Reference Electrodes as a Function of Temperature and KCl Reference Solution Concentration Expressed in Moles, Potentials in Millivolts (After Nordstrom and Wilde, 1998)

	Ag/AgCl			Calomel		
Temperature (°C)	3-M KCl	3.5-M KCl	4-M KCl	3-M KCl	3.5-M KCl	4-M KCl
10	220	215	214	260	256	254
20	213	208	204	257	252	248
30	205	201	194	253	248	242
40	198	193	184	249	239	234

researchers is −59 mV per pH unit at 25°C for conversion of field observations, which is in accordance with the Nernst-equation. However, the Eh/pH slope varies within different chemical systems. Experimental values have been found to range from −6 to −256 mV per pH unit. Charoenchamratcheep *et al.* (1987), for instance, observed that in acid sulfate soil solutions Eh/pH unit slopes between −206 and −256 mV per pH unit occurred. Field mineralogy and solution geochemistry affect poise and Eh–pH relationships. Therefore, Eh corrections made on the basis of −59 mV/pH unit without synchronous Eh and pH measurements may be unreliable (Collins and Buol, 1970; Garrels and Christ, 1965, p. 176).

B. VARIABILITY

Apart from electrode and pH considerations, the interpretation of redox potentials (Eh) proves difficult due to their variability. Redox potentials can vary spatially and temporally by orders of magnitude, depending on such conditions as changing water table, temperature, and the availability of organic matter for anaerobic microbes. The variability should be recorded in order to provide a basis for the evaluation of the whole redox dynamic in soils. The variability has often been attributed to the imprecision of parallel measurements (Parker *et al.*, 1985). The wide range of Eh potentials (including both natural and artificial changes of Eh) may also create difficulties in the interpretation of the obtained data.

1. Spatial Variability

The redox potential in soils can vary significantly within (e.g., microsites, Parkin, 1987; Zausig *et al.*, 1993) and between horizons (intrapedonal) (e.g., macro pores caused by earthworm activities, epi and endo saturation conditions) as well as between pedons (interpedonal) and can lead to distinct patterns across landscapes. Norrström (1994) reported that in soil volumes as small as 100 cm^3, differences between minimum and maximum values of the redox potentials can range between 400 and 1100 mV. Fiedler (1997) states that in general, redox potentials of individual electrodes must be regarded as single-point or local measurement reflecting the separated, temporally variable compartments that are representative for the surrounding soil at a scale of $\sim$1 mm^3. Therefore, it is not surprising that Eh can vary up to 800 mV between two electrodes installed in a horizontal distance of 1 cm (Fiedler, 1997).

To circumvent the difficulties of extreme spatial variability, a sufficiently large number of measurements must be made across a horizon (or depth) in order to account for the natural range of spatial variability (Vepraskas and Faulkner, 2001). However, in many if not most studies, redox probes were applied in duplicate only (Reuter and Bell, 2001; Thompson and Bell, 1996, 1998). Patrick *et al.* (1996) also recommended using electrodes in duplicate but preferred the installation of electrodes in triplicate. Cogger *et al.* (1992) recommended the use of 8–10 replicates. Vepraskas and Faulkner (2001) suggested that 10 electrodes per depth are needed to ascertain the precision of the measurement over a complete wetting/drying cycle for soils affected by fluctuating water tables. The National Technical Committee for Hydric Soils (NTCHS) recommends in their "Hydric Soil Technical Standard" that five replicates be used. Fiedler (2000) found that the differences between the redox probes of individual horizons decrease with increasing depth. For example, two electrodes showed a similar trend and level of Eh values ($\Delta Eh_{min} = 10$ mV, $\Delta Eh_{max} = 100$ mV) in permanently water-saturated horizons. Therefore, the use of 10 electrodes in these soil horizons does not seem to be necessary for accurate Eh measurements. In contrast, a higher number of redox probes are needed in horizons that are characterized by highly fluctuating water tables that separate the horizon into a saturated and an unsaturated zone. No clear agreement on the number of required electrodes was found in the literature. In addition, some researchers preferred the installation of electrodes at definite depths (e.g., 25, 50, 75, and 100 cm) (Reuter and Bell, 2003), whereas Blume (1968a,b,c) suggested the installation of the electrodes at different depths across the individual horizons.

Despite high spatial variability within individual horizons, similar redox potentials can be observed in certain types of soils. The Eh measurement in different soil types showed that, in general: (1) levels and amplitudes of intrapedonal redox potentials decrease with depth and (2) distinct interpedonal Eh gradients exist between different types of soil. In other words, the intrahorizon Eh differences are usually smaller than the interhorizon/soil Eh differences. Eh measurements are a used as a tool for: (1) the differentiation of soils and (2) the estimation of dominant redox processes in a certain type of soil. Although water table levels and soil temperature influences are not discussed here, these factors should be included in the data-gathering process because they also affect the interpretation of data.

2. Temporal Variability

The measurement period in published studies has varied from hours (De Mars and Wassen, 1999), a few days (Clay *et al.*, 1990), a few weeks, a few months (Teichert *et al.*, 2000), 1 year (Comerford *et al.*, 1996), 2 years, to as much as 5 years (Reuter and Bell, 2001). These hourly, daily, and weekly measurement intervals depended on the objectives of the different investigations. As noted by Fiedler *et al.* (2004b), Eh measurements in soils that are affected by permafrost are only meaningful during (usually short) warm summer periods since freezing can lead to technical problems (e.g., galvanic contact). The investigation of the application of organic fertilizers, which triggers the release of N_2O, requires a narrow measurement interval (hours) but a relatively small measurement period (1 month) (Flessa and Beese, 2000). According to USDA-NRCS (1991), the delineation of hydric soils in the United States is based on the percentage of time with Eh <200 mV during the growth season.

The temporal variability of Eh trends varies in relation to the water table, oxygen diffusion (Zausig and Horn, 1992), temperature (Clay *et al.*, 1990), precipitation (Fiedler, 2000), matric potentials (Fiedler, 1997; Karathansis *et al.*, 2003; Thompson and Bell, 1998), and evapotranspiration (Mansfeldt, 2003). Soil redox conditions may be subject to changes according to the following time scales:

Diurnal changes can be explained on the basis of the *Nernst equation* and the *van't Hoff's law* (a temperature increase of 10 K enhances the rate of biological reactions by a factor of 2–3). Generally, a temperature maximum is followed by an Eh minimum (Clay *et al.*, 1990; Farrell *et al.*, 1991) with amplitudes of 30–50 mV and a phase shift of 6 h.

Event changes can be related to drying/rewetting cycles (McKenzie *et al.*, 1960). The temperature-related regular variation of the redox potentials may often be concealed by a drastic increase of the water table after precipitation (event changes). In these cases, the Eh amplitudes can range up to 900 mV (Fiedler, 2000).

Seasonal changes during summer and winter can be related to gradients in soil temperature, for example depression of microbial respiration at <5°C (Megonigal *et al.*, 1993). The seasonal mean of the redox values can be as much as 300 mV (Fiedler, 1997).

Annual changes can result from annual differences in mean precipitation (corresponding to the water table) and/or temperature of the years of observation (Reuter and Bell, 2001). Mansfeldt (2003) has found mean annual differences between 40 and 200 mV based on installation depth in a calcareous Typic Endoaquoll marsh soil over a period of 4 years.

Short-term changes due to soil chemistry result from the production of carbon dioxide and release of hydroxyls in ferric iron reduction. As stated by Ponnamperuma *et al.* (1966), the pH values of flooded alkali and calcareous soils are considerably lower after 2–3 weeks of flooding, and those of acid soils are considerably higher than their aerobic counterparts. The reduced soils tend toward a range of only 7.2–6.7 (Ponnamperuma *et al.*, 1966). The conditions that exist in the field, therefore, allow for interpretations of the soil's environmental condition (Schulte-Eburt and Hofmann, 2000).

Besides these systematic Eh changes, an additional irregular shift in redox trends has been observed. These equipment and electronic Eh values, termed here "artificial" Eh values, can lead to false conclusions if they remain unnoticed. However, their identification is relatively easy in the case of "constant" environmental conditions, where artificial Eh values are characterized by spontaneous peaks and/or data outside of the natural range of Eh within soils, as illustrated in Fig. 6.

C. POOLING OF LONG-TERM DATA SETS

The determination of Eh is usually not of interest in terms of the values themselves; rather, the value of Eh determination is in predicting the behavior of certain soils in their field condition in terms of space and time. It has been demonstrated that redox potentials can vary site specifically throughout the year as a result of annual, seasonal, event-related, and diurnal changes. Such variation temporally is sensitive to the biological processes of interest in most ecological investigations. In these cases, a designation of "redox zones" in which specific ranges in Eh define electron activities (e.g., ferrous iron production or sulphide production) or categorizing of predominant redox conditions into a distinct "redox status" (e.g., moderately or severely reduced status) is useful for the interpretation of data (Fig. 7).

Generally speaking, the interpretation of data collected over longer periods of time has more value and use with the application of basic statistics. Mansfeldt (1993) and Norrström (1994) calculated the horizon-specific lower, middle, and upper quartile of Eh values. The relative frequency of Eh values, or cumulative probability distribution of Eh values, was used by Szögi and Hudnall (1998) to develop the concept of relating the frequency of diagnostic wet soil conditions to hydric soil conditions. The probability of

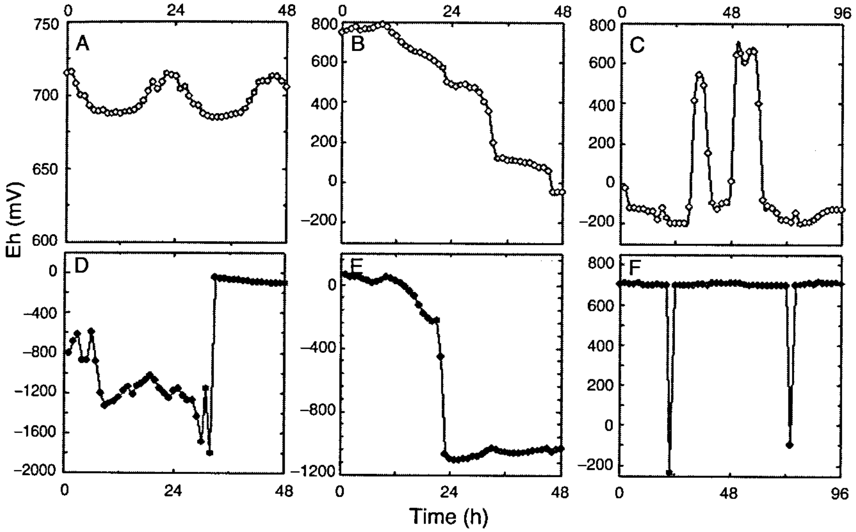

Figure 6 Examples of natural (regular) Eh potentials, which can be interpreted in relationship to abiotic factors (A–C) and artificial (irregular) Eh values (D–F) that are caused by technical problems: (A) diurnal Eh potential triggered by temperature, (B) Eh decrease after rain, (C) Eh change caused by a fluctuating water table; (D and E) Eh data outside the range of the buffering effect of water on redox reactions (−1 V + … + 1 V) may result from deflectable transmission line, (F) spontaneous Eh change caused by electro-smog. ground, and when the soil becomes reduced, the Fe is dissolved off the pipe (B). (See Color Insert.)

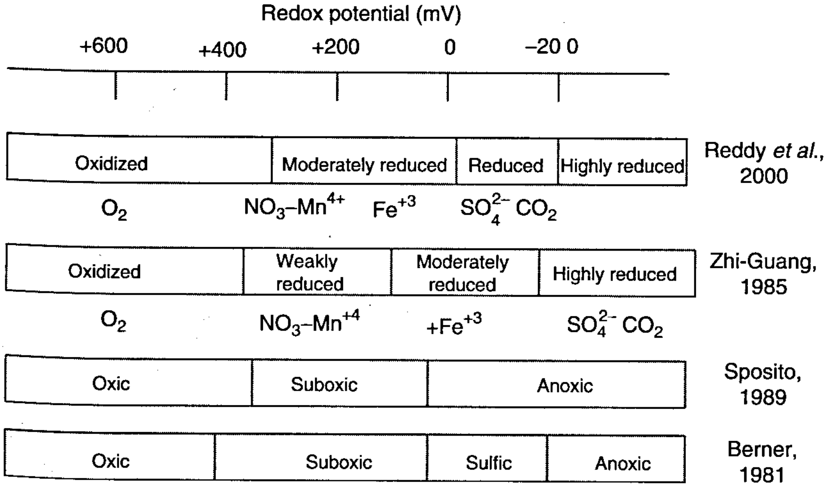

Figure 7 Different categories of redox environments with important electron acceptors.

occurrence of a distinct Eh value (at a certain depth) is obtained by computing the ratio of the number of observations that exceeded the specific Eh of the total number of observations. This ratio is the transformation of a time-dependent variable into a frequency and can be represented by a cumulative probability function.

By focusing on key Eh thresholds, Fiedler and Sommer (2000) established a useful interpretive tool for the estimation of redox dynamics of hydromorphic soils by using the percentage of time the Eh values were above or below the threshold values annually. These researchers demonstrated that their procedure was useful for horizons in pedons and pedons in landscapes. The key thresholds these researchers utilized were Mn-reduction using Eh < 450 mV; Fe-reduction using Eh < 170 mV; and CH_4-oxidation using Eh $>$ 75 mV. These key thresholds (e.g., CH_4-oxidation) can be used as input parameters for simulation models, such as wetland-DNDC, as confirmed by Zhang *et al.* (2002).

In addition to the estimation of element/matter dynamics in soils, Eh thresholds allow the classification of soils. The technical guidance for hydric soil delineations (Hurt and Carlisle, 2001; Hurt *et al.*, 2002; NTCHS, 2004) relies on redox conditions as one of the major criteria for hydric soil identification. The hydrology criterion for wetland delineation should be considered fulfilled when reducing conditions (threshold of $Eh_7 \leq 200$ mV) are continuously available (>5% of growing season) in the upper part of the soil (operationally defined as above 30 cm).

According to the World Reference Based Soil Classification system (FAO-WRB, 1998), stagnic properties are defined below a threshold of $rH < 19$, where $rH = (Eh/59) + 2pH)$. In *Soil Taxonomy* (Soil Survey Staff, 1999), reduction and oxidation are both required for "aquic" conditions but the duration of the reduction is not specified.

IV. ALTERNATIVE METHODS FOR ASSESSING REDUCTION IN THE FIELD

A. Iron-Coated (IRIS) Tubes

Jenkinson and Franzmeier (2006) proposed using iron-coated tubes to assess the redox potential in soils. They put a thin coating of ferrihydrite ($Fe(OH)_3$) onto the surface of a PVC pipe (Fig. 8A). The coated pipe simulated a rusty steel nail. It was named an IRIS tube for "indicator of reduction in soils" by Jenkinson and Franzmeier (2006). In reduced soil, microbial oxidation of organic matter produces materials that can reduce and dissolve the Fe off the IRIS tubes (Fig. 8B). The IRIS tubes have an

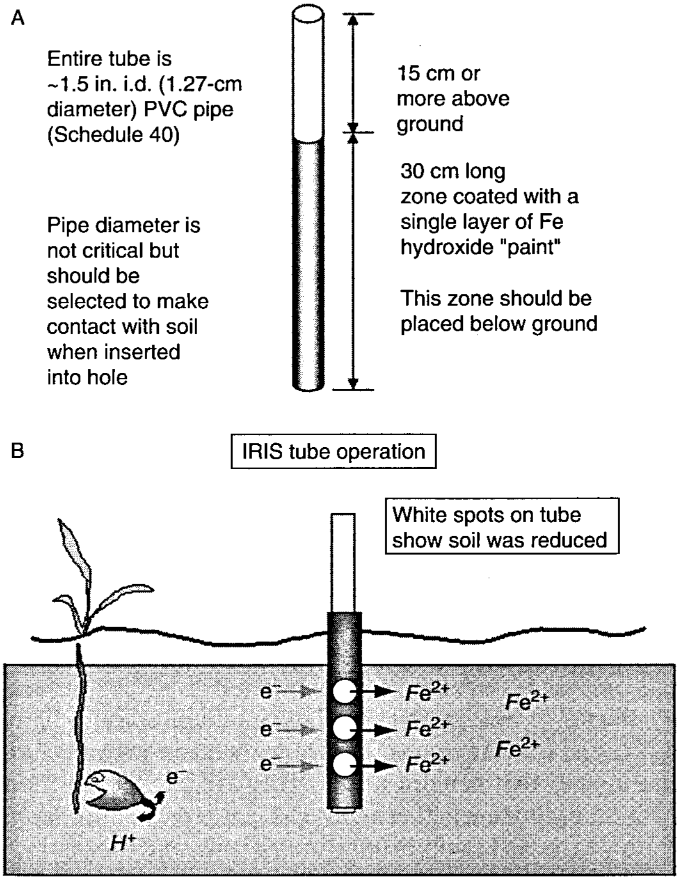

Figure 8 (A) The basic parts of an IRIS tube are an above ground area that remains bare and a 30 cm or so long area of the PVC pipe that is coated with an $Fe(OH)_3$ paint. (B) The IRIS tube is inserted into the soil such that all the $Fe(OH)_3$ paint is in the soil. (See Color Insert.)

orange color when manufactured due to the ferrihydrite. When the Fe is reduced, it dissolves off the tube and the place of Fe loss is seen as a white spot, the color of the underlying PVC pipe. The soil redox potential is estimated as being either low enough to reduce Fe or high enough to keep it in an oxidized form on the tube. The advantages of using IRIS tubes over direct redox potential measurements include being simpler and less expensive to conduct, recording reducing conditions continuously without direct measurement, and showing the location and pattern of reduction. White spots of Fe removal on the tubes show that the reduction occurred in small microsites, as opposed to complete reduction of a horizon whereby all Fe would be removed from the tube. The amount of reduction that has occurred is estimated from the area of Fe removed. The IRIS tube is also an excellent tool to use in remote locations where frequent visits are not possible to assess reducing conditions.

The IRIS tubes are easy to use. Jenkinson and Franzmeier (2006) augered a hole into the soil where data were needed and inserted the IRIS tube into the hole. While direct contact with the soil is necessary, the contact should not be so tight that Fe is scraped off the tube as it is inserted or removed for examination. The amount of Fe loss from the tube can be assessed weekly or as often as time permits. To measure the amount of Fe loss, Jenkinson and Franzmeier (2006) photographed the IRIS tubes on all sides, downloaded the pictures to a computer, and used software to estimate the area of the pipe that lost Fe.

B. Dyes

Solutions of some organic dyes react with redox couples and turn color. Childs (1981) proposed using a 0.1% solution of α,α'-dipyridyl dye to identify when Fe^{2+} is present. The USDA-NRCS uses a 0.2% solution of α,α'-dipyridyl dye in a 1-M solution of ammonium acetate (Vepraskas, 2002). The solution is clear before use; however, when it is dripped or sprayed onto a freshly extracted sample of soil, it will turn pink if reduced Fe is present. The reaction occurs in 30 s or less. The dye only reacts with Fe^{2+} and thus is of little use in soils that contain no Fe. This dye has proven a simple and effective way to evaluate whether reduced Fe is present in soils. It must be used on freshly extracted samples of saturated soils, and the sample must not be allowed to dry before the dye is applied; otherwise, the reduced Fe will oxidize. False positive reactions can occur if the soil to which dye is applied contains metal fragments from steel sampling equipment, such as augers or shovels. Samples containing high levels of organic matter may contain Fe as a ferric–organic complex (Childs, 1981). When the dye is sprayed onto such samples and exposed to direct sunlight, the organic compounds may oxidize and reduce the Fe in the sample. This reaction is capable of causing the dye to turn red even when the freshly extracted material contained no reduced Fe.

In another alternative method, which works well with dark soils that can mask or hide the color in the above method and also evaluates ferrous iron attached on the cation-exchange complex, a solution of *ortho*-phenanthroline is used with a small amount of NaCl in a small glass container like a test tube. A small amount of soil is added, and the mixture is shaken. If any ferrous iron is present in that soil, the supernatant solution will be pink (Richardson and Hole, 1979).

C. ZERO VALENCE IRON RODS

Starkey and Wight (1946) did not observe any corrosion of iron pipes when the Eh values were less than 400 mV. McKee (1978) proposed using uncoated steel welding rods to measure water table depth. Iron forms rust in the oxidized (Fe^{3+}) conditions above the water table but is reduced under anaerobic conditions to Fe^{2+} with a lack of rust coloration. McKee (1978) believes that the water table is the boundary between these two conditions and can be recognized by red above and no rust coloration below. Carnell and Anderson (1986) measured rusting on steel rods in a Stagnopodzol. They determined that the maximum rust depth correlated well with both water level and rooting depth of Sitka spruce *(Picea sithchensis*). Carnell and Anderson (1986) observed that the lower level of brownish coloration on the metal correlated with water table depths.

Bridgham *et al.* (1991) studied the suitability of steel rod rusting as a hydrologic indicator in wetland and nonwetland soils. They used both field and microcosm approaches with Histosols and one mineral soil type (Typic Fluvaquent). The steel rods worked well with a water table that did not fluctuate rapidly. Rapid fluctuations did not allow enough time to reduce and dissolve rust when it had formed. The oxidation of the rod also required considerable time because the drainage was slow and the oxygen was hindered in returning to the pores. They concluded that the steel rod technique was valuable as an indicator of hydrology for basic science studies. They thought the technique was not suitable for jurisdictional wetland determination in zones with fluctuating water tables due to the lag periods in rod oxidation and the time needed for previously formed rust to dissolve when ponded again.

Owens *et al.* (1999) used buried iron metal rods for estimating anaerobic and aerobic conditions in soils. Later, Owens (2001) stated that the idea may have implications in hydric soil determination, horticultural and agricultural applications, and remediation techniques. Owens used zero valence iron rods placed in three soil toposequences. His observations of the surface coatings formed by oxidation were compared to piezometer, soil moisture, α,α'-dipyridyl reactions, oxygen concentration, and redox potential measurements every 3 weeks for 1 year. He believes that the coatings on iron metal rods inserted in the soil appear to correlate well with specific oxygen ranges. Rods in soils with O_2 concentrations below about 2% do not develop bright (7.5YR 4/4 to 5/8) oxide/oxyhydroxide coatings but instead formed black (10YR 2/1 to 2/2) coatings. Rods in soils with O_2 concentrations between about 2 and 5% develop variegated bright (7.5YR 4/4 to 5/8) oxide/ oxyhydroxide coatings, indicating microsite differences in O_2 concentrations. Rods in soils with O_2 concentrations above about 5% with adequate moisture are almost completely coated with bright (7.5YR 4/4 to 5/8) iron oxide/oxyhydroxides. Once iron oxide/oxyhydroxides were formed on the rod, they were not reduced during subsequent reducing conditions. Owens concludes that these data indicate the iron rods can be used to provide information on a bracketed time period rather than an integrated measurement. Vepraskas *et al.* (1999) noted that the dissolution of iron was slow and required soils with considerable organic matter available for microbial use. Over a short time period (about 1 week), they observed that the soils having a high content of organic matter had over 10 times the ferrous iron, whereas soils having a low content of organic matter had only a trace amount of ferrous iron. Formation of rust is endothermic and easier to achieve than the reverse.

V. FIELD INSTALLATION AND PROCEDURES FOR REDOX POTENTIAL MEASUREMENTS

Redox potential measurements are made with three pieces of equipment: Pt electrodes, a reference electrode, and a device to read voltage, such as a voltmeter (Fig. 2). The basic components of the two electrodes are shown in Figs. 2 and 3. Pt electrodes can be purchased or made by hand. Methods for constructing electrodes have been described previously in this text and in Faulkner *et al.* (1989), Mueller *et al.* (1985), Patrick *et al.* (1996), and Vepraskas (2002). Reference electrodes are usually purchased, but the construction of a stable field type (Ag/AgCl type) is described in Section II. Because the electrodes will be in contact with the soil, they should be rugged enough for field use, which is the case with the Fiedler design described in Section II (Fiedler *et al.*, 2003). The voltmeter must be capable of measuring millivolts. Laboratory grade Eh/pH meters are frequently used, but commercial voltmeters also work. A field installation of the Pt electrode, reference electrode, and voltmeter is shown in Fig. 2. The Pt electrodes may be installed and left in place for up to a year, with notable exceptions (Section III). The reference electrode and voltmeter are taken to the field for each measurement.

A. NUMBER OF ELECTRODES TO INSTALL

Redox potential is an extremely variable property. Figure 9 shows the range in Eh that was found in one soil that was saturated for a portion of the year in a horizon that contained five Pt electrodes. The graph shows the mean and range in redox potential over time. Before the soil horizon that contained the redox Pt electrodes became saturated, the Eh was in a fairly

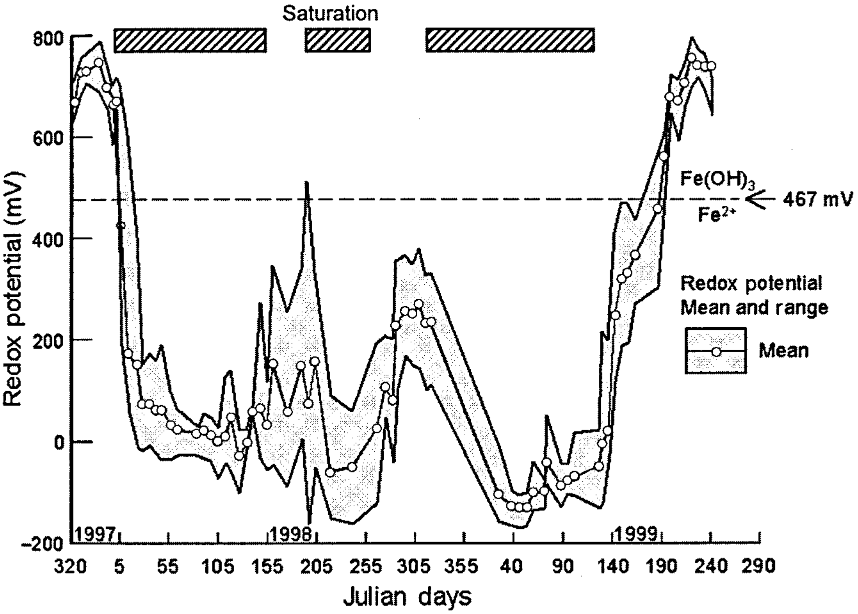

Figure 9 Variation in redox potential for a soil that undergoes periods of saturation and drainage. Means of five electrodes are shown for a mineral soil at a depth of 30 cm. The largest range in redox potential occurs soon after soil saturates or drains. Modified from Vepraskas and Faulkner, 2001.

narrow range. The variability in redox potential increased when the water table rose and redox potential decreased. The high variability was a result of reducing conditions that occurred in the soil around some electrodes but not in others. Possible causes for high variability in redox potential are illustrated in Fig. 10. When soils are saturated quickly, some air is trapped in bubbles in the soil. As shown in Fig. 10, any electrodes that have their tips in bubbles that contain oxygen will record high redox potentials. On the other hand, electrodes that are placed near pieces of organic C that are being oxidized by bacteria will be in reduced soil and will record low redox potentials. Intermediate redox potentials will occur when electrodes are placed somewhere in between these extreme conditions. If saturation is maintained for a long enough period, then the range in Eh values narrows as the entire horizon becomes reduced. See both Sections II and III for comments on other technical problems.

The broad range in Eh values is typical and shows that to measure the Eh of a soil horizon, an adequate number of electrodes must be installed. Statistical techniques could be used to determine a recommended number of electrodes, but a general rule of thumb is to install between 5 and 10

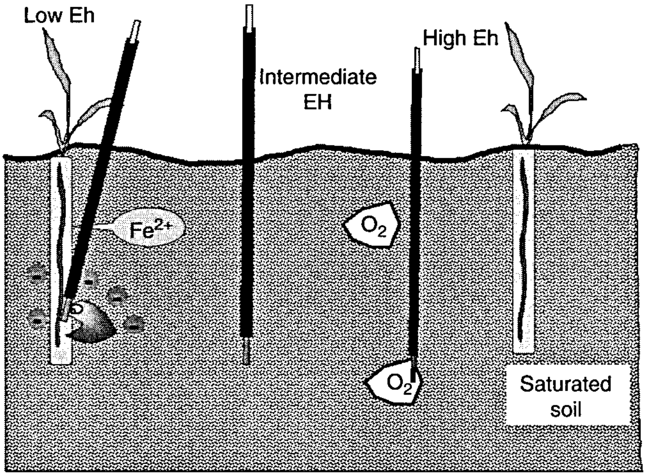

Figure 10 Illustration of possible explanations for why Eh measurements can be variable across lateral distances of 1 m or less. The soil is saturated, but air bubbles containing oxygen gas persist because the water table rose quickly and trapped air. Platinum electrodes inserted into the trapped air bubble may record high Eh values. Near a root, bacteria may be oxidizing organic C and releasing electrons that are used to reduce Fe. An electrode inserted next to the root may record a low Eh value. Other electrodes that are not near a root or gas bubble may record intermediate Eh values. (See Color Insert.)

electrodes for each depth of interest because of the variation explained earlier and given in Fig. 10. Using fewer than five electrodes will probably not account for all of the variability, and using more than 10 can be expensive. In addition, researchers must be aware that some electrodes will fail, and so replicated electrodes are also necessary to ensure that sufficient data are recorded when electrode failures occur. All electrodes need to be thoroughly tested before installation (Section II.D).

B. INSTALLING Pt ELECTRODES

The depth of Pt electrode installation will depend on the objectives of the research. Studies on wetlands typically focus on the upper 30 cm of the soil, whereas studies related to soil genesis may focus on a greater range of depths. For any application, electrodes should be installed in ways that will prevent oxygen penetrating from the surface to the electrode tip and also so that the Pt wire is in contact with natural soil. Pt electrodes can be installed in three ways to make readings: (1) direct insertion, (2) rigid rod, and (3) slurry-sealed. Direct insertion works best in soft materials that are under water. The electrode is pushed into the soil, and a reading is taken with the voltmeter and reference electrode. Being under water, there is little chance that air will enter the soil as the electrode is being pushed into the soil. In harder materials, some workers push a rigid rod into the soil to make a hole slightly smaller than the electrode. When the rod is removed from the soil, the Pt electrode is slid into the hole. A tight fit is believed to seal against oxygen penetration. This method probably works best when shallow readings are made.

The third way to install electrodes is shown in Fig. 11. A hole is first bored to within 1 cm of the desired depth of installation. The hole can be 2 cm or more in diameter. Soil at the depth of the electrode tip is then used to make slurry of mud with water. The slurry is poured into the hole and the electrode pushed through the slurry into natural soil. To complete the seal, more slurry is added to the hole until the hole is filled around the electrode. It is important that the slurry be taken from onsite and from the depth of the electrode tips to ensure that the soil chemistry (particularly the pH and organic C content) is not altered by the slurry.

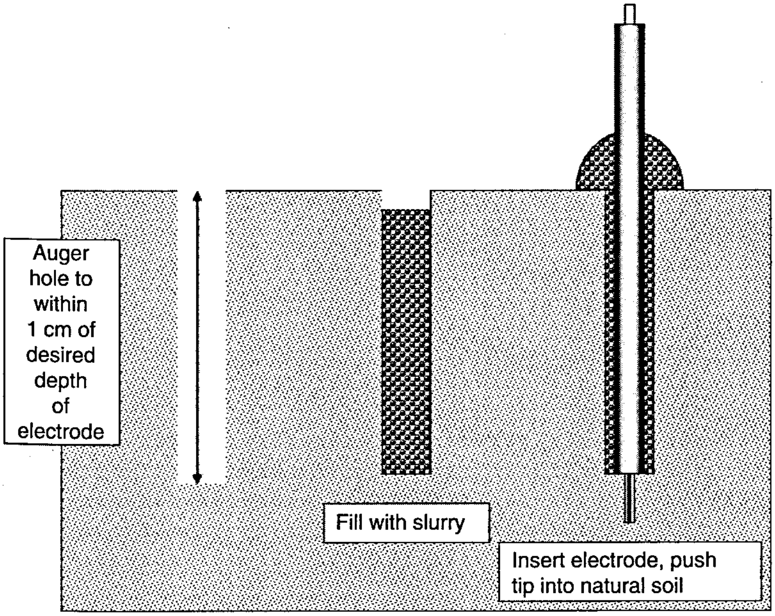

Figure 11 Installation of a Pt electrode. After the hole is bored into the soil, it is filled with a slurry made from the extracted soil. Only soil from the horizon that will contain the Pt tip should be used. Once the hole is filled with slurry, the Pt electrode is pushed through the slurry and the Pt wire seated in natural soil.

The basic process used to install five electrodes at a depth of 25 cm is as follows:

1. Auger five holes to a depth of 24 cm using a push-probe. Holes should be about 30 cm apart and are generally put in a line.
2. Fill each hole with a mud slurry made from the soil removed. Do not use the subsoil material below 25 cm because it will differ chemically from the topsoil.
3. Insert one electrode into a filled hole and push to the bottom of the hole. Try to seat the Pt into natural soil at the bottom of the hole, but do not push so hard that you bend the wire.
4. Pour more slurry around the wire to keep the hole filled.
5. Make one more hole to a depth of 12 cm, but do not put slurry into it. This hole will be for the reference electrode. It should be placed about halfway along the line of Pt electrodes, about 30 cm from the middle electrode.

The distance between electrodes that are installed at the same depth is determined for convenience. The electrodes should be close enough so that they can be read without moving the reference electrode, yet not so close that one electrode is disturbed when an adjacent electrode is installed.

Before they are inserted into the soil, the electrodes can be rechecked for accuracy by measuring the voltage of a buffer solution. This step ensures that electrodes were not damaged in transit to the field. To test the equipment:

1. Brush the Pt wires with steel wool to clean them.
2. Insert the clean electrodes into the test solution.
3. Insert the reference electrode (remove black cap covering ceramic tip).
4. Connect black wire to "common" terminal on voltmeter and attach to reference electrode.
5. Connect red wire to "volt" terminal on voltmeter and connect to a Pt electrode.
6. Turn meter on, and read voltage. Record voltage.
7. If voltage is within 20 mV of the number on the test solution bottle, the electrodes and the rest of the equipment are good.

Once installed, electrodes may be left in place for up to a year. Each electrode should be checked for accuracy in a buffer solution each year to ensure that the electrodes are functioning properly. It is advisable to secure the electrodes to racks made of PVC pipe to keep the electrodes from being stepped on and moved. Wires may also be attached to each electrode with the other end of the wire secured to a wooden table. This arrangement prevents workers from compacting the soil near the installation and also lessens the need for bending over.

C. Reading the Electrodes

Electrodes installed by direct insertion can be read as soon as the electrode tip reaches the proper depth. When electrodes are installed by using a rigid rod or by mud slurry, then readings should be delayed at least 24 h to allow the solution around the Pt wire to equilibrate with the soil solution. The basic procedure for measuring redox potential is:

1. Place some water in the open hole, dug to 10 cm, and insert the reference electrode. Be sure you took off the protective plastic caps that cover the base of the electrode.
2. Connect the black wire from the voltmeter (common terminal) to the reference electrode.
3. Connect the red wire from the voltmeter to one Pt electrode.
4. Turn the meter on and wait for the readings to stabilize.
5. Record the voltage. Note whether the voltage is "plus" or "minus."
6. Convert the voltage to "Eh" or redox potential by adding to the voltage reading a correction factor that is appropriate to the reference electrode. For most work, a correction factor of +200 mV can be used for Ag/AgCl electrodes, +250 mV for calomel electrodes.

D. Common Field Problems

The most common problem that occurs while making redox potential measurements is that the voltage does not stabilize but steadily moves, or drifts, to higher or lower values. The drift can be caused by natural processes that include a gradual change in the chemistry of the soil solution around the electrode tip. Drift may also be caused by human error. When it does occur, workers should check that the voltmeter is connected properly to the reference electrode and Pt electrode. The contact between the reference electrode and soil should also be checked. The voltage can drift if the circuit is broken among voltmeter, reference electrode, and Pt electrode.

In many cases, the voltage will drift when the kinds and amounts of oxidized and reduced species around the Pt tip are changing. This has to be expected whenever the soil water content changes from unsaturated to saturated or the reverse. The greatest amount of drift may be expected when the water table fluctuates and the soil horizon either saturates (and air bubbles may become trapped) or drains and oxygen penetrates along large cracks and root channels while the matrix is reduced. Redox potentials at a given electrode are stable when oxygen is the dominant electron acceptor, as is commonly the case in unsaturated soils. When saturation occurs, bacteria that are respiring near the tip of the Pt electrode will deplete the soil water of oxygen and eventually other electron acceptors will be used. As such substances as nitrate, manganese oxides, and iron oxides are reduced, the redox potential will fall and may cause drift. If soil water is moving past the Pt tip, the composition of the soil solution near the tip will slowly change, which can also cause drift.

Voltage drift is a frustrating problem to resolve in the field, and workers are advised to use a standard procedure when making measurements. At least two options are available to address drift. The first is to leave the voltmeter connected to an electrode until the drift stops, and then record the redox potential. This may require 15 min or longer. When many electrodes must be read, such a long waiting period may not be feasible; however, if it is critical to know the exact redox potential on a given day, then this approach may have to be used. An alternative procedure is to allow a set time, for example, 1 min, for each electrode to stabilize and then take the reading. This approach is reasonable when changes in redox potential are being monitored seasonally or over long time periods. Drift that occurs on a given day may simply be part of a long-term trend as the soil is changing from oxidized to a reduced condition. Such trends become apparent if data are collected over the course of months.

E. FIELD pH MEASUREMENTS

A pH value is needed to interpret redox potentials. Reducing reactions tend to convert H^+ to water as shown by the half-reaction for the reduction of Fe:

$$Fe_2O_3 + e^- + H^+ \rightarrow Fe^{2+} + H_2O$$

When soils become saturated, the soil pH shifts toward 7 in both acid and basic soils (Ponnamperuma, 1972). In acid soils, the amount of pH change is related to the amount of Fe reduction that occurs, while in basic soils the pH shift toward 7 is controlled by the accumulation of CO_2 gas. In many field soils, the pH may change by less than 2 pH units after several weeks of saturation and reduction. However, the pH change can be more in rice paddies where large amounts of organic matter and iron oxides allow for large amounts of Fe oxides to be reduced (Ponnamperuma, 1972). When soils drain, the pH shifts again toward its original value as Fe^{2+} is oxidized or the concentration of CO_2 gas is lowered.

Soil pH should be measured in the field on samples of either soil or water. Allowing samples to oxidize or dissolved gases to escape can cause pH to change when exposed to air. Measuring pH electrometrically is most accurate. Water samples may be extracted from piezometers placed at the same depth as the electrodes. When water samples are used, the piezometer should be emptied and allowed to refill before a sample is removed for pH measurements. For soil samples, pH should be measured on soil obtained from the same depth as the electrode tip. Soil pH is commonly measured on a slurry of 1:1 soil to water by volume.

F. INTERPRETING REDOX POTENTIAL

Redox data are interpreted using an Eh–pH diagram that relates a given reducing half-reaction to redox potential. An example is shown in Fig. 12 for the reduction of $Fe(OH)_3$. When the soil pH is known, then the redox potential from an electrode can be plotted on the diagram to determine the form of Fe that should exist in the soil. Diagrams such as that shown in Fig. 12 can be prepared for any half-reaction of interest (McBride, 1994; Vepraskas and Faulkner, 2001). Field experience has shown that such diagrams work well for Fe minerals. The theoretical redox potential at which Fe reduction occurs, shown on the Eh–pH diagram, is close to the actual redox potential where reduction has been observed (McBride, 1994). Similar results have been found for the reduction of SO_4 and CO_2. On the other hand, theoretical redox potentials for the reduction of O_2, NO_3, and MnO_4 have been found to be markedly higher than the redox potentials found in nature. Accordingly, when redox potentials are measured to assess the reduction of O_2, NO_3, and MnO_4, it may be advisable to use a phase diagram such as that for Fe, and then assume that if Fe has been reduced, then O_2, NO_3, and MnO_4 must have been reduced as well.

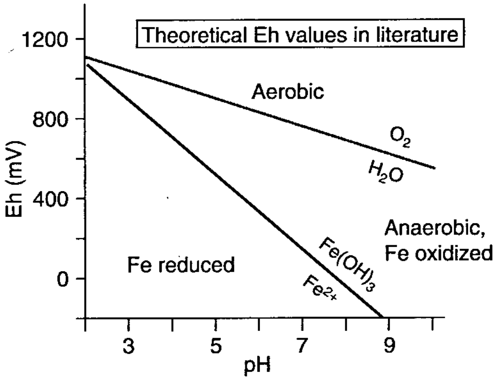

Figure 12 An Eh–pH diagram that can be used to interpret redox potentials. The soil pH must be known before the field-measured Eh values can be interpreted. This graph can be used to identify the critical Eh values at which Fe reduction occurs in a soil of a given pH. Such data are then used to determine when Fe reduction occurred in a soil (McBride, 1994). (See Color Insert.)

VI. SUMMARY

Redox potential measurements (Eh) are the tendency of a pair of chemical compounds to undergo a transfer of electrons. In hydric soils, the pair of ions of most interest is Fe^{2+}/Fe^{3+}. Redox measurements have never been more important than at present because of the need for better measures for hydric soils. The various levels of reduction and oxidation relate to important environmental conditions. The interpretation of redox potentials obtained from redox potential measurements in soils is subject to many problems (e.g., chemical restraints and technical problems). It is difficult if not impossible to interpret redox reactions in soils in a quantitative way by applying basic equilibrium thermodynamics. However, this does not preclude the usefulness of these estimates for understanding how the ecosystem functions. Therefore, the attempt to identify dominant redox processes in a given soil is of scientific interest as well as practical relevance.

Many practical, persistent, and controversial problems exist. One problem is that the iron ion pair is not the only pair that may undergo an electron transfer in field conditions. Commercial working and reference electrodes are often not suitable or rugged enough for field use in soils. Electrode construction, insulation, and contamination are also problems. Suggestions were given on electrode construction, which should help with these problems. Insulation with epoxy products, which often adsorb water, has been unsatisfactory. We suggest alternatives. Cleaning to prevent contamination and standardization procedures of working electrodes are suggested.

Standard field installation procedures, such as those suggested here, are necessary to ensure consistent results. Additionally, field pH, water table, and soil temperature data are needed for interpretation of the results. Numerous repetitions of each soil element measured are needed because of these variations, and these repetitions are costly.

Currently, *in situ* Eh measurements are still the most efficient way of estimating reducing reactions for virtually any soil. In the future, evaluations of redox measurements should include comparisons to ferrous iron dyes, such as dipyridyl, comparison to "IRIS" or "indicator of reduction in soils," and to zero valence iron materials. Such comparisons with field pH measurements should lead to better interpretations of soil conditions.

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