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BIOCHAR-MEDIATED REDUCTIVE TRANSFORMATION OF NITRO HERBICIDES AND EXPLOSIVES

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Abstract—Biochar, a subset of black carbon produced via pyrolysis of biomass, has received much attention in recent years due to its potential to address many important issues, from energy and climate to agriculture and environmental quality. Biochar is known to influence the fate and transport of organic contaminants, although its role has been generally assumed to be as an adsorbent. In this study, the authors investigated the ability of biochar to catalyze the reductive reactions of nitro herbicides and explosives. Two biochars, derived from poultry litter and wastewater biosolids, were found to promote the reductive removal of the dinitro herbicides pendimethalin and trifluralin and the explosives 2,4-dinitrotoluene and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) by dithiothreitol. Parallel experiments using another black carbon material, graphite powder or granular activated carbon, in place of a biochar resulted in comparable rate enhancement to show reduction products, such as 2,4-diaminotoluene and formaldehyde. A cyclization product of trifluralin and reduction products of dinitrotoluene and RDX were detected only when biochar and dithiothreitol were both present, supporting the ability of biochar to promote redox reactions. Three possible catalysts, including graphene moieties, surface functional groups, and redox-active metals, in biochar may be responsible for the biochar-mediated reactions. The environmental significance, implications, and applications of this previously unrecognized role of biochar are discussed. Environ. Toxicol. Chem. 2013;32:501–508.

Keywords—Biochar Redox transformation mediator Nitro herbicide Explosive

INTRODUCTION

Biochar, the carbon-rich product generated through thermal (pyrolytic) decomposition of organic materials, has received significant interest in recent years [1]. The driving forces behind the surge in interest appear to be threefold. First, in an effort to mitigate climate change and rising energy cost, crop residues and other waste biomass have been increasingly explored as a renewable energy source (bio-oil and syn-gas) and potentially low-cost and sustainable alternatives to fossil fuels [2]. Biochar is produced as a solid by-product in the pyrolysis of biomass [3]. Second, pyrolytic conversion of organic wastes to biochar has been suggested as a means of reducing the volume and disposal cost of organic wastes [4]. According to the United Nations Environmental Programme [5], the global production of waste biomass—agricultural wastes, forestry residues, municipal waste, and so on—is 140 billion tonnes a year. This provides a strong impetus for efforts in both energy production and waste reduction. For example, more than 12 million dry tonnes of litter is generated every year from the U.S. poultry industry [6], and proper disposal of this waste presents a major challenge. Pyrolysis of poultry litter to produce bioenergy and biochar has been suggested as a potential solution to this challenge [7]. As another example, in South Korea land disposal of wastewater biosolids has been a controversial issue since the government joined the London Protocol in 2006. After ocean dumping of biosolids was banned in 2012, a total of 9,000 tonnes/d of biosolids are being treated via various processes including carbonization. As world population and waste production continue to grow, it is imperative to develop sound methods and guidelines to safely dispose of and/or beneficially use pyrolyzed waste materials. Third, biochar has been applied as a soil additive and shown to produce multiple potential environmental and economic benefits. These include improved soil fertility and crop yield, carbon stabilization and storage, reduced emissions of greenhouse gases (specifically, N_2O and CH_4) from soil, better retention and reduced leaching of nutrients (e.g., nitrogen and phosphorus), improved surface- and groundwater quality, and adsorption of organic and metallic contaminants [1,2,8–12].

Biochar is a subset of black carbon (BC), which encompasses a broad spectrum of condensed, carbon-rich materials derived from incomplete combustion and other thermal processes [13,14]. Like other BC, the physical and chemical properties of biochar can vary greatly depending on the type of source biomass [15,16]. In addition, pyrolysis temperature strongly affects the properties of biochar, including elemental composition, extent of carbonization, aromaticity, surface area and functional groups, porosity, and crystallinity [16,17]. In general, higher pyrolysis temperature increases the aromaticity, C/O and C/H ratios, and carbonization of biochar, while decreasing its biodegradability [15–18].

Similar to other BC, biochar has a strong affinity for aromatic compounds and has been increasingly investigated as an adsorbent for organic chemicals in soils and sediments. Chen et al. [19] showed that nonpolar and polar aromatic compounds could sorb to the surface of pine needle biochar through partition and/or adsorption depending on the pyrolysis temperature. Loganathan et al. [20] reported that application of biochar to soil can significantly increase the sorption of atrazine and, hence, decrease its bioavailability. Chun et al. [17] suggested that the relatively high affinity of biochar for polar aromatic compounds (e.g., nitrobenzene) could be attributed to the functional groups (acidity/basicity) on the biochar surface. In contrast, Zhu and Pignatello [21] proposed that π–π

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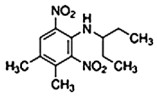
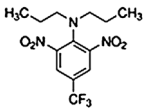
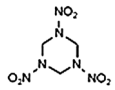
Table 1. Properties[a] of the chemicals used in the present study

Name	Molecular structure	Molecular weight	Log K_{OW}	Water solubility (mg/L)
Pedimethalin		281.31	5.20	0.3
Trifluralin		335.28	4.69	<1.0
DNT		182.13	2.00	270
RDX		222.12	0.87	60

[a] Data from World Health Organization [27] and Yinon and Zitrin [28].
DNT = 2,4-dinitrotoluene; RDX = hexahydro-1,3,5-trinitro-1,3,5-triazine.

electron donor–acceptor interactions between organic sorbates and BC best explain the sorption behavior. Namely, electron-rich and poor regions of graphene moieties in BC could explain the sorption of π-acceptors (e.g., nitrobenzene, 2,4-dinitrotoluene [DNT], and 2,4,6-trinitrotoluene) and π-donors (such as naphthalene and phenanthrene), respectively [21,22].

In recent years, BC has been investigated as an electron-transfer mediator for the reduction of organic contaminants. We showed that reduction of nitroaromatic compounds, such as DNT, and heterocyclic nitramines, such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), by a thio reductant was greatly enhanced by BC materials such as soot or graphite [23]. More recently, we observed that reduction of DNT and 2,4-dibromophenol by H_2S was enhanced by soot and granular activated carbon (GAC) [24]. Kemper et al. [25] reported that RDX degradation by H_2S was accelerated in the presence of BC including GAC and graphite. These authors suggested that the addition of BC might be an attractive in situ technique to remediate RDX-contaminated marine sediment under sulfide-rich conditions. Xu et al. [26] further showed that BC could also mediate the reduction of another energetic compound, nitroglycerin, by H_2S.

To date, studies on the environmental applications and impacts of biochar have largely focused on issues related to climate, soil quality/nutrient retention, and contaminant fate. With respect to contaminant fate, the role of biochar considered so far has been limited to adsorption. Here, we hypothesize that, similar to other BC, biochar can also act as a redox mediator to promote the reductive transformation of organic compounds and impact the fate of redox-sensitive chemicals in the environment. In the present study, we assessed the effect of organic waste-derived biochar on the transformation of nitro herbicides and explosives. Specifically, we tested the ability of two biochars, produced from poultry litter and wastewater biosolids, to mediate the reduction of the herbicides pendimethalin and trifluralin and the explosives DNT and RDX, in the presence of a thiol reductant, dithiothreitol. For cross-comparison, we also assessed the ability of two other BC materials, graphite and GAC, to enhance the reduction of these herbicides under the same reaction conditions.

MATERIALS AND METHODS

Chemicals

Pendimethalin ($C_{13}H_{19}N_3O_4$, 99%) and trifluralin ($C_{13}H_{16}F_3N_3O_4$, 99%) were purchased from Supelco. The following were purchased from Aldrich: DNT ($C_7H_6N_2O_4$, 97%), 2,4-diaminotoluene (DAT, $C_7H_{10}N_2$, 98%), 4-amino-2-nitrotoluene (4A2NT, $C_7H_8N_2O_2$, 97%), 2-amino-4-nitrotoluene (2A4NT, $C_7H_8N_2O_2$, 99%), and dithiothreitol (>98%). We obtained RDX ($C_3H_6N_6O_6$,1000 μg/ml in acetonitrile) from ChemService. We acquired K_2HPO_4 and $NaH_2PO_4 \cdot 2H_2O$ (>98%) from DC Chemical and Junsei Chemical, respectively. Acetonitrile and methanol, high-performance liquid chromatography-grade, were purchased from Fisher Scientific. All chemicals were used as received. Properties of the chemicals are summarized in Table 1.

Two types of biochar were prepared via pyrolysis from dried pellets of poultry litter and wastewater biosolids. The poultry litter pellets (<6 mm in diameter) were obtained from Perdue AgriRecycle, and the biosolids were collected from a municipal wastewater-treatment facility in the city of Ulsan, South Korea. The poultry litter biochar was prepared through slow pyrolysis of dried poultry litter pellets at 400°C for 8 h at a Delaware State University facility. A detailed description of the poultry litter biochar has been published elsewhere [7]. The sampled biosolids were dried and pyrolyzed at a pilot-scale plant located in a company in Ulsan for 4 h at 400°C. High-purity graphite powder (<20 μm, 99.9%) was acquired from Aldrich. A charcoal-based GAC was obtained from DC Chemical. The GAC contained C (79.8%), H (0.6%), O (2.8%), and N (0.6%). The surface areas of graphite and GAC were 13.6 ± 0.3 and 739 ± 1 m^2/g, respectively, as determined by the Brunauer-Emmett-Teller method with N_2.

Batch experiments

All experiments were prepared and performed in an anaerobic glove box under N_2. Batch experiments were conducted using 250-ml borosilicate amber bottles. Each bottle contained 120 mg (0.778 mmol) of dithiothreitol and a BC material—biochar (1 g), graphite (0.1 g), or GAC (0.01 g). Due to the

Table 2. Properties of the biochars used in the present study

Types of biochar	Surface area (m^2/g)	Elemental contents[a] (%)			
		C	H	O	N
Poultry litter	2.3	37.1	2.3	13.9	5.2
Biosolids	19.5	31.8	3.4	19.4	4.4

[a] Analyzed by vario EL elemental analyzer (Elementar).

difference of sorption capacity among the BC materials, different masses of biochar, graphite, and GAC were added to observe the enhancement of the reduction in the presence of the BC materials over the given experimental period. The bottles were then filled completely with deoxygenated phosphate buffer solution (20 mM, pH 7). Phosphate is known to be a good buffer and to not significantly affect the reductive reaction in the presence of BC [23,25,26]. The bottles were prepared in duplicate to ensure reproducibility and to estimate experimental errors. We did not leave any headspace in the bottles because pendimethalin and trifluralin are volatile [29]. Preliminary tests confirmed that the sorption of two dinitro herbicides to glassware and volatilization were negligible during the experimental period. The surface area-to-solution volume ratios were 5.44, 29.6, 9.2, and 78 m^2/g for graphite, GAC, poultry litter biochar, and biosolids biochar, respectively. A 2.5-ml aliquot of the solution was displaced by 2.5 ml of pendimethalin or trifluralin stock solution (1,000 mg/L in methanol) added at time zero. The volume of methanol was approximately 1% in the final solution, and the initial concentrations of pendimethalin and trifluralin were 0.055 and 0.0298 mM, respectively. Mininert valves (VICI Precision Sampling) and low-permeability vinyl tape (3M) were used to seal the bottles and prevent air intrusion and volatilization losses. The bottles were placed in a horizontal position on a platform shaker rotating at 150 rpm. At selected times, 1 ml of aqueous sample (possibly including few fine particles of BC materials) was withdrawn using a glass syringe and immediately passed through a 25-nm cellulose membrane filter (Millipore) to remove the particles for quantification of pendimethalin or trifluralin. To maintain zero headspace, 1 ml of deoxygenated phosphate buffer was added after each sampling. For every experiment two sets of control were prepared under identical conditions, one without dithiothreitol and the other without a carbon material. In reduction control experiments without a BC material, direct reduction of the herbicides by dithiothreitol was observed. In sorption control experiments without dithiothreitol, sorption of the herbicides to BC was determined.

For DNT and RDX transformation experiments, 200 ml of phosphate buffer solution and 1 g of poultry litter biochar were used. Due to the low volatility of DNT and RDX, approximately 50 ml of headspace remained in the vial. Conditions for batch reduction experiments with DNT and RDX have been described in detail previously [23].

Chemical analysis

Pendimethalin and trifluralin were analyzed using a Dionex UltiMate 3000 high-performance liquid chromatographic system equipped with an Acclaim 120 guard column (4.3 × 10 mm, Dionex) and an Acclaim 120 C18 column (4.6 × 250 mm, 5 μm, Dionex). A mixture of acetonitrile and water (80/20, v/v) was used as the mobile phase at a flow rate of 1.0 ml/min. The retention times for pendimethalin and trifluralin were 11.1 and 11.8 min, respectively. The wavelength of the ultraviolet detector was set at 254 nm. Also using high-performance liquid chromatography, we determined DNT, RDX, and their reduction products (2A4NT, 4A2NT, and DAT for DNT, formaldehyde for RDX). The analytical methods and conditions for the quantification of DNT, RDX, and their daughter products are described in detail elsewhere [23].

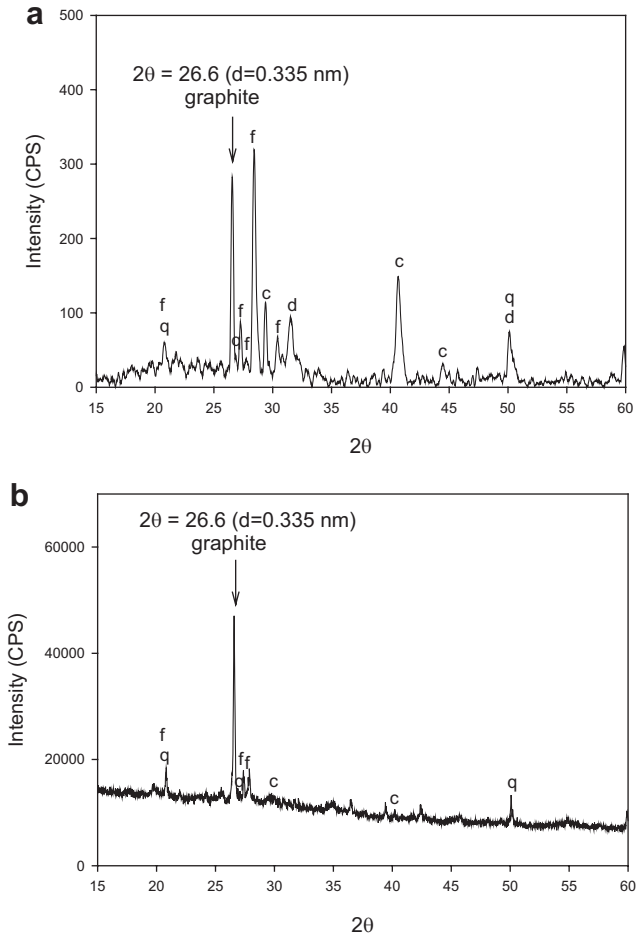


Fig. 1. X-ray powder diffraction patterns of (**a**) poultry litter biochar and (**b**) biosolids biochar. c = calcite; d = dolomite; f = feldspar; q = quartz; CPS = counts per second.

To confirm the reductive transformation of pendimethalin and trifluralin, selected samples were analyzed using a gas chromatograph–mass spectrometer (GC–MS; 7890 GC, 5975N MS; Agilent) with a DB-5 column (30 m × 0.25 mm × 0.25 μm). Reacted solution (200 ml) was extracted two times with *n*-hexane (50 ml) using a vortex shaker for 5 min, and the extract was concentrated to 1 ml for injection. The extraction

Table 3. Inorganic elemental contents[a] in the biochar used in the present study (dry wt %)

Types of biochar	Al	B	Ca	Cu	Fe	K	Mg	Mn	P	S	Zn
Poultry litter	0.48	0.01	4.91	0.08	0.24	5.32	1.35	0.09	2.71	1.10	0.10
Biosolids	0.65	0.01	8.14	0.27	0.43	1.62	1.60	0.40	1.02	0.59	0.65

[a] Analyzed by inductively coupled plasma optical emission spectrometry (Activa M, Horiba Scientific) after aqua regia extraction.

efficiency was 85%. The carrier gas was He (99.999%), and the flow rate was 1.0 ml/min. The injection volume was 1 μl, and the injection mode was splitless. The injector temperature was 300°C, and the oven temperature was constant at 50°C for 2 min, increased at 5°C/min for 50 min, and held at 300°C for 16 min. The obtained mass spectrum was compared to standard ones in a mass spectral library (NIST 05, Version 2.0) to identify possible reduction products.

RESULTS AND DISCUSSION

Characterization of biochar

The Brunauer-Emmett-Teller surface areas and elemental compositions of poultry litter and biosolids biochars are summarized in Tables 2 and 3. The characteristics of the two biochars were quite different. Their surface areas are comparable to those of wood and grass biochars prepared at the same temperature (<10 to >20 m^2/g [16]). The content of nitrogen and phosphorus of poultry litter biochar was slightly higher than that of biosolids biochar, whereas the metal (Al, Ca, Cu, Fe, Mg, Mn, and Zn) content of biosolids biochar was generally higher. X-ray diffraction analysis showed a distinct graphite peak ($2\theta = 26.6$, $d = 0.335$ nm) for both poultry litter and biosolids biochars (Fig. 1). Other crystalline species identified by X-ray diffraction included feldspar, quartz, dolomite, and calcite, although the intensities were different for biosolids and poultry litter biochars (Fig. 1).

Graphite/GAC-mediated reduction of pendimethalin and trifluralin

Before testing the biochars, we examined graphite and GAC with respect to their ability to enhance the reduction of pendimethalin and trifluralin by dithiothreitol. Graphite and GAC are two BC materials that had been shown previously to promote the reduction of nitro and halogenated aromatic compounds [23–26]. Without graphite or GAC, direct reduction of pendimethalin by dithiothreitol in the aqueous phase was relatively slow, with approximately 20% of pendimethalin transformed over 120 min (Fig. 2a, b). In the absence of dithiothreitol, adsorption of pendimethalin to graphite and GAC was rapid but occurred only to a limited extent, approximately 40 and 20% removal in 120 min, respectively. In the presence of both graphite and dithiothreitol, 95% of the pendimethalin disappeared from solution in 120 min. Similarly, GAC also enhanced the transformation of pendimethalin. Compared to the 20% removal in BC-free and dithiothreitol-free controls, the removal of pendimethalin was approximately 90% over 120 min (Fig. 2b). After the rapid initial drop in aqueous pendimethalin

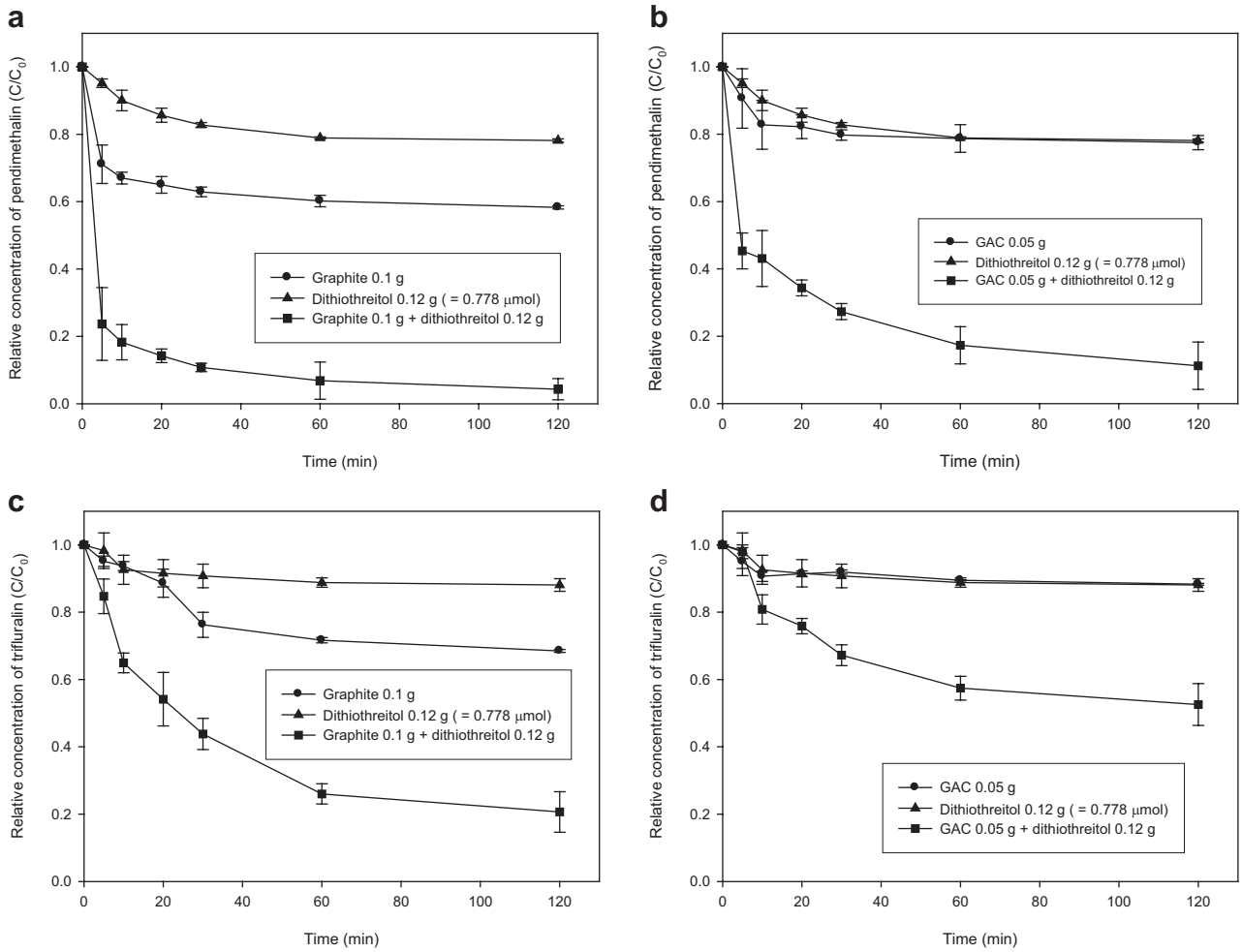


Fig. 2. Graphite- and granular activated carbon (GAC)–mediated reduction of pendimethalin and trifluralin by dithiothreitol. (**a**) Graphite-pendimethalin, (**b**) GAC-pendimethalin, (**c**) graphite-trifluralin, (**d**) GAC-trifluralin. Data points are the average of duplicate samples, and error bars represent one standard deviation.

concentration in the first 5 min, pendimethalin continued to transform throughout the course of the experiment, in contrast to the controls where pendimethalin concentrations did not change markedly over the same period.

The reductive removal of trifluralin by dithiothreitol was similarly enhanced in the presence of graphite and GAC. Compared to pendimethalin, trifluralin was less reactive toward aqueous dithiothreitol (~10% removal in 120 min) and adsorbed to a lesser extent to graphite and GAC (~30 and 10% removal in 120 min, respectively). In contrast to the controls, removal of trifluralin by dithiothreitol continued in the presence of either graphite or GAC (Fig. 2c, d). The initial decrease in solution concentration was less pronounced, and the final percentage of removal was lower for trifluralin compared to pendimethalin. These may be due to poorer adsorption of trifluralin to BC (which mediated its transformation), lower intrinsic reactivity of trifluralin, or a combination of the two as suggested by the BC-free and reductant-free controls. These results indicate that BC such as graphite and GAC can mediate the transformation of the dinitroaniline herbicides pendimethalin and trifluralin.

Biochar-mediated reduction of pendimethalin and trifluralin

Experiments were then conducted to test our hypothesis that, similar to other BC such as graphite and GAC, biochar could enhance the reductive transformation of pendimethalin and trifluralin. As shown in Figure 3a and b, in the absence of dithiothreitol pendimethalin adsorbed quickly to both poultry litter biochar and biosolids biochar but only to a limited extent (~28 and 20%, respectively), and there was virtually no further removal for the rest of the experiment. In contrast to these controls, the initial removal of pendimethalin with dithiothreitol and either biochar was more pronounced due to both adsorption and reduction, and the removal continued throughout the course of the experiment. In 120 min, 95 and 92% of pendimethalin was removed, respectively, clearly illustrating the ability of these biochars to enhance pendimethalin transformation. Interestingly, unlike pendimethalin, trifluralin was removed slowly from water in dithiothreitol-free controls containing only poultry litter or biosolids biochar (Fig. 3c, d). Whether this was due to slower adsorption kinetics of trifluralin than that of pendimethalin or higher reactivity of trifluralin is not clear. If these biohars contained a constituent(s) (as discussed in *Possible reaction mechanisms*) that could potentially serve as reductant, the latter possibility would be consistent with the finding of Wang and Arnold [29], who observed faster abiotic reduction of trifluralin than pendimethalin. Compared with the controls, trifluralin reduction by dithiothreitol was enhanced by either poultry litter or biosolids biochar, although the extent of enhancement was modest relative to pendimethalin (Fig. 3c, d).

To confirm the reductive transformation of pendimethalin and trifluralin, GC-MS analysis was conducted for water

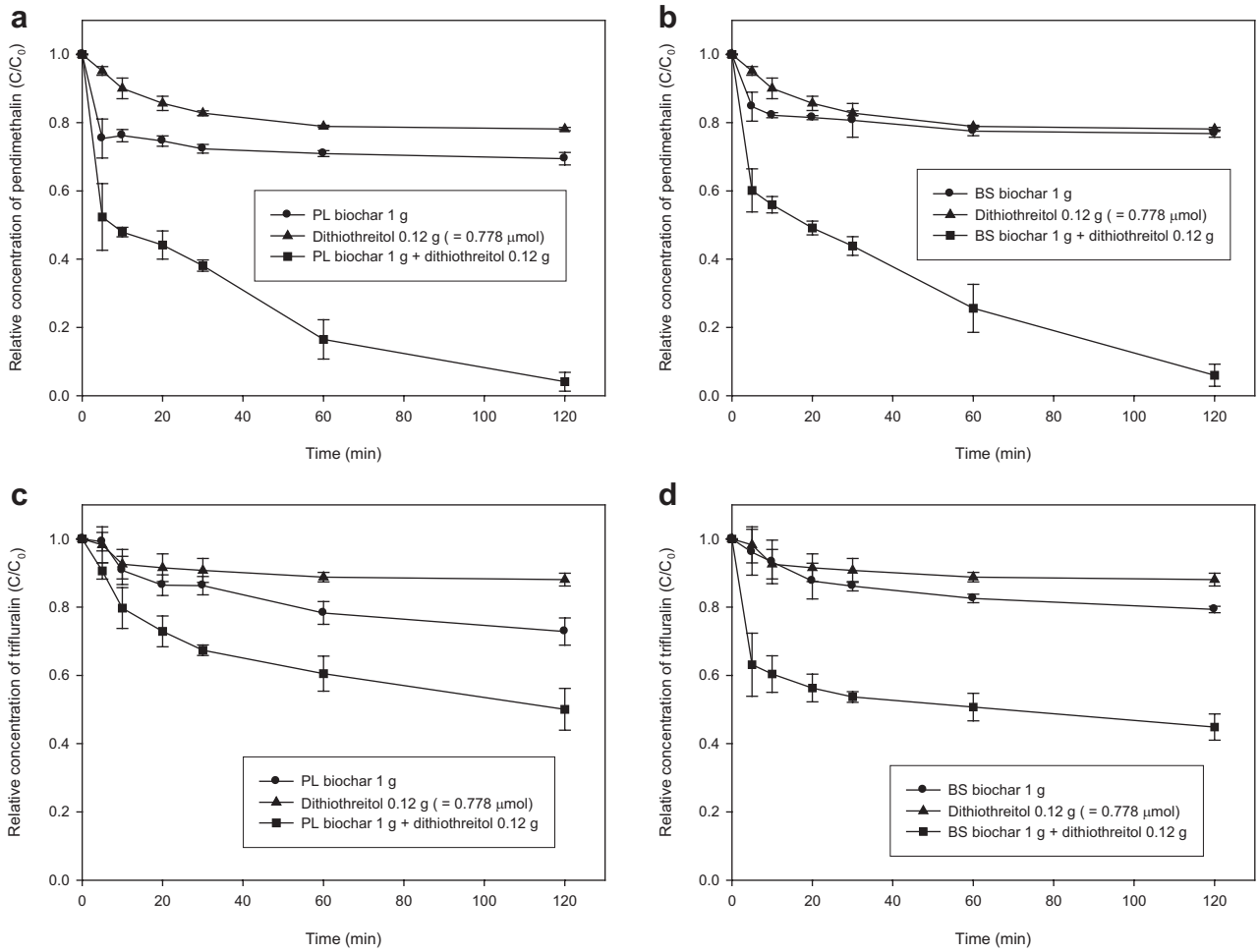


Fig. 3. Biochar-mediated reduction of pendimethalin and trifluralin by dithiothreitol. (**a**) Poultry litter (PL) biochar-pendimethalin, (**b**) biosolids (BS) biochar-pendimethalin, (**c**) PL biochar-trifluralin, (**d**) BS biochar-trifluralin. Data points are the average of duplicate samples, and error bars represent one standard deviation.

samples collected after 120 min. For sorption and reduction controls, we did not observe any possible reduction products of pendimethalin and trifluralin by GC–MS. In the presence of dithiothreitol and poultry litter biochar, we identified a potential reduction product of trifluralin. As reported by Klupinski and Chin [30] and by Wang and Arnold [29], abiotic reduction of trifluralin can result in many possible products through either reduction of the nitro groups or cyclization. Only relatively hydrophobic products could be identified by the hexane extraction and GC-MS analysis used in this study. The GC-MS results suggest that 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)-1*H*-benzimidazole was formed with poultry litter biochar and dithiothreitol (Fig. 4), a cyclization product that was also produced during trifluralin reduction by goethite-bound Fe(II) [29,30]. Identification of this product only in reactors containing both a reductant and a biochar, but not in any of the sorption and reduction controls, supports the notion that the enhanced removal of trifluralin shown in Figure 3 was due, at least in part, to reductive transformation promoted by the biochars. No reduction product of pendimethalin was identified by hexane extraction and GC–MS analysis. Pendimethalin was presumably transformed through reduction of the nitro groups [29,31], which would have produced the more polar and less extractable amino compounds. Extraction using a solvent with a hydrogen-donating property may be necessary to recover the amino products.

Biochar-mediated reduction of DNT and RDX

In a previous study we showed that reduction of DNT and RDX could be markedly enhanced in the presence of BC such as graphite and diesel soot [23]. In the present study, we assessed the possibility of poultry litter biochar to promote the reduction of these energetic compounds. As shown in Figure 5, DNT and RDX were transformed only slowly by dithiothreitol in aqueous solution in the absence of biochar. Similar to pendimethalin, DNT was adsorbed to biochar rapidly but was not removed further without dithiothreitol. In comparison, RDX was similar to trifluralin in that it was quickly adsorbed, as suggested by the initial precipitous drop in aqueous concentration, and gradually removed throughout the experiment in the presence of poultry litter biochar alone. While this removal could be due to either slow adsorption or transformation, the latter may be more probable given that the poultry litter biochar had a relatively small surface area (2.3 m^2/g) but contained elements that could be redox-active (discussed below). With both dithiothreitol and biochar, removal of both DNT and RDX from solution was

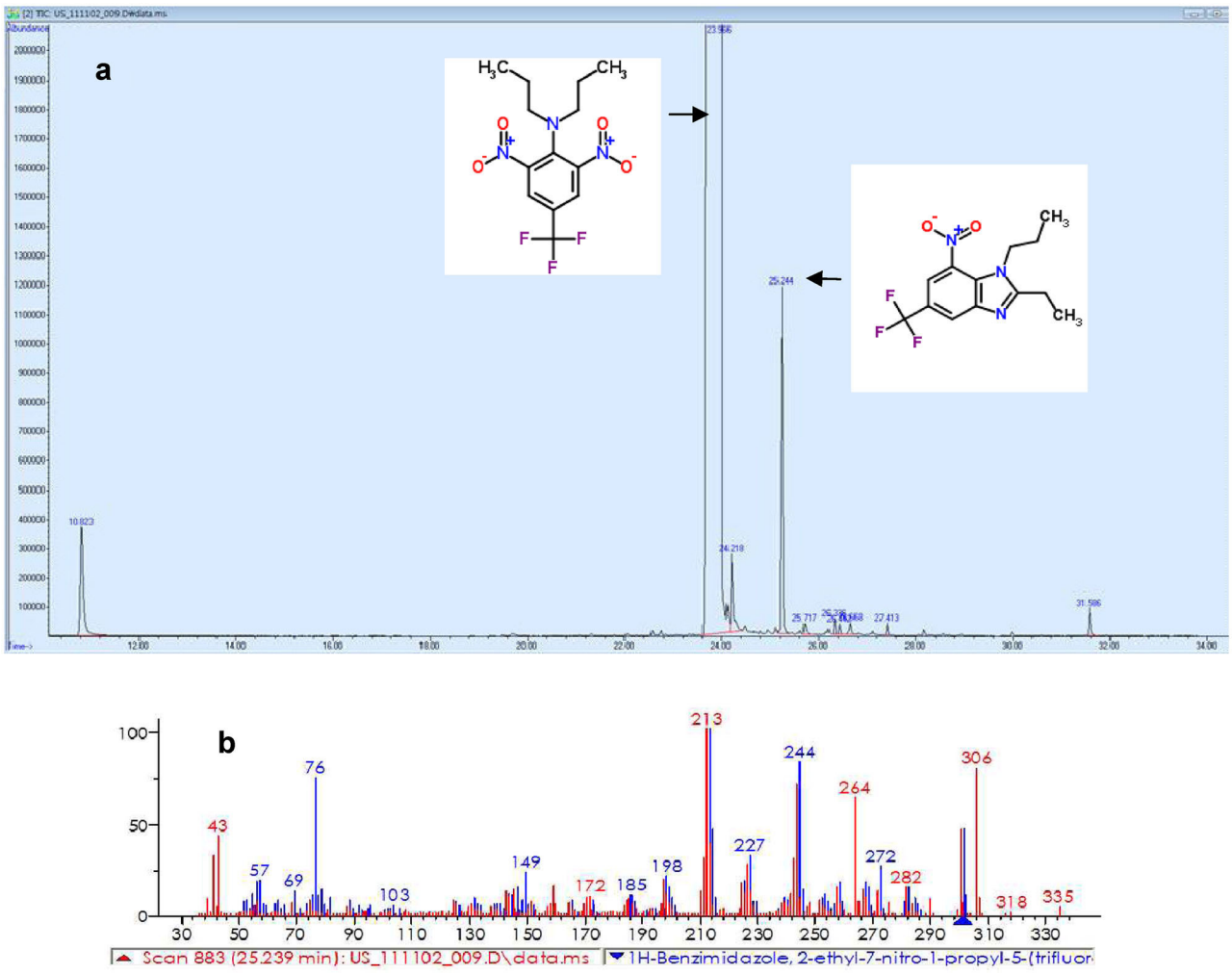


Fig. 4. (**a**) Gas chromatogram of hexane extract of trifluralin solution with dithiothreitol and poultry litter biochar after reaction for 120 min. Peaks corresponding to trifluralin and a possible cyclization product are labeled. (**b**) Mass spectrum of the cyclization product (retention time = 25.24 min, 93.9% match).

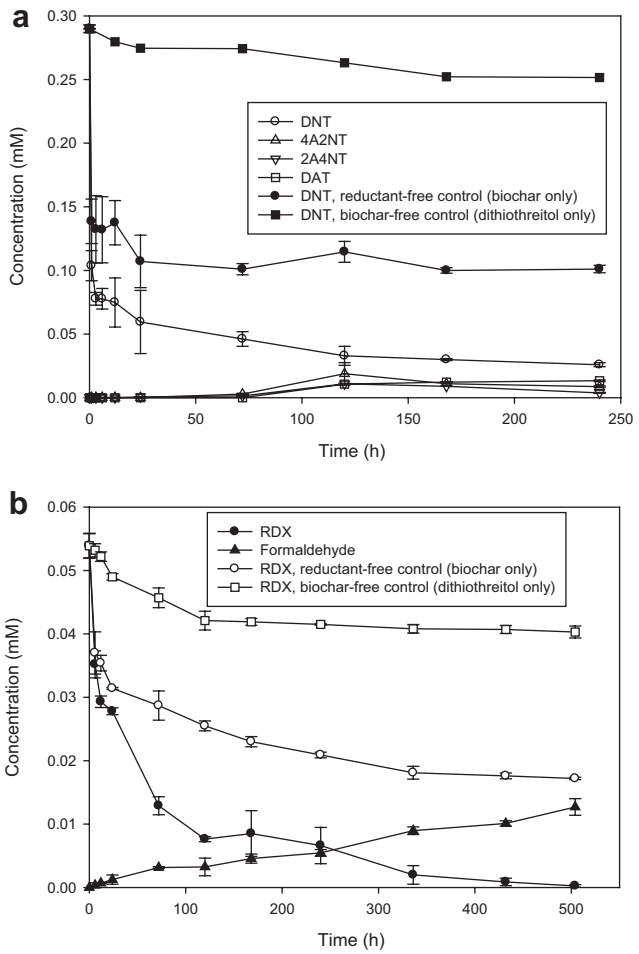


Fig. 5. Poultry litter biochar–mediated reduction of (**a**) 2,4-dinitrotoluene (DNT) and (**b**) hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in the presence of dithiothreitol. Data points are the average of duplicate samples, and error bars represent one standard deviation. DAT = 2,4-diaminotoluene; 4A2NT = 4-amino-2-nitrotoluene; 2A4NT = 2-amino-4-nitrotoluene.

enhanced. In addition, the reduction products of DNT (2A4NT, 4A2NT, and DAT) and RDX (formaldehyde) were detected only when biochar and dithiothreitol were both present. This result parallels that with soot and graphite [23] and clearly demonstrates that biochar can promote the reductive transformation of nitro explosives.

Possible reaction mechanisms and environmental implication of biochar

Taken together, our results suggest that similar to other BC materials such as graphite, soot, and GAC, biochar can play dual roles, that is, as an adsorbent and a redox catalyst, to influence the fate of organic chemicals such as nitro herbicides and explosives. While the adsorptive property of biochar can be ascribed to the condensed carbon formed during pyrolysis [16,19,21], its catalytic ability could have arisen from at least three possible structural components. First, as we had proposed previously for soot and graphite [23,32], the microscopic graphene moieties in biochar may serve as both adsorption and redox reaction sites, due to their high affinity for aromatic compounds [21,22] and their ability to transfer electrons to adsorbed reactants [30]. The presence of graphite in both biosolids and poultry litter biochars (Fig. 1) and their similar catalytic effect to high-purity graphite (Fig. 5, [23]) support this mechanism. A second possibility involves redox-labile surface functional groups, such as (hydro)quinone. Quinone moieties have been suggested to catalyze the reduction of nitro and azo compounds [25,33]. In contrast to high-purity graphite, both poultry litter and biosolids biochars contained a substantial amount of oxygen, as shown in Table 2. Therefore, the possible involvement of surface quinone functions cannot be ruled out, although how these hydroquinone groups could transfer electrons to nitro molecules adsorbed elsewhere in biochar (especially on condensed carbon surface) remains to be explained. Because of the complex compositions of the biochars, still a third possibility exists where redox-active metals, such as Fe, Cu, and Mn (Table 3), could have been involved in the enhanced reduction of nitro herbicides [29,30]. Note that the second and third mechanisms (i.e., hydroquinones and reduced metal ions) might be responsible for the slow removal of trifluralin and RDX in the sorption (biochar-only) controls. It should be noted that in the present study we did not provide scientific evidence to directly support the suggested possible mechanisms. Therefore, this remains to be explored in future work.

As we continue to explore more sustainable solutions to the many daunting challenges facing society, beneficial use of excess biomass will become increasingly essential for environmental management. Because of the many compelling impetuses aforementioned—from mitigating climate change and boosting energy production to managing nutrients and wastes and improving soil and water quality—biomass pyrolysis, and thus biochar production, will likely become a more adopted practice in the future. Consequently, it is imperative that we develop an understanding of the potential impacts of biochar as it becomes more ubiquitous in various natural and engineered environments.

Our results suggest that, when applied to agricultural soil, biochar may alter the fate and possibly shorten the residence time of nitro herbicides by promoting their transformation, in addition to reducing the availability and transport of these compounds through sorption. Similar to GAC [34,35], biochar has been proposed as an adsorbent to decrease the concentrations and bioavailability of organic and metallic pollutants [17,36,37]. The present study further suggests that biochar may also be applied to promote the degradation of organic compounds including agrochemicals, explosives, and potentially other nitrogenous compounds such as azo dyes [38] and nitrate esters [26,39]. For example, in shooting ranges, proving grounds, and other military installations where soil and groundwater are contaminated with explosives, biochar may be used to accelerate the breakdown of these compounds. Finally, biochar may play a role in the natural attenuation of redox-labile contaminants in reducing environments, in a manner similar to other types of BC [23]. Indeed, BC has recently been implicated in the abiotic reduction of pesticides in sediment porewaters in the Prairie Pothole Region [31].

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