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Chemical Equilibria of Nutrients in Submerged Soils

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SUMMARY

When a soil is submerged, a variety of chemical changes like transformation of nutrients namely N, P, K, S, Fe, Mn, Cu, Zn, B and Mo occurs. In this section, the transformation of some important nutrient elements in submerged soils are being discussed.

INTRODUCTION

The submerged soils play a great role in influencing plant growth and microbial activity, soil moisture regimes, aeration etc., which in turn affect crop production. Therefore, most plant growth factors and influenced by all these soil physical properties since soil acts as medium for plant growth. So, soil should be physically healthy and fertile so that the soil can able to provide optimum nutrients, water, microbial activity, air, temperature etc., for optimum crop production. The environment is a complex of so many factors, all interacting with each other, that it is impossible to isolate any one factor that does not influence another. For the study of environmental effects, however, this complex is usually sub-divided into clearly defined units. On of these units is the soil, which is vitally important for plant growth and development. Soil in itself represents a complicated physical, chemical and biological system by which the plant is supplied with the water, nutrients and oxygen it requires for its development. Most of the nutrients transformation are being discussed.

Nitrogen

Nitrogen occurs in soils mainly as complex organic substances, ammonia, molecular nitrogen, nitrite and nitrate. The transformations of nitrogen are largely micro-biological inter-conversions regulated by the physical and chemical environment of the soil. In submerged soil, the main transformations are accumulation of ammonia, volatilization loss of ammonia, denitrification, nitrogen fixation and leaching losses of nitrogen. These transformations have an important bearing on the nutrition of rice. It is evident that nitrogen is deficient in rice soils because of conditions favourable for rapid transformations and losses of nitrogen from the soil.

Mineralization of Nitrogen and Accumulation of Ammonia

In aerated soils NO_3^- is the inorganic form and all of the nitrogen reactions that follow the decomposition of organic matter proceed towards the production of NO_3^-. Thus organic form of nitrogen undergoes mineralization to NH_4^+, oxidation of NH_4^+ to NO_2^- and oxidation of NO_2^- to NO_3^-. But in an anaerobic soils the absence of O_2 inhibits the activity of the *Nitrosomonas* micro-organisms that oxides NH_4^+ and therefore, nitrogen mineralization stops at the NH_4^+ form. The accumulation of ammonia in submerged soils is, therefore, a good index of the capacity of a soil to meet up the demand for nitrogen to the rice crop. The transformation of nitrogen occur in the aerobic and anaerobic layers of a submerged soil. In the aerobic surface layer, conditions are similar to those of a well-drained soil and nitrogen mineralization proceeds to the NO_3^- form. The presence of an aerobic layer above the anaerobic layer is the major cause of instability of nitrogen in submerged soils and results in considerable loss of nitrogen through nitrification-denitrification reactions. Nitrate is stable and not subject to denitrification as long as it remains in the surface aerobic layer, but it readily diffuses downward into the anerobic layer and undergoes denitrification as a result of a gradient in the NO_3^- concentration between the aerobic layer and the anaerobic layer. This process can proceed as long as NO_3^- is formed in the aerobic layer, and that can readily happen if there is a sources of NH_4^+ in the aerobic layer that can be nitrified (NO_3^-). The removal of NH_4^+ in that layer by nitrification created a concentration gradient that causes NH_4^+ to diffuse upward form the anaerobic layer.

Phosphorus

Soil submergence is known to influence the transformation and availability of both native and applied phosphorus. Phosphorus is not directly involved in oxidation-reduction reactions in redox potential range encountered in submerged soils, but because of its reactivity with a number of redox elements its behaviour is significantly affected by waterlogging. On submergence, the availability of native as well as applied phosphorus increases in the soil. The phosphorus transformation are known to be associated with pH changes in submerged soils. When an aerobic soil is submerged the concentration of available phosphorus initially increased and thereafter declines with the period of submergence. However, the magnitude of initial increase and decrease in the layer period of submergence depends on the soil properties. The decrease in the concentration of available P at the later period of submergence may be due to the fixation (through adsorption) of released phosphorus by clay colloids (kaolinite, montmorillonite and hydrous oxides of Fe and Al). In addition, the decreased concentration of phosphorus may also be due to the decreased solubility of phosphorus associated with calcium.

Potassium

In soils two important parameters influence the availability of K to plants. These are the intensity factor (I), which is the concentration of an element in the soil solution and the capacity factor (Q), which is the ability of solid phases (soil) to replenish that element as it is depleted from solution. As plants remove K^+ ions from the soil solution, the concentration of K^+ ions in the immediate vicinity of roots is reduced and diffusion gradients are established. With flooding or submergence soluble ferrous (Fe^{2+}) and manganous (Mn^{2+}) ions increase and exchangeable K^+ is then displaced into the soil solution. The increase in soluble K^+ after submergence is closely related to ferrous ion (Fe^{2+}) content of the soil solution. The release of K^+ from micas may be the contributing factor for the increase in K^+ in soil and that release depends on the various factors like tetrahedral rotation, degree of tetrahedral tilting, -OH groups orientation, degree of K^+ depletion from the soil solution, hydronium ions (H_3O^+), biological activity and complexing organic acids, inorganic cations etc. Besides these, charge density and the configuration of the oxygen about exchange sites probably determines the release of K^+ and thus increases the concentration of K^+ in the soil solution.

Sulphur

In submerged soils the main transformations of sulphur are the reduction of sulphate (SO_4^{2-}) to sulphate (S^{2-}) and the dissimilation of the amino acids, cysteine, cystine and methionine to H_2S. Methylthiol has been found in submerged soils and the bad odour of putrefying blue-green bacteria in a reservoir has been attributed to dimethyl sulphide and methyl, butyl and isobutyl thiols. The main product of transformations of the sulphur in submerged soils is H_2S and it is derived largely from SO_4^{2-} reduction. After formation of H_2S due to SO_4^{2-} reduction results from the soil submergence, it may react with various heavy metals (Zn, Cu, Cd, Pb etc.) to give their insoluble sulphides. As a result the availability of these metals may be reduced. Because Fe^{3+} reduction to Fe^{2+} precedes SO_4^{2-} reduction, there usually will be Fe^{2+} present in the soil solution by the time hydrogen sulphide (H_2S) is produced and to that hydrogen sulphide will be converted to insoluble iron sulphide (FeS). When an acid soil is submerged the concentration of water soluble SO_4^{2-} increases initially and therafter the concentration of the same decreases slowly. The initial increase in SO_4^{2-} concentration is due to the release (following increase in pH) of SO_4^{2-}, which is strongly sorbed at low pH by clay and hydrous oxides of Fe and Al. Rice like other plants, absorbs sulphur primarily in the forms of SO_4^{2-} and reduction of SO_4^{2-} to sulphide (S^{2-}) in submerged soils reduces the availability of sulphur.

Iron

The most important chemical change that takes place when a soil is submerged is the reduction of iron and the accompanying increase in its solubility. The intensity of reduction depends upon time of submergence, amount of organic matter, active iron, active manganese, nitrate etc. Due to reduction of Fe^{3+} to Fe^{2+} on submergence, the colour of soil changes from brown to grey and large amounts of Fe^{2+} enter into the soil solution. It is evident that the concentration of ferrous iron (Fe^{2+}) increases initially to some peak value the thereafter decreases slowly with the period of soil submergence. Organic matter also enhances the rate of reduction of iron in submerged soils. The initial increase in the concentration of ferrous iron (Fe^{2+}) on soil submergence is caused by the reduction. The decrease in the concentration of Fe^{2+} following the peak rise is caused by the precipitation of Fe^{2+} as $FeCO_3$ in the early stages where high partial pressure of CO_2 prevails and as $Fe_3(OH)_8$ due to decrease in the partial pressure of $CO_2(pCO_2)$.

Manganese

The main transformations of manganese in submerged soils are the reduction of manganese (Mn^{4+}) to manganous (Mn^{2+}) and almost similar to that of iron transformation. Like iron, the transformation for Mn is also governed by the redox equilibria system. In submerged soils, the transformation of Mn results an increase in the concentration of water soluble Mn^{2+}, precipitation of manganous carbonate ($MnCO_3$), and re-oxidation of Mn^{2+} diffusing or moving by mass flow to oxygenated interfaces in the soil. The initial increase in the concentration of Mn^{2+} may be due to the reduction of soil as well as Mn^{4+} and the decrease of the same of the later period may be due to the precipitation of Mn^{2+} on $MnCO_3$ and $Mn(OH)_2$ in the soil solution. The kinetics of manganese reduction varies markedly from soil to soil. The changes in water soluble Mn^{2+} concentration depend upon the pH, organic matter content and active Mn content of the soils. The mobilization of Mn in soils is markedly increased after submergence due to the reduction of manganic compounds to more soluble forms as a consequence of the anaerobic metabolism of soil bacteria. It is evident that organic matter influences the manganese transformation in soils through following ways :

- The production of complexing agents that effectively reduces the activity of free iron in solution.
- The decrease in the oxidation-reduction potential of the soil either directly or indirectly through microbial activity.
- The stimulation of microbial activity that results in the incorporation of the Mn is biological tissue.

Zinc

The transformation of zinc in submerged soils is not involved in the oxidation-reduction process like that of iron and manganese. However, the reduction of hydrous oxides of iron and manganese, changes in pH, partial pressure of CO_2, formation insoluble sulphate compound etc. In soil on submergence is likely to influence the solubility of Zn in soil either favourably or adversely and consequently the Zn nutrition of low and rice. The reduction of hydrous oxides of iron and manganese, formation of organic complexing agents, and the decrease in pH of alkaline and calcareous soils on submergence are found to favour the solubility of Zn, whereas the formation of hydroxides, carbonates, sulphides may lower the solubility of Zn in submerged soils. Zinc deficiency in submerged rice soils is very common owing to the combined effect of increased pH, HCO_3^- and S_2^- formation. When an aerobic soils is submerged, the availability of native as well as applied Zn decreases and the magnitude of such decrease varies with the soil properties. The transformation of Zn in soils was found to be greatly influenced by the depth of submerged and application of organic matter. If an acid soil is submerged, the pH of the soil will increase and thereby the availability of Zn will decrease. On the other hand, if an alkali soil is submerged, the pH of the soil will decrease and as a result the solubility of Zn will generally increase.

Copper

Most of the copper in soils is very insoluble and can only be extracted by strong chemical treatments which dissolve various mineral structures of solubilise organic matter. The concentration of copper in soil solutions is usually very low. All pH values below 6.9, divalent Cu^{2+} is the dominant species. Above pH 6.9, $Cu(OH)_2^0$ is the principal solution species and $CuOH^+$ at 7.0.

It is evident that copper exists in soils as different discrete chemical pools which are as follows :

- Water soluble plus exchangeable Cu.
- Copper associated with clay minerals.
- Organically bound Cu.
- Copper associated with different oxides in soils.
- Residual copper.

The chemical equilibria of Cu in submerged rice soils are similar to those of Zn. The mechanism for removal of Cu from soil solutions in submerged soils is so pronounced that copper is apparently removed from chelating agents that is capable of keeping the element is solution phase in upland soils. When an acid soil is submerged, the release of copper decreases due to increase in soil pH, whereas submerging an alkali and calcareous soils, the amount of copper in soil solution increases to a lesser degree. However, in most of the soils, submergence decreases the availability of copper and thereby creates deficiency to plants. The possible explanation for the increase in the concentration of copper in submerged soils the decrease in the amount of copper may be due to the insoluble precipitation as CuS, $CuCO_3$ and $Cu(OH)_2$ since the production of sulphide, carbonate, bicarbonate and hydroxide is more in submerged soils resulting from the reduction of soils.

Boron and Molybdenum

Very little work has been done so far on the chemical equilibrium of boron and molybdenum in submerged soils. Since the solubility of the oxyanionic forms of these two elements is very much dependent on pH, organic matter content, clay content etc. Their availability in submerged soils is related to the changes in soil pH. Submerging an acid soil caused an increase in the amount of available Mo content during the initial period, which remained almost unchanged at the later period. This increase might be due to the increase in soil pH and desorption of MoO_4^{2-} from oxides and hydroxides of Fe and Mn. It has been reported that the concentration of B in soil solution remains more or less constant after submergence.

CONCLUSION

In this chapter, we utilized a number of example applications to expanding usefulness of chemical equilibrium in a variety of research activities that encompass plant mineral nutrition. Equilibria of nutrients allow us to explain observed plant response in terms of pertinent changes in the aqueous speciation of hydroponic or soil solutions.

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