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Effects of incubating an acid sulfate soil treated with various liming materials under submerged and moist conditions on pH, Al and Fe

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Acid sulfate soil in Malaysia is known to be very acidic with pH < 3.5 and have high amount of aluminum. A study was conducted to investigate the efficacy of various lime sources for alleviating the infertility of the soil and to determine its lime requirement. The treatments were ground magnesium limestone, hydrated lime, liquid lime and fused magnesium phosphate under submerged and moist condition for 3 months. Soil and water were sampled throughout the incubation period for the determination of pH, Al and Fe. The initial soil pH and exchangeable Al were 3.43 and 7.71 cmolc kg^{-1}, respectively. After 3 months of incubation under submerged condition, the soil pH and water pH increased from 3.43 to 5.01 and from 2.38 to 5.17, respectively. Under moist condition, the pH increased from 3.43 to 4.02 due to application of 6 t ground magnesium limestone (GML) ha^{-1}. The efficacy of hydrated lime as soil ameliorant was comparable to that of GML. It was recommended that 6 t ha^{-1} of GML be applied prior to the growing season for maximum benefit. This study showed that GML can be effectively applied to ameliorate the infertility of acid sulfate soils for rice cultivation.

Key words: Glasshouse incubation study, ground magnesium limestone, liquid lime, fused magnesium phosphate, hydrated lime, acid sulfate soil.

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INTRODUCTION

Along the coastal plains of Peninsular Malaysia occur soils containing pyrite (FeS_2). These soils, called acid sulfate soils, are found abundantly in the coastal plains of the west coast of the Peninsular (Shamshuddin and Auxtero, 1991; Shamshuddin et al., 1995; Muhrizal et al., 2006; Enio et al., 2011). Pyrite occurs in the soils of the Holocene age, formed when seawater inundated the areas some 6,000 years ago (Roslan et al., 2010). Under anaerobic conditions, sulfate and ferric ions are respectively reduced to sulfide and ferrous ions which subsequently end up in the form of pyrite. When this pyrite is exposed to the atmosphere, a new straw-yellow color (2.5Y 8/6) mineral called jarosite [$FeK_3(SO_4)_2(OH)_6$] is formed. As a result of pyrite oxidation, high amount of acidity is released into the soils and environment. Soil pH becomes very low and Al concentration which is toxic to rice at high concentration is very high (Shamshuddin, 2006). It is difficult to grow crops on these soils. However, there are plants species that thrive well under acid sulfate soil conditions, including gelam *(Meluleuca leucadendron),* nipah *(Nipa frutescens)* and mangrove *(Rhizophora macronata)* species.

About 0.5 million hectare of acid sulfate soils occur in Malaysia some of which have been reclaimed for rice and

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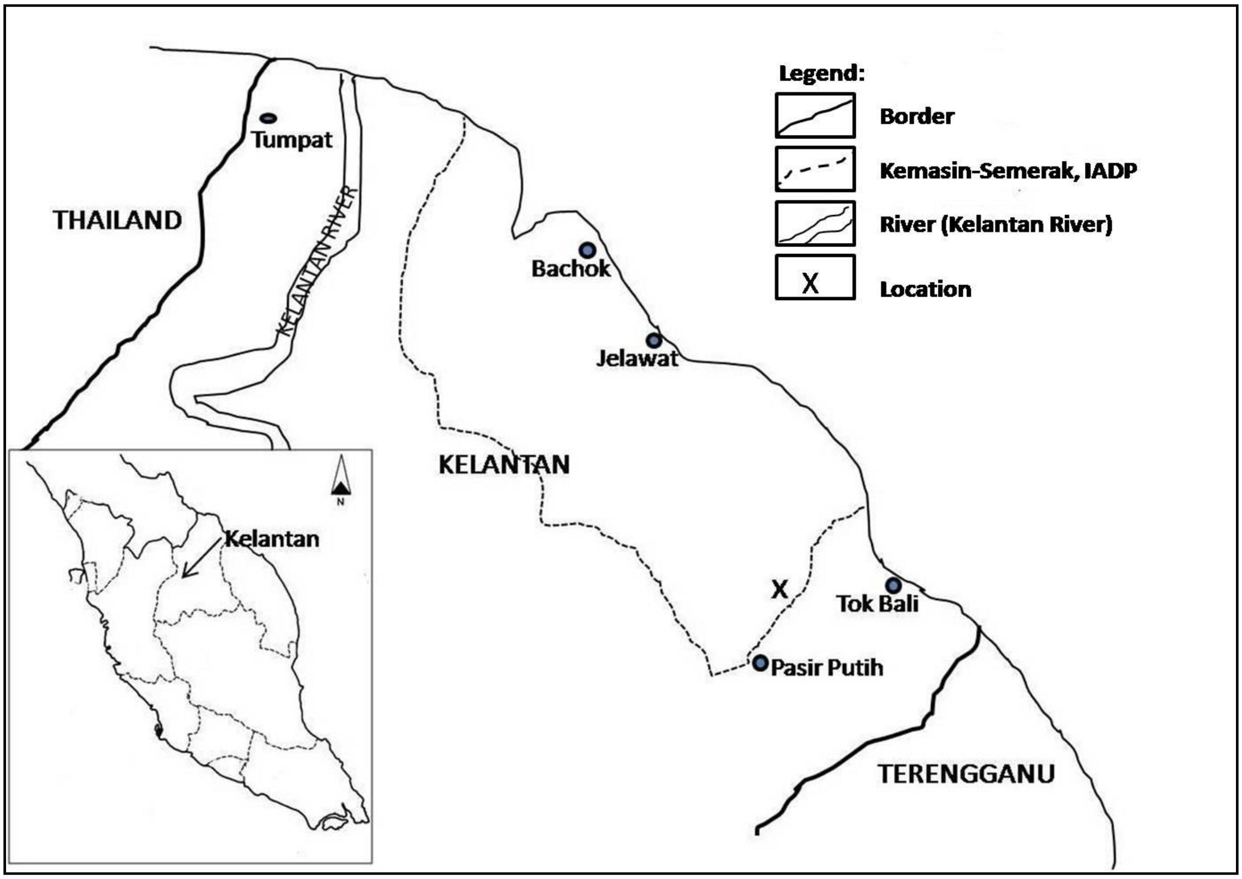

Figure 1. Map showing the location (marked X) of the sampling site in Kelantan, Malaysia.

oil palm cultivation with mixed success. Farmers in the northern state of Kedah who used the soils for rice cultivation produced yield far below the national average of 3.80 t ha^{-1} (Ting et al., 1993). Some of the acid sulfate soils were planted with cocoa in the west coast of Peninsular Malaysia (e.g. Arcadia Estate, in the state of Perak), but the yield was less than 1 t ha^{-1} of cocoa bean (Chew et al., 1984).

In acid sulfate soils, Al^{3+} and Fe^{2+} occur in high concentrations which can be toxic to plants. The presence of these ions causes some problems, such as lowering of pH and nutrient deficiency. Al^{3+} is known to inhibit root development (Kochian et al., 2005). Elisa Azura et al. (2011) found that high Al concentration (50 µM) in water can retard the elongation of rice root.

The infertility of such soils may be alleviated by application of appropriate amendments such as GML and ground basalt. Submerging the soil is another way of decreasing the acidity. GML application is known to increase soil pH that precipitate Al as Al- hydroxides (Shamshuddin et al., 1991, 1998, 2010; Ismail et al., 1993; Shamshuddin and Ismail, 1995).

Liming also increases microbial activity in soils (Curtin and Smillie, 1986). However, for acid sulfate soils, it requires high amount of lime to increase pH above 5 and therefore not economical (Dent, 1986). Suswanto et al. (2007) and Shazana et al. (2011) found that applying 4 t ground basalt with 0.25 t organic fertilizer ha^{-1} were able to ameliorate acid sulfate soil infertility for rice cultivation.

The objectives of this study were to investigate the efficacy of various liming materials for alleviating the infertility of an acid sulfate soil and to determine the lime requirement of the soil. The ameliorants used were GML, hydrated lime, liquid lime and fused magnesium phosphate. It is hoped that the results from this study are useful to the farming community in the Kemasin-Semerak IADP, Kelantan, Malaysia.

MATERIALS AND METHODS

The location and soil sampling

The soil used in this study was obtained from the Kemasin-Semerak IADP, Kelantan, Malaysia (05.86060°N, 102.44507°E) (Figure 1). It belongs to the Parit Botak Series which can be classified as a Typic Sulfaquept**.** The soil was sampled at 15 cm interval to the depth of 75 cm at selected locations in the experimental plots in order to determine its initial chemical

Table 1. Initial chemical characteristics of the typic sulfaquept studied.

Depth (cm)	pH water (1:2.5)	EC (dS/m)	Exchangeable cation (cmolc/kg)				Fe (mg/kg)	CEC (cmolc/kg)	Total N (%)	Total C (%)	Available P (mg/kg)
			K	Ca	Mg	Al					
0 - 15	3.43	0.295	0.98	1.45	0.67	7.71	69.70	15.86	0.25	4.36	13.10
15 - 30	3.41	0.226	2.34	0.56	0.23	7.69	89.25	9.79	0.10	1.18	3.40
30 – 45	3.30	0.247	2.56	0.50	0.24	8.01	116.45	9.64	0.08	0.85	2.72
45 – 60	3.21	0.251	2.83	0.68	0.24	8.23	221.60	9.79	0.07	0.83	1.95
60 - 75	3.17	0.238	3.05	0.67	0.24	8.09	232.00	9.71	0.06	0.79	1.77

properties (Table 1). For the incubation experiment, sample was taken from the topsoil (0 to 15 cm depth).

Experimental design and treatments

An incubation study was conducted in the glasshouse at Ladang 2, Universiti Putra Malaysia for 3 months. The soils obtained from Kemasin-Semerak (IADP), Kelantan, Malaysia were air-dried, ground and passed through 2 mm sieve. The samples were air-dried because following a normal procedure before doing chemical analysis. Five hundred gram of the soil was placed into each pot which has surface area 0.02 m^2 and arranged in completely randomized design (CRD). The incubation study consisted of submerged and moist condition, having four treatments and five rates with 3 replications. Treatments and rates used for this study were as follows: (1) Ground magnesium limestone (GML) - 0, 2, 4, 6 and 8 t ha^{-1}; (2) hydrated lime (HL) - 0, 2, 4, 6 and 8 t ha^{-1}; (3) liquid lime (LL) - 0, 10, 20, 30 and 40 L ha^{-1}; and (4) fused magnesium phosphate (FMP) - 0, 75, 100, 125 and 150 kg ha^{-1}. The amendments were applied onto the soils for a week before water was added and maintained 5 cm above the soil surface for submerged conditions; water was added regularly to maintain moist conditions. For the submerged soils, water was collected every week for the first month, followed by every 2 weeks for the rest of the experimental period.

Analyses of soil

Soil pH was determined in water (1:2.5) using pH meter. Electrical conductivity was determined using EC meter after shaking with deionized water for 15 min (Sonnevelt and van den Ende, 1971). Cation exchange capacity (CEC) was determined using NH_4OAc, buffered at pH 7 (Soil Survey Laboratory Staff, 1922). Exchangeable Ca, Mg, and K in the NH_4OAc extracts were determined by atomic absorption spectrometry (AAS). Exchangeable Al was extracted using 1 M KCl and the Al in the extracts was determined by AAS (Kotze et al., 1984). Extractable Fe was extracted using 0.05 M HCl in 0.0125 M H_2SO_4 using double acid method. The extracted Fe was also determined by AAS. Bray and Kurtz (1945) method was used to determine available P. Total carbon in soil was determined by the Carbon Analyzer LECO CR-412 (Leo Corporation, St. Joseph, MI) and total N was determined using the Kjeldhal method (Bremner and Mulvaney, 1982).

Analyses of water

Water, sampled from every pot, was filtered using filter paper No. 20 and pH was determined using pH meter while Al and Fe samples were determined using AAS.

Statistical analysis

The data so obtained were subjected to Analysis of Variance (ANOVA) and Tukey to compare the means of the treatments.

RESULTS

Initial chemical characteristics

Table 1 shows the initial chemical characteristics of the untreated acid sulfate soil. Soil pH decreases with the soil depth. Exchangeable Al is very high throughout the soil depth. Soil pH and exchangeable Al of the topsoil are 3.43 and 7.71 $cmol_c$ kg^{-1}, respectively. Extreme acidity occurring in the soil has environmental consequences. For instance, the excessive amount of Al and Fe in the soil affects plant growth and aquatic life.

Fe in the topsoil is 69.70 mg kg^{-1} and it increased with soil depth. Exchangeable Ca, exchangeable Mg and available P were found to decrease with the soil depth. P availability is not a problem in the topsoil. Lime application can stimulate microbial activity that releases P to the soils (Kyuma, 2004). According to Dobermann and Fairhurst (2000), the sufficient level for available P is 7 to 20 mg kg^{-1}.

Exchangeable Ca and Mg were low with the values of 1.45 and 0.67 cmolc kg^{-1}, respectively. Total carbon (4.36%) and total N (0.25%) in the topsoil were higher than those of the subsoil. Total carbon was found to decrease with depth.

Changes in pH, Al and Fe for soil under submerged condition

Figure 2 shows the soil pH, exchangeable Al and extractable Fe for soil under submerged condition due to treatment with GML. The soil pH increased with increasing rate of GML application. It required 6 t GML ha^{-1} to increase the pH to about 5. At this rate of GML application, exchangeable Al was decreased to < 1 cmolc kg^{-1} soil after 12 weeks. The change in extractable Fe was erratic. This was due to oxido-reduction processes taking place in the soil during the incubation period. The same trend occurred for soil treated with hydrated lime

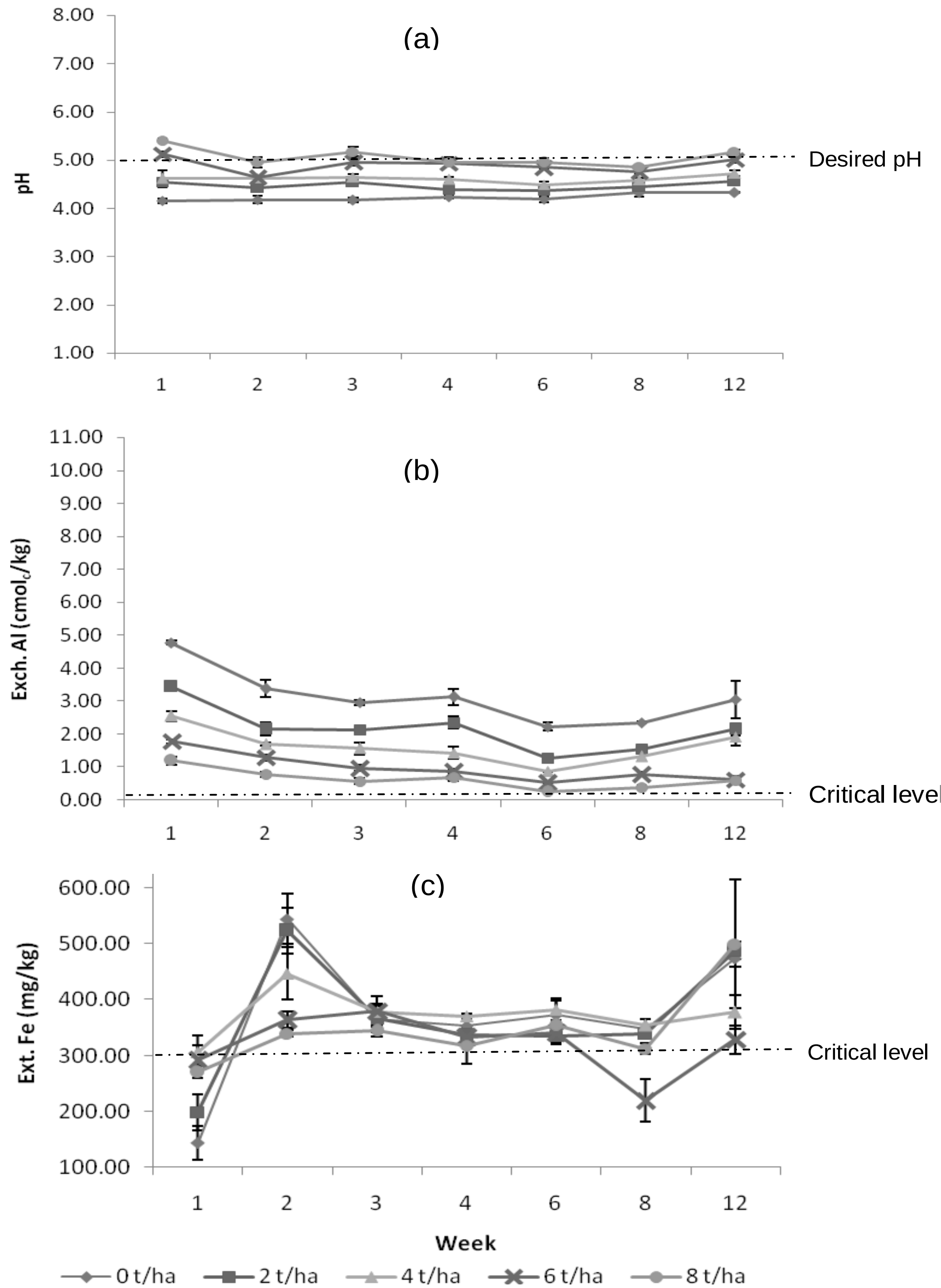

Figure 2. Changes in pH (a), exchangeable Al (b) and Fe (c) of a Typic Sulfaquept after treatment with GML under submerged condition.

(Figure 3). It means that as the soil pH increased, exchangeable Al decreased due to increasing rate of hydrated lime application. Application of 4 t ha^{-1} of hydrated lime was able to raise pH to above 5, thus able to alleviate Al toxicity. Like GML, treating the soil with hydrated lime did not result in remarkable decrease in extractable Fe.

Application of liquid lime did not change soil pH much (Figure 4). The pH did not increase to 5 even at the application rate of 40 L liquid lime ha^{-1}. However,

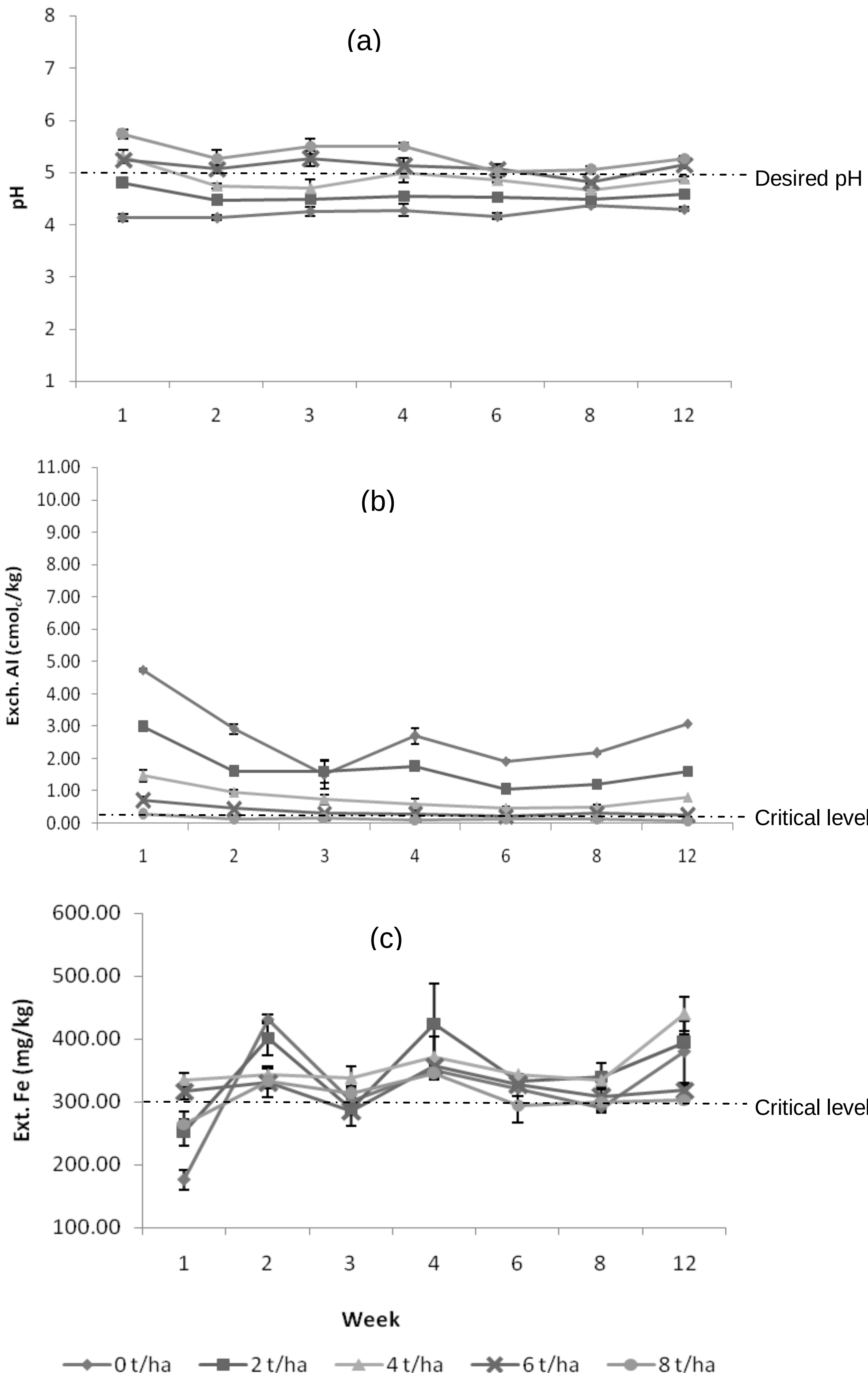

Figure 3. Changes in pH (a), exchangeable Al (b) and Fe (c) of a Typic Sulfaquept after treatment with hydrated lime under submerged condition.

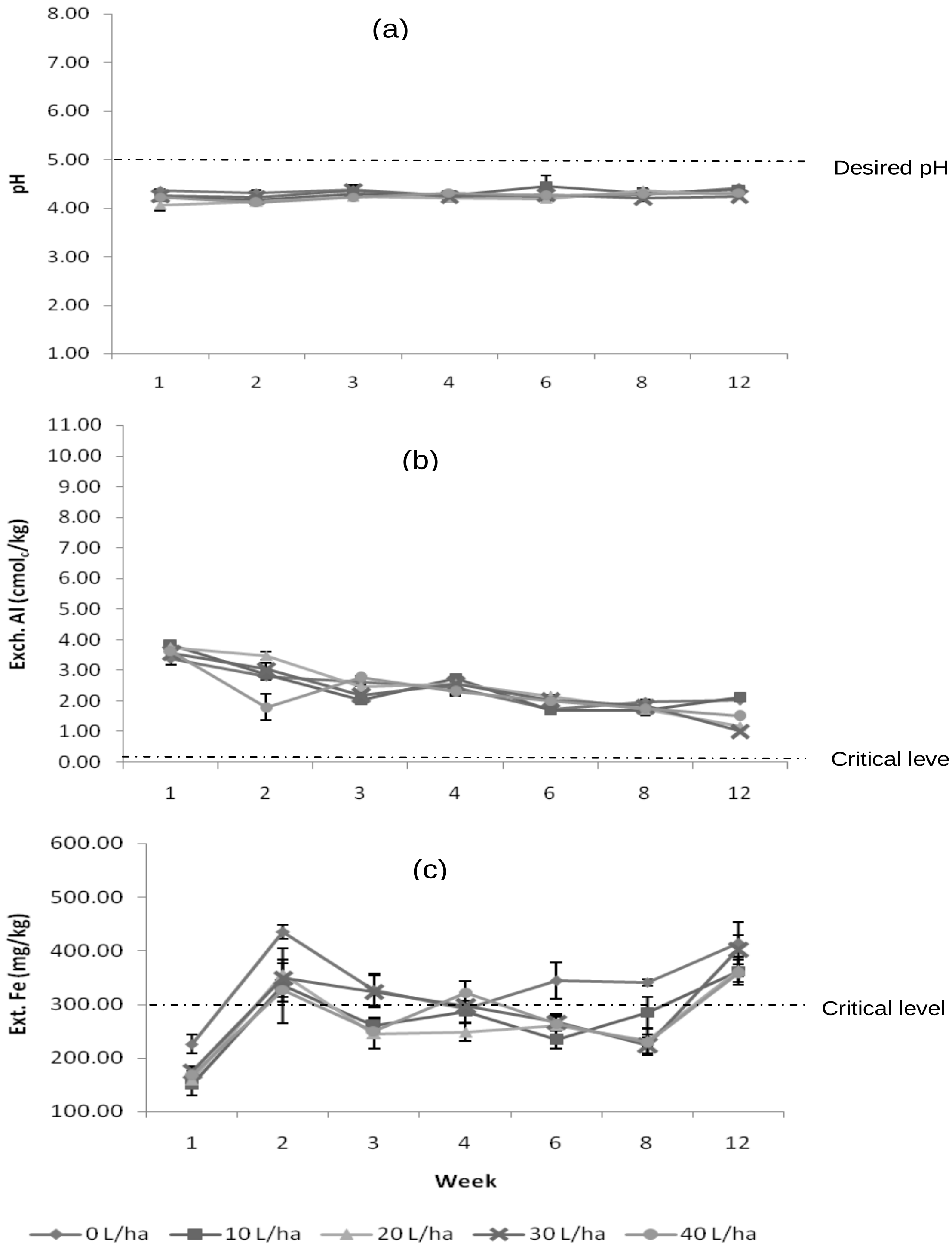

Figure 4. Changes in pH (a), exchangeable Al (b) and Fe (c) of a Typic Sulfaquept after treatment with liquid lime under submerged condition.

exchangeable Al decreased significantly due to liquid lime application. The effect of liquid lime on extractable Fe was also erratic.

FMP is currently used by the farmers in Kemasin-Semerak, Kelantan, at the recommended rate of 125 kg ha^{-1}. However, this rate is not sufficient to obtain the desired pH of 5 (Figure 5). Exchangeable Al decreased up to week 6 and after that it started to increase. The highest rate of 150 kg ha^{-1} was not sufficient to raise the soil pH to pH 5 and exchangeable Al to less than 1 cmolc

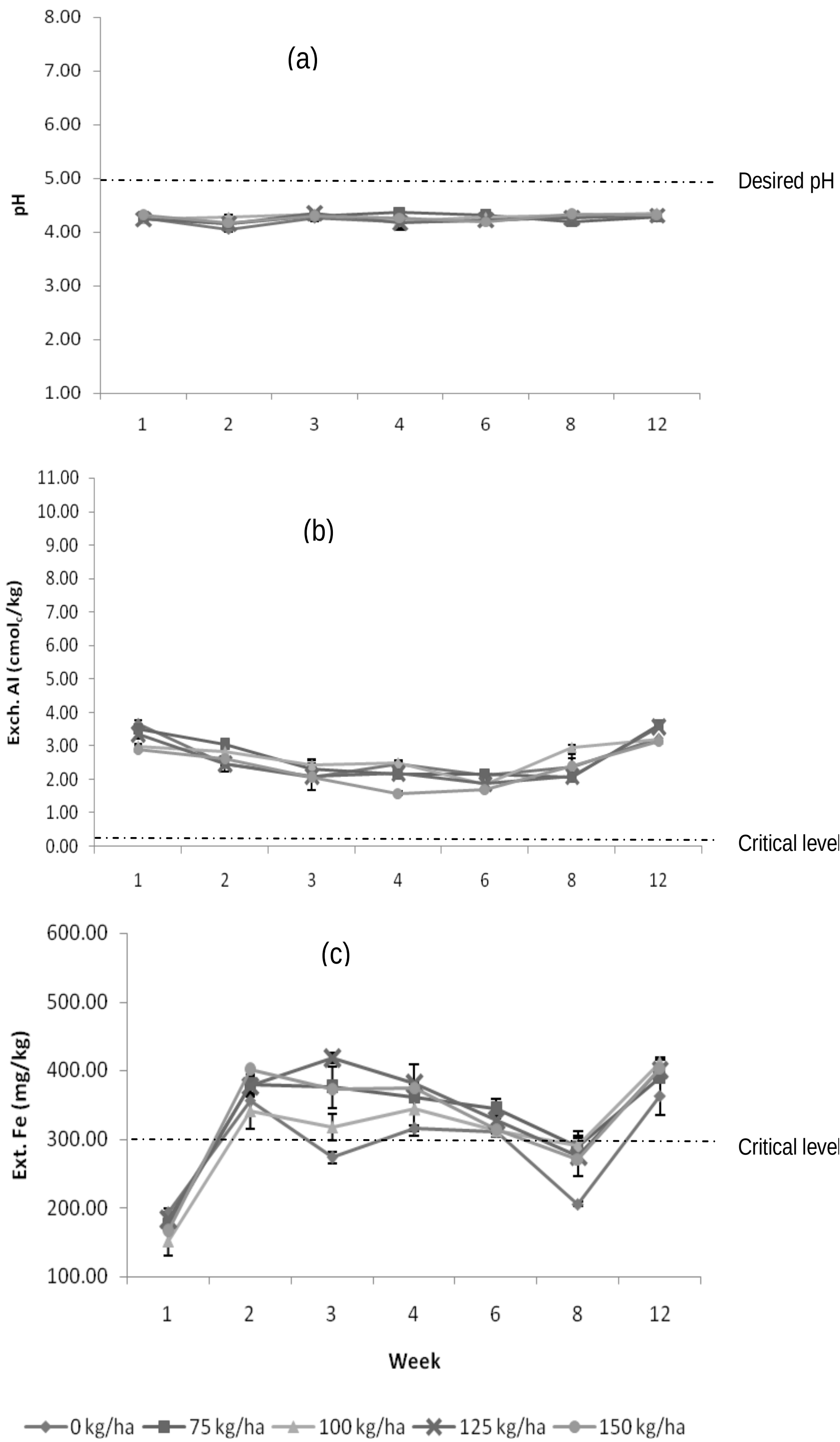

Figure 5. Changes in pH (a), exchangeable Al (b) and Fe (c) of a Typic Sulfaquept after treatment with fused magnesium phosphate under submerged condition.

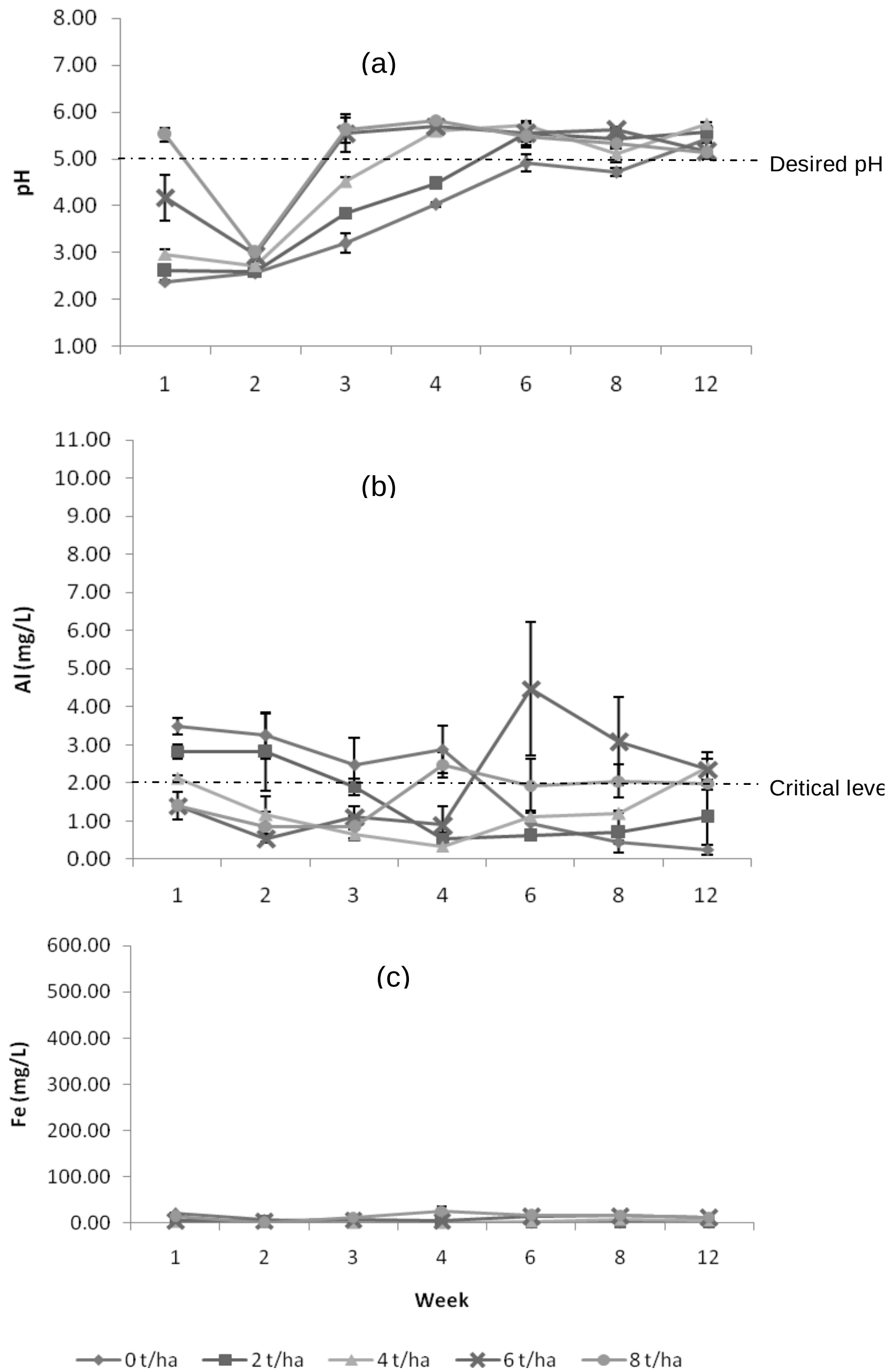

Figure 6. Changes in pH of water (a), Al concentration (b) and Fe concentration (c) of a Typic Sulfaquept after treatment with GML under submerged condition.

kg^{-1} soil. The change in extractable Fe was also erratic.

Changes in pH, Al and Fe of water

Figure 6 shows the pH, Al and Fe of the water for soil treated with GML. The highest rate of GML used in this experiment was 8 t ha^{-1}. Application of 6 t ha^{-1} GML was able to raise the pH above 5 at week 3. This pH stayed at least up to 12 weeks of incubation. The increase in pH was due to reduction process where proton was consumed. The pH increase had resulted in the precipitation of Al as inert Al-hydroxides. As such, Al in

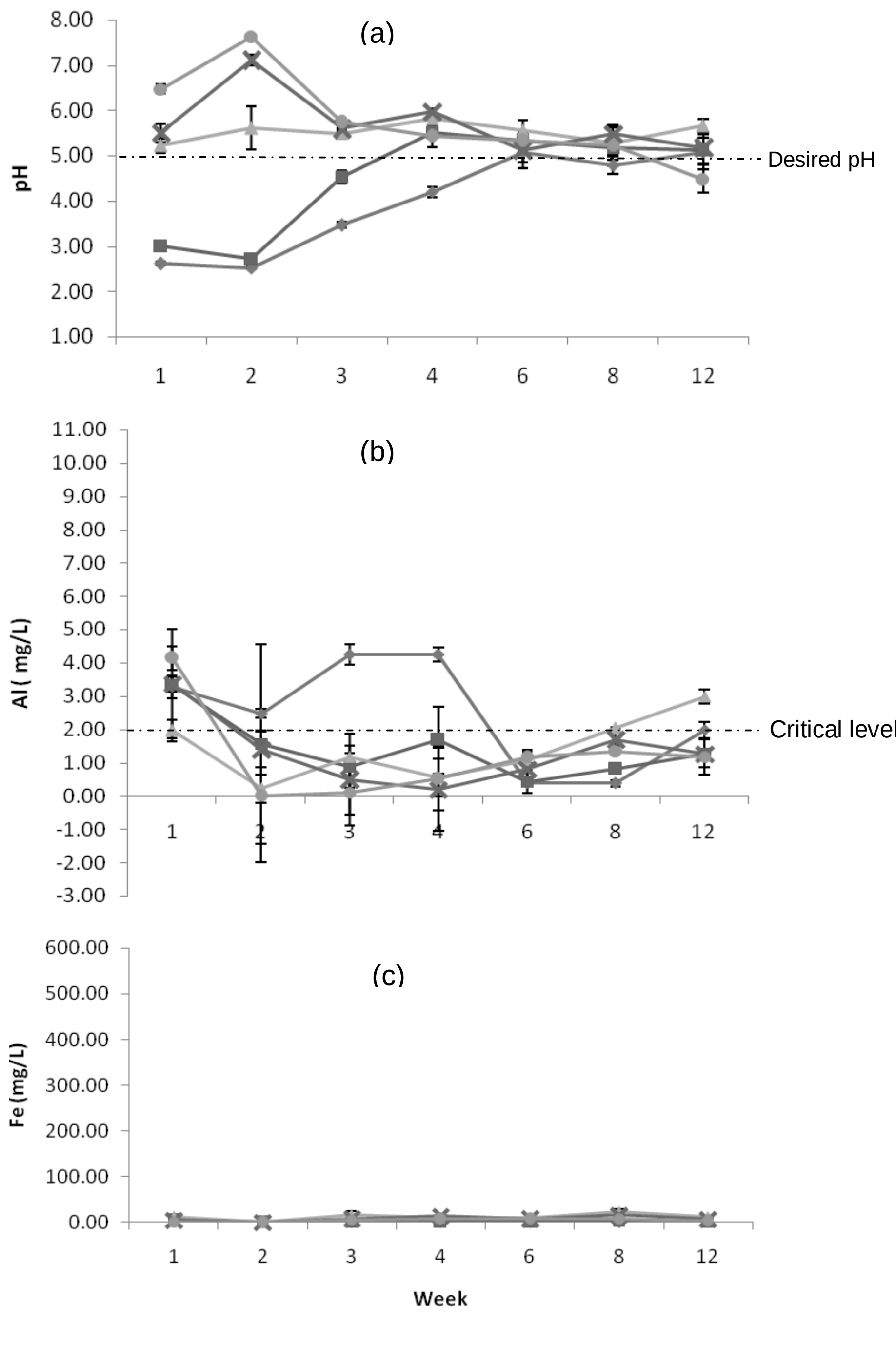

Figure 7. Changes in pH of water (a), Al concentration (b) and Fe concentration (c) of a typic sulfaquept after treatment with hydrated lime under submerged condition.

the water was reduced significantly. This happened at the GML rate of 6 t ha^{-1} or higher, in which the Al was low.

Figure 7 shows that applying hydrated lime at the rate of 4 t ha^{-1} or higher was able to obtain the desired water pH of 5. Water pH was as high as 7.5 after 2 weeks of incubation using 8 t ha^{-1} of hydrated lime. Water pH remained about 5 from 6 weeks onwards. About 2 t ha^{-1} of HL was sufficient to reduce Al toxicity in water.

After 8 weeks, water pH was about 5 for all rates (Figure 8). However, at week 1 and 2, water pH was < 3. The increase in pH was probably due to proton consumption during the reduction process. The favorable

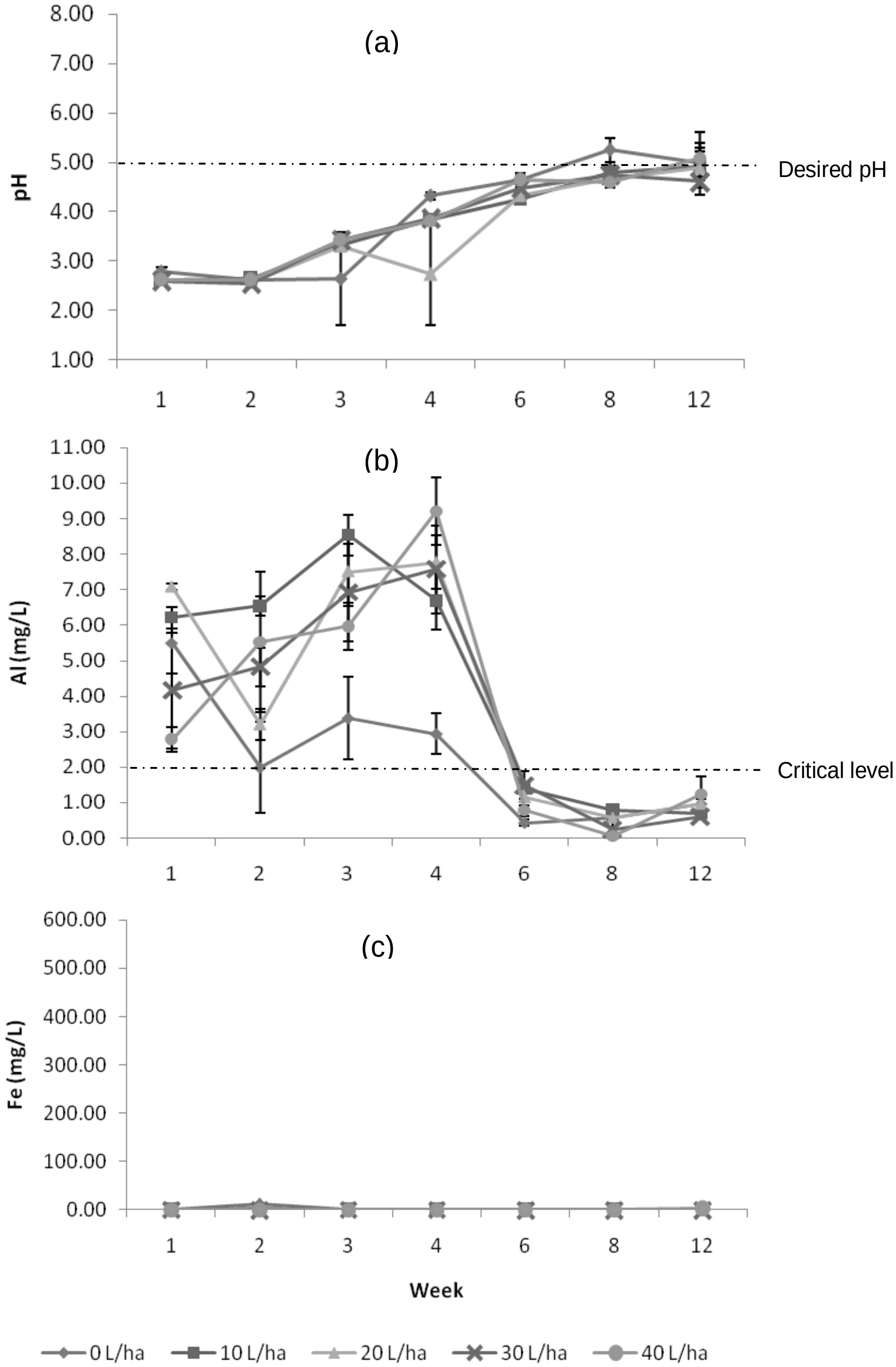

Figure 8. Changes in pH of water (a), Al concentration (b) and Fe concentration (c) of a typic sulfaquept after treatment with liquid lime under submerged condition.

concentration of Fe in water was below than 0.5 mg L^{-1}. Liquid lime was able to increase pH significantly at the rate tested in this study.

Figure 9 shows that water pH increased with time. The trend in pH increase was similar to that of liquid lime application. After 6 weeks, the Al concentration was very low for all the rates in water and that was below than critical toxic level of 74 µM (Dent, 1986).

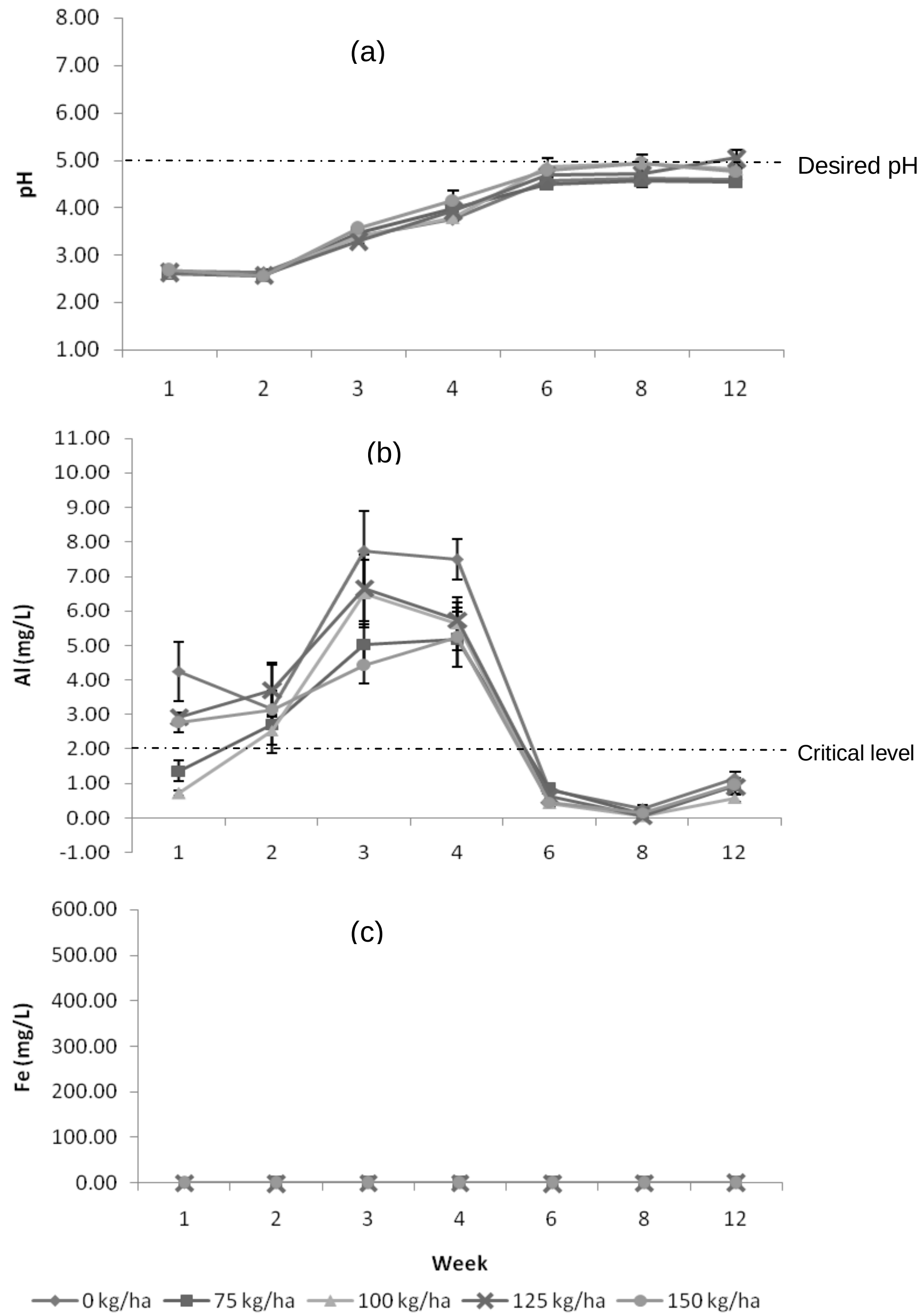

Figure 9. Changes in pH of water (a), Al concentration (b) and Fe concentration (c) of a typic sulfaquept after treatment with fused magnesium phosphate under submerged condition.

Changes of soil pH, Al and Fe for soils under moist condition

Due to the application of 6 t GML ha^{-1}, soil pH increased to about 5 at week 2 (Figure 10). After that, soil pH began to decrease. At this rate of GML application, exchangeable Al at week 12 was about 3 cmolc kg^{-1} soil. This level of exchangeable Al is still too high for rice production. At week 3, applying 6 t ha^{-1} of hydrated lime managed to maintain pH at about 5 (Figure 11). From then on, the soil pH decreased slightly. Exchangeable Al was higher than critical value even already applied with 8 t ha^{-1}.

Application of liquid lime was unable to raise soil pH under moist condition (Figure 12). But, exchangeable Al was able to be decreased sufficiently by applying liquid

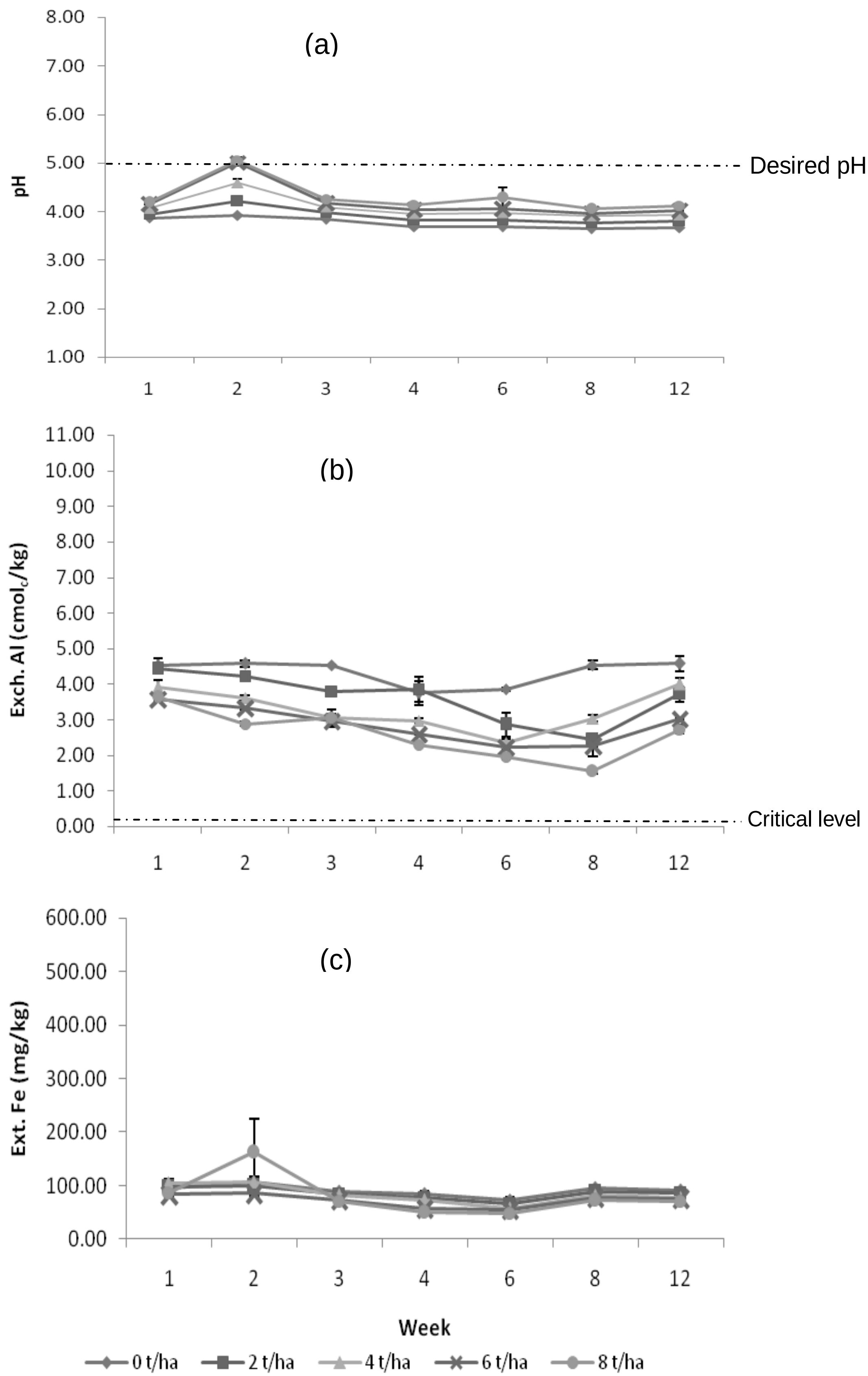

Figure 10. Changes in pH (a), exchangeable Al (b) and Fe (c) of a typic sulfaquept after treatment with GML under moist condition.

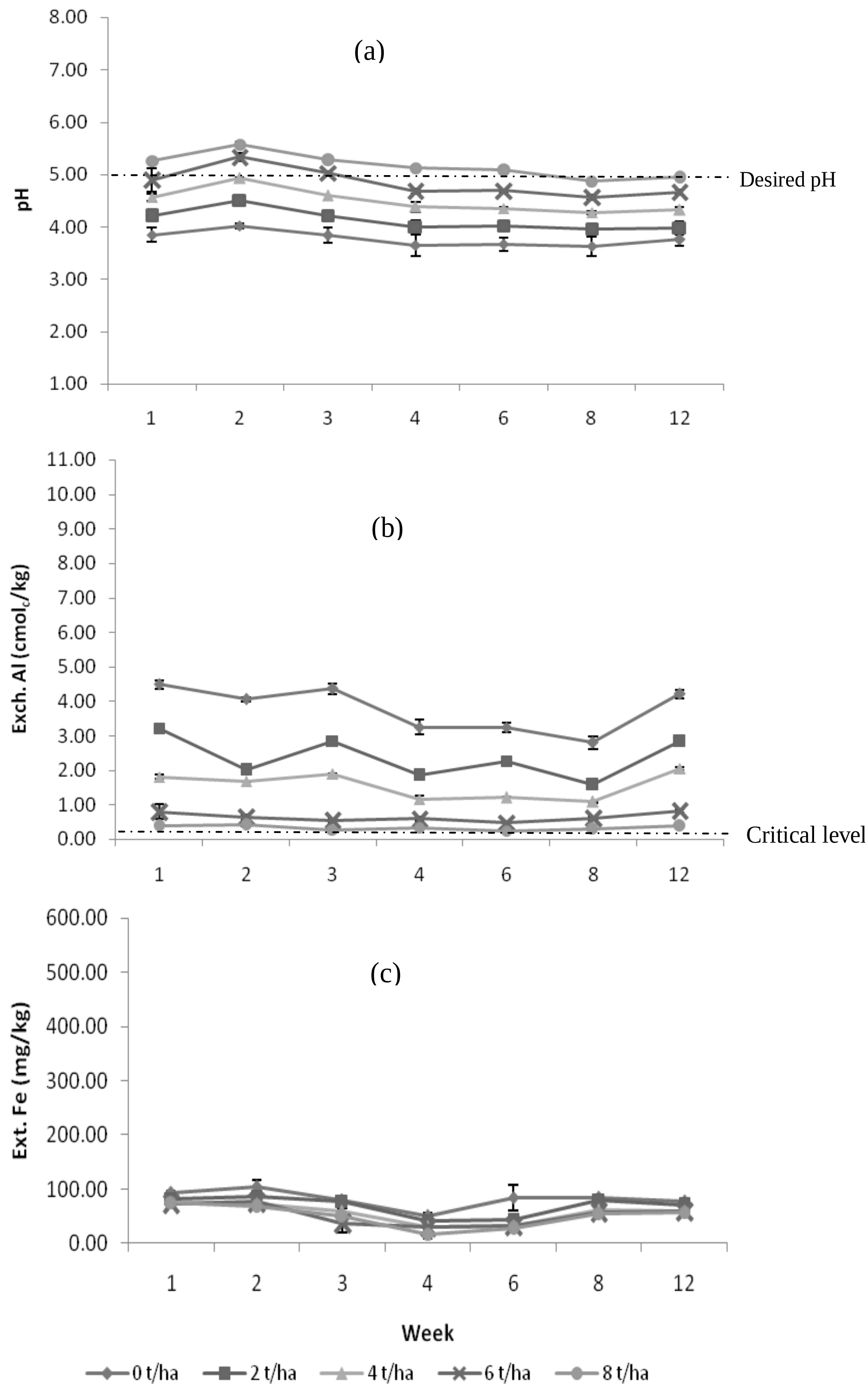

Figure 11. Changes in pH (a), exchangeable Al (b) and Fe (c) of a typic sulfaquept after treatment with hydrated lime under moist condition.

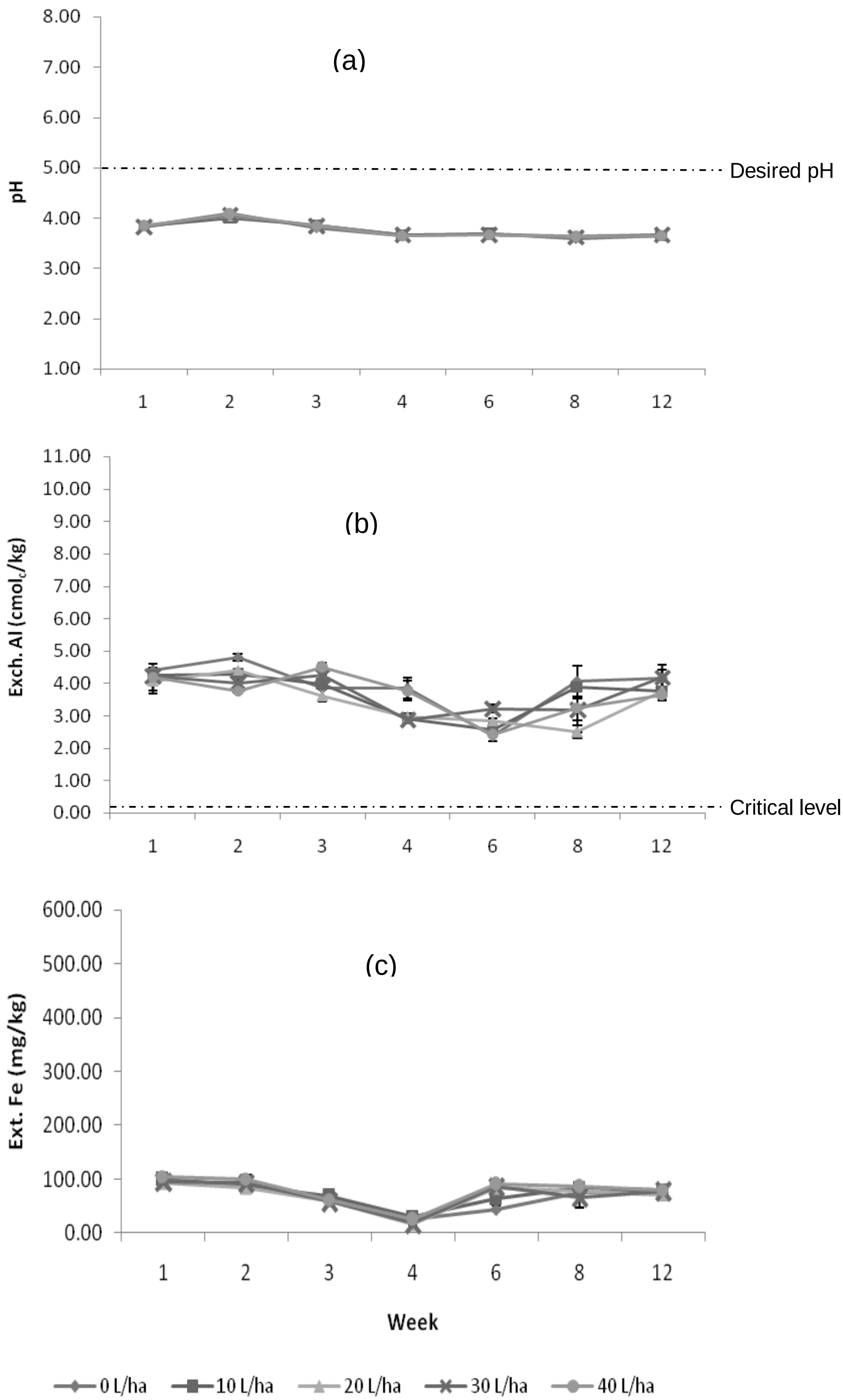

Figure 12. Changes in pH (a), exchangeable Al (b) and Fe (c) of a typic sulfaquept after treatment with liquid lime under moist condition.

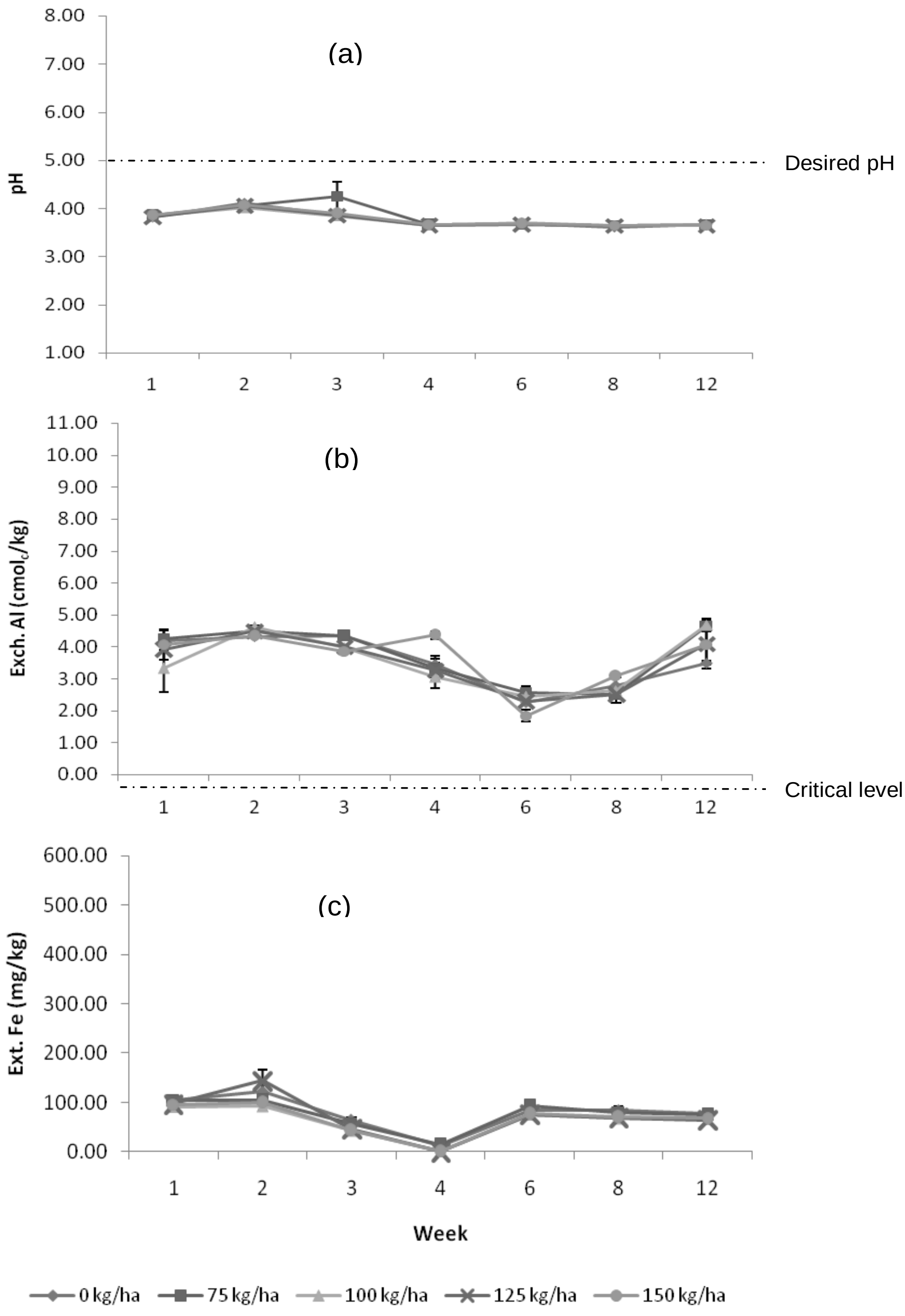

Figure 13. Changes in pH (a), exchangeable Al (b) and Fe (c) of a typic sulfaquept after treatment with fused magnesium phosphate under moist condition.

lime at the rate tested in the current study The effect of FMP application on soil pH and exchangeable Al was similar to that of liquid lime application (Figure 13). As such, we do not expect FMP to be able to ameliorate the acidity occurring in acid sulfate soils at the rate tested in this study.

DISCUSSION

The efficacy of various lime types

Majority of lime types were not able to raise soil pH above 5 at the rate of application used in this study. In

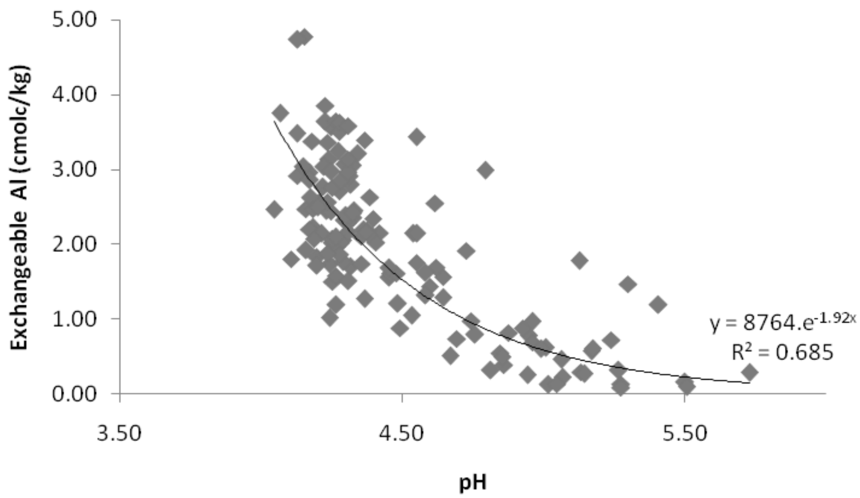

Figure 14. Relationship between exchangeable Al and pH of soil under submerged condition.

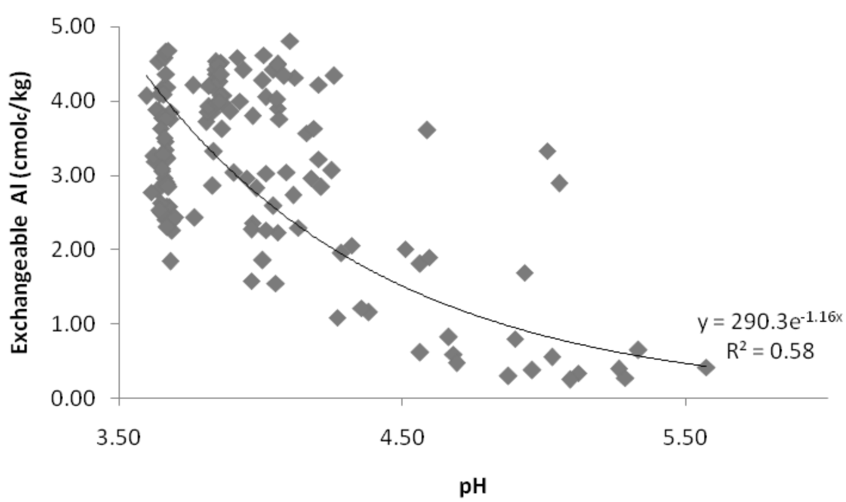

Figure 15. Relationship between exchangeable Al and pH of soil under moist condition.

terms of reducing exchangeable Al, GML and hydrated lime were the most effective. At the rate of 6 t ha^{-1}, exchangeable Al was reduced to less than 1 cmolc kg^{-1} soil under submerged condition. The effects of lime application on soil chemical properties were highly variable. GML was found to be the most effective to ameliorate acid sulfate soils compared to other soil ameliorants.

Relationship between Al and pH of the soils

Figure 14 and 15 show the relationship between soil pH and exchangeable Al of the incubated soils under submerged and moist conditions, which are presented by the equation $Y = 87644.e^{-1.92x}$ (R^2=0.685) and $Y=290.3e^{-1.16x}$ (R^2=0.58), respectively. It means that as the pH increased, Al decreased. It was observed that soil pH was higher under submerged condition compared to that under the moist condition. According to Dobermann and Fairhust (2000), the critical exchangeable Al in the soil is 1 to 2 mg kg^{-1}. At this Al level, the soil pH was 5.5 (Figure 14). This means that we only need to increase soil pH up to 5.5.

Chemical reaction

Ground magnesium limestone (GML)

Under normal condition, Al^{3+} is very high in acid sulfate soils. This Al^{3+} is hydrolyzed in water to produce proton:

$$Al^{3+}. 6H_2O + H_2O = Al (OH)^{2+} . 5H_2O + H_3O^+ \quad (1)$$

The pKa of Al is 5. When pH is below 5, reaction goes to the right and vice versa. The soil in this study has a pH of < 3.5 (Table 1). So, acid sulfate soils have high amount of acidity. When the amendments were applied onto the soils, pH went up depending on the rate. When water pH was above 5, Al^{3+} will be precipitated as inert Al-hydroxides. GML had ameliorated the soil according to the following reactions:

$$(Ca, Mg)(CO_3)_2 \rightarrow Ca^{2+} + Mg^{2+} + CO_3^{2-} \quad (2)$$

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \quad (3)$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \quad (4)$$

The carbonate from GML had hydrolyzed to produce hydroxyls (Equation 3). Then, the hydroxyl reacted with Al^{3+} to be precipitated as Al (OH_3) and therefore, Al in the water was reduced significantly. That is how GML ameliorates acid sulfate soil infertility.

Hydrated lime

Hydrated lime also known as slaked lime, milk of lime, pickling lime or calcium hydroxide. This lime is white in color and in powder form. Hydrated lime is made from calcium oxide and it is commercially produced by treating with water (Equation 5):

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (5)$$

When it was applied onto the soil, it released Ca and hydroxyl ions. The OH^- ions so released can ameliorate the soil by increasing the pH and subsequently precipitate Al.

Liquid lime

Liquid lime used in this study was supplied by Humibox (M) Sdn Bhd. It was called Mg Reaktif 113 TF. This lime which contains some dolomite quickly corrected soil acidity and supplied magnesium and calcium. Liquid lime reacted in the soil according to the following reactions:

$$Ca(OH)_2 + CaCO_3.MgCO_3 \rightarrow 2Ca^{2+} + Mg^{2+} + 2CO_3^{2-} + 2OH^- \quad (6)$$

In the end, the Ca and Mg so released during the reaction were able to somewhat ameliorate the infertility of acid sulfate soil. The recommended rate of liquid lime application was 20 L ha^{-1}; however, at this rate, it was unable to change pH to < 5 the desired level. Liquid lime easily infiltrates into the soil once it is applied and quickly react with soil, but it can easily to evaporate into the atmosphere.

Fused magnesium phosphate

Fused magnesium phosphate (FMP) is commonly used by farmers in Kelantan at the rate of 125 kg ha^{-1}; it was given as a subsidy by the Malaysian government. From this study, it was observed that FMP was not as good as GML in terms of the ameliorative liming effect. FMP had reacted in the soil according to the following equation:

$$CaMgP_2O_7 + H_2O \rightarrow Ca^{2+} + Mg^{2+} + 2HPO_4^{2-} \quad (7)$$

When applied, this fused magnesium phosphate was able to release calcium, magnesium and phosphate needed by rice for its growth (Equation 7). The active ingredients of fused magnesium phosphate are P_2O_5 (15%), CaO (28%), MgO (15%), SiO_2 (24%) and Fe (3%).

Determination of lime requirement

Acid sulfate soil is considered ameliorated if pH level is high; Al and Fe level are low after liming materials are applied. When exchangeable Al was < 1 cmolc kg^{-1} soil, soil pH was about 5. A pH of above 5 is required in order to precipitate Al also Al-hydroxides. To achieve the pH value of above 5, we need to apply GML or hydrated lime at the rate of 6 t ha^{-1} (Figure 16). This rate of lime application can be regarded as the lime requirement of the acid sulfate soils (Typic Sulfaquept) in Malaysia.

Cost-effective of lime type

Both GML and hydrated lime gave comparable ameliorative affects. However, GML is cheaper (Table 2) and easier to handle. So, GML is the most effective and the most suitable of the lime type for amelioration of acid sulfate soil in Malaysia.

Conclusion

Application of lime is able to make acid sulfate soil suitable for agriculture use. From this experiment, it was found that application of 6 t ha^{-1} GML can ameliorate the acid sulfate soil better compared to other soil ameliorants under submerged condition with cost of about RM 990 ha^{-1}. Water pH was above 5 and Fe concentration was below critical level due to application of 6 t GML ha^{-1}. However, under moist condition it was found that soil ameliorant does not help to achieve the desire level of pH, Al and Fe concentration.

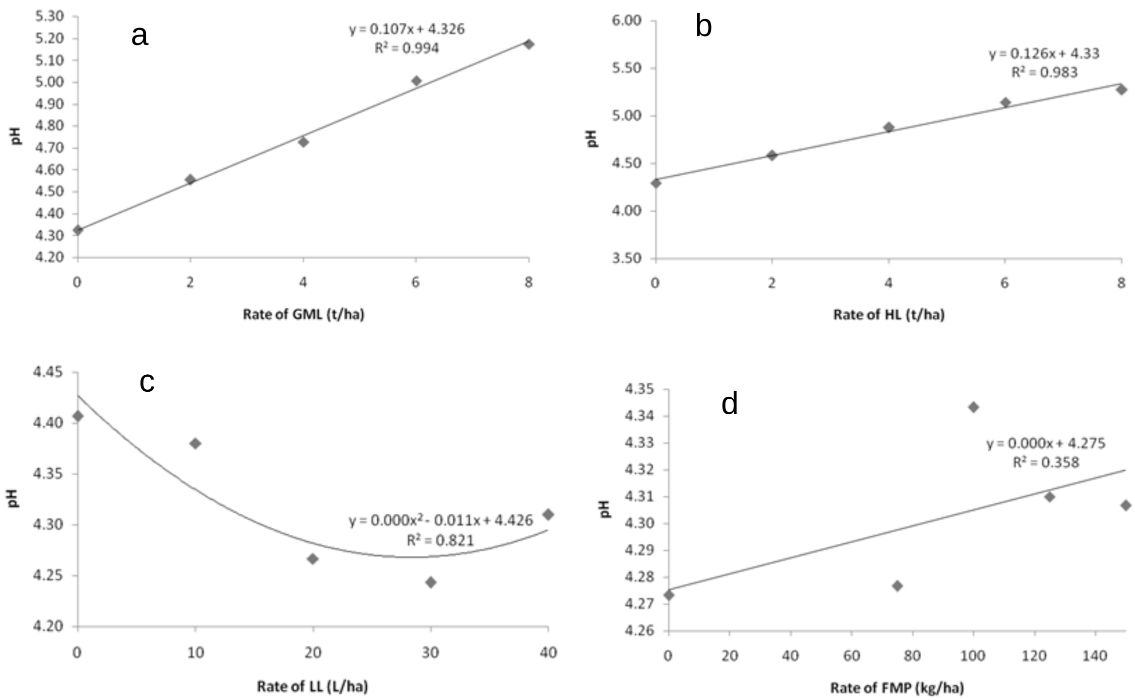

Figure 16. Relationship between soil pH and the rate of GML (a), hydrated lime (b), liquid lime (c) and fused magnesium phosphate (d).

Table 2. The price of the soil amendments.

Soil amendments	International value (USD)	Local value (MYR)*
Ground magnesium limestone (tonne)	52.88	165
Hydrated lime (tonne)	147.44	460
Liquid lime (20 L)	102.56	320
Fused magnesium phosphate (tonne)	230.77	720

* Multiplying by 3.12 to obtain the value in Malaysia Ringgit (MYR).

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