Pesticide Adsorptivity of Aged Particulate Matter Arising from Crop Residue Burns

Yaning Yang and Guangyao Sheng*

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

Particulates (ashes) arising from the burning of crop residues are potentially effective adsorbents for pesticides in agricultural soils. To determine the long-term adsorptive sustainability of ashes, a wheat (*Triticum aestivum* L.) ash was aged under environmentally relevant conditions (in $CaCl_2$ solution at room temperature and pH 7) in soil extract for 1 month and in a soil (1% ash) for a period of up to 12 months. The aged ash and ash-amended soil were used to sorb diuron from water. The diuron sorption was also measured in the presence of atrazine as a competing pesticide. There was no observed microbial impact on the stability of the wheat ash in soil. All isotherms with the ash were nonlinear type-I curves, suggestive of the surface adsorption. On a unit mass basis, the ash in soil extract was 600–10000 times more effective than the soil in sorbing diuron. Adsorption of dissolved soil organic matter (DOM) during aging on the ash surfaces reduced the diuron adsorption by 50–60%. Surface competition from the atrazine adsorption also reduced the ash adsorption of diuron by 10–30%. A total of 55–67% reduction in diuron sorption by the ash-amended soil was observed. Due to its high initial adsorptivity, the ash fraction of the aged ash-amended soil contributed >50% to the total diuron sorption. Thus, the wheat ash aged in the soil remained highly effective in adsorbing diuron. As crop residues are frequently burned in the field, pesticides in agricultural soils may be highly immobilized due to the presence of ashes.

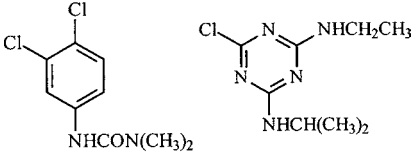KEYWORDS: Sorption; pesticide; ash; aging; soil; DOM; uptake competition

INTRODUCTION

Soil sorption of organic contaminants is an important physicochemical process that strongly influences contaminant transport and fate in the environment. Whereas the naturally occurring soil organic matter (SOM) is considered to be the predominant sorbent for organic contaminants from water (*1–4*), the combustion-derived black carbon (BC) has recently been invoked as an additional carbonaceous material of distinct properties that contributes to the soil sorption (*5–7*). BC was recognized to occur widely in many soils, sediments, and natural solids three decades ago (*8*). BC is believed to arise from the thermal alteration of various organic materials and thus possesses a relatively structured carbon matrix with a medium-to-high surface area (*7, 9*). This suggests that BC may act as a surface adsorbent similar in some respects to activated carbon, in contrast to SOM as a partition medium. Models that consider the concurrent sorption of organic contaminants by SOM and BC have successfully accounted for both the partitioning behavior and the adsorptive phenomena, the former characterized by linear isotherms and a lack of uptake competition between coexisting solutes and the latter by nonlinear type-I isotherms and competitive sorption between cosolutes (*7, 10–*

13). To date, efforts have been placed on the identification and isolation of BC from environmental matrices (*14–16*). Unfortunately, reliable isolation techniques that preserve the adsorptive power of BC during isolation have not been established, which hinders a full understanding of the adsorptive properties of BC.

BC is described as a ubiquitous form of carbon comprising a range of materials from polyaromatic to elemental or graphitic carbon (*8, 17*). The general behavior of BC in the environment is determined by two of its surface characteristics: chemical inertness at low temperatures and adsorptive properties (*8*). However, the BCs produced under different conditions from different source materials may possess widely different chemical compositions and surface properties and thus need to be extensively characterized in terms of their surface adsorptivity. As a prevalent method of immediate land-clearing worldwide, the field burning of crop residues is likely to be the major source of BC in agricultural soils (*7, 18*) and hence may significantly influence the environmental fate of pesticides. An early study indicated that some Hawaiian soils receiving the burning of sugarcane trash retained high adsorptivity for substituted ureas and *s*-triazines following the oxidative removal of organic matter by H_2O_2 (*19*). This was ascribed to the peroxide-resistant BC in the particulate matter (ash) arising from combustive carbonization of cane trash, although no direct evidence of BC was presented. Our recent study found that pure-form ashes of wheat

* Corresponding author [telephone (479) 575-6752; fax (479) 575-3975; e-mail gsheng@uark.edu].

Table 1. Selected Physicochemical Properties of Diuron (Left) and Atrazine (Right) (*22*)

pesticide	water solubility (mg/L)	pK_a	log K_{oc}	log K_{ow}
diuron	40 (20°C)		2.21–2.87	2.58
atrazine	33.8 (22°C)	1.7	1.95–2.71	2.27

and rice residues were highly effective adsorbents of the pesticide diuron, and the BC fraction of wheat ash was primarily responsible for the diuron adsorption (*20*).

The BC is usually assumed to be chemically and biologically inert in the environment (*21*), from the fact that activated carbon is refractory under environmental conditions. Evidence exists that BC persists as a solid carbonaceous material in some unconsolidated sediments (*8*). It is not clear whether the BC fraction of ashes arising from the burning of crop residues, as a surface adsorbent, remains sustainable in adsorbing pesticides when existing in a prolonged period in agricultural soils. In this study, pure-form wheat ash was used to sorb diuron in the absence and presence of atrazine as a cosolute to measure the competitive adsorption. The ash was also aged under environmentally relevant conditions to determine its adsorptive sustainability. The objectives of this study were to determine the effect of aging on the pesticide adsorptivity of ashes arising from the burning of crop residues, to measure the competitive adsorption between coexisting pesticides by ashes, and to overall evaluate the adsorptive sustainability of the ash surfaces subjected to prolonged exposure to complex soil matrices.

EXPERIMENTAL PROCEDURES

Pesticides. Diuron (with a purity of 99%) and atrazine (98%) were purchased from ChemService (West Chester, PA) and used as received. Diuron was used as the nominal solute in both single-solute and binary-solute sorption experiments, whereas atrazine was used as the competing solute (cosolute) in binary-solute sorption experiments. Both pesticides are polar and electrically neutral at normal soil pH values. Selected physicochemical properties of these pesticides are listed in **Table 1**.

Sorbents. Wheat ash was obtained by burning wheat (*Triticum aestivum* L.) straw in an open field under natural conditions on a fine July afternoon, as described in our previous study (*20*). Wheat straw is one of the most frequently burned crop residues. The ash has a BC content of 12.9% and surface area of 10.1 m²/g. The ash was either used alone or mixed with a soil. The soil was a Stuttgart silt loam collected at the Rice Research and Extension Center, Stuttgart, Arkansas, 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 crop residue burns in the past decade, was assumed to contain minimal levels of ashes. The soil was air-dried, ground, and sieved (1 mm). To obtain ash-amended soil sorbent, the wheat ash was added into the soil in exact ash (weight) content of 1% and thoroughly mixed before its use for the experiments.

Aging of Sorbents. Soil (150 g), wheat ash (10 g), and ash-amended soil (50 g) were weighed into 250-mL Teflon bottles and aged in 120 mL of a 0.005 M CaCl₂ solution in the laboratory under the ambient conditions for 1, 3, 6, and 12 months, respectively. Considering the yearly production and burning of crop residues, the aging for up to 12 months was chosen. The pH of the aging solution was adjusted to neutral with 1 M HCl and 1 M NaOH. During aging, the bottles were shaken once a week. After the appropriate aging period, the sorbents in bottles were frozen in a −80 °C freezer and subsequently freeze-

dried. To evaluate the potential influence of dissolved organic matter (DOM) of soil and soil microbial activity on the adsorptivity of the ash, a soil extract was obtained by adding the soil to the 0.005 M CaCl₂ solution in a ratio of 412.5 g of soil/L, shaking overnight, and filtering twice through Whatman no. 2 filter paper. Half of the soil extract was autoclaved. Aliquots of 0.01 g of sterilized wheat ash were aged in 25-mL Corex glass centrifuge tubes containing 2.4 mL of autoclaved or unautoclaved soil extract for 1 month. The aged wheat ash sorbents in the soil extracts, without prior freeze-drying, were directly used for sorption measurements by adding pesticide solution.

Sorption Isotherms. Diuron sorption in single-solute systems by the fresh (unaged) and aged wheat ash, soil, and ash-amended soil was measured by the batch equilibration technique as described in many earlier studies (e.g., see refs *6* and *23*). The procedures for the competitive sorption between diuron and atrazine were the same except that the 0.005 M CaCl₂ solution containing 8.6 mg/L atrazine was used as the background solution. Various quantities of diuron in 0.005 M CaCl₂ solution (or in CaCl₂−atrazine solution) were introduced into 25-mL Corex glass centrifuge tubes containing 0.01−3.50 g of sorbent. In most cases, the mass of sorbents was adjusted to allow for 30−70% of added diuron to be sorbed at equilibrium. At low concentrations with ash sorbents, diuron sorption was allowed to exceed 70% to compromise on the accuracy of sorbent weighing. Additional 0.005 M CaCl₂ solution (or CaCl₂−atrazine solution) was added to bring the total liquid volume to 10 mL. For the sorption by the wheat ash aged in soil extract, the total liquid volume was 12.4 mL. The initial concentrations of diuron ranged up to ∼50% 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 ash and soil samples showed that diuron sorption on all sorbents leveled off within 18 h, indicating the establishment of apparent sorption equilibrium.

After the establishment of sorption equilibrium, sorbents and aqueous phases were separated by centrifugation at 6000 rpm (RCF = 5210*g*) for 20−30 min. The pesticide concentrations in supernatants were analyzed by direct injection of 20 μL into a Hitachi reversed-phase high-performance liquid chromatograph (Hitachi High-Technologies Co., Tokyo, Japan) fitted with a UV−visible detector set at 252 nm for diuron in single-solute systems and at 215 nm for diuron and atrazine in binary-solute systems. A Phenomenex Prodigy C18 column was used. For single-solute sorption, the mobile phase was a mixture of acetonitrile and water (50:50) with a flow rate of 1.0 mL/min. For the binary-solute sorption, the mobile phase was a mixture of methanol and water (55:45) with a flow rate of 1.3 mL/min. All diuron concentrations were above the detection limit of ∼0.5 ppb. Each sorption isotherm was measured at seven to nine concentrations. All measurements were in triplicate with a difference of variation in sorption generally <5%, and 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 verify that glass tubes did not adsorb pesticides and no processes other than sorption contributed to the loss of solution-phase pesticides. Sorption isotherms are plotted as the amount of pesticide sorbed against the equilibrium concentration in water.

RESULTS AND DISCUSSION

Figure 1 shows the isotherms of diuron sorption from water by wheat ash aged for 1 month in autoclaved and unautoclaved soil extract, as compared to that by unaged wheat ash where DOM was not present. Overall, the wheat ash is a highly effective adsorbent for diuron. The isotherms are type-I curves, consistent with the proposition of surface adsorption (*5−9, 12, 13*) and our previous study (*20*). The characteristics of surface adsorption are further manifested by the observation that the aging of the wheat ash in soil extract decreased the diuron adsorption. DOM in soil solution is known to be adsorbed by various natural solids (e.g., see refs *24* and *25*). Similar adsorption of DOM by the wheat ash is believed to have occurred to occupy the ash surfaces and to subsequently reduce

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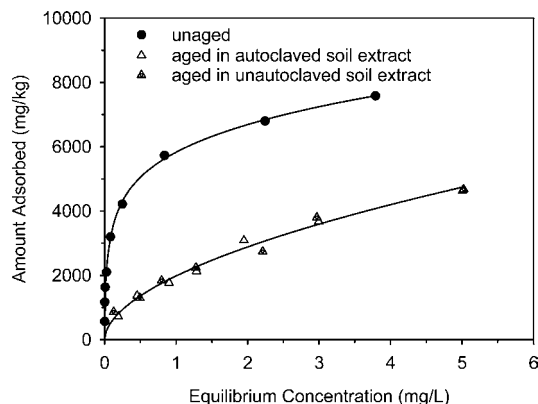
Figure 1. Isotherms of diuron sorption from water by wheat ash aged for 1 month in autoclaved and unautoclaved soil extract as compared to unaged wheat ash.

the diuron adsorption. With 2.1% SOM and the soil-to-extractant ratio used in the study, an appreciable level of DOM is expected to be present in the soil extract, although we did not measure the total dissolved organic carbon. From the isotherms in **Figure 1**, calculations show that the adsorption of DOM reduced the diuron adsorption by 50−60% over the diuron concentration range from 0 to 3 mg/L. Partitioning of diuron into the adsorbed DOM is expected to be insignificant compared to the diuron adsorption on the ash. Although the reduction in diuron adsorption is significant, the aged ash remained highly effective in adsorbing diuron, due primarily to its high initial adsorptivity, and thus may have a long-term influence on the environmental fate of pesticides.

Whereas the DOM adsorption competitively reduces the diuron adsorption, possibilities exist that the total reduction in diuron adsorption may partially result from the ash degradation under the environmental conditions. Two potential processes for BC degradation, photochemical and microbial breakdown, have been proposed in the literature (*8*). The photochemical degradation of the wheat ash is expected to be extremely slow under the normal conditions (*8*), particularly in soils where light is essentially absent. On the other hand, some early studies indicated that charcoals could be degraded by microorganisms (*26*, *27*). It remains unclear, however, how charcoals are degraded and what elements (carbon vs impurities) are actually utilized by microorganisms. Analysis of the wheat ash indicated a composition of 14.3% carbon, 0.64% nitrogen, 1.46% phosphorus, 21.0% potassium, 3.36% calcium, 0.89% magnesium, 0.63% sulfur, and other microelements (sodium, iron, manganese, zinc, copper, boron, and aluminum). When in their available (soluble) forms, these are essential elements for the growth of microorganisms. **Figure 1** shows that whether the soil extract was autoclaved did not result in a differential diuron adsorption. This suggests that the wheat ash surfaces were not impaired by microorganisms over a period of 1 month. Further evidence of the ash resistance to microbial attack is presented in the following sections. Activated carbon, a common adsorbent, is known to be resistant to microbial degradation (*8*), due largely to the well-structured carbon matrix. Because the ash BC, as the primary adsorbent, is similar in some respects to activated carbon, the biological stability of the wheat ash has been expected.

Persistence of the wheat ash as an adsorbent of pesticides was further examined by aging the ash, soil, and ash-amended soil. **Figure 2** shows the diuron sorption by the soil, the wheat ash, and the ash-amended soil, all aged for 1, 3, 6, and 12
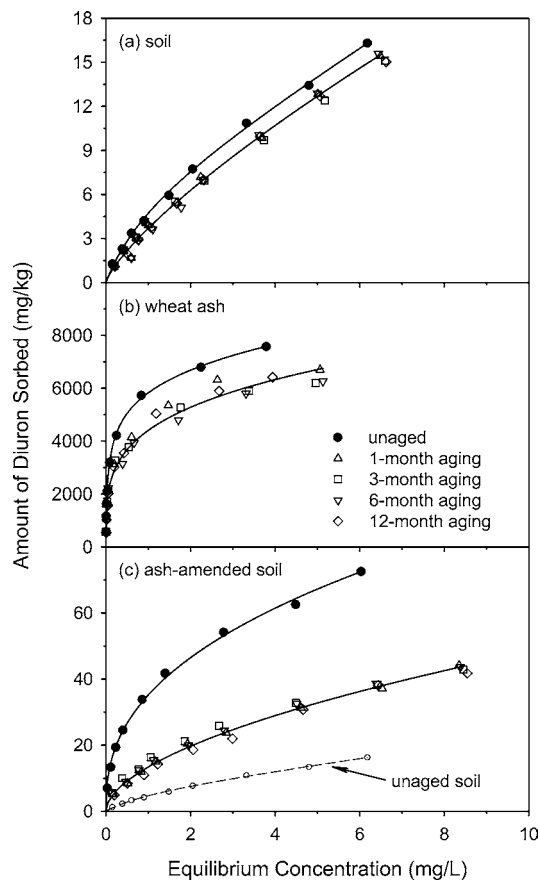
Figure 2. Isotherms of diuron sorption from water by soil (a), wheat ash (b), and ash-amended soil (c) aged for 0 (unaged), 1, 3, 6, and 12 months.

months under environmentally relevant conditions, as compared to that by their respective unaged sorbents. The isotherms of diuron sorption by the soil are highly linear over the range of intermediate to high concentrations (**Figure 2a**), in accord with the characteristics of solute partitioning into SOM (*1*, *2*, *4*). The concave-downward nonlinearity at low concentrations may be ascribed to the specific interaction of diuron molecules with active SOM sites (*28*), due to the polar nature of diuron molecules (*6*, *9*). Aging of the soil resulted in a constant but small reduction in diuron sorption (<10%). Furthermore, aging for 1 month and for up to 12 months did not cause a differential diuron sorption. Chemical processes involving Ca^{2+} of the aging solution most likely caused such a reduction. Microbial decomposition of SOM apparently did not influence the diuron sorption.

The wheat ash effectively adsorbed diuron (**Figures 1** and **2b**). On a unit mass basis, the ash was 600−10000 times more effective than the soil in sorbing diuron over the range of the experimental concentrations. The presence of the ash in soil, even at the trace level, will thus strongly influence the sorptive behavior of the soil. Assuming that diuron molecules are adsorbed in a monolayer configuration on the surface of the ash, and the cross-sectional area of diuron molecule is estimated as 49.5 $Å^2$ (= 49.5 × 10^{-20} m^2) (*20*, *29*), using the diuron adsorption of 7585 mg/kg on the unaged ash at 3.80 mg/L (**Figures 1** and **2b**), the surface area occupied by diuron molecules is estimated at 9.7 m^2/g. This number is close to the measured surface area of the unaged ash (10.1 m^2/g). Similar to the observation with the soil, aging of the wheat ash caused a small reduction (<20%) in diuron adsorption over the experimental concentration range (**Figure 2b**). The adsorptivity

of the aged ash did not decrease with aging time, suggesting that microbial breakdown of the ash did not occur. The reason for the reduction in diuron adsorption is unknown. It is due likely to the mechanical destruction of the ash porous structure during aging. It may also be due to experimental artifacts originating from the freezing-drying processes that have altered the ash particle size and surfaces.

Amendment of 1% wheat ash into the soil substantially enhanced the diuron sorption (**Figure 2c**), due apparently to the high adsorptivity of the ash. Fitting of the full-range sorption data to the Freundlich equation, $Q = K_f C_e^N$, where Q and C_e are the amount of diuron sorbed (mg/kg) and equilibrium concentration (mg/L), respectively, and K_f and N are constants, results in N values of 0.689 with the soil and 0.403 with the ash-amended soil, indicating the increased degree of isotherm nonlinearity with the ash amendment. Assuming that the ash did not affect the sorptivity of the soil, diuron sorption by the ash-amended soil (**Figure 2c**) compared to that by the unaged soil (**Figure 2a**, also the dashed line in **Figure 2c**) indicates that the ash fraction of the ash-amended soil dominated the diuron sorption. Calculations using the measured isotherms and that for the unaged soil in **Figure 2a** show that the ash fraction of the unaged sorbent adsorbed >80% of the total diuron. Similarly, aging reduced the diuron sorption on the ash-amended soil by 50−60% over the range of experimental concentrations. The degree of isotherm linearity for the aged sorbent increased, as indicated by the Freundlich N value of 0.555, suggestive of the partial deactivation of the ash surfaces. The diuron sorption did not further decrease with increasing aging time. This suggests that microbial activity in the soil, where microbes are most active, did not contribute to the observed aging effect; otherwise, the diuron sorption would have decreased continuously with aging time. Therefore, the reduction in diuron sorption by the aged sorbent is due probably to the suppression of the ash surfaces from the DOM adsorption. However, the ash fraction of the aged sorbent remained highly effective for pesticide adsorption by contributing >55% to the total diuron sorption (**Figure 2c**).

Although soil DOM is capable of suppressing the diuron adsorption on the wheat ash, foreign organics (e.g., pesticides) may also act as competing solutes in a similar fashion of adsorptive suppression, as illustrated in **Figure 3**. The diuron uptake by the soil in the presence of atrazine was slightly lower than that with diuron as single solute (**Figure 3a**). On the other hand, atrazine uptake by the soil decreased little, if any, with increasing diuron concentration (and hence with diuron uptake). The lack of strong uptake competition between diuron and atrazine in soil is predicted because the two pesticides are expected to partition into SOM as their primary uptake mechanism (*1*, *3*, *4*). The small reduction in diuron uptake is ascribed to the competitive interaction of atrazine with active SOM sites (*6*, *9*, *27*). In contrast, diuron adsorption by the wheat ash, where SOM is absent, in the presence of atrazine is clearly reduced (**Figure 3b**), apparently due to the competitive adsorption of atrazine. The reduction accounted for 10−30% of the total diuron adsorption with an initial atrazine concentration of 8.6 mg/L. Meanwhile, atrazine adsorption on the ash also decreased with increasing diuron concentration. Over the diuron concentration range of 0−2 mg/L, atrazine adsorption was reduced by as much as ∼67% (**Figure 3b**).

As the wheat ash dominated pesticide sorption in the ash-amended soil, a reduction in diuron sorption on the ash-amended soil in the presence of atrazine is predicted. In fact, the measured overall reduction in diuron sorption in the presence of 8.6 mg/L
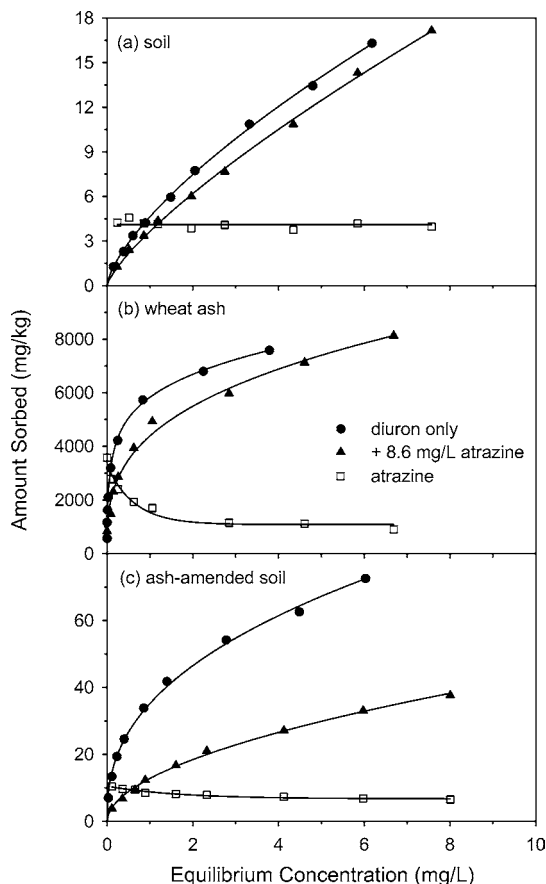
Figure 3. Isotherms of diuron sorption from water by soil, wheat ash, and ash-amended soil in the absence and presence of atrazine as a competing solute. Variation in atrazine sorption with diuron concentration also shown.

atrazine ranged from 55 to 67% over the experimental concentration range (**Figure 3c**). The atrazine sorption also decreased by as much as 38% with increasing diuron concentration, in direct contrast to the observation with the soil where the atrazine uptake was not reduced by the diuron uptake. Both the larger reduction in diuron uptake (55−67 vs 10−30%) and the smaller reduction in atrazine uptake (∼38 vs ∼67%) with the ash-amended soil than with the wheat ash suggest that the overall reduction in diuron uptake resulted from a combination of the DOM adsorption on the ash surfaces and the adsorptive competition between diuron and atrazine. In soils where multiple contaminants are present, a larger reduction in diuron uptake may be observed. Nevertheless, calculations show that the wheat ash contributed >50% to the total diuron sorption when atrazine was present. The wheat ash thus remained highly effective for diuron adsorption.

CONCLUSIONS

Ashes arising from the burning of crop residues are potentially effective adsorbents for pesticides. When existing in soils, ashes are not subjected to microbial degradation and are therefore biologically stable. The adsorption potential of ashes for pesticides may be suppressed by soil DOM adsorption and reduced by competitive adsorption of coexisting pesticide counterparts. However, aged ashes in soils remain highly effective in adsorbing pesticides, due to their high initial adsorptivity, and thus may greatly influence the retention and environmental fate of pesticides in agricultural soils.

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