

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/5302693>

Enhanced Pesticide Sorption by Soils Containing Particulate Matter from Crop Residue Burns

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · SEPTEMBER 2003

Impact Factor: 5.33 · DOI: 10.1021/es034006a · Source: PubMed

CITATIONS

207

READS

180

2 AUTHORS, INCLUDING:



Yaning Yang

University of Illinois, Urbana-Champaign

10 PUBLICATIONS 647 CITATIONS

SEE PROFILE

Enhanced Pesticide Sorption by Soils Containing Particulate Matter from Crop Residue Burns

YANING YANG AND GUANGYAO SHENG*

Department of Crop, Soil, and Environmental Sciences,
University of Arkansas, Fayetteville, Arkansas 72701

Lack of proper techniques to isolate black carbon (BC) from soils has hindered the understanding of their roles in the sorption and environmental fate of organic contaminants in soils and sediments. The burning of crop residues may be the primary source of BC in agricultural soils. In this study, wheat (*Triticum aestivum* L.) and rice (*Oryza sativa* L.) residues were burned, and the resulting particulate matter (ashes) along with a soil were used to sorb diuron from water. Calculations indicated that the burning of crop residues may result in an appreciable level of ashes in soils. The diuron sorption isotherms on ashes were curvilinear Langmuir type, suggestive of surface adsorption and similar to that with activated carbon. Ashes were 400–2500 times more effective than soil in sorbing diuron over the concentration range of 0–6 mg/L. Sorption by wheat ash-amended soils and the degree of isotherm nonlinearity increased with increasing ash content from 0% to 1% (weight), indicating the significant contribution of wheat ash to the sorption. Calculations show that wheat ash and soil independently contributed to the sorption. Above the wheat ash content of 0.05%, the sorption was largely controlled by the ash. Density-based fractionation and repeated HCl–HF washing of wheat ash yielded carbon-enriched fractions and enhanced diuron sorption by these fractions. BC appeared primarily responsible for the high adsorptivity of ashes. Ashes arising from the burning of crop residues may be an important determinant of pesticide immobilization and environmental fate in soils.

Introduction

Observations of the isotherm nonlinearity and multi-solute competitive effects for the sorption of neutral organic contaminants (NOCs) of low polarity from water by soils and sediments have fostered great interests in the sources of such sorptive characteristics and their potential impact on the environmental fate of NOCs. The observed characteristics have been attributed to the NOC–soil organic matter (SOM) specific interactions (1), to the rubbery and glassy states of SOM (2–4), to the NOC hole-filling in SOM (4–6), and/or to the presence of small amounts of high-surface-area carbonaceous materials (HSACM) (i.e., black carbon (BC)) in soils and sediments (7, 8). While all these propositions need to be extensively tested, the HSACM model has been well-accepted (9). Attempts have been made to quantify BC in various environmental matrixes (10–13). Many soils and sediments are known to contain BC (12, 14–16). Enhanced

sorptive nonlinearity on the humin fraction of a peat, as compared to the original peat and its humic acid fraction, was attributed to HSACM enriched in the humin fraction during the density fractionation procedures (17). Combined adsorption and partition models have been used to assess the contribution of BC to the NOC sorption by soils and sediments and appeared to satisfactorily account for the sorptive nonlinearity and the overall sorption (10, 18–20). A comprehensive procedure for the isolation of BC involving the use of strong acids and oxidant has been developed recently (21). However, use of severe chemical conditions may alter the surface properties of BC, and thus it is questionable to characterize the obtained BC in terms of the adsorptive properties. In addition, BC produced under different conditions from different starting materials may possess widely different chemical compositions and surface properties and, hence, adsorptive characteristics. To address the adsorptive properties of environmental BC, it is essential to extensively characterize each single source of BC.

Biomass burning is among many potential contributions to BC in soils. Burning crop residues in the field is a common post-harvest practice for disposal of these materials, for immediate land clearing, and for land-use change in many parts of the world. Particulate matter (ashes) resulting from such burns may contain BC due to combustive carbonization. In heavily agricultural regions with frequent burning of crop residues, ashes arising from such burns may predominantly contribute to BC in agricultural soils, and high levels of BC may be expected (22). With heavy reliance on the use of pesticides in modern agricultural production, ashes may highly sorb pesticides and strongly influence their environmental fate. In fact, the impact of ashes arising from the burning of sugarcane trash on pesticide sorption in soils was noticed early in 1960s by Hilton and Yuen (23). These authors found that many Hawaiian soils retained high sorptivity for substituted ureas and *s*-triazines following the oxidative removal of organic matter by H₂O₂. They attributed the observation to the presence of ash charcoals (including BC) in the soils receiving the regular burning of cane trash, although no direct evidence of pesticide sorption by ashes was presented. Toth et al. (24) ascribed the observed reduction in the phytotoxicity of diuron applied over the ash of recently burned kangaroo grass to the diuron sorption by the ash. Another study using a soil-plus-charcoal (commercial) sorbent indicated that the presence of the charcoal not only enhanced pesticide sorption but also altered the sorptive characteristics of the soil by reversing the effect of pH on sorption, changing sorption isotherm from Freundlich type on the soil to Langmuir type on the soil-plus-charcoal, and reaching maximum sorption at relatively low equilibrium concentrations in solution (25).

The importance of ashes in influencing pesticide fate in soils is poorly understood primarily because of the low ash contents in soils and the inability of current techniques to isolate these materials from soils. In this study, soil-free (pure-form) ashes arising from the burning of wheat and rice residues were collected and used to sorb diuron from water. The advantage of using pure-form ashes is obvious because it enables one to directly investigate the adsorptive properties of ash BC without undesired surface alteration. The two residues are most frequently burned in the United States. The objectives of our research were to measure the sorptive ability of ashes for pesticides in soils, to identify the primary ash component(s) responsible for their high sorptivity, and to evaluate the potential impact of ashes on pesticide immobilization in soils.

* Corresponding author phone: (479)575-6752; fax: (479)575-3975; e-mail: gsheng@uark.edu.

TABLE 1. Carbon and Silicon Contents and Specific Surface Areas (SSA) of Ash Samples

ash sample	carbonate C (%)	total C (%)	BC ^a (%)	elemental Si (%)	SSA (m ² /g)
rice ash	0.37	6.02	5.65	32.9	16.54
wheat ash	1.41	14.33	12.92	19.5	10.05
light fraction of wheat ash	0.93	26.40	25.47	16.6	6.74
heavy fraction of wheat ash	1.61	9.19	7.58	20.7	5.73
carbon fraction of wheat ash	<0.02	76.40	76.40	1.39	408.30

^a Calculated as the difference between total C and carbonate C.

Experimental Section

Burning of Crop Residues. Wheat (*Triticum aestivum* L.) and rice (*Oryza sativa* L.) residues (straws) were used in this study. Air-dried residues (10 kg each) were collected from the Arkansas Agricultural Research and Extension Center in Fayetteville, AR. The residues were burned on a stainless steel plate (1 m × 1 m) in an open field under uncontrolled conditions in a still, fine, July afternoon. Wheat ash and rice ash were separately collected and weighed.

Sorbents. Crop residues, ashes, and a soil were used as sorbents. Dry wheat and rice residues were cut into small pieces (<2 mm). Ashes were used either pure or mixed with soil. The soil was a Stuttgart silt loam collected at the Rice Research and Extension Center, Stuttgart, AR, with a composition of 17.1% sand, 60.4% silt, 22.5% clay, and 2.1% organic matter and a cation-exchange capacity of 8.5 cmol_c/kg. The soil, without records of residue burns, was presumed to contain minimal levels of ashes. The soil was air-dried, ground, and sieved (1 mm). To obtain ash-amended soil sorbents, the soil was amended with wheat ash in exact ash (weight) contents of 0.01%, 0.02%, 0.05%, 0.1%, 0.5%, and 1%. Ash-amended soils were thoroughly mixed before their use for pesticide sorption. A density-fractionated technique was used to separate wheat ash into the light and heavy fractions. Wheat ash (2 g) was suspended in 20 mL of mixed dibromodichloromethane and hexane solution with a density of 2.05 g/cm³, followed by vigorous shaking for 5 min. The suspension was kept still overnight on the bench, and the light fraction (floating on the surface of the solution) and the heavy fraction (sinking in the bottom) were collected, dried, and weighed. Each fraction was approximately 50% of the original weight. To obtain the carbon (C) fraction, wheat ash (2 g) was treated in 10 mL of mixed hydrochloric acid and hydrofluoric acid (0.1:0.3 M) four times, followed by thorough washing with distilled water four times to remove soluble salts and silicon.

Carbon and silicon contents of wheat ash, rice ash, light fraction of wheat ash, heavy fraction of wheat ash, and C fraction of wheat ash were measured in a commercial laboratory (Huffman Laboratories, Inc., Golden, CO). The specific surface areas (SSAs) of these ash samples were measured by N₂ adsorption at liquid nitrogen temperature with an Autosorb-1 surface area analyzer (QuantaChrome Corp., Boynton Beach, FL). All ash samples (0.5 g each) were outgassed under vacuum at 100 °C for 5 h before N₂ adsorption. Helium was used as the carrier gas and also the dilution gas to fix the partial pressure of N₂ within the range of 0.05–0.30. The molecular surface area of 16.2 Å² for N₂ and the BET (Brunauer–Emmett–Teller) equation were used to calculate the SSAs of ash samples. Carbon and silicon contents and the SSAs of ash samples are listed in Table 1.

Pesticide. Diuron, a substituted urea herbicide, was used as a model pesticide in this study. Diuron was purchased from ChemService (West Chester, PA), with a purity of >99% and used as received. Diuron is neutral at normal soil pH with a water solubility of ~38 mg/L and log *K*_{ow} of 2.68 (26).

Sorption Isotherms. Pesticide sorption by the above sorbents (i.e., crop residue pieces, ashes, soil, ash-amended

soils, fractions of wheat ash) was measured by the batch equilibration technique as described in many studies (e.g., refs 4 and 8). Before use, all sorbents were sterilized by γ-irradiation to eliminate possible solute biodegradation. Various quantities of diuron in 0.005 M CaCl₂ solution were introduced into 25-mL Corex glass centrifuge tubes containing 0.01–3.50 g of sorbent. The mass of sorbents was adjusted to allow for 30–60% of added diuron to be sorbed at equilibrium. At low concentrations with ash sorbents, diuron sorption was allowed to exceed 60% to compromise on the accuracy of sorbent weighing. Additional 0.005 M CaCl₂ solution was added to bring the total liquid volume to 10 mL. The initial concentrations of diuron ranged up to 30% of its water solubility. The centrifuge tubes were closed with Teflon-lined screw caps and rotated (40 rpm) at room temperature (~25 °C) for 24 h. Kinetic measurements with the crop residues, ashes, and soil showed that diuron sorption on all sorbents leveled off within 18 h, indicating sorption equilibrium and overcoming of possible surface hydration effects. After establishment of sorption equilibrium, sorbents and aqueous phases were separated by centrifugation at 6000 rpm (rcf = 5210g) for 20–30 min. Such a centrifugation was sufficient to separate ash samples from supernatant, due to the fact that ash particles settled quickly and their surfaces were expected to be essentially neutral (similar to that of activated carbon). The diuron concentrations in supernatants were analyzed by direct injection of 20 μL to a Hitachi reversed-phase high-performance liquid chromatography (Hitachi High-Technologies Co., Tokyo, Japan) fitted with a UV–visible detection set at 252 nm. A Phenomenex Prodigy C18 column was used. The mobile phase was a mixture of acetonitrile and water (50:50) with a flow rate of 1.0 mL/min. Each sorption isotherm was measured with eight concentrations, each in triplicate; the average data were reported. The amount of pesticide sorbed was calculated by the difference between the amount initially added and that remaining in the equilibrium solution. Blanks not containing sorbents were also run to ensure that glass tubes did not adsorb pesticides.

Results and Discussion

Burning of 10 kg of dry wheat and rice residues produced approximately 600 g of wheat ash and 1600 g of rice ash, respectively. Thus, the ash productivities are ~6% with wheat residue and ~16% with rice residue. Carbon analyses showed the total carbon and carbonate carbon contents of 14.33% and 1.41% in wheat ash as well as 6.02% and 0.37% in rice ash, respectively (Table 1). The differences between the total carbon content and carbonate carbon content are 12.92% and 5.65% in wheat ash and rice ash, respectively. Presumably, the major form of this carbon in the ashes is BC in nature, based on the fact that crop residues were completely burned and the resulting ashes were gray-to-black in color. As burning is performed in the field, ashes are directly incorporated into soils following burning. Using the average biomass production of ca. 6000 kg/ha for wheat and ca. 12 000 kg/ha for rice, respectively, and assuming that ashes are mixed with soils of furrow slice (i.e., 0.15 m deep), calculations show that each burning would result in an ash content of 0.015% wheat ash or 0.08% rice ash in soils receiving crop residue

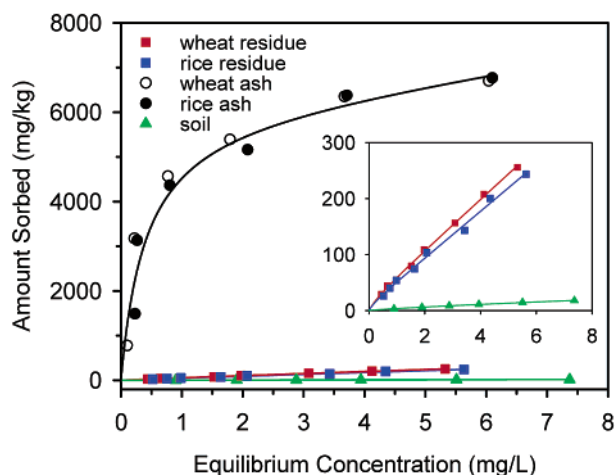


FIGURE 1. Sorption of diuron from water by wheat residue, rice residue, wheat ash, and soil.

burning. With no-till practices or the lack of ash–soil complete mixing, the actual ash content in the top layer soil of a particular field may be much higher. Ashes may accumulate in soils because burning has been a consistent practice following each harvest and also because BC is highly persistent under the environmental conditions (12).

The sorption isotherms of diuron with soil, wheat residue, rice residue, wheat ash, and rice ash are presented in Figure 1, in which the amount of diuron sorbed by the sorbents (mg/kg) is plotted against the equilibrium concentration (mg/L) in water. The diuron isotherm on soil exhibited a small nonlinearity at low concentrations and an increased linearity at intermediate to high concentrations, consistent with the results of Sheng et al. (27). By extrapolating the upper linear portion of the isotherm, the concentration of 1.2 mg/L, below which the isotherm displayed a visible nonlinearity, was obtained. The upper portion of the isotherm (above 1.2 mg/L) was fit to the Freundlich equation, $Q = K_f C_e^N$, where Q and C_e are the amount of diuron sorbed (mg/kg) and the equilibrium concentration (mg/L), respectively, and K_f and N are constants. The curve-fitting resulted in a N value of 0.989, indicative of the high linearity. This suggests that the solute partitioning into SOM was the dominant mechanism for diuron sorption to soil. The log K_{oc} value calculated from the slope of the isotherm normalized to the organic carbon content of the soil was 2.74, close to the reported average value of 2.78 (26). Sheng et al. (27) reported that the sorption of diuron was much lower and less extensive by homoionic K-SWy-2 clay than by SOM because diuron molecule contains large substituents on the aromatic ring (two chlorines and *N,N*-dimethylurea), which may sterically hinder the adsorption by clay minerals. The nonlinearity at low concentrations was attributed to the specific interaction of diuron molecules with active sites of SOM (1). On the Stuttgart silt loam, the nonlinear capacity was ~ 1.48 mg/kg, negligible as compared to ~ 600 mg/kg on the Florida peat soil reported by Chiou and Kile (8). This difference may have resulted from the large difference in SOM contents and clay properties and from the fact that the Florida peat may contain BC from the burning of sugarcane trash and wild forest fires (17).

Sorption of diuron by wheat residue and rice residue also displayed highly linear isotherms with a small nonlinearity at low concentrations (Figure 1). As crop residues are mostly organic in nature, solute partitioning is expected to dominate the diuron sorption. Slightly higher sorption by wheat residue than by rice residue is consistent with the measured carbon contents of the two crop residues (42.5% and 36.0% for wheat residue and rice residue, respectively). In fact, normalization of diuron sorption to the respective carbon contents of the

two crop residues yielded a single isotherm (figure not shown). Linear sorption of NOCs by corn residues from water has been previously reported (28). The small nonlinearity at low concentrations could be attributed to the specific interactions of diuron molecules with an abundance of polar groups in crop residues (e.g., carboxyl groups, phenolic hydroxyl groups).

Diuron sorption on wheat ash and rice ash was comparable in magnitude and displayed the characteristics of the Langmuir adsorption isotherm (Figure 1). Wheat ash and rice ash were 400–2500 times more effective than the soil in sorbing diuron over the diuron concentration range of 0–6 mg/L. Fitting to the Langmuir isotherm equation gave the maximum sorption of 6962 mg/kg ($r^2 = 0.960$). Assuming that the diuron molecule is spherical, the cross-sectional area of diuron molecule is estimated as 4.95×10^{-15} cm², using the density of 1.48 g/cm³ and the molecular weight of 233.1 g/mol (29). Further assuming that the diuron sorption on ash was monolayer surface adsorption, which is the characteristics of Langmuir type sorption, the surface area covered by diuron molecules was estimated to be 8.90 m²/g. This number is close to the measured SSA of wheat ash (10.05 m²/g) and $\sim 54\%$ of that of rice ash (16.54 m²/g) (Table 1). The small difference between the calculated surface area and the measured of wheat ash may be just an artifact of calculation. The larger difference with rice ash could be a result of high content of silica, which may appreciably contribute to the measured SSA but little or only slightly to the diuron sorption due to its strong hydration in the presence of water.

The potential contributions of ashes to pesticide sorption, if crop residues are completely burned, as compared to residue return can be estimated by using diuron as a model pesticide and wheat ash as a model ash. According to Barber (30), when corn residue was returned to the field, ~ 8 –11% of the C in corn stalk residue and $\sim 18\%$ in corn roots were transformed to organic matter. Without prior knowledge of the conversion rate of wheat residue carbon, we assume that 15% of the C in wheat residue (with a measured carbon content of 42.5%) will be converted to organic matter. Our data showed that at the equilibrium concentration of 0.0258 mg/L, sorption of diuron on a unit mass basis was 2.27 mg/kg by wheat residue and 370 mg/kg by wheat ash (Figure 1). Therefore, sorption of diuron by wheat residue, the synthesized organic matter (from the log K_{oc} value of 2.74 obtained earlier, $K_{oc} = 550$ L/kg) and wheat ash would be

$$M_{\text{residue}} = 2.27 \text{ mg/kg} \times 6000 \text{ kg/ha} = 13\,620 \text{ mg/ha}$$

$$M_{\text{om}} = 550 \text{ L/kg} \times 0.0258 \text{ mg/L} \times 6000 \text{ kg/ha} \times 42.5\% \times 15\% = 5428 \text{ mg/ha}$$

$$M_{\text{ash}} = 370 \text{ mg/kg} \times 6000 \text{ kg/ha} \times 6\% = 133\,200 \text{ mg/ha}$$

The above calculations show that wheat residue, if burned, would adsorb ~ 10 times more diuron than would wheat residue when leaving in the field without burning or ~ 24 times more than would organic matter converted from wheat residue. Clearly, burning crop residues, as compared to residue return, would result in enhanced pesticide sorption. Alternative residue management may significantly reduce pesticide sorption.

The sorption of diuron from water by ash-amended soils is presented in Figure 2a. Sorption of diuron increased with increasing wheat ash content in the soil. The sorption data over the entire range of concentrations were fit to the Freundlich equation. Although such a curve fitting may result in an N value that indicates an overall nonlinear isotherm even though the isotherm is highly linear at high concentrations (e.g., sorption of diuron by soil), it should provide a

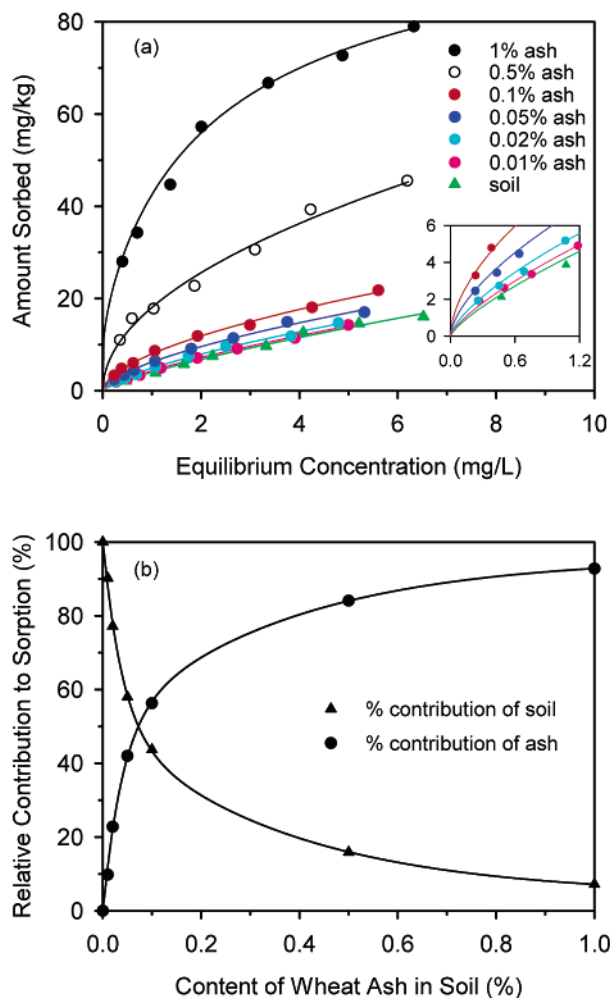


FIGURE 2. (a) Sorption of diuron from water by soil and wheat ash-amended soils containing various amounts of ash. (b) Relative contributions of wheat ash and soil to the overall sorption of diuron calculated from the isotherms in panel a at the equilibrium concentration of 0.5 mg/L.

comparison of the degree of isotherm nonlinearity between various sorbents. The obtained N values are 0.764, 0.731, 0.691, 0.622, 0.571, 0.444, and 0.367 for the soil and ash-amended soils with ash contents of 0.01%, 0.02%, 0.05%, 0.1%, 0.5%, and 1%, respectively, indicating a progressively increasing degree of isotherm nonlinearity with increasing ash content in the soil. These characteristics are consistent with the high adsorptivity and Langmuir-type isotherm of wheat ash. Quantitative calculation of sorption data with the soil and the pure-form wheat ash presented in Figure 1 reveals that the diuron sorption is essentially the combination of individual sorptions by ash and soil in direct proportion to the ash content, suggesting the independent contributions of ash and soil to sorption. To separate the contributions of ash and soil, the amounts of diuron sorbed by the soil and the ash-amended soils at the equilibrium concentration of 0.5 mg/L were obtained from the isotherms in Figure 2a. The amounts of diuron sorbed by the ash-amended soils over that by the soil (i.e., sorption differences) were assigned to those by the ash. The relative contributions of ash and soil, calculated from individual sorption divided by the total sorption, are shown in Figure 2b. Over the range of 0–1% wheat ash contents, the contribution of wheat ash increased and that of soil decreased as ash content increased. Above the wheat ash content of ~0.05%, wheat ash dominated the overall sorption. The overall sorptive characteristics shifted

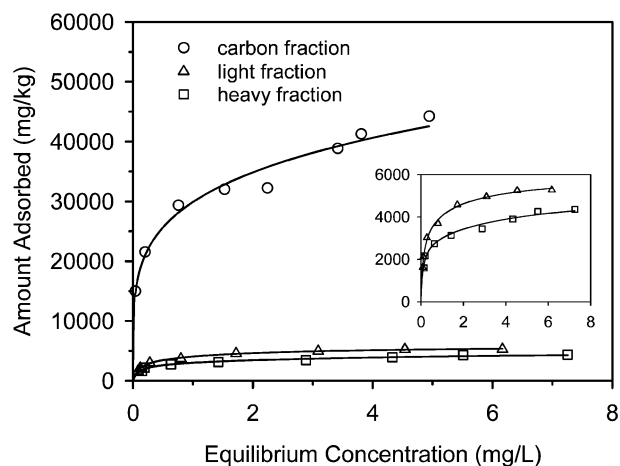


FIGURE 3. Sorption of diuron from water by carbon fraction, light fraction, and heavy fraction isolated or fractionated from wheat ash.

from those of soil to predominantly those of ashes as ash content in the soil increased. Because the ash content in topsoil of a particular agricultural field can be higher than 0.05%, the pesticide sorption on ashes is of practical interest. Wheat ash in soil not only enhanced the sorption of diuron but also altered the sorptive characteristics of the soil, as observed with a commercial charcoal by Yamane and Green (25).

To identify the potential ash component(s) that are responsible for the high adsorptivity, wheat ash was fractionated into the light and heavy fractions. As the density of activated carbon is lower than that of silica, it was expected that the light fraction should have higher carbon content than the heavy fraction. Elemental analysis supported such an inference. The light fraction has a BC content of 25.47% as compared to 7.58% for the heavy fraction (Table 1). Both fractions and the bulk wheat ash have similar silica contents. The light fraction also has a higher SSA than does the heavy fraction, due presumably to the higher BC content in the light fraction. It is not clear what caused the measured SSAs of both fractions lower than that of the bulk ash sample. The sorption isotherms of diuron on both fractions are shown in Figure 3. The light fraction was ~1.3 times more effective than the heavy fraction in sorbing diuron over the experimental concentration range. Ash BC appeared primarily responsible for the higher adsorptivity of the light fraction. Both fractions were somewhat less effective than the bulk wheat ash for diuron sorption, due probably to the lower SSAs of both fractions than that of the bulk wheat ash.

To further explore the role of ash BC in the diuron sorption, the C fraction was obtained by repeatedly washing wheat ash with mixed dilute hydrochloric and hydrofluoric acids. The treatment effectively removed silica and other soluble metal salts including carbonates (Table 1), although insoluble calcium fluoride precipitate may have formed as indicated in the elemental analysis (data not shown). Nevertheless, BC was enriched to 76.4%, and silica was largely removed in the C fraction (Table 1). The precipitated calcium fluoride in the C fraction is expected to be ineffective in sorbing diuron and should have a minimal effect on the overall sorption. The C fraction has a high SSA (408.30 m²/g), consistent with the high carbon content. Sorption isotherms in Figure 3 indicated that the C fraction was 6.5–45 times more effective than the bulk wheat ash, 8–22 times more than the light fraction, and 11–28 times more than the heavy fraction in sorbing diuron over the measured concentration range. These results demonstrate that BC in the wheat ash is the primary sorptive component for diuron sorption.

In summary, ashes arising from the burning of wheat and rice residues are highly effective adsorbents for diuron and can be the primary contributors to the overall pesticide sorption when existing in agricultural soils. Ashes and soils independently contribute to diuron sorption. The sorptive characteristics of soils containing ashes may be dominated by ashes. BC formed in ashes during burning appears primarily responsible for the high adsorptivity of ashes. It is expected that other pesticides will be strongly sorbed by ash BC in soils. While not excluding the role of the rubbery/glassy states of SOM and NOC hole-filling, this study provides direct evidence to support the HSACM model that BC contributes to the isotherm nonlinearity. As crop residues are often burned in the field, pesticides in agricultural soils may be highly immobilized because of the presence of ashes.

Acknowledgments

This research was supported by USDA-NRICGP Grant 2002-35107-12350 and the Division of Agriculture of the University of Arkansas.

Supporting Information Available

Two figures showing the kinetic adsorption of organic compounds from water by wheat ash and its carbon fraction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Spurlock, F. C.; Biggar, J. W. *Environ. Sci. Technol.* **1994**, *28*, 996–1001.
- (2) Young, T. M.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1995**, *29*, 92–97.
- (3) LeBoeuf, E.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 1697–1702.
- (4) Xing, B.; Pignatello, J. J.; Gigliotti, B. *Environ. Sci. Technol.* **1996**, *30*, 2432–2440.
- (5) Xing, B.; Pignatello, J. J. *Environ. Sci. Technol.* **1997**, *31*, 792–799.
- (6) Xing, B.; Pignatello, J. J. *Environ. Sci. Technol.* **1998**, *32*, 614–619.
- (7) Chiou, C. T. *Environ. Sci. Technol.* **1995**, *29*, 1421–1422.

- (8) Chiou, C. T.; Kile, D. E. *Environ. Sci. Technol.* **1998**, *32*, 338–343.
- (9) Allen-King, R. M.; Grathwohl, P.; Ball, W. P. *Adv. Water Resour.* **2002**, *25*, 985–1016.
- (10) Gustafsson, O.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. *Environ. Sci. Technol.* **1997**, *31*, 203–209.
- (11) Gelinas, Y.; Prentice, K. M.; Baldock, J. A.; Hedges, J. I. *Environ. Sci. Technol.* **2001**, *35*, 3519–3525.
- (12) Masiello, C. A.; Druffel, E. R. M. *Science* **1998**, *280*, 1911–1913.
- (13) Masiello, C. A.; Druffel, E. R. M.; Currie, L. A. *Geochim. Cosmochim. Acta* **2002**, *66*, 1025–1036.
- (14) Gustafsson, O.; Gschwend, P. M. *Geochim. Cosmochim. Acta* **1998**, *62*, 465–472.
- (15) Karls, J. E.; Christensen, E. R. *Environ. Sci. Technol.* **1998**, *32*, 225–231.
- (16) Schmidt, M. W. I.; Noack, A. G. *Global Biogeochem. Cycles* **2002**, *14*, 777–793.
- (17) Chiou, C. T.; Kile, D. E.; Rutherford, D. W.; Sheng, G.; Boyd, S. A. *Environ. Sci. Technol.* **2000**, *34*, 1254–1258.
- (18) Xia, G.; Ball, W. P. *Environ. Sci. Technol.* **1999**, *33*, 262–269.
- (19) Accardi-Dey, A.; Gschwend, P. M. *Environ. Sci. Technol.* **2002**, *36*, 21–29.
- (20) Accardi-Dey, A.; Gschwend, P. M. *Environ. Sci. Technol.* **2003**, *37*, 99–106.
- (21) Song, J.; Peng, P.; Huang, W. *Environ. Sci. Technol.* **2002**, *36*, 3960–3967.
- (22) Skjemstad, J. O.; Clarke, P.; Taylor, J. A.; Oades, J. M.; McClure, S. G. *Aust. J. Soil Res.* **1996**, *34*, 251–271.
- (23) Hilton, H. W.; Yuen, Q. H. *Agric. Food Chem.* **1963**, *11*, 230–234.
- (24) Toth, J.; Milham, P. J.; Kaldor, C. J. *Plant Prot. Q.* **1999**, *14*, 151–154.
- (25) Yamane, V. K.; Green, R. E. *Soil Sci. Soc. Am. Proc.* **1972**, *36*, 58–64.
- (26) Montgomery, J. H. *Agrochemicals Desk Reference*, 2nd ed.; Lewis Publishers: Boca Raton, FL, 1997; pp 185–187.
- (27) Sheng, G.; Johnston, C. T.; Teppen, B. J.; Boyd, S. A. *J. Agric. Food Chem.* **2001**, *49*, 2899–2907.
- (28) Boyd, S. A.; Jin, X.; Lee, J.-F. *J. Environ. Qual.* **1990**, *19*, 734–738.
- (29) Tomlin, C. D. S. *The Pesticide Manual*, 12th ed.; British Crop Protection Council: Farnham, Surrey, U.K., 2000; pp 331–332.
- (30) Barber, S. A. *Agron. J.* **1979**, *71*, 625–627.

Received for review January 3, 2003. Revised manuscript received May 28, 2003. Accepted June 4, 2003.

ES034006A