EFFECTS OF POST HARVEST MANAGEMENT PRACTICES ON THE STABILITY OF IRON MINERALS IN RICE CULTURE

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Incorporation of crop residues in the soil results in the more reducing conditions as compared to other post harvest management practices. Understanding the nature and extent of reducing conditions and impacts of these reducing conditions on the iron minerals in the paddy soils is the focus of recent research. Two adjacent rice plots with different residue management practices were selected to measure the redox potentials and pH throughout the rice cultivation period. A thermodynamic approach, by constructing the pe-pH diagrams, was used to calculate the stability of iron minerals: Throughout the rice cultivation period a large variability between pe and pH values was observed such that $-6 < pe < 11$ and $6.8 < pH < 8.4$. It was found that before flooding, in both paddy fields, all the iron should be stable in the form of Fe^{3+} (system was oversaturated with respect to Hematite, Goethite, Lepidocrocite and Fougerite) and at the end of the rice cultivation period all the iron should be stable in the form of the Fe^{2+} (system was under-saturated with respect to all mentioned iron minerals). The results also showed that incorporation of rice residues and rhizospheric activity have very determinant role in the dissolution of different iron minerals.

Keywords: Rice residues, pe-pH diagram, rhizosphere, growth stages.

INTRODUCTION

The importance of crop residue management practices is increasing with the current renewed focus on agricultural sustainability and environmental protection (Gadde *et al.*, 2009). The traditional method for crop residues disposal, especially for rice straw, is burning because this method is considered advantageous for disease and pest control, and labour and energy savings. However, open burning of crop residues contributes to emissions of toxic and green house gasses in the environment (Gadde *et al.*, 2009). So, this practice is banned or dramatically reduced in most of the developed countries and alternative methods are recommended to be employed (Eagle *et al.*, 2000). Incorporation of rice crop residues in the soil can favourably influence the biological, chemical and physical properties of the soil and increase the nutrient cycling, fertility of soil, microbial biomass, and mineralization of nitrogen and organic carbon (Nawaz *et al.*, 2012; Bierke *et al.*, 2008; Zeleke *et al.*, 2004). However, in lowland paddy fields, incorporation of rice straw can result in the relatively lower redox potentials or more reducing conditions than in paddy fields where rice straw is removed (Gao *et al.*, 2004; Gao *et al.*, 2002).

Low land paddy soils pass through alternative cycles of aerobic conditions (before flooding) and anaerobic conditions (cultivation period) that leads to the different redox reactions in the soil. It is evident that root influence is strongly affected by drought conditions (Abd-Allah *et al.*, 2005), however, during aerobic conditions, the soil is under oxic state and values of redox potentials (pe) are high while during anaerobic conditions, the soil is under anoxic/reduced state and gives lower values of redox potentials. The alternative aerobic/anaerobic cycles or redox reactions can result in change of soil fertility and increase in soil pH owing to denitrification and reduction of Fe^{3+} to Fe^{2+}, respectively (Ponnamperuma, 1985). Among the elements whose oxidation state can change under earth-surface conditions, iron is the most abundant. Iron is present in the soil in different mineral forms such as hematite (Fe_2O_3), goethite (α FeOOH), lepidocrocite (γ FeOOH), fougerite ($Fe_3(OH)_7$) etc. depending upon the redox conditions of the soil (Bourrie *et al.*, 1999). The switching between the di- and trivalent redox state of iron initiates a number of significant geochemical reactions. Indeed, the large difference of mobility between Fe^{2+}, soluble, and Fe^{3+}, insoluble, leads to the segregation of iron in horizons and/or in soil sequences (Marshall, 1977).

At neutral pH (pH = 7), three domains of reduction state in the soil can be identified: first domain of soil moderately reduced with the pe > 2, second reduced domain of soil when $(-2) < pe < (2)$ and third domain is largely reduced at

pe less than -2 (Sposito and Sparks, 1981). In low land rice cultivation, pe values can be observed in largely reduced domain. As iron contents in most soils are larger than nitrate and manganese, the availability of reducible Fe^{3+} induces the buffering capacity which protects soil against a rapid decrease in redox potential and ultimately mobilization of toxic ions in the soil (Förstner *et al.*, 1994; Lovley, 2000).

The roots of the rice plants are capable of maintaining oxidizing conditions and acidic pH in the rhizosphere by transferring the atmospheric oxygen to the roots and by liberating the H^+ in soil during the absorption process respectively (Begg *et al.*, 1994; Couchat *et al.*, 1993; Murtaza *et al.*, 2005). Furthermore, incorporation of rice straw can result in relative lower pH than physically removing of rice straw due to higher temperatures of soil solution or due to organic acids produced during the biodegradation of the rice straw (Nawaz *et al.*, 2012; Johnson *et al.*, 2006).

Objectives of our study were (1) to observe the evolution of redox conditions and pH throughout the rice cultivation period (2) to determine the effect of different residue management practices on the stability of iron minerals and (3) to see that how the activity of roots can alter the redox conditions and ultimately the stability of iron minerals in rice culture. Thermodynamic approach was used to calculate the stability fields of different iron minerals under different pe and pH values.

MATERIALS AND METHODS

***Site characteristics*:** The study was conducted in the Camargue (France) under Mediterranean climate in two neighbour plots (R-178 and R-179) located at 31°62` E and 48° 29` N. In plot R-178 rice residues are burnt while in plot R-179 the rice residues are incorporated in soil for 20 years. In general, soils on both plots were alluvial, clayey loamy (about 40% clay, 55-56% silt and 4 % sand), naturally less or more saline, with hydromorphic conditions and were deposited in Holocene by Rhône River. These soils are transformed soils by rice culture as rice has been cultivated on both plots and surrounded plots for more than 50 years.

***Use of multiparameteric probe*:** Two calibrated multiparametric probes, type IDROPROBE of DERLIN manufactured by IDROMAR, were used for *in-situ* measurements throughout the rice cultivation period in both plots (R-178 and R-179). These probes were equipped with stirrer to agitate the soil waters and several electrodes to measure the redox potentials, pH, temperature and electrical conductivity. Afterwards, the oxido-reduction potentials, measured with a platinum electrode against a standard Ag/AgCl electrode, were converted to the normal hydrogen scale (NHE) with temperature correction. These probes were installed at depth range of 5-10 cm and were programmed to take the readings after every one hour. The electrodes of the multiparameteric probe were covered with inert tissue to avoid the direct contact with muddy soil as well as the direct effects of rhizospheric activity.

***Manual sampling and use of multimeter*:** Manual sampling was carried out at three different stages of rice cultivation: a) during vegetative stage, b) during reproductive stage, and c) during ripening stage. For manual sampling in the root zone, decontaminated with HNO_3, perforated and inert tissue covered zero-tension lysimeters were used (Bourrie *et al.*, 1999). These polypropylene made pots were installed in the field some days before the sampling day, to allow chemical equilibrium between soil waters and soil. At specific hours aqueous solutions were sampled for soil solutions and non-conservative parameters were measured using portable multimeter and calibrated electrodes in the field: temperature, pH, redox potential and electrical conductivity. Calibration of electrodes and their performance was verified by using procedures of Nawaz and Bourrie (2012).

***pe-pH diagrams*:** pe-pH equilibrium diagrams were made to establish stability fields of iron and to analyse positions of sampled solutions as described by Takeno (2005). To construct the pe-pH diagrams, all the values of normalized redox potentials (Eh) were converted to pe values (Nawaz, 2010; Fiedler *et al.*, 2007). All the values used for solubility product for different forms of iron are given in Table 1.

RESULTS AND DISCUSSION

The Fig. 1 shows domains of stability for various forms of iron as a function of pH and pe in three plots during the complete rice culture period. The Fig. 2 (Figs. 2A, 2B, 2C) shows the three different stages in the evolution of pe and

Table 1. Expressions of Ionic Activity Products and values of Solubility products of Fe oxides and Green Rusts at 298.15 K, 1 bar

Mineral	$\Delta_f G°$ (kJ.mol⁻¹)	±σ	Ionic Activity Product log *IAP*	log *K*	±σ	Ref.
α Fe_2O_3, hematite	- 755.45	±2	log [Fe^{2+}] + 3 pH + pe	12.17	±0.2	1
α FeOOH, goethite	- 480.3	±1	log [Fe^{2+}] + 3 pH + pe	14.97	±0.2	2
γ FeOOH, lepidocrocite	- 470.7	±1	log [Fe^{2+}] + 3 pH + pe	16.65	±0.2	3
$Fe_3(OH)_7$,Fougerite	-1799.7	±6	log [Fe^{2+}] + pe + 7pH	28.2	+0.8	4

1. From E°= 0.72 V ± 0.01 for Hematite + $6H^+$ + 2e = $2Fe^{2+}$ + $3H_2O$ (Bratsch, 1989);
2. Detournay *et al.* (1975); 3. Hashimoto and Misawa (1973); 4. Bourrie *et al.* (1999).

pH during the rice cultivation period. All the straight lines are limits for domains of stability of respective minerals of iron. Here first straight line is for Hematite (from lower side) below which all the iron is in the form of Fe^{2+} and above which in the form of Hematite up to domain of stability then there are lines of Goethite, Lepidocrocite and last is for Fougerite. It can be observed that the values of pe and pH, for R-178 and R-179, have huge variation throughout the rice cultivation period such as -6 < pe < 11 and 6.8 < pH < 8.4 (Fig.1).
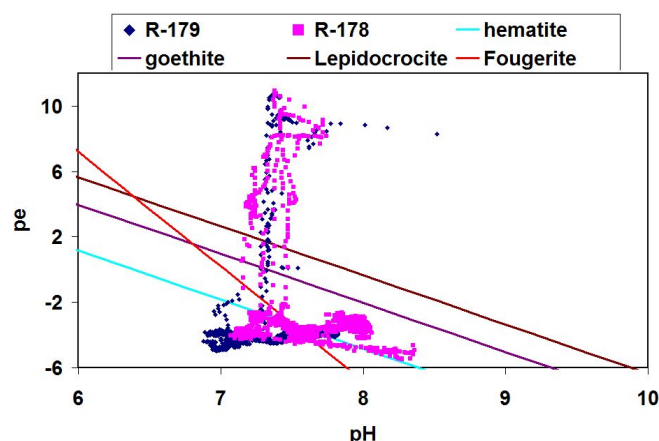

Figure 1. Diagram pe as a function of pH with the equilibrium lines for different forms of the iron for two plots with different residue management practices.

The huge variation in pe values are in according to oxic and reduced conditions before flooding and after flooding respectively. In the start (just after flooding), all the plots are in oxic conditions (pe > 6) and in the end period of rice cultivation all the plots are in highly reduced conditions (-6 < pe < -4). The Figure 1 shows well that system, in all plots, is in continuous evolution with time and both pH and pe play an important role to determine the existence of different reduced forms of the iron. When values of redox potentials are very high (pe > 6), all the iron should be present, in both plots, in the form of Fe^{3+} and oversaturated with respect to αFeOOH (goethite), γFeOOH (lepidocrocite), $Fe_3(OH)_7$ (fougerite) and $αFe_2O_3$ (hematite). When redox potential values decreased as such that 2 > pe > -2, in both plots (R-178 and R-179), decrease of pe at constant pH was observed that leads the system being under-saturated with respect to αFeOOH and γFeOOH. Once the systems attained minimum redox values, -4 < pe < -5 in R-178 and R-179, system in all plots is under-saturated with respect to different iron forms and about all the iron should be present in the form of Fe^{2+}. The larger variations of pe values demonstrate that low land rice culture system passes repeatedly through a phase of higly oxic and highly reduced conditions and ultimately

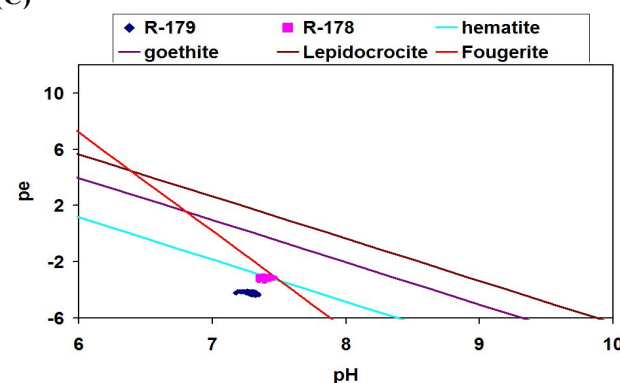affects dissolution and precipitations of several minerals as describe by Ponnamperuma (1985).

(A)
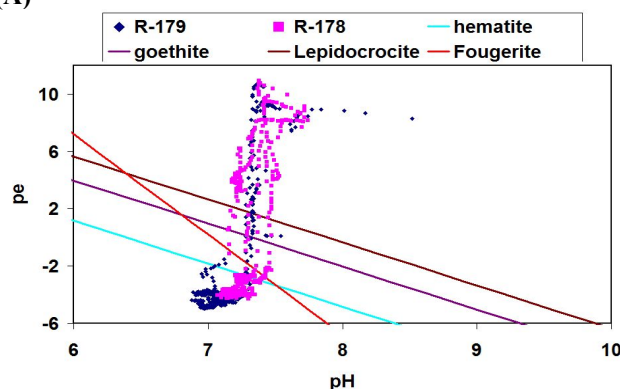
(B)
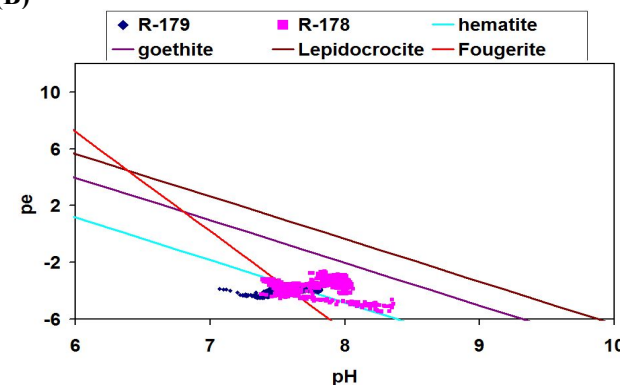
(C)

Figure 2. The pe-pH diagram for two rice plots with different post harvest practices. A. when pe values change but pH is constant; B. when pe values are constant but pH changes; C. when both pe values and pH are constant.

The incorporation of rice residues, apparently, did not affect the presence of different forms of the iron in the system throughout the rice cultivation period except the system in R-179 (where rice residues were incorporated) was more

under-saturated with respect to fougerite and hematite as compared to R-178 (where rice residues were burnt) (Fig. 1 & 2C). It has been intensively reported that incorporation of crop residues in rice culture result in more reduced conditions as compared to other alternative post harvest management practices (Nawaz *et al.*, 2013; Gao *et al.*, 2004) The pe-pH diagram, at given pH and pe, shows well the positions of the system with respect to the stability fields of different forms of the iron but it does not clarify the evolution of the system with the passage of time. To observe the effect of time evolution on pe-pH diagram, the (Fig. 1) was divided in three periods: when pH is constant and pe decreases (oxic or transition conditions) (Fig. 2A), when pH is more unstable than pe (reduced conditions at unstable pH) (Fig. 2B) and when pe and pH are stable (Fig. 2C). The Figure 2A represents about first month in the rice culture for both plots which is the transition period from oxic to anoxic conditions at constant pH and the Figure 2B is the representative of about 2nd month of the rice cultivation which is remarked by the fluctuations in the pH due to urea fertilizer application in the field. In the Figure 2C, last period of rice cultivation that is in highly reductive conditions that is highly stable period with respect to redox potentials and pH for both plots. These changes are ultimate representative of growth phases of rice plants. The rice culture system is very dynamic during vegetative and reproductive growth stages (from 1st to 3rd month); however, the absorption of nutrients and rhizospheric activity is minimized at grain maturity stage (Nawaz *et al.*, 2012).

The measurements taken with the help of the multiparametric probe were not affected by daily cycles of rhizospheric activity in contrary to measurements taken with the help of field multimeter (manually). So, the pe-pH diagrams, were calculated for the pe and pH measurements by both multiparametric probe and field multimeter in soil solution (SS) of the surface waters to observe the effect of the rhizosphere on the stability fields of different forms of iron (Fig. 3).

The results (Fig. 3) showed that during vegetative stage, in spite of having larger pe values, the measurements taken from multimeter were near the stability field of fougerite as in the case of measurements taken from the probe. This is because of lower pH in the rhizosphere due to root absorption or root exudates as described by Begg *et al.* (1994). Furthermore, again due to varied activity of roots during a complete day, the variations between pH and pe during a day for multimeter measured values were significantly larger than probe measurements. Only the R 179_probe is under saturated with respect to all the iron minerals and depicts that all the Fe^{3+} is stable in the form of Fe^{2+}. The results show that during first stage, incorporation of rice residues (R 179_probe and R 179_multimeter) results in slightly acidic pH and more reduced conditions as compared to burning of rice residues (R 178_probe and R

178_multimeter) either measured in the rhizosphere (multimeter) or in the closed cell with no immediate effects of rhizosphere (probe). These results are in accordance with Gao *et al.* (2004) and Begg *et al.* (1994).

(A)

(B)

(C)
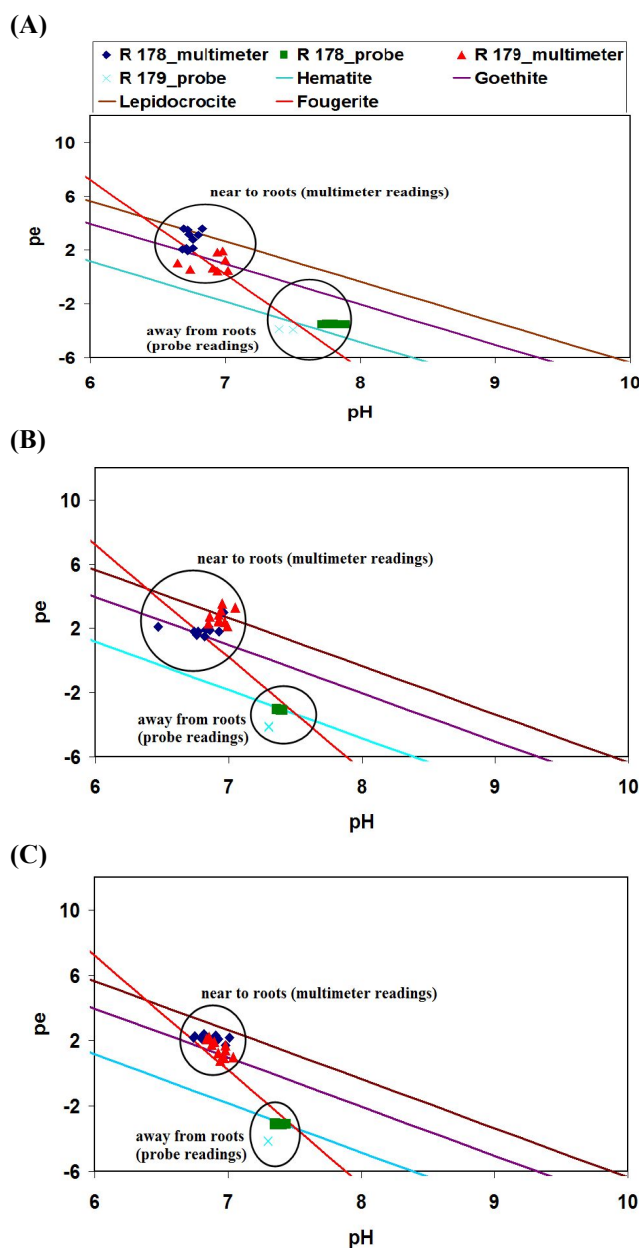
Figure 3. The pe-pH diagram to show the rhizospheric effect on soil solutions of rice culture for two plots. A. At vegetative stage; B. At reproductive stage; C. At ripening stage.

During other stages, R 179_multimeter and R 178_multimeter were mostly oversaturated with respect to fougerite and were near the stability fields of goethite while

R 178_probe and R 179_probe were largely under-saturated with respect to all iron minerals including fougerite. During reproductive and maturation stage, root absorption is significantly reduced so all the values (R 178_multimeter, R 178_ probe, R 179_multimeter and R 179_probe) are about at the same pH but these are only the reducing conditions (pe values) which make the above mentioned difference (Fig. 3). The measurements taken by probe in the plot where rice residues were incorporated (R 179_probe) were more under-saturated with respect to all minerals than the R 178_probe.

***Conclusion*:** Incorporation of rice residues in the lowland paddy fields results in more reducing conditions as compared to burning of rice residues and these reducing conditions can change the stability of iron minerals. Sometimes, in iron rich soils, more reducing conditions can result in iron toxicity in rice plants. A thermodynamic study, using only redox potentials and pH values throughout the rice cultivation period confirmed the hypothesis that in rice culture all the present iron can be present in reduced form (Fe^{+2}). So, if there is absence of other physico-chemical processes controlling the iron concentrations in soil solution (*i.e.* precipitation in the form of FeS) this iron can damage the crop yield especially at initial stages. Measurement of real iron concentrations and using physico-chemical models like PHREEQC can largely increase the accuracy and precisions in the results.

REFERENCES

Abd Allah, A., S. Badawy, B. Zayed and A. El.Gohary. 2010. Role of root system traits in the drought tolerance of rice (*Oryza sativa L.*). Int. J. Agri. Biol. 1: 83-87.

Begg, C., G. Kirk, A. Mackenzie and H. Neue. 1994. Root-induced iron oxidation and pH changes in the lowland rice rhizosphere. New Phytol. 128:469-477.

Bierke, A., K. Kaiser and G. Guggenberger. 2008. Crop residue management effects on organic matter in paddy soils--The lignin component. Geoderma 146:48-57.

Bourrie, G., F. Trolard, J. Jaffrezic, V. Maitre and M. Abdelmoula. 1999. Iron control by equilibria between hydroxy-green rusts and solutions in hydromorphic soils. Geochim. Cosmochim. Acta 63:3417-3427.

Bratsch, S. 1989. Standard electrode potentials and temperature coefficients in water at 298.15 K. J. Phys. Chem. Ref. Data 18:1-22.

Couchat, P., J. Bois and M. Puard. 1993. Rice responses to environmental conditions. Agronomy 1:73-85.

Detournay, J., L. De Miranda, R. Derie and M. Ghodsi. 1975. The region of stability of green rust II in the electrochemical potential-pH equilibrium diagram of iron in sulphate medium. Corros. Sci. 15:295-306.

Eagle, A., J. Bird, W. Horwath, B. Linquist, S. Brouder, J. Hill and C.V. Kessel. 2000. Rice yield and nitrogen utilization efficiency under alternative straw management practices. Agron. J. 92:1096-1103.

Fiedler, S., M. Vepraskas and J. Richardson. 2007. Soil redox potential: importance, field measurements, and observations. Advs. Agron. 94:1-54.

Forstner, U., W. Calmano, J. Hong and M. Kersten. 1994. Effects of Redox Variations on Metal Speciation--Implications on Sediment Quality Criteria Assessment. Sp. Pub. Roy. Soc. Chem. 154:83-102.

Gadde, B., S. Bonnet, C. Menke and S. Garivait. 2009. Air pollutant emissions from rice straw open field burning in India, Thailand and the Philippines. Environ. Pollut. 157:1554-1558.

Gao, S., K. Tanji and S. Scardaci. 2004. Impact of rice straw incorporation on soil redox status and sulfide toxicity. Agron. J. 96:70-76.

Gao, S., K. Tanji, S. Scardaci and A. Chow. 2002. Comparison of redox indicators in a paddy soil during rice-growing season. Soil Sci. Soc. Amer. J. 66:805-817.

Hashimoto, K. and T. Misawa. 1973. The solubility of [gamma]-FeOOH in perchloric acid at 25°C. Corros. Sci. 13:229-231.

Johnson, S., O. Angeles, D. Brar and R. Buresh. 2006. Faster anaerobic decomposition of a brittle straw rice mutant: implications for residue management. Soil Biol. Biochem. 38:1880-1892.

Lovley, D. 2000. Environmental microbe-metal interactions. Washington, DC: ASM Press.

Marshall, C. 1977. The Physical Chemistry and Mineralogy of Soils. Volume II: Soils in Place: John Wiley & Sons, Inc.

Murtaza, G., A. Ghafoor, U. Kahloon, M. Bilal and M. Manzoor. 2005. Comparative growth performance of rice and wheat varieties at different EC and SAR ratios in soil. Pak. J. Agri. Sci. 42: 99-106.

Nawaz, M.F., G. Bourrié, F. Trolard, J. C. Mouret and P. Henry. 2013. Effects of agronomic practices on the physico-chemical properties of soil waters in rice culture. Turk. J. Agric. For. 37: 195-202.

Nawaz, M.F., G. Bourrie, S. Gul, F. Trolard, I. Ahmad, M.A. Tanvir and J.C. Mouret. 2012. Impacts of rice plant roots on the variation in electro-physicochemical properties of soil waters. Pak. J. Bot. 44:1891-1896.

Nawaz, M.F. and G. Bourrie. 2012. Development of sensor calibration against standards using measurement software TestPointTM-CEC and application to the verification of pH electrodes. J. Chem. Soc. Pak. 34:9-15.

Nawaz, M.F. 2010. Geochemistry of hydromorphic soils and waters under rice culture and forest - continuous measurements, thermodynamicmodelling and kinetics. Ph.D. Thesis. Université d'Aix Marseille III. France, p. 18.

Ponnamperuma, F.N. 1985. Chemical kinetics of wetland rice soil relative to soil fertility. In: Wetland Soils-Characterization, Classification and Utilization. International Rice Research Institute (IRRI), Los Banos, Philippines.

Sposito, G. and D. Sparks. 1981. The thermodynamics of soil solution: Oxford University Press, p.223.

Takeno, N. 2005. Atlas of Eh-pH Diagrams, Inter-comparison of Thermodynamic Databases. National Institute of Advanced Industrial Science and Technology: Tokyo.

Zeleke, T., M. Grevers, B. Si, A. Mermut and S. Beyene. 2004. Effect of residue incorporation on physical properties of the surface soil in the South Central Rift Valley of Ethiopia. Soil Till. Res. 77:35-46.