

Adsorption, Desorption and Mobility of s-Triazine Herbicides in Soils

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Abstract

Adsorption, desorption and movement of atrazine, ametryn, dimethametryn and simazine associated with their respective ¹⁴C-herbicides were studied for five commonly occurring soils of central Thailand; Bangkhen clay, Pakchong clay loam, Kampang Saen silty loam, Sattahip loamy sand and Nampong sand. Organic carbon contents of the soils by weight varied from 0.3 to 2.9% clay fractions ranged from 1 to 57%. The greatest amount of herbicides were adsorbed onto Bangkhen clay, followed by Pakchong clay loam, Kampang Saen silty loam, Nampong sand, and Sattahip loamy sand respectively, Adsorption of s-triazines onto soil were governed by amount and type of clays and organic matter. The average K value across soil types showed that dimethametryn was adsorbed in greatest amount, followed by simazine, ametryn and atrazine. All herbicides were desorbed in all soils. Atrazine and simazine were desorbed from Bangkhen clay and Nampong sand more rapidly than from other soils. Ametryn and dimethametryn were desorbed more from Bangkhen clay than other soils. The greatest movement of herbicides occurred in Sattahip loamy sand followed by Nampong sand, Pakchong clay loam, Kampang Saen Silty loam, and Bangkhen clay respectively. The most mobile herbicide was atrazine followed by simazine, ametryn, and dimethametryn.

Keywords : adsorption, desorption, mobility, triazine

Atrazine and ametryn are used mainly for weed control in corn, sugarcane, and pineapple plantations. Simazine is often used in corn, sugarcane, and fruit trees. Dimethametryn is normally used in rice and sugarcane cultivation. Information on the behavior of atrazine, ametryn, and simazine in soils of other countries is available, but little information is available on the behavior of dimethametryn in soils.

The chemical structure of the 4 herbicides are :

atrazine, 6-chloro-N-ethyl-N'-(1-methylethyl)-1, 3, 5-triazine-2, 4-diamine; ametryn, N-ethyl-N'-(1-methyl ethyl)-6-(methylthio)-1, 3, 5-triazine-2, 4-diamine; dimethametryn, N-ethyl-N'-(1, 2-dimethyl propyl)-6-(methylthio)-1, 3, 5-triazine-2, 4-diamine; simazine, 6-chloro-N, N'-diethyl-1, 3, 5-triazine-2, 4-diamine. Their properties are given in Table 1. Harris (1966) reported that there was greater adsorption of the methoxy- and methyl-

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Table 1. Properties of ^{14}C -s-triazines.

Herbicides	Specific activity	Label position	Water solubility (Anonymous, 1983)
	($\mu\text{Ci}/\text{mg}$)		(ppm)
Atrazine	27.2	ring	33.0
Ametryn	26.7	ring	185.0
Dimethametryn	13.9	ring	50.0
Simazine	17.6	ring	3.5

thio-derivatives of s-triazine herbicides than there was of the chloro-s-triazine derivatives, indicating a direct relationship between water solubility and adsorbability, but also that the methoxy- and methylthio-derivatives are more basic than are the chloro-derivatives. The type and number of alkyl groups in the 2- and 4- positions also influence the amount of adsorption. For a series of ethyl substituent compounds, as the alkyl groups were replaced by H atoms, adsorption decreased in the order: $(\text{C}_2\text{H}_5)_4 > (\text{C}_2\text{H}_5)_5 > (\text{C}_2\text{H}_5)_6$ (Weber, 1970). Therefore the 6-substituent determined the primary adsorption mechanism and that change in alkyl-groups in the 2- and 4- position also affected the basicity of compounds and hence the amount of adsorption.

The objectives of this study were to determine the adsorption-desorption and mobility of these herbicides in five commonly occurring soils of Thailand.

Materials and Methods

Five soils of Thailand (Table 2) were collected by random sampling of the 0-15 cm layer. Adsorption-desorption and mobility studied followed the methods of Peter and Weber (1985).

Table 2. Physical and chemical properties of five soils.

Soil types	Particle size distribution			pH	C.E.C. (mg/100 g)	Organic matter (%)
	Sand	Silt	Clay			
	(%)					
Bangkhen clay (Bangkhen Series)	17	26	57	5.6	25.7	2.9
Pakchong clay loam (Pakchong Series)	23	40	37	6.8	15.3	2.0
Kampang Saen silty loam (Kampang Saen Series)	57	34	9	5.6	4.2	0.7
Sattahip loamy sand (Sattahip Series)	81	14	5	5.2	1.2	0.6
Nampong sand (Nampong Series)	87	12	1	6.5	1.2	0.3

Adsorption-desorption experiments

The adsorptions of four ^{14}C -labeled s-triazine herbicides on the five soils (Table 2) were determined at room temperature ($28 \pm 2^\circ\text{C}$). One gram samples of soil were sieved through a 2 mm mesh sieve then weight in 10 ml screw top vials. Solution containing 2,000 dpm/ml of ^{14}C -herbicide was prepared in 0.01 M CaCl_2 , along with non-labeled herbicide at 4, 8, 12, 16 and 20 $\mu\text{g}/\text{ml}$, the concentration of the herbicide associated with its respective ^{14}C -herbicide. Aliquots (5.0 ml) of the herbicide solution were pipetted into the vials. The vials were capped and placed on a shaker for 24 hours. Preliminary studies showed that all chemicals reached equilibrium with soils after shaking for this time.

After shaking, the vials were centrifuged and a 1.0 ml aliquot of the supernatant liquid was placed in a scintillation vial with 4.5 ml of counting cocktail (60.09 naphthalene, 5.0 g PPO and 0.5 g POPOP per l of diexane).

The quantity of herbicide adsorbed was determined by calculating the difference between the initial herbicide concentration (dpm/ml) and the concentration present in the equilibrium solution after the herbicide was adsorbed onto the soil. K values were determined by using the Freundlich equation. Each treatment was replicated four times in a completely randomized design.

As the first step in the desorption study the equilibrium solutions were decanted from the weighed tubes, then the tubes reweighed. Sufficient 0.01 M CaCl_2 solution was added to each tube to achieve a 1:5 ratio between soil and solution after correction for interstitial solution. The tubes and contents were shaken again, centrifuged, then after a 24-h equilibration period, a 1 ml aliquot was removed and counted. Two desorptions were conducted, and treatment was replicated four times.

Mobility experiments

Soil thin layer chromatography plates (TLC) were prepared by mixing each soil (Table 2) with sufficient water to form a paste. Glass plates, 20 × 20 cm were partitioned into 4 × 20 cm columns, where soil paste was spread. After drying, four independent soil columns were obtained. Approximately 0.5 μCi of the four ^{14}C -labeled herbicides (Table 1) were applied to their respective columns on the soil TLC plates at 3.0 cm from the bottom. The plates were placed in a TLC developing tank containing water at a depth of 1.0 cm. The plates were left in the tank until the water saturated the soil column at least 15.0 cm up the plate. The movement of water from the point of herbicide application to the position of the wetting front was recorded and the plates were allowed to dry. The dry plates were exposed to X-ray film for 4 weeks to trace the movement of ^{14}C -labeled herbicides. The movement of herbicides were compared by determining

their retention factor (Rf). Rf values were calculated by dividing the distance of herbicide movement by the distance of water movement (solvent front). Each treatment was replicated four times.

Results and Discussion

Soil adsorption – desorption study

The amount of *s*-triazines adsorbed by the five soil is represented by K values (Freundlich isotherms) in Table 3. The Freundlich equation is written as $X/m = KC^{\frac{1}{n}}$, where X/m is the mass of herbicide adsorbed (microgram) per unit weight of adsorbent (gram), C is equilibrium concentration of herbicide in solution (microgram per milliliter), and K and $\frac{1}{n}$ are constants representing the intercept and slope isotherms respectively. The average K values across soil types indicated that the greatest amount of dimethametryn was adsorbed onto soil followed by simazine, ametryn, and atrazine (Table 3). Ametryn and dimethametryn are methylthio *s*-triazines and were reported by Harris (1966) to be adsorbed by clay particle more than the chloro-*s*-triazines, atrazine and simazine, because the substituent in the 6-position on the molecule has the greatest effect on the basicity of the compound. The more basic compounds are also generally adsorbed in greater amount than less basic compounds (Weber, 1970). Within the subclass of chloro-*s*-triazine, simazine was adsorbed more than atrazine, which might be explained by differences in water solubility between atrazine and simazine (Table 1). This result is similar to that of Nearpass (1967). For methylthio-*s*-triazines, dimethametryn was adsorbed more than ametryn, possibly because long chain alkyls are adsorbed more than short chain alkyls (Weber, 1970). Furthermore water solubility of ametryn was also higher than dimethametryn (Table 1).

Table 3. Freundlich K-values for herbicide adsorption onto five soils.

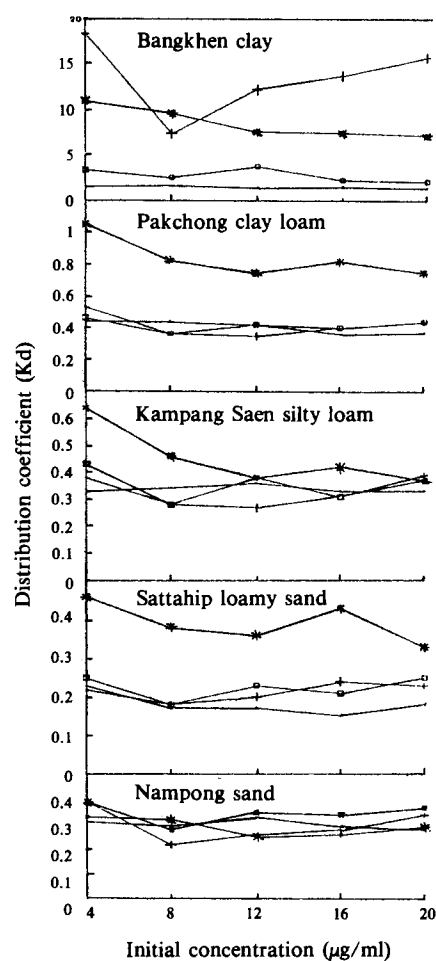
Soil types	Herbicides*				Mean*
	Atrazine	Ametryn	Dimethametryn	Simazine	
	(K)				
Bangkhen clay	0.98 a	1.19 a	8.56 a	3.46 a	3.55 a
Pakchong clay loam	0.52 b	0.54 b	0.45 d	0.45 b	0.49 b
Kampang Saen silty loam	0.34 c	0.36 c	0.81 b	0.43 b	0.48 b
Sattahip loamy sand	0.26 d	0.20 d	0.53 c	0.22 d	0.30 e
Nampong sand	0.33 c	0.36 c	0.39 e	0.35 c	0.36 d
‡ Mean	0.49 C	0.53 C	2.15 A	0.98 B	

* Means within a column followed by the same letter are not significantly different at the 5% level by DMRT.

‡ Means within the row followed by the same letter are not significantly different at the 5% level by DMRT.

The average K-value across herbicides showed that the greatest amount of herbicides were adsorbed by Bangkhen clay, followed by Pakchong clay loam, Kampang Saen silty loam, Nampong sand and Sattahip loamy sand (Table 3). But the percentage of clay and organic matter of Sattahip loamy sand were higher than those of Nampong sand (Table 2). Type and amount of clay and organic matter govern herbicide adsorption, and different organic matter fractions, and types of cation saturated onto soil fraction might also affect herbicide adsorption (Hayes, 1970).

The distribution coefficient (K_d) values were calculated by dividing the mass of herbicide adsorbed (microgram of herbicide per gram of soil) by the mass of herbicide in solution (microgram of herbicide per milliliter of water). K_d value of s-triazines in all soils were slightly decreased with increasing herbicide concentration (Figure 1). This finding demonstrated that the potential for herbicide leaching, particularly at a very high application rate.

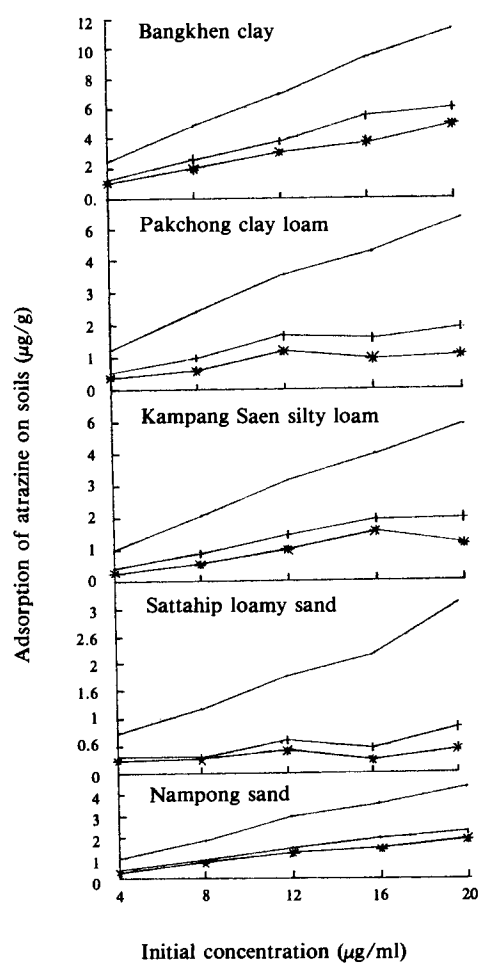


— Atrazine — Ametryn * Dimethametryn — Simazine

Figure 1. Distribution coefficient (K_d) of s-triazines in five soils.

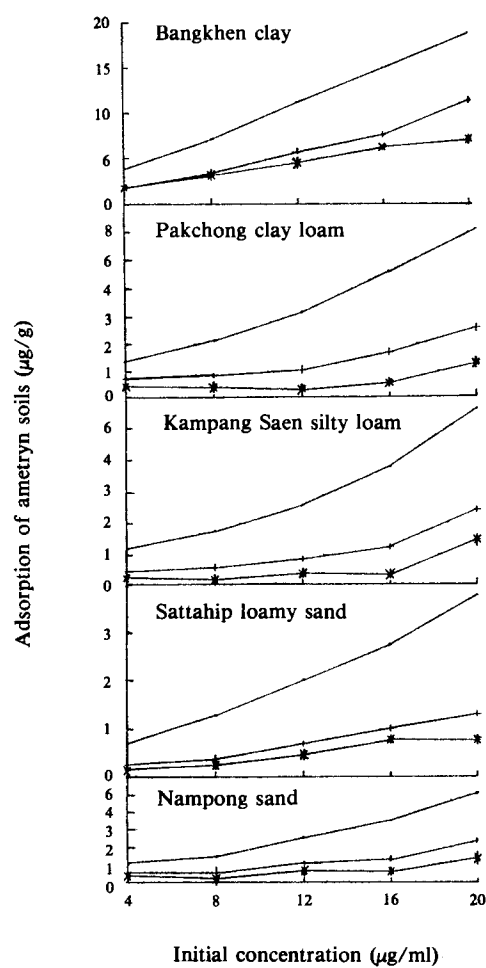
All herbicides were desorbed in all soils (Figures 2, 3, 4 and 5). The second desorption amount of atrazine and simazine were higher for Bangkhen clay and Nampong sand than other soils (Figures 2 and 5). However less atrazine and simazine were desorbed from Pakchong clay loam, Kampang Saen silty loam, and Sattahip loamy sand (Figures 2 and 5). Furthermore,

ametryn and dimethametryn were desorbed from Bangkhen clay more than other soils (Figures 3 and 4). This finding supported the previous result that herbicide properties, amount and type of clay particles including organic fractions in soil did not only affect herbicide adsorption, but also desorption.



—+— Adsorption —+— 1st desorption —*— 2nd desorption

Figure 2. Initial adsorbed atrazine on soil and the amount remaining after desorption.



—+— Adsorption —+— 1st desorption —*— 2nd desorption

Figure 3. Initial adsorbed ametryn on soil and the amount remaining after desorption.

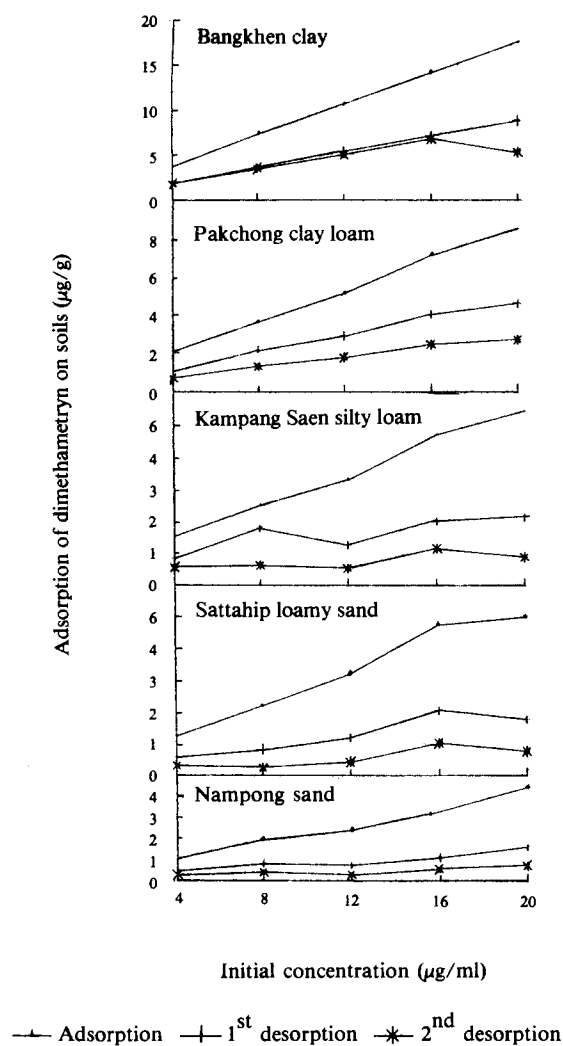


Figure 4. Initial adsorbed dimethametryn on soil and the amount remaining after desorption.

Mobility study

Herbicide mobility was influenced by soil types. The greatest movement of herbicides were occurred on Sattahip loamy sand followed by Nampong sand, Pakchong clay loam, Kampang Saen silty loam, and Bangkhen clay respectively (Table 4). However the organic matter and clay content of Sattahip loamy sand

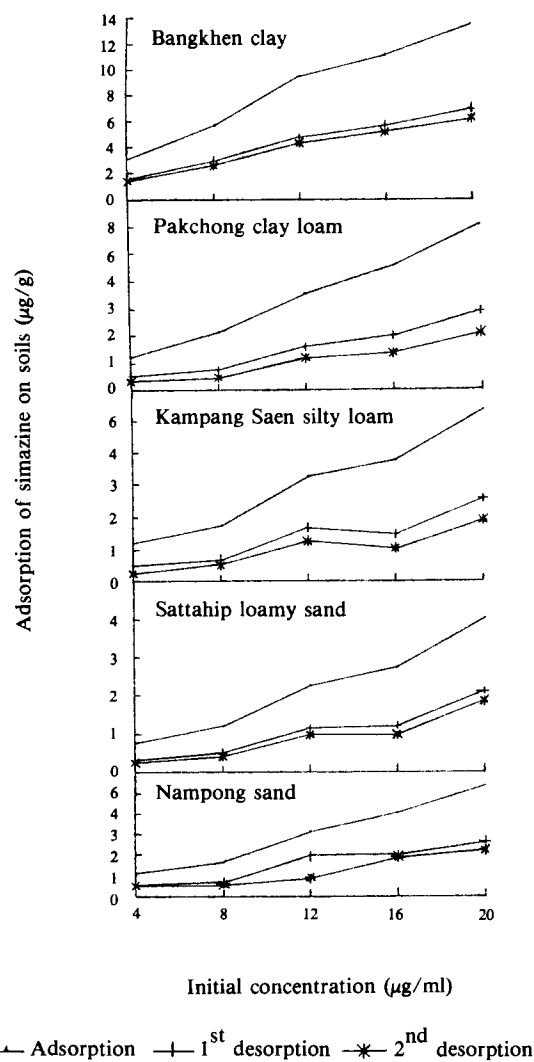


Figure 5. Initial adsorbed simazine on soil and the amount remaining after desorption.

were higher than of Nampong sand (Table 2). These results were coincided with the previous results which shown that s-triazines were adsorbed onto Nampong sand more than onto Sattahip loamy sand (Table 3). On average the most mobile herbicide was atrazine followed by simazine, ametryn and dimethametryn respectively (Table 4).

Table 4. The mobility of *s*-triazine herbicides in five soils as indicated by soil TLC Rf values.

Soil types	Herbicides				Mean *
	Atrazine	Ametryn	Dimethametryn	Simazine	
	(Rf)				
Bangkhen clay	0.30 d	0.10 d	0.16 d	0.19 e	0.19 d
Pakchong clay loam	0.49 c	0.36 b	0.22 c	0.39 d	0.37 c
Kampang Saen silty loam	0.50 c	0.33 c	0.25 c	0.40 c	0.37 c
Sattahip loamy sand	0.90 a	0.71 a	0.49 a	0.79 a	0.72 a
Nampong sand	0.76 b	0.31 c	0.36 b	0.52 b	0.49 b
‡ Mean	0.59 A	0.36 C	0.30 D	0.46 B	

* Means within a column followed by the same letter are not significantly different at the 5% level by DMRT.

‡ Means within the row followed by the same letter are not significantly different at the 5% level by DMRT.

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