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Marked changes in herbicide sorption–desorption upon ageing of biochars in soil

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HIGHLIGHTS

- Fresh biochars undergo rapid ageing process with contact time in soil.
- Fresh biochars in soils exhibited high sorption and non-singular sorption–desorption isotherms.
- Aged biochars in soil showed singular sorption–desorption isotherms for atrazine.
- At 10 t ha^{-1}, biochars in a Ferrosol lost their high sorption capacity in three years.
- Herbicide application rates may need to be frequently adjusted after biochar addition to soils.

GRAPHICAL ABSTRACT

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ABSTRACT

We studied the sorption–desorption behaviour of two herbicides (diuron and artrazine) in a soil rich in Fe and Al oxides (Ferrosol), either amended freshly with two different types of biochars or that contained biochars aged under field conditions. Standard batch sorption–desorption experiments were conducted on soil samples freshly amended with two biochars, (namely, poultry litter – PL and paper mill – PM sludge) as well on those collected from field 32 months after biochar application. Soils that were freshly amended with biochars @ 10 t ha^{-1} showed a two (PM) to five (PL) fold increase in sorption of herbicides as compared with that in the unamended soil. For example, the fresh amendments with PL biochar at 10 t ha^{-1} led to a highly significant ($P < 0.001$) increase in the Freundlich sorption coefficient (K_f) of atrazine; i.e. 20.71 ($n = 0.40$) as compared with 4.02 ($n = 0.70$) for the control soil. Sorption was reversible in the unamended soil but sorption–desorption hysteresis was prominent in the soil amended with fresh biochars. In contrast, the soil containing aged biochars (at 10 t ha^{-1}) exhibited sorption–desorption properties that were statistically similar to that of the control soil, especially for atrazine. Ageing of biochars in the soil over a 32 months period reduced the sorption capacity by 47% (PM) to 68% (PL) for diuron. These findings may have implications for herbicide efficacy in biochar amended soils.

1. Introduction

The amendment of biochar to soil, especially farmland, is advocated both as an important means of sequestering carbon, and also to improve soil fertility [1,2]. In many instances, biochar has been found to possess a high affinity for organic pollutants. For example, Yang and Sheng [3] reported that the level of diuron adsorbed by wheat char/ash (produced by burning in an open field) was 400–2500 times greater than that of a silty loam soil (2.1% organic carbon – OC). Biochar has been shown to be an effective sorbent for several herbicides including acetochlor, atrazine, ametryn, benzonitrile, diuron and simazine [4–6]. The highly sorptive nature of biochar can be either beneficial or problematic depending on how the material is utilized. In the case of its agronomic

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application to farmland, the sorptive nature of biochar can influence the bioavailability and biodegradation of pesticides [7–10]. Indeed, several studies in recent years have demonstrated that application of biochars to soil can significantly compromise the effectiveness of soil applied pesticides. For example, Yang and Sheng [11] showed that effectiveness of diuron herbicide was severely reduced in soil amended with chars. Similarly, Xu et al. [12] reported that residues of rice straw burned in an open field significantly decreased the herbicidal power of clomazone against barnyard grass. More recently, based on dose–response curves, Nag et al. [13] quantified the extent of such effects on two herbicides (atrazine and trifluralin) with different modes of action. They reported that for an effective control of ryegrass in a soil freshly amended with 10 t ha^{-1} of biochar (top 10 cm soil) a 3.5 times higher atrazine application rate was required compared to that in unamended soil. Similarly, Graber et al. [14] reported that to achieve full nematicidal activity, at a biochar amendment level of 26 t ha^{-1} in soil, the dose of dichloropropene fumigant had to be doubled.

The above studies have been performed on soils receiving fresh applications of biochars and it is not clear if, and how rapidly, the ability of biochars in sorbing pesticides will change with residence time in soil. Given the highly reactive nature of biochar surfaces, it is expected that biochars in soils may undergo a myriad of biogeochemical interactions and access to sorption sites on biochars may be blocked with time [15–17]. Therefore, the so-called “aged” biochars may have very different properties than freshly applied biochars in soils [18] and consequently their inactivation potential for pesticides may change with time in soil. Among the very few published studies relating to this aspect, Yang and Sheng [19] reported that the ageing of ash in soil for a period of 12 months did not lead to a differential diuron sorption. Similarly, Jones et al. [20] noted that after two years of residence time of a biochar in a soil, the sorption and degradation behaviour of simazine was comparable, suggesting that the effects of biochar on herbicide behaviour did not change in that time period. Currently, there is little understanding of how long the biochars may maintain their extraordinary ability to inactivate soil applied herbicides or pesticides in soils.

The objectives of this study were (i) to study the sorption–desorption behaviour of atrazine [6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and diuron [*N*-(3,4-dichlorophenyl)-*N*,*N*-dimethyl-urea] on two distinct biochars freshly applied to a soil and (ii) to quantify the changes in both sorption and desorption behaviour that occurred due to “ageing” of biochars in the soil. A soil rich in iron oxides, classed as a Ferrosol [21], was freshly amended with two biochar types and the sorption–desorption behaviour of the herbicides was compared with that on the same biochars aged for 32 months in soil under field conditions.

2. Materials and methods

2.1. Materials

Atrazine (98.1% purity) was obtained from ChemService, Inc. (West Chester, PA) and diuron (99.5% purity) was obtained from Sigma Aldrich Inc. (Steinheim, Germany) and used as received. Dried calcium chloride was obtained from Ajax Chemicals (Auburn, NSW).

2.2. Biochars and soil

Two biochars were produced by Pacific Pyrolysis Pty. Ltd. using a continuous 300 kg h^{-1} pilot slow-pyrolysis unit located at Somersby, NSW (Australia). The first biochar was derived from paper mill sludge (PM) and the second from poultry litter (PL). Both biochars were produced at a highest treatment temperature of 550 °C and at a heating rate of 5–10 °C min^{-1}. Analysis of some of the properties of biochars before application to the field soil is provided in Table 1. Additional information on the characteristics of PM has been previously reported by Joseph et al. [18].

Table 1
Key properties of the two biochars used in this study.

Analysis[b]	Unit	Poultry litter biochar	Papermill sludge biochar
pH (CaCl$_2$)	pH units	8.9	6.8
EC	dS m^{-1}	6.1	1.3
Specific surface area	m^2 g^{-1}	3.14	6.13
Total carbon	%	42	38
Total nitrogen	%	2.6	2.5
KCl extractable ammonium-N	mg kg^{-1}	9.4	3.3
KCl extractable nitrate-N	mg kg^{-1}	0.45	<0.2
Phosphorus	%	2.4	0.56
Bray [b]1 phosphorus	mg kg^{-1}	1020	180
Colwell phosphorus	mg kg^{-1}	3700	840
Potassium	%	2.8	0.41
Calcium	%	4	11
CaCO$_3$ equivalent	%	8.8	18
Aluminium	cmol(+) kg^{-1}	<0.03 ([a]LOR)	0.19
Calcium	cmol(+) kg^{-1}	4.3	14
Potassium	cmol(+) kg^{-1}	44	5.7
Magnesium	cmol(+) kg^{-1}	2.8	3.4
Sodium	cmol(+) kg^{-1}	13	2
CEC	cmol(+) kg^{-1}	64	25

[a] LOR refers to limit of reporting.
[b] Analyses were carried out using standard published methods [21].

Soil was obtained from a biochar field trial at Wollongbar Primary Industries Institute (28°50′S, 153°25′E; elevation 140 m), Wollongbar, New South Wales, Australia. The soil is a highly permeable red Ferrosol derived from basalt [21], with a bulk density of 1010 kg m^{-3}. The soil was an acidic Ferrosol (pH 4.3; 1:5 CaCl$_2$) with 4.5% total organic carbon content; total Fe 8.4%, total Al 6.7%; 0.04 dS m^{-1} Electrical Conductivity (Table 2). Field plots were amended with the PL in October 2007 at rates of 10 t ha^{-1} (equivalent to ca. 1% w/w following incorporation to 100 mm) and 50 t ha^{-1}. In an adjacent trial, PM was amended @ 10 t ha^{-1} only, there was not a 50 t ha^{-1} amendment in the original experimental plan for this biochar. Biochar originally used to amend the soil was stored in a sealed glass container with Teflon lined lid in a minus 20 °C freezer. These field plots were part of a biometrically designed agronomic trial and were cropped with sweet corn (*Zea mays* L.) and faba bean (*Vicia faba L.*). Three replicate plots of each treatment were sampled by taking 5 cores from the 0–100 mm profile and compositing these. The soil sampling was conducted 32 months after the application of biochar, providing almost 3 years of ageing time to biochars in soil. In addition, soil was sampled from 3 control plots (0–100 mm) and combined. Both the soil and biochars were air-dried, ground and passed through a 2 mm sieve. For sorption experiments the biochars that were originally used in the field trials were applied to the control soil at an application rate of 10 t ha^{-1} only.

2.3. Analysis of soils and biochars

For soil analysis, three soil cores (50 mm diameter) to 100 mm depth were taken from each field plot (*n* = 3), air-dried, composited and passed through a 1 mm sieve prior to analysis. Soil and biochar chemical analyses were undertaken in a NATA (National Association of Testing Authorities, Australia) laboratory accredited to ISO17025.

Table 2
Analysis of soils from control and biochar amended plots 32 months following amendment.

Analysis	Unit	Un-amended soil	Soil + poultry litter biochar 10 t ha^{-1}	Soil + poultry litter biochar 50 t ha^{-1}	LSD (5%)	Soil + papermill sludge biochar 10 t ha^{-1}	LSD (5%)
Total carbon	%	4.5	4.7	5.4	0.27	4.6	0.23
Total nitrogen	%	0.47	0.49	0.54	0.04	0.45	0.03
Phosphorus	%	0.12	0.14	0.18	0.02	0.13	nd
Bray #1 phosphorus	mg kg^{-1}	10.8	18.1	89.3	16.1	15.3	6.0
Potassium	%	0.02	0.02	0.02	nd	0.02	nd
Calcium	%	0.07	0.10	0.20	0.03	0.09	0.03
EC	dS m^{-1}	0.04	0.05	0.05	0.005	0.05	nd
pH (CaCl$_2$)	pH units	4.3	4.5	5.0	0.21	4.4	0.21
CEC	cmol(+) kg^{-1}	5.4	6.2	9.3	0.9	5.2	1.2

Total C and N were measured by Dumas combustion using an Elementar vario MAX CN analyser with combustion chamber set at 900 °C and oxygen flow rate of 125 mL min^{-1}. The pH was measured in 0.01 M CaCl$_2$ (1:5) according to the Australian standard method 4B2 [22]. Major cations and CEC were assessed using exchange into 1 M NH$_4$OAc described in method 15E1 [22]. Phosphorus was tested using Bray #1 extraction as described in Australian method 9E2 [22] and available orthophosphate P by Colwell bicarbonate extraction, described in method 9B1 [22]. Liming value measured as carbonate equivalent was determined using method 19A1 [22]. The acid-extractable elements and metals were determined according to USEPA method 6010 using a Varian 720-EC, Inductively Coupled Plasma, Optical Emission Spectrometers (ICP-OES). Estimates of soil properties under each treatment were obtained after accounting for natural and extraneous sources of variation as described by Gilmour et al. [23]. The data processing was accomplished by use of the ASReml package [24] in the R environment [25].

The specific surface area of both PL and PM biochars were determined using nitrogen adsorption isotherms at 77.3 K and interpreted by the BET equation as described by Brunauer et al. [26]. The contribution of biochar in OC content of amended soils was quantified using solid-state ^{13}C cross polarization (CP) nuclear magnetic resonance (NMR) spectra, acquired with magic angle spinning (MAS) at a ^{13}C frequency of 50.3 MHz on a Varian Unity200 spectrometer. The soils were treated with hydrofluoric acid (HF) – prior to analysis by NMR spectroscopy. Samples were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 5000 ± 100 Hz in a Doty Scientific MAS probe. A 1-ms contact time and a 1-s recycle delay were used, and 4000 transients were collected for each spectrum.

2.4. Sorption kinetics and sorption–desorption of herbicides in biochar-amended soils

The time required for sorption equilibrium was initially determined using soil with aged biochar applied at 10 t ha^{-1} and a herbicide concentration of 1 mg L^{-1} in soil solution ratio of 1:5. Simultaneously, hydration of the soil/biochar mixture was initiated through the addition of 4 mL 0.01 M CaCl$_2$ to 1 g of amended soils (both aged and freshly spiked) in Oak-Ridge Nalgene® centrifuge tubes (50 mL) for atrazine and glass centrifuge tubes (25 mL) for diuron. The chosen centrifuge tubes were found previously to absorb minimal pesticide from solution. The solutions were mixed on an end-over-end shaker for up to 72 h prior to the commencement of the sorption experiments. This is because being hydrophobic, biochar needs to be prehydrated [27,28]. No difference in sorption beyond 20 h pre-equilibration, was noted. The use of calcium chloride in solution assists in the flocculation of small biochar particles upon centrifugation. After the hydration step, sorption kinetics were determined by adding 1 mL of 5 mg L^{-1} herbicide concentration in 0.01 M calcium chloride solution (in less than 1% ethanol) and the tubes were allowed to shake in the dark for up to further 24 h period. Three tubes were removed at 0, 2, 4, 6, 8, 16, 24 h, centrifuged at 1998 g (K = 7823) for 20 min, with the supernatant filtered using 33 mm 0.45 μm Millex Durapore PVDF syringe filters. Preliminary experiment showed minimal sorption of the pesticides in question to the filter used (less than 5%). The use of control samples meant that any sorption to the filter was corrected for in final calculations. Equilibration of biochar sorption occurred within 24 h for both PM and PL (data not shown).

In two separate experiments, the sorption and one step desorption of atrazine and diuron to soil with aged biochar or to a soil with freshly amended biochar was monitored using the method described above in accordance with OECD Technical guideline 106 [29]. Four treatments for soil with aged biochar were tested, namely: control soil (no biochar), PM at an application rate of 10 t ha^{-1} and PL at two application rates of 10 t ha^{-1} and 50 t ha^{-1}. PM was not applied at 50 t ha^{-1} in the original field tests. The 50 t ha^{-1} treatment was not tested for the freshly applied biochar to soil treatments. The soil samples with aged and fresh biochars were equilibrated overnight (20 h), as previously, following OECD protocol [29]. The centrifuge tubes were prepared in triplicate, with six herbicide concentrations used to determine sorption and desorption of atrazine and diuron. These concentrations differed between biochar aged in soil and freshly amended soil. Sorption on biochar aged in soil was monitored at concentrations of 0.5, 1, 2, 3, 4 and 5 mg L^{-1}, whilst sorption on freshly amended soils was measured at 1, 2, 4, 6, 8 and 10 mg L^{-1}. Control tubes consisted of solutions without sorbent and no changes in herbicide concentration were detected during the equilibration. The amounts of adsorbed atrazine and diuron were calculated indirectly from the difference between the average amount measured in the control solution and the amount measured from equilibrium aqueous phase concentrations.

At the end of sorption experiment, the supernatant was decanted and 5 mL of 0.01 M calcium chloride was added to initiate desorption. The tubes were then mixed end-over-end shaker for a further 24 h period, the supernatant extracted and herbicide concentrations were analysed. The volume of solution remaining entrained from the previous step was calculated by difference of weights. From the known concentration in solution at the start of desorption, the calculations for the actual amount desorbed were corrected.

2.5. Analysis of atrazine and diuron

Analysis of herbicide concentrations in soil solution was carried out using separate analytical methods on an Agilent 1100 Series HPLC System with Grace Altima HP C18 column, 250 mm × 4.6 mm, 5 μm at a flow rate of 1 mL min^{-1}. Isocratic elution was achieved for atrazine with 40% acetonitrile in water and for diuron with 60% acetonitrile in water. PDA detection was set at 220 nm for atrazine and 254 nm for diuron. Under these conditions, atrazine was found to elute at a retention time of approximately 10.2 min, with diuron

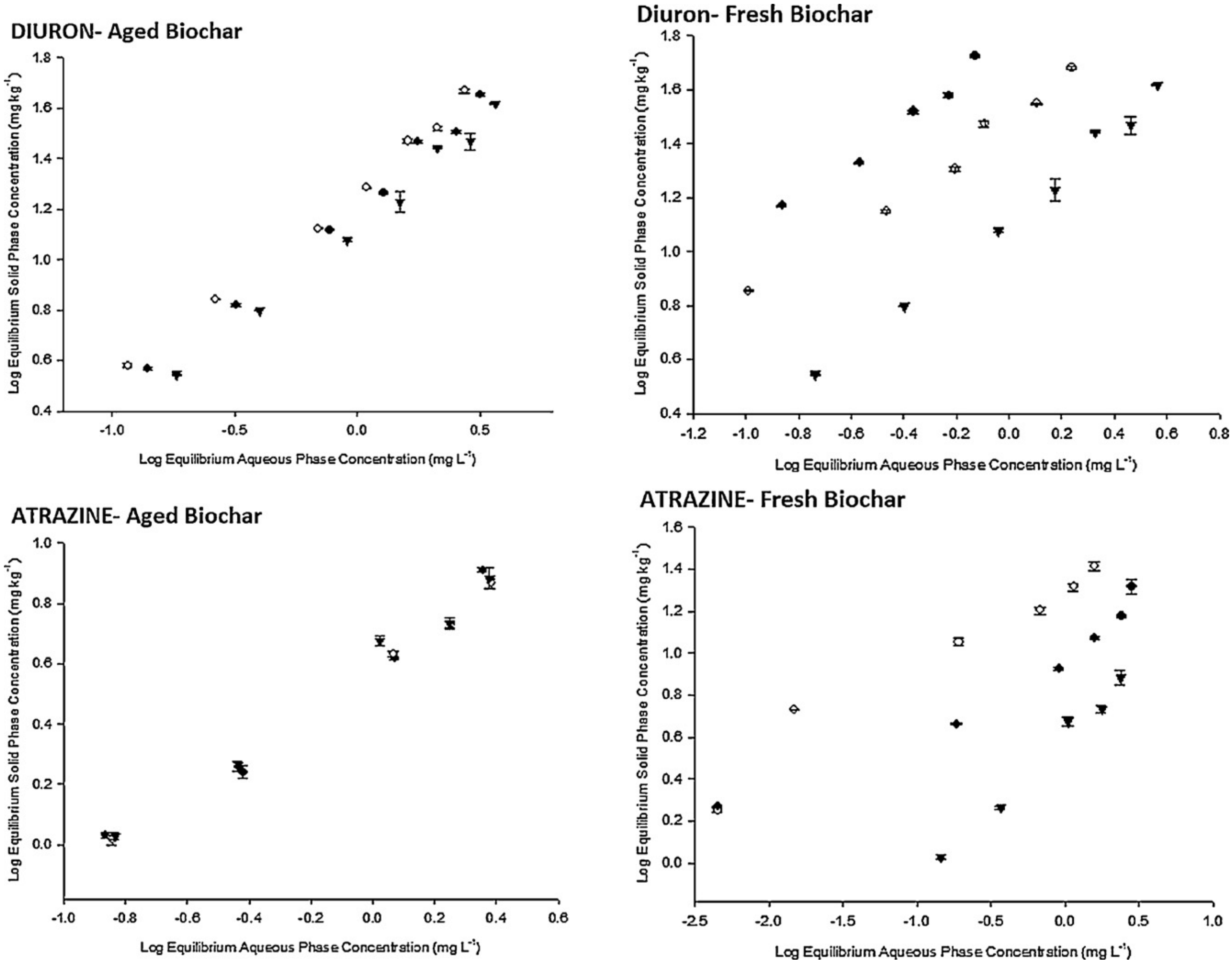

Fig. 1. Sorption isotherms of diuron and atrazine for the aged and freshly amended soils at an application rate of 10 t ha^{-1} for two biochars, PL (○) and PM (●) and the control soil (▼). Error bars represent standard error of the mean of triplicate samples ($n = 3$). Symbols may cover error bars.

eluting at approximately 5.1 min. Identification of compounds was achieved by comparing their retention time values with those of standards. The sample injection volume was 50 μL. Data was collected and processed using Agilent Chemstation software. The limit of detection for atrazine was 0.045 mg L^{-1}, whilst the limit of detection for diuron was 0.05 mg L^{-1}.

2.6. Statistical analysis

The sorption–desorption data of control soils and biochar-amended soils were fitted to either the linear or the Freudlich isotherm model commonly employed in such studies [30]. Statistical differences between curves were determined by comparing the coefficients obtained by pooling the two sets of data under consideration with those obtained from summing the coefficients for the two sets of individual data. Statistical analysis was undertaken in Microsoft© Excel 2007, using the regression package to undertake analysis of variance.

3. Results

3.1. Sorption on soils amended with fresh and aged biochars

Both biochars effectively sorbed atrazine and diuron in soils freshly amended with biochars (Fig. 1). The isotherms for the biochar amended soils were highly non-linear and fitted to the Freundlich model well. The fresh amendments with PL biochar @ 10 t ha^{-1} led to a highly significant ($P < 0.001$) increase in the Freundlich sorption coefficient (K_f) for atrazine of 20.71 ($n = 0.40$) compared with 4.02 ($n = 0.70$) for the control soil and for diuron of 60.20 ($n = 0.73$) compared with 13.38 ($n = 0.81$) for the control soil (Table 3). This amounted to an increase in sorption capacity of 448% for diuron and 515% for artrazine, not taking into account the concentration dependence of sorption (decreased n value in the presence of biochar). The addition of PM biochar to the soil @ 10 t ha^{-1} showed a smaller increase in K_f value of for atrazine (10.59; $n = 0.35$) and diuron (31.12; $n = 0.67$) (Table 3). Between the two herbicides, diuron showed comparatively lesser non-linearity for all freshly amended biochar and soil combinations (Table 3). For both atrazine and diuron, the control soil was found to show the lowest nonlinearity. For both herbicides, the differences between control soils and soil freshly amended with biochars were highly significant ($P < 0.001$).

The sorption isotherms on the biochars aged in soil at the application rate of 10 t ha^{-1} are shown in Fig. 2. Sorption of diuron by both aged biochars was found to be significantly ($P < 0.001$) higher than that in the control soil. The K_f value for the control soil was 13.38 ($n = 0.81$), whereas the values for soils with aged biochars were 16.63 (0.79) for the PM and 19.30 (0.78) for PL. In contrast, the sorption of atrazine by the soil with aged biochar was not significantly different to that of the unamended control soil. The K_f

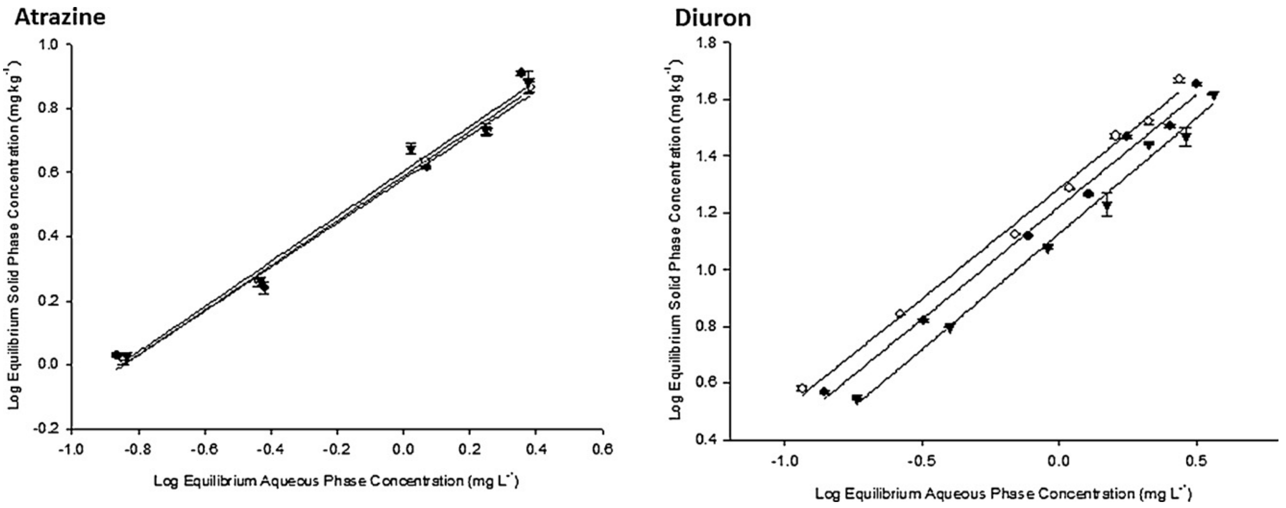

Fig. 2. Sorption isotherms of atrazine and diuron for the unamended control soil (▼) and biochar aged in soil at an initial application rate of 10 t ha^{-1} for two biochars, PL (○) and PM (●). Error bars represent standard error of the mean of triplicate samples ($n = 3$). Symbols may cover error bars.

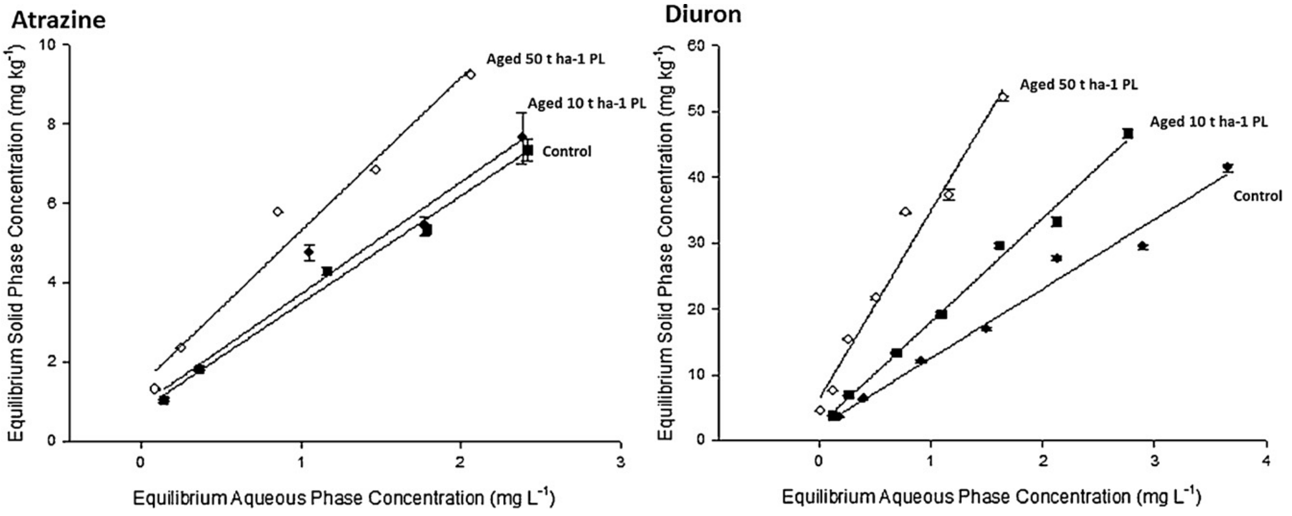

Fig. 3. Sorption isotherms of atrazine and diuron for the unamended control soil (●) and soil with aged PL biochar at 10 t ha^{-1} (■) and 50 t ha^{-1} (○). Error bars represent standard error of triplicate samples ($n = 3$). Symbols may cover error bars.

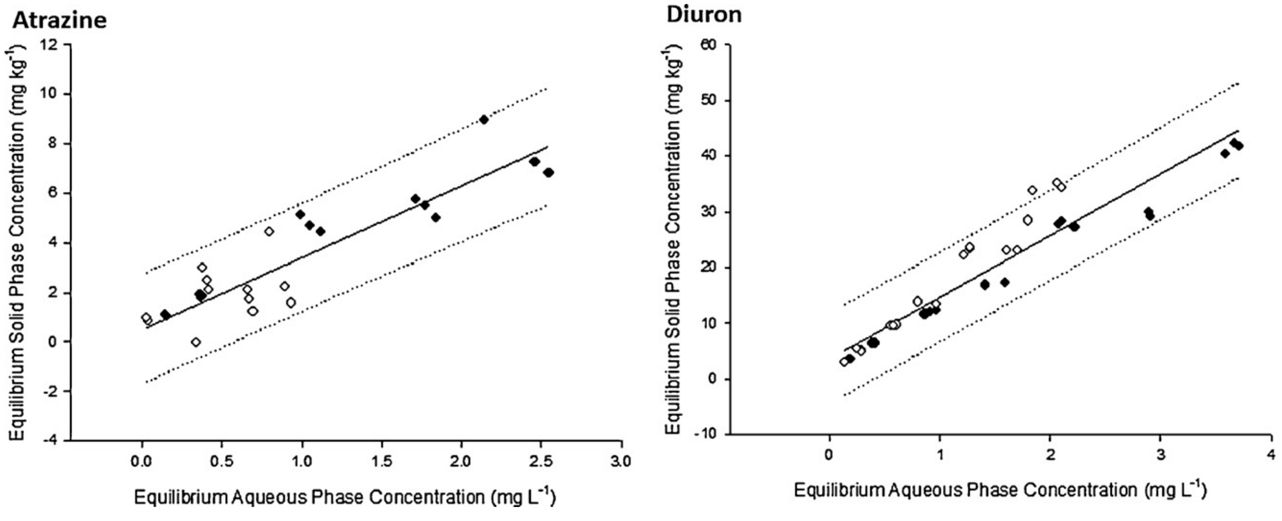

Fig. 4. Sorption (●) and desorption (○) isotherms of atrazine and diuron for control unamended soil. Dotted lines represent 95% confidence interval.

Table 3
Freundlich parameters for sorption isotherms of atrazine and diuron in soils freshly added biochar and with biochar aged in soil. Values in each of the four quadrants with the same letter are not significantly different between groups at $p < 0.05$.

	Fresh						Aged					
	K_f	n	R^2	K_{oc}			K_f	n	R^2	K_{oc}		
Atrazine												
Control soil	4.02	0.70	0.99	90	a		4.02	0.70	0.99	90	a	
Papermill sludge 10 t ha^{-1}	10.59	0.35	0.94	141	b	***	3.89	0.70	0.98	84	a	
Poultry litter 10 t ha^{-1}	20.71	0.40	0.96	265	c	***	3.80	0.69	1.00	81	a	
Poultry litter 50 t ha^{-1}	–	–	–	–			5.80	0.62	0.99	107	b	**
Diuron												
Control soil	13.38	0.81	0.99	301	a		13.38	0.81	0.99	301	a	
Papermill sludge 10 t ha^{-1}	31.12	0.67	0.99	415	b	***	16.63	0.79	0.99	361	b	*
Poultry litter 10 t ha^{-1}	60.20	0.73	0.98	771	c	***	19.30	0.78	0.99	411	c	*
Poultry litter 50 t ha^{-1}	–	–	–	–			36.72	0.72	0.98	680	d	***

[*] Level of significance for $P < 0.05$.
[**] Level of significance for $P < 0.01$.
[***] Level of significance for $P < 0.001$.

value of the control soil was found to be 4.02 whereas the corresponding values for the soil with aged PM and PL biochars were 3.89 and 3.80, respectively (Table 3). It is noteworthy that the values of the Freundlich exponent (n) in soils with aged biochars at 10 t ha^{-1} application rate were found to be similar to those in unamended soil. When the K_{oc} values of fresh and aged PL biochar are compared for diuron, a decrease of almost 200% of the sorption capacity was noted when the biochar aged in the soil. For atrazine, however, the decrease in sorption capacity upon ageing of the biochar in soil was even greater, being >300%. These comparisons based on K_{oc} values are concentration dependent and are valid for only unit solution concentration, due to isotherms being non-linear. The soil with the aged PL biochar @ 50 t ha^{-1} showed a significantly ($P < 0.001$) higher sorption capacity for diuron than the control soil, with a K_f value of 36.72, compared to 13.38 for the unamended soil (Fig. 3; Table 3). Similarly, a significantly ($P < 0.05$) higher K_f value was found for atrazine (5.80) compared with that for the unamended soil (4.02), but the difference was smaller in this case.

3.2. Desorption in soils with aged and fresh biochars

With regard to atrazine, the sorption and desorption isotherms for the unamended control soil (Fig. 4) were found to overlap (i.e. no statistical difference). This indicates that sorption in unamended soil was largely reversible. However, a hint of hysteresis was noted in the case of diuron. The soil containing aged PL biochar (@ 10 t ha^{-1}) showed essentially reversible sorption (sorption and desorption isotherms essentially overlapping) for atrazine similar to than found in the unamended soil (Fig. 5). In contrast, hysteresis was evident in the sorption–desorption isotherms of freshly amended soils (Fig. 5). The effect was of similar nature for the PM biochar (data not shown). However, in the case of diuron the sorption–desorption isotherms showed hysteresis in soils with both freshly added as well as aged biochars.

4. Discussion

The application of fresh biochar to soil resulted in a significant ($P < 0.001$) increase in sorption capacity of soil for atrazine and diuron compared to the unamended control soil. Furthermore, the sorbed herbicides were not readily desorbed from soils amended with the fresh biochars, which may influence pesticide bioavailability [8,13]. However, the increase in sorption as well as sorption–desorption hysteresis was found to be dependent not only on the types and application rates of biochars but also the chemistry of herbicide molecule. For example, the freshly applied PM biochar in soil had a much lower affinity for diuron and atrazine per unit mass than the PL biochar. Even when the OC content differences were taken into considerations, the K_{oc} values were markedly different between the two biochars. Among the two herbicides, diuron has much greater affinity (3–6 times that for atrazine in a corresponding treatment) for soil and the biochars (Table 3). This

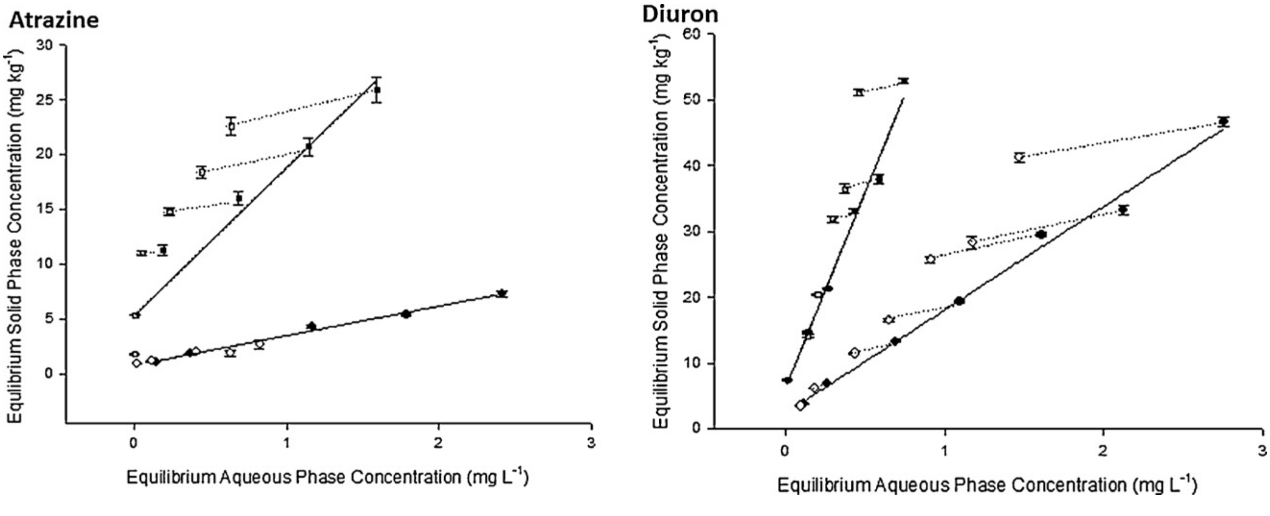

Fig. 5. Sorption (● and ■) and desorption (○ and □) isotherms of atrazine and diuron for biochar aged in soil (● and ○) and freshly amended soils (amended with PL at 10 t ha^{-1}) (■ and □). Error bars represent standard error of the mean of triplicate samples ($n = 3$). Symbols may cover error bars.

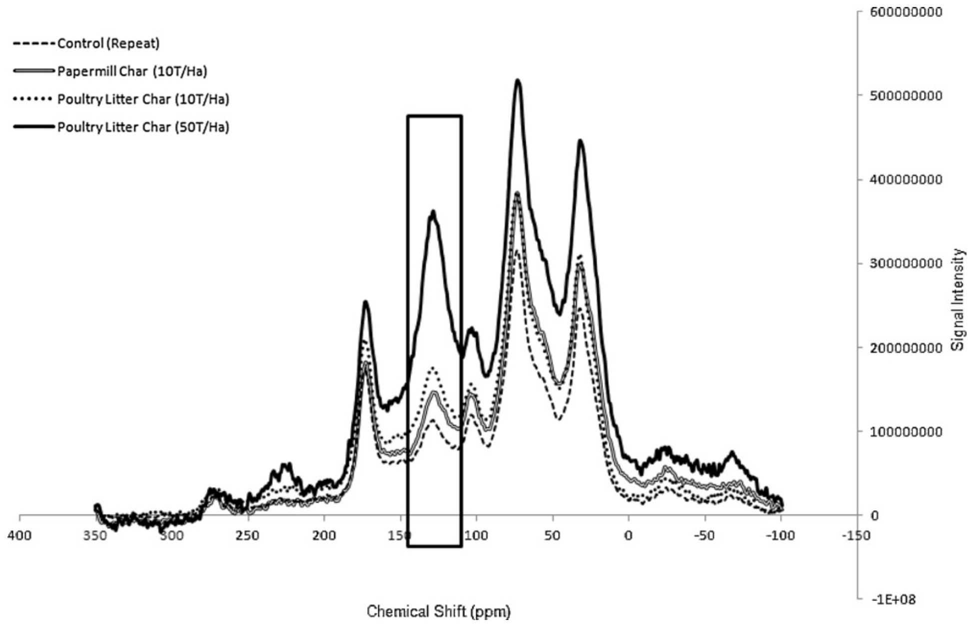

Fig. 6. Solid state C13 NMR spectra (CP-MAS) characterizing the chemistry of the organic carbon in control and biochar treated soils, measured 32 months after the biochar amendment to the Ferrosol. The main peak of interest is the aromatic signal centered at around 130 ppm (as shown), which includes the aromatic structures of charcoal, as well as those of other soil organic matter components, especially lignin.

may have contributed to the observed differences between the two herbicides in their sorption–desorption behaviour in amended soils.

The increase in sorption and its dependence on biochar type, as well as resistance to desorption of sorbed herbicides on freshly applied biochar, is consistent with previous reports in literature [3,4,8,10,31–34]. The differences in sorption ability of biochars often depend on the differences in their characteristics (e.g. aromaticity, specific surface area) which are a function of biomass source and the production technology employed [4,5]. In this study, both biochars were produced using the same production methodology and the biomass source was the only difference. The OC content and specific surface area (SSA) of the two biochar were not markedly different but the pH differed by >2 units (Table 1). The difference in pH, however, is not expected to directly influence the sorption of diuron (an unionisable compound) and also of the basic atrazine, which has a pK_a of 1.7 and not expected to be sensitive to experimental pH environment.

The key objective of this study was to establish if biochars, once in contact with soil, would lose their outstanding ability to sorb soil-applied pesticides over time. The results presented here show that the affinity of both biochars for the two herbicides studied here decreased markedly with ageing in soil. In fact, the sorption of atrazine on soils amended with biochar 32 months earlier was found to be statistically similar to that in the control soils, especially at the 10 t ha^{-1} initial application rate of biochar. In the case of diuron, however, the sorption in biochar-amended soil was still higher than that in the control soil. Ageing of biochars for about three years in soil resulted in a decrease in the sorption capacity by 47% (PM) to 68% (PL) for diuron and 63% (PM) to 82% (PL) for atrazine. However, at a higher application rate (50 t ha^{-1}) the PL biochar still retained its higher sorption capacity relative to the control soil for both herbicides. This demonstrates that the effectiveness of a biochar's sorption capacity after an extended period of time is likely to be dependent on the initial application rate of biochar to the soil. The sorption of diuron to the biochars aged in soil for 32 months differed from that of atrazine, in that there was a statistically significant difference between the aged soil and the control soil. This reflects the inherent sorption properties of the two compounds, as on average diuron has about four time greater sorption affinity for organic carbon than atrazine [35].

To address the question, i.e. if the reduction in amended soil's sorption capacity is due to ageing or any possible loss of biochar, we carried out ^{13}C solid sate NMR spectroscopy on unamended as well as the soils amended with two types of biochars at different rates. In the absence of any widely accepted or standard method to quantify the biochar content of soils, to authors knowledge, the NMR spectroscopy was considered as the best option to make a relative assessment of the aromatic fractions of OC in soil samples from field, 32 months after the biochar application. Recognizing that NMR may underestimate the biochar content (due to lack of full observability of chars), the NMR spectra presented in Fig. 6 were generally consistent with the amounts of biochar originally applied to the soil. For example, the soils with 10 t ha^{-1} biochar had significantly more pronounced fraction of aromatic carbon (indicated by chemical shifts from 90–160 ppm) than the control soil and the 50 t ha^{-1} PL biochar treatment had nearly 5 times higher aromatic carbon than the 10 t ha^{-1} treatment, indicating proportionally higher biochar content. Since the biochars were incorporated in soil and a crop cover was present for most of the time, any off-site movement losses are likely to be small, if any. Whilst some loss of biochars from the soil cannot be ruled out, the following suggest that the loss in sorption capacity of biochars with time in soil is most likely due to the changes that may have occurred on biochar surfaces. Firstly, the difference in aromatic OC in biochar amended soil (10 t ha^{-1}) is much higher than control soil, yet we see the sorption–desorption behaviour of herbicides in soil with aged biochar reverting almost to that in the control soil, especially for atrazine. Furthermore, it is noteworthy that the non-linearity of the isotherms (indicated by n values in Table 3) for both herbicides decreased upon ageing of biochar at 10 t ha^{-1} in soils to the extent that these were comparable to those in control soil. The nature of interactions that may have caused a reduction in biochar sorption capability are discussed below.

Due to their strong affinity for organic compounds and inorganic ions, biochars are likely to undergo a range of biogeochemical interactions in soil and as a result their properties are expected to change with time in soil. Oxidation of biochar surfaces together with adsorption of partially oxidized organic matter may lead to oxidised functional groups on biochar increasing CEC in soils [36,37]. Sorption of environmental constituents, especially natural organic matter (NOM) and oxidation reactions are major contributors in ageing of biochars [37]. It is also possible that with time mineral and organic matter in soil may cover the reactive surfaces of biochar [38] and thereby mask the true sorption capacity of biochars for organic compounds such as pesticides and other agrochemicals. Indeed, the examination of biochars, collected from our study site, by X-ray photo electron spectroscopy, Scanning electron microscopy and Transmission electron microscopy, revealed that soil mineral incorporation of biochar surface occurred within first year in soil, albeit localized on specific sites on the biochar surface [39]. Also other studies on sorption of pesticides before and after removal of paramagnetic materials (e.g. sesquioxides) from char surfaces by HF treatment (needed for NMR studies) have shown that sorption on natural charcoal in soils increases by a factor of 2–3 after such a treatment [40,41]. Ahangar et al. [40] proposed that the sites of sorption on organic matter such as charcoal can be blocked by its interaction with soil components, especially the organo-mineral interactions in soils. Singh and Kookana [41] showed that the removal of paramagnetic materials from the surface of C in soil using 2% HF followed by a UV treatment led to a marked increase in the sorption of carbaryl and ethion in soil. In their study, the HF + UV treatment is expected to have resulted in the removal of minerals and oxidation of organic matter at the surface of the biochar. The above examples highlight that the buildup of soil minerals at the surface of biochar and the presence of easily oxidisable organic fractions may block the sites where sorption is most likely to occur [18]. The reduction of sorption capacity of aged biochars to levels comparable with the unamended soil after less than three years of residence time in soil appears to be due to the above organo-mineral interactions with biochars in soils.

In summary, the results from our study indicate that despite the high deactivation (sorption) potential of freshly applied biochars for herbicides in soils, they are likely to lose their sorption capability over time, depending on the nature of soil, biochars and the rate of biochar application. These results may have major agronomic implications. Previous studies, based on freshly applied biochars in soils, demonstrating that much higher rates of applications of herbicides may be needed to gain an effective weed control, [11,13] may not be valid for biochars aged in soils. Due to changing properties of biochars in soils with time, the herbicide application rate may need to be adjusted differently for different herbicides every cropping season until biochars lose their extraordinary herbicide deactivation capacity. After nearly three years of ageing in soils, the biochar did retain certain sorption/deactivation potential (indicated by high sorption and low desorption) for some herbicides (e.g. diuron). Clearly, more work is needed to establish the length of time during which the biochars in soil may maintain their outstanding ability to sorb pesticides and thereby influencing their efficacy.

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