MICRONUTRIENT TRANSFORMATIONS IN SUBMERGED SOILS

Dr. V. K. Venugopal
Former Professor & Head
Department of Soil Science and Agricultural Chemistry
College of Agriculture, Vellayani
Consultant, Digital University Kerala

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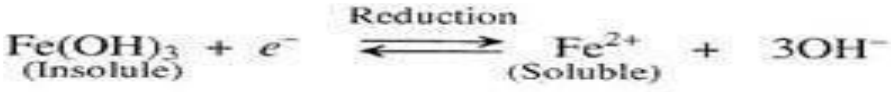
Iron under submergence

- Dominant chemical reaction is reduction of Ferric iron to soluble Ferrous
- .Intensity of reduction, depends on time of submergence, amount of OM, active iron, active Mn, nitrate etc.
- On reduction, colour of soil changes from brown to grey and large amounts of Fe2- enter the soil solution.
- (Fe2+) concentration increases initially to peak value and further decreases slowly with the period of soil submergence.
- Organic matter also enhances the rate of reduction of iron in submerged soils.

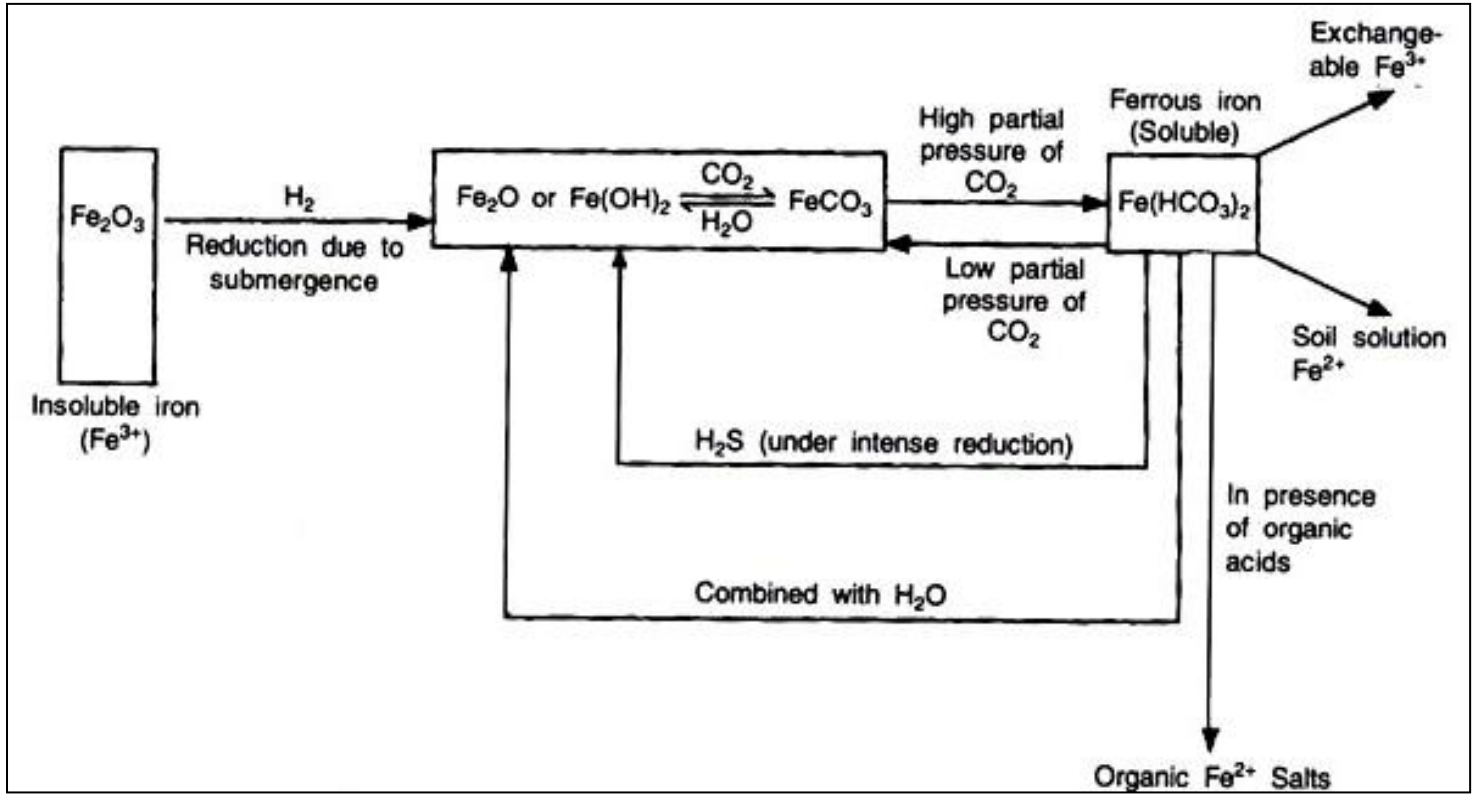


- In calcareous soils inrease in the concentration of Fe2+ following the peak rise is by the precipitation of Fe2+ as FeC03 in the early stages due to high partial pressure of CO2
- Fe3(OH)8 precipitation occurs due to decrease in the partial pressure of CO2(PCO2)

Consequences of Iron Reduction

- Water soluble iron increases, with increase in pH
- Cations are displaced from exchange sites
- Solubility of P and Si increases and new minerals are formed.

Transformations of Iron in submerged soil



Manganese in Submerged soil

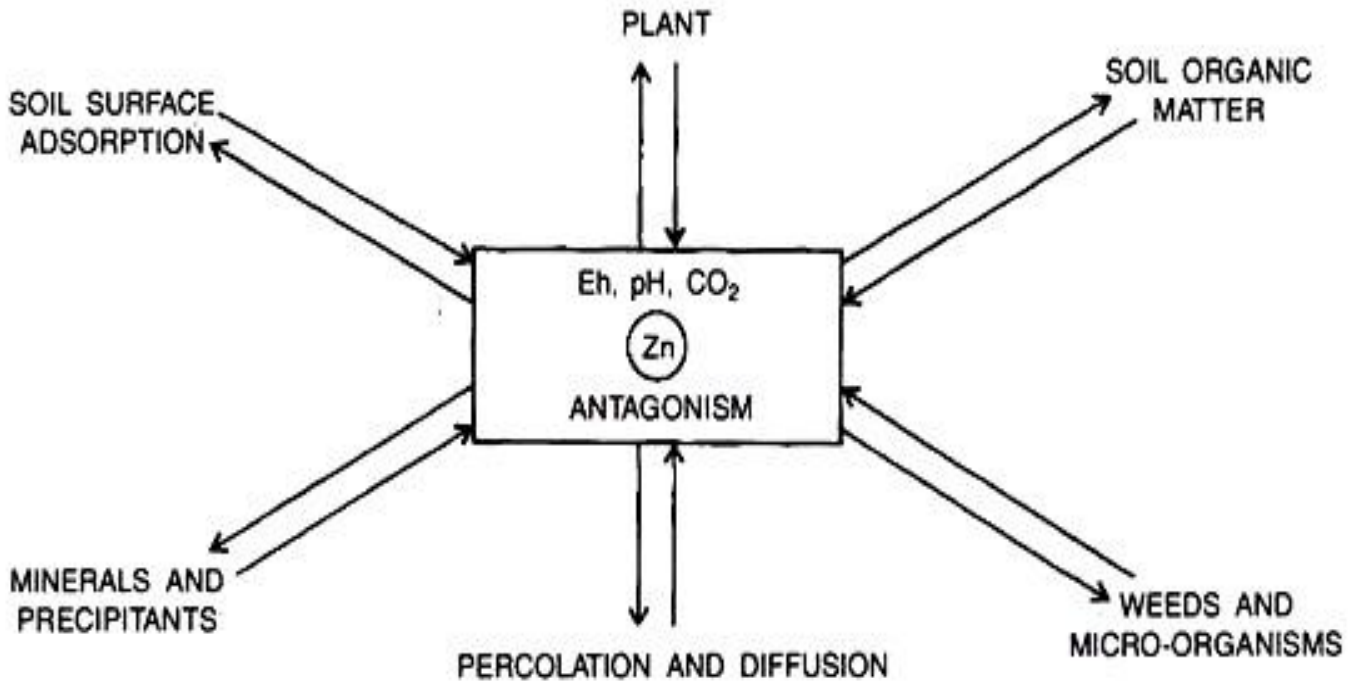
- Transformation of Mn4+ to Mn2+
- In submerged soil transformation of Mn results in increase in concentration of water soluble Mn2+ and later precipitation of Manganous carbonate (MnCO3).
- When the aerobic laterite soils are submerged, the reduction of Mn4+ occurs concurrently with nitrate reduction, but precedes Fe reduction.
- Water soluble (Mn2+) increases initially and decline with period of submerges.
- Reduction of Mn4+ occurs when redox potential is within range from +200 to +400 mV.

$$MnO_2 + 4H^+ + 2e^- \underset{}{\overset{\text{reduction}}{\rightleftharpoons}} \underset{\text{(Water soluble)}}{Mn^{2+}} + 2H_2O$$

Dynamic equllibrium of Zinc in submerged soil

- Rice plant receives Zn from
- soil solution,
- Exchangeable complex,
- Adsorbed solid phase including soil organic fractions.
- Zinc is stable in submerged soils.
- Higher pH and poorer the aeration, greater is the likelihood of Zn deficiency
- High manganese concentration antagonises Zn absorption and translocation.
- High Calcium and magnesium may also affect Zn uptake.

Dynamic equilibrium of Zinc in submerged soils



Transformations of Zinc under submergence

- Reduction of hydrous oxides of iron and manganese, formation of organic complexing agents, decrease availability of zinc
- Alkaline and calcareous soils on submergence the decrease in pH favour the solubility of Zn,
- Acid soil on submergence, the increase in pH of the soil decrease availability of Zn
- Formation of hydroxides, carbonates, sulphides lower the solubility of Zn
- Zinc deficiency in submerged rice soils is very common owing to the combined effect of increased pH, HCO_3^- and S_2^- formation due to reductive process
- Aerobic soil on submergence, the availability of native as well as applied Zn decreases, magnitude of such decrease vary with the soil properties. like clay and organic matter
- Transformation of Zn in soils was found to be greatly influenced by the depth of submerged and organic matter content
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i. Formation of insoluble franklinite ($ZnFe_2O_4$) compound in submerged soils.

$$Zn + 2Fe2+ + 4H2O \rightleftharpoons ZnFe2O4 \text{ (Francolite)}$$

ii. Formation of very insoluble compounds of Zn as ZnS under intense reducing conditions

$$Zn2+ S2- \rightleftharpoons ZnS \text{ (Sphalerite)}$$

(Very insoluble in water)

(ZnS, Sphalerite) in the presence of traces of hydrogen sulphide (H_2S) in submerged soils control the solubility of Zn.

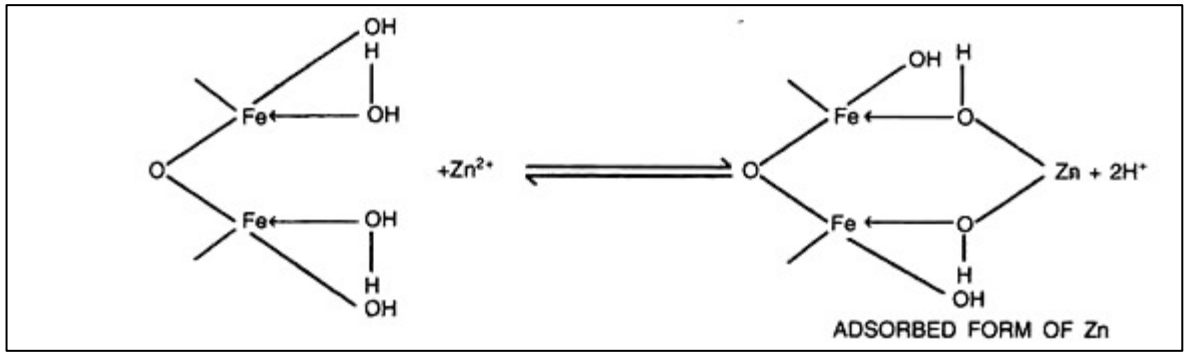
iii. Formation of insoluble compounds of Zn as $ZnCO_3$ at the later period of soil submergence is due to high partial pressure of CO_2(pCO_2) arising from the decomposition of organic matter

iv. Formation of $Zn(OH)_2$ at a relatively higher pH which decreases the availability of Zinc

$$Zn2+ + 2H2O- \rightleftharpoons Zn(OH)2$$

(Insoluble)

Adsorption of soluble Zn^{2+} by oxide minerals e.g. sesquioxides, carbonates,soil organic matter and clay minerals etc. decreases the availability of Zn the possible mechanism of Zn adsorption by oxide minerals is shown below: Mechanism 1



Zn^{2+} adsorption occurs as bridging between two neutral sites,Zn^{2+} could also be adsorbed to two positive sites or to a positive and neutral site.

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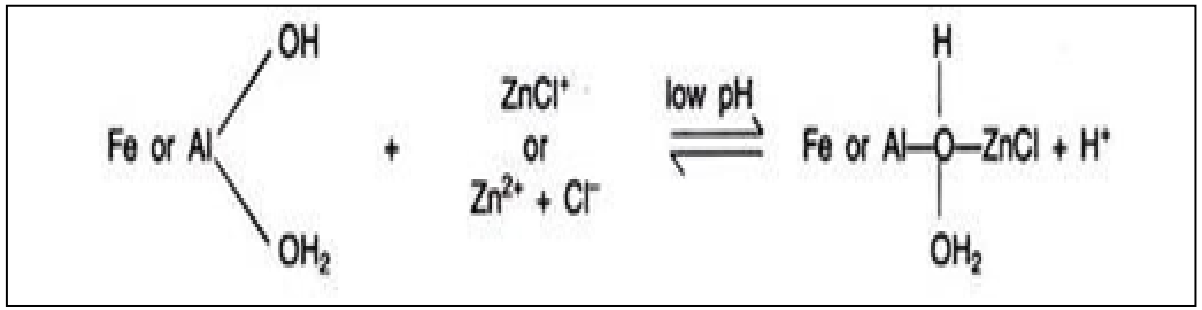
Mechanism ii

Occurs at low pH and results non-specific adsorption of Zn^{2+} which renders it unavailable to plants.



v. Formation of various Zn compounds with P fertilizers reduces availability of Zn

$$Zn^{2+} + PO_4^{3-} \longrightarrow \underset{\text{(Insoluble)}}{Zn_3(PO_4)_2}$$

Transformations of copper on submerged soils

Copper is very insoluble in soils

Can be extracted only with strong chemical extractants from minerals and organic matter

Concentration of copper is very low in soils

Divalent Cu, dominant species in soil solution at pH values below 6.9

Above pH of 6.9 mainly occurs as Cu (OH)2 while at pH 7 occurs as Cu (OH) +

Hydrolysis Reaction of Cu ions in soil

$$Cu^{2+} + H_2O \rightleftharpoons CuOH^+ + H^+$$

$$CuOH^+ + H_2O \rightleftharpoons Cu(OH)_2^0 + H^+$$

Copper pools in soil

Copper in soil solution, exchange complex

Adsorbed on clay minerals,organic matter, sesquioxides.

Residual copper

All forms of copper are in dynamic equilibrium

Factors affecting availability of copper

- Soil pH,
- Amount of organic matter,
- Clay content,
- Oxides of Fe and Mn etc.
- All these above forms of Cu are in Dynamic equilibrium in soils

Dynamics of copper under submergence

Copper comes into the soil solution and becomes available to the plant as follows:

$$\text{Soil Cu } 2+ + H \rightleftharpoons Cu2+$$

$$Cu(OH)2\ CO3 + 4H+ \rightleftharpoons Cu2+ + CO2 + 3H2O$$

Malachite, abundant source of Cu — Soluble

Dynamics of Copper under submergence

- In most soils, submergence decreases creates deficiency to plants.
- Acid soil on submergence, the release of copper decreases due to increase in soil pH,
- Alkali and calcareous soils, on submergence copper in soil solution increases to a lesser degree.
- Decrease in the amount of copper is due to the insoluble precipitation as CuS, $CuCO_3$ and $Cu(OH)_2$
- Submerged soil high in organic matter, available Cu decreases due to formation of complexes
- In some instances organic complexes increase the available copper on submergence due to reduction of coating of hydrous oxides of Fe^{3+} and Mn^{4+} on the copper compounds and production of soluble Cu-organic chelates
- Microbiological immobilization and antagonistic effect of high levels of iron, manganese decrease availability of copper
- High levels of phosphorus reduces availability of Copper as P mediates formation of complexes of copper with allophane and sesquioxides,

Transformations of Boron and Molybdenum

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

Reference

Ponnamperuma, F.N. (1972). The Chemistry of Submerged Soils, Reprinted from: Advances in Agronomy, Vol. 24, ©1972,Academic Press, Inc


Thank You