IV. Chemical

The main chemical changes brought about by flooding or water-logging an air-dry soil are the disappearance of oxygen; accumulation of carbon dioxide; the anaerobic decomposition of organic matter; transformations of nitrogen; and reduction of Fe(III), Mn(IV), and ${\rm SO_4}^{2-}$

A. Disappearance of oxygen

Oxygen trapped in the soil or present in the flood water is rapidly used up by soil organisms. In warm soils well supplied with organic matter oxygen disappears within a few hours of flooding or saturating the soil with water. The bulk of a flooded soil continues to be free of molecular oxygen because the small amount of oxygen that diffuses into the soil is used up chemically and biochemically at the soil surface (Sec. IA).

B. Accumulation of carbon dioxide

Up to 3 t carbon dioxide per ha may accumulate in the plowed layer of a flooded soil. Being soluble in water and chemically reactive it forms carbonic acid and bicarbonates and it reacts with divalent cations forming insoluble carbonates. The partial pressure of carbon dioxide ($P_{\rm CO2}$) is a good measure of carbon dioxide accumulation.

Fig. 7

The $P_{\rm CO_2}$ in a soil increases on flooding, reaches a peak of 0.2 to 0.5 bar 1 to 3 weeks later, and declines to a fairly stable value of 0.05 to 0.2 bar (Fig. 7). Acid soils high in organic matter but low in iron and manganese show a rapid increase in

 $P_{\rm CO_2}$ to about 0.5 bar within 1 to 2 weeks of flooding followed by a slow decline to about 0.3 bar. Neutral soils low in organic matter give $P_{\rm CO_2}$ values that are less than 0.2 bar (Ponnamperuma, 1977a).

An increase in $P_{\rm CO_2}$ depresses pH and increases the concentration of water-soluble iron, manganese, and calcium.

C. Anaerobic decomposition of organic matter

The decomposition of organic matter in flooded soils differs from that in a well-drained soil in speed, pathways, and end products.

Speed

The decomposition of organic matter in a flooded soil is slower than that in a well-drained soil. The accumulation of organic matter in marshes and peat in waterlogged depressions is proof of that.

The decomposition of organic matter in a well-drained soil is accomplished by actinomycetes, fungi, and a wide range of bacteria, assisted by the soil fauna. Because of the high energy release associated with their aerobic respiration, decomposition of substrate and synthesis of cell substance proceeds fast. Thus organic matter disappears rapidly in warm, moist soils. In flooded soils the decomposition is almost entirely the work of a narrow group of microorganisms — anaerobic bacteria. Because they are more sensitive to environmental conditions than aerobic microorganisms and because they function at the much lower energy level of fermentation, both decomposition and assimilation are slow.

Gambrell and Patrick (1978) reported that anaerobic conditions reduced the rate of decomposition of native organic matter in soil to half that under aerobic conditions and that of wheat straw to 13%. A long-term experiment at the International Rice Research Institute (IRRI) showed that growing two crops of wetland rice per year for 6 years on a soil previously used for dryland crops increased the organic matter content from 2.59% to 3.22% in the dryfallowed plots and to 3.50 in the flood-fallowed (i.e. continuously flooded) plots (IRRI, unpublished).

A high C:N ratio of substrate, soil acidity, and low temperature retard organic matter decomposition. Although natural organic substances decompose slowly in anaerobic soils, reducing conditions accelerate the degradation of insecticides, herbicides, and fungicides (Sethunathan and Siddaramappa, 1978).

2. Pathways

Decomposition of organic matter in soils is a process in which microorganisms use the substrate to derive energy and carbon for cell synthesis. It is accomplished by respiration.

Aerobic and anaerobic respiration follow a common pathway until the formation of pyruvic acid, the key intermediate substance in the metabolism of carbohydrates by bacteria (Doelle, 1975). In aerobic respiration pyruvic acid is oxidized to carbon dioxide through the TCA cycle with oxygen as terminal electron acceptor. In the absence of oxygen, facultative and obligate anaerobes use NO_3 , Mn(IV), Fe(III), SO_4^{2-} , dissimilation products of carbohydrates and proteins, CO_2 , N_2 , and even H^+ ions as electron

acceptors in their respiration. If the electron acceptor is inorganic the process is called anaerobic respiration; if they are organic substances, fermentation (Doelle, 1975). Fermentation produces an array of reaction products, most of which have been identified in anaerobic soils (Ponnamperuma, 1972; Yoshida, 1978; Tsutsuki, 1983; Watanabe, 1983).

The breakdown of proteins aerobically and anaerobically follows common pathways until amino acids are formed. In aerobic oxidation, aerobic and facultative aerobic bacteria oxidize amino acids using them as their sole source of carbon, nitrogen, and energy (Doelle, 1975) liberating ammonia and producing carbon dioxide or carbon moieties that can be oxidized through the TCA cycle. In fermentation, amino acids are converted to ammonia, organic acids (including pyruvic acid), carbon dioxide, methane, amines, and hydrogen sulfide.

The main pathways of pesticide degradation in flooded soils are reductive dechlorination, dehydrochlorination, hydrolysis, and reduction (Sethunathan and Siddaramappa, 1978).

3. The end products

The stable end products in the decomposition of organic matter in well-drained soils are carbon dioxide and humic materials. The carbon dioxide escapes into the atmosphere. The humic materials remain in the soil, bound to clay and hydrous oxides of aluminum and iron. The nitrogen which is released as ammonia is converted to nitrate and sulfur compounds are oxidized to sulfate.

The major end products of the anaerobic decomposition of organic matter in soils are carbon dioxide, methane, and humic materials. Ammonium is the stable form of nitrogen and sulfide that of sulfur. But the anaerobic metabolism of bacteria produces an array of substances — many of them transitory — not found in well-aerated soils. Some of them gleaned from various sources (IRRI, 1966; Ponnamperuma, 1972; Yoshida, 1978; Neue and Scharpenseel, 1983; Tsutsuki, 1983; Watanabe, 1983) are listed below.

- a. Gases. Ammonia, carbon monoxide, hydrogen, hydrogen sulfide, methylamine, nitrogen, nitric oxide, nitrogen dioxide, nitrous oxide, phosphine, and sulfur dioxide.
- b. Hydrocarbons. Butane, butadiene, ethane, ethylene, methane, propane, propadiene, and propylene.
- c. Alcohols. n-Butanol, 2-butanol, 2,3-butane-diol, ethanol, methanol, n-propanol, and 2-propanol.
- d. Carbonyls. Acetaldehyde, acetone, butyraldehyde, formaldehyde, methyl ethyl ketone, propionaldehyde, and n-valeraldehyde.
- e. Volatile fatty acids. Acetic, butyric, formic, isovaleric, propionic, and valeric.
- f. Nonvolatile acids. Capric, fumaric, lactic, malonic, and oxaloacetic.
- g. Phenolic acids. p-Coumaric, ferulic, p-hydroxy benzoic, sinapic, and vanillic.

h. Volatile sulfur compounds. Carbon disulfide, carbonyl sulfide, ethyl mercaptan, methyl mercaptan, and methyl disulfide.

Humus of soils that are alternately flooded and drained, as in rice cultivation, differs from that of dryland soils in the following respects (Kuwatsuka et al., 1978; Tsutsuki and Kuwatsuka, 1978; Tsutsuki and Kumada, 1980): the humification degree is less, the content of hydrogen and nitrogen is higher and degree of unsaturation lower, the content of carboxyl and phenolic groups is lower whereas that of alcoholic and methoxyl groups is higher, and the molecular weight is higher.

D. Transformations of nitrogen

The main nitrogen transformations in flooded soils are mineralization, nitrification/denitrification, immobilization, volatilization, and biological fixation.

1. Mineralization

The conversion of organic nitrogen to inorganic forms in flooded soils stops at the ammonium stage because of the lack of oxygen to carry the process through to nitrate. So ammonium accumulates in flooded soils. Ammonium is derived from anaerobic deamination of amino acids, degradation of purines, and hydrolysis of urea. Less than 1% comes from nitrate reduction. Although aerobic deamination may be more rapid than the anaerobic process, inorganic nitrogen is released in larger quantities and faster in

anaerobic soils than in aerobic soils because less immobilization of nitrogen occurs in anaerobic soils (Broadbent and Reyes, 1971).

Soils vary widely in their capacity to produce ammonium (Fig. 8). Soils rich in organic matter rapidly release ammonium and attain concentrations exceeding 300 mg/kg in the soil within 2 weeks after submergence (at 25-35°C). Soils low in organic matter may release as little as 40 mg/kg even after several weeks of submergence. The soil solution may contain from 5 mg/L of ammonium for clay soils to over 100 mg/L for sandy soils high in organic matter.

Water management and temperature markedly influence the rate and amount of ammonium released when a soil is kept flooded. A dry soil that is flooded releases more ammonium than a wet soil (Dei and Yamasaki, 1979). Intermittent drying and flooding increases ammonium production (Reddy and Patrick, 1975). The Q₁₀ for mineralization of soil nitrogen was 2.0 in the range 5 to 35°C (Stanford et al., 1973). Dei and Yamasaki (1979) found that the amount of ammonium released in flooded soils can be described by the equation

$$Y = k \{ (T-15)D \}^n$$
 (17)

where Y is the amount of nitrogen mineralized, T is the daily soil temperature, D is the number of days, (T-15) is the effective temperature, k is a coefficient, and n is a constant related to the mineralization pattern.

Fig. 8

2. Nitrification/denitrification

Ammonium fertilizers broadcast on the surface, ammonium formed by mineralization of nitrogen in the surface oxidized layer, and ammonium diffusing to that zone from the reduced soil are nitrified. The nitrate formed moves by mass flow and diffusion into the reduced zone where it is highly unstable (Ponnamperuma, 1972). Here it is denitrified (converted to nitrous oxide or nitrogen) and lost from the system.

Air-dry soils may contain as much as 350 mg/kg of nitrate nitrogen. Within a few days of submergence most of this nitrogen is lost by denitrification. A high organic matter content favors denitrification. Low temperature retards it (Fig. 9). Alternate wetting and drying favor the formation and subsequent destruction of nitrate (Reddy and Patrick, 1975).

Nitrite, which is an intermediate product of both aerobic nitrification and anaerobic denitrification, is unstable in both aerobic and anaerobic media. Nitrite may be an important intermediate in denitrification in soils that are alternately flooded and dried (Ponnamperuma, 1972).

3. Immobilization

Nitrogen can be fixed in soils chemically and biologically and rendered temporarily unavailable to plants. The high concentration of ammonium ions present in flooded soils should favor both processes.

Fig. 9

a. Chemical fixation

Ammonium may be fixed in the clay lattice, specifically adsorbed on soil colloids, or participate in humus synthesis.

Grewal and Kanwar (1973) reported that the ammonium fixing capacity of 23 wet soils treated with 100 mg N/kg was 8.0 to 30.5%.

The following factors favor ammonium fixation: a high content of 2:1 type clays, a high concentration of ammonium, alternate wetting and drying, and a high soil pH.

Pasricha (1976) suggested that ammonium was held at specific adsorption sites in two reduced clays.

Ammonium and amino acids condense with phenolic substances in soils to form humus (Stevenson, 1979).

b. Biological immobilization

The amount of inorganic nitrogen immobilized biologically in a soil represents a balance between mineralization of organic nitrogen compounds and the synthesis of microbial tissue. The balance between the two processes is determined by water regime, duration of submergence, C:N ratio of the organic matter, and temperature.

Because microbial activity is less intense in anaerobic soils than in aerobic soils (Sec. IVc) the nitrogen requirement of the microflora is lower, and less nitrogen is immobilized in flooded soils. As active proliferation of anaerobic bacteria induced by flooding slows down, the demand for nitrogen decreases. Although the nitrogen requirements for

decomposition of organic matter is much less anaerobically than aerobically, materials with wide C:N ratios such as straw can temporarily immobilize nitrogen, whereas leguminous green manures release the greater part of the nitrogen in 2 to 3 weeks (Ponnamperuma, 1972). Nitrogen immobilization rates are independent of temperature in the range 10-40°C (Kai and Wada, 1979).

4. Volatilization

In recent years the role of the standing water in the loss of nitrogen as ammonia from flooded soils has received increasing attention (Mikkelsen et al., 1978; De Datta, 1981; Savant and De Datta, 1983). Field studies suggest that up to 20% of nitrogen in urea or ammonium sulfate broadcast on flooded rice fields may be lost in a season as ammonia gas.

A high concentration of ammonium in the flood water, high soil pH, high photosynthetic activity by algae and submerged plants, and high temperature favor ammonia volatilization.

Loss of ammonia is not limited to fertilized fields, for ammonium is continuously formed in the flood water by organic matter decomposition and is transferred by diffusion to the flood water from the anaerobic soil. Figure 10 shows the effect of pH on nitrogen loss.

Fig. 10

5. Biological nitrogen fixation

Flooding increases a soil's capacity to fix nitrogen bio-logically.

Biological nitrogen fixation involves the reduction of dinitrogen to ammonium. Photosynthesis and anaerobic respiration
provide the powerful reductants needed for the process
(Ponnamperuma, 1972). A flooded soil is an ideal medium for
nitrogen fixation because blue-green algae living free or in association with azolla thrive in the flood water and soil surface while
aerobic nitrogen fixers function at the aerobic/anaerobic interfaces and anaerobic bacteria flourish in the reduced layer sustained
by intermediate products of the anaerobic decomposition of organic
matter.

A pH above 7 and the presence of available phosphate, iron, and adequate amounts of carbon dioxide in the flood water favor the growth of blue-green algae (Roger and Reynaud, 1979). Blue-green algae (Cyanobacteria) fix about 0.5 kg N/ha/day (Stewart et al., 1979).

The heterotrophic nitrogen fixers Azotobacter and Clostridium contribute to nitrogen fixation in flooded soils (Watanabe, 1978). Their activity is favored by anaerobic conditions, the presence of decomposable organic matter, and rice plants. They may account for as much as 60% of the nitrogen fixing activity of wetland rice soils (Matsuguchi, 1979).

Azolla, a water fern, with a blue-green alga (Anabaena azollae) living in symbiosis, can fix up to 400 kg N/ha/year under field conditions (Becking, 1979). A good supply of phosphorus, calcium, iron, and molybdenum favors nitrogen fixation by azolla.

Apparently because of autotrophic and heterotrophic nitrogen fixation, the nitrogen content of a continuously flooded soil increased from 0.153 to 0.189% in 6 years (IRRI, unpublished).

E. Reduction of manganese, iron, and sulfate

When the oxygen and nitrate present in a flooded soil are consumed, anaerobic bacteria use oxidized soil components such as hydrous oxides of Mn(IV) and Fe(III) and ${\rm SO_4}^{2-}$ as electron acceptors in their respiration, converting them to their reduced counterparts Mn(II), Fe(II), and S²⁻.

1. Manganese

Within 1 to 3 weeks of flooding almost all the active (EDTA-dithionite-extractable) manganese present in a soil is reduced to Mn(II) compounds which are more soluble in water than those of Mn(IV). The reduction is both chemical and biochemical and precedes that of iron (Yoshida, 1978).

Acid soils high in manganese and organic matter build up water-soluble Mn²⁺ concentrations as high as 90 mg/L, at 25 to 35°C, in 1 to 2 weeks of flooding (Fig. 11). Alkaline soils and soils low in manganese rarely contain more than 10 mg/L of water-soluble manganese at any stage of submergence.

The decrease in concentration of water-soluble manganese is due to its precipitations as manganous carbonate. The activity of ${\rm Mn}^{2+}$ after the peak is given by

$$pH + 1/2 \log Mn^{2+} + 1/2 \log P_{CO_2} = 4.4$$
 (18)

Fig. 11

2. Iron

The most conspicuous chemical change that takes place when a soil is flooded is the reduction of Fe(III) to Fe(II). The brown color of iron-rich soils changes to shades of gray, green, or blue, and large amounts of iron are brought into solution. The reduction of iron is a consequence of anaerobic metabolism and appears to be a chemical reduction by bacterial metabolites, although direct reduction coupled with respiration may also be involved (Yoshida, 1978). Five to fifty percent of active Fe(III) present in a soil may be reduced within a few weeks of submergence depending on temperature, organic matter content, nitrate concentration, and crystallinity of the oxides. The reduced iron acts as a sink for oxygen diffusing into the soil and is a source of Fe^{2+} ions. solid phase of reduced iron includes green hydrated magnetite $(Fe_3O_4.nH_2O)$, black hydrotroilite $(FeS.nH_2O)$, white siderite (FeCO₃) and blue vivianite (Fe $_3$ PO $_4.8H_2$ O)

The kinetics of water-soluble iron depend on soil properties and temperature. Acid soils high in organic matter and iron build up concentrations as high as 600 mg/L in 1 to 3 weeks after flooding and show a roughly exponential decrease to levels of 50-100 mg/L which persists for several months (Fig. 12). Low temperature retards the peak and broadens the area under it (Ponnamperuma, 1976). Soils high in organic matter but low in iron give high concentrations that persist for several months. In neutral and calcareous soils the concentration of water-soluble iron may be less than 1 mg/L.

The activity of water-soluble Fe^{2+} in reduced soils is given by

$$pH + 1/2 \log Fe^{2+} = K$$
 (19)

K varies from the theoretical value of 5.4 to 4.8 (Ponnamperuma, 1977a).

3. Sulfate

The reduction of sulfate is accomplished by a small group of obligate anaerobic bacteria of the genus <u>Desulfovibrio</u>. These bacteria use a variety of fermentation products and molecular hydrogen to reduce SO_4^{2-} . Strong acidity, nitrate, and low temperature retard sulfate reduction.

The kinetics of water-soluble sulfate depend on soil properties. In acid soils the concentration of water-soluble sulfate increases, reaches a peak, and then decreases. The initial increase is due to desorption of sulfate adsorbed on hydrous oxides following the increase in pH (Sec. IIE). The subsequent decrease is due to reduction. A nearly neutral pH, the presence of organic matter and a temperature of 25 to 45°C favor sulfate reduction (Ponnamperuma, 1972; 1981).

The hydrogen sulfide formed by sulfate reduction dissociates as follows:

$$H_2S = H^+ + HS^-$$
 (20)

$$HS^{-} = H^{+} + S^{2-}$$
 (21)

At the pH values of flooded soils the bulk of the water-soluble hydrogen sulfide is present as $\rm H_2S$ and $\rm HS^-$ but the activity of $\rm S^{2-}$ is sufficient to precipitate $\rm Fe^{2+}$ and $\rm Zn^{2+}$ as insoluble sulfides (Ayotade, 1977). That keeps the concentration of $\rm H_2S$ in the soil solution below 0.1 mg/L, the toxic limit for rice.

V. Fertility

Soil fertility is the status of a soil with respect to its ability to provide plants with nutrients in the amount, rate, and balance needed for optimum growth. Fertility depends on the presence of water, oxygen and adequate nutrients in forms the plant can absorb, the soil's ability to deliver oxygen and nutrients by mass flow and diffusion to the root surface, the presence of a favorable ionic composition, and the absence of substances that interfere with the movement of nutrients in balanced amounts into the root. The physical, chemical, electrochemical, and biological changes brought about by flooding markedly influence soil fertility.

A. Physical

The restriction of oxygen entry into the soil, swelling of soil colloids, and destruction of structure, drastically cut down respiration and nutrient absorption in plants not possessing a mechanism for the internal transfer of oxygen to the roots. For most crop plants, except rice, root growth is reduced when the oxygen diffusion rate falls below 0.2 mg/cm/min (Meek and Stolzy, 1978). Puddling and compaction by traffic on a flooded soil aggravate the adverse effects. Lowering of soil temperature by

flooding may retard germination, seedling growth, and nutrient absorption even after a flooded soil is drained. In soils of high permeability, flooding increases the loss of nutrients by leaching.

B. Electrochemical

A decrease in redox potential below 0.2V: destroys nitrate; favors the accumulation of ammonium and nitrogen fixation; increases the availability of phosphorus, silicon, iron, and manganese; decreases the availability of sulfur, zinc, and copper; and generates substances that interfere with nutrient uptake.

The decrease in redox potential benefits marsh plants such as rice because it prevents iron deficiency in neutral and alkaline soils and increases the availability of nutrients on most soils.

The increase in pH of acid soils, the decrease in pH of alkaline soils, and pH stabilization at 7 should markedly influence soil fertility through effects on nutrient absorption, the concentration of nutrients or toxins, and microbial processes that release or destroy plant nutrients or that generate toxins.

A pH of 6.5-7.0 in the soil solution favors nutrient absorption, increases the availability of phosphorus, and favors the mineralization of organic matter, regardless of the soil's pH before flooding. Benefits related to initial pH include: elimination of aluminum and manganese toxicities and alleviation of the toxicities of iron, organic acids, and carbon dioxide in acid soils; and increasing the availability of iron, manganese, zinc, and calcium in alkaline soils (Ponnamperuma, 1978).

Flooding decreases the specific conductance of saline soils and increases that of nonsaline soils. A specific conductance exceeding 4 dS/m hinders nutrient and water uptake and injures plants (Maas and Hoffman, 1977).

The increase in ionic strength caused by flooding decreases the activity coefficients of ions in the soil solution. That affects chemical and electrochemical equilibria that regulate the concentration of nutrient ions.

The high concentration of cations and bicarbonate ions produced by soil metabolism displace ions from soil colloids. Thus the concentration of potassium, calcium, magnesium, and phosphorus in the soil solution increases, and that benefits plants. One disadvantage is that these ions may be removed from the root zone by percolating water. Flooding causes impoverishment of sandy soils. The increase in concentration of water-soluble phosphate and silica caused by flooding is due partly to desorption (Ponnamperuma, 1972).

C. Chemical

The beneficial chemical effects of flooding on soil fertility are the influx of dissolved and suspended nutrients, the accumulation of nitrogen, the increase in solubility of phosphorus and silicon, and the increase in concentration of potassium in the soil solution (Ponnamperuma, 1977a). The disadvantages are the depletion of oxygen, the accumulation of carbon dioxide, and the destruction of nitrate. In acid soils high in organic matter, volatile fatty acids and excess water-soluble iron may persist for several weeks after submergence. The effects of the products

of the anaerobic decomposition of organic matter on plant growth are summarized in Table II. Flooding increases the availability of molybdenum but decreases that of zinc and copper (Table III).

Tables II & III

Prolonged flooding is lethal to non-hydrophytes but usually highly beneficial to marsh plants such as rice.

VI. Soil Formation

The water regime is an important soil forming factor. Thus its effects are used as differentiating characteristics at the suborder level (Soil Survey Staff, 1975).

A. Aquic suborders

The transformation of weathered rock material into soil is brought about by the accretion of organic matter, leaching of soluble salts, transformation and translocation of organic and inorganic substances, and the synthesis of secondary minerals. The balance among these processes determines the character of the soil that develops. Aquic soils owe some distinguishing character to flooding or waterlogging. They are the suborders, Aqualfs, Aquents, Aquepts, Aquods, Aquols, Aquox, and Aquults. These soils are usually found in flat or concave land-scapes and have one feature in common — soil reduction due to temporary exclusion of oxygen by water.

During the period of waterlogging or flooding the soil is reduced (Sec. III). When the water table recedes and oxygen reenters the soil, the changes caused by flooding are reversed.

Aquic soils have three main horizons: a partially oxidized A horizon in which organic matter accumulates, a zone where oxidizing and reducing conditions alternate, and a zone of permanent reduction. Because the soil is intermittently saturated with water, oxidation of organic matter is slow and it accumulates in the A horizon. In the second horizon iron and manganese are alternately reduced and oxidized. During oxidation iron and manganese oxides are deposited as rusty mottles, streaks, or concretions. The zone of permanent waterlogging is bluish green because ferrous compounds are present.

B. Paddy soils

Paddy soils are soils that are managed in a special way for the wet cultivation of rice. The management practices include levelling the land, construction of levees to impound water, puddling (plowing and harrowing the wet soil), maintenance of 5 to 10 cm of standing water during the 4 to 5 months the crop is on the land, draining and drying the fields at harvest, and reflooding after an interval which varies from a few days to several months. These operations and oxygen secretion by rice roots lead to the development of certain features peculiar to paddy soils (Ponnamperuma, 1972).

During the period of submergence iron and manganese are reduced and the soil turns dark gray. When the soil is drained at harvest, the entire profile above the water table is reoxidized giving it a highly mottled appearance, with vertical streaks corresponding to root channels. Reduced iron and manganese move

out of the root zone in percolating waters and are deposited below the plow sole. Cations displaced from soil colloids by ${\rm Fe}^{2+}$ and ${\rm Mn}^{2+}$ migrate out of the root zone and are lost by "ferrolysis" (Brinkman, 1979).

C. Acid sulfate soils

Acid sulfate soils are extremely acid soils (pH is <3.5) derived from sediments high in sulfidic materials and low in bases.

The first phase of their formation — the build-up of pyrites—
proceeds in tidal swamps. The main steps in pyrite formation are
the reduction of sulfate to hydrogen sulfide by <u>Desulfovibrio</u>
species, precipitation of iron monosulfide, oxidation of hydrogen
sulfide to sulfur chemically and biochemically, and formation of
pyrite thus

$$SO_4^{2-} + 10 \text{ H}^+ + 8 \text{ e} = H_2S + H_2O$$
 (22)

$$H_2S = H^+ + HS^-$$
 (23)

$$HS^- = H^+ + S^{2-}$$
 (24)

$$Fe^{2+} + S^{2-} = FeS$$
 (25)

$$H_2S + 1/2 O_2 = S + H_2O$$
 (26)

$$FeS + S = FeS_2$$
 (27)

While submerged the reduced sediment is nearly neutral in reaction and supports salt-tolerant plants. But when drained oxygen enters the soil and oxidizes the pyrite and sulfur present

Pons, 1978) rendering the soil extremely acid and producing jarosite, a yellow mineral characteristic of acid sulfate soils. Submergence reverses most of the changes.

D. Sodic soils

Sodic soils contain sufficient exchangeable sodium to interfere with plant growth. Their pH is usually above 8.5 and the sodium adsorption ratio of the saturation extract is 15 or more. The alkalinity is due to the presence of sodium carbonate and bicarbonate. These soils are found in arid areas in depressions with a water table near the surface. They undergo temporary flooding.

Sodium carbonate is of chemical and biological origin. The biological process is due to reduction of sulfate and loss of hydrogen sulfide by volatilization

$$Na_2SO_4 + 8 H^+ + 8 e = Na_2S + 4 H_2O$$
 (28)

$$Na_2S + 2 H_2O + 2 CO_2 = 2 NaHCO_3 + H_2S$$
 (29)

$$2 \text{ NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$$
 (30)

E. Saline soils

Saline soils contain sufficient salts in the root zone to interfere with plant growth. Two common causes of salinity are intrusion of surface or underground saline waters and concentration of salt in the surface soil by the evaporation of groundwater rich in salts. Thus irrigation in arid areas without drainage

leads to the build up of salinity and alkalinity. The problem is aggravated if the irrigation water itself is saline (Shalhevet and Kamburov, 1976).

F. Peat soils

Continuous waterlogging or flooding provide conditions conducive to peat formation. Marsh vegetation that thrives uninterrupted because of the availability of water generates organic matter the bulk of which accumulates because of the slow decomposition of organic matter under anaerobic conditions (Sec. IVc). As one generation of plants follows another, layer after layer of organic residues is deposited. Accompanying this process is a succession of vegetation climaxing in forest trees (Brady, 1974). Swamp forests cover 32 million ha in the rain forest belts of the tropics. Those of Southeast Asia are 4 to 5 thousand years old (Driessen, 1978).

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