Prediction of the glyphosate sorption coefficient across two loamy agricultural fields

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ABSTRACT

Sorption is considered one of the most important processes controlling pesticide mobility in agricultural soils. Accurate predictions of sorption coefficients are needed for reliable risk assessments of groundwater contamination from pesticides. In this work, we aim to estimate the glyphosate sorption coefficient, K_d, from easily measurable soil properties in two loamy, agricultural fields in Denmark: Estrup and Silstrup. Forty-five soil samples in Estrup and 65 in Silstrup were collected from the surface in a rectangular grid of 15×15-m from each field, and selected soil properties and glyphosate sorption coefficients were determined. Multiple linear regression (MLR) analyses were performed using nine geo-referenced soil properties as variables to identify the parameters related with glyphosate sorption. Scenarios considered in the analyses included: (i) each field separately, (ii) both fields together, and (iii) northern and southern sections of the field in Silstrup. Considering correlations with all possible sets of the same nine geo-referenced properties, a best-four set of parameters was identified for each model scenario. The best-four set for the field in Estrup included clay, oxalate-extractable Fe, Olsen P and pH, while the best-four set for Silstrup included clay, OC, Olsen P and EC. When the field in Silstrup was separated in a northern and southern section, the northern section included EC, and oxalate-extractable Fe, Al and P, whereas the southern part included pH, clay, OC and Olsen P. The best-four set for both fields together included clay, sand, pH and EC. Thus, the most common parameters repeated in the best-four sets included clay and pH as also reported previously in the literature, but in general, the composition of the best-four set differed for each scenario, suggesting that different properties control glyphosate sorption in different locations and at different scales of analysis. Better predictions were obtained for the best-four set for the field in Estrup (R^2 = 0.87) and for both fields (R^2 = 0.70), while the field in Silstrup showed a lower predictability (R^2 = 0.37). Possibly, the low predictability for the field in Silstrup originated from opposing gradients in clay

and oxalate-extractable Fe across the field. Also, whereas a lower clay content in Estrup may be the limiting variable for glyphosate sorption, the field in Silstrup has a higher clay content not limiting the sorption, but introducing more variability in K_d due changes in other soil properties.

Keywords: sorption coefficient, glyphosate, field scale, multiple linear regression

INTRODUCTION

Pesticide leaching risk may vary strongly at the field scale, mostly because of heterogeneities in soil structure and biochemistry (Jury and Roth, 1990; Koestel et al., 2013). Sorption is one of the main processes controlling pesticide leaching (Arias-Estevez et al., 2008). Sorption also influences the magnitude and rate of other soil processes and functions, for example, reducing the bioavailability of pesticides for microbiota and hence limiting biodegradation (Alexander, 1995). Additionally, sorption reduces pesticide efficacy, leading to an increase in pesticide application rates (Reichenberger et al., 2007) which, in turn, influence other processes like plant growth or microbial activity. The sorption coefficient, K_d [L kg^{-1}], is one of the most sensitive input parameters in pesticide fate models (Farenhorst et al., 2008). The sorption coefficient, in turn, depends on the nature of the pesticide molecule and selected soil properties such as organic carbon, pH, texture, etc. (Wauchope et al., 2002; Weber et al., 2004). Because of such complex and interactive processes, it is essential to identify a set of soil properties that can predict location-specific pesticide sorption and thereby mobility. Rather than measuring the sorption coefficient itself by batch equilibrium experiments on soil samples, regression equations narrowed down to a few easily measurable soil properties will be beneficial if the relevant soil properties can be determined from non-destructive on-the-go surface techniques. Such regression models combined with on-the-go techniques will limit the sampling and laboratory costs for field scale modelling of K_d, but first, it is essential that the regression models are based on the right properties.

Glyphosate [N-(phosphonomethyl)glycine] is a non-selective herbicide with carboxyl, amino, and phosphonate functional groups (de Jonge and de Jonge, 1999). Glyphosate has a low mobility and strong affinity to soil mineral fractions such as clay and amorphous iron and aluminum oxides (Borggaard and Gimsing, 2008; Vereecken, 2005). Variable-charge minerals are considered to be more effective to glyphosate sorption than permanent-charge minerals (Gimsing

and Borggaard, 2002). Interpretations of the role of OC on glyphosate sorption are conflicting (Morillo et al., 2000). For example, Tsui and Chu (2004) observed increasing glyphosate sorption with increasing OC content while Gerritse et al. (1996) observed decreasing glyphosate sorption with increasing OC content. In addition to soil constituents, soil chemistry (pH, EC, ionic composition) plays a role on glyphosate sorption. Since glyphosate is a zwitterion, its net charge is pH-dependent (Stalikas and Konidari, 2001), and therefore, variations in soil pH can alter glyphosate sorption. Sorption of glyphosate is assumed to occur through the adsorbent–cation–phosphate linkage (de Jonge et al., 2001; Sprankle et al., 1975; Torstensson, 1985) and hence, an enhanced effect of cations (e.g., ferric, ferrous, and aluminum ions) on glyphosate sorption is also reported (Hensley et al., 1978; Sprankle et al., 1975). The resemblance of the sorption mechanisms of phosphate and glyphosate has led to the conclusion that glyphosate and phosphate compete for sorption sites on clay minerals and amorphous oxides (de Jonge et al., 2001). However, Borggaard (2011) reported that phosphate can have no effect or even increase glyphosate sorption. Overall, it is clear that heterogeneity in soil geochemistry imparts strong variation in glyphosate sorption.

Identification of field-scale areas vulnerable to leaching is important to understand and forecast groundwater pesticide loadings and to implement best management practices to minimize groundwater contamination. In particular, a thorough knowledge of the spatial variability of soil properties that control sorption is necessary to develop accurate predictive models of glyphosate sorption. However, based on soil properties and terrain attributes across a 2.72-ha agricultural field section Farenhorst et al. (2008) was not able to develop regression models strong enough to predict glyphosate sorption in soil (R^2=0.11). Neither was it possible for Singh et al. (2014) to detect any correlations between the glyphosate sorption coefficient and pH, clay and sand and only weak correlations was obtained with soil organic carbon (r= −0.21, P<0.001) and silt (r= −0.11,

P<0.001). Furthermore, Vinther et al. (2008) only showed a weak spatial correlation between the glyphosate sorption coefficient and clay (r=0.36, P<0.01) and OC (r=0.38, P<0.01).

In this study we investigated the influence of soil physical and chemical properties on the glyphosate K_d. The main objective of the study was to estimate K_d from easily measurable physical and chemical properties of soils taken from two Danish agricultural fields that are part of the Danish Pesticide Leaching Assessment Programme (www.pesticidvarsling.dk). Multiple linear regression (MLR) analysis was used to relate the glyphosate sorption coefficient, determined from laboratory batch experiments, with the soil physical and chemical properties. Based on the strength of these relationships, we determined if any of these measurements could be used for field-scale screening of glyphosate mobility.

MATERIAL AND METHODS

Field sites

Sampling was carried out at two agricultural loamy fields (Silstrup and Estrup) in Denmark (Fig. 1), which belong to the Danish Pesticide Leaching Assessment Program (Lindhardt et al., 2001). Silstrup is located in northwestern Jutland (56°55´56.16´´N, 8°38´43.91´´E) and covers 1.69 ha of loamy agricultural land and slopes gently 1-2^o. Two pedological profiles classified the soil as Alfic Argiudoll and Typic Hapludoll according to the USDA classification (Lindhardt et al., 2001). The field site in Estrup is located in southern Jutland (55°29´09.96´´N, 9°04´09.37´´E) and covers 1.26 ha of loamy agricultural land. The field site is virtually flat and the complex geological structure comprises a clay till core with deposits of different age and composition. Three pedological profiles classified the soil as Aquic Argiudoll, Abruptic Argiudoll, and Fragiaquic Glossudalf (Lindhardt et al., 2001). Both fields were managed conventionally with regard to crop rotation, fertilization, and soil tillage. Further information about field management at the two sites can be found elsewhere (Brüsch et al., 2013; Norgaard et al., 2014b; Norgaard et al., 2013).

Soil sampling and characterization

Bulk soil was collected from the top 20-cm in a rectangular grid of 15×15-m covering the cultivated area of each field (Fig. 1). This sampling grid was chosen to represent the spatial variations across the fields, and still keep the sampling intensity at a reasonable level. Sixty-five samples were collected from Silstrup and 45 from Estrup. Air dried and 2-mm sieved soil samples were used for subsequent soil analysis and sorption experiments. Texture was determined by a combined sieve/hydrometer method (Gee and Or, 2002). Organic carbon was determined on a LECO analyzer coupled with an infrared CO_2 detector (Thermo Fisher Scientific Inc., MA). The pH was measured in a soil/water solution of 8 ml soil suspended in 30 ml of demineralized water and electrical conductivity (EC) was measured in a 1:9 (v/v) soil/water extract. Oxalate extractable Al, Fe and P were measured using the procedure described by Shoumans (2000). Available soil phosphorous was determined by the Olsen method (Olsen, 1954).

Glyphosate solution

The sorption studies were performed with ^{14}C-labeled glyphosate ([glycine-2-14C] glyphosate, N-(phosphonomethyl)glycine). Radiolabelled ^{14}C-labelled glyphosate was purchased from Perkin Elmer (Boston, USA). Stock solutions were prepared by dissolving ^{14}C-labeled glyphosate in a 0.01 M $CaCl_2$ solution to an initial glyphosate concentration of 0.23 mg L^{-1}. Sodium azide (1.00 g L^{-1}) was added to prevent microbial degradation.

Sorption experiments

The glyphosate sorption coefficients were determined by batch equilibrium experiments with three replicates. Air dry soil aliquots (0.5 g) were equilibrated with 0.5 mL of 0.01 M $CaCl_2$ for 24 h in

glass centrifuge tubes closed with Teflon caps. Nine milliliters of the 0.01 M $CaCl_2$ containing the desired concentration of glyphosate were added and the samples were rotated end-over-end (30 rpm) for 24 h at 20°C followed by centrifugation at 5,000 rpm for 1 h. Samples of 3 mL supernatant were mixed with 17 mL of scintillation cocktail (Packard Ultima Gold, PerkinElmer, MA). The glyphosate concentration was quantified using a liquid scintillation analyzer (Packard Tri-carb 2250CA, Packard Instrument Co., IL). The stopping criterion was set to 1%, with a maximum counting time of 1 h. The amount of glyphosate sorbed was calculated as the difference between the solution concentration at the equilibrium and the concentration in vials without soil. Controls were included without soil material but were otherwise treated similarly.

The sorption coefficient, K_d, was calculated from Eq. (1).

$$K_d = \frac{C_s}{C_e} \quad (1)$$

where C_s is the amount of compound sorbed by the soil [g kg^{-1}] and C_e is the compound concentration of the soil solution at equilibrium [g L^{-1}].

Multiple linear regression analysis

The analyses used in this paper follow directly those used to predict colloid dispersibility, mobility, and transport at the experimental site in Silstrup (Norgaard et al., 2014a). To examine the interactions among parameters, a multiple linear regression (MLR) analysis was performed to relate K_d to every combination of nine measured soil properties (pH, EC, clay, sand, OC, Al_{OX} FE_{OX}, P_{OX}, and Olsen P). We make the simplest assumption of a linear dependence of K_d on the (combinations of) measured properties. However, it would be a relatively simple matter to consider nonlinear relationships if they were strongly supported in the literature. We emphasize that the adopted approach with MLR does not necessarily suggest that the underlying processes are inherently

linear; some of these processes may exhibit nonlinear, or even discontinuous, dependence on soil properties. However, our aim was merely to determine whether a small set of easily measureable properties showed a strong enough correlation with the glyphosate sorption coefficient for them to be used for field-scale screening. The variance inflation factor (VIF) was used to quantify the magnitude of multicollinearity for the included properties in each of the considered sets.

In our study, consideration of the results of the MLR analyses with all possible combinations of parameters allowed us to examine, with the fewest assumptions possible, the importance of soil properties on K_d across the two different fields. We examined the combinations of properties in sets of varying size best able (defined by maximum R^2) to explain sorption of glyphosate in different scenarios: each field separately and both fields together. In addition, Silstrup was split into a northern and southern section, because this site showed marked differences between North and South in solute transport behavior and colloid dispersibility and leaching (Norgaard et al., 2014a; Norgaard et al., 2013).

RESULTS AND DISCUSSION

Soil properties and glyphosate sorption

The average values and ranges of the selected soil properties are listed in Table 1. Clay content was lower in Estrup (0.06 - 0.14 kg kg^{-1}) than in Silstrup (0.14 - 0.19 kg kg^{-1}). The combination of these two fields provides a wide range in clay content for studying glyphosate sorption. Estrup showed a gradient in clay content from the southern to the northeastern part of the field (Fig. 2A). Higher clay contents in Silstrup were found in the northern part of the field (Fig. 3A). The average OC contents were 0.032 and 0.022 kg kg^{-1} for Estrup and Silstrup, respectively. Interestingly, both fields showed opposing gradients of OC and clay (OC maps not showed). In Estrup, the variations in OC were larger with values from 0.018 up to 0.084 kg kg^{-1}. Higher amounts of Al_{OX} were present in Estrup, most likely related with the high OC content (Fernandez-Sanjurjo et al., 1998). The content of Fe_{OX}, was twice as high in Silstrup compared to Estrup. The spatial variability of Fe_{OX} followed the same pattern as clay in Estrup (Fig. 2B), while in Silstrup higher Fe_{OX} were found in the southern section (Fig. 3B), where the clay content was lower. There were no differences in the phosphorus content, either P_{OX} or Olsen P, between the two fields. Oxalate-extracted phosphorous ranged from 235 to 558 mg kg^{-1} and Olsen P from 39 to 100 mg kg^{-1} (Table 1). Oxalate extractable P presented higher values in the southwestern part of Estrup (Fig. 2C), while in Silstrup P_{OX} presented higher values in the southern part (Fig. 3C). The pH of both fields was slightly acidic or neutral, ranging from 6.3 to 7.6 in Estrup and from 6.4 to 7.5 in Silstrup. Higher pH values in Estrup were located in the northwestern part of the field (Fig. 2D), and lower values in the eastern part. A belt from West to East in the center of Silstrup presented higher pH values, decreasing towards the southern part of the field (Fig. 3D). Electrical conductivity (EC) average values were 52 and 47 µS cm^{-1} for Estrup and Silstrup respectively. Higher EC values were found

in the southwestern part of Estrup; Silstrup showed a positive gradient in EC from Southeast to Northwest.

The glyphosate sorption coefficient was higher in Silstrup (344 to 667 L kg^{-1}) than in Estrup (161 to 536 L kg^{-1},). Glyphosate was strongly sorbed in the northwestern part of the field in Estrup (Fig. 2F) following the gradients in clay and Fe_{OX}. Silstrup showed a maximum sorption capacity in the northern part of the field, with a sorption "hotspot" towards the eastern part (Fig. 3F). There was no evident spatial correlation of K_d on the maps of the soil properties in Silstrup.

Single Linear Regression analysis

The best single predictor of K_d differed across the selected geographical scenarios. In Estrup, Fe_{OX} (Fig. 4B) was the parameter that explained most of the observed variation in K_d (R^2=0.73), and clay also provided a good correlation with K_d (R^2 = 0.52) (Fig. 4A). In Silstrup, the inverse correlation with P_{OX} gave the best R^2 (R^2 = 0.20) (Fig. 4C). Dividing Silstrup in northern and southern sections, P_{OX} (R^2=0.17) was selected in the North and Olsen P (R^2=0.25) in the South (Fig. 4D). When we predicted K_d from both fields together, clay was the best predictor (R^2=0.62) (Fig. 4A). From these results, Fe_{OX} or clay content could be considered as single predictors of K_d explaining more than 50% of the sorption variability; however, the uncertainty would be relatively high. Piccolo et al. (1994) found that amorphous oxides mainly interact with glyphosate enhancing its retention in soil. Glyphosate affinity to clay was stated from the first glyphosate sorption study reported in the literature (Sprankle et al., 1975) where sorption was stronger in a clay loam soil than a sandy soil, and it was confirmed by later studies. For example, Farenhorst et al. (2009) found that clay, together with pH, controlled glyphosate sorption across a prairie land scape. With a similar range of clay content as in our study (0.01 to 0.25 kg kg^{-1}), they measured sorption coefficients from 19 to 547 L kg^{-1}. The negative correlation with both Pox and Olsen P in Silstrup field suggested that P

competes with glyphosate for the sorption sites in the soil, reducing glyphosate sorption (de Jonge et al., 2001).

Multiple Linear Regression analysis

Multiple linear regression analysis was used to examine which set of measured soil properties could explain K_d best using as few assumptions as possible. The number of combinations, c, studied can be calculated by the binomial coefficient:

$$c = \frac{m!}{k!(m-k)!}, 0 < k \leq m \quad (2)$$

where m is the number of measurements and k is the number of parameters selected. The same predictor properties were used for all the analyses. The number of unique parameter sets obtained from k ranging from 1 to 9 was 511 for each of the five geographical scenarios considered: Estrup; Silstrup; Silstrup North; Silstrup South; and both fields together. For each subset of parameters considered, the goodness of the fit (R^2) and the significance level (p for significance, $\alpha = 0.05$) were calculated. This analysis was applied previously to predict colloid dispersibility, mobilization and transport at different soil sample scales (Norgaard et al., 2014a). Figure 5 presents the MLR results for the different geographical scenarios. The R^2 for each subset based on the MLR to K_d is shown in Fig. 5A, C, E, G, and I. The y-axis represents R^2 and the x-axis the number of predictor properties used for each set. A black point represents the R^2 from a combination of k properties with p-values > 0.05. Larger black dots represent sets with p-values ≤ 0.05, and red dots indicate the maximum R^2 obtained for each parameter set size. The best performances for each k value were significant (p-values ≤ 0.05) in all the sets. The improvement achieved when multiple parameters were included compared to the best single parameter was dependent on the geographical scenario; in general, the increment in R^2 from using one to nine parameters was between 0.2 and 0.3 (Fig. 5),

with little increase for both fields together, and considerably improvement in Silstrup South. For all of the geographical scenarios, the increasing rate of R^2 with increasing parameter set size decreased after around four parameters suggesting that only four parameters need to be considered in defining a screening set. A similar result was found by Norgaard et al. (2014a) for predicting colloid dispersibility and transport with a limited number of informative parameters that are feasible to measure at the field scale. In this study, all of the best-four sets were significant, with a *p*-value $\leq$ 0.05. The selection of four parameters did not reduce substantially the R^2 compared to using all 10 parameters. The best-four set for each MLR analysis is shown in Table 2. Positive signs are assigned to parameters which are positively correlated to K_d and vice versa. The weight of each parameter is shown in Table 3. None of the properties included in the best-four sets for the geographical scenarios had a VIF > 3 (data not shown). A VIF larger than 10 has previously been used to indicate that multicollinearity influences the regression estimates (O'Brien, 2007), however, based on our VIF this does not appear to be the case in any of the best-four models. The best-four set predicting K_d in Estrup included clay, Fe_{OX}, Olsen P (all positively correlated) and pH (negatively correlated), $R^2 = 0.87$. The best-four set in Silstrup included a positive correlation with clay, and a negative correlation with EC, sand, and OC ($R^2 = 0.36$). Surprisingly, P_{OX}, the best single predictor in Silstrup, was not included in the best-four subset. Only for $k = 4$, P_{OX} is out of the best predictors, while it was selected for the other nine sets of k values. This variability in the composition of the parameter sets together with the low performance achieved (less than 50% of the variability explained) suggest that other factors not measured possibly exerted a strong control on the sorption within this field site. Compared to Estrup where the low clay content may result in clay being a limiting factor for glyphosate sorption, the field in Silstrup has a higher clay content where more properties are likely to influence glyphosate K_d and the predictability of the best-four

set model Furthermore, the opposite gradients of clay and Fe_{OX} in Silstrup could interfere in their effects on the glyphosate sorption.

Dividing Silstrup in two geographical areas, the selected parameters differed from the whole field (Table 2). For the northern part, only the negative correlation with EC is common with the results for the whole field. Also, there is a positive correlation between K_d and the amorphous oxides (Fe_{OX} and Al_{OX}) and a negative correlation with P_{OX} for the northern part. For the southern part, the best-four set comprised a negative correlation with pH, clay, OC and Olsen P. The negative correlation with clay does not follow some previously published results (Glass, 1987; Vereecken, 2005). However, in this case, because clay is not the strongest predictor in the set, the negative sign may indicate interactions among clay, OC and Olsen P in controlling K_d.

he best-four set for both fields together was positively correlated with clay and negatively correlated with pH, EC and sand ($R^2 = 0.70$). The selection of clay suggested that the finest fraction of the soil controlled glyphosate sorption across both fields together. This parameter presented a wide range, not overlapped between the two fields (Table 1). The range of EC and pH are similar in both field sites (Fig. 4E and F). The effect of pH on glyphosate sorption is reported elsewhere (de Jonge and de Jonge, 1999; Gimsing et al., 2004; Mcconnell and Hossner, 1985). Increasing pH causes an increase in the negative charges of the soil surfaces as well as on glyphosate molecules. This phenomenon enhances the repulsion between the pesticide and the soil surfaces (Gimsing et al., 2004). Decreasing K_d with increasing EC (Fig. 4F) suggested that cations in the solution complexed glyphosate molecules reducing sorption on the soil surfaces. Glyphosate can form strong complexes with Zn, Cu, Co, or Fe (Caetano et al., 2012) that can inactivate sorption glyphosate ligands. For example, Copper-glyphosate complexes were found to reduce the herbicide sorption on montmorillonite (Morillo et al., 1997).

In general, the parameters selected by MLR are consistent with previously published controlling factors for glyphosate sorption (de Jonge et al., 2001; Gimsing and Borggaard, 2002; Hance, 1976; Sprankle et al., 1975). Clay and pH were selected in most of the geographical scenarios studied. Gimsing et al. (2004) found that Fe_{OX} and pH predicted glyphosate sorption in surface soils, and Ghafoor et al. (2013) included OC, pH and clay in their model for predicting K_d.

For a better understanding of the differences in R^2 in the analyses we plotted the predicted values as a function of the measured values (Fig. 5B, D, F, and H). Open points represents the predicted values for the best-four parameters, and full dots represent the predicted values for all parameter sets. As expected, using all parameters reduced deviations of the predicted values from the 1:1 line. In general, residuals were well distributed along the 1:1 line for the different geographical scenarios. A slight deviation from the 1:1 line, however, was observed for K_d > 550 L kg^{-1} (Fig. 5D, J) that corresponds to the northern Silstrupsection. When we studied the northern section individually (Fig. 5F), the bias of the predicted K_d from the 1:1 line was reduced. However, the low predictive power suggests that other, unmeasured properties exert a strong control on glyphosate sorption in Silstrup.

CONCLUSIONS

The influence of soil physical and chemical properties on glyphosate sorption was studied across two agricultural fields. The best-four set of parameters was considered to give an acceptable prediction of K_d compared to using the nine parameters measured in Estrup and with both fields together, while in Silstrup the performance was low. The most commonly selected parameters for predicting glyphosate sorption across the geographic scenarios studied included clay, pH, Fe_{OX}, EC and P. However, the four most predictive parameters varied depending on the field site. The proposed analysis could explain most of the variability in Estrup but less than half of the variation

in Silstrup suggesting that potential factors controlling glyphosate sorption in Silstrup were not determined. Further studies with larger data sets including a wider range of parameters are planned to verify the minimum number of measurements required for accurate estimation of K_d.

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FIGURE CAPTIONS

Fig. 1. Sampling distribution in Estrup (A) and Silstrup (B).The horizontal dotted line in Silstrup indicates the division between the northern and southern section.

Fig. 2. Spatial variation of selected soil properties (A) clay, (B) oxalate extractable iron, Fe_{OX}, (C) Oxalate extractable phosphorous, P_{OX}, (D) pH, (E) EC, and (F) the glyphosate sorption coefficient ,K_d, in Estrup. The interpolated maps were obtained by empirical Bayesian kriging in ArcMap 10.1.

Fig. 3. Spatial variation of selected soil properties (A) clay, (B) oxalate extractable iron, Fe_{OX}, (C) Oxalate extractable phosphorous, P_{OX}, (D) pH, (E) EC, and (F) the glyphosate sorption coefficient, K_d, in Silstrup. The interpolated maps were obtained by empirical Bayesian kriging in ArcMap 10.1.

Fig. 4. The glyphosate sorption coefficient as a function of (A) clay content, (B) oxalate extractable iron, Fe_{OX}, (C) oxalate extracted P, P_{OX} (D) Olsen P, (E) pH and (F) EC for the two fields studied. Notice that Silstrup was divided in northern and southern sections.

Fig. 5. Prediction of the glyphosate sorption coefficient, K_d, with the multiple linear regression (MLR) model. The panels A, C, E, G and I show the increase in R^2 as a function of the number of parameters included in the analysis (k = 10), for Estrup, Silstrup, Silstrup North, Silstrup South, and Both fields. Sets with a p value > 0.05 are shown as small dots; sets with a p value ≤ 0.05 have larger dots. The best prediction set (highest R^2 and $p \leq 0.05$) for a particular number of parameters included is marked with a red dot. Panels B, D, F, H and J show the predicted K_d versus the measured K_d for Estrup, Silstrup, Silstrup North, Silstrup South, and both fields, respectively. Filled symbols show the prediction sets using 9 parameters; open symbols show the prediction sets using only four parameters. Black circles represent Estrup points, red squares represent Silstrup North points, and blue triangles represent Silstrup South points. The solid lines represent the 1:1 line.

TABLES

Table 1. Selected soil properties and glyphosate sorption coefficients for Estrup and Silstrup .

		pH	EC	clay	silt	sand	OC	Al_{OX}	Fe_{OX}	P_{OX}	Olsen P	K_d
			µS cm^{-1}	----------kg kg^{-1}----------				----------mg kg^{-1}----------				L kg^{-1}
Estrup	min	6.31	33	0.06	0.14	0.46	0.02	513	464	238	39	161
	max	7.60	110	0.14	0.30	0.77	0.08	2078	1675	558	100	536
	mean	6.71	52	0.11	0.25	0.59	0.03	928	1105	335	59	322
Silstrup	min	6.39	40	0.14	0.23	0.45	0.02	648	1843	235	49	344
	max	7.49	71	0.19	0.33	0.59	0.02	971	2960	465	90	667
	mean	6.75	47	0.16	0.30	0.51	0.02	762	2420	328	64	475

EC: electric conductivity; OC: Organic Carbon content; Al_{OX}, Fe_{OX}, P_{OX}: Oxalate extractable aluminum, iron and phosphorous; Olsen P: Available phosphorous; K_d: glyphosate sorption coefficient

Table 2. The best-four sets from the multiple regression analysis (MLR) predicting the glyphosate sorption coefficient (K_d) for the different geographic scenarios: Estrup, Silstrup, Silstrup North, Silstrup South and all data. A "-" symbol indicates that the parameter is inversely correlated with K_d, and a "+" symbol indicates that the parameter is positively correlated with K_d. The R^2 values using a single parameter, the best four sets and all parameters are presented in the first three rows.

	Estrup	Silstrup	Silstrup N	Silstrup S	Both fields
R^2 single	0.73	0.20	0.17	0.25	0.62
R^2 best four set	0.87	0.36	0.43	0.53	0.70
R^2 all parameters	0.93	0.45	0.50	0.69	0.72
pH	-		-	-	-
EC		-			-
clay	+	+	-	-	+
sand					-
OC		-	-	-	
Al_{OX}					
Fe_{OX}	+				
P_{OX}					
Olsen P	+	-	-	-	

EC: electric conductivity; OC: Organic Carbon content; Al_{OX}, Fe_{OX}, P_{OX}: Oxalate extractable aluminum, iron and phosphorous; Olsen P: Available phosphorous.

Table 3. Weights of variable predictors for best-four sets from the multiple regression analysis (MLR) predicting the glyphosate sorption coefficient (K_d) for the different geographic scenarios: Estrup, Silstrup, Silstrup North, Silstrup South and all data.

Geographic scenario	Equation
Estrup	-187.0 pH + 1412 clay + 0.213 Fe_{OX} + 0.733 Olsen P
Silstrup	-6.49 pH +2792 clay -11450 OC -1.83 Olsen P
Silstrup N	-8.27 EC -0.395 Al_{OX} + 0.100 Fe-ox -2.274 P_{OX}
Silstrup S	-335.4 pH -3510.1 clay -28162 OC -2.274 Olsen P
Both fields	- 201.0 pH – 1.27 EC + 2850 clay – 282.9 sand

FIGURES

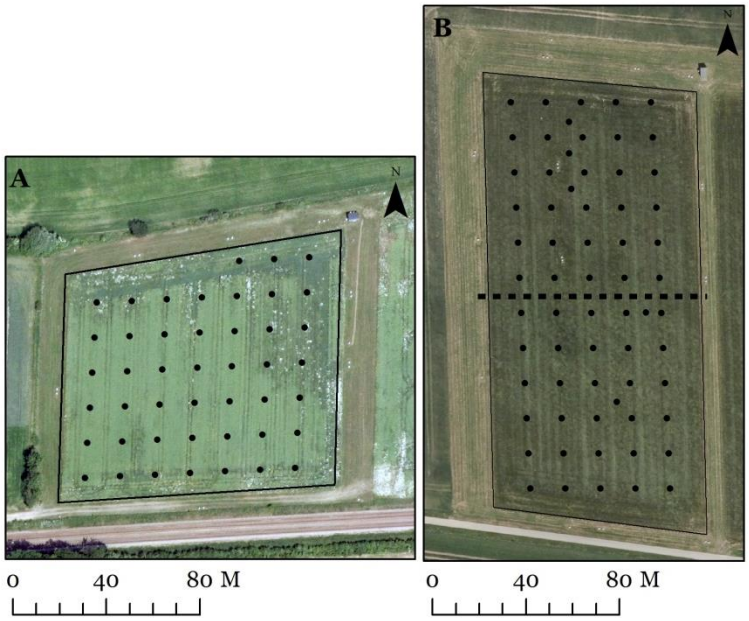
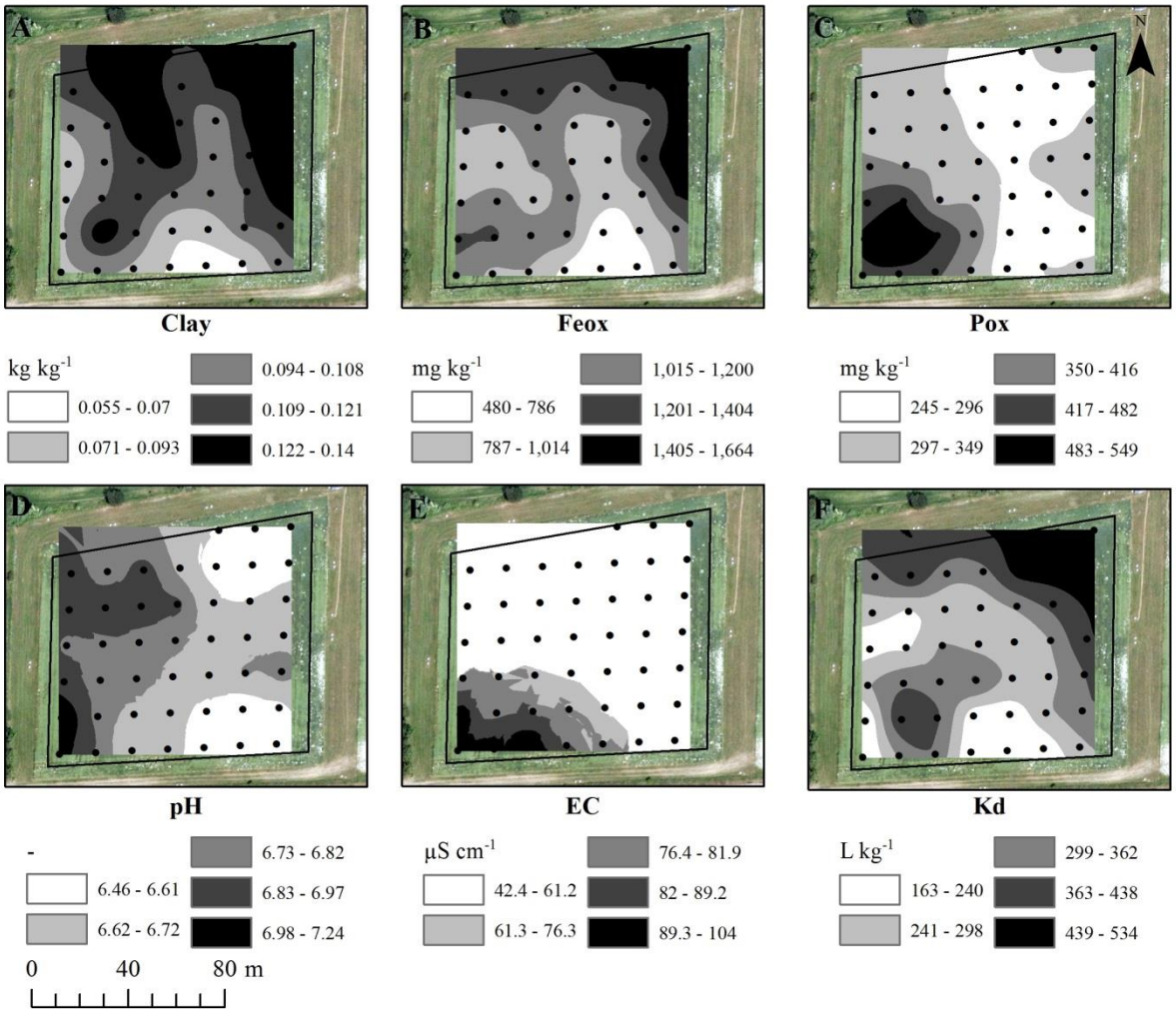
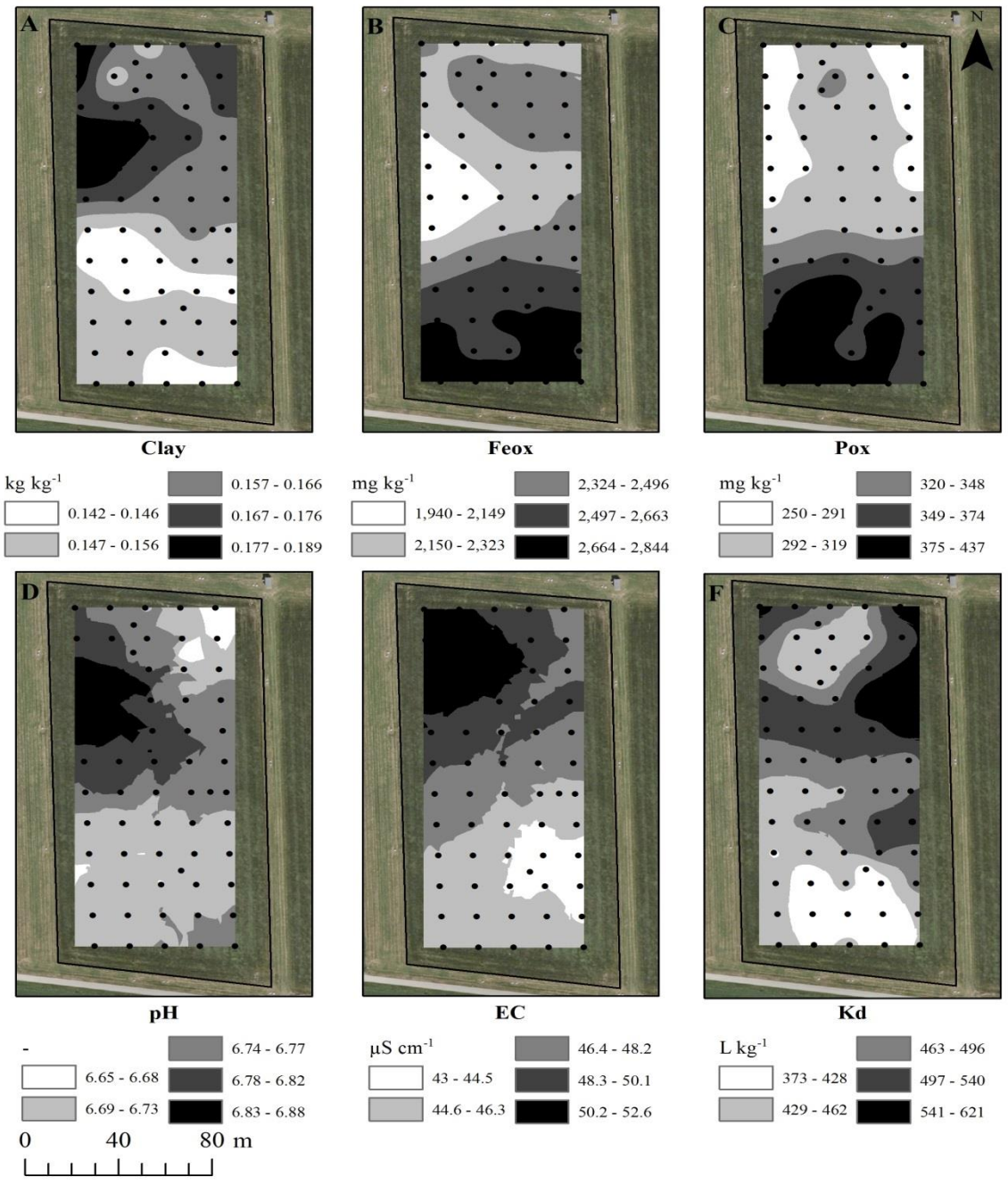


Fig. 6.


A
Clay
kg kg-1
0.055 - 0.07
0.071 - 0.093
0.094 - 0.108
0.109 - 0.121
0.122 - 0.14
B
Feox
mg kg-1
480 - 786
787 - 1,014
1,015 - 1,200
1,201 - 1,404
1,405 - 1,664
C
N
Pox
mg kg-1
245 - 296
297 - 349
350 - 416
417 - 482
483 - 549
D
pH
-
6.46 - 6.61
6.62 - 6.72
6.73 - 6.82
6.83 - 6.97
6.98 - 7.24
E
EC
µS cm-1
42.4 - 61.2
61.3 - 76.3
76.4 - 81.9
82 - 89.2
89.3 - 104
F
Kd
L kg-1
163 - 240
241 - 298
299 - 362
363 - 438
439 - 534
0
40
80 m

1

2 Fig. 7.


A
B
C
N
Clay
kg kg-1
0.142 - 0.146
0.147 - 0.156
0.157 - 0.166
0.167 - 0.176
0.177 - 0.189
Feox
mg kg-1
1,940 - 2,149
2,150 - 2,323
2,324 - 2,496
2,497 - 2,663
2,664 - 2,844
Pox
mg kg-1
250 - 291
292 - 319
320 - 348
349 - 374
375 - 437
D
F
pH
-
6.65 - 6.68
6.69 - 6.73
6.74 - 6.77
6.78 - 6.82
6.83 - 6.88
0
40
80 m
EC
µS cm-1
43 - 44.5
44.6 - 46.3
46.4 - 48.2
48.3 - 50.1
50.2 - 52.6
Kd
L kg-1
373 - 428
429 - 462
463 - 496
497 - 540
541 - 621

1

2 Fig. 8.

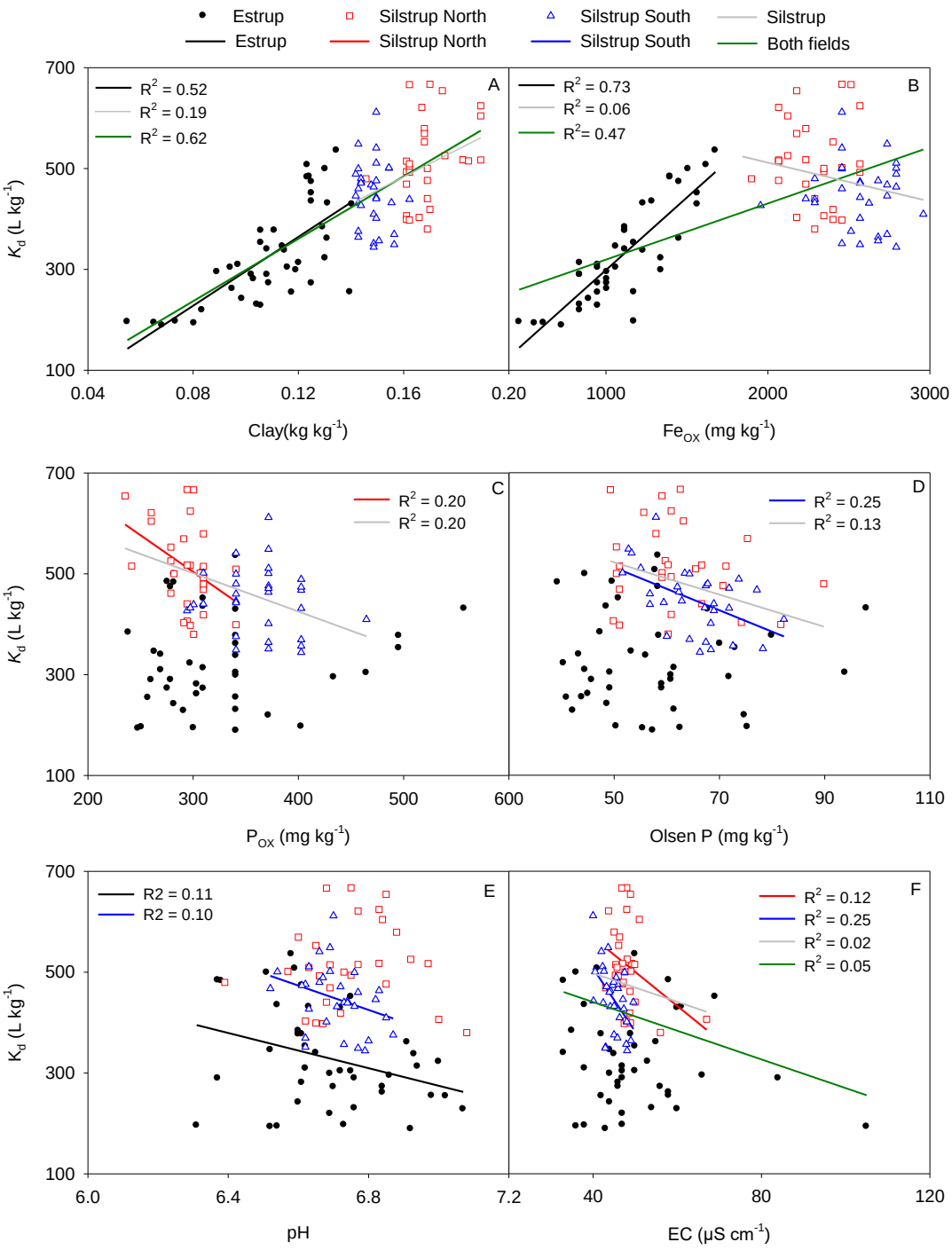
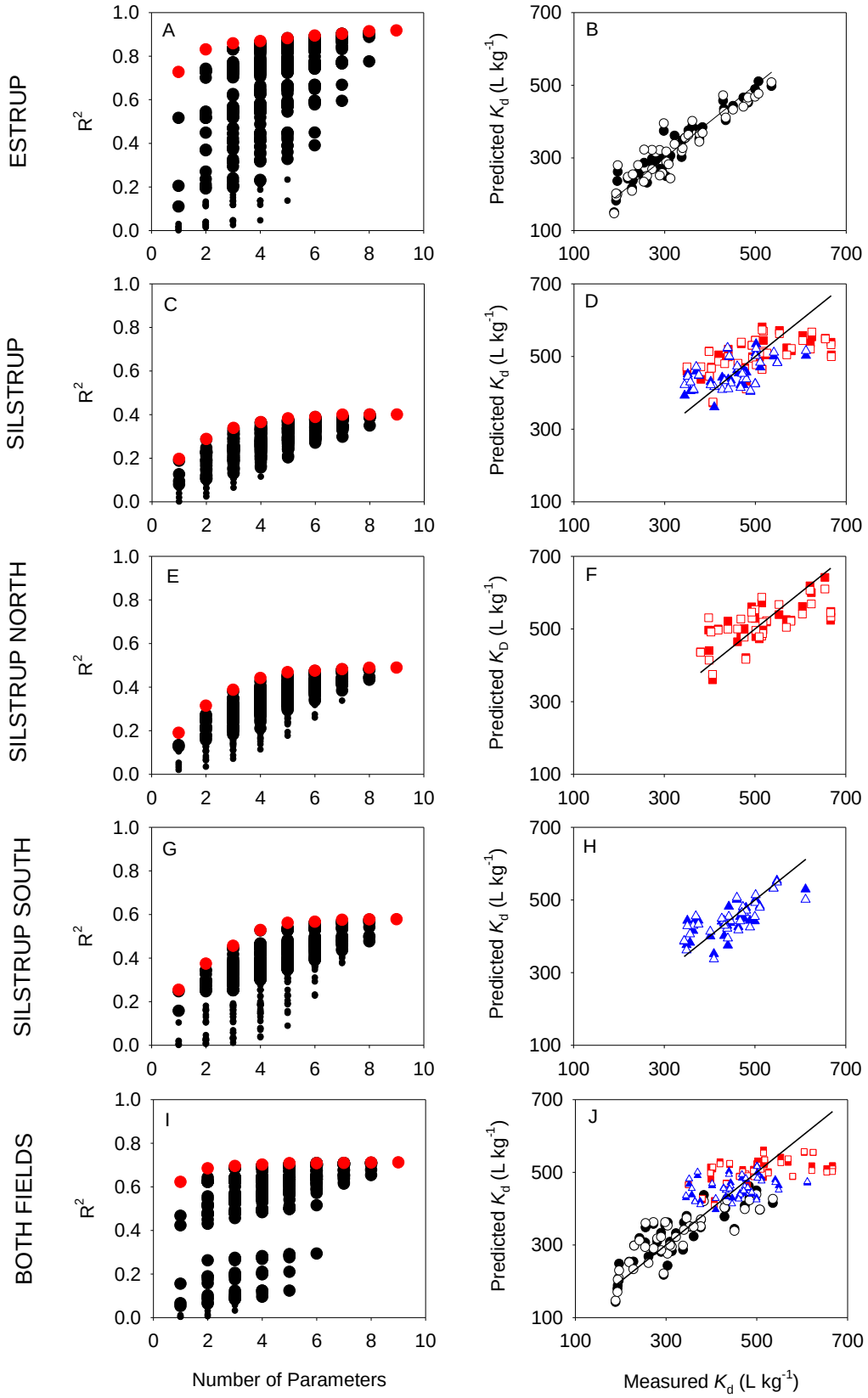

Estrup
Silstrup North
Silstrup South
Silstrup
Estrup
Silstrup North
Silstrup South
Both fields
A
R2 = 0.52
R2 = 0.19
R2 = 0.62
Clay(kg kg-1)
B
R2 = 0.73
R2 = 0.06
R2= 0.47
FeOX (mg kg-1)
C
R2 = 0.20
R2 = 0.20
POX (mg kg-1)
D
R2 = 0.25
R2 = 0.13
Olsen P (mg kg-1)
E
R2 = 0.11
R2 = 0.10
pH
F
R2 = 0.12
R2 = 0.25
R2 = 0.02
R2 = 0.05
EC (µS cm-1)
Kd (L kg-1)

Fig. 9.


ESTRUP
SILSTRUP
SILSTRUP NORTH
SILSTRUP SOUTH
BOTH FIELDS
A
B
C
D
E
F
G
H
I
J
R2
Predicted Kd (L kg-1)
Predicted KD (L kg-1)
Number of Parameters
Measured Kd (L kg-1)

1

2 Fig. 10.

1