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Dissipation of Three s-Triazine Herbicides, Atrazine, Simazine, and Ametryn, in Subtropical Soils

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In a collaborative experiment on persistence of simazine (2-chloro-4,6-bis(ethylamino)-*s*-triazine) in soil, the residue of simazine was measured in fields from 21 sites located in 11 countries, the rate of simazine degradation was attributed to soil temperature and moisture content (Walker *et al.* 1983). Khan *et al.* (1981) reported half-life for disappearance to be approximately two mon for atrazine (2-chloro-4-isopropylamino-6-ethylamino-*s*-triazine) over the first six mon (during the months of late spring, summer and early fall) after application. Frank and Sirons (1985) showed that breakdown of atrazine in the field appeared slower under winter than summer conditions; in the field-monitored samples in Canada they found that the half-life dissipation appeared to be 1.4 mon in the summer increasing to 3-4 mon in the winter. The influence of climate and soil properties on the degradation of simazine in soils has been studied in our previous work (Chen *et al.* 1983).

Here, we describe a comparison of the persistence of three *s*-triazine herbicides--atrazine, simazine and ametryn (2-methylthio-4-ethyl-amino-6-isopropylamino-*s*-triazine) under various soil temperatures and moisture contents in subtropical soils.

MATERIALS AND METHODS

Atrazine and ametryn used in this experiment were provided by Cyanamid Taiwan Corporation as a commercial product of 50 and 80% wettable powders, respectively. Simazine is a product of Ciba-Geigy, Japan, formulated as a commercial product of 50% wettable powder by Kumiai Chemical Industry Co., Ltd., Japan. Pure herbicides (mp 175 °C for atrazine, 227 °C for simazine and 85 °C for ametryn) for reference standards were obtained by extracting the commercial product with

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chloroform and recrystallizing from hexane. The soil used in the laboratory experiments was collected from the Experimental Farm of Taiwan Agricultural Research Institute, Wufeng, Taichung, and the upland fields of Tucheng near Ta-han River, Taipei prefecture. Soil samples were located in the subtropical area (around the latitude 24° N); their physicochemical properties are shown in Table 1.

Table 1. Physicochemical properties of the soils

Location	pH	Field	Mechanical analysis				Organic
	(1:1)	capacity (%)	Clay (%)	Silt (%)	Sand (%)	Texture	matter(%)
Taipei	4.4	10.87	15.6	25.1	59.3	Sandy loam	2.14
Taichung	4.9	28.69	30.8	26.7	42.5	Clay loam	1.45
Taichung	6.5	21.67	21.8	46.2	32.0	Loam	0.94

In laboratory experiments, the collected soils were passed through a 2-mm sieve, and were dried in air at ambient temperature for one day. Then 6.9 kg of each soil was divided into three groups for three herbicide tests. In each group, 2.3 kg of soil was treated with herbicide of commercial product as a wettable powder suspended in water (20 mL) to give a concentration of 4 μ g ai/g dried soil. The treated soil was mixed by passing through a 2-mm sieve several times. The samples were then stored at 4 ℃ in polyethylene bags for 24 hr while duplicate 10 g subsamples were dried at 105 ℃ for determination of the moisture content. Then, 20 g (dried weight basis) of each sample was weighed into small polyethylene bags. Sufficient water to bring the soil to 90% field capacity was added to 64 (4x8x2) small bags and sealed. The bags were incubated separately at four temperatures (10, 20, 30 and 40 ℃) in equal amounts and sampled for analysis eight times (at 0, 3, 7, 14, 28, 56, 84 and 112 d) in duplicate bags. The other 48 (3x8x2) small bags were incubated at 20 ℃ but at soil moisture levels 60, 40 and 20% of field capacity. Total bags of (64+48)x3x3 were made by three soils treated with three herbicides. The bags were weighed at two-wk intervals and water was added when necessary. After sampling, the soil (20 g) was extracted with 80% methanol (50 mL) in a rotary shaker for 1 hr, and filtered, and the residue washed with 80% methanol (2x25 mL). The filtrates were combined and concentrated to dryness at 70 ℃ on a rotary evaporator, dissolved in chloroform (2 mL), and passed through an Al_2O_3 column (6 g, 1.2x15 cm) and then washed with hexane (50 mL). The hexane eluate was discarded and the column was eluted with chloroform (75 mL). The chloroform eluate was collected, and concentrated to dryness, and the residue dissolved in benzene for GC analysis.

ECD gas chromatography was performed with a Varian 3700 Gas Chromatograph equipped with a CDS 111 Integrator and a Varian

Model 9176 Recorder. A glass column (2 m x 2 mm id) packed with equal proportions of the mixture of 2% SE-30 and 3% QF-1 coated on 100/200 mesh Chromosorb G-HP was employed. Operating temperatures were as follows, injection port and detector 240 ℃, column 200 ℃. Nitrogen at a flow rate of 40 mL/min was used as a carrier gas.

Field experiments were performed at the Experimental Farm of Taiwan Agricultural Research Institute, Wufeng, Taichung, in the winter from Nov. 1989 to Mar. 1990 (16 wk). Sixteen plots (four each) were treated with 50% atrazine, 50% simazine, 80% ametryn wettable powder (at rates 2, 2, 1.25 kg ai/ha, respectively) and control. The control plots were hand weeded. The size of each plot was 1.5 m x 5 m. Meteorological data such as temperature and precipitation in the Taichung area during the experimental period were also collected (Table 2, summarized). The treated plots were sampled by 15 cores per plot of 1.5 cm to a depth 10 cm by random sampling. The cores from each plot were mixed and passed througha 2-mm sieve. The soil was stored at -10 ℃ while awaiting chemical analysis. First sampling was made within 60 min after treatment. Similar samples were taken at 3, 7, 14, 28, 56, 84 and 112 d after application. Subsamples of the bulk sample from each plot were analyzed in duplicate.

Table 2. Meteorological data in the Taichung area during the experimental period

Month	Temperature (℃)			Precipitation	
	Max. (daytime)	Min. (night)	Monthly average	Rainday (d)	Rainfall (mm)
Nov. 1989*	27.6	8.3	19.48	1	4.0
Dec. 1989	25.7	7.7	16.96	6	59
Jan. 1990	28.1	9.0	17.49	10	22
Feb. 1990	28.2	9.8	19.09	8	57.5
Mar. 1990**	21.0	11.7	14.49	5	27

*Nov. 15 to 30, 1989. **Mar. 1 to 7, 1990

RESULTS AND DISCUSSION

The recovery in this experiment performed by extracting with 80% methanol, which was proved to be the most efficient solvent (Cotterill 1980), averaged about 92, 93 and 92% for atrazine, simaznie and ametryn, respectively. The residues of atrazine, simazine and ametryn in three different soils with various moisture contents and varied temperatures during the designated period after treatment were measured. We found about 50 to 60% of atrazine residues in three soils until 112 d incubation under lower soil moisture content and lower temperature (20% of field capacity and 20℃). After 112 d, residues decreased gradually as the test conditions of moisture content and temperature rose in the experiment. Atrazine residues showed to be almost negligible under 90% of field capacity and 40 ℃. Similar tendencies were found for simazine and ametryn. Degradation of herbicide in the different soils was assumed to follow first-order kinetics (Walker 1976a; 1976b). The dissipation coefficient and the first-order half-lives of the three herbicides in these soils were calculated by liner regression equation, and is shown in Table 3. As discussed by Hurle and Walker (1980) and Walker *et al.* (1983), soil is a complex chemical and biological medium and factors that influence degradation may vary during the course of extended incubation experiments. Taichung clay loam in this work is exactly the same as the soil in the previous work (Chen *et al.* 1983), but soil samples were collected after a ten-yr interval. The half-life of simazine showed deviation from 340 d (present) to 66 d (previous) under the condition of 20% field capacity and 20℃, although no significant variation was found under other test conditions. A significant relationship was found between the temperature and the residue of herbicide in soil, and also a positive tendency was observed between soil moisture content and degradation. The results showed that higher moisture content and higher temperature lead to rapid dissipation of the herbicide. Temperature seems to play the more important role than moisture content in the effect on the dissipation coefficient. Kaufman and Kearney (1970) reported that major chemical hydrolysis occurred for the degradation of atrazine and simazine having a Cl-C linkage in the chemical structure. Whereas ametryn, a compound with a CH_3S-C linkage, principally undergoes microbial degradation. In the results in the present work, the variation of half-life for atrazine and simazine showed more obviously than that of ametryn when the soil moisture content was increased from 20 to 40% of field capacity, but no obvious difference was found at soil moisture content higher than 40% of field capacity. That atrazine showed a more rapid rate of degradation than simazine in all tests under the same conditions and may be attributed to their water solubility (33 ppm for atrazine and 5 ppm for simazine).

The effect of temperature on the degradation of atrazine and simazine was more marked than that ametryn, explaining the effect of temperature on chemical hydrolysis occuring prior to biodegradation. According to Walker *et al.* (1983), the influence of soil moisture content on herbicide degradation rate is characterized according to an empirical equation $H=AM^{-B}$, in which H is the half-life (d) at moisture content M (%, w/w) and A and B are parameters. Regression analyses with the half-life against the soil moisture content yield the parameters A and B and their sq r shown in Table 4. The results show that A and B values are in the order simazine>atrazine>ametryn in Taichung clay loam and Taichung loam, but in the Taipei sandy loam the order is

Table 3. Dissipation coefficient and half life of atrazine, simazine and ametryn in three soils under different moisture contents and temperatures

% of FC*		20	40	60	90	90	90	90
Temp. ℃		20	20	20	10	20	30	40
Herbicide	Soil**	Dissipation coefficient K (×0.01/d) <Half life, (d)>						
Atrazine	SL	0.60 <115>	0.82 <85>	1.10 <63>	0.80 <87>	1.19 <58>	3.56 <19>	5.45 <13>
	CL	0.71 <98>	1.28 <54>	1.41 <49>	1.01 <69>	1.64 <42>	3.68 <19>	5.69 <12>
	L	0.62 <115>	0.76 <91>	1.11 <62>	0.90 <77>	1.15 <60>	2.03 <34>	2.95 <24>
Simazine	SL	0.66 <106>	0.71 <97>	0.84 <82>	0.48 <146>	1.18 <59>	2.70 <26>	3.79 <18>
	CL	0.20 <341>	0.73 <95>	0.86 <81>	0.54 <129>	1.40 <49>	2.96 <23>	3.91 <18>
	L	0.40 <173>	0.65 <106>	0.85 <81>	0.52 <133>	1.00 <70>	1.56 <44>	2.11 <33>
Ametryn	SL	0.75 <92>	0.90 <77>	0.97 <71>	0.95 <72>	1.04 <67>	1.20 <58>	1.49 <47>
	CL	0.78 <89>	0.83 <84>	0.94 <74>	1.09 <64>	1.26 <55>	1.76 <39>	1.94 <36>
	L	0.73 <95>	0.86 <81>	0.97 <72>	1.00 <69>	1.41 <49>	1.85 <37>	2.61 <27>

*FC: Field capacity. ** SL: Taipei sandy loam; CL: Taichung clay loam; L: Taichung loam.

Table 4. Parameters of three herbicides fitted to equation $H=AM^{-B}$ and activation energy calculated from Arrhenius equation

Parameter	Herbicide	Taipei sandy loam	Taichung clay loam	Taichung loam
A	Atrazine	197	306	290
	Simazine	165	310	576
	Ametryn	107	150	183
B	Atrazine	0.59	0.68	0.58
	Simazine	0.41	1.31	0.74
	Ametryn	0.22	0.29	0.41
r^2	Atrazine	0.97	0.93	0.93
	Simazine	0.82	0.96	0.99
	Ametryn	0.99	0.81	0.87
Activation energy ($KJ\ mol^{-1}$)	Atrazine	57.8	72.5	51.1
	Simazine	63.8	76.5	54.9
	Ametryn	12.9	15.1	24.4

atrazine>simazine>ametryn. The smaller value of A and larger value of B showed an easier influence on the degradation of herbicide. In the soil of greater moisture content, the value of B affects the degradation more intensely than the value of A. In contrast, the coefficient B has only a little effect on the degradation of herbicide in drier soil. In combination of $H=AM^{-B}$ with the Arrhenius equation, $\log H_1/H_2 = E(1/T_1 - 1/T_2)/4.575$, in which H_1 and H_2 are the half-lives at temperatures T_1 and T_2, and E is the activation energy, together with the first-order rate law, the prediction of the degradation of herbicide in the field seemed more reasonable. The activation energies of the three herbicides on three soils are shown in Table 4. The activation energy for simazine was calculated to be 63.8, 76.5 and 54.9 KJ mol^{-1} for Taipei sandy loam, Taichung clay loam and Taichung loam, respectively, which are close to the data obtained by Walker (1976b) for simazine with 61.5 KJ mol^{-1}. The activation energies of the three herbicides on the same soil have the order, simazine>atrazine>ametryn. With a larger activation energy, more obvious differences in the half-life are found when the temperature changes. The chemicals with smaller activation energy are decomposed easily relative to that of a greater activation energy because the chemical forms an activated complex compound more easily in the process of chemical decomposition or biodegradation.

The residues of atrazine, simazine and ametryn in the Taichung loam at designated intervals during the field experiment are listed in Table 5. Regression analyses with the logarithms of residue against time showed a value of sq r greater than 0.91. The dissipation coefficient followed first-order kinetics (K) and the first-order half-lives (H) in the soil are also shown in the Table 5. The results show that the dissipation coefficient was much greater than that from the laboratory test (Table 3); the

Table 5. Persistence of three herbicides in field experiment in Taichung loam and their dissipation coefficient K and half-life H

Sampling days	Residue (%)		
	Atrazine	Simazine	Ametryn
0	100	100	100
3	79	88	82
7	61	60	10
14	40	49	8.37
28	18	21	7.88
56	3.66	3.37	0.43
84	3.14	1.44	0.01
112	1.57	0.77	ND*
K ($\times$0.01/d)	4.23	4.83	10.70
H (d)	14.4	16.4	6.5

*ND : Not detected.

Table 6. Persistence of three herbicides in Taichung loam simulated with laboratory parameter and meteorological data

Days	Residue (%)		
	Atrazine	Simazine	Ametryn
0	99.9	99.9	99.9
5	93.2	94.7	94.2
10	87.6	90.7	89.3
20	79.1	84.2	80.9
30	72.1	78.9	73.9
60	50.3	59.9	52.8
90	36.7	47.5	38.9
110	28.5	39.2	30.8

persistence orders are, simazine>atrazine>ametryn. For the dissipation coefficient and the activation energy obtained from the laboratory experiment, together with the soil temperature and moisture content which were simulated by meteorological data (Linacre, 1977; Walker and Barnes, 1981), the persistence of the three herbicides are simulated as shown in Table 6. The predicted values are much greater than the observed values (Table 5). This effect is attributed to photodecomposition of herbicide in the field and erosion by wind and water during the experiments. The parameters found from the laboratory test seem unable to predict directly the field dissipation of herbicide in the subtropical soil.

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