Redox Potential

Soil Chemistry (Soil 503)

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Redox potential

- Reduction & oxidation occur simultaneously in any soil
- Reduction is the gain of electrons & Oxidation is the loss of electrons
- These reactions proceed simultaneously because of the free transfer of electrons and are said to be reversible
- Aerated condition of a soil can be better characterized with the help of oxidation reduction potential known as redox potential

- Redox Potential is a measure of the intensity of reduction in soil in the absence of O_2
- Physical measurement of O_2 is not simple and hence it is more feasible to measure the Redox Potential
- The reduction of the inorganic Redox systems in the soil following flooding can be determined in both intensity and capacity terms
- The intensity factor determines the relative ease of the reduction where as the capacity factor denotes the amount of the redox system undergoing reduction

Oxidized		Reduced
O_2 (volatile) + 4H+ + 4 e	⟺	2 H_2O (Soluble)
NO^{3-} (soluble) + H_2O + 2 e	⟺	NO_2^-(soluble) + $2OH^-$
MnO_2 (insoluble) + $4H^+$ +$2e^-$	⟺	Mn^{2-}(soluble) +$2H_2O$
$Fe(OH)_2$ (insoluble) + e-	⟺	Fe^{2+}(Soluble) +3 OH^-
SO_3^{2-} (soluble) + 3 H_2O + 6e	⟺	S^{2-} (insoluble) + 6 OH^-
CO_2(soluble)	⟺	CH_4 (volatile)

O_2 readily accepts electrons from the decomposed plant material while the reduction of CO_2 to CH_4 occurs under very reducing conditions

The Eh range in water logged soils extends from approximately -300 volts to approximately +700 mvolts

O_2 is depleted as Eh decreases to 500 mvolts, NO_3 is reduced at 300 - 400 mvolts

Importance

- **The redox potential of a soil is an important determinant in rice culture for supporting growth and grain yield.**
- **Moderate reducing conditions are known to enhance growth through a number of mechanisms, while intense reducing conditions produce substances that are toxic to the plant**
- **The inorganic redox value of a soil will give an indicator of the oxidation reduction status of the various inorganic compounds present in it**

- **The inorganic redox systems play an important role in flodded soils in helping the organic matter decomposition.**

- **The decomposition of organic matter supported by NO_3, Mn^{4+} and Fe^{3+} systems is similar to the decomposition supported by O_2, since CO_2 and the reduced oxidant are the major products of this type of decomposition**

- **Another beneficial function of the large amount of the inorganic oxidants in the soils is the nutritional effect of N,S and P, released from the decomposition of the organic matter**

Redox Potentials

The half cell for an oxidation-reduction system can be illustrated with reaction and attains the following general expression

Oxidized state + e  **Reduced state**

The Nernst equation

Eh $= E_0 + RT/nF \log$ (oxidized state/reduced state)

Where,

Eh is the redox potential

It is in fact the half cell potential relative to a standard reference electrode

E_0 is a constant called the standard redox potential of the system

- **If the activities of the oxidized and reduced species are unity, the ratio becomes 1 and the log equals to 0**

- **The standard redox potential is defined as the redox potential of the system at which the activities of oxidized and reduced species are unity**

Application of redox potential in soil

- **Eh of soils varies with the reduced and oxidation state in soils**
- **It is also associated with soil pH**
- **E h - pH relationships are usually linear in character**

Activity of reduction products

- Van Breemen and Brickman stated that flooding of aerobic soils reduced first the NO_3 in soils
- After the dispersion of nitrate, Mn would be reduced, followed by Fe
- The latter increased the conc. of Mn^{2+} and Fe^{2+} ions during the initial period of reduced condition
- The conc. of Mn^{2+} and Fe^{2+} ions decreased again upon continued flooding and stabilized at a constant level
- The net reduction is a condition in which Fe (III) and Fe (II) ions are present together