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THE CHEMISTRY OF SUBMERGED SOILS

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I. Introduction

The chemistry of submerged soils is a subject of unusual scientific and ecological interest. Its scientific interest springs from its applications in geochemistry, pedology, agriculture, limnology, oceanography, and pollution

control. Its ecological importance needs no emphasis, for 72% of the earth's surface is covered by submerged soils or sediments. The chemical changes in these submerged materials influence (a) the character of the sediment or soil that forms, (b) the suitability of wet soils for crops, (c) the distribution of plant species around lakes and streams and in estuaries, deltas, and marine flood plains, (d) the quality and quantity of aquatic life, and (e) the capacity of lakes and seas to serve as sinks for terrestrial wastes.

II. Kinds of Submerged Soils

The Glossary of Soil Science Terms (Anonymous, 1965) defines soil in two ways: (a) "The unconsolidated mineral material on the immediate surface of the earth that serves as a natural medium for the growth of land plants"; and (b) "The unconsolidated mineral matter on the surface of the earth that has been subjected to and influenced by genetic and environmental factors of: parent material, climate (including moisture and temperature effects), macro- and microorganisms, and topography, all acting over a period of time and producing a product—soil—that differs from the material from which it is derived in many physical, chemical, biological, and morphological properties and characteristics."

The first definition limits submerged soils to soils carrying dryland crops that undergo temporary waterlogging, for permanently waterlogged soils support marsh plants, not land plants. The second definition embraces waterlogged soils, marsh soils, paddy soils, and lake and ocean sediments. In this chapter, I use the wider definition.

A. WATERLOGGED (GLEYS) SOILS

Waterlogged soils are soils that are saturated with water for a sufficiently long time annually to give the soil the distinctive gley horizons resulting from oxidation-reduction processes: (a) a partially oxidized A horizon high in organic matter, (b) a mottled zone in which oxidation and reduction alternate, and (c) a permanently reduced zone which is bluish green (Robinson, 1949).

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 deposited as rusty mottles or streaks if the diffusion of oxygen into the soil aggregates is slow; if diffusion is fast, they are deposited as concretions (Blume, 1968). While some rusty

mottles consist of goethite and lepidocrocite (Iwasa and Kamoshita, 1961) the deposits are rarely pure oxides. Because iron and manganese form coprecipitates, the concretions are mixtures or complex oxides (Hem, 1964). They also contain small amounts of zinc, copper, nickel, and cobalt (Jenne, 1968). The zone of permanent waterlogging is bluish green because ferrous compounds are present. In this zone, secondary minerals, such as hydrated magnetite, pyrite, marcasite, siderite, vivianite, and ferrous silicates, may be present (Ponnamperuma, 1972).

Saturation with water may be due to impermeability of the soil material, the presence of an impervious layer, or a high water table. Waterlogged soils occur in almost any climatic zone from the tundra to the desert or humid tropics (Soil Survey Staff, 1960), usually as the poorly drained members of drainage catenas. Robinson (1949), Joffe (1949), Russell (1961), Rode (1962), and Ponnamperuma (1972) have discussed the influence of waterlogging on soil genesis. This influence is so great that wetness has been used as a differentiating characteristic at the suborder level in classifying all soils except aridisols and histosols (Thorp and Smith, 1949; Soil Survey Staff, 1960, 1967).

Robinson (1930), Van't Woudt and Hagan (1957), Grable (1966), and Stolzy and Letey (1964) have reviewed the effects of waterlogging on crop plants. Humphries (1962) has described its effects on perennial grasses, and Potsma and Simpendorfen (1962), on pine trees.

B. MARSH SOILS

Marsh soils may be defined as soils that are more or less permanently saturated or submerged. Freshwater marsh soils occur on the fringes of lakes and the networks of streams that feed them (Joffe, 1949). Saltwater marshes are found in estuaries, deltas, and tidal flats (Guilcher, 1963).

The outstanding features of these soils are the accumulation of plant residues in the surface horizon and the presence of a permanently reduced G horizon below it. In freshwater marshes, the G horizon is blue or green (Joffe, 1949); in marine marshes it is green if iron silicates are present and dark gray if pyrites are the main iron minerals (Pons and Van der Kevie, 1969).

Joffe (1949) and Rode (1962) have classified freshwater marshes according to their origin into upland, lowland, and transitional. Upland marshes receive mainly rainwater and are therefore poor in bases and have pH values of 3.5–4.5. Lowland marshes are saturated or submerged with water-carrying bases and have pH values of 5.0–6.0. Ruttner (1963) has described the transition from lowland to upland and the accompanying changes in vegetation. But there is no niche for these organic soils in the

classification of histosols proposed by the U.S.D.A. Soil Survey Staff (1968), in which the emphasis is on the kind of plant residue, not the water regime.

Pearsall (1938), Misra (1938), Pearsall and Mortimer (1939), Pierce (1953), and Armstrong and Boatman (1967) have shown an association between the chemical properties of the soils, especially their oxidation-reduction state, and the distribution of natural vegetation in marshes. Gorham (1953) found that in passing from the relatively inorganic lake muds through semiaquatic soils to raised bog peats, soil acidity increased, base saturation decreased, and humus nitrogen content fell. These changes were reflected in the nutrient status of the plants.

Saltwater marsh soils cover over 20 million hectares of flat land, chiefly in the deltas of the tropics. When submerged and anaerobic they are neutral in reaction and support salt-tolerant marsh plants. But when the land is elevated or when the water recedes, air penetrates the soil and oxidizes the pyrites present in it to basic ferric sulfate and sulfuric acid, producing an acid sulfate soil. I have previously reviewed the genesis of these soils (Ponnamperuma, 1972). Moorman (1963), Nhung and Ponnamperuma (1966), and Pons and Van der Kevie (1969) have suggested methods of reclaiming them for crops, especially, rice.

C. PADDY SOILS

Paddy soils are soils that are managed in a special way for the wet cultivation of rice. The management practices include: (a) leveling of the land and construction of levees to impound water; (b) puddling (plowing and harrowing the water-saturated soil); (c) maintenance of 5–10 cm of standing water during the 4–5 months the crop is on the land; (d) draining and drying the fields at harvest; and (e) reflooding after an interval which varies from a few weeks to as long as 8 months. These operations and oxygen secretion by rice roots lead to the development of certain features peculiar to paddy soils.

During the period of submergence, the soil undergoes reduction (Section III, E) and turns dark gray. Iron, manganese, silica, and phosphate become more soluble and diffuse to the surface and move by diffusion and mass flow to the roots and to the subsoil. When reduced iron and manganese reach the oxygenated surface, the surface of rice roots, or the oxidized zone below the plow sole (De Gee, 1950; Koenigs, 1950; Mitsui, 1960; Kyuma and Kawaguchi, 1966), they are oxidized and precipitated along with silica and phosphate. Sandwiched between the oxidized surface layer and the zone of iron and manganese illuviation is the root zone of rice with reddish-brown streaks along root channels. When the land is

drained at harvest, almost the entire profile above the water table is reoxidized, giving it a highly mottled appearance.

Precipitation in the plow layer is not pedologically of any consequence because plowing and puddling redistribute the deposits. But the downward movement of iron and manganese means that these two elements are permanently lost from the topsoil. The eluviated iron and manganese, along with some phosphate, are deposited below the plow sole to produce an iron-rich B_{1r} horizon overlying a manganese-rich B_{1m} horizon. Kyuma and Kawaguchi (1966) regarded reduction eluviation and oxidative illuviation as the soil forming processes characteristic of paddy soils and have proposed the new term "Aquorizem" at the Great Soil Group level to define soils which have the sequence of reductive eluviation/oxidative illuviation.

A well developed paddy soil has the horizon sequence $A_{pR}/A_{12r}/B_{1rR}/B_{2g}/G$. Kanno (1957) has described these horizon sequences and their variation with duration of waterlogging, and has proposed a classification of paddy soils based on the depth of the permanent water table. Brinkman (1970) has recently drawn attention to another soil forming process associated with alternate oxidation-reduction which he calls "ferrolysis." During submergence and soil reduction, the cations displaced from exchange sites by Fe^{2+} migrate out of the reduced zone and are lost. When the soil is drained and dried, the reduced iron is reoxidized and precipitated, leaving H^+ ions as the only major cation. The soil is acidified and the clay disintegrates.

D. SUBAQUATIC SOILS

These soils are formed from river, lake, and ocean sediments. I justify the use of the term "soil" to describe the uppermost layers of unconsolidated aqueous sediments on the following grounds: (a) the sediments are formed from soil components; (b) typical soil-forming processes such as hydrolysis, oxidation-reduction, precipitation, synthesis, and exchange of matter and energy with the surroundings proceed in the uppermost layers of subaquatic sediments; (c) even deep sea sediments contain organic matter and a living bacterial flora (Goldschmidt, 1958); (d) the bacteria in lake and ocean sediments are similar to those in soils (Hutchinson, 1957; Kaplan and Rittenberg, 1963); (e) the metabolism of subaquatic sediments is similar to those of submerged soils; (f) the uppermost layers show a horizon differentiation distinct from physical stratification (Goldschmidt, 1958); and (g) sediments differ in texture, composition, clay mineralogy, organic matter content, and oxidation-reduction level (Rankama and Sahama, 1950; Kuenen, 1965) as soils do. Goldschmidt (1958) defined

soil as the habitat for living organisms in the uppermost part of the lithosphere and proposed the inclusion of subaquatic soils in the pedosphere. Mortimer (1949) regarded lake sediments as soils of a special type and called them "underwater soils." The uppermost layers of unconsolidated river, lake, and ocean sediments may be regarded as permanently submerged cumulative soils.

The composition of sediments is so variable (Mortimer, 1949; Kuenen, 1965) that they are best studied from the metabolic standpoint, as proposed by Mortimer. Mortimer (1949), Ruttner (1963), and McKee *et al.* (1970) have reviewed the metabolism of lake muds; Kaplan and Rittenberg (1963) and Martin (1970), the chemistry and metabolism of marine sediments.

III. Characteristics of Submerged Soils

A. ABSENCE OF MOLECULAR OXYGEN

When a soil is submerged, gas exchange between soil and air is drastically curtailed. Oxygen and other atmospheric gases can enter the soil only by molecular diffusion in the interstitial water. This process, according to the figures given by Lemon and Kristensen (1960) and by Greenwood (1961), is 10,000 times slower than diffusion in gas-filled pores. Thus the oxygen diffusion rate suddenly decreases when a soil reaches saturation by water (Taylor, 1949; Lemon and Kristensen, 1960; Kristensen and Enoch, 1964). Within a few hours of soil submergence, microorganisms use up the oxygen present in the water or trapped in the soil and render a submerged soil practically devoid of molecular oxygen. Both direct and indirect tests for oxygen, in the laboratory and in the field, have shown this.

Evans and Scott (1955) noted that the concentration of oxygen in the water used for saturating a soil decreased to one-hundredth of its initial value in 75 minutes. Takai *et al.* (1956) found no oxygen in three soils 1 day after submergence. Turner and Patrick (1968) could detect no oxygen in four soil suspensions within 36 hours of withdrawal of the oxygen supply. Yamane (1958) reported the absence of oxygen in two flooded rice fields at five sampling times in 3 months. Yunkervich *et al.* (1966) and Armstrong and Boatman (1967) found no oxygen in bogs with stagnant water. Mortimer (1941, 1942) could not detect oxygen 1 cm below the surface of submerged lake muds. And Scholander *et al.* (1955) reported the absence of oxygen in a mangrove swamp. Also, comparison of oxygen consumption rates by lake and ocean muds (2×10^{-10} to

2×10^{-9} g cm⁻² sec⁻¹) given by Hutchinson (1957), Pamatat and Banse (1969), and Howeler and Bouldin (1971) with oxygen diffusion rates in saturated soils (1×10^{-12} g cm⁻² sec⁻¹) shows that submerged soils and lake and ocean muds are anoxic below the soil-water interface. And respiration studies by Greenwood (1961) indicate that saturated crumbs have no oxygen at the center. The low oxidation-reduction potentials reported by Hutchinson (1957) for lake muds, by Zobell (1946) and Bass-Becking *et al.* (1960) for fine ocean sediments, and by me for saturated and submerged rice soils (Ponnamperuma, 1965) are further proof of the absence of molecular oxygen in waterlogged soils and sediments. But coarse sediments low in organic matter, in shallow water, may be well supplied with oxygen (Zobell, 1946).

B. OXIDIZED MUD-WATER INTERFACE

A submerged or saturated soil, however, is not uniformly devoid of oxygen. The concentration of oxygen may be high in the surface layer which is a few millimeters thick and in contact with oxygenated water. Below the surface layer, the oxygen concentration drops abruptly to practically zero (Mortimer, 1941, 1942; Patrick and Sturgis, 1955; Greenwood and Goodman, 1967). The brown color of the oxygenated layer, its chemical properties, and its oxidation-reduction potential undergo a similar abrupt change with depth in submerged soils (Pearsall and Mortimer, 1939; De Gee, 1950; Alberda, 1953; Howeler, 1970), in lake muds (Mortimer, 1942; Hayes and Anthony, 1958), and in sea sediments (Friedman *et al.*, 1968; Friedman and Gavish, 1970). The chemical and microbiological regimes in the surface layer resemble those in aerobic soils.

C. EXCHANGES BETWEEN MUD AND WATER

The presence of this oxygenated surface layer in lake and ocean muds is of the utmost ecological importance because it acts as a sink for phosphate and other plant nutrients (Hutchinson, 1957; Armstrong, 1965; Mortimer, 1969; Harter, 1968; McKee *et al.*, 1970; Fitzgerald, 1970) and as a chemical barrier to the passage of certain plant nutrients from the mud to the water. The surface operates efficiently in this way only so long as the lake or ocean bottom is supplied with oxygenated water by turbulence due to wind or by thermal movements, and the oxygen supply exceeds the demand at the interface. But these conditions are not always present: the surface may use up oxygen faster than it receives it, undergo reduction, and release large amounts of nutrients from the lake mud into the water (Mortimer, 1941, 1942).

In summer, some lakes undergo thermal differentiation into three layers: the epilimnion, the thermocline, and the hypolimnion. The epilimnion is the surface layer of warm water 10–20 m deep (Mortimer, 1949), which, because of mixing by wind action, is uniform in temperature and is saturated with atmospheric oxygen from top to bottom. Immediately below this is the thermocline, a layer in which there is a rapid fall in temperature with depth. In the thermocline, the concentration of oxygen is relatively constant in lakes poor in plant nutrients (oligotrophic lakes), but it decreases with depth in lakes rich in plant nutrients (eutrophic lakes) (Ruttner, 1963). The hypolimnion is the layer of cold stagnant water practically isolated from the epilimnion, except for solids, both organic and inorganic, that sink through it and accumulate on the mud surface. Bacteria in the surface layer use the oxygen in it to oxidize the organic matter. The oxygenated layer of the mud becomes thinner and thinner and finally disappears. The boundary between the aerobic and anaerobic zones then rises above the mud surface and well into the hypolimnion. When the oxidized layer disappears, phosphate, Fe^{2+} , Mn^{2+} , silica, and other soluble substances escape from the mud into the hypolimnion. But when cold weather returns and the layers mix, Fe^{2+} and Mn^{2+} are oxidized to Fe(III) and Mn(IV) oxide hydrates. These precipitates sink to the bottom carrying with them phosphate, silica, and sulfate (Hutchinson, 1957). Thus iron, manganese, phosphate, and silica which were released from the lake mud during the thermal stratification in summer are returned with sulfate to the bottom during the autumn mixing. This cycling of nutrients is less active in oligotrophic lakes, because the muds of these lakes receive less organic matter and therefore remain oxidized. The oxygenated layer in bottom muds regulates the nutrient cycles in lakes.

Because of the ecological importance of the oxygenated layer at the surface of lake muds, limnologists have attempted to study the factors that affect its thickness. Mortimer (1942) suggested that the thickness of the layer represented a balance between the diffusion of oxygen into the mud and its consumption, and derived some empirical relationships. Hutchinson (1957) evaluated two equations based on microbial respiration derived by Grote. Recently, Bouldin (1968) proposed six models for the description of diffusion of oxygen across mud surfaces. Two of these are steady-state models similar to those discussed by Hutchinson. The others are transient-state models introducing a new concept—oxygen consumption by mobile and nonmobile reductants, in addition to microbial use. Howeler (1970) and Howeler and Bouldin (1971) found experimentally that about 50% of the total oxygen consumed by the swamp soils they studied was used in oxidizing (a) water-soluble iron diffusing upwards and (b) reduced iron in the soil matrix. They suggested that oxygen consumption by re-

duced muds was best described by models that combine both microbial respiration and chemical oxidation. But Edwards and Rolley (1965) found no relationship between oxygen consumption by river muds and their chemical properties. Because the reduced soil acts as a sink for oxygen, the oxygenated layer at the surface of submerged soils should be quite thin. Howeler (1970) showed that it ranged from 0.2 mm to 6.0 mm in 10 submerged soils, and contained large amounts of freshly precipitated Fe(III).

The presence of Fe(III) and Mn(IV) (Weijden *et al.*, 1970) oxide hydrates in the surface layer implies that lake and ocean muds can sorb and retain phosphate, silica, manganese, cobalt, nickel, and zinc that are present in the supernatant water or that diffuse to the surface layer from the reduced zone below (Parks, 1967; Jenne, 1968; Hynes and Greib, 1970; Shukla *et al.*, 1971). The oxidized layer thus accumulates phosphorus, silicon, manganese, cobalt, nickel, and zinc. By contrast, permanently reduced ocean muds containing H₂S tend to accumulate copper, silver, uranium, molybdenum, and apatite (Goldberg, 1965).

Many studies on the absorption capacity of lake muds for nutrients and toxins have been done without recognizing the great difference in the adsorptive properties of oxidized and reduced muds.

The presence of oxygen in the soil-water interface profoundly affects the nitrogen economy of paddy soils and lake and ocean bottoms. Ammonium nitrogen broadcast as fertilizer or released from organic matter is converted to nitrate in the oxygenated surface layer. The nitrate diffuses into the anaerobic layer just below it and is denitrified. Denitrification causes substantial losses of ammonium fertilizer broadcast on paddy soils (Mitsui, 1960; Aomine, 1962; Patrick and Mahapatra, 1968) and makes lake and ocean bottoms sinks for nitrate (Kaplan and Rittenberg, 1963; Brezonik and Lee, 1968). Without denitrification, nitrogen deposits in aquatic sediments would deplete the atmosphere of nitrogen in 400 million years (Vaccaro, 1965). Denitrification, however, accounts for only 10% of the nitrogen imbalance in oceans (Martin, 1970).

D. PRESENCE OF MARSH PLANTS

Plants growing in submerged soils have two adaptations that enable the roots to ward off toxic reduction products, accumulate nutrients, and grow in an oxygen-free medium: oxygen transport from the aerial parts and anaerobic respiration.

It has been known for quite some time that the roots of marsh plants receive their oxygen from the aerial parts (shoot, air roots, or stilt roots) through gas spaces connecting these organs (Conway, 1940; Sifton, 1945;

Scholander *et al.*, 1955; Ruttner, 1963). Van Raalte (1941) and several other workers cited by me (Ponnamperuma, 1965) showed that rice roots behave similarly. More recently, W. Armstrong (1967, 1970) measured the oxygen flux across the roots of swamp plants, including rice, and found that it is sufficient to meet the oxygen requirements of root cells, to oxidize the rhizosphere, and to ward off the entry of reduced substances.

The rhizomes, corms, and leaves of semisubmerged plants apparently can respire anaerobically for long periods of time without injury (Laing, 1940). Anaerobic respiration enables rice to germinate at very low O_2 tensions (Erygin, 1936; Aleshin, 1961).

But how do land plants survive temporary waterlogging? Land plants respond to oxygen stress in the roots by forming intercellular gas spaces in the cortex (Bryant, 1934; McPherson, 1939). Through these spaces, limited amounts of oxygen may be transferred from the shoot to the root cells to enable the plant to survive short periods of soil waterlogging. But land plants may have a permanent system of varying efficiency for oxygen transport. Bartlett (1961) found that land plants vary widely in their resistance to waterlogging and that this resistance was linked with the capacity of the root to oxidize the rhizosphere, presumably by oxygen translocation from the shoot. Greenwood (1967) reported that seedlings of the land species he studied contained continuous, nontortuous gas channels in the stems and roots and that the roots grew in oxygen-free media. Apparently, oxygen transport from shoot to root is present in varying degrees even in mesophytes (Greenwood and Goodman, 1971). This enables them to withstand short spells of soil submergence.

E. SOIL REDUCTION

The most important chemical difference between a submerged soil and a well-drained soil is that a submerged soil is in a reduced state. Except for the thin, brown, oxidized layer at the surface (and sometimes an oxidized zone in the subsoil), a submerged soil is gray or greenish, has a low oxidation-reduction potential, and contains the reduced counterparts of NO_3^- , SO_4^{2-} , Mn^{4+} , Fe^{3+} , and CO_2 : NH_4^+ , H_2S , Mn^{2+} , Fe^{2+} , and CH_4 . Reduction of the soil is a consequence of anaerobic respiration by soil bacteria. During anaerobic respiration organic matter is oxidized and soil components are reduced.

1. Oxidation-Reduction Potential

Oxidation-reduction is a chemical reaction in which electrons are transferred from a donor to an acceptor. The electron donor loses electrons

and increases its oxidation number or is oxidized; the acceptor gains electrons and decreases its oxidation number or is reduced. The source of electrons for biological reductions is organic matter.

The driving force of a chemical reaction is the tendency of the free energy of the system to decrease until, at equilibrium, the sum of the free energies of the products equals that of the remaining reactants. In a reversible oxidation-reduction reaction, this force can be measured in calories or in volts. The change in free energy, ΔG , for the reduction, $\text{Ox} + ne \rightleftharpoons \text{Red}$ is given by

$$\Delta G = \Delta G^0 + RT \ln \frac{(\text{Red})}{(\text{Ox})} \quad (1)$$

where (Red) and (Ox) are the activities of the reduced and oxidized species and ΔG^0 is the free energy change when the activities are unity. Converting calories to volts using the relationship, $\Delta G = -nEF$, we have

$$E = E_0 + \frac{RT}{nF} \ln \frac{(\text{Ox})}{(\text{Red})} \quad (2)$$

in which E is the voltage of the reaction, E_0 is the voltage when (Ox) and (Red) are each unity, and F is the Faraday constant in heat units. If E is measured against the standard hydrogen electrode, it is denoted by E_h . Equation (2) then becomes

$$E_h = E_0 + \frac{RT}{nF} \ln \frac{(\text{Ox})}{(\text{Red})} \quad (3)$$

E_h is a quantitative measure of the tendency of a given system to oxidize or reduce susceptible substances. E_h is positive and high in strongly oxidizing systems; it is negative and low in strongly reducing systems. There is, however, no neutral point, as in pH. E_h , like pH, is an intensity factor. Any chemical reaction which involves the exchange of electrons will be influenced by redox potential (E_h).

If oxidation-reduction reactions are arranged one below the other in descending order of E_0 as in Table I, a given system theoretically can oxidize any one below it under standard conditions. Changes in pH and activities of the reactants and resultants can, however, alter the order.

2. The pE Concept

Sillen (1964, 1967) has suggested that it is more logical and more convenient to use pE instead of E_h in the study of redox equilibria. The com-

TABLE I
Some Redox Systems in Surface Media

System	E ^o (V)	pE ^o	pE ^o ^b
$\frac{1}{4}\text{O}_{2g} + \text{H}^+_{aq} + e = \frac{1}{2}\text{H}_2\text{O}_l$	1.229	20.80	13.80
$\frac{1}{2}\text{NO}^-_{3aq} + \frac{5}{2}\text{H}^+_{aq} + e = \frac{1}{10}\text{N}_{2g} + \frac{3}{2}\text{H}_2\text{O}_l$	1.245	21.06	12.66
$\frac{1}{2}\text{P}_2\text{O}_7^{2-}_{aq} + \text{H}^+_{aq} + e = \frac{1}{2}\text{NO}^-_{2aq} + \frac{1}{2}\text{H}_2\text{O}_l$	0.884	14.11	7.11
$\frac{1}{2}\text{MnO}_2s + 2\text{H}^+_{aq} + e = \frac{1}{2}\text{Mn}^{2+}_{aq} + \text{H}_2\text{O}_l$	1.229	20.80	6.59
$\frac{1}{2}\text{CH}_3\text{COCOOH}_{aq} + \text{H}^+_{aq} + e = \frac{1}{2}\text{CH}_3\text{CHOHCOOH}_{aq}$	0.256 ^c	4.93	-2.67
$\text{Fe}(\text{OH})_3s + 3\text{H}^+_{aq} + e = \text{Fe}^{2+}_{aq} + 3\text{H}_2\text{O}_l$	1.057	17.87	-3.13
$\frac{1}{2}\text{CH}_3\text{CHO}_{aq} + \text{H}^+_{aq} + e = \frac{1}{2}\text{CH}_3\text{CH}_2\text{OH}_{aq}$	0.221 ^c	3.74	-3.26
$\frac{1}{2}\text{SO}_4^{2-}_{aq} + \frac{5}{2}\text{H}^+_{aq} + e = \frac{1}{2}\text{H}_2\text{S}_{aq} + \frac{1}{2}\text{H}_2\text{O}_l$	0.303	5.12	-3.63
$\frac{1}{2}\text{CO}_2g + \text{H}^+_{aq} + e = \frac{1}{2}\text{CH}_4g + \frac{1}{2}\text{H}_2\text{O}_l$	0.169	2.86	-4.14
$\frac{1}{6}\text{N}_2g + \frac{1}{2}\text{H}^+_{aq} + e = \frac{1}{3}\text{NH}^+_{4aq}$	0.274	4.64	-4.69
$\frac{1}{2}\text{HPO}_4^{2-}_{aq} + \frac{5}{2}\text{H}^+_{aq} + e = \frac{1}{2}\text{PH}_3g + \frac{1}{2}\text{H}_2\text{O}_l$	0.212	3.59	-5.16
$\frac{1}{2}\text{NADP}^+_{aq} + \frac{1}{2}\text{H}^+_{aq} + e = \frac{1}{2}\text{NADPH}_{aq}$	-0.106 ^c	-1.79	-5.29
$\frac{1}{2}\text{NAD}^+_{aq} + \frac{1}{2}\text{H}^+_{aq} + e = \frac{1}{2}\text{NADH}_{aq}$	-0.123 ^c	-2.08	-5.58
$\text{H}^+_{aq} + e = \frac{1}{2}\text{H}_2g$	0.000	0.00	-7.00
$\text{Ferredoxin}(\text{ox})_{aq} + e = \text{Ferredoxin}(\text{red})_{aq}$	-0.132 ^d	-7.31	-7.31

^a Using ΔG° values (Latimer, 1952), unless otherwise indicated.

^b pE^o corrected to pH 7.0.

^c Clark (1960).

^d Anon (1965)

mon reagent in redox equilibria is the electron and, according to Sillen, should be treated like other participating species. Just as pH is a measure of proton activity, so is pE, the negative logarithm of the electron activity, a measure of electron activity.

It can be shown that $pE = -\log(e) = Eh/2.303RTF^{-1}$ or $pE = Eh/0.0591$, and $pEo = Eo/0.0591$ at 25°C (Sillen, 1964, 1967; Stumm and Morgan, 1970; Ponnampereuma, 1972). Thus for the equilibrium, $\text{Ox} + ne + m\text{H}^+ \rightleftharpoons \text{Red}$,

$$Eh = Eo + \frac{RT}{nF} \ln \frac{(\text{Ox})}{(\text{Red})} + \frac{mRT}{nF} \ln \text{H}^+ \quad (4)$$

or

$$Eh = Eo + 2.303 \frac{RT}{nF} \log \frac{(\text{Ox})}{(\text{Red})} - \frac{2.303RTm}{nF} \text{pH} \quad (5)$$

or

$$pE = pEo + \frac{1}{n} \log \frac{(\text{Ox})}{(\text{Red})} - \frac{m}{n} \text{pH} \quad (6)$$

or

$$pE = pEo - \frac{1}{n} p(\text{Ox}) + \frac{1}{n} p(\text{Red}) - \frac{m}{n} \text{pH} \quad (7)$$

where $p(\text{Ox})$ and $p(\text{Red})$ denote the negative logarithms of the activities of the oxidized and reduced species.

The pE_o can also be expressed in terms of ΔG^o or the equilibrium constant (K) of the reaction. Thus

$$pE_o = \Delta G^o / 1.364n = \frac{1}{n} \log K \quad (8)$$

In strongly oxidizing systems the electron activity is low, so pE is large and positive. In reducing systems, pE is small or negative. Table I lists some redox systems in soils arranged in descending order of pE_o corrected to pH 7.0. pE is an intensity factor, for it is a measure of the electron free energy level per mole of electrons. It has nothing to do with capacity.

3. Poise

Poise is a useful concept in understanding potential measurements and the behavior of mixed systems. The poise of a redox system is its resistance to changes in potential upon the addition of small amount of oxidant or reductant. Poise increases with the total concentration of oxidant plus reductant, and for a fixed total concentration it is maximum when the ratio of oxidant to reductant is 1. The analysis of the electrode kinetics of the Fe^{3+} - Fe^{2+} system by Stumm and Morgan (1970) leads to a similar conclusion. The poor poise of natural aerated systems is due to the absence of a reversible system in sufficiently high concentration.

Poise also has a bearing on the potentials of mixed systems. When two or more systems are mixed, a redistribution of electrons takes place (if energy barriers are absent) which brings the potentials of the systems to a common value. The final potential is determined by the system which is present in excess.

4. Measurement

The state of reduction of a soil can be defined quantitatively by measures of intensity (redox potential) or capacity (total concentration of reduction products).

a. Redox Potential. At first sight, E_h or pE appears to be the simplest, quickest, and most meaningful method of characterizing soil reduction. A bright platinum electrode placed in the soil should acquire a potential which is determined by the state of reduction of the soil. This potential can be measured against a reference electrode (usually the saturated calomel electrode) with a high impedance voltmeter such as a pH meter. But in practice, intrinsic and extrinsic errors deprive E_h measurements in most natural media of precise thermodynamic significance. Intrinsic er-

rors include electrode malfunctioning, pH effects, absence of true equilibrium, liquid junction potential errors, heterogeneity of the medium, and the discrepancy between the potentials measured in muds and those of their equilibrium solutions. Extrinsic errors are those of sampling muds and extracting the interstitial solutions without altering their composition.

Electrode errors can be minimized by preparing the electrodes carefully and cleaning them properly. Many papers during the past fifty years have discussed the choice of metal, size and shape of the electrode, methods of establishing external contact, and ways of cleaning them before use. There is no need to review the merits and demerits of these methods. Suffice it if we refer to two recent accounts (Janz and Ives, 1961; Adams, 1969) and describe a procedure that we have found to be highly reliable.

A 2 cm length of B and S gauge 18 bright platinum wire is fused to the end of a 4 mm-bore soft glass tube with 1 cm of the wire outside. A few drops of mercury provide electrical contact with the copper wire connecting it to the voltmeter. Electrodes, new or old, are cleaned by rinsing them successively with a detergent, 1 *N* HCl, and distilled water. They are checked against a standard redox buffer just before use. A solution of 0.0033 *M* $K_4Fe(CN)_6$ and 0.0033 *M* $K_3Fe(CN)_6$ in 0.1 *M* KCl which has an Eh of 0.430 V at 25°C (Zobell, 1946) or a suspension of pure quinhydrone in 0.05 *M* potassium acid phthalate, which has an Eh of 0.463 V at 25°C, can serve as a standard. Good electrodes give potentials which agree to within 1 mV of the standard and to within 0.1 mV among themselves.

Although bright platinum electrodes prepared as described above give precise and accurate potentials in buffer solutions and in the solutions of reduced soils, they do not register steady or reproducible potentials in poorly buffered media like aerated soils and natural waters. Morris and Stumm (1967) and Stumm and Morgan (1970) have attributed these defects to the absence of electroactive systems in sufficiently high concentrations in aerobic media and to the presence of mixed systems that are not in equilibrium among themselves. They concluded that even if reproducible potentials are observed in natural systems, the potentials have no precise thermodynamic significance. So they have discouraged the use of redox potential as an environmental parameter.

Despite limitations in aerobic media, good platinum electrodes give steady readings within 5 to 10 minutes of insertion in reduced soils and sediments. But the potentials vary widely from spot to spot (Zobell, 1946; Jeffery, 1961; Aomine, 1962; IRRI,¹ 1966; Yamane and Sato, 1970). The

¹ The International Rice Research Institute.

low precision of mud potentials, due apparently to heterogeneity of the medium, render mud potentials useless in thermodynamic calculations.

Another serious problem is the divergence of potentials measured by electrodes placed in the submerged soil or mud from the potentials of the soil solution drawn out by gravity (Ponnamperuma, 1955; IRRI, 1966), by pressure (Brooks *et al.*, 1968), or by flow under slight hydrostatic pressure into a porous cup embedded in the submerged soil (IRRI, 1970)—all under conditions that precluded oxidation. Soil potentials are higher than solution potentials before appreciable soil reduction but several tenths of a volt lower after the soil is reduced (IRRI, 1966, 1970). Published values for potentials of reduced groundwaters (Hem, 1960; Bass-Becking *et al.*, 1960; Back and Barnes, 1965; Balashova, 1969), the interstitial solutions of reduced ocean muds (Brooks *et al.*, 1968; Friedman and Gavish, 1970), reduced lake waters (Mortimer, 1941, 1942; Kjensmo, 1970), and the solutions of reduced soils (Ponnamperuma *et al.*, 1966a) usually range from 0.2 to 0.0 V and rarely drop below -0.05 V. By contrast, reduced soils and lake and ocean muds give potentials of 0.0 to -0.3 V with occasional plunges to values as low as -0.4 V (Bass-Becking *et al.*, 1960). Since the liquid junction potential error accounts for only about 0.025 V, other explanations have been suggested.

Ponnamperuma and Castro (1964) noted some similarities between the potentials and dE/dpH values of reduced soils and those of bacterial suspensions. We hypothesized that soil potentials were highly localized bacterial potentials. Later work (IRRI, 1966) suggested that the differences between mud and solution potentials may be due to the presence of oxidant or reductant in the solid phase. Brooks *et al.* (1968) noted that potentials of marine mud cores were about 0.2 V lower than their interstitial waters. They attributed the low mud potentials to some interaction between the electrode and the mud. But we now have evidence that if a reduced soil is equilibrated anoxically with water and CO_2 (at the partial pressure of CO_2 in the mud) and allowed to settle, Eh of the sediment and supernatant solution are nearly identical and this potential is almost that of the soil solution drawn by gravity (IRRI, 1967). In other words, potentials of soil solutions are equilibrium potentials.

The variability of soil potentials and their divergence from those of the equilibrium soil solutions explain why several workers who used soil potentials as a measure of reduction (Jeffery, 1961; Ponnamperuma and Castro, 1964; Ponnamperuma, 1965; Bohn, 1968, 1969) failed to obtain the expected theoretical relationships among Eh, pH, and ion activities. Those who measured solution potentials (Hem, 1960; Back and Barnes, 1965; Ponnamperuma *et al.*, 1966a, 1967, 1969b; Skopintsev *et al.*, 1966) were more successful. It is also noteworthy that the Eh, pH, and Fe^{2+} concentra-

tions in reduced lake waters reported by Pearsall and Mortimer (1939), Mortimer (1941, 1942), and Kjensmo (1970) conform to the equilibrium values for the $\text{Fe}(\text{OH})_2\text{-Fe}^{2+}$ system.

The hydrogen ion concentration affects Eh by direct participation in the oxidation-reduction or by influencing the dissociation of oxidant or reductant (Clark, 1960). So dE/dpH varies with the system. Although most workers use -0.059 V/pH at 25°C as the correction factor, the experimental values range from about -0.06 for aerobic soils to as steep a slope as -0.232 for some reduced soils (Patrick, 1960). This uncertainty makes many potentials corrected to pH 7 unreliable. We have shown theoretically and experimentally that the dE/dpH slope for the solutions of reduced ferruginous soils after the peak of water-soluble Fe^{2+} is -0.059 (Ponnamperuma *et al.*, 1967). For most mineral muds, adjustment of Eh for pH is an unnecessary refinement because the pH values of reduced muds are about 7 and mud potentials are in any case imprecise.

Although soil or mud potentials have no precise thermodynamic significance, they are semiquantitative measures of soil reduction. They are therefore useful in describing the state of reduction of wet soils and lake and ocean sediments. These potentials are best measured *in situ* and with minimum disturbance of the mud. Several probes for the simultaneous measurement of Eh and pH have been described (Mortimer, 1942; Starkey and Wight, 1946; Matsuo and Kato, 1956; Whitfield, 1969). If *in situ* measurement is not possible, the potential should be determined in cores of mud, immediately after collection, without dilution with water or exposure to air. Avoiding direct contact of the calomel reference electrode with the mud minimizes the liquid junction potential error (Jenny *et al.*, 1950; Peech *et al.*, 1953). Devices for extracting undisturbed mud cores from waterlogged soils and lake and ocean muds have been described by Mortimer (1942), Kawaguchi *et al.* (1956), Walker (1964), and Mackereth (1969).

The potential of the liquid phase of a reduced mud is far more meaningful and reliable than the potential of the mud itself. The liquid phase, that is, the interstitial or pore water or the soil solution, is a homogeneous phase in quasi, dynamic, or near equilibrium with the solid and gas phase of the mud, as the liquid phases of similar natural systems are believed to be (Garrels, 1959; Schuffelen and Koenigs, 1962; Morgan, 1967). The potential and pH of such a solution can be measured precisely with a minimum of the liquid junction potential error. (We have routinely obtained potentials that agree within 0.1 mV at duplicate electrodes in the solutions of reduced soils.) The main problem is to extract the solution and transfer it to the electrometric cell without altering its composition.

The method of extraction depends on the sample. The solutions of

permeable submerged soils in pots can be drawn by gravity into flasks filled with purified nitrogen, transferred into the electrometric cell under slight nitrogen pressure, and the potential and pH measured within a few minutes of sample collection. The interstitial solutions of muds of low permeability and of core samples from paddy fields or lake and ocean bottoms have to be squeezed out by applying gas, mechanical, or centrifugal pressure. Excessive pressure alters the ionic composition of the solution. Manheim (1966) and Presley *et al.* (1967) used presses for extracting the interstitial water of ocean sediments. Takai *et al.* (1963) obtained the soil solution by centrifugation. We have found that low-temperature centrifugation gives clear solutions differing little from those drawn by gravity. Suction or contact for more than a few minutes with even an inert gas should be avoided because these treatments lead to loss of CO₂ from the solution and a consequent increase in pH and a decrease in Eh (Ponnamperuma *et al.*, 1966a; IRRI, 1970). Thus Millipore filtration in an inert atmosphere may lead to loss of CO₂. These extrinsic problems do not arise when the measurements are done *in situ* in natural or waste waters using the probes described by Back and Barnes (1965) and Schmidt (1970).

b. Reducing Capacity. Three methods have been proposed for measuring the reducing capacity of muds: titrating with an oxidizing agent (Sturgis, 1936; Starkey and Wight, 1946; Zobell, 1946); determining total reduced Fe(II) (Ponnamperuma, 1955; Jeffery, 1961; IRRI, 1964); and oxygen consumption by the mud (Howeler and Bouldin, 1971).

The titration method is unsatisfactory because the value obtained depends on the conditions of oxidation. If strong, reducing capacity is overestimated because organic matter and Fe(II) in clay minerals are included; if mild, genuine reduction products are not estimated. Consumption of dichromate under standard conditions as proposed by Sturgis (1936) may, however, provide comparative values of reducing capacity. Total reduced Fe(II) is not a good measure of reduction capacity because other reduction products are excluded. Oxygen consumption by the mud (Howeler and Bouldin, 1971) may give an ecologically more significant measure of reducing capacity than the chemical methods.

The reducing capacity of soil solutions can be found by determining either the biological oxygen demand (BOD) or the chemical oxygen demand (COD) by standard methods (American Public Health Association, 1971). But oxygen consumption by the solution constitutes only a small fraction of the total reduction capacity.

5. Anaerobic Respiration

Submerging a soil cuts off its oxygen supply. The aerobic organisms use up the oxygen present in the soil and become quiescent or die. The faculta-

tive and obligate anaerobes then proliferate (Takai *et al.*, 1956; Takeda and Furusaka, 1970) using carbon compounds as substrate and using oxidized soil components and dissimilation products of organic matter as electron acceptors in respiration (Doelle, 1969). The switch from aerobic to anaerobic respiration occurs at the very low oxygen concentration of $3 \times 10^{-6} M$ (Greenwood, 1961).

Aerobic and anaerobic respiration probably follow common paths until the formation of pyruvic acid (Clifton, 1957; Doelle, 1969). The overall reaction may be represented by



In aerobic respiration the electrons picked up by nicotinamide adenine dinucleotide are transferred to atmospheric oxygen through the mediation of carriers and the terminal oxidases. Pyruvic acid itself is oxidized through the TCA cycle with oxygen as terminal electron acceptor. The regeneration of NAD^+ enables the system to operate cyclically and complete the oxidation of substrate. In the absence of oxygen, facultative and obligate anaerobes use NO_3^- , $Mn(IV)$, $Fe(III)$, SO_4^{2-} , dissimilation products of organic matter, CO_2 , N_2 , and even H^+ ions as electron acceptors in their respiration reducing NO_3^- to N_2 , $Mn(IV)$ to $Mn(II)$, $Fe(III)$ to $Fe(II)$, SO_4^{2-} to H_2S , CO_2 to CH_4 , N_2 to NH_3 , and H^+ to H_2 . Also, anaerobic respiration produces substances that reduce soil components chemically (Bloomfield, 1951). Thus the switch from aerobic to anaerobic respiration ushers in the reduction of the soil.

The requirements for soil reduction are the absence of oxygen, the presence of decomposable organic matter, and anaerobic bacterial activity. The course, rate, and degree of reduction are influenced by the nature and content of organic matter, temperature, the nature and content of electron acceptors, and pH. Also, air-drying a wet soil intensifies reduction after submergence (Aomine, 1962; Yoshizawa, 1966) and N, P, K fertilizers accelerate reduction in soils deficient in these nutrients (Chiang and Yang, 1970).

6. Sequential Reduction

Reduction of a submerged soil proceeds roughly in the sequence (Table I) predicted by thermodynamics (Ponnamperuma, 1955; Ponnamperuma and Castro, 1964; Takai and Kamura, 1966; Turner and Patrick, 1968). The same sequence is observed in the vertical distribution of redox components in a well eutrophied lake and in the succession of redox reactions in anaerobic batch digesters (Stumm and Morgan, 1970). The sequence is also reflected in the microbial succession—acrobies, facultative anaer-

obes, strict anaerobes—after submerging a soil (Takeda and Furusaka, 1970).

Oxygen is the first soil component to be reduced, and it becomes undetectable within a day after submerging a soil (Section III, A). The next oxidant to be attacked is nitrate, but nitrate reduction begins only after the oxygen concentration has dropped to a very low value (Mortimer, 1941; Skerman and MacRae, 1957; Bremner and Shaw, 1958; Greenwood, 1962; Turner and Patrick, 1968).

Just as the presence of oxygen retards nitrate reduction, so does the presence of nitrate retard the reduction of other redox components. Nitrate stabilizes potentials at 0.2 to 0.4 V, and prevents the release of Mn^{2+} , Fe^{2+} , S^{2-} , CH_4 , and H_2 in lake waters and muds (Pearsall, 1938; Pearsall and Mortimer, 1939; Mortimer, 1941, 1942) and in submerged soils (Ponnamperuma, 1955; Ponnamperuma and Castro, 1964; Yamane and Sato, 1968; Turner and Patrick, 1968). Nitrate also suppresses odor development in effluents and sewage (Sanborn, 1941; Heukelekian, 1943) and methane formation in anaerobic sewage digesters (Brezonik and Lee, 1966). Nitrate prevents the formation of volatile acids (Greenwood and Lees, 1960) but is not as effective an oxidant of organic matter as oxygen (Schroeder and Busch, 1967).

Manganese dioxide follows nitrate in the reduction sequence. But its influence is weaker than that of nitrate because it is insoluble in water and is used as an electron acceptor in respiration by only a limited number of bacteria. However, native or added MnO_2 retards the decrease in Eh of flooded soils and prevents the buildup of high concentrations of Fe^{2+} and other reduction products (Ponnamperuma and Castro, 1964; Ponnamperuma *et al.*, 1965).

The next mineral system in thermodynamic sequence is the $Fe(OH)_3-Fe^{2+}$ system. Because of the low standard potential of this system (Table I), its influence on soil reduction is not as obvious as that of NO_3^- or MnO_2 . But I noted that soils high in Fe(III) showed a slower fall in Eh in the zone -0.05 to -0.2 V (Ponnamperuma, 1965), while Asami and Takai (1970) found that addition of amorphous Fe_2O_3 to paddy soils depressed CH_4 formation.

Although the reduction of a submerged soil proceeds in a stepwise manner, roughly in thermodynamic sequence, attempts to define the potentials at which one system comes into operation and yields to the next have not been successful. This is apparent from the wide range of critical potentials reported by various workers. I have previously listed these potentials and discussed the reasons for their variability (Ponnamperuma, 1972). But the following critical potentials reported by Patrick (1964), Connell and

Patrick (1968), and Turner and Patrick (1968) for stirred soil suspensions may provide a rough guide to the progress of reduction:

Observation	E ₇ (volt)
Oxygen (undetectable)	0.99
Nitrate (undetectable)	0.92
Manganese (detectable)	0.90
Iron (detectable)	0.12
Sulfate (undetectable)	-0.15

IV. Electrochemical Changes in Submerged Soils

Submerging a soil brings about a variety of electrochemical changes. These include (a) a decrease in redox potential, (b) an increase in pH of acid soils and a decrease in pH of alkaline soils, (c) changes in specific conductance and ionic strength, (d) drastic shifts in mineral equilibria, (e) cation and anion exchange reactions, and (f) sorption and desorption of ions.

I discuss changes in pH, Eh, and specific conductance in this section and mineral equilibria in Section VI. The information on ion exchange reactions and sorption and desorption of ions in submerged soils is too meager and unreliable for review.

A. REDOX POTENTIAL

The single electrochemical property that serves to distinguish a submerged soil from a well-drained soil is its redox potential. The low potentials (0.2 to -0.4 V) of submerged soils and sediments reflect this reduced state, the high potentials (0.8 to 0.3 V) of aerobic media, their oxidized condition.

1. Submerged Soils and Muds

When an aerobic soil is submerged, its Eh decreases during the first few days and reaches a minimum; then it increases, attains a maximum, and decreases again asymptotically to a value characteristic of the soil, after 8-12 weeks of submergence (Ponnamperuma, 1955, 1965; Motomura, 1962; Yamane and Sato, 1968). The course, rate, and magnitude of the Eh decrease depend on the kind and amount of organic matter,

the nature, and content of electron acceptors, temperature,² and the duration of submergence.

The presence of native or added organic matter sharpens and hastens the first minimum, nitrate abolishes it (Ponnamperuma, 1955; Yamane and Sato, 1968). The rapid initial decrease of Eh is apparently due to the release of reducing substances accompanying oxygen depletion before Mn(IV) and Fe(III) oxide hydrates can mobilize their buffer capacity. According to Yamane and Sato (1968), the first minimum potential can be as low as -0.42 V and can be accompanied by the evolution of hydrogen.

Nitrate stabilizes potentials for some time at an E_h value of about 0.2 V; Mn(IV) and Fe(III) oxides, at lower values (Ponnamperuma and Castro, 1964; Ponnamperuma, 1965).

The influence of soil factors on Eh changes have been summarized as follows (Ponnamperuma and Castro, 1964; Ponnamperuma, 1965): (a) soils high in nitrate (more than 275 ppm NO₃⁻) have positive potentials for several weeks after submergence; (b) soils low in organic matter (less than 1.5%) or high in manganese (more than 0.2%) maintain positive potentials even 6 months after submergence; (c) soils low in active manganese and iron (sandy soils) with more than 3% organic matter attain Eh values of -0.2 to -0.3 V within 2 weeks of submergence; and (d) the fairly stable potentials reached after several weeks of submergence lie between 0.2 and -0.3 V.

Temperatures above and below 25°C retard the decrease in Eh but the degree of retardation varies with the soil (IRRI, 1967, 1969; Cho and Ponnamperuma, 1971). The retardation of reduction is most pronounced in acid soils and hardly noticeable in neutral soils high in organic matter. The fairly stable potentials attained after about 12 weeks of submergence are practically independent of temperature in the range 15 to 45°C.

The surfaces of submerged soils and oxygenated lake and ocean muds have potentials (0.3 to 0.5 V) which differ little from those of the overlying water. But below the oxygenated layer which is a few millimeters thick, the potential drops sharply and may be strongly negative (Section III, B). The oxidized state of the surface layer is not permanent: during stagnation the surface may undergo reduction. According to Mortimer (1941, 1942), the critical potential for reduction of the soil-water interface is 0.2 V. Lake and ocean muds have potentials of 0.3 to -0.3 V, with occasional plunges to -0.4 V (Bass-Becking *et al.*, 1960).

² Unless otherwise indicated, the temperature of the studies of the chemical and electrochemical kinetics described in this chapter was 25–32°C. All laboratory equilibrations were done at 25°C.

2. Natural Waters

The redox potentials of lake and sea waters and their muds reflect their state of oxidation-reduction. Waters in contact with the atmosphere have potentials of 0.5 to 0.3 V (Hutchinson, 1957; Bass-Becking *et al.*, 1960; Kaplan and Rittenberg, 1963). Anoxic waters have potentials of 0.2 to 0.0 V (Mortimer, 1941, 1942; Hutchinson, 1957; Kjensmo, 1970), although potentials as low as -0.15 V have been reported for stagnant sea water (Richards, 1965). The potentials of interstitial waters of marine sediments lie between 0.45 and -0.11 V (Friedman and Gavish, 1970). The fairly stable potentials attained by the solutions of flooded soils after several weeks of submergence range from 0.2 to 0.0 V with an occasional dip to -0.05 V.

The vertical changes in potentials in natural waters depend on the degree of mixing and the nutrient content of the water. If thermal or mechanical mixing is active, the surface potential is maintained to great depths. But in eutrophic lakes that undergo thermal stratification (Section III, C), the potential drops sharply in the thermocline and may have, in the hypolimnion, values as low as those of the reduced sediment (Mortimer, 1941, 1942).

3. Practical Significance

Despite theoretical and practical problems, the redox potential of a soil or sediment provides a quick, useful, semiquantitative measure of its oxidation-reduction status. Since the oxidation-reduction status of soils affects the growth of plants and that of sediments influences aquatic life and the capacity of sediments to absorb certain terrestrial wastes, Eh can be a useful environmental parameter. Several workers have confirmed this.

Bradfield *et al.* (1934) successfully used Eh of the soil in early spring to demarcate low-yielding orchard sites associated with impeded drainage where measurements of groundwater alone were of little avail. Pearsall and Mortimer (1939) noted an association between Eh and the distribution of plant species in marshes and stressed the ecological significance of the oxidation-reduction state of a soil. Aomine (1962) reported that a mosaic of high and low redox spots in flooded fields benefits rice. Starkey and Wight (1946) found that anaerobic corrosion of iron pipes was severe below 0.1 V; above 0.4 V it was absent. Mortimer (1941, 1942) found that when the E. of the mud-water interface dropped below 0.2 V, the mud underwent reduction, lost its absorptive capacity, and released manganese, iron, phosphate, and silica into the overlying water. Whitfield (1969) admitted the shortcomings of Eh measurements but found them a valuable guide in mapping the distribution of estuarine sediments. Bass-Becking *et al.* (1960) examined 6200 pairs of Eh-pH readings in natural

media and established Eh-pH limits for different natural environments and bacterial ecosystems. Pohland and Mancy (1969) discussed the theoretical difficulties in the use of Eh for characterizing heterogeneous biochemical systems but concluded that Eh-pH can be used as an operational parameter in anaerobic digestion of waste organic materials. The optimum range was -0.275 to -0.285 V (Pohland, 1969). Weijden *et al.* (1970) found that the manganese content of deep-sea sediments increased sharply in the Eh range 0.32 – 0.42 V. Borchert (1965) defined zones of deposition of limonite, siderite, and pyrites in ocean sediments in terms of pH and Eh. Garrels and Christ (1965) have used Eh and pH to describe mineral associations in nature, and Hem (1960) and others, in the study of groundwaters.

Although Eh reveals whether a soil is aerobic or anaerobic, it is unsatisfactory as a measure of oxygen concentration in soils (Ponnamperuma, 1972). Also, for the reasons discussed by me (Ponnamperuma, 1965), it is of little diagnostic value in rice culture. But the redox potentials of reduced lake and ocean waters, the interstitial waters of reduced soils and muds, and groundwaters are thermodynamically meaningful and have been used successfully in the quantitative study of redox equilibria (Section VI).

B. pH

1. The pH Values of Submerged Soils and Sediments

When an aerobic soil is submerged, its pH decreases during the first few days (Motomura, 1962; Ponnamperuma, 1965), reaches a minimum, and then increases asymptotically to a fairly stable value of 6.7 – 7.2 a few weeks later. The overall effect of submergence is to increase the pH of acid soils and to depress the pH of sodic and calcareous soils. Thus submergence makes the pH values of acid soils (except those low in iron) and alkaline soils converge to 7 (Fig. 1). The following figures, gleaned from several sources (Pearsall, 1938; Bass-Becking *et al.*, 1960; Ponnamperuma *et al.*, 1966a; Friedman and Gavish, 1970; Weijden *et al.*, 1970), show that the pH of submerged soils and sediments and their interstitial solutions is about 7:

Submerged soils	6.7–7.2
Solutions of submerged soils	6.5–7.0
Fresh water sediments	6.0–7.0
Sea sediments	7.0–7.8
Interstitial waters of sea sediments	6.2–7.7
Marsh soils (flat bogs)	5.0–7.0

The low lower pH limit of marsh soils may be due to humic acids (Ruttner, 1963).

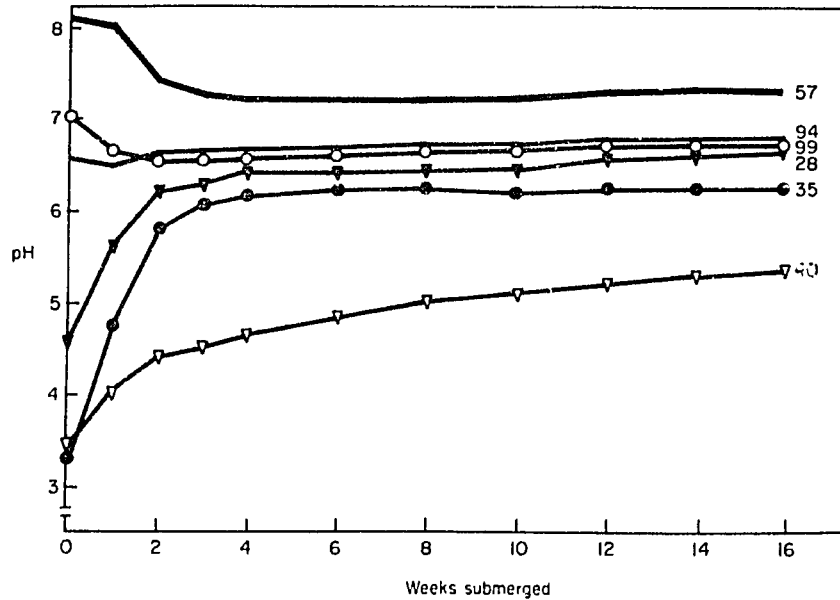


FIG. 1. Kinetics of the pH values of some submerged soils

Soil No.	Texture	pH	O.M %	Fe %	Mn %
28	Clay	4.9	2.9	1.70	0.08
35	Clay	3.4	6.6	2.60	0.01
40	Clay	3.8	7.2	1.50 0.04	0.00
57	Clay loam	8.7	2.2	0.63	0.07
94	Clay	6.7	2.6	0.96	0.09
99	Clay loam	7.7	1.8	1.55	0.08

Draining and exposure to air reverse the pH changes in paddy soils (Dennett, 1932), in mangrove swamps (Hesse and Jeffery, 1963), in lake muds and bogs (Pearsall, 1938; Misra, 1938), and in anaerobic soils (Starkey and Wight, 1946; IRRI, 1965).

The pH values of submerged soils measured in air-free aqueous suspensions are slightly higher than those of the corresponding soil solutions (Ponnamperuma *et al.*, 1966a). This may be due to the inversion of the suspension effect by the divalent cations Ca^{2+} , Fe^{2+} , and Mn^{2+} (Raupach, 1954) and to dilution and loss of CO_2 during measurement of the pH of the soil suspension (Ponnamperuma *et al.*, 1966a). Because the soil solution is the thermodynamically meaningful phase and the pH of a solution can be measured with the minimum of the liquid junction potential

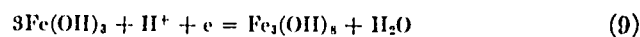
and CO_2 errors, I use pH values of the soil solution in the description of pH changes in flooded soils and their quantitative interpretation.

Although the pH values of acid soils increase after submergence and those of sodic and calcareous soils decrease, soil properties (and temperature) markedly influence the pattern of changes (Fig. 1). Soils high in organic matter and in reducible iron attain a pH of about 6.5 within a few weeks of submergence. Acid soils low in organic matter or in active iron slowly attain pH values which are less than 6.5. In fact, acid sulfate soils low in iron may not attain a pH of more than 5 even after months of submergence. Organic matter magnifies the decrease in pH of sodic and calcareous soils (IRRI, 1966). Low temperature (IRRI, 1968; Cho and Ponnampereuma, 1971) or the presence of nitrate (Yamane, 1958; IRRI, 1965) retards the increase in pH.

2. Interpretation of pH Changes

The decrease in pH shortly after submergence is probably due to the accumulation of CO_2 produced by respiration of aerobic bacteria, because CO_2 depresses the pH even of acid soils (Nicol and Turner, 1957). The subsequent increase in pH of acid soils is due to soil reduction (Ponnampereuma *et al.*, 1966a). The pH values of submerged calcareous and sodic soils are lower than those of the aerobic soils because of the accumulation of CO_2 , for Whitney and Gardner (1943), Yaalon (1957), and Ponnampereuma *et al.* (1966a) have shown that the pH of alkaline soils is highly sensitive to changes in the partial pressure of CO_2 (P_{CO_2}).

Table I shows that all the important reduction reactions that occur in nature involve the consumption of H^+ ions. This means a decrease in acidity or an increase in net OH^- ion concentration. The increase in pH is not determined by the absolute number of H^+ ions consumed or OH^- ions produced but by the ratio, $R = \text{H}^+ \text{ consumed} / \text{e} \text{ consumed}$, as Bostrom (1967) has pointed out. This ratio is merely the coefficient of H^+ in the equations in Table I. It is highest for the reduction of $\text{Fe}(\text{OH})_3$. The overall value of R for this reaction, however, is 1 because after the peak of water-soluble Fe^{2+} , the equilibrium



comes into operation (Ponnampereuma *et al.*, 1967). Since most soils contain more Fe(III) oxide hydrates than any other oxidant, the increase in pH of acid soils is largely due to the reduction of iron. Thus the pH of reduced ferruginous soils can be related to Eh and Fe^{2+} activity by

$$\text{Eh} = 1.06 - 0.059 \log \text{Fe}^{2+} - 0.177\text{pH} \quad (10)$$

before the peak of water-soluble iron and afterward by the equations (Ponnamperuma *et al.*, 1967)

$$\text{Eh} = 1.37 - 0.0885 \log \text{Fe}^{2+} - 0.236\text{pH} \quad (11)$$

$$\text{Eh} = 0.43 - 0.059\text{pH} \quad (12)$$

The pH values of soils high in sodium sulfate may increase after submergence because Na_2SO_4 is reduced to H_2S and NaHCO_3 forms (Section V, E).

The pH values of sodic soils can be related to the $\text{Na}_2\text{CO}_3\text{-H}_2\text{O-CO}_2$ equilibrium and those of calcareous soils to the $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$ equilibrium (Section VI, B).

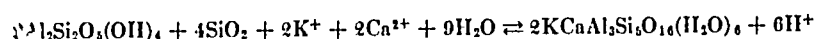
Although the increase in pH of acid soils is brought about by soil reduction, the fairly stable pH attained after a few weeks of submergence is regulated by P_{CO_2} . For reduced ferruginous soils the empirical relationship is

$$\text{pH} = 6.1 - 0.58 \log P_{\text{CO}_2} \quad (13)$$

This relationship is almost identical with that for an aqueous suspension of $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ equilibrated with CO_2 (Ponnamperuma *et al.*, 1969a).

The pH values (and therefore Eh) of submerged soils, whether acid or alkaline, are highly sensitive to loss of CO_2 (Fig. 2). This must be borne in mind during the sampling of reduced soils and the extraction and handling of their interstitial solutions (Section III, E, 4, a). The pH of most reduced soils equilibrated with CO_2 at 1 atm is 6.1 (Ponnamperuma *et al.*, 1969a).

Sillen (1961) has proposed that the reaction of sea water, which is buffered around pH 8.1, is regulated by an equilibrium of the type



with

$$\log K = 6 \log (\text{H}^+) - 2 \log (\text{K}^+) - 2 \log (\text{Ca}^{2+}) \quad (14)$$

The carbonate system, $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$, according to Sillen is only an indicator of pH, not the mechanism of the buffer action. Garrels (1965) has suggested that dissolved silica and metallic cations recombine with degraded silicates and release H^+ ions. The H^+ ions produced by this reversal of weathering prevent an increase in the alkalinity of sea water. Presumably on the basis of these observations, Bohn (1969) surmised that silicate equilibria rather than the redox equilibria control the pH of submerged soils.

Martin (1970) and Stumm and Morgan (1970) have briefly reviewed the role of silicates vis-à-vis carbonates and have proposed two mechanisms buffering the pH of sea water: the carbonate system, a short-term

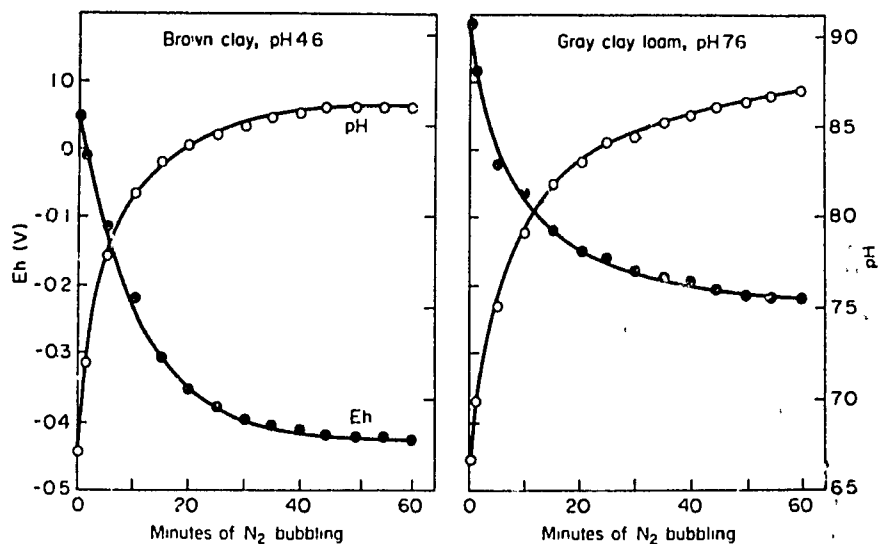


Fig. 2. Influence of the loss of CO_2 (caused by bubbling N_2) on pH and Eh of the solutions of two soils, 10 weeks after submergence.

mechanism; and the silicate system, a long-term mechanism operating perhaps over thousands of years. In waterlogged soils, in paddy soils, and in recent lake and ocean sediments, redox and carbonate systems control the pH.

3. pH Effects

The pH value profoundly influences hydroxide, carbonate, sulfide, phosphate, and silicate equilibria in submerged soils. These equilibria regulate the precipitation and dissolution of solids, the sorption and desorption of ions, and the concentrations of such nutritionally significant ions or substances as Al^{3+} , Fe^{2+} , H_2S , H_2CO_3 , and undissociated organic acids. Some of these mineral equilibria are discussed in Section VI. Since excess water-soluble aluminum and iron are the toxic factors in acid sulfate rice soils (Nhung and Ponnampereuma, 1966) and iron deficiency limits the growth of rice on sodic and calcareous soils (Ponnampereuma, 1965), the influence of pH on the solubility of aluminum and iron is of special interest.

The concentration of water-soluble aluminum in a soil is related to pH (Raupach, 1963) by

$$\text{pAl}_m = 2\text{pH} - 4.41 \quad (15)$$

Thus at a pH of 3.5 (a common pH value for acid sulfate soils), the concentration of water-soluble aluminum is 69 ppm. This concentration is

much above the toxic limit for rice. But if the pH is raised to 4.4 by limin or if the soil is kept submerged for a few weeks before planting, the aluminum concentration should drop to 1 ppm and aluminum toxicity be averted. Nhung and Ponnampereuma (1966) have confirmed this experimentally.

The concentration of water-soluble Fe^{2+} , like that of Al, is highly sensitive to pH changes as Eq. (16) (Ponnampereuma, 1955) indicates:

$$pFe^{2+} = 2pH - 10.8 \quad (16)$$

If solid-phase $Fe_2(OH)_2$ is present, the activities of water-soluble Fe^{2+} (concentrations would be higher) are 3.5 ppm at pH 7.5, 35 ppm at pH 7, 350 ppm at pH 6.5, and 3500 ppm at pH 6. The detection of 6600 ppm Fe^{2+} in the solution of a flooded acid sulfate soil when its pH was 5.67 (Nhung and Ponnampereuma, 1966) is therefore not surprising. A pH change of 0.5 unit above or below 7 can spell the difference between iron deficiency and toxicity of rice on flooded soils (Ponnampereuma 1965).

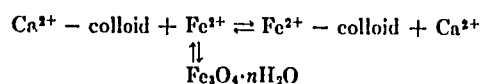
The increase in pH of acid soils is one of the benefits of flooding rice soils because it eliminates aluminum toxicity, minimizes iron toxicity, and increases the availability of phosphorus.

C. SPECIFIC CONDUCTANCE

1. Kinetics

The specific conductance of the solutions of most soils increases after submergence, attains a maximum, and declines to a fairly stable value, which varies with the soil. The changes in conductance reflect the balance between reactions that produce ions and those that inactivate them or replace them with slower moving ions.

The increase in conductance during the first few weeks of flooding is due to the release of Fe^{2+} and Mn^{2+} from the insoluble Fe(III) and Mn(IV) oxide hydrates, the accumulation of NH_4^+ , HCO_3^- , and $RCOO^-$, and (in calcareous soils) the dissolution of $CaCO_3$ by CO_2 and organic acids. An additional factor is the displacement of ions, especially cations, from soil colloids by reactions of the following type



This is evident from the similarity of the curves for the kinetics of ($\text{Fe}^{2+} + \text{Mn}^{2+}$), other cations, and specific conductance (Fig. 3). Conductance increases in spite of the replacement of NO_3^- and SO_4^{2-} by the less mobile HCO_3^- ion formed during denitrification and sulfate reduction and in spite of the neutralization (in acid soils) of the highly mobile H^+ ions. The decline after the maximum is due mainly to the precipitation of Fe^{2+} as $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ and Mn^{2+} as MnCO_3 (Section V, C, 1). The decrease in conductance of calcareous soils is caused by the fall in partial pressure of CO_2 and the decomposition of organic acids (Section V, A, 3).

The kinetics of specific conductance varies widely with the soil. Neutral and alkaline soils starting with high conductances attain values exceeding 2 mmhos/cm and show a slow decline. Strongly acid soils have low initial conductances. They show steep increases to 2–4 mmhos/cm during the first 4 weeks of flooding, and then decline sharply, in striking similarity to the kinetics of water-soluble iron and manganese (Fig. 3). Among non-saline soils, the highest specific conductances (4–5 mmhos/cm) are observed in soils that have a low cation exchange capacity and are high in organic matter.

A specific conductance exceeding 4 mmhos/cm indicates the presence of too much salt for the healthy growth of rice (IRRI, 1967). Values considerably in excess of 4 mmhos/cm are possible in submerged soils that have a low cation exchange capacity and are high in organic matter (especially if they are fertilized), and in acid sulfate soils.

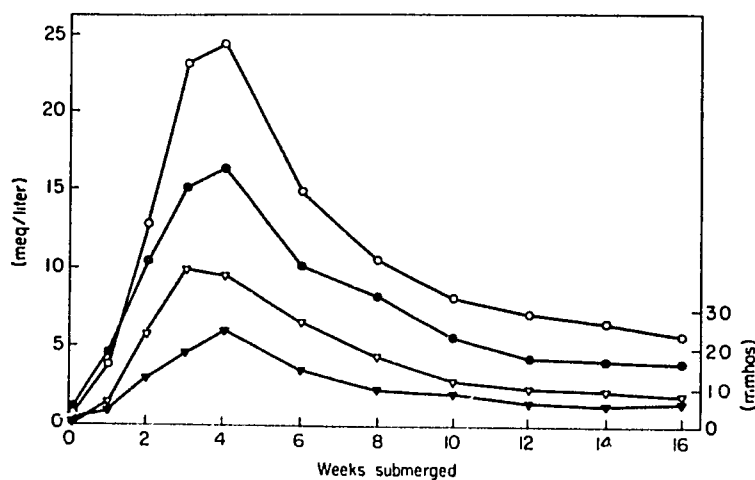


FIG. 3. Kinetics of specific conductance and cation concentrations in a submerged ferrallitic soil. ○ Total alkalinity (meq/l); ● $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{NH}_4^+ + \text{Na}^+ + \text{K}^+$ (meq/l); ▽ $\text{Fe}^{2+} + \text{Mn}^{2+}$ (meq/l); ▼ Specific conductance (mmhos/cm at 25°C).

2. Specific Conductance and Ionic Strength

The specific conductance of an aqueous solution, at a fixed temperature depends on the kind and concentration of ions present. Since the kind and concentrations of ions determine to a large extent the ionic strength ($I = \frac{1}{2} \sum c_i z_i^2$, where I is ionic strength, c_i the concentration in moles per liter and z_i the valence), there should be a quantitative relationship between specific conductance and ionic strength. When we tested this prediction experimentally (Ponnamperuma *et al.*, 1966b), we found that, in spite of wide variations in the ionic composition of the solutions of reduced soils, the ionic strength in moles per liter was numerically equal to 16 times the specific conductance (κ) in mhos/cm at 25°C, up to ionic strengths of 0.05.

The ionic strength of a solution is chemically and, perhaps, ecologically an important property of a soil solution because it determines the activity coefficients of the ions present. A knowledge of the activity coefficient of ions is necessary for the thermodynamic study of mineral equilibria in flooded soils. The activity coefficient (γ) of an ion can be derived from the Debye-Hückel equation if the concentrations of all the ions present are known. Use of $I = 16\kappa$ eliminates the need for chemical analysis and enormously simplifies the calculation of ionic strength. Substituting 16κ for I , we can rewrite the Debye-Hückel equation and its simpler form as follows

$$-\log \gamma = \frac{4Az^2\kappa^{1/2}}{1 + 4aB\kappa^{1/2}} \quad (17)$$

$$-\log \gamma = 4Az^2\kappa^{1/2} \quad (18)$$

And for dilute solutions the Henderson-Hasselbalch equation becomes

$$\text{pH} = 7.84 + \log [\text{HCO}_3^-] - \log P_{\text{CO}_2} - 2\alpha^{1/2} \quad (19)$$

where $[\text{HCO}_3^-]$ is the concentration of bicarbonate in moles per liter (Ponnamperuma *et al.*, 1966b).

V. Chemical Transformations in Submerged Soils

The chemical properties of a soil undergo a drastic transformation on submergence. The oxidized constituents, Fe(III), Mn(IV), NO_3^- , and SO_4^{2-} , that characterize a well drained soil, virtually disappear and are replaced by their reduced counterparts, Fe(II), Mn(II), NH_4^+ , and S^{2-} and the course of organic matter decomposition is diverted from CO_2 production to the formation of an array of unstable organic substances, for

lowed by the evolution of CO_2 and CH_4 . These changes have important implications for geochemistry, limnology, rice culture, and pollution control.

A. CARBON

The two main transformations of carbon in nature are photosynthesis and respiration. On the balance between these two processes depend (a) the amount of organic matter that accumulates in soils and sediments, and (b) the quality of streams, lakes, and estuaries. In submerged soils, respiration (decomposition of organic matter) is the main transformation.

1. *Decomposition of Organic Matter*

The decomposition of organic matter in a submerged soil differs from that in a well drained soil in two respects: it is slower; and the end products are different.

In a well drained soil, decomposition of plant residues is accomplished by a large group of microorganisms assisted by the soil fauna. Owing to the high energy release associated with the aerobic respiration of these organisms, decomposition of substrate and synthesis of cell substance proceed rapidly. The bulk of freshly added organic matter disappears as CO_2 , leaving a residue of resistant material, chiefly altered lignin. Also, there is a heavy demand on nutritional elements, especially nitrogen. In submerged soils, the decomposition of organic matter is almost entirely the work of facultative and obligate anaerobes. Since anaerobic bacteria operate at a much lower energy level than aerobic organisms, both decomposition and assimilation are much slower in submerged soils than in aerobic soils. The accumulation of plant residues in marshes and in underwater sediments (Degens, 1965) illustrates this point.

The most striking difference between anaerobic and aerobic decomposition lies in the nature of the end products. In a normal well drained soil the main end products are CO_2 , nitrate, sulfate, and resistant residues (humus); in submerged soils, they are CO_2 , hydrogen, methane, ammonia, amines, mercaptans, hydrogen sulfide, and partially humified residues.

2. *Pyruvic Acid Metabolism*

Carbohydrate metabolism is probably the same in both aerobic and anaerobic soils until the formation of the key metabolite, pyruvic acid. For example, cellulose is hydrolyzed to soluble sugars by extracellular enzymes; the sugars enter the microbial cell and are hydrolyzed further to glucose, which is then oxidized to pyruvate by the EMP, HMP, ED, or the phos-

phosphoketolase pathway (Doelle, 1969). The overall oxidation of glucose to pyruvic acid may be represented as follows



When oxygen is absent, the reduced nicotinamide adenine dinucleotide (NADH) formed during this process transfers its H^+ ions and electrons to oxidized soil components or to organic metabolites (Section III, E, 5). If the electron acceptor is inorganic, the process is called anaerobic respiration; if they are organic substances, fermentation (Doelle, 1969). Fermentations are largely the reactions of pyruvic acid and its alteration products.

Pyruvic acid undergoes a variety of changes determined by pH, redox potential, osmotic pressure, the available electron acceptors, and the microorganisms present (Werkman and Schlenk, 1951). Since most soils contain a wide variety of microorganisms, the physical and chemical environment determine the fate of pyruvic acid. The main anaerobic transformations of pyruvic acid gleaned from Werkman and Schlenk (1951), Wood (1961), Wilkinson and Rose (1963), and Doelle (1969) include: (a) reduction to lactic acid, (b) decarboxylation to CO_2 and acetaldehyde, (c) dissimilation to lactic and acetic acids and CO_2 , (d) cleavage to acetic and formic acids, H_2 , and CO_2 , (e) carboxylation to oxaloacetic acid, (f) condensation with itself or acetaldehyde to give acetylmethylcarbinol, and (g) dissimilation to butyric and acetic acids.

The reaction products of pyruvic acid may undergo further biochemical transformations (Barker, 1956; Clifton, 1957; Wilkinson and Rose, 1963; Doelle, 1969). Among these reactions are: (a) reduction of acetaldehyde to ethanol, (b) reaction of ethanol and acetic acid yielding butyric and caproic acids, (c) decomposition of ethanol to CH_4 and CO_2 , (d) dissimilation of lactic acid to propionic and acetic acids, (e) decomposition of formic acid to CO_2 and H_2 , (f) reduction of oxaloacetic acid to succinic acid, (g) reduction of acetylmethylcarbinol to 2,3-butanediol, and (h) reduction of butyric acid to butanol and acetone to 2-propanol.

Thus the transformations of pyruvic acid and its reaction products produce an array of substances that include: ethanol, butanol, 2-propanol, glycerol, 2,3-butanediol, and acetylmethylcarbinol, acetone and acetaldehyde; formic, acetic, butyric, valeric, caproic, lactic, oxaloacetic, malonic, fumaric, and succinic acids; and CO_2 , H_2 , CH_4 , and C_2H_2 . Almost all these products and others have been identified collectively in anaerobic soils and cultures containing soils (Acharya, 1935; Roberts, 1947; Takijima, 1964; IRRI, 1965; Wang and Chiang, 1967; Yamane and Sato, 1967; Gotoh and Onikura, 1967, 1971; Smith and Scott Russell, 1969; Gotoh, 1970) and in sewage and polluted waters (Pohland and Bloodgood, 1963; Tezuka *et al.*, 1963; Mahr, 1965; Smith and Mah, 1966). The main

products of the anaerobic decomposition of carbohydrates, however, are CO_2 , the lower fatty acids, and CH_4 . Their formation sequence corresponds roughly to the three main stages of the dissimilation of carbohydrate following soil submergence: (a) respiration by aerobes and facultative anaerobes, (b) acid production, and (c) decomposition of acids and reduction of CO_2 to CH_4 by strict anaerobes.

3. Kinetics of CO_2

One to three tons of CO_2 are produced in the plowed layer of 1 hectare of a soil during the first few weeks of submergence (IRRI, 1964). Being chemically active, it forms carbonic acid, bicarbonates, and insoluble carbonates. The excess accumulates as gas. The partial pressure of CO_2 , which is a good measure of CO_2 accumulation, can be calculated from pH, HCO_3^- concentration, and specific conductance of the solutions of flooded soils (Ponnamperuma *et al.*, 1966b) or from pH and total CO_2 determined by gas chromatography (IRRI, 1967).

The partial pressure of CO_2 in a soil increases after submergence, reaches a peak of 0.2–0.8 atm 1–3 weeks later, and declines to a fairly stable value of 0.05–0.2 atm (IRRI, 1964). The pattern of P_{CO_2} kinetics depends on soil properties and temperature (Cho and Ponnamperuma, 1971). Acid soils high in organic matter but low in iron and manganese show a rapid increase in P_{CO_2} to about 0.5 atm within 1–2 weeks of flooding followed by a slow decline to about 0.3 atm. Acid soils high in both organic matter and iron build up P_{CO_2} values as high as 0.8 atm, but the peaks are followed by a rapid decline to a fairly constant value of about 0.1 atm. Sandy soils tend to give higher mean P_{CO_2} values than clay soils of comparable organic matter content.

The decline in P_{CO_2} after 1–4 weeks of submergence is due to escape, leaching, removal as insoluble carbonates, dilution by CH_4 produced during the decomposition of organic acids, and bacterial reduction of CO_2 to CH_4 . Since low temperature retards methane production, P_{CO_2} tends to be high when the temperature is low (Cho and Ponnamperuma, 1971).

The P_{CO_2} values reported above are considerably lower than those suggested by the composition of the gases of anaerobic soils reported by Takai *et al.* (1963). The degassing method used by these workers probably displaced varying amounts of CO_2 from HCO_3^- , thus inflating the concentration of CO_2 .

The practical implications for rice culture are that CO_2 injury may occur in acid soils low in iron, that organic matter or low temperature may aggravate this injury, that high P_{CO_2} values are short-lived in ferruginous soils, and that planting should be delayed at least 2 weeks after flooding to avoid CO_2 injury.

4. Kinetics of Volatile Organic Acids

The main organic acids found in anaerobic soils and sewage are formic, acetic, propionic, and butyric acids. Of these, acetic acid is by far the most abundant (Tezuka *et al.*, 1963; Painter, 1971; Gotoh and Onikura, 1971).

When a soil is submerged, the concentration in the soil solution of volatile organic acids increases, reaches a peak value of 10–40 mmoles/liter in 1–2 weeks and then declines to less than 1 mmole/liter a few weeks later. Soils high in native or added organic matter produce high concentrations of acids (Motomura, 1962). Low temperature retards acid formation slightly, but acid destruction markedly (Yamane and Sato, 1967; Cho and Ponnampereuma, 1971). Thus organic acids persist longer in cold soils than in warm soils. Ammonium sulfate appears to increase acetic acid formation but suppresses the formation of propionic and butyric acids (IRRI, 1971).

The volatile organic acids are ecologically important because they are intermediates in the degradation of organic matter to CH_4 in rice soils, in sewage, polluted and anoxic waters, and lake and ocean sediments. These acids have been shown to be toxic to rice in culture solutions at pH values below 6.0 (Takijima, 1964; Tanaka and Navasero, 1967). But because of their transitory existence, organic acid injury to rice is unlikely except in peaty soils (Takijima, 1964), cold acid soils (Cho and Ponnampereuma, 1971), and soils to which green manure or straw has been added (IRRI, 1971). Accumulation of volatile organic acids in anaerobic sewage digesters indicates digester failure.

5. Methane Fermentation

Methane is the typical end product of the anaerobic decomposition of organic matter. The gas escapes in large amounts from flooded soils, marshes, lake muds, anoxic lake and ocean waters, sewage disposal units, and from the stomachs of ruminants, accompanied usually by smaller amounts of carbon dioxide and hydrogen. Some of the methane is oxidized bacterially at the surface of paddy soils (Harrison and Aiyer, 1913, 1915) and in the oxygenated strata of lakes (Hutchinson, 1957). Methane formation is ecologically important because it helps the disposal of large amounts of organic matter sedimented in lakes or accumulated in cities.

Methane is produced by a small group of obligate anaerobes found in reduced muds, in anaerobic sewage digesters, and in rumens. Methane bacteria function best at temperatures above 30°C, but *Methansarcina methanica*, the species which is most abundant in natural anaerobic waters, produces methane even at 5°C (Ruttner, 1963). Methane bacteria are highly substrate specific and can metabolize only a small number of simple organic and inorganic substances, usually the products of fermentation.

These include: formic, acetic, propionic, *n*-butyric, *n*-valeric, and *n*-caproic acids; methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol, and *n*-pentanol; and hydrogen, carbon monoxide, and carbon dioxide (Barker, 1956). These substances may be derived from the breakdown of carbohydrates, proteins, or fats.

Some typical reactions of methane bacteria listed by Barker (1956) and Stadtman (1967) include: (a) oxidation of ethanol to acetic acid coupled to the reduction of CO_2 to CH_4 ; (b) β -oxidation of propionic acid to acetic acid coupled to the reduction of CO_2 to CH_4 ; (c) cleavage of acetic acid to CH_4 and CO_2 ; (d) decomposition of formic acid to CH_4 and CO_2 ; and (e) reduction of CO_2 to CH_4 .

The end result of these reactions is the almost complete degradation of the lower fatty acids and some alcohols to carbon dioxide and methane (Stadtman, 1967). Thus soluble carbon compounds produced by anaerobic degradation of insoluble carbohydrates, proteins, and fats are gassified and released to the atmosphere as CO_2 and CH_4 .

Almost all natural organic substances and many synthetic compounds can be fermented to CO_2 and CH_4 (Loehr, 1968). Pfeffer (1966) and Loehr (1968) have discussed the advantages of anaerobic digestion over aerobic digestion for the disposal of sewage and industrial wastes and Loehr (1968) has listed the conditions for efficient anaerobic digestion. Cessation or retardation of methane formation, the accumulation of acids, and bad odors signify digester failure. The primary cause of digester failure is probably the accumulation of substrates for which the appropriate species of bacteria are not present in sufficient numbers (Gaudy and Gaudy, 1966).

The gassification of the greater part of the organic matter in sewage and industrial wastes relieves streams and lakes of a heavy oxygen demand, and prevents their pollution.

Toerien and Hattingh (1969) and Kotzé *et al.* (1969) have reviewed the microbiology and mechanisms of anaerobic digestion in wastewater treatment.

6. Reducing Substances

The solutions of submerged soils contain substances that reduce KMnO_4 under mild conditions. These substances compete with rice roots for oxygen, and if present in excess, may deprive them of the oxygen vital for respiration and nutrient uptake. Since water-soluble Fe^{2+} (the main inorganic reductant) accounts for less than 25% of the reducing capacity, the bulk of the reducing substances must be organic. But aldehydes, ketones, alcohols, reducing sugars, aliphatic hydroxy and unsaturated acids, and mercaptans and organic sulfides are present only in traces (IRRI, 1965).

Two phenolic substances—ferulic acid (3-methoxy-4-hydroxycinnamic acid) and sinapic acid (3,5-dimethoxy-4-hydroxycinnamic acid)—have been detected in the solutions of reduced soils (IRRI, 1970), but the nature of the bulk of the reducing substances is unknown. They are probably complex molecules containing phenolic and olefinic groups (Fotiyev, 1966; Christman and Ghassemi, 1966; Lamar and Goerlitz, 1964).

7. Detergents and Pesticides

In recent years, pollution of drinking water, streams and lakes, and even the sea by detergents and pesticides has received wide attention, and methods of minimizing it have been investigated. Physical, chemical, and microbiological factors determine the fate of these substances in soils and waters. For pollution control, microbiological decomposability is a desirable characteristic of detergents and pesticides. And data on biodegradability of these pollutants in aerobic media are available. But the fate of these substances may be different in anaerobic media.

Branched-chain anionic detergents apparently resist biodegradation both in aerobic and anaerobic media, but linear-chain anionic detergents are broken down to a much lesser degree anaerobically than aerobically (Rismondo and Zilio-Grandi, 1968).

The herbicides atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) and trifluraline (α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) disappear more rapidly under anaerobic conditions than under aerobic conditions (Kearney *et al.*, 1967).

Anaerobic biodegradation of the insecticide parathion (*O,O*-diethyl-*O-p*-nitrophenyl phosphorothioate) stops at the aminoparathion stage; aerobically it is biodegraded further (Graetz *et al.*, 1970). Aerobically, diazinon [*O,O*-diethyl-*O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate] is first hydrolyzed to 2-isopropyl-6-methyl-4-hydroxypyrimidine, and the pyrimidine ring is then oxidized to CO₂ by soil microflora; anaerobically, the hydrolysis product accumulates (Sethurathan and Yoshida, 1969).

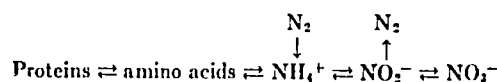
The insecticide, γ -BHC (γ -isomer of 1,2,3,4,5,6-hexachlorocyclohexane) persists for several years in aerobic soils, but is biodegraded partly to CO₂ in submerged soils (MacRae *et al.*, 1967b). A high content of organic matter hastens the biodegradation; addition of nitrate or manganese dioxide retards it (Yoshida and Castro, 1970). DDT (dichlorodiphenyltrichloroethane) is fairly stable in aerobic soils but is degraded to DDD in submerged soils (Castro and Yoshida, 1971).

Alternate oxidation and reduction may provide an environment more favorable to the degradation of mixed detergents and pesticides than oxi-

dition or reduction alone. If so, these substances are less likely to persist in paddy soils (Section II, C) and in eutrophic lakes than in aerobic soils and oligotrophic lakes (Section III, E).

B. NITROGEN

Nitrogen occurs in soils and sediments chiefly as complex organic substances, ammonia, molecular nitrogen, nitrite, and nitrate. The transformations that they undergo are largely microbiological interconversions regulated by the physical and chemical environment. The main interconversions may be depicted as follows



The equilibrium point of this system in a soil depends on the nature and content of organic matter, oxidation-reduction potential, pH, and temperature. In submerged soils, the main transformations are the accumulation of ammonia, denitrification, and nitrogen fixation. These transformations have an important bearing on the nutrition of rice and aquatic plants, the pollution of streams, lakes, and estuaries, and the nitrogen balance in nature.

1. Accumulation of Ammonia

The mineralization of organic nitrogen in submerged soils stops at the ammonia³ stage because of the lack of oxygen to carry the process via nitrite to nitrate. So ammonia accumulates in anaerobic soils, anoxic waters, and in anaerobic sewage digesters. Ammonia is derived from anaerobic deamination of amino acids, degradation of purines, and hydrolysis of urea. Less than 1% comes from nitrate reduction (Woldendorp, 1965).

Some examples of deamination reactions taken from Clifton (1957), Barker (1961), and Doelle (1969) include: (a) oxidation of alanine to pyruvic acid; (b) reduction of aspartic acid to succinic acid; (c) oxidation of alanine to pyruvic acid coupled to the reduction of glycine (the Stickland Reaction); (d) oxidation of alanine to acetic acid coupled to the reduction of alanine; (e) desaturation of aspartic acid to fumaric acid; (f) dissimilation of tryptophan to indole and pyruvic acid; (g) dissimilation of glutamic acid to acetic and propionic acids, CO₂, and H₂; (h) dissimilation of arginine to ornithine; (i) dissimilation of cysteine to H₂S; and (j) dissimilation of purines to acetic acid and CO₂. The end products of these reac-

³ Ammonia stands for (NH₃ + NH₄OH + NH₄⁺).

tions are ammonia, CO₂, and volatile fatty acids. The fatty acids are subsequently fermented to methane. Bacteria that effect these changes have been isolated from soils, muds, decomposing organic matter, sewage, and rumen fluids.

Greenwood and Lees (1960) found that during the anaerobic decomposition of amino acids added to soil volatile fatty acids were formed, and, in 10 days, 80% of the N in the amino acids was released as ammonia. Anaerobic deamination was much slower than the aerobic process. Nitrate suppressed volatile acid formation but not ammonia production. Some amino acids decomposed much more slowly than others both aerobically and anaerobically.

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 (Joachim, 1931; Waring and Bremner, 1964; Broadbent and Reyes, 1971) because less immobilization of nitrogen occurs in anaerobic media.

Ammonification in an aerobic soil is accomplished by a wide group of microorganisms of which fungi are normally the most vigorous. The aerobic metabolism of fungi with its high energy release enables them to carry on vigorous decomposition of organic matter coupled to high synthetic activity. Thus decomposition is rapid but no nitrogen is released unless the nitrogen content of the substrate exceeds 1–2% (Bartholomew, 1965). On submergence, fungi are replaced by anaerobic bacteria. These bacteria, operating at a lower energy level, synthesize much less cell material. Thus the nitrogen factor (the number of grams of additional nitrogen required to decompose 100 g of material) is much less anaerobically than aerobically (Acharya, 1935). But Broadbent and Nakashima (1970) found that the nitrogen factor varied with quantity of straw added, the nitrogen content of straw, the nature of soluble nitrogen added, the degree of anaerobiosis, and the soil, but in no case was it inconsiderable. Williams *et al.* (1968) observed an increase in the yield of rice on flooded fields when the nitrogen content of the straw that was plowed in exceeded 0.6%, and a decrease in yield when the nitrogen content was below 0.5%. Thus in spite of the lower nitrogen factor in flooded soils, materials with wide C:N ratios such as straw and weeds, instead of supplying nitrogen may depress its availability to rice, especially in soils low in organic matter (IRRI, 1964), while green manures like *Sesbania sesban* release the greater part of their nitrogen within 2–3 weeks of incorporation in flooded soils (Joachim, 1931; IRRI, 1964).

Temperature has a marked effect on ammonia release in flooded soils. Mitsui (1960) reported a virtual doubling of ammonia production when the temperature of anaerobic incubation was raised from 26 to 40°C. Kawa-

guchi and Kyuma (1969) and Cho and Ponnampereuma (1971) have reported similar increases in the range 15–40°C.

Ammonia production in submerged soils follows a roughly asymptotic course and the kinetics of ammonia release can be described by

$$\log (A - y) = \log A - ct \quad (20)$$

where A is the mean maximum $\text{NH}_4^+\text{-N}$ concentration, y is the actual concentration t days after submergence, and c is a parameter depending on the soil (Ponnampereuma, 1965). A is a characteristic for a soil under a given temperature regime and was found to be highly correlated, in 31 tropical mineral paddy soils, with the organic matter content of the soil. Waring and Bremner (1964) proposed ammonia released after 2 weeks anaerobic incubation at 30°C as a measure of nitrogen available to dryland plants. Kawaguchi and Kyuma (1969) used ammonia produced after 2 weeks' anaerobic incubation at 40°C as an index of available nitrogen in paddy soils.

Almost all the mineralizable nitrogen in a soil is converted to ammonia within 2 weeks of submergence if the temperature is favorable, the soil is not strongly acid or very deficient in available phosphorus. The amount of ammonia produced during the first 2 weeks of submergence may range from 50 to 350 ppm N on the basis of the dry soil. The soil solution may contain 2 to 100 ppm N depending on texture and organic matter content of the soil (IRRI, 1964). The A values of nitrogen in flooded soils may be as high as 30% of the total N (Broadbent and Reyes, 1971).

I have previously discussed the implications of the kinetics of ammonia release for rice culture (Ponnampereuma, 1965).

2. Denitrification

Nitrate undergoes two transformations in submerged soils: assimilation or reduction of nitrate with incorporation of the products into cell substance; and dissimilation or nitrate respiration in which nitrate functions as an alternative to oxygen as an electron acceptor. A substantial proportion of added nitrate may, in some submerged soils, be assimilated, and enter the pool of soil organic matter (MacRae *et al.*, 1967a), but the bulk of native or added nitrate disappears within a few days in most soils as a result of nitrate respiration. Nicholas (1963) defines denitrification as a special case of nitrate respiration in which nitrate, nitrite, or some intermediate is converted to nitrogen or its oxides.

Denitrification has been extensively reviewed during the past decade with emphasis on varying aspects: microbiology (Alexander, 1961); environmental factors (Broadbent and Clark, 1965; Woldendorp, 1968); biochemistry (Nicholas, 1963; Campbell and Lees, 1967); paddy soils

(Patrick and Mahapatra, 1968); sewage (Painter, 1971); and the sea (Martin, 1970). The main features are critically reviewed below.

Denitrification is brought about by a large number of bacteria and fungi which include heterotrophic and autotrophic species (Painter, 1971). These facultative organisms transform nitrate to nitrogen and its oxide only at very low oxygen concentrations (Skerman and MacRae, 1957; Bremner and Shaw, 1958; Greenwood, 1962; Turner and Patrick, 1968). I have shown theoretically that nitrate will become undetectable ($10^{-7} M$) in water only at an infinitesimal partial pressure of oxygen (Ponnamperuma, 1972). If denitrification occurs in aerobic soils, it is due to the presence of anaerobic pockets (Russell, 1961; Greenwood, 1962). Nitrite, however, is denitrified by bacteria even in the presence of oxygen (Kefauver and Allison, 1957; Skerman *et al.*, 1958; Mechsner and Wuhrmann, 1963). This observation agrees with the thermodynamic prediction that nitrite is highly unstable in aqueous systems in equilibrium with air (Ponnamperuma, 1972). Because nitrite is an intermediate both in the reduction of nitrate and the oxidation of ammonia to nitrate, aerobic denitrification via nitrite may be more substantial and widespread than realized, especially in soils that are alternately wet and dry.

Denitrifying organisms need a source of H^+ ions and electrons to reduce nitrate and a carbon source and ammonia for cell synthesis. In soils, organic matter is the source of all these ingredients. Thus denitrification is absent or slow in soils low in organic matter and is enhanced in such soils by adding organic matter (Bremner and Shaw, 1958; McGarity, 1961; MacRae *et al.*, 1967a). The limiting factor in denitrification by marine bacteria, according to Lloyd (1939), is the supply of organic matter.

Most reviewers state that the rate of denitrification increases with temperature up to $60^\circ C$. While this is generally true for experiments lasting a few hours or days, over a period of 2 weeks the overall rate is essentially the same in the range $15-40^\circ C$, as the figures of Bremner and Shaw (1958) and the findings of Yamane and Sato (1961) and Cho and Ponnamperuma (1971) indicate. Although Cooper and Smith (1963) found that a decrease of temperature from 25° to $20^\circ C$ halved the rate of nitrate disappearance in the first few hours, at the end of 60 hours there was no nitrate left at 30° , 25° , or $20^\circ C$. Only temperatures near freezing can delay denitrification over a period of weeks. Thus in submerged soils and sediments, and anoxic lake and ocean waters, where changes are measured over weeks, months, or years, temperature may be irrelevant to denitrification losses.

Patrick (1960) and Broadbent and Clark (1965), impressed by the approximate linearity of the nitrate/time curves, reported that the rate of denitrification was independent of the nitrate concentration. But Patrick's

curves and those of Cooper and Smith (1963) cited by Broadbent and Clark reveal a roughly exponential trend. So do the nitrate curves of Turner and Patrick (1968). Mathematical formulation of the kinetics of nitrate in the solutions of flooded soils showed that the disappearance of nitrate follows first-order kinetics ($-dc/dt = kc$) with high velocity constants for nearly neutral soils and low ones for acid soils (IRRI, 1965). This means that the rate of denitrification depends on the nitrate concentration, and it is slower in acid soils than in neutral soils, as has been reported by De and Sarkar (1936), Ponnampereuma (1955), Bremner and Shaw (1958), and several others.

Some reviewers discount redox potential as a factor in denitrification. But it is, at least theoretically, the best quantitative measure of the tendency toward denitrification because it is the quintessence of the factors that bring about a milieu favorable or unfavorable for denitrification. Several workers have confirmed this (Section III, E, 6). It may, however, be repeated that over a wide range of soils under natural vegetation Pearsall (1938) found that whenever the potential was higher than 0.35 V, nitrate was present and whenever the potential was less than 0.32 V at pH 5.0, nitrate was absent. Patrick (1960) noted that the potential at pH 5.1 at which nitrate in soil suspensions became unstable was 338 mV. The partial pressure of oxygen at this potential and pH is $10^{-21.86}$ atm.

During denitrification, nitrogen is the ultimate product of nitrate reduction and CO_2 , the oxidation product of carbohydrate; ammonia is produced in only very small amounts; and nitrite and nitrous oxides are intermediates (Broadbent and Clark, 1965). Nitric oxide is an unlikely intermediate (Ponnampereuma, 1972), but may arise in soils by chemical reactions. Hydroxylamine is believed to be an intermediate both in nitrate reduction and ammonia oxidation (Doelle, 1969), but its presence in submerged soils has not been established.

Jordan *et al.* (1967) found that of 59 microorganisms isolated from a flooded soil only 22 reduced NO_3^- to NO_2^- , but not all these reduced NO_2^- . Martin (1970) reports that about half of the marine bacterial species reduce NO_3^- to NO_2^- but less than 5% can reduce NO_3^- or NO_2^- to nitrogen. In spite of this, nitrite does not accumulate in anaerobic media. Concentrations exceeding 3 ppm are rare and transitory in flooded soils (Ponnampereuma, 1955).

Almost all the nitrate present in a soil disappears within a few days of submergence, the bulk of it being lost as N_2 . After submergence, ammonia diffusing up to the oxidized surface layer or broadcast on the surface undergoes nitrification; the nitrate formed moves down by diffusion and mass flow into the reduced soil below and is denitrified (Section III, B). Alternate wetting and drying increases the denitrification loss (Patrick and

Wyatt, 1964); continuous submergence minimizes it and even leads to a substantial accumulation of nitrogen (IRRI, 1969).

Denitrification in cultivated soils is undesirable because it causes the loss of a valuable plant nutrient, so good farmers try to minimize this loss. But in effluents from sewage works, in groundwaters, streams, lakes, and estuaries, loss of nitrogen by denitrification is highly desirable because it helps to prevent the contamination of drinking water by nitrate and the pollution of natural bodies of water by excessive growth of aquatic plants.

3. Nitrogen Fixation

Biological nitrogen fixation is the reduction of nitrogen gas to ammonia (Mortenson, 1962). This reaction needs reductants at a very high electron activity or a very low pE (Table I). Photosynthesis and anaerobic respiration are the two major natural sources of these reductants. Submerged soils with blue-green algae (and sometimes, nitrogen-fixing photosynthetic bacteria) at the surface and nitrogen-fixing bacteria in the bulk of the soil are thus favorably placed for nitrogen fixation.

Harada (1954), Mitsui (1960), and Singh (1961) have reviewed the role of blue-green algae in the nitrogen economy of rice fields. From their reviews the following conclusions may be drawn: (a) members of the genera, *Nostoc*, *Anabaena*, *Oscillatoria*, *Tolypothrix*, *Calothrix*, *Phormidium*, *Aulosira*, and several others can fix nitrogen; (b) some of these algae are present in most paddy fields; (c) some species may fix as much as 22 kg/ha of nitrogen in a season; (d) a slightly alkaline reaction and available phosphorus favor fixation and nitrogen fertilizers retard it; (e) fixation is apparently increased by the presence of the rice plant; and (f) the greater part of the nitrogen fixed is not available for the current needs of the crop.

Nitrogen fixation by free-living bacteria are perhaps equally important because the environment of a flooded soil is suited to both aerobic and anaerobic nitrogen fixers. Aerobic bacteria can thrive in the oxygenated surface layer and in the oxygenated rhizosphere of rice, sustained by ethanol, acetate, and other soluble substrates diffusing from the anaerobic soil matrix. The low oxygen concentration in their habitat would favor nitrogen fixation (Jensen, 1965). The anaerobic bulk of the soil would be an ideal medium for such anaerobic nitrogen fixers as *Clostridium*, especially if organic matter is present. In this connection the finding of Rice *et al.* (1967) that a combination of aerobic and anaerobic conditions dramatically increased nitrogen fixation in a thin layer of soil amended with straw is significant. But under field conditions, except at the soil-water interface, the nitrogen supply may be insufficient because the gas can reach the interior of the soil only by the extremely slow process of

molecular diffusion in the interstitial water. The presence of rice plants alters the situation: nitrogen is transported along with oxygen from the shoot to the root and presumably diffuses out with oxygen (Section III, D). This ensures a supply of nitrogen for the aerobic fixers in the rhizosphere and perhaps for the anaerobes just outside the oxygenated rhizosphere. No data are available on the amount of nitrogen diffusing out of rice roots in flooded fields but the following observations are significant: (a) more nitrogen is fixed in the presence of rice plants than in their absence (Green, 1953; Singh, 1961; IRRI, 1970); (b) nitrogen is fixed in the root zone of rice (Yoshida and Ancajas, 1971); and (c) aerobic nitrogen fixing bacteria are present on rice roots (IRRI, 1970).

C. 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. Rice benefits from the increase in availability of iron but may suffer, in acid soils, from an excess. The presence of iron in natural waters is undesirable because it imparts a color and makes purification of water for domestic and industrial use difficult. Besides, it is an indication of natural or man-made organic pollution. The reduction of iron present at the soil-water interface in lake bottoms during thermal stratification of lakes has even greater implications: the mud loses its absorptive capacity and releases nutrients into the water (Section III, C), shifting the photosynthesis-respiration balance of the lake toward the accumulation of organic matter. The reduction of iron has important chemical consequences: (a) the concentration of water-soluble iron increases; (b) pH increases; (c) cations are displaced from exchange sites; (d) the solubility of phosphorus and silica increases (Section V, F and G); and (e) new minerals are formed.

The reduction of iron is a consequence of the anaerobic metabolism of bacteria and appears to be chiefly a chemical reduction by bacterial metabolites (Bloomfield, 1951; Motomura, 1961), although direct reduction coupled with respiration may be involved (Kamura *et al.*, 1963; Ottow and Glathe, 1971). The kinetics of iron(II) follows a roughly asymptotic course (Takai *et al.*, 1963; IRRI, 1964). Five to 50% of the free iron oxides present in a soil may be reduced within a few weeks of submergence depending on the temperature, the organic matter content, and the crystallinity of the oxides. The lower the degree of crystallinity, the higher is the reduction percentage (Asami, 1970).

Soil properties influence the kinetics of water-soluble Fe^{2+} more drastically than that of total Fe(II). Acid soils high in organic matter and iron

build up concentrations as high as 600 ppm within 1–3 weeks of submergence and show a steep roughly exponential decrease to levels of 50–100 ppm which persist for several months. Low temperature retards the peak and broadens the area under it (Cho and Ponnampereuma, 1971). 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 rarely exceeds 20 ppm.

The increase in concentration of water-soluble iron can, in most soils, be related to the potential and pH of the $\text{Fe}(\text{OH})_3\text{--Fe}^{2+}$ system (Ponnampereuma *et al.*, 1967)

$$Eh = 1.058 - 0.050 \log \text{Fe}^{2+} - 0.177\text{pH} \quad (21)$$

The subsequent decrease is due probably to precipitation of $\text{Fe}_3(\text{OH})_8$ or $\text{Fe}_3\text{O}_4 \cdot n\text{H}_2\text{O}$ brought about by the increase in pH following a decline in P_{CO_2} (Section V, A, 3). The final stable concentration appears to be regulated by the $\text{Fe}_3(\text{OH})_8\text{--Fe}^{2+}$ equilibrium with

$$Eh = 1.373 - 0.0885 \log \text{Fe}^{2+} - 0.236\text{pH} \quad (22)$$

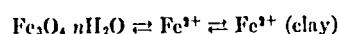
In ferruginous soils, the concentration of water-soluble Fe^{2+} after the peak conforms closely to Eq. (23) (Ponnampereuma, 1972)

$$\text{pH} + \frac{1}{2} \log \text{Fe}^{2+} = 5.4 \quad (23)$$

For other soils the value of the constant may be as low as 4.9 (IRRI, 1967), reflecting the variability of the composition of $\text{Fe}_3\text{O}_4 \cdot n\text{H}_2\text{O}$ that Sillen (1966) refers to.

The bulk of the water-soluble iron is present as bicarbonate and salts of the lower fatty acids, for the kinetics of iron (and manganese) parallels that of total alkalinity ($\text{HCO}_3^- + \text{RCOO}^-$) (Fig. 3). In strongly colored solutions of reduced soils, Fe^{2+} may also be present as complexes of humic acid (Oldham and Gloyna, 1969).

The dynamics of the concentration of Fe^{2+} (and Mn^{2+}) affects the concentrations of other cations. This is clear from the similarity of the kinetics of $(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{NH}_4^+ + \text{K}^+)$ to that of $(\text{Fe}^{2+} + \text{Mn}^{2+})$ (Fig. 3). But values for exchangeable and water-soluble Fe^{2+} must be viewed cautiously because they are highly dependent on the pH of the extractant, as can be seen from Eq. (23) and the following equilibrium:



The cations displaced may be lost by leaching while the supply of Fe^{2+} is maintained by the dissociation of $\text{Fe}_3\text{O}_4 \cdot n\text{H}_2\text{O}$. On drying and oxidation, the soil is acidified (Brinkman, 1970).

Water-soluble Fe^{2+} diffusing to the oxygenated soil–water interface and

moving by mass flow and diffusion from the surface of rice roots and to the oxidized zone below the plow sole is deposited as mottles, tubules, and nodules, respectively.

The grayish color of submerged soils is attributed to iron sulfide, but I have cited evidence (Ponnamperuma, 1972) to show that the bulk of the reduced iron in most paddy soils is probably hydrated magnetite [$\text{Fe}_3\text{O}_4 \cdot n\text{H}_2\text{O}$ or $\text{Fe}_3(\text{OH})_4$] along with some hydrotroilite ($\text{FeS} \cdot n\text{H}_2\text{O}$). If anaerobic conditions persist, these precipitates may age, producing the typical minerals of reduced sediments, magnetite (Fe_3O_4), and pyrite (FeS_2). Also, Fe(II) silicates (greenalite and chamosite), siderite (FeCO_3) and vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$] may form (Rankama and Sahama, 1950; Rode, 1962; Rosenquist, 1970).

D. MANGANESE

The main transformations of manganese in submerged soils are the reduction of Mn(IV) oxides to Mn(II), an increase in the concentration of water-soluble Mn^{2+} , precipitation of manganous carbonate, and reoxidation of Mn^{2+} diffusing or moving by mass flow to oxygenated interfaces in the soil.

Within 1–3 weeks of flooding, almost all the EDTA-dithionate extractable manganese present in soils, except those low in organic matter, is reduced (IRRI, 1964). The reduction is both chemical and biological and precedes the reduction of iron. The kinetics of water-soluble Mn^{2+} reflect the influence of soil properties on the transformations of manganese (IRRI, 1964).

Acid soils high in manganese and in organic matter build up water-soluble Mn^{2+} concentrations as high as 90 ppm within a week or two of submergence then show an equally rapid decline to a fairly stable level of about 10 ppm. Soils high in manganese but low in organic matter also give high peaks but they are late and broad like those of Fe^{2+} at low temperatures (Cho and Ponnamperuma, 1971). Alkaline soils and soils low in manganese rarely contain more than 10 ppm water-soluble Mn^{2+} at any stage of submergence.

Manganese is present in anoxic soil solutions as Mn^{2+} , MnHCO_3^+ , and as organic complexes. Its concentration represents a balance between the release of Mn^{2+} by reduction and removal by cation exchange reactions, precipitation, and formation of insoluble complexes. After the peak, the concentration of Mn^{2+} (Ponnamperuma, 1972) conforms to

$$\text{pH} + \frac{1}{2} \log \text{Mn}^{2+} + \frac{1}{2} \log P_{\text{CO}_2} = 4.4 \quad (24)$$

Patrick and Turner (1968) noted that as the content of reducible Mn of an anaerobic silty clay decreased, the content of exchangeable Mn in-

creased. But binding at cation exchange sites does not explain the steep decline in water-soluble Mn^{2+} that occurs in acid soils high in Mn and organic matter. We have suggested that the steep fall in concentration after the peak is due to precipitation of $MnCO_3$ (Ponnamperuma *et al.*, 1969b) (Section VI, B). $MnCO_3$ is appreciably soluble in ammonium acetate. That may explain the high values Patrick and Turner (1968) got for exchangeable Mn^{2+} .

Water-soluble Mn^{2+} , like Fe^{2+} , diffuses from reduced soils and sediments to the oxygenated interface and is sorbed by Fe(III) and Mn(IV) oxide hydrates and oxidized to produce Mn-rich nodules. Penetrating the oxidized zone below the plow sole of paddy soils, it is oxidized below the B_{1r} horizon to give a B_{mn} horizon (Koenigs, 1950; Kanno, 1957). When a reduced soil is drained, air enters the soil and reoxidizes it. Iron(II) being more easily oxidized than Mn(II) is rapidly converted to Fe(III) oxide hydrates. These precipitates may sorb Mn^{2+} or form coprecipitates to give stains, nodules, and concretions whose composition apparently is determined by the milieu in which they are formed (Ponnamperuma *et al.*, 1969b).

Most flooded soils contain sufficient water-soluble Mn for the growth of rice, and manganese toxicity is not known to occur in flooded soils. But native or added MnO_2 retards soil reduction and counteracts the adverse effects of excess Fe^{2+} and other reduction products (Nhung and Ponnamperuma, 1966; Yuan and Ponnamperuma, 1966). Hutchinson (1957) and Tanaka (1964) have described the oxidation and reduction of manganese in lakes.

Little is known about the mineralogy of manganese in submerged soils. A search for the following precipitates may be fruitful: $MnCO_3$, $(Ca,Fe,Mn)CO_3$, MnS , Mn_3O_4 , $(Mn_3O_4,Fe_3O_4)_2$, and $Mn_3(PO_4)_2$.

E. SULFUR

Sulfur is one of the most abundant elements on earth, and its transformations are of great geochemical, pedological, biological, and ecological interest.

In aerated soils and waters the main transformations are (a) the oxidation of elemental sulfur, sulfides, and organic sulfur compounds to sulfate, and (b) the reduction of SO_4^{2-} and incorporation of sulfur into plant and microbial tissues. In anaerobic media, the main changes are the reduction of SO_4^{2-} to sulfide and the dissimilation of the amino acids, cysteine, cystine, and methionine (derived from the hydrolysis of proteins) to H_2S , thiols, ammonia, and fatty acids (Barker, 1961; Freney, 1967). Methyl thiol has been found in submerged soils (Takai and Asami, 1962; IIRI,

1965), and the bad odor of putrefying blue-green algae in a reservoir has been attributed to dimethyl sulfide and methyl, butyl, and isobutyl thiols (Jenkins *et al.*, 1967). The main product of the anaerobic transformations of sulfur is H_2S and it is derived largely from SO_4^{2-} reduction (Timar, 1964; Postgate, 1965). The H_2S formed may react with heavy metals to give insoluble sulfides, it may function as hydrogen donor to photosynthetic green and purple sulfur bacteria, and it may be oxidized chemically and bacterially at aerobic/anaerobic boundaries.

The reduction of sulfate is brought about by a small group of obligate anaerobic bacteria of the genus *Desulfovibrio*, which use SO_4^{2-} as the terminal electron acceptor in respiration. These bacteria use a variety of fermentation products and molecular hydrogen to reduce SO_4^{2-} , they tolerate high concentrations of salt and H_2S , and function best in the pH range 5.5–9.0 (Starkey, 1966). Nitrate (Vamos, 1958) or low temperature (Cho and Ponnampereuma, 1971) retards the reduction.

The kinetics of water-soluble sulfate (which is a measure of sulfate reduction) in anaerobic soils depends on soil properties (IRRI, 1965). In neutral and alkaline soils concentrations as high as 1500 ppm SO_4^{2-} may be reduced to zero within 6 weeks of submergence. Acid soils first show an increase in water-soluble SO_4^{2-} , then a slow decrease spread over several months. The initial increase in SO_4^{2-} concentration is due to the release (following increase in pH) of SO_4^{2-} which according to Harward and Reisenauer (1966) is strongly sorbed at low pH by clay and hydrous oxides of iron and aluminum. Sulfate reduction follows first-order reaction kinetics with velocity constants which are several hundred times higher for alkaline soils than for acid soils (IRRI, 1965). Sulfate reduction proceeds slowly in submerged acid sulfate soils, despite their strong acidity; lime accelerates reduction considerably (Nhung and Ponnampereuma, 1966).

Although large amounts of H_2S are produced in submerged soils, lake and ocean muds, and anoxic waters, the concentration of water-soluble H_2S may be so small that it is chemically almost undetectable (Misra, 1938; Mortimer, 1941; Hutchinson, 1957; IRRI, 1965). This is due to its removal as insoluble sulfides, chiefly FeS. Thus the solutions of submerged soils rarely contain more than 0.1 ppm H_2S . But enormous amounts of H_2S can accumulate in the stagnant waters of inland seas, salt lakes, and in ~~sulfur~~-containing waste waters (Hutchinson, 1957). When *sulfu* such waters mix with overlying inhabited strata, there can be a catastrophic kill of fish (Ruttner, 1963; Richards, 1965).

At the pH values of most anaerobic soils and sediments the bulk of the H_2S in the interstitial water is present as undissociated H_2S and HS^- . But the concentration of S^{2-} is high enough to precipitate FeS. FeS may also be formed by the action of H_2S on $FePO_4$ (Sperber, 1958) and on

crystalline Fe(III) oxides (Berner, 1964). Finely precipitated iron sulfide is probably black hydrotroilite ($\text{FeS} \cdot n\text{H}_2\text{O}$) disseminated throughout the solid phase (Berner, 1964). $\text{FeS} \cdot n\text{H}_2\text{O}$ is present occasionally in colloidal solution (Shioiri and Tanada, 1954). Hydrotroilite gradually changes to mackinawite and later to pyrites (FeS_2) (Berner, 1964). The requirements for pyrite accumulation in a sediment are absence of oxygen, the presence of sulfate-reducing bacteria, a supply of SO_4^{2-} and fresh organic matter, and sufficient iron to immobilize the H_2S produced. These conditions are found in ideal combination in deltas and estuaries in the tropics. When these sediments or "mud clays" (which are neutral to alkaline in reaction) are drained and exposed to air, the pyrites are oxidized to basic ferric sulfate and H_2SO_4 , giving acid sulfate soils or "catclays" with pH values as low as 2 (Ponnamperuma, 1972).

Sulfate reduction can lead to the formation of a diametrically opposite type of soil—an alkali soil. Sodium sulfate present in arid soils may be converted to H_2S and sodium bicarbonate during periods of waterlogging. This reaction decreases salinity (Ogata and Bower, 1965) and increases alkalinity (Timar, 1964; Janitzky and Whittig, 1964).

Reduced lake and ocean muds accumulate insoluble sulfides and function as sinks for silver, copper, lead, cadmium, and iron (Hutchinson, 1957; Goldberg, 1965).

The reduction of sulfate in submerged soils has three implications for rice culture: the sulfur supply may become insufficient, zinc and copper may be immobilized, and H_2S toxicity may arise in soils low in iron.

F. PHOSPHORUS

Phosphorus, like nitrogen, exists in valence states from +5 to -3. Although, thermodynamically, phosphite, hypophosphite, and phosphine can form from phosphate in anaerobic media, and their presence has indeed been demonstrated (Hutchinson, 1957; Tsubota, 1959), the main transformation of phosphorus in anaerobic media are the movements of the orthophosphate ion.

Phosphorus is present in soils, sediments, and natural waters as soluble phosphates, both organic and inorganic, and as slightly soluble solids. The solids include (a) iron(III) and aluminum phosphates, (b) phosphates adsorbed or coprecipitated with Fe(III) and Mn(IV) hydrous oxides, (c) phosphates held by anion exchange on clay and hydrous oxides, (d) calcium phosphates, and (e) organic phosphates. Phosphates associated with iron(III) and aluminum predominate in acid soils and sediments; calcium phosphates predominate in neutral and alkaline soils (Jackson, 1964; Stumm and Morgan, 1970). Iron(III) and aluminum phosphates release

phosphate as pH increases while calcium phosphates liberate phosphate as pH decreases (Stumm and Morgan, 1970).

When a soil is submerged or when a lake undergoes thermal stratification, the oxygen supply is cut off and reduction sets in (Section III, E). A striking consequence of reduction is the increase in the concentration of water-soluble and available P. Mortimer (1941) observed a hundred-fold increase in soluble P in the hypolimnion of a lake after reduction of the mud-water interface. Kaplan and Rittenberg (1963) reported that the interstitial waters of reduced sediments contain 50 times as much P as sea water and that stagnant lake and sea waters containing H_2S have high P concentrations.

The increase in concentration of water-soluble P on soil submergence, though appreciable, is not as pronounced as that in stagnant lake waters.

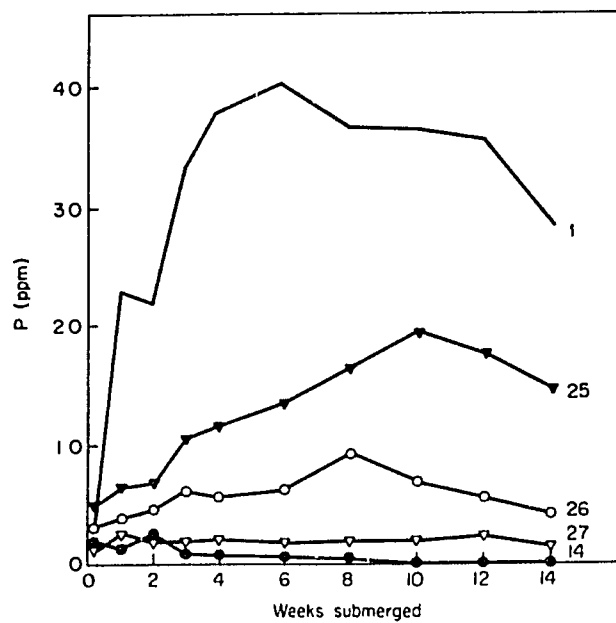


FIG. 4. Kinetics of water-soluble P in some submerged soils.

Soil No.	Texture	pH	O.M. %	Fe %
1	Sandy loam	7.6	2.3	0.18
14	Clay	4.6	2.8	2.13
25	Sandy loam	4.8	4.4	0.18
26	Clay loam	7.6	1.5	0.30
27	Clay	6.6	2.0	1.00

Besides, it is markedly affected by soil properties (Fig. 4). The increases on flooding and the peak values are highest in the sandy calcareous soil low in iron, moderate in the acid sandy soil low in iron, small in the nearly neutral clay, and least in the acid ferrallitic clay.

The availability of native and added P whether judged by solubility in soil-test extractants or uptake by the rice plant increases on submerging a soil (Shapiro, 1958; Mitsui, 1960; Davide, 1961; Broeshart *et al.*, 1965; Mahapatra and Patrick, 1969). In noncalcareous soils the increase in solubility of P is associated with a decrease in Eh or an increase in Fe(II) (Ponnamperuma, 1955; Patrick, 1964; Savant and Ellis, 1964) suggesting a role for Fe(III) bonded phosphates. But neither soil test data (Chang, 1965) nor P fractionation studies with submerged soils throw much light. Fractionation of P in reduced soils by the method of Chang and Jackson (1957) is unreliable unless precautions are taken to avoid the oxidation of Fe(II) and unless a distinction is drawn between calcium bonded P and P that may, in some soils, be bonded by Fe(II) and Mn(II).

The increase in concentration of water-soluble P when acid soils are submerged result from (a) hydrolysis of Fe(III) and Al phosphates, (b) release of P held by anion exchange on clay and hydrous oxides of Fe(III) and Al, and (c) reduction of Fe(III) to Fe(II) with liberation of sorbed and chemically bonded P. The first two reactions are due to the pH increase brought about by soil reduction. In alkaline soils the increase in solubility of P is a consequence of the decrease in pH of these soils on flooding, for the solubility of hydroxylapatite increases as pH decreases (Stumm and Morgan, 1970).

The phosphate ions released by these reactions and from the decomposition of organic matter may be resorbed by clay and hydrous oxides of Al in the anaerobic zone (Gasser and Bloomfield, 1955; Bromfield, 1960) or they may diffuse to oxidized zones and be reprecipitated (Hynes and Greib, 1970). Noncalcareous sediments absorb and retain more P than calcareous lake sediments (Williams *et al.*, 1970; Shukla *et al.*, 1971). That explains why the increase in concentration of water-soluble P is small and transitory in acid clay soils compared to calcareous soils (Fig. 4).

Quantitative studies of phosphate equilibria in submerged soils face the following difficulties: (a) up to 60% of water-soluble P may be organic; (b) P may be present as soluble complexes of Ca, Mg, Al, and Fe, and as colloids; (c) the identity of the solids, which may range from adsorption products to chemical compounds, is not known; and (d) sorption may be more important than precipitation in regulating the concentration of soluble P. But the solubility of P in alkali and calcareous soils appears to be regulated by the solubility of hydroxyapatite $[\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_3]$ and

in reduced acid soils by adsorption on kaolinite, montmorillonite, and hydrous oxides of Al. Vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$] may not be involved. If vivianite with an activity product constant of $10^{-29.9}$ is in equilibrium with dissolved Fe^{2+} at pH 7.0, the total P concentration should be about 10^{-5} M. The actual concentrations in ferruginous soils are much less (Fig. 4). That explains why vivianite is found only in old sediments (Rosenquist, 1970).

Phosphate is one of the main pollutants of streams and lakes, so stringent efforts are being made to minimize its escape from waste-water treatment plants. Also, much attention is focused on the role of lake sediments as sinks for phosphate.

Hutchinson (1957) has reviewed the phosphorus cycle in lakes, and Martin (1970) that in the sea. Stumm and Morgan (1970) have discussed the chemistry of phosphates in surface waters and the role of hydrous oxides in phosphate equilibria. Leckie and Stumm (1970) have reviewed precipitation reactions. Ponnampertuma (1965) and Patrick and Mahapatra (1968) have reviewed P transformations in paddy soils.

G. SILICON

Silicon occurs in soils as crystalline and amorphous silica, as silicates, ^{as silica} sorbed or coprecipitated with hydrous oxides of Al, Fe(III) and Mn(IV), and as silica dissolved in the soil solution.

Dissolved silica is present as monomeric $\text{Si}(\text{OH})_4$. The concentration of $\text{Si}(\text{OH})_4$ in equilibrium with amorphous silica at 25°C is 120–140 ppm as SiO_2 and is independent of pH in the range 2–9. The concentrations of silica in natural waters are much less than 120 ppm (Stumm and Morgan, 1970; Martin, 1970), and in soil solutions decrease with increase in pH up to about pH 8 (Jones and Handreck, 1967). The low concentration of silica in natural waters has been attributed to sorption of silica by hydrous oxides of Fe(III) and Al (Jones and Handreck, 1967) and to recombination of silica with aluminum silicates (Mackenzie *et al.*, 1967).

But the concentration of dissolved silica in interstitial solutions of river, lake, and ocean sediments are higher than those of the overlying waters (Kaplan and Rittenberg, 1963; Harris, 1967). And when lake muds undergo reduction, large amounts of soluble silica are released into the hypolimnion (Hutchinson, 1957). The concentration of silica in the solutions of submerged soils increases slightly after flooding and then decreases gradually, and after several months of submergence the concentration may be lower than at the start (IRRI, 1964). The increase in concentration after flooding may be due to the release of silica following (a) reduction

of hydrous oxides of Fe(III) sorbing silica, and (b) action of CO_2 on aluminosilicates (Bricker and Godfrey, 1967). The subsequent decrease may be the result of recombination with aluminosilicates, following the decrease in P_{CO_2} .

H. TRACE ELEMENTS

Although the forms of boron, cobalt, copper, molybdenum, and zinc present in soils are probably not involved in oxidation-reduction reactions, their mobility may be affected by some of the consequences of soil submergence. Thus the reduction of the hydrous oxides of Fe(III) and Mn(IV) and the production of organic complexing agents should increase the solubility of Co, Cu, and Zn. The increase in pH of acid soils and the formation of sulfides should lower their solubility. The net result of soil submergence is to increase the availability of Co and Cu (Mitchell, 1964; Adams and Honeysett, 1964) and of Mo (Jenne, 1968) and to depress that of zinc (IRRI, 1970). Elements mobilized in reduced sediments may diffuse upward and accumulate in the oxidized surface layer (Hynes and Greib, 1970).

VI. Mineral Equilibria in Submerged Soils

In recent years, the application of equilibrium thermodynamics to the quantitative study of chemical transformations in nature has assumed increasing importance. Despite many theoretical and practical difficulties, equilibrium thermodynamics has been useful in understanding mineral associations in nature (Garrels and Christ, 1965), the composition of sea water (Sillen, 1961) and other natural waters (Stumm and Morgan, 1970), the chemical changes in submerged soils (Ponnamperuma *et al.*, 1965, 1966a, 1967, 1969a,b), and biological oxidation-reduction reactions (Ponnamperuma, 1972). Stumm and Morgan (1970) have listed the difficulties in applying equilibrium thermodynamic concepts to the nonequilibrium conditions encountered in nature. Ponnamperuma *et al.* (1966a, 1967) have discussed the difficulties relevant to oxidation reduction reactions. These difficulties are minimal in submerged soils, because submerged soils are more or less closed, isobaric, isothermal systems in which many reactions are catalyzed by bacteria.

A. REDOX SYSTEMS

Reduction of the soil is the most important chemical change brought about by submergence. According to Table I, the reduction of the main

components proceeds in the following sequence: O_2 , NO_3^- , $Mn(IV)$, $Fe(III)$, SO_4^{2-} , CO_2 , N_2 , and H^+ . Since the oxidized and reduced forms of each component coexist along with H^+ ions and electrons, they may be assumed to be in equilibrium if energy barriers are absent and reaction rates are not too slow.

1. The O_2 - H_2O System

The O_2 - H_2O system dominates the redox picture in all environments exposed to atmospheric oxygen. Oxygen is such a powerful oxidant that at a P_{O_2} of 0.21 atm it should, theoretically, convert carbon, hydrogen, nitrogen, sulfur, iron, and manganese to CO_2 , H_2O , NO_3^- , SO_4^{2-} , Fe_2O_3 , and MnO_2 . These are the stable forms of the elements in the surface oxygenated soil-water interface of submerged soils and sediments.

If the system, $O_2 + 4H^+ + 4e = 2H_2O$, dominates aerobic media, the potential (Eh) and pE ($-\log e$) values should conform to

$$Eh = 1.229 + 0.015 \log P_{O_2} - 0.059pH \quad (25)$$

$$pE = 20.80 - \frac{1}{4}pO_2 - pH \quad (26)$$

where pO_2 is the negative logarithm of P_{O_2} .

Aqueous systems in equilibrium with air should, therefore, have a dE/dpH of -0.059 and an Eh value of 0.82 V. Experimental values of dE/dpH for aerobic soils and natural waters are of the right order, but their Eh values at pH 7.0 are considerably lower: they range from 0.35 to 0.56 V and depend on pretreatment of the platinum electrode. For this reason and also because of poor poise and low sensitivity (-15 mV or $\frac{1}{4}pE$ unit for a 10-fold decrease in O_2 concentration), Eh or pE is not a satisfactory measure of soil aeration. The high pE of the O_2 - H_2O system and its small decrease with P_{O_2} mean that very small concentrations of O_2 are sufficient to maintain an environment in the oxidized state. According to Turner and Patrick (1968), the E_r at which oxygen becomes undetectable is 0.33 V or a pE of 5.63.

2. The Nitrogen Systems

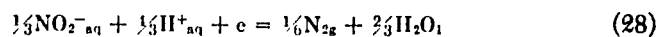
Nitrogen and its oxidation and reduction products are abundant and widespread, they are soluble in water, and they are in constant contact with atmospheric oxygen or electrons liberated from organic matter by microorganisms. Besides, the three main transformation of N—nitrification, denitrification, and nitrogen fixation—are oxidation-reduction reactions catalyzed by enzymes. So they are best studied from the standpoint of electron activity.

a. *The NO₃⁻-N₂ System.* In aerobic media the NO₃⁻-N₂ system for which

$$pE = 21.06 - \frac{1}{5}pNO_3^- + \frac{1}{10}pN_2 - \frac{9}{5}pH \quad (27)$$

should be in equilibrium with the O₂-H₂O system for which pE is 13.63 at a P_{O₂} of 0.2 atm and pH 7.0. Substituting 13.63 for pE and 0.78 atm for P_{N₂}, we have 10^{1.0} as the activity of NO₃⁻. This means that nitrate is very stable in aerobic media. Equation (27) also reveals that the pE at which NO₃⁻ is just detectable (10⁻⁷ M) in an aqueous system at pH 7.0 in equilibrium with atmospheric N₂ is 11.27. At this pE, P_{O₂} is 10^{-10.1}, which explains the stability of NO₃⁻ at very low O₂ concentrations even in the presence of denitrifying bacteria (Bremner and Shaw, 1958; Skerman and MacRae, 1957). But at a pE of 5.63 at pH 7.0 (the potential at which O₂ becomes undetectable), the P_{N₂} in equilibrium with 10⁻² M NO₃⁻ is 10^{0.03}. This means that NO₃⁻ is highly unstable in anaerobic media, as we have seen in Section V, B, 2.

b. *The NO₂⁻-N₂ System.* The equations for this system are



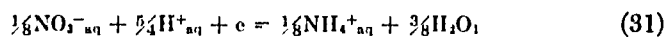
$$pE = 25.60 - \frac{1}{3}pNO_2^- + \frac{1}{6}pN_2 - \frac{1}{3}pH \quad (29)$$

In aerated media the system should be in equilibrium with the O₂-H₂O system and have a common pE. Combining Eq. (29) with Eq. (26) and substituting 0.78 for P_{N₂} and 0.21 for P_{O₂} we have

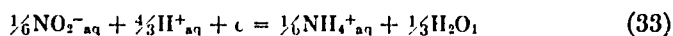
$$pNO_2^- = 14.1 - pH \quad (30)$$

This equation reveals that the concentration of NO₂⁻ in equilibrium with air and water at pH 7.0 is 10^{-7.1} M. Thus NO₂⁻ occurs in the merest traces or not at all in aerobic soils and waters (Hutchinson, 1957; Campbell and Lees, 1967) and, unlike NO₃⁻, is denitrified even in the presence of oxygen (Skerman *et al.*, 1958). In anaerobic media it is even more unstable.

c. *The NO₃⁻-NH₄⁺ and NO₂⁻-NH₄⁺ Systems.* The equations for these systems are



$$pE = 14.01 - \frac{1}{5}pNO_3^- + \frac{1}{8}pNH_4^+ - \frac{5}{4}pH \quad (32)$$

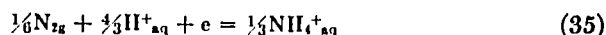


$$pE = 15.17 - \frac{1}{6}pNO_2^- + \frac{1}{6}pNH_4^+ - \frac{1}{3}pH \quad (34)$$

These equations show that in aerated media NO₃⁻/NH₄⁺ is 10^{50.70} and NO₂⁻/NH₄⁺ is 10^{10.71}, dramatizing the tremendous driving force of the oxidation of ammonia to nitrite and nitrate. But at the potential of flooded soils (pE = -1 to 3) the concentrations of NO₂⁻ or NO₃⁻ that can be

in equilibrium with NH_4^+ is infinitesimal. Measurements in lake waters, soils, and sediments support this prediction (Pearsall, 1938; Hutchinson, 1957; Patrick, 1960). Thermodynamically, the reduction of NO_3^- and NO_2^- to NH_4^+ is possible in anaerobic media. But not more than a few percent of NO_3^- goes to NH_4^+ apparently because of the tremendous driving force of the competing denitrification reactions. Plants and bacteria reduce nitrate to ammonia with the help of the powerful reductants, NADH, NADPH, and ferredoxin, generated by light or by anaerobic respiration.

d. The N_2 - NH_4^+ System. The following equations reveal that a high electron activity is necessary for the reduction of N_2 to NH_4^+



$$\text{pE} = 4.04 - \frac{1}{2}\text{pN}_2 + \frac{1}{2}\text{pNH}_4^+ - \frac{3}{2}\text{pH} \quad (36)$$

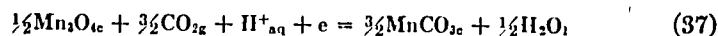
At a pH 7.0 and a P_{N_2} 0.78 atm, a detectable amount of NH_4^+ (10^{-8} M) will be present only at a pE of -2.35 . The source of electrons at high activity are NADH, NADPH, and ferredoxin (Arnon, 1965; Rabinowitch and Govindjee, 1969).

Thermodynamically, algae and anaerobic bacteria present in submerged soils can fix N_2 . Further even aerobic N_2 fixers should function more efficiently at a low O_2 concentration as Jensen (1965) has reported.

3. The Manganese Systems

Manganese is present in surface media in at least 36 oxide minerals with the metal in the valence states $+2$, $+3$, $+4$, and mixtures of these (Jenne, 1968). The complexity of the oxides of manganese and their variability make quantitative studies of the manganese systems difficult.

Reduced soils have a pE of -1 to 3 , a pH of 6.5 to 7.0 and a P_{CO_2} of 0.1 to 0.5 atm. Under these conditions, pE-pH diagrams show that the stable solid phases are Mn_3O_4 and MnCO_3 (Ponnamperuma *et al.*, 1969b). The equations for these systems are



$$\text{pE} = 18.57 - \frac{3}{2}\text{pCO}_2 - \text{pH} \quad (38)$$

The observed relationship for three reduced soils high in manganese equilibrated with different P_{CO_2} values (Ponnamperuma, 1972) was

$$\text{pE} = 10.86 - 1.11\text{pCO}_2 - \text{pH} \quad (39)$$

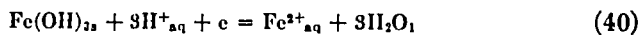
The coefficients of pCO_2 and pH are of the right order for the Mn_3O_4 - MnCO_3 system, but pEo is considerably less than that for hausmannite (Mn_3O_4). This discrepancy suggests that the Mn_3O_4 present

in these soils was far less reactive than the ideal oxide. But the value of the expression $\text{pH} + \frac{1}{2} \log \text{Mn}^{2+} + \frac{1}{2} \log P_{\text{CO}_2}$ was fairly constant and equal to 4.4 suggesting that the concentration of dissolved Mn^{2+} in reduced soils is apparently determined by the solubility of MnCO_3 .

4. The Iron Systems

We have previously reviewed the chemistry of iron and the thermodynamics of its transformations in submerged soils (Ponnamperuma *et al.*, 1967; Ponnamperuma, 1972). In this section, I review the main equilibria.

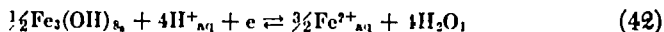
a. *The $\text{Fe}(\text{OH})_3\text{-Fe}^{2+}$ System.* The equilibrium between "ferric hydroxide" and Fe^{2+} is given by



$$\text{pE} = 17.87 + \text{pFe}^{2+} - 3\text{pH} \quad (41)$$

The pEo values calculated from Eh, pH, and Fe^{2+} activities of the solutions of 32 submerged soils ranged from 17.46 to 18.13 (Ponnamperuma, 1972). They were closest to the theoretical value of 17.87 for the ferruginous soils. The solubility of iron in submerged paddy soils is controlled by the $\text{Fe}(\text{OH})_3\text{-Fe}^{2+}$ equilibrium. In this connection, the report of Kawaguchi and Kyuma (1969) that no crystalline oxides of Fe(III) were present in the A horizon of Southeast Asian rice soils is noteworthy. In other soils the concentration of soluble Fe^{2+} may be governed by minerals intermediate in properties between ferric hydroxide and hematite (Barnes and Back, 1964).

b. *The $\text{Fe}_3(\text{OH})_8\text{-Fe}^{2+}$ System.* The gray-green color of reduced soils, often attributed to FeS, may be due to the presence of hydrated magnetite, $\text{Fe}_3\text{O}_4 \cdot n\text{H}_2\text{O}$. If this solid is present after the peak of water-soluble Fe^{2+} in submerged soils, as solubility criteria suggest, then

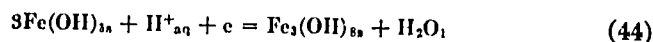


$$\text{pE} = 23.27 + \frac{3}{2}\text{pFe}^{2+} - 4\text{pH} \quad (43)$$

The pEo values calculated from Eh, pH, and Fe activities of the solutions of 32 submerged soils after the peak of water-soluble Fe^{2+} ranged from 21.8 to 23.5. The mean values for the three ferruginous soils in the group was 23.31. This is almost identical with the theoretical value for the $\text{Fe}_3(\text{OH})_8\text{-Fe}^{2+}$ system.

These findings suggest that the concentration of water-soluble iron after its peak is controlled by the solubility of $\text{Fe}_3\text{O}_4 \cdot n\text{H}_2\text{O}$ whose thermochemical properties vary with the soil.

c. *The Fe(OH)₃-Fe₃(OH)₈ System.* After the formation of Fe₃(OH)₈, the following equations are relevant



$$\text{pE} = 7.96 - \text{pH} \quad (45)$$

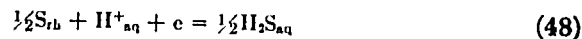
Thus the dpE/dpH slopes for the solutions of reduced ferruginous soils is -1 and pE can be derived from pH if the pE₀ characteristic of the soil is known (IRRI, 1966).

5. The Sulfur Systems

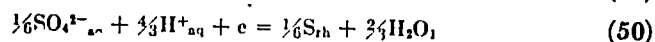
The main sulfur systems can be described by



$$\text{pE} = 5.12 - \frac{1}{8}\text{pSO}_4^{2-} + \frac{1}{8}\text{pH}_2\text{S} - \frac{5}{4}\text{pH} \quad (47)$$



$$\text{pE} = 2.40 + \frac{1}{2}\text{pH}_2\text{S} - \text{pH} \quad (49)$$



$$\text{pE} = 6.04 - \frac{1}{6}\text{pSO}_4^{2-} - \frac{3}{2}\text{pH} \quad (51)$$

These equations show that SO₄²⁻ is highly stable in air, that a chemically detectable amount of H₂S (10⁻⁶ M) will appear in a 10⁻² M SO₄²⁻ solution at pH 7.0 only at the low pE of -3.26 , and that H₂S and S are readily oxidized in air to SO₄²⁻. The oxidation of S and pyrites in mines and acid sulfate soils produce strong acidity.

B. CARBONATE SYSTEMS

Submerged soils have all the ingredients required for carbonate equilibria: (a) high concentrations of CO₂; (b) the presence of the divalent cations, Fe²⁺, Mn²⁺, Ca²⁺, and Mg²⁺, in most soils, CaCO₃ in calcareous soils, and NaHCO₃ in sodic soils; (c) intimate contact between solid, solution, and gas phases; and (d) virtual isolation of the system from the surroundings. Thus sodic soils behave like NaHCO₃, calcareous soils like CaCO₃, ferruginous soils like Fe₃O₄·*n*H₂O, and manganiferrous soils like MnCO₃ when submerged and equilibrated with CO₂ (Ponnamperuma *et al.*, 1969a).

1. The Na₂CO₃-H₂O-CO₂ System

The partial pressure of CO₂ and the concentration of Na⁺ associated with HCO₃⁻, CO₃²⁻, and OH⁻ determine the pH of this system according

to the equation (Ponnamperuma, 1967)

$$\text{pH} = 7.85 + \log [\text{Na}^+] - \log P_{\text{CO}_2} - 0.51I^{1/3} \quad (52)$$

The pH values of soils containing NaHCO_3 equilibrated with CO_2 at different P_{CO_2} values conformed closely to Eq. (52) (Ponnamperuma *et al.*, 1966a, 1969a). Nakayama (1970) has derived equations for the CaCO_3 - NaHCO_3 - H_2O - CO_2 system and proved them experimentally.

2. The CaCO_3 - H_2O - CO_2 System

The theoretical equations for this system (neglecting the effect of complexes) are

$$\text{pH} = 5.99 - \frac{2}{3} \log P_{\text{CO}_2} + \frac{1}{3} (\log \gamma_{\text{HCO}_3^-} - \log \gamma_{\text{Ca}^{2+}}) \quad (53)$$

$$\text{pH} + \frac{1}{2} \log \text{Ca}^{2+} + \frac{1}{2} \log P_{\text{CO}_2} = 4.92 \quad (54)$$

Equation (53) can be simplified to

$$\text{pH} = 6.08 - \frac{2}{3} \log P_{\text{CO}_2} \quad (55)$$

Calcareous soils, both aerobic and anaerobic, conformed closely to Eq. (55) (Ponnamperuma *et al.*, 1966a, 1969a; IRRI, 1966), but the slightly higher values obtained for the constant (6.1) indicated that the CaCO_3 in these soils was slightly more soluble than calcite. Olsen and Watanabe (1960) reported that calcareous material in soils is apparently more soluble than calcite.

3. The MnCO_3 - H_2O - CO_2 System

When a manganiferous soil is submerged, the concentration of water-soluble Mn increases rapidly, reaches a peak, and declines rapidly (Section V, D). The decrease has been attributed to the precipitation of MnCO_3 (IRRI, 1964, 1965; Ponnamperuma *et al.*, 1969b).

If MnCO_3 is present, the following equations should apply (Ponnamperuma, 1967)

$$\text{pH} = 5.42 - \frac{2}{3} \log P_{\text{CO}_2} + \frac{1}{3} (\log \gamma_{\text{HCO}_3^-} - \log \gamma_{\text{Mn}^{2+}}) \quad (56)$$

$$\text{pH} + \frac{1}{2} \log \text{Mn}^{2+} + \frac{1}{2} \log P_{\text{CO}_2} = 4.06 \quad (57)$$

When we plotted the pH values of the solutions of reduced manganiferous soils against $\log P_{\text{CO}_2}$, we obtained straight lines with slopes of 0.6–0.7 but intercepts of about 5.9 (IRRI, 1965). An equilibrium study in the laboratory with three reduced soils containing more than 0.3% reducible Mn yielded slopes of 0.64–0.67 and intercepts of 6.08–6.11. A plot of

pH + $\frac{1}{2}$ log Mn²⁺ against log P_{CO_2} , in the same study, gave slopes of 0.46 to 0.53 and intercepts of 4.37 to 4.56.

These data indicate that the MnCO₃ present in submerged soils (probably as a fine precipitate coating soil particles) is more soluble than rhodocrosite.

4. The FeCO₃-H₂O-CO₂ System

Conditions in submerged soils seem to be ideal for the precipitation of FeCO₃, and indeed siderite is found in marshes. But apparently it does not precipitate during short periods of submergence, for the solubility of iron in the solutions of submerged soils is almost 100 times that permitted by the solubility product of FeCO₃ ($10^{-10.24}$) given by Singer and Stumm (1970). There is no satisfactory explanation of this anomaly (Ponramperuma, 1972).

Reduced ferruginous soils do not satisfy the equations for the FeCO₃-H₂O-CO₂ equilibrium, but when such soils are equilibrated with CO₂ at different P_{CO_2} values they give a pH—log P_{CO_2} relationship almost identical with that for Fe₂O₃·*n*H₂O (Ponramperuma *et al.*, 1969a) namely

$$\text{pH} = 6.1 - 0.58 \log P_{CO_2} \quad (58)$$

VII. Perspectives

Two recent developments have stimulated interest in the chemistry of submerged soils: the breeding of lowland rice varieties with a high yield potential; and the pollution of streams, lakes, and seas by domestic, agricultural, and industrial wastes. The chemistry of submerged soils is valuable (a) in understanding soil problems limiting the performance of high-yielding rice varieties, and (b) in assessing the role of lake, estuarine, and ocean sediments as reservoirs of nutrients for aquatic plants and as sinks for terrestrial wastes.

The chemical and electrochemical changes in paddy soils have been described adequately, but information on the dynamics of cold, cumulative, underwater lake and ocean muds is meager.

In spite of the availability of a large body of information on the chemistry of submerged soils, the following observations have not been satisfactorily explained: (a) the difference in oxidation-reduction potential between submerged soil or sediment and the interstitial solution; (b) the release of water-soluble phosphate when a soil or sediment undergoes reduction; (c) the dynamics of water-soluble silica in submerged soils; (d) the

decrease in the solubility of zinc brought about by soil submergence; (e) the supersaturation of solutions of submerged soils with respect to siderite; and (f) the much lower reactivity of the manganese oxides occurring in paddy soils compared to that of the pure oxides.

Quantitative studies of redox, carbonate, and silicate equilibria in submerged soils are likely to yield valuable information on the dynamics of ecologically important elements. A prerequisite to these studies is mineralogical and thermodynamic research on the metastable precipitates, the complex oxides and coprecipitates, the solid solutions, and the surface-active solids present in soils that undergo alternate oxidation and reduction. The chemistry of hydrated magnetite and its role in mineral equilibria in submerged soils and lake muds require further investigation. The redox potential of the interstitial solutions of muds is an ecologically and thermodynamically meaningful parameter, so its use should be encouraged.

The role of alternate oxidation and reduction in the biodegradation of detergents and pesticides merits study.

A submerged soil appears to be an ideal medium for both aerobic and anaerobic nitrogen fixation, especially in the presence of rice plants. But quantitative data on the amounts fixed and methods of increasing fixation are meager. Augmenting nitrogen fixation in paddy fields can be a boon to the farmers of developing countries.

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