Chapter 2

Effects of Aeration on Reactivity and Mobility of Soil Constituents[1]

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Aeration status of a soil primarily refers to the O_2 concentration in the soil atmosphere. The principal gases of the soil atmosphere and some typical values for an aerated soil are N_2 (79.2%), O_2 (20.6%), and CO_2 (0.25%). The percentages for atmospheric air are N_2 (79.0%), O_2 (20.97%), and CO_2 (0.03%). The composition of the soil atmosphere is determined by the physical, chemical, and biological conditions of the soil and the plant-root density. For example, incorporation of organic residues into soil can deplete soil O_2 and increase CO_2 concentration. Flooding a soil can displace soil air, and increase the concentrations of CO_2 and CH_4 as a result of anaerobic organic matter decomposition.

Adequate soil O_2 is essential for normal root growth for most plants, for growth of most microorganisms, and to activate several essential biochemical reactions in the soil. The optimum soil O_2 requirements for plant-root development greatly varies with species and age of the plant (Kramer, 1965, 1969). The optimum soil O_2 requirements of microorganisms vary with the type of biochemical reactions functioning in the soil system. A few reviews have appeared in the literature on soil aeration and its effects on plant growth (Grable, 1966; Stolzy, 1974; Meek and Stolzy, 1978). These reviews, however, were limited to plant growth and development and provide very little or no information on the effects of soil aeration on the reactivity of the soil processes associated with the move-

ment of nutrients. The purpose of this paper is to examine the effects of soil aeration (primarily O_2) on the reactivity and mobility of nutrients in well-aerated, moderately aerated, poorly aerated, and flooded soils.

SOIL OXYGEN

Oxygen status of a soil is controlled by the gaseous interchange between the atmosphere above the soil surface and the soil atmosphere. The atmosphere above the soil has an abundant supply of O_2, and this O_2 is continuously supplied to the soil through diffusion, although changes in soil temperature, volume of pore space, barometric pressure, and wind speed can also result in minor contributions through mass flow (Russell, 1952).

Diffusion is the random thermal motion of molecules of a gas or of a liquid. Molecular sizes and weights are different for various gases, which will enable them to diffuse at different rates. Net movement of gases by diffusion is also a function of the concentration or partial pressure gradient, the cross sectional area available for the diffusion, the properties of the material through which the gases are diffusing, and the time. Soil O_2 content is generally lower than the atmospheric O_2, and the net diffusion of O_2 will be from atmosphere to the soil. Soil CO_2 concentration is generally higher than atmospheric CO_2, hence the net diffusion of CO_2 will be from soil to the atmosphere.

Rate of O_2 diffusion in an unflooded soil is dependent on the effective air-filled porosity (Kohnke, 1968). For every soil there appears to be an optimum effective air-filled porosity. Flocker et al. (1959) observed an air-filled porosity of 10% to be critical and below this value O_2 diffusion into soil was negligible. Their study also showed that optimum growth of plants occurred with air-filled porosities between 20 and 35%. Grable and Siemer (1968) found that O_2 diffusion decreased to zero at or near air-filled porosities of 10 to 20% in the soil they studied.

Air-filled porosity of a soil changes with volumetric water content and soil-water suction. In a field study, Patrick et al. (1973) have shown the volume distribution of soil solids, air space, and water in several soils of Louisiana. Bruin (coarse-silty, mixed, thermic Fluvaquentic Eutrochrept), Dundee (fine-silty, mixed, thermic Aeric Ochraqualf), and Tensas (fine, montmorillonitic, thermic Vertic Ochraqualf) soils had air-filled porosities generally >10%. Mhoon (fine-silty, mixed, nonacid, thermic Typic Fluvaquent) and Tunica (clayey over loamy, montmorillonitic, nonacid, thermic Vertic Haplaquept) soils had air-filled porosities of <10%, a value at which normal exchange of gases do not occur (Fig. 1). The effective pore space for air movement within a given soil is inversely related to soil water content. As the soil-water content approaches saturated condition, air-filled porosity of the soil will approach zero, resulting in interruption of the normal processes of gaseous exchange between soil and air. At this point, O_2 diffusion into a saturated or a flooded soil will depend on consumption at the soil surface and depth of the overlying water. Oxygen diffusion in these systems was found to be about 10 000 times slower than diffusion in gas-filled pores (Greenwood, 1961).

Incorporation of organic wastes (crop residues, animal and municipal wastes) can increase soil O_2 demand, thus resulting in decreased O_2 concentration (Meek and Grass, 1975). In most well aerated soils, O_2 consumption rates are usually lower than the potential O_2 diffusion rate from the atmosphere. As a result, the soil is maintained under aerobic (oxidized) conditions. In poorly aerated soils, O_2 diffusion cannot keep up with demand, resulting in slower renewal of O_2 as compared to consumption. This results in the formation of anoxic microsites in the soil. In flooded soils, O_2 diffusion is extremely slow, and the slow O_2 supply rate as compared to demand in the soil, results in depletion of soil O_2 in less than 36 h (Turner and Patrick, 1968), thus creating anaerobic conditions.
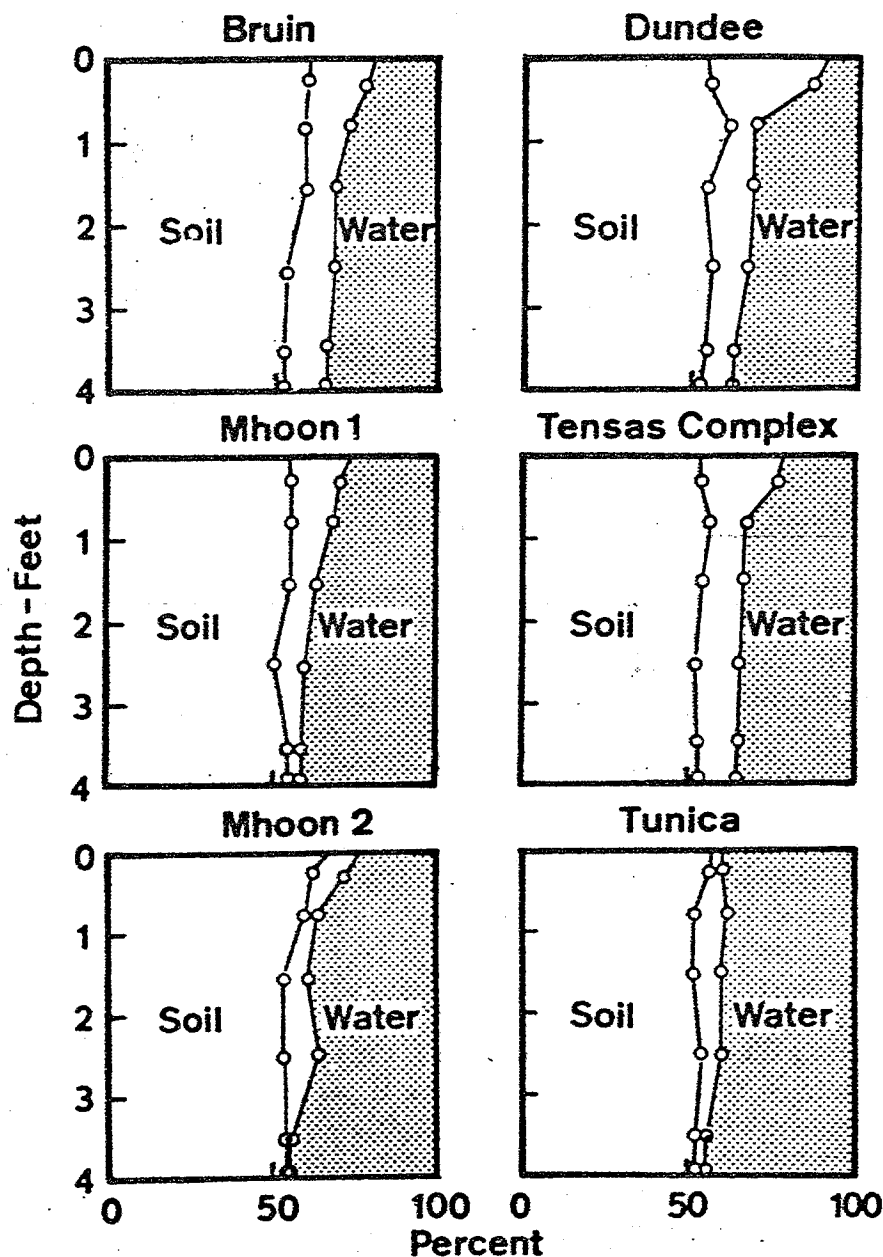

Fig. 1. Volume distribution of soil solids, air space, and water at beginning of 1970 growing season for Bruin, Mhoon 1, and Mhoon 2 soils at the Northeast Louisiana Exp. Stn. and Dundee, Tensas Complex and Tunica soils at Highland Plantation (Patrick et al., 1973).

The greater potential O_2 consumption by the flooded soil, compared to the slow supply rate through the floodwater results in the development of two distinctly different soil layers: 1) an oxidized or aerobic surface soil layer where O_2 is present; and 2) an underlying anaerobic or reduced soil layer, where no free O_2 is present (Pearsall, 1938; Mortimer, 1941; Alberda, 1953).

The thickness of the oxidized soil layer is controlled by the O_2 concentration in the overlying water and O_2 consumption by the underlying sediment. Howeler and Bouldin (1971) using swamp sediment (6.2% organic matter), measured an oxidized layer thickness of 0.48 mm at an O_2 concentration of 4%, compared to 2.4 mm at an O_2 concentration of 21% (Fig. 2a). By varying the sediment organic matter content (adding varying amounts of C source), Engler and Patrick (1974) showed an inverse relationship between the oxidized layer and sediment organic matter content (Fig. 2b). The role of oxidized and reduced layers on reactivity and mobility of nutrients in flooded soils is discussed in the latter part of this paper.

Oxygen consumption in well-aerated, poorly aerated, and flooded soils depends on source of O_2-demanding components (energy source), temperature, and soil texture (Meek and Stolzy, 1978). Incorporation of organic wastes (crop residues, animal manures, municipal, and industrial wastes) into soil increases microbial activity, thus exerting greater demand on soil O_2. During aerobic microbial respiration, O_2 is used as an electron acceptor and organic C is used as an energy source. Oxygen is also consumed during the nitrification process where nitrifying organisms use O_2 and derive energy from the oxidation of NH_4^+ and NO_2^-. These reactions, therefore, can potentially use large quantities of O_2 and nitrification can at times deplete O_2 in soils receiving large amounts of nitrogenous wastes, although other microbial processes compete favorably for O_2 under such conditions. In flooded soils, O_2 reaching the soil surface is consumed by (i) heterotrophic microbial respiration in the aerobic layer; (ii) biological autotrophic oxidation of NH_4^+ in the aerobic layer; and (iii) chemical oxidation of reduced Fe^{+2}, and Mn^{+2}, and sulfides. Several mathematical models for describing O_2 diffusion and consumption in flooded soils were presented by Bouldin (1968). Models which include the consumption of O_2 during microbial respiration in the aerobic zone and oxidation of mobile and nonmobile reductants such as Fe^{+2} (Howeler and Bouldin, 1971) were found to be best suited for describing O_2 consumption in flooded soils. In a recent study (Reddy et al., 1980b), O_2 consumption by 37 anaerobic soils was also found to be a two phase process. The rate of O_2 consumption during Phase I was approximately the same for all soils ($k_I = 0.15$ h^{-1}), where O_2 consumption during Phase II ranged from 0.003 to 0.054 h^{-1}. The first phase represented chemical oxidation of Fe^{+2}, while the second phase represented chemical and biological oxidation. Soil temperature affects O_2 status directly by its effect on movement and indirectly by its effect on plants and microbial activity. Several researchers (Drobnik, 1962; Moureux, 1967; Pal et al., 1975) calculated Q_{10} values in the range of 1.5 to 2.0 for a temperature range of 5 to 37°C during aerobic decomposition of organic matter. Luxmoore and Stolzy (1972)

calculated Q_{10} values of 1.5 to 1.8 for a 5 to 25°C range during respiration rate of root tips.

CHARACTERIZATION OF SOIL AERATION

Aeration status of a soil can be characterized by measuring the (1) composition of soil atmosphere, (2) gaseous diffusion (O_2 diffusion rates),
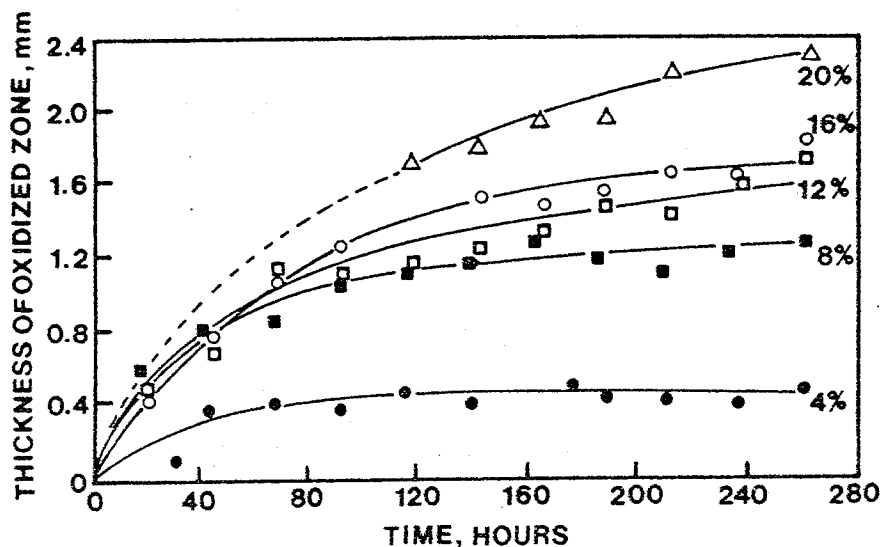
Fig. 2a. Thickness of oxidized layer in flooded soil, as influenced by varying levels of oxygen in the atmosphere above floodwater (Howeler and Bouldin, 1971).
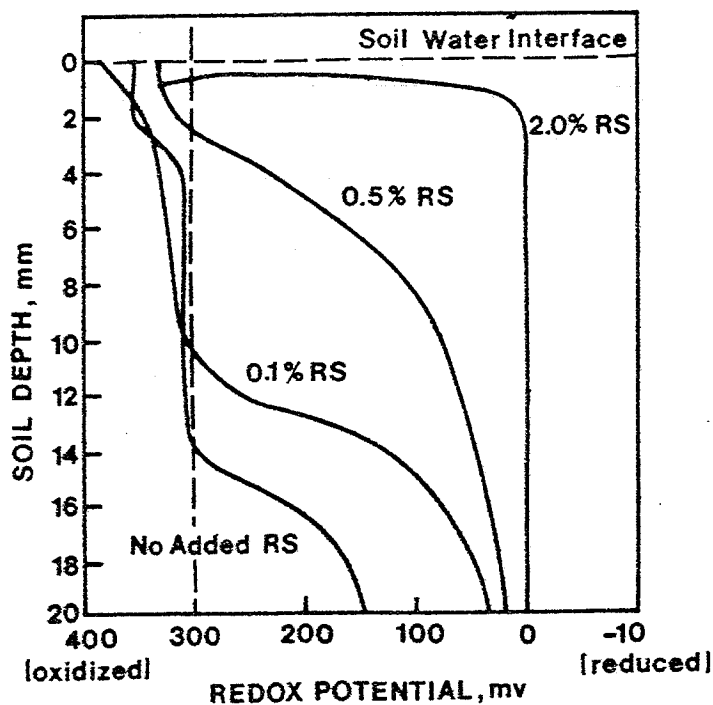
Fig. 2b. Thickness of oxidized layer in flooded soil, as influenced by energy source (organic matter) (Engler and Patrick, 1974).

and (3) oxidation-reduction potential (Eh). Measuring O_2 uptake and respiratory quotient (Bridge and Rixon, 1976) and measuring reduced chemical forms in soil solution (Meek and Grass, 1975) have been reported as possible alternate methods for assessing soil aeration status.

Composition of Soil Atmosphere

Aeration status of a soil can be established by measuring the composition of the soil atmosphere. With good aeration, O_2 content of the soil may approach that of atmospheric air. Decreased soil O_2 concentration can result in partial or complete anaerobic conditions. These conditions can measurably increase N_2O content of the soil air as a result of denitrification. An inverse relationship was observed between soil O_2 and N_2O (Dowdell and Smith, 1974). Under highly reduced conditions, gases such as H_2S (sulfate reduction end product) and CH_4 (CO_2 reduction end product) can be detected in significant quantities in soils with high C content. In addition to CH_4, Smith and Robertson (1971) and Sheard and Leyshon (1976) have found C_2H_4 concentrations in the range of 17 to 20 ppm in soils incubated under anaerobic conditions for a period of 13 to 19 days.

Gaseous Diffusion

The technique of measuring soil O_2 diffusion rate (ODR) with a stationary platinum electrode (Lemon and Erickson, 1952) has been found to be satisfactory in the higher range of soil aeration and was found to be less sensitive in the lower range of soil aeration (Poorly drained and flooded soils). This method measures the O_2 reduction rate at the platinum electrode surface when constant electrical potential is applied (Sojka et al., 1975; West and Black, 1978). Once the O_2 present at the electrode surface is reduced, further reduction depends on the diffusion of O_2 to the electrode surface. To obtain precise measurements, the potential applied must be one at which O_2 is the only component reduced (Van Doren and Erickson, 1966). McIntyre (1970) presented a detailed review of the potential advantages and problems involved in using platinum electrodes for O_2 flux measurements. Shalhevet et al. (1969) observed ODR values in the range of 0.04 to 0.09 $\mu g\ cm^{-2}\ min^{-1}$ for soil with Eh values of -270 to 90 mv, while ODR sharply increased (0.09 to 0.36 $\mu g\ cm^{-2}\ min^{-1}$) in the soil at Eh values of 90 to 200 mv.

Oxidation-Reduction Potential (Eh)

Oxidation-reduction potential or redox potential is a measure of electron availability potential in a chemical or biological system. This method was used by several researchers (Patrick and Mahapatra, 1968; Ponnamperuma, 1972, for example) to characterize the intensity of reduction and identify different forms of redox couples (e.g. Fe^{+2} and Fe^{+3}) in

flooded soils and sediments. An inert electrode, usually platinum, is used to measure the potential of all redox couples. Under well-drained conditions (oxidized systems), low concentrations of redox couples reduce the stability and reproducibility of Eh measurements (Bohn, 1971), while in flooded soils and in soils with low O_2 levels, the higher concentrations of redox couples increases the sensitivity of Eh measurements, thus making this technique more applicable to anaerobic systems. Well-drained soils have characteristic Eh value of > 400 mv, and as the soil O_2 decreases, soil Eh values decrease. In some flooded soils with high C content, Eh values as low as − 350 mv can be observed. Changes in the concentrations of various redox couples as a function of Eh is shown in Fig. 3. Oxygen disappeared at Eh values of about 300 mv, while NO_3^- is removed at Eh values between 200 to 300 mv followed by the reduction of Mn^{+4}, Fe^{+3}, and SO_4^{-2}. Detailed discussions of the stability of redox couples in soil systems have been presented by Patrick and Mahapatra (1968) and Ponnamperuma (1972).

REACTIVITY AND MOBILITY

In this paper, reactivity is defined as a combination of transformations (physical, chemical, and biological), simultaneously functioning in well-drained, moderately to poorly drained, and flooded soil systems, and converting non-mobile chemical species into mobile forms and mobile species to non-mobile forms. The role of these conversion processes or transformations on the mobility of several important soil constituents at varying levels of soil aeration (redox changes) will be discussed.
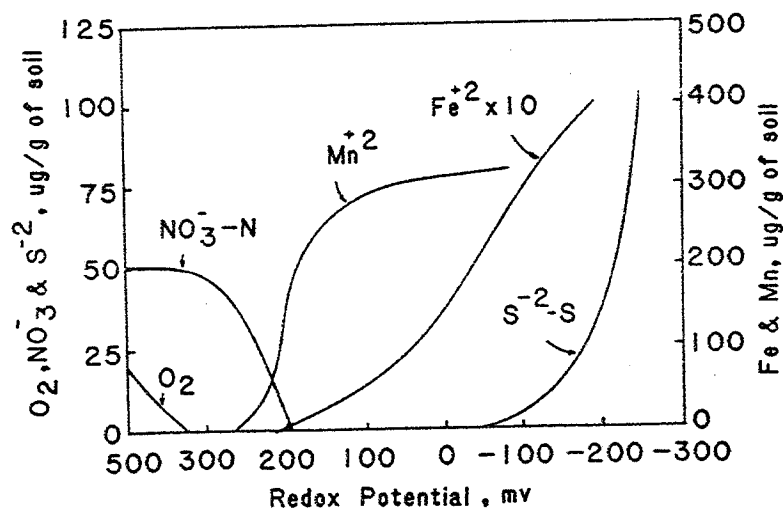

Fig. 3. Stability of various redox couples shown as a function of redox potential (data obtaine . from Patrick, 1964; Connell and Patrick, 1968; Turner and Patrick, 1968, Gotoh and Patrick, 1972).

Nitrogen

Most of the N in soils and sediments is in organic form with only a very small amount present in the inorganic form. A series of biochemical and physico-chemical processes are involved in transforming one source of N to another source. The most important forms of inorganic N compounds include NH_4^+, NO_3^-, NO_2^-, N_2, and N_2O. These compounds are the end products of specific biological reactions. The important microbial conversion processes functioning in a soil system are organic $N \rightarrow NH_4^+$ (ammonification), $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ (nitrification), $NO_3^- \rightarrow N_2O \rightarrow N_2$ (denitrification), $NO_3^- \rightarrow NH_4^+$ (assimilatory NO_3^- reduction), $N_2 \rightarrow$ organic N (biological fixation), and $NH_4^+ \rightarrow NH_3$ (volatilization).

Organic N conversion to NH_4^+ occurs at all levels of soil aeration, but at varying rates. Under well-aerated conditions, very little or no NH_4^+ accumulates in a soil system, because of rapid oxidation of NH_4^+ to NO_3^-. Ammonium N accumulates in O_2-deficient soils since O_2 is required for the oxidation of NH_4^+ to NO_3^-. Data shown in Fig. 4 with varying soil moisture levels present indirect evidence for the effects of varying levels of soil O_2. Ammonification was shown to occur at a maximum rate in a soil with 0.3 atm moisture tension. Although soil O_2 levels are probably high at moisture tension > 0.3 atm, the rates of these processes were lower than at low tension, probably due to available water limiting the process.
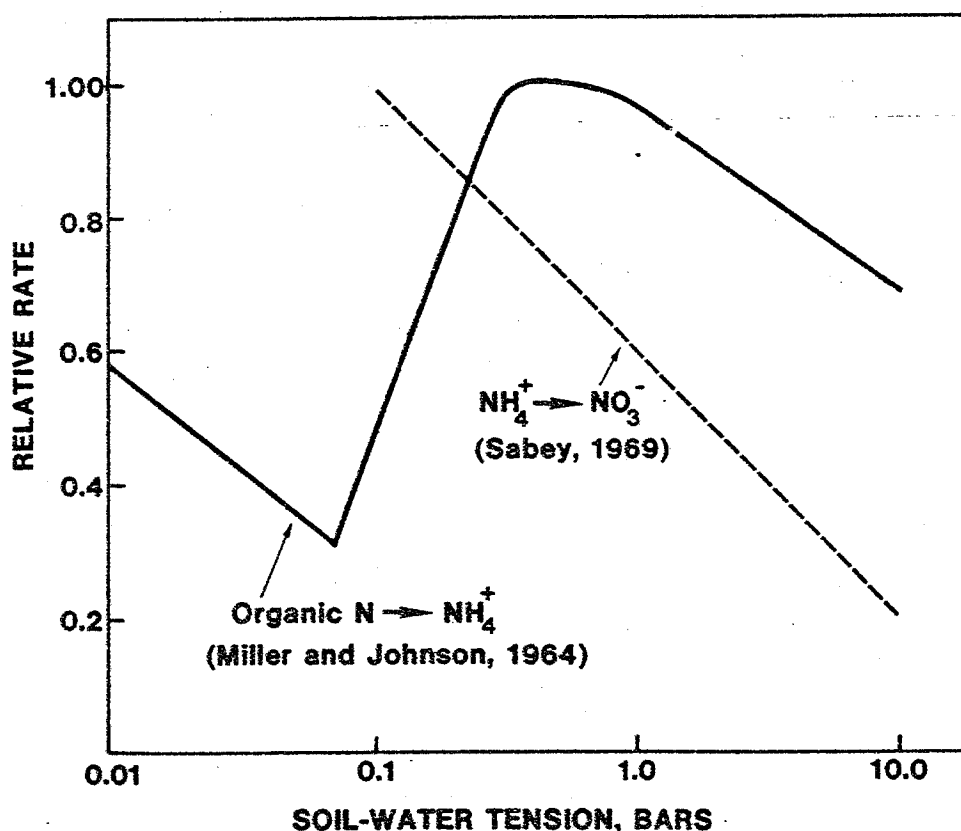

Fig. 4. Effect of soil-water tension on relative rate of ammonification and nitrification in drained soils (Miller and Johnson, 1964; Sabey, 1969).

On the other hand, at moisture tensions < 0.3 atm, soil O_2 was probably limiting because of larger fraction of soil pores filled with water. Reactions of NH_4^+ that are concentration dependent are increased in O_2-deficient soils because of high NH_4^+ concentration. Since NH_4^+ undergoes fixation reactions within the clay lattices, the increased concentration should increase fixation.

In addition to the normal reactions of NO_3^- assimilation by plants and microbes, restricted aeration causes the dissimilatory reduction of NO_3^- by facultative anaerobes. The rate of this process can be much greater than assimilation. With the exception of O_2, NO_3^- is the first redox constituent to disappear from the soil following restricted O_2 supply. In a poorly drained soil, the rate of this process is controlled by the fraction of soil pores free of O_2 and the available energy source. In soils that have both aerobic and anaerobic zones, rate of denitrification is dependent on the NO_3^- diffusion from aerobic soil pores to anaerobic microsites. Although this mechanism was not demonstrated experimentally, Reddy et al (1978) have shown the effect of NO_3^- diffusion on the denitrification process.

The above described N processes control the concentration of NH_4^+ and NO_3^- in drained, poorly drained, and flooded soils. The mobility of these ions is also related to the soil aeration. Apparent NH_4^+ diffusion was shown to increase with the soil-water content (Fig. 5). As the soil-water
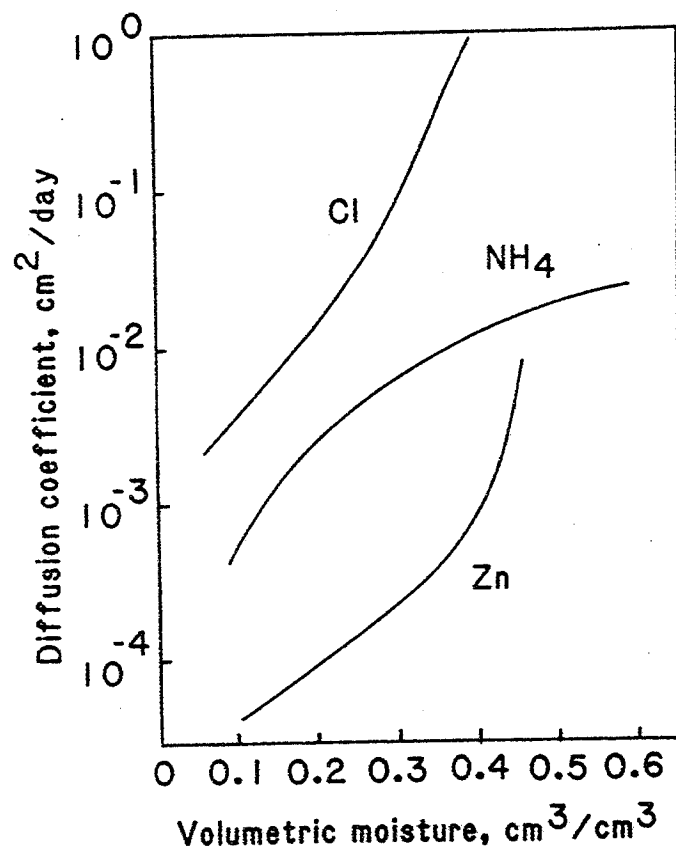

Fig. 5. Diffusion coefficient of Cl, NH_4, and Zn, as influenced by volumetric soil-water content (Cl, average of six soils, Warncke and Barber, 1972; NH_4^+, Crowley silt loam soil, Reddy et al., 1981b; Zn, Fincastle soil (fine-silty, mixed, mesic Aeric Ochraqualf), Warncke and Barber, 1972).

content increases, the liquid phase becomes more continuous and diffusion path less tortuous (Porter et al., 1960). The mobility of NH_4^+ is increased in O_2-deficient soils because of the higher concentration and also because a larger fraction of NH_4^+ is in the pore water instead of being adsorbed onto the exchange complex. This latter effect is due to displacement from the exchange complex by other cations that are mobilized as a result of reduction processes. For example, in poorly drained and flooded soils, concentration of Mn^{+2} and Fe^{+2} can increase as a result of reduction and compete with NH_4^+ and other cations for exchange sites, and may result in displacement of NH_4^+ from the exchange complex. This will decrease NH_4^+ adsorption and increases its mobility. In flooded soils, a significant amount of NH_4^+ is lost as a result of diffusion into the overlying oxygenated floodwater and surface aerobic layer. Ammonium diffused into surface soil layer or floodwater can be rapidly oxidized to NO_3^- or volatilized to NH_3. Nitrate thus formed diffused back into underlying anaerobic soil and is lost through denitrification (Reddy et al., 1976). In flooded soils and sediments, high pH conditions can exist in the overlying floodwater as a result of imbalance between photosynthesis and respiration of algae, thus creating favorable conditions for N loss through NH_3 volatilization (Mikkelsen et al., 1978).

Nitrate diffusion is also influenced by soil-water content, soil O_2, and denitrification potential of a soil. Nitrate diffusion rate increases with soil-water content. Movement of NO_3^- was found to be more rapid in a sandy soil than a loam soil (Clarke and Barley, 1968). Low soil O_2 and greater demand for electron acceptors in anaerobic sites can increase NO_3^- diffusion from aerobic sites to anaerobic microsites where it is lost through denitrification. Although the role of denitrification in anaerobic microsites has been demonstrated (Rolston and Marino, 1976); the rate of NO_3^- diffusion from aerobic sites to anaerobic microsites has not been documented.

In flooded soils and sediments, NO_3^- in floodwater and in the surface oxidized zone is derived from (1) nitrification in the oxidized soil zone or floodwater, and (2) input from external sources (drainage effluents, wastewaters). In this system, NO_3^- from floodwater diffuses into underlying anoxic sediments where it undergoes denitrification (Reddy et al., 1978). It has been shown that very little or no denitrification occurs in floodwater low in available C (Engler and Patrick, 1974), and under these conditions, floodwater NO_3^- removal is dependent on the diffusion of NO_3^- into anaerobic portions of the sediment. The flux of NO_3^- from the floodwater is controlled by (i) concentration gradient across sediment-water interface, (ii) floodwater depth, (iii) temperature, and (iv) mixing and aeration.

Phosphorus

Phosphorus in soils occurs both in organic and inorganic forms. In mineral soils, inorganic P probably is more important than organic P, primarily due to slower availability of the organic P. However, in organic

soils and mineral soil high in organic matter content, organic P mineralization can play a significant role in releasing soluble inorganic P. Inorganic P is the most mobile form of P; however, under certain conditions soluble organic P can be mobile. Inorganic P in the soil can be divided into four main groups: calcium phosphate, aluminum phosphate, iron phosphate, and reductant-soluble P extracted after the removal of the first three forms. The latter two fractions are not very important in the fertility of well-aerated soils, but have been found to be of significance in poorly drained and flooded soils.

Although P itself is not normally biologically reduced in redox reactions in soils, it does undergo reactions that have a pronounced effect on its reactivity (Fig. 6). Most of this change in reactivity of P as a result of anaerobic conditions is associated with the Fe chemistry of the soil. Reduction of Fe^{3+} oxyhydroxide and Fe^{3+} phosphate compounds increase the solubility of PO_4^{-3} (HPO_4^{-2}, $H_2PO_4^-$) and make it more available to plants. The reduction-solubilization of Fe^{+3} compounds releases PO_4^{-3} in two ways: (i) by converting insoluble Fe^{+3} phosphates to more soluble Fe^{+2} phosphates, and (ii) by solubilizing the Fe^{+3} oxyhydroxide material in the soil that has occluded in its matrix forms of phosphate that are more reac-
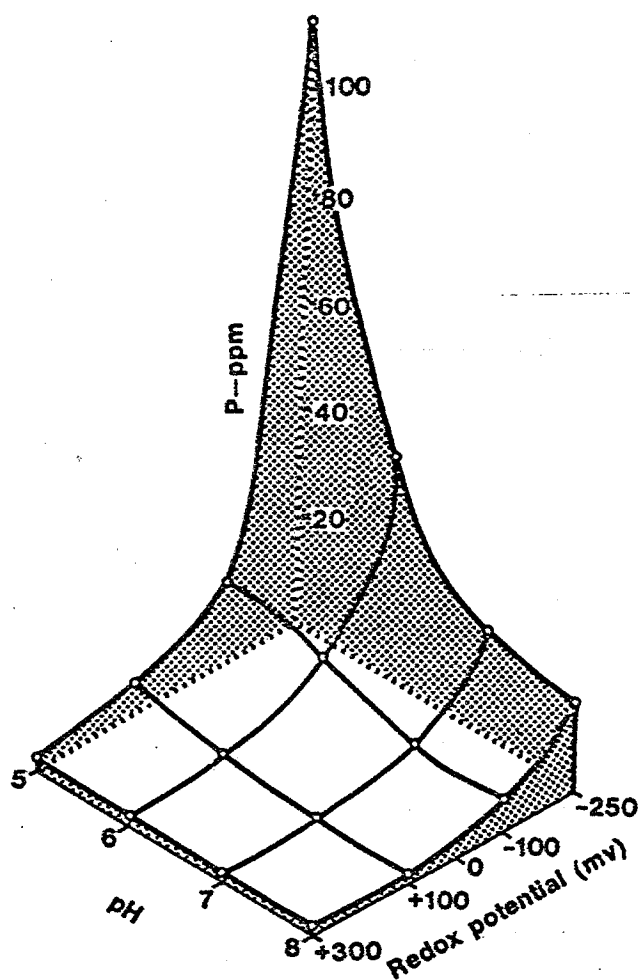

Fig. 6. Solubility of P as influenced by pH and redox potential.

tive than the occluding Fe^{+3} oxyhydroxide material (Patrick, 1964; Mahapatra and Patrick, 1969; Patrick and Khalid, 1974). Phosphorus release was also found to be significantly higher in flooded organic soils than soils maintained under drained conditions (Reddy, 1983) (Table 1). Although organic soils are low in Fe and Al, anaerobic conditions increased the solubilization of organic matter, thus increasing the availability of soluble P.

In alkaline soils, Turner and Gilliam (1976a) observed that increase in available P (expressed as anion resin-adsorbable P) under flooded conditions was not due to soil reduction of ferric phosphate but due to increased soil-water content. Reasons for not detecting an increase in available P as the alkaline soils were reduced were due to (1) lack of reductant soluble P, and (2) soluble P being controlled by the calcium system. Increased available P under water saturated conditions (oxidized or reduced) was attributed to the greater rate of diffusion to the resin particles.

The movement of soil P to plant roots occurs by mass flow and diffusion. Movement of P by mass flow is determined by the concentration in soil solution and the soil-water content as well as by the rate of water uptake. Under well-drained conditions, soil solution P is generally low, indicating that P movement to plant roots in these soils probably occurs primarily due to diffusion (Barber et al., 1963; Olsen, 1971). As discussed earlier, in most of the poorly drained and flooded soils, soluble P concentrations are usually high, which results in an increased rate of movement by diffusion and mass flow. No evidence is available on the effect of soil O_2 on P diffusion; however, several researchers (Olsen et al., 1965; Mahtab et al., 1971; Turner and Gilliam, 1976b) have observed increased rate of P diffusion with increase in soil-water content (Fig. 7). For example, Olsen et al. (1965) showed that P diffusion coefficients increased from 0.4×10^{-7} to 15.5×10^{-7} cm²/s as the volumetric moisture increased from 0.22 to 0.55 cm³/cm³. In these soils, it was not clear whether increased rate diffusion was due to soil reduction (caused by high soil-water

Table 1. Phosphorus release rates in organic soils in Florida maintained under flooded and drained conditions (Reddy, 1983).

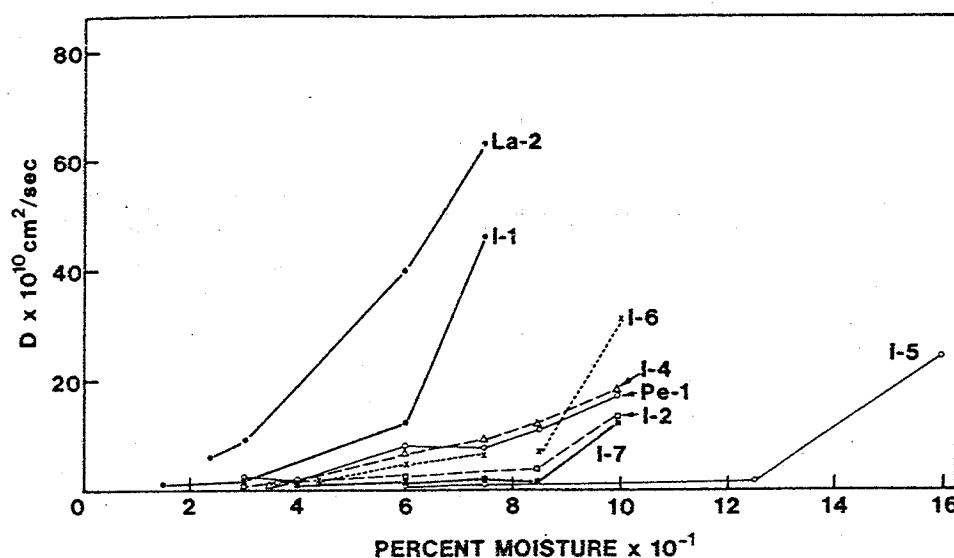| Soil type	Soluble P		Total P	
	Non-flooded	Flooded	Non-flooded	Flooded
		— kg P ha⁻¹ d⁻¹ —		
Cultivated soils				
Oklawaha muck	0.12	1.12	0.14	1.38
Monteverde muck	0.07	0.45	0.07	0.80
Lauderhill muck	0.16	0.62	0.20	0.70
Brighton muck	0.14	0.27	0.16	0.36
Pahokee muck	0.01	0.05	0.01	0.10
Virgin soils				
Monteverde muck	0.19	1.28	0.21	1.64
Pahokee muck	0.02	0.09	0.02	0.20

Fig. 7. Effect of soil moisture and oxidized/reduced conditions on P diffusion (reproduced from Turner and Gilliam, 1976a; Plant Soil 45:353–363).

content) or water content or both. Turner and Gilliam (1976a) have shown that for an alkaline soil increased rate of diffusion was due to saturated soil-water content (oxidized or reduced) rather than reduction as compared to moist conditions.

Rate of P diffusion is controlled by the adsorption-desorption process which controls the soil solution concentrations. Observed P adsorption behavior was shown to be influenced by oxidized and reduced soil conditions (Patrick and Khalid, 1974). In a Crowley silt loam soil, more P was adsorbed under oxidized conditions than under reduced conditions when the P concentration in the soil solution was low. This pattern was reversed at higher solution P concentration. The difference in behavior of phosphate under oxidized and reduced conditions was attributed to the change brought about in ferric oxyhydroxide by soil reduction. The greater surface area of the gel-like reduced ferros compounds in a reduced soil probably resulted in more P being solubilized where solution P was low and more solution P was adsorbed when solution P was high. These data suggested that at high solution P concentrations, P movement can occur at a more rapid rate under oxidized conditions than reduced conditions. This study was conducted at saturated soil-water content under both oxidzied and reduced conditions, and it is not clear whether similar effects will be seen if P adsorption is measured at water contents encountered under drained field conditions. Assuming a linear adsorption isotherm, Krom and Berner (1980) calculated adsorption coefficients (K_D) for the data reported in the literature on P adsorption in oxic and anoxic soils and sediments. For anoxic sediments, K_D values were in the range of 1 to 80 ml/g, while for oxic soils and sediments K_D values were in the range of 10 to 5000 ml/g. These data suggest a stronger adsorption capacity of oxic soils as compared to anoxic soils.

Potassium

Potassium is not involved in oxidation-reduction reactions and is therefore less affected by poor soil aeration and flooded conditions than are P and N. Although K occurs in several forms in soil, adsorbed and solution phases are primarily involved in mobility. The release of large amounts of Fe^{+2}, Mn^{+2}, and NH_4^+ in soils with low O_2 results in displacement of K^+ ions from the exchange complex to the soil solution. No data are available on the availability and mobility of K as influenced by soil O_2 alone. However, Pasricha and Ponnamperuma (1976) have shown increased K^+ concentrations in soil solution as a result of flooding. Potassium diffusion rates were found to be dependent on soil moisture and soil solution concentrations and a significant linear relationship was observed between K diffusion, uptake by plants, and soil moisture (Mengel and Von Braunschweig, 1972).

Calcium and Magnesium

Effects of soil aeration on reactivity and mobility of Ca^{+2} and Mg^{+2} will be of a similar nature as K^+. These nutrients are also not involved in soil oxidation-reduction reactions. However, reduction of insoluble Fe^{+3} and Mn^{+4} to soluble forms displaces other cations from the exchange complex to the soil solution. This process occurs both in poorly drained soils with low O_2 levels and in flooded soils. Under flooded conditions, increased water content can solubilize some compounds, which otherwise are relatively insoluble, and increase the concentration in soil solution. In poorly drained and flooded alkaline soils, low O_2 and high CO_2 levels can result in dissolution of $CaCO_3$ and $MgCO_3$ and increase the Ca^{+2} and Mg^{+2} concentration of the soil solution (Ponnamperuma, 1972). Low O_2 levels associated with increased soil-water content can also increase the mobility of these cations in soils. Increases in the concentration of other cations on the exchange complex can decrease the adsorption coefficient and result in rapid diffusion. Van Schaik et al. (1966) reported that the diffusion of ions is dependent upon the fraction of the adsorbed cations present in the diffuse layer and bulk solution. Their results show that approximately 70% of the exchangeable Na^+ ions were mobile, whereas only 25% of the Ca^{+2} ions were mobile.

Sulfur

Sulfur is subject to oxidation-reduction reactions and exists in soils and sediments at different valance states. The most common valances are +6 (sulfate), 0 (elemental S), and −2 (sulfide). The valance state of S in soil is governed to a large extent by the environmental conditions (O_2 and water content) that affect the composition and activity of the microflora. Detailed reviews on biogeochemical transformations of S in soils and sedi-

ments have been presented by Trudinger (1979); Krouse and McCready (1979); and Ralph (1979).

In aerated soils, the principal S transformations include (1) the oxidation of elemental S, thiosulfates, and sulfides; (2) mineralization of organic S; and (3) incorporation of S and sulfates into microbial tissue, and uptake by plants. Under conditions of O_2 free environment, sulfate reducing obligate anaerobic bacteria use SO_4^{-2} as an electron acceptor, resulting in the formation of sulfides (Alexander, 1977). These organisms are very sensitive to O_2 and cannot function in the presence of soil O_2. Sulfate reduction was shown to occur in soils with Eh < -75 mv (Harter and McLean, 1965), while Connell and Patrick (1968) reported sulfide formation in an anaerobic soil with Eh < -150 mv. The optimum pH range for maximum sulfide formation was found to be between 6.5 to 8.5 (Connell and Patrick, 1968). Besides soil O_2, sulfide formation can be retarded by the presence of NO_3^- (Fig. 8). Sulfur oxidizing bacteria, such as *Thiobacillus denitrificans* can reduce NO_3^- to N_2O and N_2, while oxidizing S to SO_4^{-2}.

In anoxic systems, S^{-2} concentrations of the soil can be decreased as a result of precipitation with metallic cations, such as Fe, Mn, Cu, Pb, Hg, Zn, Cd (Lindberg and Harriss, 1974; Krauskopf, 1967). Engler and Patrick (1975) observed that the metal sulfides were relatively unstable in an aerobic soil due to microbial oxidation. However, these sulfides were found to be relatively stable under anaerobic conditions with little or no dissolution of the ^{35}S from the metal sulfides.

Although some of the S in reduced form (S^{-2}) may accumulate in a soil system as metal sulfides and elemental S, most is eventually oxidized to SO_4^{-2}, a process in which microbial activities play a major role. The sulfate thus formed rapidly moves in the soil water. As the air-filled pore space is decreased as a result of an increase in soil water, the rate of SO_4^{-2} movement increases, primarily due to a decrease in the diffusion path
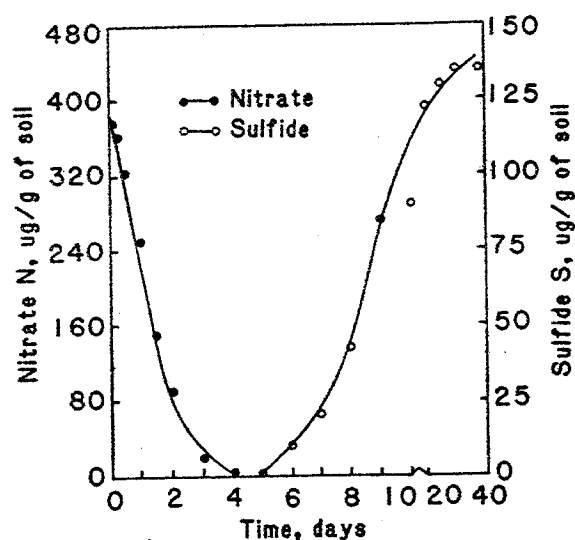

Fig. 8. Relationship between NO_3^- reduction and S^{-2} formation in a flooded soil (reproduced from Connell and Patrick, 1969. Soil Sci. Soc. Am. Proc. 33:711–715).

length. Sulfate diffusion coefficient in sediments saturated with water was reported to be 0.345 cm^2/day (Goldhaber et al., 1977). Sulfate ions can diffuse into deeper soil layers devoid of O_2, where it can be subsequently reduced to sulfides. Several researchers (Lambert et al., 1971; Donnelly et al., 1972) have reported significant quantities of sulfide formation in groundwaters. Goldhaber et al. (1977) observed a decrease in SO_4^{-2} concentration with increase in sediment depth. High SO_4^{-2} concentrations were observed at the sediment water interface and in the surface 1 to 2 cm of the sediment, while H_2S concentrations were found to increase with depth. In anoxic sediments, some of the sulfide formed in the anaerobic zones can diffuse into the surface oxidized zone where it can be oxidized to elemental S and subsequently to SO_4^{-2}. However, precipitation of sulfides with Fe^{+2} and other metals will slow this process. Sulfate thus formed can also diffuse back into the anaerobic zone where it will be reduced to sulfide.

Trace Metal Nutrients

Reactivity and mobility of trace metallic nutrients are also influenced by soil aeration. Some of the micronutrients that are influenced by the depletion of soil O_2 include Fe, Mn, Zn, Cu, Co, and Mo. In this paper, primary emphasis will be placed on the stability of Fe and Mn, while the effect on other nutrients will be discussed to limited extent.

In aerated soils, Fe and Mn exist as sparingly soluble Fe^{+3} and Mn^{+4} compounds. Decrease in soil O_2 levels as a result of temporary waterlogging, or as a result of rapid O_2 consumption due to the incorporation of high O_2 demand wastes (crop residues, animal wastes), can result in reduction of Mn^{+4} to Mn^{+2} and Fe^{+3} to Fe^{+2}. Reduction of these compounds is inhibited by the presence of soil O_2 and to some extent by NO_3^- (Fig. 2). The abundance of reduced Fe^{+2} in solution and on the exchange complex is favored by increase in soil acidity and soil reduction. The reduction of Fe and Mn has an indirect impact on the chemistry of the soil, such as (1) increases in water soluble Fe^{+2} and Mn^{+2}, (2) pH increases, (3) displacement of other cations from the exchange complex into soil solution, (4) increasing the solubility of P and Si, and (5) formation of new minerals (Ponnamperuma, 1972).

Gotoh and Patrick (1972, 1974) have reported that both water soluble and exchangeable Fe^{+2} and Mn^{+2} increased with decrease in Eh and pH. At pH 5, the effect of Eh was minimal on Mn^{+2} solubility, while between pH 6 and 8 the conversion of insoluble Mn^{+4} to Mn^{+2} was dependent on both Eh and pH. Similarly, appreciable amounts of Fe^{+2} were detectable at Eh of +300 mv and pH 5. However, reducible Fe became unstable when Eh was between +300 and +100 mv at pH 6 and 7, and −100 mv at pH 8 (Fig. 9). Application of an energy source followed by an irrigation decreased Eh values approximately 100 mv and resulted in high levels of Mn and Fe in the soil solutions obtained at 80 cm depth (Meek and Grass, 1975).

The mobility of Fe and Mn is increased greatly by reduction to the more soluble Fe^{+2} and Mn^{+2} forms. As the intensity of anaerobiosis in-

creases, the effectiveness of the soil exchange complex in adsorbing cations will be reduced due to the larger total concentration of cations, thus increasing the mobility of Fe^{+2} and Mn^{+2}. Under reduced conditions, Mn^{+2} is subject to greater movement through both mass flow and diffusion. Because of its greater relative solubility than reduced Fe in anoxic soils, Mn^{+2} is usually depleted before Fe with a corresponding increase in the Fe/Mn ratios in the soil.

Reduction of insoluble Fe^{3+} oxyhydroxide compounds to the more soluble Fe^{2+} form greatly increases mobility of Fe^{2+}. In general, Fe^{2+} does not appear to be as mobile as Mn^{2+}, probably as a result of the easier reduction of oxidized Mn compounds to the soluble reduced forms. This condition results in the appearance of Mn^{2+} ions in the soil solution of a flooded soil before Fe^{2+} shows up. It also means that at a given reducing redox potential a greater fraction of the Mn is going to be in the reduced soluble form and subject to mobility. Another factor that decreases the mobility of Fe^{2+} relating to Mn is the difference in partitioning of the Fe^{2+} and the Mn^{2+} between the solution phase and the exchange complex at any given pH-redox conditions. A larger fraction of the reduced Fe^{2+} will be on the exchange complex as compared to the Mn^{2+} where more will remain in solution. Unless large amounts of S^{2-} are present, Fe^{2+} is quite
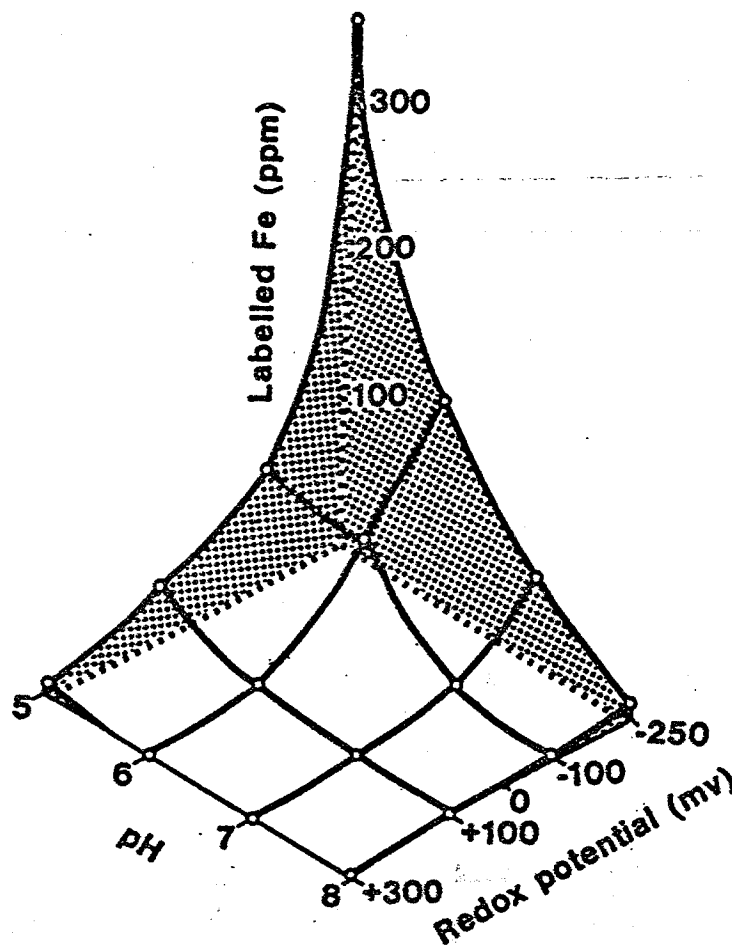

Fig. 9. Solubility of Fe as influenced by pH and redox potential.

mobile, however, and its movement in reduced soils in response to concentration gradients is evident. Ellis et al. (1970a) observed an increased diffusion coefficient of Fe^{+2} in montmorillonite clay with increased concentration of Fe^{+2} (up to 0.2 meq/g of clay). Similar results were also observed for other micronutrients (Mn, Zn, and Cu) (Ellis et al., 1970b). In the same study, diffusion coefficient of Fe^{+2} was found to be about five times larger than the diffusion coefficient of Fe^{+3}. Three examples of iron movement are (i) diffusion to aerobic surface layer where it is precipitated as Fe^{3+} oxyhydroxide (Fig. 10), (ii) diffusion and mass flow to plant roots where it is oxidized and precipitates as Fe^{3+} oxyhydroxides encrustations around the roots, and (iii) mass flow with downward percolating water to oxygenated subsoil layer where it precipitates along with Mn. This last process occurs only in soils where subsoil is oxygenated as compared to anaerobic root zone. As with Mn, reduced Fe affects mobility of other cations by disturbing the equilibrium between the soluble and exchangeable forms, resulting in an increased mobility. In tropical regions this process can result in "ferrolysis" in which Fe has displaced most of the other cations (Brinkman, 1970).

Micronutrients such as Zn, Cu, Mo, Co, and B are not as readily involved in soil oxidation-reduction reactions, but their solubility and mobility are affected by poor aeration. However, reduction can act to solubilize trace metals specifically adsorbed onto Fe^{+3} and Mn^{+4} oxides and hydrous oxides. In studies using controlled pH and Eh levels, Jugsujinda and Patrick (1977) found uptake of native added ^{65}Zn by rice (*Oryza sativa* L.) seedlings was greater from aerobic than anaerobic soil suspensions. In a recent study, Reddy and Patrick (1977) observed that chelated Zn and Cu in soil solution decreased with decreasing Eh from +500 mv (oxidized) to −200 mv (reduced). The instability of Zn and Cu chelates was attributed to chemical fixation (possibly with sulfide) of added Zn
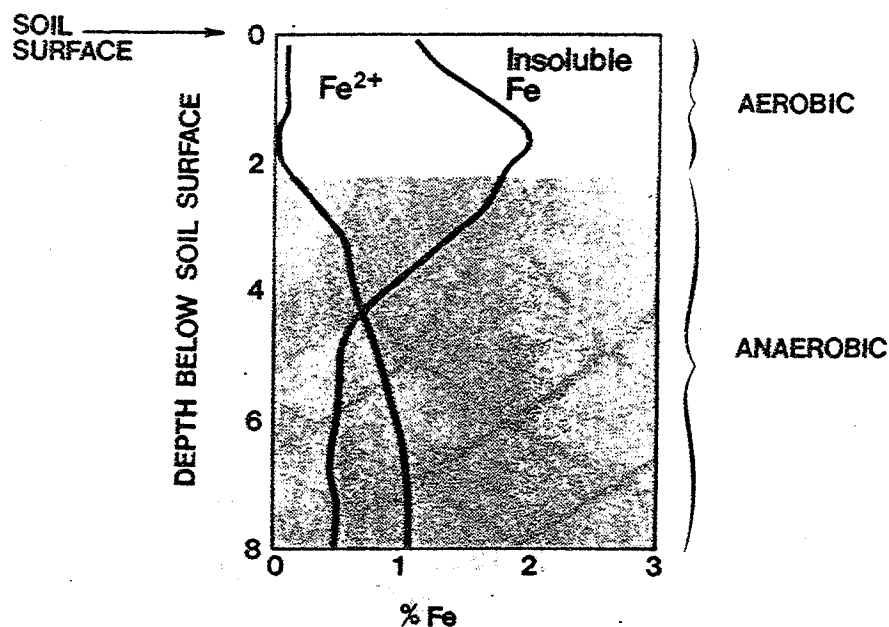

Fig. 10. Distribution of Fe^{+2} and Fe^{+3} in a flooded soil.

and Cu, and not due to chemical or microbial breakdown of the metal chelate complex. Some of these metallic cations may be less mobile under reduced conditions because of possible precipitation with sulfide (Engler and Patrick, 1975).

Mobility of metallic cations is also influenced by soil-water content. For example, rate of Zn diffusion (Fig. 5) was shown to increase with an increase in volumetric water content (Warncke and Barber, 1972). However, no information is available on the effect of varying levels of soil O_2 on diffusion of micronutrients.

CONCLUSIONS

Aeration status of a soil is controlled by the O_2 concentration in the soil atmosphere. Under well-aerated conditions, soil O_2 approaches that of atmospheric air and in poorly drained soils soil O_2 decreases. Decrease in soil O_2 is dependent on the fraction of pore volume filled with water, presence of O_2 demanding soil constituents, and soil physical properties. Under certain conditions a soil with small fraction of pore space filled with water can have O_2 concentrations near zero (example: soils receiving heavy loading of carbonaceous wastes). On the other hand, in soils with low O_2 demand, excessive soil-water content may not result in completely anoxic conditions. Although, these two cases are extreme, differentiation should be made in evaluating the aeration status of the soil.

Depletion of soil O_2 retards the root growth of several plants. The optimum soil O_2 requirement for plant-root development varies with species and age of the plant. The chemistry and microbiology of the soils are also altered as a result of changes in soil O_2. Restricted supply of O_2 to a soil results in reduction of NO_3^- to N_2O and N_2, Mn^{+4} to Mn^{+2}, Fe^{+3} to Fe^{+2}, SO_4^{-2} to S^{-2}, and CO_2 to CH_4. Reduction of these species depends on the intensity of soil anaerobiosis.

The most common method of characterizing the soil aeration is to measure (1) composition of soil atmosphere, (2) O_2 diffusion rates, and Eh. Oxygen diffusion measurements were found to be useful and more reliable in aerated soils while Eh measurements were found to be more effective in poorly drained and flooded soils.

Both reactivity and mobility of plant nutrients are influenced by the O_2 status of the soil. Biochemical processes involving aerobic bacteria were found to be slower in soils with low O_2 levels. For example, in poorly drained soils, ammonification and nitrification rates were found to be slower while denitrification rates were found to be faster. Oxygen depletion and saturated soil-water conditions increases the ionic strength of the soil solution, primarily due to increased levels of Fe^{+2}, Mn^{+2}, and NH_4^+ in solution. The release of large amounts of reduced cations results in displacement of other cations such as K^+, Ca^{+2}, and Mg^{+2} from the exchange complex, thus increasing their mobility. Mobility of some metallic cations (e.g., Zn, Cu) can be decreased as a result of reduced conditions because of possible precipitation with sulfides. However, this process occurs under a completely anoxic environment.

As discussed earlier, poor soil aeration can be the result of low O_2 levels, high water content, or the effects of both. Most of the research conducted in the past is oriented to evaluate the effect of varying levels of soil moisture on reactivity and mobility of nutrients. Data are scarce on the effects of varying levels of soil O_2 on the reactivity and mobility of nutrients. Future research should be oriented to study the effects of varying O_2 levels on nutrient transformations, adsorption-desorption processes, precipitation reactions, and diffusion mechanisms. The results from these studies will be useful in nutrient management of agricultural soils, thus, improving the utilization of nutrients by plants and reducing the pollution of surface and groundwater.

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