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Soil Properties Control Glyphosate Sorption in Soils Amended with Birch Wood Biochar

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Abstract Despite a contemporary interest in biochar application to agricultural fields to improve soil quality and long-term carbon sequestration, a number of potential side effects of biochar incorporation in field soils remain poorly understood, e.g., in relation to interactions with agrochemicals such as pesticides. In a field-based study at two experimental sites in Denmark (sandy loam soils at Risoe and Kalundborg), we investigated the influence of birch wood biochar with respect to application rate, aging (7–19 months), and physicochemical soil properties on the sorption coefficient, K_d (L kg^{-1}), of the herbicide glyphosate. We measured K_d in equilibrium batch sorption experiments with triplicate soil samples from 20 field plots that received biochar at different application rates (0 to 100 Mg ha^{-1}). The results showed that pure biochar had a lower glyphosate K_d value as compared to soils. Yet, at the Kalundborg soils, the application of biochar enhanced the sorption of glyphosate when tested after 7–19 months of soil–biochar interaction. The relative enhancement effect on glyphosate sorption diminished with increasing biochar application rate, presumably due to increased mineral–biochar interactions. In the Risoe soils, potential biochar effects on glyphosate sorption were affected by a distinct gradient in soil pH (7.4 to 8.3) and electrical conductivity (0.40–0.90 mS cm^{-1}) resulting from a natural $CaCO_3$ gradient. Thus, glyphosate K_d showed strong linear correlation with pH and EC. In conclusion, the results show that biochar, despite initially being a poor sorbent for glyphosate, can increase glyphosate sorption in soil. However, the effect of biochar on glyphosate sorption is depends on prevailing soil physicochemical properties.

Keywords Biochar · Glyphosate · Sorption · Soil properties

Abbreviations

SSA	Specific surface area
EC	Electrical conductivity
CEC	Cation exchange capacity
OC	Organic carbon

1 Introduction

Biochar is a carbon-rich solid material resulting from thermal conversion of biomass under oxygen-limited conditions, e.g., by pyrolysis (Kookana et al. 2011). Depending on the feedstock and process conditions,

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biochar generally has low bulk density and high porosity, specific surface area (SSA), cation exchange capacity (CEC), and pH (Chan et al. 2007; Uchimiya et al. 2010). These properties have recently promoted the application of biochar in agricultural fields to improve soil quality and crop productivity (Kookana et al. 2011). The structure of biochar is made up of different proportions of carbonized and non-carbonized organic matter (Chen et al. 2008) and represents a heterogeneous sorbent with a potential to sorb nutrients and agrochemicals, such as pesticides. The sorption occurs on both carbonized and non-carbonized fractions of biochar (Zheng et al. 2010), and the sorption ability of biochar is controlled by factors such as the extent of crystallinity of the carbonaceous structure, the bonding state of carbon, the SSA, CEC, surface group functionality, and surface heterogeneity (Graber et al. 2012).

In addition to the intrinsic biochar properties, the interaction with inherent soil characteristics can influence the biochar sorption efficiency. In general, the soil content of organic carbon, clay, or amorphous oxides control the soil sorption capacity (Wauchope et al. 2002), but biochar-induced changes in soil solution chemistry (e.g., pH and cationic composition) may play an important role in the sorption process (de Jonge and de Jonge 1999). A pH shift alters the net charge of ionizable agrochemicals and/or soil components and thus directly changes the sorption interactions. Likewise, biochar may affect the cationic composition of the soil solution by contributing metals directly and also by solubilizing soil metals, such as Fe and Mn (Graber et al. 2014). On the other hand, biochar can also provide a sorptive surface and remove cations from the soil solution. It is well known that interactions between organic molecules and metallic cations, such as cation–organic dipole interactions and coordination bonds, have significant effects on soil sorption capacity (Calvet 1989).

The actual ability of biochar to sorb ionic and nonionic pesticides has only been sporadically addressed. Yu et al. (2006) observed increased sorption of the nonionic herbicide diuron to soil after biochar addition. Clay and Malo (2012) observed the sorption coefficient (K_d) of the weakly cationic herbicide atrazine to vary from 7 to 92 L kg^{-1} for biochar in contrast to the normal atrazine soil K_d of 1 to 5 L kg^{-1} (Koskinen and Clay 1997). In the same study, Clay and Malo (2012) observed high sorption coefficients (from 3 to >80 L kg^{-1}) of the anionic herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) for biochar, regardless of the negative charge of the pesticide, which is expected to minimize sorption to soil (Clay et al. 1988).

Increased sorption of pesticides in soil due to biochar addition can be beneficial in terms of reduced pesticide leaching and less pesticide residue in crops (Yu et al. 2009). Negative effects, on the other hand, can be a decrease in pesticide efficiency, requiring a higher application rate (and cost) of these chemicals (Yu et al. 2006; Spokas et al. 2009; Kookana 2010). Indeed, recent studies have documented reductions in the efficacy of pesticides in the presence of biochar in soil (Yang et al. 2006; Xu et al. 2008; Graber et al. 2011). Such sorption-mediated effects of biochar would clearly be a disadvantage. Yet, after application to soil, the properties of biochar may change over time (Martin et al. 2012); a process commonly referred to as aging or weathering. Effects of aging on chemical sorption properties in biochar-amended soils have been studied in relation to different chemical compounds, for example phenanthrene (Zhang et al. 2010; Kumari et al. 2014a), diuron and atrazine (Martin et al. 2012), and other herbicides (Trigo et al. 2014). These studies revealed that the aging effects on sorption vary with the chemical nature of the sorbate. Therefore, the ability of biochar to lose or retain the sorption capacity with aging is sorbate-specific, and probably also biochar-specific, at least to the level of functional similarities among the potential sorbate and biochars.

Glyphosate (N-(phosphonomethyl)glycine) is the most frequently used herbicide worldwide (Piccolo et al. 1994); it is a broad-spectrum, non-selective, organophosphorus herbicide and contains carboxyl, amino, and phosphonate functional groups (de Jonge and de Jonge 1999). Glyphosate adsorbs onto the soil mineral phase strongly and sorption mainly takes place through the phosphonic acid moiety (Cheah et al. 1997). The formation of adsorbent–cation–phosphate linkages is considered to be the most probable mechanism for glyphosate sorption (Sprankle et al. 1975; de Jonge et al. 2001). Despite extensive studies on glyphosate sorption to different soil types (Gerritse et al. 1996; de Jonge and de Jonge 1999; de Jonge et al. 2001; Cáceres-Jensen et al. 2009), little is known about glyphosate sorption to biochar-amended soil. In natural soils, metal ions will often be complexed to both fulvic acids and humic acids, and these types of complexes have been shown to adsorb glyphosate efficiently (Piccolo et al. 1995; Maqueda et al. 1998). It may be hypothesized that biochar will form similar complexes and thereby contribute to increased glyphosate sorption.

The objective of this study was to determine the capacity of soil systems amended with biochar to sorb glyphosate as influenced by different physicochemical soil properties. We used pure birch wood biochar and soil samples from two field experiments with different soil texture and strategies of birch wood biochar amendment (0–100 Mg ha^{-1}) thereby addressing also the short-term effects of biochar aging (7–19 months) on glyphosate sorption characteristics.

2 Materials and Methods

2.1 Biochar

Commercial biochar produced from birch wood pyrolyzed at ~500 °C was used for this study (Skogens Kol AB; now part of Auson AB, Sweden). The same biochar was used in recent field experiments and was characterized by 81 % C, 0.24 % N, pH 9.6, electrical conductivity (EC) 0.28 mS cm^{-1}, zeta potential −42 mV, CEC 9.26 cmol kg^{-1}, SSA 322 m^2 g^{-1}, and <0.88 mg kg^{-1} polycyclic aromatic hydrocarbons (Sun et al. 2014; Kumari et al. 2014a, b).

2.2 Study Sites, Soil Samples, and Analyses

We collected a total of 20 composite soil samples from two biochar-amended agricultural sites located at Risoe (55° 41′ N, 12° 05′ E) and Kalundborg (55° 42′ N, 11° 18′ E) in Denmark. The two sites are sandy loam soils, but differ with respect to soil physicochemical properties (Table 1), as well as the extent and timing of biochar application. A detailed account of the design of the biochar field experiments has been presented by Sun et al. (2014) and Kumari et al. (2014a, b). Briefly, at Risoe, eight plots (6 × 8 m) were established along a natural pH gradient in April 2011 (pH ranging from 7.4 to 8.3). Biochar was applied at 0 and 20 Mg ha^{-1} to four replicate plots and incorporated by harrowing to ~10-cm soil depth. Seven months after biochar application, topsoil samples (0–20 cm) were collected from five sampling points in each plot and pooled to one composite sample per plot. At Kalundborg, 12 plots (6 × 6 m) were established in April 2011. Biochar was harrowed into the 0–10-cm soil layer at application rates of 0, 10, 20, and 50 Mg ha^{-1} $year^{-1}$. Four plots (K1–K4) were amended with biochar in April 2011, whereas four plots (K5–K8) were amended with biochar in April 2012 (i.e., in each year to rates of 0, 10, 20, and 50 Mg ha^{-1}). The four remaining plots (K9–K12) were amended with biochar both in April 2011 and April 2012 (i.e., to cumulative rates of 0, 20, 40, and 100 Mg ha^{-1}). Soil sampling was done in October 2012 where bulk soil samples were collected from 0–20-cm depth from six sampling points in each plot and pooled to one composite sample per plot. The cropping system at Risoe was oat (2011) and barley (2012); at Kalundborg, maize was grown in both years. Soil sampling for the sorption studies was done in interrow areas with the intention to avoid plant residues.

In the laboratory, air-dried and 2-mm sieved soils were used for analysis of soil properties and sorption experiments. Soil texture was determined by the method of Gee and Or (2002). Total C in ball-milled subsamples was determined by oxidation to CO_2 using a FLASH 2000 organic elemental analyzer coupled to a thermal conductivity detector (Thermo Fisher Scientific, Waltham, MA). Total C was taken as organic C unless a preceding effervescence test indicated the presence of carbonates. When carbonate was present, the carbonate-C content was determined by the method of Loeppert and Suarez (1996), and organic C was taken as the difference between total C and carbonate-C. Cation exchange capacity was measured in both soils by the ammonium acetate extraction method (Kalra and Maynard 1991). Soil specific surface area (SSA) was determined by EGME adsorption following the method described by Pennell (2002) without removing organic carbon prior to analysis (Cihacek and Bremner 1979; de Jonge et al. 2000). The pH and EC were measured in soil/water mixes of 1:4 and 1:9 (*v*/*v*), respectively. Available soil phosphorous was determined by the Olsen method (Olsen et al. 1954). Oxalate extractable Al and Fe were measured following Mckeague and Day (1966) as an estimation of the amorphous Fe and Al oxides in the soil. The procedure for analysis of the soil properties is explained in further detail in Kumari et al. (2014b).

2.3 Glyphosate solution

Radiolabeled ^{14}C-labeled glyphosate was purchased from Perkin Elmer (Boston, USA). Glyphosate solution (0.23 mg L^{-1}) was prepared by dissolving ^{14}C-labeled glyphosate in 0.01 M $CaCl_2$. Sodium azide (1.00 g L^{-1})

Table 1 Physicochemical properties and glyphosate sorption coefficient (K_d) of biochar, reference soils, and biochar-amended soils from Risoe (R) and Kalundborg (K) experimental sites

Sample	Biochar ($Mg\ ha^{-1}$)	Clay ($kg\ kg^{-1}$)	Silt	Sand	OC	$CaCO_3$	Fe-ox ($mmol\ kg^{-1}$)	Al-ox	Olsen P ($mg\ kg^{-1}$)	pH	EC ($mS\ cm^{-1}$)	CEC ($cmol\ kg^{-1}$)	SSA ($m^2\ g^{-1}$)	K_d ($L\ kg^{-1}$)
Biochar	NA	NA	NA	NA	0.81	NA	NA	NA	NA	9.60	0.28	9.3	322.0	8
R1	0	0.15	0.13	0.64	0.013	0.05	20	19	24	8.25	0.86	10.2	40.6	242
R2	20	0.15	0.12	0.64	0.018	0.06	20	19	21	8.25	0.90	9.5	36.0	287
R3	0	0.16	0.13	0.65	0.012	0.04	22	20	20	8.27	0.88	10.4	41.1	260
R4	20	0.16	0.12	0.67	0.022	0.01	23	20	22	8.14	0.83	10.2	40.3	254
R5	0	0.17	0.13	0.68	0.012	BL†	27	21	23	8.00	0.61	11.8	40.5	321
R6	20	0.17	0.13	0.67	0.020	BL	26	20	25	7.72	0.40	11.0	39.3	416
R7	0	0.16	0.15	0.67	0.013	BL	28	21	27	7.50	0.49	11.6	38.5	440
R8	20	0.16	0.14	0.66	0.020	BL	27	21	28	7.40	0.48	11.8	38.1	408
K1	0	0.08	0.12	0.77	0.016	BL	41	19	102	6.49	0.43	9.0	20.5	188
K2	10	0.09	0.13	0.74	0.018	BL	40	18	98	6.64	0.41	10.5	29.4	250
K3	20	0.10	0.14	0.72	0.022	BL	40	18	87	6.71	0.46	10.8	27.3	253
K4	50	0.11	0.15	0.69	0.027	BL	40	18	87	6.34	0.45	11.4	32.7	293
K5	0	0.09	0.12	0.77	0.015	BL	39	19	95	6.69	0.53	9.6	21.9	172
K6	10	0.10	0.14	0.73	0.017	BL	38	18	97	6.73	0.44	10.8	31.1	231
K7	20	0.11	0.14	0.71	0.023	BL	39	18	95	6.98	0.48	11.1	32.0	218
K8	50	0.11	0.11	0.72	0.035	BL	40	18	94	6.73	0.44	10.7	31.7	269
K9	0	0.09	0.12	0.77	0.016	BL	44	19	105	6.56	0.48	10.2	18.9	191
K10	20	0.09	0.13	0.75	0.024	BL	43	18	97	6.70	0.47	11.0	27.6	213
K11	40	0.08	0.10	0.77	0.031	BL	43	19	98	6.58	0.45	11.9	31.7	252
K12	100	0.09	0.10	0.73	0.048	BL	37	18	90	6.83	0.48	11.8	40.0	194

The physicochemical properties include contents of organic carbon (OC), oxalate extractable Fe (Fe-ox), and Al (Al-ox), electric conductivity (EC), cation exchange capacity (CEC), and specific surface area (SSA)

BL below detection limit (0.01 kg kg^{-1}), *NA* not applicable

was added to prevent microbial degradation (Gimsing and Borggaard 2007).

2.4 Sorption experiment

The sorption coefficients of glyphosate were determined by batch equilibration experiments with three replicates. Soil aliquots (0.5 g) were hydrated with 0.5 mL of a 0.01 M $CaCl_2$ solution for 24 h in glass centrifuge tubes closed with Teflon caps. Nine milliliters of the glyphosate solution (0.23 mg L^{-1}) was added and the samples were incubated end-over-end (30 rpm) for 24 h at 20 °C followed by centrifugation at 5000 rpm for 1 h. Samples of 3-mL supernatant were mixed with 17 mL of scintillation cocktail (Packard Ultima Gold). The glyphosate concentration was quantified using a liquid scintillation analyzer (Packard 2250 CA, Downers Grove, IL). The specific amount of glyphosate sorbed (C_s; g kg^{-1}) was calculated from the soil dry weight (m_s) and the difference between the solution concentration (g L^{-1}) at the equilibrium (C_e) (i.e., after the 24-h incubation period) and the solution concentration (g L^{-1}) in equivalent samples from assays run without soil (C_i):

$$C_s = V\,(C_i - C_e)/m_s \tag{1}$$

where V is the volume in liters. The sorption coefficient of glyphosate, K_d (L kg^{-1}), was calculated as

$$K_d = C_s/C_e \tag{2}$$

2.5 Statistical analyses

For the Risoe soils, statistical testing of K_d was done using a mixed-effects model including biochar, soil pH, and clay content as fixed main effects and block as a random effect (Montgomery 2013). The R version 3.0.2 (R Core Team, 2013) and the R package *lme4* (function *lmer* with REML=FALSE) were used for data analysis. Likelihood ratio tests (function *anova*) of models with and without the tested effects were used to obtain P values for the main effects of biochar, soil pH, and clay content (Winter 2013).

The absence of true replication at the Kalundborg site hindered a full statistical analysis. Therefore, in the present study, inferences about effects of biochar and soil properties on glyphosate K_d were made on the basis of correlation analyses, including all soil plots at the Kalundborg site. Linear relationships between measured variables were evaluated by Pearson's test. All procedures were performed at $P<0.05$.

3 Results and Discussion

3.1 Physicochemical Properties of Soil and Biochar Amended Soil

The Risoe soils were generally characterized by higher clay content and EC, and lower OC, Olsen P, and oxalate extractable Fe than the Kalundborg soils (Table 1). Also, Risoe soils were slightly alkaline with a pH gradient from 7.4 to 8.3 whereas Kalundborg soils were slightly acidic to neutral (pH 6.3 to 7.0). The CEC of pure biochar (9.26 cmol kg^{-1}) was generally lower than the CEC of the non-amended (reference) soils (Table 1). Nevertheless, we observed a slightly higher CEC in the biochar-amended soils than in the reference soils for the Kalundborg site. This is not surprising, though, since the CEC of biochar may increase with aging in soil due to surface oxidation and/or adsorption of organic acids by the biochar (Cheng et al. 2006, 2008; Liang et al. 2006). For SSA, there were no clear effects of biochar at the Risoe site (Table 1), whereas biochar amendment significantly increased soil SSA at the Kalundborg site (on average by 55 %). The increase in SSA, relative to the rates of biochar application, was most pronounced at lower application rates (Table 1).

3.2 Glyphosate Sorption on Pure Biochar and Biochar-Amended Soils

As expected, the sorption coefficient for glyphosate on pure biochar ($K_d=7.5$ L kg^{-1}) was markedly lower than for reference soils ($K_d=172$–440 L kg^{-1}) (Table 1), implying a lack of favorable sites and/or the presence of unfavorable conditions (e.g., the high pH of 9.6) for glyphosate sorption on pure biochar. Beaton et al. (1960) found that charcoal has the capacity to sorb P, which is understood to have the same binding mechanism as glyphosate (Sprankle et al. 1975) and suggested that hydrogen bonding was the mechanism attaching phosphate to the charcoal surface. However, the ability of charcoal to sorb P was limited compared to that of soil, which is in agreement with our results.

The mixed effects testing showed no main effect of biochar on glyphosate K_d ($P=0.70$) in biochar-amended soils from Risoe. Rather, a significant effect of pH on K_d was observed ($P<0.001$) for the Risoe soil. For Kalundborg soils, however, a consistently larger glyphosate K_d was seen for biochar-amended soils compared to reference soils (on average 33 % higher glyphosate K_d in biochar-amended soil, $n=9$). This trend occurred despite the much lower glyphosate K_d for pure biochar than for soil, implying enhancing effects of aged biochar on glyphosate sorption (Table 1). In soil, biochar undergoes various oxidation reactions which increase oxygen-containing functional groups such as phenol and carboxyl groups on the biochar surfaces (Cheng et al. 2006, 2008; Cheng and Lehmann 2009). Therefore, after aging in soil, biochar potentially has more available sorption sites for glyphosate than fresh biochar. We observed a strong positive linear correlation ($r=0.86$, $P<0.001$) of K_d with biochar application rate for Kalundborg soils (Fig. 1a). Biochar-induced variations in soil sorption properties (SSA and CEC) may have played a role for the observed increase in the glyphosate sorption capacity of soils. Yet, the enhancement of glyphosate sorption was relatively less pronounced at higher biochar application rates. For example, in Kalundborg 2011 and Kalundborg 2012 soils, the glyphosate K_d increased by ca. 34 % at a biochar application rate of 10 Mg ha^{-1}, whereas the increase was 56 % at 50 Mg ha^{-1}. The empirical (mechanistic) link between biochar application rate and glyphosate K_d was not entirely consistent, though, as the soil which received the highest cumulative biochar dose (100 Mg ha^{-1}, encircled data point in Fig. 1a) highly deviated from the other data and was excluded in the correlation analyses. Possibly, the results obtained at 100 Mg ha^{-1} biochar could be due to a high prevalence of mineral–biochar interaction which masks sorption sites on clay and amorphous oxides at higher biochar application rates. Many studies have reported possible biochar–mineral interactions in soils (Brodowski et al. 2006;

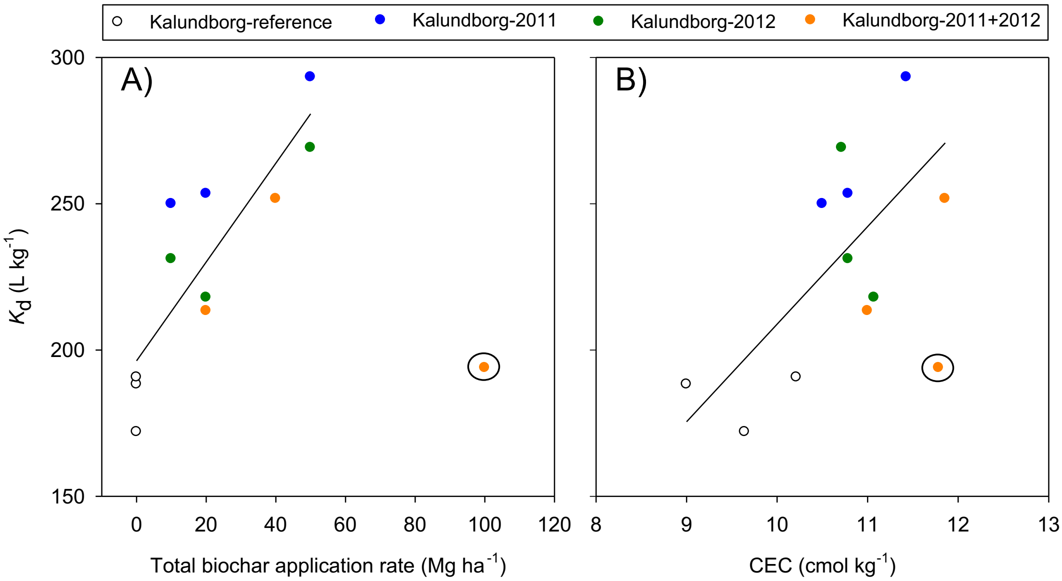

Fig. 1 Glyphosate sorption coefficient (K_d) plotted against **a** cumulative biochar application rates and **b** cation exchange capacity (CEC) at the Kalundborg site. The *lines* show the correlation between K_d and biochar application rates (BAR) and K_d and CEC, respectively, excluding the (*encircled*) data point at 100 Mg ha^{-1} biochar ($K_d = 1.7$ BAR + 196, $r = 0.86$ and $K_d = 33$ CEC—125, $r = 0.71$). The year of biochar application is indicated by different *symbol colors*

Liang et al. 2008). However, further data are required to ascertain the role of biochar–mineral interactions on sorption processes.

3.3 Correlations Between Glyphosate Sorption and Physicochemical Soil Properties at the Kalundborg site

In order to examine the contrasting effects of biochar on glyphosate sorption at the two sites, we performed statistical analyses separately for Kalundborg and Risoe soils. For Kalundborg soils, we performed Pearson product moment correlation analysis including biochar application rate and soil physicochemical properties. Literature provides evidence that the sorption of glyphosate by soils depends on CEC and clay content (Glass 1987), organic matter (Morillo et al. 2000), iron and aluminum oxides (Prata et al. 2000; Gerritse et al. 1996), phosphorus (Sprankle et al. 1975; de Jonge and de Jonge 1999), pH (Morillo et al. 2000), and EC (Yaron et al., 2012). The present results (Table 2) showed strong positive correlations of biochar application rate with CEC ($r = 0.74$, $P < 0.01$) and SSA ($r = 0.77$, $P < 0.01$) agreeing with positive effects of biochar on soil sorption properties. Further, we observed positive correlations of K_d with biochar ($r = 0.86$, $P < 0.001$), CEC ($r = 0.71$, $P < 0.05$), and SSA ($r = 0.81$, $P < 0.01$) in accordance with a positive role of field applied biochar on glyphosate sorption presumably through providing sorption sites. To further illustrate the effect of CEC on sorption, we plotted K_d against CEC (Fig. 1b). The data showed that biochar-amended soils had higher CEC and K_d compared to reference soils and indicated a linear increase in K_d with CEC. It is generally accepted that glyphosate readily binds to clay minerals (Sprankle et al. 1975; Gerritse et al. 1996). In line with this, we observed a significant positive correlation ($r = 0.63$, $P < 0.05$) of glyphosate K_d with clay content at the Kalundborg site (Table 2). Further, a significant negative correlation was found between K_d and Olsen P ($r = -0.65$, $P < 0.05$). This is not surprising as it is well documented that glyphosate and phosphate can compete for the same potential sorption sites (Sprankle et al. 1975; de Jonge and de Jonge 1999; de Jonge et al. 2001). With regard to soil EC and pH, there were no correlations with K_d at the Kalundborg site. In summary, although the mechanism was not explicitly deduced, it may be envisaged that potential cation exchange sites in aged biochar surfaces could be involved in glyphosate sorption through cation bridging directly and/or biochar-induced soil chemistry indirectly could be involved, thereby enhancing the glyphosate sorption at the Kalundborg site.

Table 2 Pearson product moment correlation for soils from the Kalundborg site ($n = 11$; i.e., excluding the data point at 100 Mg biochar ha^{-1})

	CEC	SSA	pH	EC	Olsen P	Fe-ox	Clay	K_d
Biochar	0.74**	0.77**	−0.16	−0.26	−0.58	0.00	0.57	0.86***
CEC		0.81**	0.092	−0.13	−0.44	0.11	0.45	0.71*
SSA			0.22	−0.39	−0.55	−0.38	0.71*	0.81**
pH				0.28	0.01	−0.36	0.35	-0.23
EC					−0.02	0.071	−0.14	−0.58
Olsen P						0.47	−0.63*	−0.65*
Fe-ox							−0.58	−0.16
Clay								0.63*

CEC cation exchange capacity, *SSA* specific surface area, *EC* electric conductivity, *Fe-ox* oxalate extractable Fe, K_d glyphosate sorption coefficient

$*P < 0.05$; $**P < 0.01$; $***P < 0.001$

3.4 Correlations Between Glyphosate Sorption and Physicochemical Soil Properties at the Risoe Site

As we inferred before, the mixed effects testing showed no effect of biochar on glyphosate K_d at the Risoe site. Kumari et al. (2014a), who worked with the same soil, observed lower K_d of phenanthrene at the Risoe site compared to the Kalundborg site at the same application rate and aging time. They speculated that the pronounced mineral–biochar interaction in Risoe soils with higher clay content may potentially block the sorption sites on biochar. Disregarding biochar application, we observed a marked variation in K_d (ranging from 242 to 440 L kg^{-1}) among the eight soil samples from Risoe site (Table 1). However, this is not surprising as we observed a marked variation in soil physicochemical properties (Table 1) as well at this site. Further, the results of Pearson product moment correlation analysis for Risoe soils (Table 3) showed strong correlations between K_d and soil physicochemical properties (CEC, pH, EC, Olsen P, and Fe-ox). In contrast to the Kalundborg site, K_d positively correlated with Fe-ox ($r = 0.84$, $P < 0.01$) and Olsen P ($r = 0.84$, $P < 0.01$) while negatively correlated with pH ($r = -0.94$, $P < 0.001$) and EC ($r = -0.94$, $P < 0.001$) at the Risoe site. Similar to the Kalundborg site, we observed a positive correlation between K_d and CEC ($r = 0.72$, $P < 0.05$) at the Risoe site as well. CEC positively correlated with Fe-ox; Fe oxides are negatively charged under neutral–alkaline conditions contributing to the pH-dependent negative charge in soils (Alloway 2013; Sumner 1963). Further, CEC negatively correlated with EC ($r = -0.82$, $P < 0.05$). Cations raise the point of zero charge (PZC) of iron oxides (Parks 1967; Sposito 1984). Negative charge of iron oxides depends on adsorption of OH$^-$ from solution (McBride 1994) and hence increases with pH. However, at the Risoe site, increasing pH was associated with increasing EC and

Table 3 Pearson product moment correlation for soils from the Risoe site ($n = 8$)

	CEC	SSA	pH	EC	Olsen P	Fe-ox	Clay	K_d
CEC		0.16	−0.79*	−0.82*	0.71*	0.94***	0.68	0.72*
SSA			0.30	0.13	−0.29	0.01	0.36	−0.38
pH				0.91**	−0.93***	−0.86***	−0.42	−0.94***
EC					−0.84**	−0.90**	−0.68	−0.94***
Olsen P						0.72*	0.22	0.84**
Fe-ox							0.75*	0.84**
Clay								0.49

CEC cation exchange capacity, *SSA* specific surface area, *EC* electric conductivity; *Fe-ox* oxalate extractable Fe, K_d glyphosate sorption coefficient

$*P < 0.05$; $**P < 0.01$; $***P < 0.001$

decreasing Fe-ox, both of which are contributing to lower CEC. Probably, this may be the reason for the observed negative correlation between pH and CEC ($r = -0.79$, $P < 0.05$).

Among major drivers of glyphosate sorption, soil pH has been reported to play a significant role (McConnell and Hossner 1985; Morillo et al. 2000). We therefore examined glyphosate K_d at varying soil pH (Fig. 2a) and observed a linear decline of K_d with increasing soil pH. Glyphosate, being a zwitterion with pK values of 2.0, 2.6, 5.6, and 10.6 (Stalikas and Konidari, 2001), is positively charged below pH 2.0, while negatively charged above pH 2.6. Therefore, within the pH range, we investigated glyphosate has a net negative charge that increases with increasing pH. The increased negative charge of the glyphosate and sorbent resulted in decreased electrostatic attraction between the sorbent and the glyphosate. Several other studies which examined the effect of pH on the sorption of glyphosate also concluded that the increased negative charge of both glyphosate and mineral surfaces with increasing pH decreases the sorption of glyphosate (McConnell and Hossner 1985; Morillo et al. 2000; Ghafoor et al. 2013). Similarly, as expected, K_d showed a linear decline with

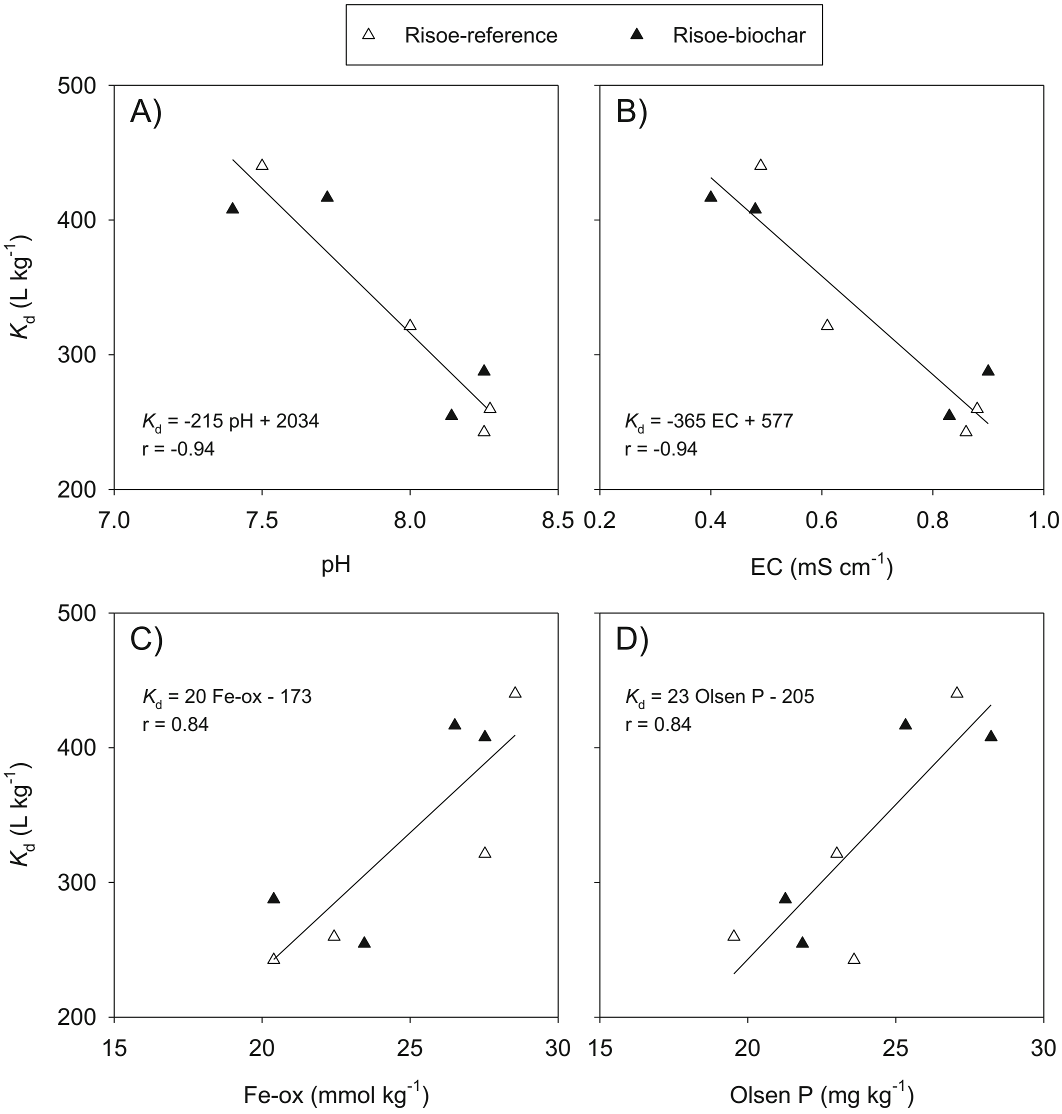

Fig. 2 Glyphosate sorption coefficient (K_d) plotted against **a** pH, **b** electrical conductivity (EC), **c** oxalate extractable Fe content (Fe-ox), and **d** Olsen P at the Risoe site. *White triangles* represent reference soils (without biochar); *black triangles* represent biochar-amended soil plots (20 Mg ha^{-1})

increasing soil EC (Fig. 2b), which is in good agreement with our previous discussion on decreasing CEC with increasing EC. In addition to this concept, the presence of strongly complexing metals (in this case probably Ca^{2+}) leads to a decrease in sorption as a result of metal-glyphosate complexes (Yaron et al., 2012). This agrees well with Morillo et al. (1997) who found reduced glyphosate sorption on montmorillonite due to the formation of copper-glyphosate complexes. In a recent study on glyphosate sorption on Danish agricultural soils, Paradelo et al. (2015) also found a linear decrease of K_d with EC and pH. In brief, the variations in chemical properties of soils, notably pH and EC (Table 1), can significantly control the variation in glyphosate $K_{d.}$ This is particularly the case of the soil from Risoe which was located in a natural $CaCO_3$ gradient (Kumari et al. 2014b). We presume that the dominant chemical effects due to the presence of $CaCO_3$ have overshadowed the effects of biochar on glyphosate sorption in Risoe soils.

3.5 Role of Fe Oxides and P

Glyphosate sorption was observed to increase with Fe-ox at the Risoe site (Fig. 2c). In general, Fe oxides are considered to serve as potential sites for glyphosate sorption (Piccolo et al. 1994), and past studies showed strong sorption of glyphosate with increasing iron content of soils (Gerritse et al. 1996); glyphosate can be readily adsorbed on iron oxide by ligand exchange through the phosphonic acid moiety (Cheah et al. 1997). Adsorption on the iron oxide is, however, markedly decreased by increasing pH and decreasing EC due to increase in net negative charge at the surface of iron oxides (Oliveira et al. 2004; Parks 1967; Sposito 1984). Interestingly, however, such a relation was not evident for Kalundborg soils irrespective of higher contents of oxalate extractable Fe in Kalundborg soils than in Risoe soils (see Table 1). Note that the pH of Kalundborg soils was below the PZC (pH 7–8.5) of iron oxides which results in a net positive charge on iron oxides. Thus, the soil properties affecting the glyphosate sorption at the Kalundborg site differs from that of the Risoe site. We further noticed higher Olsen P in Kalundborg soils compared to Risoe soils (Table 1), which is likely a reason for the lower glyphosate K_d in Kalundborg soils, since glyphosate and phosphate compete for the same potential sorption sites as we inferred before. In apparent contrast to this theory, glyphosate K_d did not decrease, but rather increased, linearly with increasing Olsen P in Risoe soils (Fig. 2d). This is, however, not surprising knowing that the Risoe soil is characterized by the distinct $CaCO_3$ gradient with resulting opposite gradients in Olsen P and pH, i.e., decreasing $CaCO_3$ levels causing higher Olsen P but lower pH levels. In relation to glyphosate sorption,

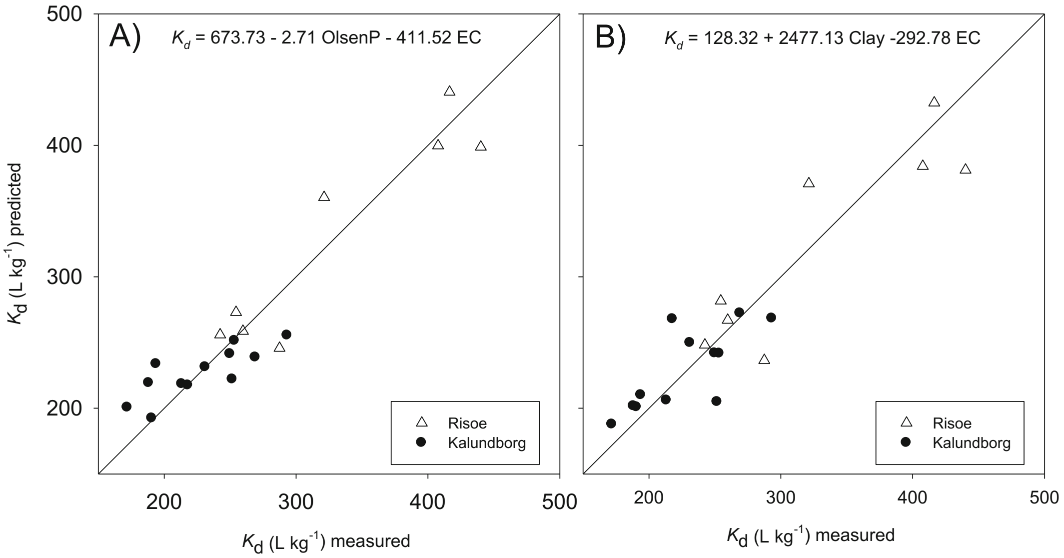

Fig. 3 Predicted glyphosate sorption coefficient (K_d) against measured glyphosate K_d for combined Kalundborg (*triangles*) and the Risoe (*circles*) soil data based on the multiple linear regression (MLR) analyses showing K_d as a function of **a** Olsen P and EC, and **b** clay and EC. 1:1 lines and MLR parameters used for Kd predictions are shown in each panel

the effect of pH dominates over that of Olsen P, thus giving an overall effect of increasing K_d even at increasing Olsen P (Borggaard 2011).

3.6 Predictors of Glyphosate Sorption

Acknowledging that the soil properties affected glyphosate sorption differently in Risoe and Kalundborg soils, we attempted to identify the best predictors of K_d if both soils nevertheless were considered together. A multiple linear regression (MLR) analysis combining the Kalundborg and Risoe datasets showed Olsen P and EC (Fig. 3a) as the best predictors of K_d ($R^2 = 0.88$, $P < 0.001$), suggesting that Olsen P and EC are the main controlling parameters of glyphosate K_d. The analysis further recognized clay and EC (Fig. 3b) as almost equally good predictors of K_d ($R^2 = 0.85$, $P < 0.001$) as Olsen P and EC. Interestingly, Olsen P presented a negative correlation with K_d when the two fields are studied together while the opposite trend was found in Risoe field. As it was discussed above, P can compete with or enhance glyphosate sorption and these interactions are likely site-specific. The results thus further highlight the importance of detailed physicochemical characterization of the site/soils to gain a valid mechanistic understanding on the controlling mechanisms of sorption characteristics in a complex soil–biochar chemical system.

4 Conclusions

Compared to agricultural soils from the Risoe and Kalundborg field sites, pure birch wood biochar had a ~20 to 60-fold lower glyphosate K_d. The effect of biochar amendment on the sorption of glyphosate was influenced by indigenous physicochemical properties of the soils. Apparently, the gradient in pH and EC at the Risoe site masked the enhancing biochar effects on glyphosate K_d that were indicated at the Kalundborg site. Overall the results highlighted the importance of further research for understanding the as yet poorly characterized effects of soil–biochar interactions in controlling the overall chemical sorption kinetics in biochar-amended field soils.

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