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ARTICLE

Characterization of Adsorption and Degradation of Diuron in Carbonatic and Noncarbonatic Soils

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The adsorption and degradation of the pesticide diuron in carbonatic and noncarbonatic soils were investigated to better understand the fate and transport of diuron in the environment. Batch adsorption experiments yielded isotherms that were well-described by the linear model. Adsorption coefficients normalized to soil organic carbon content (K_{oc}) were lowest for carbonatic soils, averaging 259 ± 48 (95% CI), 558 ± 109, 973 ± 156, and 2090 ± 1054 for carbonatic soils, Histosols, Oxisols, and Spodosols, respectively. In addition, marl-carbonatic soils had much lower K_{oc} values (197 ± 27) than nonmarl-carbonatic soils. Diuron degradation data fit a first-order reaction kinetics model, yielding half-lives in soils ranging from 40 to 267 days. There was no significant difference between the average diuron degradation rate coefficients of each of the soil groups studied. Given the low adsorption capacity of carbonatic soils, it may be advisable to lower herbicide application rates in agricultural regions with carbonatic soils such as southern Florida to protect aquatic ecosystems and water quality.

KEYWORDS: Herbicides; organic matter; K_{oc}; calcareous; marl; leaching potential

INTRODUCTION

Carbonatic soils often develop in karstic regions known for their susceptibility to contaminant dispersal due to their high permeability. This situation is particularly acute in southern Florida, where carbonatic soils are thin and underlain by the Tamiami formation, a highly permeable limestone and sandstone bedrock (*1, 2*). Thus, there is little to retard the flow of water and contaminants to interlinking water canals, the surficial Biscayne aquifer system, and the nearby Everglades National Park. These soils play a unique role in U.S. and Puerto Rican agriculture. Carbonatic soils support >85% of Florida's tropical fruit and vegetable production (*3*). The subtropical environment of southern Florida and Puerto Rico that makes it suitable for the year-round growth of vegetables and tropical fruits also encourages proliferation of pests. Between 1999 and 2002, diuron use for major crop production in Florida came second (424 t per year) after atrazine, the use of which was 567 t per year (*4*). It is estimated that 15000 t of pesticides are used annually in South Florida, of which herbicides constitute 2900 t (*5*). In monitoring studies done in southern Florida between 1990 and 2009, diuron has been frequently detected in surface water (*4*).

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], classified as a phenylurea herbicide, remains a priority pollutant because its adsorption and degradation have not been well characterized (*6*). Understanding the fate of a pesticide in the soil environment requires knowledge of both its adsorption capacity and degradation rate. For example, pesticides such as DDT that are strongly adsorbed have a low leaching potential (*7, 8*). However, such chemicals may be transported while adsorbed to particles during surface water runoff events (*7, 9−11*). In contrast, weakly adsorbed pesticides have a high leaching potential, provided they resist degradation during movement through the soil profile.

Pesticide dissipation has been reported to be primarily controlled by microbial degradation (*12−14*) and may be accelerated by repeated application and subsequent soil enrichment of specific pesticide-degrading microbial species. In some cases, adsorption of compounds such as atrazine and chlorpyrifos to soil organic matter (OM) has been found to inhibit degradation by physically protecting the pesticides from microbial attack (*15, 16*). However, a positive relationship has also been reported between OM content and degradation rates for DDT, diazinon, diuron, and parathion (*17*). In these cases, OM may act as a primer or cometabolite, supplying labile carbon and nutrients for microbial growth (*17*).

Pesticide immobility and recalcitrance were previously perceived as desirable attributes, allowing extended pesticide effectiveness. However, due to environmental and human health concerns, such chemicals have been phased out and replaced with less persistent alternatives such as organophosphates and carbamates, which have short half-lives of about 1−120 days (*15, 18*). Even then, some of these pesticides have been known to degrade to more persistent and more toxic metabolites than the parent compounds and to cause health and reproductive effects in nontarget species (*14*). Specifically, the aqueous phase metabolites of diuron have been reported to be more toxic than the parent compound (*19*). Thus, there is a need to understand the fate and transport of diuron in the environment. In addition, little is known about the fate of pesticides in carbonatic soils such as

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those in southern Florida (*20*). Carbonatic soils from southern Florida have been found to adsorb pesticides much less than associated noncarbonatic soils (*20*). The goal of this study was to characterize and contrast the adsorption and degradation processes of diuron in carbonatic and other soils and to assess the potential that diuron may pose for pollution of surface and groundwater resources.

MATERIALS AND METHODS

Materials. The surface horizons (0−15 cm) of carbonatic and associated soils were collected from southern Florida (Miami-Dade and Monroe counties) and Puerto Rico. Carbonatic soils contain > 40% carbonate rock weight content (limestone and/or dolomite), which includes the minerals calcite and aragonite. Two carbonatic soil types were collected in southern Florida and Puerto Rico, namely, marl-derived soils (marl-carbonatic), which are made up of limnic materials and formed by secondary calcium carbonate precipitation, and marine-derived oolitic limestone soils (nonmarl-carbonatic), which result from rock scarification and plowing using heavy equipment. Detailed soil descriptions and classification information can be found in Kasozi et al. (*21*). To better understand the adsorption and degradation properties of hydrophobic organic chemicals at a regional scale, soils formed under contrasting ecological settings were included in this study. For purposes of comparison, typical Florida soils (Spodosols) were collected from Alachua County, in northern Florida, Histosols associated with carbonatic soils were collected from southern Florida, and Oxisols were collected from Uganda, Africa. Spodosols are characterized as sandy with amorphous mixtures of OM and iron and aluminum oxides, whereas Histosols and Oxisols are characterized by greater accumulations of OM and iron oxides, respectively. The geographically diverse soil samples used in this study encompass a wide range of vegetation and OM sources and include 23 carbonatic, 15 Histosol, 10 Spodosol, and 38 Oxisol soil samples.

Soil pH was determined using a soil solution ratio of 1:2 in 0.01 M Ca Cl$_2$ and an equilibration time of 5 min. Organic carbon (OC) was determined according to the Walkley−Black wet oxidation procedure (*22,23*). Thermogravimetry was used both to confirm OC determinations and to quantify carbonate content (*24*). Detailed description of the OC and calcium carbonate determination procedures are available in Kasozi et al. (*21*).

For diuron quantification, high-performance liquid chromatography (HPLC) grade methanol, water, and acetonitrile with purities of > 99% obtained from Fisher Scientific (San Jose, CA) were used. The diuron analytical grade standard obtained from AccuStandard (New Haven, CT) had a purity of 98%.

Diuron Adsorption Experiments. A batch-slurry method was carried out at 25 °C to examine diuron adsorption to soils as described in previous studies (*25−27*). Four levels of diuron standard solutions ranging from 2 to 8 mg L^{-1} were prepared by parallel dilution in 0.01 M CaCl$_2$ solution. Depending on their OC content, 0.2−1.5 g soil samples were weighed into 50 mL centrifuge tubes followed by the addition of 10 mL of standard solution. Adsorption equilibrium was attained by shaking the mixture end-over-end for 24 h, a period determined previously to be sufficient to reach equilibrium (*20,28,29*). For quality control purposes and to ensure that there was no diuron adsorption onto container walls, blank controls were included in the analyses.

After centrifugation at 10000 rpm for 15 min, the supernatant was decanted and filtered using Whatman no. 42 filter papers. Diuron equilibrium concentrations (C_e) were determined by HPLC with UV detection. A mixture of methanol (60%), water (30%), and acetonitrile (10%) by volume was used as mobile phase with a flow rate of 2.0 mL min^{-1} using a 3.9 × 150 mm Nova-Pak C18 column. The injection volume was 10 μL, and the UV detector was set at 250 nm wavelength. The adsorbed concentration was assumed to be the difference between initial and final solution concentration, as no loss occurred in the blank controls.

The adsorption isotherms were fit to the linear equation

$$S_e = K_d C_e \qquad (1)$$

where S_e (mg kg^{-1}) is the equilibrium adsorbed concentration, K_d (L kg^{-1}) is the adsorption coefficient, and C_e (mg L^{-1}) is the solution equilibrium concentration.

Diuron Degradation Experiments. Diuron degradation was determined by monitoring its disappearance from diuron−soil mixtures over time. Samples of 5 g of air-dried soil were weighed into 50 mL polycarbonate centrifuge tubes. Aqueous solutions of diuron standard with concentrations ranging from 20 to 100 mg L^{-1} were added to soil samples in volumes equivalent to 60% of each soil's water-holding capacity and homogenized by stirring. Diuron degradation incubations were conducted in the dark at 25 °C for 120 days. At set time intervals, samples, prepared in triplicate, were extracted with 20 mL of methanol by shaking for 3 h and centrifuged at 10000 rpm for 10 min, and the supernatant was filtered through Fisher Brand Q2 filter paper. The residue was extracted with an additional 10 mL of methanol for 2 h and similarly treated. The extracts were combined and stored at −20 °C until analysis by HPLC as described above for the adsorption experiments.

Degradation was operationally defined as the disappearance of the parent compound and was modeled using a first-order kinetics model (eq **2**) such that

$$C_t = C_o\, e^{-kt} \qquad (2)$$

where C_0 (mg) is the initial concentration of diuron, C_t (mg) is the concentration at time t (days), and k (1/day) is the first-order degradation rate coefficient. However, because diuron was likely incompletely extracted, an extraction efficiency factor (f^*) was used to adjust the diuron concentration using eq **3**

$$C_t = \frac{C_t*}{f*} \qquad (3)$$

where C_t* is the extracted concentration at time t. For each soil sample, f^* was calculated by extracting diuron from a sample immediately after diuron addition. Substituting eq **3** into eq **2** and linearization yields eq **4**

$$\ln(C_t*) = \ln(C_0 f*) - kt \qquad (4)$$

which can be used to obtain k graphically by plotting $\ln(C_t^*)$ versus t.

Statistical Analysis. Regression analyses, nonparametric statistics (Kruskal−Wallis), and confidence interval calculation were performed using SAS (*30*) software.

RESULTS AND DISCUSSION

The chemical properties of soils studied, including calcium carbonate content, pH, and fraction organic carbon content (f_{oc}) are presented in **Tables 1−3**. These parameters illustrate the wide diversity of soil properties within the sample set. The pH of the soils averaged 7.3 ± 0.1 (±95% confidence interval, CI), 6.7 ± 0.3, 5.8 ± 0.6, and 3.6 ± 0.2 [standard error (SE); ± 0.05, 0.13, 0.21, and 0.09] for carbonatic, Histosols, Oxisols, and Spodosols, respectively. The f_{oc} in the soils ranged from 0.01 to 0.11 for carbonatic soils (similar for marl- and nonmarl-carbonatic soils), from 0.10 to 0.47 for Histosols, from 0.003 to 0.06 for Oxisols, and from 0.002 to 0.02 for Spodosols (**Tables 1−3**). The mean OC contents in soils were 3.9 ± 1.2 (±95% CI), 32.4 ± 7.6, 2.4 ± 0.4, and 1.6 ± 0.9 [SE ± 0.6, 3.5, 0.2, and 0.4] for carbonatic soils, Histosols, Oxisols, and Spodosols, respectively.

Adsorption of Diuron. Adsorption coefficients (K_d) ranged from 1.9 to 29.8 L kg^{-1} for carbonatic soils, from 53.5 to 486 L kg^{-1} for Histosols, from 1.59 to 59.3 L kg^{-1} for Oxisols, and from 1.16 to 86.6 L kg^{-1} for Spodosols. The adsorption data were well-described by the linear model with linear correlation coefficients (between S_e and C_e) generally better than 0.9. Similar linear diuron isotherms have been observed in other studies (*11, 20, 31*). In other studies, however, diuron adsorption has been described by the nonlinear Freundlich model (*32−34*). This contrast is likely due to the higher diuron concentration range in which these other studies were conducted. The adsorption coefficients (K_d) within each soil type were significantly linearly correlated to f_{oc} (**Figure 1**). In all cases the p value on the slope was < 0.001, but the intercepts for all soil types were not

Table 1. Carbonatic Soil Sample Sources, Chemical Properties, and Calculated Diuron Soil Interaction Parameters[a]

soil series	origin	f_{oc}	% CaCO$_3$	pH	K_{oc} (L kg^{-1})	$t_{1/2}$ (days)	GUS
Aguilita	PR	0.05	52.9	6.94	261	100	3.2
Biscayne[b]	FL	0.06	83.6	6.99	220	267	4.0
Biscayne 2[b]	FL	0.03	81.8	7.18	204	161	3.7
Cudjoe[b]	FL	0.10	68.0	7.19	255	nd	
Chekika	FL	0.02	88.8	7.18	292	77	2.9
Chekika 2	FL	0.04	58.4	7.00	448	nd	
Colinas	PR	0.02	80.3	7.15	403	154	3.1
Keyvaca	FL	0.11	64.5	7.26	262	45	2.6
KeyWest 1[b]	FL	0.01	89.5	8.16	152	nd	
KeyWest 2[b]	FL	0.01	94.2	7.69	162	239	4.3
Krome 1	FL	0.02	64.3	7.48	436	119	2.8
Krome 2	FL	0.02	50.5	7.36	463	nd	
Lignumvitae 1[b]	FL	0.06	83.6	7.16	251	119	3.3
Lignumvitae 2[b]	FL	0.05	85.4	7.28	168	239	4.2
Pennsuco[b]	FL	0.03	84.1	7.36	216	231	3.9
Perrine 1[b]	FL	0.03	87.9	7.30	167	103	3.6
Perrine 2[b]	FL	0.03	91.0	7.25	161	nd	
Perrine-Tamiami assoc	FL	0.04	90.3	7.33	496	nd	
Saddlebunch 1[b]	FL	0.02	nd	7.45	152	315	4.6
Saddlebunch 2[b]	FL	0.08	79.2	7.42	189	267	4.2
San Sebastian	PR	0.02	nd	7.18	226	289	4.1
Tuque	PR	0.02	86.0	7.27	155	187	4.1
Yauco	PR	0.03	61.9	7.25	207	117	3.5

[a] Abbreviations: FL, Florida; PR, Puerto Rico; f_{oc}, fraction of organic carbon (OC); K_{oc}, sorption coefficient normalized to OC; $t_{1/2}$, half-life; GUS, groundwater ubiquity scores; nd, not determined. [b] Marl-carbonatic soil.

Table 2. Florida Histosol and Spodosol Soil Chemical Properties and Calculated Diuron–Soil Interaction Parameters[a]

soil series	f_{oc}	% CaCO$_3$	pH	K_{oc} (L kg^{-1})	$t_{1/2}$ (days)	GUS
Histosols						
Dania 1	0.43	6.6	5.94	982	nd	
Dania 2	0.53	7.9	5.72	911	nd	
Islamorada	0.39	10.1	6.65	273	1733	5.1
Lauderhill 1	0.29	10.3	7.06	545	187	2.9
Lauderhill 2	0.21	18.3	7.22	391	nd	
Lauderhill 3	0.23	10.1	7.18	543	nd	
Matecumbe 1	0.33	11.5	7.00	674	169	2.6
Matecumbe 2	0.20	nd	6.97	564	nd	
Pahokee 1	0.42	9.9	7.20	464	nd	
Pahokee 2	0.47	8.8	6.27	765	nd	
Tamiami 1	0.40	nd	6.30	485	165	2.91
Tamiami 2	0.40	4.9	6.65	660	nd	
Torry 1	0.13	4.8	7.20	509	nd	
Torry 2	0.10	nd	6.65	556	nd	
Spodosols						
Monteocha 1	0.05	nd	3.57	1586	224	1.88
Monteocha 2	0.01	nd	3.32	3910	128	0.86
Pomona 1	0.01	nd	3.55	1678	119	1.61
Pomona 2	0.02	nd	3.16	2675	210	1.33
Pomona 3	0.01	nd	3.23	3885	92	0.81
Pomona 4	0.02	nd	3.3	4243	141	0.8
Pomona Bh-1[b]	0.01	nd	3.93	590	nd	
Pomona Bh-2[b]	0.02	nd	3.87	631	nd	
Pomona Bh-3[b]	0.01	nd	3.89	1149	nd	
Pomona E	0.002	nd	3.79	555	nd	

[a] Abbreviations same as **Table 1**. [b] Bh horizons depth = 80–100 cm.

significantly different from zero ($p > 0.05$). The relatively high correlation coefficients of 0.78 and 0.75 for carbonatic soils and Histosols, respectively, suggest that OC plays a predominant role in the adsorption processes of these soil types. However, lower correlation coefficients of 0.61 and 0.56 observed for Oxisols and Spodosols indicate that OC alone does not account for the adsorption of diuron in these soils. Linagaye et al. (*31*) observed similarly low correlation (0.58), and similar K_d values, in Sri Lankan Oxisols. Another study in Brazilian Oxisols (*34*) observed a similar trend. The processes that might result in the observed discrepancies in the adsorption of diuron in Oxisols and Spodosols need further investigation. However, with the exception of Oxisols, X-ray diffraction (XRD) analysis (data not shown) did not indicate the presence of significant amounts of clay minerals in Florida soils. For carbonatic soils, the dominant mineral was calcite. There was no effect of soil pH on the adsorption of diuron. No investigations on the effect of clay minerals on diuron adsorption were pursued in this study because diuron is nonionic. A previous study by Nkedi-Kizza et al. (*35*) showed no diuron adsorption when soil organic matter was removed from soils using hydrogen peroxide. The adsorption process is believed to be controlled largely by OC especially for soils with OC content > 1% (*32, 36, 37*) as was the case in most of our soil samples. In addition, several previous studies found a strong relationship between adsorption of neutral organic chemicals and OC content (*36, 38–42*). Compared to the silt and sand fractions, Wang and Keller (*32*) reported higher diuron adsorption in the clay-sized fraction, in which adsorption was attributed to the OC associated with the different size fractions. The study reported a high OC content within the clay-sized fraction and showed an increasing trend in both OC content and CEC from sand < silt < clay-sized fractions. It is noteworthy that OM is more associated with the clay-sized fraction than with silt or sand fractions. It therefore likely that correlating sorption to CEC is likely to yield a good relationship, but this should not be surprising because OC

contributes a great deal to the soil CEC. The study attributed the sorption of diuron to OC. Oliver et al. (*43*) also did not find a strong relationship between diuron adsorption and clay content (< 2 μm). Sheng et al. (*44*) also reported that diuron was more predominantly adsorbed to OM than to clays. A similar study by Chiou (*45*) found that surfaces of clay minerals were ineffective in adsorbing neutral organic chemicals.

The OC-normalized adsorption coefficient (K_{oc}), calculated for each soil sample as its K_d divided by f_{oc}, averaged 259 ± 48 (±95% CI) for carbonatic soils (197 ± 27 for marl- and 332 ± 80 for nonmarl-carbonatic soils) and 558 ± 109, 973 ± 156, and 2090 ± 1054 [SE ± 23, 51, 77, and 466] for Histosol, Oxisol, and Spodosol soils, respectively. **Figure 2** shows the K_{oc} distribution across soil types. The K_{oc} values of marl-carbonatic soils were significantly lower than for other soils ($\alpha = 0.05$) with an average value that was about 2, 3, 5, and 10 times lower than for nonmarl-carbonatic soils, Histosols, Oxisols, and Spodosols, respectively. The diuron average K_{oc} value for carbonatic soils was also significantly lower than the average literature value of 480 (*46*).

Although it was observed that adsorption capacity generally increased with OC content for each soil type (soil order), this relationship was not true for the data set as a whole (i.e., across soil orders). That is, the influence that OM had on adsorption varied for different soil types. For example, Spodosols, with the lowest average OC content (0.016), showed the highest diuron adsorption capacity ($K_{oc} = 2090$), followed by Oxisols (0.022; average $K_{oc} = 973$), again indicating that processes other than OC content (e.g., the nature of OM present) may play a major role in controlling the adsorption of diuron in soils. Also, the average OC content of nonmarl-carbonatic soil was only 15% less than that of the marl-carbonatic soils, but the average K_{oc} of

Table 3. Oxisol Sample Sources, Soil Chemical Properties, and Calculated Diuron−Soil Interaction Parameters

				diuron		
soil classification	sample location	f_{oc}	pH	K_{oc} (L kg^{-1})	$t_{1/2}$ (days)	GUS
Bayamon	Bayamon[a]	0.02	6.57	328	nd	
Bayamon	Bayamon 2[a]	0.02	4.28	333	40	2.37
Buganda Catena (Ferrallitic soils)	Fiduga 1[b]	0.02	5.96	1253	nd	
Buganda Catena (Ferrallitic soils)	Fiduga 2[b]	0.01	7.04	770	nd	
Buganda Catena (Ferrallitic soils)	Fiduga 3[b]	0.02	7.02	908	nd	
Buganda Catena (Ferrallitic soils)	Fiduga pooled[b]	0.01	6.78	1282	147	1.93
Kasese series (Lithosols)	Hima 1[b]	0.04	7.54	768	nd	
Kasese series (Lithosols)	Hima 2[b]	0.06	7.56	969	nd	
Kasese series (Lithosols)	Hima 3[b]	0.04	7.51	837	nd	
Kasese series (Lithosols)	Hima Lime[b]	0.01	7.62	1192	nd	
Kasese series (Lithosols)	Hima pooled[b]	0.03	7.93	691	193	2.65
Kabira Catena (Ferrisols)	Kakira 1[b]	0.02	5.88	1396	nd	
Kabira Catena (Ferrisols)	Kakira 2[b]	0.03	5.2	1669	nd	
Kabira Catena (Ferrisols)	Kakira 3[b]	0.03	6.2	806	nd	
Kabira Catena (Ferrisols)	Kakira pooled[b]	0.03	5.63	1058	169	2.17
Mabira Catena (Ferrisols)	Kasaku 1[b]	0.03	4.11	717	nd	
Mabira Catena (Ferrisols)	Kasaku 2[b]	0.03	5.31	1186	nd	
Mabira Catena (Ferrisols)	Kasaku 3[b]	0.03	4.27	567	nd	
Mabira Catena (Ferrisols)	Kasaku 4[b]	0.03	4.49	742	nd	
Buganda Catena (Ferrallitic soils)	MK Flora 1[b]	0.03	5.15	1508	nd	
Buganda Catena (Ferrallitic soils)	MK Flora 2[b]	0.02	4.85	796	nd	
Buganda Catena (Ferrallitic soils)	MK Flora 3[b]	0.03	5.2	2076	nd	
Buganda Catena (Ferrallitic soils)	MK Flora 4[b]	0.02	5.46	1621	nd	
Buganda Catena (Ferrallitic soils)	MK Flora pooled[b]	0.02	5.13	1397	165	1.90
Kasese series (Lithosols)	Muhookya 1[b]	0.01	7.22	348	nd	
Kasese series (Lithosols)	Muhookya 2[b]	0.03	7.41	585	nd	
Kasese series (Lithosols)	Muhookya 3[b]	0.003	7.53	541	nd	
Kasese series (Lithosols)	Muhookya pooled[b]	0.01	7.43	736	248	2.71
Bugangari series (Lithosols)	Rubaabo[b]	0.02	6.37	1165	nd	
Mabila Catena (Ferrisols)	Scoul Lugazi 1[b]	0.03	5.11	1529	nd	
Mabila Catena (Ferrisols)	Scoul Lugazi 2[b]	0.02	5.01	1351	nd	
Mabila Catena (Ferrisols)	Scoul Lugazi 3[b]	0.03	4.11	1885	nd	
Mabila Catena (Ferrisols)	Scoul Lugazi 4[b]	0.03	4.69	1437	nd	
Mabila Catena (Ferrisols)	Scoul pooled[b]	0.03	4.68	1154	165	2.08
Katera series (Ferrallitic soils)	Wagagai 1[b]	0.01	4.37	247	nd	
Katera series (Ferrallitic soils)	Wagagai 2[b]	0.01	3.95	253	nd	
Katera series (Ferrallitic soils)	Wagagai 3[b]	0.02	4.17	342	nd	
Katera series (Ferrallitic soils)	Wagagai pooled[b]	0.01	4.14	552	169	2.80

[a] Puerto Rican origin. [b] Ugandan origin. Ugandan soil classification: local classification (Food Agricultural Organisation/European Union classification, in parentheses) *59*. [c] nd, not determined.

nonmarl-carbonatic soil was 77% greater. This difference in diuron adsorptive behavior is likely due to varied OM compositions in these two classes of carbonatic soils. The origin of OM in marl soil is likely to be algae, derived from terrestrial algal mats that develop on the soil surface, whereas OM in the nonmarl-carbonatic soils may be of mixed marine algal and plant origin. It is interesting to note that even within the marl- and nonmarl-carbonatic soil classes, there are samples with similar OC contents but different K_{oc} values, which suggests the occurrence of intrasoil type OM composition heterogeneity or other soil components play a role in diuron adsorption.

Degradation of Diuron. The degradation experiments were conducted at 25 °C in the dark, and diuron degradation was operationally defined as reduction in the extracted parent compound. Diuron degradation was well-described by a first-order kinetic model (**Figure 3**). The degradation rate coefficient, k (1/day), ranged from 0.0004 to 0.02 and had a mean value of 0.005 ± 0.001 for all of the soils tested. The $t_{1/2}$ of diuron in soils ranged from 40 to 267 days, with Bayamon, an Oxisol from Puerto Rico, showing the fastest degradation rate for diuron ($t_{1/2} = 40$ days) and Saddlebunch, a Mollisol with carbonatic mineralogy from Key West, FL, showing the slowest degradation rate ($t_{1/2} = 267$ days). By soil group, the average diuron half-life

was 168 ± 42 ($\pm 95\%$ CI) days for carbonatic soils, 176 ± 22 days for Histosols, 162 ± 48 days for Oxisols, and 152 ± 55 days for Spodosols. However, there was no significant statistical difference between the average half-lives of each of the soil groups, indicating that degradation rates were not affected by soil type.

The diuron half-life in Oxisols determined in field experiments by Dores et al. (*47*) of 15 days was much lower than that found in this study. However, it is difficult to conduct a controlled degradation experiment in the field, and leaching may also occur due to rainfall, producing lower degradation rates. The diuron half-life obtained in this study for Histosols was also lower than was found in another study (*48*). The average half-life (164 days) obtained for all soils in this study was about 2 times higher than the average diuron half-life (90 days) reported in the literature (*6*, *15*, *46*).

In agreement with a previous study (*49*), no relationship was observed between diuron degradation rate and soil chemical parameters such as pH or f_{oc} or diuron adsorption parameters such as K_d or K_{oc}. This finding contrasts with previous studies (*17*, *50*), which reported an increase in diuron degradation rate with increased OC content. Other studies (*51−53*) have reported a decrease in degradation with increased adsorption capacity (which is often related to increased f_{oc}), citing protection
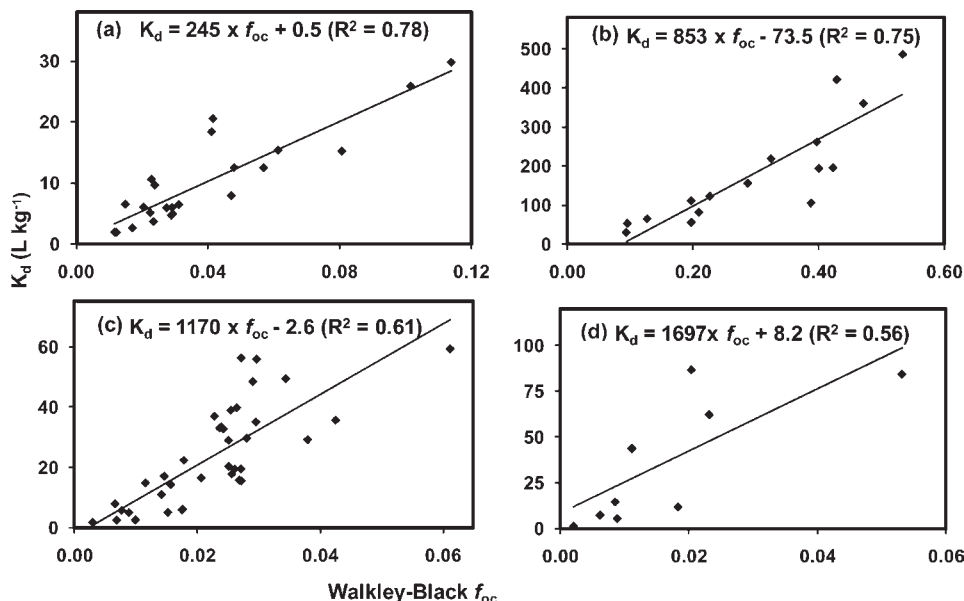
Figure 1. Correlations between diuron adsorption coefficient (K_d) and organic carbon fraction (f_{oc}): (**a**) carbonatic soils; (**b**) Histosols; (**c**) Oxisols; (**d**) Spodosols.
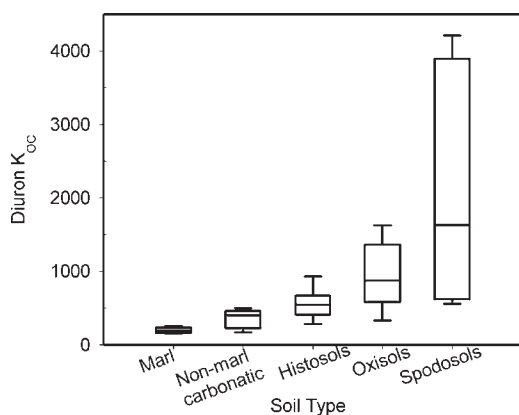

Figure 2. Box plot showing 25th and 75th percentile distribution of organic carbon-normalized adsorption coefficient (K_{oc}) values for diuron in each of the soil groups.
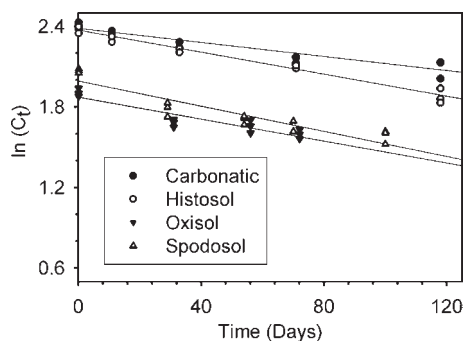

Figure 3. Selected plots of $\ln(C_t^*)$ versus time for diuron degradation in soils.

of the chemical from microbial attack due to adsorption. Both abiotic and biological processes may cause the degradation of pesticides in soils. It is generally believed that biodegradation is the major cause for diuron disappearance in soils (*13*, *54*). The interplay between soil OM, minerals, microbes, and diuron and other contaminants needs to be further studied. Because both
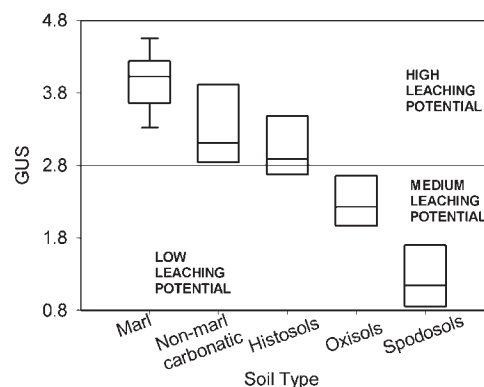

Figure 4. Box plot showing 25th and 75th percentile distribution of groundwater ubiquity scores (GUS) for diuron in each soil group.

adsorption and degradation are important factors in determining whether a contaminant is likely to move from application site to nontarget sites, Gustafson et al. (*55*) introduced the groundwater ubiquity score (GUS), which incorporates both of these factors to predict the potential for a chemical to pose a concern for groundwater pollution. Following Gustafson et al. (*55*), GUS values for the soils studied were calculated as

$$\text{GUS} = [4 - \log K_{oc}] \times \log t_{1/2} \qquad (5)$$

A GUS of < 1.8 indicates low leaching potential, $1.8 < \text{GUS} < 2.8$ moderate potential, and $\text{GUS} > 2.8$ high potential for leaching (*55–58*). The GUS for diuron ranged from 3.3 to 4.6, from 2.6 to 4.1, from 2.6 to 3.7, from 1.9 to 3.3, and from 0.8 to 1.7 for marl-carbonatic, nonmarl-carbonatic, Histosols, Oxisols, and Spodosols, respectively (all data in **Tables 1–3** and summarized in **Figure 4**). A Saddlebunch soil sample from southern Florida and a Tuques soil sample from Puerto Rico showed the highest potential to leach diuron. Results in **Figure 4** showed that, according to the GUS, marl-carbonatic soils exhibited the highest potential to leach diuron, whereas Spodosols had lowest leaching potential. Among the nonmarl-carbonatic soil types, those from Puerto Rico exhibited the highest diuron GUS. The GUS factor provides a good estimator for groundwater pollution risk,

although under field conditions, the potential for leaching may vary from that indicated by the score because other factors, such as temperature and intensity and frequency of precipitation, and intrinsic soil properties such as permeability and drainage class, depth to the water table, and farming practices may influence actual adsorption and degradation behavior of a contaminant.

The GUS index of leaching potential proved to be a useful method to integrate the adsorption and degradation data generated for diuron and to illustrate the particular concern that diuron application in carbonatic soil regions may pose. The shallow soil depth and the porous nature of the carbonatic soils, as well as the highly permeable surficial aquifer in southern Florida, add to the environmental threat that diuron may pose to groundwater resources in this region. With its relatively slow degradation rate and low adsorption capacity in carbonatic soils, particularly marls, diuron is likely to persist and be transferred through water flow paths, which may explain its frequent detection in southern Florida surface waters (*4*).

Field application rates are based on the soil OC content, which affects the available solution concentration of the compound applied. However, because diuron is poorly adsorbed in carbonatic soils, it may be possible that it remains effective even when applied at lower rates than currently used in southern Florida agricultural production. Protecting the environment in these vulnerable soils may, therefore, require lowering the application rates for herbicides used in southern Florida and Puerto Rican agriculture. Pesticide management practices specific to carbonatic soils must be developed to safeguard the environment and water resources in places such as southern Florida and Puerto Rico. Further research should be carried out to understand the cause of diuron's unexpectedly low degradation rate in carbonatic soils.

ABBREVIATIONS USED

C_e, equilibrium solution concentration (mg L^{-1}); C_0, initial mass of sorbate added to soil (mg); C_t, mass of sorbate at time t days (mg); C_t*, extracted mass of sorbate from soil at time t days (mg); f*, extraction efficiency of sorbate from soil; f_{oc}, fraction of organic matter; GUS, groundwater ubiquity score; k, degradation rate coefficient (1/day); K_d, soil−water partition coefficient (L kg^{-1}); K_{oc}, soil−water partition coefficient normalized with soil organic carbon content (L kg^{-1}); OC, soil organic carbon; OM, soil organic matter; p, probability; rpm, revolutions per minute; S_e, equilibrium adsorbed concentration of a solute (mg kg^{-1}); $t_{1/2}$, half-life; 95% CI, 95% confidence interval; α, level of significance.

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