



## Interlinked chemical-biological processes in anoxic waterlogged soil – A review

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### ABSTRACT

Wetland soils are predominantly oxygen-free includes swamps, marshes, coastal wetlands, floodplains, etc. and globally important for rice cultivation. The chemical changes happen due to changing electrochemical properties and also by anaerobic microorganisms. Anaerobic microorganisms play a key role in bringing about nutrient transformations with a general trend of increase in soil pH, electrical conductivity, and ionic strength but decrease in redox potential in waterlogged soils. The biogeochemical cycling of nutrients (C, N, P, S) by facultative and obligate anaerobes help to sustain life in submerged conditions. Under flooded conditions the availability of P, Ca, Mg, Fe, Mn, Mo, and Si increases while that of S, Zn and Cu decreases. Moreover, fermentative bacteria decompose organic matter into CO<sub>2</sub>, H<sub>2</sub>, acetate, propionate, butyrate, fatty acids, amino acids, alcohols, etc. with a terminal step of methane formation by methanogens. Anaerobic soils are thus important for maintaining fertility, ecosystem productivity, and functions.

**Key words:** Anaerobic soil, C-N transformations, Microorganisms, Nutrient cycling, Soil organic matter, Waterlogging

When a soil is waterlogged, a series of changes may occur in soil due to changes in soil physico-chemical and microbiological properties. As a consequence, the solubility of some compounds increase, a fraction of soluble nutrients can be leached out from rhizosphere and some new undesirable toxic compounds may be formed due to complex chemical reactions. The main driving force for such changes is primarily a decrease in redox potential. In an aerobic soil oxygen acts as electron acceptor, but when the soil is waterlogged the remaining oxygen is soon utilized in respiration by root and, microorganisms. In absence of free oxygen, other oxygen containing compounds available in the soil become electron acceptors and are transformed into a more reduced form, but the ability to accept electrons varies from compound to compound. In submergence, reduced conditions can be the consequence of either biological or chemical reduction. Biological reduction is caused by microorganisms oxidizing organic material and transferring electrons to other chemical components of the soil. Though this is the most common type of reduction in submerged soils, but there is also evidence that chemical reduction may occur as well, especially in subsoil (Lind and Pederson 1976). Theoretically, the sequence of reduction of a submerged soil is governed by the laws of thermodynamics.

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The sequence would be the reduction of O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Mn<sup>4+</sup>, Fe<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>2</sub> and H<sup>+</sup> to their reduced counterparts H<sub>2</sub>O, N<sub>2</sub>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, H<sub>2</sub>S, CH<sub>4</sub> and H<sub>2</sub> (Ponnamperuma 1972). Some typical redox reactions in soil systems and their redox potentials were listed out (Table 1) (Russell 1973).

The environment of submerged soils notably differs from that of the normal arable soils. Lack of free oxygen (may be available in a few micro pockets) and the reduced state of all essential elements in submerged soils usually differ it from normal arable soil. In submerged soils, which is generally anoxic, O<sub>2</sub> usually diffuses from the surface into the soil and creates a thin (1 to 5 mm deep) oxic soil layer. It also penetrates from roots of aquatic plants with gas vesicular systems into deeper soil layers. Aerobic bacteria obligatorily need oxygen for its survival and functioning, so well-drained soils become their habitat. On the other hand, anaerobic bacteria live in oxygen-free environment. This group includes very ancient types of bacteria that live inside the soil aggregates. Anaerobic bacteria favour wet, poorly drained soils and they can produce various toxic compounds that can limit root growth and predispose plants to root diseases.

Submerging a soil under water triggers certain physical, chemical and biological changes that greatly alter the dynamics of soil fertility and finally impacts on the crops growth in that soil such as wetland rice (Sahrawat 2005). Wetland rice systems in Asia is considered a global hub of rice supply. Interestingly the system is able to maintain soil fertility on a sustainable basis, which is unique of its kind. The essential components of wetland rice culture comprise

Table 1 Range of redox potentials (Eh), ranges of redox potentials at which the main oxidized components in submerged soils and redox potentials of typical soil systems

Soil water condition	Redox potential (mV)	Reaction	Redox potential (mV)	System	Redox potential (mV) (at 25°C, pH 7.0)
Well-drained (aerated)	+700 to +800	O <sub>2</sub> -H <sub>2</sub> O	+380 to +320	O <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> = H <sub>2</sub> O	820
Moderately reduced	+400 to +200	NO <sub>3</sub> <sup>-</sup> -N <sub>2</sub> , Mn <sup>4+</sup> -Mn <sup>2+</sup>	+280 to +220	NO <sub>3</sub> <sup>-</sup> + 2H <sup>+</sup> + 2e <sup>-</sup> = NO <sub>2</sub> + 2H <sub>2</sub> O	420
Reduced	+100 to -100	Fe <sup>3+</sup> -Fe <sup>2+</sup>	+180 to +150	MnO <sub>2</sub> + 4H <sup>+</sup> + 2e <sup>-</sup> = Mn <sup>2+</sup> + 2H <sub>2</sub> O	410
Highly reduced	-100 to -300	SO <sub>4</sub> <sup>2-</sup> -S <sup>2-</sup> CO <sub>2</sub> -CH <sub>4</sub>	-120 to -180	Fe(OH) <sub>3</sub> + 3H <sup>+</sup> + e <sup>-</sup> = Fe <sup>2+</sup> + 3H <sub>2</sub> O	-180
				SO <sub>4</sub> <sup>2-</sup> + 10H <sup>+</sup> + 8e <sup>-</sup> = H <sub>2</sub> S + 4H <sub>2</sub> O	-220
				CO <sub>2</sub> + 10H <sup>+</sup> + 8e <sup>-</sup> = CH <sub>4</sub> + 2H <sub>2</sub> O	-240
				2H <sup>+</sup> + 2e <sup>-</sup> = 2H <sub>2</sub> O	-413

Source: Russell (1973); Patrick and Reddy (1978).

cultivation of land in the wet or flooded state (puddling), transplanting of rice seedlings into puddled rice paddies, and growing the rice crop under flooding. The land is dry or flood fallowed during the turn around period between two crops. Following these cultural practices, two or three crops of rice or rice with upland crops in sequence are grown. Growing rice in submerged soils has great ameliorative effect on chemical fertility: largely by bringing pH in the neutral range, resulting in better availability of plant nutrients and accumulation of organic matter (Sahrawat 2005).

#### Redox couples and electron acceptors

Principal redox couples in sequence in submerged soils are: O<sub>2</sub>/H<sub>2</sub>O, NO<sub>3</sub><sup>-</sup>/N<sub>2</sub>, Mn(IV, III)/Mn(II), Fe(III)/Fe(II), SO<sub>4</sub><sup>2-</sup>/H<sub>2</sub>S, and CO<sub>2</sub>/CH<sub>4</sub>. The main electron-acceptors in submerged soils include dissolved O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Fe(III), SO<sub>4</sub><sup>2-</sup>, and CO<sub>2</sub>. The final products of reduction in submerged soils are Fe(II), H<sub>2</sub>S, and CH<sub>4</sub>, although intermediate products such as dissolved H<sub>2</sub> and H<sub>2</sub>S are also found in submerged soils and sediments. The redox reactions influence soil properties and fertility in submerged soils and sediments which affect their primary productivity and environmental quality (Ponnamperuma 1972). It is known that when soil is submerged, oxygen in the system is rapidly consumed during aerobic microbial respiration. This is followed by successive use of NO<sub>3</sub><sup>-</sup>, Mn(IV), Fe(III), and SO<sub>4</sub><sup>2-</sup> as electron acceptors in anaerobic microbial respiration. Also, in the absence of oxygen, facultative and obligate anaerobes use the dissimilation products of carbohydrates and proteins as electron acceptors in their respiration.

In most rice soils, Fe is the main electron acceptor. Iron occurs as Fe(III) oxides and oxyhydroxides, and in the structure of clay minerals. In a study of the long-term effects of intermittent flooding of a Vertisol, Favre *et al.* (2002) showed that cation exchange capacity (CEC) of the soil in the reduced state following flooding increased to twice that of its oxidized, unflooded state. The increase in CEC was caused by the increase in structural Fe(II) upon reduction and the removal of Fe oxyhydroxide coatings by reductive dissolution. It has also been suggested that

the changes in CEC and related redox reactions may be important in substantially modifying proton, anion, and cation balances in intermittently flooded soils.

Soil reduction in submerged soils and sediments is measured by redox potential (Eh) and expressed in mV. The measured Eh can be explained by the concentration of some redox systems. Dissolved O<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are relatively electrode-insensitive and others, especially Fe(III) play important role in the soil reduction, measured by Eh (Gao *et al.* 2002). The data on the range of redox potentials (Eh) encountered in soils and sediments ranging from well drained to submerged or flooded conditions was summarized (Table 1). The data can serve as a guideline for classifying soil reduction under diverse soil moisture regime (Patrick and Reddy 1978). The approximate Eh values at which the main oxidized components in submerged soils become unstable were shown (Table 1).

#### Effect of vertical redox gradients

In general, below ground O<sub>2</sub> is depleted rapidly with distance from the soil surface or the root surface, resulting in redox stratification. This stratification theoretically creates relatively well-defined habitats for the different groups of trace gas-metabolizing microorganisms. The different redox zones are characterized by the dominance of the electron acceptors O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Mn<sup>4+</sup>, Fe<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup>, and CO<sub>2</sub> (Fig 1) (Zehnder and Stumm 1988, Conrad 1996).

The redox potential describes which way chemical reactions will proceed in oxygen deficient soils and controls the nutrient cycling in flooded systems. Redox potential, or reduction potential, is used to express the possibility of an environment to receive electrons and therefore become reduced. For example, if a system already has plenty of electrons (anoxic, organic-rich shale) it is reduced and will likely donate electrons to a part of the system that has a low concentration of electrons, or an oxidized environment, to equilibrate to the chemical gradient. The oxidized environment has high redox potential, whereas the reduced environment has a low redox potential.

The depth of the oxic surface layer is the result of

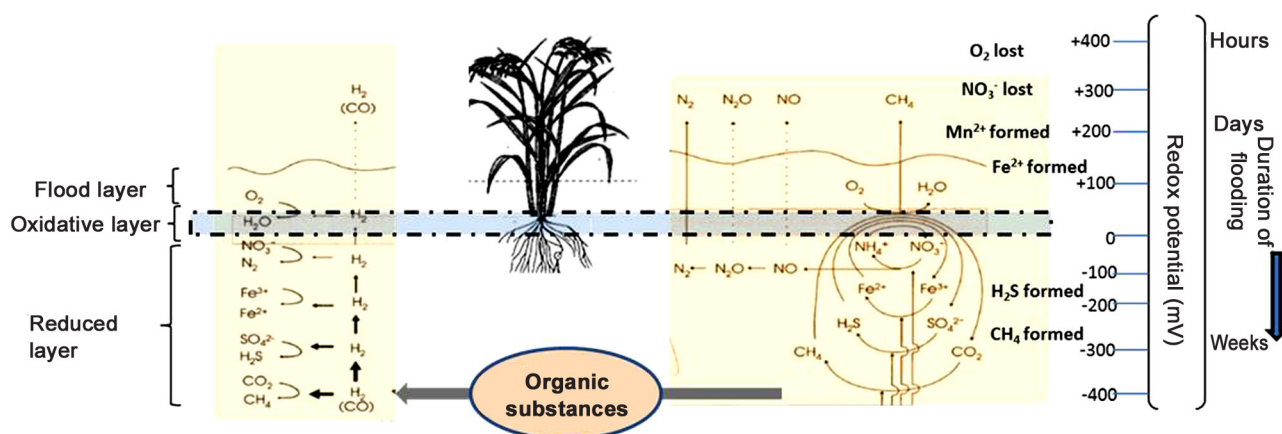


Fig 1 Schematic diagram of vertical distribution of different redox reactions operated in a submerged soil (modified from Conrad 1996)

a balance between the influx of  $O_2$  from above and the  $O_2$  consumption by the soil microflora. The  $O_2$  influx is mainly due to molecular diffusion but may be enhanced by bio-irrigation of the soil fauna and by photosynthetic  $O_2$  production by benthic algae (Asakawa and Hayano 1995). This photosynthetic active layer is called as Photic zone, where both photosynthetic and respiration processes are major biochemical activity. The  $O_2$  consumption and thus the  $O_2$  penetration depth are a function of the availability of degradable organic matter present in the surface layers (Revsbech *et al.* 1980). However,  $O_2$  consumption in the surface layer is also a function of the production of reduced compounds such as  $CH_4$ , ammonium, ferrous iron, and sulfide in the anoxic layers below. These compounds diffuse upward until they reach the oxic zone, and there they contribute to the microbial and chemical  $O_2$  demand (Sweerts *et al.* 1991). The redox potential at which  $O_2$  disappears from the wetland soil system was found to be in the range of +320 to +340 mV. Oxygen reaching at the soil or sediment surface to water column is consumed during the following processes: 1. Heterotrophic microbial respiration in the aerobic soil layer where  $O_2$  is used as an electron acceptor. 2. Chemical oxidation of reduced Fe, Mn and sulfides which diffuse from the anaerobic to aerobic soil layer, these reduced ion species have previously served as electron acceptor in the respiration of facultative anaerobes. 3. Biological autotrophic oxidation of ammonium-N by strictly anaerobes.

Most wetland soils are devoid of  $O_2$  (below 2 to 3 mm depth) and also contain no other electron acceptors (below a few centimeters depth) other than  $CO_2$  and  $H^+$ . Therefore, this zone is dominated by fermentation and methanogenesis (Fig 1).

Production of  $H_2$  by fermentation is intensive, but most of the produced  $H_2$  (together with  $CO_2$ ) is immediately converted by methanogens to  $CH_4$ , so that the steady-state concentration of  $H_2$  is typically in the nanomolar range (10 to 180 nM, corresponding to about 8 to 140 ppmv in the gas phase) (Conrad 1996). Methane is an end product of the microbial metabolism in this zone and occurs in

concentrations equivalent to mixing ratios of up to 90% (Freney *et al.* 1981). Further, trace gases that seem to be produced in the anoxic soil zone are CO and OCS (atmospheric carbonyl sulfide).

The sulfate reduction zone can also be quite extensive in wetland soils, especially in marshes that are influenced by seawater. Sulfate reducers consume  $H_2$  and, in steady state, reduce the  $H_2$  concentration to lower values than found in the methanogenic zone, typically less than 2 to 10 nM (Acht nich *et al.* 1995). Therefore, there will be a flux of  $H_2$  from the methanogenic into the  $SO_4^{2-}$ -reducing zone (Fig 1). The  $Fe^{3+}$ -reducing zones should further reduce the  $H_2$  concentration, since iron reducers are able to metabolize  $H_2$  more efficiently than are sulfate reducers. The  $NO_3^-$  reduction zone is the site where  $H_2$  concentrations are kept at a low partial pressure by the action of, e.g. denitrifiers. In this zone production and consumption of NO and  $N_2O$  occur by the action of denitrifiers; nitrification of ammonium in the oxic surface layer is an important source of nitrate and that denitrification is often tightly coupled to this process. But, the fluxes of NO and  $N_2O$  into the atmosphere are relatively small, mainly because most of the produced NO and  $N_2O$  is further reduced to  $N_2$ .

The oxic zone of waterlogged soil is dominated by consumption of trace gases, i.e. oxidation of  $CH_4$ ,  $H_2$ , CO, and  $H_2S$  with  $O_2$  as the electron acceptor (Fig 1) having generally much higher concentrations than the concentrations detected in the atmosphere or the gaseous pore space of upland soils.

In wetlands, large quantities of dissolved organic carbon (DOC) are solubilized under reducing conditions. The following mechanisms are involved in the mobilization of DOC under reducing conditions in wetlands soils: i) production of soluble organic metabolites by reducing bacteria; ii) release of OM bound to reductively dissolved Mn and Fe-oxyhydroxides; iii) desorption of OM sorbed onto soil minerals due to pH rise during reduction (Grybos *et al.* 2009).

Although the zonation in wetland soil is usually relatively well defined, but activity overlaps may occur.

Although CH<sub>4</sub> production is usually inhibited by the presence of SO<sub>4</sub><sup>2-</sup>, Fe<sup>3+</sup> or NO<sub>3</sub><sup>-</sup>, mainly since sulphate reducers, iron reducers, and nitrate reducers compete with methanogens for common electron donors (Ward and Winfrey 1985), but the simultaneous operation is possible if electron donors are not limiting, e.g. in organic-rich soils and sediments (Achnich *et al.* 1995).

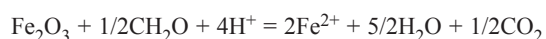
#### *Chemical fertility under anoxic-submerged soil*

The most important influence of submerging a soil in water is to reduce oxygen supply. As a result, the entrained oxygen is quickly exhausted. The lack of free oxygen or an aerobiosis causes soil reduction and sets in motion a series of physical, chemical and biological processes. The main electrochemical changes that effect the chemistry and fertility of submerged soils are:

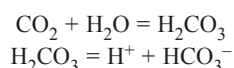
- A decrease in redox potential (redox potential, Eh) or creation of an overall reducing soil environment.
- An increase in pH values of acid soils and a decrease in pH values of alkali soils, and changes in the floodwater pH.
- An increase in specific conductance and ionic strength of soil solution.
- Ionic equilibria influence sorption–desorption reactions and the availability of major and micronutrients

Iron (Fe<sup>3+</sup>) reduction and carbon dioxide concentration [CO<sub>2</sub>] in submerged soils both play a crucial role in controlling the pH of submerged soils. However that depends on the optimum soil temperature (between 25–35°C) and availability of easily decomposable organic matter, reducible iron and other electron acceptors such as sulphate and carbon dioxide.

The pH of acidic soils increase following submergence because under anaerobic conditions, ferric iron is used as an electron-acceptor for oxidizing organic matter and during this process acidity is neutralized:



In these redox reactions, ferric iron (from amorphous ferric hydroxides) serves as an electron-acceptor and organic matter (CH<sub>2</sub>O) as the electron-donor. This reaction results in the neutralization of acidity and increase in pH. While, a decrease in pH of alkali or calcareous soils is the result of accumulation of carbon dioxide in flooded soil, which effectively neutralizes alkalinity. Moreover, carbon dioxide produced is retained in the flooded soil due to restricted diffusion through standing flood-water layer on the soil surface. This allows large quantities of carbon dioxide to accumulate and form mild acid, which help in neutralizing alkalinity in the soil–floodwater system:



Submergence of aerobic soils in water decreases its Eh that drops and stabilizes at a fairly stable range of + 200 mV to –300 mV depending on the soil, especially the content of organic matter and reducible species (nitrate, sulphate and ferric iron), particularly iron. But Eh of the surface water

and the first few millimetres of top soil in contact with the surface water remain relatively oxidized in the Eh range of + 300 to + 500 mV. Arrange of Eh is encountered in various soils from well-drained, aerated to waterlogged conditions (Table 1). The Eh of soils controls the stability of various oxidized components [oxygen, nitrate, manganese (Mn IV), ferric (FeIII) iron, sulphate (SO<sub>4</sub><sup>2-</sup>), carbon dioxide] in submerged soils and sediments (Table 1).

Under a few millimeters of water heterotrophic bacteria metabolize and consume oxygen. They, therefore, deplete the soil of oxygen and create the need for anaerobic respiration. Some anaerobic microbial processes including denitrification, sulfate reduction and methanogenesis are responsible for the release of N<sub>2</sub> (nitrogen), H<sub>2</sub>S (hydrogen sulfide) and CH<sub>4</sub> (methane). Other anaerobic microbial processes are linked to changes in the oxidation state of iron and manganese. As a result of anaerobic decomposition, the soil stores large amounts of organic carbon because decomposition is incomplete. Relatively higher accumulation of organic matter (organic C and total N) in wetland soils makes them attractive for sequestration of C for increasing the fertility of wetland soils.

Flooding of soil is a great equalizer of diversity in chemical fertility of wetland soils. This change is brought about by consumption of acidity in acid soils and the neutralization of alkalinity in alkaline and calcareous soils following flooding. As a result of flooding, the pH of acidic soils increases and that of alkaline soils decreases and the chemical reaction of submerged soils generally stabilizes in the neutral range. The availability of free water on the soil surface not only relieves moisture stress, but also provides a more conducive environment to rice roots, and availability and accessibility of nutrients through diffusion and mass flow to plant roots. The convergence of soil pH to neutrality following submerging of soils benefits wetland rice crop through better availability of nutrients such as ammonium, P, K and exchangeable cations, which are mobilized in soil solution. The convergence of pH to near neutral also affects the availability of plant nutrients mostly in a favourable manner. However, soil reduction, following flooding of soils that are rich in reducible iron, accumulates excessive concentrations of iron in the soil solution that could be toxic to wetland rice. Also, production of reduction products in submerged soils, such as sulphide and organic acids in flooded soils, may cause toxicity and retardation of rice plant growth, especially in soils that are high in easily decomposable organic matter or if high amounts of organic materials are added to the soil. Distinct changes in the availability of plant nutrients and organic matter due to flooding of soil was summarized (Table 2).

#### *Major nutrient cycles in submerged soil*

##### *C cycle*

The anaerobic microbes play a key role for nutrient cycling in the submerged soil. The process of nutrient transformation and decomposition of organic matter is much

Table 2 Changes in soil fertility parameters and consequent plant available nutrients under submergence

Chemical property	Alterations following soil submergence
pH	Towards neutral pH
Organic matter	Favours accumulation of organic C and N
Reduction products	More sulphide and organic acids, especially products in degraded soils may cause toxicity or injurious effects to growing plants
<i>Macronutrients</i>	
Ammonium-N	Release and accumulation of $\text{NH}_4^+$ favoured
P	P availability improves, especially in soils high in Fe and Al oxides
K	K availability improves through exchange of $\text{K}^+$
<i>Secondary and micronutrients</i>	
Ca, Mg, Na	Favours release of Ca, Mg and Na in solution
S	Sulphate reduction may reduce sulphur availability
Fe	Iron availability improves in alkali and calcareous soils, but Fe toxicity may occur in acidic soils high in reducible Fe
Al	Al toxicity is generally absent, except perhaps in acid sulphate soils
Cu, Zn and Mo	Improves availability of Cu and Mo but not of Zn

Source: Sahrawat (2005)

slower and less efficient than the aerobic microbes. As a result, the rate of decay of organic matter tends to be slow in flooded soils. Microbial transformations of elements in anaerobic soils play a major role in biogeochemical cycling of nutrients and in greenhouse gas emissions. Heterotrophic respiration may completely deplete oxygen in flooded soils; and these effects may be observed within only a few millimeters of the soil surface. Due to the absence of oxygen in flooded soils, those organisms inhabiting flooded soils must be able to survive with little to no oxygen. Anaerobic microbial processes including denitrification, methanogenesis, and methanotrophy are responsible for releasing greenhouse gases ( $\text{N}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{CO}_2$ ) into the atmosphere (Gotoh and Patrick 1972). 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 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  $\text{CO}_2$ , nitrate, sulphate, and resistant residues (humus); while in submerged soils, they are  $\text{CO}$ , hydrogen, methane, ammonia, amines, mercaptans, hydrogen sulfide, and partially humified residues. Carbohydrate metabolism is probably the same in both aerobic and anaerobic soils until the formation of the

key metabolite, pyruvic acid.

#### *N cycle*

In upland soils, the process of mineralization gradually converts organic nitrogen to ammonium and then to nitrate. Under flooded conditions, due to the low oxygen concentration, the end product of the mineralization process is ammonium. In flooded soils, such as rice paddy, two layers are formed an oxidative layer at the soil/water interface, which is less than one inch thick, and a reductive layer beginning immediately beneath. If nitrate fertilizer is added to flooded soil, bacteria can convert it to nitrogen gas (denitrification), which may be lost to the atmosphere (Samson *et al.* 1990). Ammonium fertilizer placed in the oxidative layer also may be converted to nitrates, just as in an upland soil.

The ammonia produced by nitrogen fixing bacteria is usually quickly incorporated into protein and other organic nitrogen compounds ( $\text{NH}_4^+$  Organic N), either by a host plant, the bacteria itself, or another soil organism. When organisms nearer the top of the food chain eat, nitrogen has been fixed initially by nitrogen fixing bacteria (Glass 2003).

The association between nitrogen (N) management, crop N uptake and gaseous losses is needed to reduce  $\text{N}_2\text{O}$  losses is often elicited. Synchronizing N fertilizer supply with peak crop demand may significantly reduce  $\text{N}_2\text{O}$  losses from the waterlogging-prone soils. The enhanced crop N uptake from urea top-dressed around stem extension is likely to benefit grain quality, especially protein (Harris *et al.* 2016).

#### *S cycle*

Similar to nitrogen, sulphur occurs in several oxidation states in submerged soils and its transformations are mostly microbial mediated processes. Sulphate washed into wetlands or deposited from the atmosphere is further reduced to  $\text{S}^{2-}$  in reactions mediated by sulphate reducing bacteria. Subsequent precipitation of  $\text{S}^{2-}$  with metals, especially  $\text{Fe}^{2+}$ , results in more or less permanent removal of the S from the global S cycle. Wetlands are therefore a potentially important sink for excess S released into the environment by means of fossil fuel burning. Some of the  $\text{S}^{2-}$  may be emitted as  $\text{H}_2\text{S}$  in organic soils, but in submerged mineral soils the concentration of  $\text{Fe}^{2+}$  is usually sufficient to prevent this. Hence measured emissions of  $\text{H}_2\text{S}$  and other forms of volatile S from wetlands are generally modest, and in general wetlands are a net sink for S. The concentration and availability of S in wetland soils rarely limit biological production.

#### *P cycle*

Though orthophosphate itself is generally not reduced in submerged soils, reduction of ferric iron compounds and changes in the electrochemical properties of the surfaces with which orthophosphate reacts strongly affect its solubility and dynamics. In agricultural wetlands with a history of P fertilization, submergence often results in enhanced availability of P to plants, and responses to additions of

further fertilizer in rice fields are often weak. However in natural wetlands, P concentrations are much smaller and P washed into the soil becomes strongly sorbed on the surfaces of reduced soil constituents. Phosphorus brought in with sediment may also be effectively filtered out by water passing through wetlands, particularly freshwater wetlands, is thus found with deficient in P.

#### *Oxic vs. anoxic soil –source(s) and sink(s) of trace gases*

Upland soils are generally well-aerated, not water-saturated andoxic, in contrast to submerged soils; those are partially or fully water-saturated soils and are mostly anoxic. These two groups of soils are characteristically different with respect to microbial production and consumption of trace gases. Wetland soils are especially important sources of atmospheric CH<sub>4</sub> and had been studied in various types of wetlands (e.g. paddy fields, fens, and wet tundra). However NO and N<sub>2</sub>O fluxes from wetland soils are less over upland soils, may be due to their reduction by denitrifiers to N<sub>2</sub>(Conrad 1996). Submerged rice fields seem to act occasionally even as a sink for atmospheric N<sub>2</sub>O. Upland soils, on the other hand, are both sources of and sinks for atmospheric trace gases. They are net sinks for atmospheric H<sub>2</sub>, CO, and CH<sub>4</sub> but net sources of N<sub>2</sub>O and NO (Table 3).

#### *Microbial interferences*

In general, microorganisms are more abundant and diverse, and distribute more evenly in the oxic layers than the anoxic layers. The decrease in abundance with increasing oxygen and substrate limitation, however, is considerably more drastic than the decrease in diversity, suggesting that growth of soil microorganisms is more energy demanding than maintenance. The lower diversity in the anoxic than the oxic soils is attributed primarily to the differences in oxygen availability in these soils (Song *et al.* 2008).

Three distinct situations arise at any anoxic submerged soil that may profusely encourage microbiological changes, such as: 1. pH approaches towards neutrality; 2. O<sub>2</sub>

Table 3 Role of microorganisms for the production and consumption of atmospheric trace gases in anoxic wetland soils

Trace gases	Production by	Consumption in
H <sub>2</sub>	Fermenting bacteria	Methanogens, sulfate reducers, ferric iron reducers
CO	Anaerobic bacteria	Anaerobic bacteria (Carboxydrotrophs)
CH <sub>4</sub>	Methanogens	Methanotrophs
OCS	Microbes with thiocyanate hydrolase	Microbes with carbonic anhydrase
N <sub>2</sub> O	Denitrifiers, nitrifiers	Denitrifiers
NO	Denitrifiers, nitrifiers	Denitrifiers, methanotrophs, heterotrophic bacteria

Source: Conrad (1996)

concentration varies both vertically and radial around root, causes changing Eh; 3. availability of Fe, Mn, etc. are more. Due to these reasons different types of microorganisms (mainly facultative to strict anaerobes) are adapted to grow in this situation; even the biological N<sub>2</sub> fixing microbes are also abundant. Differences in microbial population between upland and submerged soil are also quite prominent (Table 4).

Generally soils are well aerated, so anaerobic microbial activities are restricted to small anoxic sites for short periods. Anaerobiosis exclusively predominates in some cases, including (i) flooded soils (rice paddies, wetlands and peatlands) and (ii) heavily organic amended soils, where a transient excess of moisture exists (Dassonville and Renault, 2002). Anaerobiosis can have an impact on soil functions as well as on the deep vadose zone, the underlying aquifer and the atmosphere. Within soil, it affects the growth of roots by modifying the bio availability of nutrients (e.g. P) and O<sub>2</sub> for roots without aerenchyma, i.e. that cannot transport gases from shoots to roots, and also all aerobic microbial activities. Anaerobic microbial activities can lead to the accumulation of transient products that are toxic (e.g. lactate, propionate and butyrate), the mobilization of metals (e.g. Al or Mn) through changes in Eh and/or pH, and the production of simple organic molecules.

#### *Anaerobic microbial activities and organic matter decomposition*

Under similar soil and climatic conditions, the maintenance of organic matter and fertility would seem more feasible in wetland rice than in upland rice-growing conditions. The results from long-term studies of soil organic matter dynamics in upland and wetland rice-based production systems support this conclusion (Sahrawat 2004, 2005).

Both aerobic and anaerobic microbial catabolism preliminarily involve the hydrolysis of organic polymers (lignin, polysaccharides, lipids, proteins and some other complex compounds), followed by the oxidation of the monomers produced. The products of the initial hydrolysis

Table 4 Differences between upland and submerged microorganisms

Nature of microbes	Upland soil	Submerged soil
Anaerobic microbes	Less	More
SO <sub>4</sub> <sup>2-</sup> reducers	Less	More
Denitrifiers	Less	More
Strict aerobes	More	Less
Gm(+) and Gm (-) bacteria	More Gm(+) bacteria	Both Gm(+) and Gm(-) bacteria
Fungi and actinomycetes population	Comparatively more	Comparatively less

Source: Ponnampereuma (1972)

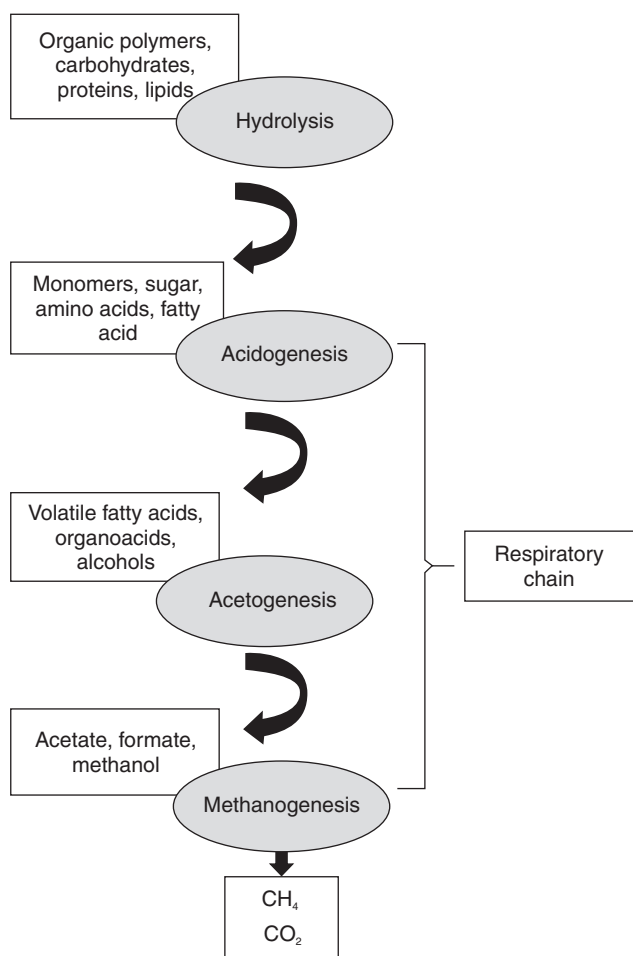
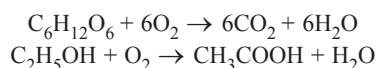


Fig 2 Schematic diagram showing the main pathways involved in the anaerobic degradation of organic matter (modified from Dassonville and Renault, 2002).

are identical, but aerobic and anaerobic conditions involve different microbial communities and different mechanisms, leading to different reaction rates (Kristensen 1995). The products of the initial hydrolysis are (i) mainly glucose, some other pentoses (fructose, etc.) and hexoses (galactose, etc.) from polysaccharides, (ii) free organic acids and other simple compounds such as glycerol and galactose from lipids and (iii) amino acids with various functional groups (including  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{SH}$ , and aromatic cycles) from proteins. Organic monomers are oxidised through different pathways (Fig 2) (Dassonville and Renault 2002). Reactions during heterotrophic oxidation of organic matter are as below:



- *Catabolism* producing  $\text{CO}_2$  similar to aerobic catabolism when there are terminal electron acceptors such as N-oxides ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{N}_2\text{O}$ ) to totally oxidise various monomers. Fe- and Mn-oxides can act significantly as terminal electron acceptors in microbial respiration. Toxic metals (Cr(VI)), metalloids (As(V), Se(VI)) and radionuclides (U(VI)) can also be used as electron acceptors in contaminated environments (Lovley 1995).

- *Fermentation* pathways, including hydrolysis i.e. conversion of polymer to monomer is mainly performed by primary fermenter, *Acetovibrio cellulolyticus*; and *acidogenesis*, in which various carbohydrates and amino-acids are metabolised to alcohols and organic acids.  $\text{CO}_2$  and  $\text{H}_2$  can be produced simultaneously from the lysis of formate. During fermentation, microorganisms use some of the substrates or transient organic compounds as electron acceptors.
- *Acetogenesis*, using fermentation products such as volatile fatty acids, alcohols, amino-acids, and in some case aromatic compounds as substrates for acetate and  $\text{H}_2$  production.
- *Reduction* of oxidized sulphur compounds to oxidize fermentation products (acetate, propionate, butyrate, etc.) with  $\text{SO}_4^{2-}$  and  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ , or S as final electron acceptors, involving *Desulphovibrio desulfuricans*; this respiration leads either to acetate,  $\text{H}_2\text{S}$  and  $\text{CO}_2$  production, or to  $\text{H}_2\text{S}$  and  $\text{CO}_2$  production, according to the functional microbial populations.
- *Methanogenesis*, that produces  $\text{CH}_4$  from either substrates such as acetate (acetoclastic pathway), or  $\text{CO}_2$  and  $\text{H}_2$  (hydrogenoclastic pathway). During carbohydrate degradation, the acetoclastic pathway generally contributes to 2/3rd of  $\text{CH}_4$  production, whereas the hydrogenoclastic pathway accounts for only 1/3rd (Wogel 1988). Some other compounds contribute to the remaining few percent such as substrates for methanogenesis, like methanol and formate. *Methanosarcina barkeri*, is an important microorganism involved in this stage.

Anaerobic microbial metabolism is characterised by key intermediates such as pyruvic acid, tartaric acid, propionic acid, acetate,  $\text{CO}_2$  and  $\text{H}_2$ , which can have a major role in terminal anaerobic metabolic steps, as demonstrated for forest and litter soil, rice paddies, and other flooded soils, acetate is generally the main volatile fatty acid produced in anaerobic metabolism that may be the final product of anaerobic metabolism when (i)  $\text{H}_2$  accumulates due to environmental conditions that reduce acetate consumption and/or (ii) there is no inorganic electron acceptor ( $\text{NO}_3^-$  for example) for acetate oxidation to be completed.

Redox states control the substrate availability and energy transformation, thus, regulates the soil microbial abundance and diversity. Fatty acid methyl ester (FAME) and 16S rRNA genes-based terminal-restriction fragment length polymorphism (T-RFLP) bacterial fingerprints confirmed that abundance of Gram-positive bacteria increased with increasing soil depth when shifting from oxic to anoxic conditions. Gram-positive bacteria constituted nearly 16% of the total community in anoxic soils since they were less sensitive to oxygen supply unlike others (Song *et al.* 2008).

#### *Cellulose degradation in anaerobic soil*

Vast quantities of cellulose are degraded by cellulose-fermenting microorganisms in anaerobic environments. In

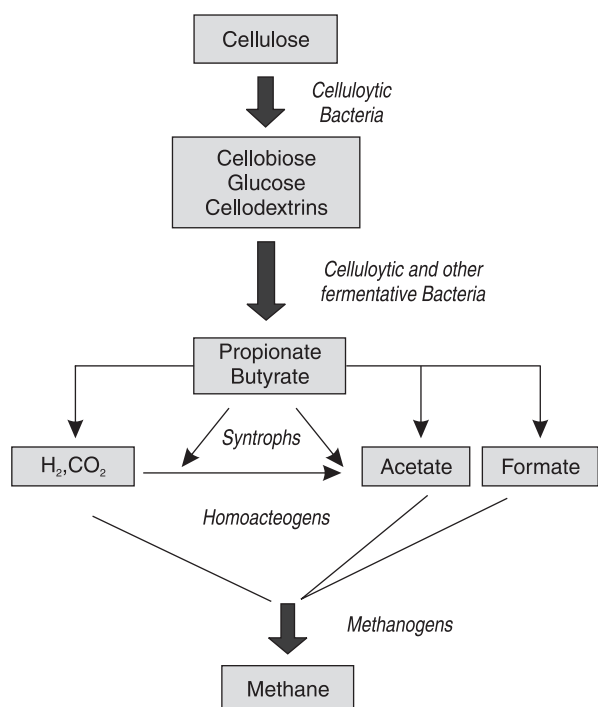


Fig 3 Pathway of anaerobic cellulose degradation by microbial communities in anoxic soils (adapted from Leschine 1995)

the absence of oxygen and certain other exogenous inorganic electron acceptors [e.g. nitrate, Mn (IV), Fe (III), sulfate], cellulose is decomposed by the anaerobic community into  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  through a complex microbial food chain. Cellulolytic and saccharolytic microbes produce enzymes that depolymerize cellulose, thereby producing cellobiose, cellodextrins, and some glucose. Different species of *Clostridium* (*C. lentocellum*, *C. celluloferrum*, *C. cellobioparum*) are involved mostly in cellulose degradation. These fermentations yield  $\text{CO}_2$ ,  $\text{H}_2$ , organic acids (e.g. acetate, propionate, butyrate), and alcohols. Very little  $\text{H}_2$  escapes into the atmosphere because it is immediately consumed by methanogens or homoacetogens. Through the combined activities of several major physiological groups of microbes, cellulose is completely dissimilated to  $\text{CO}_2$  and  $\text{CH}_4$  (Fig 3). Thus, as a source of  $\text{CO}_2$  and  $\text{CH}_4$ , the anaerobic decomposition of cellulose plays a major role in carbon cycling on the planet. In marine environments, sulphate is plentiful and sulphate-reducing bacteria out-compete methanogens for  $\text{H}_2$ . Thus,  $\text{H}_2\text{S}$  is a major product of the anaerobic degradation of cellulose in marine systems (Leschine 1995).

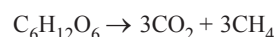
#### Emission and consumption of methane

Ricefield soils, peat soils and swamps are often exhibit very high potential methanotrophic activities (redox potential range from -200 to -280 mV). Atmospheric  $\text{CH}_4$  is mainly (70-80%) of biological origin. It is produced in anoxic environments, including submerged soils, by methanogenic bacteria during the anaerobic digestion of organic matter. On the other hand, methane is also eliminated in soils by microbial oxidation, which takes place in the aerobic zone

of methanogenic soils (methanotrophy) and in upland soils, which oxidise atmospheric methane. An environment is a  $\text{CH}_4$  source when the balance between production by methanogenic bacteria and consumption by methanotrophic bacteria is positive, leading to  $\text{CH}_4$  emission. When the balance is negative, the environment is a  $\text{CH}_4$  sink (Le Mer and Roger 2001).

#### Methanogenesis

The complete mineralisation of organic matter in anaerobic environments where sulphate and nitrate concentrations are low occurs through methanogenic fermentation, which produces  $\text{CH}_4$  and  $\text{CO}_2$  according to the reaction:



Methanogenesis, which requires strict anaerobiosis and low oxido-reduction potentials ( $\text{Eh} < -200$  mV), involves a specialized, strictly anaerobic microflora that can develop in synergy or in syntrophy with other anaerobic bacteria. Methanogens have a limited trophic spectrum comprised of a small number of simple substrates:  $\text{H}_2 + \text{CO}_2$ , acetate, formate, methylated compounds (methanol, methylamines, dimethylsulphur), and primary and secondary alcohols. Methanogens belong to the genera *Methanobacterium*, *Methanosarcina*, *Methanobrevibacter*, *Methanoculleus*, *Methanogenium*, *Methanosaeta* and *Methanospirillum* (Le Mer and Roger, 2001).

#### Methanotrophy

If  $\text{CH}_4$  concentration is higher than 40 ppm, oxidation is performed by bacteria called methanotrophs and is considered as methanotrophic activity. It generally occurs in all soils with a pH higher than 4.4. Methanotrophs use  $\text{CH}_4$  as only a C and energy source. Oxygen availability is the main factor limiting their activity. In wetlands, methanotrophs develop in the oxidized soil layer, in the aerobic rhizosphere of plants possessing an aerenchyma, and inside the roots and the submerged part of the leaf sheaths of the rice plants. Methanotrophs belong to the genera *Methylocystis* and *Methylosinus*. In rice fields, they produce soluble methane-mono-oxygenase, which avoid the accumulation of  $\text{NO}_2$  toxic to methanotrophs.

#### Environmental factors affecting methane emission

Several factors that affect  $\text{CH}_4$  emission by soils (D'Angelo and Reddy 1999) are: 1. Gas diffusion in relation with the oxido-reduction potential level and  $\text{CH}_4$ , in particular the water content, the nature of the clays and the type of vegetation. 2. Microbial activities in general: temperature, pH, Eh, substrate availability, physicochemical properties of soils, etc. 3. Methanogenesis and in particular the competition with other processes i.e. denitrification and sulphate-reduction. 4. Methane-mono-oxygenase activity: content in  $\text{H}_2$ ,  $\text{CH}_4$ , ammonium, nitrate, nitrite, and Cu, etc. 5. Competition and predation may probably affect methanogenic and methanotrophic populations.

### Nitrogen transformation

Four interrelated steps involved in N-transformation and loss from anoxic soil include: i) mineralization of organic-N or ammonification, ii) nitrification of  $\text{NH}_4\text{-N}$ , iii)  $\text{NH}_3$  volatilization and iv) denitrification was schematically represented (Fig 4).

While, inorganic N (supplied by fertilizers) in anaerobic soil is converted to gaseous forms by only two steps: i) nitrification-denitrification and ii)  $\text{NH}_3$  volatilization. Although the former process is usually more prominent in submerged soil however some other factors like slower nitrification rate than flux of  $\text{NH}_4\text{-N}$ , high pH and high temperature promote  $\text{NH}_3$  volatilization. In the flooded soils,  $\text{NH}_4\text{-N}$  diffusion ( $0.06$  to  $0.85 \text{ cm}^2/\text{day}$ ) and nitrification ( $1.1$  to  $2.7 \mu\text{g}/\text{cm}^3/\text{day}$ ) were found to be functioning at a slower rate whereas  $\text{NO}_3\text{-N}$  diffusion ( $0.25$  to  $1.94 \text{ cm}^2/\text{day}$ ) and denitrification ( $0.03$  to  $2.87 \mu\text{g}/\text{cm}^3/\text{day}$ ) operate at a rapid speed (Reddy *et al.* 1983).

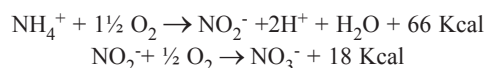
### Ammonification

It is defined as the biological conversion of organic-N to ammonium-N. Due to complete suppression of nitrification in the strictly anoxic zone, ammonium-N accumulates. Generally, few facultative or strictly anaerobic bacteria are involved in the process, characterizing: 1. Incomplete decomposition of carbohydrates into organic acids,  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{H}_2$ . 2. Low energy of fermentation (resulting less synthesis of microbial cells per unit of organic C decomposed). 3. Low N requirement of the anaerobic metabolism. The ideal condition of ammonification prevails in the anoxic soil when: i) C/N ratio of organic residues is less than 80 (if the ratio is more than 80, it favours N-immobilization); ii) Temperature ranges between  $40\text{-}60^\circ\text{C}$ . The rate of ammonification has been found to increase with increasing temperature; iii) pH of the soil solution ideally lies in between 6.5 and 8.5.

### Nitrification

Nitrification is the biological conversion of nitrogen in either inorganic or organic compounds from a reduced state to a more oxidized state. In an ecosystem with

aerobic and anaerobic interface in close proximity, as in a wetland rice field, considerable loss of nitrogen in gaseous forms ( $\text{N}_2$  and  $\text{N}_2\text{O}$ ) can occur through a nitrification-denitrification sequence. In a two-step autotrophic nitrification process, ammonium is sequentially oxidized to nitrite by *Nitrosomonas* sp. ( $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ ) like *Nitrosomonas europaea*, *N. javaensis* and related bacteria (*Nitrosococcus*, *Nitrospirilla*, *Nitrosocystis*) and then is oxidized to nitrate by *Nitrobacter* sp. ( $\text{NO}_2^- \rightarrow \text{NO}_3^-$ ) and related bacteria (*Nitrocystis*) as follows:



Both the microbes are chemoautotrophic, rod-shaped, gram negative, and aerobic. Optimum temperature for nitrifying microbes was found between  $30\text{-}40^\circ\text{C}$ . In acid soils, nitrification is poor due to decrease in the nitrifying bacteria, which can be counteracted by liming upto pH 6.0. Several microorganisms of genera *Pseudomonas*, *Streptomyces*, *Corynebacterium*, *Mycobacterium*, *Bacillus*, *Vibrio*, and *Aspergillus* are shown to perform nitrification.

### Denitrification

Denitrification of nitrogen fertilizer and subsequent loss as nitrogen gas, can result in a loss of 37% of the applied nitrogen, particularly when applied in a nitrate form. The conversion occurs in the anaerobic zone of the soil. Factors contributing to denitrification include pH, temperature, organic matter, wet/dry cycles, and fertilizer management. Severe nitrogen losses occur in soils subjected to alternate draining (aerobic) and flooding (anaerobic). The anaerobic conversion of nitrate into molecular nitrogen is also known as nitrate respiration. The process is mediated by several facultative bacteria, such as *Pseudomonas*, *Achromobacter*, *Bacillus*, *Micrococcus*, following the pathway:  $\text{NO}_3^-$  (nitrate)  $\rightarrow \text{NO}_2^-$  (nitrite)  $\rightarrow \text{NO}$  (nitric oxide)  $\rightarrow \text{N}_2\text{O}$  (nitrous oxide)  $\rightarrow \text{N}_2$  (di-nitrogen). Other bacteria like *Thiobacillus denitrificans*, also reduce nitrate to nitrogen using sulphur or thiosulphate as a source of energy.

Heavy and prolonged rainfall often leads to waterlogging resulting in to sharp increase in the emission of nitrous oxide ( $\text{N}_2\text{O}$ ), an important greenhouse gas, primarily released from agricultural soil ecosystems resulted from an anoxic environment. The denitrifiers' population is generally more abundant in waterlogged soil but identifying the composition of denitrifier communities in soil needs specific biotechnological tools. The pyrosequencing based analysis exhibiting high coverage for denitrification genes than usually followed PCR primers based approach to examine the waterlogging effect on denitrifier communities dwelling in soil. Microbial communities thus harboring denitrification genes in the top 5 cm soil distributed varying the soil depth, water-soluble carbon, and nitrate nitrogen (Wang

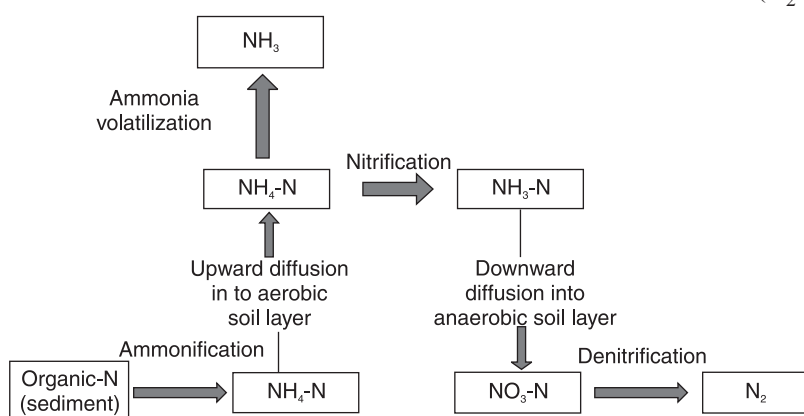


Fig 4 Sequential processes of N transformation from flooded soil (modified from Reddy and Patrick 1983).

et al. 2017).

Understanding the N-mineralization process and applying appropriate model simulation are key factors in evaluating N mineralization. An experiment was conducted for developing effective N fertilization strategies to increase productivity of paddy soil. During the period of waterlogged incubation of paddy soil, mineralization  $\text{NH}_4^+$ -N was positively correlated with OC, TN, pH, and exchangeable Ca, and mineralization total soluble N was positively correlated with OC, TN, and exchangeable Ca, but was not significantly correlated with C/N ratio, CEC, extractable Fe, clay, and sand. The ratio of cumulative soluble organic N to  $\text{NH}_4^+$ -N or TSN (total soluble N) was 54.0% and 32.5%, respectively, and that TSN showed a stronger linear correlation with OC or TN when considering soluble organic N. Hence, soluble organic N should be considered during evaluations of N mineralization (Zhang et al. 2017).

#### *Anaerobic microbial activities and geochemical transformation in soil*

Anaerobic microbial activities are closely linked to geochemical reactions in the solution and at solid-solution interfaces (Zehnder and Stumm 1988). Both the processes are interdependent. As microbial activities depend on the geochemical characteristics of the solution and on their transient changes, which affect (i) substrate availability for microbes in solution and at solid/solution interfaces and (ii) the feasibility of microbial reactions via inhibition by chemical species in solution ( $\text{NO}_2^-$ , volatile fatty acids), and (iii) thermodynamic regulation ( $\text{H}_2$ ). Whereas, microbial activities promote the geochemical transformation by (i) regulating the pH of soil solution via the net microbial production of  $\text{H}^+$  (e.g. during the reduction of  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$ ),  $\text{CO}_2$ ,  $\text{NH}_4^+$ ,  $\text{HS}^-$ , organic acids etc., (ii) the constant change in soil reduction/oxidation status by influencing redox couples (including  $\text{NO}_3^-/\text{NO}_2^-$ ,  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $\text{H}^+/\text{H}_2$ ,  $\text{SO}_4^{2-}/\text{HS}^-$ ,  $\text{CO}_2/\text{CH}_4$ ), and (iii) the amount of simple complexing fatty acids, including acetate, propionate and butyrate.

Bacteria, heterotrophic organisms, consume oxygen while decomposing organic material which depletes the soils of oxygen, thus increasing the redox potential. In low redox conditions the deposition of ferrous iron ( $\text{Fe}^{2+}$ ) will increase with decreasing decomposition rates, thus preserving organic remains and depositing humus. At high redox potential, the oxidized form of iron, ferric iron ( $\text{Fe}^{3+}$ ), will be deposited commonly as hematite. By using analytical geochemical tools such as x-ray fluorescence (XRF) or inductively coupled mass spectroscopy (ICP-MS) the two forms of Fe ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) can be measured in ancient rocks therefore determining the redox potential for ancient soils.

Microbial activities found to affect solid phases, either by: (i) *adsorption/desorption* reactions via microbial by-products (generation of  $\text{H}^+$  and other cations) that interact with solid phases, and (ii) the *dissolution* of minerals (metal oxides and oxyhydroxides, calcite, etc.) that further modify soil solution composition. Microbial effects are characterised by geochemical reactions at the

solid-solution interface, including the dissolution of calcite and/or metal oxides (goethite, etc.) and the precipitation of other minerals (siderite, fougurite) (Dassonville and Renault 2002, Schwertmann and Fechter 1994). Abiotic geochemical transformations may also partly regenerate some microbial substrates (e.g. the chemical oxidation of  $\text{HS}^-$  into  $\text{S}^0$ , with the simultaneous reduction of  $\text{Fe}^{3+}$  into  $\text{Fe}^{2+}$ ), or indirectly enhance other transformations.

#### *Mineralogical transformation in waterlogged soils and nutrient availability*

Clay mineralogy is one of the determinant of nutrient availability in paddy soils by affecting many physico-chemical and biological properties of soils (Raheb and Heidari 2012). Soils with high content of 2:1 clay minerals (micas, vermiculite and smectite) hold larger quantities of non-exchangeable K than those with kaolinite (Ghosh and Singh 2001). Application of potassium fertilizers in the waterlogged soil for long-term increased the amount of illite and vermiculite (Liu et al. 2007). Poorly drained soils with high Si, Mg, and suitable pH increased the stability of smectitic minerals. Because of that smectite is the most prevalent minerals in waterlogged paddy soils (Liu et al. 2007, Zhang et al. 2011). Illite-mica, magnesian chlorite and an interstratified mica-aluminous chlorite minerals are the dominant clay minerals in flood-irrigated paddies cultivated for 3, 10, 15, 30 and 80 years in clayey soils in China (Li et al. 2003). Due to long term waterlogging, the K-bearing phases (mica, illite and interstratified minerals) are gradually reduced to a large extent and Fe content decreased. The chlorite is increased, while the mica component in the mixed-layer mineral is decreased (Li et al. 2003). The trend is the loss of potassic minerals despite the use of NPK fertilizers and an increase in the formation of less siliceous, more ferromagnesian chlorite. Many studies showed that application of K for long-term increases the illite content or the illite layer content of illite-smectite in soil (Poonia 1996, Velde and Peck 2002). Application of  $\text{NH}_4$ -based fertilizers increase the short-range order pools of hydroxy-Al in soils and causes interlayering of 2:1 minerals due to intense acidification (McGahan et al. 2003).

#### *Waterlogging tolerance by crop plants*

Waterlogging, not only creates a different scenario for soil environment, it also causes a setback for the plants grown on it. Hypoxic and/or anoxic condition created as a result of waterlogging often leads to improper growth and development for plant due to the inability of plant root to withstand low oxygen condition. Thus it is found to affect growth and yield of many crop plants especially in low lying rainfed areas. The major reason of negative impact comes due to oxygen deprivation which is severely created under waterlogging. Oxygen limiting condition in soil promotes to shift the energy metabolism from aerobic mode to anaerobic mode. Oxygen is vital for central energy-providing pathways of cell in almost all organisms. By serving as major electron acceptor in oxidative phosphorylation pathway

for ATP production and regeneration of cellular  $\text{NAD}^+$ / $\text{NADH}$  pool,  $\text{O}_2$  act as key element in aerobic metabolism process in plants. Thus under oxygen limited environment plants tend to shift to alternate respiratory pathways, viz. fermentation (lactic acid or alcoholic) or other plant specific anerobic energy regaining mechanism (Dennis *et al.* 2000). This situation further affects nutrient and water uptake, so the plants often show wilting symptoms under submerged condition (Ahmed *et al.* 2013).

Plants do have some in-built mechanism to adjust the ill-effects of submergence, viz. aerenchyma formation, abundance of soluble sugars, increased activity of glycolytic pathway, fermentation enzymes and involvement of antioxidant defense mechanism, which individually or collectively help plants to cope with the hypoxia/anoxia stress (Alamgir and Uddin 2011). It is reported that relatively waterlogging tolerant rice genotypes were able to produce ethylene, the gaseous plant hormone, in sufficient quantities which plays crucial role in formation of aerenchyma cells to supply oxygen to roots from its aerial parts (Jackson 1985). Not only this, ethylene is also reported to promote production of adventitious roots that grows horizontally (diageotropism), which serve a new roots system replacing the old primary roots under severe flooding stress (Jackson and Drew 1984). As an anaerobic response of plant cells it is often found to produce anaerobiosis induced proteins (ANPs). Taking one of the first reports on this, it was found that about twenty anaerobic proteins were synthesized during low oxygen treatment in maize roots, while synthesis of normal aerobic proteins was drastically repressed (Sachs *et al.* 1980). This actually gives us an indication that how plants try to adapt to the abnormal environmental cues for the purpose of survival.

As a tolerance strategy, plants often produce several classes of hemoglobin (both symbiotic and non-symbiotic types), which have oxygen binding properties are capable of transporting oxygen to root system in cases of hypoxia/anoxia (Sairam *et al.* 2008). Such stress-induced expression of haemoglobins had been reported in callus, cell suspension, seed, root and stem tissue of both dicot and monocot plants (Hill 1998, Dordas *et al.* 2003a, 2004). Besides haemoglobins, which proved to have widespread role in waterlogging tolerance in plant kingdom, nitric oxide (NO) also reported to be one of the important stress induced metabolite in hypoxic plant cells and one of the functions of hypoxic stress-induced Hb is to modulate nitric oxide levels in the cell (Dordas *et al.* 2003b). Taken together there are more than one mechanism operates in plants as an adaptive response to hypoxic condition which singly or in combination act to impart waterlogging stress tolerance in plant.

Assessment of waterlogging potential across agricultural landscapes as well as in parameters measured in waterlogging studies, however, showed inconsistencies in the current indicators. The predictions of waterlogging potential for landscapes should be based on a minimum dataset that includes pedological, topographical, and climate data for the

defined area, as well as observations of plant morphological appearance and visible surface water. The effects of low oxygen concentration in soil on rhizospheric processes of waterlogging have direct effects on plant physiology. It is suggested that there is scope for modifications to these models based on recent improved understandings of plant physiological responses to waterlogging condition (Shaw *et al.* 2013).

#### *Perspective*

Waterlogged or anaerobic soils are widely distributed throughout the world and are found in all climates. Anaerobic soils are of agronomic importance because they are widely used throughout the world for rice production and are the primary sources of nutrients for plants grown in wetlands. These soils remain submerged for a considerable period of the year and during crop duration, thereby changing the chemistry of submerged soils. Prolonged waterlogging results in several physical, chemical and biological changes in soil. The chemical and biological processes in flooded soils are intricately linked and take place largely due to the biogeochemical transformations carried out by facultative and obligate anaerobic microorganisms. The important chemical changes taking place in flooded soils include an increase in the pH of acidic soils and decrease in the pH of alkaline soils, decrease in redox potential, increase in electrical conductivity or ionic strength. The factors like soil organic-matter content, type of soil, microbial biomass, and the genotype of plant species growing in such soils determine the extent of chemical changes taking place. The reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ ,  $\text{Mn}^{4+}$  to  $\text{Mn}^{2+}$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  to  $\text{N}_2$  and  $\text{N}_2\text{O}$ ,  $\text{SO}_4^{2-}$  to  $\text{S}^{2-}$ , and  $\text{CO}_2$  to  $\text{CH}_4$  take place in flooded soils. The redox reactions influence the fertility of soils under submerged conditions. The availability of essential plant nutrients is influenced by these changes. While the availability of P, K, Fe, Mn, Mo, and Si increases in flooded soils, the availability of S, Zn and Cu decreases. In submerged soils, devoid of oxygen (below few centimeters depth), fermentation and methanogenesis take place with  $\text{CO}_2$  and  $\text{H}^+$  being the main electron acceptors and methane as the end product. The availability of N depends on its proper management. When applied in the reduced soil zone, the uptake of N is more because of less loss of N by denitrification and more stability of ammonium form in flooded soils. Under submerged conditions, microbial processes that release essential plant nutrients are favoured. The anaerobic microbial processes of denitrification, sulfate reduction, methanogenesis, and methanotrophy are responsible for the release of  $\text{N}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$  and  $\text{CO}_2$ ;  $\text{CH}_4$  and  $\text{CO}_2$  being greenhouse gases of environmental concern. Anaerobic decomposition also leads to large amounts of organic carbon content in soil, besides amines, mercaptans, and partially humified residues. Anaerobic fermentation leads to the production of  $\text{CO}_2$ ,  $\text{H}_2$ , organic acids and alcohols. Thus, the interlinked chemical-biological processes in submerged soils, mostly mediated by soil microorganisms, play key role in sustaining productivity of

wetland ecosystems. The knowledge of the biogeochemical processes taking place in waterlogged soils is thus important for maintaining soil fertility and improving the yields of crops like rice.

## REFERENCES

- Achtnich C, Bak F and Conrad R. 1995. Competition for electron donors among nitrate reducers, ferric iron reducers, sulfate reducers, and methanogens in anoxic paddy soil. *Biol. Fertil. Soils* **19**: 65–72.
- Ahmed F, Rai M, Ismail MR, Juraimi AS, Rahim HA, Asfaliza R and Latif MA. 2013. Waterlogging tolerance of crops: Breeding, mechanism of tolerance, molecular approaches, and future prospects. *BioMed Research International* <http://dx.doi.org/10.1155/2013/963525>
- Alamgir H and Uddin S N. 2011. Mechanisms of waterlogging tolerance in wheat: morphological and metabolic adaptations under hypoxia or anoxia. *Australian Journal of Crop Science* **5**(9): 1094–110.
- Asakawa S and Hayano K. 1995. Populations of methanogenic bacteria in paddy field soil under double cropping conditions (rice-wheat). *Biol. Fertil. Soils* **20**: 113–7.
- Conrad R. 1996. Soil microorganisms as controllers of atmospheric trace gases (H<sub>2</sub>, CO, CH<sub>4</sub>, OCS, N<sub>2</sub>O, and NO). *Microbiology Review*, **60**(4): 609–40.
- D'Angelo E M and Reddy K R. 1999. Regulators of heterotrophic microbial potentials in wetland soils. *Soil Biol. Biochem* **31**: 815–30.
- Dassonville F and Renault P. 2002. Interactions between microbial processes and geochemical transformations under anaerobic conditions: a review. *Agronomie* **22**: 51–68.
- Dennis E S, Dolferus R, Ellis M, Rahman, M, Wu Y and Hoeren F U *et al.* 2000. Molecular strategies for improving waterlogging tolerance in plants. *Journal of Experimental Biology* **51**(342): 89–97.
- Dordas C, Hasinoff B B, Igamberdiev A U, Manach N, Rivoal J and Hill R D. 2003b. Expression of a stress-induced hemoglobin affects NO levels produced by alfalfa root cultures under hypoxic stress. *Plant Journal* **35**: 763–70.
- Dordas C, Hasinoff B B, Rivoal J and Hill R D. 2004. Class-1 hemoglobins, nitrate and NO levels in anoxic maize cell-suspension cultures. *Planta* **219**: 66–72.
- Dordas C, Rivoal J and Hill R D. 2003a. Plant haemoglobins, nitric oxide and hypoxic stress. *Annals of Botany* **91**: 173–8.
- Favre F, Tessier S, Abdelmoula M, Genin J M, Gates W P, and Boivin P. 2002. Iron reduction and changes in cation exchange capacity in intermittently waterlogged soil. *European Journal of Soil Science* **53**: 175–83.
- Freney J R, Denmead O T, Watanabe I and Craswell E T. 1981. Ammonia and nitrous oxide losses following applications of ammoniumsulfate to flooded rice. *Australian Journal of Agricultural Research* **32**: 37–45.
- Gao S, Tanji K K, Scardaci S C and Chow A T. 2002. Comparison of redox indicators in a paddy soil during rice-growing season. *Soil Science Society of America Journal* **66**: 805–17.
- Ghosh B N and Singh R D. 2001. Potassium release characteristics of some soils of Uttar Pradesh hills varying in altitude and their relationship with forms of soil K and clay mineralogy. *Geoderma* **104**: 135–44.
- Glass A D M. 2003. Nitrogen use efficiency of crop plants: physiological constraints upon nitrogen absorption. *Critical Reviews of Plant Sciences* **22**: 453–70.
- Gotoh S and Patrick WH. 1972. Transformation of manganese in a waterlogged soil as affected by redox potential and pH. *Soil Science Society of America Proceedings* **36**: 737–42.
- Grybos M, Davranche M, Gruau G, Petitjean P, and Pédrot M. 2009. Increasing pH drives organic matter solubilization from wetland soils under reducing conditions. *Geoderma* **154**: 13–9.
- Harris R H, Armstrong R D, Wallace A J and Belyaeva O N. 2016. Effect of nitrogen fertiliser management on soil mineral nitrogen, nitrous oxide losses, yield and nitrogen uptake of wheat growing in waterlogging-prone soils of south-eastern Australia. *Soil Research* **54**(5): 619–33.
- Hill R D. 1998. What are hemoglobins doing in plants? *Canadian Journal of Botany* **76**: 707–12.
- Jackson MB and Drew MC. 1984. Effects of flooding on growth and metabolism of herbaceous plants. (In) *Flooding and Plant Growth*. Kozlowsky T T, (Ed.). Academic Press, Orlando, Fla, USA.
- Jackson M B. 1985. Ethylene and responses of plants to soil waterlogging and submergence. *Annual Review in Plant Physiology* **36**: 145–74.
- Kristensen E, Ahmed S I and Devol A H. 1995. Aerobic and anaerobic decomposition of organic matter in marine sediments: which is fastest? *Limnological Oceanography* **40**: 1430–7.
- Le Mer J and Roger P. 2001. Production, oxidation, emission and consumption of methane by soils: A review. *European Journal of Soil Biology* **37**: 25–50.
- Leschine SB. 1995. Cellulose degradation in anaerobic environments. *Annual Reviews in Microbiology* **49**: 399–426.
- Li Z, Velde B Y and Li D. 2003. Loss of K bearing clay minerals in flood irrigated rice growing soils in Jiangxi Province, China. *Clays and Clay Minerals* **51**: 75–82.
- Lind A M and Pederson M B. 1976. Nitrate reduction in the subsoil. III. Nitrate reduction experiments with subsoil samples. *Tidsskrift for Planteav* **180**: 100–6.
- Liu YL, Zhang B, Cheng-liang L, Feng H and Velde B. 2007. Long term fertilization influences on clay mineral composition and ammonium adsorption in rice paddy soil. *Soil Science Society of America Journal* **72**: 1580–90.
- Lovley D R. 1995. Bioremediation of organic metal contaminants with dissimilatory metal reduction. *Journal of Industrial Microbiology* **14**: 85–93.
- McGahan D G, Southard R J and Zasoski R J. 2003. Mineralogical comparison of agriculturally acidified and naturally acidic soils. *Geoderma* **114**: 355–68.
- Patrick W H and Reddy C N. 1978. Chemical changes in rice soil. (In) *Soil and Rice*; 361–79 p. International Rice Research Institute: Manila, Philippines.
- Ponnamperuma F N. 1972. The chemistry of submerged soils. *Advances in Agronomy* **24**: 29–96.
- Poonia S R. 1996. Exchange equilibria of potassium in relation to organic matter, potassium status and clay mineralogy of soils. *Advances in Geocology* **30**: 133–44.
- Raheb A and Heidari A. 2012. Effects of clay mineralogy and physico-chemical properties on potassium availability under soil aqic conditions. *Journal of Soil Science and Plant Nutrition* **12**(4): 747–61.
- Reddy K R, Patrick W H and Broadbent F E. 1983. Nitrogen transformations and loss in flooded soils and sediments. *CRC Critical Reviews in Environment Control* **13**: 273–309.
- Revsbech N P, Joergensen B B and Blackburn T H. 1980. Oxygen

- in the sea bottom measured with a microelectrode. *Science* **207**: 1355–6.
- Russell E W. 1973. Soil conditions and plant growth, 10<sup>th</sup> Edn., p 672. Longman, London.
- Sachs M M, Freeling M and Okimoto R. 1980. The anaerobic proteins of maize. *Cell* **20**(3): 761–7.
- Sahrawat K L. 2004. Ammonium production in submerged soils and sediments: The role of reducible iron. *Communications in Soil Science and Plant Analysis* **35**: 399–411.
- Sahrawat K L. 2005. Fertility and organic matter in submerged rice soils. *Current Science* **88**: 735–9.
- Sairam R K, Kumutha D, Ezhilmathi K, Deshmukh P S and Srivastava G C. 2008. Physiology and biochemistry of waterlogging tolerance in plants. *Biologia Plantarum* **52**(3): 401–12.
- Samson M I, Buresh R J and De Datta S K. 1990. Evolution and soil entrapment of nitrogen gases formed by denitrification in flooded soil. *Soil Science and Plant Nutrition*, **36**: 299–307.
- Schwertmann U and Fechter H. 1994. The formation of green rust and its transformation to lepidocrocite. *Clay Miner.* **29**: 87–92. doi:10.1180/claymin.1994.029.1.10
- Shaw R E, Meyer W S, McNeill A and Tyerman. S D. 2013. Waterlogging in Australian agricultural landscapes: a review of plant responses and crop models. *Crop Pasture Science*, **64**(6): 549–62.
- Song Y, Deng S P, Acosta-Martínez V and Katsalirou E. 2008. Characterization of redox-related soil microbial communities along a river flood plain continuum by fatty acid methyl ester (FAME) and 16S rRNA genes. *Applied Soil Ecology*, **40**: 499–509.
- Sparks D L. 1989. *Kinetics of Soil Chemical Processes*. Academic Press, New York.
- Sweerts JPRA, Bar-Gilissen MJ, Cornelese AA and Cappenberg TE. 1991. Oxygen-consuming processes at the profundal and littoral sediment water interface of a small meso-eutrophic lake (Lake Vechten, the Netherlands). *Limnological Oceanography*, **36**: 1124–33.
- Velde B Y and Peck T. 2002. Clay mineral changes in the Morrow experimental plots, University of Illinois. *Clays and Clay Minerals* **50**: 364–70.
- Wang Y, Uchida Y, Shimomura Y, Akiyama H and Hayatsu. M. 2017. Responses of denitrifying bacterial communities to short-term waterlogging of soils. *Science Reporter* **7**(1): 1–13.
- Ward D M and Winfrey M R. 1985. Interactions between methanogenic and sulfate-reducing bacteria in sediments. *Advances in Aquatic Microbiology* **3**: 141–79.
- Wogel F. 1988. Biochemistry of methane production. (In) *Biology of Anaerobic Microorganisms* Zehnder A J B (Ed.), p 469–57. John Wiley & Sons, Inc., New York.
- Zehnder A J B and Stumm W. 1988. Geochemistry and biogeochemistry of anaerobic habitats. p. 1–38. In: A. J. B. Zehnder (ed.), *Biology of Anaerobic Microorganisms*, pp 1–38. John Wiley & Sons, Inc., New York.
- Zhang Q C, Wang G H, Feng YK, Qian P and Schoenau J J. 2011. Effect of potassium fertilization on soil potassium pools and rice response in an intensive cropping system in China. *Journal of Plant Nutrition and Soil Science* **174**: 73–80.
- Zhang Y, Xu W, Duan P, Cong Y, An T, Yu N, Zou H, Dang X, An J, Fan Q and Zhang Y. 2017. Evaluation and simulation of nitrogen mineralization of paddy soils in Mollisols area of Northeast China under waterlogged incubation. *PLoS one* **12**(2): 171–22.