CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Glyphosate and AMPA in the Leachate

4.1.1 Comparison of the amounts of glyphosate and AMPA leaching in the control groups and under rainy and summer seasons

4.1.1.1 Amount of glyphosate leaching in control group

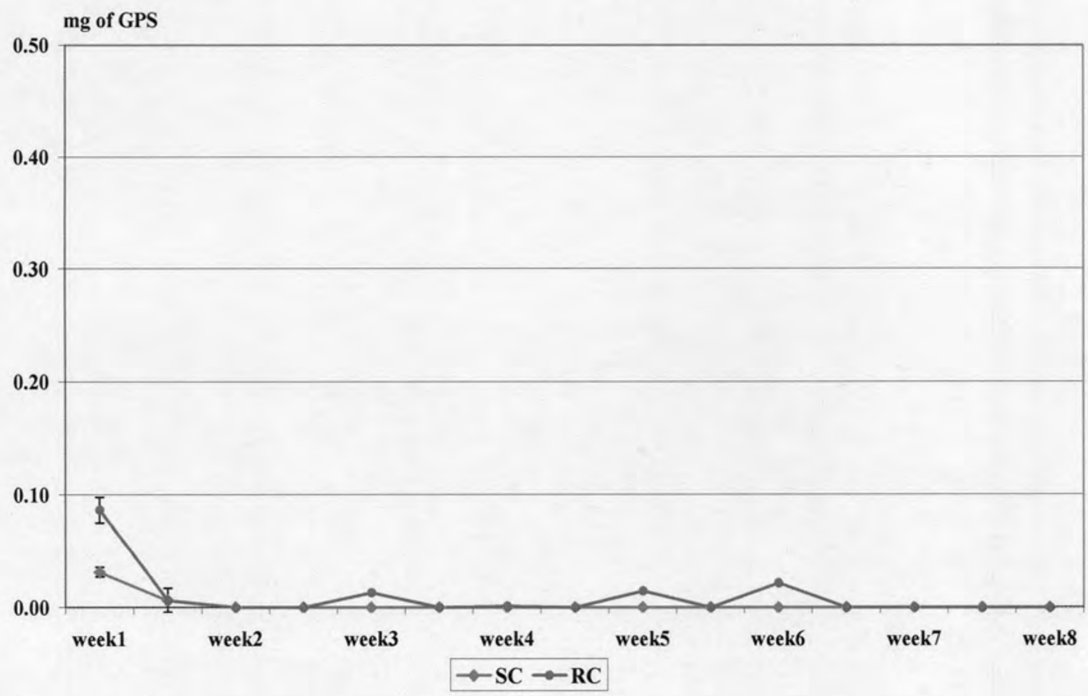

Figure 4.1. Amount of glyphosate in the control groups along monitoring period.

According to the results as shown in Figure 4.1, Glyphosate leaching in the control groups was very low and appeared only in the first week: 0.03 and 0.06 mg for summer and rainy season control groups, respectively. The amount of glyphosate in rainy season group was twice as high as that of the summer group. This result showed that the amount of water had a little influent on glyphosate leaching which can be explained by its characteristic of being more preferable to adsorbed on soil particle and would not reverse into soil solution [19, 20, 22, and 23]. These results also are related to the findings of the U.S. EPA from 1993 that reported that under natural conditions, glyphosate had less possibility to leach into soil deeper than six inches.

4.1.1.2 Amount of AMPA leaching in control group

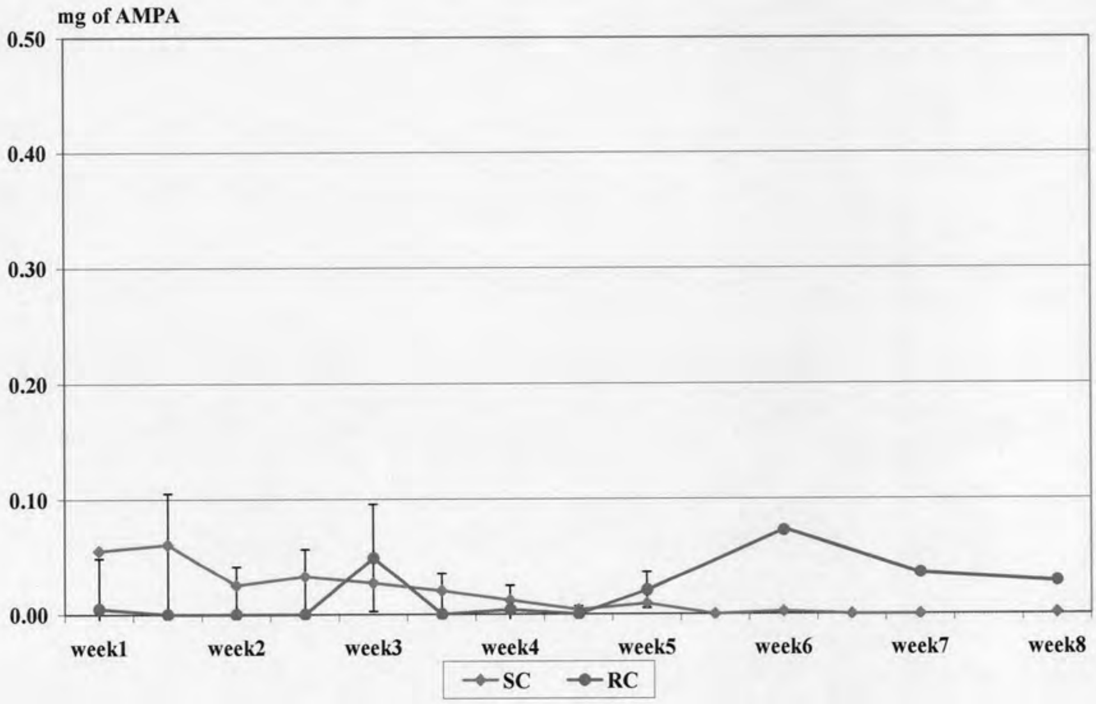

Figure 4.2. Amount of AMPA in the control groups along the monitoring period.

From the results shown in Figure 4.2, in the initial period, the amount of AMPA in the summer was higher than in the rainy season. After the 4^{th} week, the amount of AMPA in the rainy group was higher than the summer group control groups. The amount of water is the only different factor which has an effect on the leaching of AMPA between rainy and summer control groups. According to this result, the amount of water would be effect on the degradation of glyphosate that the degradation of glyphosate preferable occurring more in the conditions which has less amount of water while the other conditions has the same such as light and temperature.

4.1.2 Comparison of the amount of glyphosate and AMPA leaching influenced by the chemical fertilizer during the rainy and summer seasons

4.1.2.1 Amount of glyphosate leaching in experiment group

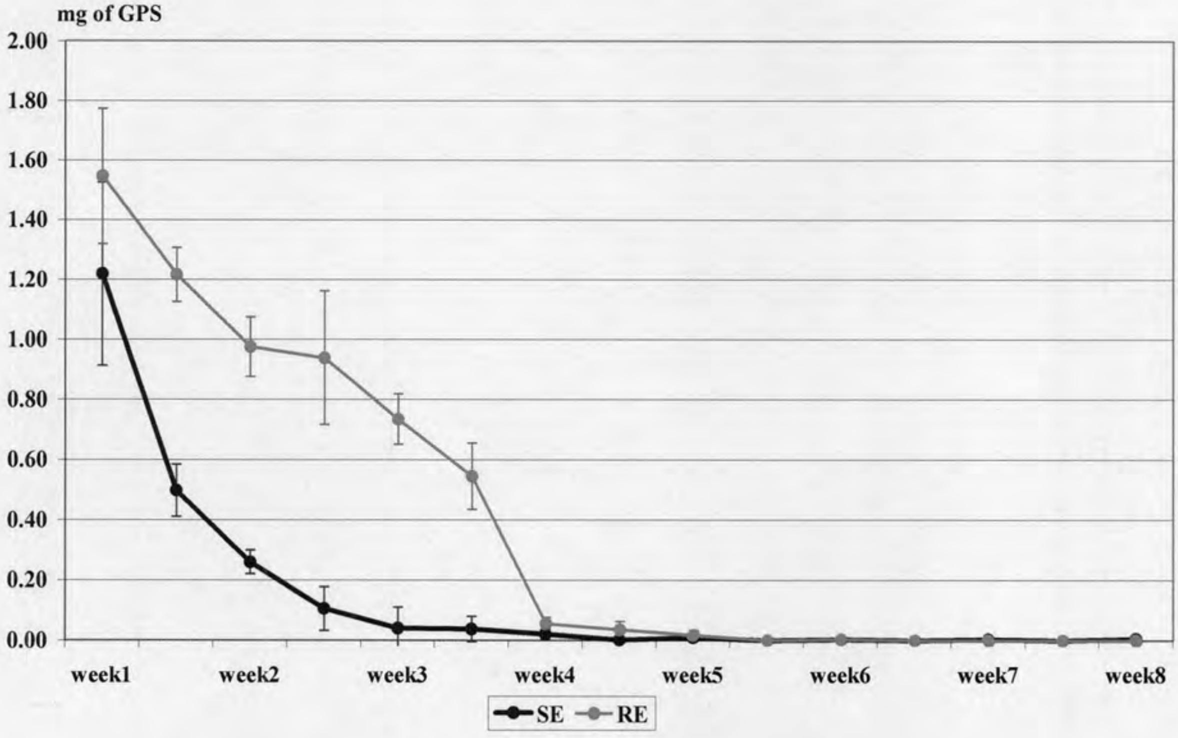

Figure 4.3. Amount of glyphosate in the experiment groups along the monitoring period.

According to the results as shown in Figure 4.3, in the presence of the chemical fertilizer, glyphosate leaching occurred until the 4th week of the monitoring period in both groups; however, the glyphosate leaching trends of the two groups were slightly different.

According to a study by U.S. EPA (1993) glyphosate strongly adsorbs in soil so it has a low possibility of leaching deeper than 6 inches of the soil layer; consequently, it has a low possibility of leaching into groundwater. However, as observed in this study, in the presence of a chemical fertilizer, it could move into the deeper soil layers and leach into groundwater. The chemical fertilizer enhanced glyphosate leaching due to the competition that occurred between glyphosate and the phosphorus fertilizer for adsorption onto the soil.

According to a study on the behavior of glyphosate sorption in soil by Prata *et al*., (2003), glyphosate adsorbed on soil at the phosphonic functional group and it occurs at the same site and same mechanism as phosphate. Since glyphosate was applied onto the soil, it adsorbed at the positively charged sites of the soil surface by exchanging ions or forming complexes with the oxides of minerals such aluminum or iron by the ligand exchange mechanism as the mechanism of phosphate adsorption in soil that has been demonstrated by MacLaren and Cameron (1997).

After glyphosate was applied to soil, it does not reverse into the soil solution or leach from soil because it is strongly adsorbed to the soil by the adsorption mechanism described above [7, 14, 20, and 22]. However, in the presence of a chemical fertilizer containing phosphorus, a competitor with glyphosate for the same specific sorption sites in soil, can cause glyphosate leaching since phosphorus has the smaller structure than glyphosate, thus it can be a stronger competitor and more capable of adsorbing onto soil confirmed by the high amount of glyphosate leaching in experiment groups in this study.

In the rainy season, glyphosate leaching gradually and only slightly decreased along the monitoring period, while glyphosate leaching in the summer greatly decreased after the first leachate sampling. The amounts of glyphosate in the leachate in the rainy group were 1.55, 1.21, 0.97, 0.94, 0.73, 0.54, 0.06, and 0.04 mg from the first week to the fourth week, respectively. And the amounts of glyphosate in the leachate in the summer group were 1.22, 0.5, 0.28, 0.1, 0.04, 0.04, 0.02, and 0.00 mg.

However, it is should be noted that the amounts of glyphosate in the first leachate samplings of both groups were rather similar. The difference occurred in the second leachate samplings and from that point on, including the different glyphosate leaching behaviors.

In the first leachate sampling, the amounts of glyphosate during the rainy and summer seasons were similar because in the initial period of experiment they had the same the amounts of glyphosate and phosphorus fertilizer in the soil and the amount of water applied was the only different factor.

The fertilizer was applied in the solid form that dissolved in water, thus the higher the amount of water, the more the fertilizer dissolved. Consequently, the phosphorus in the fertilizer could replace the glyphosate in the soil by adsorbing to sorption sites more in the rainy than the summer season. Thus, in the first leachate sampling, the amount of water was the key factor that determined the high amount of glyphosate leaching. After that, the degradation of glyphosate was considered to be the influential co-factor that affected the amount of glyphosate leaching.

In the summer, the smaller amount of water caused less substantial glyphosate leaching due to the phosphorus fertilizer. The glyphosate accumulated in the soil and rapidly degraded by soil microbial organisms, thus the amount of glyphosate in the soil dramatically decreased. The rapid degradation of glyphosate together with the effect of the low amount of water applied to this group resulted in a great decrease in the amount of glyphosate at the second leachate sampling and the amount continued to decrease until the 4^{th} week of the monitoring period. It can be concluded that in this case, the degradation of glyphosate had more of an influence on glyphosate leaching than the amount of water applied.

During the rainy season, a higher amount of water was applied resulting in the higher glyphosate replacement by phosphorus fertilizers, glyphosate leaching started off high at the first sampling and gradually decreasing until the 4^{th} week of the monitoring period as the glyphosate leaching trend exhibited by this group was influenced by the high amount of water applied.

4.1.2.2 Amount of AMPA leaching in experiment group

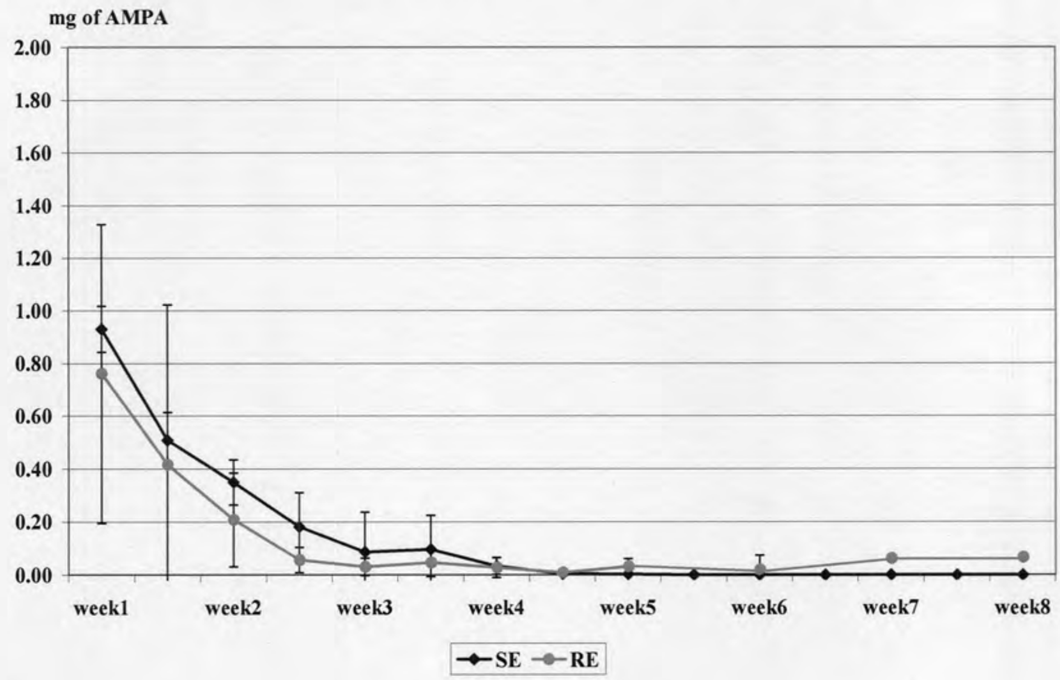

Figure 4.4. Amount of AMPA in the experiment groups along the monitoring period.

According to the results as shown in Figure 4.4, the amounts of AMPA in the leachate in both groups followed similar trends due to the degradation of glyphosate in the soil.

The AMPA in both groups slightly decreased from the first sampling to the 4^{th} week, after that the AMPA in the rainy season sample slightly increased until the end of monitoring period while the AMPA in the summer sample was present in very low amounts. This result might have been caused by the different degradation rates that occurred during the rainy and summer seasons. The summer had more suitable conditions for degradation than the rainy season so the degradation of glyphosate in the summer made it possible for the glyphosate to completely degrade by the 4^{th} week; the lower degradation rate of glyphosate during the rainy season meant that degradation continued until the end of monitoring period.

4.1.3 Comparison the amount of the glyphosate leaching in all groups

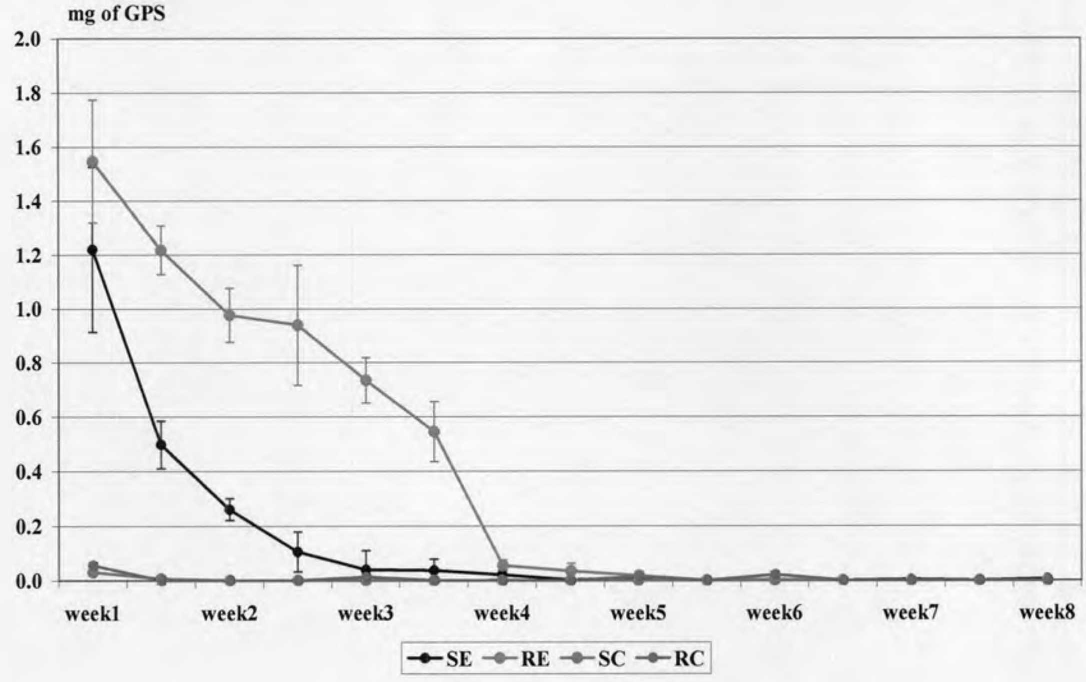

Figure 4.5. Amount of glyphosate in all groups along the monitoring period.

According to the results as shown in Figure 4.5, the highest amount of glyphosate in the leachate was found in the rainy experiment group and the lowest amount of glyphosate was found in the summer control group.

Thus the most important factor that influenced the leaching of glyphosate was the phosphorus fertilizer. This was confirmed by the amount of glyphosate leaching in the experiment groups. However, in the presence of the phosphorus fertilizer, the amount of water also influenced the leaching of glyphosate as confirmed by the different amounts of glyphosate leaching in the rainy and summer experiment groups.

When glyphosate lacked a competitor to compete with it for sorption sites on the soil, the amount of water did not significantly affect glyphosate leaching. Thus under natural conditions during the rainy and summer seasons, the environmental problem of glyphosate leaching should not occur.

4.1.4 Comparison the amount of AMPA leaching in all groups

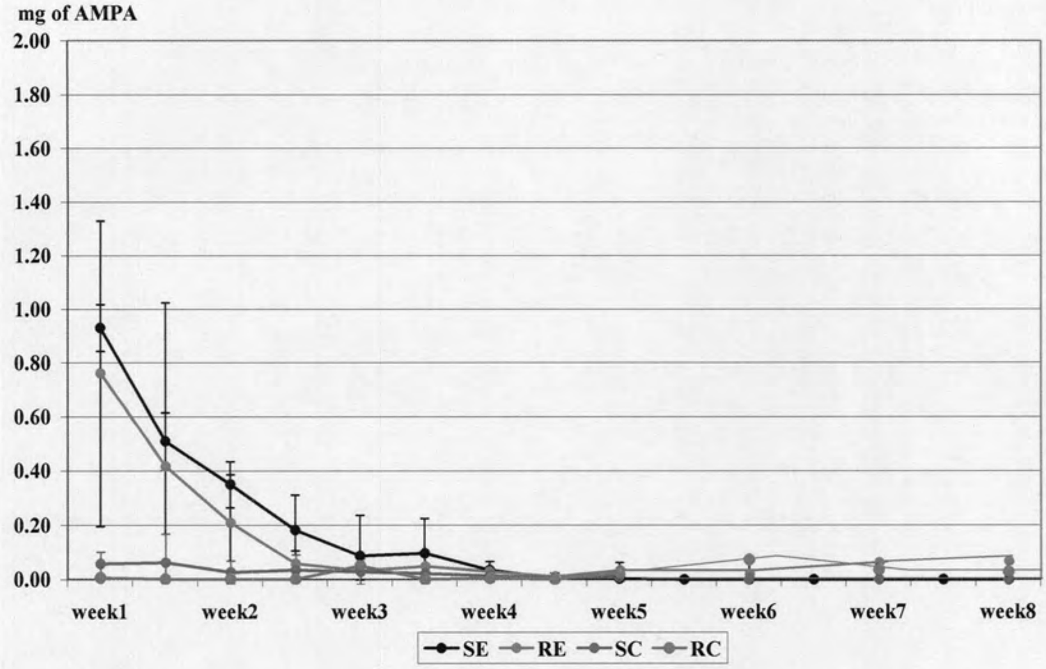

Figure 4.6. Amount of AMPA in all groups along monitoring period.

According to the results as shown in Figure 4.6, the highest amount of AMPA was found in the rainy experiment group and the lowest amount of AMPA was found in the rainy control group. The amount of AMPA observed followed a similar trend to that of glyphosate caused by the degradation of glyphosate that occurs faster in the summer groups.

4.2 Residual Glyphosate and AMPA in the Soil

4.2.1 Total residual glyphosate and AMPA in the soil after 60 days

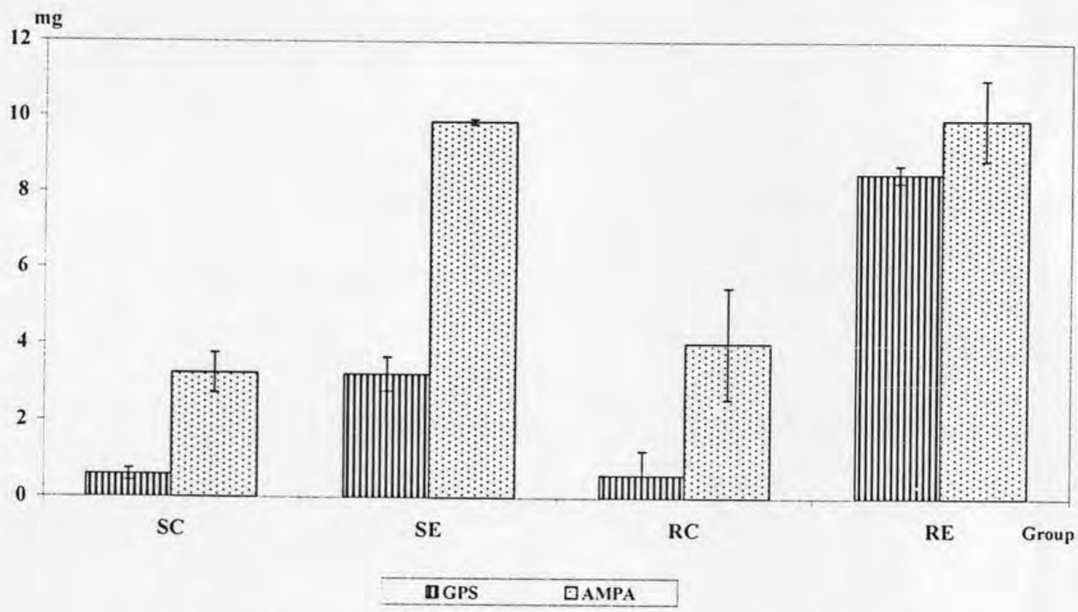

Figure 4.7. Total glyphosate residue and AMPA in the soil after 60 days.

The amount of the glyphosate residue found in the soil was contrary to our initial expectation. The groups that had higher amounts of glyphosate leaching had been expected to have less glyphosate residue in the soil. However, the trend of the residue glyphosate in the soil was the same as that of the leachate. The highest residue glyphosate levels in the soil were found in the rainy and summer experiment groups (8.5 and 3.23 mg, respectively) and the lowest levels were in the summer control groups (0.58) as shown in Figure 4.7. These results show that the chemical fertilizer could enhance both the leaching and the accumulation of glyphosate.

The high amount of glyphosate leaching in experiment groups were caused by the substantial of glyphosate by phosphate fertilizer but the interesting is the high levels of residual glyphosate also found in soil in the experiment groups. According to the results, we would like to suggest that the high level of residual glyphosate in experiment groups might be caused by the complexation between glyphosate and a chemical fertilizer had occurred and was able to reduce the soil's microbial organism ability for glyphosate degradation.

However, the interaction between glyphosate and the chemical fertilizer in the soil is quite complicated and was not investigated in this study. Glyphosate is dipolar and easily performs ions exchanges to form complexes; hence, it has ability to form complexes with the chemicals contained in the fertilizer [3, 19, and 20].

The added chemical fertilizer contains N as the total nitrogen, K_2O, P_2O_5, Ca, and Mg. After the phosphonate group of glyphosate substantial by phosphate in fertilizer, the glyphosate replaced from soil has the possibility to form complex with calcium and magnesium and precipitate in soil. The pH is a key to investigating the mechanisms between glyphosate and the chemical fertilizer in soil [13] but this study did not cover the interaction of glyphosate in the soil and leachate. Glyphosate is a dipolar molecule giving the pH of glyphosate in the leachate the tendency to be neutral so its pH can not use for investigating the complexation of glyphosate in the leachate.

The residual AMPA in summer and rainy experiment groups were similar (9.86 and 9.92 mg, respectively), while the amount of residue glyphosate was higher in the rainy experiment group than in the summer experiment group. This difference was possibly the result of the summer experiment group having better conditions for degradation than the rainy experiment group. However, the amount of AMPA residue in the soil was similar to the amount of glyphosate residue due to the degradation process. The glyphosate can be degraded to AMPA and sarcosine and, degraded to methylamine, glycine and CO_2 in finally as shown in Figure 2.2.

Thus, the degradation rate of glyphosate to AMPA and the degradation rate of AMPA to other compound should be occurred in the same rate. From this result, the trend of residual glyphosate and AMPA in soil was similar.

4.2.2 Comparison of the distribution of glyphosate and AMPA within the soil column after 60 days

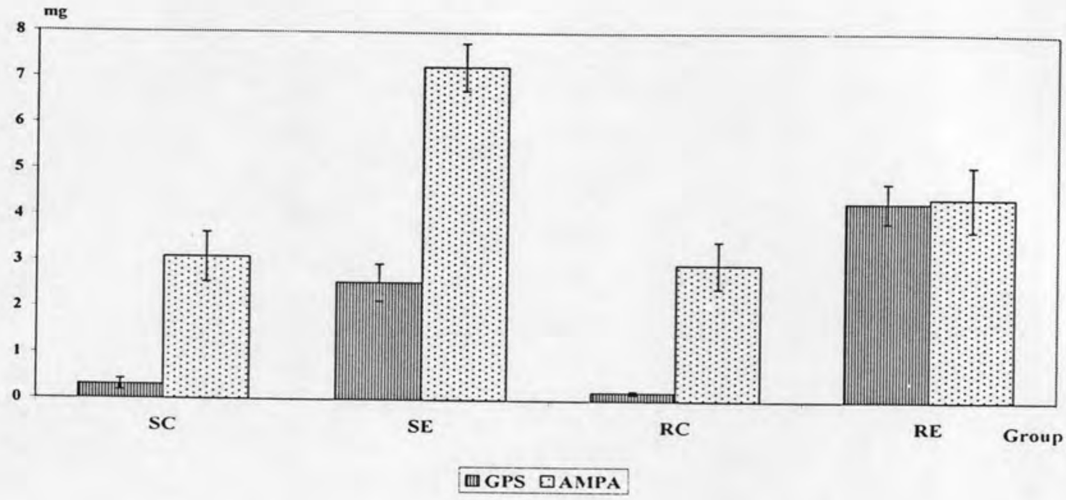

Figure 4.8 Residue glyphosate and AMPA in the upper soil.

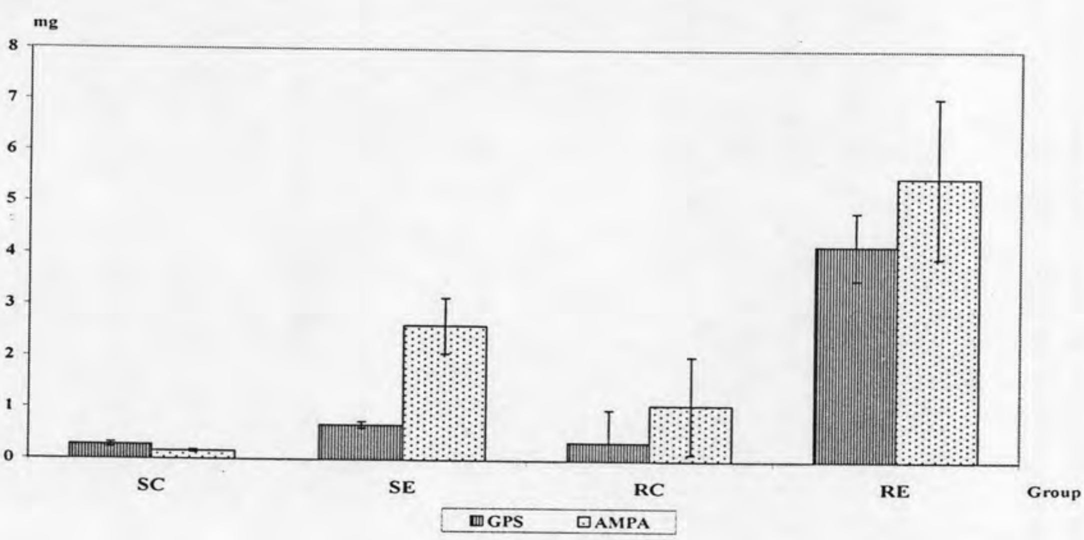

Figure 4.9. Residue glyphosate and AMPA in the lower soil.

The results of the glyphosate and AMPA residues in the upper and lower soil layers as shown in Figure 4.8 and 4.9 demonstrated that both glyphosate and AMPA could reach 15 cm of soil depth, although the amounts of their leaching in the two layers were slightly different. This result related to the study on glyphosate behavior by Veiga *et al.*, (2001). They found that both glyphosate and AMPA quickly reached 30 cm of soil depth and the concentrations of glyphosate in both layers (0-20 and 20-35) were quite similar.

In the upper soil layer, the amounts of residue glyphosate in the control groups were found to be very low due to the degradation rate. These results were in agreement with the study of D. Landry *et al.*, (2005) that reported that glyphosate can be degraded rapidly in the upper soil. In the experiment groups both glyphosate and AMPA were still found in high amounts. The highest residue AMPA levels in the summer experiment groups were quite interesting because the expectation was for the highest levels to be found in the control groups, where the degradation of glyphosate by soil microbial organisms was not effected by the chemical fertilizers. However, this result might have been caused by the almost complete degradation of both glyphosate and AMPA in the control groups; therefore, the residues of glyphosate and AMPA in the control groups were less than in the summer experiment groups.

In the lower soil layer, the glyphosate and AMPA residues in the control groups were very low while the glyphosate and AMPA residues in experiment groups were high, with the highest reading in the rainy experiment group. These results confirm the poor ability of the soil's microbial organisms to degrade the glyphosate in the experiment groups.

4.3 Degradation of Glyphosate

Table 4.1. Degradation of glyphosate in soils after 60 days.

Group	Feed in (mg)	Degradation (mg)	% Degradation
SC	135	134.35	99.52
SE	135	129.18	95.69
RC	135	134.34	99.51
RE	135	120.43	89.21

The degradation of glyphosate was not directly measured in this experiment but we had set up the assumption for measuring the degradation of glyphosate that is;

The degradation = Total amount of glyphosate applied into this experiment – amount of glyphosate in the leachate and the residual of glyphosate in soil.

According to the results shown in Table 4.1, in both the control groups glyphosate degradation occurred at approximately 99 % for both summer and rainy seasons. In the experiment groups, glyphosate had slower degradation in both the rainy and summer seasons and the slowest degradation rate was found in the rainy season (approximately 95 and 89 % for summer and rainy seasons, respectively). It can be concluded that glyphosate can be rapidly degraded under natural conditions both in rainy and summer seasons as glyphosate can be degraded by several types of bacteria which can use glyphosate as a source for nitrogen, phosphorus and carbon [5, 6, and 12].

Although degradation of glyphosate in this experiment seems to be high percentage, but results of degradation of glyphosate shown in Table 4.1 were obtained from the degradation of glyphosate after 60 days, it was related to other studies that is half-life of glyphosate ranking from 3-130 days depending on condition [18, 19, 20, and 22].

4.4 Mass Balance of Glyphosate

The mass balance equation is as follows:

In = Out

Where;

Out = [Glyphosate in the leachate + Degradation] + Residual glyphosate in soil

And

Degradation = Feed In – (Glyphosate in leachate and soil)

Thus;

Feed in = Leaching + Degradation + Residual in soil

Table 4.2. Mass Balance of glyphosate.

Group	Feed in (mg)	Glyphosate out		Residue in soil (mg)
		Leachate (mg)	Degradation (mg)	
SC	135	0.07	134.35	0.59
SE	135	2.59	129.18	3.23
RC	135	0.07	134.34	0.59
RE	135	6.07	120.43	8.50

The details of the mass balance of all groups were used to compare how the behavior of glyphosate was affected or unaffected by the chemical fertilizer during the 60-day monitoring period. From the results in Table 4.2, we concluded that the chemical fertilizer caused serious environmental problems by enhancing glyphosate leaching into groundwater, increasing the glyphosate accumulation in soil, and decreasing the degradation of glyphosate in soil. However, the harmful effects of the chemical fertilizer were more serious in the presence of high amounts of applied water.

As can be seem in Table 4.2, the rainy experiment group had the highest amounts of glyphosate both in the leachate and soil; moreover, it had the slowest degradation rate. In contrast, both control groups had the lowest amounts of glyphosate both in the leachate and soil; they also had the highest degradation rate.