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HUMIC AND FULVIC ACIDS OF *GLIRICIDIA* AND *TITHONIA* COMPOSTS FOR ALUMINIUM DETOXIFICATION IN AN ULTISOL

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ABSTRACT

A laboratory experiment was conducted to elucidate roles of *Gliricidia sepium* and *Tithonia diversifolia* composts and their extracted humic and fulvic acids on aluminum concentration in an Ultisol. Those composts and humic and fulvic acids extracted from them mixed with soil were arranged in a complete randomized design with three replicates, and incubated for 90 days. Al concentration and pH of the soil were measured at 0, 3, 10, 20, 30, 45, 60, 75 and 90 days after incubation. Results of the study showed that the highest decrease in exchangeable Al concentration (90.5%) was observed for *Tithonia* fulvic acid treatment during 90 days, followed by *Tithonia* compost (88.4%), *Gliricidia* fulvic acid (82.3%), *Gliricida* compost (82.2%), *Tithonia* humic acid (75.66%), and *Gliricidia* humic acid (73.46%) treatments, whereas control only decreased exchangeable Al concentration by 0.9%. The rate of change in exchangeable Al concentration was fast for the first 45 days, but it then slowed down for the second 45 days (45-90 days). This was particularly observed with organic acid treatments, whereas compost treatment still showed a subsequent decrease. Patterns of Al chelate and pH were very similar to that of exchangeable Al. It was thus concluded that roles of humic and fulvic acids in reducing exchangeable Al was only short term, whereas compost played roles in the long term.

Keywords: Ultisol, aluminium, humic acid, fulvic acid, *Gliricidia sepium, Tithonia diversifolia*

INTRODUCTION

Ultisol generally can be found as agricultural land distributed in Sumatera, Kalimantan, Sulawesi, Irian Jaya and a small area in Java especially in West Java. One problem of Ultisol for agriculture cultivation is high solubility of Al related to soil acidity levels (Mokolobate and Haynes, 2002). The high solubility of Al causes P nutrient in soil bind to become Al-P which is not soluble so that it can reduce P available for plants (Bates and Lynch,

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The effort usually conducted to overcome the problem of soil acidity and Al toxicity in Ultisol is liming. However, the application of high rates of lime continuously can decrease the availability of P and Mn (Shamshuddin *et al*., 2004). Another alternative that can be done to overcome the problem of acid mineral soils containing high Al is the application of organic matter (Zaharah *et al*., 1999). Organic acids present in organic matter or produced during their decomposition process can react with Al to form organo-Al complexes or $Al_{chelate}$ (Kalbitz *et al*., 2000). These complexes can reduce aluminium solubility to certain levels that will not hinder plant growth (Agbenin, 2003)

It is widely known that organic matter is very useful for improving soil fertility, soil physical properties and ion exchange capacity.

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However, large amounts of organic matter are needed to maintain and improve soil organic matter content for positive change in these properties. Such large amounts are usually beyond the reach of upland farmers. The relationship between organic matter application and nutrient release, especially nitrogen, has been enormously studied, but studies on the effects of organic matter application on improving phosphorus availability in Ultisol are relatively few.

Besides the release nutrients, other short term beneficial effects of organic matter application have not been drawn to the attention of the users. Currently, very little information is available on these practical influences. In Ultisol, an increase in soil pH and the reduction of soil Al concentrations are very important at establishment to guarantee good germination and emergence after sowing. Organic acids present in the organic matter or produced during their decomposition have been shown to interact strongly with phosphorus adsorption as they compete for the same site (Brinick and Lal, 2005). This increases phosphorus availability, with a consequent soil property change that also contributes to the improvement in crop production. Therefore, when organic matter management is considered in the context of shortage, both short-term and long-term benefits of organic matter amendment on beneficial changes other than nutrient release need to be taken into account.

Considering the variable amount and quality of organic matters, selection of organic matter needs to be considered are their availability in the field, their potential use for organic fertilizers as well as their common use by the majority of farmers. Amongst various sources of organic matter, prunings of *Gliricidia sepium* and *Tithonia diversifolia* are commonly used for improving soil productivity. *Gliricidia sepium* is a legume tree that can easily be found as living hedges, shelter plants and shade plants in rural areas throughout Indonesia. This tree is also commonly used by villagers as firewood (pruning of branch and twig) and the leaves as livestock feed. *Tithonia diversifolia* is a shrub type of vegetation that can also easily be found in rural areas. Pruning of those two organic matter sources have potential for supplying nitrogen and phosphorus. They also contain substantial amounts of humic and fulvic acids that can reduce soil aluminium toxicity. Supriyadi (2003) reported that the application of *Tithonia diversifolia* prunings as organic matter in Andisol can increase $Al_{chelate}$ from 1.30% to 1.49% during 30 days of incubation. Minardi *et al.* (2007) reported that application of *Gliricidia sepium* prunings in an Andisol reduced Al_o by 29.85% which in turn released phosphate into the soil solution.

The aim of the research was to judge the role of organic matter addition in decreasing aluminium toxicity and phosphorus availability of an Ultisol.

MATERIALS AND METHODS

The research was a laboratory incubation experiment. The experiment, soil analysis and organic matter analysis were carried out at Soil Chemical Laboratory of the Faculty of Agriculture, Brawijaya University. All activities were conducted from July 2007 until December 2007.

Topsoil of an Ultisol collected from Kentrong Village of Cipanas Distric, Lebak Regency, Banten Province was used for this study. The soil has the following characteristics: pH 4.3, 392.45 mg total P/kg soil, 5.79 mg available P/kg soil, 49.09% Al saturation, 11.85 $cmol_c$ exchangeable Al/kg soil, 4.45 $cmol_c$ exchangeable H/kg soil, 1.998% organic C, 0.20% total N, and C/N ratio of 9.99.

Prunings of *Gliricidia sepium* and *Tithonia diversifolia* were collected from Jatikerto Village of Malang. Prior to application, the prunings were air dried and composted using *Trichoderma sp*. decomposer for around 30 days. Compost produced was then analyzed for organic-C, total N, total P, humic acid and fulvic acid content. Humic and fulvic acids from the compost were extracted using 0,01 N NaOH. Chemical composition of composted *Gliricidia sepium* and *Tithonia diversifolia* prunings is presented in Table 1.

Seven treatments comprising two compost treatments, two humic acid treatments, two fulvic acid treatments and one control (no added compost or organic acids) (Table 2), were arranged in a completely randomized design with three replicates. For each treatment, 0,5 kg of air dried top soil (0-30 cm depth) that passed through a 2 mm sieve was mixed with either compost or humic and fulvic acids extracted from the compost. The mixture was then placed in a plastic bag and incubated for 90 days. During incubation, soil moisture content was kept at field capacity by regularly adding distilled water. Analysis of soil pH, exchangeable Al and Al chelate were carried out at 0, 3, 10, 20, 30, 45, 60, 75, and 90 days. Statistical analysis was performed at significant levels of 5% and 1%. Differences between treatments were tested using Duncan Multiple Range Test (DMRT). Correlation and regression analysis were performed to judge the relationship between measured parameters.

Table 1. Chemical Composition of *Gliricidia* and *Tithonia Composts*

Composition	Compost	
	Gliricidia sepium	*Tithonia diversifolia*
Organic-C (%)	40.87	39.97
Total N (%)	3.07	2.71
Total P (%)	0.41	0.49
C/N ratio	13.31	14.75
C/P ratio	99.68	81.57
Humic acid (%)	15.44	29.47
Fulvic acid (%)	5.11	6.81

Table 2. Treatments of Incubation Experiment

Po	=	Control (no added compost, humic acid or fulvic acid)
GC	=	4.17 g *Gliricidia* compost/kg soil (equivalent to 10 t/ha)
TC	=	4.17 g *Tithonia* compost/kg soil (equivalent to 10 t/ha)
GH	=	84 ml *Gliricidia* humic acid/kg soil (equivalent to 1544 kg/ha)
GF	=	82 ml *Gliricidia* fulvic acid/kg soil (equivalent to 511 kg/ha)
TH	=	84 ml *Tithonia* humic acid/kg soil (equivalent to 2947 kg/ha)
TF	=	84 ml *Tithonia* fulvic acid/kg soil (equivalent to 681 kg/ha)

RESULTS AND DISCUSSION

Change of Exchangeable Al (Al_{exch}) Concentration

Application of *Gliricidia* and *Tithonia* composts as well humic and fulvic acids extracted from the composts significantly ($p < 0.01$) affected concentration of Al_{exch}. Humic acid and fulvic acid derived from *Gliricidia* and *Tithonia* composts (GH, TH, GF, and TF treatments) reduced concentration of Al_{exch} faster than that of *Gliricidia* and *Tithonia* composts (GC and TC treatments). Al_{exch} concentration decreased sharply at 10 to 45 days through application of GH, TH, GF, and TF (Figure 1). For GC and TC treatments, the sharp decrease of Al_{exch} concentration occurred at 20 to 90 days (Figure 1).

During 90 days of incubation, the highest reduction of Al_{exch} concentration (90.5%) was observed for TF treatment, followed by TC, (88.4%), GF (82.3%), GC (82.2%), TH (75.66%), and GH (73.46%) treatments, whereas control treatment (no added compost, humic acid or fulvic acid) only reduced Al_{exch} concentration by 0.9% (Figure 1). Reactivity of fulvic acid to Al seemed to be higher than that of humic acid. This is probably due to the greater carboxyl fraction, phenolic and total acidity content of fulvic acid than those of humic acid (Zimmer, 2004). Such properties result in a higher ability of fulvic acid to form complexes with metal ions than humic acid.

Reduction of Al_{exch} concentration was strongly correlated with *Gliricidia* humic acid (GH), *Tithonia* humic acid (TH), *Gliricidia* fulvic acid (GF) and *Tithonia* fulvic acid (TF) with r values of 0.994, 0.994, 0.995, and 0.995 respectively. This indicated that fulvic acid posed stronger affinity than humic acid in reducing Al_{exch} concentration.

Considering the pattern of Al_{exch} reduction (Figure 2), it can be seen that the reduction of aluminium concentration at all treatments was relatively fast for the first 45 days (0-45 days). The reduction of Al_{exch} concentration due to GF and TF treatments reached maximum at day 20, i.e. -24.56% for GF and -28.95% for TF (Figure 2). Reduction of Al_{exch} concentration due to TH treatment reached maximum at day 30 (-19.66%), while that due to GH treatment at day 45 (-18.23%). For *Gliricidia* compost (GC) and *Tithonia* compost (TC) treatments however, a maximum reduction of Al_{exch} concentration reached by the treatments only occurred at 45 days by -18.57% (GC) and -20.93% (TC).

Cumulatively, all treatments resulted in more than 70% reduction of Al_{exch} concentration at day 90, TF treatment being the highest (-90.5%). At the second 45 days, however, the rate of Al_{exch} reduction at GC and TC treatments was slower than that observed for GH, TH, TF, and GF treatments.

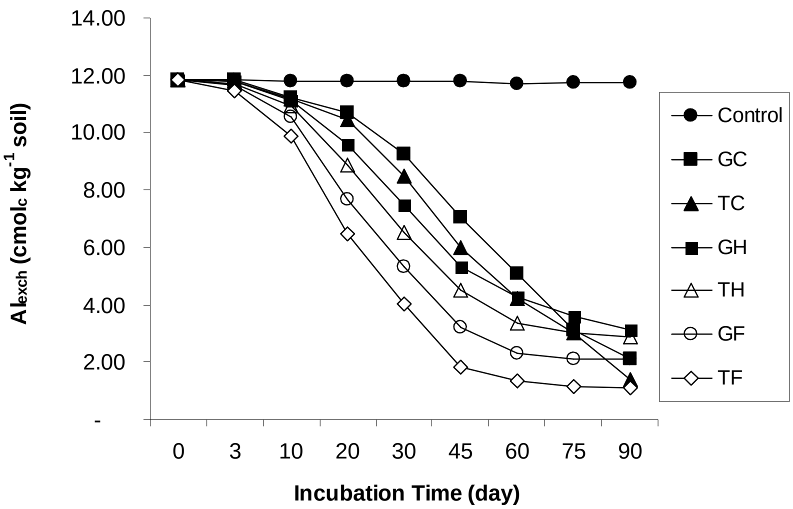

Figure 1. Change in Al_{exch} concentration due to application of *Gliricidia* compost (GC), *Tithonia* compost (TC), *Gliricidia* humic acid (GH), *Tithonia* humic acid (TH), *Gliricidia* fulvic acid (GF) and *Tithonia* fulvic acid (TF).

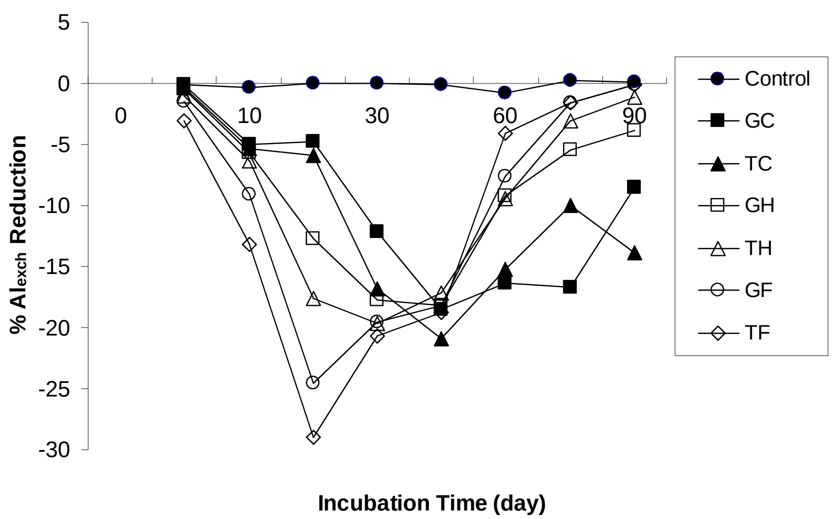

Figure 2. Percentage reduction of Al_{exch} concentration due to application of *Gliricidia* compost (GC), *Tithonia* compost (TC), *Gliricidia* humic acid (GH), *Tithonia* humic acid (TH), *Gliricidia* fulvic acid (GF) and *Tithonia* fulvic acid (TF).

This indicated that the role of humic acid in reducing Al_{exch} concentration has become weak after 30 days, whereas fulvic acid still actively played a role up to 45 days. It has been previously discussed that the greater role of fulvic acid than humic acid in reducing Al_{exch} concentration during the first 45 days was thought to be due to the higher carboxyl fraction content of fulvic acid than that of humic acid which makes fulvic acid stronger than humic acid in forming complexes with metal cations in soil (Zimmer, 2004). The relatively fast reduction of Al_{exch} concentration at the second 45 days for GC and TC treatments was thought to be related to the capability of the composts in releasing their organic substances (humic and fulvic acids), and also the capability of these organic acids to form complexes with soluble Al. One of composts characteristics is slow release of its organic substances (Katyal *et al*., 2001; Kaiser and Guggenberger. 2003). Palm *et al*. (1997) stated that mineralization and humification are parts of organic matter degradation; mineralization produces simple structured substances, while humification is a reorganization of soluble substances into a bigger molecule. It seemed likely that humic and fulvic acids were slowly released from the composts.

This is why the process of Al_{exch} concentration reduction still occurred up to 90 days. Hence, it can be concluded that roles of humic and fulvic acids in reducing Al_{exch} concentration were short term around 45 days, whereas compost still played roles in the long term.Rate of Al_{exch} concentration reduction may be predicted using an exponential decay function of Y = exp (k.t), where Y is the remaining Al_{exch} in soil, k is rate of constant of Al_{exch} reduction, and t is time. Data presented in Figure 3 show that the fastest rate of Al_{exch} reduction was observed for *Tithonia* fulvic acid treatment (0.79% per day), and the slowest was for control (0.005% per day) (Figure 3). Based on those rates of constant, it can be concluded that in general *Tithonia* compost as well as its humic and fulvic acids reduced Al_{exch} concentration faster than *Gliricida* compost and its humic and fulvic acids.

Change of $Al_{chelate}$ Concentration

The significant reduction of Al_{exch} concentration due to application of humic and fulvic acids (Figures 1 and 2), indicated important roles of humic and fulvic acids in binding soluble aluminium to form organic-metal complexes (chelates) that led to the increase of $Al_{chelate}$ (Figure 4). Haynes and Mokolobate (2001) has reported that reduction of aluminium solubility by humic acid is merely due to the formation of organic-metal complexes ($Al_{chelate}$). Data presented in Table 4 show that the reduction of Al_{exch} concentration strongly correlated with the increase of $Al_{chelate}$. The highest content of $Al_{chelate}$ (1.54%) was observed for TC treatment at day 90, followed by TF (1.50%), GC (1.47%), GF (1.42%), TH (1.25%), and GH (1.18%) treatments.

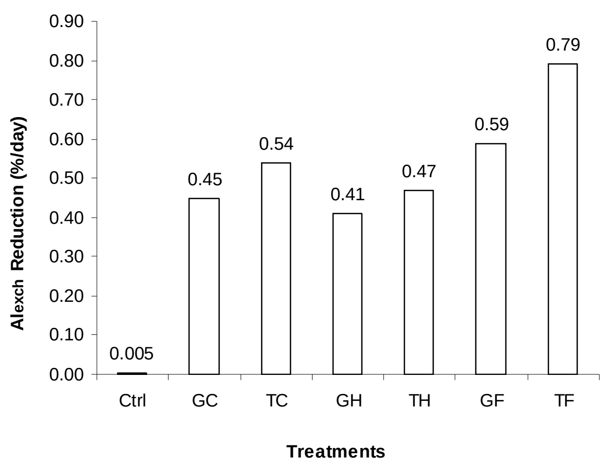

Figure 3. Rate of Al_{exch} concentration reduction for *Gliricidia* compost (GC), *Tithonia* compost (TC), *Gliricidia* humic acid (GH), *Tithonia* humic acid (TH), *Gliricidia* fulvic acid (GF), *Tithonia* fulvic acid (TF) and control (Ctrl) treatments.

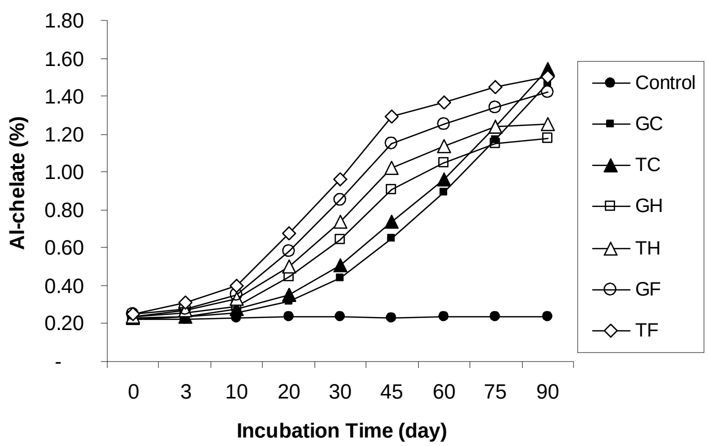

Figure 4. Change in concentration of $Al_{chelate}$ due to application of *Gliricidia* compost (GC), *Tithonia* compost (TC), *Gliricidia* humic acid (GH), *Tithonia* humic acid (TH), *Gliricidia* fulvic acid (GH) and *Tithonia* fulvic acid (TF).

The highest percentage of $Al_{chelate}$ increase due to GC and TC treatments occurred at day 90. The amount of $Al_{chelate}$ increased from 0.22% (control) to 1.47% and 1.54% whereas $Al_{chelate}$ at control only resulted in 0.02% increase. In general, all treatments increased $Al_{chelate}$ 4-5 times compared to control. This is in line with results presented by Supriyadi (2003) that application of *Tithonia diversifolia* in an Andisol increased $Al_{chelate}$ from 1.30% to 1.49% for 30 days in incubation.

The pattern of $Al_{chelate}$ increase is very similar to that of Al_{exch} reduction, i.e. ran fast in the first 45 days and then slowed down in the second 45 days (45-90 days) (Figure 5). However, the increase of $Al_{chelate}$ due to GC and TC treatments still occurred after 45 days.

The increase of $Al_{chelate}$ due to GF and TF treatments reached maximum at day 45, i.e. 136.36% (GF) and 150% (TF). Similarly for GH (122.73%) and TH (127.27%) treatments, but they were weaker than TF and GF treatments. As already discussed previously, fulvic acid seemed to be more reactive than humic acid in binding metal ions. Hence, as for Al_{exch}, application of compost gave a long term benefit, whereas humic and fulvic acids gave a short term benefit to $Al_{chelate}$ increase. A short term effect of humic and fulvic acids and a long term effect of organic matter on release of Al-P bound have also been reported by Minardi *et al.*(2007) in an Andisol amended with *Gliricidia* and its derived humic and fulvic acids.

Soil pH Change

The reduction of Al_{exch} and the increase of $Al_{chelate}$ due to application of *Gliricidia* and *Tithonia* composts as well as their humic and fulvic acids resulted in pH increase (Figure 6). The highest increase in soil pH (from pH 4.3 to 5.71) was reached by TF treatment at day 90. There was almost no pH change at control. Reduction of Al_{exch} activity due to application of organic matter is related to exchange reactions between organic anions produced by decomposition processes (humic and fulvic acids) and free OH at exchange sites which leads to an increase of OH ion in soil solution (Mokolobate and Haynes, 2002). In general, the pattern of soil pH change (Figure 7) is similar to that Al_{exch} and $Al_{chelate}$ (Figures 2 and 5).

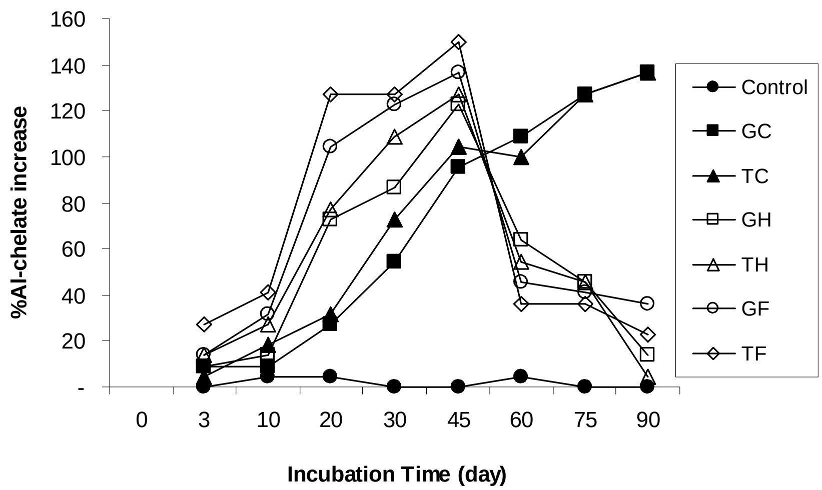

Figure 5. Percentage of $Al_{chelate}$ increase due to application of *Gliricidia* compost (GC), *Tithonia* compost (TC), *Gliricidia* humic acid (GH), *Tithonia* humic acid (TH), *Gliricidia* fulvic acid (GF) and *Tithonia* fulvic acid (TF).

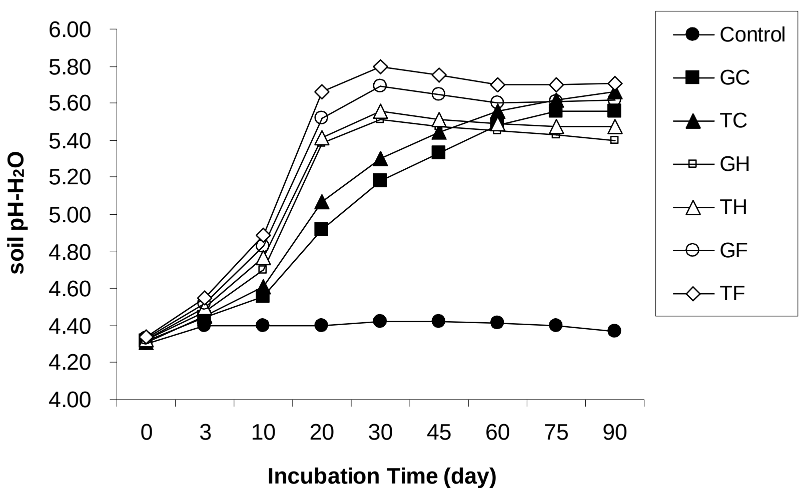

Figure 6. Change in pH due to application of *Gliricidia* compost (GC), *Tithonia* compost (TC), *Gliricidia* humic acid (GH), *Tithonia* humic acid (TH), *Gliricidia* fulvic acid (GF) and *Tithonia* fulvic acid (TF).

The increase of pH correlated more with Al_{exch} than with $Al_{chelate}$, particularly at 10, 20, 60, 75 and 90 days. However, the pH change was not always related to Al_{exch} and $Al_{chelate}$ changes (Table 3). This was probably due to unmeasured soil moisture changes during the experiment. A maximum increase of pH was reached at day 20 by all treatments. However, pH increases due to application of humic and fulvic acids were more pronounced than those of *Gliricidia* or *Tithonia* compost treatments (Figure 7). Humic and fulvic acid treatments showed no effect on pH after 45 days, while pH changes were still observed for compost treatments.

Table 3. Coefficient of correlation (r) between percentage of soil Al_{exch}, $Al_{chelate}$ and pH after 90 days incubation.

Time (day)	Coeeficient correlation (r)		
	Al_{exch}-$Al_{chelate}$	Al_{exch}-pH	$Al_{chelate}$-pH
3	0.937**	0.081	0.352
10	0.933**	0.917**	0.914**
20	0.992**	0.867*	0.903**
30	0.958**	0.516	0.345
45	0.893**	0.363	-0.069
60	0.989**	0.837*	0.858*
75	0.918**	0.945**	0.933**
90	0.896**	0.810*	0.616

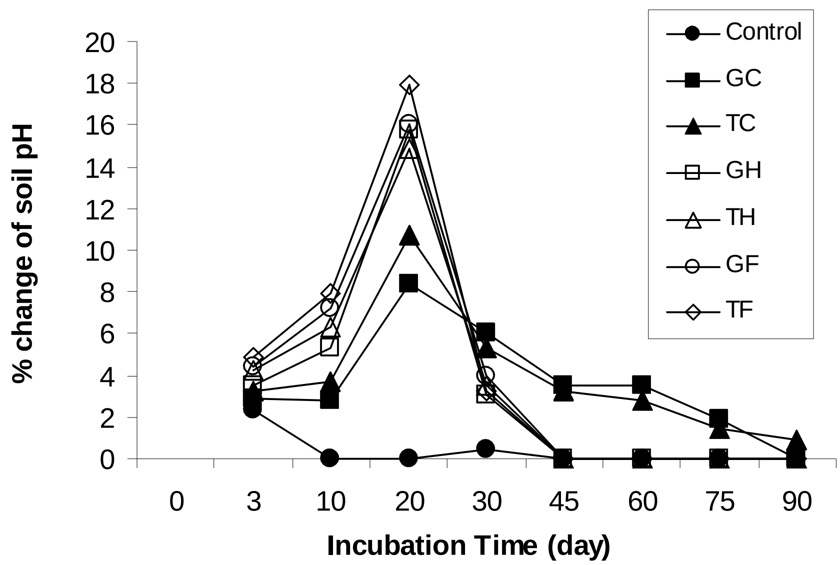

Figure 7. Percentage of pH increase due to application of *Gliricidia* compost (GC), *Tithonia* compost (TC), *Gliricidia* humic acid (GH), *Tithonia* humic acid (TH), *Gliricidia* fulvic acid (GF) and *Tithonia* fulvic acid (TF).

CONCLUSIONS

Application of *Gliricidia sepium* and *Tithonia diversifolia* composts as well as their extracted humic and fulvic acids reduced Al_{exch}, increased $Al_{chelate}$, and increased pH of an Ultisol. Reduction of Al_{exch} strongly correlated with $Al_{chelate}$ increase. However, the increase of pH did not always strongly correlate with changes in aluminium concetration. The highest Al_{exch} reduction (90.5%) was observed for *Tithonia* fulvic acid traetment during 90 days, followed by *Tithonia* compost (88.4%), *Gliricidia* fulvic acid (82.3%), *Gliricidia* compost (82.2%), *Tithonia* humic acid (75.66%), and *Gliricidia* humic acid (73.46%) treatments, whereas control (no added composts, humic acids or fulvic acids) only decreased exchangeable Al concentration by 0.9%. In general, rate of change in exchangeable Al concentration was fast for the first 45 days, but it then slowed down during the second 45 days (45-90 days). This was particularly observed for humic and fulvic acid treatments, whereas compost treatment still showed subsequent decrease. Patterns of Al chelate and pH were very similar to that of exchangeable Al. It was thus concluded that roles of humic and fulvic acid in reducing exchangeable Al was only a short term, whereas compost played roles in a long term.

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