Effect of biochar amendment and ageing on Sorption and Degradation of three Carbamate Pesticides in Soils

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Abstract **:** Biochar land application is commonly assumed to be an effective way to improve soil fertility. Biochar amendment can alter soil physico-chemical properties, sorption, degradation and leaching of different chemicals. The objectives of this study were to determine the sorption, persistence and mobility of three carbamate pesticides in six different soils in 1, 2, 5% (w/w) biochar amended and 2% aged (4 months) biochar amended soils. By the addition of biochar as compared to control, the sorption of three carbamate pesticides on all the studied soils increased significantly; the enhancement in sorption was directly correlated with amount of biochar added. The increase in pesticide sorption in biochar amended soils may be due to availability of sorption sites on biochar and the presence of micro pores in biochar. However, the sorption retards in aged biochar amended soils which might be due to covering of micro pores by organic and inorganic substances and oxidation of functional groups on the biochar surface. The sorption of three carbamate pesticides on all the studied soils belongs to 'L type'. The low heat of sorption (<50 kJ $mole^{-1}$) indicates that the sorption of pesticides was primarily via physical process in to soil organic matter. The degradation of the pesticides during the study obeys first order kinetics; the biochar retards the degradation of the pesticides and the degradation was more inhibited in fresh biochar amended soils than in aged biochar amended. The DT_{50} (50% dissipated) for three carbamate pesticides was in the order II > I > III denoting that pesticide III is most stable followed by I and II. The relatively strong and quick soil sorption of the carbamate pesticides in biochar amended soils accounts for limited soil leaching of the pesticides. These results indicate that the amendment of fresh biochar retards the degradation of carbamate pesticides, while this effect is retarded in aged biochar amended soils.

Key words: Biochar, biochar ageing, Carbamate pesticides, sorption, degradation, leaching

1 Introduction

Biochar is a carbon rich bio product that is produced from feedstock through the process of pyrolysis which is stable carbonaceous substance with high porosity, big surface area. Addition of biochar in soils boost soil fertility and improve soil quality by changing the pH, increasing water holding capacity, enhancing the cation Exchange Capacity (CEC), nutrient availability and microbial population [1-3]. The high specific surface area and CEC of biochar as compared to soil reduces leaching of nutrients such as nitrate, ammonium and phosphate [4-5]. The indiscriminate use of the pesticides has resulted in reduction of biodiversity, outbreak of secondary pests, development of pesticide resistance, pesticide induced resurgence and contamination of food and the ecosystem [6]. Carbamates have replaced persistent pesticides such as DDT and lindane, being mainly used as herbicides, fungicides and insecticides. Carbamates show a high biological activity and have medium to high polarity, but some of them are converted in the environment into high polar and toxic products than the parent compounds.

Sorption is one of the most important factors which affect transport and transformation processes of pesticides and their bioavailability [7]. The extent of sorption depends on soil organic matter, type and contents of clay, pH, CEC as well as on physico-chemical properties of pesticides itself [8,9]. Besides these, microbial degradation also contributes to the transformation of carbamate pesticides.

The main objective of the present study was to investigate the effects of biochar and aged biochar amended six soils differing significantly in organic matter (OM) and other physical and chemical properties on the sorption, dissipation and leaching of three polar carbamate pesticides, Oxamyl (I); S-Ethyl-N-(methyl carbamoyl) oxythioactimidate (II) and N-Phenyl (ethyl carbamoyl) propylcarbmate (III). The results of this study will be helpful for understanding the impact of biochar amendment on sorption and leaching of Carbamate pesticides.

2 Materials and Methods

For this study six soil samples (S_1 to S_6) from cultivated land of different parts of India (0-30 cm depth) (differing significantly in OM and other physical and chemical properties) were selected. The soil samples were air dried at room temperature, sieved to pass through 2mm sieve. The physico-chemical properties, determined by the usual soil laboratory methodology (Table 1).

2.1 Preparation and ageing of soil - Biochar Mixtures

The biochar used was prepared from paddy straw by the methods as described by Reddy [10]. The characteristics of the biochar are given in Table 2. Soil mixtures were prepared by mixing soil with sieved biochar (< 2mm) at a rate of 1, 2 and 5% biochar per unit soil dry weight. Biochar ageing was performed by amending soils with 2% of biochar. These mixtures were incubated in darkness at room temperature for 4 months. The moisture content was adjusted to 60% of water holding capacity and monitored and adjusted weekly by addition of deionized water.

2.2 Sorption isotherms:

Sorption experiments were conducted by placing 5 g of air dried soils and soil-biochar mixtures in large number of glass stoppered tubes and adding various amounts of standard pesticide solution (0-15 ml of 20 μg ml^{-1} in 0.01 M $CaCl_2$ at a constant ionic strength) and making upto 25 ml with distilled water. The suspensions were shaken for 30 h at 20±2^{o}C (Preliminary studies indicated that equilibrium was attained < 27 h). When equilibrium was attained the suspensions were centrifuged at 13,000 rpm for 10 min. The amount of pesticides in supernatants was estimated.

2.3 Residue estimation

The supernatants were evaporated, residues (dissolved in n-hexane) were analyzed on a Perkin Elmer GC model 8700 gas chromatograph, equipped with a ^{63}Ni electron capture detector fitted with SE 54 capillary column (60 m, 0.2 mm id). The operating conditions were as follows: column temperature 260^{o}C, injector and detector temperature 300^{o}C. The flow rate of nitrogen gas was 50 mL min^{-1}. The retention time for carbamate pesticides I, II, III were 2.14, 1.84 and 2.62 min respectively. Before using, the GC column was primed with several injections of standard pesticides till a consistent response was obtained for each pesticide. The concentration of sample was quantified by comparing the peak height of the sample chromatograms with those of standard run under identical operating conditions. Recovery was 93-99% and minimum detection was 0.05 μg g^{-1}.

2.4 Degradation and movement studies

For persistence and degradation studies 2 kg of soil and soil-biochar mixtures were incubated with 0, 10, 20, 50 and 100 μg g^{-1} soils of three carbamate pesticides in several polypropylene pots separately at 60% of water retention capacity. Moisture was regularly maintained based on the difference in between two consecutive days. Samples were incubated at room temperature. The residues were monitored at the time interval of 0 (4 h), 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, 77, 84 and 91 days after incubation followed by residue analysis.

2.5 Mobility studies

The mobility studies were conducted in 60 x 12 cm PVC pipes. The lower end of pipes was sealed with polythene and cotton cloth. The pipes were filled with 10 kg of each soil and soil-biochar mixtures. 500 mg of pesticides (50 μg g^{-1} soils) were applied separately in all the pipes at 60% of water retention capacity. Soil samples were collected using a steel soil sampler at the depth of 0-15 and 15-30 cm after 0, 7, 14, 21, 28, 35, 42, 49 days of application and at the depth of 0-15, 15-30, 30-45, 45-60 cm after 56, 63, 70, 77 and 91 days of application followed by residue analysis.

All the experiments were done in duplicate with suitable blanks.

3 Results and Discussion

3.1 Sorption Studies:

All the sorption isotherms (Fig. 1) displayed non-linearity and were described satisfactorily by the Freundlich equation (log Cs = log K_f + 1/n log Ce, where Cs (mg kg^{-1}) is the amount of pesticide adsorbed by soil, Ce (mg L^{-1}) is the equilibrium concentration in solution and log K_f and 1/n all empirical coefficients representing the intercepts and slope of isotherm respectively) with the correlation coefficient (R^2) > 0.91. The values of 1/n during the sorption studies were < 1 indicating a convex or L type of isotherms [11-12]. This kind of isotherms may arise because of minimum competition of solvent for sites on the adsorbing surface. The values of 1/n also suggest that the pesticide molecules are likely to be sorbed in a flat position [12]. Compared to control the sorption of three carbamate pesticides on all the studied six soils was increased significantly by the addition of biochar. The enhancement in sorption was directly correlated with amount of biochar added (Table 3). The values of 1/n during the sorption studies of oxamyl (pesticide I) decreased from 0.812 in un-amended soil to 0.740 in the 5% biochar (w/w) amended soil 3, suggesting a decrease in the isotherm linearity with addition of biochar. The enhancement in pesticide sorption in biochar amended soils may be availability of sorption sites on biochar and the presence of micro pores in biochar [13-14]. Data of Fig 1 and Table 3 also denote that sorption capacity of aged biochar decreases with time. The values of K_f for 2% aged biochar were approx. 25% lower than 2% fresh biochar. The decrease in sorption of studied carbamate pesticides in aged biochar amended soils might be due to covering of micro pores by organic and inorganic substances and oxidation of functional groups on the biochar surface [15]. The values of K_f ranged from 1.1 to 12.1 depending on individual soils, amount of biochar amended. The values of K_f and 1/n were in the order carbamate pesticide III > I > II. The K_f value decreased in the sample order as soil OM content $S_3 > S_5 > S_2 > S_4 > S_1 > S_6$.

The preliminary studies has shown that in the studied biochar unamended soils the organic matter contributed predominately [16] to the sorption of carbamate pesticides and the order of sorption was pesticide III > I > II. The heat released during carbamate pesticides sorption on tested soils ranged between 8.18 to 12.64 kJ $mole^{-1}$. The low heat of sorption (<50 kJ $mole^{-1}$) indicates that the sorption of pesticides was primarily via physical process [17] into soil organic matter [18].

3.2 Dissipation studies

The dissipation half lives (DT_{50}) were calculated using a first order dissipation model. Equation (1) describes the dissipation kinetics and equation (2) is used to calculate dissipation half lives.

$$C_t = Co \times e^{-(kt)} \ldots\ldots (1); \quad DT_{50} = 0.693/k \ldots\ldots (2)$$

Where Co and Ct are the concentration of analyses at time 0 and time t (days) respectively k is the first order rate constant determined as the slope value from test substance dissipation curves, as the regression lines generated have a coefficient of determination R^2 > 0.93. Similar results have also been reported by other workers for various pesticides [19]. The values of k and DT_{50} are given in Table 4. An examination of data of Table 4 showed that addition of biochar retards the degradation of the studied carbamate pesticides. The DT_{50} (50% dissipated) for three carbamate pesticides increased with amount of biochar amended. Degradation of studied pesticides was more inhibited after fresh biochar addition than aged biochar [20]. An examination of data of Table 3 also showed that the rate of degradation followed the soil order $S_6 > S_2 > S_4 > S_1 > S_5 > S_3$ indicating thereby a role of soil organic matter and soil pH [21]. The rate of degradation is related inversely to the order of sorption as soil S_3 has maximum sorption due to organic matter content there is minimum degradation. The DT_{50} (50% dissipated) for three carbamate pesticides was in the order II > I > III denoting that pesticide III is most stable followed by I and II. The values of DT_{50} in biochar amended and un-amended soils ranged from 40.3 to 72.2 d for pesticide I; 38.5 to 66.6 d for pesticide II and 44.1 to 74.5 d for pesticide III. The data of Table 4 also revealed that there is a significant negative correlation between pH and DT_{50}, possibly owing to rapid hydrolysis with increase of pH from 5.9 to 8.8. From the data of DT_{50} it may be inferred that there is a fairly similar microbial activity in the tested soils [22].

3.3 Mobility Studies

Results of mobility studies denote that the studied carbamate pesticides in all the tested biochar un-amended soils did not leach below 45 cm. The concentration of studied carbamate pesticides below 15 cm after 91 days of application was 30-45% of the initial amount of pesticide applied. With the amendment of biochar into the soil, leaching of carbamate pesticides in soil columns retards which may be due to enhanced sorption. The concentration of studied carbamate pesticides below 10 cm after 91 days of application in biochar amended soils was 12-25% of the initial amount of pesticide applied. The leaching of the studied carbamate pesticides in the aged biochar amended soils was more than fresh biochar amended soils. These results confirm the results that ageing of biochar in soil environment decreases the sorption capacity of biochar. Similar results are also reported by other researchers [23-24]. Data of Fig 2 also showed that the leaching of pesticides was in the order soil $S_6 > S_2 > S_4 > S_1 > S_5 > S_3$ (Fig. 2). The amount of pesticide leaching below 15 cm depth showed a strong inverse relationship to sorption and soil organic matter.

4 Conclusions

From this study it may be concluded that addition of fresh biochar significantly increases sorption of the studied carbamate pesticides to soils and the sorption depends on the amount of biochar added and soil organic matter, the sorption onto the aged biochar amended soils was lesser than fresh biochar amended soils. The relatively strong and quick soil sorption of the carbamate pesticides in biochar amended soils accounts for decreased dissipation rate and limited soil leaching of the pesticides in all the studied soils. The DT_{50} is significantly positively correlated with soil organic matter.

References

[1]. Sohi, SP, Krull E, Lopez-Capel, E, Bol, R and Sparks, DL editor, A review of biochar and its use and function in soil, *Advances in Agronomy*, Vol. 105, 2010, pp. 47- 82.

[2]. Uzoma, KC, Inoue, M, Andry, H, Zahoor, A. and Nishihara, E, Influence of biochar application on sandy soil hydraulic properties and nutrient retention. *J. Food Agric. Environ.*, Vol. 9, 2011, pp. 1137–1143.

[3]. Ventura, M, Sorrenti, G, Panzacchi, P, George, E, and Tonon, G, Biochar reduces short-term nitrate leaching from a horizon in an apple orchard. *J. Environ. Qual.*, Vol. 42, 2013, pp. 76–82.

[4]. Zheng, J, Stewart, CE and Cotrufo, MF, Biochar and nitrogen fertilizer alters soil nitrogen dynamics and greenhouse gas fluxes from two temperate soils. *J. Environ. Qual.,* Vol. 41, 2012, pp.361–1370.

[5] Parvage, MM, Ulen, B, Eriksson, J, Strock, J and Kirchmann, H, Phosphorus availability in soils amended with wheat residue *Char. Biol. Fert.,* Vol.49, 2013, pp. 245–250.

[6] Singh, SP, Survey of Indian Agriculture, In the Hindu, 2000, pp. 159-163.

[7] Villaverde, J, Kah, M and Brown, CD, Adsorption and degradation of four acidic herbicides in soils from southern Spain. *Pest Management Science,* Vol. 64, 2008, pp. 703-710

[8]. Ertli, T, Marton, A and Foldenyi, R, Effect of pH and the role of organic matter in the adsorption of isoprutron on soils. *Chemosphere*, Vol. 57, 2004, pp. 771-779.

[9]. Fernandes, MC, Cox, L, Hermosin, MC and Corenjo, J, Adsorption-desorption of metalaxyl as affective dissipation and leaching in soils; role of mineral and organic components. *Pest Management Sci.*, Vol.59, 2003, pp. 552-554.

[10]. Reddy, SBN, *Biocharculture, Biochar for Environment and Development* , Pub. Metameta, Netherlands, 2014.

[11]. Giles, CH, MacEwan, TH, Nakhwa, S.N and Smith, D, Studies in adsorption, part XI. A system of classification of solution adsorption isotherms and its use in diagnosis-adsorption mechanism and measurement of specific area of solid. *Journal of Chemical Society,* 1960, pp.3973-3993.

[12]. Giles, CH., Smith, D and Huitson A. A general form and classification of adsorption isotherms. *Journal Colloid In terface Science,* Vol. 47, 1974, pp. 755-765.

[13]Ahmad, M., Rajapaksha, AU, Lim, JE, Zhang, M, Bolan, N, Mohan, D, et al., Biochar as a sorbent for contaminant management in soil and water; a review, *Chemosphere*, Vol. 99, 2014, pp. 19-33.

[14] Khorram, MS, Lin, D, Zhang, Q, Zheng, Y, Fang, H and Yu,,Y, Effects of aging process on adsorption-desorption and bioavailability of fomesafen in an agricultural soil amended with rice hull biochar, *Journal of Environmental Science,* Vol. 56, 2017, pp. 180-191.

[15] Joseph, SD, Camps-Arbestain, M, Lin. Y, Munroe, P, Chia, CH, Hook, J, et al., An investigation into the reactions of biochar in soil. *Aust. J. Soil Res.,* Vol. 48, 2010, pp. 501-515.

[16] Cox, L, Koskinen, WC and Yen, PY, Influence of soil properties on sorption-desorption of imidacloprid. *J. Environ. Sci. Health B,* Vol. 33**,** 1998, pp. 123-134.

[17] Hulscher, TEM. and Cornelissen, G, Effect of sorption equilibrium and sorption kinetics of organic micro pollutants: a review. *Chemosphere*, Vol. 32, 1996, pp. 609-626.

[18] Sheng, G, Johnston, CT, Teppen, BJ, Boyd, SA, Potential contributions of smectite clays and organic matter to pesticide retention in soils. *J. Agric. Food Chem.,* Vol. 49**,** 2001, pp. 255-259.

[19]. Hu, D and Coates, J, Evaluation of the environmental fate of thymol and phenethyl propionate in the laboratory. *Pest Manag. Sci*., Vol. 64**,** 2008, pp.775-779.

[20] Kookana, RS, The role of biochar in modifying the environmental fate, bioavailability and efficacy of pesticides in soils: a review, *Aust. J. Soil Res.* , Vol. 48, 2010, pp. 627-637.

[21] Dolaptsoglou, C, Karpozuzas, DG, Menkissoglu-Spiroudi, UM., Eleftherohorinos, I and Voudrias, EA,. Influence of different organic amendments on the degradation metabolism and adsorption of Terbuthylazine. *J. Environ. Qual.,* Vol. 36, 2007, pp. 1793-1802.

[22] Prakash, NB and Suseela Devi, L, Persistence of butachlor in soils under different regime. *J. Indian Soc. Soil Sci.,* Vol. 48**,** 2000, pp.249-256.

[23] Martin, SM, Kookana, RS, Van Zwieten, L and Krulla, E, Marked changes in herbicide sorption –desorption upon ageing of biochars in soil, *J. Hazard. Mater.*, Vol. 231-232, 2012, pp. 70-78.

[24] Delwiche, KB, Lehmann, J and Walter, MT, Atrazine leaching from biochar amended soils, *Chemosphere*, Vol. 95, 2014, pp. 346-352.

Table 1. Selected Physical and Chemical properties of the soils used

Soil	Location	Organic Carbon (g kg^{-1})	Clay %	Sand %	Silt %	pH (1:2.5)	CEC (cmol (p+) kg^{-1})
S_1	Bangalore	1.34	20.2	30.8	49	6.3	6.7
S_2	Aligarh	1.68	13.0	39	48.0	8.9	11.2
S_3	Kota	3.30	45.2	10.6	44.2	7.1	31.8
S_4	Jhansi	1.32	27.2	48.2	24.6	7.6	22.5
S_5	Doiawala	2.50	20.2	25.4	54.4	5.8	20.4
S_6	Ludhiana	0.84	30.0	32.5	37.5	8.1	15.8

Table 2. **Selected Physical and Chemical properties of the biochar used in this study**

pH (1:2.5)	Specific surface area (m^2/g)	Bulk density (g/mL)	Ash content (% w/w)	Total Pore volume (mL/g)	Micro Pore volume (mL/g)	CEC (cmol (p+) kg^{-1})	Total Organic Carbon (%)	Total Nitrogen (%)	Total Phosphorous (%)	Exchangeable Acidity(m mol/kg)
9.14	11.84.	0.484	21.24	0.044	0.006	9.1	51.2	0.88	0.22	21

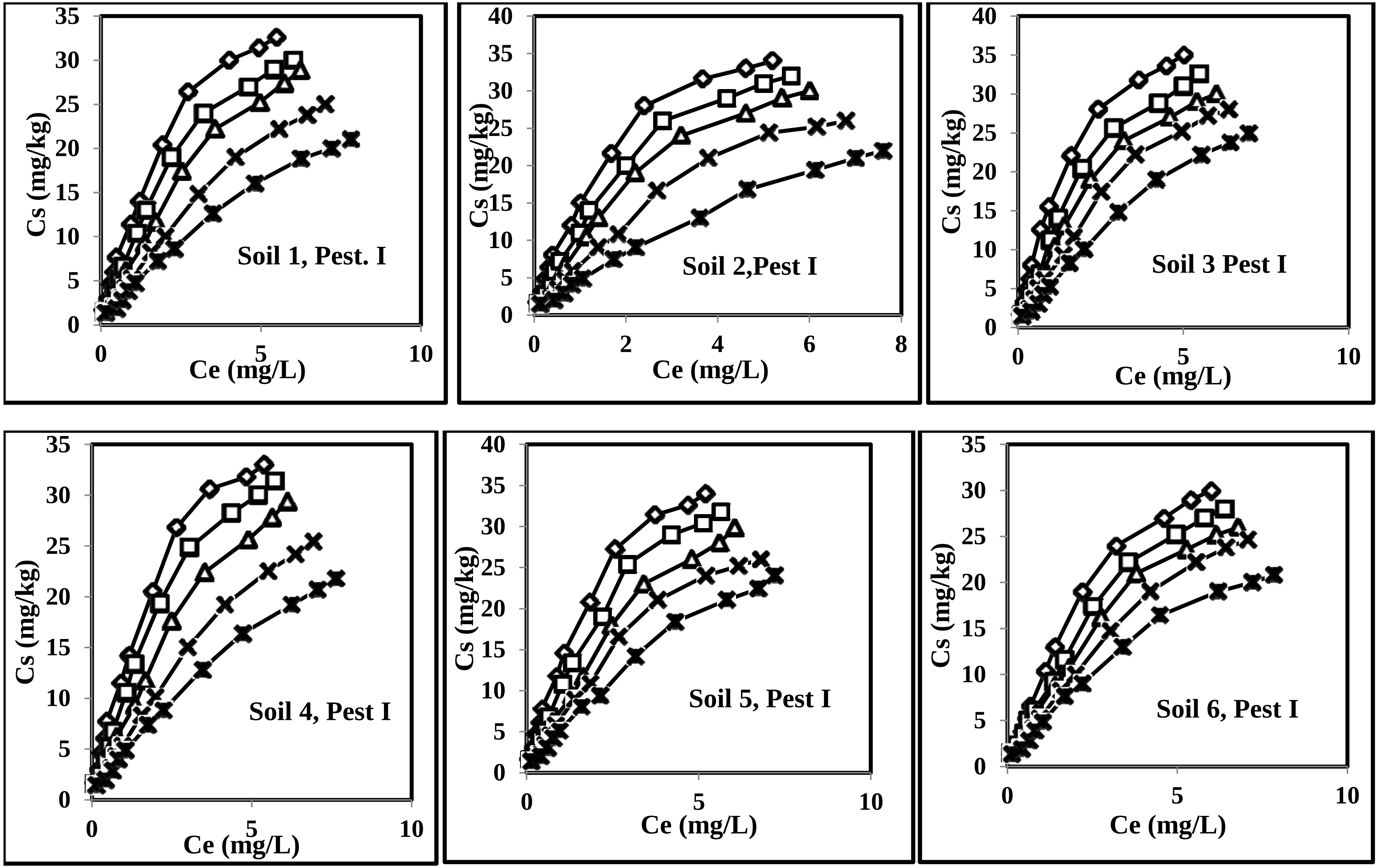
Table 3. Freundlich parameters for three carbamate pesticides adsorption in unamended and biochar- amended soils

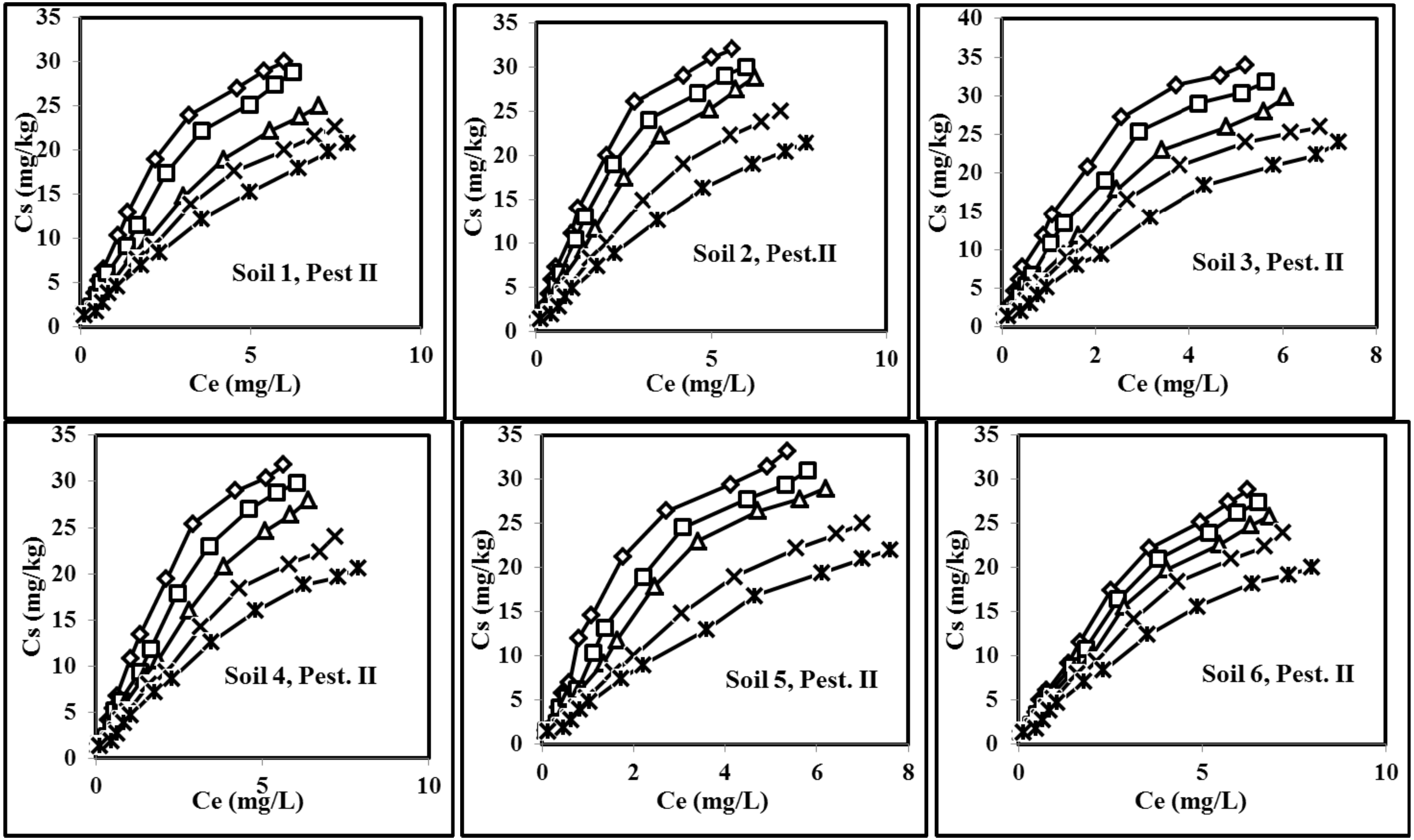
Properties	Soils																	
	S_1			**S_2**			**S_3**			**S_4**			**S_5**			**S_6**		
	Pesticides I																	
	K_f	1/n	R^2	K_f	1/n	R^2	K_f	1/n	R^2	K_f	1/n	R^2	K_f	1/n	R^2	K_f	1/n	R^2
Fresh soil	1.524	0.832	0.964	1.784	0.828	0.932	2.946	0.812	0.948	1.688	0.824	0.958	2.068	0.818	0.928	1.044	0.842	0.918
Soil+1% Biochar	2.884	0.820	0.944	3.424	0.812	0.898	4.856	0.800	0.912	3.586	0.814	0.922	4.034	0.806	0.904	1.966	0..830	0.904
Soil+2% Biochar	5.986	0.804	0.976	7.154	0.788	0.924	8.968	0.766	0.934	6.454	0.796	0.964	8.144	0.774	0.948	4.138	0.812	0.932
Soil+5% Biochar	8.186	0.776	0.934	9.324	0.754	0.944	11.364	0.740	0.966	8.642	0.770	0.904	10.542	0.748	0.932	6.786	0.788	0.942
Soil+2% Aged Biochar	4.458	0.812	0.958	5.345	0.800	0.936	7.688	0.788	0.920	5.014	0.806	0.916	6.866	0.794	0.944	3.656	0.818	0.936
	Pesticides II																	
Fresh soil	1.124	0.838	0.936	1.348	0.834	0.942	2.188	0.822	0.928	1.264	0.836	0.914	1.688	0.830	0.966	0.978	0.850	0.902
Soil+1% Biochar	2.284	0..828	0.912	2.666	0..822	0.918	3.424	0.810	0.904	2.388	0..824	0.936	3.284	0.814	0.914	1.544	0..834	0.922
Soil+2% Biochar	5.048	0.810	0.934	5.566	0.806	0.932	7.088	0.782	0.948	5.322	0.808	0.904	6.244	0.792	0.908	3.924	0.816	0.954
Soil+5% Biochar	7.294	0.784	0.934	8.044	0.780	0.964	10.122	0.756	0.932	7.766	0.782	0.932	8.648	0.760	0.926	5.824	0.794	0.918
Soil+2% Aged Biochar	3.988	0.816	0.910	4.604	0.814	0.908	6.342	0.800	0.944	4.442	0.816	0.928	5.188	0.806	0.912	3.088	0.822	0.920
	Pesticides III																	
Fresh soil	1.612	0.828	0.924	1.986	0.822	0.902	3.288	0.808	0.916	1.794	0.822	0.924	2.388	0.814	0.916	1.198	0.840	0.936
Soil+1% Biochar	3.388	0.816	0.904	3.884	0.808	0.918	5.584	0.798	0.934	3.988	0.810	0.916	4.912	0.800	0.934	2.124	0..826	0.966
Soil+2% Biochar	6.388	0.800	0.918	8.248	0.780	0.922	9.584	0.764	0.952	7.484	0.790	0.948	9.224	0.768	0.948	4.754	0.806	0.944
Soil+5% Biochar	8.758	0.772	0.932	10.324	0.750	0.948	12.126	0.736	0.926	9.642	0.760	0.922	11.662	0.740	0.922	7.584	0.782	0.924
Soil+2%Aged Biochar	5.454	0.808	0.942	6.788	0.798	0.918	8.454	0.784	0.912	6.124	0.800	0.908	7.586	0.790	0.918	4.152	0.814	0.958

Table 4. Average degradation rate constants, half-lives for three carbamate pesticides adsorption in unamended and biochar-amended soils

Soil	Soils														
	Fresh soil			Soil+1% Biochar			Soil+2% Biochar			Soil+5% Biochar			Soil+2% Aged Biochar		
	Pesticides I														
	k (d^{-1})x10^1	**DT_{50}**	**R^2**	**k (d^{-1})x10^1**	**DT_{50}**	**R^2**	**k (d^{-1})x10^1**	**DT_{50}**	**R^2**	**k (d^{-1})x10^1**	**DT_{50}**	**R^2**	**k (d^{-1})x10^1**	**DT_{50}**	**R^2**
S1	0.156±0.04	44.4±1.2	0.974	0.150±0.05	46.2±1.6	0.972	0.136±0.03	51±1.8	0.954	0.124±0.05	55.9±1.5	0.946	0.144±0.05	48.1±1.4	0.948
S2	0.144±0.05	48.1±1.6	0.966	0.140±0.04	49.5±1.3	0.942	0.130±0.03	53.5±1.1	0.934	0.116±0.04	59.7±1.6	0.964	0.139±0.04	49.9±1.6	0.956
S3	0.124±0.06	55.9±1.4	0.976	0.118±0.03	58.7±1.5	0.934	0.105±0.03	66±1.4	0.948	0.096±0.03	72.2±1.7	0.938	0.112±0.03	61.9±1.8	0.964
S4	0.150±0.05	46.2±1.1	0.944	0.145±0.05	47.8±1.6	0.922	0.132±0.03	52.5±1.6	0.966	0.120±0.05	57.3±1.2	0.962	0.140±0.05	49.5±1.6	0.952
S5	0.136±0.04	51±0.9	0.958	0.132±0.04	52.5±1.3	0.948	0.120±0.04	57.7±1.8	0.916	0.108±0.04	64.2±1.4	0.952	0.129±0.04	53.7±1.5	0.932
S6	0.172±0.04	40.3±1.2	0.962	0.166±0.04	41.7±1.2	0.952	0.152±0.04	45.6±1.5	0.936	0.138±0.04	50.2±1.3	0.944	0.158±0.04	43.9±1.2	0.936
	Pesticides II														
S1	0.166±0.04	41.7±1.1	0.948	0.158±0.05	43.9±1.1	0.942	0.145±0.03	47.3±1.4	0.932	0.132±0.05	52.5±1.4	0.942	0.153±0.05	45.3±1.7	0.948
S2	0.154±0.05	45±1.4	0.952	0.147±0.04	47.1±1.5	0.948	0.140±0.03	50.2±1.6	0.954	0.124±0.04	55.9±1.6	0.952	0.142±0.04	48.8±1.5	0.964
S3	0.132±0.06	52.5±1.5	0.986	0.122±0.03	56.8±1.4	0.956	0.113±0.03	61.3±1.8	0.928	0.104±0.03	66.6±1.8	0.938	0.118±0.03	58.7±1.3	0.932
S4	0.158±0.05	43.9±1.2	0.954	0.150±0.05	46.2±1.2	0.944	0.140±0.03	49.5±1.2	0.950	0.130±0.05	53.3±1.5	0.944	0.146±0.05	47.5±1.6	0.952
S5	0.144±0.04	48.1±1.4	0.946	0.138±0.04	50.2±1.7	0.922	0.128±0.04	54.1±1.4	0.960	0.117±0.04	59.2±1.4	0.956	0.132±0.04	52.5±1.5	0.936
S6	0.180±0.04	38.5±1.1	0.938	0.172±0.04	40.3±1.5	0.958	0.163±0.04	42.5±1.5	0.968	0.146±0.04	47.5±1.6	0.944	0.162±0.04	42.8±1.2	0.944
	Pesticides III														
S1	0.144±0.04	48.1±1.2	0.954	0.136±0.05	51±1.3	0.944	0.130±0.03	53.3±1.7	0.956	0.121±0.05	57.3±1.6	0.946	0.147±0.05	47.1±1.6	0.932
S2	0.136±0.05	51±1.2	0.962	0.129±0.04	53.7±1.4	0.924	0.122±0.03	56.8±1.4	0.934	0.110±0.04	63±1.2	0.948	0.144±0.04	48.1±1.7	0.962

S3	0.112±0.06	61.9±1.2	0.968	0.104±0.03	66.6±1.7	0.942	0.101±0.03	68.6±1.6	0.948	0.093±0.03	74.5±1.7	0.950	0.116±0.03	59.7±1.5	0.942
S4	0.140±0.05	49.5±1.4	0.954	0.133±0.05	52.1±1.4	0.954	0.126±0.03	55±1.5	0.928	0.114±0.05	60.8±1.6	0.942	0.136±0.05	51±1.2	0.958
S5	0.126±0.04	55±1.5	0.944	0.120±0.04	57.8±1.6	0.946	0.116±0.04	59.7±1.8	0.948	0.102±0.04	67.9±1.8	0.938	0.123±0.04	56.3±1.5	0.924
S6	0.158±0.04	44.1±1.3	0.982	0.150±0.04	46.2±1.1	0.958	0.144±0.04	48.1±1.6	0.938	0.134±0.04	51.9±1.7	0.940	0.152±0.04	45.6±1.5	0.938


Cs (mg/kg)
Ce (mg/L)
Soil 1, Pest. I
Soil 2,Pest I
Soil 3 Pest I
Soil 4, Pest I
Soil 5, Pest I
Soil 6, Pest I


Soil 1, Pest II
Soil 2, Pest.II
Soil 3, Pest. II
Soil 4, Pest. II
Soil 5, Pest. II
Soil 6, Pest. II
Cs (mg/kg)
Ce (mg/L)

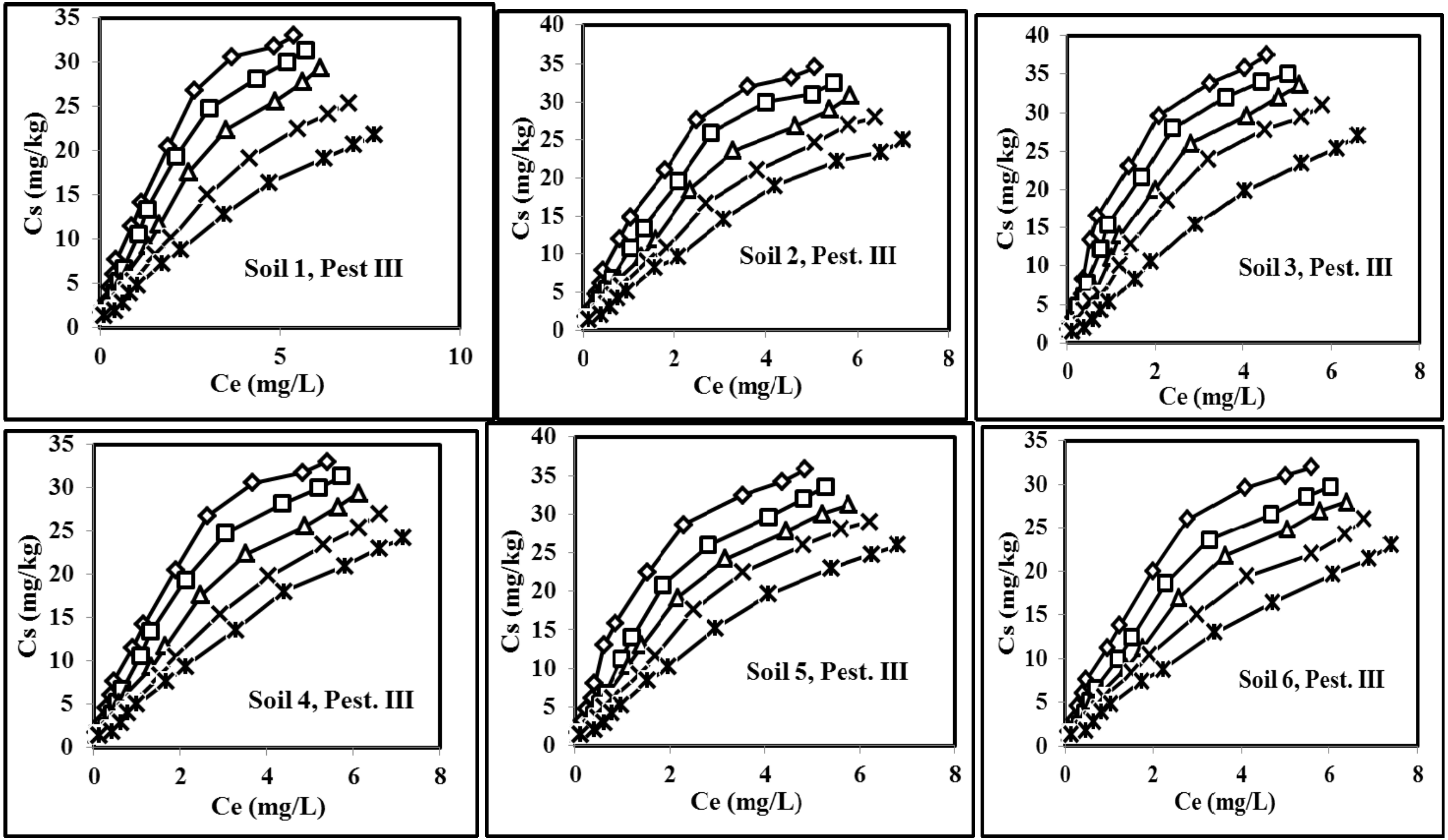
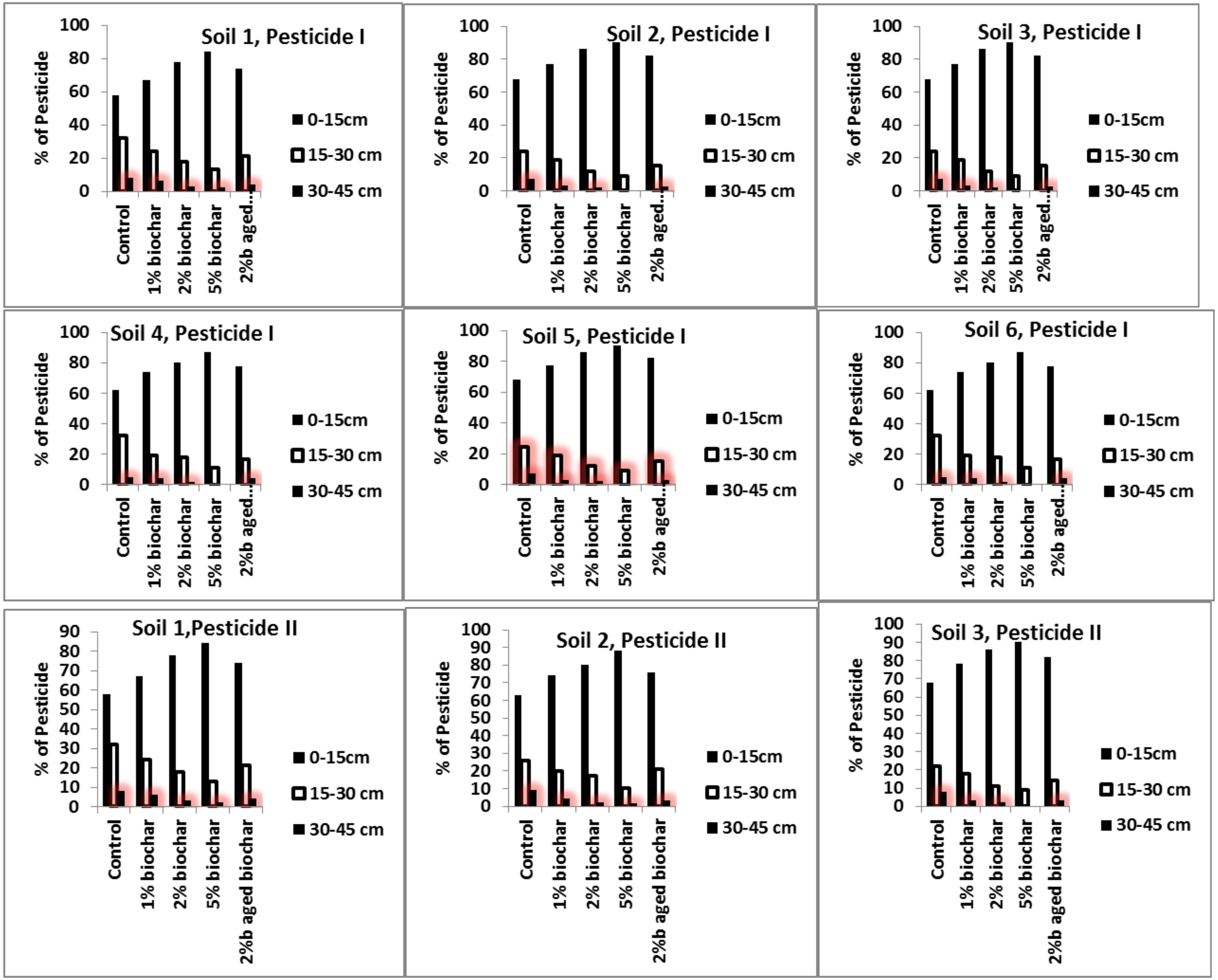


Fig. 1.Adsorption isotherms of three carbamate pesticides (I, II, III) adsorption on six soils in (□) 5% biochar amended, (◇) 2% biochar amended, (△) 1% biochar amended, (X) 2% aged biochar amended and (*) fresh soils


Soil 1, Pesticide I
Soil 2, Pesticide I
Soil 3, Pesticide I
Soil 4, Pesticide I
Soil 5, Pesticide I
Soil 6, Pesticide I
Soil 1,Pesticide II
Soil 2, Pesticide II
Soil 3, Pesticide II
% of Pesticide
0-15cm
15-30 cm
30-45 cm
Control
1% biochar
2% biochar
5% biochar
2%b aged...
2%b aged biochar

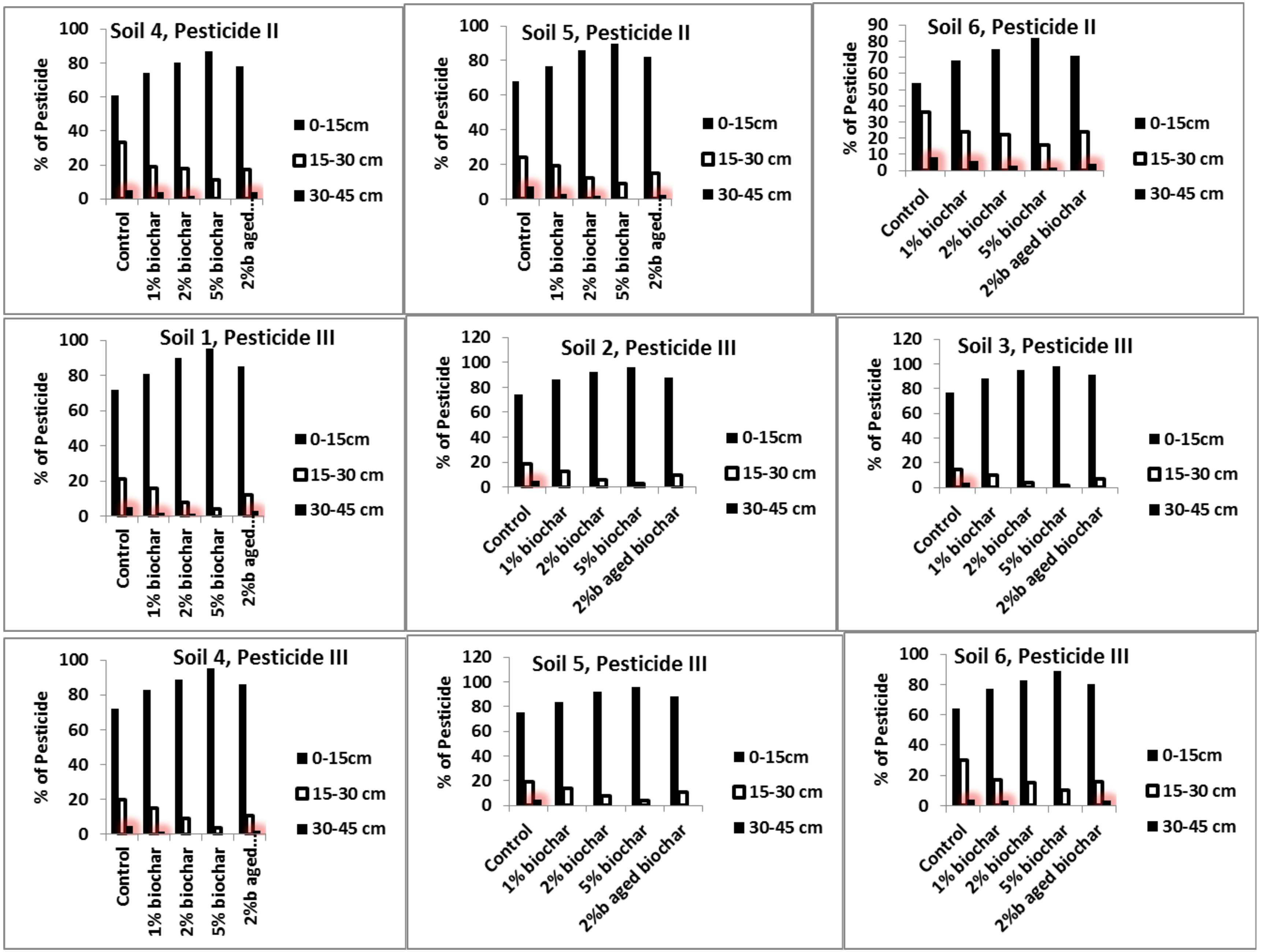


Fig. 2 Distribution of three Carbamate Pesticides in Soils in Biochar amended and unamended soils