

SIGNIFICANCE OF IRON- AND SULPHATE REDOX PROCESSES IN FLOODED SOILS FOR THE NUTRITION OF RICE

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Introduction

Wetland rice is well adapted to flooded soil conditions and generally intensive reductive transformations are beneficial for the rice crop. Amongst the most important physico-chemical changes in flooded soils are those resulting from ferric iron- and sulphate-reduction, and both processes may affect directly or indirectly the development of the rice plant. So far, a number of nutritional disorders of wetland rice have been ascribed at least in part to intensive iron- or sulphate-reduction in the soil although an acceptable understanding of the physiological effects caused by ferrous- and sulfidic ions is still lacking. In this paper, we focus on the role of the rice plant itself in the regulation of biological iron- and sulphate-reduction and on possible toxicities of Fe(II) and sulphides. In soils, the physiological status of the plant and particularly of the roots seems to play a key role in the control of types and intensities of rhizospheric processes. Vice versa the chemical properties of the soil determine the physiology of the plant and the proper functioning of the root system.

Causes and conditions of iron- and sulphate-reduction

In flooded soils reductive processes proceed as predicted by the thermodynamics of the redox couples involved (Table 1). All processes mentioned are mediated directly by microorganisms, which use the oxidants (Table 1) as electron acceptors during specific energy conserving reactions. In order to achieve a steady state

Table 1: Sequence of microbial reductive transformations in flooded soils and theoretical equilibrium conditions of the redox-reactions at pH = 7 (OTTOW & FABIG, 1985).

Processes	Measured Redox Potential (Eh) During Transformations ¹⁾	rH Level ²⁾	Redox Systems Involved ³⁾	E ⁰ (mV) ⁴⁾
Respiration	> 400	> 26	O ₂ · 4H ⁺ · 4e ⁻ = 2H ₂ O	+ 814
NO ₃ ⁻ respiration	+ 500 - + 200	29 - 19	2NO ₃ ⁻ · 12H ⁺ · 10e ⁻ = N ₂ · 6H ₂ O	- 741
Formation of Mn(II)	- 400 - - 200	26 - 19	MnO ₂ · 4H ⁺ · e ⁻ = Mn(II) · 2H ₂ O	- 410
Production of Fe(II)	+ 400 - + 180	26 - 18	Fe(OH) ₃ · 3H ⁺ · e ⁻ = Fe(II) · 3H ₂ O	- 185
S ²⁻ production	+ 100 - - 200	16 - 5	SO ₄ ²⁻ · 10H ⁺ · 8e ⁻ = H ₂ S · 4H ₂ O	- 214
CH ₄ production	- 150 - - 280	7 - 2	CO ₂ · 8H ⁺ · 8e ⁻ = CH ₄ · 2H ₂ O	- 244

¹⁾ Redox potentials (Eh) are comparable only if corrected for pH

²⁾ rH (= -negative log of pH₂) calculated from Eh(mV) at (a) and a pH of 6 (assumed) according to rH = Eh(mV)/29 · 2xpH(30°C)
At rH = 0 completely reduced, at rH = 42,6 entirely oxidized, conditions prevail

³⁾ These electron acceptors are increasingly electrochemically sluggish (NO₃⁻, MnO₂) or even highly inactive (Fe₂O₃ · xH₂O, SO₄²⁻)

⁴⁾ E⁰ = E_m = standard electrode potential at 50% reduction at a pH of 7,0

flux from the oxidized to the reduced side of each equilibrium (Table 1) an energy input is required to activate the electron acceptor. The strict sequence of soil reduction is accordingly determined by a considerable increase in activation energy of the progressively electrochemically sluggish electron acceptors (OTTOW, 1982; MUNCH & OTTOW, 1982; OTTOW & FABIG, 1985).

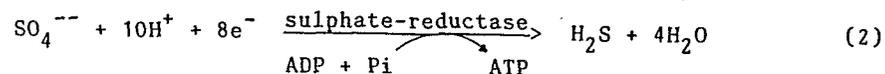
The higher the amounts of easily decomposable organic matter in soils, the more intensive will be the demand for (alternative) electron acceptors during microbial energy conservation and the more complete will be the sequential exhaustion of the electron acceptors involved. On the other hand, the redox level (rH- or pE-value) at which the soil will poise during reduction depends on the quantity and the quality (e. g. cristallinity) of the electron acceptors present in the soil. In most soils ferric iron and sulphate are the quantitatively predominant oxidants and their forms and spatial distribution are therefore essential for the kinetics of soil reduction.

Microbial reduction of ferric compounds (e. g. amorphous "Fe(OH)₃ ") is proposed to proceed as (1)



and will continue as long as ferric compounds are available in the system. During their energy conserving metabolism the iron-reducing microorganisms will prefer those ferric oxides and hydroxides that require least energy of activation (MUNCH & OTTOW, 1980; 1982). Consequently, amorphous ferric compounds are reduced in preference to crystalline ones. Within the latter, even lepidocrocite is used preferentially to goethite or hematite (MUNCH & OTTOW, 1980; 1982).

In a homogeneously reduced soil, sulphate-reduction (2)



will not start until most of the ferric compounds have been reductively consumed. The sulphate-reducing bacteria have more specific nutrient requirements than the iron-reducing microorganisms. They depend tightly on metabolites of the preceding fermentations (e. g. acetate, lactate, alcohols, specific amino acids and/or H₂) and use only sulphate as electron acceptor at particular conditions (anaerobiosis, low redox levels and presence of Fe(II) to precipitate H₂S) (JACQ, 1973; 1975; 1977).

Around decaying roots or accumulations of organic matter the ferric iron stock of the soil may be locally exhausted, and intensive sulphate-reduction can start although, in the mean bulk soil, iron-reduction is not completed (FRENEY et al., 1982). Due to the heterogeneous distribution of organic matter in the soil, different soil compartments consequently may have a differently advanced reduction status.

In paddy soils major parts of the soil organic matter are mineralized via ferric iron- or sulphate-reduction (FRENEY et al., 1982; INUBUSHI et al., 1984). Therefore *in situ* Eh and pH are usually mainly buffered by iron- or sulphate reduction (Fig. 1). In addition to its importance for Eh- and pH-buffering (Fig. 1, middle part) the reduction of ferric oxides and -hydroxides brings about considerable increases in nutrient availabilities (PONNAMPERUMA, 1977) (Fig. 1, lower part). Especially the release of phosphate previously sorbed or occluded by ferric (hydr)oxides is of major importance to the nutrition of the rice

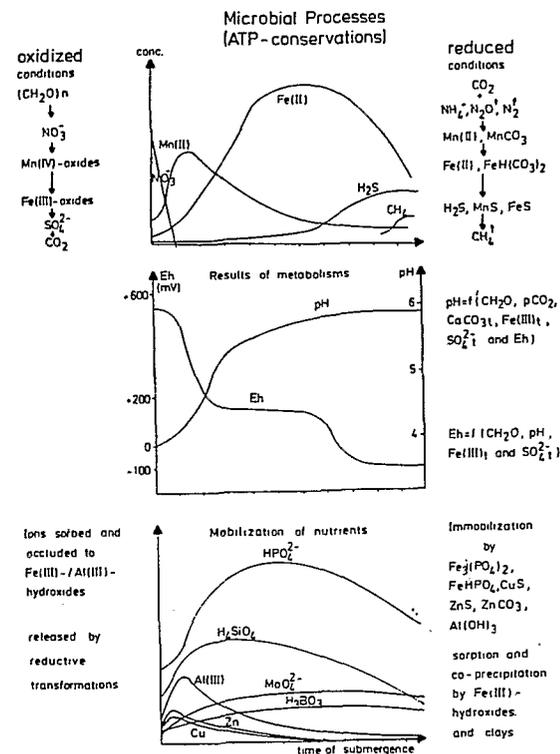


Fig. 1: Sequence of microbial reduction processes with anorganic oxidants as electron acceptors and their effects on pH, Eh and the mobility of nutrients (concentrations in soil solution).

plant (SWARUP, 1985; ROY & DE DATTA, 1985). Sulphate-reduction, however, can counteract the release of cations brought about by iron-reduction by reprecipitating them as sulfides (FeS, MnS, ZnS etc.). Additionally, ferrous hydroxides present in reduced soil compartments may act as strong sorbants for anions (phosphate, molybdate etc.) (Fig. 1). Consequently, iron-reduction and desulfurication are effectively influencing nutrient availability in paddy soils. Estimations of positive and negative effects of soil reduction on physiology or growth of rice remain difficult because of the high variability of reduction intensity in the bulk soil, which is mainly due to the heterogeneous availability of organic substrates. This is one reason, why

attempts to relate plant growth in the field to in situ Eh, pH or soil solution concentrations of Fe(II) or S(--) are often bound to fail.

The rhizosphere of wetland rice in relation to iron- and sulphide-toxicity

Based on comparative physico-chemical surveys of iron toxic soils and the mineral contents of affected plants from various regions in South East Asia and West Africa iron toxicity was explained at least partly by multiple nutrient stresses (insufficient supply with P, K, eventually Zn and Ca) (TANAKA & YOSHIDA, 1970; OTTOW et al., 1982; BENCKISER et al., 1984; PRADE, 1986). Two distinct types of iron toxicity were identified (PRADE et al., 1986). Primary iron toxicity, mainly observed immediately after transplanting in the phase of intensive microbial iron reduction, is attributed to the failure of young non-aerenchymatic and/or damaged roots to exclude Fe(II)-ions. In this phase an increased carbon flow from damaged roots may even stimulate Fe(III)-reduction in the rhizosphere, hence increasing the influx of Fe(II). Recovered plants may suffer heavily from a second influx of Fe(II) during the reproductive growth stage between heading and flowering (secondary iron toxicity). Secondary iron toxicity proved clearly to be dependant on the nutrient status of the plant (PRADE et al., 1986).

Both phases of iron intoxication are shown in Fig. 2. The comparison of leaf iron contents (Fig. 2, upper part) with the Fe(II)-concentrations in the soil solution (Fig. 2, lower part) suggests that a heavy iron mobilization had occurred immediately after transplanting in the rhizosphere, because at this time only traces of Fe(II) could be detected in the soil solution. Afterwards, while Fe(II)-concentrations in the soil solution increased, plants succeeded to regulate iron influx, probably by establishing an effective oxidation of Fe(II) in the rhizosphere (by means of the air conducting aerenchym tissues). Recovery was obviously delayed in nutrient deficient plants (Fig. 2, treatment N). Physiological stresses caused by nutrient deficiencies (e. g. high N-supply, not balanced with adequate P- and K-fertilization) may hamper the plants ability to create an oxi-

dized rhizosphere by increasing the exudation of carbohydrates and other metabolites, thus stimulating oxygen consumption and iron reduction in the root zone (BENCKISER et al., 1984).

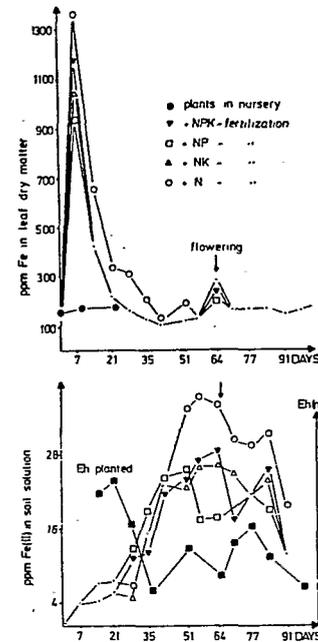


Fig. 2: Effect of fertilization on the uptake of Fe (ppm Fe in leaf dry matter) by wetland rice (IR8), Fe(II)-concentrations in the soil solution and development of redox-level (Eh; mean of all treatments) on an iron toxic loamy sand (Djibelor/Basse Casamance/Sénégal). The field was flooded immediately after the transplantation of seedlings.

Fig. 3 gives strong evidence that rhizospheric iron-reduction also can influence the availability of other elements such as aluminium. The excessive Al-uptake in freshly transplanted rice (Fig. 3, upper part) cannot be ascribed to a high solubility of Al-ion species since proton activities in situ were low (Fig. 3, lower part). An intensive microbial reductive dissolution of Al-substituted ferric oxides, by the way releasing Al-ions, could well explain this phenomenon. In both examples (Fig. 2, 3) measurements of in situ Eh, pH or Fe(II)-concentrations alone could not warrant an accurate description of the reduction processes in the soil and their effects on the plant's physiology, probably because of significant differences in reduction intensities between the rhizosphere and the mean bulk soil.

Because sulphate-reduction requires a considerably higher activation energy than iron-reduction (Table 1), rhizospheric or spermospheric desulfurication, often observed with young rice

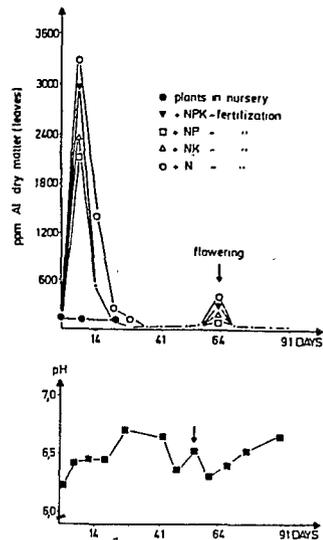


Fig. 3: Effect of fertilization on the uptake of Al (ppm Al in leaf dry matter) by wetland rice (IR8) in relation to *in situ* pH (mean of all treatments) on an iron toxic loamy sand (Djibelor/Basse Casamance/Sénégal). The field was flooded immediately after the transplantation of seedlings.

seedlings, can be only explained by a local acceleration of the reduction sequence (JACQ, 1973; 1975). Since desulfurication is bound to be preceded by iron reduction (see Table 1 and Fig. 1) the black precipitates of ferrous sulfides in the rhizosphere need not necessarily

be an indication for sulfide toxicity. Quite likely, intensive iron-reduction at the root surface should be regarded as the cause of root damage and death. The following liberation of metabolites suitable for sulphate-reducing bacteria and the presence of sulphate might trigger H_2S -formation and intensive precipitation of ferrous sulfides. This blackening of root systems ("sulfide toxicity"), often observed with rice suffering from "bronzing" or "yellowing", thus is not a symptom of sulfide toxicity *per se* but rather a consequence of root damage, which could be due to intensive iron-reduction in the rhizosphere (e. g. induced by nutrient deficiencies). Based on these views, the application of organic manures (green manure, straw, compost etc.) will not provoke iron- or sulfide toxicity and can be recommended, even if strong sulphate reduction is induced in the bulk soil, if the nutritional status of the soil warrants the oxidative capacity of the rice rhizosphere. Repeated incorporations of organic fertilizers will naturally improve the soils fertility, which will contribute to an increased tolerance of rice against adverse soil conditions.

Conclusions

The major importance of ferric iron-reduction and sulphate-reduction processes in paddy soils is based on their influences on Eh/pH-buffering and on nutrient availability. Additionally, the reduction products are frequently considered to be potentially toxic to rice. Both microbially catalysed processes are of special importance in the rice rhizosphere where, depending on the physiological status of the plant, they can be either effectively promoted or virtually suppressed in comparison to the non rhizospheric soil. Therefore the actual influence of both processes on plant growth can hardly be interpreted in terms of *in situ* physico-chemical characteristics (Eh, pH, concentrations of Fe(II) etc.). Toxicity symptoms (bronzing, yellowing, blackening of root systems etc.) are not so much proof of real Fe(II) or S^{--} stresses but are rather hinting towards other causal physiological stresses, for instance nutrient deficiencies. If we wish to understand the detrimental effects of iron and sulphides in paddy soils we should pay more attention to the plants physiology rather than to the soil chemistry alone.

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