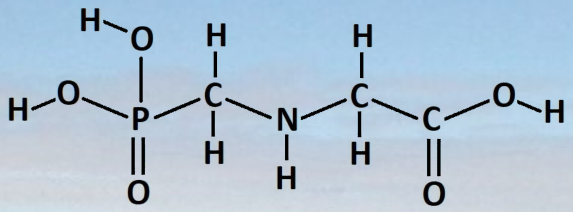
Controlling factors for glyphosate sorption

and the prediction of sorption coefficients for cultivated soils of Southern Greenland and elsewhere



MASTER THESIS

BY
LAURA THODE CHRISTENSEN

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STUDENT REPORT

School of Engineering and Science
Department of Civil Engineering
Thomas Manns Vej 23
9220 Aalborg East
Denmark
http://www.civil.aau.dk

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Controlling factors for glyphosate sorption
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of Southern Greenland and elsewhere

Author:

Laura Thode Christensen
Student number 20151421

Project period:

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Supervisor:

Per Møldrup
Aalborg University, Department of Civil Engineering

Assistant supervisor:

Lis Wollesen de Jonge
Aarhus University, Department of Agroecology

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Preface

This is a master's thesis written for the programme in Water and Environment, a specialization within Civil Engineering at Aalborg University, Denmark. It is intended for an audience familiar with the terminology of soil science, and formatted for duplex printing.

Reading guide

For citation of literature the Harvard method is used, which is denoted as [Surname,Year]. Where it is considered relevant, there is a specific reference to a certain chapter, page or table/figure.

The figures, tables, equations, chapters, sections, and subsections are sequentially numbered. The first figure in chapter 2 is denoted figure 2.1, the succeeding figure 2.2 and so forth.

Acknowledgements

A special gratitude goes to my fellow student Charel Pesch for assistance on logistics, collaboration on gathering data and general discussions. Also the technical staff, Palle Jørgensen in particular, at the facilities of Aarhus University in Foulum has proven invaluable for my understanding and execution of work in the laboratories. Last but not least: Marcos Paradelo, Cecilie Hermansen, Emmanuel Arthur and Maria Knadel of Aarhus University have all facilitated my understanding of the subject and complemented my two supervisors in the best way possible. Thank you all.

Laura Thode Christensen

Aalborg, Denmark

English abstract

The most used non-selective herbicide in the world is glyphosate, the active ingredient of popular formulations such as Monsanto's Roundup. The global use of glyphosate is still in 2017 on the rise. There are concerns for the environmental safety of both glyphosate itself, its degradation product AMPA, the cation it is distributed by, surfactants and other adjuvants. Glyphosate is generally expected to degrade before leaching to groundwater resources can occur, but under the Danish Pesticide Leaching Assessment Programme glyphosate has been found in groundwater above the limit value.

Glyphosate is water soluble, and binds to soil surfaces in complex ways still not fully understood. This study focuses on the strength of the bonds made between glyphosate and soil, and the soil parameters controlling the strength. Models for predicting the linear glyphosate sorption coefficient at the glyphosate concentration 0.23 mg L^{-1} are discussed and improved.

A sample set is carefully selected. Danish fields with pronounced gradients in clay content, pH and content of organic carbon are included. In junction with Greenlandic fields a gradient in soil age is obtained, ranging from areas recently introduced to farming, areas that have been farmed for only a few generations and the centuries old farmlands of Denmark. Soils of different origin are included, ranging from the glacial deposits of Denmark to the crystalline rocks of Greenland. Inability to obtain data rendered an attempt at including soils of volcanic origin unsuccessful for the most part.

Soil parameters are obtained from the knowledge base of Aarhus University, Foulum, or measured in the laboratory. Glyphosate sorption coefficients are measured by batch experiments on C^{14}-marked glyphosate and liquid scintillation counting. Linear regression analyses are performed in Matlab.

The soil parameters of pH, content of clay, content of fine silt, content of oxalate extractable phosphorus and most of all content of oxalate extractable iron prove important in predicting glyphosate sorption coefficients. Parameters of electrical conductivity, content of organic carbon and oxalate extractable aluminium are found to have only a weak or no influence. The historical management and origin of the soils are found to influence the relationships between soil parameters and glyphosate sorption coefficient.

Pedotransfer functions for predicting a glyphosate sorption coefficient based on oxalate extractable iron and either pH or oxalate extractable phosphorus are found to have coefficients of determination above 0.6 at regional level or higher.

Danish abstract

Den mest benyttede generelle plantegift i verden er glyfosat, den aktive ingrediens i populære produkter som Monsantos Roundup. Det globale forbrug af glyfosat stiger fortsat i 2017. Der er bekymringer for miljøpåvirkningen fra både glyfosat selv, nedbrydningsproduktet AMPA, den kation det distribueres med, overfladeaktive -og andre hjælpestoffer. Sædvanligvis forventes glyfosat at nedbrydes inden nedsivning til grundvand kan forekomme, men under det danske varslingssystem for udvaskning af pesticider er glyfosat fundet over grænseværdien i grundvand.

Glyfosat er vandopløseligt, og binder sig til jordpartiklernes overflader efter indviklede og endnu ikke fuldt afdækkede principper. Dette studie beskæftiger sig med styrken af bindingerne mellem glyfosat og jord, og de jordparametre der kontrollerer styrken. Modeller for bestemmelse af den lineære sorptionskoefficient for glyfosat ved koncentrationen 0.23 mg L^{-1} diskuteres og forbedres.

En samling af jordprøver er nøje udvalgt. Danske marker med udtalte gradienter i lerindhold, pH og organisk materiale er medtaget. Sammen med marker fra Grønland opnås en gradient i jordenes alder, lige fra de helt nyopdyrkede arealer, arealer der har været under plov i et par generationer, og til de århundrede gamle landbrugsjorde fra Danmark. Jorde med forskellig oprindelse er medtaget, fra Danmarks glaciale aflejringer til det grønlandske grundfjeld. Problemer med at fremskaffe data for jorde af vulkansk oprindelse gør at disse i hovedparten ikke er medtaget.

Jordparametre er indhentet fra videncentret på Århus Universitet, Foulum, eller målt i laboratoriet. Sorptionskoefficienter for glyfosat er målt ved masseeksperimenter på C^{14}-mærket glyfosat og liquid scintillation counting. Lineære regressionsanalyser er udført i Matlab.

Jordparametrene pH, indhold af ler, indhold af finsilt, indhold af oxalat ekstraherbar fosfor og i aller højeste grad indhold af oxalat ekstraherbar jern viser sig at være vigtige for forudsigelsen af sorptionskoefficienter for glyfosat. Parametrene elektrisk ledningsevne, indhold af organisk materiale og oxalat ekstraherbar aluminium viser sig kun at have lille eller slet ingen indflydelse. Jordens oprindelse og landbrugshistorie findes at påvirke forholdet mellem jordparametre og sorptionskoefficienter for glyfosat.

Modeller for bestemmelse af sorptionskoefficienter for glyfosat ud fra oxalat ekstraherbar jern og enten pH eller oxalat ekstraherbar fosfor findes at have R^2 over 0.6 på regionalt eller højere niveau.

Contents

Introduction 1

1.1 Motivation

I want to protect our soils and groundwater, for it still to be valuable for generations to come. Glyphosate is a widely used pesticide raising some environmental concerns, and it is yet to be fully understood under what conditions the problems arise.

Glyphosate, being the active ingredient in popular formulations such as Monsanto's Roundup, is the most used non-selective herbicide in the world according to Gros et al. [2017]. This is backed up by Global Analysists Industry Inc. [2016] who in their analysis of companies competing in the market for glyphosate include no less than 90 profiled companies spread over the globe. The use of glyphosate is still on the rise globally, figure 1.1 presenting global usage of the active ingredient since 1995.

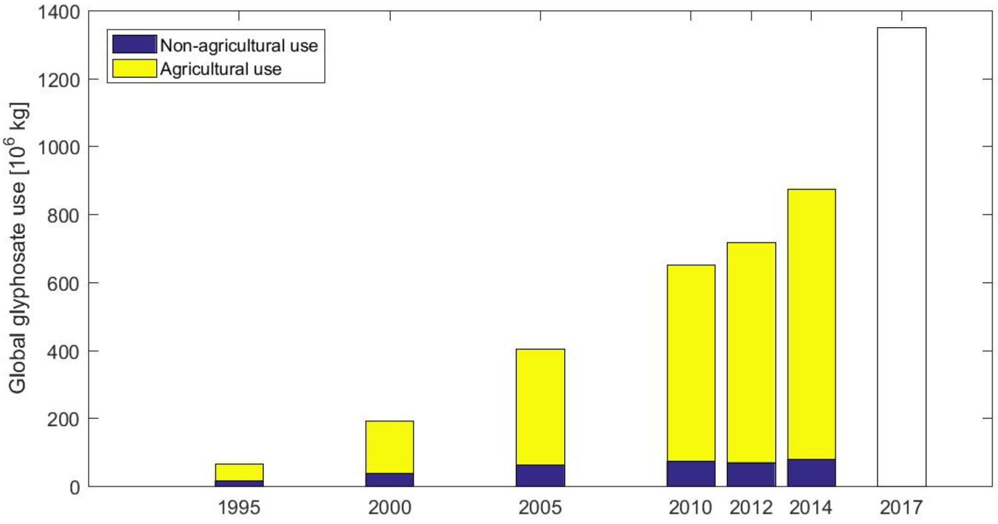

Figure 1.1. Global glyphosate use, values from Benbrook [2016]. Total values for 2017 is a prediction presented by Gros et al. [2017].

The Danish Pesticide Leaching Assessment Programme (PLAP) has monitored the leaching risk of pesticides under field conditions since 1998, and through this programme [Rosenbom et al., 2016] glyphosate has been found in groundwater considered part of the national drinking water resource. Continuous monitoring of the test fields provides a certain trust that problems with leaching from Danish agricultural land will be quickly uncovered. So far the findings have not been of a magnitude prompting a change in regulation, but they refute the belief that glyphosate is always degraded faster than leaching will occur.

For more than a decade I made a home for my family in the farming region of Southern

Greenland, where every year more potential agricultural land is uncovered by the melting inland ice. The soil is young in terms of the low number of microbial turnovers it has seen, and the lack of time for general weathering and minimal workings of humans have left the soil structure chaotic. Including the tundra climate there are many differences to the well processed experimental fields of temperate Denmark, and the knowledge gained from PLAP is not easily applicable nor are the fields included to be considered particularly representative for the the soils of Southern Greenland. More knowledge is needed if we are to make meaningful risk assessments for the use of glyphosate in Greenlandic agriculture, and considering the world wide use of glyphosate based herbicides other areas of the world might also benefit from a better understanding of the compound in general.

1.2 About glyphosate

The molecule of glyphosate as seen in figure 1.2 was first synthesised in 1950, but it was not until the 70s that its potential as a killer of weeds was discovered. Glyphosate was marketed in 1974 as a non-selective weed killer of green plants, and has since then gradually replaced other (harsher) chemicals hitherto used in established high-yield farming, but it is also widely used in non-agricultural practices including forestry, domestic use, roads and pavements. The use of glyphosate in agriculture continues to increase, gaining popularity with the spread of no-till farming as well as the 1996 introduction of genetically engineered glyphosate-tolerant crops, allowing glyphosate to be used as a selective herbicide. [World Health Organization, 2016]

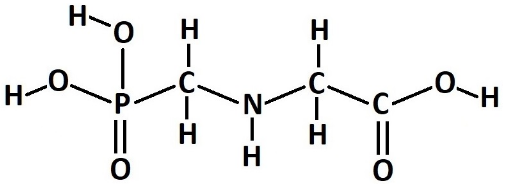

Figure 1.2. Glyphosate molecular structure.

The herbicide is usually formulated as a salt of the deprotonated acid of glyphosate and a cation such as for instance isopropylamine or trimethylsulfonium, the choice of cation influencing the side effect of the formulation [World Health Organization, 2016]. The salt can be part of a formula or marketed either as a crystalline, odourless and colourless solid or in a liquid solution. When glyphosate salt is an active ingredient in a formula it will be in combination with a surfactant an possibly other pesticides.

When a solution of glyphosate and a surfactant is applied to green leaves it is distributed throughout the plant where it inhibits the essential enzyme enolpyruvylshikimate phosphate synthase (EPSPS), thus preventing the production of amino acids required for protein synthesis, resulting in restriction of plant growth and if applied in sufficient quantities ultimately resulting in plant death [World Health Organization, 2016]. EPSPS is not present in mammalian cells.

Besides the obvious use on pavement and other areas with undesired green growth glyphosate finds a number of uses in agriculture. One is keeping the area around trunks of grapevine or trees free from weed, another is preparing a field for sowing, and a third is for desiccating a crop ensuring even drying before harvest. With the introduction of genetically engineered glyphosate resistant crops such as soy, maize, canola, cotton, alfalfa and sugar beets, glyphosate has found a new use killing off undesired plants in fields sown with these crops.

Glyphosate is reduced usually by microbes to aminomethylphosphonic acid (AMPA), consisting of the phosphonate functional group with an attached nitrogen atom. AMPA is comparable to glyphosate when it comes to toxicity, degradation rates and sorption to soil.

While investigation into formulations as well as the degradation product AMPA would probably lead to interesting discussions it is not in the scope of the current project. Glyphosate alone, not considering derived effects of other chemicals often included in formulations nor the products of degradation are investigated here.

Glyphosate, according to European Food Safety Authority [2015], has a negligible volatility with a Henry's law constant at $2.1 \cdot 10^{-7}$ Pa m^3 mol^{-1} and a high solubility in water at 10.5 g L^{-1}, while the octanol-water coefficient $log(P_{ow})$ is -3.2 at 25 °C and the solubility in organic solvents is generally low.

Unlike the highly hydrophobic pollutants of poly-aromatic hydrocarbons and the toxic elements of heavy metals that readily form aggregates with the soil matter [Loll and Moldrup, 2000] glyphosate will travel with the water in much more dynamic ways, and how the glyphosate of the water binds to the soil is in focus for the current project.

Glyphosate being a zwitterion sorbs onto variable-charge surfaces [Borggaard and Gimsing, 2008]. The phosphonic moiety of glyphosate binds weakly on unoccupied phosphate binding sites and is easily displaced by phosphate. Glyphosate binds to organic molecules via hydrogen bonds [Gros et al., 2017]. The binding varies as the molecular structure changes with varying pH as presented in figures 1.3 and 1.4.

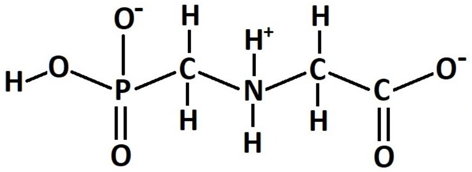

Figure 1.3. Glyphosate molecular structure at soil pH between approximately 2.23 and 5.46, reproduced from Albers et al. [2009].

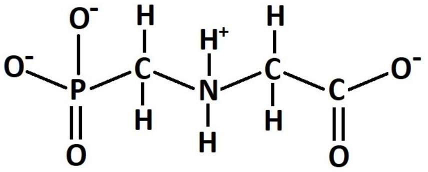

Figure 1.4. Glyphosate molecular structure at soil pH between approximately 5.46 and 10.14, reproduced from Albers et al. [2009].

1.3 Hypothesis

The risk of a chemical leaching is highly dependent on the strength of its sorption to the soil particles. Glyphosate sorption to soil is a very complex matter with several details still not fully understood [Borggaard and Gimsing, 2008].

Sorption coefficients depend on the concentration of the chemical and is often described by a fitted model. Adsorption models generally accepted [de Jonge et al., 2001] include the following four: Linear, Langmuir [Loll and Moldrup, 2000, equation 5.3], Freundlich [Vereecken, 2005] and Modified Freundlich (MF) [Sibbesen, 1981].

However, since the scope of the current project does not include a final determination of the sorption coefficients, and de Jonge et al. [2001] argues that sorption coefficients are only meaningful in investigations of relative differences between soils, the current project will only investigate the sorption coefficient found at a concentration of 0.23 mg L^{-1}.

How different soil characteristics influence the measured glyphosate sorption coefficient has been investigated in several papers, some of which are presented in table 1.1 with the given ranges of clay content, pH and more. All investigated soils are from the European continent, and hence have most likely been under human management for centuries.

Table 1.1. Glyphosate sorption coefficients reported in various studies.

K_d	C	No.	clay	pH	literature
113-377	0.04-65	23	n.a.	3.6-6.4	de Jonge et al. [2001]
41.7-113.5	0.03-67	10	15	6.13-7.3	de Jonge and de Jonge [1999]
161-667	0.23-0	110	6-19	6.3-7.6	Paradelo et al. [2015]
172-440	0.23-0	7	8-17	6.49-8.27	Kumari et al. [2016]
23.7-516	0.05-5	17	8.9-15.4	6.1-8	Sidoli et al. [2016]
96.4-780.5	10-150	23	2-58	4.03-7.19	Gros et al. [2017]
33.1-100.8	0.1-10	6	4-54	6.3-7.5	Albers et al. [2009]
81-113	0.08-24	2	4-15	5.32-6.3	de Jonge et al. [2000]

K_d [L kg^{-1}] is either the measured or (where a model has been fitted) the calculated adsorption coefficient at a glyphosate concentration of 0.23 mg L^{-1}.
C [mg L^{-1}] is the concentration (interval) at which sorption has been investigated.
No. is the number of (relevant) samples used in publication.
Clay [%] and pH is the range covered by (relevant) samples.
All soils are European.

Over the past few years attempts have been made to find a useful glyphosate sorption coefficient pedotransfer function [Dollinger et al., 2015] [Sidoli et al., 2016] [Paradelo et al., 2015] [Paradelo et al., 2016]. I shall attempt to improve the correlation of soil parameters to glyphosate sorption coefficients. Borggaard and Gimsing [2008] summarises that the risk of glyphosate leaching apparently is low due to strong sorption to soil and relatively fast degradation, but also that degradation has been found inversely correlated to sorption strength.

1.3.1 Effects of pH

Soil pH effects the molecular structure of glyphosate as presented in figures 1.3 and 1.4, and as soil pH rises the negative charges on the glyphosate molecule experience larger repulsive forces from the soil [Gimsing et al., 2004]. The overall effect is a reduced sorption, as measured by de Jonge et al. [2001], Sidoli et al. [2016] and Gimsing et al. [2004] who all found a strong negative correlation between glyphosate sorption coefficient and soil pH (correlation factor 0.7 for the two first references, 0.9 for the last).

Sidoli et al. [2016] finds that pH should be measured in $CaCl_2$ to prove valuable in predicting glyphosate sorption, but for practical reasons this aspect is not covered in the current project.

The hypothesis is that a rising soil pH measured in water shows a large negative influence on glyphosate sorption.

1.3.2 Effects of clay and fine silt

The small particles of the soil provide the charged surfaces to which glyphosate binds [Borggaard and Gimsing, 2008]. In general clay has been found to correlate positively with glyphosate sorption, as measured by Paradelo et al. [2015], Kumari et al. [2016] and Gimsing et al. [2004] who all found a medium strong positive correlation between clay content and glyphosate sorption coefficient (correlation factors 0.8, 0.6 and 0.5).

It is expected that the silt of the Greenlandic soils might hold some of the roles usually filled by clay, due to the young age of the soils.

The hypothesis is that a higher clay content shows a positive influence on glyphosate sorption, and that a higher content of fine silt in the Greenlandic soils shows a positive influence on glyphosate sorption.

In search of a K_d pedotransfer function Paradelo et al. [2015] found that a function of four predictors can get a coefficient of determination of up to 87%, but that the predictors may vary between fields. Two Danish fields were included, and for the total dataset analysed in the paper the following coefficients were found:

$$K_d = -201.0 \cdot \mathrm{pH} - 1.27 \cdot \mathrm{EC} + 2850 \cdot \mathrm{clay} - 282.9 \cdot \mathrm{sand} + 1585 \tag{1.1}$$

where

K_d	linear glyphosate sorption coefficient at concentration 0.23 mg L^{-1} [L kg^{-1}]
pH	measured in demineralised water
EC	electrical conductivity [µS cm^{-1}]
clay	particles below 2 µm [kg kg^{-1}]
sand	particles above 50 µm [kg kg^{-1}]
1585	constant given by Marcos Paradelo after personal inquiry September 2017

The hypothesis is that a better performing pedotransfer function can be found by use of a carefully selected dataset covering more than a few fields.

1.3.3 Effects of organic matter

Since the turnover and hence the mineralisation of organic matter in Greenland is less advanced the organic matter is expected to hold less sorption sites available to glyphosate. Several studies have investigated glyphosate sorption to soil organic matter, but while Gimsing et al. [2004] found a correlation factor of 0.4 both de Jonge et al. [2001] and Albers et al. [2009] concluded that no relationship could be found. The hypothesis is that organic matter content shows no correlation to glyphosate sorption.

1.3.4 Relation to electrical conductivity

A soils electrical conductivity is a measure of its ability to sustain a current, and reflect the content of dissolved ions [University of Minnesota et al., 2017]. When the salts present provide sorption sites for glyphosate measuring electrical conductivity might provide valuable information when estimating K_d. However Paradelo et al. [2015] found only a weak negative correlation, correlation factor -0.2, while others such as Kumari et al. [2016] has found no correlation between the two.

The hypothesis is that an increased electrical conductivity shows only a weak positive influence on glyphosate sorption.

1.3.5 Relation to cation exchange capacity, CEC

Cation exchange capacity is a measure of a soils ability to hold cations at a certain pH-level. Since the cations are the positively-charged ions of the soil, and glyphosate is predominantly negatively charged, CEC might prove valuable when estimating K_d of a soil.

Kumari et al. [2016] and Gimsing et al. [2004] found positive correlations between an increase in CEC and increase in glyphosate sorption coefficients, with coefficients of 0.7 and 0.5 respectively. Dollinger et al. [2015] performed an analysis on data mined in the literature, including soils of Brazil, Canada and Europe, and found that a pedotransfer function for predicting a glyphosate sorption coefficient based on the two soil parameters clay content and cation exchange capacity had a coefficient of determination of 0.48 :

$$K_d = 7.20 \cdot \text{CEC} - 1.31 \cdot \text{clay} + 24.82 \tag{1.2}$$

where

K_d	linear glyphosate sorption coefficient [L kg^{-1}]
CEC	cation exchange capacity [cmol kg^{-1}]
clay	clay content [%]

The hypothesis is that a better performing pedotransfer function can be found even without considering the soil parameter of cation exchange capacity.

1.3.6 Competition by phosphorus

Phosphate form a complex relationship with glyphosate sorption to soil, providing additional sorption sites while mainly competing with glyphosate [Gimsing et al., 2004]. Negative correlations, where higher phosphorus content correlate to lower glyphosate sorption has been found in several studies, where de Jonge et al. [2001] found a correlation coefficient of -0.8 to Olsen P, Kumari et al. [2016] found the coefficient -0.7 and Sidoli et al. [2016] the coefficient -0.36.

The hypothesis is that an increased amount of oxalate extractable phosphorus will show a negative influence on glyphosate sorption.

1.3.7 Iron and aluminium sorption sites

Borggaard and Gimsing [2008] have shown that minerals providing variable-charge sorption sites are favoured by glyphosate over those providing permanent-charge sites, and while clay contains minerals of both species it might prove valuable to measure directly on iron and aluminium which provides sorption sites for the phosphonic functional group of glyphosate.

A positive correlation coefficient between a higher content of extractable iron respectively extractable aluminium to glyphosate sorption coefficient has been found by several studies. Correlation factors of 0.7 has been found for oxalate extractable iron by de Jonge et al. [2001], Paradelo et al. [2015] and Gimsing et al. [2004]. de Jonge et al. [2001], Sidoli et al. [2016] and Gimsing et al. [2004] found correlation factors for oxalate extractable aluminium of 0.8, 0.4 and 0.7.

Sidoli et al. [2016] has found that a model including pH (measured in $CaCl_2$), iron, aluminium and phosphorus predicts a glyphosate sorption coefficient for soils in a 110 square kilometre area of France with a coefficient of determination of 0.94. When the pH is measured in water the coefficient of determination goes down to 0.61, and with the exponent $(nf)^{-1}$ averaged at 0.93 the following model is given:

$$K_f = (1.3 \cdot 10^6) \cdot e^{-1.3 \cdot \mathrm{pH} + 0.3 \cdot \mathrm{Fe} - 0.4 \cdot \mathrm{Al} - 7.3 \cdot \mathrm{P}} \tag{1.3}$$

where

K_f	Freundlich glyphosate distribution coefficient [mg kg^{-1} (L mg^{-1})$^{-\mathrm{nf}}$]
pH	measured in demineralised water
Fe	oxalate extractable iron [g kg^{-1}]
Al	oxalate extractable aluminium [g kg^{-1}]
P	phosphorus extractable by the Olsen method [g kg^{-1}]
( )	constant given in parenthesis [mg kg^{-1} (L mg^{-1})$^{-\mathrm{nf}}$]

The hypothesis is that a rising content of oxalate extractable iron and aluminium will show a positive influence on glyphosate sorption, and that iron will show a stronger correlation than aluminium.

1.3.8 Summary

The hypothesis is that when leaching does occur it will be from soils with high sorption coefficients as predicted by an improved pedotransfer function found by use of a carefully selected dataset covering more than a few fields, and the found function will perform better than existing even without considering the soil parameter of cation exchange capacity. The different soil parameters are expected to influence the pedotransfer function as presented in table 1.2.

Table 1.2. Recapitulation regarding hypothesis on parameters influencing glyphosate sorption. If an increased (amount of the) parameter prompt an increased glyphosate sorption the increase is marked positive.

Parameter	Increase	Significance
pH	-	large
clay	+	medium
Fine silt	+	medium
OM		none
EC	+	weak
P_{ox}	-	medium
Fe_{ox}	+	large
Al_{ox}	+	medium

1.4 Project objectives

Due to the complex and not fully understood nature of glyphosate sorption to soils, all experiments in the current project will be performed on natural soils to ensure that effects found are naturally occurring.

A dataset will be collected containing information on the linear glyphosate sorption coefficient K_d, soil texture, soil pH, electrical conductivity and content of available iron, aluminium and phosphate. The dataset must cover large variations in not only soil pH and clay content, but also several climatic zones and both soils on old farmland and very young soils must be included.

On the dataset an analysis will be performed using single and multiple linear regression, a relationship between K_d and soil properties should be established, and the findings compared to known pedotransfer functions. Impact of variations in climate and management practice will be assessed.

Finally the results must be compared to field scale data on leaching of glyphosate, and a discussion must be performed on the implication of the findings.

Soil materials 2

In this chapter the soils included in the current study are presented by their origin, their cultivated history, and the range the investigated soil parameters fall into. Also detail on soil sampling are given.

2.1 Chosen soils

To facilitate the attempted investigations a total of 533 soil samples are chosen to be included in the current analysis. Most of the samples are grouped in fields sampled every 15 meters, but collections of separate points are also included, as presented in table 2.1, where "Fertility" and "New Zealand" are presented as "separate points" since they represent collections of points spread over a larger area rather than sampled fields. "Fertility" are a collection of soils from Denmark.

The table includes information on the number of soil samples included in each field or collection, as well as total numbers included from the different geographical regions of Denmark, South Igaliku of Greenland, Greenland total, New Zealand and all combined. Greenland is separated in the two regions due to the differences in historical farming, where the oatfield has been farmed for more than 40 years while managing of the fields of South Igaliku are of more recent initiation.

All soils have been sampled from a depth of 0-25 cm, air dried and passed through a 2 mm sieve before storage at room temperature. The dried and sieved samples resulting from the work of laboratory technicians, students and researchers of University of Aarhus, Foulum, have provided the soil materials for this project.

2.2 Characterisation

The data found is in the range presented in table 2.2, where values for the different regions are also included, DK+GL representing all soils not including New Zealand.

A texture triangle including Danish and Greenlandic soils is presented as figure 2.1. Sand are particles in the range 63-2000 µm or 0.06-2 mm, Lund from 20 µm.

Table 2.1. Sample sites included in analysis.

Field name	no. of samples	type	primary gradient
Denmark:			
Odder	12	field	pH (6.2-8.2)
Eskebjerg	12	field	pH (5.7-8.3)
Lerbjerg	16	field	clay (10-69)
Estrup	45	field	clay (5-14)
Silstrup	77	field	clay (14-19)
Risø	(4)	field	clay (15-17)
Kalundborg	(3)	field	pH (6.5-6.7)
Juelsminde1	9	field	pH (5.9-7.7)
Lund	14 (18)	field	clay (10.9-14.9)
Fjennelev	12	field	clay (11-14)
Ringkøbing 1	15	field	pH (5.7-6.5)
Ringkøbing 2	11	field	pH (4.9-7.6)
Sørvad	20	field	pH (5.2-6.1)
Ø Bakker	(17)	field	clay (2-20)
Fertility	68	separate points	clay (3-18)
total, Denmark	311 (339)		
Greenland:			
Oatfield	70	field	
South Igaliku:			
Field 100	32	field	
Field 200	18	field	
Field 300	23 (24)	field	
total, South Igaliku	73 (74)		
total, Greenland	143 (144)		
New Zealand	(67)	separate points	
total, all regions	454 (550)		

No. of samples given in parenthesis are including samples missing information on one or more soil parameter. Unit for primary gradient are according to table 1.1.

Table 2.2. Covered values of soil parameters in analysed dataset.

	DK+GL	Denmark	Oatfield	South Igaliku	Greenland	New Zealand
K_d	37-2412	37-2412	56-1414	204-1504	56-1504	13-3810
pH	4.38-8.28	4.79-8.28	4.38-7.42	5.07-6.13	4.38-7.42	4.50-6.30
EC	0.13-3.94	0.24-3.94	0.22-1.42	0.13-0.86	0.13-1.42	0.60-10.00
Clay	1.6-68.9	2.3-68.9	2.7-8.5	1.6-5.6	1.6-8.5	0.1-51.2
Fine silt	1.0-43.1	1.0-43.1	6.3-30.4	1.7-8.7	1.7-30.4	7.3-92.7
Total C	0.8-37.1	0.8-37.1	2.0-7.9	0.9-6.1	0.9-7.9	2.1-21.7
Fe_{ox}	8.3-300	9.9-240	25-88	22-300	22-300	
Al_{ox}	11-130	11-130	18-97	26-96	18-97	
P_{ox}	1.5-52	3.9-32	1.5-52	4.5-30	1.5-52	

where

K_d	linear glyphosate sorption coefficient [L kg^{-1}]
EC	electrical conductivity [mS cm^{-1}]
clay	particles below 2 µm [%]
fine silt	particles in the range 2-20 µm [%]
total C	total carbon content [%]
Fe_{ox}	oxalate extractable iron [mmol kg^{-1}]
Al_{ox}	oxalate extractable aluminium [mmol kg^{-1}]
P_{ox}	oxalate extractable phosphorus [mmol kg^{-1}]

Texture (clay and silt) on soils of New Zealand is measured by not comparable method.

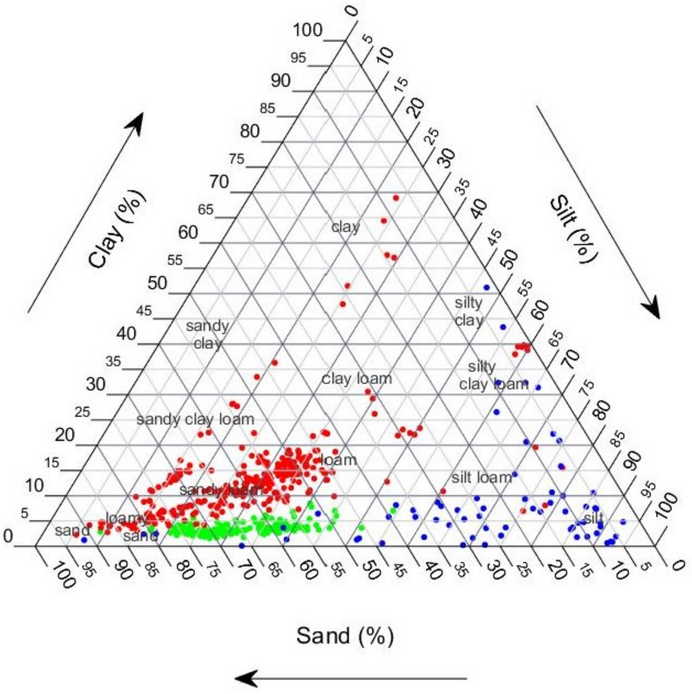

Figure 2.1. Soil texture triangle. Red points represent Danish soils, green points Greenlandic soils and blue soils of New Zealand. Note that values from New Zealand are not directly comparable due to differences in measurement methods.

2.2.1 Field sites in Denmark, Northern Europe

From Denmark a wide variety of fields have been included in the analysis, rendering a good coverage of the different agricultural soil types present in the small temperate country.

Soil samples have been included from the fields of Odder, Eskebjerg, Lerbjerg, Estrup and Silstrup [Paradelo et al., 2015], Risø and Kalundborg [Kumari et al., 2016], Juelsminde, Lund, Fjennelev, Ringkøbing, Sørvad and Ø Bakker. Locations of all sampled fields are visualised on figure 2.2, and in addition to the fields a collection of separate sampled points (not shown on map) have been included in the analysis.

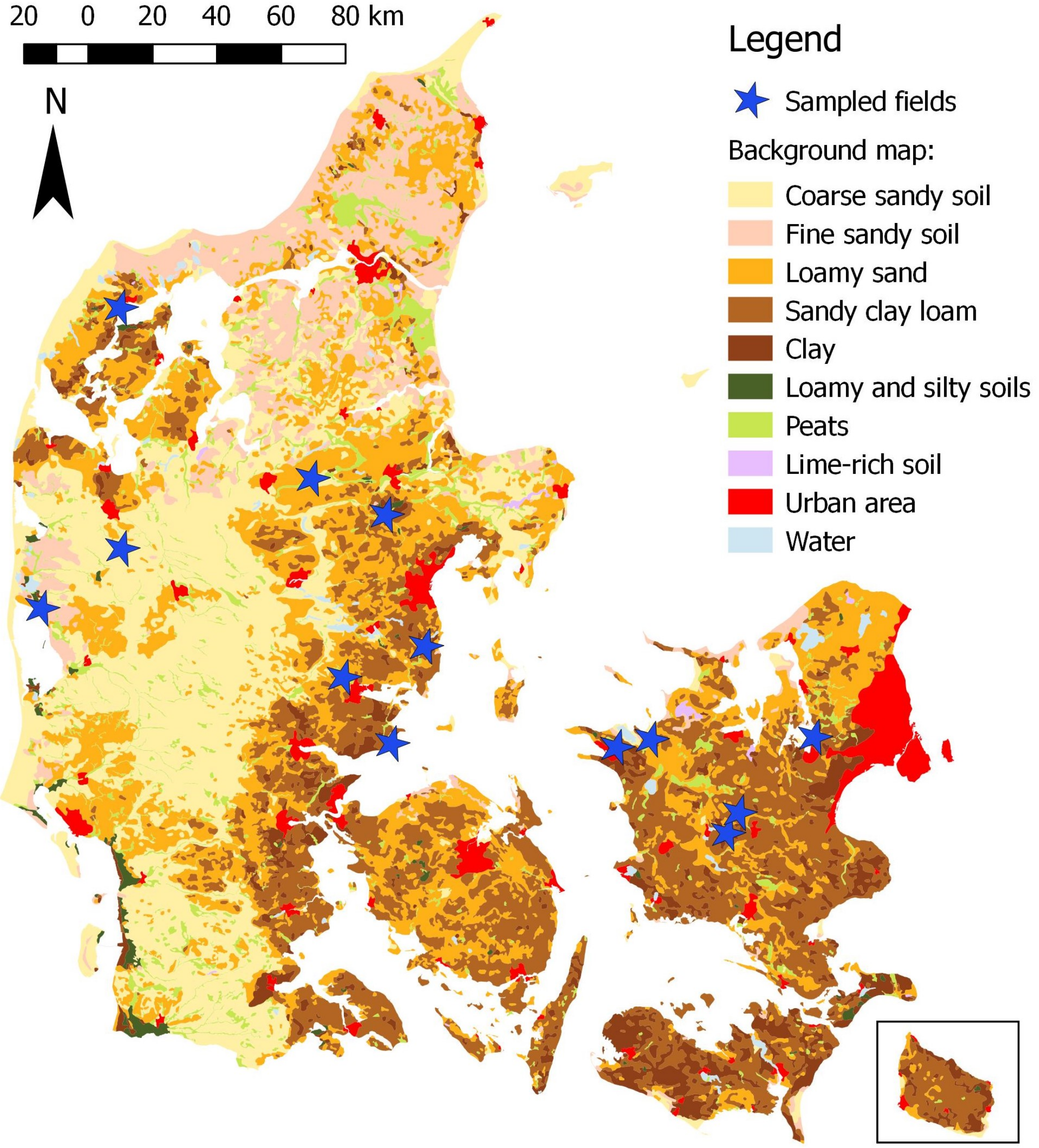

Figure 2.2. Location of sampled fields in Denmark. Separate points not shown. [Kortforsyningen, 2017] [Aarhus Universitet, 2017]

2.2.2 Field sites in Greenland

An oatfield by Upernaviarsuk Experimental Farm outside the town of Qaqortoq, see figure 2.4, was sampled by technicians and scientists from Aarhus University in the summer of 2014. By 2015 three more locations were sampled by the university staff, two fields next to the farm of South Igaliku and one three kilometres south of the farm. On figure 2.5 the locations of the three fields relative to the fjord and icecap are visualised.

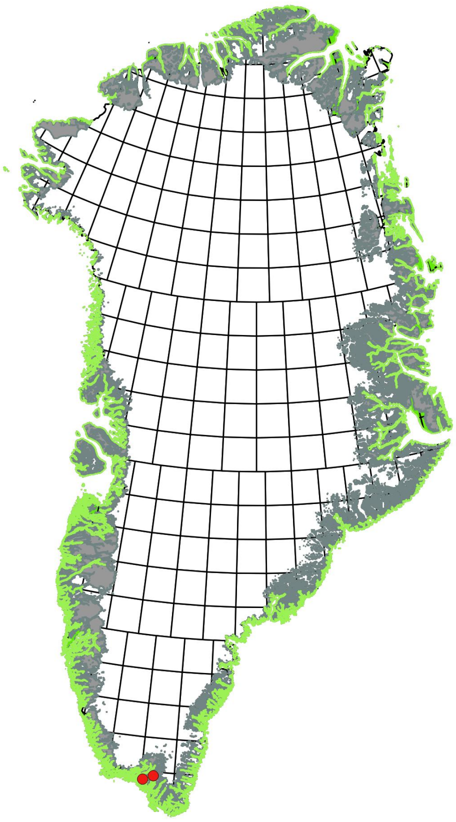

Figure 2.3. Location of sampled fields in Greenland. For smaller scale see figures 2.4 and 2.5. [Kortforsyningen, 2017]

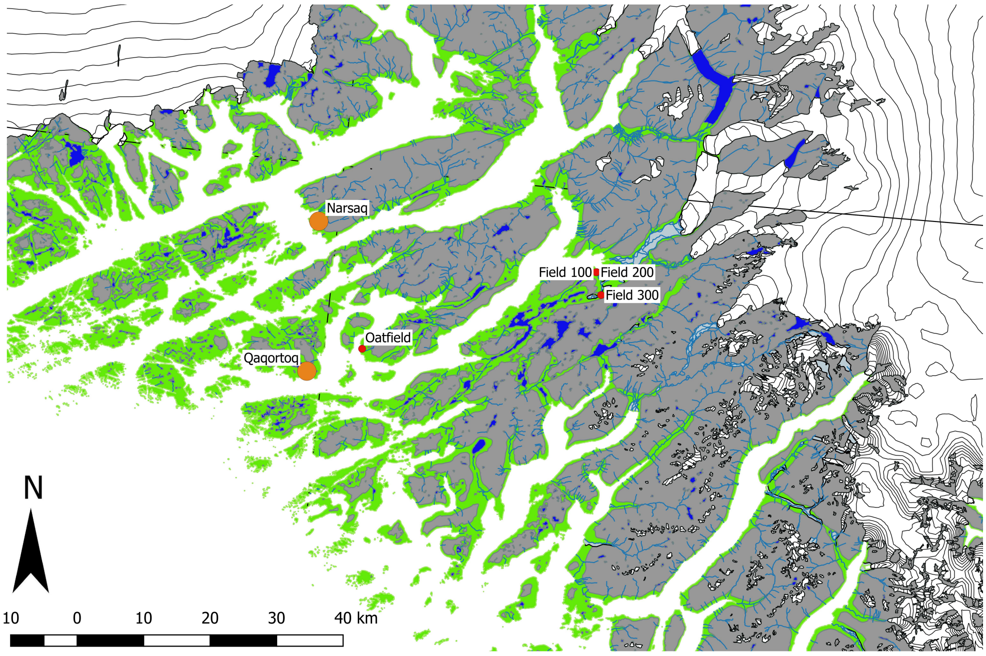

Figure 2.4. Location of sampled fields in Southern Greenland. Narsaq and Qaqortoq are the towns of the area. For legend and smaller scale see figure 2.5. Contours on land not shown. [Kortforsyningen, 2017]

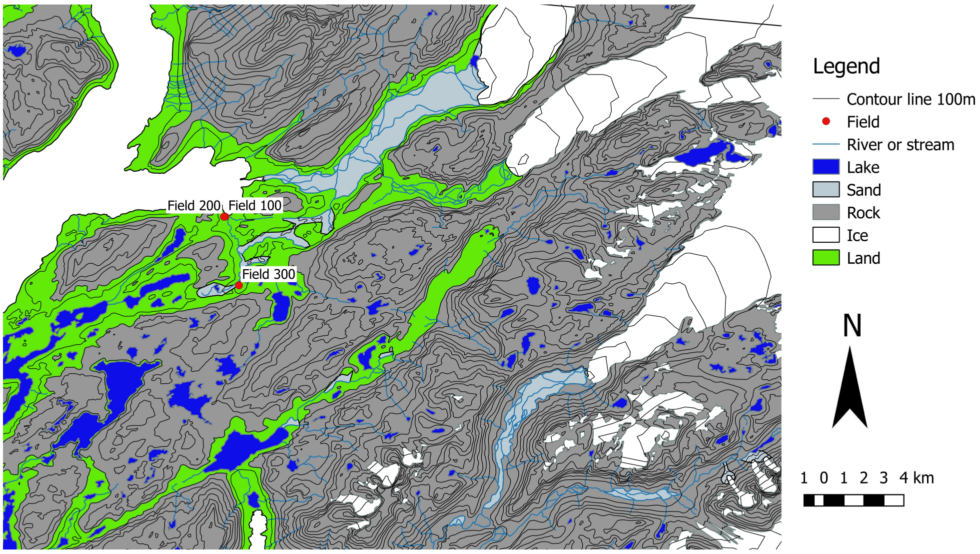

Figure 2.5. Location of sampled fields at South Igaliku. [Kortforsyningen, 2017]

The Greenlandic soils included in the analysis differ from the Danish soil not only in texture but also in the quality of the organic material present and in the length of the soils history in farming. The fields of South Igaliku are all established in resent years, field 300 used for pasture and 200 and 100 for growing winter fodder for the livestock. The oatfield has been under plough for approximately half a century, since the establishment of the experimental farm.

2.2.3 Field sites in New Zealand

From New Zealand 68 of the soils presented in Clothier and Lamont [2014] are included in the analysis on some of the soil parameters. The volcanic activity in the area induce a different composition of the clay minerals compared to what can be found in Denmark, and as such the soils of New Zealand adds potential robustness to the assessment of clays influence on sorption coefficients.

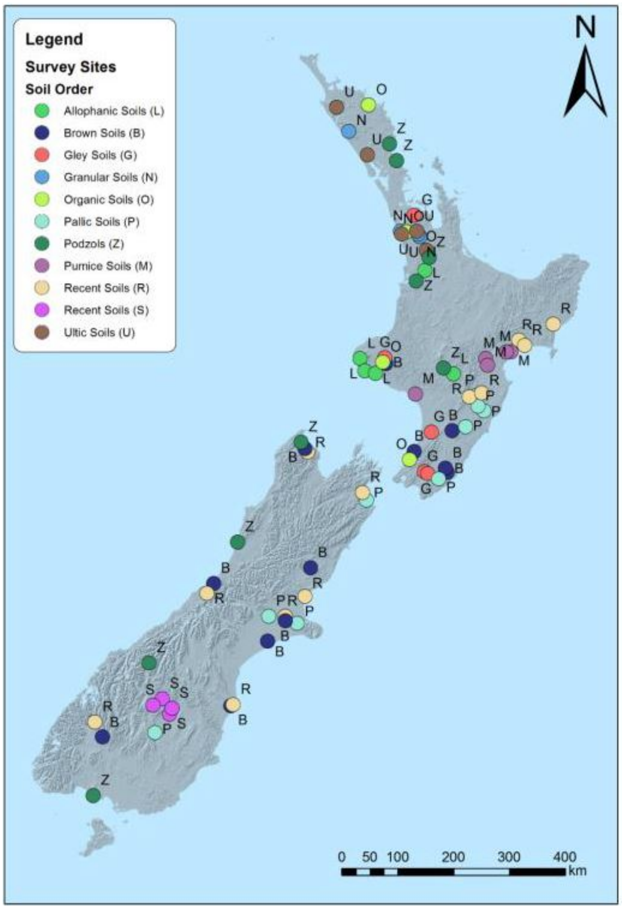

Figure 2.6. Location of sampling sites in New Zealand, illustration reproduced from Clothier and Lamont [2014]

The soils have been sampled by a New Zealand based research group in the years 2009, 2010 and 2012.

Measurements and methods 3

In this chapter origins of the investigated soil parameters are listed, laboratory procedures are described and methods for data analyses explained. Utilised equipment and chemicals are described.

3.1 Availability and origin of soil data

In order to evaluate the hypothesis the relevant soil parameters must be obtained for each of the chosen soils. Soil texture and for some of the soils also other parameters have been determined prior to the initiation of the current project and data on oxalate extractables have been acquired from an external laboratory. Glyphosate sorption coefficients and other data has been measured during the current project, and all methods are presented in the following. Table 3.1 presents the origin of each dataset for all chosen soils.

3.2 Methods for obtaining soil parameters

3.2.1 Soil texture

Texture on Danish and Greenlandic soils has been determined by a combined sieve/hydrometer method [Gee and Or, 2002] at or requested by University of Aarhus, Foulum.

Particle-size distributions of the soils from New Zealand have been measured in New Zealand by laser diffraction, and are therefore not directly comparable to the greater part of data.

3.2.2 Measurement of soil pH

The soil acidity was measured in a capped 50 mL test tube. 8 mL of soil and 30 mL of demineralised water was mixed by rotating the test tube end over end 30 times per minute for 10 minutes and left to settle for 10 minutes, all at room temperature. This is generally in accordance with Thomas [2002].

Acidity of the liquid was measured with a pH-meter, HQ11d from Hack (calibrated daily). The electrode was kept in the supernatant and moved approximately one centimetre up and down per second until a stable reading is acquired. No replicates were made.

Table 3.1. Data overview.

Field name	no. of samples	texture and humus	water content at air dry	pH	Electrical conductivity	glyphosate sorption coefficient	Al, oxalate extractable	Fe, oxalate extractable	P, oxalate extractable
Odder	12	o	X	X	X	1	L	L	L
Eskebjerg	12	o	X	X	X	1	L	L	L
Lerbjerg	16	o	X	X	X	1	L	L	L
Estrup	45	o	=	o	o	o	o	o	o
Silstrup	77	o	=	o	o	o	o	o	o
Risø	4	o	=	o	o	o	o	o	-
Kalundborg	3	o	=	o	o	o	o	o	-
Juelsminde 1	9	o	X	o	o	3	o	o	o
Lund	18	o	X	X	X	3	L	L	L
Fjennelev	12	o	X	X	X	3	L	L	L
Ringkøbing 1	15	o	X	X	X	3	L	L	L
Ringkøbing 2	11	o	X	X	X	3	L	L	L
Sørvad	20	o	X	X	X	3	L	L	L
Fertility	68	o	o	X	X	2	L	L	L
Oatfield	70	o	x	X	X	1/2	L	L	L
Field 100	32	o	x	X	X	1	L	L	L
Field 200	18	o	x	X	X	1	L	L	L
Field 300	24	o	x	X	X	1	L	L	L
New Zealand	67	o	o	o	X	2/3	-	-	-

o marks data available before initiation of current project.
X marks data measured as part of the current project.
x marks data measured by fellow student Charel Pesch.
L marks data acquired from external laboratory Agrolab A/S, Denmark.
= marks data not relevant for the current project.
- marks data that is relevant but for practical reasons have not been made available for the current project.
For glyphosate sorption coefficient is given a number representing the batch where measurements was obtained.

3.2.3 Measurement of electrical conductivity, EC

The electrical conductivity of the soil was measured in a capped 50 mL test tube. 4.0 g of soil and 36 mL of demineralised water was mixed by rotating the test tube end over end 30 times per minute for 60 minutes and left to settle for 60 minutes, all at room temperature.

The electrical conductivity of the liquid was measured with a conductivity-meter from

Radiometer Copenhagen, type CDM 2e No. 133602 (calibrated daily). The electrode was kept in the supernatant. No replicates were made.

Values read on conductivity meter is multiplied by the samples dilution factor, in the current case the readings are multiplied by 10 to reach the operative values presented.

3.2.4 Iron aluminium and phosphorus, Fe Al P

Oxalate extractable iron, aluminium and phosphorous was measured in an external laboratory by the method of Schoumans et al. [1987].

3.2.5 Batch sorption coefficient determination, K_d

Glyphosate sorption coefficients have been measured in batches of up to almost 200 soil samples at a time.

Glyphosate solution

Glyphosate marked with the C^{14} isotope was obtained from PerkinElmer (Boston, MA 02118 USA). The 3 mL solution featured 300 µCi and 0.92 mg glyphosate (*N*-phosphonomethyl-2-amino-[2-^{14}C]-acetic acid).

4 L stock solution was prepared by dissolving the marked glyphosate together with 5.88 g $CaCl_2$ (background electrolyte) and 4 g sodium azide (preservative) in deionized water, resulting in a glyphosate concentration of 0.23 mg/L. This is in the low concentration range, and according to table two in Vereecken [2005] this is relevant for prediction in the unsaturated soil zone.

Stock solution was kept dark and refrigerated, and allowed to raise to room temperature (while still kept dark) only for the day it would be utilised.

Sorption

The process of the batch sorption experiment is illustrated on figure 3.1. References to the figure are given in square brackets in the following paragraphs.

10 mL glass centrifuge tubes (cleaned and calcined at 500 °C) were prepared with 0.5 mg air-dry soil [1], and at least 24 hours before experiment start 0.5 mL 0.01 mol $CaCl_2$ were added to the samples to ensure their saturation [2] [3].

9 mL stock solution was added to each centrifuge tube [4]. The tubes were sealed with caps with acetone wiped Teflon coated liners [5] before being rotated end-over-end for 24 hours [6]. After centrifuging [7] for 60 minutes at 5000 rpm 3 mL of the supernatant was transferred [8] to a scintillation glass [9] and mixed with 17 mL scintillation cocktail (Ultima Gold, Packard) [10].

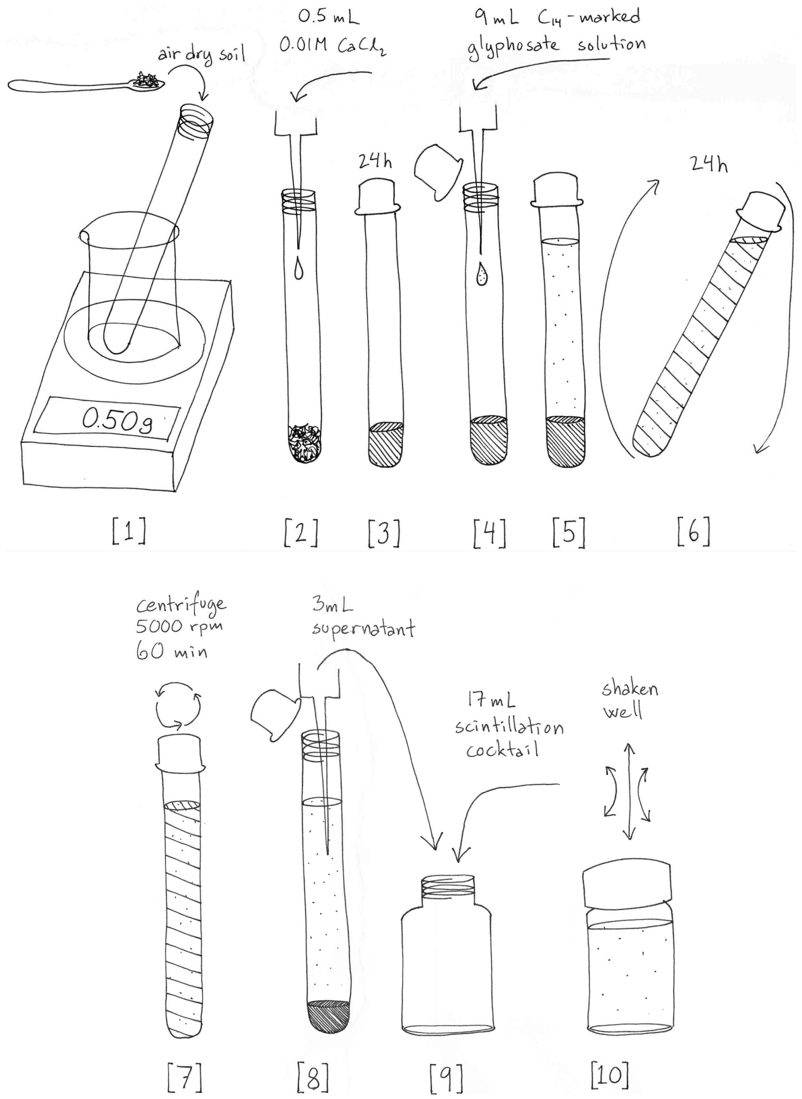

Figure 3.1. Illustration of method for obtaining glyphosate sorption coefficient.

Liquid scintillation count

The glyphosate concentration was determined by liquid scintillation counting on a Tri-carb from PerkinElmer, counting time 30 minutes. The quench indicator tSIE/AEC had previously been determined based on a quench curve of acetone and water.

Experiments were carried out at room temperature on 3 or more replicates of each soil sample. Controls were included without soil material, but otherwise treated similarly. All pipette-tips were primed with a corresponding diluted stock solution before use.

3.3 Data processing and analysis

3.3.1 Organic matter, data homogenisation

For the purpose of the current project all data for content of organic matter is converted to Total Carbon (Total C). If no other information is available Total C is considered equal to Organic Carbon (OC) or Soil Organic Carbon (SOC). If data is given as Organic Matter (OM) or "humus" the following conversion factor is used: Humus = OM = 1.7036 * Total C .

3.3.2 Fe Al P Data homogenisation

For the purpose of the current project all data for content of oxalate extractable iron (Fe_{ox}), aluminium (Al_{ox}) and phosphate (P_{ox}) is converted to mmolkg^{-1}. If data is given as mgkg^{-1} it is divided by the atomic weight of the element in question, namely 55.85 for iron, 26.98 for aluminium and 30.97 for phosphate.

3.3.3 Sorption isotherm

Glyphosate sorption can be described by several functions, one of the better performing being the Freundlich Isotherm as known from Loll and Moldrup [2000] and presented in the following equation 3.2, while the linear sorption isotherm is presented concurrent. Both are illustrated on figure 3.2.

$$C_S = K_d \cdot C_L \tag{3.1}$$

$$C_S = K_f \cdot (C_L)^{1/nf} \tag{3.2}$$

where

C_S	concentration on solids [mg kg^{-1}]
C_L	concentration in liquid [mg L^{-1}]
K_d	linear glyphosate sorption coefficient [L kg^{-1}]
K_f	Freundlich glyphosate distribution coefficient [mg kg^{-1} (L mg^{-1})$^{-\mathrm{nf}}$]
nf	Freundlich exponent [-]

Since the main interest of the current project is the parameters controlling glyphosate sorption across fields and regions, the linear model is quite sufficient for allowing adequate comparisons between samples.

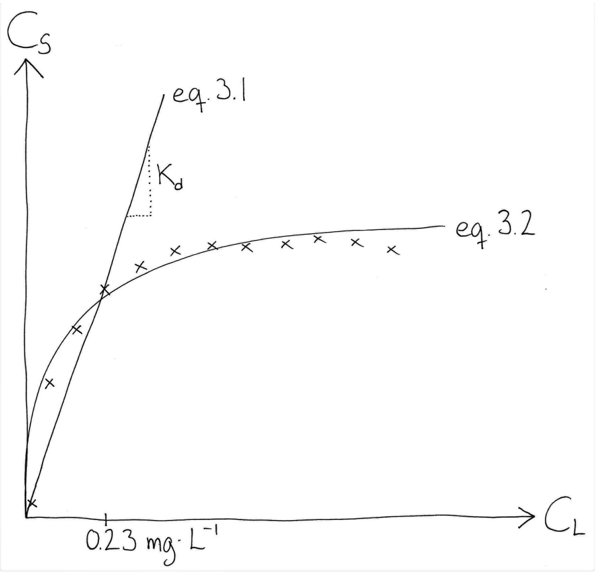

Figure 3.2. Fictitious sorption isotherm, x illustrating measured points, lines illustrating approximations based on equations 3.1 and 3.2.

3.3.4 Post-processing of data, glyphosate sorption coefficient

Theoretical decays per minute (DPM) of the stock solution gives a theoretical concentration per DPM, which is used when calculating the concentration of glyphosate in both the control samples and the extracted supernatant from soil samples.

The concentration in the controls is averaged, and the difference to the concentration in the supernatant is regarded equivalent to what is sorbed to the soil. When the 9.5 ml liquids is compared to the exact weight (four significant figures, water content at air dry subtracted) of the soil sample the sorbed amount can be calculated in the unit mg/kg, letting us calculate K_d as the concentration in the supernatant divided by the sorbed quantity.

Where one of the replicates increased the standard deviation by magnitudes it was considered erroneous and removed from the set.

3.3.5 Linear regression analysis

Analyses are performed with the aid of the software Matlab, version R2016a, by MathWorks Inc.

Test if current dataset is suited for linear regression analysis

Linearity between predictors and response is assessed in chapter 4. Two outlier have been omitted: From the sample G302 a recorded content of oxalate extractable iron more than double the size of adjacent values is considered erroneous; From sample number 3 at the field of Estrup a recorded electrical conductivity more than double the rest of the values from that field is considered erroneous. No other outliers have been omitted.

Data has been checked for multicollinearity (data not presented). Two Pearson correlation coefficients (r) are found to be larger than 0.8, namely 'clay against total C' and 'electrical conductivity against the function of clay, fine silt and OM' both at 0.81. Since these correlations are both absurd and small they are not considered further. All tolerances $(T = 1 - r^2)$ are larger than 0.2 and with variance inflation factors $(VIF = 1/T)$ below 10 there is found no indication of multicollinearity.

SLR, individual correlations for predictors against K_d

For analysis of dependencies between sorption coefficient K_d and the soil factors the Matlab functions 'corr' and 'fitlm' are used.

Analysis by multiple linear regression

The Matlab function 'bestregress' is used on the dataset to perform stepwise multiple regression analysis. The linear pedotransfer functions are build by applying the Akaike information criterion to the models.

Adsorption coefficient relation to single parameters

4

In this chapter the investigated physical and chemical soil properties are presented one at a time and related to the glyphosate sorption coefficient. Figures illustrating the relationships or absence thereof are presented with trend lines for the different regions. Implications are discussed. Finally dependencies between some of the important parameters are discussed and an overview is given on the findings.

4.1 General figure legend and more

With K_d as the dependent variable each of the soil parameters are evaluated as predictors and presented in the following. Legend for scatter diagrams is found as figure 4.1. All points include information on standard deviation where available.

Legend of trend lines is included for each figure. Level of significance is given as an appendix to r^2 , *** , ** and * representing correlation significance levels of 0.001, 0.01 and 0.05 respectively. r^2 is the adjusted coefficient of determination.

Figure 4.1. General legend for all scatter diagrams

4.2 pH

The hypothesis states that since a rise in soil pH will increase the repulsive forces between glyphosate and soil, the over all effect is a reduced sorption. Several studies have presented this negative correlation between soil pH and glyphosate sorption coefficient. Some are presented in table 4.1 together with studies that found no or only weak correlation between the two. Sidoli et al. [2016] found that pH should be measured in a solution of $CaCl_2$ to be most valuable in prediction of the glyphosate sorption coefficient. In the current study pH is measured in demineralised water for practical reasons and in accordance with local custom.

Table 4.1. Glyphosate sorption coefficients and correlation to pH as reported in various studies.

pH	cor.	K_d	no.	region	literature
6.13-7.3	-	41.7-113.5	10	One Danish soil sample	de Jonge and de Jonge [1999]
5.32-6.3		80.7-112.7	2	Two fields in Denmark	de Jonge et al. [2000]
3.6-6.4	-	112.9-377	23	Two fields in Denmark	de Jonge et al. [2001]
4.6-6.5	-	n.a.		Denmark	Gimsing et al. [2004]
4.03-7.19		96.4-780.5	23	Sweden and Germany	Gros et al. [2017]
6.1-8	-	23.7-516	17	France, Lyon	Sidoli et al. [2016]

cor. indicates with a symbol if correlation between pH and K_d was found: - indicates a negative correlation.
K_d [L kg^{-1}] is either the measured or (where a model has been fitted) the calculated adsorption coefficient at a glyphosate concentration of 0.23 mg L^{-1}.
no. is the number of (relevant) samples used in publication.

Data from the current project is presented on figures 4.2 and 4.3. All significant Pearson coefficients for pH are negative, and the highest level of significance is found when all soils are included (r^2=0.06). For all regions it is found that only a minor part of the variance in K_d (if any at all) is due to changes in pH. On field level the influence of pH is more varied, ranging from not significant to highly significant with a coefficient of determination at 0.97 for Juelsminde 1 presented on 4.3.

Juelsminde 1 has only very short ranges for all other measured parameters (clay at 16.6-17.9 %) but electrical conductivity (0.91-2.7 mS cm^{-1}) and pH. For fields with a larger range of clay content it is found that the influence of pH is reduced.

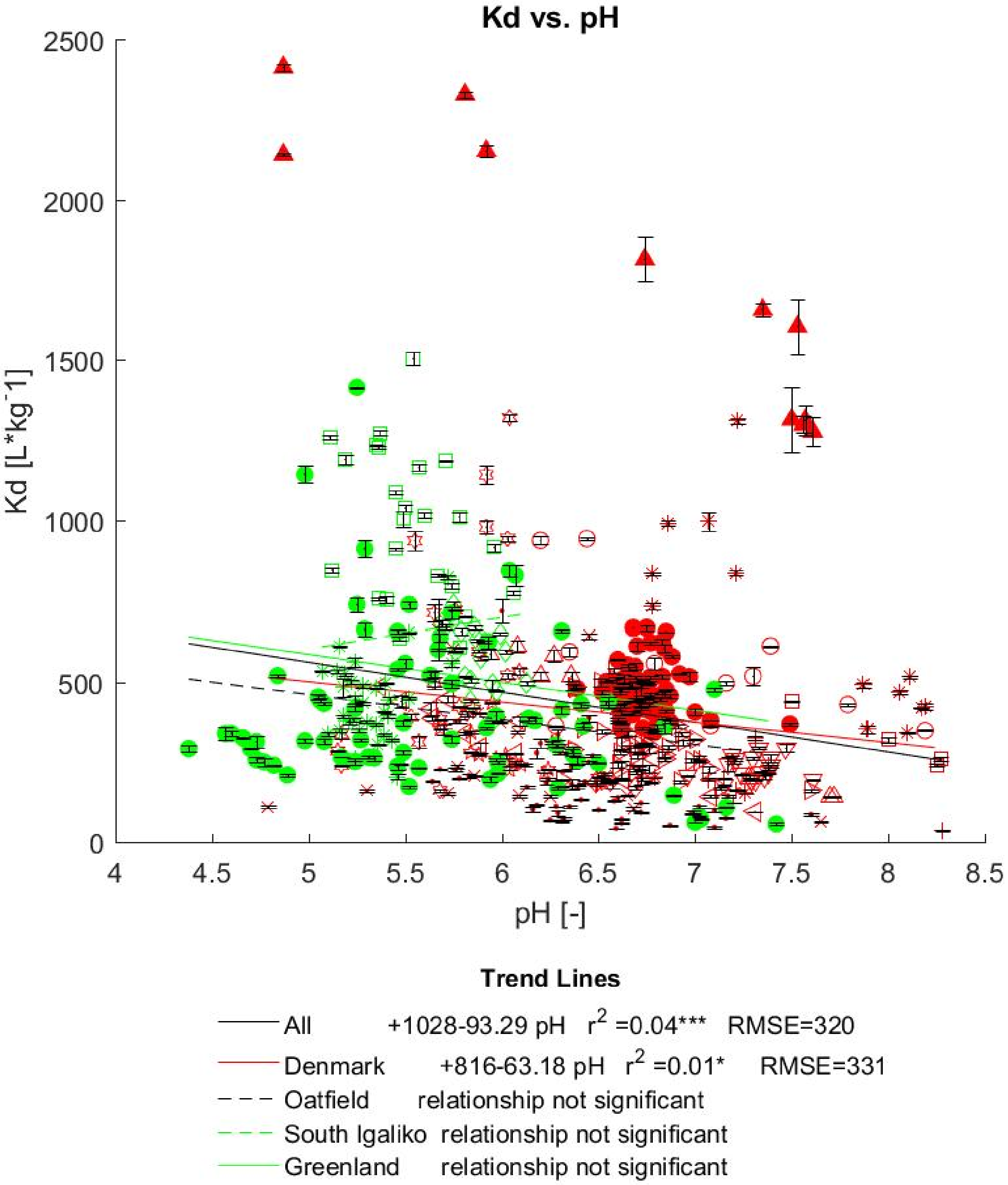

Figure 4.2. Sorption coefficient K_d vs. pH and simple linear regressions. Figure 4.3 presents data for Juelsminde 1 alone.

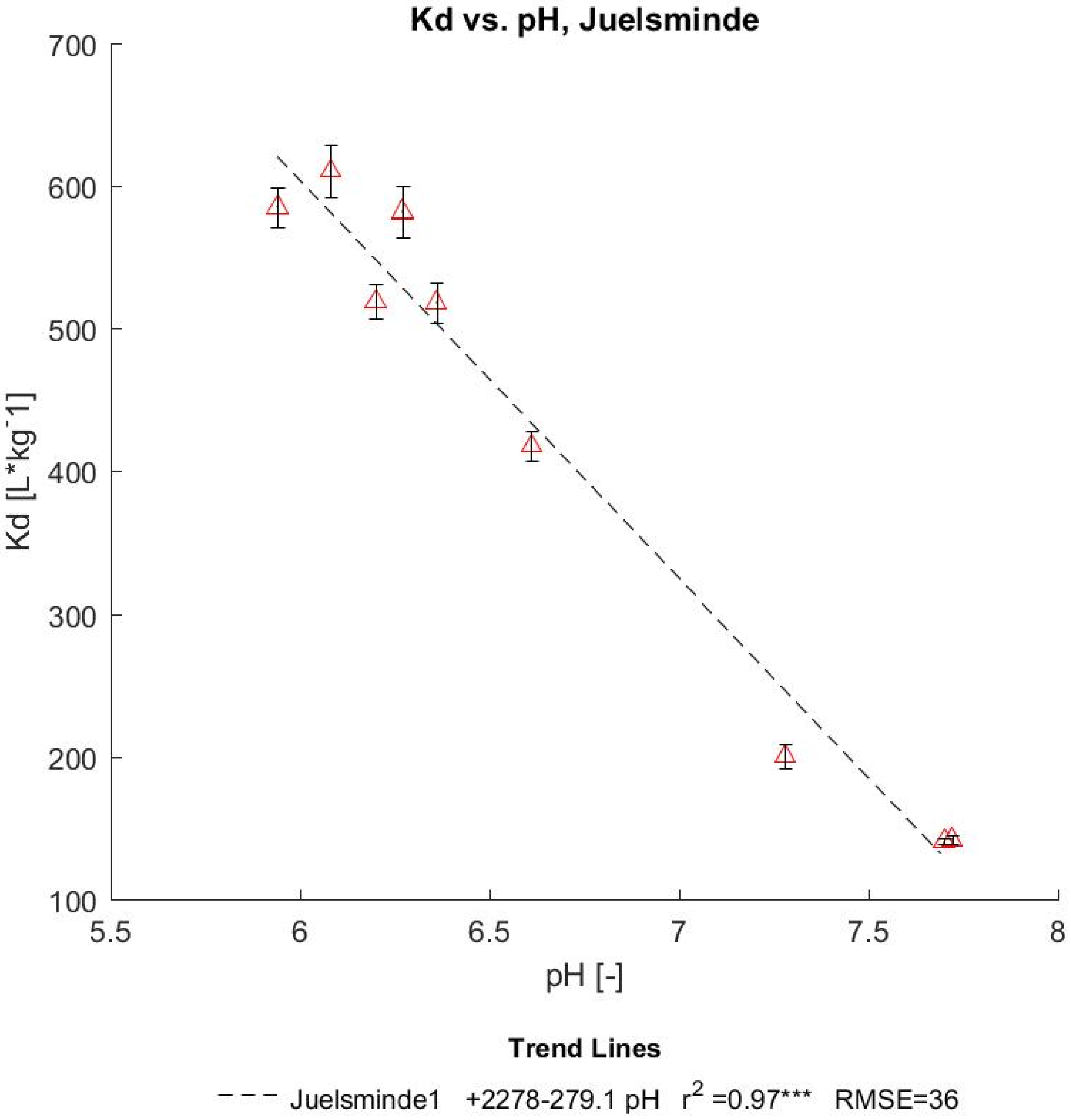

Figure 4.3. Sorption coefficient K_d vs. pH and simple linear regressions for Juelsminde 1 field.

All relationships found between pH and sorption coefficient are negative, giving a higher sorption coefficient with lower pH, in accordance with the hypothesis, but in general the relationship is not as strong as expected.

4.3 Clay

The hypothesis states that since glyphosate sorbs to charged surfaces and an increased amount of clay increases the soil surface, increased clay content would induce increased glyphosate sorption. Studies have presented this positive correlation between soil clay content and glyphosate sorption coefficient, some of which are presented in table 4.2 together with a study that found no correlation between the two.

Table 4.2. Glyphosate sorption coefficients and correlation to clay content as reported in various studies.

clay	cor.	K_d	no.	region	literature
0.06-0.19	+	161-667	110	Two fields in Denmark	Paradelo et al. [2015]
0.08-0.17	+	172-440	7	Two fields in Denmark	Kumari et al. [2016]
0.04-0.54		33.1-100.8	6	Denmark, A- B- and C-horizon	Albers et al. [2009]
0.03-0.15	+	n.a.	5	Denmark	Gimsing et al. [2004]

clay [kg kg^{-1}] is particles below 2 µm.
cor. indicates with a symbol if correlation between clay content and K_d was found: + indicates a positive correlation.
K_d [L kg^{-1}] is either the measured or (where a model has been fitted) the calculated adsorption coefficient at a glyphosate concentration of 0.23 mg L^{-1}.
no. is the number of (relevant) samples used in publication.

Data from the current project is presented on figure 4.4, 4.5 and 4.6. All significant Pearson coefficients for clay content are positive and found at the highest level of significance. The Greenlandic fields combined show a low coefficient of determination at only 0.07 and Denmark and Greenland combined are at 0.09, indicating that the influence of clay content on glyphosate sorption coefficient is strongly dependent on the historical management of the land.

On field level the correlation between K_d and clay content varies between no significance to a highly significant correlation of varying strength, the highest coefficient of determination found for Lerbjerg at 0.89 as seen together with Sørvad on figure 4.6. The deviations for Lerbjerg could possibly stem from variations in pH (6.8-8.2), but a field such as Sørvad has only a very minor variation in pH (less than 1) and still does not show a stronger relation between clay and sorption coefficient. Also the two trend lines sees very different slopes indicating that another parameter besides clay and pH influences the glyphosate sorption coefficient.

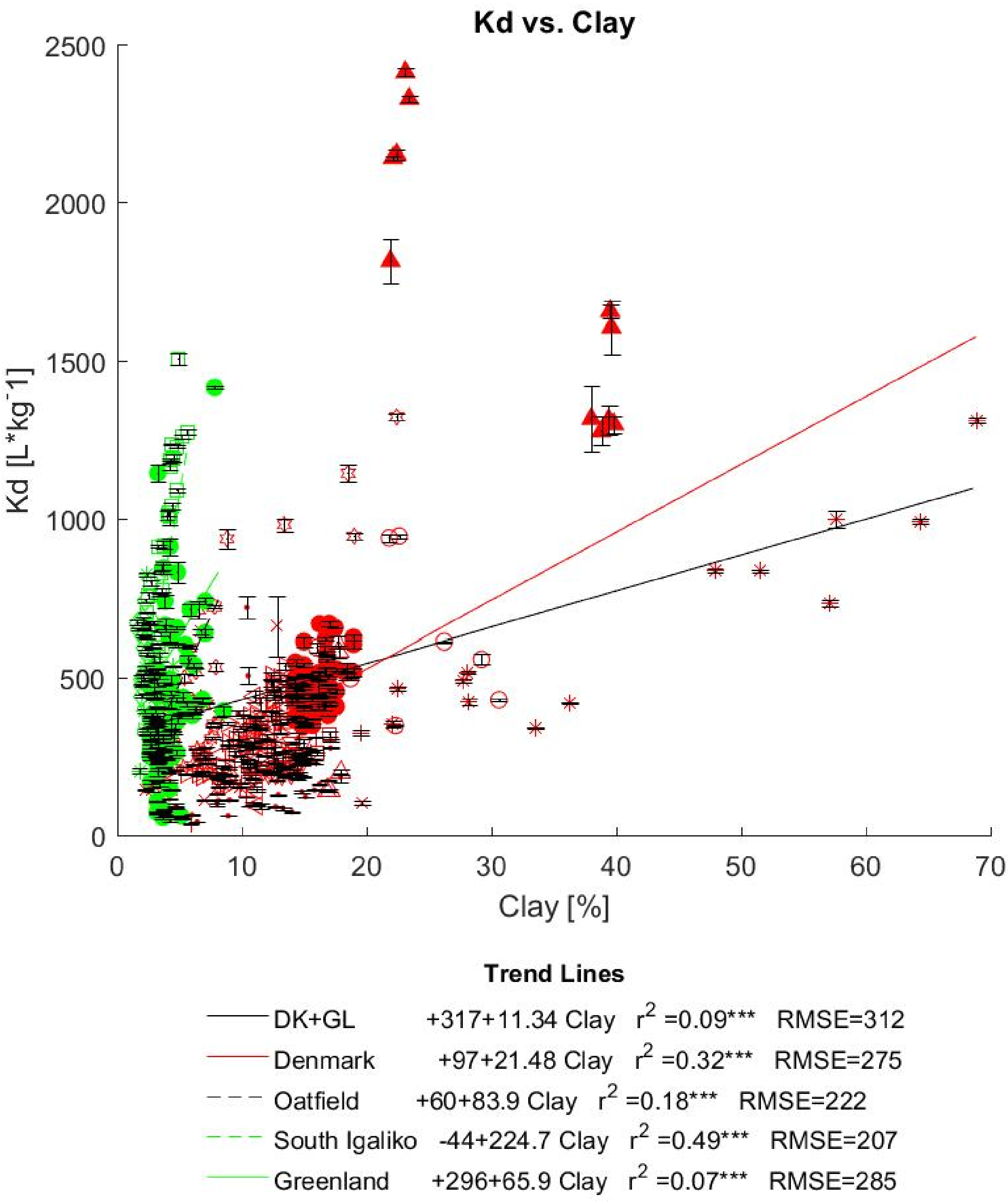

Figure 4.4. Sorption coefficient K_d vs. clay and simple linear regressions. Figures 4.5 and 4.6 presents data for Greenlandic fields respectively Lerbjerg and Sørvad alone.

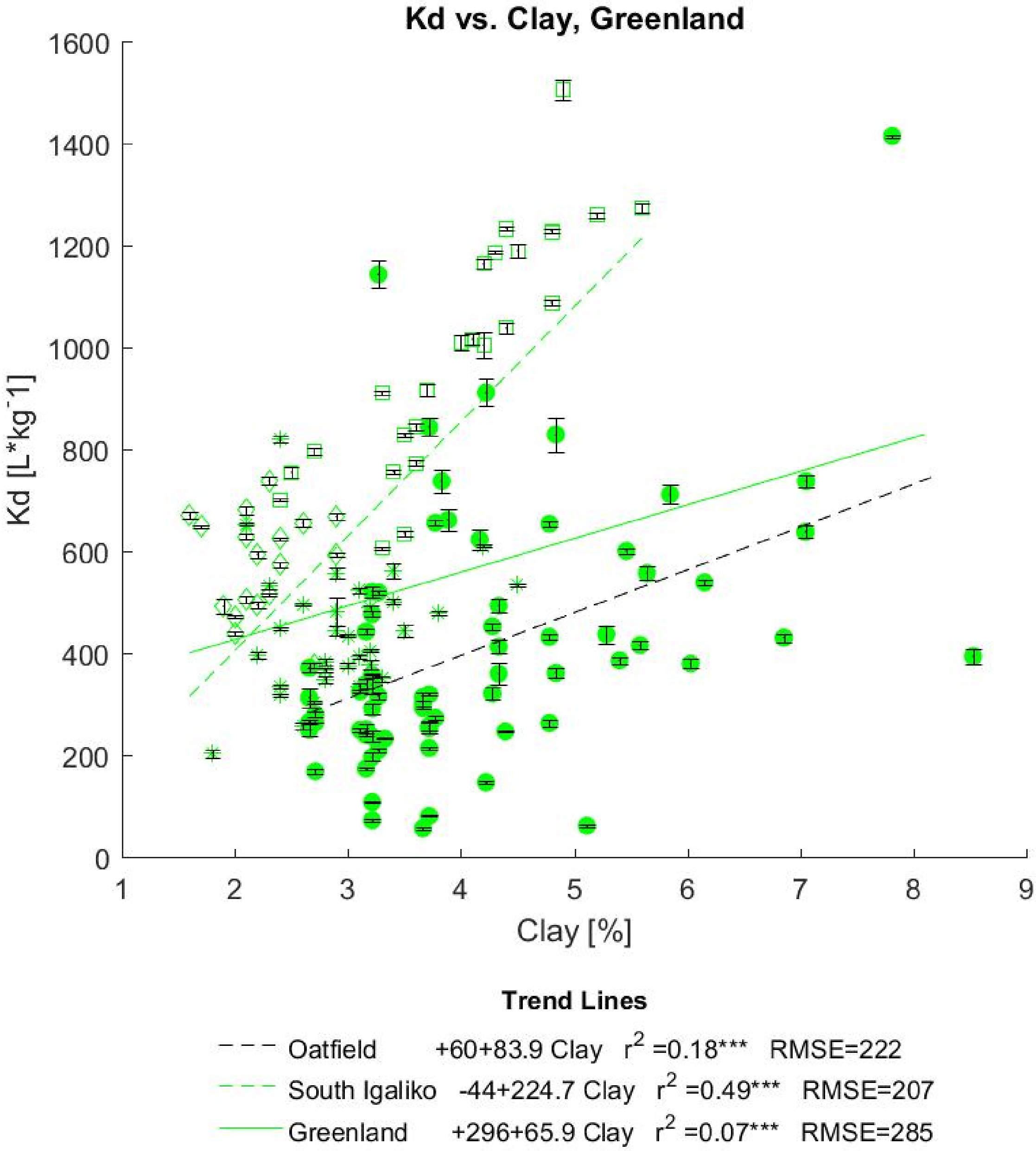

Figure 4.5. Sorption coefficient K_d vs. clay and simple linear regressions for Greenlandic fields.

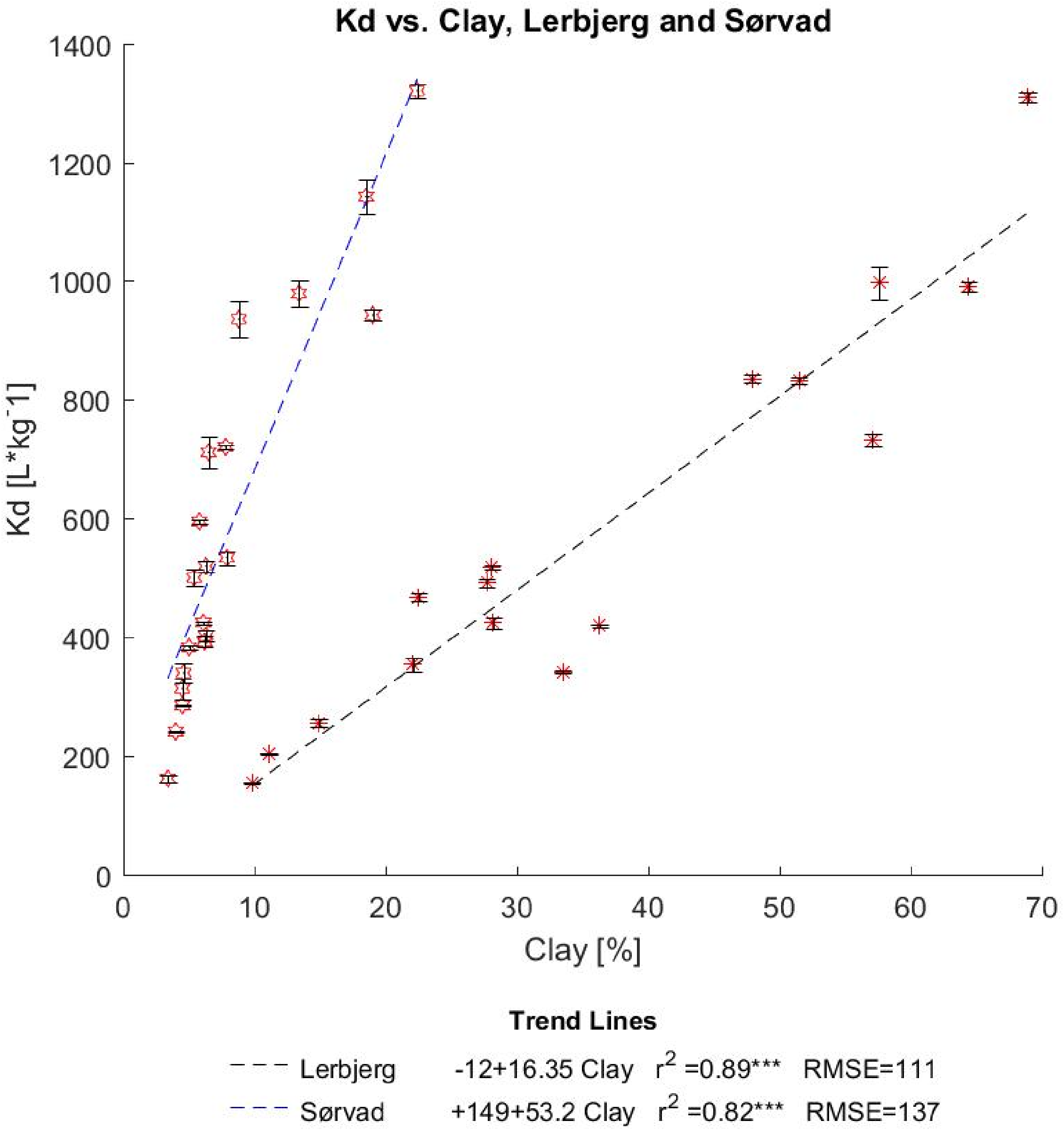

Figure 4.6. Sorption coefficient K_d vs. clay and simple linear regression for Lerbjerg and Sørvad fields.

All relationships found between clay content and sorption coefficient are positive, giving a higher sorption coefficient with larger clay content, in accordance with the hypothesis, and in general the relationship is even stronger than expected.

4.4 Fine silt alone or combined with clay

The hypothesis states that the unweathered clay minerals of the silt fraction will have some of the same effect on glyphosate sorption on Greenlandic soils as the clay fraction has in general, namely a higher content of fine silt (particles between 2 and 20 µm) inducing a higher glyphosate sorption coefficient.

Data from the current project is presented on figures 4.7 (fine silt alone) and 4.8 (combined with clay), and the combined parameter is further illustrated on figures 4.9 and 4.10 where subsets of the data set are to be found.

All significant Pearson coefficients for content of both fine silt alone and combined with clay are positive and found at the highest level of significance. Not significant relationships and low coefficient of determination when regions are combined indicate that the influence of content of fine silt on glyphosate sorption coefficient is somehow dependent on the historical management of the land.

All predictions for whole regions are equally good or better for fine silt + clay considered as a single predictor than for clay or fine silt alone, while some Danish fields get better predictions by clay alone. Data from Lerbjerg (fine silt between 4.6 and 17 %) and Sørvad (fine silt between 2.8 and 12 %) are presented on figure 4.10 where the relationship to glyphosate sorption coefficient is found to be weaker than for clay alone (see figure 4.6).

When looking at the soils from Greenland alone, presented on figure 4.9, the problems with using the texture parameters across regions becomes apparent as the relationship found for Oatfield differs from that of the fields from South Igaliku in such a way that no significant relationship at all is to be found for Greenland combined.

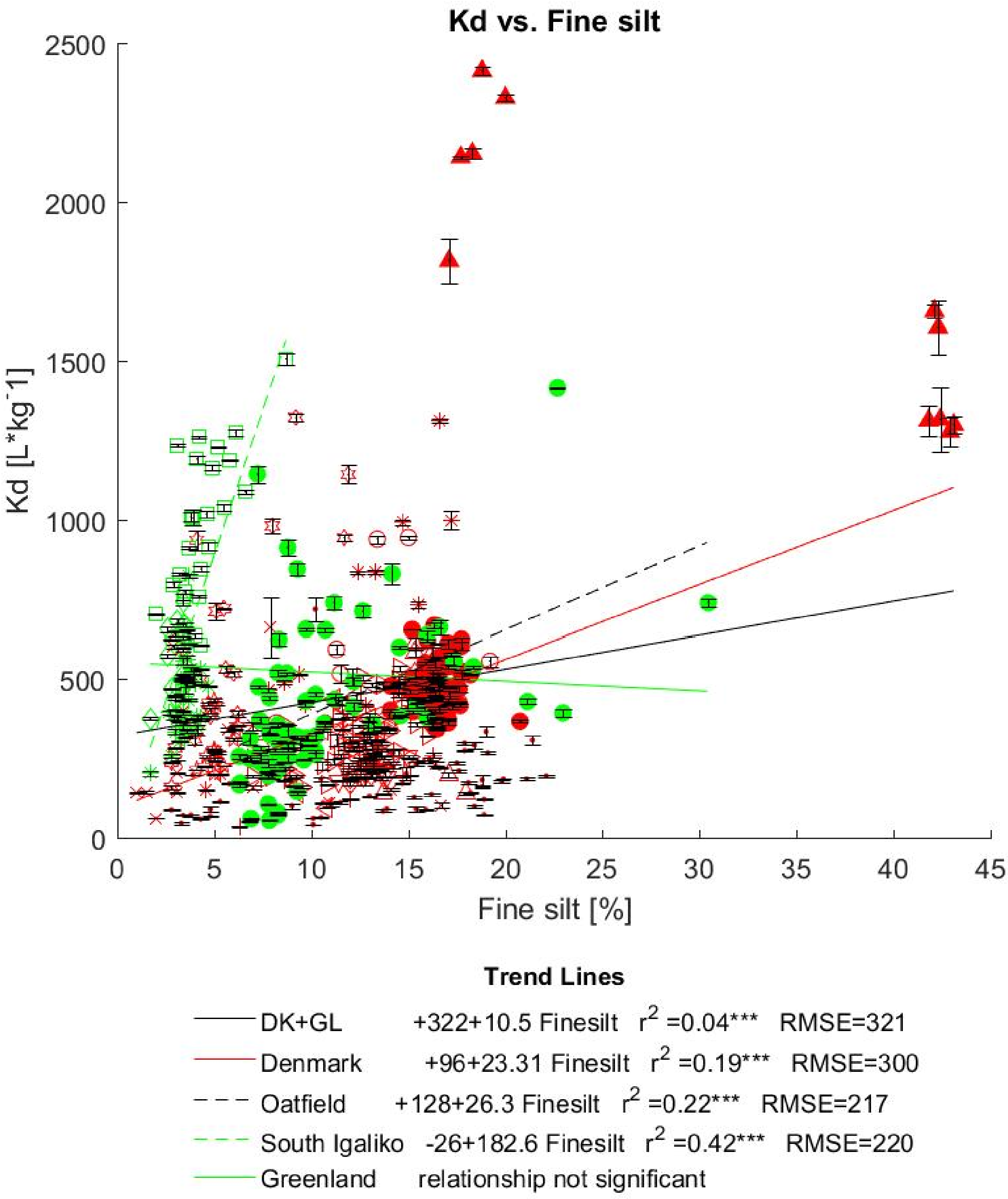

Figure 4.7. Sorption coefficient K_d vs. fine silt and simple linear regressions.

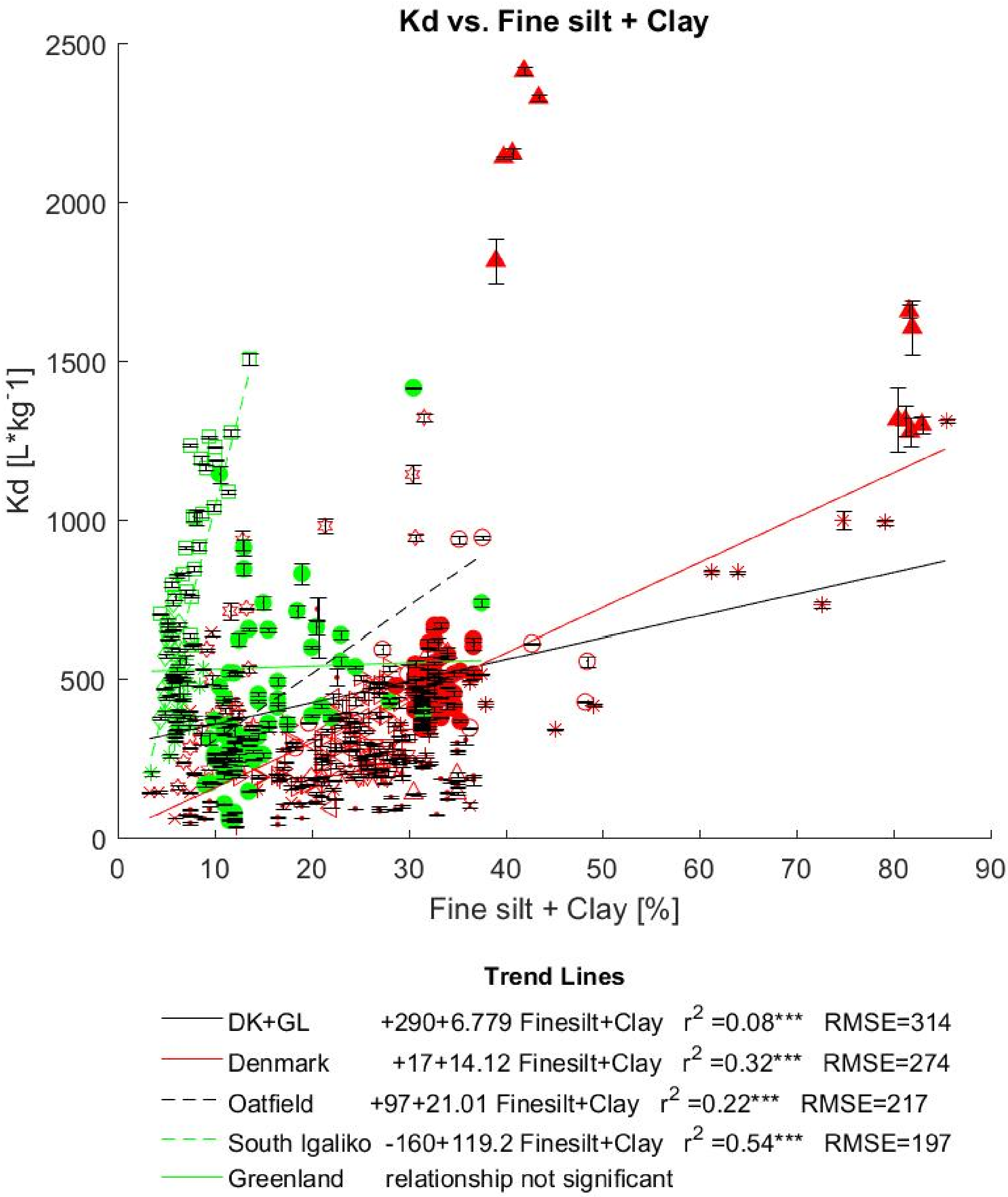

Figure 4.8. Sorption coefficient K_d vs. fine silt + clay and simple linear regressions. In the trend line equations the term "Finesilt+Clay" is a single variable. Figures 4.9 and 4.10 presents data for Greenlandic fields respectively Lerbjerg and Sørvad alone.

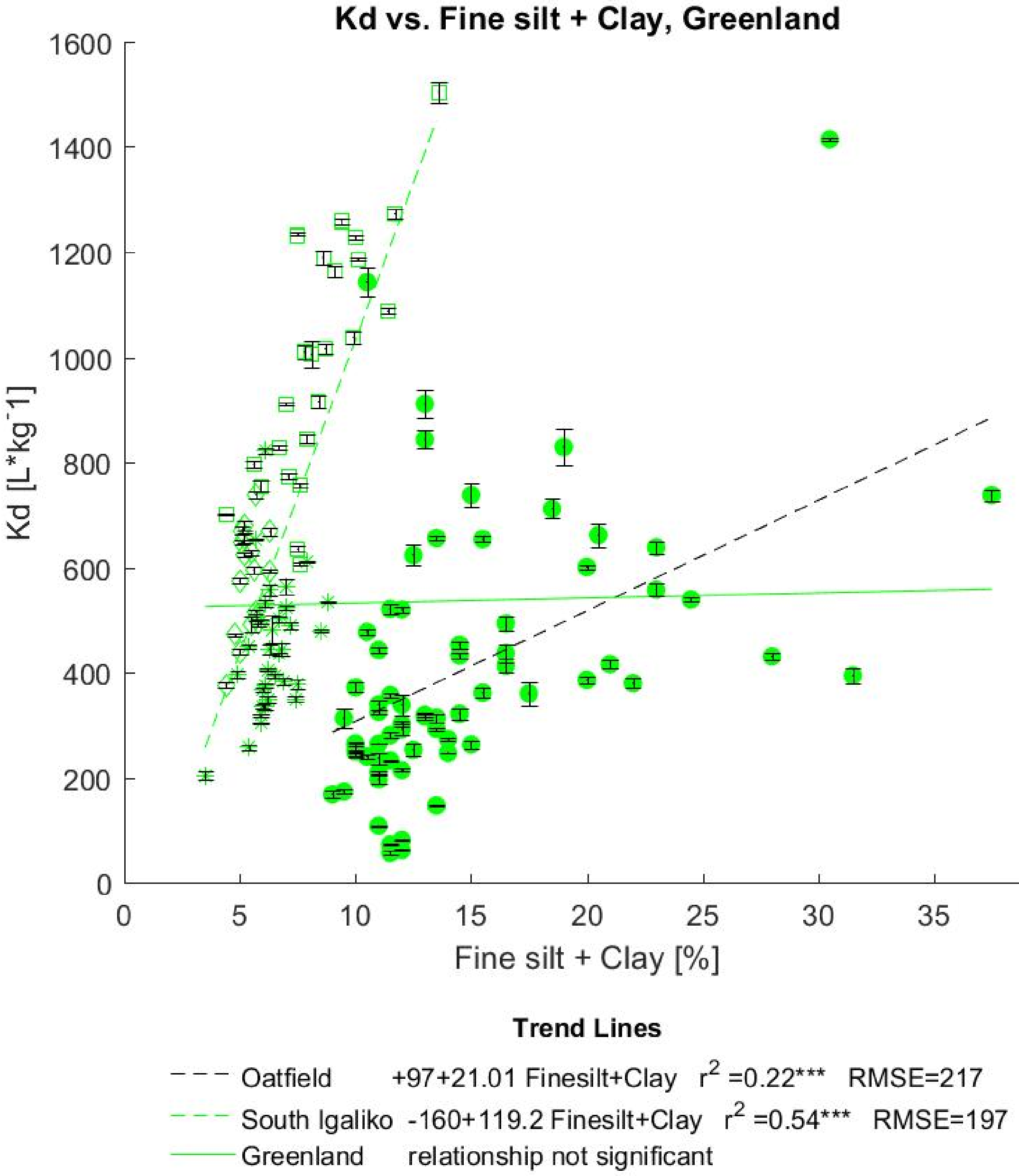

Figure 4.9. Sorption coefficient K_d vs. fine silt + clay and simple linear regressions. In the trend line equations the term "Finesilt+Clay" is a single variable.

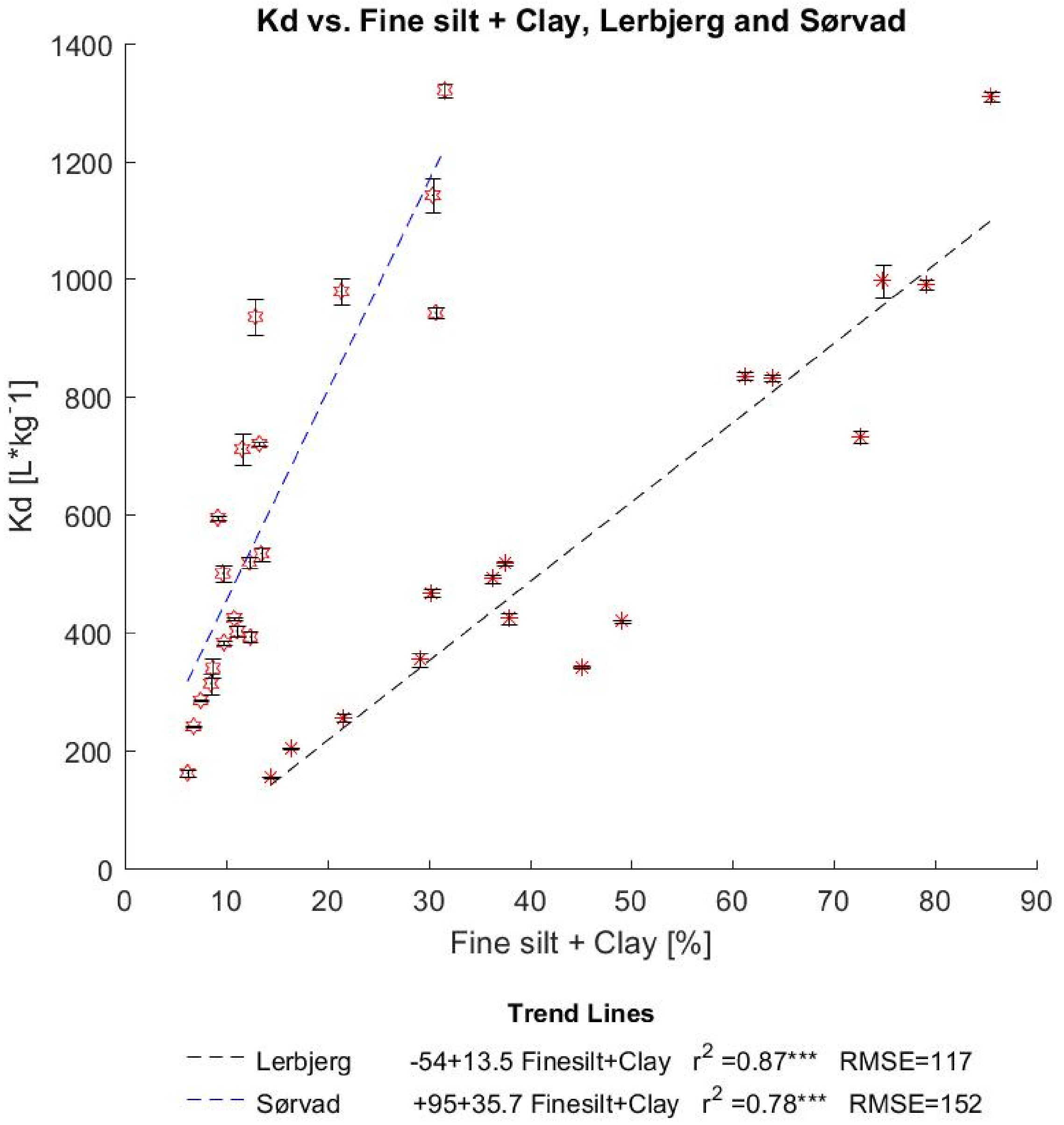

Figure 4.10. Sorption coefficient K_d vs. fine silt + clay and simple linear regressions. In the trend line equations the term "Finesilt+Clay" is a single variable.

The influence of the fine silt seems to go down as the age of the soil goes up, corroborating the idea that the content of very influential clay minerals in the fine silt particle fraction diminishes over time. All of this is in good accordance with the hypothesis of a positive relationship between sorption coefficient and content of fine silt.

In search of better performing pedotransfer functions for regions alone it makes sense to consider including the combined predictor.

4.5 Organic matter

The hypothesis states that the organic matter holds no major sorption sites for the charged glyphosate, and data from the current project is presented on figures 4.11 and 4.12. All significant Pearson coefficients for content of organic matter are positive with varying levels of significance and great difference in strength.

Data from Ø Bakker and the two fields of Ringkøbing are presented on figure 4.12 where Ringkøbing 1 is seen as a crowd of low K_d and a total C at approximately 2.5 %. The field of Ø Bakker has a content of total C between 1.5 and 37.1 % but shows no significant relationship to sorption coefficient. Ringkøbing 2 shows a large correlation, but this is assumed to be an artefact of clay content correlating strongly to content of total C as the samples fall into one of two categories, one with total C below 3.3 and clay between 38 and 39.9 % and another with total C above 7.3 and clay between 21.9 and 23.5 %, while Ringkøbing 1 has a clay content between 5.3 and 7.8 %.

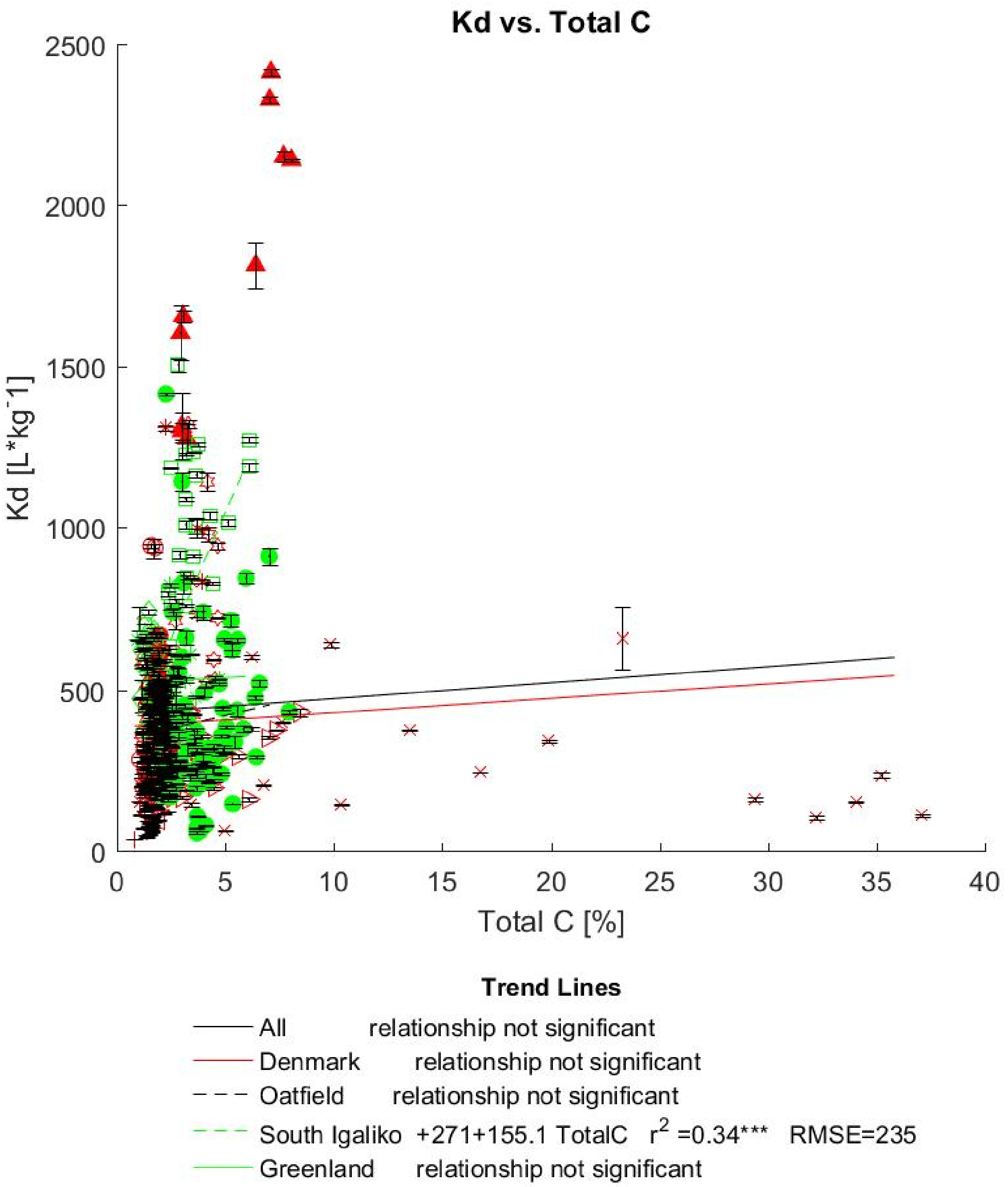

Figure 4.11. Sorption coefficient K_d vs. total C and simple linear regressions. Figure 4.12 presents data for Ringøbing 1 and 2 and Ø Bakker alone.

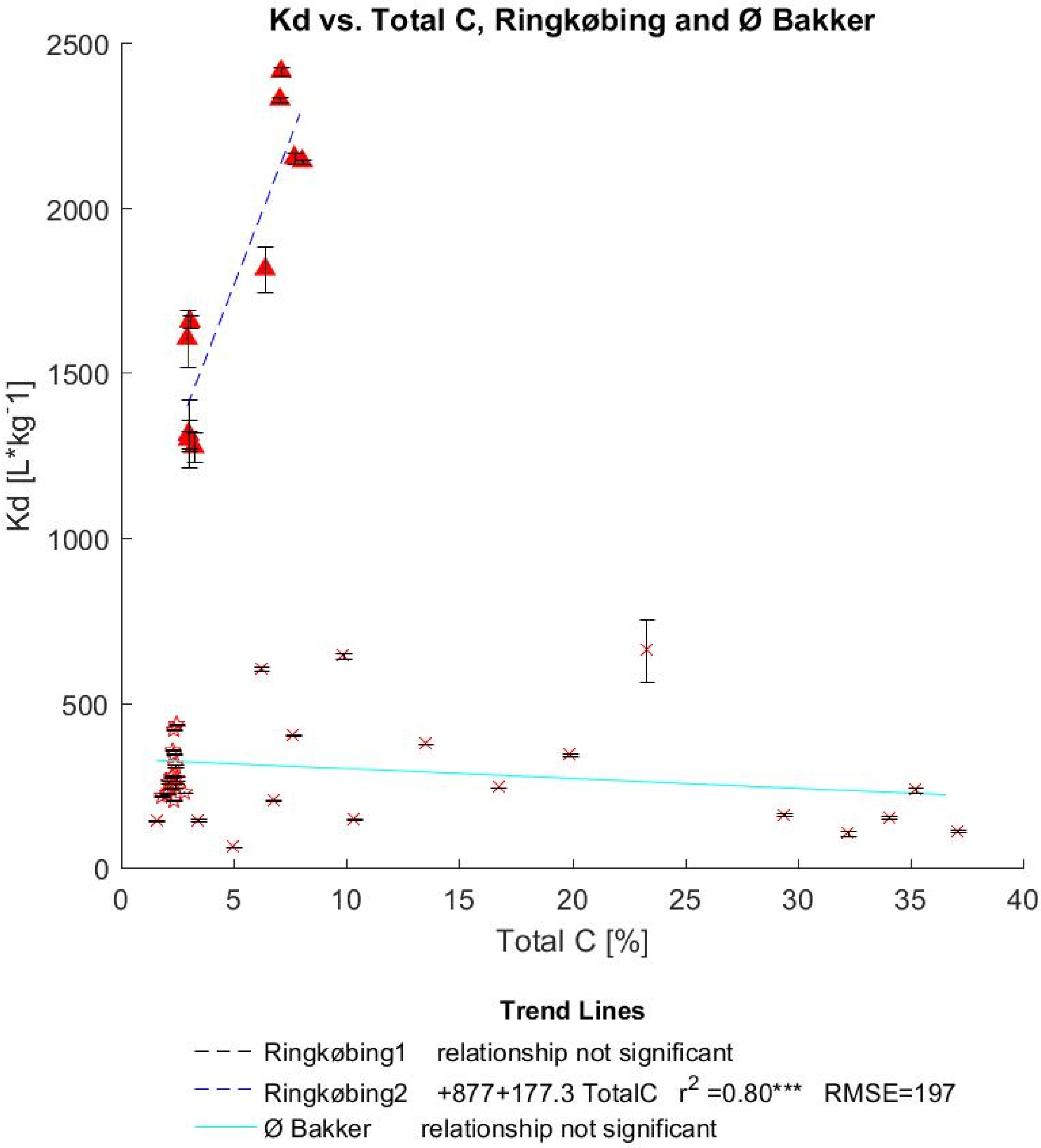

Figure 4.12. Sorption coefficient K_d vs. total C and simple linear regressions for the fields of Ringkøbing and Ø Bakker.

All significant relationships found between content of total C and sorption coefficient are positive, giving a higher sorption coefficient with larger content of total C, but whether or not a significant relationship is found varies greatly across fields and regions. It must be concluded that content of total C is correlated to other controlling parameters, and in good accordance with the hypothesis total C content as such is not in it self a good predictor for a glyphosate sorption coefficient.

4.6 Electrical conductivity

The hypothesis states that the dissolved salts causing a rise in EC might provide sorption sites for glyphosate hence improving sorption. Data from the current project is presented on figure 4.13. A highly significant but weak positive correlation is found when all measured soils are considered, but for the individual regions only the youngest of the Greenlandic soils show a significant relationship.

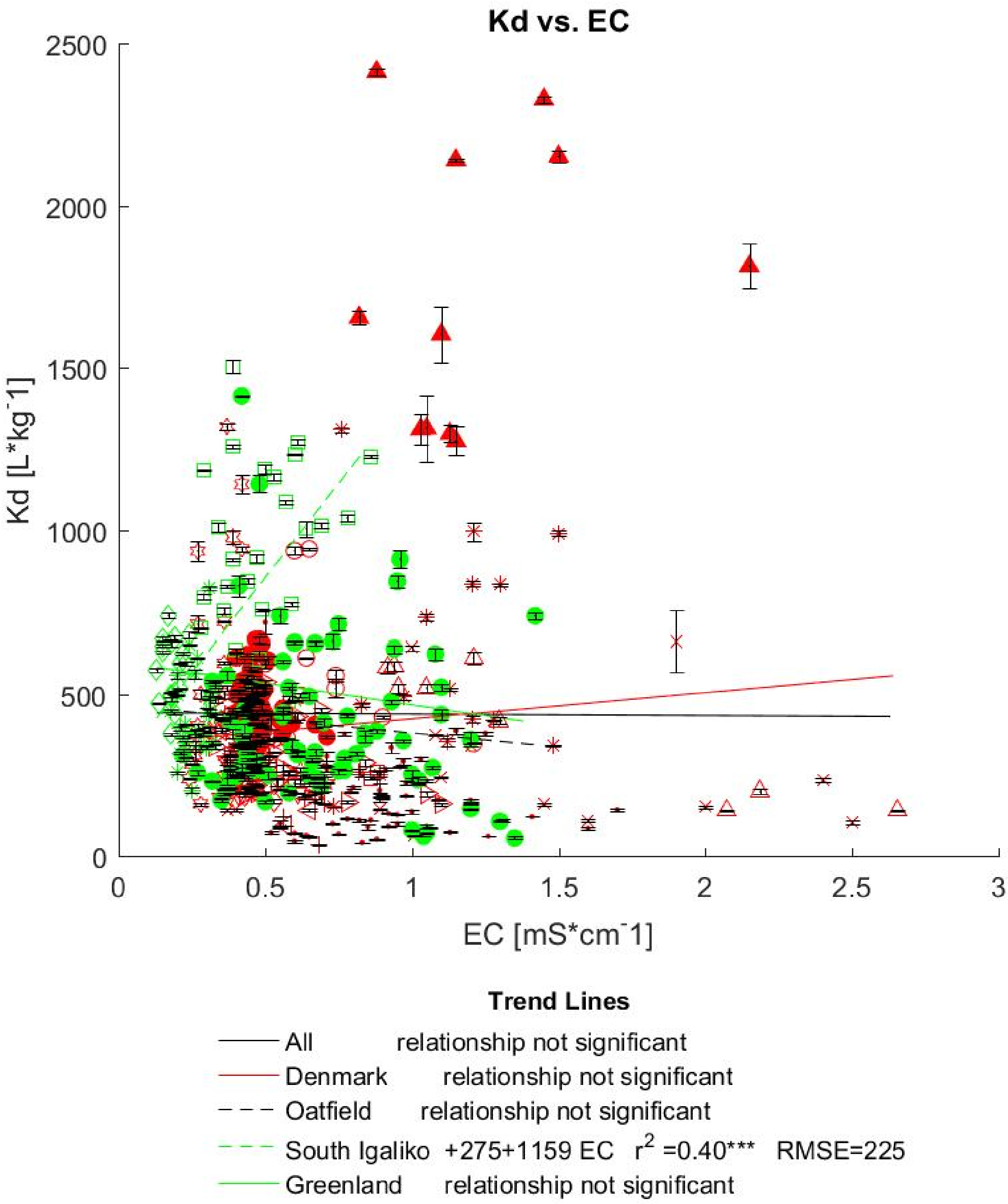

Figure 4.13. Sorption coefficient K_d vs. electrical conductivity and simple linear regressions.

The hypothesis of a general weak correlation must be rejected, but it is recorded that there might be an interesting relationship between sorption coefficient and electrical conductivity when it comes to the very young soils.

4.7 Oxalate extractable phosphorus

The hypothesis states that phosphorous mainly competes with glyphosate for sorption sites, hence a higher content of oxalate extractable phosphorus is expected to cause a lower glyphosate sorption. Studies have presented this negative correlation between soil phosphorus content and glyphosate sorption coefficient, and some are presented in table 4.3.

Table 4.3. Glyphosate sorption coefficients and correlation to phosphorus content as reported in various studies.

Phosphorus	cor.	K_d	no.	region	literature
Olsen: 0.11-1.6	-	113-373	23	Two fields in Denmark	de Jonge et al. [2001]
oxalate: 4.2-10	-	161-667	110	Two fields in Denmark	Paradelo et al. [2015]
Olsen: 0.36-1.9	-	172-440	7	Two fields in Denmark	Kumari et al. [2016]
Olsen: 0.72-3.6	-	23.7-516	17	France, Lyon	Sidoli et al. [2016]
Olsen: 0.12-0.65	-	n.a.	5	Denmark	Gimsing et al. [2004]

Phosphorus [mmol kg^{-1}] method of extraction given.
cor. indicates with a symbol if correlation between clay content and K_d was found: + indicates a positive correlation.
K_d [L kg^{-1}] is either the measured or (where a model has been fitted) the calculated adsorption coefficient at a glyphosate concentration of 0.23 mg L^{-1}.
no. is the number of (relevant) samples used in publication.

Data from the current project is presented on figures 4.14 and 4.15. All significant Pearson coefficients for content of oxalate extractable phosphorus are negative, with great variation in strength.

Ringkøbing 2 shows a large correlation, but as was the case with content of organic material discussed in section 4.5 this may be an artefact of clay content correlating to content of oxalate extractable phosphorus. The Greenlandic fields show a more consistent relationship, while the Danish fields only show a significant relationship for isolated fields.

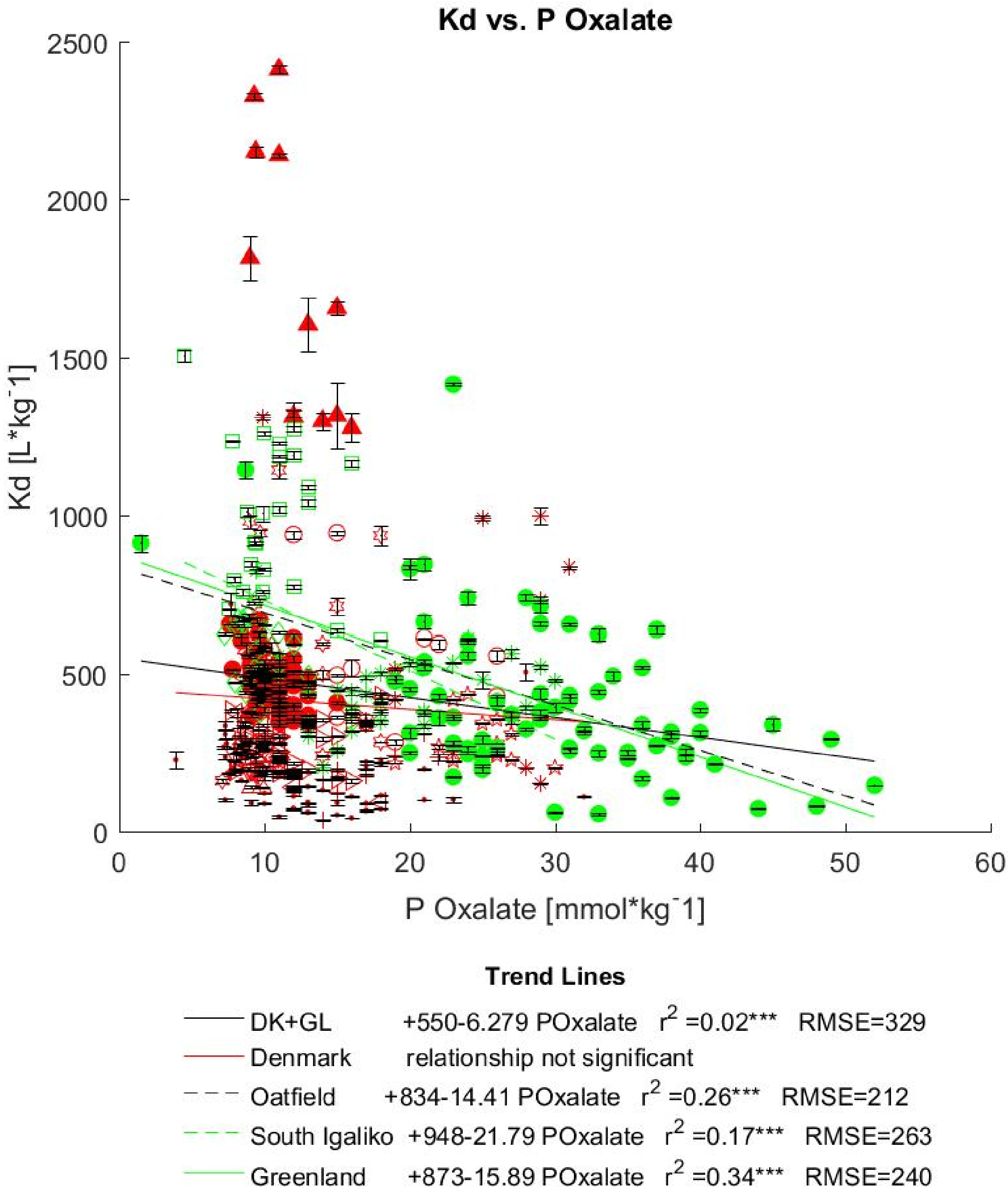

Figure 4.14. Sorption coefficient K_d vs. oxalate extractable phosphorus and simple linear regressions. Figure 4.15 presents data for Ringkøbing 1 and 2 alone.

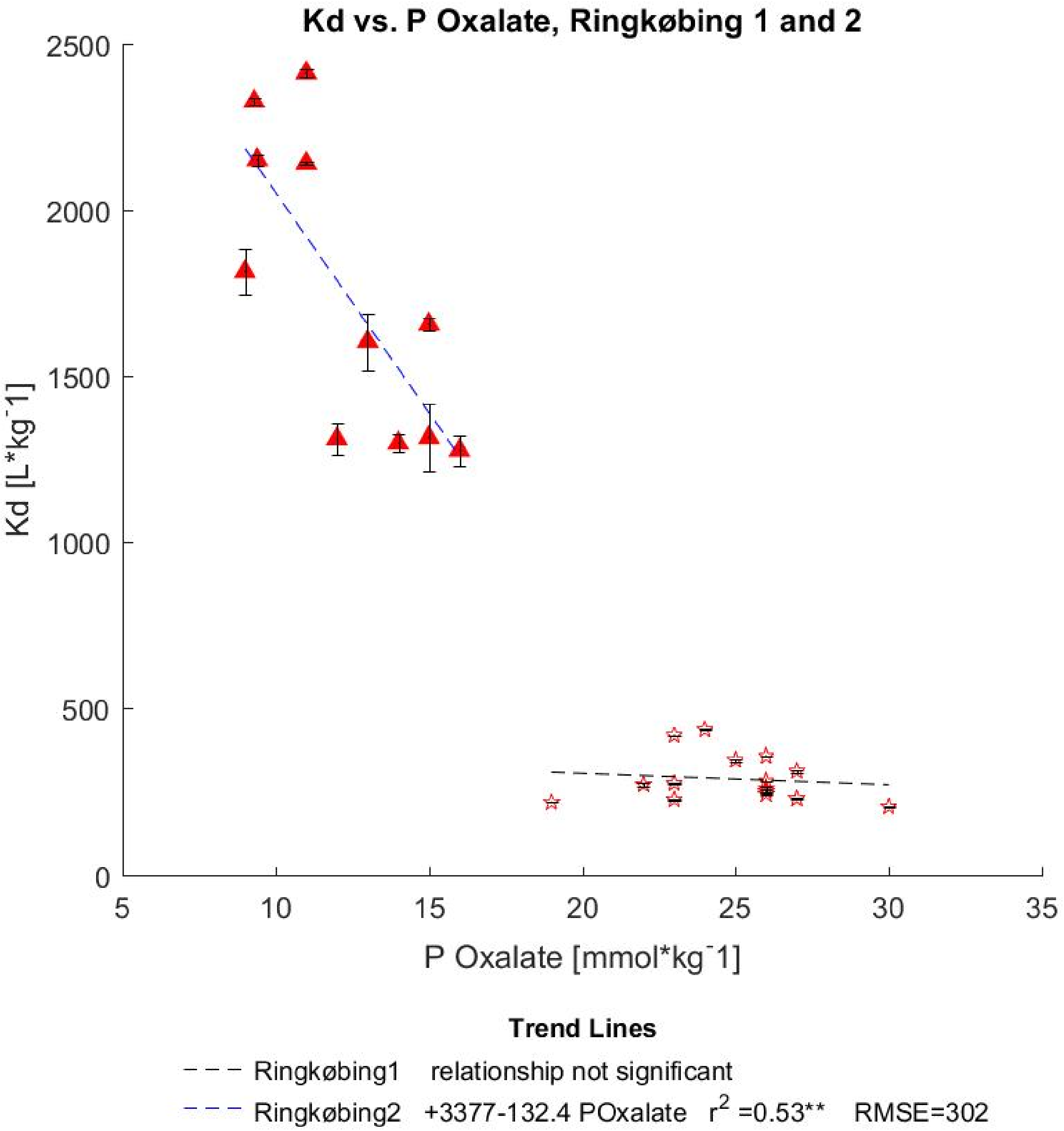

Figure 4.15. Sorption coefficient K_d vs. oxalate extractable phosphorus and simple linear regressions for the two fields of Ringkøbing.

In accordance with the hypothesis the glyphosate sorption coefficient goes down when content of oxalate extractable phosphorus goes up, as the competition for sorption sites would prompt, but the relationship is not found to be as reliable as expected.

4.8 Iron

The hypothesis states that because iron is one of the clay minerals providing the variable-charge sorption sites favoured by glyphosate, a higher content of oxalate extractable iron will correlate to a larger glyphosate sorption. Studies have consistently presented this positive correlation between soil iron content and glyphosate sorption coefficient, some are presented in table 4.4.

Table 4.4. Glyphosate sorption coefficients and correlation to iron content as reported in various studies.

Iron	cor.	K_d	no.	region	literature
32-78	+	113-373	23	Two fields in Denmark	de Jonge et al. [2001]
8.3-53	+	161-667	110	Two fields in Denmark	Paradelo et al. [2015]
20-44	+	172-440	7	Two fields in Denmark	Kumari et al. [2016]
38-57	+	23.7-516	17	France, Lyon	Sidoli et al. [2016]
29-64	+	n.a.	5	Denmark	Gimsing et al. [2004]

Iron [mmol kg^{-1}] oxalate extractable.
cor. indicates with a symbol if correlation between clay content and K_d was found: + indicates a positive correlation.
K_d [L kg^{-1}] is either the measured or (where a model has been fitted) the calculated adsorption coefficient at a glyphosate concentration of 0.23 mg L^{-1}.
no. is the number of (relevant) samples used in publication.

Data from the current project is presented on figures 4.16, 4.17 and 4.18. All significant Pearson coefficients for content of oxalate extractable iron are positive and found at the highest level of significance.

The correlations for whole regions is consistently high, also higher than what was found for clay alone. On field level on the other hand the correlation is weaker than what was found for clay, compare figures 4.6 and 4.18, and Silstrup and other fields show no significant correlation at all between sorption coefficient and oxalate extractable iron.

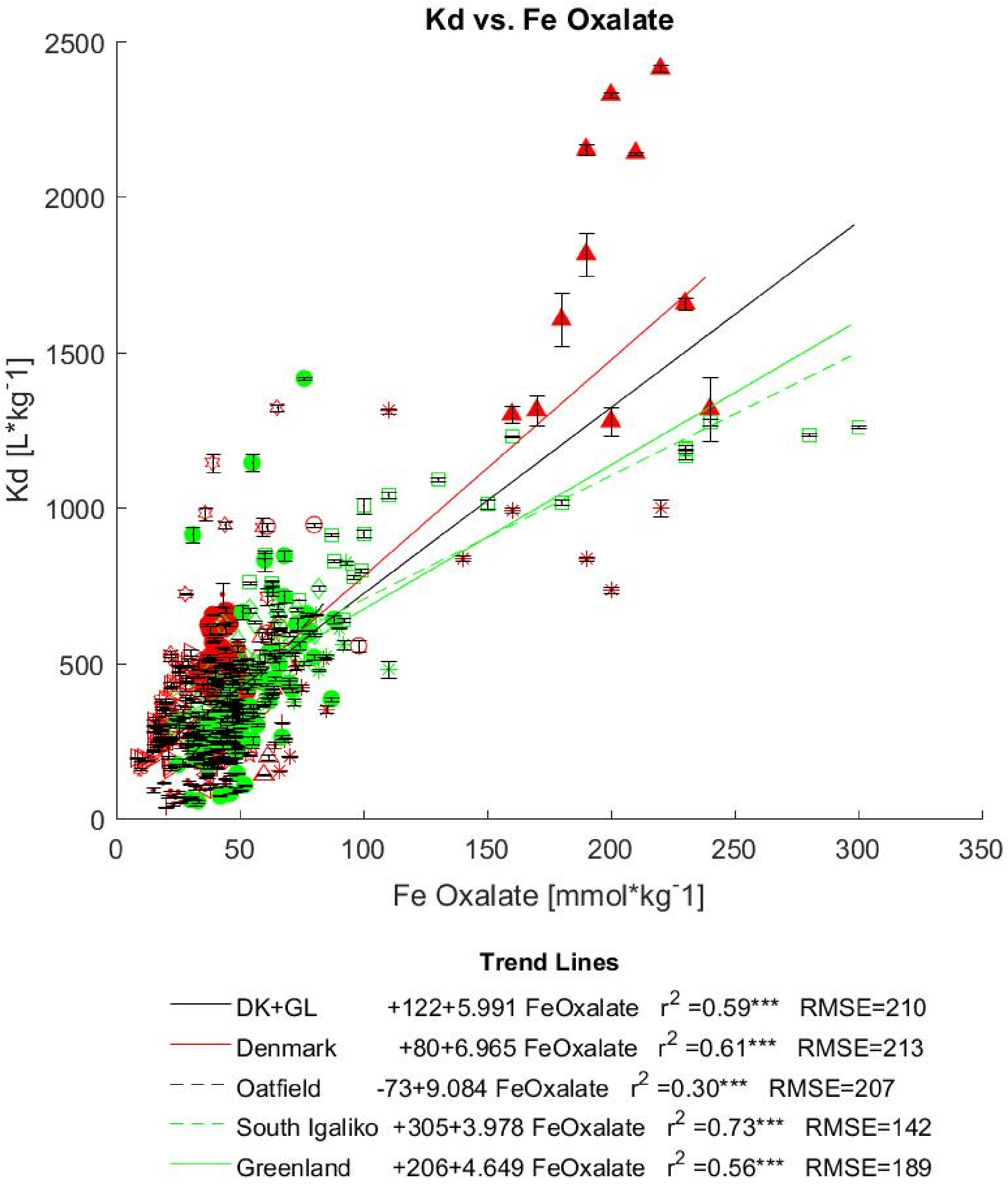

Figure 4.16. Sorption coefficient K_d vs. oxalate extractable iron and simple linear regressions. Figures 4.17 and 4.18 presents data for Greenlandic fields respectively Lerbjerg and Sørvad fields alone.

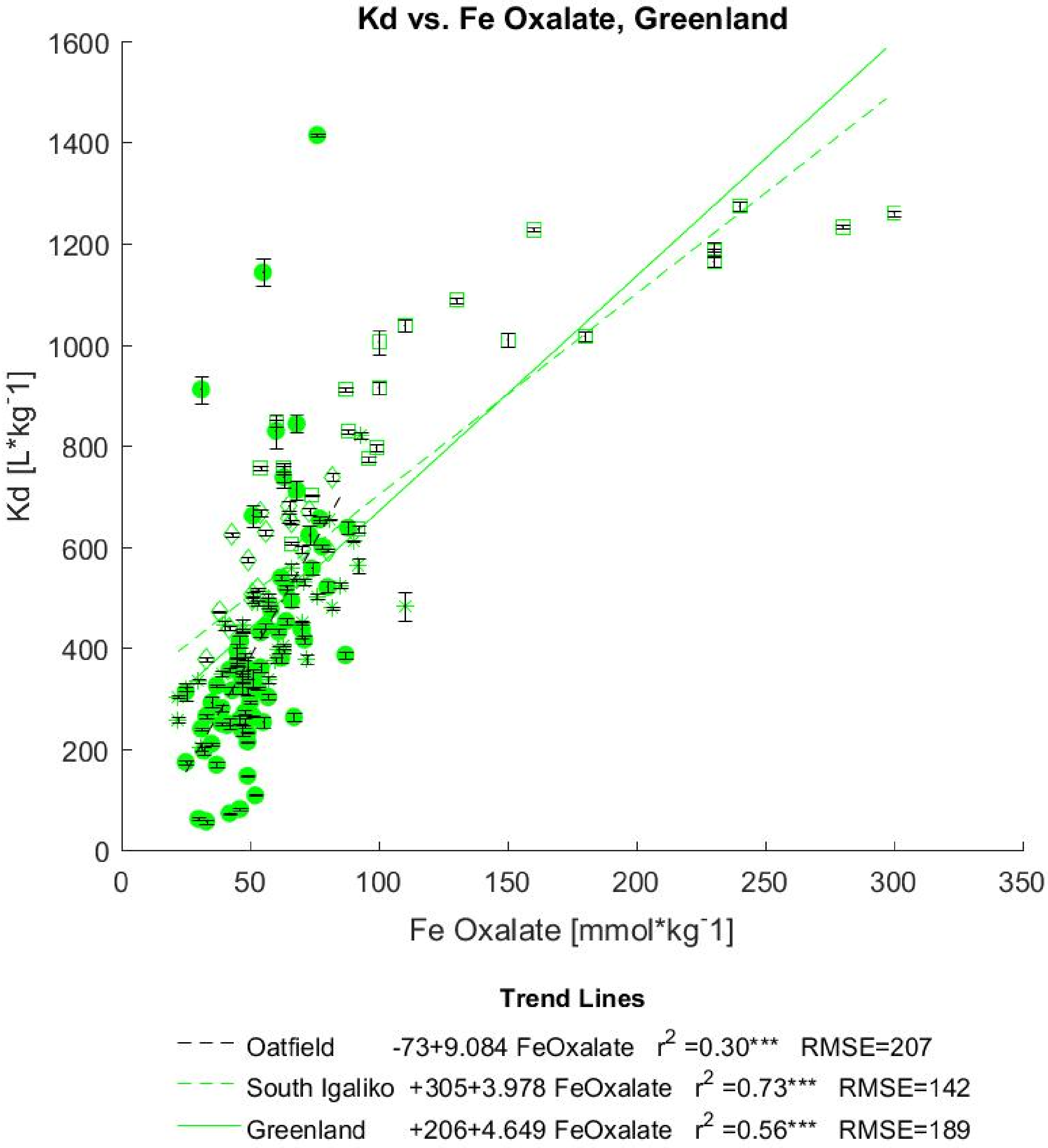

Figure 4.17. Sorption coefficient K_d vs. oxalate extractable iron and simple linear regression for soils of Greenland.

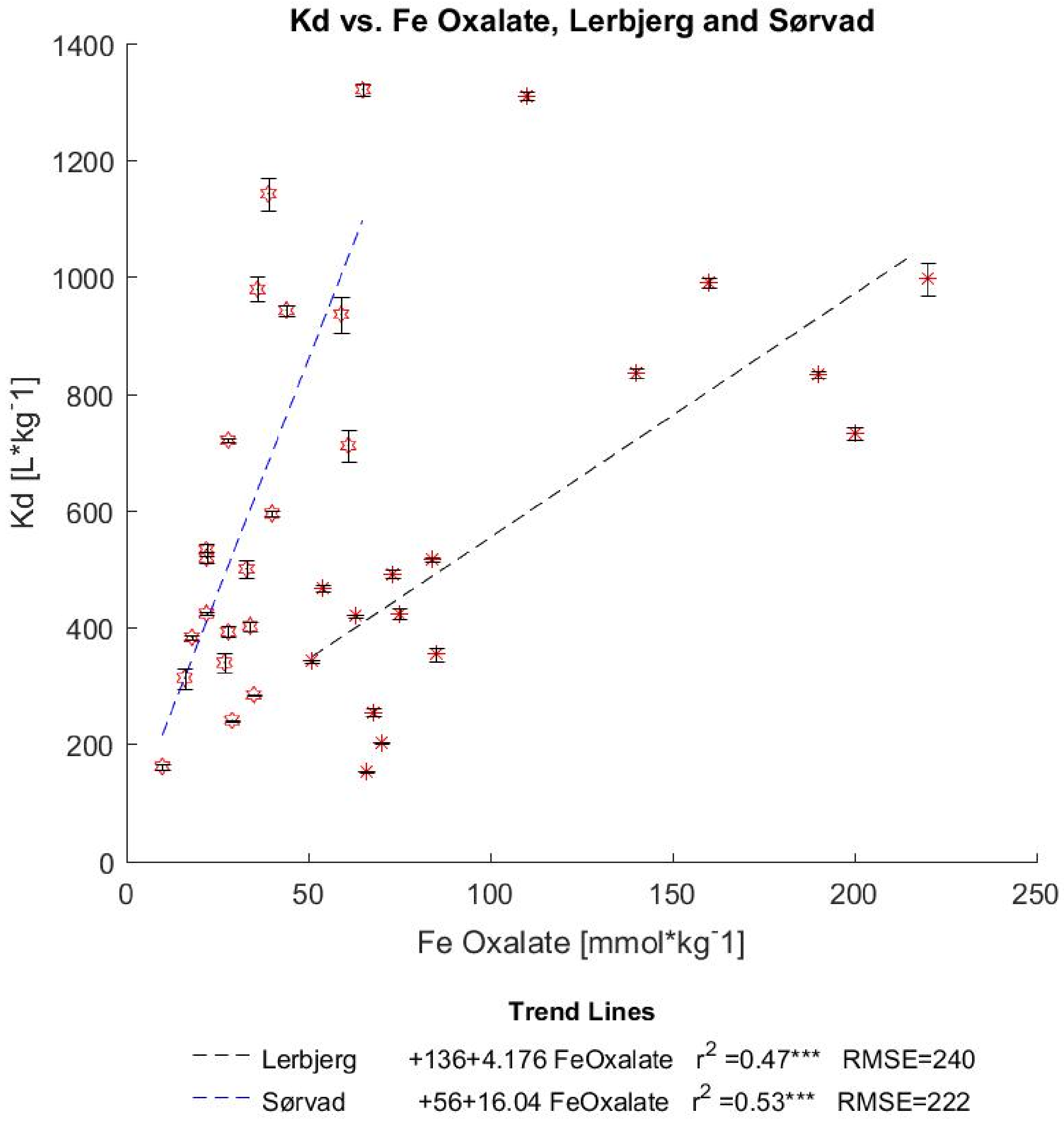

Figure 4.18. Sorption coefficient K_d vs. oxalate extractable iron and simple linear regression for Lerbjerg and Sørvad fields.

The hypothesis of a strong positive relation, where a rise in content of oxalate extractable iron prompts a higher glyphosate sorption coefficient, is accepted for regions and across regions.

4.9 Aluminium

The hypothesis states that because aluminium is one of the clay minerals providing the variable-charge sorption sites favoured by glyphosate, a higher content of oxalate extractable aluminium will correlate to a larger glyphosate sorption. Studies have consistently presented this positive correlation between soil iron content and glyphosate sorption coefficient, some are presented in table 4.5.

Table 4.5. Glyphosate sorption coefficients and correlation to aluminium content as reported in various studies.

Aluminium	cor.	K_d	no.	region	literature
13-37	+	113-373	23	Two fields in Denmark	de Jonge et al. [2001]
9.2-37	+	161-667	110	Two fields in Denmark	Paradelo et al. [2015]
18-21	+	172-440	7	Two fields in Denmark	Kumari et al. [2016]
21-39	+	23.7-516	17	France, Lyon	Sidoli et al. [2016]
14-29	+	n.a.	5	Denmark	Gimsing et al. [2004]

Aluminium [mmol kg^{-1}] oxalate extractable.
cor. indicates with a symbol if correlation between clay content and K_d was found: + indicates a positive correlation.
K_d [L kg^{-1}] is either the measured or (where a model has been fitted) the calculated adsorption coefficient at a glyphosate concentration of 0.23 mg L^{-1}.
no. is the number of (relevant) samples used in publication.

Data from the current project is presented on figure 4.19. The significant Pearson correlation coefficients found for oxalate extractable aluminium are positive, in accordance with the hypothesis.

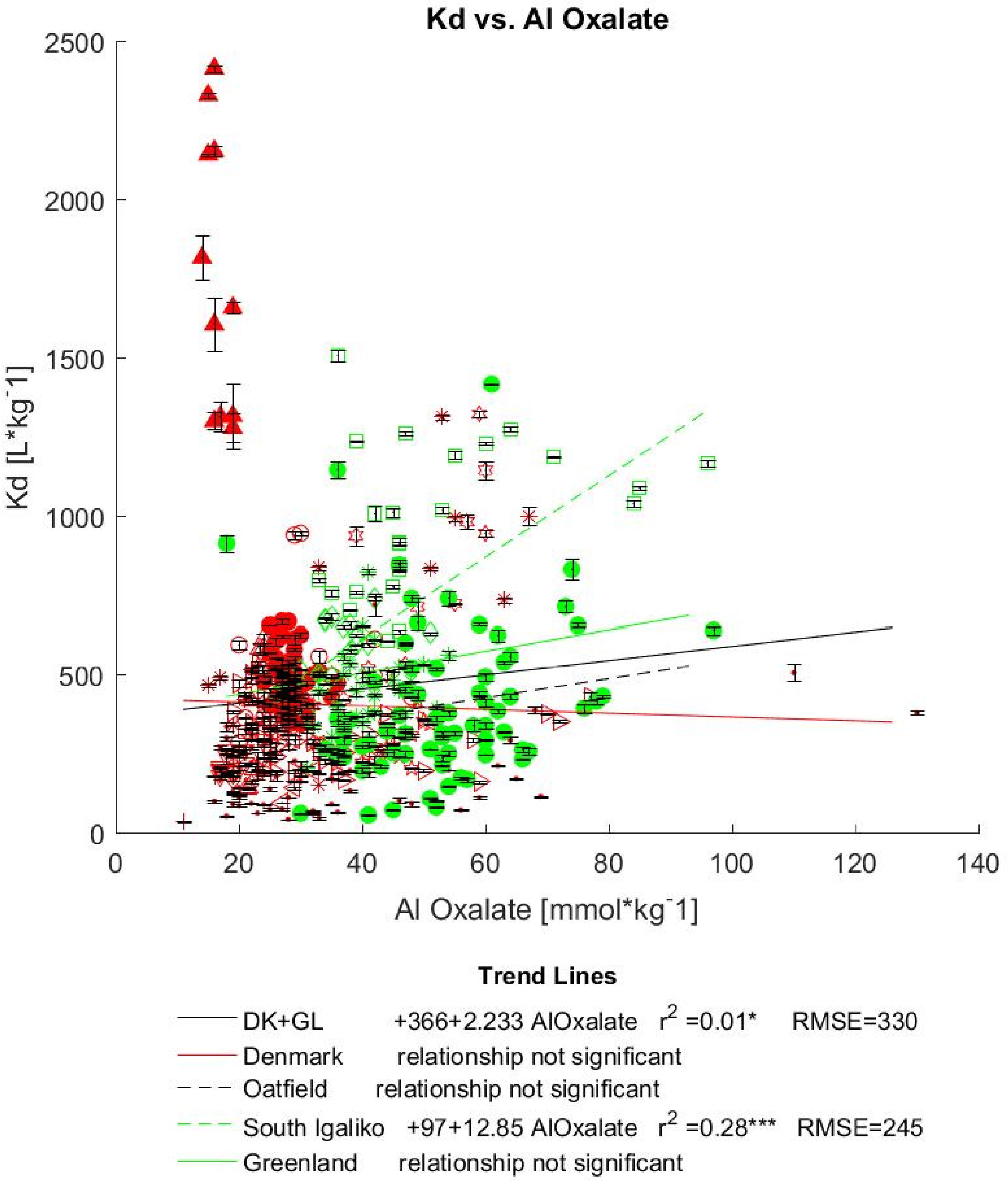

Figure 4.19. Sorption coefficient K_d vs. oxalate extractable aluminium and simple linear regressions.

The relationship between the glyphosate sorption coefficient and oxalate extractable aluminium when all Danish and Greenlandic soils are included is very weak, and when considering soils of Denmark alone or soils of Greenland alone no significant relationship is found at all. The influence of oxalate extractable aluminium is very weak, and much more so than expected.

4.10 Summary and conclusion on single parameters

The dependencies between sorption coefficient K_d and the investigated soil parameters are presented by Pearson correlation coefficient r and level of significance, *** ** and * representing correlation significance levels of 0.001, 0.01 and 0.05 respectively.

Table 4.6. Pearson correlation coefficients (r) for linear regressions and recapitulation on hypothesis

Parameter	(All) DK+GL	Denmark	Greenland	Increase	Expected significance	Conclusion
pH	(-0.22 ***)	-0.12 *		-	large	medium
Clay	0.30 ***	0.56 ***	0.27 ***	+	medium	large
Total C					none	none
Fine silt	0.20 ***	0.43 ***		+	medium	medium
Fine silt + clay	0.29 ***	0.57 ***		+	medium	medium
EC					weak	none
P Oxalate	-0.16 ***		-0.59 ***	-	medium	medium
Fe Oxalate	0.77 ***	0.78 ***	0.75 ***	+	large	large
Al Oxalate	0.11 *			+	medium	weak

For pH, total C and EC the first value given is for all soils, including those from New Zealand.
n.a. indicates that data has not been available, compare table 3.1.
A blank field indicates a not significant relationship.
If an increased (amount of the) parameter prompt an increased glyphosate sorption the increase is marked positive.
Clay are particles below 2 µm.
Fine silt are particles below 20 µm.

Measured pH, content of clay, oxalate extractable iron and phosphorus are the most promising parameters to be investigated in an attempt at an improved pedotransfer function for predicting a soils glyphosate sorption coefficient. Fine silt maybe in combination with clay might also prove valuable, but in the following chapter these two parameters will only be included in selected analyses.

Adsorption coefficient predicted by multiple parameters

5

In this chapter pedotransfer functions from literature is evaluated on the current data set. New models are generated based on the best predictors identified in the previous chapter. The new models are evaluated and the best ones identified. Results are discussed.

5.1 Test of models found in literature

5.1.1 Paradelo et al. 2015

In the article Paradelo et al. [2015] it is argued that a pedotransfer function incorporating a limited number of predictors can render acceptable predictions, but also that predictors may vary between fields. The model Paradelo finds for the two fields included in the publication is now evaluated on the much larger data set from the current project.

Paradelo presents weights of variable predictors for best-four sets, and the derived pedotransfer function is written out in equation 1.1. Paradelo's model is rewritten in equation 5.1 to account for differences in units and method to the current project.

$$K_d = -201.0 \cdot pH - 12.7 \cdot EC + 28.50 \cdot Clay - 2.829 \cdot Sand + 1585 \tag{5.1}$$

where

K_d	linear glyphosate sorption coefficient at concentration 0.23 mg L^{-1} [L kg^{-1}]
pH	measured in demineralised water
EC	electrical conductivity [mS cm^{-1}]
$Clay$	particles below 2 µm [%]
$Sand$	particles above 50 µm [%]
1585	constant given by Marcos Paradelo after personal inquiry September 2017

The factor difference between 1.1 and 5.1 on the electrical conductivity stems from the fact that Paradelo et al. utilises the measured value while the current project is carried out on the value adjusted for dilution factor.

Paradelo et al. [2015] achieves a coefficient of determination of $R^2 = 0.70$. On figure 5.1 the Paradelo model is illustrated on the original dataset of Silstrup and Estrup fields that Paradelo derived the model from, while figure 5.2 presents all analysed Danish and Greenlandic fields (for legend see figure 4.1).

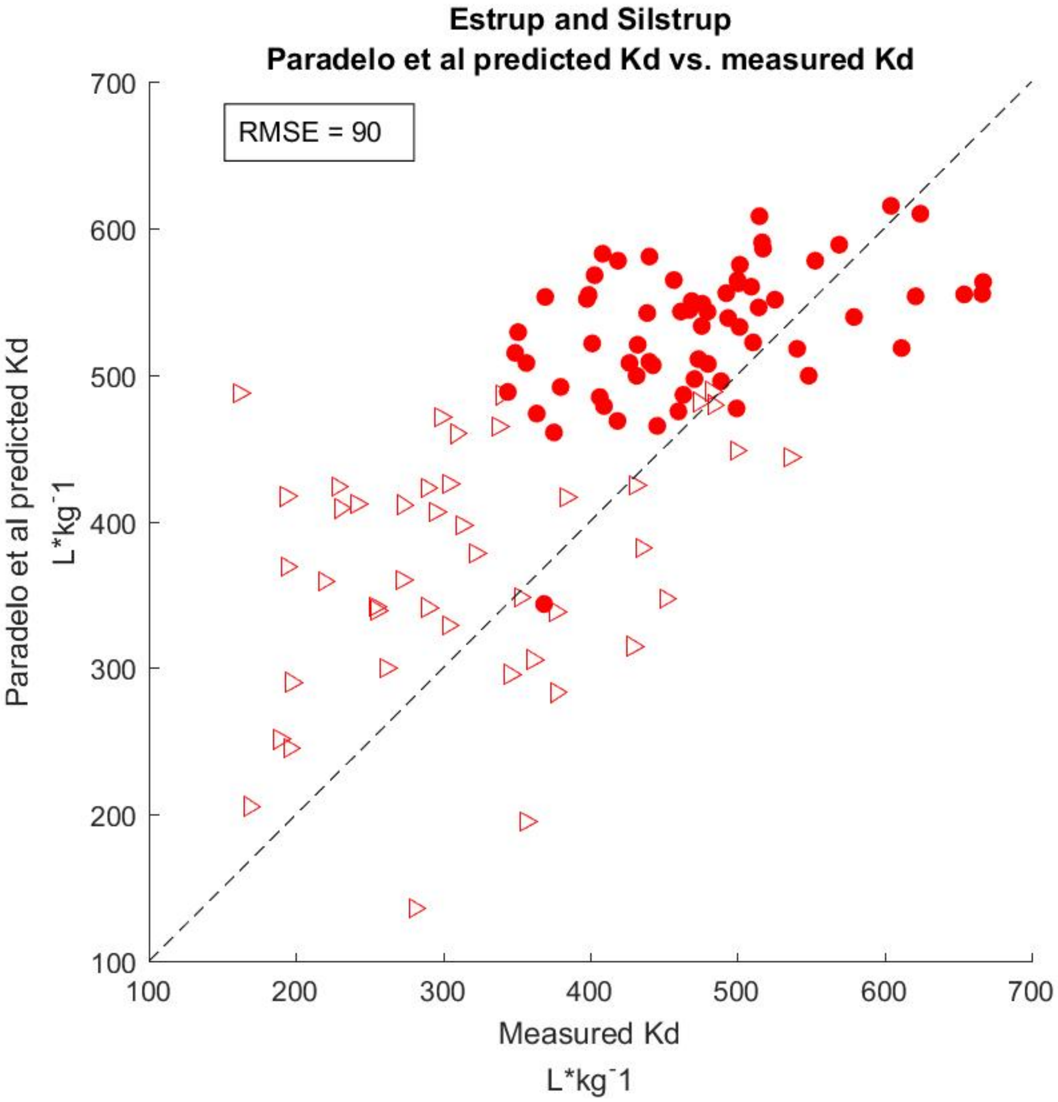

Figure 5.1. Scatter diagram of K_d predicted by the Paradelo model vs. measured K_d for Silstrup and Estrup fields. Reference line for a perfect fit is included.

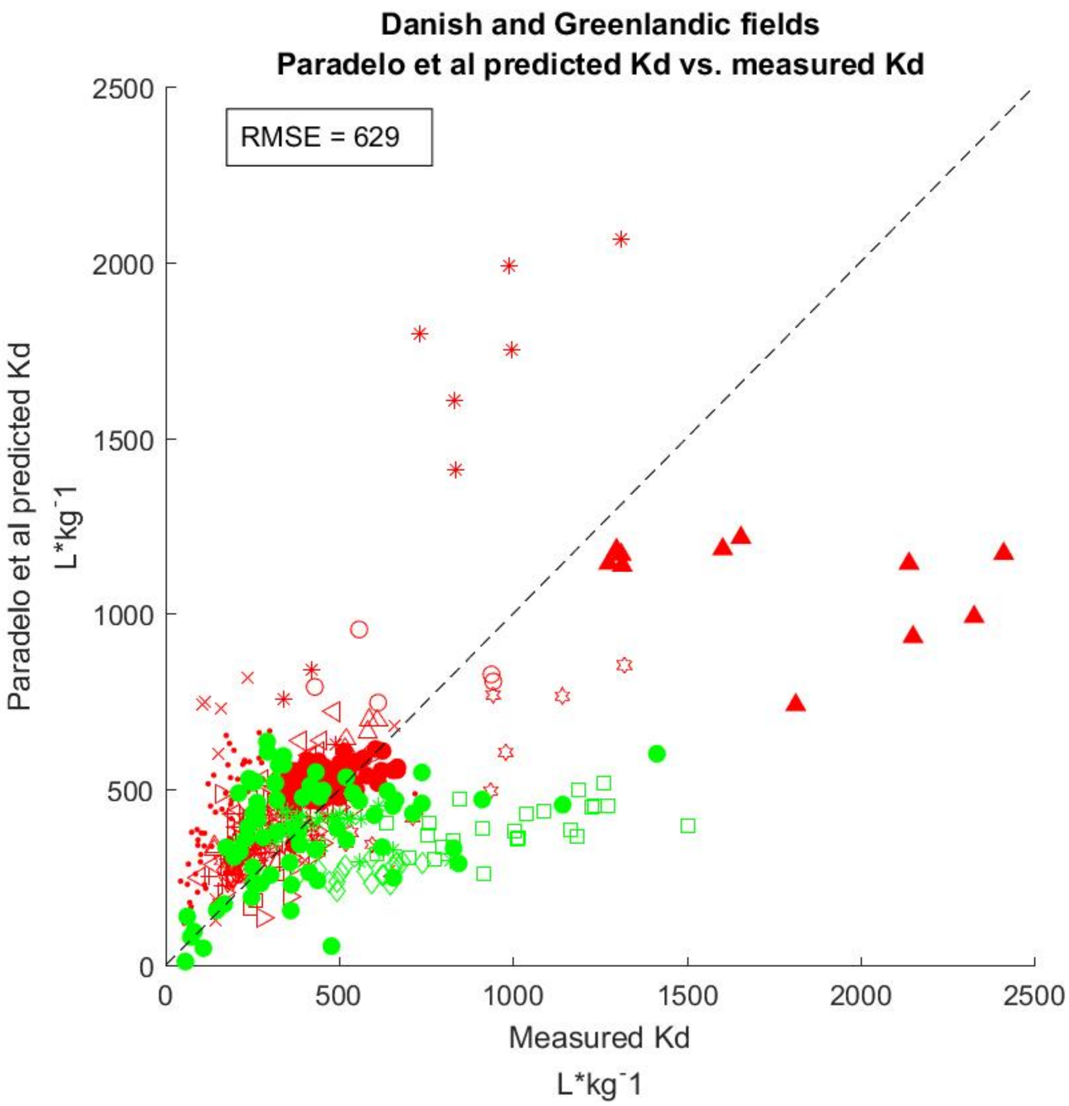

Figure 5.2. Scatter diagram of K_d predicted by the Paradelo model vs. measured K_d for all Danish and Greenlandic fields. Reference line for a perfect fit is included.

Some of the Danish fields (in particular Ringkøbing 2, represented by red triangles) and Greenland in general appears to be represented poorly by this model. Figure 5.3 presents the Greenlandic fields alone.

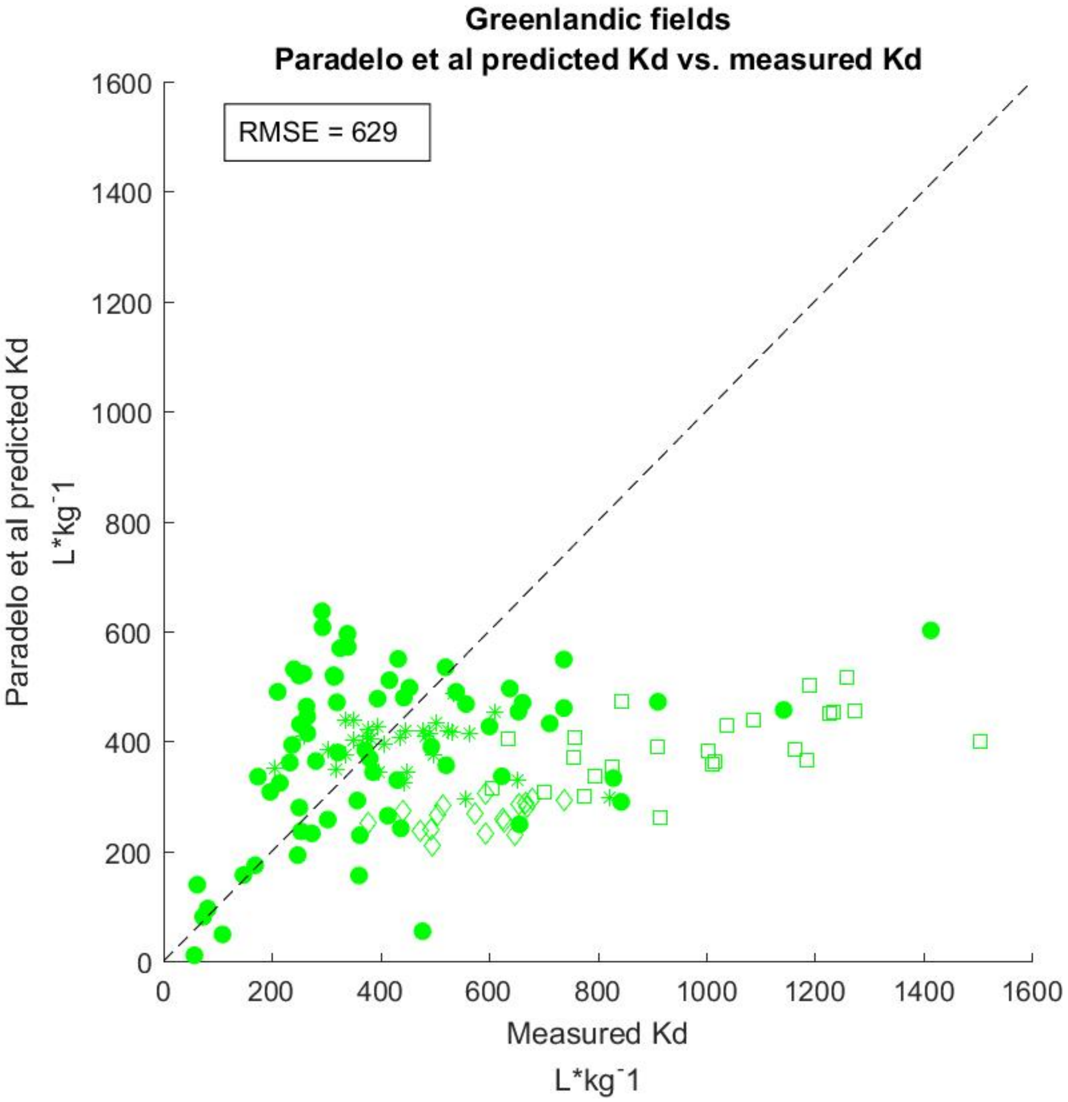

Figure 5.3. Scatter diagram of K_d predicted by the Paradelo model vs. measured K_d for all Greenlandic fields. Reference line for a perfect fit is included.

The youngest soil on field G300 (green open square) is represented very poorly by the Paradelo model. The Paradelo model is obviously not suited for use outside the fields from where it was derived, in agreement with the expectations phrased by Paradelo et al. [2015].

The model performs poorly supposedly because is based on a data set with a limited range of the predicting values, where especially the range for iron content (8 to 53 mmol kg^{-1}) is very narrow when compared to the larger dataset that includes a large number of soils with content of oxalate extractable iron between 50 and 110 mmol kg^{-1} (compare figure 4.16).

5.1.2 Dollinger et al. 2015

Dollinger et al. [2015] presented a pedotransfer function (introduced in equation 1.2) for predicting a glyphosate sorption coefficient based on the soil parameters of *Clay* and *CEC*. For the two fields of Estrup and Oatfield all necessary parameters are available and the model is evaluated on figure 5.4.

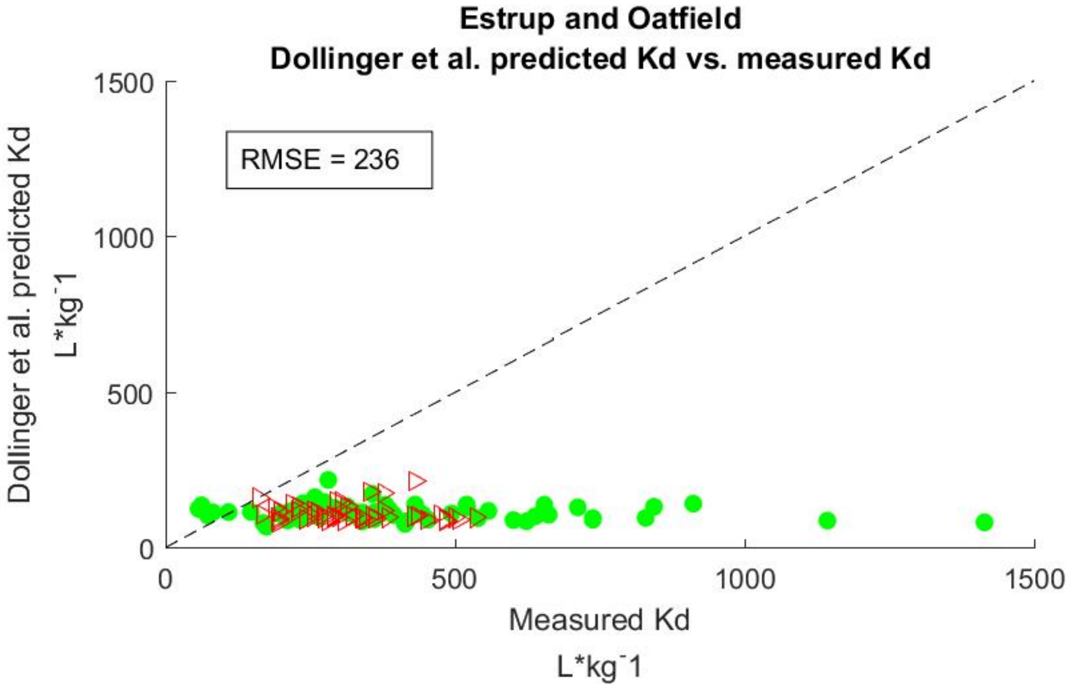

Figure 5.4. Scatter diagram of coefficients predicted by model by Dolliger et al. vs. measured sorption coefficients for Estrup and Oatfield. Reference line for a perfect fit is included.

It appears that the model does not suit the current data set at all, and support the hypothesis of cation exchange capacity being unnecessary or unsuited in the quest for a better performing pedotransfer function.

The cause of the substantially poorer fit found on the fields of Estrup and Oatfield compared to the reported $R^2 = 0.48$ in the publication is uncertain. It might be that the model performs poorly on these two fields in particular, and that the fit would improve if more fields were included, but it is also possible the Greenlandic soil does not follow the same relationship as the American and European soils employed when the model was generated.

5.2 New multi parameter models

5.2.1 Investigated predictors and regions

All analyses are performed on predictors proven promising in the previous chapter. The suitability of the current dataset for performing a multiple linear regression (MLR) was made probable in section 3.3.5. Soils of New Zealand are omitted due to lack of data (see chapter 3).

A best model based on the parameters of *pH, Clay,* Fe_{ox} and P_{ox} is found, as well as a best model based on the commonly known soil parameters of *pH, Clay* and *Fine silt*. Additionally a best model based on the parameters Fe_{ox} and P_{ox}, which are found in one simple and relatively inexpensive laboratory analysis, is found.

Besides the geographical regions of Denmark, Greenland, South Igaliku and DK+GL (Denmark and Greenland combined) also the Danish field Silstrup and the collection of Danish points referred to as Fertility are included in the following section. Silstrup is the largest collection of samples from a single Danish field available, and Fertility is an equally large collection of separate points also from Denmark, and they might provide an insight into the field level precision of the models. A total of 7 regions are analysed, all containing 68 or more sampled points, allowing the search for models considering up to 3 predictors following the conservative rule of thumb requiring at least 20 times as many samples as predictors in a study [Schneider et al., 2010]. For completeness models containing up to four parameters are presented in the following, keeping in mind that the validity of four-parameter models might be compromised.

5.2.2 Coefficients of determination

For each predictor in the following tables a symbol indicates if it is negatively (-) or positively (+) correlated to K_d. Coefficients of determination, r^2, for best fitting models on the region in question are presented in table 5.1 where predictors *pH, Clay,* Fe_{ox} and P_{ox} are evaluated, in table 5.3 where predictors Fe_{ox} and P_{ox} alone are evaluated and in table 5.2 where predictors *pH, Clay, Fine silt* and *'Fine silt + Clay'* are evaluated.

Two predictors are significantly better than one for the three regions of Fertility, Oatfield and Greenland. A great improvement is not found from two to three predictors. The preferred predictors vary across the regions, and *pH* even varies between an odd positive correlation and the more common (and expected) negative correlation to K_d.

P_{ox} is much more stable as it is negatively correlated to K_d for all regions. *Clay, Fine silt* and *'Fine silt + Clay'* all correlate consistently positive, and Fe_{ox} is the best single predictor (presented in bold in table 5.1) for 5 out of 7 regions.

Table 5.1. *pH, clay,* Fe_{ox} and P_{ox}. Coefficients of determination, r^2, for best fitting models found.

	DK+GL	Silstrup	Fertility	Denmark	Oatfield	South Igaliku	Greenland
r^2 single predictor	0.59	0.16	0.24	0.61	0.30	0.73	0.56
r^2 2 predictors	0.64	0.22	0.42	0.71	0.60	0.82	0.71
r^2 3 predictors	0.68		0.56	0.76	0.64	0.87	0.76
r^2 4 predictors	0.70			0.76		0.88	0.77
pH	-	-	-	-	-	+	-
Clay	+	+	+	+		+	+
Fe_{ox}	+		+	+	+	+	+
P_{ox}	-	-	-	-	-	-	-

Table 5.2. *pH, Clay and Fine silt*. Coefficients of determination, r^2, for best fitting models found.

	DK+GL	Silstrup	Fertility	Denmark	Oatfield	South Igaliku	Greenland
r^2 2 predictors	0.19	0.21	0.42	0.48	0.31	0.66	0.26
r^2 3 predictors	0.19			0.49		0.69	0.28
pH	-	-	-	-	-	+	-
Clay	+		+	+		+	+
Fine silt	-						-
Fine silt + Clay	+	+		+	+	+	+

Table 5.3. Fe_{ox} and P_{ox}. Coefficients of determination, r^2, for best fitting models found.

	DK+GL	Silstrup	Fertility	Denmark	Oatfield	South Igaliku	Greenland
r^2 2 predictors	0.64		0.26	0.71	0.60	0.82	0.71
Fe_{ox}	+		+	+	+	+	+
P_{ox}	-		-	-	-	-	-

Predictions based on *pH, Clay* and *Fine silt* are generally much too poor to be of any generic interest, as illustrated by the generally low coefficients of determination presented in table 5.2. Only the region of South Igaliku finds a decent prediction based on *pH, Clay* and *Fine silt* alone, with r^2 at 0.66 for two predictors, but the rest of the regions are below 0.5. The model is abandoned.

When the predictors *pH, Clay*, Fe_{ox} and P_{ox} are all considered, only the Danish regions of Fertility and Silstrup have other than Fe_{ox} and P_{ox} as their best two predictors (equations presented in table 5.4).

The prediction for Danish fields is never very good, but given that the evaluated predictors are chosen as the most promising for a general model across fields and regions, this is to be expected.

5.2.3 Best new models

For the different regions the best models on K_d based on two parameters are presented in table 5.4, including information on coefficients of determination and root-mean-square error. Observe that the two models presented for DK+GL are the same, as are the models for Denmark, Oatfield, South Igaliku and Greenland respectively.

Table 5.4. Best fitting models for predicting K_d found by multiple linear regression.

Region	R^2	RMSE	Equation
pH, Clay, Fe_{ox} and P_{ox} :			
DK+GL	0.64	197	$+6.17 \cdot Fe_{ox} - 9.00 \cdot P_{ox} + 255$
Silstrup	0.22	72	$-131 \cdot pH - 25.6 \cdot P_{ox} + 1634$
Fertility	0.42	89	$-162 \cdot pH + 11.5 \cdot Clay + 1111$
Denmark	0.71	187	$+7.86 \cdot Fe_{ox} - 20.8 \cdot P_{ox} + 312$
Oatfield	0.60	157	$+9.55 \cdot Fe_{ox} - 15.3 \cdot P_{ox} + 355$
South Igaliku	0.82	117	$+3.82 \cdot Fe_{ox} - 14.6 \cdot P_{ox} + 518$
Greenland	0.71	155	$+3.95 * Fe_{ox} - 10.4 \cdot P_{ox} + 478$
Fe_{ox} and P_{ox} :			
DK+GL	0.64	197	$+6.17 \cdot Fe_{ox} - 9.00 \cdot P_{ox} + 255$
Fertility	0.26	101	$+5.85 \cdot Fe_{ox} - 7.82 \cdot P_{ox} + 79.9$
Denmark	0.71	187	$+7.86 \cdot Fe_{ox} - 20.8 \cdot P_{ox} + 312$
Oatfield	0.60	157	$+9.55 \cdot Fe_{ox} - 15.3 \cdot P_{ox} + 355$
South Igaliku	0.82	117	$+3.82 \cdot Fe_{ox} - 14.6 \cdot P_{ox} + 518$
Greenland	0.71	155	$+3.95 \cdot Fe_{ox} - 10.4 \cdot P_{ox} + 478$

where

K_d	glyphosate sorption coefficient at concentration 0.23 mg L^{-1} [L kg^{-1}]
pH	measured in demineralised water [-]
Fe_{ox}	oxalate extractable iron [mmol kg^{-1}]
P_{ox}	oxalate extractable phosphorus [mmol kg^{-1}]
Clay	particles below 2 µm [%]
R^2	coefficient of determination
RMSE	root-mean-square error

The model based on predictors Fe_{ox} and P_{ox} and generated based on all Danish and Greenlandic fields is evaluated on figures 5.5 and 5.6.

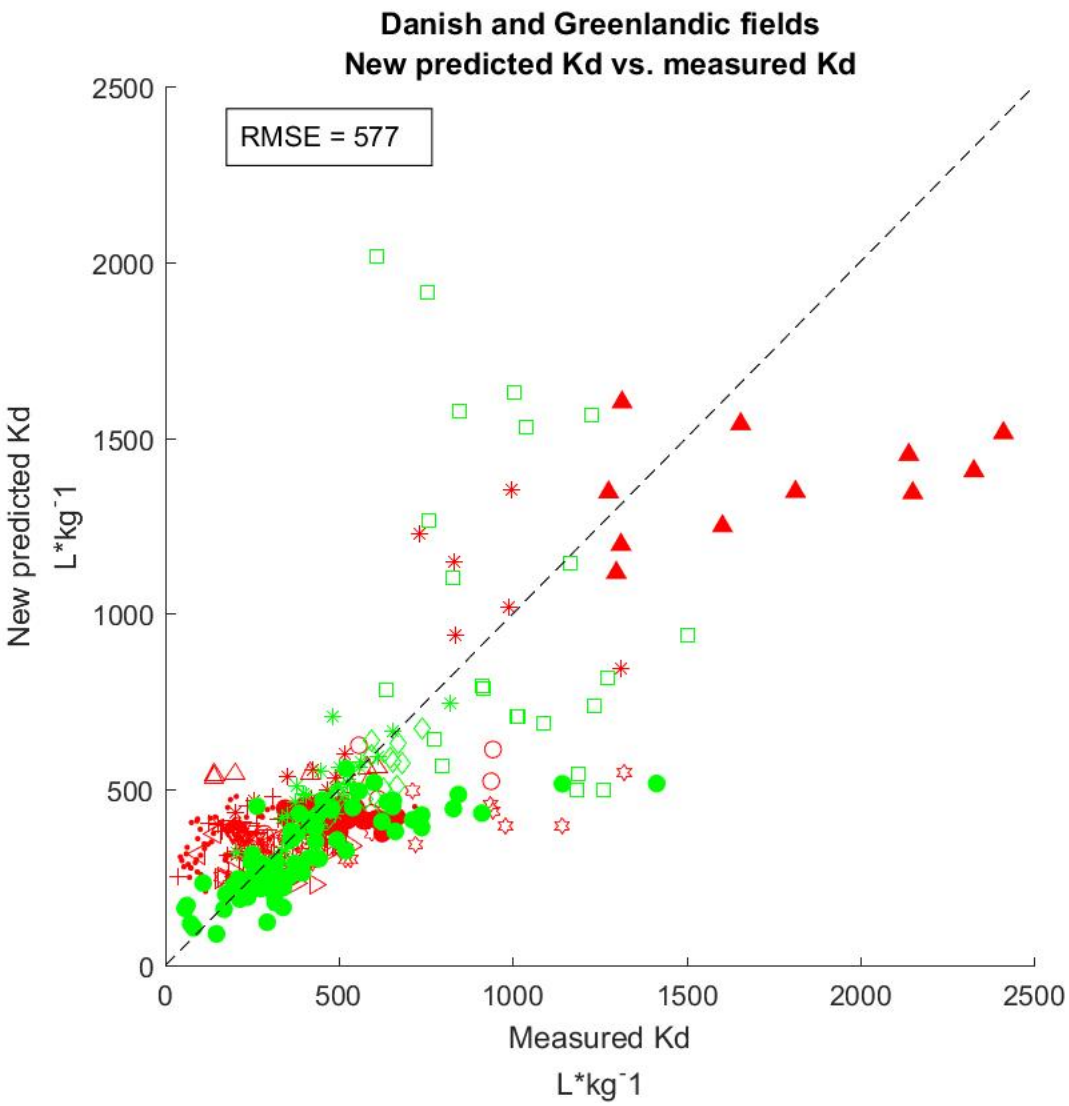

Figure 5.5. Scatter diagram of K_d predicted by Fe_{ox} and P_{ox} vs. measured sorption coefficients. Reference line for a perfect fit is included.

For the fields with K_d above 750 L kg^{-1}, including the Greenlandic field G300 (green open squares), the Danish fields Ringkøbing 2 (red closed triangles) and parts of Lerbjerg (red asterisks) and Sørvad (red open six-pointed star), the precision of the predictions goes down drastically.

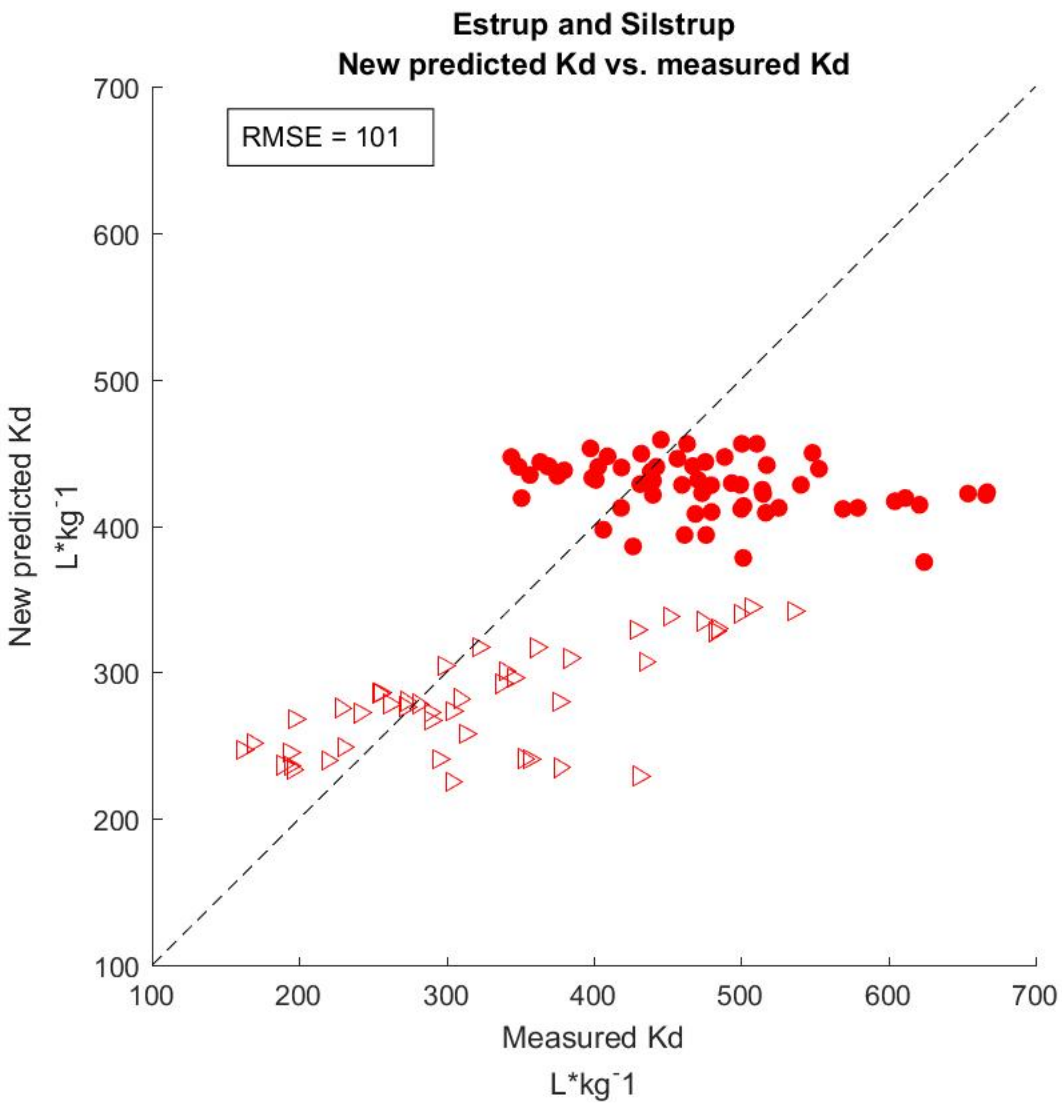

Figure 5.6. Scatter diagram of K_d predicted by Fe_{ox} and P_{ox} vs. measured sorption coefficients for the Danish fields of Estrup and Silstrup. Model is based on all Danish and Greenlandic soils. Reference line for a perfect fit is included.

Predictions for the Danish fields Estrup and Silstrup are not remarkably worse than was the case for the model by Paradelo (compare figure 5.1 and 5.6) when one takes into account that this was the data set the Paradelo model was originally derived from.

When estimates for K_d across fields and regions are sought, a model based on Fe_{ox} (improving sorption strength by providing sorption sites) and P_{ox} (lowering sorption strength by competing for sorption sites) seem very promising.

Sensitivity of new model

The Greenlandic field G300 is located isolated far up the valley (see map on figure 2.5). On figure 5.5 the samples from this field show a very large error from the prediction based on Fe_{ox} and P_{ox}. An alternative model is found based on the same data set except G300 is omitted, and the equation changes as follows:

$$\text{Model based on all fields:} + 6.17 \cdot Fe_{ox} - 9.00 \cdot P_{ox} + 255\ , r^2 = 0.64 \text{ and RMSE} = 197$$
$$\text{Model omitting G300:} + 7.46 \cdot Fe_{ox} - 10.3 \cdot P_{ox} + 215\ , r^2 = 0.65 \text{ and RMSE} = 185$$

The model is evaluated on the fields of Denmark and Greenland on figure 5.7.

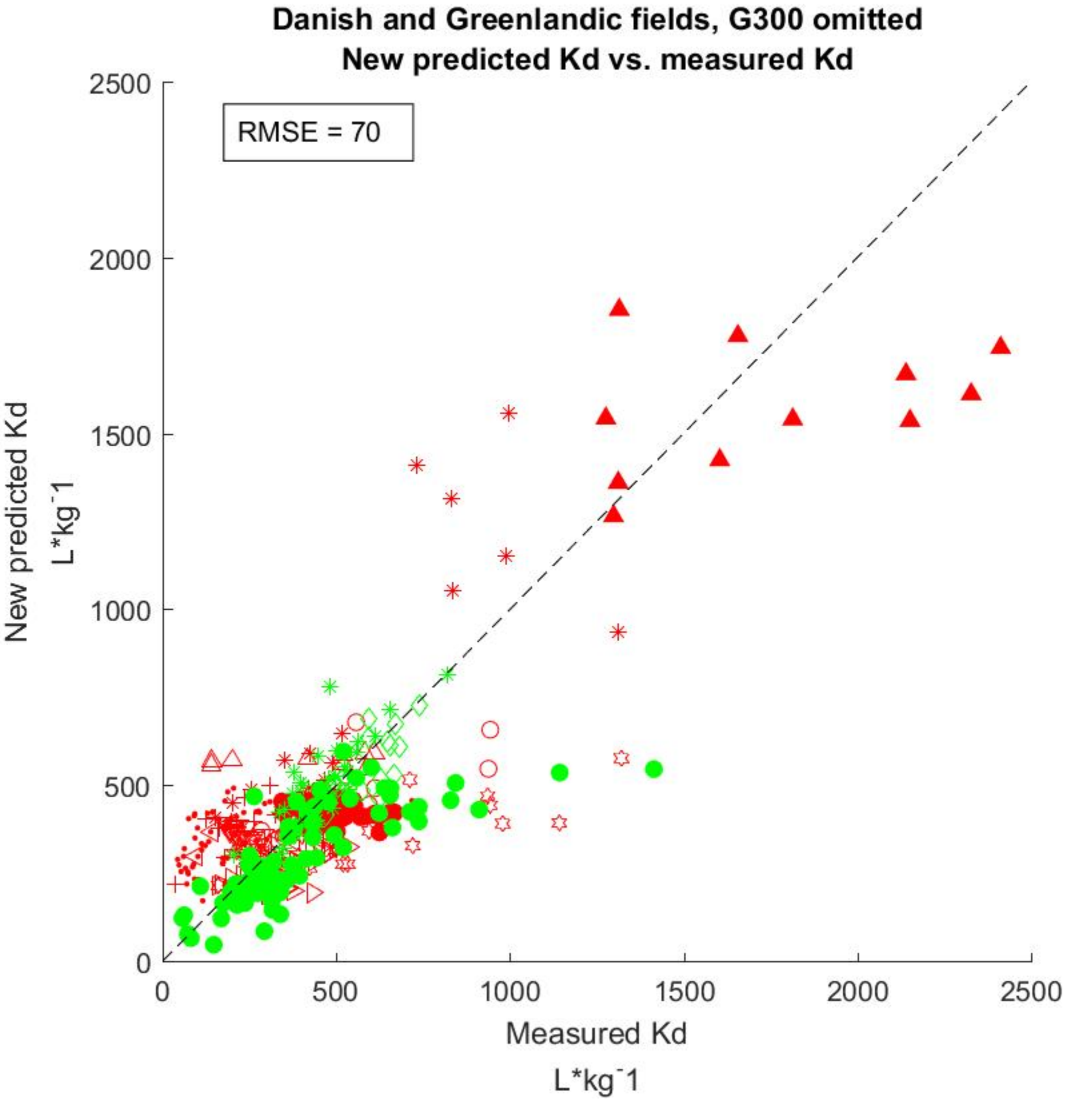

Figure 5.7. Scatter diagram of coefficients predicted by Fe_{ox} and P_{ox} vs. measured sorption coefficients. Model is based on all Danish and Greenlandic soils omitting G300. Reference line for a perfect fit is included.

When G300 is left out of the evaluation the root-mean-square error as expected goes down drastically, but the coefficient of determination does not improve.

5.3 Summary and conclusion on multiple parameters

More than 60 % of the variation in glyphosate sorption coefficient of the investigated soils can be explained by a linear model incorporating the two predictors Fe_{ox} and P_{ox}. This model performs remarkably better across fields and regions than the model found by Paradelo et al., confirming the hypothesis that carefully selected fields improve performance of the model.

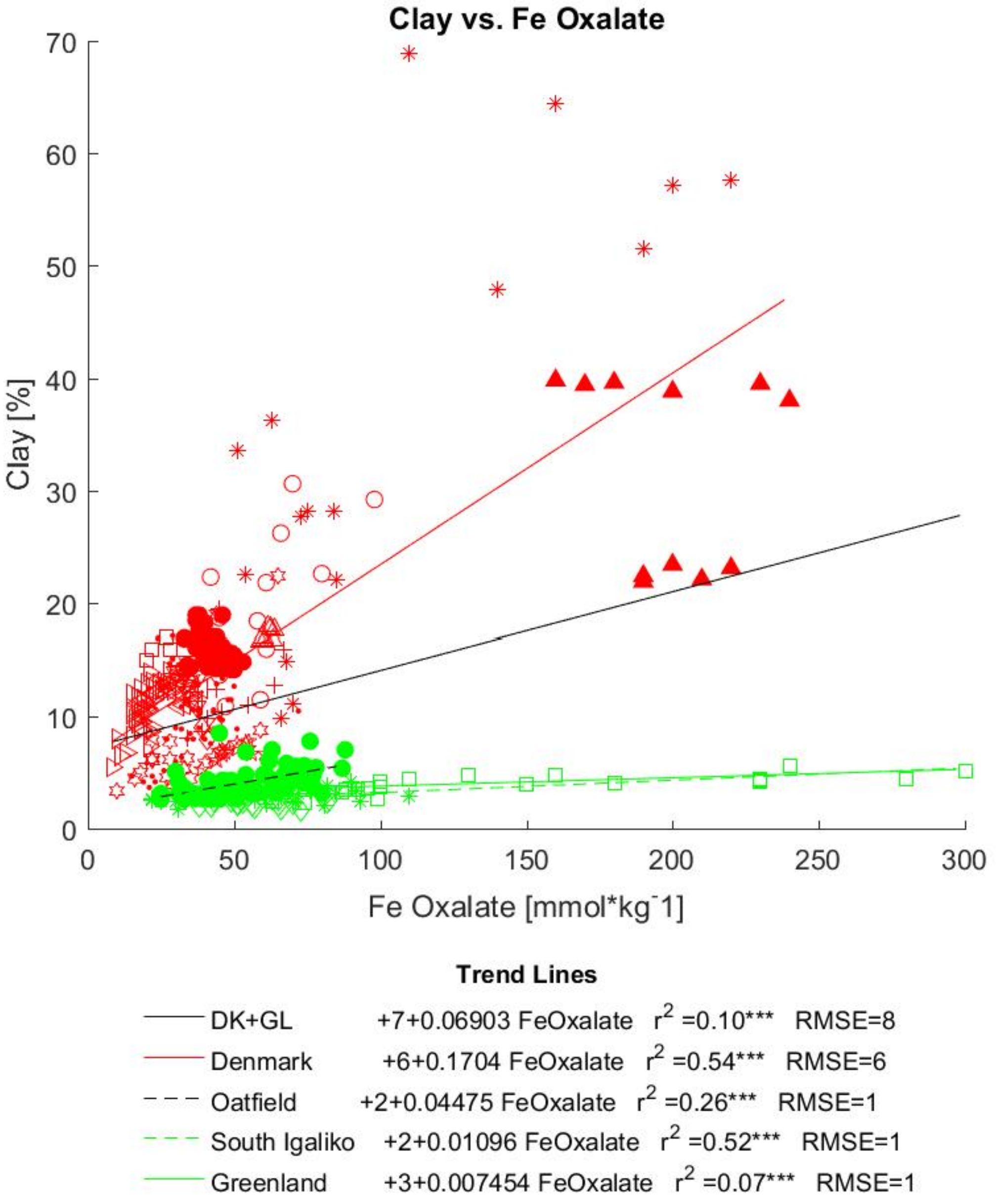

Figure 5.8. Clay content vs. oxalate extractable iron and simple linear regressions.

It is still unclear what controls the remaining part of the variation in K_d. Correlation between clay content and Fe_{ox} respectively P_{ox} is presented on figures 5.8 and 5.9.

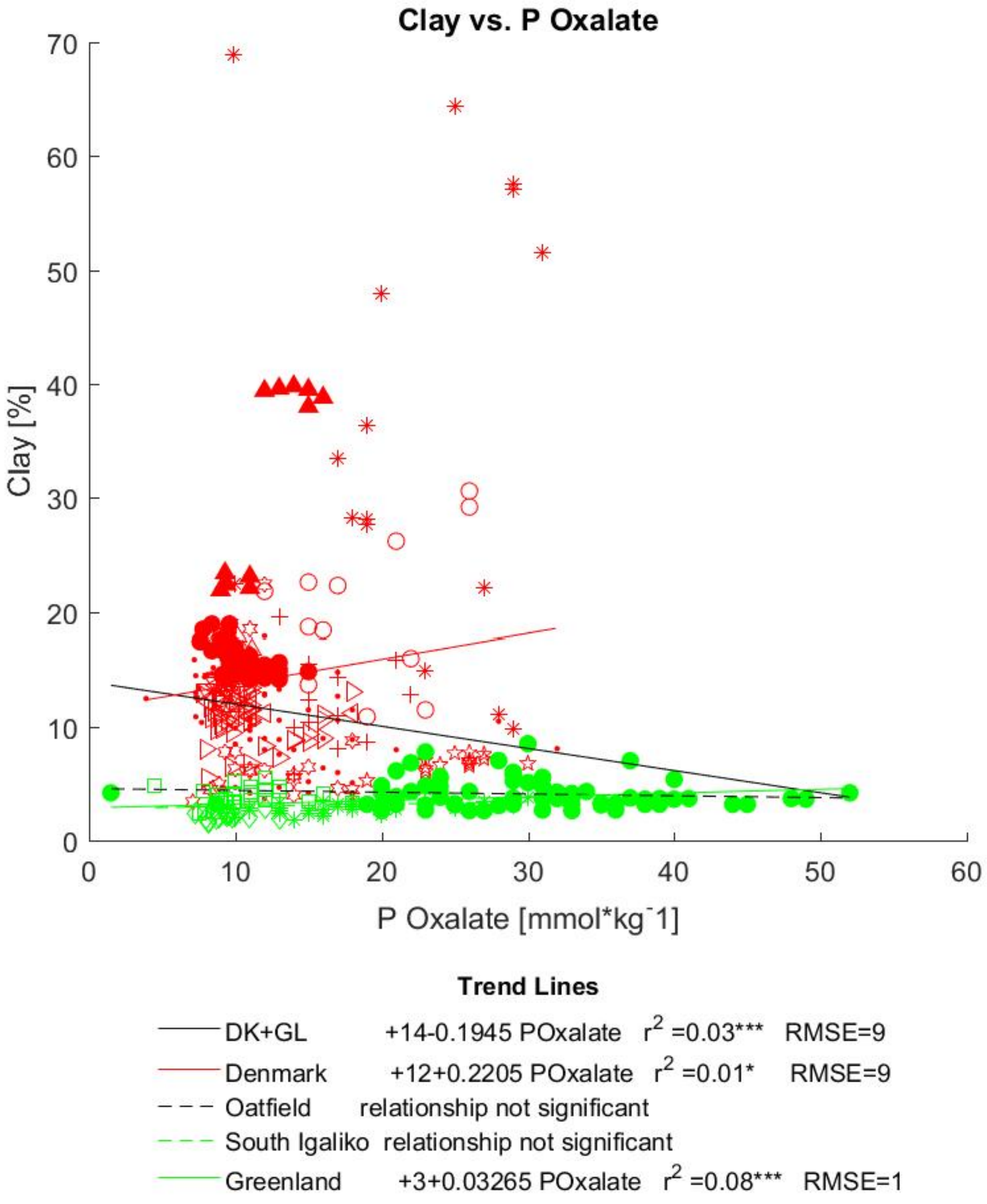

Figure 5.9. Clay content vs. oxalate extractable phosphorus and simple linear regressions.

The composition of clay clearly differs between Denmark and Greenland, where Greenland sees much larger amounts of phosphorus and iron per clay. A difference was expected due to the different origin of the soils. In general the investigated Greenlandic soils have been poor on clay, to a degree rarely seen in the Danish samples. Future investigations could get more into details with these differences.

5.3.1 New models summarised

No usable pedotransfer function has been found when the predictors of *Clay*, *Fine silt* and *pH* were considered without the oxalate extractables. Only when predicting single fields or regions did the model perform reasonably, but even then not consistently across all regions or fields.

For the Greenlandic soils the best predictors are the two oxalate extractables iron and phosphorus [mmol kg^{-1}], and equation 5.2 has a coefficient of determination of 0.71.

$$K_d = +3.95 \cdot Fe_{ox} - 10.4 \cdot P_{ox} + 478 \tag{5.2}$$

The coefficient of determination for the prediction of Greenlandic soils can be improved to 0.77 when predictors *Clay* and *pH* are included.

The best pedotransfer function for predicting the glyphosate sorption coefficient for the Danish soils is based on the same two predictors but with slightly different weights as presented in equation 5.3.

$$K_d = +7.86 \cdot Fe_{ox} - 20.8 \cdot P_{ox} + 312 \tag{5.3}$$

For Danish soils alone the coefficient of determination is 0.71 when the two predictors are included, and this can be improved only to 0.76 for four predictors.

The pedotransfer function with the best performance across regions is again based on the two predictors Fe_{ox} [mmol kg^{-1}] and P_{ox} [mmol kg^{-1}]. The equation is given in 5.4.

$$K_d = +6.17 \cdot Fe_{ox} - 9.00 \cdot P_{ox} + 255 \tag{5.4}$$

This pedotransfer function has a coefficient of determination of 0.64, and can be improved only to 0.70 by including predictors *Clay* and *pH*. No systematic difference in errors is seen between Danish and Greenlandic soils.

Discussion and environmental consequences

6

In this chapter the new knowledge on the magnitude of glyphosate sorption on the Greenlandic soils is related to potential environmental consequences. Leaching through colloidal transport is discussed with references to PLAP, and a brief recap is conducted on the differences between soils of different historical management and origin.

6.1 Retardation and transport of glyphosate

Glyphosate sorption coefficients measured translates to an expected travel speed of the chemical through the soil, and since a low speed will allow more time for biodegradation to happen this is a critical measure in risk assessments and discussions of the robustness of the environment.

Retardation factor R is a measure of the relation between mobility of a conservative tracer and the chemical in question [Loll and Moldrup, 2000, equation 5.20] and is simplified to apply on a homogeneous, non-layered soil, constant water velocity and linear sorption/desorption.

$$R = u_{water} \cdot u_{chemical}^{-1} = 1 + \rho_b \cdot \theta^{-1} \cdot K_d \tag{6.1}$$

where

R	Retardation factor [-]
ρ_b	Bulk density [g $DM \cdot \mathrm{cm}^{-3}$ $soil$]
θ	Volumetric water content [cm^3 $water \cdot \mathrm{cm}^{-3}$ $soil$]
K_d	Sorption coefficient [$\mathrm{L\ kg}^{-1} = \mathrm{cm}^3 \cdot \mathrm{g}^{-1}$]
u	Pore water velocity

6.1.1 Glyphosate binding to three hypothetical Greenlandic soils

For Greenland three hypothetical soils are considered, one with an average glyphosate sorption coefficient, one in the high range and one in the low range.

Considering a soil of the low (realistic in Southern Greenland) bulk density $\rho_b = 1.35$ g cm^{-3} at low water content 0.2 cm^3 cm^{-3} the range of sorption coefficients found corresponds to retardation factors in the unsaturated zone of Greenland between 100 and 2000, averaged at a sorption coefficient of 500 L kg^{-1} corresponding to a retardation factor of approximately 700.

If soil water travels approximately one meter per year, glyphosate applied to the hypothetical soils in the investigated concentration of 0.23 mg L^{-1} travels 15, 1.5 and 0.5 mm per year. In every event it is expected to take decades for the glyphosate to travel through the top soil, and in spite of the less than favourable Sub Arctic climate it is expected that microbes will have time to degrade both the chemical itself and its equally problematic degradation product AMPA before it leaches to ground or surface waters.

6.1.2 Retardation in Greenland and Denmark

On figure 6.1 retardation factors are illustrated for Greenlandic soils and Danish soils, the latter calculated for a higher soil water content and a slightly higher bulk density.

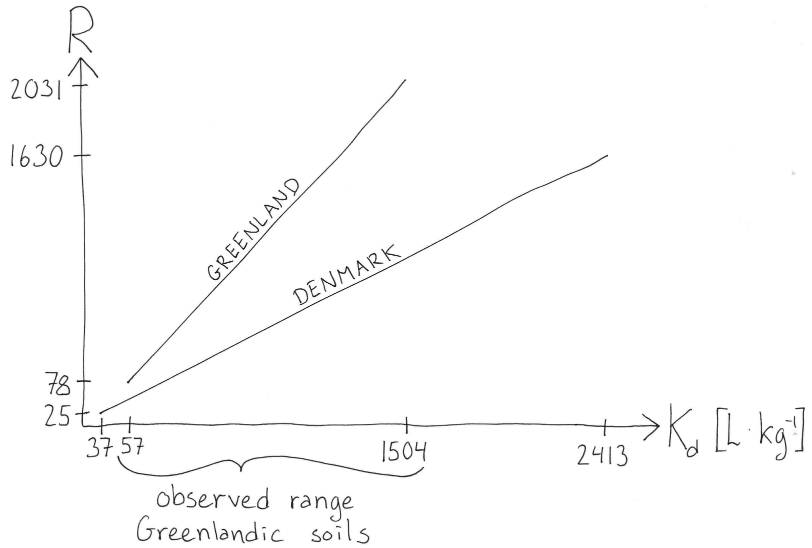

Figure 6.1. Retardation of Danish and Greenlandic soils.

The speed at which glyphosate travels through soil in Greenland can be expected to be comparable or slower than that found in Denmark.

6.2 Leaching from monitored fields

Under the Danish Pesticide Leaching Assessment Programme (PLAP) the fields of Estrup and Silstrup has been monitored for leaching of glyphosate. According to Rosenbom et al. [2016] glyphosate has been found at relatively high concentrations in drainage water under both fields, but only above drinking water levels in groundwater under Estrup field. Of the two fields Estrup has a slightly lower K_d (162-536 L kg^{-1}) compared to Silstrup (344-667 L kg^{-1}), but the difference both in sorption coefficient and in leaching data really is too small to draw any conclusions on.

6.2.1 Colloidal transport

Silstrup and Estrup fields see an estimated travel time for glyphosate through the top soil of many decades. Even when the soil is near saturation the estimated travel time through a one meter top layer is still several years. Of cause these figures are only valid for the relatively low concentration of 0.23 mg L^{-1}, but it is still a good indication that when leaching occurs it might just be due to colloid-facilitated transport, as also reasoned by others including [de Jonge et al., 2000].

From the current project does not assess if the particles that bind the glyphosate will stay immobile in the soil or move with the water flow. The events at Estrup has been examined by Norgaard et al. [2014] who identified no clear relationship between colloidal transport and the transport of glyphosate. Leaching of glyphosate was found to be controlled by rain intensity and timing after application, but also indications of a common dominant transport mechanism between colloids and glyphosate was discovered.

6.3 Relationships between predictors, and summary

Figure 6.2 presents the derived parameter '$K_d/Clay$' (*Clay* in [%]) which is quite constant around 25 (between 5 and 50) for the Danish fields, especially those with a pH above 6 or 6.5. No such relationship has been found for the Greenlandic fields.

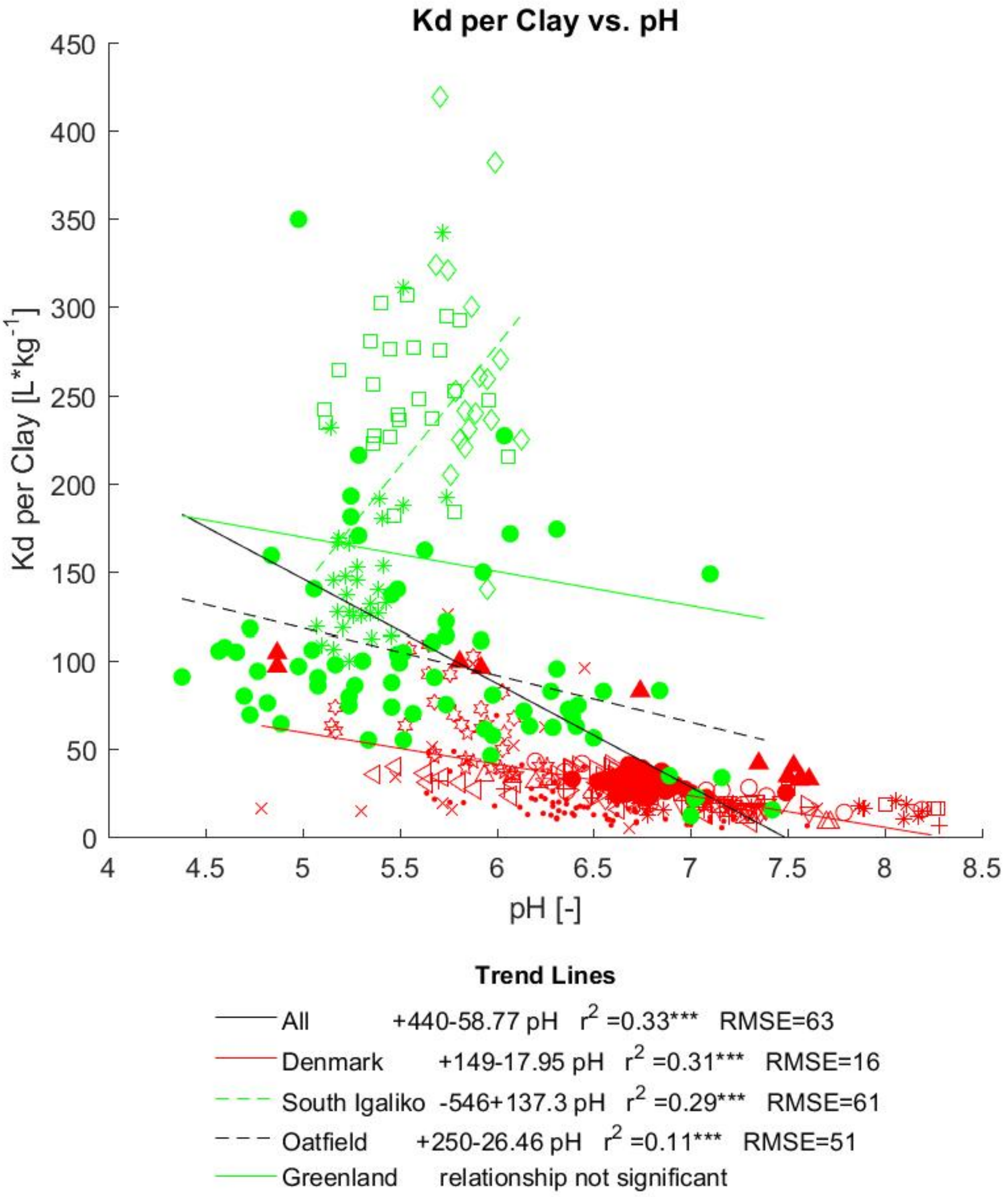

Figure 6.2. K_d per Clay plotted against Fe_{ox}.

It appears the risk of glyphosate leaching is not very different across the regions investigated in Denmark and Greenland, but the relationships between soil parameters and sorption coefficients differ in ways that continue to puzzle.

Conclusions 7

The parameters of pH, content of clay, content of oxalate extractable iron and content of oxalate extractable phosphorus are all individually found to have a medium or high influence on glyphosate sorption coefficients K_d (found at a glyphosate concentration of 0.23 mg L^{-1}) across fields and regions. pH does not correlate to K_d when only Greenlandic soils (or subsections there off) are investigated, and equally for phosphorus versus the Danish soils. Iron was generally the best single predictor.

When the Greenlandic soils were divided according to historical management the parameter of content of fine silt, alone or combined with clay, revealed a reliable medium strong influence on K_d for both Greenlandic and Danish soils as well as all combined.

Parameters found to have only a weak or no influence on K_d included electrical conductivity, content of organic carbon and content of oxalate extractable aluminium. No indications were found that the different quality of organic matter found in Greenland influences the current investigations.

Pedotransfer functions employing two predictors for K_d were found to have coefficients of determination above 0.6, and for all regions iron was revealed as one of the predictors. The generated pedotransfer function improves performance considerably from the models given by Dollinger et al. [2015] and Paradelo et al. [2015].

Sorption of glyphosate to the young Greenlandic soils is comparable to Danish soils in strength, but indicates different relationships to the soil parameters than what is found for the well processed soils of Denmark. Data also suggests differences between the soils of South Igaliku that have most recently been taken under plough and that of Oatfield that has been in active farming for half a century already.

7.1 Limitations and suggestions

Investigated Greenlandic soils all contain less than 9 % clay, and all originate from a very limited geographical area of a country with a vast variation in geology. One limitation of the current study is that the knowledge gained might not be applicable to soils of larger clay content nor from a larger region.

This suggests that a future study would benefit from including data on Greenlandic soils of a higher clay content, as well as the complete set of parameters on soils of volcanic origin like the ones from New Zealand that had to be omitted for the current analysis on multiple parameters. Also the composition of clay clearly differs between Denmark and Greenland, and future investigations could investigate this. A different suggestion for a future study would be to follow the lead of Sidoli et al. [2016], who suggests the exchange of pH(water) for pH($CaCl_2$).

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