

IRON DYNAMICS AND ITS RELATION TO SOIL REDOX POTENTIAL AND PLANT GROWTH IN ACID SULPHATE SOIL OF SOUTH KALIMANTAN, INDONESIA

Dinamika Besi dan Hubungannya dengan Potensi Redoks Tanah dan Pertumbuhan Tanaman di Tanah Sulfat Masam Kalimantan Selatan, Indonesia

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ABSTRACT

Organic matter has a function to maintain reductive conditions and to chelate toxic elements in acid sulphate soils. The study aimed to assess the dynamics of ferrous iron (Fe^{2+}) in acid sulphate soil and its correlation with soil redox potential (Eh) and plant growth. The experiment was arranged in two factorial randomized block design with three replications. The first factor was two types of organic matter: (1) control (without organic matter), (2) rice straw and (3) rush weed (*Eleocharis dulcis*). The second factor was time of decomposition of organic matter: $I_1 = 2$ weeks, $I_2 = 4$ weeks, $I_3 = 8$ weeks, and $I_4 = 12$ weeks (farmer practice). The results showed that concentration of ferrous iron in the soil ranged from 782 to 1308 mg kg^{-1} during the rice growing season. The highest constant rate of iron reduction ($k \text{ Fe}^{2+}$) was observed on application of rice straw and rush weed with decomposition time of 8 weeks with the $k \text{ Fe}^{2+}$ value of 0.016 and 0.011 per day, respectively, while the ferrous iron formation without organic matter had the $k \text{ Fe}^{2+}$ value of 0.077 per day. The ferric iron (Fe^{3+}) reduction served as a function of soil Eh as indicated by the negative correlation of ferrous iron and Eh ($r = -0.856^*$). Organic matter decreased exchangeable iron due to chelating reaction. Iron concentration in roots was negatively correlated with soil soluble iron ($r = -0.62^*$). Application of rice straw decomposed for 8 weeks increased the height of rice plant up to 105.67 cm. The score of Fe^{2+} toxicity at 8 weeks after planting ranged from 2 to 3, so rice crop did not show iron toxicity symptoms.

[**Keywords:** Ferrous iron, redox potential, plant growth, acid sulphate soil]

ABSTRAK

Bahan organik memiliki fungsi mempertahankan kondisi reduktif tanah dan mengkelat unsur beracun di tanah sulfat masam. Penelitian bertujuan untuk mempelajari dinamika besi ferro di tanah sulfat masam serta korelasinya dengan potensi redoks (Eh) tanah dan pertumbuhan tanaman. Penelitian menggunakan rancangan faktorial dua faktor dan diulang tiga kali. Faktor pertama adalah jenis bahan organik, yaitu (1) kontrol (tanpa

bahan organik), (2) jerami padi, dan (3) gulma purun (*Eleocharis dulcis*). Faktor kedua adalah waktu dekomposisi bahan organik, yaitu $I_1 = 2$ minggu, $I_2 = 4$ minggu, $I_3 = 8$ minggu, dan $I_4 = 12$ minggu (pola petani Banjar). Hasil penelitian menunjukkan bahwa secara umum konsentrasi besi ferro (Fe^{2+}) di tanah sulfat masam berkisar 782–1308 mg kg^{-1} selama pertumbuhan tanaman padi. Konstanta tertinggi kecepatan reduksi besi ($k \text{ Fe}^{2+}$) terdapat pada perlakuan jerami padi dan gulma purun dengan waktu inkubasi 8 minggu, masing-masing 0,016 dan 0,011 per hari. Sementara konstanta terendah ditunjukkan pada perlakuan tanpa bahan organik, yakni 0,077 per hari. Reduksi besi ferri (Fe^{3+}) merupakan fungsi dari nilai Eh tanah yang ditunjukkan dengan adanya korelasi negatif antara besi ferro dan nilai Eh dengan $r = -0,856^*$. Bahan organik dapat menurunkan konsentrasi besi tukar dalam tanah melalui pengkelatan. Terdapat korelasi negatif antara konsentrasi besi dalam akar dengan yang larut dalam tanah dengan nilai $r = -0,62^*$. Pemberian kompos jerami padi dengan waktu inkubasi 8 minggu meningkatkan tinggi tanaman padi yang mencapai 105,67 cm. Nilai skor keracunan besi pada tanaman padi umur 8 minggu setelah tanam berkisar 2–3 dan disimpulkan tanaman padi cukup toleran di lahan sulfat masam karena tidak menunjukkan gejala keracunan besi.

[**Kata kunci:** Besi ferro, potensial redoks, pertumbuhan tanaman, tanah sulfat masam]

INTRODUCTION

Acid sulphate soils are characterized by the presence of sulfuric horizon and generally contain iron in large amounts resulting in low soil pH, < 3.5 (Sarwani *et al.* 2006; Natural Resources Conservation Service 2010), and are classified into Sulfaquepts (Soil Survey Staff 2010). The reduction processes of SO_4^{2-} and Fe (III) oxide in acid sulphate soils occur in waterlogged (anaerobic) conditions which raise the pH of the soil due to the consumption of protons in the process (Sarwani *et al.* 2006). The dominant forms of iron oxide in water-logged conditions are goethite ($\alpha\text{-FeOOH}$), ferri-hydrate ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$), lepidocrocite ($\alpha\text{-}$

FeOOH) and maghemite ($\alpha\text{-Fe}_2\text{O}_3$) (Cornell and Schwertmann 1996). The solubility and reactivity of iron oxides were influenced by several factors, namely pH, soil redox potential (Eh) and environmental conditions. Changes in soil pH and Eh affect the stability and solubility of metal minerals (Satawathananont *et al.* 1991) in the soil solution and water puddles on the soil surface (Ponnamperuma 1977; Bremen 1975). The high solubility of iron is one of the problems in the use of acid sulphate soil for cultivation of food crops, especially rice.

Crop residues and rush weed (*Eleocharis dulcis*) are major sources of organic material in acid sulphate soils. Rice straw residues and weeds are effectively used as ameliorant material in rice cultivation on acid sulphate soils (Sarwani *et al.* 1993). The process of organic matter decomposition in flooded soils is contrast to that in aerobic soils because the presence of oxygen is limited in flooded soil conditions. Oxygen is an electron acceptor that is used by anaerobic microorganisms for oxidation of organic material. The C/N ratio of organic materials for optimum composting ranged from 20 to 50/1 (Rynk and Colt 1997). In the early decomposition process, the easily decomposed materials such as chlorophyll (leaves) and epidermal tissue (skin) were first decomposed followed by the aromatic part which is difficult to decompose because of a high lignin content. The results of the FTIR analysis of methyl aliphatic, amines and amides are indicators of organic matter decomposition process characterized by broad absorption decrease due to biodegradation of labile fractions (Smidt *et al.* 2002; Smidt and Meissl 2006). While the aromatic C = C and C = O functional groups which are interpreted as humic groups increased after the decomposition of organic material. This study aimed to assess iron dynamics in acid sulphate soil and its correlation with soil redox potential and plant growth under the influence of different decomposition levels of organic matter.

MATERIALS AND METHODS

The experiment was conducted in the greenhouse of Indonesian Swampland Agricultural Research Institute, Banjarbaru, South Kalimantan from April to July 2011. The soil was classified into potential acid sulphate soil, Sulfaquents (Soil Survey Staff 2010). Acid sulphate soil samples of the rhizosphere (0–20 cm depth) were collected from Tanjung Harapan Village, Alalak Sub-District, Barito Kuala Regency, South Kalimantan (030 10'S; 1140 36'E).

The experiment was arranged in two-factorial randomized block design with three replications. The first factor was a type of organic matter, i.e. (1) control (without organic matter), (2) rice straw and (3) rush weed. The second factor was time of decomposition of organic matter according to Banjarese farmers' practice, i.e. I_1 = 2 weeks (*tajak* period), I_2 = 4 weeks (*puntal balik* period), I_3 = 8 weeks (*puntal balik* period) and I_4 = 12 weeks (farmer practice).

The process of decomposition of organic matter was carried in the field (Belandean Experimental Station in Barito Kuala District, South Kalimantan) according to the treatments and farmers' practice. All treatments except for farmer practice used decomposer for decomposition process.

Soil samples were directly collected from the field and transferred into the pots with diameter of 25 cm and height of 35 cm. Each pot contained 6 kg fresh soil. Organic matters were applied into the pots and then submerged with water from river and the water level of flooding was 5 cm. Urea was given at 200 kg ha⁻¹ splitting two times at transplanting and at four weeks after transplanting. SP-36 fertilizer of 160 kg ha⁻¹ and KCl of 100 kg ha⁻¹ rates, respectively, were given once at planting time.

Measurements of soil pH and redox potential (Eh) were conducted using a pH-meter and a Pt-electrode (pH/ORP Meter), respectively. Soluble iron (Fe (II)) in the soil was determined by extraction with 1 M NH₄OAc at pH 4.8 (Olson and Sommers 1982). Soil suspension was filtered using Whatman filter paper 42. Fe contents were determined by an Atomic Absorption Spectrophotometer. Plant samples were digested using HNO₃ + HClO₄ (Kacar 1995). Rice of Margasari variety was used for a testing crop.

RESULTS AND DISCUSSION

Soil Chemical Properties

Soil in the study site was classified into a Typic Sulfaquent because the soil pH after oxidized dropped to < 3.5. Pyrite oxidation produces Fe²⁺ and SO₄²⁻ and H₂ which result in a decrease in soil pH. According to Dent (1986), the soil pH < 2.5 or 3 after being given H₂O₂ indicated strong sulfuric acidity. The pH of the air-dried soil was low (pH 4.4). The low soil pH affects PO₄-P sorption/desorption. According to Gustafsson *et al.* (2012), the solubility of PO₄-P increased with increasing soil pH in the low to medium pH range because of sorption/desorption

processes involving iron. This is consistent with the high amounts of ferrous iron at $1,495 \text{ mg kg}^{-1}$. The soils of Belandean had a high organic matter content (19.5%), 11.05% organic C, 0.19% N, 56.09 C/N, and 24.19 mg kg^{-1} P-Bray. The high organic matter content plays an important role in inhibiting the formation of Fe-oxides in the soil, keeping redox potential low most of the time (Sarwani *et al.* 2006). The organic compounds have a capability to reduce soil redox potential. Fiedler *et al.* (2004) reported a negative correlation between the gradient of redox potential and concentrations of soil microbial biomass but increased parallelly to microbial population and DOC.

Iron Dynamics in Acid Sulphate Soil

Ferrous iron dynamics in acid sulphate soil was affected by organic matter (Fig. 1). Application of rice straw and rush weed increased ferrous iron concentration at 45 days after planting then decreased gradually. Organic substrates from rush weed were widely available in South Kalimantan. Banjarnese farmers often apply rush weed as rice straw under anaerobic conditions. A research by Reddy *et al.* (2008) revealed the exchangeable pool of iron following similar trends. Flooding of drained paddy soils increased water-soluble iron rapidly reaching the peak concentrations, followed by a steady decrease resulting from secondary reactions such as precipitation with carbonates and sulfides. According to Wagai *et al.* (2013), iron could bind organic ligands to form organo-metal complexes. Organic matter in the soil

provides chelating agents which function as a sink for micro-nutrient cations and heavy metals. Under anoxic conditions, ferric iron is readily reduced either by inorganic chemical reactions or by microbial processes. The extent of these phenomena is closely dependent on the availability of organic molecules (organic carbon) from which the microbes obtain sustenance (Colombo *et al.* 2014). These results clearly indicated that organic carbon was associated with ferrous iron ($r = 0.80^*$) (Fig. 2).

The high cumulative ferrous iron occurred at two weeks of organic matter decomposition and the magnitude was in the order of composted rush weed > composted rice straw > without organic matter (Fig. 3). In acid sulphate soil, organic matter has a function as an electron donor in the reduction process. Addition of good quality organic matter decreased

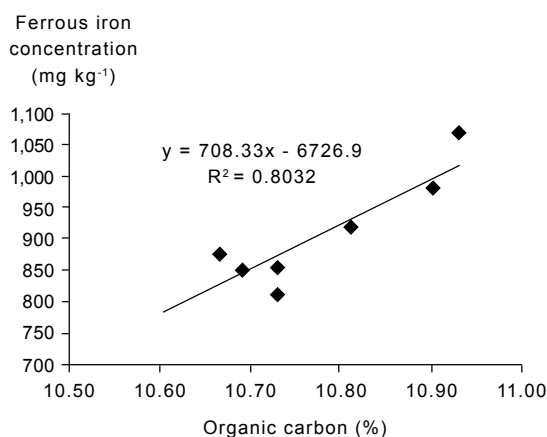


Fig 2. Correlation between organic carbon and ferrous iron concentration in acid sulphate soil.

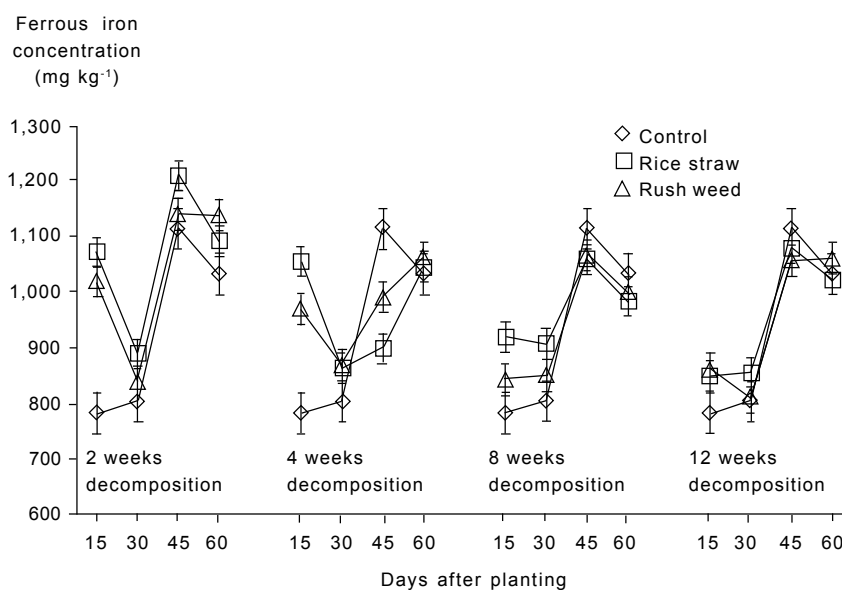


Fig 1. Dynamics of ferrous iron concentration as a function of organic matter decomposition time in acid sulphate soil.

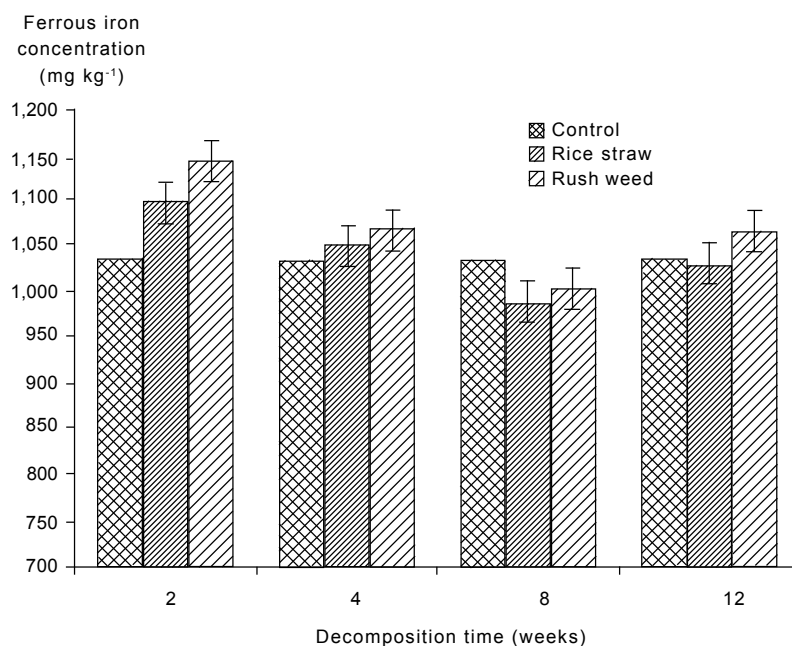


Fig. 3. Ferrous iron concentration at different decomposition times of organic matter in acid sulphate soil.

ferrous iron due to chelating process. Good quality organic matter has a C/N ratio of < 20. According to Palm and Sanchez (1991), good quality crop residues and rush weed, N content form, C/N ratio, lignin content and poliphenol affected the rate of organic matter decomposition in waterlogged soil. In the early decomposition process, the easily decomposable organic fraction, namely chlorophyll (leaves) and epidermal tissue (skin) was decomposed first, then followed by the aromatic fraction which was difficult to decompose because of a high lignin content. In acid sulphate soils, organic matter has a function to maintain reductive conditions and also to chelate toxic elements. Sarwani *et al.* (2006) reported that application of good quality organic matter on acid sulphate soils in Malaysia reduced ferrous iron content due to chelating reaction. The low cumulative ferrous iron occurred for rice straw and rush weed after 8 weeks decomposition (Fig. 3). Composting organic matter was the most common way to mineralize organic matter and had been proven to reduce ferrous iron in waterlogged soils.

Rates of Iron Reduction

The highest constant rate of iron reduction was observed at the application of rice straw and rush

weed with 8 weeks decomposition time with the $k \text{ Fe}^{2+}$ value of 0.016 and 0.011 per day, respectively, while the ferrous iron formation without organic matter application had the lowest $k \text{ Fe}^{2+}$ value, i.e. 0.077 per day (Fig. 4). The $k \text{ Fe}^{2+}$ value is a rate constant of ferrous iron formation in acid sulphate soil. The high k value indicated that the formation of ferrous iron occurred rapidly. The rate of iron reduction in wetland soils correlated well with the quality of rice straw and rush weed. The chemical composition of organic matter in the soil could also be an important factor regarding the rate of iron reduction in waterlogged soils. One theory indicates that the rates of organic matter oxidation and Fe(III) reduction are faster in the presence of organic matter than that without organic matter because of electron shuttling by humic substances of organic matter, alleviating the need for Fe(III) reducing microorganisms to contact insoluble Fe(III) oxides. Roden and Wetzel (2002) reported that microbial reduction of Fe (III) oxides followed the first-order kinetics and the rates of reduction were directly linked to organic matter mineralization with the first-order rate constants ranged from 0.175 to 0.346 per day. The rate of reduction in wetland soils was affected by many factors, including the amounts and forms of organic matter, the amounts and forms of Fe, microbial activities, and concentrations of NO_3 and Mn in the soil (Ponnamperuma 1977).

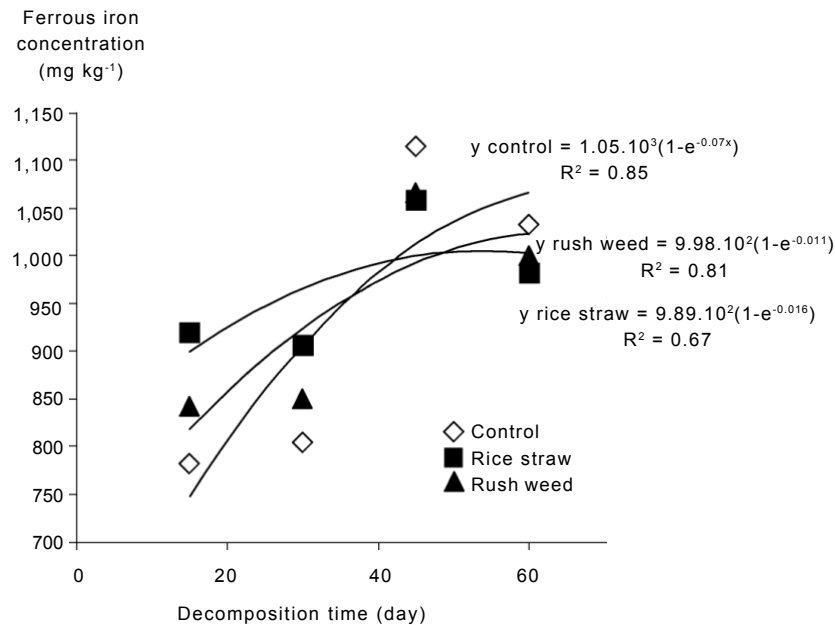


Fig. 4. Rates of ferrous iron formation in acid sulphate soil with application of rice straw and rush weed after eight weeks decomposition.

Soil Redox Potential and Ferrous Iron

Soil redox potential (Eh) directly affected ferrous iron. Result of the study showed a negative correlation between Eh and Fe^{2+} with the value of $r = -0.856^*$ (Fig. 5). Similar result was demonstrated by Gardiner and James (2012) that the negative impact on redox values was caused by organic matter addition, not by native organic matter in the soil. Reduction of Fe(III) is a function of Eh. Fe(II) concentration was low under oxidized conditions and high with the decrease in soil Eh (Reddy 2008). Accumulation of Fe(II) in acid sulphate soil is coupled to Fe(III) reduction and organic matter decomposition.

Relationship Between Soluble Iron and Iron Uptake

In submerged soils, ferric iron is reduced to the ferrous form. As a consequence, the level of ferrous iron in the soil solution may increase to 300 ppm or higher. The soluble iron in soil generally influences iron concentration in root. According to Halim *et al.* (2014), the main pathway for metals into plants is from the soil via the root, but the present study showed that significant negative correlation occurred between iron concentration in root and that of soil soluble iron with correlation coefficient $r = -0.62^*$ ($p = 0.03$) (Fig.

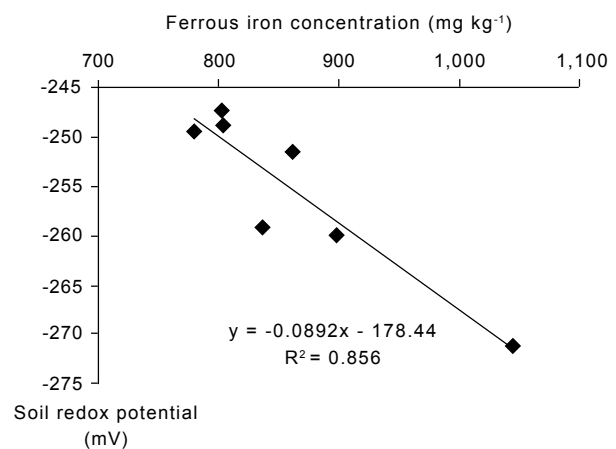


Fig 5. Correlation between redox potential and ferrous iron concentration in acid sulphate soil.

6). Rice roots have three functions to counteract iron toxicity (Tadano and Yoshida 1978): (1) oxidation of iron in the rhizosphere, which keeps iron concentrations low; (2) exclusion of iron at the root surface, which prevents the iron from entering the roots; and (3) retention of iron in the root tissue, which decreases iron translocation from root to shoot. The water-soluble metals are the most readily available for root, but exchangeable and reducible fractions can also be considered as available forms (Kabata-Pendias and Pendias 2001; Rogan *et al.* 2010).

Plant Growth

The addition of organic matter during incubation for 4, 8 and 12 weeks resulted in the higher plant height than that of incubation for 2 weeks because the C/N ratio of organic matter was higher (Fig. 7). The C/N ratio is an indicator of the rate of biomass decomposition and the main factor affecting mineralization processes of organic materials (Becker *et al.* 2005).

By the standards of International Rice Research Institute (IRRI), the score of iron toxicity was rated from 1 to 3. Results of the study showed that Margasari rice variety used in this experiment was quite tolerant to Fe^{2+} toxicity. At 4 weeks after planting, the score of Fe^{2+} toxicity ranged from 1 to 2

for all treatments of provision of organic matter and incubation period and also that without organic matter. At 8 weeks after planting, Fe^{2+} toxicity score ranged from 2 to 3, suggesting that Margasari rice variety did not show any symptoms of iron toxicity (Table 1).

The treatment of organic matter incubation for 4, 8 and 12 weeks resulted in higher shoot dry weight compared to 2 weeks incubation time (Fig. 8). Application of rice straw with 8 weeks incubation increased rice dry weight to 27.05 g and the lowest was that applied with rush weed with 2 weeks incubation. Organic matter increased the availability of soil nutrients and lowered the redox potential, so that pyrite oxidation can be suppressed.

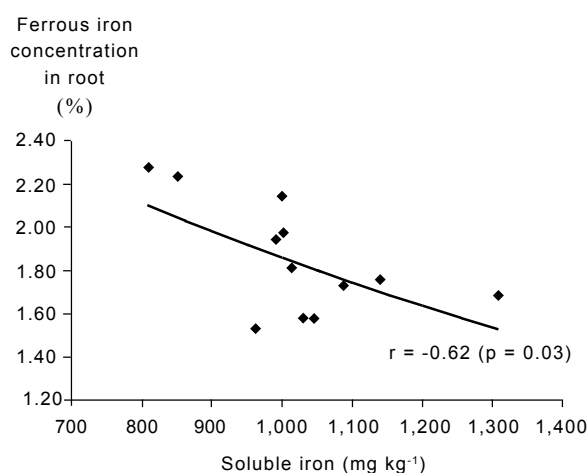


Fig. 6 Correlation between soluble iron of soil and ferrous iron concentration of root in acid sulphate soil.

Table 1. Influence of incubation period of organic matters on the level of iron toxicity in rice.

Treatment	Score of iron toxicity	
	4 weeks after planting	8 weeks after planting
Control	1-2	3
2 weeks incubation		
Rice straw	1-2	2-3
Rush weed	1-2	2
4 weeks incubation		
Rice straw	1-2	2-3
Rush weed	1-2	2-3
8 weeks incubation		
Rice straw	1-2	2-3
Rush weed	1-2	2
12 weeks incubation		
Rice straw	1-2	2
Rush weed	1-2	2-3

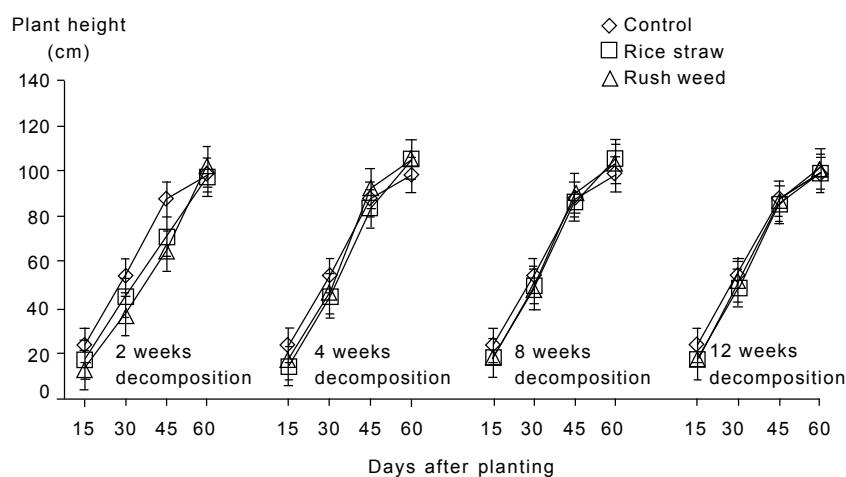


Fig 7. The height of rice plant as a function of organic matter decomposition time in acid sulphate soil.

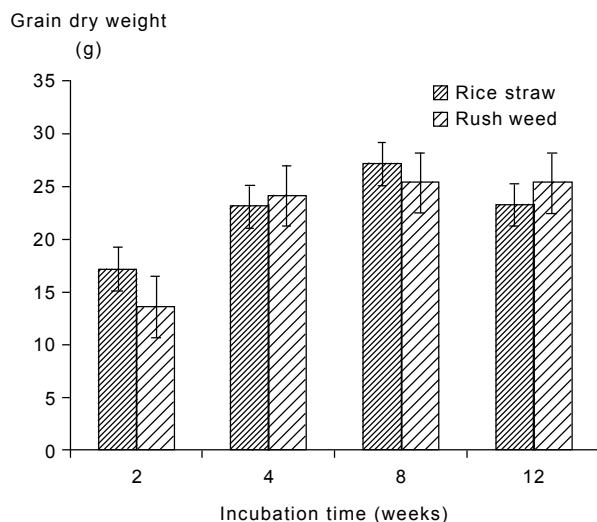


Fig. 8. Dry weight of rice grains as a function of organic matter decomposition time in acid sulphate soil.

CONCLUSION

Organic matter in acid sulphate soil was able to maintain soil reduced conditions. The exchangeable ferrous iron (Fe^{2+}) in the soil decreased through chelating reaction. The concentration of Fe^{2+} ranged from 781.8 to 1308.2 mg kg^{-1} during the rice growing season. The highest constant rate of iron reduction was observed on application of rice straw and rush weed that decomposed for 8 weeks, with the $k \text{ Fe}^{2+}$ value of 0.016 and 0.011 per day, respectively, while the $k \text{ Fe}^{2+}$ of ferrous iron formation without organic matter was 0.077 per day. The ferric iron (Fe^{3+}) reduction served as a function of soil redox potential as indicated by the negative correlation between ferrous iron and Eh ($r = -0.856^*$). Application of rice straw and rush weed decreased soil redox potential ($\pm -200 \text{ mV}$). Moreover, iron concentration in root negatively correlated with soil soluble iron ($r = -0.62^*$). This suggests that rice roots in submerged soil have functions to counteract the increasing ferrous iron in soil solution.

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