

soil extracts, it is not clear whether oxidation will also occur in the soil. In any case, arsenite will not be found in soil samples as long as ammoniacal solutions are used for soil extraction. Therefore, there is no need to clean up soil extracts on TLC to separate CA from arsenite.

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## Ionization and Adsorption-Desorption of Tricyclazole by Soil Organic Matter, Montmorillonite Clay, and Cape Fear Sandy Loam Soil

Jerome B. Weber

Aqueous solutions of tricyclazole (5-methyl-1,2,4-triazolo[3,4-*b*]benzothiazole) were spectrophotometrically titrated to obtain a  $pK_a$  of 1.6. The fungicide was adsorbed by Ca-montmorillonite and Cape Fear sandy loam in substantially greater amounts than prometryn [2,4-bis(isopropylamino)-6-(methylthio)-*s*-triazine] and in lesser amounts than prometryn by Ca-organic matter from deionized water. Adsorption isotherms for tricyclazole by the adsorbents were of the S type, C type, and L type, respectively. In 0.01 M buffer solutions at pH 6.0, 4.0, and 2.0, tricyclazole was adsorbed in substantially greater amounts than prometryn by all adsorbents. Adsorption increased greatly as pH decreased. Water effectively desorbed from 17 to 44% of bound tricyclazole from Ca-organic matter and Cape Fear soil but removed only 1-6% from Ca-montmorillonite. Desorption with 0.01 M paraquat(2+) greatly increased displacement of tricyclazole and confirmed the postulated ionic adsorption at low pH levels. Prometryn was more readily desorbed than was tricyclazole. Adsorption mechanisms are postulated and discussed.

Rice blast disease, caused by the fungus *Piricularia oryzae* Cav., is the most serious disease of rice in the world (Parthasarathy and Ou, 1965). The rice blast pathogen infects rice at all stages of growth, and thus the plants must be protected through most of their growth period. Tricyclazole (5-methyl-1,2,4-triazolo[3,4-*b*]benzothiazole) is a new systemic fungicide reported to provide long-term control of rice blast disease when applied as a foliar spray, seed coat treatment, soil drench, or as a transplant bare-

root soak treatment (Froyd et al., 1976, 1978). Tricyclazole is readily absorbed by plant roots, translocated to leaves, and provides residual disease control after a single soil or foliar application.

Tricyclazole is a heterocyclic compound which probably has weakly basic properties similar to those of other triazoles and thiazoles (Acheson, 1976). The objectives of this study were to (1) determine the ionization constant of tricyclazole, (2) measure the adsorption of tricyclazole relative to that of the herbicide prometryn [2,4-bis(isopropylamino)-6-(methylthio)-*s*-triazine] by Ca-organic matter, Ca-montmorillonite clay, and a Cape Fear sand loam soil, (3) measure the desorption of tricyclazole from

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Table II. Adsorption of Tricyclazole and Prometryn by Ca-Organic Matter, Ca-Montmorillonite, and Cape Fear Sandy Loam Soil

pesticide	concn added <sup>a</sup> ( $\times 10^{-6}$ ), M	amount adsorbed					
		Ca-OM		Ca-mont.		Cape Fear	
		$\mu\text{mol/g}$	%	$\mu\text{mol/g}$	%	$\mu\text{mol/g}$	%
tricyclazole	10	7.13	71	1.06	11	0.58	29
	20	13.68	68	3.60	18	0.96	24
	30	18.59	62	8.78	29	1.43	24
	40	23.99	60	17.13	43	1.68	21
	50	26.75	54	26.55	53	2.27	23
prometryn	50	36.93	74	2.30	5	1.28	13
	LSD(0.05):	1.80		1.40		0.33	

<sup>a</sup> Twenty milliliters of solution equilibrated with 20 mg of Ca-organic matter (pH 4.2), 20 mg of Ca-montmorillonite (pH 6.5), or 100 mg of Cape Fear sandy loam soil (pH 5.5) for 24 h at 25 °C.

equals concentration, that concentration remains constant, that only molecular species (M) are present at pH levels higher than 3.0, that only protonated species (MH) are present at pH levels of 0.5 or lower, that total ultraviolet light absorption at each pH level is due to the combined absorption of the respective species present, and that the absorbance measured at each pH level (A) is comprised of the absorbance of molecular ( $A_M$ ) and protonated ( $A_{MH}$ ) species, as is customary in spectrophotometric titrations (Woislawski, 1953; Weber 1977a), the expression may be rewritten as

$$pK_a = \text{pH} - \log \frac{A - A_{MH}}{A_M - A} \quad (5)$$

where  $\text{pH} = -\log [\text{H}^+]$  in solution at each absorbance (A) measurement,  $A_M$  = absorbance of molecular species (0.455),  $A_{MH}$  = absorbance of protonated species (0.755), and A = measured absorbance at each pH level. By use of the above expression, a sample calculation for a solution of tricyclazole at pH 1.5 is

$$\begin{aligned} pK_a &= 1.5 - \log [(0.625 - 0.755)/(0.455 - 0.625)] \\ &= 1.5 - \log (-0.130/-0.170) \\ &= 1.5 - \log 0.76 \\ &= 1.5 - (-0.1) \\ &= 1.6 \end{aligned}$$

Mean values for six replications of the ultraviolet spectral data and the  $pK_a$  for tricyclazole are given in Table I.

**Adsorption-Desorption of Tricyclazole by Ca-Organic Matter.** Tricyclazole was adsorbed by Ca-organic matter in a typical L-type isotherm in amounts approximately three-fourths that obtained for prometryn (Table II; Figure 1). L-type isotherms are most common and signify that the solid has a relatively high affinity for the solute (Giles et al., 1960; Weed and Weber, 1974). Adsorption of tricyclazole and prometryn by Ca-organic matter (in reality K-OM in the K buffer) was shown to be pH dependent and adsorption increased as suspension pH decreased in each case (Table III). Although more prometryn than tricyclazole was adsorbed by Ca-organic matter from deionized water (pH 4.2) at the  $50 \times 10^{-6}$  M concentration (39.93 vs. 26.75  $\mu\text{mol/g}$ , Figure 1, and 74 vs. 54%, Table II), similar amounts of the respective compounds were adsorbed at this same concentration in the pH 4.0, 0.01 M buffer solution (49 vs. 50% at pH 4.0, Table III). Adsorption of tricyclazole increased from 50 to 72% when the pH decreased from 4.0 to 2.0, whereas prometryn adsorption was the same (49 and 50%) at the two pH levels. This was because maximum adsorption of basic pesticides normally occurs at pH levels in the vicinity of the  $pK_a$  for the compound (Weber, 1972) and the  $pK_a$  values for tricyclazole and prometryn were 1.6 and 4.0,

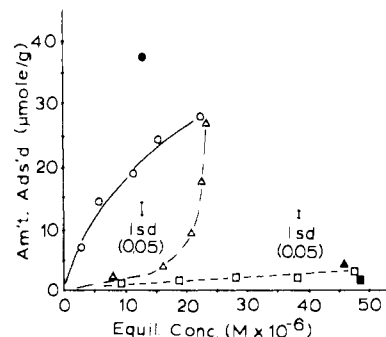
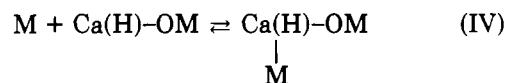
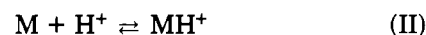


Figure 1. Adsorption isotherms for tricyclazole by (O) Ca-organic matter, ( $\Delta$ ) Ca-montmorillonite, and ( $\square$ ) Cape Fear sandy loam soil [( $\bullet$ ), ( $\blacktriangle$ ), and ( $\blacksquare$ )] were prometryn, respectively, in each case.

respectively. Desorption studies showed that water removed 31% of the tricyclazole adsorbed by Ca-organic matter at pH 6.0, but only 17% of that adsorbed at pH 2.0, and that 0.01 M paraquat(2+) solution desorbed 2-3 times as much tricyclazole at each pH level as water. Analogous results occurred in the desorption of prometryn, suggesting similar mechanisms of adsorption (Weber et al., 1969). The two pesticides are probably adsorbed by Ca-organic matter as both the molecular and protonated species as follows:



where M = molecular species of pesticide,  $\text{MH}^+$  = protonated species of pesticide, and  $\text{Ca(H)-OM}$  = organic matter saturated with Ca ions, but most acid groups are still counteracted by  $\text{H}^+$  ions. Conditions were as follows: for reaction I, pH 6.0, primarily physical adsorption, and desorption with water occurs; for reaction II, pH <4.0 and formation of protonated species occurs in bulk solution or at acidic groups on adsorbent; for reaction III, pH <4.0, adsorption of cationic pesticide occurs through ion-exchange reaction, and desorption with 0.01 M paraquat(2+) occurs but no desorption occurs with water; for reaction IV, pH <4.0, adsorption of pesticide occurs by direct association of the basic molecule with  $\text{H}^+$  ions on the adsorbent surface, and desorption with 0.01 M paraquat(2+) occurs but no desorption occurs with water.

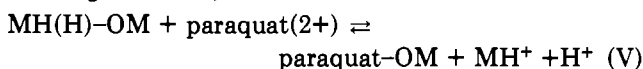
Desorption of tricyclazole and prometryn from Ca-organic matter with water was probably through shifting the equilibrium toward the left in reaction (I), thus releasing

Table III. Effect of Suspension pH on Adsorption of Tricyclazole and Prometryn by Ca-Organic Matter, Ca-Montmorillonite, and Cape Fear Sandy Loam and Desorption of the Pesticides with Deionized Water and 0.01 M Paraquat(2+)

pesticide	adsorbent	pH <sup>a</sup>	desorbing solution	amt adsorbed <sup>b</sup>		amt desorbed <sup>c</sup>		
				μmol/g	%	μmol/g	%	
tricyclazole	Ca-OM	6.0	water	23.00	46	7.13	31	
		4.0	water	23.00	50	7.15	29	
		2.0	water	35.80	72	6.09	17	
		6.0	paraquat(2+)	23.00	46	13.50	59	
		4.0	paraquat(2+)	25.00	50	11.90	48	
		2.0	paraquat(2+)	35.80	72	14.90	42	
	Ca-mont.	6.0	water	40.50	81	2.23	6	
		4.0	water	48.40	97	0.60	1	
		2.0	water	49.30	99	0.40	1	
		6.0	paraquat(2+)	40.50	81	29.00	72	
		4.0	paraquat(2+)	48.40	97	30.00	62	
		2.0	paraquat(2+)	49.30	99	32.50	66	
	Cape Fear	6.0	water	2.05	21	0.91	44	
		4.0	water	3.00	30	1.13	38	
		2.0	water	5.20	52	1.56	30	
		6.0	paraquat(2+)	2.05	21	1.36	67	
		4.0	paraquat(2+)	3.00	30	1.97	66	
		2.0	paraquat(2+)	5.20	52	3.06	59	
	prometryn	Ca-OM	6.0	water	13.60	27	6.23	46
			4.0	water	24.60	49	4.70	19
			2.0	water	25.00	50	0.43	2
6.0			paraquat(2+)	13.60	27	11.83	87	
4.0			paraquat(2+)	24.60	49	14.00	57	
2.0			paraquat(2+)	25.00	50	16.23	65	
Ca-mont.		6.0	water	21.60	43	17.20	80	
		4.0	water	48.20	96	32.40	67	
		2.0	water	49.20	98	26.67	54	
		6.0	paraquat(2+)	21.60	43	21.40	99	
		4.0	paraquat(2+)	48.20	96	39.73	82	
		2.0	paraquat(2+)	49.20	98	38.63	79	
Cape Fear		6.0	water	1.45	15	0.93	64	
		4.0	water	2.85	29	0.86	30	
		2.0	water	2.75	28	0.31	11	
		6.0	paraquat(2+)	1.45	15	1.31	91	
		4.0	paraquat(2+)	2.85	29	2.33	82	
		2.0	paraquat(2+)	2.75	28	2.11	77	
				LSD(0.05):	1.40	0.50		

<sup>a</sup> Suspension pH maintained with 0.01 M potassium citrate plus HCl buffer. <sup>b</sup> Twenty milliliters of 50 × 10<sup>-6</sup> M pesticide used with 20 mg of Ca-organic matter, 20 mg of Ca-montmorillonite, or 100 mg of Cape Fear sandy loam equilibrated for 24 h at 25 °C for adsorption phase. <sup>c</sup> Twenty milliliters of water or 0.01 M paraquat(2+) added to adsorbent pellet and equilibrated for 24 h at 25 °C for desorption phase.

bound pesticide into solution. Desorption of the pesticides with 0.01 M paraquat(2+) was probably by way of a cation exchange reaction, as follows:



where MH(H)-OM = pesticide ionically bound to organic matter as in reaction III, paraquat(2+) = divalent paraquat cation, paraquat-OM = paraquat ionically bound to organic matter, MH<sup>+</sup> = displaced pesticide which reestablishes equilibrium according to reaction II, and H<sup>+</sup> = displaced hydrogen ions from organic matter.

**Adsorption-Desorption of Tricyclazole by Ca-Montmorillonite.** Tricyclazole adsorption by Ca-montmorillonite exhibited an S-type isotherm in amounts ranging from the same as prometryn at the lowest concentration to nearly 10 times as much in prometryn at the highest concentration (Figure 1). The percent tricyclazole adsorbed increased with each increase in concentration (Table II), suggesting that molecular pressure had a direct effect on the adsorption phenomenon. S-type isotherms signify that the solid has a higher affinity for the solvent than for the solute, at low solute concentrations; at higher solute concentrations there is supportive adsorption among adsorbed molecules, and multilayers may be forming on the surface at high solute concentrations (Giles et al., 1960).

Adsorption of tricyclazole and prometryn by Ca-montmorillonite was much greater in the pH 6.0, 0.01 M buffer solution (Table III) than in deionized water at approximately pH 6.5 (Table II; Figure 1). Adsorption of both pesticides increased greatly as pH decreased from 6.0 to 2.0 and went from 81 to 99% and from 43 to 98% for tricyclazole and prometryn, respectively (Table III). Water was ineffective in desorbing tricyclazole from Ca-montmorillonite (1-6% desorbed), but 0.01 M paraquat(2+) desorbed from 62 to 70% of the pesticide. The 0.01 M paraquat(2+) solution was also much more effective than water in desorbing prometryn from Ca-montmorillonite, with amounts desorbed ranging from 79 to 99% and from 54 to 80% for the two solutions, respectively. In all cases, except desorption of tricyclazole with water, desorption of the pesticides from Ca-montmorillonite decreased as pH at adsorption decreased. This suggests that the mechanism of adsorption was primarily physical at neutral pH levels and ionic at low pH levels similar to that postulated for adsorption of the s-triazine herbicides by montmorillonite (Weber, 1970). It is likely that enhanced protonation occurred at the clay surface as suggested by Feldkamp and White (1979) and that tricyclazole was protonated to a much greater extent than that predicted on the basis of the bulk solution pH and the pK<sub>a</sub> of the compound. In addition, Feldkamp and White (1979) have

suggested the possibility that citrate buffer may complex with Al in the clay lattice, thereby affecting the apparent negative charge on the clay surface and enhancing adsorption of basic molecules such as tricyclazole. Although cation-exchange reactions between tricyclazole and the clay surface are undoubtedly occurring at low pH levels, mechanisms of adsorption for neutral and high pH levels cannot be postulated based on the information available at this time.

**Adsorption-Desorption of Tricyclazole by Cape Fear Soil.** Tricyclazole was adsorbed by Cape Fear soil in substantially greater amounts than prometryn in the pH 5.5 deionized water system (compare 23 vs. 13% for the two pesticides, respectively) (Table II; Figure 1), and in the 0.01 M buffer system (compare 21, 30, and 52% at pHs 6.0, 4.0, and 2.0 for tricyclazole with 15, 29, and 28% at the same pH levels for prometryn, Table III). The adsorption isotherm for tricyclazole on Cape Fear soil was relatively linear (C type) (Figure 1). C-type isotherms signify a constant partition of adsorbate between solution and adsorbent, indicating that additional adsorption sites become available as adsorption proceeds (Giles et al., 1960). However, since the soil is a mixture of organic matter, which displayed L-type isotherms for tricyclazole, and clay minerals, which displayed S-type isotherms, the C-type isotherm may be a composite isotherm for the mixture of adsorbing surfaces.

Adsorption on the Cape Fear soil increased as pH decreased for both tricyclazole and prometryn showing the pH-dependent adsorption mechanism which was also characteristic when Ca-organic matter and Ca-montmorillonite were used as the adsorbents (Table III). Water was much less effective in desorbing tricyclazole from the Cape Fear soil than was 0.01 M paraquat(2+) (compare 44, 38, and 30% desorption with 67, 66, and 59% desorption with water and paraquat(2+), respectively). This was also the case for prometryn. However, prometryn was much more readily displaced from the Cape Fear soil than was tricyclazole with both water and paraquat(2+) solutions (compare 64 and 91% desorption of prometryn, respectively, at pH 6.0 vs. 44 and 67% desorption of tricyclazole, respectively, at pH 6.0, Table III).

High adsorption of tricyclazole by soil organic matter and montmorillonite clay, the effects of buffer salts vs. water, and the pH dependence of the adsorption mecha-

nisms in these studies suggest that these factors will have a significant effect on the bioavailability of the fungicide in soil systems and in aquatic systems containing soil particulate matter.

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