Interactions of triazine herbicides with biochar: Steric and electronic effects

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ABSTRACT: We studied the adsorption of triazine herbicides and several reference heteroaromatic amines from water onto a temperature series of hardwood biochars (300 – 700 °C, labelled B300 – B700). Adsorption on biochars correlated poorly with pyrolysis temperature, H/C, O/C, mean minimum fused ring size, surface area (N₂ or CO₂), microporosity, and mesoporosity, but correlated well with a weighted sum of microporosity and mesoporosity. Steric effects were evident by the negative influence of solute molecular volume on adsorption rate. Adsorption rate maximized for the biochar with the greatest mesoporosity-to-total-porosity ratio, suggesting that mesopores are important for facilitating diffusion into pore networks. The cationic forms of amines adsorb more slowly than the neutral forms. To further probe steric and electronic effects, adsorption on a biochar (B400) was compared to adsorption on graphite—a nonporous reference material with an unhindered, unfunctionalized graphene surface—and in comparison with reference compounds (benzene, naphthalene, pyridine, quinoline and 1,3-triazine). Relative to benzene, the surface area-normalized adsorption of the triazine herbicides was disfavored on B400 (favored on graphite) by 11–19 kJ/mole, depending on concentration. It is estimated that steric suppression of B400 adsorption comprises 6.2 kJ/mol of this difference, the remainder being the difference in polar electronic effects. Based on the behavior of the reference amines, the difference in polar effects is dominated by π – π electron donor–acceptor (EDA) interactions with sites on polyaromatic surfaces, which are more electropositive and/or more abundant on graphite. Overall, our results show that mesoporosity is critical, that adsorption rate is a function of solute molecular size and charge, that steric effects in the solute largely suppress equilibrium adsorption, and that π – π EDA forces play a role in triazine polar interactions with the biochar.

40 *Keywords:* Herbicides; Soil contamination; Leaching; Groundwater; Solid waste conversion;

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Graphical Abstract

1. Introduction

Triazine herbicides are used world-wide in agriculture to control broadleaf and grassy weeds. The triazines have low to moderate soil sorption coefficient, moderate solubility in water, and low volatility, making them vulnerable to leaching. In the U.S., triazine herbicides, especially atrazine, simazine and prometon, are frequently detected in ground and surface waters at concentrations up to several hundred micrograms per liter (*Gilliom, 2007, Hoffman et al., 2000, Kolpin et al., 1998*). Exposure to some triazine herbicides can lead to adverse human health and ecosystem effects, including hormone disruption (atrazine) (*Chapin et al., 1996*) and damage to testes, kidneys, and thyroid (simazine) (*USEPA, 2002; 2005*). Effective approaches for mitigating the leaching of triazine herbicides from agricultural fields are clearly needed. Biochar, which is made by anaerobic pyrolysis of biomass waste materials, has attracted attention as soil amendments for reducing the physical and biological availabilities of soil-borne chemicals, among other functions (*Lehmann and Joseph, 2015 (in press)*). Biochar addition to soils increases adsorption of certain herbicide compounds (*Cabrera et al., 2014, Graber and Kookana, 2015, Loganathan et al., 2009, Spokas et al., 2009*), which can reduce leaching (*Delwiche et al., 2014, Graber and Kookana, 2015, Jones et al., 2011, Lu et al., 2012*) but at the same time increases the application rate needed to achieve the same level of weed control (*Graber and Kookana, 2015*). Chars also present intrinsically in soil as the charred products of biomass burning.

The objective of the present study was to better understand the interaction of triazines with biochar at a fundamental level. Published studies with this objective in mind are few and were seldom carried out by varying solutes and sorbents in a systematic manner. Hao et al. found that the adsorption of atrazine on corncob biochars increases with decreasing H/C and (O + N)/C

ratios, stating that “aromatic C and hydrophobic structures” are the major adsorption sites (*Hao et al., 2013*). Cao et al. proposed that the adsorption of atrazine by low-temperature (200 and 350 °C) biochars is due to partitioning into an uncarbonized biochar organic matter phase (*Cao et al., 2009*). Zhang et al. found that decreasing the solution pH from ~9.7 to ~3.7 led to a 1.5-fold increase in the adsorption of atrazine and simazine on biochar made from a mixture of hardwood chips and barks, and believed that the increase was due to the coulombic attraction between the triazine cations and the negatively charged surfaces (*Zheng et al., 2010*). In spite of the insights gained from these studies, our mechanistic understanding of the adsorption of triazines and other agrochemicals to biochar is still rudimentary.

First, the effect of biochar pore geometry on the adsorption is not clear. Biochar and many pyrogenic carbonaceous materials (PCMs) are generally nanoporous, with pores having apertures within the range of solute molecular diameters. Several rate models based on pore-diffusion and pore-filling mechanisms have been developed for the adsorption on porous PCMs (activated carbon) (*Ahn et al., 2005, Crittenden et al., 1991, Kleineidam et al., 2002*). However, little attention has been paid so far to steric effects that could result in molecular exclusion from pores or hindered diffusion within pore networks. Some studies of simple neutral aromatic compounds have shown that adsorption on biochar becomes hindered with increasing degree of substitution on the ring and increasing fused ring size (*Lattao et al., 2014, Pignatello, 2013, Zhu et al., 2005*). However, the role of biochar geometry, especially the relative importance of microporosity and mesoporosity of biochar, in relation to the size of solute molecules has not been well characterized.

Second, the influence of the electronic properties of heteroaromatic amines on adsorption is also incompletely understood. Previous studies have shown that π -electron rich polyaromatic

surfaces of biochar and graphite can interact with certain cyano- or nitroaromatic compounds that are π -electron poor to form π - π electron donor-acceptor (EDA) complexes (*Latta et al., 2014, Zhu and Pignatello, 2005*). The π - π EDA force results primarily from attraction between opposing quadrupoles. We recently showed that cationic triazine herbicides (ametryn and prometon) and polyaromatic surfaces undergo π^+ - π EDA interactions, which are a combination a π - π EDA force and a cation- π force (*Xiao and Pignatello, 2015*). Zhang et al. suggested that uncharged atrazine undergoes π - π EDA interactions on manure-derived biochars (*Zhang et al., 2013*). Since the neutral form of the triazines predominates in the soil under most conditions, it is of interest to establish beyond speculation whether neutral triazine herbicides can associate through π - π EDA interactions with the polyaromatic surfaces of PCMs including biochar.

The effect of biochar amendment on the leaching of herbicides also strongly depends on the adsorption rate; however, reports of adsorption rates of organic compounds including herbicides by biochar are rare (*Chen et al., 2012*). Chen et al. state that the diffusion of organic compounds in an uncarbonized ‘partition’ phase is slower than diffusion in the carbonized phases of biochar; hence, naphthalene adsorption was slower in low-temperature biochars (200 and 300 °C) than in high-temperature biochars (> 400 °C), which had a higher degree of carbonization (*Chen et al., 2012*).

The objective of this study was to systematically probe key physical-chemical properties of the biochar and key electronic and steric properties of the triazine herbicides that govern the overall adsorption rate and extent. The test set included five triazine herbicides—ametryn, atrazine, prometon, simazine, and terbutryn. The study was aided by the use of reference compounds and sorbents. The reference compounds included three heteroaromatic amines (pyridine, quinoline and 1,3-diazine). Quinoline is a steric homolog of pyridine; 1,3-diazine is

isosteric with pyridine and an electronic homolog of pyridine. Pyridine and quinoline are used in a variety of industrial, commercial, and agronomic applications, and have been found in the natural environment (*Brumley et al., 1991, Pereira et al., 1983, Stuermer et al., 1982*). We also included two nonpolar aromatic compounds (benzene and naphthalene) for comparison; their adsorption data were taken from a previous study (*Lattao et al., 2014*). The reference adsorbent was graphite, which has an unhindered, unfunctionalized polyaromatic (graphene) surface. Graphite has been used previously as a reference for the polyaromatic surfaces of PCMs (*Lattao et al., 2014, Pignatello, 2013, Xiao and Pignatello, 2015, Zhu et al., 2005*).

2. Methods and materials

Biochars were made from maple wood shavings heated for 2 h under a flow of N₂ at six final heat treatment temperatures (HTTs) from 300 to 700 °C as previously described (*Cao et al., 2012*). The chars are hereafter referred to as B300 through B700. Graphite (Sigma-Aldrich; 99.99% C; particle size < 20 µm) had 100.1% C, <0.5% H, and <0.5% O (*Zhu and Pignatello, 2005*). Pore size distribution and surface area (SA) of biochars and graphite were determined by nitrogen and carbon dioxide porosimetry using BET, non-local density functional theory and Monte Carlo models (*Braida et al., 2003*).

The adsorbates in highest purity available were purchased from Sigma–Aldrich, Riedel-de Haën, or Fisher Scientific, including five triazine herbicides (ametryn (98.5%; $pK_a = 1.7$), atrazine (>98%; $pK_a = 1.23$), prometon (99%; $pK_a = 4.3$), simazine (99%; $pK_a = 1.62$), terbutryn (99.3%; $pK_a = 4.3$)) and a series of heteroaromatic amines [pyridine (>99.9%; $pK_a = 5.23$), 1,3-diazine ($\geq 98.0\%$; $pK_a = 1.23$), quinoline (98%; $pK_a = 4.95$)]. ‘Nanopure water’ is tap water passed through a commercial purifier (Milli-Q) to achieve a resistivity of > 18.2 MΩ cm.

Adsorption was conducted in glass vials at 20 °C by a method described previously (Xiao and Pignatello, 2014). The liquid phase was synthetic agricultural runoff prepared with nanopure water containing both monovalent and divalent ions (1.0×10^{-3} mol/L NaHCO_3 , 0.5×10^{-3} mol/L CaCl_2 , 0.2×10^{-3} mol/L MgSO_4 , 0.1×10^{-3} mol/L KCl , 1.0×10^{-3} mol/L NaCl) and also containing 3.1×10^{-3} mol/L NaN_3 to inhibit microbial growth. The calculated ionic strength is 7.5×10^{-3} mol/L, not including salts from the biochar that may have dissolved. The adsorbent (biochar or graphite) was pre-wetted in the liquid phase for 48 h. The vials were then spiked with adsorbates from stock solutions in methanol (atrazine, simazine and terbutryn; final methanol concentration in liquid phase, < 0.2%) or water (ametryn, prometon, pyridine, 1,3-diazine and quinoline), and allowed to mix end-over-end at 40 revolutions per minute (rpm) at 20 °C in the dark. The solid-to-liquid ratio was adjusted to achieve 25–75% adsorption. The solid-to-liquid ratio did not influence adsorption on graphite (Fig. S1 in the Supplementary data). The adsorption equilibrium time was chosen on the basis of separate kinetic tests to be sufficient to reach apparent equilibrium. Equilibration times of 50 d (for pyridine and quinoline) and 60 d (for triazine herbicides) were chosen for biochar, and 48 h was chosen for graphite. An adsorption time of 7 d for 1,3-diazine on biochar was selected on the basis of the uptake curve for pyridine. Controls without adsorbents showed no significant abiotic loss during the uptake period. After adsorption, the aqueous phase was sampled and microfiltered (0.45 μm , nylon). Adsorption to filters was negligible. Aqueous concentrations were determined within two days by high-performance liquid chromatography (HPLC) with UV detection at 228 nm for herbicides and quinoline and 256 nm for 1,3-diazine and pyridine, using external standards. The analytical HPLC methods can be found in the Supplementary data.

Adsorption isotherms were fit to the Freundlich model:

$$C_s = K_F C_w^n \quad (1)$$

where C_s (mg/kg) and C_w (mg/L) are the adsorbed and aqueous-phase concentrations, respectively; n is the Freundlich exponent providing an indication of isotherm nonlinearity; and K_F ($\text{mg}^{1-n} \text{L}^n \text{kg}^{-1}$) is the Freundlich adsorption coefficient. They were obtained by nonlinear least-squares regression of experimental data weighted by the dependent variable. The observed (concentration-dependent) distribution ratio K (L/kg) (K_b for biochar and K_g for graphite) is defined as the adsorbed-to-solution concentration ratio,

$$K = \frac{C_s}{C_w} \quad (2)$$

The K is related to K_F by $K = K_F C_w^{n-1}$.

The uptake data were fitted to an analytical solution of the Fickian diffusion equation for a sphere in a well-mixed batch system (*Crank, 1975*):

$$\frac{C_{s,t}}{C_{s,e}} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1) \exp(-D_b^{\text{app}} q_n^2 t / a^2)}{9 + 9\alpha + q_n^2 \alpha^2} \quad (3)$$

where $C_{s,t}$ and $C_{s,e}$ are the concentrations of solute adsorbed after time t and equilibrium, respectively; a (cm) is the characteristic diffusion length scale within the solid; D_b^{app} (cm^2/sec) is the apparent diffusion coefficient over a ; α (unitless) is a parameter incorporating the final fractional uptake of solute; and q_n is the non-zero root of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \quad (4)$$

The value of D_b^{app}/a^2 was obtained by minimizing the sum of the square of the differences between measured and fitted values, with D_b^{app}/a^2 as the only adjustable parameter. The

regression was performed for values of n up to 4 because $\frac{6\alpha(\alpha+1) \exp(-D_{\text{biochar}}^{\text{app}} q_n^2 t / a^2)}{9 + 9\alpha + q_n^2 \alpha^2}$

approached zero for $n > 4$. The adjusted (for degrees of freedom) coefficient of determination R_{adj}^2 was used to evaluate fitting performance (Xiao et al., 2013).

3. Results and discussion

3.1. Microporosity and mesoporosity and other properties of biochars as a function of HTT

Increasing HTT caused significant and nonlinear increases in C and decreases in O and H contents of biochar (Fig. S2, Supplementary data). The loss of oxygen-containing substance and volatile organic compounds during pyrolysis results in the formation of pores (Lehmann and Joseph, 2015 (in press)). The total porosity of biochar tripled from HTT of 300 °C to 500–700 °C. The microporosity of biochar ($d < 2$ nm) increased by 2.5 times as the HTT increased from 300 °C to 700 °C (Fig. 1). Considerable mesoporosity ($2 \text{ nm} < d < 50 \text{ nm}$) had developed by the HTT of 500 °C. The mesoporosity decreased two-fold when the HTT further increased from 500 °C to 600 °C and was unchanged from 600 °C to 700 °C. B500 had the highest mesoporosity, whereas B700 had the highest microporosity (Fig. 1). Lua et al. also found that the N₂ BET surface area of pistachio-nut shell-derived carbon increases with the pyrolysis temperature from 250 to 500 °C but then decreases (moderately) from 500 to 800 °C (Lua et al., 2004). On the other hand, Keiluweit et al. found that a general increase in N₂ BET surface area of wood- and grass-derived chars as the pyrolysis temperature increasing from 100 to 700 °C (Keiluweit et al., 2010). The effects of pyrolysis temperature on the evolution of biochar pore geometry are not well understood, and they are potentially intertwined with other pyrolysis conditions and feedstock type. In addition, the isoelectric point determined by zeta potential measurement is $\text{pH}_{\text{iep}} < \sim 2$ for all the biochars (Fig. S3, Supplementary data). As shown in Fig. S3, at neutral pH, the low-temperature biochars (e.g., B300) tends to be more negatively charged than high-temperature

biochars (e.g., B700), which is likely due to the loss of surface oxygenic functional groups with temperature (see Fig. S2 of Supplementary data). The mean minimum aromatic fused ring cluster size estimated by nuclear magnetic resonance spectroscopy increased approximately linearly from 20 to 76 carbons with HTT from 300 to 700 °C (Cao *et al.*, 2012).

Fig. 1 is near here.

3.2. Adsorption as a function of biochar physical-chemical properties

We initially examined the relationships between adsorption and biochar physical-chemical properties using atrazine and the reference, planar compound quinoline as probes. Adsorption isotherms of atrazine on B300, B400, B500, B600 and B700 are shown in Fig. S4 (Supplementary data), and those of quinoline in Fig. S5. Many studies of organic compound adsorption by PCMs (biochar and activated carbon) (Ahmaruzzaman, 2008, Graber *et al.*, 2012, Hao *et al.*, 2013, Kearns *et al.*, 2014, Wang *et al.*, 2010, Yang *et al.*, 2010, Zhang *et al.*, 2011) report a trend of increasing adsorption with increasing SA or microporosity. In addition, atrazine adsorption was found to decrease with increasing carbonization (as H/C ratio) or increasing polarity [as (O + H)/C ratio] (Hao *et al.*, 2013). However, our results are not in agreement with these reported trends. Biochar B700 has the highest SA, largest microporosity, lowest H/C, lowest O/C, and highest mean minimum fused ring cluster size, indicating it has the largest and most hydrophobic surface of all the chars; thus, B700 was expected to have the greatest adsorption affinity for the test compounds according to the previously-reported trends. However, no straightforward relationship was found between atrazine or quinoline adsorption and each of the following biochar properties: micropore SA (CO₂ accessible), N₂ BET SA, CO₂-accessible

microporosity, mesoporosity, H/C, O/C, and fused ring cluster size (Figs. S6 and S7, Supplementary data). As shown in Figs. S4 and S6 in Supplementary data, adsorption of atrazine peaked at B500, which has the highest mesoporosity. The same is true for quinoline. The results are consistent with a recent study (*Lattao et al., 2014*) that found no straightforward relationship between these same biochar properties and adsorption affinity for benzene, naphthalene, or 1,4-dinitrobenzene.

Lattao et al. (*Lattao et al., 2014*) found that the “reduced” carbon-normalized distribution coefficient ($K_{b-C,r}$) for benzene, naphthalene, or 1,4-dinitrobenzene could be predicted by the weighted sum of microporosity and mesoporosity:

$$K_{b-C,r} = a \times \text{microporosity} + b \times \text{mesoporosity} \quad (5)$$

where a and b are the coefficients (g/cm^3) corresponding to micropore adsorption and mesopore adsorption, respectively. $K_{b-C,r}$ is calculated from C_{s-C} (carbon-normalized C_s) using the Freundlich equation and the reduced aqueous concentration. The reduced concentration is given by

$$C_r = C_w / C_w^{\text{sat}}(L) \quad (6)$$

where $C_w^{\text{sat}}(L)$ is saturated water solubility of the liquid or subcooled liquid (atrazine, 1068 mg/L (*Capel et al., 2008*); quinoline, 6110 mg/L (*SRC, 2014*)). In this study, Eq. 5 was extended to include two heteroaromatic amines (atrazine and quinoline), and the values of $K_{b-C,r}$ were calculated at C_r of 0.001 and 0.01.

A visual presentation of model performance of Eq. 5 is given in Fig. 2, and the regression results appear in Table S1 (Supplementary data). The coefficient of determination (R^2) falls in the range 0.88–0.99 (Table S1), suggesting a strong correlation. However, in each case there are only five data points (five biochars) against two independent variables, which may lead to over-

fitting (Xiao *et al.*, 2013). The adjusted coefficient of determination (R_{adj}^2), which takes into account the degree of freedom, falls in the range 0.51–0.66, indicating a moderately strong correlation. The prediction of $K_{b-C,r}$ is good to within a factor of 3 (0.48 log units) for all but three data points (Fig. 2).

Fig. 2 is near here.

3.3. Adsorption rates

Uptake rates of prometon, pyridine, and quinoline by biochars were determined at pH ~7, where they are predominantly neutral in solution, and at pH ~2 where they are predominantly cationic. The data were fitted to the diffusion model in Eq. 3. The uptake curves along with model fits are shown in Fig. S8 (Supplementary data). The fits by Eq. 3 are generally better for the neutral than the cationic species. The fitted values of D_b^{app}/a^2 are given in Table S2 (Supplementary data) and displayed in the bar graphs of Fig. 3.

Fig. 3 is near here.

Steric hindrance to diffusion becomes important as the ratio of pore aperture to the minimum critical molecular diameter drops below ~10, and becomes severe as that ratio approaches 1 (Kärger and Ruthven, 1992). The computed molecular volumes and shortest (width) and longest (length) molecular dimensions are given in Table 1. The reference compounds, benzene, naphthalene, pyridine, 1,3-diazine and quinoline are characterized by co-planarity of all atoms in the molecule. The single-ring compounds vary 2.74–2.81 Å in length and the double-ring compounds vary 5.02–5.07 Å in length (Table 1). The triazine herbicides are larger in both dimensions than the reference compounds due to ring substituents. In addition, the triazines have

greater bulk in the direction (z) perpendicular to the plane of the ring due to the inability of all substituent atoms to simultaneously assume co-planarity with the ring atoms. This can further restrict diffusion within slit-like pores, which become more prevalent as the biochar evolves to a more polyaromatic structure with increasing pyrolysis temperature.

Table 1 is near here.

For a given biochar, D_b^{app}/a^2 follows the order, pyridine > quinoline > prometon, which is the reverse order in their molecular volume. The value of D_b^{app}/a^2 follows the same order for the corresponding cationic form. An inverse correlation between D_b^{app}/a^2 and molecular volume is expected if steric effects are important. Quinoline is 79% longer and 56% more voluminous than pyridine, and prometon is the largest among the three compounds in all dimensions (Table 1). The value of D_b^{app}/a^2 reaches a maximum at B500 with all compounds, both in neutral and cationic form. B500 has the largest mesoporosity and the highest ratio of mesoporosity to total porosity (Fig. 1). This suggests that mesopores provide pathways for molecules to access deeper and smaller pores. The slowest uptake for all three compounds occurred for B700, which has the highest microporosity. Restricted diffusion will be manifested more in micropores than mesopores, and the steric hindrance in B700 micropores may lead to its low adsorption affinity towards solutes in comparison with B500 that has lower microporosity but greater mesoporosity.

It can also be seen in Fig. 3 that D_b^{app}/a^2 is several times smaller for the cation than for the corresponding neutral molecule of pyridine, quinoline and prometon. This observation is novel. The slower uptake of the cation is likely due to one or more of the following effects that would retard its diffusion in pores compared to the neutral molecule: *i*) back diffusion of native

cations (e.g., Na^+) to maintain electroneutrality; *ii*) co-diffusion of a counterion (e.g., Cl^-) to maintain electroneutrality; or *iii*) a larger hydration sphere of strongly-bound water molecules surrounding the cation and counterion. The relative contribution of these effects requires further study.

3.4. Probing electronic and steric effects using graphite as a reference adsorbent

The adsorption isotherms of the triazines and the reference compounds, pyridine and quinoline, were determined on B400 and graphite for comparison. Graphite is nonporous and sparsely-functionalized and should therefore interact primarily on the infinite polyaromatic sheet surface, with some adsorption along edges and defects. The weight-based adsorption of the (nonplanar) triazine herbicides was generally lower on B400 than on graphite (Fig. S9a), despite the higher SA of B400 than graphite (N_2 -accessible SA: $9.3 \text{ m}^2/\text{g}$ vs $4.5 \text{ m}^2/\text{g}$; CO_2 -accessible SA: $388 \text{ m}^2/\text{g}$ vs $15.8 \text{ m}^2/\text{g}$ (Lattao *et al.*, 2014)). On the other hand, on a weight basis the planar heterocyclic amines (pyridine, quinoline, and 1,3-diazine) prefer B400 over graphite.

The N_2 SA-normalized adsorption isotherms on B400 and graphite are shown in Fig. 4. These isotherms are mirrored by the corresponding CO_2 SA-normalized isotherms shown in Fig. S9b (Supplementary data). Based on N_2 SA, adsorption of the triazine herbicides is 10^1 - to 10^2 -times greater on graphite than on B400. The origin of this preference for graphite may be steric or electronic, or both. The steric bulk of the triazines may limit their access to interior pore SA of B400 that is otherwise available to N_2 at 77 K. In this regard, the preference for graphite is not exhibited for the smaller, flatter molecules pyridine, quinoline and 1,3-diazine. An electronic origin of the preference would be remarkable because graphite lacks polar (at least, dipolar) functionality.

Fig. 4 is near here.

To better understand the relative importance of steric and electronic effects on adsorption, the B400–water and graphite–water isotherms were used to construct the SA normalized B400–graphite distribution isotherms for eight heteroaromatic amines (pyridine, 1,3-diazine, quinoline, and five triazines) studied in the present work, in comparison with those for two aromatic compounds (benzene and naphthalene) obtained from a previous study (*Lattao et al., 2014*). The isotherms of a reference compound, 1,3,5-triazine could not be obtained because the compound is unstable in water. The B400–graphite isotherms were constructed using the experimental adsorption data points for B400 (C_w , $C_{s,b}$) and calculated values of $C_{s,g}$ for graphite at the same C_w using the Freundlich parameters for graphite converted to unit SA basis (*Lattao et al., 2014*). The biochar–graphite distribution ratio is given by:

$$K_{b-g} = \frac{C_{s,b}/C_w}{C_{s,g}/C_w} = \frac{C_{s,b}}{C_{s,g}} \quad (7)$$

Figure S10a shows B400–graphite adsorption isotherms normalized by the N_2 BET SA, ($SA_b^{N_2}$ and $SA_g^{N_2}$, respectively). The same isotherms normalized by CO_2 SA in Fig. S10b have identical spatial relationships, but are just shifted by a constant equal to $SA_b^{N_2}/SA_b^{CO_2} \cdot (SA_g^{N_2}/SA_g^{CO_2})^{-1}$. The isotherms indicate increasing preference for graphite over B400 in the order, benzene < pyridine ~ naphthalene < 1,3-diazine < quinoline < triazine herbicides.

The free energy of B400–graphite partitioning of a compound i , relative to i = benzene, can be expressed by (*Lattao et al., 2014*),

$$\Delta_{i-BEN}\Delta_{b-g}G = \Delta_{i-BEN}\Delta_{b-g}G^{ster} + \Delta_{i-BEN}\Delta_{b-g}G^{polar} + \Delta_{i-BEN}\Delta_{b-g}G^{hydr} \quad (8)$$

where the terms on the right correspond to the contributions to overall free energy by steric, polar, and hydrophobic effects. The polar term lumps dipole–dipole, dipole-induced dipole, hydrogen bonding, and quadrupole–quadrupole forces. The hydrophobic effect term lumps dispersion forces at the surface and interactions in the liquid phase that result in disruption of the cohesive forces of bulk water. The hydrophobic free energy may be taken as proportional to the free energy of solvent–water partitioning, such that

$$\Delta_{i-BEN}\Delta_{b-g}G^{hydr} = (\Delta_{i-BEN}\Delta_{b-g}a)\Delta_{i-BEN}\Delta_{S-w}G + (\Delta_{i-BEN}\Delta_{b-g}b) \quad (9)$$

where S is a suitable reference solvent and a and b are proportionality constants. For a closely-related series of compounds, the hydrophobic effects driving adsorption to B400 and graphite are expected to be roughly equal, which is equivalent to saying that the values of $\Delta_{i-BEN}\Delta_{b-g}a$ and $\Delta_{i-BEN}\Delta_{b-g}b$ are close to zero. Therefore, the hydrophobic term in Eq. 8 can be ignored. Substituting the appropriate B400–graphite adsorption equilibrium constants for $\Delta_{BEN-i}\Delta_{b-g}G$, Eq. 8 becomes,

$$\Delta_{i-BEN}\Delta_{b-g}G^{ster} + \Delta_{i-BEN}\Delta_{b-g}G^{polar} = -RT \ln \frac{K_{b-g,i}}{K_{b-g,BEN}} + const \quad (10)$$

where $const$ is a constant that depends on the reference states chosen for adsorption.

Figure 5 plots $\Delta_{i-BEN}\Delta_{b-g}G^{ster} + \Delta_{i-BEN}\Delta_{b-g}G^{polar}$ versus the adsorbed concentration on graphite for all the eight heteroaromatic amines studied in the present work and two aromatic compounds (benzene and naphthalene) from a previous study (*Lattao et al., 2014*). One can see that the curve for quinoline is positively displaced relative to the curve for pyridine. Since quinoline and pyridine are expected to undergo similar polar interactions with B400, this suggests that steric effects suppress quinoline adsorption relative to pyridine adsorption on B400.

As such, the curve for naphthalene is positively displaced (less favorable adsorption by B400) relative to the curve for benzene. Since naphthalene does not undergo significant polar interactions with either biochar or graphite, the positive displacement of the curve for naphthalene has been attributed to steric effects (*Lattao et al., 2014*).

Fig. 5 is near here.

The free energy curves for pyridine and 1,3-diazine are also positively displaced relative to the curve for benzene. Since pyridine and 1,3-diazine are isosteric with benzene, this indicates that pyridine and 1,3-diazine have greater affinity for graphite than for B400 for electronic reasons. Pyridine and 1,3-diazine can undergo dipole–dipole, H bonding and π – π EDA interactions with B400. However, since graphite has no significant functionality, of these forces, π – π EDA interactions with graphite appear to dominate the $\Delta_{i-BEN}\Delta_{b-g}G^{polar}$ term for pyridine and 1,3-diazine.

The π – π EDA force may occur when electron-poor and electron-rich π systems interact through their quadrupoles. The polyaromatic surfaces of PCMs are π -electron rich, while the solute molecule is π -electron poor by virtue of the electronegative N atoms incorporated into the ring. The polyaromatic sheet of graphite is infinite, whereas the mean minimum fused ring size of B400 is about 18 C atoms (*Cao et al., 2012*). The polyaromatic component of the total SA of B400 is expected to be less than that of graphite due to the presence of incompletely carbonized structure (*Keiluweit et al., 2010*) in biochar. In addition, B400 contains almost 20% O—some of it in functional groups like hydroxyl, carboxyl, ether and carbonyl attached to rings—that likely reduce the π -donor character of the ring systems.

Electrostatic potential (E_p , kJ/mol) has been used as an indicator of a compound's π -donor or π -acceptor character, and thus its potential to engage in π - π EDA interactions (Cockcroft *et al.*, 2007, Mecozzi *et al.*, 1996, Xiao and Pignatello, 2015). The molecular E_p surface of solutes was determined by density functional theory (B3LYP, 6-31G* basis set; Spartan 10, Wavefunction Inc., Irvine, CA) (Xiao and Pignatello, 2015). The value of E_p at the midpoint of the ring ($E_{p,mid}$) was taken as a measure of the π -donor or π -acceptor character of the ring as a whole, according to past practice (Xiao and Pignatello, 2015). The value of $E_{p,mid}$ (kJ/mol) increases with increasing N incorporation in the order, benzene (−96.0) < pyridine (−44.2) < 1,3-diazine (11.2) < 1,3,5-triazine (70.4); and the order, naphthalene (−76.8) < quinoline (−57.7) (Table 1). These results confirm that heterocyclic N atoms strongly polarize the ring electron cloud. The $E_{p,mid}$ values of the triazine herbicides range from −27.1 to −58.4 kJ/mol, which are more negative than the $E_{p,mid}$ of 1,3-diazine (11.2 kJ/mol) and 1,3,5-triazine (70.4 kJ/mol), reflecting the net π -electron donor character of the triazine herbicide ring substituents. The potential to engage in π - π EDA interactions with graphite is, indeed, a function of molecular electrostatic potential (Fig. 6). The $\log K_g/K_{ow}$, which represents the free energy of adsorption normalized by hydrophobic effects and neglects steric and all other polar effects, correlates strongly with $E_{p,mid}$. The heteroaromatic compounds give a steeper slope than the substituted benzenes, which suggests that an electronegative atom within the ring has a greater effect on ring quadrupolarity.

Fig. 6 is near here.

The net positive displacement of $\Delta_{i-BEN}\Delta_{b-g}G^{ster} + \Delta_{i-BEN}\Delta_{b-g}G^{polar}$ for pyridine (by 3.7–8.5 kJ/mol) and 1,3-diazine (by 8.8–10.4 kJ/mol) from the benzene baseline in Fig. 5 reflects $\Delta_{i-BEN}\Delta_{b-g}G^{polar}$ since these solutes are isosteric with benzene. Moreover, since graphite cannot engage in dipolar and hydrogen bonding interactions, the positive displacement further suggests that $\Delta_{i-BEN}\Delta_{b-g}G^{polar}$ is dominated by π – π EDA interactions rather than hydrogen bonding or dipole–dipole interactions. This is consistent with the more positive $E_{p,mid}$ of pyridine (-44.2 kJ/mol) and 1,3-diazine (11.2 kJ/mol) relative to benzene (-96.0 kJ/mol). Furthermore, the net positive displacement indicates either that graphite is more electropositive than B400, or that π – π EDA sites are more abundant on graphite than on B400, or both. Quinoline is positively displaced relative to the isosteric naphthalene (Fig. 5). Thus, a similar line of reasoning can be used to argue that $\Delta_{BEN-i}\Delta_{b-g}G^{polar}$ for quinoline reflects π – π EDA forces that predominate on graphite relative to B400.

The sum $\Delta_{i-BEN}\Delta_{b-g}G^{ster} + \Delta_{i-BEN}\Delta_{b-g}G^{polar}$ for the triazine herbicides is displaced by 11–19 kJ/mole from the benzene baseline, a greater displacement than the other compounds tested. This displacement corresponds to 2.0–3.4 $\log_{10}$ units relative to benzene of the distribution ratio, K_{b-g} , depending on concentration. The positive displacement is likely due to a combination of steric effects and π – π EDA forces. The $E_{p,mid}$ values of the triazines (-27.1 to -58.4 kJ/mol) scatter around that of pyridine (-44.2 kJ/mol), yet the values of $\Delta_{i-BEN}\Delta_{b-g}G^{ster} + \Delta_{i-BEN}\Delta_{b-g}G^{polar}$ are all positively displaced relative to that of pyridine. Thus, in the absence of steric effects, the curves of the triazines would be closer to the curve of pyridine. On that basis, it is suggested that adsorption of the triazines on B400 is suppressed by about by ~6.2 kJ/mol (1.2 $\log_{10}$ units of K_{b-g}) relative to benzene due to steric effects. With their greater width and thickness, the triazines are

unable to penetrate pore networks as deeply as benzene. The steric free energy likely depends on the biochar sample. It has been found that steric hindrance for naphthalene relative to benzene increases as the ratio of microporosity to total meso- plus micro-porosity of the biochar increases (Lattao *et al.*, 2014).

Within the triazine series, the order in $\Delta_{i-BEN}\Delta_{b-g}G^{ster} + \Delta_{i-BEN}\Delta_{b-g}G^{polar}$ is: ametryn < terbutryrn < prometon ~ atrazine < simazine. Excluding prometon, this is the same order as the order in $E_{p,mid}$ (Table 1), which suggests that π - π EDA interactions may participate in triazine herbicide adsorption to biochar and graphite. Prometon is the only one of the triazines with two isopropylamino substituents; the dual isopropyl groups introduce additional steric bulk in the z direction that increases the value of $\Delta_{i-BEN}\Delta_{b-g}G^{ster} + \Delta_{i-BEN}\Delta_{b-g}G^{polar}$ above that corresponding to the expected position along the above series. Subtracting $\Delta_{i-BEN}\Delta_{b-g}G^{ster}$ (~6.2 kJ/mol) from the total displacement ($\Delta_{i-BEN}\Delta_{b-g}G^{ster} + \Delta_{i-BEN}\Delta_{b-g}G^{polar}$) corresponds to $\Delta_{i-BEN}\Delta_{b-g}G^{polar}$ of 5–13 kJ/mol. We suggest that $\Delta_{i-BEN}\Delta_{b-g}G^{polar}$ for B400 is dominated by the π - π EDA force for the triazines. Lastly, Fig. 5 shows that $\Delta_{i-BEN}\Delta_{b-g}G^{ster} + \Delta_{i-BEN}\Delta_{b-g}G^{polar}$ generally declines with increasing sorbed concentration. This reflects a transition to diffusion in progressively larger, less sterically-hindered pores as concentration increases. For heterocyclic compounds that are isosteric with benzene, the concentration dependence means that the graphite surface sites occupied at lower concentration are more electropositive than those occupied at higher concentration.

4. Conclusion

In this study we have examined the adsorption of a series of triazine herbicides and reference compounds on biochars prepared at different temperatures from the same source material. We conclude that adsorption of triazine herbicides is a function primarily of a combination of mesoporosity and microporosity. We also conclude that π - π EDA and steric effects play important roles in adsorption. We provide substantial evidence for these effects. Adsorption of the triazines on B400 is suppressed by about 1.2 $\log_{10}$ units of distribution coefficient relative to benzene. A larger calibration set than we employ here will be required to quantify the contributions of π - π EDA and steric effects for any given porous PCM; moreover, it will be a challenge to merge molecular structure with sorbent physical-chemical properties to predict adsorption in the broader context. Lastly, we find that uptake rates depend inversely on molecular volume, and that the cationic forms of heteroaromatic amines adsorb more slowly than the neutral forms. The latter observation is noteworthy, as it has important implications for fate of ionizable compounds.

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Supplementary data

Figure S1 shows the adsorption of cationic ametryn and terbutryn on graphite under two different solid-to-liquid ratios; Fig. S2, changes in biochar elemental compositions as a function of HTT; Fig. S3, zeta potential of biochars as a function of pH; Figs. S4 and S5, adsorption isotherms of

atrazine and quinoline on a temperature series of biochar; Figs. S6 and S7, adsorption of atrazine and quinoline on biochar as a function of biochar properties; Fig. S8, uptake rate of three organic amines on biochars; Fig. S9, N₂ or CO₂ SA-normalized adsorption isotherms of five triazine herbicides and two reference, planar compounds; Fig. S10, biochar–graphite distribution isotherms on a unit N₂ or CO₂ SA basis; Table S1, fitting parameters of five compounds at two values of C_r for Eq. 5; and Table S2, apparent diffusivities of three compounds on a temperature series of biochar. This material can be found in the online version.

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Table 1. Steric and electronic properties of the test compounds.^a

	V_m (Å ³)	L_s (Å)	L_l (Å)	$E_{p,mid}$ (kJ/mol)
Benzene	94.7	2.79	2.79	-96.0
Naphthalene	144.6	2.81	5.07	-76.8
Pyridine	89.8	2.73	2.81	-57.7
Quinoline	139.7	2.81	5.02	-42.6
1,3-Diazine	85.1	2.67	2.74	11.2
Prometon	252.1	4.78	8.65	-58.4
Atrazine	222.3	4.30	9.31	-28.9
Ametryn	246.9	5.06	9.30	-54.5
Simazine	198.9	4.30	9.29	-27.1
Terbutryn	265.6	5.08	9.18	-53.0

^a V_m : molecular volume estimated by B3LYP density functional calculation on a 6-31G* basis set (Spartan 10, Wavefunction Inc., Irvine, CA); L_s : shortest molecular dimension; L_l : longest molecular dimension. $E_{p,mid}$ value of naphthalene or quinoline was the mean value taken from the midpoint of each ring of the compound.

Figure 1

Fig. 1–Changes in biochar porosities.

Figure 2

Fig. 2—Experimental versus predicted values of the reduced biochar carbon-normalized distribution coefficient $K_{b-C,r}$ by the weighted sum of microporosity and mesoporosity model (Eq. 5).

Figure 3

Fig. 3—Characteristic diffusion rate constants for uptake on different biochars.

Figure 4

Figure 4. Adsorption isotherms (normalized by N₂-accessible surface area) of five triazine herbicides and two hetero-aromatic amines on a biochar (B400) and graphite at pH ~7.4.

Figure 5

Fig. 5—The contribution to total free energy by steric (ster) hindrance and polar interactions calculated by Eq. 9 from biochar (B400)—graphite distribution isotherms on a unit N₂ SA basis (see Fig. S10 in Supplementary data for the isotherms).

Figure 6

Fig. 6—Correlation between the hydrophobicity-normalized distribution coefficient on graphite and $E_{p, \text{mid}}$ (see Table 1). The K_g was calculated at 10 $\mu\text{mol/L}$, with error bar representing the range between 5 and 20 $\mu\text{mol/L}$ solute concentration. Filled symbols represent neutral heteroaromatic amines studied in the current work as well as benzene examined in previous studies (*Lattao et al., 2014, Zhu and Pignatello, 2005*). Open symbols represent substituted benzenes, naphthalene and phenanthrene from previous studies (*Lattao et al., 2014, Zhu and Pignatello, 2005*).