VII. BIOCHEMISTRY OF METAL TRANSFORMATIONS IN SOIL

Required Readings:


Suggested Readings:


Approximately one-fourth of the earth’s naturally occurring elements are known to be essential for the growth and development of microorganisms and/or plants. Of the essential metals, however, several may become toxic when available in excess of the requirements for a particular
organism. Some metals, such as mercury and lead, are considered toxic even when present in trace amounts. Other metals, which are not essential, may be tolerated at low concentrations but become toxic at higher levels. Various microorganisms and plants not affected by large concentrations of a particular metal may actually accumulate a metal in excess of what is required for "normal" growth. The metal that has accumulated in a tolerant organism may be passed on to other organisms, resulting in bioaccumulation and potential eventual toxicity problems.

The sources of metals in the environment are the rocks of the earth’s crust that are broken down by natural weathering processes. The soil formed as a result of weathering contains the metals originally found in the rock. Four elements (oxygen, silicon, aluminum, and iron) comprise more than 80% by weight, of the total earth's crust. The remaining elements are not found in uniform concentrations throughout the earth, but vary widely from place to place. When metals are found at high enough concentrations, they are extracted from the rock and are called ores.

Of interest to the soil biochemist are the many reactions that render the metals available for plant uptake or which increase the mobility and toxicity of the metals within the environment. The biochemical reactions of metals depend on a multitude of factors such as its total concentration in the soil, pH, redox potential, temperature, moisture, ion exchange, salt formation, and precipitation reactions. The maintenance of an adequate but not excessive level of metals in the soil, therefore, requires a balance among all the factors mentioned.

Extensive work has been conducted on the reactions that directly or indirectly influence metal transformations in soil. Three broad categories of biotransformations may be applied to the majority of metals in soils.

1. Oxidation-reduction reactions of inorganic metal species.
2. Conversion of inorganic to organic forms and vice versa. Included in this
category are mineralization-immobilization reactions and methylation-demethylation reactions.

3. Indirect effects of biological activity on metal availability such as changes in acidity and alkalinity, alteration of the oxidation-reduction potential as a result of microbial activity, changes in the concentration of microbial end-products which react with metals in nonbiological redox reactions, salt formation, acid-base reactions, or complexing reactions.

Specific Types of Reactions in Soil. Many metals undergo reactions that are common to more than one metal. An important reaction of this type is biomethylation. Information in the literature indicates that the metals Hg, Sn, Pb, Pt, Au, Cd, and Zn as well as several nonmetals such S, As, Se, and Te may become methylated via biological mechanisms. The review by Summers and Silver (suggested reading) describes some of the biochemistry of this reaction for several different metals. Methylation makes a metal much more toxic as methylation provides the metal greater mobility and also the ability to more easily cross cell membranes. The dominant organic form of mercury, especially at neutral soil pH, is monomethyl mercury. Transalkylation is possible whereby the methyl group associated with one metal is transferred to another metal.

Methylation may occur within the cell or outside the cell in the soil environment. Methylation of mercury, as well as other metals, occurs via a variety of methyl donors including methylcobalamin (CH$_3$-B$_{12}$), s-adenosyl methionine, and N$^5$-methytltetrahydrofolate. The soil factors that stimulate methylation of metals include high microbial activity under aerobic conditions and the presence of a readily available organic source. The presence of sulfides greatly inhibits mercury methylation, presumably because the sulfide reacts with mercury to form an extremely insoluble precipitate.

A second type of reaction that many metals can participate in is called “corrosion”. Corrosion is
defined as the destructive attack of a metal by a chemical or electrochemical reaction with its environment. Corrosion is frequently thought of as rusting, especially when applied to iron-containing materials. Microorganisms contribute to the corrosion process in several ways.

1. Through the formation of mineral acids, especially sulfuric acid.
2. Through the formation of organic acids.
3. By changing the electrode potential or $E_h$.
4. By creating microgalvanic cells.
5. By depolarizing surfaces through the reduction of hydrogen ions.
6. By producing $H_2S$ and $PH_3$ which are themselves corrosive.

The production of acids by microorganisms causes corrosion because many metals become soluble under acidic conditions. Leaching of the solubilized metals produces a new metal surface that can also be attacked by the acid and the process repeats itself.

Variations in oxygen and ion concentrations at the surface of a metal may establish electrical currents. Microorganisms growing on the surface of a metal such as iron may bring about the required variations in oxygen and ion concentrations as a result of their metabolic activity. As a result of the lower concentration of oxygen beneath the active cell mass, and the higher concentration adjacent to the cell mass, a potential is formed between these two areas. Iron goes into solution at the anode in areas of low oxygen concentration and the electrons flow to the more oxygenated cathode to combine with oxygen and form hydroxyl ions. The overall equation describing aerobic corrosion is given by

$$2Fe + O_2 + H_2O \rightarrow 2Fe(OH)_2$$

When this process continues, a cavity or pit is formed which is covered by what is called a tubule. A tubule is composed of the corrosion products and microbial cells.

To describe the process of anaerobic corrosion, a cathodic depolarization hypothesis has been postulated. The reactions involved can be summarized by the equation
\[
4\text{Fe} + \text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{FeS} + 3\text{Fe(OH)}_2 + 2\text{OH}^- \\
\]

The individual reactions that occur at the anode are stripping of electrons from the metal and the production of corrosion products.

\[
4\text{Fe} \rightarrow 4\text{Fe}^{2+} + 8\text{e}^- \\
\text{Fe}^{2+} + \text{S}^{2-} \rightarrow \text{FeS} \\
3\text{Fe}^{2+} + 6\text{OH}^- \rightarrow 3\text{Fe(OH)}_2 \\
\]

At the cathode, the reactions that occur are the transfer of the hydrogens (electrons) removed from the metal ultimately to sulfate resulting in sulfate reduction.

\[
8\text{H}^+ + 8\text{e}^- \rightarrow 8\text{H} \quad \text{(hydrogenase)} \\
\text{SO}_4^{2-} + 8\text{H} \rightarrow \text{S}^{2-} + 4\text{H}_2\text{O} \quad \text{(sulfate reduction)} \\
\]

The H+ and OH- ions in the above equations come from the ionization of water

\[
8\text{H}_2\text{O} \rightarrow 8\text{OH}^- + 8\text{H}^+ \\
\]

The key mechanism in the series of reactions that results in corrosion is catalyzed by the bacterial hydrogenase coupled to the reduction of sulfate to sulfide. The enzyme hydrogenase has been directly associated with the ability to produce cathodic depolarization. The removal of hydrogen (or electrons) at the cathode brings about the dissolution of ferrous iron at the anode and causes the electrons to flow from the anode to the cathode. The sulfate acts in place of oxygen as a terminal electron acceptor and can be replaced by other compounds, such as the dye benzyl viologen, in the corrosion process.

In soil, the conditions at which optimum anaerobic corrosion occur are a pH greater than 5.5, an electron potential of less than 400 mv, a low concentration of free oxygen, and a plentiful supply of sulfate.

Besides iron, other metals that undergo corrosion reactions include lead, copper, zinc, aluminum, tin, nickel, and chromium. Because of the cost incurred as a result of corrosion, various control
measures have been investigated. The most practical approach is to control the conditions that cause corrosion. Metal objects such as pipes should be located, if possible, in well-drained alkaline soils with low salt concentrations. Since sulfate reducers require organic matter, areas low in organic matter are also ideal for placing of metal objects. Other methods used to control corrosion include treating the metal surface with a protective coating of coal-tar pitch metal or wrapping the metal with a polyvinyl chloride tape. Bactericides have also been used.

Cathodic protection has been applied to increase the life-time of a metal object in soil. The metal object to be protected is made into the cathode of an electrolytic cell by connecting it to a more electronegative metal acting as the anode. A direct current is thus imposed between the metal and the expendable anode to which the corrosion is transferred. The alkalinity produced in areas adjacent to the cathode metal object offers additional protection.

Reactions of Metals in Various Chemical Groups. The biochemistry of metals in the same family or group of the periodic table (i.e. the metals that appear within the same vertical column) are often very similar. The alkali (Group 1A) and alkaline earth group (Group IIA) metals are characterized by an outer electronic shell of one or two “s” electrons, respectively. These electrons are readily lost and the alkali and alkaline earth metals are found in nature in ionized form. The biochemical reactions in which these metals participate are relatively simple compared to other metals because they do not undergo oxidation-reduction reactions or methylation-demethylation reactions. Several of the alkaline earth metals, most notably Mg, serve an important role as cofactors in enzyme catalyzed reactions. In some areas of the world, alkali metals also exert a great influence on the biochemistry of a soil because of the salinity problems associated with an accumulation of their related salts.

Of the metals that comprise Groups IIIA, VA, and VA, the most widely studied is lead. This is not because it has any great value as a nutrient or even a micronutrient but because lead is
normally extremely toxic to living organisms. Arsenic in the form of arsenite and arsenate, has chemical properties very similar to that of phosphate. It is a potent inhibitor of phosphatases.

The elements in Groups VIA and VIIA are not normally considered metals but the reactions that characterize them are similar to those of the metals. Se and Te, for example, are subject to methylation. Selenium is an element in which there is a very fine line between the amount required for proper growth (it is considered an essential element) and concentrations that are high enough to cause toxicity. Since both Se and Te can exist in a number of valence states, microbial activity may be expected to bring about changes from one valence state to another. The chemistry of Se is very much like that of S and it is often found in protein as a substitute for S in the amino acids cysteine and methionine. It is this fact that makes Se toxic when it is taken up in concentrations above that required for growth.

The Group B metals (Groups IIIB to IIB as one moves from left to right across the periodic table) are called the transition metals. Several of the transition metals such as iron and manganese are found in high concentrations in soil and their biochemistry has been studied in some detail. Available iron concentrations are normally very low in soil, even though 10% or greater of the total soil may be comprised of this element, because of the insolubility of ferric iron at the pH values normally found in soil. For example, the Ksp of Fe(OH)$_3$ at pH 7 and 25°C is approximately $10^{-38}$ M. In environments in which iron availability is limiting, microorganisms and plants synthesize and secrete iron chelators, called siderophores, into their surroundings. Siderophores have been detected in soils and this chapter includes a review and a research paper dealing with siderophore chemistry.

With the exception of uranium, there is almost no biochemical information available for most of the lanthanide and actinide elements in soil. The primary reason for this is that the natural abundance of most of these elements in soils is extremely low. Uranium is the exception
because, even though it also is normally found in soil at very low concentrations, it is involved in nuclear reactions and information as to its fate in soil has been desired. Biochemical reactions of uranium revolve around its many oxidation states. Many of the reduced uranium forms are easily oxidized to the soluble hexavalent state. The oxidation of uranium minerals is slightly exothermic and could conceivably support autotrophic growth.

**Heavy Metals.** A subset of metal elements that is often grouped together is the "heavy metals". Although a strict definition of the term “heavy metal” is lacking, it is often used to describe those metals that exhibit toxic effects against biological systems. Most heavy metals exist at low concentrations in soil but in localized areas their concentrations may be much higher due to natural deposits or man’s activities. Several of the heavy metals, i.e. copper, zinc, and iron are actually essential elements that are required for normal plant and microbial growth. However, at high concentrations, they may become toxic.

The toxicity of heavy metals arises because they

1) block the essential function of biomolecules,
2) displace another essential metal ion in biomolecules, and
3) modify the active conformation of biomolecules.

Heavy metals also affect the microbial population in soils by reducing their diversity and by selecting for strains resistant to the toxic effects of the heavy metals. Tolerance or resistance of microorganisms to heavy metals comes about through several different mechanisms. In many instances, uptake by the microorganism is limited because of the impermeability of the plasma membrane. Other microorganisms, however, may accumulate the metal in a cellular location or form in the cell that will remove its interference from the biological processes most sensitive to the presence of the metals. Microorganisms may also reduce the toxic effects of metals by rendering the metal less soluble or removing the metal from the microbial environment through the formation of volatile metabolites.
Previously it was stated that a strict definition of the term "heavy metals" is difficult to establish because of the variety of ways it is used in the literature. A classification scheme that divides all the metals into three categories, based on their relative ability to form various types of metal ion/ligand complexes has been proposed.

Class A metals are those which, on the basis of their magnitudes of the equilibrium constants, have the following ligand preference order.

\[ F > Cl > Br > I \]

and the following donor atom preference sequence

\[ O > S \geq Se, \ N > As \text{ and } O > N > S. \]

The class A metals are comprised of the alkali, alkaline earth, lanthanide, and actinide metals. They are characterized by their ionic character and are generally not considered toxic. The elements that are considered macronutrients are included in the Class A metals.

The Class B metals have a ligand preference order of

\[ I > Br > Cl > F \]

and a donor atom preference sequence of

\[ Se \geq S > O, \ As > N, \text{ and } S > N > O. \]

The more traditional “heavy metals” fit within the class B designation. These metals have covalent characteristics and are more toxic than the Class A metals. The toxicity occurs by (i) binding SH and N centers, (ii) displacement of borderline metals required in biochemical reactions, and (iii) their ability to form organometallic complexes which affects the biological activity of the organic molecule. Several classes of the Class B metals are essential nutrients but are required in small amounts and are, therefore, classes as micronutrients.

The borderline metals are those that exhibit properties of either Class A or Class B metals.
depending on the environment specific reaction considered.

The value in abandoning the term “heavy metals” in favor of Class A, Class B, or borderline metal designations is that these new classifications are based on criteria that are biologically and chemically significant.