EFFECTS OF SORPTION AND DESORPTION ON BIOAVAILABILITY OF ATRAZINE IN SOILS AMENDED WITH CROP RESIDUE DERIVED CHAR

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THESIS ABSTRACT

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The bioavailability of pesticides in soils is affected by the addition of crop residue-derived char, which alters the sorption and desorption characteristics of the soil. Sorption, desorption and bioavailability experiments were performed using two types of soils (Hartsells and Grady) in the presence and absence of a wheat char (*Triticum aestivum* L.), and char only systems with atrazine as the sorbate. The sorption isotherms for the two soils were linear, suggesting that partitioning into organic matter was the primary sorption mechanism. The isotherms for the 1% char-amended soils showed an increased sorption nonlinearity and sorption capacity. The 1% char amendment to both soils produced similar isotherms, indicating that the presence of a small amount of char may dominate the overall sorption process. The amount of atrazine sorbed by char was 800 – 3800 times greater than that sorbed by the soils alone. The fraction resistant to desorption was 38% in both the Hartsells soil and char-amended Hartsells. The Grady soil showed a slightly less resistant fraction of 33%, which increased to 38% with the addition of char. The resistant fraction in char was 33%. *Pseudomonas* sp. strain ADP, which is capable of utilizing atrazine as its sole nitrogen source, was used in the bioavailability assay. The presence of char in the system reduced the CO_2 production by 11% and 20% in the char amended soils and char, respectively. A desorption-biodegradation-mineralization (DBM) model was used to assess the bioavailability of atrazine in the test systems. The model predicted the sorbed phase bioavailability in soils and soil amended with char systems, but not in char. Multistep kinetic and equilibrium desorption experiments showed that the site fractions varied with atrazine concentration. Hence, a dynamic DBM model incorporating this variation in site fractions with atrazine concentration was developed. The dynamic DBM model confirmed that sorbed phase atrazine was not utilized in char slurries. Further, the results indicate that sorbed atrazine in both the equilibrium and non-equilibrium fractions were bioavailable in soils and soils amended with char, but not in the non-desorbed fraction. This study shows that the presence of char in soil affects the sorption and desorption processes and, ultimately, the bioavailability of atrazine.

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I. LITERATURE REVIEW

Crop residue burning

Soil, the primary geosorbent of the environment, is comprised of minerals and organic matter, which make up the solid phase responsible for the sorption of contaminants. The mineral phase includes primary minerals, such as quartz and feldspar, and secondary minerals, such as clays. The solid phase constituent varies in composition from one soil to another, leading to heterogeneity. Even at a microscopic scale, the soil differs in structure and composition. The heterogeneity is complemented by pyrogenic activities both natural (forest fires) and anthropogenic (crop residue burning), both of which result in high surface area carbonaceous materials (HSACM). These materials alter the sorptive properties of this already complex system and play a vital role in the sorption/desorption processes (Weber et al., 1992). Crutzen and Andreae (1990) reported that out of the estimated 3.9×10^{12} kg/year of global carbon input due to biomass burning, 23% was attributable to the burning of agricultural waste. The carbonaceous matter resulting from the biomass burning and fossil fuel combustion is called black carbon. Based on their parent material, nature of formation and ratios of hydrogen, oxygen and carbon, black carbon can be referred to as either charcoal, char, or soot (Allen-King et al., 2002). This thermally altered carbonaceous matter is resistant to further breakdown. Black carbon is reported to be in the humin fraction of the soil organic matter, constituting about 18.3% to 41% of the total organic carbon in soils and sediments (Song et al., 2002). Black carbon has been found in the atmosphere in the form of soot for a long period of time, and is a major component, representing about 12%-31%, of the organic carbon in deep sea sediments (Allen-King et al., 2002). Crop residue burning is a historically common post harvest practice adopted in many parts of the world for the purpose of clearing land, recycling nutrients, residue disposal, and pest control. This combustive carbonization process produces char, which is primarily composed of high surface area materials such as charcoal. The impact of char from sugarcane trash burns in Hawaiian soils on pesticide sorption was first reported in 1963 by Hilton and Yuen. It has been reported that the burning of crop residues is the major source of black carbon in agricultural soils (Yang and Sheng, 2003a). It was shown that the burning of wheat straw residues would typically result in approximately 0.02% (w/w) of char in agricultural soils (Yang et al., 2006). Burning of rice straw, wheat straw, almond and walnut tree prunings accounts for 95% of biomass burning in California (Jenkins et al., 1996). The char resulting from the burning of kangaroo grass is known to reduce herbicidal efficacy due to its high sorption capacity (Toth et al., 1999). Similarly, Yang et al. (2006) showed that even 0.1% (w/w) of wheat char in soils would result in an appreciable reduction in the bioavailability of diuron in soils. Although the practice of biomass burning brings some positive impacts, such as recycling nutrients, it has been shown that overall the process results in the loss of essential nutrients like nitrogen (Crutzen and Andreae, 1990). One of the major impacts due to biomass burning is the emission of volatile organic compounds and polycyclic aromatic hydrocarbons, which are both toxic and suspected carcinogens (Jenkins et al., 1996).

Factors influencing the properties of char

The properties of the char derived from crop residues depend on the type of crop, dryness of the crop residue and burning conditions. The char derived from rice and wheat differs in both physical and chemical characteristics. The char derived from rice has higher surface area and more elemental silicon, while the char derived from wheat has a lower surface area and higher black carbon content, as shown in Table 1.1 (Yang and Sheng, 2003b). It has even been reported that two varieties of rice straws burned under exactly the same conditions resulted in different PAH emissions (Jenkins et al., 1996). Compared to activated carbon that are derived from wood chars under oxygen limiting conditions, which possess a highly structured pore network, char obtained from crop residues has been reported to contain a lower surface area and more functional groups that contain heteroatoms representing a polar surface. The wheat char was shown to contain 5.4 times more surface functional groups when compared to activated carbon, based on surface area measurements (Chun at al., 2004).

Char formed at high temperatures (500°C -700°C) is well carbonized, with a higher surface area and little organic matter, and the process of adsorption on to the carbonized surface is the dominant sorption mechanism. By comparison, the char formed at low temperatures (300°C-400°C) is only partially carbonized, with a lower surface area and higher organic matter content. It has been observed that as the pyrolysis temperature increases, the percentage of elemental carbon increases and the percentage of oxygen and hydrogen decrease, thereby resulting in increased carbonation (Chun et al., 2004).

The methods adopted for the isolation of char from soils might also affect the char properties. A wet chemical procedure was adopted by Song et al. (2002) to isolate and quantify different fractions of soil organic matter. This method involved sequential acid demineralization to remove minerals and lipids, base extraction for separating humic acid and black carbon and finally dichromate oxidation for separating the char fraction. Recently, Jeong and Werth (2005) assessed the chemical and thermal methods for the isolation of wood char fractions from soils. Their results showed that an acid demineralization treatment (HF/HCl and TFA) produces a char enriched fraction with less alteration to the char mass, but might alter the C/O ratio by up to 25% and could also affect the surface area slightly. Base extraction and dichromate oxidation were likely to result in significant changes in the surface area, C/O ratios and functional group contents, thus altering the sorption properties/mechanisms of the isolated black carbon. Since the properties of char are very much dependant on various factors such as the type of crop, dryness of the crop residues and burning conditions, it is difficult to extend the results obtained from one char to another. Thus, the nature of char and the difficulty in its isolation limit the complete understanding of char's role in agricultural soils.

Pesticides

In the U.S. alone about 1.2 billion pounds of chemicals were used as pesticides in the years 2000 and 2001, accounting for 28% of the world's pesticide usage. A major portion, about 675 million pounds, of this was attributed to agricultural usage (Kiely et al., 2004). Organic pesticides can be broadly classified into ionic and nonionic pesticides. Ionic pesticides are sorbed mainly due to electrostatic attraction to the oppositely charged soil colloids and nonionic pesticides are sorbed mainly due to hydrophobic interaction, hydrogen bonding and van der Waals forces. The major properties of the pesticides that affect the sorption of these compounds to the soil are its functional groups, polarity, and chemical structure. These factors influence the type and nature of binding of the compounds to the sorbent (Novak et al., 1995).

Atrazine, one of the widely used pesticides in the world, was chosen for the study. Its annual agricultural usage in the U.S. alone was 74-80 million pounds of active ingredient accounting for 11-12% of the total pesticides used in agriculture (Kiely et al., 2004). Atrazine has been reported to be present in drinking water sources well above the maximum contaminant level of 3 ppb (Ray, 2003). Some reports speculate that it has a carcinogenic effect in animals, but this has not been proven in humans (USEPA, 2002). The molecular structure of atrazine is shown Fig. 1.1 and some of its properties are listed in Table 1.2. Degradation of atrazine in the environment occurs by both chemical and biological processes (Fig. 1.2).

Sorption and desorption of pesticides

The environmental fate of pesticides is often influenced by its sorption to the soil. Sorption is the process of binding of the solute particles to the sorbent phase and it includes both adsorption and absorption. In adsorption, the solute accumulation is restricted to the sorbent surface or an interface between the solvent and the sorbent. The sorbents may be clay minerals, iron or aluminum oxides or hydroxides, soil organic matter (humic substances) or other carbonaceous matter (Alexander, 1999). Adsorption is further classified into physical, chemical and electrostatic adsorption (Weber et al., 1991). Physical adsorption includes the class of adsorption processes that result due to the dipole moments between the sorbate and the sorbent molecule. These can either be induced dipole-dipole interactions or instantaneous dipole interactions resulting in London dispersion forces. Chemical adsorption, also often referred to as chemisorption, includes adsorption between the sorbate and sorbent molecules either due to covalent bonding or hydrogen bonding. Large molecules are retained on the surface of the clay due to hydrogen bonding. Electrostatic adsorption results due to ion-ion interaction between the sorbate and the sorbent molecules. In ion exchange, low molecular weight compounds in solution are exchanged for an ion of another type from the sorbent.

Absorption/partition involves the dissolution of the solute molecules from one phase to the other, based on its relative affinity to each phase. In absorption the solute molecules interpenetrate the sorbent at least a few nanometers, so the sorbate lies within the physical matrix of the sorbent (Weber et al., 1991). The absorption mechanism is mainly attributed to the sorption of hydrophobic compounds onto the organic fraction of the soil and the process is entropy driven. The absorption coefficient is directly related to the octanol/water partition coefficient of the sorbate compound and the organic fraction of the soil (Chiou et al., 1979). In some cases, the sorbate molecules and the organic matter of the sorbent form covalent linkages, resulting in a complex natural humic substance (Alexander, 1999).

Desorption

Desorption of a sorbed pesticide plays a vital role in controlling its biodegradability (Zhang et al., 2004). Once the aqueous phase chemical has been utilized by the microbes, the rate of mineralization may be controlled by the desorption rate. It has been observed in soils and other natural sorbents that the sorption-desorption process is not completely reversible. The equilibrium desorption of the chemical often indicates that a portion of the sorbed compound has not been desorbed, even at zero aqueous phase concentration and repeated solvent extraction (Barriuso et al., 2004). The desorption equilibrium isotherms are often different from the sorption equilibrium isotherms, indicating non singularity (Pignatello, 1989). True hysteresis has been reported to exist in those sorbents, and this is not an experimental artifact (Sander et al., 2005).

Sorption of neutral organic compounds

The sorption of neutral/nonionic organic compounds (NOC) to soil constituents is of primary importance because many environmental pollutants are NOC or behave like NOC in the environment. The sorption of NOC to soil has been found to be linear even at high relative concentrations. In addition, an inverse relationship has been observed between the solubility and the partition or distribution coefficient of the sorbate to the soil. This led Chiou et al. (1979) to conclude that sorption of NOC to soil was similar to dissolution/partitioning of compounds to organic solvents. When the partition coefficient (K_p) was normalized to the soil organic carbon content (f_{oc}), similar values were obtained for a specific sorbate immaterial of soil organic matter composition and this could be represented by K_{oc} (Karickhoff, 1981). Moreover, Karickhoff determined the correlation between solubility of the chemicals, its K_{oc}, and its octanol water partition coefficient using a range of pesticides and soils/sediments.

The sorption of NOC to natural geosorbents was found to be linear in many cases, although sorption nonlinearity in atrazine has been reported at relatively low concentrations in a soil organic matter (SOM) rich sorbent (Xing et al., 1996). These authors hypothesized the soil organic matter to be a two phase system consisting of a rubbery phase and a glassy phase. The sorption to the former involves a partitioning process and the latter a hole filling process, leading to a dual-mode mechanism by SOM. However, the presence of charcoal like high surface area carbonaceous material (HSACM) in soil has also been identified (Karapanagioti et al., 2000; Kleineidam et al., 1999). Chiou and Kile (1998) proposed that the presence of these high surface area carbonaceous materials might also explain the observed nonlinearity in the sorption of NOC at relatively low concentrations (Chiou et al., 2000).

Sorption isotherms

The relationship between equilibrium aqueous phase concentration and the corresponding sorbed phase concentration is given by the sorption isotherm, which aids in understanding the sorption mechanism. The linear relationship between the sorbed phase and the aqueous phase concentration indicates the process of absorption or dissolution of solute to the soil organic matter. This is given by the following equation.

$$S = K_d C_e$$

where S is the equilibrium sorbed phase concentration (mg/Kg), K_d is the partition or distribution coefficient (L/Kg), and C_e is the equilibrium aqueous phase concentration (mg/L). The nonlinear relationship between the sorbed concentration and the aqueous concentration can be explained using the following semi-empirical Freundlich equation.

$$S = K_f C_e^n$$

where S is the sorbed phase concentration (mg/Kg), K_f is the Freundlich sorption coefficient (mg/Kg / $(\text{mg/L})^n$), C_e is the equilibrium aqueous phase concentration (mg/L) and n is the Freundlich exponent.

The Langmuir model is used to explain the process of adsorption on to sorbents, wherein sorbate was assumed to form a monolayer on a sorbent surface consisting sites of equal energy. The Langmuir model is given as follows:

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e}$$

where q_e is the sorbed concentration (mg/Kg), $Q_{\max}$ is the Langmuir adsorption capacity (mg/Kg), b is the Langmuir affinity coefficient (L/mg) and C_e is the aqueous concentration (mg/L).

The sorption equilibrium in activated carbon type sorbents is well described by the Polanyi-Dubinin-Manes (PDM) model, where the mechanistic processes involved in the sorbate filling the micro or meso pores of the sorbent is considered. The PDM model is described by the following equation (Kleineidam et al., 2002):

$$C_s = V_o \rho_o \exp\left[-RT \frac{(-\ln \frac{C_w}{S})}{E} \right]^b$$

where C_s is the sorbed concentration (mg/Kg), V_0 is the maximum volume of sorbed chemical per unit mass of sorbent (cm^3/Kg), ρ_o is the density of the compound (Kg/cm^3), R is the ideal gas constant (J/mol/K), T is the temperature (K), C_w is the aqueous phase equilibrium concentration (mg/L), S is the aqueous solubility of the compound (mg/L), E is the characteristic free energy of adsorption of a compound when compared to a reference compound (KJ/mol) and b is an exponent representing the pore size distribution.

Combined sorption models

Sorption models representing both adsorption and absorption must be used to fully explain the aqueous and sorbed phase relationship, since natural sorbents are highly heterogeneous and both these processes are believed to be operating in the soil environment. Two models commonly used are the combined model (PDM and linear model) and the dual-mode model. The combined model incorporates both the Polanyi and Manes model and the linear model, signifying pore filling and partitioning processes, respectively. Grathwohl and Rahman (2002) and Kleineidam et al. (2002) used a solubility normalized combined sorption model for analyzing the sorption of several organic contaminants to sediments and activated charcoal. It is represented as follows (Kleineidam et al., 2002):

$$C_s = V_o \rho_o \exp\left[-RT \frac{(-\ln \frac{C_w}{S})}{E} \right]^b + f_{ocp} K_p C_w$$

where C_s is the sorbed concentration (mg/Kg), V_0 is the maximum volume of sorbed chemical per unit mass of sorbent (cm^3/Kg), ρ_o is the density of the compound (Kg/cm^3), R is the ideal gas constant (J/mol/K), T is the temperature (K), C_w is the aqueous phase equilibrium concentration (mg/L), S is the aqueous solubility of the compound (mg/L), E is the characteristic free energy of adsorption of a compound when compared to a reference compound (KJ/mol), exponent b represents the pore size distribution, f_{ocp} is the fraction of organic carbon available for partitioning and K_p is the partitioning coefficient (L/Kg).

The dual-mode model combines the linear partitioning model and Langmuir model, signifying the processes of absorption and adsorption, respectively. The adsorption to the holes in the glassy phase of soil organic matter is represented by the Langmuir model, whereas the linear model represents the partitioning process. The dual-mode model is represented as follows (Zhao et al., 2001):

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e} + K_p C_e$$

where q_e is the sorbed concentration (mg/Kg), Q_{max} is the Langmuir adsorption capacity (mg/Kg), b is the Langmuir affinity coefficient (L/mg), C_e is the aqueous concentration (mg/L) and K_p is the partitioning coefficient (L/Kg).

Xia and Ball (1999) performed sorption experiments using nine low polarity organic chemicals and Dover aquitard material. Both the dual-mode model and combined model were useful in explaining the sorption processes. It was hypothesized that the adsorption involved the process of pore filling of the microporous HSACM in the sediments by the NOC. Similarly, Accardi-Dey and Gschwend (2003) explained the sorption of phenanthrene using a combined model that represents organic matter partitioning and adsorption to black carbon by linear model and Freundlich equation, respectively.

Sorption and desorption of atrazine

Atrazine can be sorbed by both specific and non specific interactions with the sorbent. These interactions include, but are not limited to, hydrophobic interaction, hydrogen bonding and van der Waals attraction. Atrazine is sorbed by both the soil organic matter and clay (Koskinen and Rochette, 1996; Park et al., 2003). The primary sorption mechanism of non-ionic organic chemicals such as atrazine to soil organic matter is through partitioning or dissolution of the chemical to the organic phase of the solid sorbent. Atrazine has a K_{oc} range of 39-155 L/Kg (Roberts, 1998). The distribution coefficient of atrazine was highly correlated to the fraction of organic carbon and there is no significant correlation between atrazine sorption and other important soil properties (e.g., cation exchange capacity) and constituents (e.g., iron, aluminum and manganese oxides) (Gerritse et al., 1996; Payaperez et al., 1992). It was reported that the sorption of atrazine to soil organic matter could occur through both physical and chemical processes, but physical sorption is the primary mechanism by which atrazine sorbs to silicate clays (Laird et al., 1994). Armstrong and Chesters (1968) showed that when the pH of the system is around 4.5, chemical hydrolysis of atrazine to hydroxy atrazine results wherein the sorption of atrazine to carboxyl or phenolic group of the sorbent occurs by means of hydrogen bonding between protonated groups and the ring nitrogen of the atrazine. Sorption to montmorillonite could occur through van der Waals attraction, hydrogen bonding or coulombic attraction between the atrazine ring nitrogen atoms and the highly dissociated water at the clay surface.

Atrazine desorption in soils and other sorbents was reported to be hysteretic in nature and desorption of atrazine was shown to decrease with an increase in the soil organic matter. Also, the non-desorbed fraction varied between 9% and 51% in different soils (Park at al., 2003). Ma et al. (1993) showed that desorption of atrazine was dependent on both incubation time and concentration. Their experiments in Sharkey soil exhibited a higher Freundlich desorption K_f and lower n than the sorption K_f and n. The soil showed high non-desorbed fractions for lower initial concentrations. In their experiments at an initial atrazine concentration of 4.1 mg/L, the sorption K_f and n were 3.9 cm^3/g and 0.877, respectively. The desorption K_f varied from 4.4 cm^3/g to 5.181 cm^3/g and n varied from 0.607 to 0.232 for zero and twenty four days incubation, respectively. Selim and Zhu (2005) reported that the average desorption percentage after six successive desorption steps followed by methanol extraction was 67%, but a higher non-desorbed fraction was observed for the lowest initial concentration in sugarcane mulch residue. They noted that the atrazine recovered by solvent (methanol) extraction is potentially desorbable.

Sorption of chemicals to char

An early study by Manes and Hofer (1969) reported that adsorption by charcoals occurs by London forces, which is nonspecific and hence weak. Yang and Sheng (2003a) reported that char effectively sorbed about 400 – 2500 times more diuron than a silty loam soil with a maximum sorption capacity of 6962 mg/Kg. The sorption isotherms indicated increasing nonlinearity as the percentage of char amendment increased. A 1% char amendment to soils in a diuron sorption system resulted in a Freundlich n value of 0.403, whereas in soil it was 0.689. Yang and Sheng indicated that the black carbon from wheat char was primarily responsible for the high sorptivity of diuron. The adsorption of a chemical to the surface of the char is dependent on the surface functional groups on the char. The surface acidity/basicity of the char is related to the affinity of the adsorbate, since a polar solute (nitro-benzene) is more highly adsorbed than a non-polar solute (benzene) (Chun et al., 2004). The polar functional groups on the char are hydrophilic and affect the sorption of non-polar molecules (Chun et al., 2004; Yang et al., 2004). Wheat residue derived char has been reported to be involved in the protonation/deprotonation of the surface functional group with respect to pH, affecting the adsorption of diuron and bromoxynil and ametryne (Yang et al., 2004). The possible sorption mechanisms in black carbon may be (1) van der Waals interactions that include dispersive interactions between the sorbate and the black carbon systems and dipole-dipole interactions and (2) steric effects due to the separation distance between the sorbate and the black carbon nanopore surface. The strength of sorption might be related to the ability to attain near planar conformation (Cornelissen et al., 2005).

Bioavailability of pesticides

Bioavailability is the ease with which a chemical is available to microorganisms for degradation. It represents the accessibility of a chemical for assimilation as well as its possible toxicity (Alexander, 2000). Bioavailability is one of the key factors controlling the bioremediation of contaminated soils or sediments (Feng et al., 2000). Bioavailability of a compound is often influenced by the sorption mechanism and desorption rate (Novak et al., 1995; Alexander, 1999). Sorption of chemicals can alter both the substrate and nutrient availability. The strength of sorption influences the desorption of the solute, which is an important criterion affecting bioavailability. In addition to dissolved chemicals, sorbed substrates may be utilized by the bacteria (Guerin and Boyd, 1997; Feng et al., 2000; Park et al., 2003).

The microbial characteristics that influence the bioavailability include the enzymes secreted by the microbes, the affinity of the bacteria towards substrates and the bio-surfactants produced. The extra cellular enzyme secreted by the microbes may facilitate the degradation of the target compounds. Bacteria with high substrate affinity may have a competitive edge in acquiring the sorbed substrate. Some microbes are capable of producing bio-surfactants that enhance desorption of the sorbed chemical, thereby increasing its bioavailability (Alexander, 1999).

Differential bioavailability of naphthalene to two microbes was reported by Guerin and Boyd (1992), who found that the *Pseudomonas* sp. strain 17484 could access the sorbed phase chemical but not the other organism. In another study, a naphthalene degrading bacterium was able to degrade soil-sorbed naphthalene but unable to degrade the naphthalene when it was sorbed to granulated activated carbon (Guerin and Boyd, 1997). This suggests that the sorption mechanisms of naphthalene to the two different sorbents might also control the bioavailability of the compound. Microorganisms can also act on the sorbed compound directly, by adhering to the surface. The study by Calvillo and Alexander (1996) showed a higher mineralization rate of biphenyl sorbed in polyacrylic beads when compared to the desorption rate. They concluded that desorption of the sorbed compound was not a prerequisite for biodegradation, as supported by the lack of surfactants, indicating possible sorbed phase chemical utilization by the microbes. Feng et al. (2000) used a coupled desorption/biodegradation model to assess the bioavailability of sorbed biphenyl and showed that sorbed biphenyl was bioavailable for both the organisms studied. Recently, Vacca et al. (2005) showed direct sorbed phase utilization of phenanthrene in humic acids.

Bioavailability of pesticides in char systems

It has been observed that the mineralization of benzonitrile was lower in soils amended with char when compared to soil systems. It was reasoned that the sorption of the solute to char amended soil was higher and stronger than its sorption to soil alone. Also, desorption of the sorbed pesticide was reported to be slower and the bacteria showed an increased acclimation period when char was present in the soil (Zhang et al., 2004). The presence of char in the system altered the degradation pattern in soils and it was shown that the mineralization was more strongly affected by the sorption of the chemical to char than by either the pH or the initial concentration of the chemical (Zhang et al., 2006). The same group found that the addition of char to soils might also provide nutrients that would result in increased microbial activity (Zhang et al., 2005). The presence of even a very small amount of char (0.1%) was found to influence the bioavailability of pesticides in the environment, merely due to its high sorption capacity (Yang et al., 2006). The reduced biodegradation in char amended systems may result in higher residual pesticide levels, thus leading to higher application rates of pesticides.

Predictive models for bioavailability

Experimental designs to assess the mineralization of sorbed compounds directly are quite challenging, as the degradation of the aqueous substrate, desorption and the direct uptake of sorbed chemicals occur simultaneously (Calvillo and Alexander, 1996).

The rate and extent of these processes can be the same or different. Therefore, mathematical models are useful tools for assessing the bioavailability of sorbed compounds. Ogram et al. (1985) modeled 2,4-dichlorophenoxy acetic acid mineralization in slurry systems and concluded that the assumption of sorbate mineralization in aqueous phase alone, by both aqueous and attached cells, could describe the experimental data. Those models did not consider the process of desorption in predicting the bioavailability, although this was incorporated in later bioavailability models (Feng et al., 2000). The sorption kinetics of numerous sorbate-sorbent systems indicate that the sorption process is biphasic, with an initial rapid rate phase followed by a slow phase. A two compartment/site box model was proposed by Karickhoff (1980) based on the rate of sorption/desorption. In the model, one of the sites exhibits a rapid sorption/desorption phase and the other site represents a slow sorption/desorption phase. Van Genuchten and Wagenet (1989) developed a two site/two region model for predicting pesticide transport by incorporating physical non-equilibrium represented by an immobile region and a chemical non-equilibrium represented by one of the two sites. Ma and Selim (2005) used a second-order two-site model, with one site as equilibrium and the other as kinetic, to predict atrazine transport in soils amended with sugarcane mulch reside. A three site model was developed by Park et al. (2001) incorporating a non-desorbed fraction into the two site model, which was then used to predict sorbed phase naphthalene and atrazine bioavailability (Park et al., 2003) in soil slurries. This model was composed of three different types of sites: equilibrium, non-equilibrium and non-desorption sites. The equilibrium sites represent the rapid phase, while the non-equilibrium site represents the time dependent desorption phase, as described in the two site model. The sorbate in the non-desorbed fraction was not expected to desorb within the experimental desorption time period. In terms of the chemical fractionation, Selim and Zhu (2005) considered all the water extractable atrazine to be readily desorbable, methanol extractable atrazine as less readily desorbable, and the fraction remaining after methanol extraction as non-desorbable atrazine.

Application of the 3-site model to assess sorbed phase bioavailability

One way to assess the bioavailability of sorbed chemicals is by modeling the processes of sorption and desorption and extending those processes to the bioassay systems to check for sorbed chemical utilization. Feng et al. (2000) assessed the bioavailability of sorbed biphenyl using a coupled desorption/biodegradation model. In their study the mineralization of sorbed biphenyl by two bacteria in four different soils was assessed by predicting the mineralization for two limiting conditions, i.e., as if desorption in slurries was instantaneous and there was no desorption. Biphenyl mineralization in slurries was found to be higher than the mineralization predicted by the instantaneous desorption model, indicating sorbed chemical utilization by the bacteria. The three site model developed by Park et al. (2001) was tested for four scenarios, starting with only aqueous phase mineralization and then including the mineralization of sorbed naphthalene at three fitted mineralization rates, corresponding to each type of site. The model predictions showed that mineralization of naphthalene is only possible through the utilization of sorbed phase chemical, since the experimental mineralization was higher than could be explained by abiotic desorption in all four of the soils studied. The three site model was extended to the assessment of sorbed phase bioaccessibility of atrazine in 6 different soils by three atrazine degrading bacteria. In eleven out of the eighteen cases examined, mineralization of aqueous phase atrazine was able to explain the experimental CO_2 production in the slurries. For highly sorptive soils and bacteria exhibiting chemotaxis towards atrazine enhanced bioavailability was observed, which indicated direct sorbed atrazine utilization by the bacteria (Park et al., 2003).

Table 1.1 Carbon and silicon contents and specific surface areas (SSA) of char samples (Yang and Sheng, 2003b)

Char sample	Carbonate C (%)	Total C (%)	BC[a] (%)	Elemental Si (%)	SSA (m^2/g)
Rice char	0.37	6.02	5.65	32.9	16.54
Wheat char	1.41	14.33	12.92	19.5	10.05
Light fraction of wheat char	0.93	26.40	25.47	16.6	6.74
Heavy fraction of wheat char	1.61	9.19	7.58	20.7	5.73
Carbon fraction of wheat char	<0.02	76.40	76.40	1.39	408.30

[a] Calculated as the difference between total C and carbonate C.

Table 1.2 Selected properties of atrazine (Xing et al., 1996; USEPA 2002; Roberts, 1998)

Generic Name	2-chloro-4-ethylamino-6-isopropylamino -1,3,5-triazine
Molecular Formula	$C_8H_{14}N_5Cl$
Molecular weight	215.69 g/mol
pK_a	1.7
log K_{ow}	2.3-2.7
K_{oc}	39 – 155
Water solubility (20-25°C)	33 mg/L
Vapour pressure (25°C)	0.039 mPa
Melting point	171-174°C
Density (20°C)	1.19 g/mL
Appearance	Colorless/white crystalline solid
Maximum application rate	4 lb a.i./ac
Mode of action	Absorbed by roots and leaves; acts as a photosynthetic inhibitor
Degradation in soils	Both microbial and chemical (Fig. 1.2)
Maximum contaminant level	3 µg/L
% Agricultural usage in the U.S.	11 – 12 %

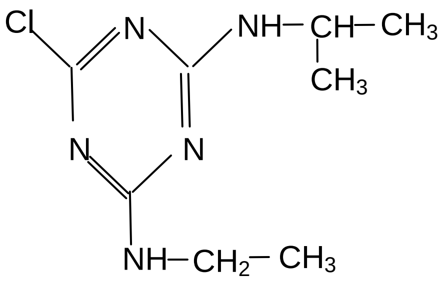

Fig. 1.1 Molecular structure of atrazine.

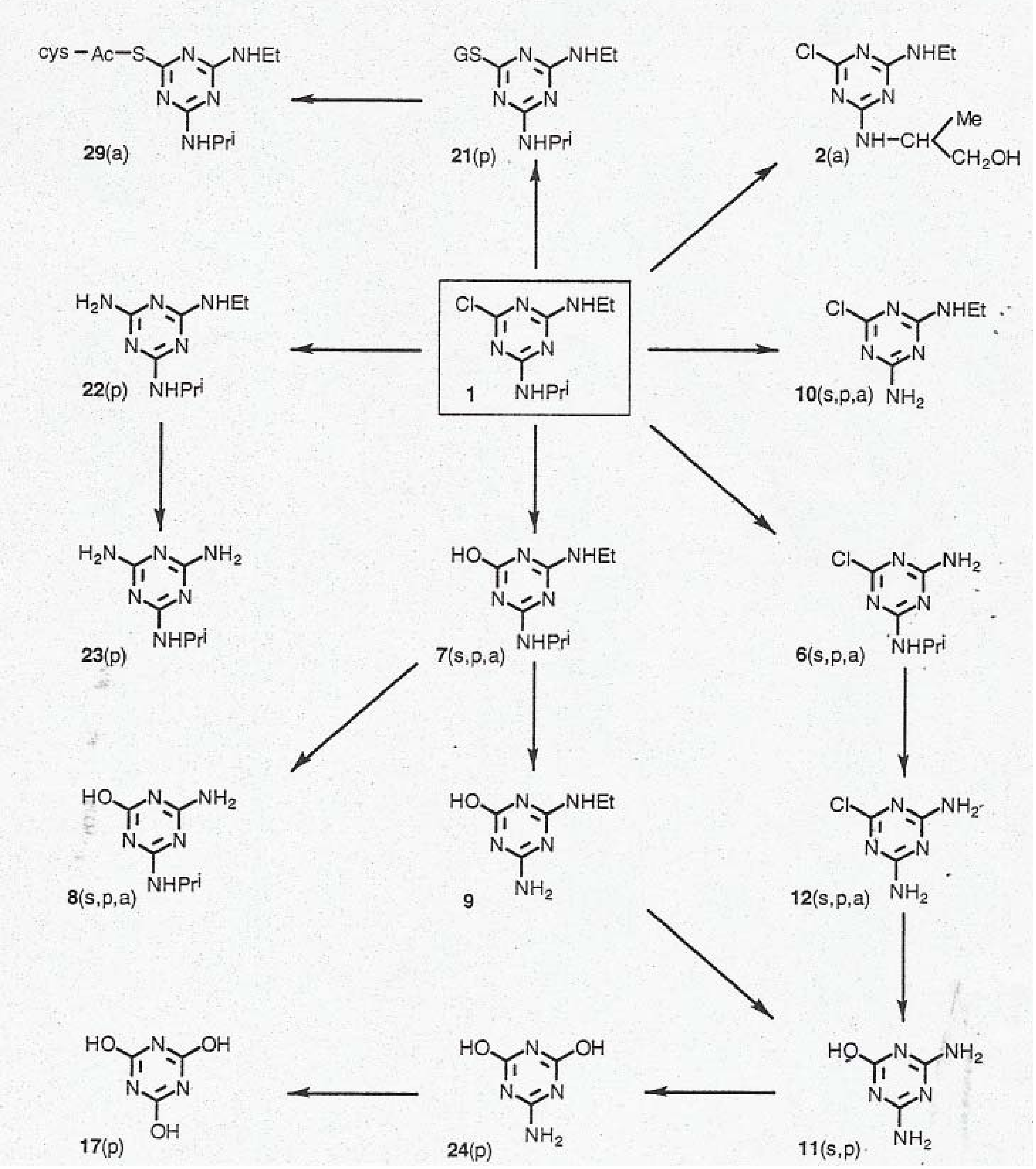

Fig. 1.2 Degradation and metabolism of atrazine in soils (s), plants (p) and animals (a)

Source: Roberts, 1998.

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II. BIOAVAILABILITY OF ATRAZINE IN SOILS AMENDED WITH CROP RESIDUE DERIVED CHAR

INTRODUCTION

Sorption and biodegradation are two important processes that govern the environmental fate of pesticides. Sorption of chemicals to soils is a complex process due to the highly heterogeneous nature of soils. Anthropogenic activities like crop residue burning produce incompletely combusted residues that add to the natural heterogeneity of agricultural soils. Crutzen and Andreae (1990) reported that out of the estimated 3.9 x 10^{12} Kg/year of global carbon input due to biomass burning, 23% can be attributed to the burning of agricultural wastes. The carbonaceous matter formed through biomass burning and fossil fuel combustion is often referred to as black carbon, which includes charcoal, char, and soot. Here, char refers to a form of black carbon derived from crop residue burning.

Crop residue burning is a historically common post harvest practice adopted in many parts of the world for the purpose of clearing land, recycling nutrients, residue disposal and pest control. The process results in char due to combustive carbonization that contains high surface area material like charcoal. It is reported that the burning of crop residues is the major source of black carbon in agricultural soils (Yang and Sheng, 2003a). Black carbon was reported to be in the humin fraction of the soil organic matter

(SOM), and constituted about 18.3% to 41% of the total organic carbon in the soils/sediments (Song et al., 2002). Burning of rice straw, wheat straw, almond and walnut tree prunings constituted about 95% of the biomass burning in California (Jenkins et al., 1996). Char serves as an effective sorbent in the soil even when present in very small quantities. The impact of char from sugarcane trash burns in Hawaiian soils on pesticide sorption was first reported in 1963 by Hilton and Yuen. Char from the burning of kangaroo grass is known to reduce the herbicidal efficacy due to its high sorption capacity (Toth et al., 1999). Yang et al. (2006) showed by a simple calculation that the burning of wheat straw residues would result in approximately 0.02% (w/w) of char in agricultural soils. Skjemstad et al. (1996) showed that the charcoal carbon from woody material was highly protected in Australian soils and constituted about 0.32% to 0.83% (w/w) of the soil. The isolation of char from soils without altering its surface properties is difficult to achieve (Song et al., 2002; Jeong and Werth, 2005). Hence, Yang and Sheng (2003a, 2003b) studied the sorptive properties of crop residue derived char, using the wheat char collected from the burning of wheat straw in open atmosphere.

The sorption isotherms of neutral/nonionic organic compounds (NOC) to natural geosorbents are often found to be linear. Xing et al. (1996), however, reported sorption nonlinearities of atrazine at relatively low concentrations in organic matter rich soil. They hypothesized that the soil organic matter acted as a two phase system consisting of a rubbery and a glassy phase. The sorption to the former involves a partitioning process and the latter a hole filling process, leading to a dual-mode mechanism. Chiou and Kile (1998), however, proposed that the presence of high surface area carbonaceous material might also lead to this observed nonlinearity in the sorption of NOC at low concentrations. The presence of charcoal like high surface area carbonaceous materials (HSACM) in soils has been identified (Karapanagioti et al., 2000; Kleineidam et al., 1999) and is thought to be responsible for the nonlinearity in sorption isotherm (Chiou et al., 2000). Yang and Sheng (2003b) reported that char sorbed about 400 – 2500 times more diuron than a silty loam soil over a concentration range of 0-6 mg/L. The sorption isotherms indicated increasing nonlinearity as the percentage of char amendment increased. They reported that the black carbon component of wheat char was primarily responsible for the high sorptivity of diuron. The surface acidity/basicity of the char is also known to affect the adsorption of chemicals (Chun et al., 2004). Protonation/deprotonation of the surface functional groups at different pH was observed in wheat residue derived char, which influenced the adsorption of ionic pesticides in soils (Yang et al., 2004).

The presence of char in soil affects not only sorption but also the biodegradation of organic chemicals. It has been observed that the mineralization of benzonitrile was lower in soils amended with char when compared to soil systems with no char (Zhang et al., 2004). The reasons given were that the sorption of the solute to char amended soil was higher and stronger than its sorption to soil alone. In addition, desorption of sorbed pesticide was reported to be slower and the bacteria showed an increased acclimation period when char was present in the soil (Zhang et al., 2004). The presence of char in the system also altered the degradation pattern in soils. It was shown that the sorption of benzonitrile to char governed mineralization more than either pH or the initial substrate concentration (Zhang et al., 2006).

Atrazine is one of the most widely used herbicides in the U.S., with an annual usage of 76 million pounds (Kiely et al., 2004). The environmental fate of atrazine in both soil and aquatic environments has been well characterized. However, little is known regarding how the presence of char influences the environmental fate of atrazine. The objectives of this work were therefore to study the sorption and desorption characteristics of atrazine in soils, soils amended with char, and char, and to assess the bioavailability of atrazine in these systems.

MATERIALS AND METHODS

Chemical

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) (98% purity) was obtained from Chem Service, Inc. (West Chester, PA) and used as received. U-^{14}C-labeled atrazine (Sigma-Aldrich, MO) with a specific activity of 15.1 mCi/mmol and radiochemical purity of $\geq$ 95% was purchased from Sigma-Aldrich Corp. (St. Louis, MO).

Sorbents and sorbent extracts

Two soils, Hartsells (HS) and Grady (GY) that differ in organic content and mineralogy, were used in this study (Table 2.1). The Hartsells soil (Fine-loamy, siliceous, thermic Hapludults) is classified as a sandy loam soil, whereas the Grady soil (Fine, kaolinitic, thermic Paleaquults) is a clay loam. Dried wheat straw residues were burned on a stainless steel plate (1 m x 1 m) in the open atmosphere and the resulting wheat char was collected. Figure 2.1 shows images of the char under a light microscope and a scanning electron microscope. The particle size of the char varied from a few micrometers to a few millimeters. In an earlier study, the char used here was reported to have an elemental composition of 12.9% elemental C, 1.4% carbonate C, 19.5% silica, 20.9% K and 3.4% Ca. Its pH and specific surface area were 10.2 and 10.1 m^2/g, respectively (Zhang et al., 2004).The sorbents used in the experiments include soil, soil amended with 1% char, and char alone. Sorbents used in the bioavailability assays were gamma irradiated (~ 5 Mrad) using a ^{60}Co source and checked for sterility prior to use.

In the experiments involving sorbent extracts, appropriate sorbents were mixed with 20 mM phosphate buffer (pH 7.0) at the same solid solution ratio used in the experiments (1:10 for soils, soils amended with char, and 1:1000 for char) for 48 hours at room temperature and centrifuged at 8000 rpm (RCF ~ 3000 g) for 15 minutes. The supernatant was filtered through two layers of Whatman 2v filter paper and the extract was collected. Sorbent extracts used in desorption experiments contained 150 mg/L of sodium azide.

Organism

Pseudomonas sp. strain ADP, kindly provided by Dr. Larry Wackett of the University of Minnesota, was used in the study. This is a Gram negative motile rod capable of utilizing atrazine as a sole nitrogen source and has the ability to mineralize atrazine (Mandelbaum et al., 1995).

Batch sorption experiments

Batch equilibrium sorption experiments were performed using two soils (Hartsells and Grady), soils amended with 1% char, and char. After a preliminary sorption study with soils amended with 0.05, 0.5 and 1.0% (w/w) of char, 1% char amendment was chosen due to the ease of detecting discernable differences between sorption in the soils and the soils amended with char. It also made it possible to accurately weigh small amounts of char (0.02 g). Soil and 1% (w/w) char were mixed at 12 rpm for at least 24 hours before performing sorption experiments. All the experiments were performed at room temperature ($22 \pm 2^{\circ}$ C). Sorption was initiated by mixing the sorbents (2 g of soil, 2 g of soil + 0.02 g of char, or 0.02 g of char) with 20 mL of 20 mM phosphate buffer (pH 7) containing various atrazine concentrations in 30 mL glass centrifuge tubes with Teflon-lined screw caps. The atrazine concentrations ranged from 0.1 mg/L to 4 mg/L and were well below the solubility limit (33 mg/L). About 1 kBq of ^{14}C-labelled atrazine was added to the sorption tubes. In all abiotic experiments performed, 150 mg/L of sodium azide was included to inhibit microbial growth. The sorption tubes were tumbled in the dark at 12 rpm for 48 hours to attain equilibrium. Then the tubes were centrifuged at 8000 rpm (RCF ~ 3000 g) for 15 minutes and 1 mL of the supernatant was sampled in duplicate and analyzed using a Beckman LS-6500 liquid scintillation counter (LSC). In the case of char, after centrifugation the char samples were filtered through glass wool packed in Pasteur pipettes to trap the fine char particles remaining in suspension prior to LSC analysis. The sorption tubes were prepared in duplicate and the average results were reported. The amount of sorbed atrazine was calculated from the difference between the initial and the equilibrium aqueous phase concentrations. Control sorption tubes without the sorbent were also included to check for atrazine losses.

Equilibrium desorption experiments

The batch equilibrium desorption experiments were performed using sorption tubes containing an initial atrazine concentration of 4 mg/L. The above mentioned batch sorption procedure was used, followed by removal of different volumes of the supernatant (from 2 mL to 16 mL) and replacing the same volume with appropriate sorbent extracts. The sorption tubes were then tumbled at 12 rpm for 48 hours and sampled in duplicates and analyzed using LSC. In the case of char, after centrifugation the char samples were again filtered through glass wool packed in Pasteur pipettes to trap fine char particles remaining in suspension prior to LSC analysis.

Multistep equilibrium desorption experiments

Multistep equilibrium desorption experiments involved the equilibration of sorbents with an initial atrazine concentration of 2 mg/L and approximately 5 kBq of ^{14}C-atrazine in triplicate. Following centrifugation and sampling, 16 mL of the supernatant was decanted and replaced with the same volume of sorbent extract to initiate desorption. The centrifuge tubes were tumbled at 12 rpm and samples in duplicate were collected after 48 hours and analysed using LSC. The desorption step was repeated five times for soils and char-amended soils, and eleven times for char.

Kinetic desorption experiments

Kinetic desorption experiments involved the equilibration of sorption tubes with an initial atrazine concentration of 2 mg/L and approximately 3 kBq of ^{14}C-atrazine in triplicate. Following centrifugation and sampling, 16 mL of the supernatant was decanted and replaced with sorbent extract to initiate desorption. The centrifuge tubes were tumbled and samples were collected at regular time intervals. In the case of char, sorption and subsequent desorption were performed by sacrificing discrete sorption tubes in duplicate at specific time periods. After centrifugation, the char samples were filtered through packed glass wool to trap the fine char particles in suspension prior to analysis.

A separate kinetic desorption experiment in char involved replacement of the 16 mL of the decanted supernatant with phosphate buffer instead of char extract. The decanted aqueous phase was filtered using 0.2 µm Anodisc 25 membrane filter and the char collected on the filter was washed back into the sorption tubes before initiating desorption.

Multistep kinetic desorption experiments followed by solvent extraction

Multistep kinetic desorption experiments were performed in soil and char-amended soil systems. The sorption tubes were equilibrated with an initial concentration of 2 mg/L and approximately 7 kBq of ^{14}C-atrazine. Following centrifugation and sampling, 16 mL of the supernatant was decanted and replaced with the same volume of sorbent extract to initiate desorption. The centrifuge tubes were tumbled and an aliquot of 0.5 mL was sampled at regular time intervals for 48 hours. A second desorption cycle was initiated by a similar fill-and-draw method as performed before, where16 mL of the supernatant was replaced with the appropriate sorbent extract and the samples were collected at the same time intervals as the first desorption cycle for a further 48 hours.

Methanol extraction was performed after the second desorption cycle. First, 16 mL of phosphate buffer was used to replace the supernatant and the centrifuge tubes were tumbled for 2 hours. This was followed by centrifugation, decantation of supernatant, and replacement with 20 mL of 4:1 (v/v) methanol: phosphate buffer. After 4 hours of methanol/buffer extraction, the tubes were centrifuged and sampled. The methanol/buffer extraction was then repeated second time.

Bioavailability assays

To perform bioavailability assays, *Pseudomonas* sp. strain ADP was grown on mineral salt agar plates containing atrazine (Park et al., 2003). After 48 hours, the cells were transferred to a liquid medium and shaken at 200 rpm in the dark at room temperature. At regular time intervals, cell growth was monitored by measuring the optical density at 600 nm. Sorbent extract controls and sorbent (gamma irradiated) slurries were set up in 160-mL serum bottles at the same solid to solution ratio as used in the sorption and desorption experiments. Atrazine at an initial concentration of 2 mg/L and a radioactivity level of 7.5 kBq was added to the serum bottles and equilibrated. After 24 hours, the slurries and the controls were inoculated with 0.75 mL of cell suspension in phosphate buffer to achieve a final concentration of approximately 7×10^7 CFU/mL. At precise time intervals, 1 mL of headspace gas and 1 mL of suspension were withdrawn and injected into sealed tubes containing 1 mL of 2 M HCl. The radioactive CO_2 that evolved was trapped onto 2 M NaOH saturated filter paper strips hanging from a sleeve stopper in the center well. After overnight equilibration, the filter paper strips were transferred to scintillation vials. The center wells were rinsed with 1 mL of 50% (v/v) ethanol that was then combined with scintillation fluid. The samples were left in the dark for at least 24 hours and analyzed using LSC.

DBM model

To assess the bioavailability of sorbed atrazine, the Desorption-Biodegradation-Mineralization model (DBM) developed by Park et al. (2001) was used. The model incorporates sequential desorption, biodegradation and mineralization kinetics by conceptualizing the sorbent into three distinct sites: equilibrium, non-equilibrium and non-desorption sites. The model assumes: (1) sorption equilibrium can be described by a nonlinear isotherm (i.e., Freundlich); (2) the rate of release of the compounds from non-equilibrium sites is proportional to the concentration gradient between these sites and the liquid phase; (3) there is no time lag between biodegradation and mineralization; (4) the desorption parameters developed in the abiotic experiments are valid in the bioavailability assays; (5) the biodegradation and mineralization rates for attached cells to sorbents are the same as those of the suspended cells; (6) the biodegradation and mineralization rate parameters evaluated from soil-free solutions are the same as those in soil slurry solutions and (7) the suspended and attached cells can only utilize liquid phase chemicals (Park et al., 2003).

a. Equilibrium site model

The equilibrium sites are assumed to follow the nonlinear Freundlich equation of the form:

$$S_{eq} = f_{eq}.\ K_f.\ C^n \tag{1}$$

where S_{eq} is the sorbed concentration in the solid equilibrium sites (mg/Kg), f_{eq} is equilibrium site fraction, K_f is the Freundlich sorption coefficient (mg/Kg / (mg/L)^n), C is the liquid phase concentration (mg/L) and n is the Freundlich exponent.

b. Non-equilibrium site model

The following mass transfer model was used to describe the time dependent release of contaminants from non-equilibrium sites based on the concentration gradient between the aqueous and solid phases:

$$\frac{dS_{neq}}{dt} = \alpha\,(f_{neq}.K_f C^n - S_{neq}) \tag{2}$$

where S_{neq} is the sorbed concentration in the solid non-equilibrium sites (mg/Kg), α is the first order desorption rate coefficient for non-equilibrium sites (min^{-1}), f_{neq} is the non-equilibrium site fraction, K_f is the Freundlich sorption coefficient (mg/Kg / (mg/L)^n), C is the liquid phase concentration (mg/L), n is the Freundlich exponent, and t is the desorption time (min). It should be noted that as α approaches infinity, equation (2) will be reduced to equation (1).

c. Non-desorption site model

The non-desorption sites are defined as those sites that contain sorbate that cannot be released to aqueous solution during the experimental desorption period. This is described by the following expression:

$$S_{nd} = f_{nd}.K_f.C_e^n \tag{3}$$

where S_{nd} is the sorbed concentration in the solid non-desorption sites (mg/Kg), f_{nd} is the non-desorption site fraction, K_f is the Freundlich sorption coefficient (mg/Kg / (mg/L)^n), C_e is the liquid phase concentration at sorption equilibrium (mg/L), and n is the Freundlich exponent.

d. Mass balance equations

The overall mass balance for a batch system that involves sorption, biodegradation, and mineralization can be written as:

$$-\left(V_l \frac{dC}{dt} + W_s.\frac{dS}{dt}\right) = V_l.R_{bio} \tag{4}$$

$$\frac{dP_{co_2}}{dt} = Y_{co_2} R_{bio} \tag{5}$$

and $$R_{bio} = k_1. C \tag{6}$$

where V_l is the volume of the liquid (L), C is the liquid phase concentration (mg/L), W_s is the weight of the soil (Kg), S is the sorbed phase concentration (mg/Kg), Pco_2 is the CO_2 concentration (mg/L), Yco_2 is the yield coefficient (mg of CO_2 released per mg of atrazine, %). R_{bio} represents the first order liquid phase degradation rate expression (mg/L/min) where k_1 is the first order rate constant (min^{-1}).

Numerical solution to the DBM

The numerical solution to the DBM was obtained by the Euler method and programmed using Matlab (The MathWorks, Inc., MA, USA).

The biodegradation model equation (4), can be written in finite form as,

$$-\left(V_l \frac{\Delta C}{\Delta t} + W_s . \frac{\Delta S}{\Delta t} \right) = V_l . R_{bio} \tag{7}$$

Since, $S = S_{eq} + S_{neq} + S_{nd}$

$$\Delta S = \Delta S_{eq} + \Delta S_{neq} + \Delta S_{nd}$$

Therefore,

$$\frac{\Delta S}{\Delta t} = \frac{\Delta S_{eq} + \Delta S_{neq} + \Delta S_{nd}}{\Delta t}$$

where,

$$\frac{\Delta S_{eq}}{\Delta t} = f_{eq}\, K_f\, n\, C^{n-1} \frac{\Delta C}{\Delta t}$$

$$\frac{\Delta S_{neq}}{\Delta t} = \alpha (f_{neq} . K_f C^n - S_{neq})$$

Since non-desorption sites are defined as those sites that cannot release sorbate during the experimental desorption period,

$$\frac{\Delta S_{nd}}{\Delta t} = 0$$

Therefore,

$$\frac{\Delta S}{\Delta t} = f_{eq}\, K_f\, n\, C^{n-1} \frac{\Delta C}{\Delta t} + \alpha (f_{neq} . K_f C^n - S_{neq}) \tag{8}$$

substituting (8) in equation (7),

$$-\left(V_l \frac{\Delta C}{\Delta t} + W_s . (\frac{f_{eq} K_f n C^{n-1} \Delta C}{\Delta t} + \alpha (f_{neq} K_f C^n - S_{neq})) \right) = V_l . R_{bio}$$

Substituting first order degradation in the above equation,

$$-\left(V_l\frac{\Delta C}{\Delta t}+W_s.\frac{f_{eq}K_f nC^{n-1}\Delta C}{\Delta t}+\alpha W_s(f_{neq}K_f C^n-S_{neq})\right)=V_l.K_1C$$

and rearranging the above equation gives,

$$\frac{\Delta C}{\Delta t}=\frac{(V_lK_1C+\alpha\ W_s f_{neq}K_f C^n-\alpha W_s S_{neq})}{-V_l-W_s f_{eq}K_f nC^{n-1}} \qquad (9)$$

The mineralization equation (5) can be written in finite form as,

$$\frac{\Delta P_{co_2}}{\Delta t}=Y_{co_2}K_1C$$

For first order kinetics,

$$\Delta P_{co_2}=Y_{co_2}K_1C.\Delta t \qquad (10)$$

Equations (9) and (10) were then solved simultaneously to compute the changes in aqueous phase concentrations over a small interval Δt.

Estimation of site parameters for DBM

The site parameters for the DBM (f_{eq}, f_{neq}, f_{nd} and α) were estimated by fitting the kinetic desorption profiles using one of the built-in functions of the graphical tool in SigmaPlot ($y= y_0 + a(1-\exp(-bt))$), where y_0, a, and b represent f_{eq}, f_{neq}, and alpha, respectively. The non-desorbed (f_{nd}) fraction was calculated using the constraint $f_{eq}+f_{neq}+f_{nd} = 1$.

RESULTS AND DISCUSSION

Sorption

The sorption isotherms for the two soils were highly linear (Fig. 2.2a and 2.2c) within the tested concentration range, suggesting that partitioning into the organic matter was indeed the primary sorption mechanism. The Freundlich parameters for Hartsells and Grady soils (Table 2.2) indicate that the sorption capacity of the Grady soil was slightly higher than that of the Hartsells soil, which can be attributed to the higher organic matter content of the Grady soil. The log K_{oc} of the Hartsells and Grady soils were 2.0 and 1.9, respectively. These values were within the log K_{oc} range reported for atrazine, i.e., 1.6 to 2.2, calculated from the partition coefficient (Roberts, 1998). The isotherms for the char-amended soils showed increased sorption capacity and nonlinearity, as indicated by the Freundlich K_f and n, respectively (Table 2.2). The 1% char amendment in both soils produced similar isotherms, indicating that the presence of a small amount of char in the soils dominated their overall sorption process (Fig. 2.2b and 2.2d). The amount of atrazine sorbed by char (Fig. 2.3) was 800 – 3800 times more when compared with the soils over a concentration range of 0.1-4 mg/L. Sorption experiments were performed over a wider concentration range in char to reveal information on the sorption at higher concentrations. The data were fitted with Langmuir, Freundlich, and dual-mode models (Fig. 2.4) and the parameters are reported in Table 2.3. The dual-mode model fit the sorption data better for the entire concentration range, however, other models cannot be considered to be less descriptive based on the correlation coefficients (Table 2.3). Although the dual-mode model was formulated to explain the polymer based theory of SOM, consisting of rubbery and glassy phases (Xing et al., 1996), a similar phenomenon is speculated to be operative in the char systems. The wheat char obtained by Chun et al. (2004) at 300°C showed partial carbonization, as indicated by a higher molar H/C ratio. Since the char used in the present study was obtained by burning wheat straw in an open atmosphere, a similar carbonization is expected. Additionally, open-air burning is likely to produce a combination of light and heavy fractions with highly and partially carbonized residues resulting in adsorption and absorption, respectively, which could best be explained with a dual-mode mechanism.

Assuming the sorption of atrazine to soil is the same in both the char-amended soil system and the soil system, the data suggest that the atrazine sorption to char in the char-amended system was less than the atrazine sorption to char in the char alone system. This may be explained by the competitive sorption between atrazine and dissolved soil organic matter. To understand the competitive sorption process, soil extract was used instead of phosphate buffer in the char sorption experiments. At an initial concentration of 2 mg/L, char sorbed approximately 70% of the atrazine in phosphate buffer, whereas the char with soil extract sorbed only 36% of the atrazine. The latter was similar to the results found for atrazine sorption by soil amended with char systems, which was around 41% of the atrazine added. This indicates that the sorption of atrazine by char was suppressed even in the presence of soil extracts. A similar phenomenon has also been reported in the sorption of benzonitrile by char, where it was attributed to competitive sorption between the solute and dissolved soil organic molecules to char (Zhang et al., 2004).

Desorption

The equilibrium desorption experiments indicate higher hysteresis in the Hartsells soil than the Grady soil (Figs. 2.2a and 2.2c, and Table 2.2). It has been reported that the sorption of atrazine to soil organic matter may involve both weak physical sorption and strong chemisorption; the latter would result in a higher hysteretic effect (Ma et al., 1993). Desorption of atrazine from fine grained soils showed less hysteresis than a coarse grained soil because the organic matter associated with the coarse clay was reported to have a higher affinity for atrazine (Laird et al., 1994). Hysteresis was observed in both soils amended with char (Figs. 2.2b and 2.2d) but not in char alone systems (Fig 2.3). Instead, in the char system the equilibrium concentration of atrazine after desorption stayed below the corresponding sorption equilibrium concentration when char extract was used to replace the decanted aqueous phase to initiate desorption. The black carbon fraction of the wheat char is reported to have a zero point charge of 4.2, above which it possesses a negatively charged surface (Yang et al., 2004). Anions present in the aqueous phase will therefore not be electrostatically favorable for adsorption onto char surfaces above pH 4.2. As our experimental conditions were at a neutral pH, the aforementioned phenomenon was not expected to occur, since the char surface should carry negative charges and atrazine should be in its molecular form. It is possible that dissolved chemicals in the char extract interfered with atrazine desorption. The results of a sorption experiment performed with atrazine in char extract instead of phosphate buffer showed some reduction in char sorption. These chemicals could be dissolved polycyclic aromatic hydrocarbons, which have been found in wood char (Rey-Salgueiro et al., 2004). Also, Martin-Neto et al. (2001) observed that there was less sorption of atrazine in peat samples at a pH greater than six, due to the blockage of sorption sites by water molecules.

The kinetic desorption plots (Fig. 2.5) show that about 38% of the sorbed atrazine was non-desorbed in the Hartsells soil and Hartsells amended with char (Table 2.4) in the first desorption cycle. Grady soil showed 33% of non-desorbed fraction, which increased to 38% in char amended Grady. Char alone showed a non-desorbed fraction of 33%. The desorption rate coefficients in the first desorption cycle were higher in the Hartsells soil than the Grady soil as it is inversely related to distribution coefficient. This phenomenon was also reported by Brusseau and Rao (1989). The addition of char to the soils decreased the desorption rate coefficient, but char alone showed a higher desorption rate coefficient than the soils. The order of desorption rate coefficients was char > soils > soils amended with char in the first desorption cycle. This contrasts with the finding of Zhang et al. (2004) who reported that the desorption rate of benzonitrile was slower in char than in a silty loam soil.

Multistep kinetic desorption followed by solvent extraction

A second desorption was performed at the end of the first desorption cycle in soils and soils amended with char systems (Fig. 2.6a and 2.6b), and was followed by two methanol extractions. The second desorption profiles were also fitted using the DBM model (Fig. 2.6c and 2.6d) and the site parameters are given in Table 2.4. Compared to the site fractions from the first desorption, the non-desorbed fractions in the second desorption increased in all systems and the sums of the equilibrium and non-equilibrium fractions decreased. The desorption rate coefficients also decreased in both soils and char-amended soils for the second desorption. This shows the concentration dependence of these site parameters.

The percentages of atrazine remaining after each desorption step and the extraction are shown in Fig. 2.7 and Table 2.5. The atrazine remaining in the Hartsells soil was higher than in the Grady soil after each step, and this trend was more pronounced after the methanol extraction. The first methanol extraction released approximately 10% and 36% of the total sorbed amount in both soils and soils amended with char, respectively. Only small increases were observed between the first and second methanol extractions in all the systems. Pignatello (1989) showed that the solvent extraction of chemicals could be correlated to the bioavailability of the compound for microorganisms. The fraction of atrazine that resisted solvent extraction in the soils equilibrated with atrazine was shown to be the non bioavailable fraction in an incubation study (Barriuso et al., 2004).

Multistep equilibrium desorption

The multistep kinetic desorption experiments indicated some variation in the site parameters with the sorbed phase concentration. Hence, a multistep equilibrium desorption experiment that would portray the relationship between the equilibrium aqueous concentration and the non-desorbed fraction (f_{nd}) was performed in soil, soil amended with char and char alone systems at an initial atrazine concentration of 2 mg/L. The results were plotted, along with their respective sorption isotherms and tabulated (Table 2.6). In both soils (Fig. 2.8a and 2.8c) after five successive desorption the aqueous phase concentration was nearly zero, which was not the case in either of the char-amended soils (Fig. 2.8b and 2.8d). When char was present in the soils, it required several more desorption steps for the aqueous concentration to reach zero compared to the soil alone systems. In the case of char alone (Fig. 2.9a), even after eleven desorption steps using phosphate buffer, about 560 mg/Kg of atrazine was still sorbed, indicating the very high sorption capacity of char and its strength. In all the systems, the non-desorbed fraction after the final desorption was similar to that of the non-extracted fraction after the first methanol extraction (Table 2.5). Fig 2.9b shows the multistep equilibrium desorption when char extract was used to replace the decanted supernatant. The desorption data points stayed below the sorption data points. This was not observed when phosphate buffer replaced the aqueous phase (Fig. 2.9c).

Bioavailability assays

The mineralization rate (k_l) and extent (P_{max}) of sorbent free controls in each system did not vary much with the initial atrazine concentration (Table 2.7). $^{14}CO_2$ production in the char extract was 79%, whereas in the Hartsells and Grady extracts it was 72% and 68%, respectively (Fig. 2.10a and 2.10b). The maximum $^{14}CO_2$ production observed in the soil slurries was around 70% for the Hartsells soil and 65% for the Grady soil (Table 2.8 and Fig. 2.10c and 2.10d). The $^{14}CO_2$ produced in the char-amended soils and char systems was 11% and 20% lower, respectively, when compared to soil slurries. This may be due to the increased sorption of atrazine to the solid phase in char containing systems.

DBM model results

(a) Estimation of site parameters using the DBM model

The site fractions are the key parameters for DBM and other similar compartment models (Karickhoff, 1980; Van Genuchten and Wagenet, 1989) that are used to predict desorption and biodegradation processes. The expected equilibrium of the total mass of atrazine in the system after decantation (including both the residual aqueous and sorbed atrazine) was used to normalize the fraction desorbed. The schematic for the parameter estimation for a typical sorption-desorption relationship observed in sorbents at an initial concentration of 2 mg/L is shown in Fig. 2.11. Sorption sites on the sorbents are divided into three site fractions based on their atrazine desorption characteristics: equilibrium (f_{eq}), non-equilibrium (f_{neq}) and non-desorption (f_{nd}) sites. The equilibrium sites represent the rapidly desorbing phase in the sorbent. The non-equilibrium sites represent the time dependent desorption fraction. The non-desorbed fraction is regarded as the irreversible fraction, wherein the sorbate at this site is not expected to desorb within the experimental desorption period (Park et al., 2003). The fitted lines for the desorption kinetics of soils, soils amended with char, and char are shown in Fig. 2.5. When the desorption kinetic in char was initiated with char extract, the fraction desorbed from char was higher than would be expected based on the sorption isotherm (Fig 2.3). Hence, the desorption kinetic experiments in char were performed using phosphate buffer instead of char extract. The order of the estimated non-desorbed fraction was, Hartsells ~ Hartsells amended with char > char. For the Grady soil, the order was Grady amended with char > Grady > char. Selim and Zhu (2005) considered the water extractable atrazine to be readily desorbable, the methanol extractable atrazine as less readily desorbable and the fraction that remained after methanol extraction as non-desorbed atrazine. The non-desorbed fraction represents the true hysteresis fraction, where the sorbate is bound to the sorbent (Pignatello, 1989).

(b) Model results for bioavailability assays

The results of the DBM model are shown in Fig. 2.12. Overlapping of the DBM predicted line with the experimental data indicates mineralization of the aqueous phase chemicals. The prediction line falling below the experimental data indicates mineralization higher than would be expected from aqueous substrate utilization alone, and hence the substrate in the sorbed phase is considered to be bioavailable. The prediction line falling above the experimental data indicates that mineralization is somehow inhibited. The results of the DBM indicate enhanced bioavailability in the case of soils (Fig. 2.12a and 2.12c) and soils amended with char (Fig. 2.12b and 2.12d). The DBM predicted line in char followed the experimental data precisely, indicating that only aqueous phase atrazine was bioavailable (Fig. 2.12e). The mass balance for the DBM shows the change in aqueous atrazine (cmass), sorbed atrazine (smass), aqueous atrazine biodegraded (biodeg), and sum of all the above (total mass) with respect to time (Fig. 2.13). Note that the difference between the total mass of atrazine and the mass of atrazine that was mineralized was equal to the sum of the aqueous mass of atrazine and the sorbed mass of atrazine at any point in time, indicating the mass balance of the system.

Development of dynamic-DBM model

The multistep experiments (both kinetic and equilibrium desorption) showed that the site fractions were dynamic as they vary with aqueous atrazine concentrations. The variation in the non-desorbed site fraction in various sorbents estimated from the multistep equilibrium desorption experiments is shown in Fig. 2.14. The non-desorbed fraction was related to the sorption desorption hysteresis, which was concentration dependent. It has been shown that the irreversible fraction responsible for hysteresis is dependent on sorbent-sorbate combination, concentration and time (Sander et al., 2005). Park et al. (2001) confirmed the constancy of the non-desorbed fraction with respect to concentration, using a series dilution experiment before using DBM model to assess the bioavailability of naphthalene. Ma et al. (1993) examined the concentration dependence of atrazine desorption in a Sharkey soil, especially at low concentrations. To represent the site fractions that were likely to vary with respect to concentration, dynamic non-desorbed site fractions were calculated from the multistep equilibrium desorption experiments. The site fractions were then fitted with a Freundlich type equation with an intercept (Fig. 2.14 and Table 2.9). Since less variation was observed in the non-equilibrium site fraction (f_{neq}) from the multistep kinetic desorption, f_{neq} was assumed to be constant (Table 2.4). Thus, a dynamic equilibrium and non-desorbed site fractions that vary with concentration could be obtained. Park et al. (2004) showed that the change in non-equilibrium site fractions over a period of one month was less than 6% for atrazine in five out of six soils, while the other fractions varied by as much as 46%. The desorption rate coefficients obtained from the first desorption cycle can be chosen, although they decrease with concentration in all systems. The higher desorption rate resulted only in a higher aqueous phase concentration, and hence the model result is more conservative with regard to the prediction of sorbed atrazine degradation.

a) Numerical formulation of the dynamic DBM model

In the dynamic fractions method the relationship extracted between f_{nd} and aqueous concentration was fitted using an empirical equation similar to the Freundlich equation with an intercept as follows:

$$f_{nd}=f_{nd0} + aC^{b} \tag{11}$$

where f_{nd} is the non-desorbed site fraction at aqueous concentration C, f_{nd0} represents the non desorbed site fractions at zero aqueous concentration, and a, b are fitting parameters.

The change in aqueous phase concentration with respect to time in the dynamic-DBM model is given by incorporating the change in sorbed phase concentration using the above relationship.

$$\frac{\Delta S}{\Delta t} = \frac{\Delta S_{eq} + \Delta S_{neq} + \Delta S_{nd}}{\Delta t}$$

where,

$$\frac{\Delta S_{eq}}{\Delta t} = f_{eq}\, K_f\, n\, C^{n-1}\, \frac{\Delta C}{\Delta t} + \frac{\Delta f_{eq}}{\Delta t}\, K_f\, C^{n}$$

$$\frac{\Delta S_{neq}}{\Delta t} = \alpha(f_{neq}.K_f C^{n} - S_{neq})$$

$$\frac{\Delta S_{nd}}{\Delta t} = f_{nd}\, K_f\, n\, C^{n-1}\, \frac{\Delta C}{\Delta t} + \frac{\Delta f_{nd}}{\Delta t}\, K_f\, C^{n}$$

Therefore,

$$\frac{\Delta S}{\Delta t} = f_{eq}\, K_f\, n\, C^{n-1}\, \frac{\Delta C}{\Delta t} + \alpha(f_{neq}.K_f C^{n} - S_{neq}) + f_{nd}\, K_f\, n\, C^{n-1}\, \frac{\Delta C}{\Delta t} + \frac{\Delta f_{nd}}{\Delta t}\, K_f\, C^{n} \tag{12}$$

Substituting (10) in the mass balance equation (7), with the condition that $f_{eq}+f_{neq}+f_{nd} = 1$, where f_{neq} is assumed to be a constant,

$$\frac{\Delta f_{eq}}{\Delta t} = \frac{-\Delta f_{nd}}{\Delta t}$$

Hence

$$\Delta C = \frac{(V_l K_1 C + \alpha \ W_s f_{neq} K_f C^n - \alpha W_s S_{neq}).\Delta t}{-V_l - W_s \ f_{eq} K_f \ nC^{n-1} - f_{nd} W_s K_f \ nC^{n-1}}$$

Using $f_{eq}+f_{nd} = 1- f_{neq}$, gives the final form for the change in aqueous phase concentration in the DBM model with dynamic fractions.

$$\Delta C = \frac{(V_l K_1 C + \alpha \ W_s f_{neq} K_f C^n - \alpha W_s S_{neq}).\Delta t}{-V_l - (1 - f_{neq}) W_s K_f \ nC^{n-1}} \tag{13}$$

b) Dynamic DBM Model Results

The model results are shown in Fig. 2.15. In the Hartsells soil (Fig. 2.15a), the DBM prediction was less than the experimental data for the initial 200 minutes of the incubation period, indicating sorbed atrazine availability only during that initial time period. A similar pattern was observed in the Hartsells amended with char (Fig. 2.15b). For the Grady soil (Fig. 2.15c) and Grady soil amended with char (Fig. 2.15d), sorbed phase utilization was observed for the initial 300 minutes. In char alone, sorbed atrazine was not bioavailable, as indicated by the prediction line falling either on or above the experimental data (Fig. 2.15e).

The dynamic-DBM was also checked for mass balance (Fig. 2.16). The variation in the site fractions with respect to aqueous concentration, along with the dynamic DBM prediction line and experimental data is shown in Fig. 2.17. In the Hartsells soil and Hartsells amended with char (Fig. 2.17a and 2.17b) the sorbed phase atrazine was bioavailable until the equilibrium site fractions reached approximately zero (~200 min), after which no sorbed phase utilization was observed. In the Grady soil, the equilibrium site fraction was approximately zero (~ 350 min), after which bioavailability of sorbed atrazine was not observed. In the soil amended with char systems, predicted mineralization showed sorbed phase bioavailability for some initial time period, after which the prediction line falls below the experimental data even though the mass balance plots (Fig. 2.16b and 2.16d) indicate the availability of aqueous atrazine. This can also be seen in the char system (Fig. 2.18e).

These results indicate that the sorbed phase chemical at both equilibrium sites and non-equilibrium sites in soils might be accessible for microbial degradation before desorption and the chemicals in the non-desorbed fraction might not be bioavailable. Since the atrazine sorbed by char out competed dissolved organic molecules in char-amended soils, the strength of atrazine sorbed to char in this system must have been high. It is also observed that soils amended with char showed less non-desorbed fraction (~ 0.7) when compared to soils (~0.9) at lower concentrations. Further experiments to evaluate the variation in desorption rate coefficients with respect to concentration that can be incorporated that into the dynamic DBM will aid in our understanding of sorbed chemical bioavailability in these systems. The present dynamic DBM can serve as a limiting condition that indicates the maximum mineralization possible from the aqueous atrazine. The experimental data above the dynamic-DBM prediction line indicates mineralization due to factors other than the aqueous phase mineralization, which can be regarded as direct uptake or sorbed substrate bioavailability.

CONCLUSIONS

Char clearly affects the sorption, desorption, and biodegradation processes of atrazine in soils. The sorption data showed that the addition of char to soils increased both the sorption capacity and nonlinearity. These results reaffirm that pesticide fate transport models that predict the fate of pesticides using the K_{oc} of the chemical alone may not be adequate (Wauchope et al., 2002). The kinetic desorption results of this study indicate that the desorption rate coefficient of atrazine in char to be higher than both the soils alone and the char-amended soils. Sorption due to black carbon and its effect on bioavailability should therefore be considered when characterizing the sorption of soils in agricultural systems where crop residue burning is practiced. The experimental results of the multistep equilibrium desorption indicate that the presence of char increased the desorption fractions in soils amended with char. However, overall mineralization was reduced due to the presence of char in the system. The DBM model with modified parameters suggested that only aqueous phase chemicals would be available for mineralization in char slurries, but sorbed phase utilization prevailed in soils and soils amended with char. The non-extracted fraction after methanol extraction was found to be similar to that of the non-desorbed fraction at close to zero aqueous concentration from a multistep equilibrium desorption experiment.

The multistep desorption experiments indicated large variations in site parameters with respect to concentration in all systems except char. The DBM model was modified to incorporate the dynamic parameters and the results suggest that only sorbed chemicals at equilibrium and non-equilibrium sites might be bioavailable in soils before desorption, and not those at the non-desorbed sites. The model confirmed that sorbed phase atrazine was not bioavailable in char systems. The bioavailability of a chemical can be considered as a competitive process between sorption and bacterial degradation. As the concentration decreases, the strength of sorption is expected to be high as indicated by the increase in the non-desorbed site fraction, which might limit the bioavailability of atrazine.

The higher sorption capacity of char will result in higher application rates of pesticides, which are likely to have a negative impact on the environment. The presence of even a very small amount of char was found to reduce the bioavailability of pesticides in the soil, which could be mainly attributed to its high sorption capacity. This study demonstrated that the presence of char in the system would limit the bioavailability of atrazine in agricultural soils and hence management of crop residues by methods other than field burning should be considered.

Table 2.1 Selected soil characteristics

	Hartsells	**Grady**
Organic Carbon, %	1.29	2.12
pH	5.3[a]	5.7
Texture	Sandy loam	Clay loam
Sand, %	59.1	24.7
Silt , %	32.1	42.8
Clay, %	8.78	32.5
Mineralogy (% of clay)		
Kaolinite	60	45
Hydroxy-interlayered vermiculite	15	35
Quartz	15	10
Mica	5	

[a] Source: Park et al. (2003).

Table 2.2 Freundlich sorption and desorption isotherm parameters

Sorbent	**Sorption Parameters**			**Desorption Parameters**		
	K_f	**n**	**r^2**	**K_f**	**n**	**r^2**
Hartsells (HS)	1.49	0.96	0.9974	2.96	0.45	0.9740
HS + 1% Char	7.51	0.72	0.9947	9.79	0.40	0.9351
Grady (GY)	1.92	0.88	0.9896	2.53	0.77	0.9331
GY + 1% Char	8.19	0.73	0.9968	10.48	0.46	0.9779
Char	2012	0.51	0.9526	1768	0.40	0.9605

K_f represents the Freundlich sorption coefficient in $(mg/Kg)/(mg/L)^n$ and n represents the Freundlich exponent.

Table 2.3 Sorption parameters of atrazine by char using various models

Model	**Parameter**	**Estimate**	**r^2**
Dual mode parameters	Q_{max}	2385	0.9966
	b	3.78	
	K_p	194	
Langmuir parameters	Q_{max}	3848	0.9903
	b	1.30	
Freundlich parameters	K_f	1901	0.9842
	n	0.39	

Q_{max} is the Langmuir adsorption sorption capacity in mg/Kg; b is the Langmuir affinity coefficient in L/mg; K_p is the partitioning coefficient in L/Kg.

Table 2.4 Estimated desorption site parameters from the kinetic desorption profiles

Sorbent	**Alpha (α, min^{-1})**	**Equilibrium (f_{eq})**	**Non-equilibrium (f_{neq})**	**Non-desorption (f_{nd})**	**r^2**
Desorption I					
Hartsells	0.0154	0.4326	0.1819	0.3855	0.9238
HS + 1% Char	0.0061	0.2310	0.3865	0.3825	0.9627
Grady	0.0089	0.5022	0.1668	0.331	0.9670
GY + 1% Char	0.0079	0.2594	0.3518	0.3888	0.9623
Char	0.0326	0.4628	0.2082	0.3290	0.8453
Desorption II					
Hartsells	0.0029	0.1955	0.1480	0.6565	0.9562
HS + 1 % Char	0.0034	0.1437	0.4031	0.4532	0.9782
Grady	0.0039	0.2899	0.1318	0.5783	0.9099
GY + 1% Char	0.0047	0.1953	0.2885	0.5162	0.9561

Alpha (α) is the first order desorption rate coefficient of non-equilibrium sites.

Table 2.5 Percentages of atrazine remaining after a series of extraction steps

Extractant used – step	Hartsells	Grady	HS + 1 % char	GY + 1% char
Sorbent extract – I	56.63	55.08	73.31	73.09
Sorbent extract –II	40.73	38.68	55.71	57.33
Phosphate buffer	37.02	33.49	51.92	52.88
Methanol –I	27.05	22.55	15.97	16.12
Methanol –II	26.27	21.63	12.60	13.31
Non-desorbed fraction[*]	30.80	21.68	16.48	16.56

[*] From multistep equilibrium desorption

Table 2.6 Freundlich sorption and desorption parameters estimated from multistep desorption experiments

	Sorption Parameters			**Desorption Parameters**		
Sorbent	$\mathbf{K_f}$	**n**	$\mathbf{r^2}$	$\mathbf{K_f}$	**n**	$\mathbf{r^2}$
Hartsells	1.47	0.95	0.9991	2.08	0.24	0.9226
HS + 1% Char	7.66	0.75	0.9990	7.74	0.37	0.9842
Grady	1.85	0.94	0.9990	2.48	0.32	0.9332
GY + 1% Char	8.14	0.74	0.9995	8.38	0.39	0.9890
Char	1893.2	0.46	0.9943	1157.4	0.46	0.9647

K_f and n represent the Freundlich sorption coefficient in (mg/Kg)/(mg/L)^n and curvature constant, respectively.

Table 2.7 Biokinetic parameters in sorbent extract controls at different initial atrazine concentrations

		Hartsells			**Grady**		
Sorbent Extract	**Initial concentration (mg/L)**	**Pmax %**	**k_l (min^{-1})**	**r^2**	**Pmax %**	**k_l (min^{-1})**	**r^2**
Soil	2.152	72.41	0.0159	0.9981	67.82	0.0110	0.9979
	1.096	72.10	0.0171	0.9987	67.24	0.0112	0.9974
	0.568	71.90	0.0162	0.9980	66.06	0.0113	0.9986
Soil + 1% Char	2.152	74.95	0.0135	0.9977	71.27	0.0076	0.9971
	1.096	74.99	0.0144	0.9964	72.47	0.0070	0.9971
	0.568	73.76	0.0143	0.9973	71.86	0.0074	0.9970
Char	2.152	79.14	0.0164	0.9977	77.53	0.0086	0.9984
	1.096	81.08	0.0150	0.9930	78.65	0.0080	0.9986
	0.568	80.01	0.0144	0.9978	79.36	0.0083	0.9967

Pmax is the maximum CO_2 yield (maximum percentage of initial atrazine mineralized as CO_2); k_l represents the first order mineralization rate constant for aqueous phase.

Table 2.8 Biokinetic parameters of sorbent extracts and slurries

	Extract controls			**Slurries**		
Sorbent	**Pmax %**	**k_l (min^{-1})**	**r^2**	**Pmax %**	**k (min^{-1})**	**r^2**
Hartsells	72.41	0.0159	0.9981	69.58	0.0225	0.9995
HS + 1% Char	74.95	0.0135	0.9977	57.61	0.0159	0.9995
Grady	67.82	0.0110	0.9979	65.46	0.0126	0.9994
GY + 1% Char	71.27	0.0076	0.9971	54.39	0.0084	0.9972
Char	79.14	0.0164	0.9977	48.65	0.0059	0.9991

Pmax is the maximum CO_2 yield (maximum percentage of initial atrazine mineralized as CO_2); k represents the first order mineralization rate constant.

Table 2.9 Regression parameters from multistep desorption equilibrium experiments for estimating dynamic non-desorbed fraction

Sorbent	Intercept	-a	b	r^2
Hartsells	1.07	0.54	0.37	0.9961
HS + 1% char	0.87	0.63	0.51	0.9814
Grady	1.09	0.68	0.34	0.9945
GY + 1% char	0.95	0.72	0.39	0.9787
Char	0.46	0.18	0.65	0.8606

The intercept represents the fitted non-desorbed fraction at zero aqueous concentration (fnd_0), a and b are fitting parameters.

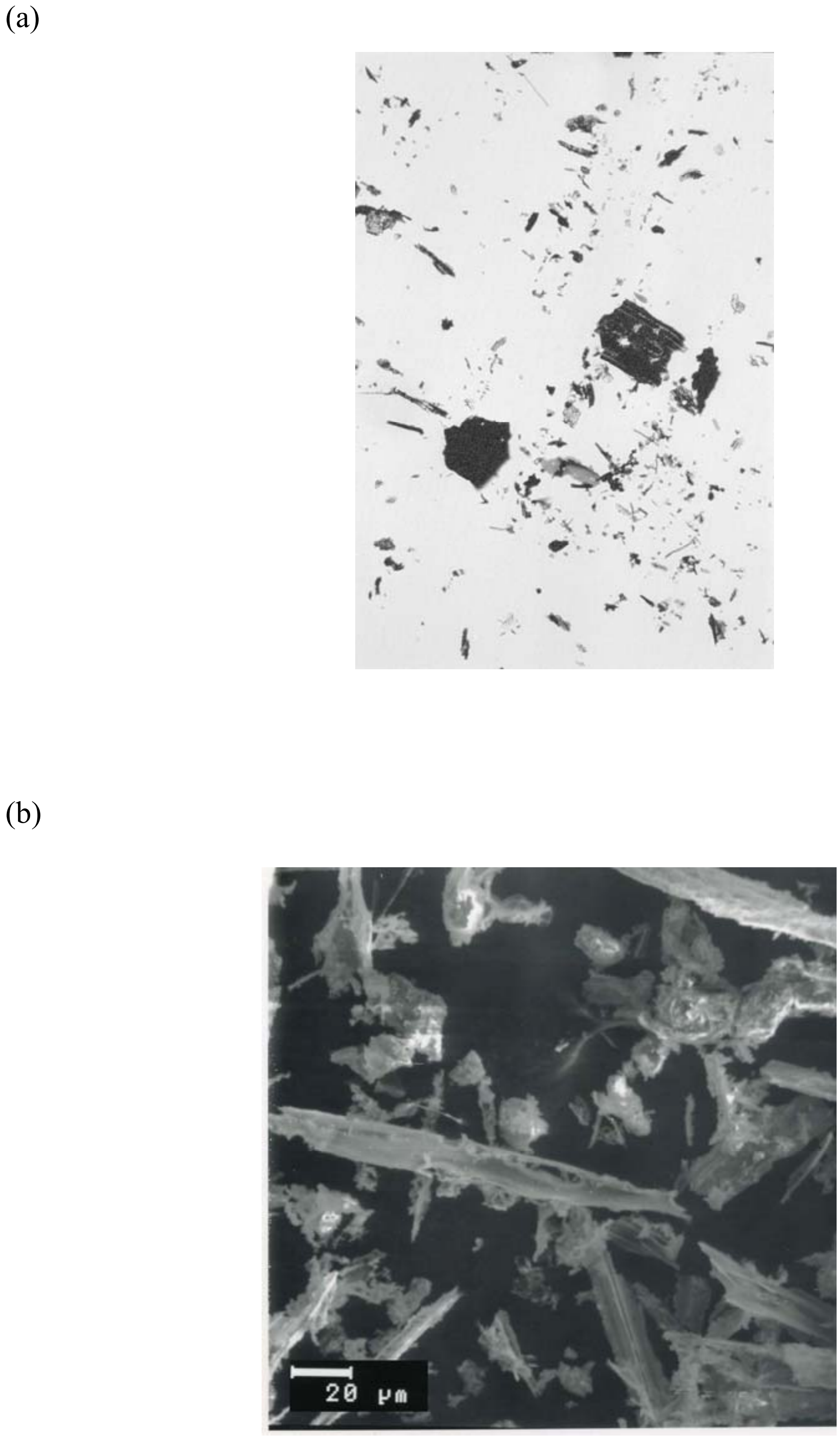


Fig. 2.1 Char images under (a) light microscope (80x), and (b) Scanning electron microscope (500x).

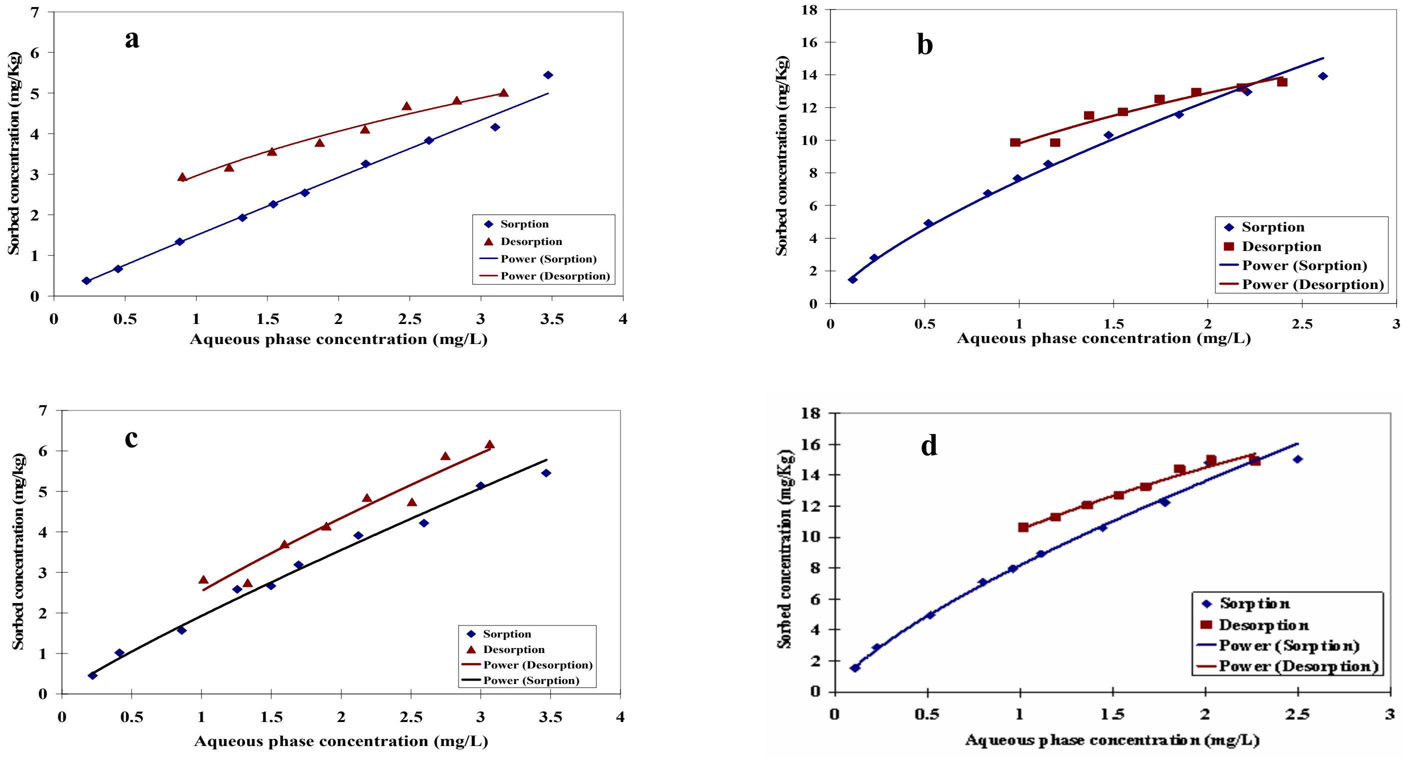


Fig. 2.2 Sorption and desorption isotherms of atrazine for (a) Hartsells soil, (b) HS + 1% Char, (c) Grady soil, and (d) GY + 1% Char.

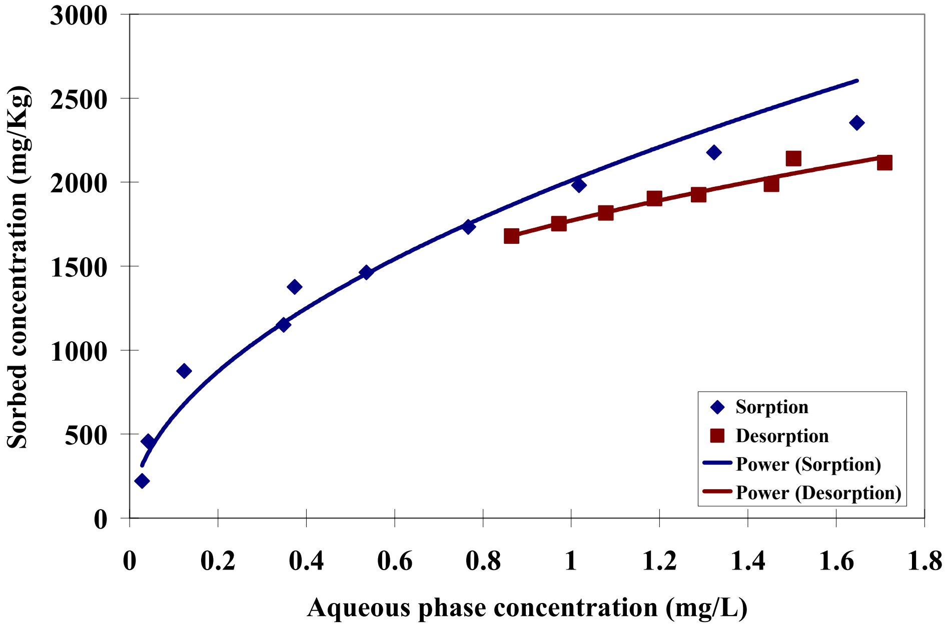


Fig. 2.3 Sorption and desorption isotherms of atrazine by char.

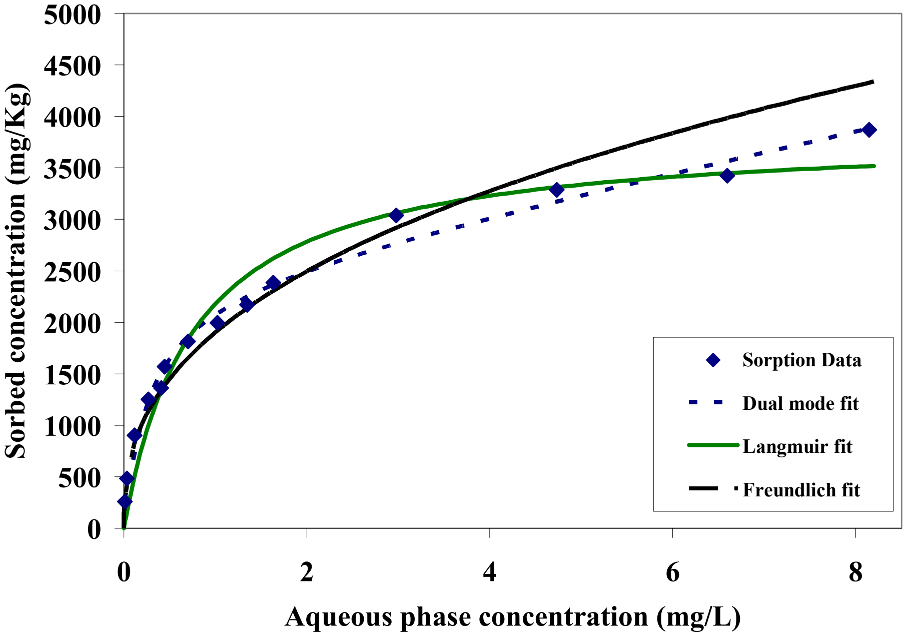


Fig. 2.4 Sorption of atrazine by char fitted with different adsorption models.

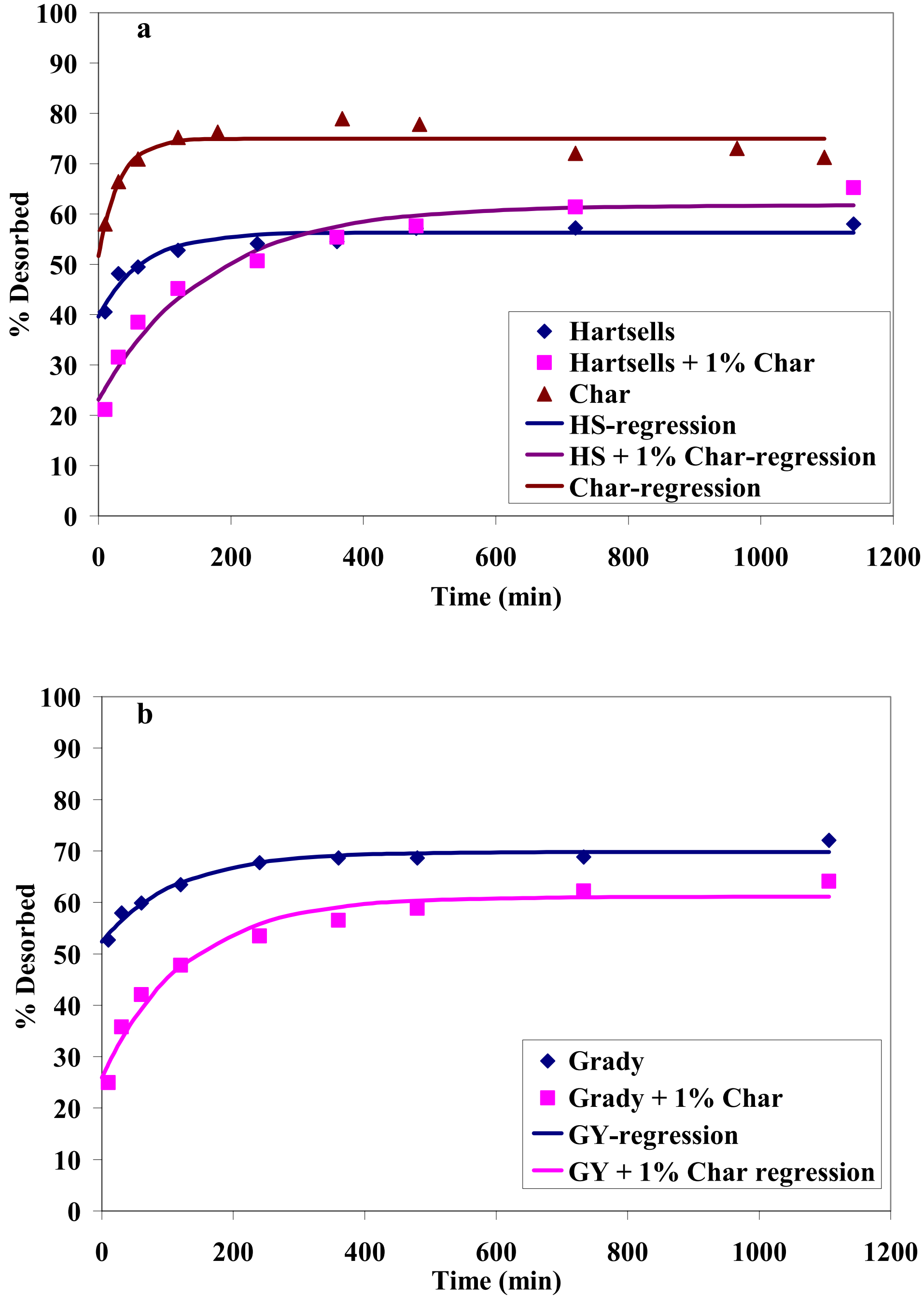


Fig. 2.5 Desorption kinetic profiles with model fitting for (a) Hartsells, Hartsells + 1% Char, and Char, (b) Grady and Grady + 1% Char.

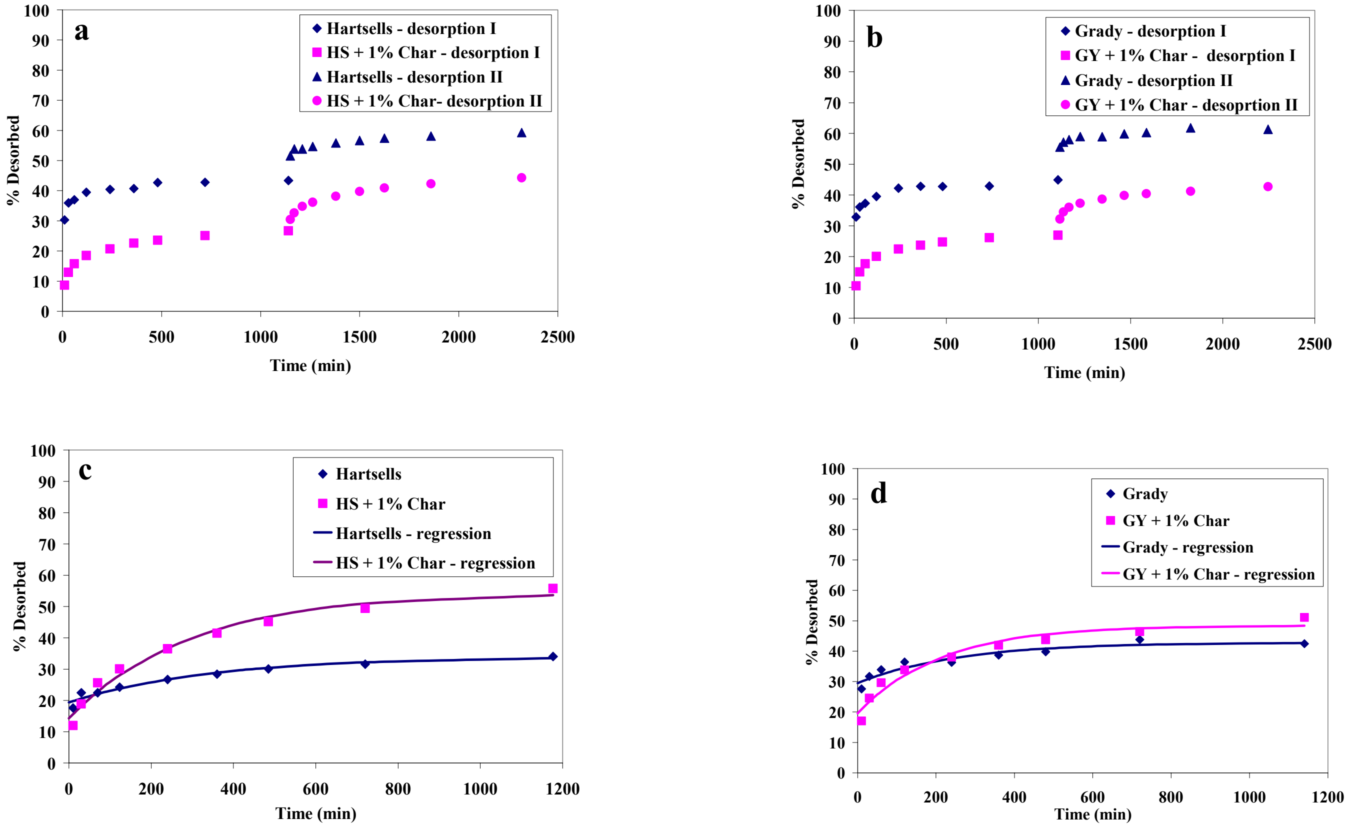
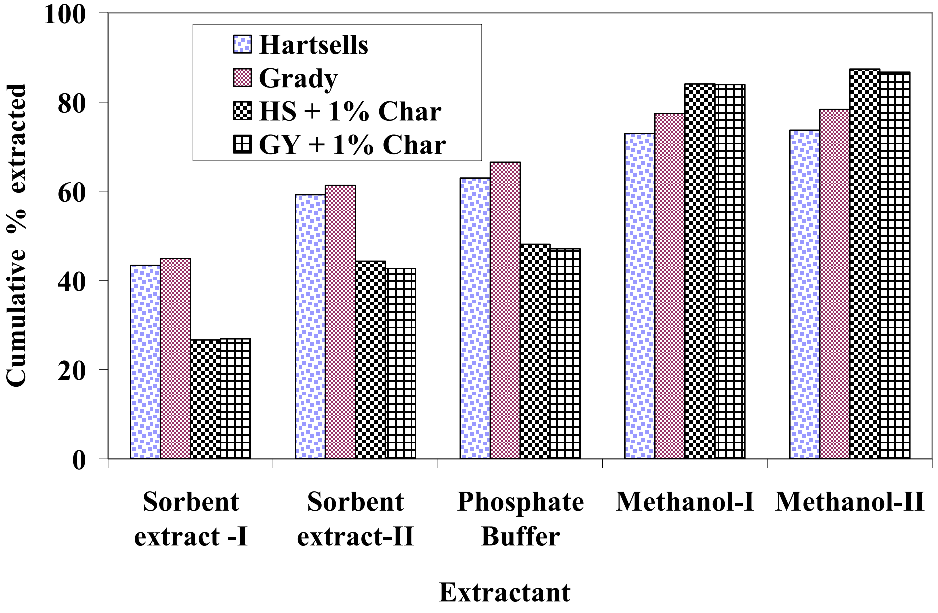


Fig. 2.6 Multistep kinetic desorption of atrazine in (a) Hartsells, HS+ 1% Char; (b) Grady, GY +1% Char. Regression lines for the second desorption are shown in (c) Hartsells, HS + 1% Char; (d) Grady and Grady + 1% Char.



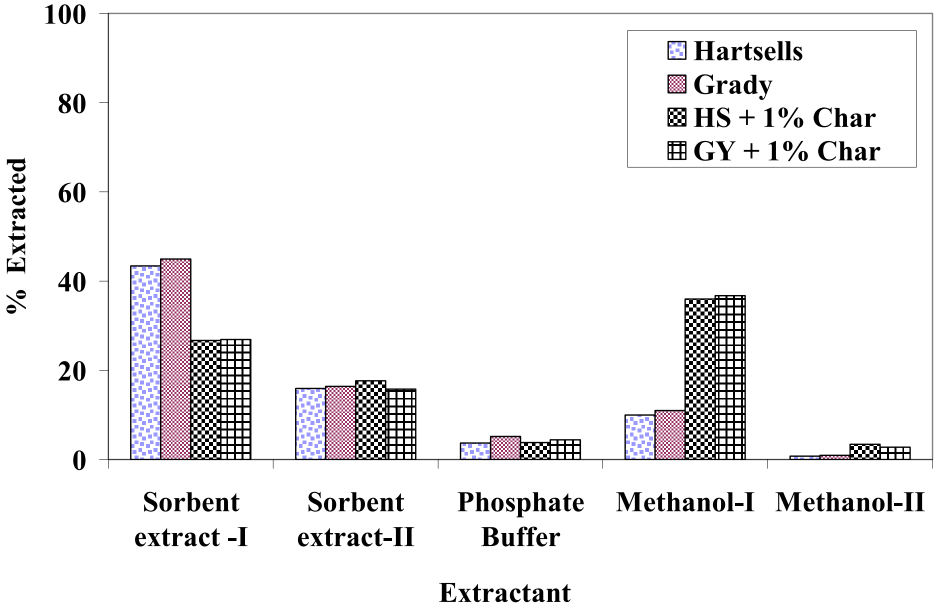


Fig. 2.7 Extraction of atrazine sorbed to soils and soils amended with 1% char.

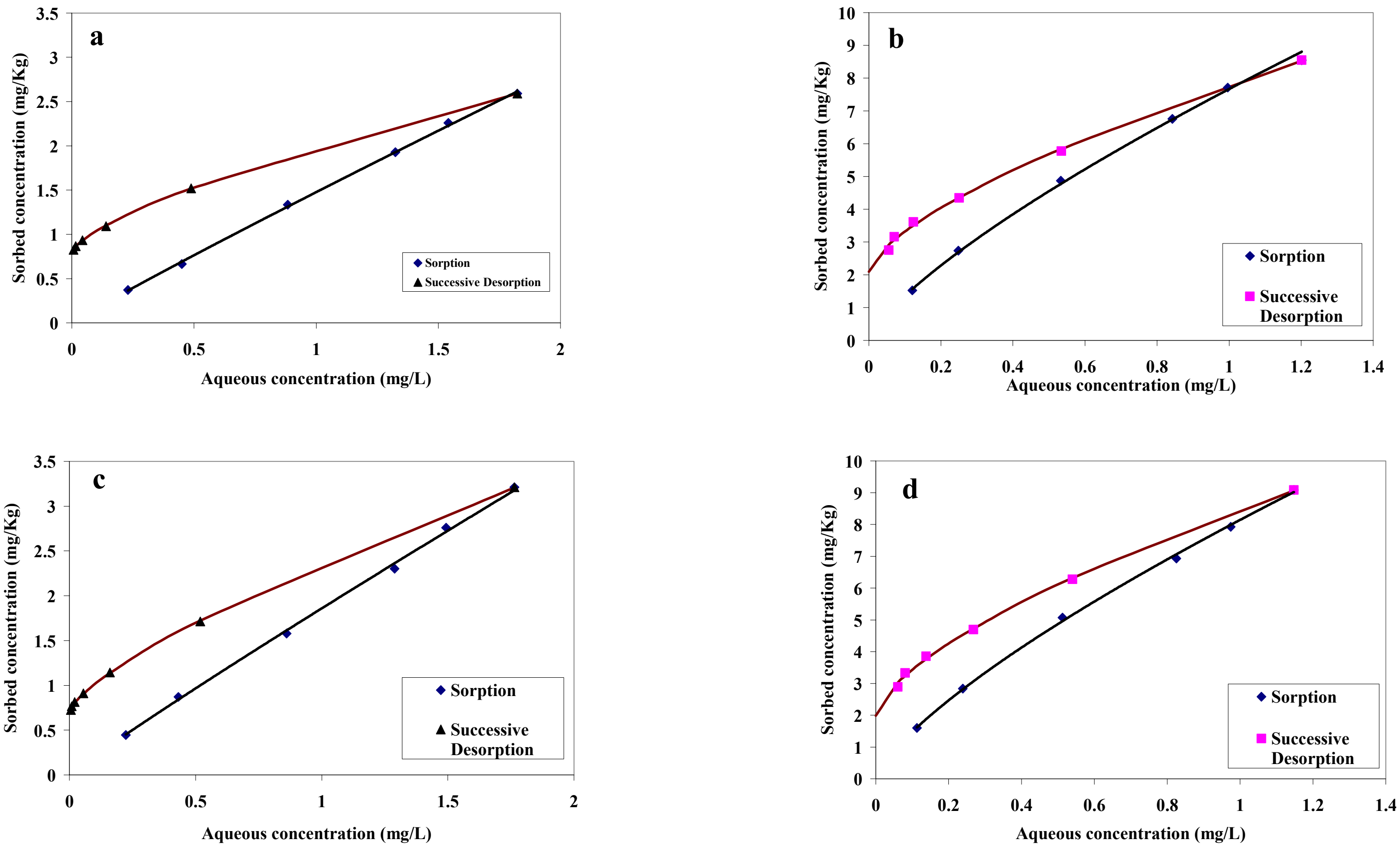


Fig. 2.8 Multistep equilibrium desorption of atrazine in (a) Hartsells; (b) Hartsells + 1% Char; (c) Grady soil; (d) Grady + 1% Char.

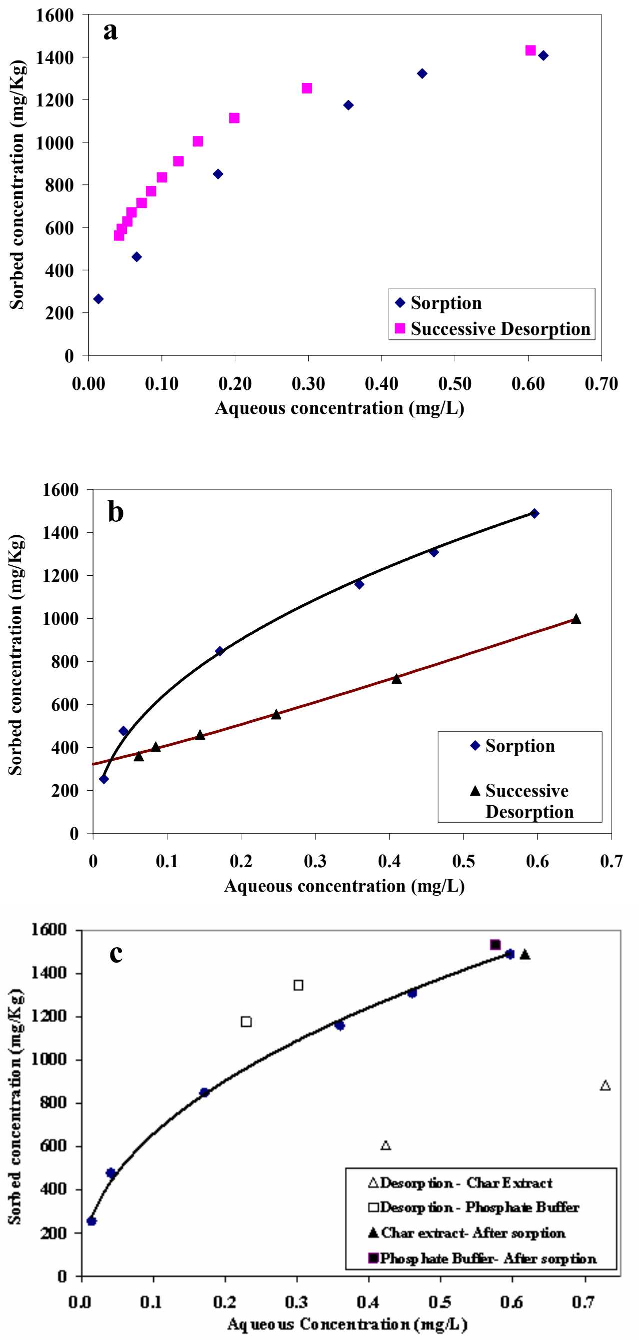


Fig. 2.9 Multistep equilibrium desorption of atrazine in char. Desorption was initiated using (a) phosphate buffer; (b) char extract. (c) shows a comparison of atrazine desorption from char using phosphate buffer and char extract.

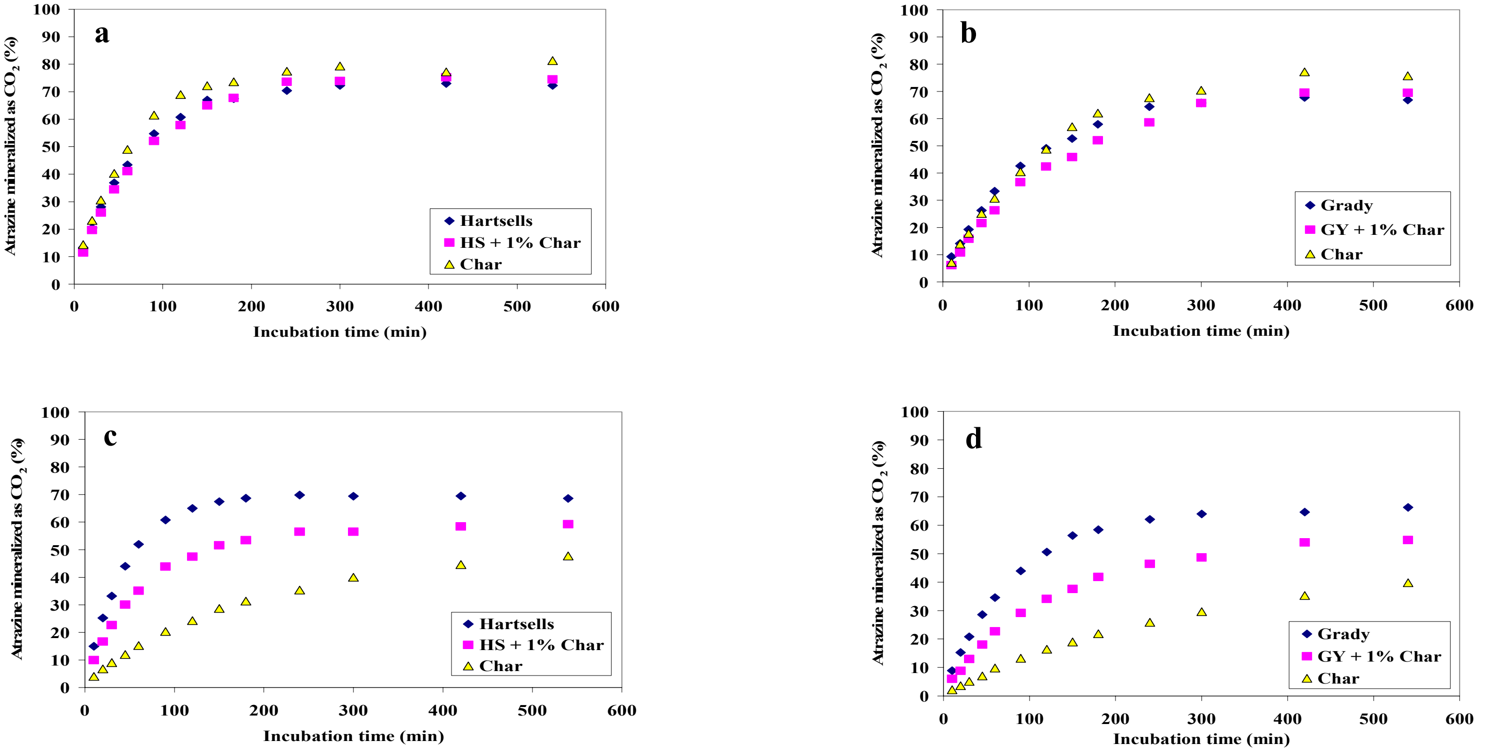


Fig. 2.10 Mineralization of atrazine in sorbent extracts and slurries. (a) Hartsells, HS +1% Char and Char extracts; (b) Grady, GY+1% Char and Char extracts; (c) Hartsells, HS +1% Char and Char slurries and d) Grady, Grady + 1% Char and Char slurries.

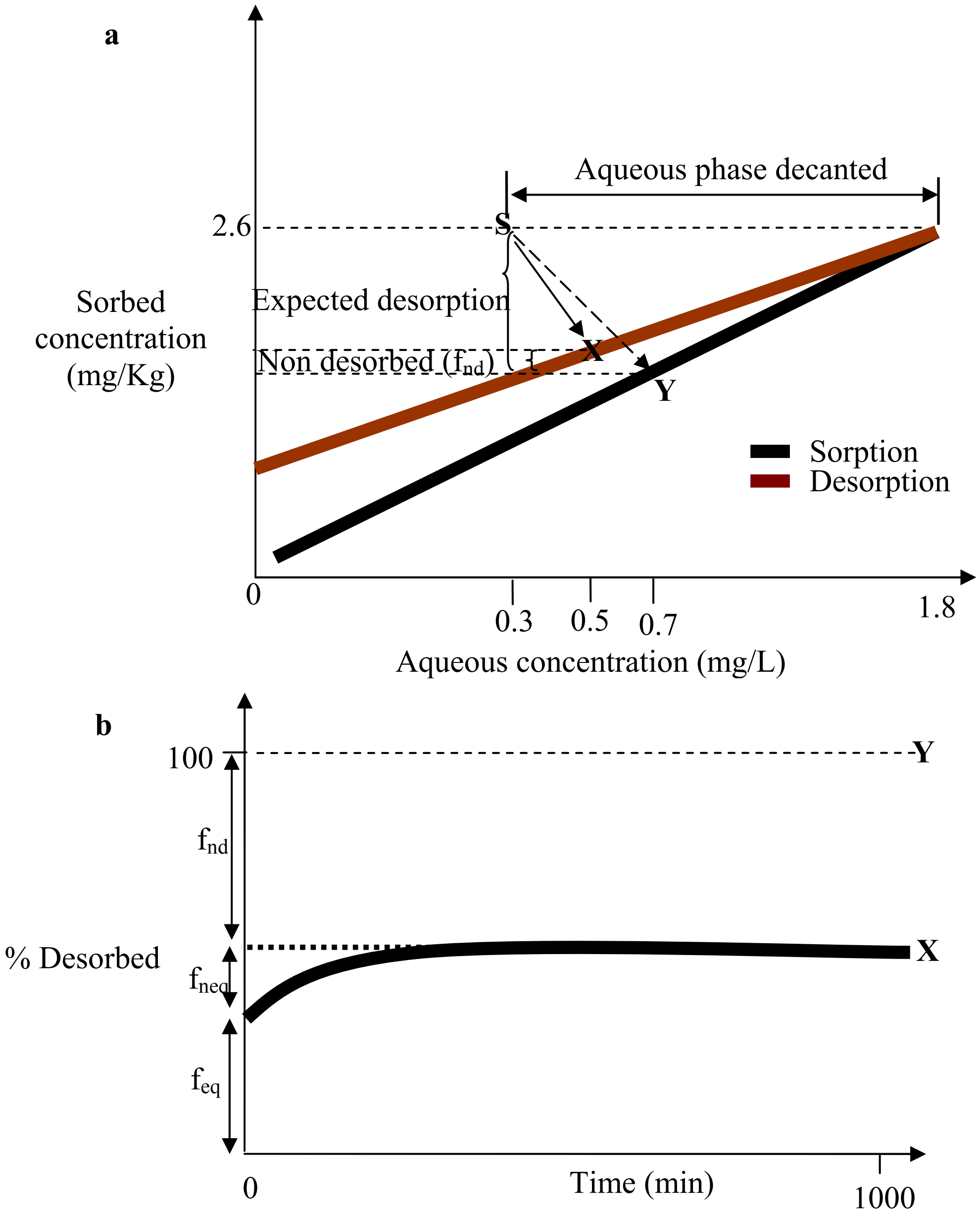


Fig. 2.11 Illustration of site fraction estimation for a typical sorption/desorption relationship observed in sorbents, where ‘S’ denotes sorbed phase concentration at the residual aqueous phase concentration before initiating desorption, ‘Y’ indicates the expected position of the initial total concentration (on sorption isotherm) and ‘X’ represents the position that is reached. (b) A typical kinetic desorption profile wherein ‘X’ and ‘Y’ correspond to ‘X’ and ‘Y’ in (a).

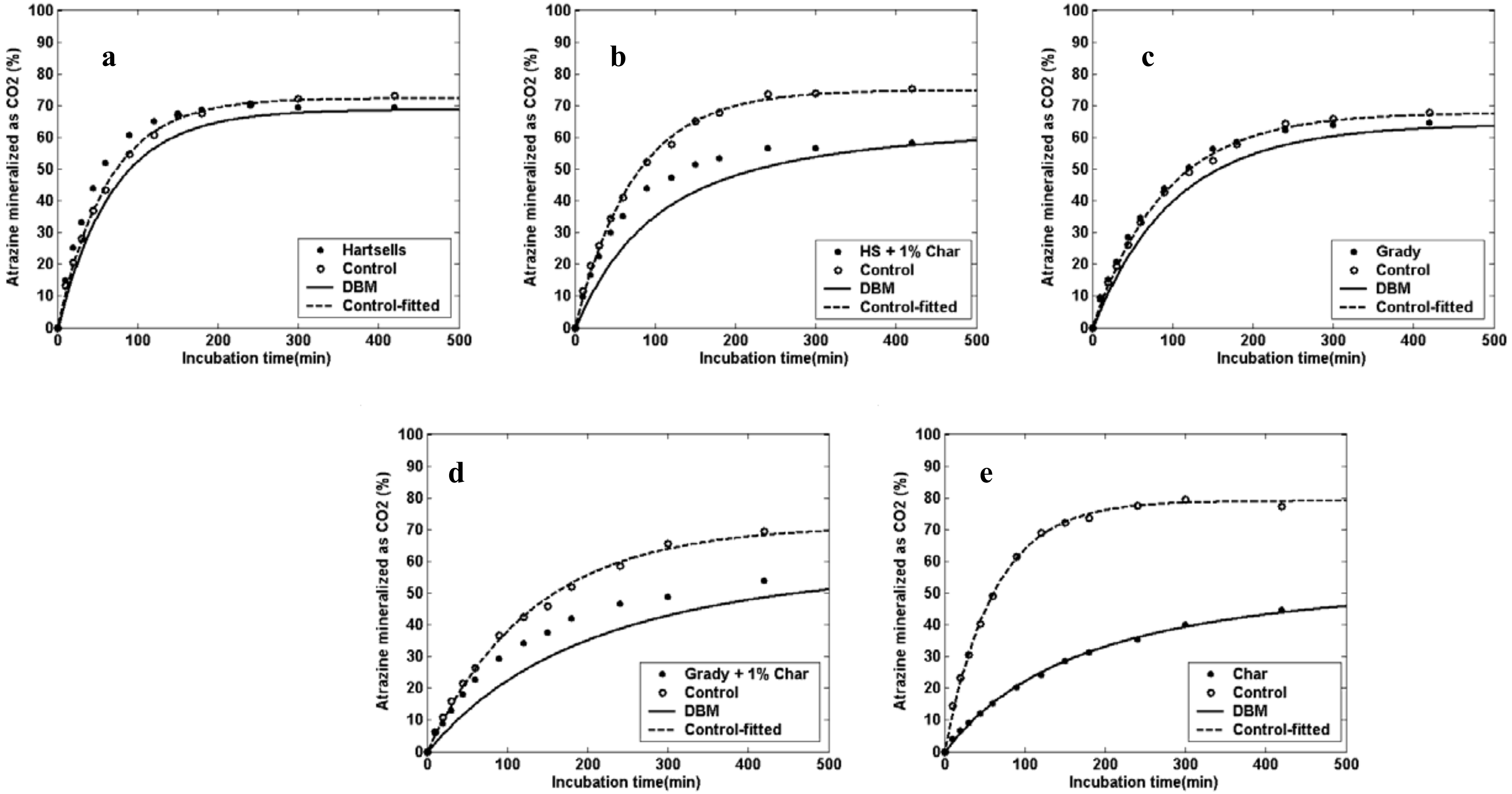
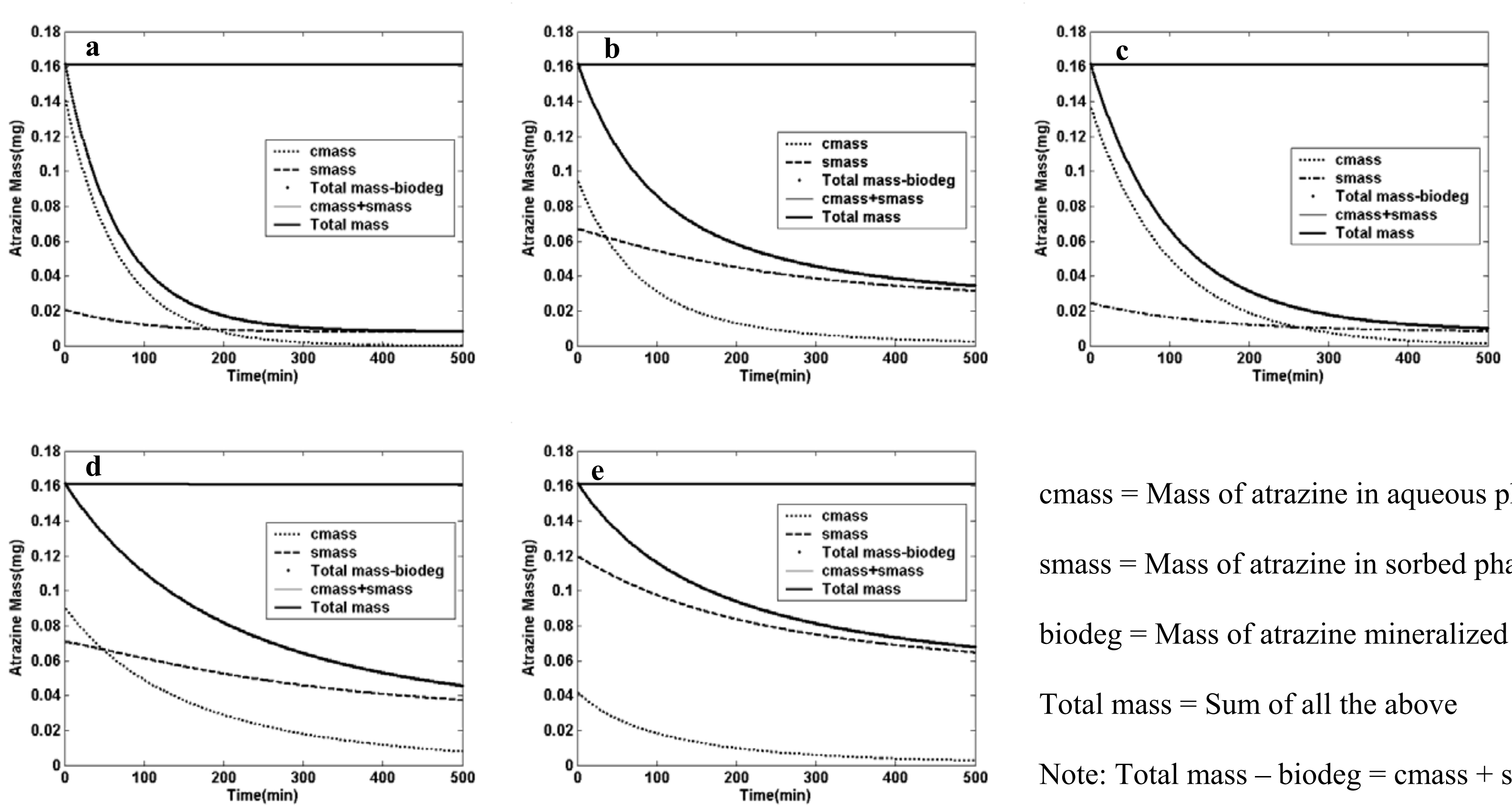


Fig. 2.12 DBM model predicted mineralization of atrazine by *Pseudomonas* sp. strain ADP (a) Hartsells soil; (b) Hartsells + 1% Char; (c) Grady soil; (d) Grady + 1% Char; (e) Char. Broken lines represent the nonlinear regression lines for sorbent extracts, and solid lines represent DBM predicted lines for sorbent slurries.



cmass = Mass of atrazine in aqueous phase

smass = Mass of atrazine in sorbed phase

biodeg = Mass of atrazine mineralized

Total mass = Sum of all the above

Note: Total mass – biodeg = cmass + smass

Fig. 2.13 Mass balance for the DBM model. (a) Hartsells soil; (b) Hartsells + 1% Char; (c) Grady soil; (d) Grady + 1% Char; (e) Char.

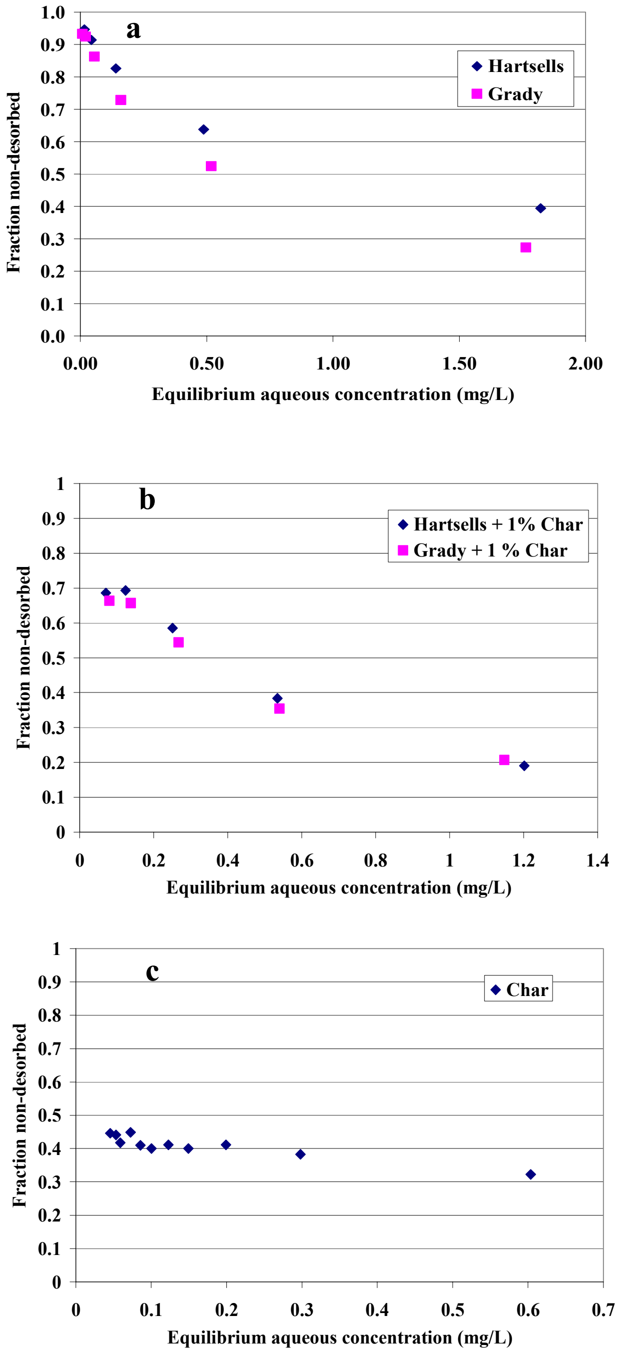


Fig. 2.14 Variation in non-desorbed fraction (f_{nd}) with respect to equilibrium aqueous concentration (a) Hartsells and Grady soil; (b) HS + 1% Char and Grady + 1% Char; (c) Char.

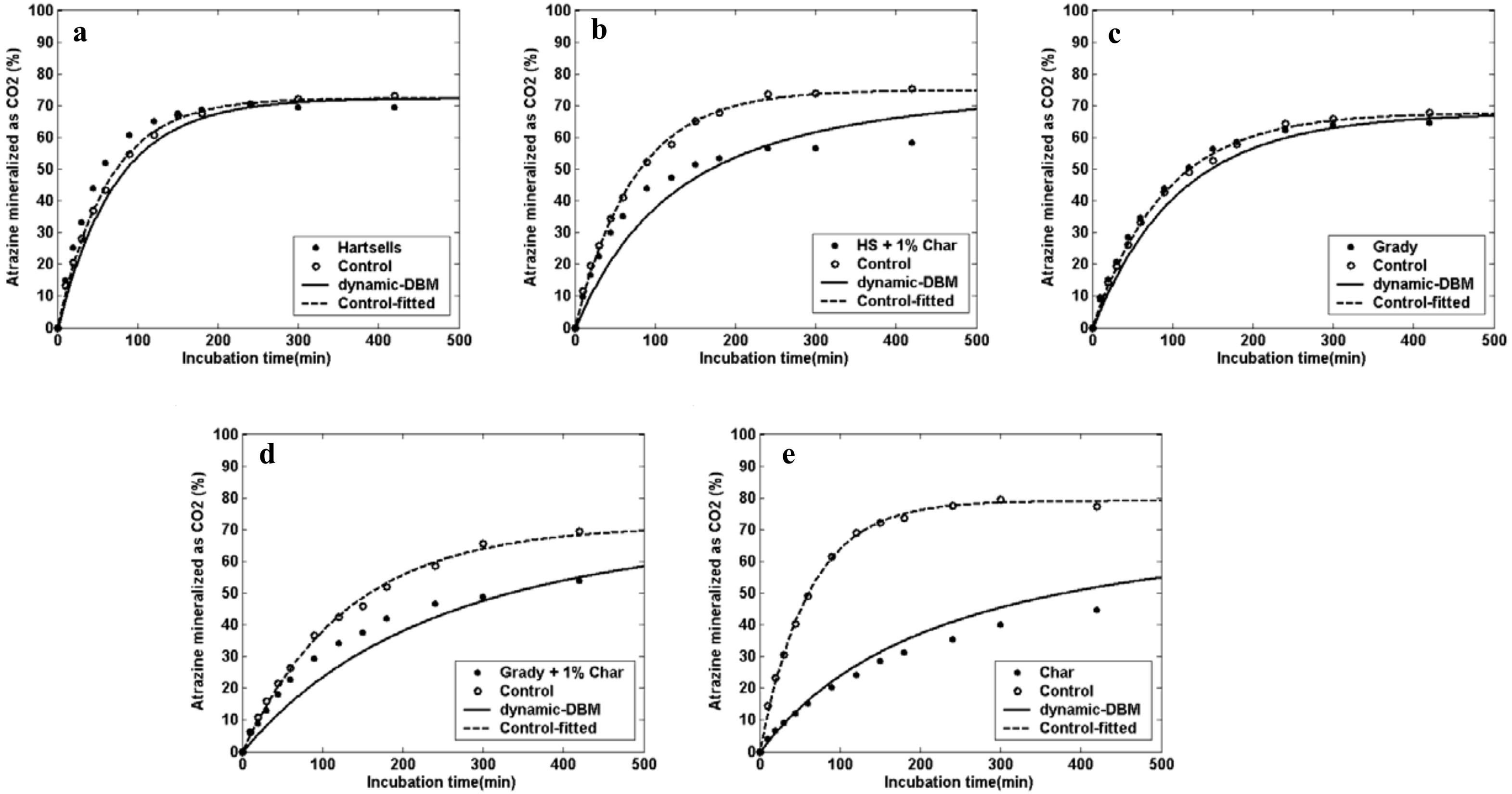
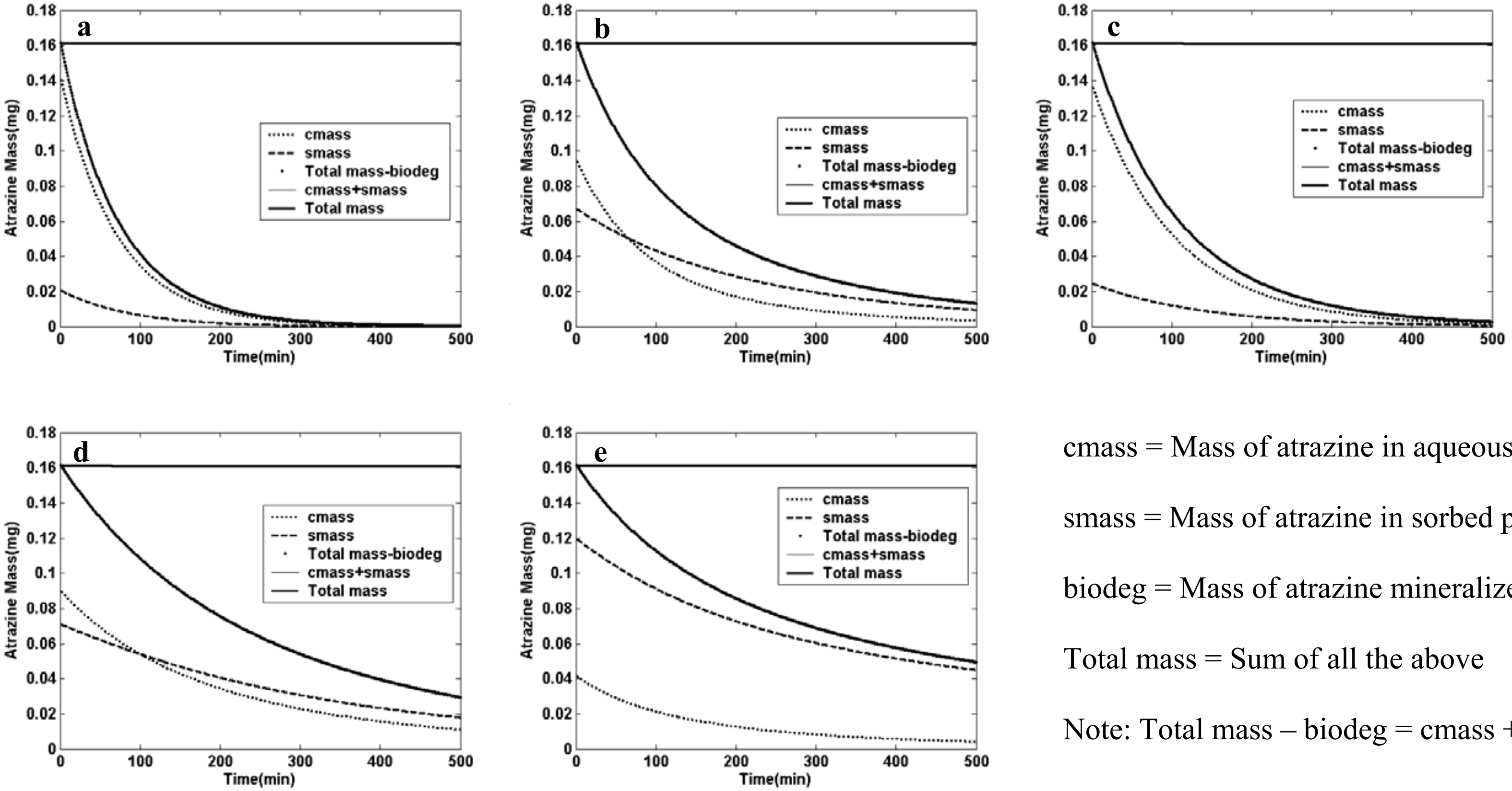


Fig. 2.15 DBM model predicted mineralization of atrazine by *Pseudomonas* sp. strain ADP using dynamic parameters. (a) Hartsells soil; (b) Hartsells + 1% Char; (c) Grady soil; (d) Grady + 1% Char; (e) Char. Broken lines represent the nonlinear regression lines for sorbent extracts, and solid lines represent dynamic DBM predicted lines for sorbent slurries.



cmass = Mass of atrazine in aqueous phase

smass = Mass of atrazine in sorbed phase

biodeg = Mass of atrazine mineralized

Total mass = Sum of all the above

Note: Total mass – biodeg = cmass + smass

Fig. 2.16 Mass balance for the DBM model with dynamic parameters (a) Hartsells soil; (b) Hartsells + 1% Char; (c) Grady soil; (d) Grady + 1% Char; (e) Char.

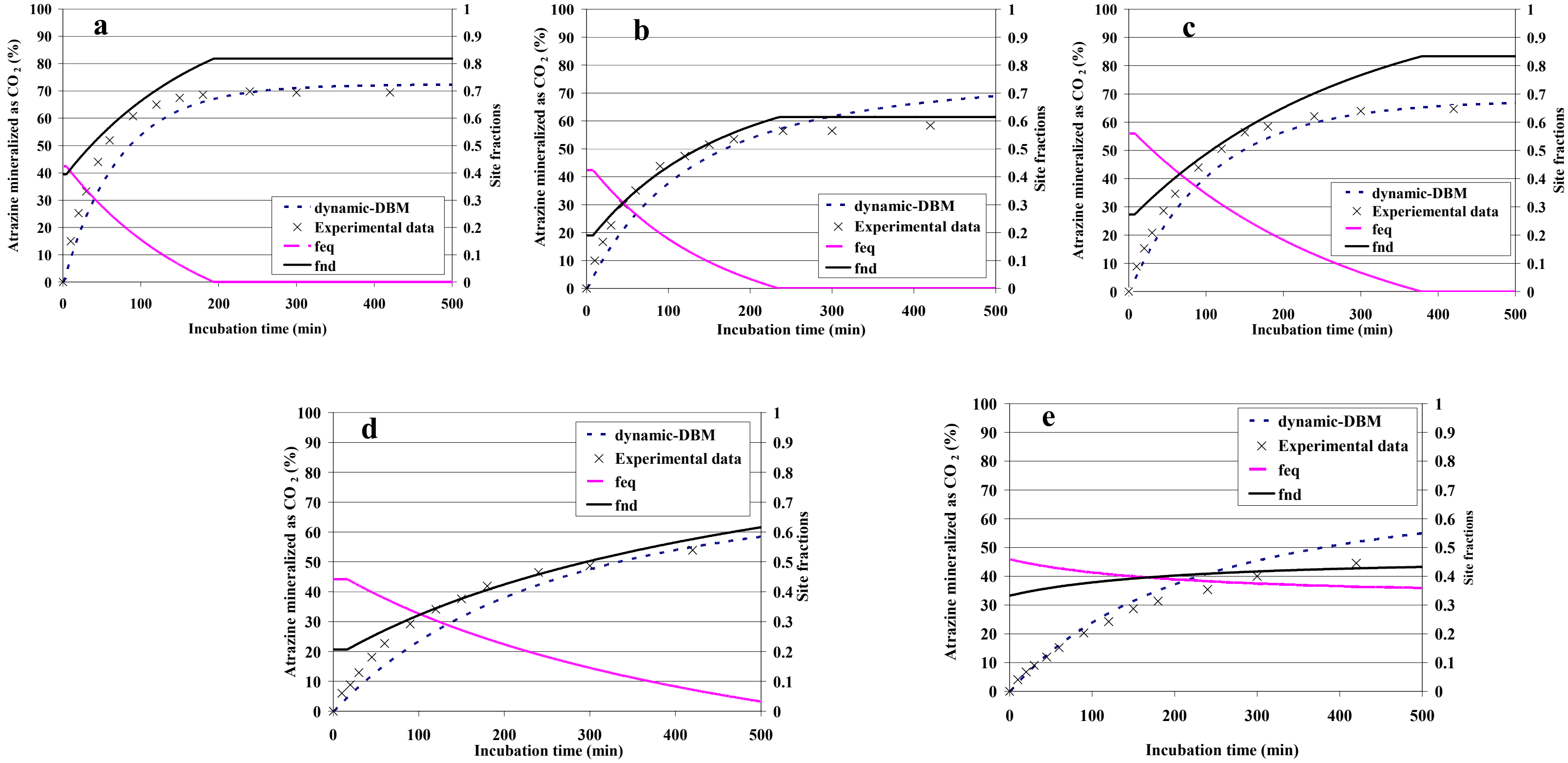


Fig. 2.17 Variation in site fractions with change in aqueous concentration during mineralization (a) Hartsells soil; (b) Hartsells + 1% Char; (c) Grady soil; (d) Grady + 1% Char; (e) Char.

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