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## Sorption of Pesticides in Tropical and Temperate Soils from Australia and the Philippines

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The sorption behavior of diuron, imidacloprid, and thiacloprid was investigated using 22 soils collected in triplicate from temperate environments in Australia and tropical environments in Australia and the Philippines. Within the temperate environment in Australia, the soils were selected from a range of land uses. The average Koc values (L/kg) for imidacloprid were 326, 322, and 336; for thiacloprid, the values were 915, 743, and 842; and for diuron, the values were 579, 536, and 618 for the Ord (tropical), Mt. Lofty (temperate), and Philippines (tropical) soils, respectively. For all soils, the sorption coefficients decreased in the following order: thiacloprid > diuron > imidacloprid. There were no significant differences in sorption behavior between the tropical soils from the Philippines and the temperate soils from Australia. Sorption was also not significantly related with soil characteristics, namely, organic carbon (OC) content, clay content, and pH, for any of the three chemicals studied. When the data were sorted into separate land uses, the sorption of all three chemicals was highly correlated (P < 0.001) with OC for the rice soils from the Philippines. Sorption coefficients for all three chemicals were highly correlated with OC in temperate, native soils only when one extreme value was removed. The relationships between sorption of all three chemicals and OC in temperate, pasture soils were best described by a polynomial. Sorption coefficients for imidacloprid and thiacloprid determined in the temperate pasture soils remained fairly consistent as the OC content increased from 3.3 to 5.3%, indicating that, although the total OC in the pasture soils was increasing, the component of OC involved with sorption of these two compounds may have been remaining constant. This study demonstrated that the origin of the soils (i.e., temperate vs tropical) had no significant effect on the sorption behavior, but in some cases, land use significantly affected the sorption behavior of the three pesticides studied. The impact of land use on the nature of soil OC will be further investigated by NMR analysis.

KEYWORDS: Pesticide fate and behavior; soil organic carbon; landuse; diuron; imidacloprid; thiacloprid

#### INTRODUCTION

Off-site movement of organic chemicals into waterways is a major concern worldwide. To minimize this contamination, it is necessary to understand the sorption processes of these chemicals and the relationships between sorption processes and soil parameters. However, a recent review of the literature of pesticide fate studies found 77% of reports were focused on temperate zone conditions, and of those reports on tropical zones, the majority (18% of the total) originated in India (I).

The major consistent difference between temperate and tropical regions is that, on average, the tropics are 15 °C warmer than the temperate regions and have no cold winters, which providing there is water present, results in a much more rapid turnover of organic matter (1). One characteristic of some

tropical soils resulting from rapid reaction rates is deep weathering and intensive leaching. The resultant low-charge minerals and oxides are not efficient in holding nutrient cations, and organic matter then becomes an important sink and source of essential elements (2). Soil organic matter (SOM) is also an important component controlling the sorption of nonpolar organic compounds by soils (3). The organic constituents of tropical soils are not considered to be different from those in temperate soils. However, the relative size of various SOM pools is determined by climatic and edaphic factors (2). There is a clear need to understand the fate and behavior of pesticides in tropical soils. In this study, the sorption behavior of diuron, imidacloprid, and thiacloprid was investigated using soils from a temperate environment in Australia and tropical environments in Australia and the Philippines. Also, this study looked at the effect of land use on the sorption behavior of these chemicals. Other studies have shown that the origin of organic carbon (OC) can affect the nature of soil OC. The <sup>13</sup>C NMR spectra of soil collected from under native grass have been found to have a

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Table 1. Sites and Selected Physicochemical Properties of the Soils Studied

sample name	soil classification <sup>a</sup>	land use	years under each land use	organic carbon % <sup>b</sup>	clay % <0.002 mm <sup>b</sup>	silt % 0.002–0.02 mm <sup>b</sup>	sand % 0.02–20 mm <sup>b</sup>	$pH^b$				
			Ord soils, Aust	tralia (tropical)								
Ord 7B	Chromic Haplotorrerts	rock-melon	~40	0.78	47.4	15.0	37.6	6.77				
Ord 1B	Typic Haplotorrerts	melons	~40	0.69	49.7	15.9	34.4	6.78				
Ord 5A	Sodic Haplotorrerts	leucenea	$\sim$ 40	1.77	49.5	18.5	32.0	6.60				
Ord 1A	Chromic Haplotorrerts	sorghum	~40	0.94	47.1	16.8	36.1	6.76				
			Mt. Lofty soils, Aus	stralia (temperate	)							
Wotton	Ultic Palexeralfs	vines	8	2.27	<sup>′</sup> 31.3	34.1	34.6	5.37				
George V	Ultic Palexeralfs	vines	20	2.33	8.9	11.9	79.2	5.17				
Broderick	Ultic Palexeralfs	vines	20	2.19	4.9	16.1	79.0	4.82				
Bishop	Ultic Palexeralfs	apples, cherries	50 and 20	2.88	13.6	33.9	52.5	5.47				
Bungay	Ultic Haploxeralfs	cherries	20	3.40	12.7	42.0	45.3	5.19				
Parker	Ultic Palexeralfs	cherries	60	2.59	15.8	25.3	58.9	5.00				
George N	Ultic Palexeralfs	native vegetation	>100	3.01	7.3	14.2	78.5	4.63				
Pound	Ultic Haploxeralfs	native vegetation	>100	2.10	3.9	14.8	81.3	4.11				
Montacute	Ultic Haploxeralfs	native vegetation	>100	2.73	11.5	31.7	56.8	4.75				
Hunter	Ultic Palexeralfs	pasture	20	2.81	9.4	17.6	73.0	6.30				
Mason	Ultic Haploxeralfs	pasture	20	4.91	14.0	33.8	52.2	4.52				
Cranwell	Ultic Haploxeralfs	pasture	20	2.76	13.0	19.1	67.9	5.35				
	Philippines soils (tropical)											
Laurel	Haplustults-Ustorthents	rice	>30	1.32	18.2	33.5	48.3	6.23				
Bay	Tropaquepts	rice	>100	2.68	27.6	33.2	39.2	6.36				
Pagsanjan	Palemunults	rice	>100	2.35	46.2	31.2	22.6	5.29				
Liliw	Hapludalfs	vegetable	>30	4.07	11.7	36.3	52.0	5.53				
Lumban	Humults	vegetable	>20	1.27	24.7	28.8	46.5	5.49				
Calauan	Hapludalfs	pineapple	>30	1.71	24.3	30.8	44.9	4.40				

<sup>&</sup>lt;sup>a</sup> As per ref 26. <sup>b</sup> As per ref 27.

greater proportion of aromatic carbon and a lesser proportion of *O*-alkyl carbon than the spectra of virgin soil from under Brigalow scrub (4). The pesticides used in this study were chosen because there is very little information in the literature about the behavior of thiacloprid and imidacloprid and there is little information about the behavior of diuron in tropical soils. The behavior of diuron is particularly important because the use of this compound in the Philippines is expected to increase since it has recently been registered for use in rice (Varca, L. Personal communication), which is a major staple of the Filipino diet.

#### **MATERIALS AND METHODS**

Pesticides. Analytical grade chemicals (99.9% imidacloprid, 99.6% thiacloprid, and 99% diuron) were obtained from Bayer Crop Science (Germany). Thiacloprid and imidacloprid are relatively new systemic insecticides of the neonicotinoid group, which act agonistically on the nicotinic acetylcholine receptor (5). They effectively control sucking insects, soil insects, termites, and some species of chewing insects (6). Imidacloprid is used in tomato production in the Philippines, and it is used in a range of crops in Australia including rice, cotton, and citrus fruits. Both compounds are quite soluble in water at 0.61 and 0.185 g/L for imidacloprid and thiacloprid, respectively (7, 8). The half-life of imidacloprid has been reported as 40 days in field experiments (9) and 48 days in the laboratory (10). Thiacloprid has a short half-life in soil of 9-27 days (11) and low toxicity to birds, fish species, beneficial arthropods, bees, and mammals (5). Diuron is a substituted phenylurea herbicide for selective control of germinating grass and broad-leaved weeds in many crops (7). In the Philippines, diuron is used in pineapple production and has recently been registered for use in rice, so its use here is expected to increase (Varca, L. Personal communication). In Australia, diuron is used in sugar cane and horticultural crops. Diuron is slightly moderately soluble in water (0.042 g/L) (7). It has been detected in waterways in the Philippines (Varca, L. Personal communication) and in water bodies in other countries. It is moderately to highly persistent in soils with half-lives ranging from 1 month to 1 vear (12).

**Soil Properties.** Surface (0-15 cm) soils were collected from 22 sites: (four from the Ord River Irrigation area in northeastern Western

Australia; 12 from the Mt. Lofty Ranges, South Australia; and six from the Los Baños region in the Philippines). The soils were chosen to represent the major land uses and soil types in these areas (**Table 1**). From each paddock or area, three replicate soil samples were collected. Each replicate comprised three 0–15 cm cores (5 cm diameter) that were bulked. The three cores that were bulked were collected in a Knight's Move Latin Square design (12). Selected physical and chemical characteristics of the soils and information about the land use are given in **Table 1**. The soils were air-dried, ground, and sieved through a 2 mm sieve. The soil parameters (pH, texture, and OC content) were determined by midinfrared analysis (27).

Sorption Studies. Sorption coefficients for imidacloprid, thiacloprid, and diuron were determined using a batch method. The sieved soils (5 g) were weighed in duplicate into polypropylene centrifuge tubes with 10 mL of 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> solution containing the chemical (0.5 mg/L for imidacloprid and thiacloprid and 1.5 mg/L for diuron). This concentration was chosen to be representative of field applications and to ensure that the studies were conducted in the linear part of the sorption isotherm. Soil suspensions were shaken for 24 h on an endover-end shaker and centrifuged at 1100g for 20 min, and then, the supernatant solution was decanted, filtered through 0.45  $\mu$ m Acrodisk filters, and stored at 4° C before being analyzed by high-performance liquid chromatography (HPLC). The amount sorbed was calculated from the difference between the initial and the final concentrations in solution. Pesticide sorption onto walls and loss during filtering were checked by running blanks (solutions with no soil) in every batch. Data were corrected for losses due to filtering. The sorption coefficient (Kd) was calculated from the ratio of the sorbed concentration ( $\mu g/g$ ) to solution concentration (µg/mL) after equilibration.

Pesticide Analysis. The concentrations of pesticides were determined using an Agilent 1100 HPLC equipped with a quaternary pump, variable wavelength diode array detector, and an autosampler with an electric sample valve. Data were collected and processed using Agilent ChemStation software. The following conditions were used for imidacloprid and thiacloprid: Alltech Prevail C18 column (150 mm  $\times$  2.1 mm i.d., 5  $\mu$ m particle size); gradient elution with mobile phase 90:10 H<sub>2</sub>O:CH<sub>3</sub>CN at the start that changed over 3 min to 80:20 H<sub>2</sub>O: CH<sub>3</sub>CN and was maintained at this composition for 10 min and then changed over the next 5 min to 50:50 H<sub>2</sub>O:CH<sub>3</sub>CN; a flow rate of 0.5 mL/min; an injection volume of 25  $\mu$ L; UV detector at a wavelength

Table 2. Average Soil Sorption Coefficients ( $K_d$ ) and  $K_{OC}$  Values (L/kg) (n = 6) for Imidacloprid, Thiacloprid, and Diuron; Standard Deviations Are Given in Parantheses

	imidacloprid		thiacl	oprid	diuron	
sample <sup>a</sup>		Koc		Koc		Koc
			Ord soils, Australia (tropio	al)		
Ord 7B	2.1 (0.3)	263 (18)	4.6 (0.6)	590 (39)	2.2 (0.2)	285 (6)
Ord 1B	3.0 (0.6)	439 (45)	7.5 (1.9)	1076 (167)	4.4 (1.3)	625 (113
Ord 5A	2.7 (0.5)	156 (20)	7.0 (1.4)	408 (46)	4.1 (2.2)	225 (41)
Ord 1A	5.5 (0.3)	591 (61)	14.9 (0.8)	1584 (145)	11.1 (0.3)	1179 (79)
mean (SD)	3.3 (1.5)	326 (192)	8.5 (4.4)	915 (528)	5.5 (3.9)	579 (438
		Mt.	Lofty soils, Australia (temp	perate)		
Wotton	9.7 (1.0)	434 (71)	20.8 (1.1)	937 (158)	12.0 (6.3)	560 (338
George V	5.3 (1.1)	228 (35)	11.4 (2.9)	486 (86)	7.4 (1.5)	317 (50)
Broderick	6.9 (0.7)	322 (55)	14.2 (1.8)	663 (154)	11.0 (1.3)	510 (105
Bishop	13.5 (6.0)	459 (110)	32.3 (15.1)	1094 (287)	22.5 (10.4)	756 (169
Bungay	11.5 (2.7)	346 (103)	29.4 (9.1)	879 (312)	21.9 (7.8)	654 (270
Parker	5.9 (1.8)	251 (111)	12.4 (3.3)	526 (196)	9.6 (3.6)	391 (134
George N	9.0 (1.9)	321 (117)	19.0 (4.9)	662 (233)	14.9 (3.9)	524 (190
Pound	6.5 (1.0)	309 (51)	17.7 (7.6)	877 (436)	11.8 (2.5)	564 (102
Montacute	15.1 (5.6)	539 (113)	35.9 (12.1)	1293 (255)	32.2 (14.0)	1138 (324
Hunter	6.7 (3.4)	238 (2)	15.4 (7.9)	548 (4)	9.4 (5.7)	323 (36)
Mason	9.3 (0.5)	190 (16)	20.9 (0.9)	427 (46)	16.3 (1.0)	334 (37)
Cranwell	6.7 (3.6)	231 (90)	15.0 (8.2)	520 (203)	10.2 (5.5)	356 (139
mean (SD)	8.9 (3.2)	322 (107)	20.4 (8.0)	743 (271)	14.9 (7.3)	536 (236
			Philippines soils (tropica	l)		
Laurel	4.0 (0.3)	304 (40)	10.6 (1.2)	807 (119)	6.6 (0.7)	497 (19)
Bay	12.6 (0.4)	479 (77)	33.2 (1.8)	1259 (176)	25.6 (1.7)	975 (178
Pagsanjan	10.7 (2.7)	453 (65)	28.9 (6.8)	1219 (154)	24.8 (1.8)	1060 (117
Liliw	9.4 (5.4)	223 (97)	21.3 (12.2)	508 (217)	14.5 (8.0)	349 (144
Lumban	3.0 (0.8)	236 (50)	7.4 (2.2)	580 (136)	4.2 (1.4)	326 (85)
Calauan	5.4 (1.8)	319 (126)	11.3 (4.6)	677 (316)	8.3 (3.9)	500 (268
mean (SD)	7.5 (3.9)	336 (108)	18.8 (10.7)	842 (324)	14.0 (9.3)	618 (319

<sup>&</sup>lt;sup>a</sup> For land use associated with each sample, refer to Table 1.

of 242 nm for thiacloprid and 270 nm for imidacloprid; and retention times of 7.0 min for imidacloprid and 9.1 min for thiacloprid. The following conditions were used for diuron: Altima C18 column (250 mm  $\times$  4.6 mm i.d., 5  $\mu$ m particle size); isocratic mobile phase 40:60 H<sub>2</sub>O:CH<sub>3</sub>CN; flow rate of 1 mL/min; an injection volume of 20  $\mu$ L; detection wavelength of 254 nm; and retention time of 5.8 min. Standards for the calibration curve were run in the same matrix as the samples, 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub>. The detection limits were 0.01 ppm for imidacloprid and thiacloprid and 0.025 ppm for diuron. The coefficient of variation between laboratory duplicates was less than 10% for all three compounds. Instrument repeatability was monitored throughout the analytical run by repeating a standard every tenth sample.

**Statistical Analysis.** Sorption coefficients ( $K_d$  values) were determined from single-point measurements (batch equilibrium with one concentration). The relationships between these  $K_d$  values and pH, OC (% OC), and % clay (<0.002 mm) content were also determined by regression analysis. An analysis of variance (ANOVA) was performed to determine the significance of the effect of soil origin and land use on the sorption coefficients for each chemical.

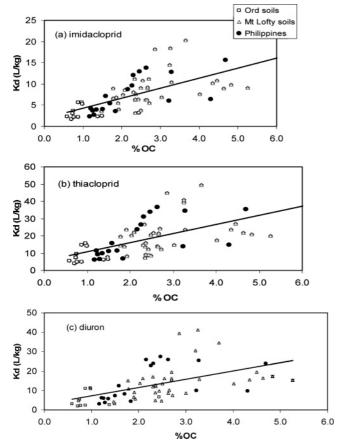
### RESULTS AND DISCUSSION

**Sorption Coefficients for Imidacloprid, Thiacloprid, and Diuron.** The average sorption coefficients ( $K_d$ ) for imidacloprid ranged from 5.3 to 15.1 L/kg in the temperate soils and from 2.1 to 12.6 L/kg in the tropical soils (**Table 2**). The average  $K_d$  values for imidacloprid were significantly (P < 0.001) lower for the Ord soils (3.3 L/kg) than that for the Mt. Lofty soils (8.9 L/kg) and the Philippines soils (7.5 L/kg). The average  $K_{OC}$  values (L/kg) for imidacloprid were 326 for the Ord soils, 322 for the Mt. Lofty soils, and 336 for the Philippines soils (**Table 2**). Previously published sorption data for imidacloprid were determined using temperate soils; however, the sorption values obtained for imidacloprid in this study are within the range obtained in other studies. For example, the  $K_{OC}$  values

determined using three U.S. soils ranged from 369 to 432 L/kg (6), in seven U.S. soils ranged from 120 to 433 L/kg (14), in five low OC Spanish soils ranged from 269 to 830 (15), and in two German soils ranged from 249 to 268 L/kg (16).

The  $K_d$  values for thiacloprid ranged from 11.4 to 35.9 L/kg in temperate soils and from 4.6 to 33.2 L/kg in tropical soils (**Table 2**). The average  $K_d$  values for thiacloprid were significantly (P < 0.001) lower for the Ord soils (8.5 L/kg) than that for the Mt. Lofty soils (20.4 L/kg) and the Philippines soils (18.8 L/kg). The average  $K_{\rm OC}$  values (L/kg) for thiacloprid in the Ord soils were 915, in the Mt. Lofty soils were 743, and in the Philippines soils were 842 L/kg (**Table 2**). There are no published data on sorption of thiacloprid for comparison.

The average  $K_d$  values (**Table 2**) for diuron ranged from 7.4 to 32.2 L/kg in temperate soils and from 2.2 to 25.6 L/kg in tropical soils (**Table 2**). The average  $K_d$  value for diuron was significantly (P < 0.001) lower for the Ord soils (5.5 L/kg) than that for the Mt. Lofty soils (14.9 L/kg) and the Philippines soils (14.0 L/kg). The average  $K_{\rm OC}$  value (L/kg) for diuron in the Ord soils was 579, for the Mt. Lofty soils was 536, and the Philippines soils was 618 (Table 2). Sorption coefficients for diuron determined in this study are in the range obtained in several other studies. For example, the  $K_{OC}$  values in six Italian soils ranged from 395 to 500 L/kg (17), in seven U.S. citrus soils ranged from 144 to 373 L/kg (18), in a coarse silt was 570 L/kg (19), in a coarse clay was 884 L/kg (19), and in a German silt loam was 550 L/kg (20). The  $K_d$  values of diuron in three cotton-growing soils from Australia (3.2-5.7 L/kg) (21) were in the range found in the tropical Australian soils in this study, but the range found in the temperate Australian soils was higher. For all three compounds studied, there was very little difference in  $K_{OC}$  values in soils from tropical and temperate



**Figure 1.** Relationship between sorption coefficients ( $K_d$  values, L/kg) and %OC for (a) imidacloprid, (b) thiacloprid, and (c) diuron in temperate soils from Mt. Lofty, Australia, and tropical soils from the Ord region, Australia, and the Philippines.

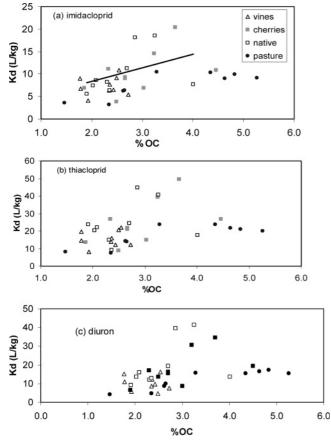
environments indicating that factors more complex than broad generalization of soils on the basis of climatic regions is needed to explain differences in sorption behavior in soils.

Relationship between Sorption Coefficients and Soil pH, **OC, and Clay Content.** The average soil pH increased in the order Mt. Lofty (5.07) < Philippines (5.55) < Ord (6.73), and % OC increased in the order Ord (1.04) < Philippines (2.24) < Mt. Lofty (2.83). There was no significant relationship between  $K_{\rm d}$  values for imidacloprid, thiacloprid, or diuron and soil pH (data not shown). Other studies (14) have similarly found no strong relationship between imidacloprid sorption and pH  $(r^2 = 0.34)$  for seven temperate soils from the United States that ranged in pH from 4.6 to 7.8. The three compounds in this study are nonionic so soil pH would not be expected to affect sorption. However, other studies have found sorption of diuron and other phenylureas by humic acid increased as pH diminished (22). There was also no significant relationship between  $K_d$ values for imidacloprid, thiacloprid, or diuron and clay content (<0.002 mm) (data not shown).

No significant relationship was found between  $K_d$  values and soil OC for imidacloprid ( $r^2 = 0.39$ ), thiacloprid ( $r^2 = 0.32$ ), and diuron ( $r^2 = 0.28$ ) (**Figure 1**). Soil OC has been found in some studies (6, 14) to be the main factor affecting the sorption of imidacloprid to several temperate soils ( $r^2 = 0.94$ , n = 7), with pH and clay not affecting imidacloprid sorption. There are no data in the literature about thiacloprid, but because it is a similar chemical to imidacloprid, it may be expected to behave in a similar manner. Sorption of diuron to Taiwanese soils was related to soil OM (23), and the addition of wheat or lucerne straw to soil was found to increase sorption in a clay loam soil

(22). The maximum amount of diuron that could be sorbed to six Italian soils (as computed by the Langmuir model and not directly comparable to the present study), has been reported to increase linearly with OC(17).

Influence of Land Use on Sorption Behavior of Mt. Lofty **Soils.** Earlier studies (24, 25) had found that land use greatly affected the sorption behavior of a range of pesticides and their metabolites, but these previous studies were confined to soils that were mainly sandy with low OC content. There were insufficient soil/land use combinations from the tropical regions to investigate any relationships between land use and sorption behavior, so only soils from the Mt. Lofty ranges were used for this section. In this study, the soils from the Mt. Lofty ranges were chosen to reflect a range of land uses in the region and to cover a wider range of soil physical and chemical characteristics. These soils have been under the particular land use for at least 10 years (Table 1). There were no significant differences between the four land uses (vines, cherries, native, and pasture) for the average sorption coefficient for imidacloprid and thiacloprid, but the average sorption coefficients for diuron were significantly (P < 0.01) lower for the soils from under grapevines ( $K_d = 10.1 \text{ L/kg}$ ) and pasture ( $K_d = 12.0 \text{ L/kg}$ ) than for the soils under cherries ( $K_d = 18.0 \text{ L/kg}$ ) and native vegetation ( $K_d = 19.7 \text{ L/kg}$ ). These results are surprising because the sorption coefficients were different in soils that were least disturbed, i.e., pasture and native soils. The relationship between sorption coefficients and soil pH and OC was compared for the four land uses. There were no significant trends between sorption coefficients and increasing pH for any of the three pesticides (data not shown). There were no significant relationships between sorption coefficients and OC for imidacloprid and thiacloprid in soils from under vines, cherries, and native vegetation and for diuron in soils from under vines and native vegetation. However, the removal of one outlier for the sorption coefficients determined from soils under native vegetation and cherries resulted in significant relationships between  $K_d$  values and soil OC for imidacloprid ( $r^2 = 0.83$ , P < 0.001 for native soils and  $r^2 = 0.53$ , P < 0.01 for cherry soils) and thiacloprid  $(r^2 = 0.49, P < 0.01 \text{ for native soils and } r^2 = 0.57, P < 0.01$ for cherry soils) (**Figure 2**). The relationship between  $K_d$  values for all three compounds and OC from the soils under grapevines was highly variable with K<sub>d</sub> values almost doubling for approximately the same OC content (Figure 2). There were no significant relationships between K<sub>d</sub> values and soil OC for diuron in soils under vines, native vegetation, or cherries. Again, the removal of one outlier for the sorption coefficients determined from soils under native vegetation, which was in a soil with an OC content of 4.5%, resulted in a significant relationship between  $K_d$  values and soil OC for diuron ( $r^2 = 0.63, P < 0.01$ ) (**Figure 2**). The relationship between  $K_d$  values and soil OC for diuron in pasture soils was best described by a polynomial relationship. In pasture soils, the sorption coefficient for diuron increased significantly (P < 0.05) but gradually with increasing OC over a range of 1.5–5.3% ( $r^2 = 0.87$ , P < 0.005). However, although the relationship between  $K_d$  values and soil OC was significant for imidacloprid ( $r^2 = 0.78$ , P < 0.001) and thiacloprid ( $r^2 = 0.65$ , P < 0.01), the sorption coefficients determined in the pasture soils remained fairly consistent as the OC content increased from 3.3 to 5.3%. This indicates that, although the total OC in the pasture soils was increasing, the component of OC involved with sorption of these two compounds may have been remaining constant (**Figure 2**). The  $K_d$  values for diuron  $(r^2 = 0.78, P < 0.001)$ , imidacloprid  $(r^2 = 0.84, P < 0.001)$ , and thiacloprid ( $r^2 = 0.87$ , P < 0.001) determined in the rice



**Figure 2.** Relationship between sorption coefficients ( $K_d$  values, L/kg) and %OC for (a) imidacloprid, (b) thiacloprid, and (c) diuron in temperate soils under the four major land uses in the Mt. Lofty ranges. Removal of one extreme value in the native soils improved the relationship for imidacloprid ( $R^2 = 0.83$ , P < 0.001), thiacloprid ( $R^2 = 0.67$ , P < 0.01), and diuron ( $R^2 = 0.84$ , P < 0.001).

soils from the Philippines increased significantly with increasing soil OC, although the  $K_d$  values for all three pesticides in the vegetable soils did not change with increasing soil OC (data not shown). The smaller sample size of the tropical soils made it difficult to compare the effect of land use on sorption in this environment.

Soil OC may not be adequate to explain variation between soils in sorption behavior of pesticides. Other studies have shown that there has been a stronger relationship between the sorption coefficients and the aromatic (28, 29) and/or alkyl (29) fraction of OC than with total soil OC. Further investigations are required to determine whether the variation in sorption behavior in these soils is better related to particular chemical fractions of OC rather just OC alone.

In conclusion, this study has shown that although the sorption of diuron, imidacloprid, and thiacloprid was significantly (P < 0.001) different between tropical and temperate soils, closer inspection showed that only the sorption of soils to the tropical Ord soils was significantly (P < 0.001) different from the sorption in the temperate Mt. Lofty soils and the tropical soils from the Philippines. For all soils, the sorption decreased in the order thiacloprid > diuron > imidacloprid. The relationship between sorption coefficients and soil OC was variable. There was no significant relationship between sorption coefficients and soil OC for imidacloprid, thiacloprid, or diuron when all of the data were considered. However, differences in sorption were found between the four different land uses (cherries, vines, pasture, and native vegetation). The average sorption coefficients

for all three chemicals studied were significantly (P < 0.01)greater for soils under native vegetation and cherries than those under vines or pasture. There were no significant relationships between sorption coefficients and OC for imidacloprid and thiacloprid in soils from under vines, cherries, and native vegetation and for diuron in soils from under vines and native vegetation. Removal of one outlying point for the sorption coefficients determined from soils under native vegetation for all three chemicals resulted in a significant relationship between  $K_{\rm d}$  values and soil OC. The relationship between  $K_{\rm d}$  values and soil OC for diuron in pasture soils was best described by a polynomial relationship. In pasture soils, the sorption coefficient for diuron increased significantly ( $P \le 0.05$ ) but gradually with increasing OC over a range of 1.5–5.3% ( $r^2 = 0.87, P < 0.001$ ). However, although the relationship between  $K_d$  values and soil OC was significant for imidacloprid ( $r^2 = 0.78$ , P < 0.001) and thiacloprid ( $r^2 = 0.65$ , P < 0.01), the sorption coefficients determined in the pasture soils remained fairly consistent as the OC content increased from 3.3 to 5.3%. This indicated that although the total pool of OC in pasture soils was increasing, the component of OC involved with pesticide sorption may be remaining constant. This hypothesis will be further investigated using NMR characterization of OC in soils from the different land uses.

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Received for review February 8, 2005. Revised manuscript received May 3, 2005. Accepted May 30, 2005. We acknowledge the financial support of the Ord Bonaparte Program and the Australian Centre for International Agricultural Research (ACIAR).

JF050293L