Sorption and Desorption Behaviors of Diuron in Soils Amended with Charcoal

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Charcoal derived from the partial combustion of vegetation is ubiquitous in soils and sediments and can potentially sequester organic contaminants. To examine the role of charcoal in the sorption and desorption behaviors of diuron pesticide in soil, synthetic charcoals were produced through carbonization of red gum (*Eucalyptus* spp.) wood chips at 450 and 850 °C (referred to as charcoals BC450 and BC850, respectively, in this paper). Pore size distribution analyses revealed that BC850 contained mainly micropores (pores ≈ 0.49 nm mean width), whereas BC450 was essentially not a microporous material. Short-term equilibration (<24 h) tests were conducted to measure sorption and desorption of diuron in a soil amended with various amounts of charcoals of both types. The sorption coefficients, isotherm nonlinearity, and apparent sorption−desorption hysteresis markedly increased with increasing content of charcoal in the soil, more prominently in the case of BC850, presumably due to the presence of micropores and its relatively higher specific surface area. The degree of apparent sorption−desorption hystersis (hysteresis index) showed a good correlation with the micropore volume of the charcoal-amended soils. This study indicates that the presence of small amounts of charcoal produced at high temperatures (e.g., interior of wood logs during a fire) in soil can have a marked effect on the release behavior of organic compounds. Mechanisms of this apparent hysteretic behavior need to be further investigated.

KEYWORDS: Diuron; sorption; desorption; soil; charcoal; carbonization; hysteresis

INTRODUCTION

Black carbon (e.g., soot and charcoal) produced from the incomplete combustion of vegetation and fossil fuel is ubiquitous in terrestrial and aquatic environments (*1*, *2*). In addition to dispersal through biomass and fossil fuel combustion in the environment, some agricultural practices may also contribute to the increasing amount of black carbon in agricultural soils. For example, it is an old practice in the eastern and southern parts of China to mix firewood ashes with soils and livestock dung followed by heating and aging for several months, before the mixture is added directly into the field as a fertilizer. Direct burning of plant residues in the field after harvest for land clearing is common all over the world. Such agricultural practices will also provide direct input of black carbon into agricultural soil (*3*−*6*). Terrestrial black carbon, being erosion-prone, is readily transported by wind and water and is often deposited into aquatic ecosystems. Black carbon has been found to make a significant proportion of soils and sediments: 15−30% of total organic matter in marine sediments (*7*) and 12−31% of deep-sea sediments (*8*), 18−41% of the soils and sediments collected from the suburban area of Guangzhou, China (*9*), up to 30% of soils collected around Australia (*4*, *10*), and up to 45% of total organic carbon (TOC) in soils collected from Germany (*11*).

It has been well recognized that the presence of charcoal in soil could not only enhance the sorption of organic contaminants such as pesticides (*12*) but also influence the nature of the sorption mechanism (*13*). Research in recent years (*14*) has shown that the residues produced from burning wheat and rice were 400−2500 times more effective than soil in sorbing diuron over the concentration range of 0−6 mg/L in water. However, the effect of these amendments on the desorption behavior of diuron was not investigated in that study.

The nature and properties of black carbon are strongly affected by the nature of parent materials (wood, grass) and the temperature experienced during combustion (*2*, *15*). Charcoals formed from lignocellulosic materials under conditions of pyrolysis become increasingly carbonized as temperatures rise above 500 °C and are completely carbonized as temperatures approach 1000 °C (*15*). Under relatively high pyrolysis temperatures (500−700 °C), the charcoal derived from wheat was

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8546 *J. Agric. Food Chem.,* Vol. 54, No. 22, 2006

Yu et al.

found to be well carbonized and had a relatively high surface area and low oxygen content (*16*). Such chars have been reported to show high affinity for organic compounds (*16, 17*), especially for polar solutes (*16*).

Despite the fact that the environmental fate and impact of contaminants (bioaccessibility, bioavailability, and toxicological impact) are strongly influenced by their desorption behavior (*18–21*), the effect of black carbon on the desorption behavior of compounds has so far received limited attention. Braida et al. (*22*) observed pronounced hysteresis in the sorption of benzene in water to pure-form maple-wood charcoal prepared by oxygen-limited pyrolysis. Here they found that the sorption of wood charcoal was highly irreversible and proposed that hysteresis was due to pore deformation of charcoal during desorption of the sorbate, leading to entrapment of molecules as the polyaromatic scaffolding collapsed during desorption.

The objective of this study was to assess the effect of the presence of small amounts of charcoal materials (prepared from eucalyptus wood at two different temperatures of 450 and 850 °C) in soil on the sorption–desorption behaviors of pesticides in soil. Sorption and desorption behaviors were investigated to assess the role of the types and amounts of charcoal as sorbent for pesticides (represented by diuron as a model nonionic pesticide) in soils amended with various amounts of charcoals.

EXPERIMENTAL PROCEDURES

Chemicals. Diuron [*N*-(3,4-dichlorophenyl)-*N,N*-dimethyl urea, with purity >99%] was obtained from Sigma-Aldrich (Sydney, Australia). Diuron is a nonionic urea herbicide with a very wide use globally. The herbicide is nonvolatile (vapor pressure is 1.1×10^{-3} mPa at 25 °C), has a water solubility of 36.4 mg/L, and is stable in neutral media. Its reported average soil half-life is in the range of 90–180 days (*23*). Sodium azide was obtained from Fluka (Sydney, Australia). Calcium chloride of analytical grade and all solvents of HPLC grade were obtained from Merck Pty. Ltd. (Victoria, Australia). A stock solution of 100 mg/L of diuron was prepared in methanol.

Charcoal, Soil, and Sorbent. Charcoals were prepared from red gum wood (*Eucalyptus* spp.), at two different temperatures, namely, 450 and 850 °C (BC450 and BC850, respectively). Red gum woodchips were air-dried at 40 °C, and pieces of <5 mm were hand picked for the carbonization process. The woodchips were placed in porcelain crucibles with lids in a temperature-programmable muffle furnace (S.E.M., Australia). The temperature of the furnace was ramped to the defined temperature (450 or 850 °C) and held for 2 h for BC450 and for only 1 h for BC850. The prepared black carbon materials were ground to a fine powder on a disk-rotating mill for 3 min.

The specific surface areas (SSA) of the two charcoals were evaluated using the Brunauer, Emmett, and Teller (BET) nitrogen adsorption technique (*24*) at 77 K, using an automated manometric gas adsorption apparatus (*25*) and ultrahigh-purity gaseous nitrogen (99.999%, from BOC Gases). The details of the method and uncertainties associated with the measurement have been published elsewhere (*25*). Outgassing of the charcoal was carried out at 300 °C for 8 h at a background vacuum of 1×10^{-4} Pa, similar to that used for charcoal samples by Braida et al. (*22*). For the pore volume evaluation, we employed α_S-plot analysis, where the adsorption properties of a porous solid are compared with those of a nonporous standard material exhibiting surface chemistry similar to that of the test sample (*25*). Moisture content was determined by comparison of sample mass before and after evacuation at 300 °C.

We classified pore width (d_p) according to the International Union of Pure and Applied Chemistry (IUPAC) recommendations as follows: micropores, $d_p < 2$ nm; mesopores, $2 < d_p < 50$ nm; and macropores, $d_p > 50$ nm. Pores smaller than 2 nm were analyzed using the Horvath–Kawazoe (H–K) method (*26*). This method calculates the effective micropore size distribution of slit-shape pores using the data from adsorption isotherms. Using the H–K equation we calculated the effective mean width of slit pores (d_p) and correlated it with the

value of $\Delta V_{ads}/\Delta r_{slit}$, where ΔV_{ads} is the incremental amount of nitrogen adsorbed (converted to condensed liquid volume of nitrogen) and Δr_{slit} is the corresponding incremental width of slit pores. The individual and cumulative frequencies were calculated for a range of d_p data. Other properties of these chars as characterized using NMR techniques have been published elsewhere (*27*).

The soil used in this experiment was collected from the Roseworthy Campus, University of Adelaide, and was amended with charcoal. After air-drying, the soil was passed through a 2 mm sieve. This soil contained 87.8% sand, 1.3% silt, 8.3% clay, and 1.4% organic matter and is of sandy loam texture. The soil pH value was 6.8 in a 1:5 (soil/water) soil suspension and had a maximum water-holding capacity of 34.2% (v/v) and a cation exchange capacity of 9.3 cmol(+)/kg. The soil was sterilized by autoclaving at 120 °C under 300 kPa chamber pressure for 30 min three times within 3 days.

Charcoal-amended soils used in the experiment were prepared by mixing the above soil and the two types of charcoal at different ratios. The percentages of charcoal materials in the amended soils were 0, 0.1, 0.5, 1.0, 2.0, and 5.0% (w/w) for BC450 and 0, 0.1, 0.2, 0.5, 0.8, and 1.0% (w/w) for BC850. The charcoal-amended soils were thoroughly mixed on a rotary shaker for 7 days before their use as sorbents for sorption and desorption experiments.

Sorption and Desorption Isotherms. Diuron sorption by the sorbents was measured by the batch equilibration technique. Preliminary kinetic experiments showed sorption and desorption of diuron in charcoal-amended soils reached an apparent equilibrium within 24 h. Although sorption is known to continue for days at a very slow rate, for the comparative assessment between different chars under similar conditions, the 24 h shaking time was deemed to be adequate for the purposes of this study. The sorbents were suspended in 10 mL of 0.01 M CaCl$_2$ solutions (containing 0.5% NaN$_3$ to inhibit microbial activity) spiked at concentrations from 1 to 27 mg/L of diuron. The amounts of charcoal-amended soil used in the experiments were adjusted to allow for 30–80% of the added chemical to be sorbed at equilibrium. On the basis of our preliminary experiments, for BC450-amended soil an aliquot of 1.0 g of soil was used for 0, 0.1, 0.5, 1.0, and 2.0% and only 0.2 g of soil for 5.0%. For BC850-amended soils, an aliquot of 0.5 g of soil was used for 0.1 and 0.2% and only 0.2 g for 0.5, 0.8, and 1.0% amendment. The suspensions were shaken on a rotary shaker at room temperature (22 ± 2 °C) at 120 rpm for 24 h and then centrifuged at 4000 rpm for 60 min. After centrifugation, an aliquot of the supernatant in each tube was taken out and analyzed directly by high-performance liquid chromatography (HPLC).

Each sorption test was carried out in triplicate. Losses during the test were monitored by including two blank controls in each test: one tube that had only a chemical solution without any sorbent and the other control tube that had only the sorbent and CaCl$_2$ solution without chemical. Tests showed losses due to adsorption to glassware and degradation were negligible, and no interferences were found during the analysis of solutions. This is consistent with previous studies and the nature of the chemical (persistent and nonvolatile).

Desorption experiments were conducted for those samples with the highest sorption loading. After 24 h of equilibration, the tubes were centrifuged and 5 mL of the supernatant in each tube was taken out for analysis. Another 5 mL of 0.01 M CaCl$_2$ (including 0.5% NaN$_3$) was added into each tube, and the tubes were shaken for 24 h again. The desorption process was repeated three more times for each tube. All tests were performed in triplicate.

Pesticide Analysis. Analysis of diuron in the supernatant fraction from sorption and desorption experiments was carried out on an Agilent 1100 series high-performance liquid chromatograph (HPLC) fitted with a diode array detector and an SGE C18 RS column (250 × 4.6 mm, 5 μm). Acetonitrile (ACN) and water were used as the mobile phase, which was programmed from 36% ACN at 0 min to 80% ACN at 6 min at a flow rate of 1 mL/min. The UV wavelength for detection of diuron was 248 nm. The detection limit for diuron was 0.03 mg/L.

Data Analysis. The sorption and desorption isotherms were fitted with the linear form of the Freundlich equation

$$\log C_s = \log K_f + N \log C_w$$

Sorption/Desorption of Diuron in Charcoal-Amended Soils

J. Agric. Food Chem., Vol. 54, No. 22, 2006 **8547**

where C_w is the concentration of the chemical in solution, C_s is the concentration of the chemical in the sorbent, K_f is the Freundlich sorption coefficient, and N is the exponent indicative of sorption mechanism. The sorption−desorption apparent hysteresis index (H) was determined by the equation (*28*)

$$H = N/N_d$$

where N and N_d are the Freundlich exponents calculated from the sorption and desorption isotherms, respectively.

RESULTS AND DISCUSSION

Characteristics of Charcoals. Upon carbonization at 450 and 850 °C, 100 g of red gum chips produced about 36.1 and 28.8 g of charred materials, respectively. These are relatively higher yields of charcoal than those derived from burning crop residues (*29*). The color was gray to black for the BC850, whereas for BC450 it was a little brown to black. The relatively lower mass that remained under higher burning temperature indicates that BC850 is carbonized to a greater degree than BC450. The higher mass recovery of red gum chip-derived charcoal is believed to be due to the more condensed structure of wood chips than that of crop residues.

For the charcoal BC450, the shape of the nitrogen adsorption isotherm was similar to that for nonporous materials (**Figure 1A**), suggesting a negligibly small micropore volume (*30*). In contrast, the BC850 is a microporous material with a high specific surface area. The initial steep portion of the adsorption isotherm for BC850 is indicative of the presence of micropores in the charcoal material (*30*).

The SSA for BC850 was much higher than that of charcoal BC450 (**Table 1**) and also higher than wheat-residue-derived chars, the highest SSA of which was reported to be 438 m²/g (charred at 600 °C) (*16*). Chun et al. (*16*) also found char surface area to increase with increasing charring temperatures (300−600 °C); however, SSA measurement of char produced at 700 °C was lower than that of char produced at 600 °C, which they speculated to be due to microporous structures which were destroyed at 700 °C.

Charcoal BC450 has a very low level of microporosity (peak maxima occurred at a pore width of about 1.1 nm) (**Figure 2**). This may indicate the beginning of micropore formation at 450 °C. Increasing the preparation temperature, as in the case of charcoal BC850, clearly promoted the formation of micropores with the maximum peak occurring for pore widths of about 0.49 nm and essentially all pores <1 nm in pore width.

From the pore volume values listed in **Table 1**, we regard charcoal BC450 as a non-microporous material. Therefore, the lower temperature (450 °C) used for the preparation of charcoal materials did not lead to the formation of microporous structure. In contrast, charcoal BC850 is predominantly a microporous material with about 89.6% of volume from micropores (in terms of specific micropore volume). It is customary to express the total specific pore volume (V_{total}^{pore}) of an adsorbent as the liquid volume adsorbed at a certain value of relative pressure (P/P_0 = 0.95) (*31*). The gaseous nitrogen volume adsorbed at this value of relative pressure was converted into a liquid volume of nitrogen. For mixed-pore materials, the mesopore volume is determined as the difference between the total specific pore volume and total specific micropore volume.

Sorption−Desorption Isotherms and Their Nonlinearity. The presence of charcoal in the soil caused the sorption isotherms to change progressively into highly nonlinear, concave-downward-shaped isotherms (**Figures 3** and **4**). Most of the data on sorption and desorption isotherms fitted well to the Freund-
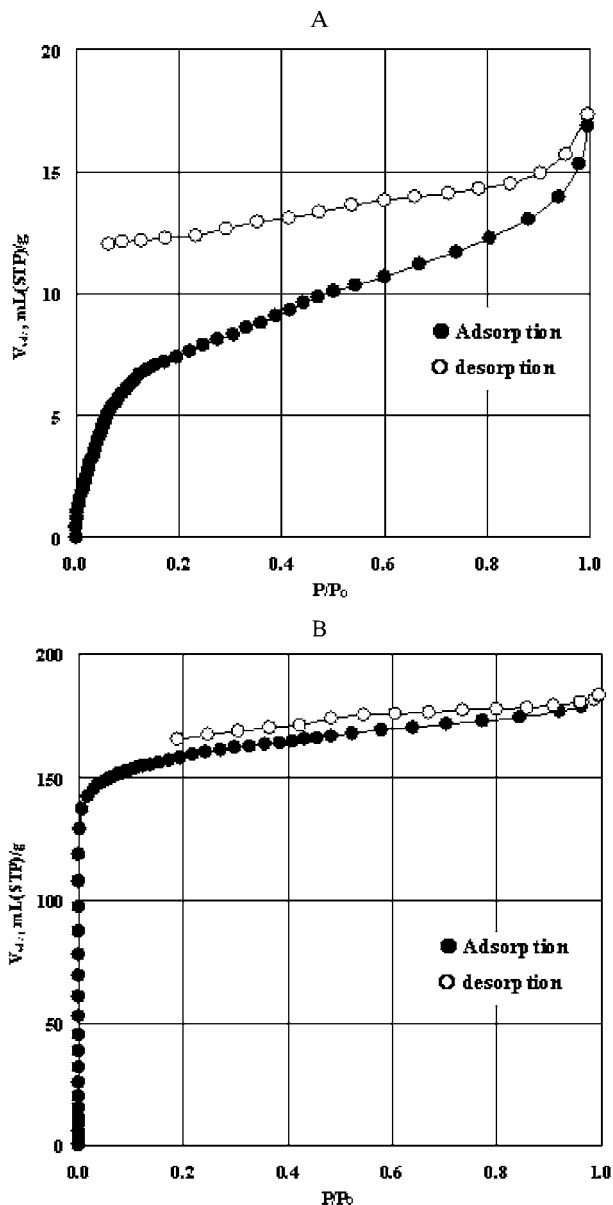

Figure 1. Nitrogen adsorption/desorption isotherm for (**A**) BC450 and (**B**) BC850.

Table 1. Characteristics of Black Carbon Materials[a]

BC burning temp (°C)	abbrev	SSA (m²/g)	moisture content (%)	V_{total}^{micro} [mL (liq)/g]	V_{total}^{pore} [mL (liq)/g]
450	BC450	27.330.035	11.7	0.00374 ± 0.00004	0.02219 ± 0.00004
850	BC850	566.390.31	9.9	0.2469 ± 0.0039	0.2757 ± 0.0015

[a] V_{total}^{micro} = volume of total specific microspore; V_{total}^{pore} = volume of specific microspore and total specific pore.

lich equation (**Table 2**); however, at the highest level of charcoal amendment, the fit was noted to be relatively poor in both types of chars. Instead, the data showed a much better fit to the Langmuir model in these cases. The increasing Freundlich sorption coefficient K_f values and decreasing N values with charcoal content in soil (**Table 2**) show that the sorption capacity of diuron on charcoal-amended soils gradually increased with increasing content of charcoal in soil. The N values decreased from 0.83 to 0.25 and 0.16, respectively, for BC450 and BC850,
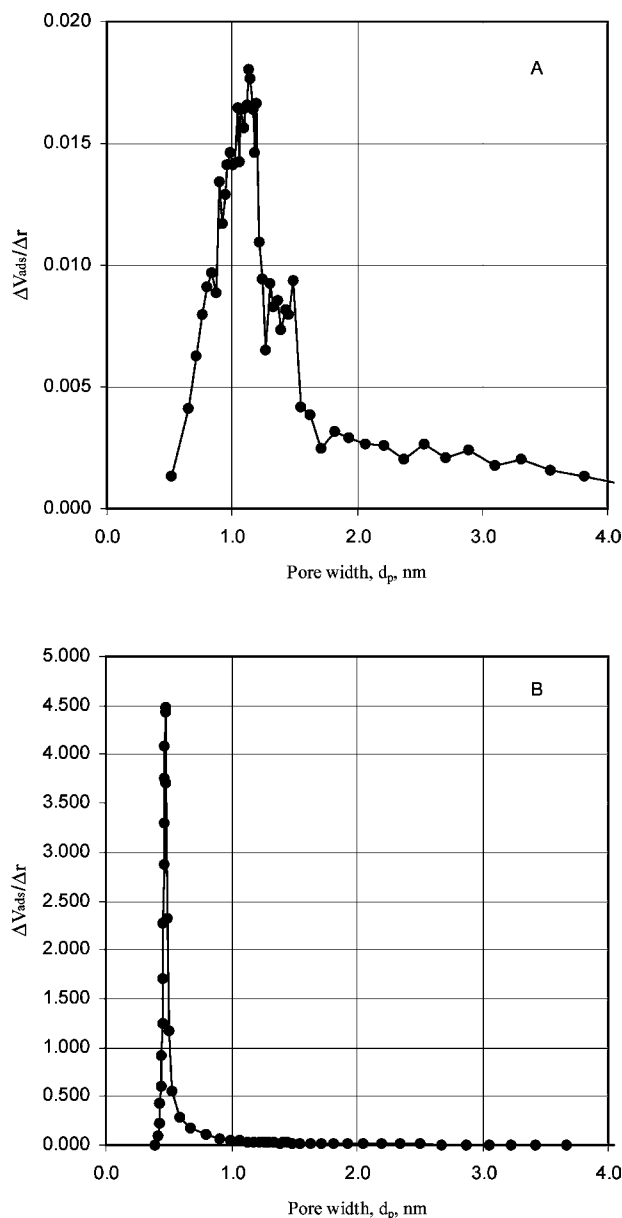
Figure 2. Pore size distribution for (**A**) BC450 and (**B**) BC850. Using the Horvath–Kawazoe (H–K) method (*26*), we calculated the effective mean width of slit pores, d_p, and plotted against the value of $\Delta V_{ads}/\Delta r_{slit}$, where ΔV_{ads} is the incremental amount of nitrogen adsorbed (converted to condensed liquid volume) and Δr_{slit} is the corresponding incremental width of slit pores.

as the amount of charcoal in soil increased from 0.1 to 5.0% of BC450 and to 1.0% of BC850 (**Table 2**).

Highly nonlinear sorption isotherms and high sorption capacity for organic compounds on sorbents (e.g., soils and sediments) containing black carbon have been observed in a number of studies (e.g., refs *32−35*). Soil organic carbon has commonly been hypothesized to consist of an amorphous phase and a condensed phase of organic carbon (*36, 37*), which are considered to be responsible for partitioning and sorption, respectively. Depending upon the relative contents of the two phases of organic carbon, sorption by soils and sediments could range from linear partitioning to highly nonlinear sorption (*34, 38, 39*).

Due to the highly nonlinear nature of isotherms, a comparison of sorption affinities among the charcoal-amended soils needs to be calculated for a specific solution concentration [e.g., C_w
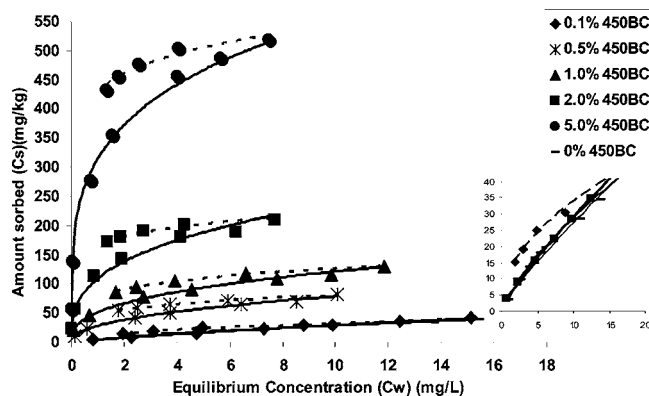

Figure 3. Influence of BC450 on sorption and desorption of diuron in soil. (Inset) Sorption–desorption on unamended soil and on 0.1% BC450.
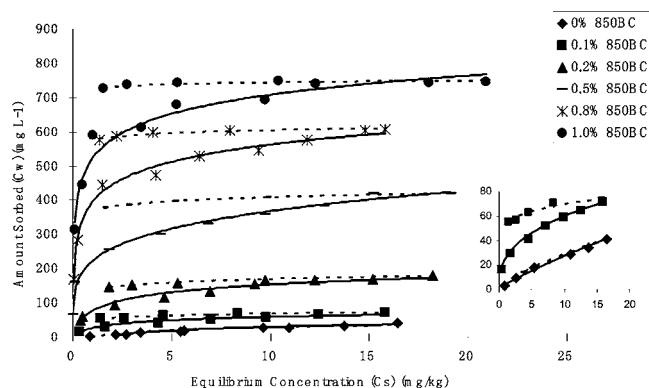

Figure 4. Influence of BC850 on sorption and desorption of diuron in soil. (Inset) Sorption–desorption on unamended soil and on 0.1% BC850.

Table 2. Freundlich Constants for the Sorption (K_f, N) and Desorption (K_{fd}, N_d) of Diuron on Soil Amended with Charcoal and the Calculated Hysteresis Index (H)

charcoal	content of charcoal in soil (%)	K_f	N	R^2	K_{fd}	N_d	R^2	H
original soil		4.08	0.83	0.9974	5.40	0.73	0.9975	1.14
BC450	0.1	4.47	0.82	0.9994	11.1	0.48	0.9944	1.69
	0.5	28.0	0.45	0.9983	47.5	0.23	0.9990	1.93
	1.0	514	0.37	0.9979	78.6	0.21	0.9977	1.79
	2.0	109	0.34	0.9958	168	0.12	0.9772	2.87
	5.0	314	0.25	0.9980	427	0.10	0.8784	2.37
BC850	0.1	25.3	0.37	0.9979	39.5	0.28	0.9958	1.32
	0.2	72.8	0.32	0.9911	138	0.09	0.9926	3.54
	0.5	224	0.22	0.9875	371	0.04	0.9990	5.14
	0.8	350	0.21	0.9928	576	0.02	0.9004	9.75
	1.0	500	0.16	0.9249	727	0.01	0.8194	14.92

of 1 mg/L, where $K_f = K_d(C_s/C_w)$]. On this basis the sorption capacities of the charcoal amended soil were 7−80 times for BC450 and 5−125 times for BC850 in comparison to that of charcoal-free soil (**Table 2**). The sorption contribution of even small additions of charcoals to the soil (0.5% of BC450 and 0.1% of BC850) was very high indeed (>85%), assuming no change in inherent sorption capacity of soil. This shows that the presence of even small amounts of highly carbonaceous black carbon (charcoal, soot, or other carbonaceous materials) can dominate sorption of an organic compound in soils and sediments.

Desorption Behavior and the Role of Microporosity. Sorption and desorption isotherms were compared to assess the

Sorption/Desorption of Diuron in Charcoal-Amended Soils

J. Agric. Food Chem., Vol. 54, No. 22, 2006 **8549**

degree of reversibility of sorption reaction. Due to the short equilibration time (24 h) employed here, it is not appropriate to refer to the discrepancy between the sorption and desorption flanks of the isotherms as true hysteresis. This is because the sorption kinetics may have been slow and the sorption reaction may have continued beyond the point in time when the desorption part of experiment was initiated. Nevertheless, a comparison of these isotherms does provide an assessment of the impact of the nature of sorbate on the desorption behavior of diuron or lack of it. For the purposes of this study, by hysteresis we mean "apparent hysteresis".

The highly nonlinear sorption isotherm and relatively flat desorption isotherm in **Figures 3** and **4** provide visual evidence of apparent sorption–desorption hysteresis on the charcoal-amended soils. We calculated the hysteresis index (H), defined as the N/N_d ratio (*28*), to quantify the degree of apparent hysteresis. The H values for all of the sorbents are listed in **Table 2**. For the original soil sample the H value was 1.14, indicating minimal desorption hysteresis. As the content of charcoal in the soil increased, the value of H also increased. For the soils amended with charcoal BC850, the H values increased rapidly from 1.32 for the soil with 0.1% of charcoal to 14.92 for 1.0% of charcoal. For the soils amended with charcoal BC450 the H value also progressively increased but at a slower rate. The results showed that besides the high sorption capacity, charcoal produced under higher temperature either had stronger sorption or provided domains for diffusion of sorbate into micropores. In this way the more microporous structure may lead to effective sequestration of a compound. This is consistent with the studies reporting poor bioavailability and bioaccessibility of organic compounds sorbed on black carbon materials (*40, 41*).

Comparison of the results for the two types of charcoal materials also revealed that although the sorption capacity of a soil could be enhanced to the same level by adding differential amounts of chars (0.8% BC850 vs 5% BC450), the degree of reversibility was quite different between the two charcoals. In the present study, the discrepancy between sorption and desorption isotherms at comparable levels of sorption (e.g., 0.8% BC850 vs 5% BC450, **Table 2**) was clearly much more prominent in the case of charcoal BC850.

To assess if a link between the microporosity and apparent desorption hysteresis exists, we plotted the values of the total pore volume for each sorbent calculated from the V_{total}^{pore} value and the content of charcoal material in the soil against the apparent hysteresis index (H) in **Figure 5**. Here, we assumed that the soil free of charcoal is a nonporous material and that the pore volume of the charcoal-amended soils was mainly provided by the added charcoal. **Figure 5** shows a good relationship between these two parameters; the H index increased exponentially ($y = 1.582\ e^{0.008x}$, $R^2 = 0.8982$) as the total pore volume of the sorbent increased. A smaller increase in H value at lower pore volume is essentially associated with the presence of charcoal BC450 and only small amounts of BC850. This is because charcoal BC450 had a negligible proportion of micropores, whereas in BC850 essentially all pores existed as micropores of <1 nm width. These micropores either entrapped the sorbed molecules of diuron or caused a slow and prolonged sorption phase, which may have led to the apparent hysteresis due to nonequilibrium processes. Braida et al. (*22*) noted swelling of a sorbent during benzene sorption and suggested pore deformation during desorption causing desorption hysteresis. It has also been suggested in other studies that surface-specific adsorption, entrapment into micropores, and partitioning into
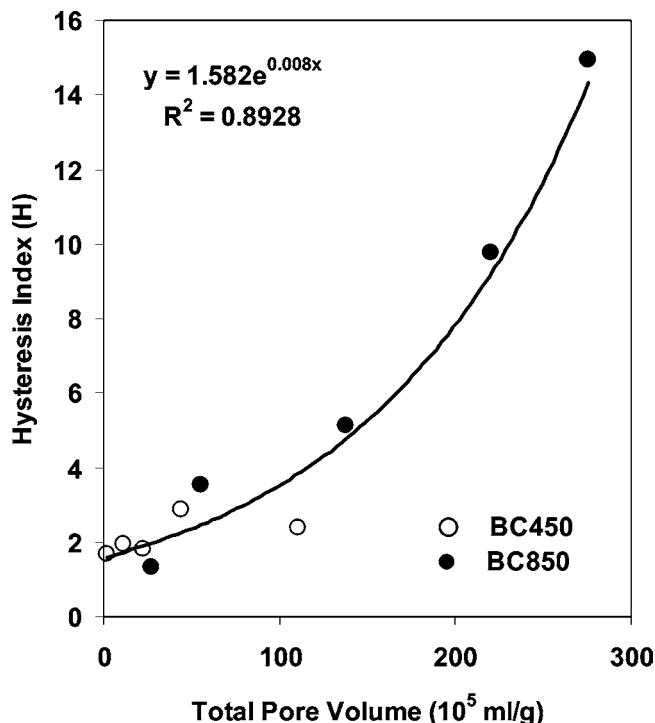

Figure 5. Relationship between total pore volume and apparent hysteresis index (*H*).

condensed structures of soil organic matter are among the main causes of chemical sequestration (*35–37, 42–45*).

Conclusions. This study showed that the presence of small amounts of black carbon in the form of charcoals in soil, especially those produced at high temperatures (e.g., interior of wood logs during a fire), can have a major effect on the sorption and desorption behaviors of organic compounds such as the diuron pesticide. The marked effect on the desorption of highly carbonaceous materials such as charcoal produced at high temperatures is expected to have strong implications for the bioavailability of such compounds in terrestrial and aquatic ecosystems. The role of such carbonaceous materials on sorption–desorption kinetics and bioavailability needs to be further investigated.

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8550 *J. Agric. Food Chem.,* Vol. 54, No. 22, 2006

Yu et al.

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