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Dissipation of *s*-triazines and Thiocarbamates from Soil as Related to Soil Moisture Content*

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ABSTRACT

Half-lives ($t_{1/2}$) *of two soil incorporated* s-*triazine (atrazine and prometon) and two thiocarbamate (EPTC and triallate) herbicides were determined in relation to soil moisture content in two California soils. Treated soils were incubated at three moisture levels in aerated glass vials at 25 ± 1°C and were analyzed at 0, 7, 16, 28, 56 and 112 day intervals. Loss of herbicides in all treatments followed first-order kinetics. The* $t_{1/2}$*-values of all herbicides decreased with increasing soil moisture and followed an empirical equation,* $t_{1/2} = aM^{-b}$ *(where* $t_{1/2}$ *is half-life;* M *the moisture content; and* a *and* b *are*

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constants). Soil moisture had a greater effect on carbamates than on s-*triazines. Prometon exhibited the longest half-life in both soils, whereas EPTC was least persistent in one soil and atrazine in another. The* $t_{1/2}$*-values for atrazine, prometon, EPTC, and triallate with medium moisture levels and 10 μg/g concentration were 34·6, 43·2, 25·4 and 38·1 days in sandy loam and 26·5, 44·4, 44·1 and 25·9 days in loamy sand, respectively. Disappearance of 50% of the applied concentrations of most of the herbicide–soil combinations (except EPTC and triallate in one soil) took longer for lower initial concentrations (1 μg/g) than for higher concentrations (10 μg/g).*

INTRODUCTION

Soil moisture is an important variable determining the behavior of agrochemicals; for example, by controlling soil oxygen levels (Brock, 1970) and by providing microbial water requirements (Gray, 1970). Degradation of most organic chemicals intentionally or unintentionally applied to the soil decreases as soil moisture content decreases (Lee *et al.*, 1984; Yaron *et al.*, 1985; Ghani & Allbrook, 1986; Walker, 1987). In addition, their diffusion and volatilization rates are greatly affected by soil moisture (Spencer *et al.*, 1982; Glotfelty *et al.*, 1984).

Degradation half-life ($t_{1/2}$) is a major input parameter for models that predict the overall behavior of solutes in soil (Jury *et al.*, 1983; Walker, 1987; van Genuchten & Wagenet, 1989). Walker and co-workers (Walker, 1974, 1987; Walker & Barnes, 1981; Walker & Zimdahl, 1981) demonstrated that the correlation of pesticide half-life and soil moisture content follows the empirical relationship:

$$t_{1/2} = aM^{-b} \tag{1}$$

where $t_{1/2}$ is the half-life; M the moisture content; and a and b are constants. The present laboratory experiment was carried out to determine the degradation life ($t_{1/2}$) as a function of soil moisture content, for two *s*-triazine (atrazine and prometon) and two thiocarbamate (EPTC and triallate) herbicides using two soils varying in organic matter content and particle-size distribution.

MATERIALS AND METHODS

Herbicides

Four herbicides *viz.*, atrazine, [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine]; EPTC, [*s*-Ethyl dipropylthiocarbamate]; prometon, [2,4-bis-

TABLE 1
Selected Properties of Four Herbicides[a]

Herbicide	*Vapor pressure (Pa)*	*Vapor density (mg/litre)*	*Aqueous solubility (mg/litre)*	*Henry's law constant*	K_{oc} *(m³/mg)*
Atrazine	9·0 E−05[b]	8·0 E−06	33	2·5 E−07	54
Prometon	8·3 E−04	7·5 E−05	750	1·0 E−07	76
EPTC	2·8 E+00	2·2 E−01	370	5·9 E−04	196
Triallate	2·6 E−02	3·2 E−03	4	7·9 E−04	2 838

[a] Singh *et al.* (1990).
[b] 1·0 E−05 = $1{\cdot}0 \times 10^{-5}$.

(isopropylamino)-6-methoxy-*s*-triazine]; and triallate, [*s*-(2,3,3-trichloroallyl) diisopropylthiocarbamate] were used in this study. Analytical standards of the herbicides were obtained from the US Environmental Protection Agency, Research Triangle Park, NC. Relevant properties are given in Table 1.

Soils

Hanford sandy loam (HSL), (a coarse-loamy, mixed non-acid, thermic typic xerorthents) from the Moreno Experimental Farm of the University of California, Riverside, and Tujunga loamy sand (TLS), (a mixed, thermic typic xerosament) from Fontana, California, were selected as the test soils. The soils had not previously received EPTC or triallate applications. Surface bulk samples (0–15 cm) were air dried and passed through a 2 mm sieve. Selected physical and chemical properties of the soils are listed in Table 2.

TABLE 2
Important Properties of the Soils

Soil type	*Organic carbon (%)*	*pH (1:1)*	*CEC (cmol/kg)*	*Clay (<2 μm) (%)*	*Silt (2–50 μm) (%)*	*Sand (50 μm–2 mm) (%)*
Hanford Sandy Loam (HSL)	0·43	6·05	5·95	7·05	25·84	67·11
Tujunga Loamy Sand (TLS)	0·33	6·30	0·45	4·47	13·52	82·01

Treatments

The soils were prepared at three gravimetric moisture levels (M1, M2, and M3) *viz.*, 1, 2 and 4% for TLS, and 3, 6 and 12% for HSL. Soil moisture content batches were treated separately with the four herbicides at a concentration of approximately 10 μg/g (C2). M2 soils were also prepared with approximately 1 μg/g herbicide concentration (C1). All treatments were replicated twice and six vials (6 cm × 2·5 cm ID) for each replication were filled with 20 g soil subsamples. At 0, 7, 14, 28, 56 and 112 days one of the six vials was sacrificed from each replication.

Soil preparation

Soils at the two lower moisture contents, M1 and M2, were prepared in 2 kg batches in 5 litre wide-mouth glass bottles. A known amount of deionized water was sprayed on the soil over a 1-h period with regular tumbling to avoid sticking of the soil on the walls. Since it was not possible to prepare the M3 treatment by direct spraying, the water content was first adjusted to the M2 level, and then after applying the herbicides the additonal amount of water was added to individual treatment vials. After overnight equilibration, the soil from each moisture treatment was sub-divided into four 500 g lots and each lot sprayed with 25 ml of herbicide solution in acetone of appropriate concentration. For this purpose, the soils in 1 litre wide-mouth glass jars were sprayed in small increments with an atomizer attached to a dry N_2 cylinder. The soil was mixed by tumbling until all the organic solvent was evaporated.

The treated soils were further equilibrated for 12 h prior to the transfer of 20 g sub-samples to individual glass vials in duplicate. Each vial was covered with aluminum foil, containing five pin holes, and incubated at 25 ± 1°C. The incubation chamber was provided with three, 1-litre capacity beakers containing distilled water to generate approximately 50% relative humidity. The zero-interval samples, drawn directly from the 1-litre jar, were assumed to contain the initial herbicide concentrations. The vials for the 112-day period from each treatment were weighed initially and at 3–4 day intervals, and the lost water was replenished in all treatments by adding appropriate amounts of deionized water.

Extraction

At each time interval, 15 g of soil from each replicate of the four herbicide treatments was composited into one 60 g sample. This sample, containing the four herbicides, was extracted with 150 ml acetone:hexane (1:1) by shaking for 1 h on an end-to-end electrical shaker. The supernatant was filtered through a bed of anhydrous sodium sulfate. These steps were repeated twice by adding 100 ml solvent and shaking for 30 min. The extracted batches were combined and concentrated to 25 ml on a rotary flash evaporator. Using this method, recovery of all the herbicides was found to vary between 85–95%.

Analysis

All the extracts were analyzed using a Varian 3700 Gas Chromatograph equipped with NP and EC detectors. The column used for atrazine, prometon and triallate was 0·9 m × 2 mm ID, Ultrabond 20M on Carbowax 100/200 mesh (column temperature for each herbicide was 150, 180, 155°C, respectively) with NP detector (300°C). DB-Wax Megabore with the same liquid phase was used for EPTC (temperature 110°C) with EC detector (280°C).

RESULTS AND DISCUSSION

The data for percent residue recovered after various incubation times are presented in Table 3. The initial herbicide concentration for each treatment was considered to be 100%. The residue data were $\log_{10}$ transformed and subjected to linear regression analysis to calculate the degradation constant, k. The $t_{1/2}$-values for different herbicides under different treatments calculated by eqn (2):

$$t_{1/2} = \frac{0{\cdot}301}{k} \tag{2}$$

are presented in Table 4. Except for three combinations (atrazine with M2C1 in HSL, M3C2 in TLS and triallate with M2C2 in TLS), the r^2-values were greater than 0·91. In these three cases also the values were above 0·75. Further, eqn (1) was employed to correlate the $t_{1/2}$-values with the soil moisture contents of the two soils. The data fit the empirical equation and the values of the constants a and b for each herbicide–soil combination are given in Table 5.

The four chemicals exhibited different dissipation behaviors. Atrazine showed an apparent lag period of 14–28 days depending upon treatment (Table 3). This was followed by a phase of rapid loss which resulted in a cumulative dissipation being comparatively faster at higher moisture levels in both soils. The $t_{1/2}$ of 26·6 days in the HSL soil was significantly greater than 22·9 days in TLS. Similar atrazine behavior was reported by Armstrong

TABLE 3
Percentage of Each Herbicide Recovered after Various Incubation Intervals at 25 ± 1°C

Interval (days)	*HSL*				*TLS*			
	M1[a]*C2*[b]	*M2C2*	*M3C2*	*M2C1*	*M1C2*	*M2C2*	*M3C2*	*M2C1*
				Atrazine				
0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0
7	99·2	91·3	107·1	68·7	84·5	94·7	96·6	90·5
14	94·6	79·1	102·4	53·4	73·1	84·7	95·2	88·2
28	82·8	79·8	104·0	40·2	72·6	71·3	78·4	61·7
56	63·9	55·3	18·9	31·6	33·4	15·5	4·7	54·5
112	11·1	9·9	7·6	24·9	8·8	6·9	6·2	21·7
				Prometon				
0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0
7	68·8	84·9	97·7	93·5	87·6	102·2	98·9	97·4
14	67·4	82·4	95·2	76·4	96·9	107·1	102·1	101·9
28	53·3	76·1	82·5	47·2	78·3	81·3	76·2	90·4
56	40·3	35·4	35·7	43·1	41·7	31·8	33·2	84·9
112	25·3	17·3	16·5	28·3	18·4	21·9	19·4	29·6
				EPTC				
0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0
7	83·9	112·6	85·2	75·2	109·9	80·2	60·4	75·5
14	64·3	64·8	58·5	63·8	102·8	53·6	56·0	77·0
28	41·2	49·5	49·0	36·4	86·7	49·5	42·7	41·1
56	29·6	21·6	23·0	34·8	75·1	46·0	23·5	30·3
112	14·1	5·3	0·7	14·5	33·0	13·8	7·8	2·4
				Triallate				
0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0
7	78·0	92·3	80·6	100·0	75·6	74·9	80·0	82·6
14	62·4	94·6	85·9	66·4	70·0	82·1	75·0	99·7
28	70·4	93·8	75·3	63·1	64·9	72·9	66·4	68·6
56	40·4	69·5	15·8	21·3	55·9	19·7	5·7	19·0
112	18·0	12·4	6·4	16·7	14·8	8·7	7·5	7·6

[a] M1, M2, and M3 equals 3, 6, and 12% water in HSL and 1, 2, and 4% in TLS.
[b] C1 and C2 represent approximately 1 and 10 μg/g initial soil herbicide concentrations. The actual concentrations were assumed to be those recovered on Day 0.

and Chesters (1968) and Scott and Phillips (1972) who found increased atrazine diffusion with increased soil moisture level. Atrazine half-life of 40 and 50 days was reported earlier by Ghadiri *et al.* (1984) under tilled and untilled field plots, whereas in the laboratory, they reported 50% dissipation within 20 days. Half-lives of 23 and 20 days were also reported by Ivany *et al.* (1985) and Buchanan and Hiltbold (1973). Our $t_{1/2}$-values are consistent

TABLE 4
Half-life Values of Herbicides as Related to Water Content and Herbicide Concentrations

Herbicide	$t_{1/2}$ *(days)*							
	HSL				*TLS*			
	M1C2[a]	*M2C2*	*M3C2*	*M2C1*	*M1C2*	*M2C2*	*M3C2*	*M2C1*
Atrazine	36·7	34·6	26·6	64·0	32·1	26·5	22·9	51·9
Prometon	63·1	43·2	40·0	62·6	44·2	44·4	42·6	64·2
EPTC	40·7	25·4	16·2	43·6	66·9	44·0	32·7	21·6
Triallate	48·2	38·1	26·3	41·6	44·9	30·5	25·9	27·9

[a] See footnotes Table 3.

with these reports. The sudden rise in degradation rates after the lag period may be attributed to build up of herbicide-degrading microbial populations (Obien & Green, 1969).

Prometon exhibited a lag period of about 14 days in both soils. In HSL, it persisted longer at low moisture levels. However, in TLS no moisture content effects were observed, perhaps because of experimental errors. Higher dissipation at higher moisture levels may be associated with higher diffusion rates (7-fold) as reported by Scott and Phillips (1972).

EPTC dissipation rate tended to decrease with time in most treatments (Table 3). EPTC probably volatilized rapidly during the first few days after application (Cliath *et al.*, 1980; Lee *et al.*, 1984; Ghani & Allbrook, 1986) and hence, volatilization could have overshadowed degradation losses during any initial lag period. Degradation flux was higher at higher soil moisture contents (Table 4). Higher moisture contents are reported to increase EPTC

TABLE 5
Relationship Between Herbicide Half-life ($t_{1/2}$) at 10 μg/g Soil Concentration and Soil Water Content (*M*) as expressed by Eqn (1)[a]

Herbicide	*HSL*			*TLS*		
	r^2	*a*	*b*	r^2	*a*	*b*
Atrazine	0·909	46·82	0·2123	0·996	31·86	0·2431
Prometon	0·934	86·17	0·3294	0·811	44·533	0·0259
EPTC	0·999	94·35	0·6655	0·995	65·54	0·5158
Triallate	0·992	79·82	0·4379	0·973	43·214	0·3962

[a] $t_{1/2} = aM^{-b}$.

degradation because of increased microbial activity (Fang *et al.*, 1961; Obrigawitch *et al.*, 1982). Irrespective of moisture levels, EPTC persisted longer in TLS than HSL, probably because of its higher organic carbon (Anderson, 1984; Sarathchandra *et al.*, 1984; Ghani & Allbrook, 1986). Our $t_{1/2}$-values for EPTC are in agreement with those reported by Lee *et al.* (1984) in stored soils without any previous EPTC exposure.

Triallate losses during the first 7 days were fairly high in all treatments. Since triallate degrading microbes usually take some time (lag period) to build up their populations, the initial high losses may be due to volatilization as triallate has a relatively high Henry's constant ($7{\cdot}9 \times 10^{-4}$). A similar early trend of dissipation by volatilization was reported by Jury *et al.* (1980) and Grover *et al.* (1988). Half-life for triallate decreased as soil moisture content increased for both soils (Table 4).

The herbicides were more persistent when applied at lower concentrations except the thiocarbamates in TLS soil. In other words, the $t_{1/2}$-values for the herbicides were generally greater when applied at 1 μg/g than when applied at 10 μg/g concentration (Table 4). It had been earlier reported that it may take longer for one-half of a chemical to disappear at lower concentrations (Hamaker, 1972).

The $t_{1/2}$-values and soil moisture levels were found highly correlated (Table 5). The magnitude of the '*b*' constant for each herbicide indicates the moisture dependence of its dissipation rate. The carbamate herbicides (EPTC and triallate) were affected more by changing soil moisture content than were the *s*-triazines. This correlation for a particular soil–herbicide combination can be used to predict variations in persistence that may occur in the field with changes in soil moisture content. Hence, half-life values through eqn (1) should be generated for many herbicides to improve predictions from pesticide behavior models. Similar to observations of Yaron *et al.* (1985) and Walker (1987), we did not find any association of $t_{1/2}$-values with physico-chemical properties of the two soils.

There exists a controversy over the assumption that degradation proceeds only in the liquid phase because the adsorbed phase may not be available for degradation (Moyer *et al.*, 1972; Marshman & Marshall, 1981; Scott *et al.*, 1983; Ogram *et al.*, 1985). Current evidence indicates that degradation rates in the sorbed phase are generally lower than those in the liquid phase (van Genuchten & Wagenet, 1989). Consequently, conditions that facilitate increased adsorption should lead to overall lowered degradation rates. One such condition is realized by lowering herbicide concentrations. Since the exponent of the Freundlich Isotherm is less than one for these herbicide–soil combinations (Singh *et al.*, 1990), lowering the concentration effectively leads to stronger sorption which, in turn, could result in lowering the overall degradation rate. Our data are consistent with this hypothesis.

In summary, degradation of the herbicides followed first-order kinetics and their disappearance was faster at higher soil moisture levels. Half-life of carbamates in these soils was more affected by soil moisture content than that of the *s*-triazines. Prometon exhibited the longest half-life in the two soils, whereas, EPTC in HSL and atrazine in TLS were least persistent. The half-lives of the herbicides were greater at low initial application dose except for EPTC and triallate in TLS.

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