LECTURE 1 Soil Chemistry

Until the late 1960s, soil chemistry focused primarily on chemical reactions in the soil that contribute to pedogenesis or that affect plant growth. Since then concerns have grown about environmental pollution, organic and inorganic soil contamination and potential ecological health and environmental health risks. Consequently, the emphasis in soil chemistry has shifted from pedology and agricultural soil science to an emphasis on environmental soil science.

A knowledge of environmental soil chemistry is paramount to predicting the fate, mobility and potential toxicity of contaminants in the environment. The vast majority of environmental contaminants are initially released to the soil. Once a chemical is exposed to the soil environment a myriad of chemical reactions can occur that may increase/decrease contaminant toxicity. These reactions include adsorption/desorption, precipitation, polymerization, dissolution, complexation, and oxidation/reduction. These reactions are often disregarded by scientists and engineers involved with environmental remediation. Understanding these processes enable us to better predict the fate and toxicity of contaminants and provide the knowledge to develop scientifically correct, and cost-effective remediation strategies.

Reduction potential (also known as **redox potential**) is the tendency of a chemical species to acquire electrons and thereby be reduced. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced.

A reduction potential is measured in volts (V). Because the true or absolute potentials are difficult to accurately measure, reduction potentials are defined relative to the standard hydrogen electrode (SHE) which is arbitrarily given a potential of 0.00 volts. **Standard reduction potential** (E^0), is measured under standard conditions: 25°C, a 1M concentration for each ion participating in the

reaction, a partial pressure of 1 atm for each gas that is part of the reaction, and metals in their pure state. Historically, many countries, including the United States, used **standard oxidation potentials** rather than reduction potentials in their calculations. These are simply the negative of standard reduction potentials, so it is not a major problem in practice. However, because these can also be referred to as "redox potentials", the terms "reduction potentials" and "oxidation potentials" are preferred by the IUPAC. The two may be explicitly distinguished in symbols as E_r^0 and E_o^0.

The relative reactivities of different half-cells can be compared to predict the direction of electron flow. A higher E^0 means there is a greater tendency for reduction to occur, while a lower one means there is a greater tendency for oxidation to occur.

Any system or environment that accepts electrons from a normal hydrogen electrode is a half cell that is defined as having a positive redox potential; any system donating electrons to the hydrogen electrode is defined as having a negative redox potential. E_h is measured in millivolts (mV). A high positive E_h indicates an environment that favors oxidation reaction such as free oxygen. A low negative E_h indicates a strong reducing environment, such as free metals.

Sometimes when electrolysis is carried out in an aqueous solution, water, rather than the solute, is oxidized or reduced. For example, if an aqueous solution of NaCl is electrolyzed, water may be reduced at the cathode to produce $H_{2(g)}$ and OH^- ions, instead of Na^+ being reduced to $Na_{(s)}$, as occurs in the absence of water. It is the reduction potential of each species present that will determine which species will be oxidized or reduced.

Absolute reduction potentials can be determined if we find the actual potential between electrode and electrolyte for any one reaction. Surface polarization interferes with measurements, but various sources give an estimated potential for the standard hydrogen electrode of 4.4V to 4.6V (the electrolyte being positive.).