CHAPTER 4

RESULTS AND DISCUSSION

4.1 Soil and wastewater treatment sludge characteristics

Soil from tangerine orchard was sandy clay loam soil that composed of 64% sand, 16% silt, and 20% clay. From Table 4.1, the soil sample was moderately acid and contained low amount of organic carbon (1.85%) as compared to the sludge. The moisture content of soil was 14.0 %. The CEC and EC value of this soil were 7.9 $cmol_c\ Kg^{-1}$ and 0.115 $dS\ m^{-1}$, respectively. All WWTS samples were slightly acidic and had higher amount of organic carbon than the soil sample. The organic matter contents of WWTS were ranged from 42.51 to 53.33 %. Food industrial WWTS had the highest CEC and EC values when compared between samples. The available phosphorus (P) of soil was 149 ppm. On the other hand, the available P of WWTS was ranged from 3,488 to 7,226 ppm. Consequently, WWTS may be used as fertilizer to increase P mineral source in soil. The amount of nitrogen (N) in soil was 0.09 ppm and in WWTS was ranged from 2.36 to 3.42 ppm. In the same way as P, source of N may be supplied from the WWTS.

Table 4.1 Soil and wastewater treatment sludge characteristics.

Parameters	Soil	Wastewater treatment sludge		
		Pig farm	Municipal	Food Industrial
Texture	Sandy clay loam	N/D	N/D	N/D
Sand (%)	64.0	N/D	N/D	N/D
Silt (%)	16.0	N/D	N/D	N/D
Clay (%)	20.0	N/D	N/D	N/D
Moisture content (%)	14.00	80.90	36.13	86.67
pH	4.40	6.25	5.90	6.73
OC (%)	1.85	50.39	42.51	53.37
CEC (cmol$_c$ Kg^{-1})	7.9	29.38	37.39	50.44
EC (dS m^{-1})	0.115	3.14	3.53	4.11
Available P (ppm)	149	4,848	3,488	7,226
Nitrogen (ppm)	0.09	3.29	2.36	3.42
Endosulfan (ppm)	0.04	0.06	1.45	0.03
Cu (ppm)	0.02	3.07	0.52	0.24
Mn (ppm)	0.15	1.29	0.91	1.34
Ni (ppm)	0.08	0.07	0.12	0.06
Zn (ppm)	0.11	5.85	3.00	1.09

N/D = Not determined

Trace amount of endosulfan was detected in both soil and WWTS samples (Table 4.1). The background concentration of endosulfan in soil was comparable to pig farm and food industrial WWTS, which were ranged from 0.03 to 0.06 ppm. Meanwhile, the amount of endosulfan in municipal WWTS was much higher than in the soil. This municipal WWTS contained 1.45 ppm of endosulfan. The results suggested that the application of pig farm and food industrial WWTS would not cause any further endosulfan contamination in soil. On the other hand, municipal WWTS may increase the amount of soil endosulfan after application.

The amounts of environmental concerned metals in soil and WWTS were analyzed as showed in Table 4.1. The amounts of Cu, Mn, Ni and Zn in soil were 0.02, 0.15, 0.08, and 0.11 ppm, respectively. In WWTS, the amount of Cu was ranged from 0.24 to 0.52 ppm. Cu in pig farm sludge was highest, which may be due to Cu in pig feed ingredients. According to US-EPA (1993), the concentration of Cu in biosolid that can be applied to land should not exceed 4,300 ppm. Our results showed that the amounts of Cu in all WWTSs were much less than the regulation. The amounts of Ni and Zn in our sludge samples were ranged from 0.06 to 0.12 ppm, and 1.09 to 5.85 ppm, respectively. Similar to Cu in the US-EPA guideline, the standard of these elements are higher than our WWTS. The regulated amounts are 420 and 7,500 ppm for Ni, and Zn, respectively. Moreover, amounts of Mn were ranged from 0.91 to 1.34 ppm in our WWTS. According to Thailand regulation, the standard concentration of Mn in soil is less than 1,800 ppm. The results suggested that the addition of WWTS would not cause Mn accumulation beyond the standard value.

From the high amount of organic content and low toxic chemicals, we may conclude that all WWTS are appropriate for the application as pesticide sorbent and may be applied to prevent soil from pesticide contamination. Meanwhile, the application of municipal WWTS to soil is not practical since it contains high amount of endosulfan and may cause further soil contamination. WWTS may also be applied as the mineral sources for soil such as N, and P. Each of WWTS has different characteristics due to their source of wastewater. The soil and WWTSs were later studied for their sorption coefficient and desorption efficiency to compare their efficiencies with each others.

4.2 Sorption coefficient and desorption efficiency

4.2.1 Sorption coefficient

Sorption coefficients of soil and wastewater treatment sludges were determined by batch partitioning experiment. Due to the low concentration of endosulfan used in this experiment, sorption coefficient (K_d) was calculated from the linear equation (4.1).

$$C_s = K_d C_w \tag{4.1}$$

Where C_s is the amount of endosulfan sorbed to soil ($\mu g\ g^{-1}$), C_w is the equilibrium concentration in solution ($\mu g\ L^{-1}$), and K_d is the adsorption coefficient ($L\ g^{-1}$). The correlation between endosulfan concentrations in solution and the amount of

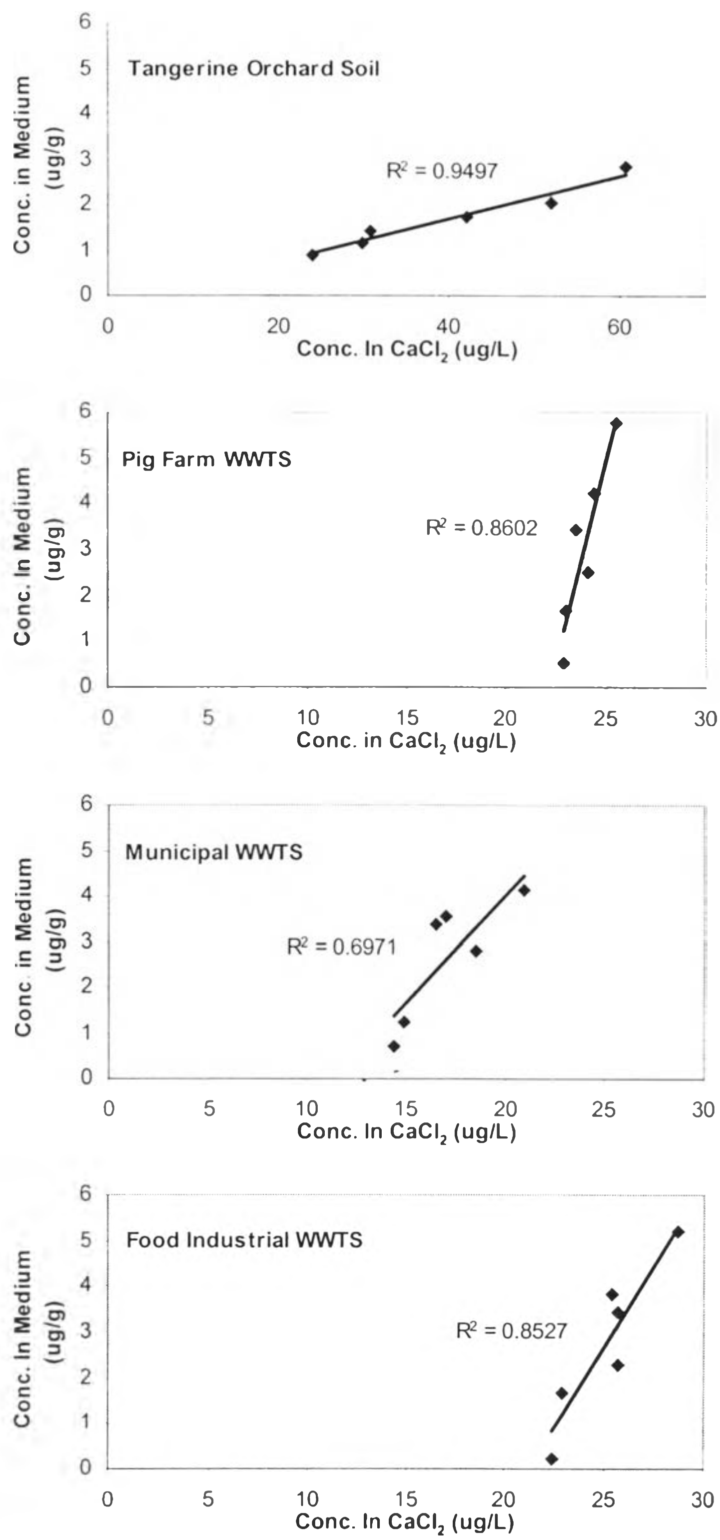


Figure 4.1 Sorption isotherm of endosulfan on soil and wastewater treatment sludges.

sorbed endosulfan was fitted to the linear isotherm in Figure 4.1 and K_d values are showed in Table 4.2.

Table 4.2 Endosulfan sorption parameter at the equilibrium.

Soil and WWTS	K_d (mL g^{-1})	K_d /OC (mL g^{-1})*
Tangerine orchard soil	47.5	25.68
Pig farm WWTS	1,755.5	34.84
Municipal WWTS	466.9	10.98
Food industrial WWTS	707.7	13.26

*OC is the organic carbon from Table 4.1.

From Table 4.2, the sorption coefficient (K_d) of soil was 47.5 mL g^{-1}, while the K_d of sludge from municipal wastewater treatment plant, sweet corn canning factory, and pig farm were 466.9, 707.7, and 1,755.5 mL g^{-1}, respectively. Therefore, sorption abilities of all wastewater treatment sludges were higher than the tangerine orchard soil. In this sense, it seems that a good correlation could exist between the organic content and the K_d parameter, the higher organic content, higher K_d values. This fact is also in agreement with the results reported from other pesticides and soil types (Gonzalez-Pradas *et al.*, 2002). The interaction between soil/sludge and endosulfan was probably by hydrophobic partitioning, which is an important sorption mechanism for organochlorine insecticides onto soil organic matter and humic substances (Gevao *et al.*, 2000).

K_d /OC is equal to K_{oc} that is the sorption coefficients measured on organic carbon basis (Spark and Swift, 2002). Tangerine orchard soil and pig farm WWTS had high K_d /OC (Table 4.2). This result suggested that organic carbon was the major factor responsible for endosulfan sorption in tangerine orchard soil and pig farm WWTS. Although, municipal and food industrial WWTS had high organic carbon content, their K_d /OC value were lower than the soil value. The results suggested that other physical and chemical properties of these sludges may prevent the sorption of endosulfan on organic carbon. Example of properties that may affect pesticide sorption are size, shape, molecular structure, chemical functions, solubility, polarity, polarizability and charge distribution of interacting species, and acid-base nature of the pesticide molecules (Pignatello and Xing, 1996).

However, we can compare the log K_d values in this study to other studies. They are showed in Table 4.3. The log K_d of soil and WWTSs in this study were 1.68 and ranged from 2.67-3.24, respectively. From other studies, the log K_d were between 0.83 and 2.46.

Table 4.3 Comparison of logK_d values obtained in this study to those in the literatures

Samples	log K_d (mL g^{-1})	Reference
Tangerine orchard soil (sandy loam clay)	1.68	From this study
Soil	2.18	US. EPA, 1996
Soil (very gravelly loam)	2.42	Zhou *et al.*,2002
Soil (marl)	2.46	Zhou *et al.*,2002
Soil	1.46-1.86	Montgomery, 1993
Soil (clay)	1.27	Ismai et al. 2002
Soil (sandy loam)	0.83	Ismai et al,
Pig farm sludge	3.24	From this study
Municipal sludge	2.67	From this study
Food industrial sludge	2.85	From this study

Although, the comparison of the log K_d was showed as well as the result of Montgomery (1993) (ranged from 1.46-1.86). On the other hand, the different was showed when compared with Zhou *et al.* (2002), found the log K_d of very gravelly loam and marl soil was 2.42 and 2.46, respectively that is differ from this study (1.68). These may be due to other unknown details of those studies which have influence on sorption behavior. There may be particle size, temperature, and dissolved organic matter.

For example, particle size of soil that has the effect on shape, pore volume, or surface area influencing the sorption behavior. Particularly, the influenced of particle size has already mentioned. The different of temperature in the laboratory experiments may be influenced to the sorption behavior. From the study of Hulscher and Cornelissen (1996), they found that the sorption coefficient for the most compounds decrease with increasing temperature. The room temperature used in our study was around 30 °C, which was probably higher than other studies. This may be one of the reasons that contributed to the lower sorption coefficients.

4.2.2 Desorption efficiency

When the chemical concentration in the soil pore water decreases, desorption of the pesticide from the solid phase to pore water phase occurs (Sabatini, 1993). This experiment was conducted right after the endosulfan sorption experiment. The initial concentrations of endosulfan in sorped soil (or WWTS) were 50, 150, and 300 ppb. Endosulfan sorped soil (or WWTS) were mixed with 5 mL 0.01 M $CaCl_2$ and shaken at room temperature for 24 h. The amounts of desorped endosulfan in $CaCl_2$ solution were analyzed. Endosulfan desorption efficiency were calculated from Equation (4.2):

$$\text{Desorption efficiency } (\mu g\ g^{-1}) = \frac{C_w V}{W} \tag{4.2}$$

Where C_w is the equilibrium concentration in solution ($\mu g\ L^{-1}$), V is the volume of $CaCl_2$ (L), and W is the initial weight of soil or WWTS (g).

The results of desorption efficiency was showed in Table 4.4. Soil endosulfan desorption efficiency was 0.277 μg g^{-1}, while the amount of desorped endosulfan was 0.107, 0.123, and 0.134 μg g^{-1} from municipal, pig farm, and food industrial WWTS, respectively. Desorption efficiency showed the amount of pesticide released from soil (or WWTS) after the equilibrium of sorption process. According to Ismai (2002), the desorption efficiency of endosulfan from sandy loam and clay soil was low due to its low water solubility. The amount of desorped endosulfan from soil was higher than from sludge samples. The results suggested that higher amount of endosulfan would retain in the sludge after sorption.

Table 4.4 Desorption efficiency of endosulfan at the equilibrium

Soil and WWTS	Desorption efficiency (μg g^{-1})
Tangerine orchard soil	0.277
Pig farm WWTS	0.123
Municipal WWTS	0.107
Food industrial WWTS	0.134

To select a WWTS for the following column experiment, we compared chemical properties, sorption coefficient (K_d), K_d /OC, and desorption efficiency between each WWTS. Pig farm WWTS had the highest K_d and K_d /OC, low desorption efficiency, and low amount of background endosulfan, consequently it was selected to be a cover material for the soil column experiment.

4.3 Soil column experiments

4.3.1 Preliminary study

Soil columns were used to study the mobility of endosulfan in soil after application with WWTS. 10 g of WWTS from pig farm was added to the column surface for enhancing endosulfan sorption. In the preliminary study, we applied endosulfan at double amount of the recommended dose to the soil column to represent the worst case scenario of pesticide application.

After endosulfan application, the distribution of this pesticide in soil columns was monitored. In the column without sludge, endosulfan was found in below the sludge after 5 days (Figure 4.2). However, endosulfan was found only in the sludge layer at all time points in the columns with sludge. The results showed that sludge sorped endosulfan and retarded its movement through the soil columns. According to Albarran, *et al.*, (2004), the vertical movement of simazine in handpacked soil columns was reduced in soil columns amended with olive-mill waste. Meanwhile, the effect of sludge on endosulfan movement would be more distinct if more endosulfan was added and the sampling period could be extended to more than 5 days.

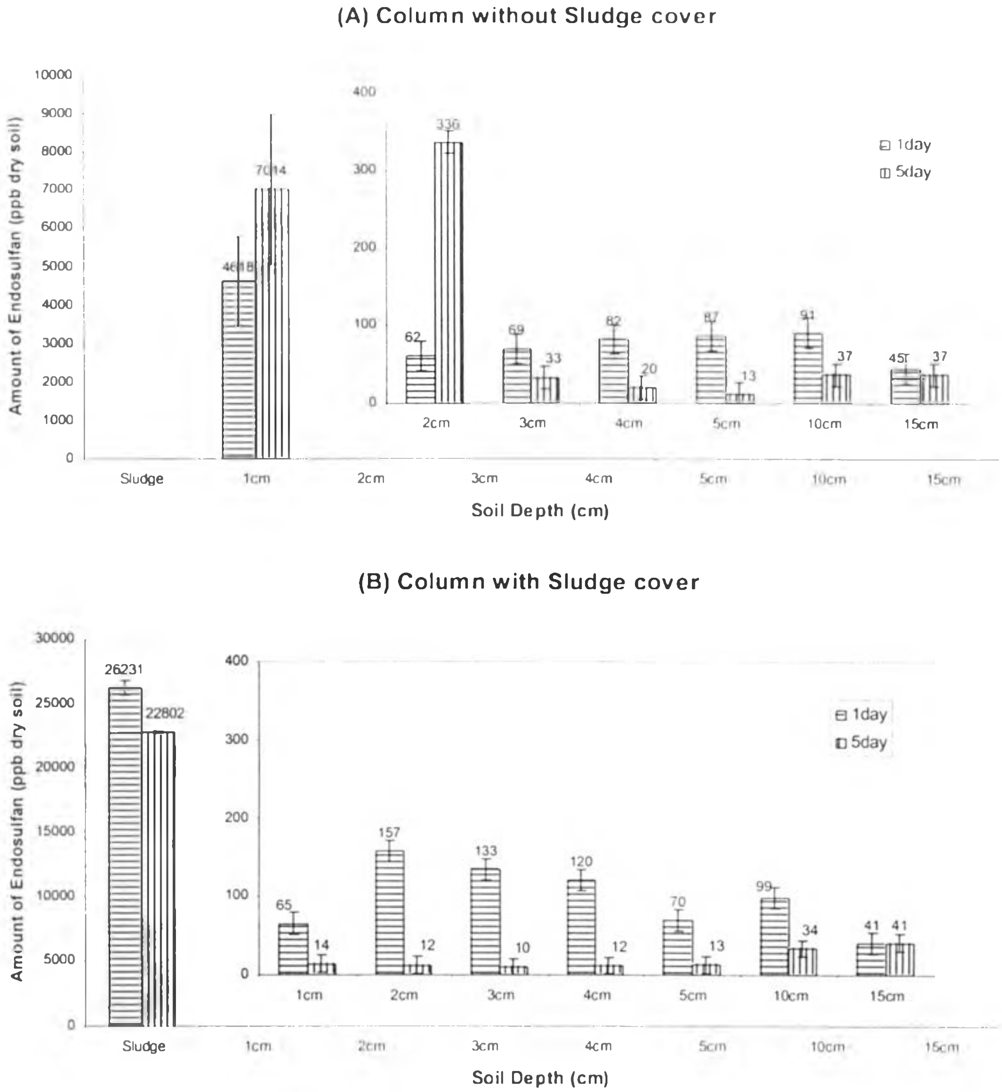


Figure 4.2 Amount of endosulfan in soil columns in preliminary study

During the study, the total concentrations of endosulfan in columns with sludge were more than 25,000 ppb, while less than 8,000 ppb of endosulfan was found in the columns without sludge. This was probably due to the loss of unsorped endosulfan via volatilization. Consequently, endosulfan would retain in the WWTS more than volatilize to the air. Kennedy *et al.* (2001), showed that up to 70% of endosulfan volatilizes from cotton fields in the first 5 days after application and 20-

30% of soil endosulfan residues were degraded by soil microorganisms. Guo *et al.* (1999) suggested that sorption might increase biodegradation as a whole by increasing the residence time of pesticides in the soil where most microbial activity occured. Therefore, we expected that the sorped endosulfan would slowly degrade by microorganisms from sludge and soil. Further study will be required to prove this hypothesis.

From the preliminary study, we found that soil columns with WWTS could retard the movement of endosulfan more than the columns without WWTS especially within the first 5 days after application. The next experiments were conducted by using triple amount of endosulfan to simulate the more serious scenario of pesticide application as well as to study the effectiveness of WWTS on endosulfan sorption. In this experiment, two main factors were considered; the frequency of pesticide application and the amount of WWTS used on top of soil columns.

4.3.2 Soil column experiment with single endosulfan application

In this experiment, single endosulfan application was used to represent the real activity of insects prevention in tangerine orchard. Normally, tangerine growers spray pesticide only after an infestation of insects. There were three treatments including columns without sludge cover, columns with 1-cm depth sludge cover, and columns with 2-cm depth sludge cover. The sludge here was wastewater treatment sludge from pig farm. Triple amount of recommended dose of endosulfan was applied to the soil column experiment only at the beginning of the study. The soil columns were poured with 30-mL of $CaCl_2$ solution at the first day and soil moisture content was maintained at 14% throughout the experiment.

After 35 days, the accumulation of endosulfan was mostly found in the top 0-7.5 cm depth of the control columns (Figure 4.3). The amounts of endosulfan were ranged from 3,243 to 10,327 ppb at 0-2.5 cm depth, 88 to 256 ppb at 2.5-5 cm depth, and 26 to 107 ppb at 5-7.5 cm depth. At 0-2.5 cm depth, the amounts of endosulfan were gradually decreased with time. On the other hand, the amount of endosulfan at 5-7.5 cm depth was increased after incubation. Endosulfan accumulated at this depth was probably due to the movement of endosulfan from the upper soil depths. This endosulfan probably desorped from sludge bound residues and leached out later.

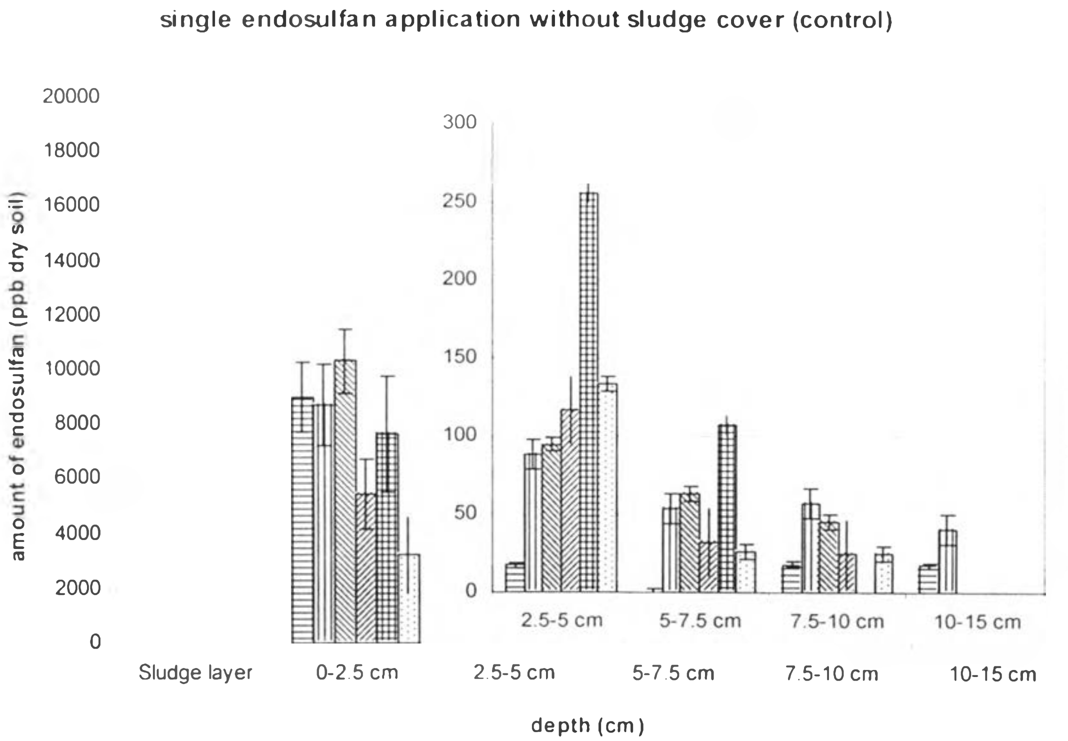


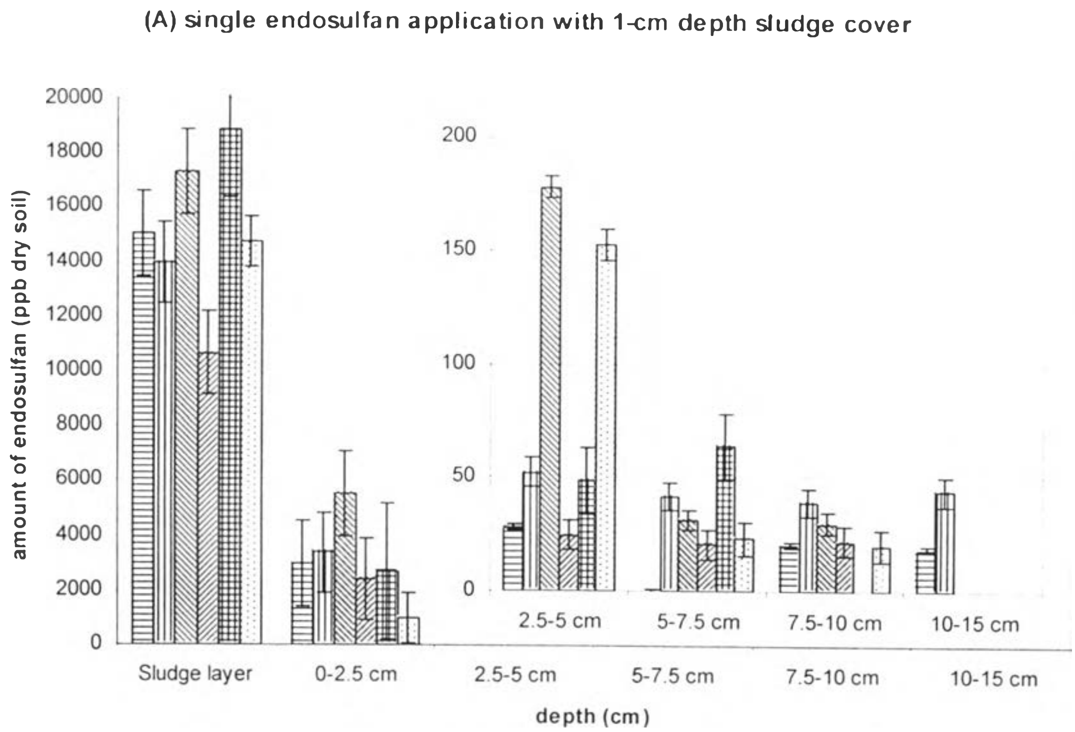
Figure 4.3 Amount of endosulfan in control column by single application

(0 day, 7 days, 14 days, 21 days, 28 days, 35 days)

Figure 4.4 showed the distribution of endosulfan in soil columns with 1-cm and 2-cm sludge depths. In the column with 1-cm depth of sludge, large amount of endosulfan was detected in sludge layer (10,661 to 18,851 ppb) (Figure 4.4A). Endosulfan was found at 0- 5 cm depth of these soil columns. At 0-2.5 cm depth, we found endosulfan at the range of 1,003 to 5,551 ppb. The amounts of endosulfan were gradually decreased after 14 days incubation. The accumulation of endosulfan was found at 2.5-5 cm depth and range from 25 to 178 ppb. The results showed that sludge sorped endosulfan and retarded its movement through the soil columns. Graber *et al.* (1997), found that retardation was observed to increase with the increasing of organic matter content, while desorption rate constant and the fast sorption sites decreased.

These processes result in greater sorption non-equilibrium. Consequently, we can conclude from this experiment that sludge could reduce the movement of endosulfan in the soil columns.

In the column with 2-cm depth of sludge cover, the results were showed in Figure 4.4B. In the sludge layer, the amounts of endosulfan were ranged from 8,152 to 14,737 ppb. Endosulfan was slighty showed in the 0-2.5 cm depth of soil column (ranged from 13 to 3,047 ppb). The results showed that endosulfan was found at lower depth (2.5-5 cm) in 1-cm depth of sludge column while the 2-cm depth of sludge column contained high amount of endosulfan at soil surface (0-2.5 cm depth). The 2-cm depth of sludge could reduce the movement of endosulfan better than 1-cm depth of sludge. In conclusion, the reduction of endosulfan contamination through the soil is the benefit of sludge cover. Beside pesticide sorption, sludge organic matter has seen to improve soil structure, reduce soil erosion and improve crop yield (Tester, 1990).



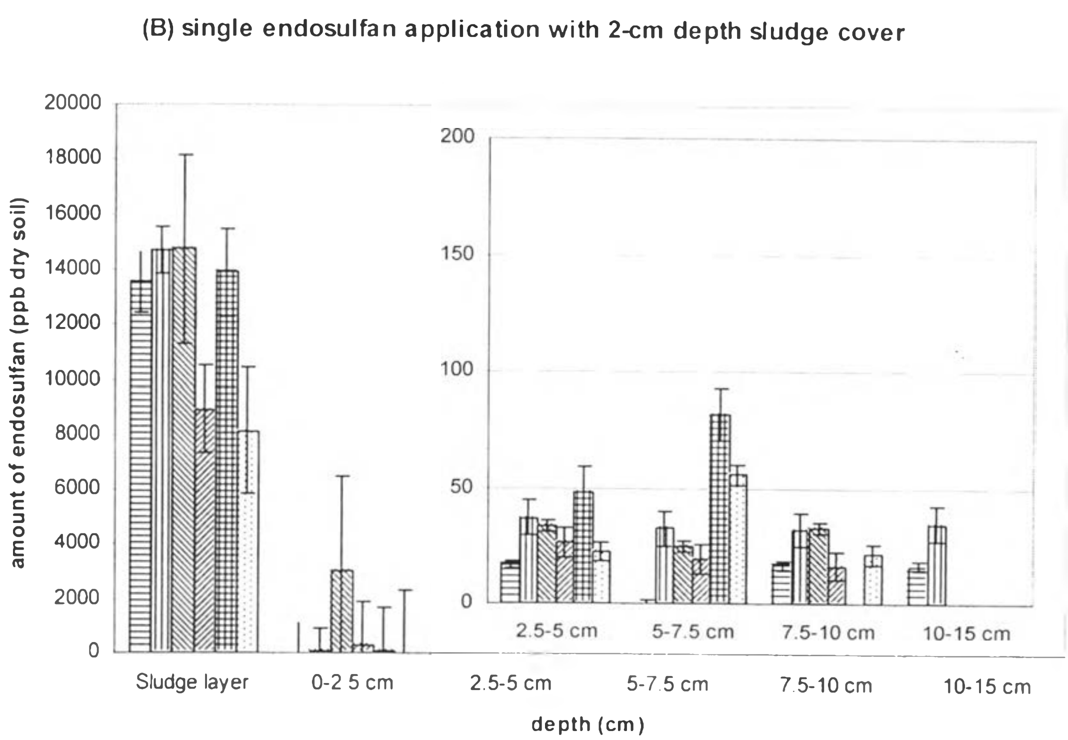


Figure 4.4 Amount of endosulfan in soil column experiment by single application

(▤ 0 day, ▥ 7 days, ▧ 14 days, ▨ 21 days, ▦ 28 days, ⬚ 35 days)

4.3.3 Soil column experiment with weekly endosulfan application

The weekly endosulfan application experiment was represented the worst case scenario of repeated pesticide application. The soil columns were set as three treatments; columns without sludge cover, columns with 1-cm depth sludge cover, and columns with 2-cm depth sludge cover by using wastewater treatment sludge from pig farm. Triple amounts of recommended endosulfan dose were applied weekly to the soil column experiment. The soil columns were poured with 30-mL of $CaCl_2$ solution at the first day and soil moisture content was maintain at 14% throughout the experiment.

Endosulfan was mostly found at the 0-5 cm depth of the control columns after 35 days (Figure 4.5). At the 0-2.5 cm depth, the amount of endosulfan was ranged from 14,100 to 34,080 ppb. During the first three week of applications, the amounts of endosulfan were increased after application. After that, endosulfan was reduced to 16,000 ppb and maintained at this level through the end of study. The reduction of endosulfan was probably due to volatilization and degradation by soil microorganisms. Enrichment of endosulfan degrading microorganisms may be occurred during the first three week of endosulfan applications. These microorganisms probably degraded only some of the added endosulfan thus certain amounts of endosulfan were still accumulated in the soil. From a study in cotton fields, indigenous plants or soil microorganisms were suggested to responsible for the degradation of 20-30% soil endosulfan residues (Kennedy *et al.*, 2001). At the 2.5-5 cm depth, 137 to 1,734 ppb of endosulfan was found. Comparison of single and weekly application, the accumulation of endosulfan in 2.5-5 cm depth in weekly application was higher than single application of endosulfan. According to Zhang *et al.* (1984), they reported an increase in the formation of bound residues after repeated application of pesticides.

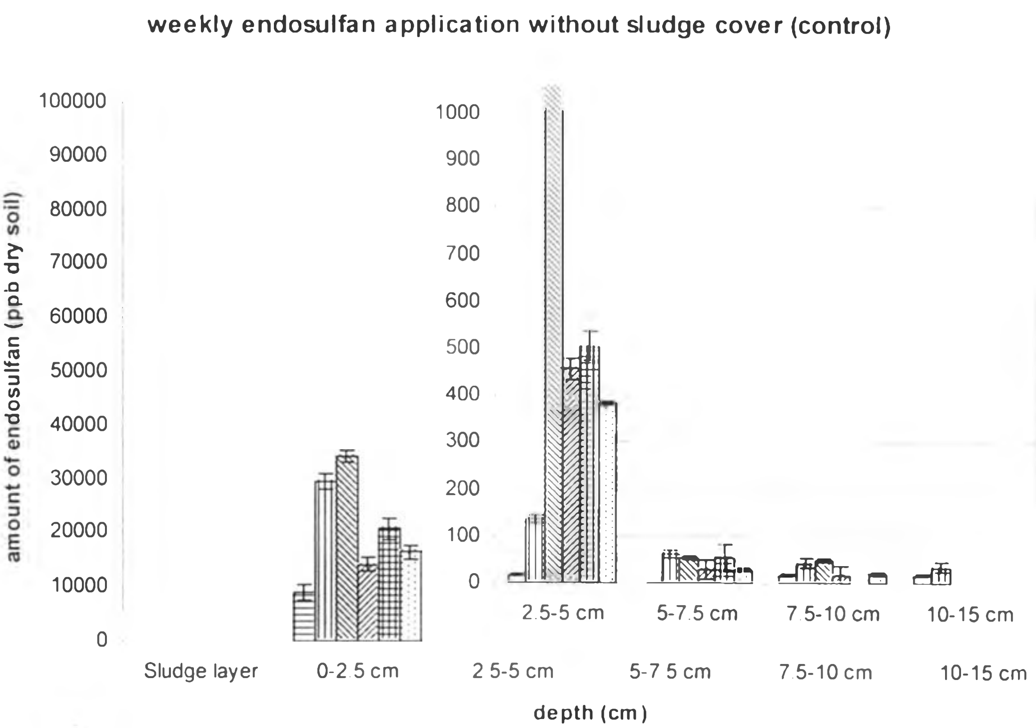
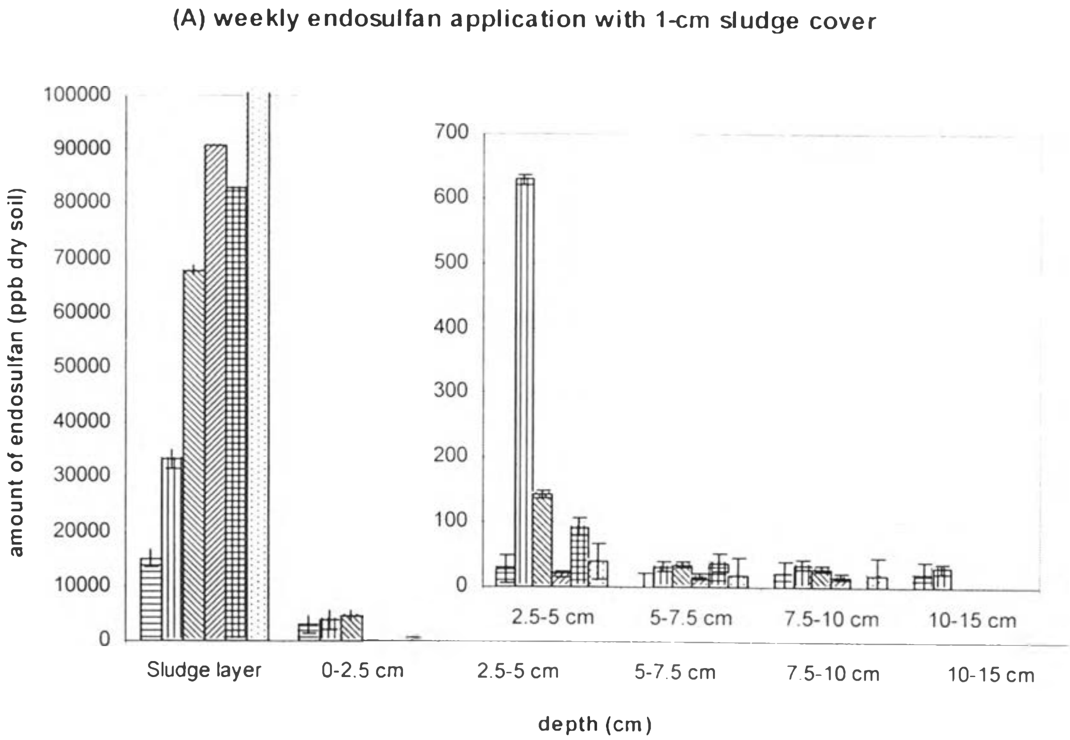


Figure 4.5 Amount of endosulfan in control column by weekly application

(0 day, 7 days, 14 days, 21 days, 28 days, 35 days)

Figure 4.6A showed the result of 1-cm depth sludge covered soil columns. The amount of endosulfan was highly sorped to the sludge layer. The amount of endosulfan was increasing with time and ranged from 33,409 to 107,775 ppb in this layer. In the soil layers, endosulfan was detected at 0-5 cm depth; in which 45 to 3,775 ppb endosulfan was found at 0-2.5 cm depth and 20 to 629 ppb endosulfan was found at 2.5-5 cm depth. Comparing with the same depth of control column, we found the accumulation of endosulfan in control column at depth higher than in 1-cm sludge covered columns. The results confirmed that sludge sorped endosulfan and retarded its movement through the soil columns.

In the column with 2-cm depth of sludge cover (Figure 4.6B), endosulfan was showed in sludge layer from 16,630 to 68,329 ppb and the 0-5 cm depth of soil column. The amount of endosulfan in sludge layer was increased with time. The amounts of endosulfan were ranged from 61 to 3,272 ppb in 0-2.5 cm depth and 20 to 270 ppb in 2.5-5 cm depth. The 2.5-5 cm depth of soil column showed the decrease of endosulfan with time. The results were probably due to the volatilization and degradation by soil microorganisms. We found that the contamination of endosulfan in each depth of 1-cm depth sludge covered columns is more than 2-cm depth sludge covered columns. It indicated that the thicker sludge layer had higher efficiency to retard pesticide movement.



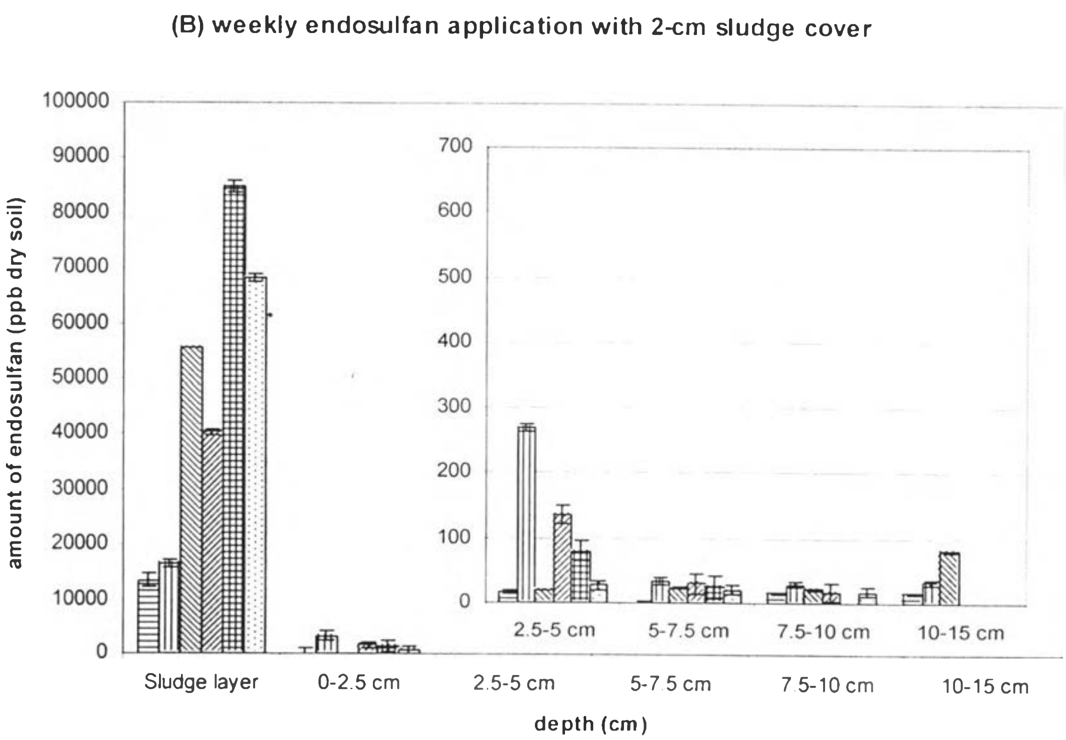


Figure 4.6 Amount of endosulfan in soil column experiment by weekly application

(▤ 0 day, ▥ 7 days, ▧ 14 days, ▨ 21 days, ▦ 28 days, ▢ 35 days)

The recommended amount of sludge as soil covering material from this experiment was therefore calculated from 2-cm depth sludge. We converted the amount of sludge for convenience use into Ton rai^{-1} unit. The details of calculation are;

Surface area of studied column	11.34	cm^2
Amount of 2-cm depth sludge	10	g
Weight of sludge per square meter	8.8	Kg
Weight of sludge per rai	14	Ton

The amount of sludge at 14 Ton rai^{-1} might seem too large for application. However, this amount was calculated from the results of our experiment, which applied triple amounts of endosulfan weekly. This pattern of pesticide application represented the worst case scenario. In real situation, we therefore recommended only 1/3 of the calculated amount, which was about 5 Ton of sludge per rai to prevent pesticide leaching.

4.3.4 Comparison of single and weekly endosulfan application

Comparison of single and weekly endosulfan application showed that endosulfan was accumulated more in columns with weekly application than single application. The movement of endosulfan in single application was higher than in weekly application. Zhang *et al.* (1984) suggested that repeated pesticide application led to an increase in the formation of bound residues. According to Zhang *et al.*

(1984), the low mobility of endosulfan in our soil columns would probably due to the bound residues of endosulfan bound that formed after application to sludge particles. Meanwhile, Samuel and Pillai (1991) suggested an opposite phenomena. They reported that repeated pesticide applications will accelerate pesticide dissipation and decelerate its binding. These may be due to particle size, temperature, dissolved organic matter, biodegradation, photodegradation, and volatilization. Long term studies are therefore required to elucidate the fate and transport process of endosulfan after application.