Sorption−Desorption of Imidacloprid and Its Metabolites in Soil and Vadose Zone Materials

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Sorption−desorption is one of the most important processes affecting the leaching of pesticides through soil because it controls the amount of pesticide available for transport. Subsurface soil properties can significantly affect pesticide transport and the potential for groundwater contamination. This research characterized the sorption−desorption of imidacloprid (1-[(6-chloro-3-pyridinyl)-methyl]-*N*-nitro-2-imidazolidinimine) and three of its metabolites, 1-[(6-chloro-3-pyridinyl)methyl]-2-imidazolidinone (imidacloprid−urea), 1-[(6-chloro-3-pyridinyl)methyl]-4,5-dihydro-1*H*-imidazol-2-amine (imidacloprid−guanidine), and 1-[(6-chloro-3-pyridinyl)methyl]-1*H*-imidazol-2-amine (imidacloprid−guanidine−olefin), as a function of changing soil properties with depth in two profiles extending from the surface to a depth of 1.8 or 8 m. Sorption of each compound was highly variable and hysteretic in all cases. Normalizing the sorption coefficients (K_f) to the organic carbon or the clay content of the soil did not reduce the variability in sorption coefficients for any compound. These results illustrate the importance of evaluation of the sorption data used to predict potential mobility. Understanding the variability of soil properties and processes as a function of depth is necessary for accurate prediction of pesticide dissipation.

KEYWORDS: Adsorption; insecticide; leach; partition; pesticide; subsoil; subsurface; transport

INTRODUCTION

Imidacloprid (1-[(6-chloro-3-pyridinyl)-methyl]-*N*-nitro-2-imidazolidinimine) is a systemic chloronicotinyl insecticide, which acts as an agonist of the nicotinyl acetylcholine receptor (*1, 2*). This insecticide is effective at low doses in controlling sucking insects, soil insects, termites, and some species of chewing insects; it is used as a seed dressing, soil treatment, and foliar treatment in a variety of crops (*3, 4*) and is currently labeled for surface and subsurface application to soil. Metabolites of imidacloprid have been shown to have a broad range of toxicities, with some showing stronger insecticidal activity than the parent compound (*5, 6*) and many demonstrating chronic toxicity to honeybee in dosing studies (*7*).

Limited information has been published concerning the fate of imidacloprid and its metabolites in soil. Surface soil dissipa-

tion half-lives (DT_{50}) in field experiments under cropped and various agricultural conditions ranged from 40 to 130 days (*8, 9*) and from 48 to 190 days in standardized greenhouse tests (*10*). The main imidacloprid metabolites identified in soil include 1-[(6-chloro-3-pyridinyl)methyl]-2-imidazolidinone (imidacloprid−urea), 6-chloronicotinic acid, and 6-hydroxynicotinic acid (*9*), which are ultimately mineralized to CO_2 (*10*). The rate of imidacloprid degradation in soil decreased with the addition of organic amendment, which was attributed to increased sorption (*9*).

Sorption−desorption processes are important in determining the fate and distribution of agrochemicals in the soil/water environment, because they determine the amount of pesticide that can reach the target organism and the amounts that can be volatilized, degraded, and leached. In general, sorption of imidacloprid and its metabolites imidacloprid−urea, imidacloprid−guanidine (1-[(6-chloro-3-pyridinyl)methyl]-4,5-dihydro-1*H*-imidazol-2-amine), and imidacloprid−guanidine−olefin (1-[(6-chloro-3-pyridinyl)methyl]-1*H*-imidazol-2-amine) is greater in soils with greater organic carbon (OC) and clay contents, with the guanidine metabolites exhibiting more sorption than imidacloprid or imidacloprid−urea (*11, 12*). Sorption of imi-

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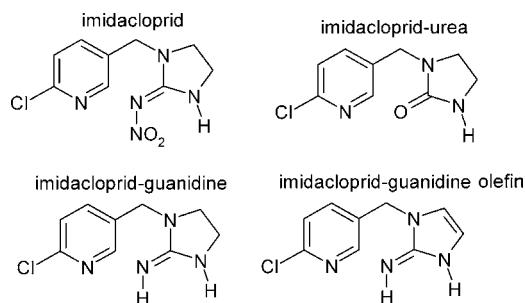⊥ University of Minnesota.

Figure 1. Stuctures of imidacloprid and its urea and guanidine metabolites investigated in this study.

dacloprid and these metabolites has been shown to increase with aging (*13−15*). These chemicals are sorbed by clays and organoclays (*16, 17*). As for many pesticides, desorption of imidacloprid and these metabolites is hysteretic in surface soils (*11*). The hysteresis mechanism is not known; however, a portion of it may be due to irreversible sorption on soil (*18*).

Some field trials have indicated that imidacloprid does not tend to leach below the surface soil when surface-applied (*8, 9*); however, leaching of imidacloprid has been observed in greenhouse soils (*19*), in field soils following the application of imidacloprid via drip irrigation (*20*), and in cracking soil, likely as a result of preferential transport (*21*). Imidacloprid applied by subsurface drip chemigation leached to at least a 150 cm depth in field trials (*22*). The U.S. EPA reports that imidacloprid has been detected in groundwater in areas vulnerable to leaching (*23*). There is no information available on the sorption−desorption of imidacloprid or any of its metabolites in subsurface soils.

Knowledge of pesticide sorption and desorption in subsurface soils is needed for risk assessments of groundwater contamination by pesticides. Most available data have been developed for triazines, atrazine in particular, in shallow subsurface soils <3 m deep (*24−28*), and only rarely for deeper subsoils (*29−31*). There are limited studies of the sorption of other pesticides in subsoils at >75 cm depth, that is, alachlor (*25, 28, 32*), isoproturon and metamitron (*31*), and hexazinone, sulfometuron methyl, and tebuthiuron (*33*).

The research presented here focused on the sorption−desorption of imidacloprid and three of its metabolites, imidacloprid−urea, imidacloprid−guanidine, and imidacloprid−guanidine−olefin, as a function of changing soil properties with depth in two soil profiles extending from the surface to 1.8 or 8 m depth. The data will contribute to assessments of the bioavailability and leaching potential of these chemicals. It is important to evaluate the environmental fate of pesticide metabolites, because their mobility, persistence, and toxicity can differ widely from those of the parent compound.

MATERIALS AND METHODS

Chemicals and Soils. Pure analytical (chemical purity > 99%) and radiochemical (methylene-^{14}C, radiochemical purity > 97%) imidacloprid (molecular weight 256), imidacloprid−urea (molecular weight 212), imidacloprid−guanidine (molecular weight 211), and imidacloprid−guanidine−olefin (molecular weight 209) were supplied by Bayer Corp. Structures are shown in **Figure 1**. Calculations of pKa using SPARC (*34*) did not predict a pKa value within the pH range of 2−12 for imidacloprid or any of these three metabolites. This is supported by laboratory measurements, which indicated no measurable pKa between pH 2.3 and 11.6 for imidacloprid and the urea metabolite (*5*). These compounds are not expected to be cationic at environmentally relevant soil pH values.

Table 1. Soil Properties as a Function of Depth

depth (cm)	texture	pH	CEC (cmol$_c$ kg^{-1})	organic carbon (g kg^{-1})	clay (g kg^{-1})
		Core CA-1			
0–30	sandy loam	7.5	10.3	5.9	128
30–74	sandy loam	7.6	10.0	4.4	108
74–97	sandy loam	7.6	10.6	5.6	108
97–132	sandy loam	7.7	12.2	8.7	168
305–427	loamy sand	8.1	5.1	0.6	48
671–793	sand	8.5	2.9	0.3	28
		Core CA-2			
0–30	sandy loam	8.2	9.7	4.1	108
30–74	sandy loam	8.0	9.6	2.2	108
74–97	silty clay loam	7.8	27.7	8.5	388
97–132	silt loam	7.9	14.8	4.4	208
305–427	loamy sand	8.0	4.7	0.9	48
671–793	loamy sand	7.9	4.4	<0.1	48
		Core MI-1			
0–15	sand/loamy sand	4.4	5.7	4.2	51.4
15–30	loamy sand	4.5	6.0	3.8	55.0
76–91	sand	7.1	9.0	1.9	52.5
168–183	sand	7.4	7.7	1.8	34.1
		Core MI-2			
0–15	loamy sand	4.1	5.8	4.9	55.1
15–30	loamy sand	4.8	5.1	2.8	50.7
76–91	sand	4.7	2.9	0.5	50.6
168–183	sand	7.1	12.7	3.3	30.6

Soils were collected from auger borings (15 cm diameter) in fallow agricultural fields in California and Michigan. The California soil was characterized as a Metz fine sandy loam (sandy, mixed, thermic, Typic Xerofluvents) and the Michigan soil as a Mancelona loamy sand (sandy, mixed, frigid, Alfic Haplorthods). Samples from selected depth increments were air-dried and stored at room temperature until used in the sorption−desorption experiments. Soil properties (**Table 1**) were determined by A&L Great Lakes Laboratories, Fort Wayne, IN, using standard methods; that is, pH was measured in a 1:1 soil/water slurry, clay content was determined by the hydrometer method, OM content was determined by combustion, and cation exchange capacity (CEC) was measured using ammonium replacement. In this paper, we apply the term "soil" to all solid materials used in these experiments, including surface soil, subsoil, and vadose zone material.

Sorption−Desorption. Sorption experiments were carried out using the batch equilibration technique. In brief, duplicate 5-g air-dried soil samples were passed through a 2-mm sieve and treated with 5 mL of 0.01 N CaCl$_2$ containing imidacloprid, imidacloprid−urea, imidacloprid−guanidine, or imidacloprid−guanidine−olefin at four concentrations ranging from 23 to 1024 μg L^{-1} (4.8−8.4 and 212−262 μmol L^{-1}, depending on chemical). These rates are within normal agronomic application rates (0.05−0.5 kg ha^{-1}), but much lower than termiticidal application rates. Radiolabeled chemicals were added to non-radioactive solutions to give final solution concentrations of ∼4000 disintegrations per minute (240 kBq mL^{-1}). Soil suspensions were mechanically shaken for 24 h at 21 ± 2 °C in 25-mL glass centrifuge tubes closed with Teflon-lined caps. Samples were then centrifuged at 1912*g* for 30 min, and 1 mL of the supernatant was removed for radiometric analysis. Previous batch kinetic studies performed with various soils indicated that for all chemicals, equilibrium was reached within 1 h, no changes in concentration occurred after shaking for 48 h, and no degradation occurred within this period. In previous laboratory studies with three agricultural surface soils, imidacloprid degraded only slightly (<12%) within 2 weeks of incubation under optimum conditions (*13*). For the three metabolites, >86% of the amount applied could be recovered during an 8-week incubation (*14*). Solutions shaken in tubes without soil served as controls and showed no loss of ^{14}C from the solution during the equilibration periods.

Desorption experiments were conducted immediately after the sorption experiment. After centrifugation in the sorption experiment and removal of 1 mL for analysis, 1 mL of 0.01 N CaCl$_2$ containing
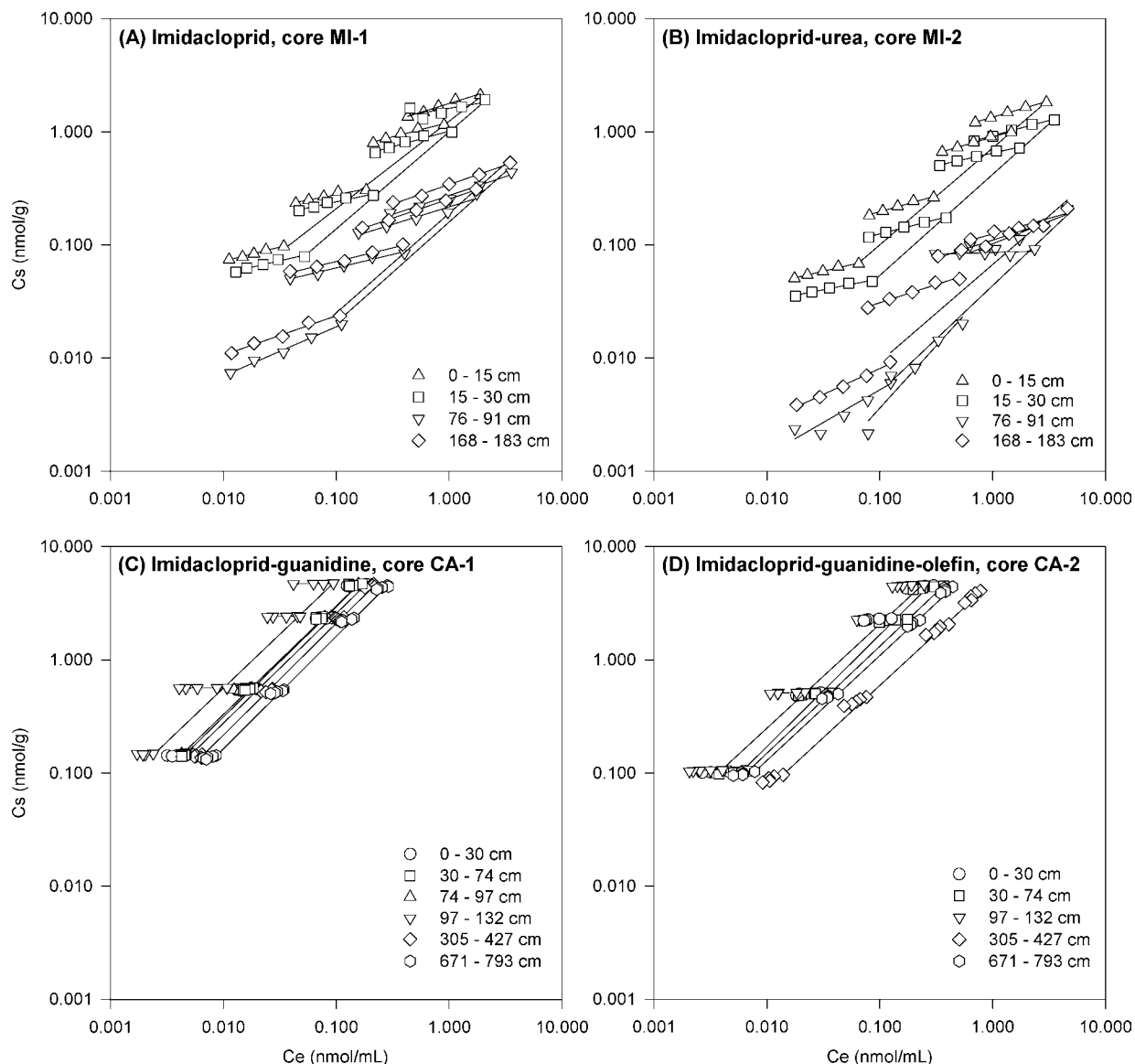
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Figure 2. Example sorption–desorption isotherms at each depth increment: (**A**) imidacloprid in core MI-1; (**B**) imidacloprid–urea in core MI-2; (**C**) imidacloprid–guanidine in core CA-1; (**D**) imidacloprid–guanidine–olefin in core CA-2. Sorption coefficients were determined by regressing a linearized Freundlich isotherm to the data. Points indicate means of duplicate samples; lines are the least-squares fit of the linearized Freundlich model to the log-transformed data.

no imidacloprid or metabolite was added to the soils. Soils were then resuspended in a vortex action shaker and then shaken for another 24 h. Soil suspensions were centrifuged, and 1 mL of supernatant was removed for analysis. This desorption cycle was repeated four times for each sample.

One-milliliter aliquots of the clear supernatants were mixed with 6 mL of EcoLite scintillation cocktail, and the amount of radioactivity was determined by liquid scintillation counting for 5 min in a 1500 TRI-CARB Packard liquid scintillation analyzer. The amount of imidacloprid or metabolite in solution was calculated considering the specific activity of each chemical. There was no chemiluminesence.

Data Analyses. The amount of chemical sorbed to the soil after equilibration was calculated from the difference between the initial and equilibrium solution concentrations. Sorption and desorption isotherms were calculated using the linearized form of the Freundlich equation

$$\log C_s = \log K_f + \frac{1}{n}\log C_e \qquad (1)$$

where C_s is the amount of chemical sorbed (μmol g^{-1} of soil), C_e is the equilibrium solution concentration (μmol mL^{-1} of solution), and K_f (μmol$^{1-1/n}$ g^{-1} mL$^{1/n}$) and $1/n$ are the sorption–desorption coefficients

expressing sorption capacity and nonlinearity, respectively. Sorption–desorption coefficients were calculated by the least-squares technique on the mean of the replicates of the log-transformed equilibrium data (**Figure 2**). Freundlich coefficients were normalized to the weight fraction of organic carbon (f_{oc}) using $K_{foc} = K_f/f_{oc}$ and to the weight fraction of clay-sized particles (f_{cm}) using $K_{fcm} = K_f/f_{cm}$. A hysteresis coefficient (H) was calculated at each concentration by

$$H = \frac{100 \times \dfrac{1}{n_{des}}}{\dfrac{1}{n_{ads}}} \qquad (2)$$

where $1/n_{des}$ is the desorption coefficient and $1/n_{ads}$ is the sorption coefficient (*35*). Associations between variables were tested using the Kendall correlation, which examines whether a variable tends to increase (positive correlation) or decrease (negative correlation) as another variable increases using pairwise comparisons.

RESULTS AND DISCUSSION

Soil Properties. There was a large variation in soil properties between sites, between duplicate cores from each site, and with

Table 2. Kendall Correlation Coefficients for Soil Properties (All Cores) and Sorption–Desorption Parameters, $n = 19$ or 20 (Bold Typeface Indicates Significant Correlations with $p < 0.005$)

	depth	pH	organic carbon	clay	CEC	K_f	$1/n_{des}$
average depth	1						
pH	0.45	1					
organic carbon	−0.41	−0.17	1				
clay	−0.30	0.02	**0.64**	1			
CEC	−0.08	0.07	**0.62**	**0.63**	1		
imidacloprid							
K_f	−0.29	−0.04	**0.66**	**0.65**	**0.48**	1	
$1/n_{des}$	0.38	**0.63**	−0.31	−0.12	−0.05	−0.27	1
imidacloprid−urea							
K_f	−0.27	−0.00	**0.66**	**0.66**	**0.47**	1	
$1/n_{des}$	0.24	0.33	−0.15	0.01	−0.08	-0.11	1
imidacloprid−guanidine							
K_f	−0.06	0.27	0.39	**0.53**	0.29	1	
$1/n_{des}$	0.26	0.00	**−0.64**	**−0.61**	−0.45	**−0.54**	1
imidacloprid−guanidine−olefin							
K_f	−0.03	0.28	0.37	**0.57**	0.30	1	
$1/n_{des}$	0.16	−0.13	**−0.53**	**−0.74**	−0.49	**−0.66**	1

depth within each core (**Table 1**). Correlation analysis of the pooled data indicated that soil OC and clay contents tended to decrease with depth, whereas pH tended to increase with depth ($p < 0.01$; **Table 2**). Clay and OC contents were correlated, and cation exchange capacity was positively correlated with clay and OC contents ($p < 0.005$; **Table 2**).

The California cores were characterized by moderate surface soil OC concentrations (0.4−0.6%), relatively high clay contents (>10% in the upper 130 cm), and high pH (≥7.5 at all depth increments). These cores included a lens at 97−132 cm in the CA-1 core and at 74−97 cm in the CA-2 core that had OC contents ≥0.85% (**Table 1**). This depth increment also had the highest clay content and CEC (**Table 1**) measured in each profile. In both California cores, OC content, clay content, and CEC were significantly correlated with each other ($p < 0.05$).

Surface soils of the Michigan cores had low pH (<5) and relatively low OC contents (0.4−0.5%); clay contents were low (5.5%) in all depth increments (**Table 1**). Soil pH values increased to near neutral at depths of >76 cm in Michigan core

MI-1 and in the deepest increment (168−183 cm) in core MI-2 (**Table 1**). Organic carbon contents were relatively uniform in the MI-1 core (0.2−0.4%), but were very low in the 76−91 cm increment of the MI-2 core (**Table 1**). In the MI-1 core, OC contents were negatively correlated with depth and pH ($p < 0.05$), whereas OC contents in the MI-2 core were not significantly correlated with any other soil property. Organic carbon contents were not correlated with clay contents in either Michigan core.

Sorption. All sorption isotherms (**Figure 2**) were well-described by the Freundlich model, with $r^2 > 0.97$. Sorption of each compound was highly variable within each core; imidacloprid and imidacloprid−urea K_f values varied over approximately 1 order of magnitude, whereas sorption of the guanidine metabolites was generally less variable (**Table 3**). Sorption coefficients followed the order imidacloprid−guanidine >imidacloprid−guanidine−olefin > imidacloprid > imidacloprid−urea, in agreement with sorption measured in other soils (*11*).

The variability in soil properties with depth had a great influence on the sorption of imidacloprid and its metabolites. In the California cores, OC and clay contents tended to vary with depth in a similar manner, whereas in the Michigan cores, soil OC and clay contents followed different trends with depth (**Figures 3** and **4**). In all cores, the greatest sorption (K_f) of each compound occurred at the depth increment with the highest OC content, which was also the depth increment with the highest clay content in three of the four cores (**Figures 3** and **4**). The higher variability in soil properties in the California cores resulted in more variable sorption coefficients in the California cores compared to the Michigan cores (**Figures 3** and **4**). In general, imidacloprid and imidacloprid−urea K_f values increased with increasing OC content, clay content, and CEC ($p < 0.005$; **Table 2**). Note that these soil properties are correlated, as discussed above (**Table 2**). Sorption of the guanidine metabolites was correlated only with clay content (**Table 2**). Despite these trends observed for the pooled data, normalizing sorption parameters by the OC content (K_{foc}) or the weight fraction of clay-sized particles (K_{fcm}) did not reduce the overall variability in sorption parameters, as has been reported previously for

Table 3. Mean Sorption and Desorption Parameters Determined for Four Soil Cores (Range Is Given in Parentheses)

	CA-1	CA-2	MI-1	MI-2
imidacloprid				
K_f ($\mu mol^{1-1/n}\, g^{-1}\, mL^{1/n}$)	1.2 (0.15–3.6)	1.2 (0.26–2.4)	0.64 (0.16–1.2)	0.61 (0.15–1.2)
$1/n_{ads}$	0.99 (0.95–1.04)	0.93 (0.90–0.96)	0.85 (0.77–0.89)	0.87 (0.83–0.89)
$1/n_{des}$	0.40 (0.13–0.89)	0.37 (0.23–0.53)	0.29 (0.19–0.43)	0.28 (0.20–0.38)
K_{foc}	320 (180–500)	1300 (280–6100)	190 (84–300)	230 (60–310)
K_{fcm}	10 (4.8–21)	8.8 (5.4–13)	13 (3.0–24)	12 (3.0–23)
imidacloprid−urea				
K_f ($\mu mol^{1-1/n}\, g^{-1}\, mL^{1/n}$)	0.72 (0.11–1.9)	0.50 (0.14–0.88)	0.30 (0.04–0.68)	0.31 (0.04–0.72)
$1/n_{ads}$	0.98 (0.97–1.00)	0.96 (0.95–0.98)	0.86 (0.78–0.91)	0.89 (0.86–0.94)
$1/n_{des}$	0.55 (0.29–0.78)	0.49 (0.37–0.80)	0.30 (0.13–0.57)	0.34 (0.03–1.1)
K_{foc}	220 (120–370)	810 (150–3300)	82 (21–160)	100 (21–150)
K_{fcm}	6.2 (3.9–11)	5.0 (2.9–6.9)	5.9 (0.76–13)	6.1 (0.79–13)
imidacloprid−guanidine				
K_f ($\mu mol^{1-1/n}\, g^{-1}\, mL^{1/n}$)	27 (16–45)	25 (13–44)	3.9 (1.6–7.2)	3.3 (1.3–5.2)
$1/n_{ads}$	0.98 (0.95–1.00)	0.97 (0.92–1.01)	0.89 (0.86–0.94)	0.89 (0.86–0.93)
$1/n_{des}$	0.11 (0.0–0.28)	0.13 (0.0–0.41)	0.42 (0.06–0.96)	0.38 (0.05–0.83)
K_{foc}	18,000 (4100–53000)	43,000 (5300–180000)	1200 (900–1700)	2100 (480–5400)
K_{fcm}	330 (190–570)	250 (110–370)	78 (42–140)	69 (52–94)
imidacloprid−guanidine−olefin				
K_f ($\mu mol^{1-1/n}\, g^{-1}\, mL^{1/n}$)	14 (5.8–26)	12 (4.9–17)	2.4 (1.2–3.6)	2.3 (1.1–3.8)
$1/n_{ads}$	0.96 (0.94–0.98)	0.94 (0.92–0.99)	0.88 (0.85–0.89)	0.91 (0.83–0.95)
$1/n_{des}$	0.18 (0.01–0.58)	0.21 (0.04–0.80)	0.41 (0.12–0.70)	0.60 (0.10–2.2)
K_{foc}	7200 (2500–19000)	22,000 (3900–92000)	790 (680–920)	1100 (320–2200)
K_{fcm}	150 (120–210)	130 (82–190)	49 (25–71)	48 (22–69)

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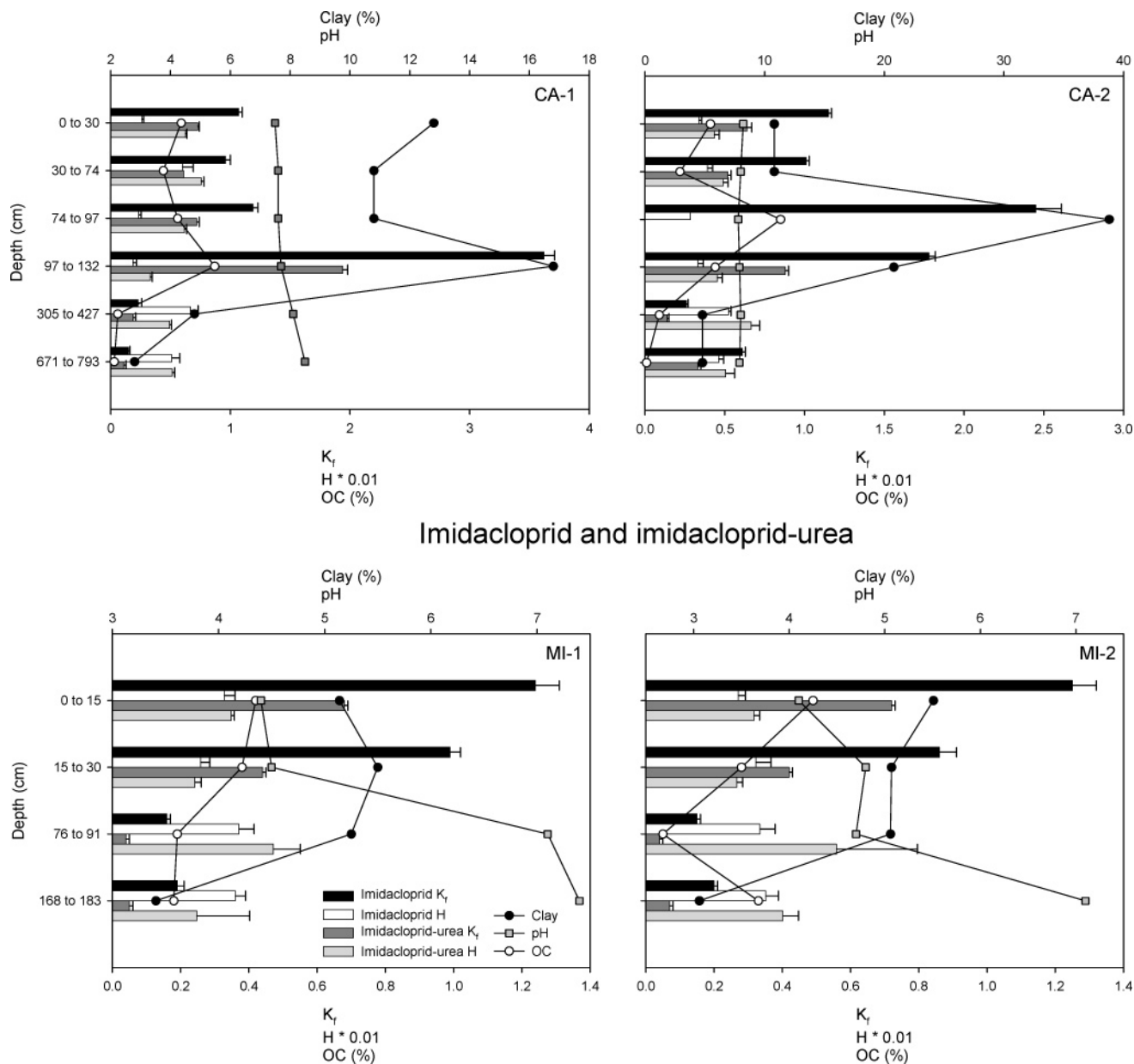*J. Agric. Food Chem.,* Vol. 54, No. 21, 2006 **8167**

Figure 3. Sorption coefficients (K_f) and hysteresis coefficients (H) in each core as a function of depth and soil properties: imidacloprid and imidacloprid–urea. Sorption coefficients were determined from linear regression to a linearized Freundlich model; error bars indicate the standard deviation of the fitted value. Hysteresis coefficients values are the mean of values determined at four concentrations; error bars indicate standard error.

pesticide sorption in subsurface materials (*28, 31*). For each compound, K_{foc} values ranged over at least 2 orders of magnitude and K_{fcm} values ranged over approximately 1 order of magnitude (**Table 3**). Many studies of sorption in surface soils have indicated that normalizing sorption coefficients to the OC content of the soil often reduces the variability in sorption coefficients, but this is not universal, and variability in K_{oc} values over an order of magnitude is common, especially at low OC contents (*36*). Models estimating pesticide leaching often use OC-normalized sorption parameters, including K_{foc}, as model inputs (*37, 38*).

Important differences in the sorptivity of the organic matter in different soils may violate the simplifying assumptions associated with normalized sorption coefficients, including a linear relationship between OC content and K_f. For each compound, the mean K_f and K_{foc} values were higher in the California cores than in the Michigan cores. At similar OC contents, samples from the California cores tended to have

higher K_{foc} for all compounds than samples from the Michigan cores (**Figure 5**). In these experiments, differences in sorptivity also occurred within each site and with depth in each core as indicated by K_{foc} values that were generally at least as variable as K_f values (**Table 3**). Organic carbon contents were especially variable in the California cores, leading to very high variability in K_{foc} values (**Table 3**; **Figure 5**).

Clay contents were generally more uniform within each core, within sites, and overall compared to OC contents (**Figure 3** and **4**), so the variability in K_{fcm} values was similar to that for K_f values. For each compound, clay-normalized sorption coefficients tended to be more uniform than OC-normalized coefficients within cores, within sites, and overall (**Table 3**).

The large differences in sorption values and trends in these cores show the importance of evaluating sorption coefficients used to predict pesticide mobility. A common approach used to estimate subsurface sorption values is to characterize the sorption in the surface soil, calculate a normalized sorption
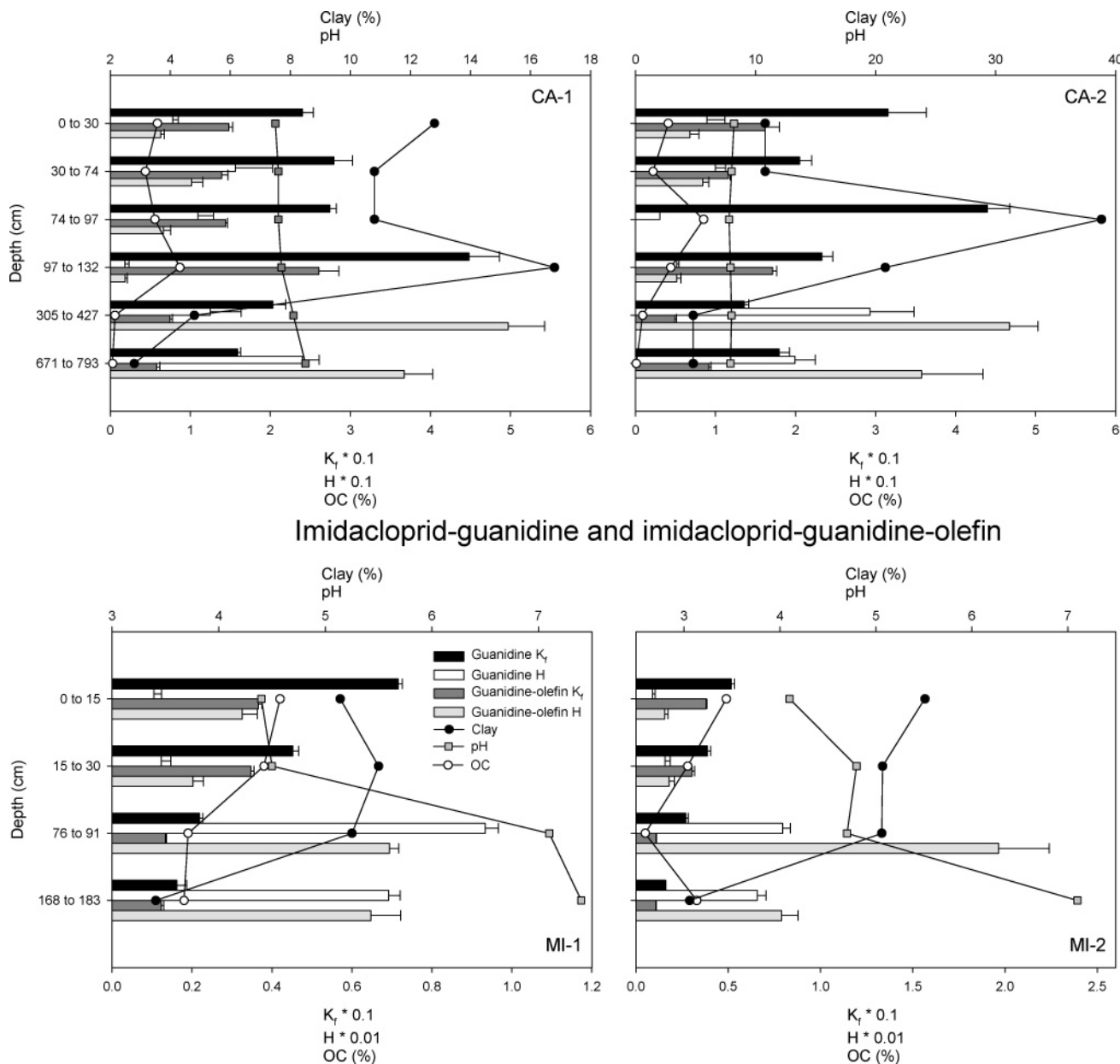
Figure 4. Sorption coefficients (K_f) and hysteresis coefficients (H) in each core as a function of depth and soil properties: imidacloprid–guanidine and imidacloprid–guanidine–olefin. Sorption coefficients were determined from linear regression to a linearized Freundlich model; error bars indicate the standard deviation of the fitted value. Hysteresis coefficients values are the mean of values determined at four concentrations; error bars indicate standard error.

coefficient based on the OC content of the surface soil (K_{oc}), and estimate the sorption in subsurface soils on the basis of the surface-soil K_{oc} and the OC content of the subsurface soil. This approach could severely underestimate or overestimate sorption in subsurface soils, as has been observed previously (*28*). In the California cores, estimates of imidacloprid K_f in subsurface soils were lower in all depth increments compared to the measured K_f (mean predicted/measured K_f was 0.6). In one subsurface sample with very low OC content, imidacloprid sorption was underpredicted by a factor of >20. Even in cases when the subsurface OC content was similar to that commonly observed in agricultural surface soils (>0.5% by weight), K_f were consistently underpredicted. Sorption was generally over-predicted in the Michigan cores, with a mean predicted/measured K_f of 2.2 and a maximum overprediction by a factor of 4. Similar results were observed for the metabolites (K_f estimates ranged from an underprediction by a factor of >20 to an overprediction

by a factor of >7). Extrapolating sorption coefficients deter-mined for surface soils to subsurface materials can introduce large errors in estimates of pesticide mobility in the subsurface.

Desorption. Sorption was hysteretic (**Figure 2**) for all compounds in all samples, as has been observed for surface soils (*11*). No consistent trends were observed relating desorp-tion coefficients to soil properties (**Figures 3** and **4**). Sorption of the guanidine metabolites tended to be more reversible (H closer to 1) with decreasing K_f, OC content, and clay content ($p < 0.005$; **Table 2**; **Figure 4**). No correlation between soil properties and imidacloprid–urea desorption values was ob-served (**Table 2**). Because sorption $1/n_{ads}$ values were near unity (**Table 3**), hysteresis coefficients were similar to $100 \times 1/n_{des}$; therefore, correlations between H and other parameters were similar to those for $1/n_{des}$.

Within each core, desorption of imidacloprid and the guani-dine metabolites tended to decrease with increasing sorption,
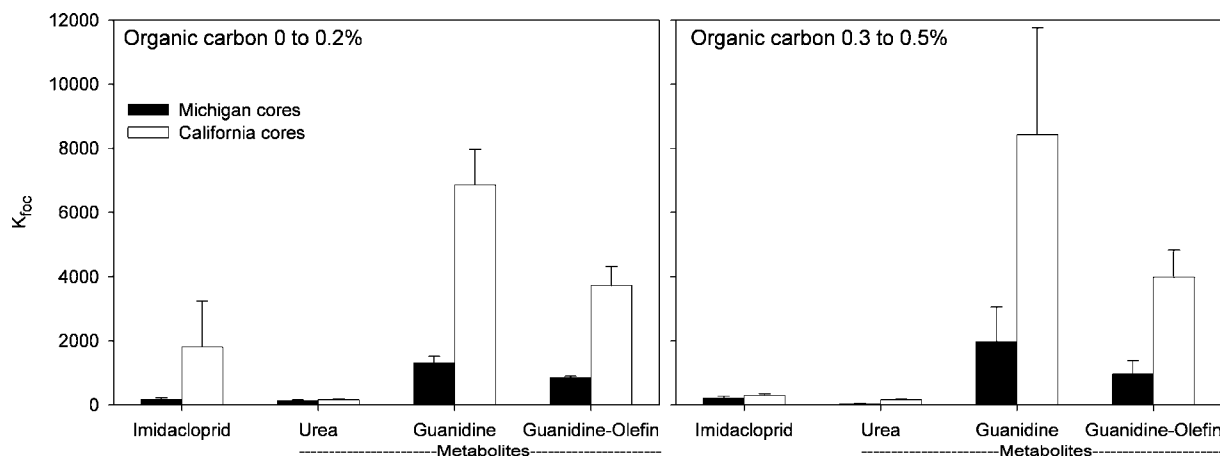
Figure 5. Mean K_{foc} for Michigan and California cores at similar organic carbon contents. Values are the mean of three or four samples; error bars indicate the standard error of the mean.
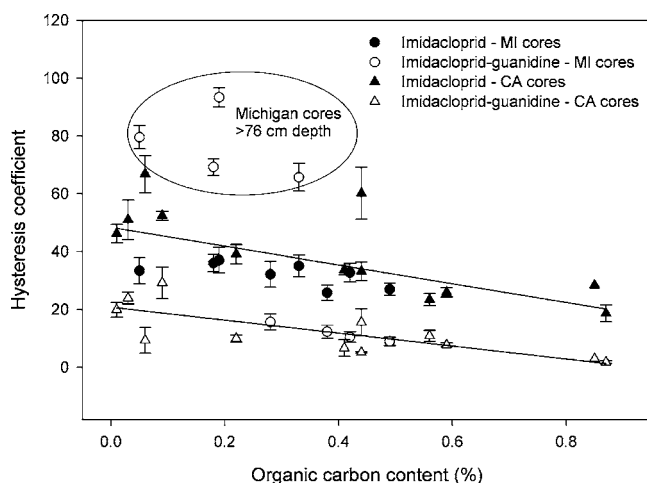

Figure 6. Hysteresis coefficients (H) for imidacloprid and imidacloprid–guanidine as a function of organic carbon content. Imidacloprid H tended to decrease with increasing organic carbon content ($r^2 = 0.43$). Imidacloprid–guanidine showed a similar trend ($r^2 = 0.64$ excluding samples from the Michigan cores at depths of >76 cm).

but this trend was not as strong for the urea metabolite (**Figures 3** and **4**). Imidacloprid–urea was less strongly sorbed than imidacloprid, because sorption coefficients (K_f) were lower and desorption coefficients ($1/n_{des}$) were higher for the urea metabolite than for the parent compound (**Table 3**; **Figure 3**). Thus, the urea metabolite would be expected to be more mobile in the subsurface than the parent compound. The guanidine metabolites are expected to be less mobile in the subsurface than the parent compound, because sorption coefficients are higher and mean desorption coefficients were generally similar to those for imidacloprid (**Table 3**; **Figures 3** and **4**).

As was observed for sorption, important differences in the characteristics of the soils affecting desorption were apparent between sites. Different chemicals exhibited different desorption trends. Over all cores, imidacloprid H increased with increasing depth and pH and decreased with increasing OC content (**Figure 6**), clay content, and cation exchange capacity. These correlations were primarily driven by the results for the California cores. In both California cores, H was negatively correlated with OC content (**Figure 6**), clay content, and CEC. In contrast, in both Michigan cores, imidacloprid $1/n_{des}$ tended to be more uniform (0.2–0.4, **Table 3**), and H values were not correlated with any soil property (**Figures 3** and **6**). For imidacloprid–

guanidine, H tended to be higher in the Michigan cores than in the California cores (**Figure 4**), especially at low OC contents (**Figure 6**). In all cores, imidacloprid–guanidine H tended to decrease with increasing OC content (**Figure 6**), clay content, and CEC, again driven primarily by the California cores. Hysteresis coefficients for imidacloprid–urea and imidacloprid–guandine–olefin did not show a strong dependence on soil properties. These results emphasize the potential inaccuracies that could result from generalizing sorption–desorption trends. Mean sorption and desorption coefficients for imidacloprid and imidacloprid–urea were higher in the California cores than in the Michigan cores (**Table 3**; **Figure 3**). For the guanidine metabolites, mean sorption coefficients were >5 times greater in the California cores than in the Michigan cores, but desorption coefficients were lower in the California cores than in the Michigan cores (**Table 3**; **Figure 4**), especially at very low OC contents (**Figure 6**).

Desorption further complicates accurate estimation of pesticide mobility in the subsurface. Whereas structurally similar compounds (imidacloprid and imidacloprid–urea) demonstrated a common response (samples with higher sorption demonstrated higher desorption coefficients and higher hysteresis coefficients), the guanidine metabolites showed a different response (samples with a higher K_f had a lower $1/n_{des}$ and a lower H). In this case, even if sorption coefficients could be accurately estimated, use of sorption coefficients alone could fail to predict the mobility of imidacloprid's guanidine metabolites because of the unexpected trends in desorption.

Summary. In all samples, sorption coefficients followed the trend imidacloprid–guanidine > imidacloprid–guanidine–olefin > imidacloprid >imidacloprid–urea. Thus, some imidacloprid metabolites are expected to be less mobile than the parent compound and some more mobile. Normalizing the sorption coefficients by the OC or clay content of the sample did not reduce the variability in sorption coefficients for any compound. The common approach of estimating subsurface sorption coefficients on the basis of the surface soil normalized sorption coefficient (K_{foc}) and the OC content of the subsurface soil resulted both in overprediction (resulting in a calculated K_f up to >7 times the measured K_f) and underprediction (up to a factor of >20) of the sorption of each compound. In all cases, sorption was hysteretic, further complicating the accurate prediction of pesticide mobility in the subsurface. These results emphasize the importance of sorption/mobility measurements for increasing the accuracy of models that attempt to predict

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the frequency of groundwater contamination by pesticides and expected pesticide concentrations in the subsurface.

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