Communications in Soil Science and Plant Analysis
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lcss20

Redox Potential and pH as Major Drivers of Fertility in Submerged Rice Soils: A Conceptual Framework for Management

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Accepted author version posted online: 13 May 2015.Published online: 13 May 2015.

Communications in Soil Science and Plant Analysis, 46:1597–1606, 2015

ISSN: 0010-3624 print / 1532-2416 online
DOI: 10.1080/00103624.2015.1043451

Redox Potential and pH as Major Drivers of Fertility in Submerged Rice Soils: A Conceptual Framework for Management

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Submerging soil creates a series of changes that have important implications for fertility and its management in wetland rice. Wetland rice makes an important contribution to the global rice supply and is often cited as an example of a sustainable production system. We little realize that flooding soil is a powerful driver of changes in fertility and nutrient availability via two most important determinants of soil fertility—pH and redox potential (Eh). The fundamental role of pH in regulating the dynamics of major and micronutrients, toxins, and reduction products in soil solution is well known and used to optimize rice production through management; however, the role of Eh, although equally important, is not appreciated and hence not fully exploited in developing improved fertility management practices. From a synthesis of global literature, this article presents a conceptual framework for the dynamics of soil organic matter and plant nutrients in terms of the combined effects of pH and Eh in submerged rice soils. It is hoped that the conceptual framework proposed would aid in developing efficient agronomic practices for better management of rice-based systems.

Keywords Amelioration, Eh, fertility, nutrients, organic matter, pH

Introduction

The most important effect of submerging a soil in water is to reduce the oxygen supply. As a result, the entrained oxygen is quickly exhausted and the soil becomes almost or fully devoid of oxygen in a few days of submergence. The lack of free oxygen or the prevalence of anaerobiosis causes soil reduction and triggers a series of physical, chemical, and biological processes. The influence of submergence on chemical and electrochemical properties of soils has been comprehensively researched and reviewed (Shioiri and Tanada 1954; Ponnamperuma 1972; De Datta 1981; Kyuma 2004; Sahrawat 1998, 2008, 2012; Reddy and DeLaune 2008). There is interest in submerged soils because this ecosystem makes a major contribution to rice supply and wetlands play an important role in maintaining environmental quality (Reddy and DeLaune 2007).

Specifically, the prevalence of anaerobiosis in submerged rice soils and the following changes in electrochemical and chemical properties has important implications for fertility and its management for paddy or wetland rice, which thrives in wetland soil conditions. It is known that paddy rice makes an important contribution to global rice; and paddy or

Received 20 April 2014; accepted 24 July 2014
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wetland rice system is often cited as an example of a sustainable production system (Bado, Aw, and Ndiaye 2010; De Datta 1981; Sahrawat 2007, 2012).

Among the electrochemical properties that are influenced by flooding of the soil under water, the oxidation-reduction potential or redox potential (Eh) and chemical reaction (pH) are the most important. The redox potential or Eh is a measure of electron activity or potential of the soils, and is measured by a platinum electrode in combination with a standard calomel electrode. Chemical reaction or pH is the negative log of hydrogen ion activity, and is measured by a glass electrode. Eh along with pH regulate several biochemical reactions in submerged soils that modulate the root environment of the rice plants grown under flooded conditions (Ponnamperuma 1972; Sahrawat 2007, 2012). The understanding and significance of pH in submerged rice soils is much appreciated in regulating the dynamics of major and micronutrients, reduction products, and toxins produced under reduced soil conditions and is used to optimize rice production through management (Ponnamperuma 1972; Sahrawat 1998). On the other hand, the role of Eh, although no less important than that of pH, remains rather hidden and relatively less appreciated, and as a result is less exploited in managing the mineral nutrition of the rice plant. The role of pH and redox potential in upland or aerobic soils has recently been comprehensively reviewed with broad transdisciplinary objectives covering soil-plant-microorganism systems by Husson (2013). It follows from this that Eh is indeed a key electrochemical property that has broad implications for the health and sustainability of the soil-plant systems.

We little realize that flooding of the soil is a powerful driver of changes in soil fertility and nutrient availability, which is driven by the two most important determinants of chemical and biological fertility of soils—pH and redox potential (Eh). From a synthesis of global literature with emphasis on tropical lowland rice soils of Asia and sub-Saharan Africa, this article presents a conceptual framework for the dynamics of organic matter and plant nutrients as modulated by integrated effects of pH and Eh. We hope the conceptual framework proposed would aid in developing efficient soil and crop management practices for paddy rice systems that better manipulate and exploit the roles of pH and Eh in the paddy rice systems.

Eh and Ph, the Key Electrochemical Changes That Drive Fertility in Submerged Soils

The main electrochemical and chemical changes following flooding of the soil under water that affect fertility and mineral nutrition of the paddy rice plant have long been known and include decrease in Eh; increase in pH of acidic soils; decrease in pH of alkaline soils; pH changes in flood water; and increase in ionic strength, measured by electrical conductivity, of soil solution (Ponnamperuma 1965, 1972; Narteh and Sahrawat 1999, 2000).

Decrease in Eh follows submergence of aerobic soil, which in turn affects the behavior of nutrient elements and their stability and availability to the rice plant. For example, mineralization of organic N stops at ammonium, and nitrate N is unstable in reduced soils. The Eh in flooded soils generally stabilizes in a range of +200 to −300 mV depending on the soil, especially on the quantity and quality of organic matter and texture, and the presence and contents of reducible nutrient elements such as nitrate (NO_3^-) N, manganic manganese (Mn IV), ferric iron (Fe III), and sulfate (SO_4^{2-}) (Table 1). The results on Eh of flooded soil provide criteria on the degree of soil reduction.

Equally importantly, the results for Eh in submerged soils also indicate the stability of the main oxidized components in submerged soils, which can be exploited for improved soil and nutrient management practices for rice production. The rvalues of Eh at which the

Table 1
Range of oxidation-reduction potentials encountered in rice soils ranging from well drained to waterlogged conditions

Soil water condition	Redox potential (mV)
Aerated or well drained	+700 to +500
Moderately reduced	+400 to +200
Reduced	+100 to −100
Highly reduced	−100 to −300

Note. Adapted from Patrick and Reddy (1978).

Table 2
Range of redox potentials in which the main oxidized components in submerged soils become unstable

Reaction	Redox potential (mV)
O_2–H_2O	+380 to +320
NO_3^-–N_2, Mn^{4+}–Mn^{2+}	+280 to +220
Fe^{3+}–Fe^{2+}	+180 to +150
SO_4^{2-}–S^{2-}	−120 to −180
CO_2–CH_4	−200 to −280

Note. Adapted from Patrick and Reddy (1978).

main oxidized components become unstable in flooded soils are given in Table 2 (Patrick and Reddy 1978; Ponnamperuma 1972).

In this section, the effects of flooding on pH and Eh in relation to chemical fertility in wetlands are discussed, with examples from tropical rice soils of Asia and sub-Saharan Africa. Salient changes in soil organic matter, availability of nutrients, and other associated factors affecting plant growth and production in submerged and aerobic (upland rice systems) soils are summarized in Table 3 (Sahrawat 2012). Clearly, soil flooding brings out a range of changes in soil that influence paddy rice productivity and its stability in the longer term compared to the upland rice system (Sahrawat 2007, 2012).

Ponnamperuma, Martinez, and Loy (1966) studied the influence of Eh and partial pressure of carbon dioxide on the kinetics of pH of thirty-five diverse lowland rice soils from Taiwan, Vietnam, and the Philippines; the soils studied captured a wide range in pH (from 3.6 to 9.4), organic matter (from 1.5 to 9.6 percent), reducible (active) Fe (from 0.08 to 2.91), active Mn (from 0.0 to 3.1 percent), and other soil properties that affect soil reduction under submerged conditions. The soils were kept flooded for 16 weeks in greenhouse pots. The results showed that the pH of calcareous and alkaline soils decreased, whereas those of the acidic soils increased; and the soil pH converged to a fairly stable range (from 6.7 to 7.2), whereas the soil solution pH stabilized in a range of 6.5 to 7.0 following 12 weeks of flooding. Further, the results showed that the decrease in pH of calcareous and alkali soils following flooding is attributed to $CaCO_3$-H_2O-CO_2 and Na_2CO_3-H_2O-CO_2 systems, respectively. The increase in solution pH values of acidic soils was quantitatively related to the potential of $Fe(OH)_3$–Fe^{2+} system. The pH values of

Table 3
Changes in soil organic matter, availability of plant nutrients, and other factors affecting plant growth under submerged and aerobic rice systems

	Submerged rice	Aerobic rice
pH	Converges to neutral range	Ambient pH
Organic matter	Favors accumulation of C and N but reduction products can be toxic	Decomposition is rapid and the accumulation relatively slow
C/N ratio	Wider C/N ratio due to OC accumulation	Varies with soil and organic-matter management
NH_4-N	Production and accumulation favored	Oxidized to nitrate, which is liable to loss by leaching and denitrification
P	Improved P availability	Not applicable
K	Improved K availability	Not applicable
S	Reduced S availability likely due to sulfide formation	Normal availability due to sulfate
Fe	Improved Fe availability in alkali and calcareous soils, but Fe toxicity may occur in acidic soils high in reducible Fe	Iron deficiency is a serious problem in calcareous and high pH soils
Mn	Reduced solubility	Depends on pH, toxicity in acidic soils
Cu, Zn, and Mo	Improved availability of Cu and Mo but not of Zn	Depends on soil pH
Al	Not a problem except perhaps in acidic sulfate soils	Serious problem on acidic soils
Reduction products	Sulfide and organic acids produced can be toxic	Not a problem
Root knot nematodes	Relatively less of a problem	Serious problem
Sustainability	Stability provided	Stability under question

Note. From Sahrawat (2012).

reduced acidic soils high in active iron were determined by the $Fe_3\ (OH)_8–H_2O–CO_2$ system (Ponnamperuma, Martinez, and Loy 1966).

Thus the dynamics of the partial pressure of CO_2 in submerged soils, with initial pH in the alkaline range, plays a critical role in bringing about changes in pH, Eh, and the solubility of Ca^{2+}, Mg^{2+}, Mn^{2+}, and Fe^{2+} and also indirectly influences specific conductance and cation exchange reactions in the flooded soil system. However, concentrations of CO_2 at partial pressures exceeding 15 percent can adversely affect water and nutrient uptake by the growing rice plants (Ponnamperuma 1965, 1972).

As mentioned earlier, following submergence of soil, the pH of acidic soils increases whereas that of alkaline soils decreases, and the pH tends to converge in the neutral range (6.5–7.5) (Ponnamperuma 1972; Narteh and Sahrawat 1999). The pH of acidic soils increases following flooding because under prevailing anaerobic conditions ferric iron is used as an electron acceptor in the oxidation of organic matter (CH_2O), which acts as electron donor, and during this oxidation-reduction reaction soil acidity is consumed as follows:

$$Fe_2O_3 + 1/2CH_2O + 4H^+ = 2Fe^{2+} + 5/2H_2O + 1/2CO_2 \quad (1)$$

Because most tropical rice soils are rich in reducible iron, the reduction of Fe(III) to Fe(II) is the most important process involved in raising the pH of acidic soils (Ponnamperuma 1972; Narteh and Sahrawat 1999). Indeed, the chemistry of submerged soils is dominated by the iron redox reaction as the amount of iron that can undergo reduction usually exceeds the total amount of other redox elements by a factor of 10 or greater (Patrick and Reddy 1978). As shown in Eq. (1), protons are consumed in the reduction of Fe(III) oxides to Fe(II); in this redox reaction, organic matter is an electron donor and Fe(III) oxide is as electron acceptor.

In highly acidic soils, protons can be derived from the free acidity present or that derived from the hydrolysis of exchangeable aluminum (Al), which leads to the formation of Al hydroxides and exchangeable Fe(II) and desorption of adsorbed sulfate, leading to the formation of soluble $Fe(II)SO_4$. In the case of soils with mild acidity or near-neutral pH, carbon dioxide may serve as proton donor, resulting in the formation of HCO_3^- and soluble Fe (II) (Konsten et al. 1994). However, it must be stated that in selected acidic sulfate soils the soil pH may not rise above 5 following prolonged submergence. In some of these acidic sulfate soils, low contents of Fe(III) oxides and most likely of sulfate relative to soil acidity was hypothesized as a major cause of for the lack of pH increase due to soil reduction following submergence of well-drained acidic sulfate soils in Indonesia (Konsten et al. 1994).

Decrease in the pH of alkaline soils following submergence is a result of production and accumulation of carbon dioxide in submerged soils, which reacts with water to form carbonic acid, which in turn dissociates into H+ and HCO^{3-}, resulting in the neutralization of alkalinity [see Eqs. (2) and (3)]. Moreover, a submerged soil system provides an ideal environment for the retention of the carbon dioxide produced and, equally importantly, for the reaction between carbon dioxide (carbonic acid) and soil alkalinity, which can be represented as follows:

$$CO_2 + H_2O = H_2CO_3 \quad (2)$$

$$H_2CO_3 + H_2O = H^+ + HCO_3 \quad (3)$$

Eh-pH Relationships

In a study of fifteen diverse rice-growing soils from West Africa, Narteh and Sahrawat (1999) reported on the relationship between Eh or pE (pE = Eh/0.059) and pH for soils 3 and 12 (see Tables 1 and 2 for details in Narteh and Sahrawat 1999) for soil and solution phases that recorded the highest and lowest Eh during 15 weeks of flooding, as described by the following regression equations:

Submerged soils:

$$\text{Soil 3: soil pE} + 2.5 - 0.37\,\text{soil pH}\ (r = -0.642;\ p < 0.012) \quad (4)$$

$$\text{Soil 12: soil pE} = 33.0 - 4.70\,\text{soil pH}\,(r = -0.735;\ p < 0.002) \tag{5}$$

Soil solution phase:

$$\text{Soil 3: solution pE} = 5.20 - 0.76\,\text{solution pH}\,(r = -0.817;\ p < 0.001) \tag{6}$$

$$\text{Soil 12: solution pE} = 9.40 - 1.20\,\text{solution pH}\,(r = -0.992;\ p < 0.001) \tag{7}$$

These results [see Eqs. (4)–(7)] establish that there are significant inverse relationships between pH and Eh of flooded rice soils and that the relationships are closer for the soil solution phase than that of the soils (Narteh and Sahrawat 1999). The results from West African rice soils indeed are in accord with those reported for Asian lowland rice soils by Ponnamperuma (1965), who concluded that soil solution measurements for various soil fertility parameters are thermodynamically more meaningful as they are potentials of homogenous soil solution phase in equilibrium with the solid and gaseous phases of the submerged soil. On the other hand, there is poor reproducibility in Eh between two electrodes in the same soil. The results from West African rice-growing soils support Ponnamperuma's conclusions in that platinum electrode measurements indicate localized potentials in the submerged soil (Narteh and Sahrawat 1999).

The results from West African soils further showed that the changes in soil solution generally corresponded to the changes in soil solution Eh. The stability in the change of the pH-Eh relationships in soil solution of fifteen soils was attained at the fourth week after submergence (Figure 1); and the relationship between the change in soil solution pH and the change in soil solution Eh was described by the following equation:

$$\text{Eh} = -16 - 48\,\text{pH}\,\left(R^2 = 0.84;\ p < 0.001\right) \tag{8}$$

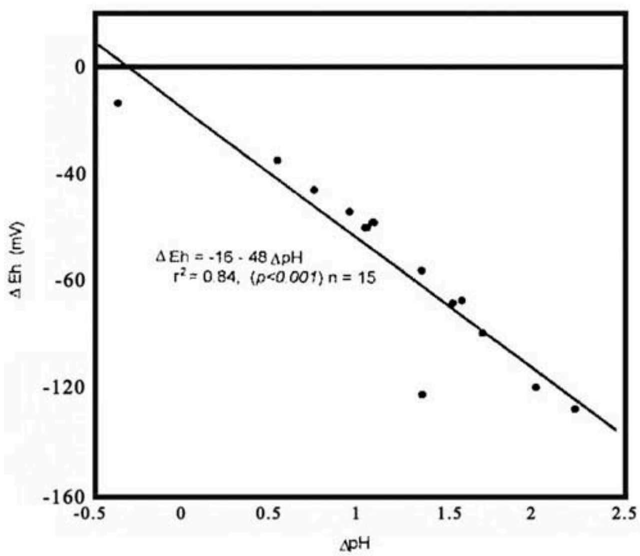

Figure 1. Relationship between change in soil solution pH and change in soil solution Eh of fifteen West African rice growing at 4 weeks after flooding (from Narteh and Sahrawat 1999).

These relationships [Eq. (8)] allow for the computation of the changes in pH of submerged soils from the changes in Eh or vice versa (Narteh and Sahrawat 1999).

Soil Fertility and Nutrient Availability

The pH of submerged soils is ecologically important because it influences the availability of plant nutrients. For example, pH markedly affects the concentrations of Fe(II), Mn(II), Al(III), and carbonic acid (H_2CO_3), which in high concentration in soil solution are toxic to the rice plant. A pH in the neutral range generally ensures that the concentrations of toxic components are not in the toxic range. Moreover, chemically the pH is the key to the understanding of various equilibria involving carbon dioxide, carbonates, and hydroxides and oxidation-reduction reactions in submerged soils (Ponnamperuma 1965; Sahrawat 1998).

Sahrawat (2007, 2012) has discussed in detail the changes in Eh and pH in submerged rice soils that influence the transformation and availability of major and micronutrients relative to the mineral nutrition of the rice plant. Here only brief discussion is provided that helps conceptualize a framework for fertility management. Salient results from sub-Saharan Africa are also discussed that help in the universalization of the framework. This is very important as the demand for rice as food has been steadily increasing during the past three or so decades; moreover, lowland rice has great potential for expansion in sub-Saharan Africa (Andriesse and Fresco 1991; Balasubramanian et al. 2007).

In a study of five acidic wetland rice soils from Sierra Leone, West Africa, it was reported that soil reduction following submergence of soils in water increased the soil pH. Further, amending the soils with rice straw or iron oxides led to a faster decrease in Eh and increase in pH to neutral (Jeffery 1961).

Narteh and Sahrawat (1999) studied the influence of flooding on electrochemical and chemical properties of rice-growing soils collected from fifteen locations in five major rice-producing countries (Nigeria, Ghana, Burkina Faso, Ivory Coast, and Republic of Guinea) in West Africa. The soils studied captured a wide range in initial pH (4.3–7.7), organic C (7.4–46.0 g kg^{-1}), total N (500–3000 mg N kg^{-1}), and extractable nutrients. The soils were held under flooded condition in greenhouse pots. The soil solution pH of the soils stabilized in the 5.8 to 8.2 pH range at 15 weeks of flooding, whereas the Eh ranged from 40 to −45 mV at 15 weeks of submergence. The soils differed widely in their capacities to release ammonium, P, K, Ca, Mg, Fe, Mn, and Zn in soil solution and thus provided useful information regarding the potential deficiencies (Narteh and Sahraat 1999), The occurrence of Fe toxicity to lowland rice as iron toxicity is a major constraint in acidic soils high in reducible iron in irrigated and rainfed lowland soils in the humid savanna and forest zones of the region (Sahrawat et al. 1996; Audebert and Sahrawat 2000; Sahrawat 2004a).

Moreover, measurements made on soil solution phase of the West African soils provided information that can be used for predicting the dynamic relationships among Eh, pH, and Fe (II). The soil solution EC (electrical conductivity) was closely related to the solution concentration of ammonium, K, Ca, and Mg individually as well as to their total concentrations at 4 weeks of flooding (Narteh and Sahrawat 1999). It follows from these results that wetland rice soils should be kept flooded for 4 weeks prior to transplanting of the rice crop as by following this practice most of the nutrients will be released in available form from the soil for the rice seedling to utilize. In the case of soils high in N and other nutrients, the basal application of N and other nutrients can be accordingly adjusted. Indeed concentrations of plant nutrients in soil solution can be used as an index of soil fertility for lowland rice soils (Narteh and Sahrawat 2000; Sahrawat and Narteh 2002).

Narteh and Sahrawat (2000) studied the kinetics of ammonium released in solution of fifteen flooded West African rice soils. The soils were held in flooded condition for 15 weeks in pots in a greenhouse. The soils differed in the pattern of release and accumulation of ammonium and had a wide range in the amounts of ammonium mobilized in soil solution. The ammonium released in soil solution of the fifteen soils was significantly related to organic carbon and total N of the soils. The pattern of ammonium released in soil solution of the soils was well described by an exponential model (Narteh and Sahrawat 2000). These results indicate the N-supplying capacity of lowland rice soils as measured by ammonium release in soil solution (Sahrawat and Narteh 2002) can be predicted by an exponential model (Narteh and Sahrawat 2000). These results corroborate the results on wetland rice soils summarized by Sahrawat (1983).

The supply of organic matter and the availability of electron acceptors in flooded rice soils play critical roles in driving soil reduction and its benefits to the rice crop (Sahrawat 1998, 2004b; Sahrawat and Narteh 2001). In soils with low organic matter, soil reduction slows down, and this results in less benefit in terms of soil fertility under submerged conditions (Sahrawat 1998; Narteh and Sahrawat 1999, 2000).

Organic-Matter Accumulation

In addition to the favorable effects of soil flooding on general soil fertility and selected nutrient availability (see Table 3), continuous wetland rice cultivation maintains or in some cases improves the organic-matter status of submerged rice soils (Sahrawat 2004c). This is due to the following: (i) As compared to aerobic soils, the decomposition of organic materials in submerged soils is slower, incomplete, and inefficient and leads to net accumulation of organic matter. (ii) Wetland rice soils that over time become deficient in electron acceptors such as easily reducible iron are likely have reduced rates of organic-matter oxidation and mineralization of soil organic N (Sahrawat and Narteh 2001; Sahrawat 2004b; Roden and Wetzel 2002). (iii) The deficiencies of major nutrients (N, P, and S) affect the growth of bacteria in submerged soils, which influence C fixation, release, and storage in submerged ecosystems (Sahrawat 2004c). (iv) The formation of recalcitrant complexes stabilizes organic matter, decreasing organic matter accessibility for microbial decomposition, leading to its accumulation. (v) The production of toxic compounds that are toxic to microbial activity result in the retardation of organic-matter decomposition (Freeman et al. 2004; Sahrawat 2004c). (vi) Relatively high net primary productivity of wetland rice soils leads to net organic-matter accumulation (Neue et al. 1997; Sahrawat 2004c).

To conclude, it can be stated that essentially slow decomposition of organic matter and greater net primary productivity of submerged rice soils lead to net accumulation of organic matter and N in submerged rice soils (Sahrawat 2004c).

Perspectives

The benefits of growing rice in flooded soils are well documented (Sahrawat 2007, 2012; Kögel-Knabner et al. 2010). In general, lowland rice soils conserve fertility by net gains from various physical, chemical, and biological (including biological N in the anaerobic and aerobic niches of the flooded soil-plant system) processes (e.g., see Sahrawat 2004c, 2007; Kögel-Knabner et al. 2010; Yan et al. 2013; Zhang and He 2004). Moreover, wetland soils have a relatively large capacity to sequester and store organic matter. Indeed, organic-matter sequestration and its conservation under reduced conditions of submerged soils is the foundation of sustainable fertility maintenance. Soil reduction in the healthy range (Eh ranging from +100 to −100 mV) along with pH in the neutral range ensures absence of toxicants and availability of most plant nutrients in submerged rice soils. Such healthy soil reduction can be further managed by manipulating through organic-matter inputs and the availability of electron acceptors especially, reducible iron (Sahrawat 1998, 2004c, 2007, 2012).

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