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Biochars mediated degradation, leaching and bioavailability of pyrazosulfuron-ethyl in a sandy loam soil

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ABSTRACT

Burning of crop residues after harvest is a quick, cheap and an easy way to manage the large quantities of agricultural biomass for timely preparation of the field for next crop. Conversion of the crop harvest residues into biochars and incorporating them back in the same field can address the issue of land clearing, waste utilization and nutrient conservation but, any amendment to the soil changes its physico-chemical characteristics and can affect the fate of soil applied herbicides. The present study reports the effect of low (400 °C) and high (600 °C) temperature wheat (WBC) and rice (RBC) straw biochar's amendment on leaching, degradation and bioavailability of pyrazosulfuron-ethyl (PYRAZO) in a sandy loam soil. The PYRAZO was poorly retained in the control soil column where 78% of the soil-applied herbicide leached out of the control soil column. Biochars addition (0.02 and 0.05 g kg^{-1}) significantly reduced the PYRAZO leaching by affecting herbicide's breakthrough time and its maximum concentration in leachate.

The biochars reduced PYRAZO degradation, both in the flooded and the nonflooded soils; but, effect was more pronounced in the nonflooded soils. The effect of biochars on PYRAZO's leaching and degradation was the function of the nature of feedstock, biochar production temperature and its dose. The high temperature biochars were more effective in reducing the leaching and degradation of PYRAZO than the low temperature biochars and the rice biochars were better than the wheat biochars. The bioavailability of PYRAZO was assayed by its effect on mustard seedlings and results suggested that low temperature biochars, even at 0.05 g kg^{-1} level, had no negative effect on herbicide efficacy. However, high temperature biochars significantly reduced the herbicide bioavailability and higher concentration of PYRAZO was required for the desired effect. These findings are relevant in assaying the fate of PYRAZO in the biochar amended soils.

1. Introduction

Pyrazosulfuron-ethyl (ethyl-5-(4,6-dimethoxypyrimidin-2-ylcarbamoylsulfamoyl)-1-methylpyrazole-4-carboxylate) (PYRAZO) belongs to the sulfonylurea group of herbicides. PYRAZO is recommended for the selective control of pre-emergent and early post-emergent grassy and broad leaved weeds in direct seeded and transplanted rice (Mathew et al., 2013). PYRAZO is weakly acidic in nature (*pKa* - 3.7) and has lower aqueous solubility (14.5 mg L^{-1}) than its other counterparts metsulfuron-methyl (*pKa* - 3.3, K_{OW} – 0.018; aqueous solubility – 2.79 g L^{-1}) and sulfosulfuron (*pKa* - 3.5, K_{OW} – 0.17; aqueous solubility – 1.63 g L^{-1}), which are highly soluble in water, have low octanol water partition coefficient and are poorly sorbed, especially in alkaline soils with K_f values ranging from 0.21–1.88 (metsulfuron-methyl) and 0.37–1.17 (sulfosulfuron) (Singh and Singh, 2012). These characteristics make them prone to leaching and runoff losses and they have been detected in the surface water as well as in the ground water (Sarmah et al., 2000; Sondhia, 2009; Singh et al., 2014). Even though PYRAZO has a high octanol-water partition coefficient (P_{ow} - 3.16), has been shown to be poorly sorbed in the same sandy loam soil that was used in the present study with a Freundlich adsorption coefficient (K_f) of 0.22 μg $^{(1-1/n)}$ g^{-1} $mL^{1/n}$ (Manna and Singh, 2015). Application of wheat and rice straw biochars, even at agronomically feasible rates (0.01–0.02 mg kg^{-1}), significantly increased the herbicide sorption and the rice straw biochars were nearly 1.5 times better than the corresponding wheat straw biochars (Manna and Singh, 2015). No information is available on PYRAZO's leaching behavior in soils. However, Chu et al. (2002) reported half-life values of 16–27 days in soil and 9–16 days in water; while, Singh et al. (2012) reported half-life ($t_{1/2}$) of 5.4 and 0.9 days in soil and water, respectively. Ok et al. (2012) observed that temperature affected PYRAZO's persistence in the paddy water and the $t_{1/2}$ in spring and summer were 3.1 and 1.6 days,

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Table 1
Physico-chemical properties of soil and biochars.

Biochar	pH	Organic carbon (%)	Cation exchange capacity (meq 100 g^{-1})	Electrical conductivity (dS m^{-1})	C (%)	N (%)	Surface area (m^2 g^{-1})	Porosity (cc g^{-1})
Soil	8.1	0.46	15.4	0.62	–	–	–	–
WBC400	9.3	37.5	62.0	8.92	40.42	0.74	10.15	0.016
WBC600	10.4	40.5	62.6	10.39	42.98	0.61	20.38	0.026
RBC400	9.8	39.0	86.5	11.86	43.26	1.15	13.53	0.024
RBC600	11.1	41.7	45.3	14.27	46.07	0.94	12.60	0.034

respectively. Application of rice husk gasification residues (RHGR) reduced the PYRAZO half-life in paddy water from 3 days (control) to 2.2 days (Ok et al., 2015); however no information is available on its persistence in biochar-amended soils.

Application of biochars, pyrolyzed products prepared from crop residues, enriches the recalcitrant portion of soil organic carbon and provides additional soil conditioning benefits like reducing soil bulk density, enhancing water holding capacity, managing soil acidity and increasing nutrients retention due to their high cation exchange capacity, high surface area and acidic surface groups. Biederman and Harpole (2013), based on meta-analysis of 371 independent studies, reported that despite variability introduced by soil and climate, addition of biochar to soils resulted in increased aboveground productivity, crop yield, soil microbial biomass, rhizobia nodulation, plant potassium, soil phosphorus, soil potassium, total soil nitrogen and total soil carbon. However, Jeffery et al. (2017) showed that biochars have no effect on crop yield in temperate latitudes, but 25% average increase in yield was observed in the tropics. Biochars have also shown high retention of pesticides (Cabrera et al., 2011; Zhang et al., 2013; Xiao and Pignatello, 2015; Mandal et al., 2017; Manna et al., 2017) thereby resulting in reduced downward mobility of contaminants (Lü et al., 2012; Li et al., 2013; Giori et al., 2014). Because of higher pesticide retention in biochar-amended soils there are reports of increased persistence and reduced bioefficacy of pesticides (Yang et al., 2006; Nag et al., 2011). Yang et al. (2006) reported that 1% biochar reduced bioavailability and degradation of diuron while, Xu et al. (2008) reported reduced bioefficacy of clomazone against barnyard grass in the presence of residues from open burning of rice straw. Nag et al. (2011) reported that at 1% biochar levels, the GR_{50} (herbicide dose required to reduce weed biomass by 50%) value for atrazine and trifluralin increased by 3.5 and 1.6 times, respectively. Plant uptake of chlorpyrifos, fipronil and carbofuran from soils by chive and spring onion markedly decreased with increasing biochar content in soil (Yu et al., 2009; Yang et al., 2010). Sopeña and Bending (2013) reported no effect of biochar on pesticide degradation. Qiu et al. (2009) and Jablonowski et al. (2013) showed enhanced microbial degradation of pesticides in biochar-amended soils and was attributed to stimulation of soil microflora by nutrients provided by biochars. These results suggest that effects of biochars on pesticide degradation are dependent on the characteristics of pesticide, biochar and soil and dose of biochar.

The rice-wheat and rice-rice cropping systems contribute ~65% of the crop residues. These residues are burnt in the fields by the farmers after crop harvest because burning is a quick, cheap and an easy way to dispose large quantities of agricultural biomass to prepare fields for sowing the next crop (Jain et al., 2014). Conversion of these crop residues into biochar and incorporating them back in the same field will simultaneously address the issues of open burning of crop residues, waste utilization and nutrient recycling. Most of the literature available on effects of biochars on pesticide's fate has used biochar doses > 0.5% and information on agronomically feasible dose is limited. The objective of this research was to determine the effect of wheat and rice straw biochars on degradation, leaching and bioavailability of PYRAZO in a sandy loam soil. The agronomically feasible dose of 0.02 g kg^{-1} and a higher dose of 0.05 g kg^{-1} were used for evaluating the realistic effect of biochars on PYRAZO's fate.

2. Materials and methods

2.1. Chemicals

Analytical grade (> 98% purity) pyrazosulfuron-ethyl (PYRAZO), 5-(aminosulfonyl)-1-methyl-1*H*-pyrazole-4-carboxylicacid (SAA) and ethyl 5-(aminosulfonyl)-1-methyl-1*H*-pyrazol- 4-carboxylate (SAE) were supplied by the United Phosphorus Ltd. (UPL), Mumbai, India.

2.2. Biochar

The biochars prepared from the rice straw (*Oryza sativa* L.) and the wheat straw (*Triticum aestivum* L.) at 400 and 600 °C were used in the study (Manna and Singh, 2015). Briefly, straw dried at 60 °C for 24 h to < 10% moisture content was roughly chopped to 5 cm pieces. It was pyrolyzed in a muffle furnace equipped with digital temperature controller, tar trap, water cooling system and N_2 purge (1.5 mL min^{-1} flow rate) to ensure an oxygen-free atmosphere. The heating rate was 3 °C min^{-1} and residence time was 1 h at 400 °C or 600 °C and the respective wheat and rice straw biochars were named as WBC400, WBC600, RBC400 and RBC600. Prior to further analysis the biochar samples were milled to pass a 0.154 mm sieve (100 BSS). The pH of biochar was measured at 1:10 biochar to water (*w/v*) ratio using glass-calomel electrode, electrical conductivity (EC) using electrical conductivity meter at 1:10 biochar to water (w/v) ratio and cation exchange capacity was estimated by normal ammonium acetate (pH = 7.0) method (Table 1) (Jackson, 1967). Total organic carbon of biochars was estimated by TOC analyzer (Elementar vario TOC). The specific surface area (SSA) and pore volume of biochars were measured from N_2 isotherms at 77 K using an automated gas adsorption analyzer (Quantachrome NOVA 10.01, Quantachrome Instruments, Florida, USA). Prior to analysis the samples were degassed at 473 K for 10 h under vacuum. The N_2 adsorbed per gram of biochar was plotted against the relative vapour pressure (P/P_0) of N_2 and data was fitted to the Brunauer, Emmett, and Teller (BET) equation to calculate surface area. The pore volume was estimated from N_2 adsorption at $P/P_0 \sim 0.5$.

2.3. Soil

Sandy loam soil from the experimental farm of the Indian Agricultural Research Institute, New Delhi, India was used in the study. The soil was collected from the surface 0–15 cm depth, air dried in shade, ground to pass through 2 mm sieve and stored for one year in polythene bags at room temperature (27 ± 4 °C). The physico-chemical characteristics of soil were determined using standard analytical procedures as mentioned above. The pH was measured at 1:2 soil:water ratio (*w/v*), organic carbon (OC) content was estimated by Walkley and Black method (Jackson, 1967) and soil mechanical fractions employing the Bouyoucos hydrometer method.

The soil was mixed with the biochars (WBC400, WBC600, RBC400 and RBC600) at 0.02 and 0.05 g kg^{-1} levels and the respective treatments were named as WBC400(0.02), WBC400(0.05), WBC600(0.02), WBC600(0.05), RBC400(0.02), RBC400(0.05), RBC-600(0.02) and RBC600(0.05). The biochar doses were chosen based on the assumption that entire straw (biomass) obtained from rice or wheat field was converted to biochar and was applied back to the same field. An

average 5–6 t ha^{-1} straw is generated during wheat or rice cultivation and assuming straw to biochars conversion efficiency of 60%, approximately ~4 t ha^{-1} biochar will be obtained and will correspond to 0.02 g kg^{-1} application rate.

2.4. Degradation studies

The effect of biochar amendment (0.02 and 0.05 g kg^{-1}) on degradation of PYRAZO in sandy loam soil was studied under flooded and nonflooded conditions. The soil + biochar (25 g) mixture was taken in sterilized 100 mL culture tubes while biochar unamended soil served as the "no biochar control". The soil samples were supplemented with sterile distilled water to maintain non-flooded (60% water holding capacity) and flooded conditions (a standing water column of 4 cm was maintained). Degradation experiments in nonflooded and flooded soils were run separately. Prior to the herbicide application soil samples were incubated at 27 ± 1 °C for 10 days for mixture stabilization and to obtain anaerobic conditions in the flooded soils. The soil samples were amended with PYRAZO (50 μg, ~200 times of the recommended dose of 22 g ha^{-1}) in 0.01 mL acetone while untreated samples served as control and each treatment was replicated thrice. The soil samples were incubated at 27 ± 1 °C in an incubator and water lost during incubation was maintained by supplementing it every week. The soil samples (3 tubes per treatment) for PYRAZO degradation were withdrawn at regular intervals (up to maximum of 80 days) for residues extraction and analysis by the high performance liquid chromatography (HPLC).

2.5. Leaching studies

The effect of biochars on PYRAZO's leaching behavior was studied in the packed and the intact soil columns. The packed columns [300 mm (l) × 59 mm (i.d.)] were constructed from polyvinyl chloride (PVC) pipes, which rested in Buchner funnel fitted with 60 μm nylon membrane to reduce the dead end volume. The columns (in duplicate) were packed by adding portions of soil (approximately 50 g) and compacting with equal force so as to obtain a uniform bulk density of 1.342 kg L^{-1} for "no biochar column" (biochar amendment did not has much effect on bulk density as mentioned below). The pore volume for soil column was calculated from the difference of mass of soil in fully saturated column and oven dry mass of the soil and the value so obtained for the control soil column was 343 mL per column. To study the effect of biochar amendments on PYRAZO leaching, the upper 15-cm of the column was packed with 0.02 and 0.05 g kg^{-1} biochar (WBC400, WBC600, RBC400 and RBC600) amended soil while lower 15-cm of the column was packed using biochar unamended soil. This setup was used to mimic the field condition where any amendment is mixed with the upper 15-cm plough layer. The bulk densities of the soils for treatments WBC400(0.02), WBC400(0.05), WBC600(0.02) and WBC600(0.05) were 1.341, 1.336, 1.337, and 1.333 kg L^{-1}, respectively, while the respective pore volumes were 346, 348, 342, and 349 mL per column. Similarly, bulk densities of the soils for treatments RBC400(0.02), RBC400(0.05), RBC600(0.02) and RBC600(0.05) were 1.338, 1.331, 1.332, and 1.329 kg L^{-1}, respectively, while the respective pore volumes were 347, 349, 344, and 350 mL per column.

One day prior to PYRAZO application the columns were pretreated with 400 mL of distilled water to minimize variation in the soil water content between the columns. The water was allowed to drain naturally. PYRAZO (100 μg) was applied to the column surface in 0.1 mL acetone in a drop wise manner using Eppendorf pipette so as to cover the entire column surface. The dose of PYRAZO used in the leaching study was ~17 times of the recommended dose (22 g ha^{-1}). After application of the herbicide the columns were left overnight. Before the start of the leaching experiment, the column surfaces were covered with 0.5 cm thick layer of acid washed sand [dissolve organic carbon (DOC) free] to minimize the disturbance of the soil surface and to allow even distribution of water. One day after PYRAZO application, the columns were leached with 1000 mL (equivalent to 320 mm rainfall) of distilled water and natural drainage was allowed. It took ~20 h to complete the experiment. The water was applied with the help of a separating funnel and the application rate of water (~50 mL h^{-1}) was such that a standing water head of approximately 1 cm persisted throughout the leaching. The leachate fractions were collected in approximately 50 mL portions and were analyzed for PYRAZO residues using HPLC. Two columns per treatment for 0.02 and 0.05 g kg^{-1} biochars were run separately.

After leaching, columns were left for 24 h for drainage and then dissected into 5 cm sections. The soil was allowed to air dry for 48 h and the PYRAZO residues were extracted and analyzed by the HPLC.

Further, comparison of PYRAZO leaching behavior was investigated using packed and intact soil columns, without and with 0.05 g kg^{-1} RBC600. The intact soil cores were collected from the I.A.R.I., New Delhi fields by pushing PVC columns into the soil and removing the intact soil core. After bringing the intact soil cores in the laboratory, the top 5 cm soil was removed and was mixed with 0.05 g kg^{-1} RBC600. The biochar mixed soil was repacked in the same column and efforts were made to maintain the bulk density equal to the original column. Similar process was performed for the control column, but no biochar was added. The bulk density and pore volume of control column were 1.29 kg L^{-1} and 288.36 mL per column, respectively, while the respective values for the RBC600(0.05) intact columns were 1.285 kg L^{-1} and 294.12 mL per column. The intact columns were pre-treated with 200 mL distilled water to minimize variation in the soil water content between the packed and the intact columns. The leaching behavior of PYRAZO in the intact soil columns was studied as mentioned above for the packed columns.

2.6. Bioavailability studies

The effect of biochars' amendment on the herbicide availability was evaluated using mustard [*Brassica juncea* (L.) Coss] (var. Pusa Mahak) seedlings, as preliminary screening indicated the mustard to be the most sensitive to PYRAZO among lentil, mustard and green gram. The plastic pots (3.3 cm i.d. × 4.5 cm length) were filled with 50 g of control soil (no biochar) or 0.02 and 0.05 g kg^{-1} WBC400, WBC600, RBC400 and RBC600 amended soils. The concentrations of PYRAZO used in the study were 0.01 (equivalent to recommended dose of 22 g ha^{-1}) and 0.1 μg g^{-1} (10 times higher dose). PYRAZO untreated soil/soil + biochar mixtures served as control and each treatment had three replicates. Five mustard seeds were sown in each pot and kept in natural condition at room temperature and watered on a regular basis. On the 12th day after sowing (DAS) the plants were carefully uprooted and the root and the shoot lengths were measured.

2.7. Extraction

2.7.1. Soil samples

The soil samples were extracted following the method reported earlier by Manna and Singh (2015). Briefly, soil samples (25 g) were transferred to 100 mL stoppered conical flasks, 40 mL of CH_3OH:H_2O (1:1, *v*/v) was added and the contents were shaken on a horizontal shaker for 30 min. The mixture was centrifuged at 4000 rpm for 5 min and the supernatant was filtered using Whatman no.1 filter paper. The soil was re-extracted twice with 20 mL and then 15 mL of CH_3OH:H_2O. The extracts were pooled and diluted with water (25 mL) and adjusted with 6 N HCl to pH 2. The aqueous phase was partitioned twice with dichloromethane (25 mL + 25 mL). The dichloromethane layer was dried over anhydrous sodium sulfate and solvent was evaporated to dryness at room temperature. The residues obtained after solvent evaporation were dissolved in 1 mL acetonitrile for further analysis by HPLC. The recovery of PYRAZO from no biochar control soil at the 0.01, 0.1 and 1 μg g^{-1} addition levels was 75.5, 80.2 and 90.8%,

respectively. The respective values from 0.05 g kg^{-1} RBC600 biochar amended soil were 74.8, 79.2 and 90.5%. The recovery of SAA metabolite at 0.05 and 0.1 μg g^{-1} levels from no biochar control soil ranged from 74.6–83.4% while respective values in 0.05 mg kg^{-1} RBC600 amended soils were 73.8–82.8%. Similarly, recovery of SAE metabolite from the control and 0.05 g kg^{-1} RBC600 biochar-amended soils was 74.6–76.1% (0.01 μg g^{-1}) and 83.4–84.1% (0.1 μg g^{-1}).

2.7.2. Water samples

The water samples (50 mL) were acidified (pH 2) and extracted by partitioning with dichloromethane (25 mL + 25 mL) in a separating funnel (Manna and Singh, 2015). The dichloromethane fraction was dried over anhydrous sodium sulfate, dichloromethane was allowed to evaporate and the residues were re-dissolved in 1 mL acetonitrile for analysis by HPLC. The recovery of PYRAZO from water at 0.1, 0.5 and 1 μg mL^{-1} addition levels was 92.8, 93.1 and 93.4%, respectively.

2.8. Analysis using high performance liquid chromatography (HPLC)

PYRAZO residue in the soil and the water extracts were analyzed using Varian HPLC (model Prostar 210, Varian, Palo Alto, CA, USA) equipped with degasser, quaternary pump, UV detector and connected with rheodyne injection system. The HPLC analyses were conducted using a Lichrospher C-18 stainless steel column [250 mm × 4 mm (i.d.)], acetonitrile: 0.1% aqueous *o*-phosphoric acid (75:25) as a mobile phase at a flow rate 0.7 mL min^{-1} and 242 nm wavelength detection. Under these conditions the retention times (Rt) were: (i) 5-(aminosulfonyl)-1-methyl-1*H*-pyrazole-4-carboxylic acid (SAA)– 3.35 min; (ii) ethyl 5-(aminosulfonyl)-1-methyl-1*H*-pyrazol-4-carboxylate (SAE) – 4.73 min; (iii) pyrazosulfuron-ethyl – 10.67 min. The limit of detection (LOD) of method used for PYRAZO, SAA and SAE were 0.05, 0.01 and 0.01 ppm while corresponding limit of quantification (LOQ) values were 0.01, 0.05 and 0.05 ppm. The standard curves for PRRAZO and SAA/SAE metabolites were linear in the range of 0.01–1 μg mL^{-1} and 0.05–1 μg mL^{-1}, respectively.

2.9. Half-life calculation and statistical analysis

PYRAZO degradation data from all treatments was fitted to the first order kinetic Eq. (1)

$$\ln C_t/C_0 = -kt \quad (1)$$

where, C_0 is the apparent initial concentration of herbicide (μg g^{-1}), C_t is the concentration (μg g^{-1}) after a lapse of time t (days), and *k* is the degradation rate constant. The half-life ($t_{1/2}$) values were calculated from the *k* values using Eq. (2).

$$\text{Half life } (t_{1/2}) = \ln(2)/k \quad (2)$$

The degradation, leaching and bioactivity data was subjected to the statistical analysis (one way ANOVA) using IBM SPSS Statistics for Windows, Version 21.0, Armonk, NY.

3. Results and discussion

3.1. Degradation studies

The Effect of the wheat (WBC400 and WBC600) and the rice (RBC400 and RBC600) straw biochars (0.02 and 0.05 g kg^{-1}) on degradation of PYRAZO in a sandy loam soil under flooded and nonflooded conditions are shown in Supplementary Tables A-G and Fig. 1. Results suggested that in the control soil, the PYRAZO was less persistent in nonflooded soil than flooded soil.

The biochars amendment increased herbicide persistence under the both moisture regimes; but, it was statistically significant in the nonflooded soils. Further, increasing the dose of biochar decreased herbicide degradation and it was more persistent. PYRAZO was more persistent in the rice biochar-amended soils than in the wheat biochar-amended soils. These results can be explained by higher sorption of PYRAZO in the rice biochar-amended soils than the wheat biochar-amended soils (Manna and Singh, 2015).

The persistence data fitted well to the first order degradation equation as the correlation coefficient (r) values were > 0.964 (Table 2, Supplementary Fig. A). Results suggested that half life ($t_{1/2}$) values for PYRAZO degradation in control (no biochar) soil under flooded and nonflooded conditions were 18.2 and 12.8 days, respectively. Application of biochars increased $t_{1/2}$ of PYRAZO under both moisture regimes, but the effect was more prominent under nonflooded conditions. The $t_{1/2}$ of PYRAZO in 0.02 g kg^{-1} WBC400 and WBC600 amended flooded soils were 19.6 and 19.1 days, respectively; while corresponding values in the nonflooded soils were 17.6 and 16.6 days. The $t_{1/2}$ of PYRAZO in 0.02 g kg^{-1} RBC400 and RBC600 amended flooded soils were 23.0 and 24.5 days, respectively, while respective values in the nonflooded soils were 32.7 and 28.6 days. Thus, in nonflooded soils the PYRAZO was more persistent in the RBC-amended soils while under flooded conditions it was more persistent in the WBC-amended soils. Increasing the dose of rice biochars from 0.02 to 0.05 g kg^{-1} further increased the $t_{1/2}$ of PYRAZO in the nonflooded soils (RBC400–37.1 days; RBC600–77.9 days) while no significant effect was observed in the flooded soils (RBC400–24.2 days; RBC600–26.3 days). Earlier, Manna and Singh (2015) reported that PYRAZO's adsorption in this sandy loam soil was higher in the rice biochar-amended soils and sorption increased with the biochar dose and high temperature biochars were more effective than low temperature biochars. In-spite-of the several fold increase in the herbicide adsorption in the biochar amended soils relative to the control, the $t_{1/2}$ of PYRAZO was significantly affected only in the nonflooded soils. Probably, plenty of water in the flooded soils made herbicide desorption easier. Further, flooded soils are predominantly anaerobic in nature and anaerobic microorganisms might have played some role in PYRAZO degradation. These results are significant as PYRAZO is recommended for weed control both in the low land (flooded) and the upland rice (direct seeded rice). Majority of the rice grown in India and worldwide is cultivated under low land conditions; where, even 0.05 g kg^{-1} biochar amendment had no significant effect on PYRAZO degradation. Earlier, Singh and Singh (2011) reported that $t_{1/2}$ of PYRAZO in flooded soils under rice cultivation was 6.9 days, while Chu et al. (2002) suggested $t_{1/2}$ of 16–27 days. No prior reports are available on relative persistence of PYRAZO in flooded and nonflooded moisture regimes or biochar amended soils.

Two metabolites of PYRAZO *viz.*, 5-(aminosulfonyl)-1-methyl-1*H*-pyrazole-4-carboxylic acid (SAA) and ethyl 5-(aminosulfonyl)-1-methyl-1*H*-pyrazol-4-carboxylate (SAE) (Supplementary Fig. B) could be identified in the samples and were quantified using HPLC (Supplementary Tables A–G). PYRAZO gets hydrolyze at sulfonyl urea bridge to produce SAE (ester metabolite) and 2-amino-4,6-dimethoxy pyrimidine (AP), (Supplementary Fig. C); but, metabolite AP could not be identified/quantified due to unavailability of an analytical standard. Metabolite SAE was further hydrolyzed to the corresponding acid (metabolite SAA). In general, the metabolite SAE was obtained in higher amounts than metabolite SAA and concentrations of metabolite SAA was higher in the flooded soils than the nonflooded soils. Further, metabolite SAE was more persistent in the nonflooded soils than the flooded soils. No effect of biochar pyrolysis temperature (400 °C and 600 °C) was observed on the formation/accumulation of both the metabolites.

3.2. Leaching studies

The results of PYRAZO leaching study suggested that in the control (no biochar) packed columns (Fig. 2) PYRAZO was fairly mobile as nearly 78% of the initially applied herbicide was recovered in the leachate (Table 3). The herbicide's breakthrough occurred after percolating 151.16 mL water and the maximum concentration was observed

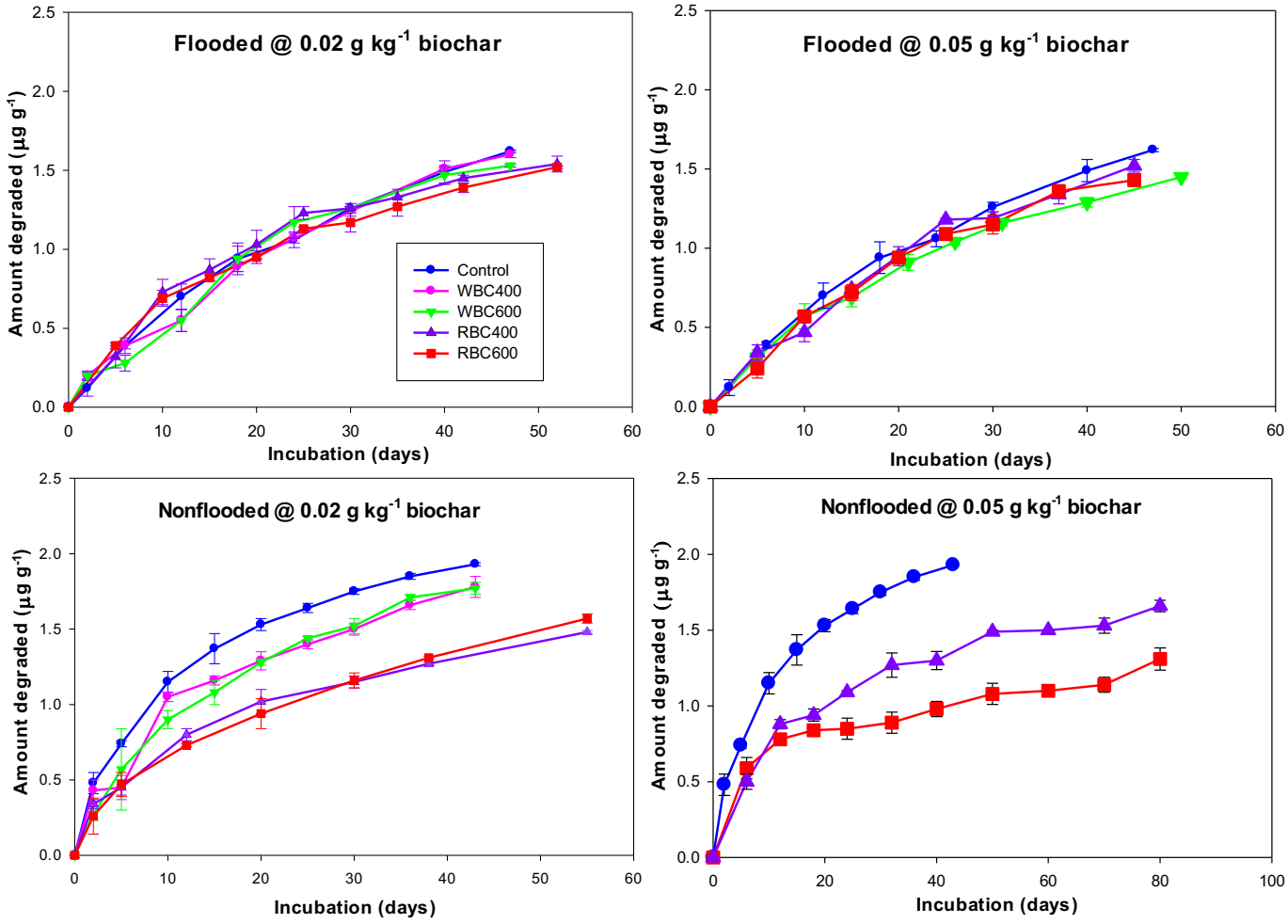

Fig. 1. Degradation of pyrazosulfuron-ethyl in biochar amended soil under flooded and non-flooded moisture regimes. Error bars represent standard deviation.

Table 2
Rate constants (k), correlation coefficient (r) and half-life (t1/2) values for pyrazosulfuron-ethyl degradation in control (no biochar) and 0.02 and 0.05 g kg^{-1} biochar-amended soils.

Treatment	Parameter					
	Nonflooded			Flooded		
	k	r	$t_{1/2}$	k	r	$t_{1/2}$
Control (C0)	0.0540	0.997	12.8^{Aa}*	0.0381	0.997	18.2^{Ba}
WBC400(0.02)	0.0394	0.996	17.6^{Bb}	0.0354	0.996	19.6^{Ca}
WBC600(0.02)	0.0417	0.990	16.6^{Bb}	0.0363	0.995	19.1^{Ca}
RBC400(0.02)	0.0212	0.982	32.7^{Fd}	0.0301	0.989	23.0^{Db}
RBC600(0.02)	0.0241	0.992	28.6^{Ec}	0.0283	0.992	24.5^{Db}
WBC600(0.05)	N.D.	N.D.	N.D.	0.0293	0.996	23.7^{Db}
RBC400(0.05)	0.0187	0.972	37.1^{Ge}	0.0283	0.988	24.2^{Db}
RBC600(0.05)	0.0089	0.949	77.9^{Hf}	0.0264	0.990	26.3^{DEb}

N.D. – Not determined.

* Values followed by different uppercase letters within a row are significantly different at 5% level based on the Duncan's multiple range test performed using SPSS. Similarly, values followed by different lowercase letters within a column are significantly different at 5% level.

after passing 349.6 mL water (1.01 pore volume) through the column. The biochar amendment, even at 0.02 g kg^{-1} level, retarded the downward mobility of PYRAZO, but results varied with the nature/properties and dose of biochars. Breakthrough of PYRAZO from 0.02 g kg^{-1} WBC400 column occurred after passing 386.9 mL water while from 0.02 g kg^{-1} WBC600 column breakthrough happened after passing 490.5 mL water.

Increasing the dose of biochar to 0.05 g kg^{-1} further reduced leaching losses of PYRAZO (Fig. 3). Compared to the PYRAZO breakthrough from the control column after passing 151.16 mL water, breakthrough from 0.05 g kg^{-1} WBC400, WBC600, RBC400 and RBC600 amended columns occurred after passing 441.74 mL (1.31 pore volume), 341.61 mL (0.98 pore volume), 324.19 mL (0.96 pore volume) and 532.32 mL (1.53 pore volume) water, respectively. The maximum PYRAZO concentration from the respective column was observed after percolating 570.21 mL (1.69 pore volume), 573.04 mL (1.65 pore volume), 459.35 mL (1.36 pore volume) and 688.03 mL (1.98 pore volume) water. The biochars' (0.05 g kg^{-1}) amendment significantly reduced the maximum concentration (C/C_0) of PYRAZO in the leachate from 0.333 (control) to 0.251 (WBC400), 0.142 (WBC600), 0.156 (RBC400) and 0.0.049 (RBC600). These results suggested that biochar amendment to soil decreased PYRAZO movement in the soil profile; but, the effect was governed by the nature and dose of biochars. Compared to PYRAZO leaching from no biochar control column, treatments WBC400, WBC600, RBC400 and RBC600 (0.02 g kg^{-1}) reduced the herbicide leaching losses by 9, 39, 45 and 56%, respectively. The corresponding reduction in PYRAZO leaching in 0.05 g kg^{-1} biochar-amended columns was 24, 56, 57 and 66%. Thus, results obtained based on the total amount of PYRAZO recovered in the leachate suggested that the rice biochars were more effective in decreasing the herbicide's leaching losses. Further, the high temperature (600 °C) biochars were more effective than the low temperature (400 °C)

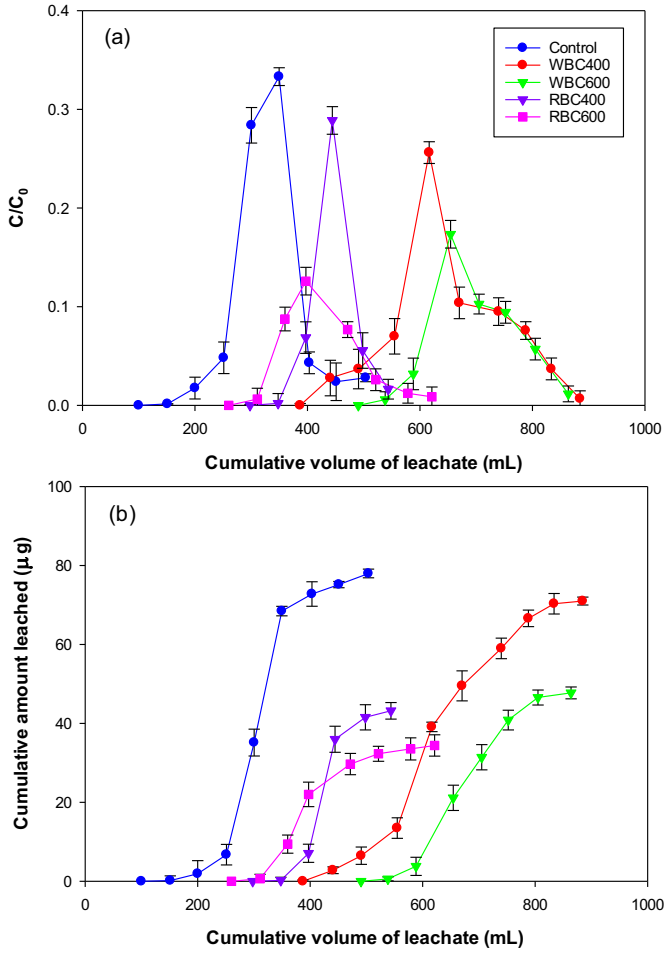

Fig. 2. Pyrazosulfuron-ethyl (a) breakthrough curves and (b) cumulative leaching curves in 0.02 g kg^{-1} biochar amended soil columns. C is the amount recovered in the leachate (µg) while C_0 is the initial amount applied to the column (µg). Error bars represent standard deviation.

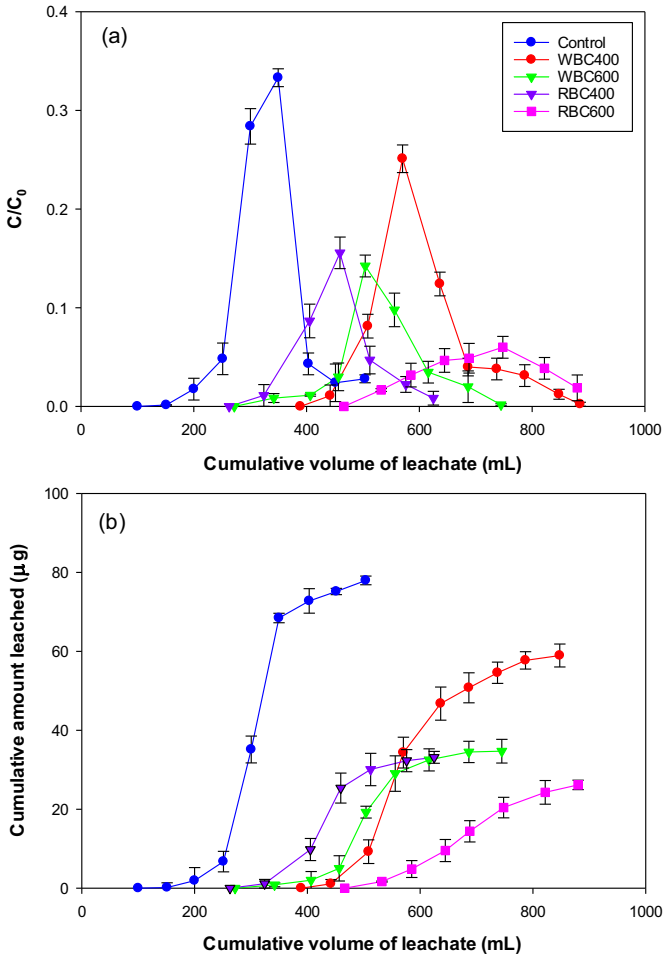

Fig. 3. Pyrazosulfuron-ethyl (a) breakthrough curves and (b) cumulative leaching curves in 0.05 g kg^{-1} biochar amended soil columns. C is the amount recovered in the leachate (µg) while C_0 is the initial amount applied to the column (µg). Error bars represent standard deviation.

Table 3
Leachate parameters and mass balance of pyrazosulfuron-ethyl residues (parent + metabolites) in no biochar control and 0.02 and 0.05 g kg^{-1} biochar amended soil columns (n = 2).

Treatments	Leachate volume (mL)	Residues recovered (µg)*				
		Water (PYRAZO)	Soil			Total
			PYRAZO	SAA	SAE	
Control	923.07 ± 12.6	77.97 ± 3.99^{e}	9.63 ± 1.41^{a}	1.50 ± 0.23^{a}	2.32 ± 0.20^{a}	91.42 ± 5.83
WBC400(0.02)	918.29 ± 05.8	70.98 ± 2.58^{e}	12.36 ± 3.44^{a}	2.67 ± 0.13^{ab}	4.38 ± 0.17^{b}	90.39 ± 0.72
WBC600(0.02)	926.49 ± 16.4	47.72 ± 1.99^{cd}	32.14 ± 4.42^{bc}	2.68 ± 0.31^{ab}	8.18 ± 0.16^{cd}	90.72 ± 1.93
RBC400(0.02)	944.13 ± 09.9	43.18 ± 2.72^{c}	37.12 ± 5.98^{bc}	3.85 ± 0.41^{c}	5.81 ± 0.18^{bc}	89.96 ± 3.48
RBC600(0.02)	923.71 ± 12.8	34.39 ± 2.84^{bc}	43.89 ± 5.70^{cd}	3.59 ± 0.16^{bc}	5.81 ± 0.16^{bc}	87.68 ± 8.22
WBC400(0.05)	885.26 ± 22.4	58.93 ± 3.56^{d}	17.54 ± 0.94^{ab}	2.19 ± 1.10^{ab}	9.15 ± 0.06^{d}	88.81 ± 2.47
WBC600(0.05)	927.65 ± 16.2	34.69 ± 4.40^{bc}	45.71 ± 7.13^{cd}	2.37 ± 0.13^{bc}	6.24 ± 0.18^{c}	89.01 ± 2.42
RBC400(0.05)	922.76 ± 14.6	33.15 ± 2.82^{bc}	49.29 ± 7.90^{cd}	3.52 ± 0.06^{bc}	9.75 ± 0.18^{d}	95.71 ± 10.5
RBC600(0.05)	978.42 ± 08.4	26.17 ± 2.86^{ab}	61.45 ± 3.30^{e}	2.99 ± 0.28^{bc}	6.12 ± 0.11^{c}	96.73 ± 0.05
Control	867.92 ± 22.3	57.41 ± 2.86^{d}	11.80 ± 1.45^{a}	8.77 ± 0.69^{e}	13.21 ± 0.16^{e}	91.19 ± 0.17
RBC600(0.05)	849.61 ± 15.2	21.93 ± 3.45^{a}	54.18 ± 2.90^{d}	6.55 ± 0.10^{d}	10.97 ± 0.18^{d}	93.64 ± 0.64

PYRAZO – Pyrazosulfuron-ethyl.
SAE – Ethyl 5-(aminosulfonyl)-1-methyl-1*H*-pyrazol-4-carboxylate.
SAA – 5-(Aminosulfonyl)-1-methyl-1*H*-pyrazole-4-carboxylic acid.
* Values followed by different letters within a column are significantly different at 5% level based on the Duncan's multiple range test performed using SPSS. The leachate volume and total residues recovered did not vary significantly. The ± values are the standard deviation.

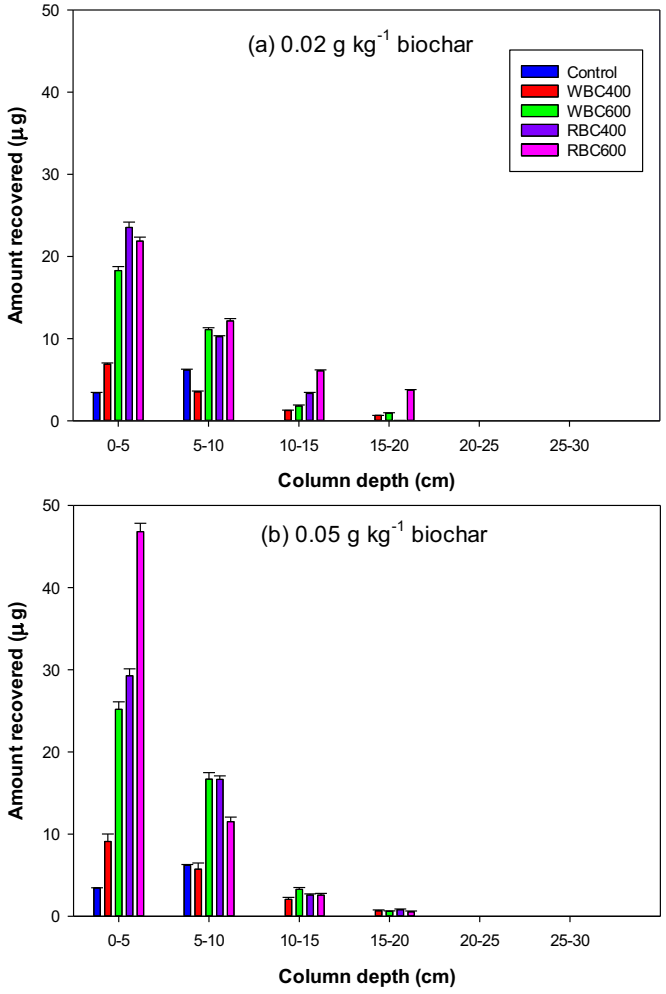

Fig. 4. Pyrazosulfuron-ethyl recovered from the different soil sections after leaching. Error bars represent standard deviation.

biochars. But, it was interesting to note that the rice straw biochars, in spite of reducing the leaching losses of the herbicide, were less effective in delaying the initial breakthrough of the herbicide in the leachate.

After the leaching experiment was over, distribution of PYRAZO/metabolites in different soil sections was determined (Fig. 4). Along with parent PYRAZO, metabolites SAE and SAA were detected in the different soil sections (Table 3). The metabolite (SAE) was formed in greater amounts than the acid metabolite (SAA) and their presence was restricted to 15–20 cm depth. The maximum amount of metabolites was detected in the top layer (0–5 cm) (Supplementary Table H). The mass balance (Table 3) results indicated that biochars amendment reduced the herbicide leaching. But, it was affected by the dose and nature of biochars. High temperature biochars were more effective in retaining the herbicide residues in soil column. Amendments at 0.05 g kg^{-1} biochar further increased the retention of PYRAZO in soil column and greater amount of applied PYRAZO was recovered from the application zone (0–5 cm). The RBC600 biochar accounted for the highest retention (46.83 µg) of PYRAZO in the 0–5 cm layer and was followed by the RBC400 (29.27 µg), the WBC600 (25.18 µg) and the WBC400 (9.09 µg).

The comparison of leaching behavior of PYRAZO for the packed and the intact columns (no biochar control and 0.05 g kg^{-1} RBC600) was made (Fig. 5). Percolation of water in the intact column was slow as it took 60–65 h to complete the leaching experiment while for packed columns it was completed in ~20 h. The results suggested that PYRAZO breakthrough from the control intact column occurred after passing 252.78 mL (0.88 pore volume) water suggesting that breakthrough of

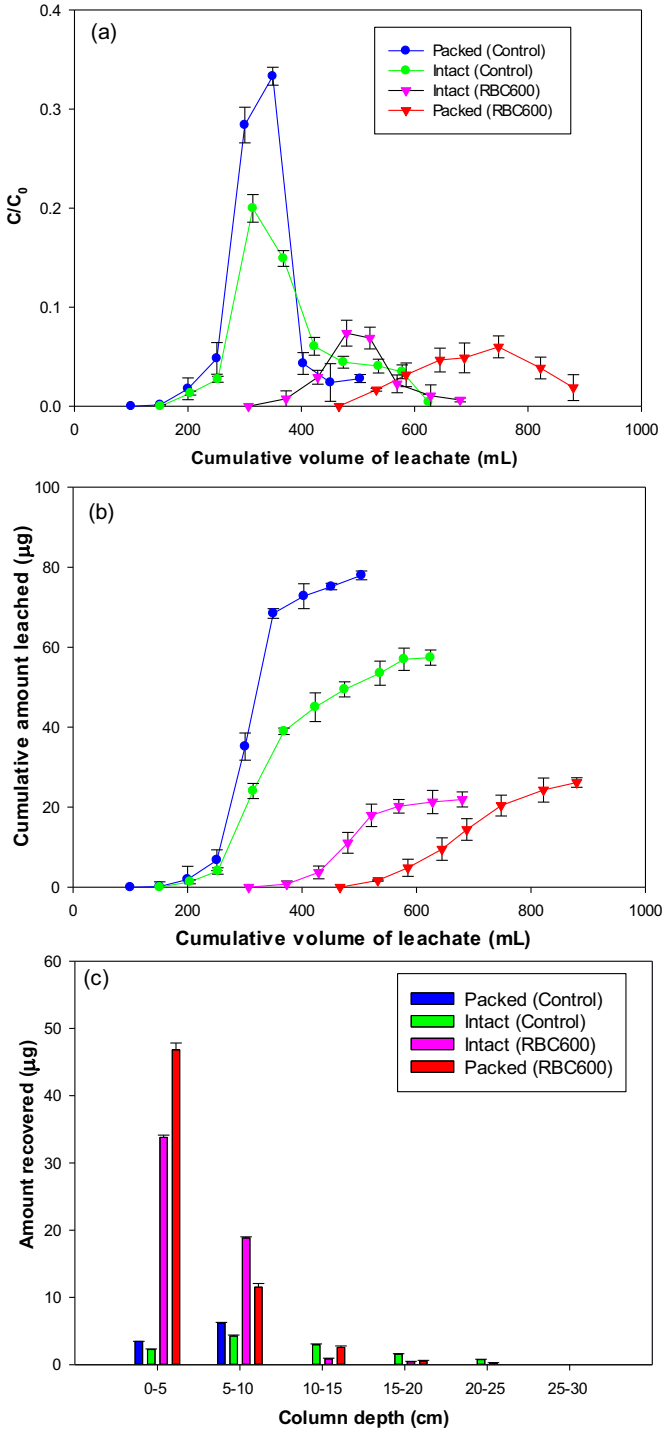

Fig. 5. Comparison of pyrazosulfuron-ethyl leaching in control and 0.05 g kg^{-1} RBC600 biochar amended packed and intact soil columns showing (a) breakthrough curve, (b) cumulative leaching curve and (c) distribution of the herbicide in different soil sections. C is the amount recovered in the leachate (µg) while C_0 is the initial amount applied to the column (µg). Error bars represent standard deviation.

PYRAZO was delayed in the intact columns relative to the packed column. These results are not in line with our previous report with other pesticides (Ghosh and Singh, 2009). Generally, pesticides are more mobile in the intact columns due to preferential flow of pesticide through macropores in the intact columns. The total amount of PYRAZO recovered in the leachate of control intact column (77.97 µg) was nearly 26% more than the amount recovered in leachate from the

packed column (57.41 μg). Amendment of 0.05 g kg^{-1} RBC600 delayed PYRAZO breakthrough and it occurred after passing 306.76 mL (1.04 pore volume) water. There was no significant difference in the amount of PYRAZO leached out of 0.05 g kg^{-1} RBC600 amended packed and intact columns. However, amounts of metabolites SAE and SAA in the soil from the intact column were higher than that recovered from the packed columns. This can be attributed to higher PYRAZO degradation in the intact columns due to longer run times. Also, more of the applied PYRAZO moved down to the 5–10 cm depth in the intact columns while packed columns retained the maximum amount of PYRAZO in the 0–5 cm depth (Fig. 5).

Decreased PYRAZO leaching in biochar amended columns can be explained by higher adsorption of the herbicide (Manna and Singh, 2015). Further, adsorption of PYAZO in biochars was affected by their pH, surface area and pore volume (Manna et al., 2017). No information is available on the effect of biochars on PYRAZO leaching, although literature suggested that biochars increased sorption of soil applied pesticides, thereby reducing their downward movement. Lü et al. (2012) demonstrated that low temperature (350 °C) rice straw biochars reduced leaching loss of acetochlor and 2,4-D by 25.4–40.7% and 30.2–45.5%, respectively. Delwiche et al. (2014) reported that pine chip biochar (pyrolyzed between 300 and 550 °C) reduced cumulative atrazine leaching by 52% in homogenized (packed) soil columns, but no significant effect was observed in intact soil columns.

3.3. Bioavailability studies

The biochars, which exhibit high pesticide retention capacity, are known to inhibit bioactivity of the soil applied herbicides and this is attributed to pesticide sequestration. Therefore, the effect of biochars amendments on PYRAZO's bioactivity was studied by its effect on mustard seedlings. Results (Table 4) suggested that the 0.02 and 0.05 g kg^{-1} WBC400 and RBC400 treatments had no effect on root and shoot length of mustard seedlings; thus, low temperature biochars (WBC400 and RBC400), even at 0.05 g kg^{-1} amendment level, had no inhibitory effect on PYRAZO's bioactivity at the dose recommended for weed control. However, root length of mustard seedling in soils amended with high temperature biochars (WBC600 and RBC600), even at 0.02 g kg^{-1} level, was longer than those grown in the no biochar soil. This suggested that availability of PYRAZO was reduced in the WBC600 and RBC600 treatments and can be attributed to higher herbicide adsorption in soil + biochar mixtures. Thus, to get weed control in the high temperature biochar (WBC600 and RBC600) amended soils higher amounts of the herbicide will be required. This was evident from the results of the experiment where PYRAZO was applied at 0.1 μg g^{-1} and it affected root length of mustard seedling in 0.02 and 0.05 g kg^{-1} RBC600 and WBC600 treatments. No effect of biochars treatment was observed on the mustard seedling's shoot length. Earlier, Graber et al. (2012) have reported similar results for phytoavailability of metolachlor and sulfentrazone to Green Foxtail in EUC-800 and BC-1 biochar amended soils. Both herbicides were effective in inhibiting seed germination in BC-1 amended soils; however, in EUC-800 amended soils, seed germination was inhibited only at the lowest dose of 13 Mg ha^{-1} and higher doses of metolachlor (3290 mL a.i. ha^{-1}) and sulfentrazone (420 g a.i. ha^{-1}) were required at 26 Mg ha^{-1} biochar dose. The present study also suggests that low temperature biochars do not have any effect on PYRAZO bioavailability while high temperature biochars reduced the herbicide bioavailability even at 0.02 g kg^{-1} dose.

4. Conclusion

PYRAZO is an important herbicide for the control of weeds in rice cultivation. It is important to generate information on effects of biochars on fate of soil applied herbicides. The study indicated that both the nature of feedstock and pyrolysis temperature affected degradation, leaching and bioavailability of PYRAZO in a sandy loam soil. In general, high temperature biochars (600 °C) were more effective (55–67%) in reducing the leaching of PYRAZO, but low temperature (400 °C) biochars also showed 25–58% reduction in the leaching losses. The biochars affected herbicide degradation; the effect was significant under nonflooded conditions where 0.05 g kg^{-1} RBC600 amendment resulted in nearly 6 fold increase in the $t_{1/2}$ of PYRAZO. The effect on leaching and degradation were more pronounced in the rice straw biochar amended soils than the wheat straw biochar amended soils. This observation was attributed to higher PYRAZO sorption in the rice biochar amended soils. The bioavailability of herbicide was unaffected by the low temperature (400 °C) biochars while high temperature (600 °C) biochars reduced the herbicide's bioavailability even at 0.02 g kg^{-1}

Table 4
Root and shoot length of mustard plant in 0.02 and 0.05 g kg^{-1} biochar amended soil at 0.01 μg g^{-1} and 0.1 μg g^{-1} level of PYRAZO (n = 3; ± values represent standard deviation).

Treatment	Root length (cm)		Shoot length (cm)	
	(−) PYRAZO	(+) PYRAZO	(−) PYRAZO	(+) PYRAZO
PYRAZO (0.01 μg g^{-1})				
Control	3.53 ± 0.70^{a,*}	1.27 ± 0.12^{a}	9.73 ± 1.55^{a}	6.77 ± 1.17^{a}
WBC400(0.02)	3.33 ± 0.50^{a}	1.03 ± 0.12^{a}	9.63 ± 0.55^{a}	6.67 ± 0.29^{a}
WBC600(0.02)	4.07 ± 0.98^{a}	2.37 ± 0.55^{b}	9.97 ± 0.50^{a}	8.80 ± 0.52^{a}
RBC400(0.02)	3.33 ± 1.01^{a}	1.13 ± 0.51^{a}	8.93 ± 0.06^{a}	7.47 ± 1.72^{a}
RBC600(0.02)	3.27 ± 0.21^{a}	2.43 ± 0.49^{b}	8.63 ± 0.81^{a}	8.83 ± 1.12^{a}
WBC400(0.05)	3.43 ± 0.21^{a}	1.43 ± 0.23^{a}	9.70 ± 0.30^{a}	7.33 ± 1.47^{a}
WBC600(0.05)	3.83 ± 0.76^{a}	2.90 ± 0.53^{b}	9.60 ± 1.15^{a}	8.50 ± 0.44^{a}
RBC400(0.05)	4.23 ± 0.67^{a}	1.51 ± 0.06^{a}	10.33 ± 0.81^{a}	8.17 ± 0.15^{a}
RBC600(0.05)	3.93 ± 0.72^{a}	2.90 ± 0.44^{b}	9.90 ± 0.36^{a}	7.97 ± 1.27^{a}
PYRAZO (0.1 μg g^{-1})				
Control	3.63 ± 0.59^{a}	1.40 ± 0.10^{a}	9.13 ± 1.52^{a}	6.90 ± 0.30^{a}
WBC400(0.02)	4.73 ± 0.40^{a}	1.50 ± 0.20^{a}	8.73 ± 0.15^{a}	7.17 ± 0.31^{a}
WBC600(0.02)	3.67 ± 0.15^{a}	1.23 ± 0.06^{a}	9.20 ± 0.98^{a}	7.57 ± 1.29^{a}
RBC400(0.02)	3.90 ± 0.79^{a}	1.33 ± 0.06^{a}	9.47 ± 0.85^{a}	7.23 ± 0.96^{a}
RBC600(0.02)	4.97 ± 1.50^{a}	1.20 ± 0.10^{a}	10.73 ± 0.47^{a}	6.67 ± 0.91^{a}
WBC400(0.05)	5.27 ± 1.17^{a}	1.43 ± 0.38^{a}	9.73 ± 0.70^{a}	8.27 ± 0.75^{a}
WBC600(0.05)	3.90 ± 0.26^{a}	1.57 ± 0.21^{a}	9.43 ± 0.12^{a}	7.57 ± 1.12^{a}
RBC400(0.05)	3.87 ± 1.27^{a}	0.80 ± 0.30^{a}	9.30 ± 0.98^{a}	7.33 ± 1.18^{a}
RBC600(0.05)	3.17 ± 0.35^{a}	0.97 ± 0.42^{a}	9.50 ± 0.90^{a}	6.70 ± 0.56^{a}

(−) and (+) signs show absence and presence of PYRAZO.
* Values followed by different letter within a column are significantly different at 5% level based on the Duncan's multiple range test performed using SPSS.

dose. This study suggested that low temperature biochars, which are effective in reducing PYRAZO leaching losses and had no effect on the herbicide bioactivity, can be safely recommended in rice cultivation, especially low land paddy cultivation. But, for realistic assessment of the effect of biochar amendments on the fate and efficacy of PYRAZO, studies under real field conditions are recommended.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2018.07.032.

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