

# Understanding the Causes of Spatial Variation in Pesticide Sorption and Degradation at the Catchment Scale

Abdul Ghafoor

*Faculty of Natural Resources and Agricultural Sciences  
Department of Soil and Environment  
Uppsala*

Doctoral Thesis  
Swedish University of Agricultural Sciences  
Uppsala 2013

Acta Universitatis agriculturae Sueciae

2013:8

Cover: A view of soil profile with distinct top soil and subsoil environment of one sampling point from the E21 monitoring catchment in Östergötland, southern Sweden (photo: Abdul Ghafoor)

ISSN 1652-6880

ISBN 978-91-576-7765-5

© 2012 Abdul Ghafoor, Uppsala

Print: SLU Service/Repro, Uppsala 2013

## Understanding the causes of spatial variation in pesticide degradation and sorption at the catchment scale

### Abstract

Intensive agricultural practices and use of pesticides, essential to achieve high crop yields, present particular risks to soil and water resources which sustain life. Degradation and sorption of pesticides in soils are both spatially variable and also among the most sensitive factors determining losses to surface water and groundwater. Currently, no general guidance is available on suitable approaches for dealing with spatial variation in pesticide degradation and sorption in catchment or regional scale modelling applications.

This thesis investigated sorption and degradation of three pesticides (bentazone, isoproturon, and glyphosate) in the cultivated soils of an agricultural catchment in Sweden with the aim to develop and test simple model approaches that could support large-scale modelling.

In the case of sorption, an extended partitioning model improved upon the  $k_{oc}$  concept for all three compounds studied: inorganic sorbents dominated sorption in sub-surface soils and their effects were only masked by organic matter in surface soils with organic carbon contents larger than ca.2%. Interactions between organic and inorganic sorbents affected glyphosate sorption, but apparently not that of bentazone or isoproturon. It was concluded that information on clay,  $f_{clay}$ , iron and aluminum oxides and soil pH, in addition to organic carbon,  $f_{oc}$ , is needed to accurately predict pesticide sorption. The variables  $f_{oc}$ ,  $f_{clay}$  and pH are generally available, whereas measurements of oxides of Al and Fe are rarely reported.

The degradation rate constant ( $k$ ) was highly variable with coefficients of variation ranging between 42 and 64% for the three herbicides. This variability could be attributed to variations in microbial biomass and pesticide bioavailability. A simple modelling approach to predict  $k$  from the sorption constant, which reflects bioavailability, and easily measurable surrogate variables for microbial biomass/activity (organic carbon and clay contents) was successfully tested in a meta-analysis of available literature data using bootstrapped partial least squares regression (PLSR). In conclusion, this approach shows promise as an effective way to account for the effects of bioavailability and microbial activity on microbial pesticide degradation in large-scale model applications.

*Keywords:* spatial variation, bentazone, isoproturon, glyphosate, persistence, half-life, laccase, sorption, bioavailability

*Author's address:* Abdul Ghafoor, SLU, Department of Soil and Environment,  
P.O. Box 7014, 75007 Uppsala, Sweden  
*E-mail:* abdul.ghafoor@slu.se

## Dedication

To my daughters Hibba (late) and Emaan

*~ Autumn is a second spring when every leaf is a flower.*

Albert Camus

# Contents

<b>List of Publications</b>	<b>7</b>
<b>Abbreviations</b>	<b>9</b>
<b>1 Introduction</b>	<b>11</b>
<b>2 Aims and objectives</b>	<b>13</b>
<b>3 Spatial variation in pesticide sorption</b>	<b>15</b>
3.1 Pesticide sorption and soil properties	16
3.1.1 Organic carbon	17
3.1.2 Soil pH	17
3.1.3 Inorganic soil constituents	19
3.1.4 Soil depth	20
<b>4 Spatial variation in pesticide degradation</b>	<b>29</b>
4.1 Soil pH	30
4.2 Soil enzymes	31
4.3 Soil texture	32
4.4 Subsoil properties	32
4.5 Soil organic carbon	33
<b>5 Conclusions, recommendations and future research</b>	<b>45</b>
5.1 Application of the new modelling approaches in practice	45
5.2 Recommendations for future research	46
<b>References</b>	<b>49</b>
<b>Acknowledgements</b>	<b>61</b>



## List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

- I Ghafoor, A., Jarvis, N.J., Thierfelder, T., Stenström, J. (2011)  
Measurements and modelling of pesticide persistence in soil at the catchment scale. *Science of the Total Environment* 409(10), 1900-1908.
- II Ghafoor, A., Moeys, J., Stenström, J., Tranter, G., Jarvis, N.J. (2011)  
Modelling spatial variation in microbial degradation of pesticides in soil. *Environmental Science & Technology* 45(15), 6411-6419.
- III Ghafoor, A., Jarvis, N.J., Stenström, J. (2013) Modelling pesticide sorption in surface and sub-surface soils of an agricultural catchment. *Pest Management Science* (in press DOI 10.1002/ps.3453).

Papers I-III are reproduced with the permission of the publishers.

The contribution of Abdul Ghafoor to the papers included in this thesis was as follows:

- I Planned the study together with Stenström and Jarvis, and was responsible for carrying out all the laboratory work, statistical analysis of data and most of the writing.
- II Planned the study together with Jarvis and Stenström, collecting literature data together with Jarvis, chose all the methods and was responsible for all the calculations in R together with Moeys, the data analyses and the writing, with assistance from co-authors.
- III Planned the study together with Jarvis and Stenström, was responsible for carrying out all the laboratory work, analyses of data and most of the writing, with assistance from co-authors.

## Abbreviations

CV	Coefficient of variation
2,4-D	2,4-dichlorophenoxyacetic acid
DT <sub>50</sub>	Half-life of compound
<i>k</i>	Degradation rate constant
<i>k<sub>clay</sub></i>	Soil clay partitioning coefficient
<i>K<sub>d</sub></i>	Linear distribution coefficient
<i>K<sub>f</sub></i>	Freundlich distribution coefficient
<i>k<sub>oc</sub></i>	Soil organic carbon partitioning coefficient
LiP	Lignin peroxidase
MCPA	(4-Chloro-2-methylphenoxy)acetic acid
MnP	Manganese peroxidase
SOC	Soil organic carbon
SIR	Substrate-induced respiration



# 1 Introduction

Currently one billion people in the world live in chronic hunger (FAOSTAT, 2012b; Foley *et al.*, 2011). Intensive agricultural practices and the use of pesticides may alleviate this situation by increasing crop yields and food security, but may also present particular risks to the soil and water resources which sustain life. In 2010, 261 kilotonnes of herbicides, 231 kilotonnes of fungicides and bactericides, and 140 kilotonnes of insecticides were applied worldwide for agricultural purposes, the largest sector in terms of pesticide use (FAOSTAT, 2012a). Pesticides can leach to groundwater and be transported by runoff during rainfall events to surface waters, such as rivers and lakes. Pesticides may harm aquatic ecosystems and human health, and also have the potential to interfere with normal bodily functions, particularly the endocrine system that regulates physiological functions through hormonal signals (McKinlay *et al.*, 2008).

There is a growing need to identify and understand the mechanisms controlling the fate of pesticides which threaten non-target organisms and are a source of contamination of water resources. When a pesticide molecule is applied to soil, it undergoes various complex and interacting physical, chemical and biological processes. Modelling is therefore a powerful approach to obtain a comprehensive understanding of the environmental fate of pesticides.

Modelling is also a cost-effective way of assessing and predicting pesticide behavior under field conditions for risk assessment purposes. Boesten (2000) reported that in every west European country, more than 100 pesticides are registered. If their transformation products are also included this means that a large number of substances must be evaluated in risk assessment. Additionally, in each country, there is large variation in soil properties, cropping systems, tillage systems and climate and weather conditions. Risk assessment of pesticide leaching to surface water and groundwater would therefore be extremely expensive and time-consuming if based on experiments only. By

using models, these problems may however be overcome (Boesten, 2000). Pesticide leaching models used in EU risk assessment i.e. PEARL (Tiktak *et al.*, 2012), PELMO (Klein, 1991), PRZM (Carsel *et al.*, 1985), PRoMPT (Whelan *et al.*, 2007) and MACRO (Jarvis, 1994), differ in some respects concerning water flow and pesticide transport, but they all use the same approaches for pesticide sorption and degradation, namely a Freundlich sorption isotherm and first-order degradation kinetics.

In any pesticide leaching model, the degradation rate coefficient and Freundlich sorption coefficient and exponent are usually considered the most sensitive parameters (Dubus & Brown, 2002; Bergström & Stenström, 1998). For example, Boesten & Van der Linden (1991) demonstrated that changing the value of either the pesticide sorption coefficient or the half-life by a factor of 2 will typically increase predicted pesticide leaching by a factor of 10. This introduces considerable uncertainty into model predictions of pesticide fate in soils, especially at larger scales (e.g. fields, catchments), since these parameters often show large spatial variability (Walker *et al.*, 2001), the causes of which are quite poorly understood.

Recent EU legislation (The Water Framework Directive 2000/60/EC and the Directive on the Sustainable Use of Pesticides 2009/128/EC) implies the need for modelling tools that can be used for risk assessment and risk reduction at catchment scales. However, the spatial modelling tools which are available for this purpose (e.g. GeoPEARL (Tiktak *et al.*, 2002), and the MACRO-SE tool currently being developed at Swedish University of Agricultural Sciences, SLU) are still in their infancy, and so far only constant values have mostly been assumed for degradation and sorption constants across large areas.

## 2 Aims and objectives

The general objective of this study is to improve the current understanding of the causes of spatial variability in pesticide sorption and degradation in soil as a basis for improving the reliability of predictions of pesticide losses to groundwater and surface water.

The specific objectives of the project were to:

1. study the factors affecting the persistence and sorption of three widely used herbicides (isoproturon, glyphosate, bentazone) in the dominant soils of a small agricultural catchment in southern Sweden (ca. 13 km<sup>2</sup> in size),
2. develop simple models which relate pesticide degradation to easily obtainable soil physical, chemical and biological parameters as support for spatial modelling applications,
3. develop sorption models, which are flexible enough to account for the influence of various soil sorbents and which might be suitable for use in spatial modelling applications.

These objectives are supported by the work presented in three papers. In the following section, I summarize the current state of knowledge about spatial variability in pesticide sorption and degradation followed by the modelling approaches developed in this study to deal with this variability in the context of large-scale modelling applications for prediction of pesticide fate.



### 3 Spatial variation in pesticide sorption

Sorption is the term used to describe adsorption and/or absorption when an independent determination of the nature of the process, that is, whether it is adsorption or absorption, is not possible (Calvet, 1989). The kinetics of sorption is inextricably linked to the forces involved in the sorptive interactions i.e. Van der Waals-London interactions, hydrophobic bonding, and charge transfer. In a complex matrix such as soil, a number of interactions are possible, and these have been discussed in detail by Pignatello & Xing (1996).

Soil sorption is characterized by a distribution coefficient that describes the partitioning of pesticide between solid and liquid phases. A batch or slurry mixing experiment is usually used to measure the distribution coefficient i.e. a mass of soil  $m_s$  (g) is mixed with a volume  $V$  (mL) of 0.01 M  $\text{CaCl}_2$ . A mass  $m_p$  (g) of pesticide is added to the slurry to give an initial concentration  $C_i = m_p/V$  of pesticide in the liquid phase. The slurry is then mixed gently in order to disturb the soil structure as little as possible for a period typically from 2 to 48 h, with 24 h being something of a standard (OECD, 2000). The liquid phase is then analyzed for the 'equilibrium' solution pesticide concentration  $C_e$ . The distribution coefficient  $K_d$  or  $K_f$  is then calculated assuming that all pesticide removed from the solution is sorbed by the soil. The mass of sorbed pesticides, historically symbolized by  $x$ , is calculated as  $x = V(C_i - C_e)$ . Then  $S = \frac{x}{m_s}$  is the concentration of pesticide on the solid phase ( $\text{g g}^{-1}$ ) which can be linearly related to the equilibrium solution concentration:

*Equation 1*

$$S = \frac{x}{m_s} = K_d \times C_e$$

where  $K_d$  is the distribution coefficient ( $\text{mL g}^{-1}$ ). The linear sorption model considers a constant ratio between  $C_e$  ( $\text{g mL}^{-1}$ ) and  $S$  ( $\text{g g}^{-1}$ ). The assumption of a constant ratio between  $S$  and  $C_e$  is not always valid. The Freundlich sorption model considers a non-linear relationship:

*Equation 2*

$$S = \frac{x}{m_s} = K_f \times C_e^{n_f}$$

where  $n_f$  (-) is an exponent that expresses the degree of isotherm non-linearity. Pesticide sorption isotherms in soils are usually well described by the Freundlich model (Coquet, 2003b). Sorption strength in different soils is often estimated using the  $k_{oc}$  value, which is the ratio between  $K_d$  or  $K_f$  and  $f_{oc}$ , the amount of organic carbon (%) in the soil (Wauchope *et al.*, 2002):

*Equation 3*

$$k_{oc} = K_d \text{ or } K_f \cdot \frac{100}{f_{oc}}$$

Pesticide sorption coefficients are highly variable in soils (Coquet, 2003b; Wauchope *et al.*, 2002). For example, Coquet (2003b) found that  $K_f$  values ranged from 0.78 to 2.13 for atrazine, 0.61 to 1.82 for isoproturon and 0.69 and 2.58 for metamiltron across a 187-ha agricultural catchment. Sonon & Schwab (1995) observed CV's of 72% for atrazine and 46% for alachlor. Gaultier *et al.* (2008b) found CV of 89% for the herbicide 2,4-D [2,4-dichlorophenoxyacetic acid]  $K_d$ , at provincial scale in Alberta, Canada.

### 3.1 Pesticide sorption and soil properties

Understanding the causes of the spatial variation of pesticide sorption in soils is important in predicting the potential for leaching at field and catchment scales. The two major factors which are known to influence sorption are soil properties and the inherent characteristics of the compound under consideration. Various soil characteristics, such as organic carbon content, clay content, pH, and Al/Fe oxides and hydroxides have been found to affect sorption of pesticides in soil (Liu *et al.*, 2008; Weber *et al.*, 2004; Bailey & White, 1964). These important factors are described in detail below.

### 3.1.1 Organic carbon

Organic carbon is in general the most important soil property that affects pesticide sorption (Spark & Swift, 2002; Worrall *et al.*, 1996). Many studies have reported a positive correlation of SOC with pesticide sorption (Thorstensen *et al.*, 2001). Coquet (2003b) conducted a study at the scale of a 187 ha agricultural catchment to investigate the spatial variation of pesticide sorption isotherms. More than 97% of the variation of the adsorption distribution coefficient  $K_d$  was explained by the organic carbon content of the soil. Vinther *et al.* (2008) found positive correlations between sorption of glyphosate, metribuzin and triazinamin and organic carbon content. Similarly, Fredslund *et al.* (2008) reported that sorption of MCPA also correlated strongly with soil organic carbon content in  $A_p$  and  $B_s$  horizons. Mermoud *et al.* (2008) found that organic carbon content was the key parameter positively correlated with sorption of dinoseb and atrazine.

Although SOC is very important, a considerable variation in  $k_{oc}$  values is found in the field (Gaultier *et al.*, 2008b; Coquet, 2003b). The quality or nature of the organic matter may also play a key role in the sorption of pesticides (Spark & Swift, 2002; Ahmad *et al.*, 2001). Ahmad *et al.* (2001) investigated sorption of carbaryl and phosalone on 27 soils using NMR (Nuclear Magnetic Resonance) spectroscopy and found highly significant positive correlations of aromaticity of soil organic matter with  $k_{oc}$  values of carbaryl and phosalone. Grathwohl (1990) suggested that an empirical relationship exists between  $k_{oc}$  and the elemental composition expressed as the atomic H/O ratio in natural organic matter. Xu *et al.* (2005) found that the amount of butachlor adsorbed on humic acids (HAs) been positively correlated with its content of carbonyls.

### 3.1.2 Soil pH

The pH-dependence of sorption has mainly been reported for ionizable pesticides, including bentazone (Grey *et al.*, 1997; Abernath & Wax, 1973) chlorimuron (Goetz *et al.*, 1989), chlorsulfuron, metsulfuron-methyl (Walker *et al.*, 1989), picloram (Nearpass, 1976) and 2,4-D (Spadotto & Hornsby, 2003). This is explained by the different ionization states of pesticides at varying pH values in soil that occur for compounds that are either acids or bases. For example, for weak acids, the lower the soil pH, the greater the adsorption. This is because at low pH, less-soluble non-ionized species dominate, which more readily bind to the lipophilic fraction of soil organic matter than the more

soluble anionic species, which are repelled by negatively charged soil colloids (Carrizosa *et al.*, 2000). The increase in sorption of basic pesticides at low pH is attributed to an increased proportion of the protonated species. In their review, Wauchope *et al.* (2002) summarized the existence of dominant species of acidic or basic pesticides in the normal range of soil pH (5-8). In contrast, the behavior of some ionic pesticides (e.g., diquat, paraquat) is unlikely to be sensitive to soil pH, since they have  $pK_a$  values well outside the range that is relevant to the soil environment. Readers are also referred to the comprehensive review by Kah & Brown (2006) for more details about the behavior of pesticides (acidic, basic and Zwitterionic compounds) in soil.

Glyphosate sorption depends on soil pH as it determines both glyphosate ionization and the surface charge of soil constituents (de Jonge & de Jonge, 1999; McConnell & Hossner, 1985). Glyphosate sorption decreases at increasing pH because of increased negative charge (or lowering of positive sorbate and sorbent at higher pH). For example, Gimsing *et al.* (2004) found that glyphosate sorption in a Danish topsoil gradually decreased when pH was raised from 6 to 8. Furthermore, for five soils, sorption was negatively correlated with pH and was the most important single factor for glyphosate sorption. Decreased soil sorption of glyphosate at increasing pH has also been shown in other studies (Wang *et al.*, 2005; de Jonge & de Jonge, 1999).

Negative relationships between soil pH and sorption have also been observed for some non-ionizable pesticides like isoproturon (Ertli *et al.*, 2004). It is suggested that in alkaline conditions the dissociation of the N-H bond of the isoproturon molecule leads to the development of a negative charge (Lopez *et al.*, 1996) which is repelled by the negatively charged soil surface. The formation of hydrogen bonds between the O, N and H atoms of the isoproturon molecule and surface groups, which is typical at lower pH values, might explain increased sorption of isoproturon in acidic conditions.

The pH effects on sorption behavior of pesticides have been observed mostly by modifying the pH artificially in the laboratory. However, with such experimental treatments, changes in soil characteristics other than pH can occur during pH adjustment which might make the interpretation of the results more difficult (Kah & Brown, 2006). The effects of pH on sorption have been less often studied in the field. In their study, Oliveira *et al.* (1999) observed two distinct patterns in the spatial distribution of imazethapyr sorption: i) areas in which  $pH > 6.25$  and  $K_d < 1.5$ , where  $K_d$  variation was due primarily to pH, and ii) areas in which  $pH < 6.25$  and  $K_d > 1.5$ , where other soil properties, i.e., SOC content, had a significant influence on  $K_d$  variation. This separation allowed identification of portions of the field where herbicide sorption would

be minimal, with a relatively higher potential for leaching (areas with  $K_d < 1.5$ ), and vice versa. Thus, soil pH could be used as a basis to provide a rationale for site-specific pesticide applications.

### 3.1.3 Inorganic soil constituents

Although for most pesticides soil organic matter is the dominant sorptive constituent in soil (e.g., Xing *et al.*, 1996; Weber *et al.*, 1992) clay minerals and oxides and hydroxides of iron and aluminium have also been proved to play a very important role in pesticide sorption (Li *et al.*, 2003; Sheng *et al.*, 2001). Pesticide sorption by inorganic constituents depends on their surface area, mineral groups and their surface reactivity (Sheng *et al.*, 2001). For example, Borggaard & Gimsing (2008) found glyphosate sorption of 1.45–1.85  $\mu\text{mol m}^{-2}$  for aluminum and iron oxides and 0.12–0.33  $\mu\text{mol m}^{-2}$  for silicate clays. They attributed this difference between the two mineral groups to the greater availability of sorption sites on the various surfaces of aluminum and iron oxide minerals compared to silicate clays which only possess sorption sites (OH groups) on octahedral layers exposed on mineral edges and not on the much larger surface area of planar faces. The types of saturating cations on the mineral or organic matter may also have a strong effect on pesticide adsorption in soil. For example, Sprankle *et al.* (1975) found that  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ -saturated clays and organic matter adsorbed more glyphosate than  $\text{Na}^{1+}$  or  $\text{Ca}^{2+}$ -saturated clays and organic matter. These studies were conducted using pure clay minerals, such as montmorillonite, kaolinite, smectites, and illite (Li *et al.*, 2003; Sheng *et al.*, 2001; Barriuso *et al.*, 1994), but there might be many differences between the properties of pure minerals and minerals present in natural soils. However, sorption studies conducted in natural soils have also shown strong correlations between clay content and pesticide sorption. Harper (1988) found that clay content was the single best predictor of metribuzin adsorption. Villaverde *et al.* (2008) observed a strong linear relationship between clay content and  $K_d$  values of dicamba, metsulfuron-methyl, 2,4-D, and flupyrsulfuron-methyl-sodium. Similarly, Worrall *et al.* (1996) concluded that clay mineral surfaces appeared to control adsorption of isoproturon at least for values of soil organic carbon content less than 27  $\text{g kg}^{-1}$ .

Undisturbed soils are not simply mixtures of discrete organic and mineral phases, but they are organized into aggregates of organo-mineral complexes. Thus, the mechanisms of pesticide sorption by soil colloids could vary as a function of aggregate size due to differences in amount as well as the chemical composition of the organic matter in the aggregates (Schnitzer & Kodama, 1992; Oades, 1988). Spadotto & Hornsby (2003) and Liu *et al.* (2008)

suggested that the effects of clay minerals on pesticide sorption, which are often masked by organic matter, could become significant when the  $f_{clay}/f_{oc}$  ratio is greater than a certain critical value (e.g.  $f_{clay}/f_{oc} > 40-60$ ).

#### 3.1.4 Soil depth

Many studies reported that as soil depth increased, the strength of sorption of pesticides decreased. For example, Blume *et al.* (2004) observed a decline in sorption coefficients of atrazine ( $K_f$ ) from 8.17 in the surface to 3.31 in the vadose zone at 175-220 cm depth. Walker *et al.* (1999) found Freundlich sorption coefficients for isoproturon of 3.25 in the topsoil and 1.06 in the subsoil (25-50 cm), which was attributed to a decrease in soil organic carbon with depth. Nevertheless, inorganic soil constituents may have a strong influence on the sorption of many pesticides in subsoil, where organic matter contents are often low. For example, Coquet (2003a) found that clay content explained 91.1, 83.1, and 97.8% of the variation in atrazine, isoproturon and metamitron sorption in vadose zone profiles 12, 5 and 3 m deep respectively. Worrall *et al.* (1996) and Felding (1997) noted that soils with very low organic matter content tend to give high values for apparent  $k_{oc}$  because the mineral phases of the soil make a significant contribution to the total adsorption (e.g. atrazine  $k_{oc}$  from 88 L kg<sup>-1</sup> in the topsoil to more than 520 L kg<sup>-1</sup> at 1 m depth (Felding, 1997). Charnay *et al.* (2005) found that atrazine  $K_d$  for 16 subsoil samples was positively correlated to clay and silt contents, but no correlation was found with  $f_{oc}$ . In contrast,  $K_d$  values were strongly correlated to  $f_{oc}$  ( $r > 0.98$ ) in surface soil samples. Si *et al.* (2009) noted that subsoil at 300–425 cm depth showed the greatest adsorption of metachlor, as it had the highest clay (mainly smectitic) content and oxalate extractable content of aluminum and iron oxides (Si *et al.*, 2009; Pusino *et al.*, 1992). Similarly, Jacobsen *et al.* (2008) found for Danish soils that glyphosate sorption was often higher in subsoil samples compared to A<sub>p</sub>-horizon samples, while Farenhorst *et al.* (2009) found that variation in sorption of glyphosate in soil profiles was predominantly controlled by variations in soil pH and clay content. Moeys *et al.* (2011) concluded that the contribution of clay minerals to isoproturon sorption can be dominant when  $f_{oc} < 6.15$  g kg<sup>-1</sup>, a value which is commonly found in subsoils. Vinther *et al.* (2008) found a strong correlation between the sorption coefficients of glyphosate and triazinamin and content of clay in the B<sub>s</sub> horizon.

A larger variation of sorption parameters in subsoils compared to surface soils has been observed. For example, Vinther *et al.* (2008) observed that the sorption coefficients ( $K_d$ ) for glyphosate, metribuzin, and triazinamin were

more variable in the B<sub>s</sub> horizon of a 4-ha agricultural field than in the A<sub>p</sub> horizon. Similarly in another study by the same research group, Fredslund *et al.* (2008) reported 3.6 times higher CV's of MCPA (2-methyl-4-chlorophenoxyacetic acid)  $K_d$  values in B<sub>s</sub> horizons compared to that in A<sub>p</sub> horizons. Coquet *et al.*, (2004) found very high CV's (197%) of  $k_{oc}$  values in the vadose zone. However, by defining  $k_{clay}$  as the  $K_d$  value normalized by the clay content, the variation in adsorption coefficient was reduced to a CV of 62%, which was half that calculated for  $K_d$ .

### ***Modelling sorption behavior of pesticides at the catchment scale***

Measurements and modelling of the sorption behavior of three selected pesticides in the soils of a small agricultural catchment in Sweden are presented in Paper III.

This study was carried out in the E21 monitoring catchment in Östergötland, southern Sweden. The total catchment area of 13 km<sup>2</sup> consists of 95% agricultural land, with main crops of winter and spring sown cereals, oilseed rape, potatoes and peas. Soil samples were collected from 60 locations in the catchment (1 location every 20 ha) on a grid pattern at 0-20 cm, 20-45 cm and 45-70 cm depth. The physical and chemical characteristics of 16 surface soils and 10 subsoils selected to cover the range of measured soil properties in the catchment are given in Tables 1 and 2 in Paper III. There was a relatively wide range of  $f_{oc}$  contents in the topsoil, ranging from 0.9 to 10.2 %. Subsoil organic carbon contents were smaller, ranging from 0.7 to 1.6 % at 20 to 45 cm depth and 0.2 to 0.8 % at 45 to 70 cm depth. Soil pH ranged from 6.0 to 7.6 in surface soils and 5.6 to 8.0 in subsoil. The soil texture was very variable, with 8 of the 12 USDA texture classes represented. Ammonium-lactate extractable phosphorus ranged from 26 to 152 mg kg<sup>-1</sup>. The content of aluminum and iron oxides (Al<sub>ox</sub> and Fe<sub>ox</sub>) ranged from 0.15 to 0.88 %, with a tendency for larger values in the topsoil.

Sorption of three test compounds (glyphosate, bentazone and isoproturon) was measured according to the OECD 106 guideline (OECD, 2000) on two replicates.

Freundlich parameters ( $K_f$  and  $n$ ) for bentazone, isoproturon, and glyphosate are presented in Tables 4 and 5 in Paper III for surface and sub-surface soils, respectively. Figure 1A shows that bentazone  $K_f$  values generally decreased with soil depth. Isoproturon  $K_f$  values were smaller in all soils at 20-45 cm than in surface samples (0-20 cm) but in soils 11 and 15  $K_f$  values increased at 45-70 cm depth (Figure 1B). These two soils also had larger clay

contents compared to other soils. The change in glyphosate  $K_f$  values with depth is shown in Figure 1C. The  $K_f$  values increased with depth, except for soil 5 where it increased first at 20-45 cm and then decreased again at 45-70 cm. The increase in  $K_f$  values at 20-45 and 45-70 cm depths was again more prominent in soils 11 and 15. Overall, the Freundlich sorption coefficients  $K_f$  showed considerable differences between soils, with coefficients of variation (CV) ranging from 22 to 84 % for the three compounds. The  $K_f$  values increased among the pesticides in the order bentazone < isoproturon < glyphosate and were within the range of previously reported values (Larsbo *et al.*, 2009; Boivin *et al.*, 2005b; Mamy & Barriuso, 2005; Coquet, 2003b; Thorstensen *et al.*, 2001; de Jonge & de Jonge, 1999; Walker *et al.*, 1999; Glass, 1987). In addition, the coefficient of variation of  $K_f$  values was higher in sub-surface soils than surface soils (CV's of 84, 66 and 22% for isoproturon, glyphosate and bentazone respectively in the subsurface). A high variability of apparent  $k_{oc}$  values was also observed, which may be attributed to the contribution of inorganic components (Al and Fe oxides, clay minerals) to adsorption. This is illustrated by the strong curvilinear dependence of glyphosate and bentazone  $k_{oc}$  values on soil pH and  $f_{oc}$  in surface soils (Figure 2). The contribution from these inorganic soil components was even more pronounced in sub-surface soils where  $f_{oc}$  was small enough so that it could not mask the effects of clay and Al<sub>ox</sub> and Fe<sub>ox</sub> (Paper III).

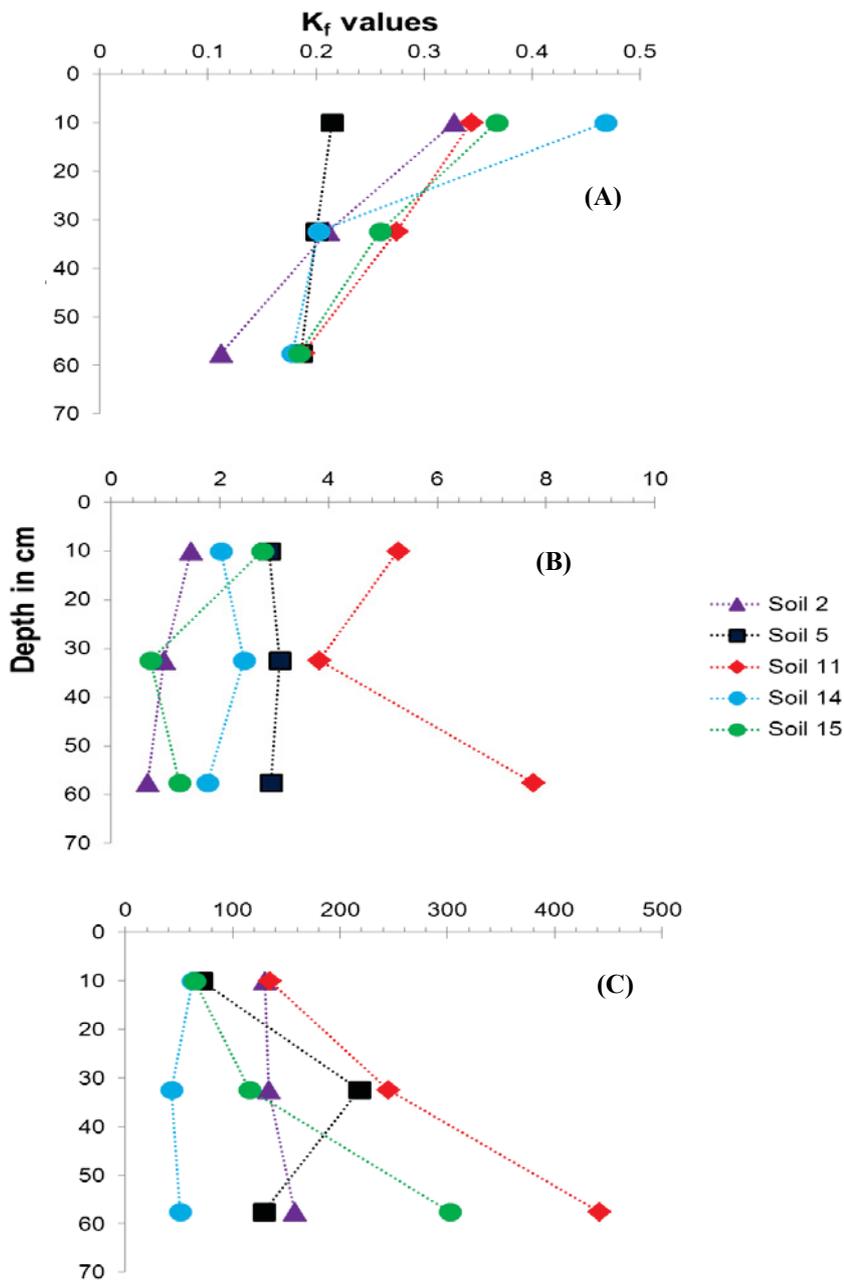


Figure 1. The dynamics of Freundlich sorption coefficients  $K_f$  values for bentazone (A), isoproturon (B), and glyphosate (C) in relation to soil depth.

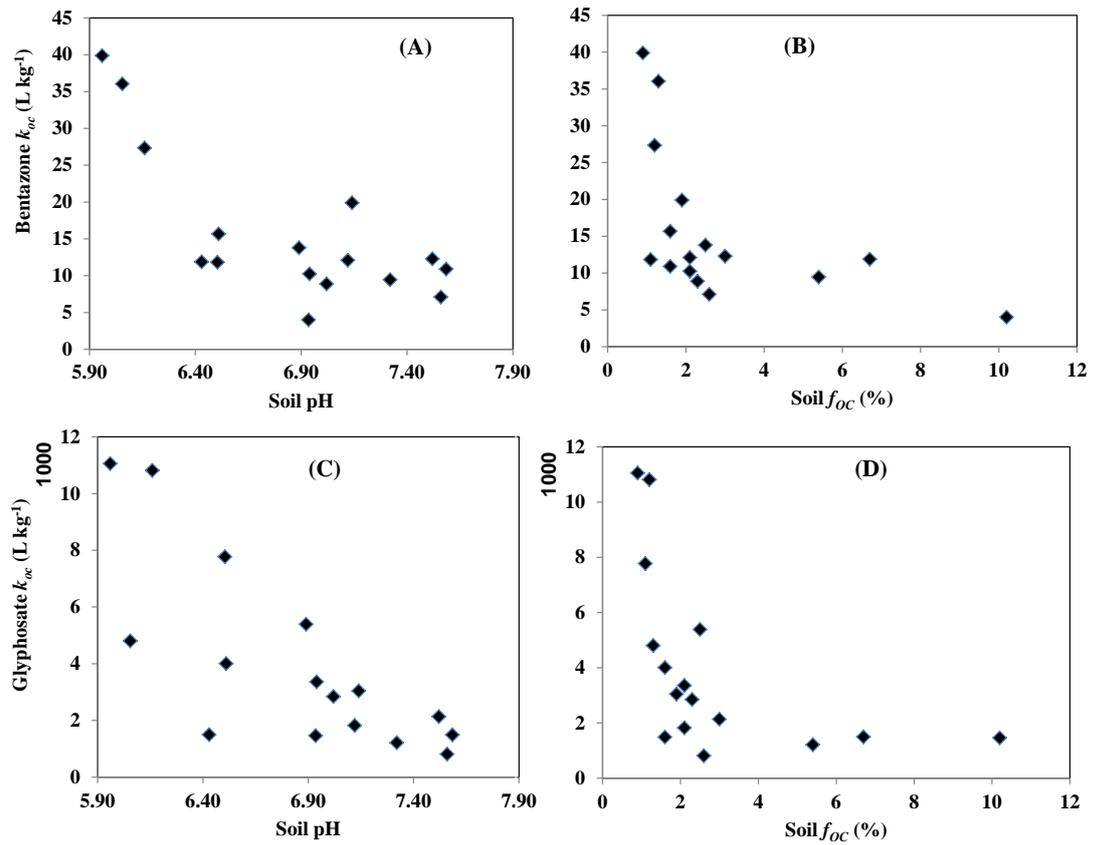


Figure 2. Relationship between  $k_{oc}$  and soil pH and  $f_{oc}$  for bentazone (A and B), and glyphosate (C and D) sorption measured in surface soils.

$k_{oc}$  has now become a widely used parameter for comparing pesticide binding in soil (Wauchope *et al.*, 2002) and for modelling purposes (i.e. in risk assessment). However, the results (Paper III) suggest that  $k_{oc}$  would be a poor predictor of sorption strength in spatial modelling applications for many compounds, even in topsoils, as  $f_{oc}$  does not need to be very low for inorganic soil constituents to become significant: as illustrated in Figure 2D, a  $f_{oc}$  content of less than 3% causes an increase in apparent  $k_{oc}$ . It can be noted that ca. 70% of arable topsoils in Sweden have  $f_{oc}$  values <3% (Eriksson *et al.*, 2010). As some previous studies (Liu *et al.*, 2008; Coquet, 2003a) have also shown, apparent  $k_{oc}$  values also increased dramatically in sub-surface soils of very low organic carbon content.

There is, therefore, a need to develop alternative sorption models based on compound and site-specific soil properties which could reliably predict pesticide sorption. Mechanistic speciation and complexation models can be used to calculate sorption to various soil phases, but such approaches are complex and require too many parameters for large-scale modelling applications, given the scarce data that is generally available from soil surveys. A simple empirical extended partitioning model for the sorption of pesticides was therefore proposed, which should be more suitable for spatial modelling applications:

Equation 4

$$K_f = \left( \frac{pH_{ref}}{pH} \right)^n \cdot \left( \sum_{i=1}^m f_i \cdot k_i \right)$$

where  $pH$  is the soil pH,  $pH_{ref}$  is a reference pH of the soil, set here equal to 7,  $f_i$  ( $\text{kg kg}^{-1}$ ) is the mass fraction of the sorbent  $i$  in soil,  $m$  is the number of sorbents considered,  $k_i$  ( $\text{L kg}^{-1}$ ) is the partitioning coefficient of the pesticide on the sorbent  $i$  and  $n$  is a parameter which accounts for the overall effects of pH on the sorption of ionic pesticides, including the influence of pH on the extent of dissociation of the molecule itself and also the nature of the surface charges on various soil constituents (Kah & Brown, 2006). For non-ionic pesticides,  $n$  can be set to zero.

Recent studies suggest that a simple additive model like equation (4) may not adequately describe the effects of different soil constituents on sorption due to interactions between them, especially the fact that organic matter may coat and therefore mask the effects of inorganic sorbents such as clay minerals and metal oxides (Moeys *et al.*, 2011; Liu *et al.*, 2008; Spadotto & Hornsby, 2003). Equation (4) was extended to account for such interactions:

Equation 5

$$K_f = \left( \frac{pH_{ref}}{pH} \right)^n \cdot \left\{ k_{oc} f_{oc} + \left( \frac{f_{oc(ref)}}{f_{oc}} \right) \cdot \sum_{i=1}^m f_i \cdot k_i \right\}$$

where  $m$  now refers to sorbents that are partially masked by organic carbon and  $f_{oc(ref)}$  ( $\text{kg kg}^{-1}$ ) is a reference organic carbon content, set here equal to  $0.01 \text{ kg kg}^{-1}$ .

The *nls* function in R (Fox, 2002) was employed to estimate model parameters by non-linear regression, unless *n* was ‘a priori’ set to zero in equation (4), when the *lm* function for multiple linear regression in R was used instead. I applied equations (4) and (5) in a ‘best subset’ regression analysis, testing all combinations of the three potential sorbents ( $f_{oc}$ ,  $f_{clay}$ ,  $f_{(Al_{ox}+Fe_{ox})}$ ), with and without the inclusion of pH effects. The significance of parameter estimates was checked at the 5% probability level. Two performance statistics were employed to compare models for which all parameters were significant, the root mean square error (RMSE) and the bias-corrected Akaike’s Information Criterion (AIC<sub>c</sub>) (Hurvich & Tsai, 1989; Akaike, 1974) for small sample sizes. Further details of model testing and development are reported in Paper III. Table 7 in Paper III presents the best single, two and three parameter models based on RMSE values, for which all parameters were significant at  $p=0.05$ .

Figure 3A shows a comparison of measured  $K_f$  values of isoproturon with those predicted using model 2 (Table 7, Paper III), which accounts for organic carbon and clay contents. For this model, the estimated  $k_{oc}$  value of isoproturon is almost 10 times larger than  $k_{clay}$  (Table 7, Paper III). Nevertheless, the influence of the soil clay fraction on the sorption of isoproturon cannot be neglected even in the topsoil, since the ratio of clay to organic carbon content varies from 2.8 to 18, with a median value of 7.6 (see Table 1, Paper III). The  $f_{clay}/f_{oc}$  ratio is even larger in subsoil, varying from 4.6 to 91.3, with a median value of 21.9 (Table 2, Paper III). Interestingly, even though isoproturon is a non-ionic herbicide, a three-parameter model which also includes pH effects (model 3) seemed even better compared to 1 and 2-parameter models, with smaller values of both RMSE and AIC<sub>c</sub>. Boivin *et al.* (2005b) and Moeys *et al.* (2011) also found that isoproturon sorption increased with decreasing pH for their datasets at small catchment and regional/continental scales respectively. For bentazone, Figure 3B shows a comparison of measured  $K_f$  with predictions using model 6 (Table 7 in paper III), which includes the effects of organic carbon, oxides of Al and Fe and pH. In my study the interaction term  $\left\{ \left( \frac{f_{oc(ref)}}{f_{oc}} \right) \cdot \sum_{i=1}^m f_i \cdot k_i \right\}$  was only needed to predict glyphosate sorption, whereas for isoproturon and bentazone, models based on equation (5) failed to improve on the simpler model given by equation (4). For glyphosate, several significant models based on various combinations of the three potential sorbents (viz.  $k_{oc}$ ,  $k_{clay}$  and  $k_{ox}$ ) were identified, which had rather similar performances. This seems reasonable as glyphosate is known to adsorb to organic matter, clay minerals and metal oxides (Borggaard & Gimsing, 2008).

Table 7 only shows the best-fitting one, two and three parameter models. Model 9, which includes  $f_{clay}$  and  $f_{oc}$  as well as pH, gave the best predictions with the smallest value of  $AIC_c$ . Figure 3C shows a comparison of measured  $K_f$  with predictions using model 9 (Table 7 in Paper III).

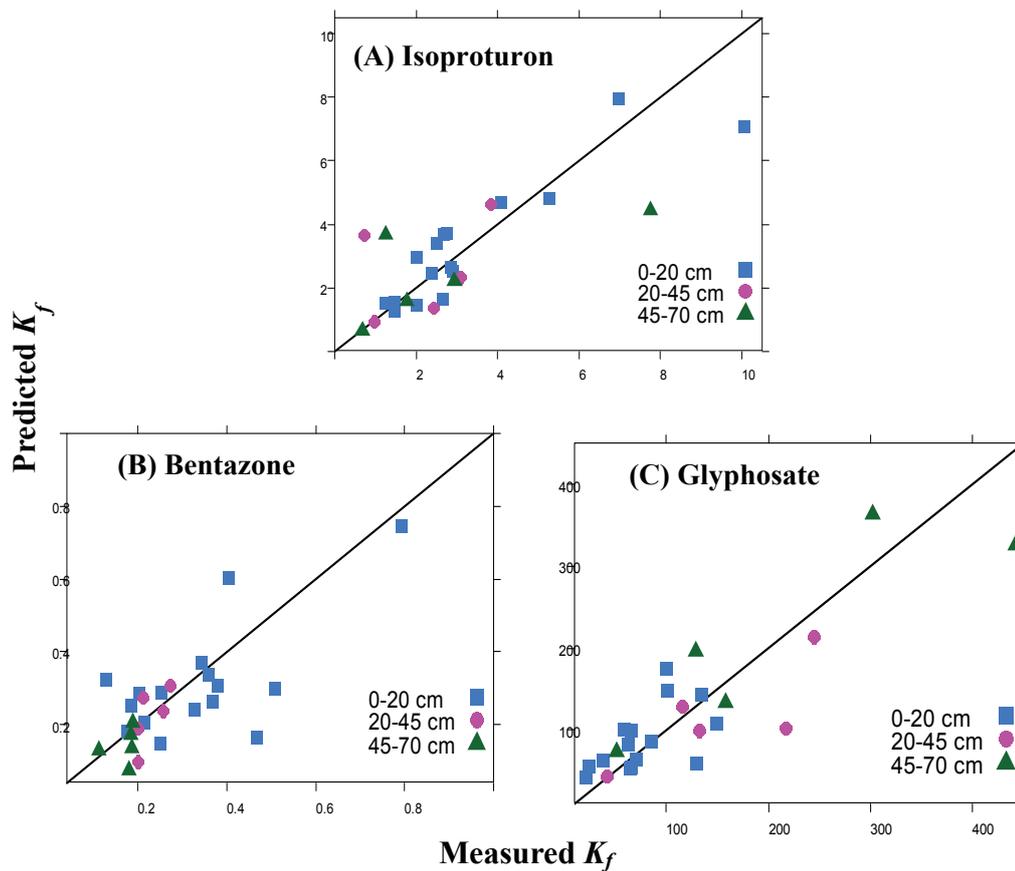


Figure 3. Relationship between measured and predicted  $K_f$  of (A) isoproturon with model 2 (Table 7 in Paper III), (B) bentazone with model 6 (Table 7 in Paper III) and (C) glyphosate with model 9 (Table 7 in Paper III).



## 4 Spatial variation in pesticide degradation

Pesticide parent compounds degrade into daughter compounds or metabolites which may or may not be toxic and, in some cases, mineralize to the original elements from which they were derived. Degradation of most pesticides in the soil is dominated by microorganisms. Standard laboratory and field studies can be performed to derive degradation half-lives (or  $DT_{50}$  values, the time required for 50% of the initial amount to be degraded; (FOCUS, 2006). Under field conditions, degradation cannot always be separated from other processes, such as chemical hydrolysis and photo-degradation (Aislable & Lloyd-Jones, 1995), leading to pesticide dissipation. In this case, the  $DT_{50}$  value reflects the time for the overall dissipation of 50% of the initial concentration (Beulke & Brown, 2001). The half-life of a compound ( $DT_{50}$ ) is calculated from the following equation:

*Equation 6*

$$DT_{50} = \frac{\ln(2)}{k}$$

where  $k$  (degradation rate constant, expressed in  $\text{day}^{-1}$ ) is derived from the equation of first-order kinetics:

*Equation 7*

$$C_t = C_0 \cdot e^{-k \cdot t}$$

where  $C_t$  is the concentration at time  $t$  ( $\text{mg kg}^{-1}$  soil) and  $C_0$  is the concentration at time zero ( $\text{mg kg}^{-1}$  soil).

Soil is a heterogeneous complex system and degradation of pesticides in soils is influenced by many spatially variable factors including the availability of SOC, nutrients, pH, salinity, soil temperature, oxygen content, soil moisture content, bioavailability (i.e. adsorption strength) and chemical structure and concentration of pesticides (Alexander, 1999; Aislabie & Lloyd-Jones, 1995). This often leads to a highly heterogeneous spatial pattern of degradation and large variations in measured DT<sub>50</sub> values (Rodriguez-Cruz *et al.*, 2008; Bending *et al.*, 2006). For example, glyphosate DT<sub>50</sub> values in a variety of different soil types have been reported in the range of 1.7 to 197 days (Sorensen *et al.*, 2006; Giesy *et al.*, 2000). The influence of different soil variables on spatial variation in pesticide degradation is discussed in detail in the following sections.

#### 4.1 Soil pH

The degradation rate of several pesticides in soils has been shown to be correlated with soil pH. For example, Houot *et al.* (2000) found that soils with a pH over 6.5 typically showed faster degradation of atrazine than those with pH lower than 6.5. Rodriguez-Cruz *et al.* (2006) demonstrated a correlation between bentazone DT<sub>50</sub> and soil pH ( $r=0.731$ ,  $P<0.001$ ). Bending *et al.* (2003) observed that pH was a key factor controlling the degradation of isoproturon within a field, with a pH above 7 generally showing rapid growth-linked degradation. Similarly, Walker *et al.* (2001) observed that soils showing rapid biodegradation of isoproturon had higher pH and more microbial biomass. In another study, Bending *et al.* (2006) showed that degradation rates of azoxystrobin were controlled by soil pH. As noted in section 3.1.2 above, soil pH is also known to affect the extent to which some pesticides adsorb to soil, and therefore to determine the bioavailability of such pesticides to the degrading microbial community. For example, Bending *et al.* (2006) observed a strong correlation between azoxystrobin sorption and DT<sub>25</sub>, with degradation rate decreasing as sorption increased. They concluded that pH induced differences in pesticide bioavailability could have had a role in controlling the degradation rate of azoxystrobin. In contrast, some studies have shown that increases in soil pH can reduce degradation rates (Hultgren *et al.*, 2002; Walker & Thompson, 1977). In such cases, chemical hydrolysis, which is generally favored under acidic conditions, might be the dominant process (Sarmah & Sabadie, 2002).

## 4.2 Soil enzymes

The presence of lignolytic enzymes (manganese peroxidase, laccase, and lignin peroxidase) in soils is of great interest because of their roles in the decomposition of organic matter, in the humification process and in the transformation of xenobiotic compounds such as pesticides (Pizzul *et al.*, 2009; Bollag, 1992). Lignolytic enzymes are non-specific, so they can simultaneously attack a wide range of other organic compounds, and this characteristic has been exploited for bioremediation purposes (Peng *et al.*, 2008; Steffen *et al.*, 2003; Barr & Aust, 1994). Pizzul *et al.* (2009) studied the ability of manganese peroxidase (MnP), laccase, lignin peroxidase (LiP) and horseradish peroxidase (HRP) to degrade the widely used herbicide glyphosate and 22 other pesticides in separate *in vitro* assays. All the compounds were transformed, with degradation percentages ranging between 20 and 100%. Complete degradation of glyphosate was obtained with MnP and laccase. Kim *et al.* (1997) showed that bentazone and its derivatives were degraded by laccase or peroxidase enzymes. Castillo *et al.* (2000) observed the degradation of bentazone by MnP. Most of these degradation studies have been done using purified enzymes but very little is known about the degradation of pesticides by these indigenous enzymes in soils.

It has also been reported that the production of these enzymes by different fungal strains of white rot fungus is highly variable (Criquet *et al.*, 2000; Boyle *et al.*, 1998; Bogan & Lamar, 1995). For example, coefficients of variation for phenol oxidase (e.g. laccase) and peroxidase (e.g. MnP) activities ranged from 30% to >300% (Keeler *et al.*, 2009; Finzi *et al.*, 2006). This variability is due to differences in growth and enzyme production responses of the fungi to different soil and environmental factors (Keeler *et al.*, 2009). For example, Jackson *et al.* (2009) found that peroxidase activity increased with soil organic matter in peat soils. A positive relationship between laccase activities and soil pH is often found (Sinsabaugh *et al.*, 2008). As pH increases, laccases deprotonate which reduces their redox potential and increases their solubility, both of which may enhance their reaction potential. Another factor is that soil enzymes are mostly immobilized on colloids and sorption of enzymes to clays and organic particles generally displaces their apparent pH optimum 1-2 units towards alkaline conditions, because soil surface pH is lower than that of the soil solution (Sinsabaugh, 2010). Because laccases are widely produced by soil fungi for varied purposes, it is arguable that the diversity of the soil enzyme pool and potentially its range of action may also expand with soil pH (Sinsabaugh *et al.*, 2008).

### 4.3 Soil texture

Soil texture can influence a range of soil environmental factors including redox potential and moisture content, which may also influence degradation rates (Rodriguez-Cruz *et al.*, 2006; Jurado-Exposito & Walker, 1998; Vink & van der Zee, 1997; Allen & Walker, 1987; Walker *et al.*, 1985). Charnay *et al.* (2005) found that metribuzin mineralization rates were positively correlated to clay, whereas isoproturon mineralization rate was positively correlated to sand. Villaverde *et al.* (2008) observed a clear positive correlation between clay content and the degradation rate constant for 2,4-D, dicamba, and flupyr-sulfuronmethyl ( $P < 0.01$ ). Forouzangohar *et al.* (2005) found that atrazine and metamitron degradation rates were higher in silty clay than in sandy loam soil. Dakhel *et al.* (2001) found that mineralization of amitrol was lower in soils with a coarse texture than in soils with a fine texture. In contrast, Allen & Walker (1987) and Walker *et al.* (1985) observed a negative correlation between the rate of degradation of metamitron, simazine, and napropamide and clay content of the soil. In these studies it was suggested that this might result from increased adsorption and hence reduced availability for degradation in heavier soils. Texture also controls the pore size distribution in soils and therefore influences their water relations and aeration characteristics. Faster degradation rates in lighter soils may be in part due to better gas exchange and hence improved conditions for aerobic micro-organisms (Walker *et al.*, 1985).

### 4.4 Subsoil properties

The subsoil exhibits a very different physical, chemical and biological environment than that of the topsoil. For example, Blume *et al.* (2004) found that the estimated half-lives of atrazine ranged from 77 to 101 days in the surface soil, but increased to over 900 days in subsurface soils. They attributed this to decreased contents of nutrients (total organic carbon, N, and P) and microbial biomass with depth. Rodriguez-Cruz *et al.* (2006) showed that degradation rates of isoproturon, bentazone and mecoprop declined with depth in soil. Charnay *et al.* (2005) found that atrazine degradation and overall microbial activity decreased with depth, given that atrazine degradation activity was found even at a depth of 2.5 m. Di *et al.* (1998) showed that eight pesticides had widely different degradation rates in surface and subsurface soils. Four of the pesticides had lower degradation rates in the subsoil than in the surface soil, but the reverse was observed for the other four pesticides. They postulated that the different patterns of degradation rates with soil depth were probably caused by interactive effects of changes in soil microbial

activities and in organic matter content and thus pesticide sorption and bioavailability.

Degradation of pesticides in subsoil may also be highly variable (Rodriguez-Cruz *et al.*, 2006; Vanderheyden *et al.*, 1997). Vinther *et al.* (2008) reported that the spatial variability in the mineralization of glyphosate was about five times higher in the B<sub>s</sub> horizon than in the A<sub>p</sub> horizon. A greater variability in the pesticide degradation rates found in subsoil relative to topsoil could be because the spatial distribution of microorganisms in subsoil is more variable than in topsoil (Rodriguez-Cruz *et al.*, 2006). It is thought that the texture of the subsoil critically determines degradation rates, with those locations possessing high clay and silt contents showing lower degradation rates relative to sites with a higher proportion of sand (Rodriguez-Cruz *et al.*, 2006). This can be attributed to increased sorption and hence reduced availability of pesticides in heavy-textured subsoils (Walker *et al.*, 1985).

Variability in microbial composition and community with depth in soil has been confirmed by using denaturing gradient gel electrophoresis (DGGE) analysis of 16S rDNA or 16S rRNA fragments (Bending *et al.*, 2003; Muyzer *et al.*, 1993). For example, in an investigation of the dissipation of metolachlor with soil depth, Si *et al.* (2009) found that microbial DNA was characterized by higher diversity in surface soil than deeper in the soil. In the subsoil, the microbial diversity remained rather constant down to the bottom of the 500 cm deep soil profile.

#### 4.5 Soil organic carbon

Soil organic carbon is a particularly important variable because it is usually a dominant factor controlling microbial activity as well as sorption of pesticides and therefore the bioavailability of a pesticide for degraders (Thorstensen & Lode, 2001). Correlation of degradation rate with soil organic matter has been found for many pesticides. For example, von Gotz & Richter (1999) observed that soil biomass and organic carbon had the strongest positive influence on bentazone degradation in soil. Thorstensen & Lode (2001) observed faster degradation of bentazone in soils rich in organic matter. They attributed this enhanced degradation in organic soils to increased fungal activity. Cederlund *et al.* (2007) found that the half-life of diuron was correlated strongly and negatively with microbial biomass estimated by substrate-induced respiration (SIR) ( $r=-0.85$ ;  $p<0.05$ ) and with the amount of organic matter measured as loss on ignition ( $r=-0.87$ ;  $p<0.05$ ). Blume *et al.* (2004) observed that atrazine mineralization rates were strongly positively correlated to microbial biomass and activity and SOC. Villaverde *et al.* (2008) observed a clear positive

correlation between SOC and degradation rate constants for 2,4-D, dicamba, and flupyr-sulfuronmethyl ( $P < 0.01$ ). Mueller *et al.* (1992) showed a positive linear correlation between a pseudo-1<sup>st</sup> order degradation rate constant for fluometuron and soil organic matter content as well as soil microbial biomass. Torstensson & Stenström (1986) showed significant positive correlations between basic respiration rates and degradation rates of linuron and glyphosate. Rodriguez-Cruz *et al.* (2008, 2006) observed that the  $DT_{50}$  of three pesticides (bentazone, isoproturon, and mecoprop-p) was negatively correlated with organic matter. In apparent contrast, Charnay *et al.* (2005) found a positive correlation between metamilon half-life and SOC. In a regional-scale study using 114 agricultural topsoils, Gaultier *et al.* (2008a) observed that the mean 2,4-D half-life in soils with more than 1% soil organic carbon (SOC) was 1.4 times greater than the mean 2,4-D half-life in soils with less than 1% SOC. They attributed this to the effects of SOC on 2,4-D sorption and thus reduced bioavailability.

### ***Spatial variation of pesticide degradation at the catchment scale***

The literature review presented above reveals that the influence of soil properties on pesticide degradation is rather complicated and often even apparently contradictory. The competitive effects of SOC on degradation seem especially difficult to unravel. An increase in soil organic matter might increase biological activity in soil by providing conditions favorable to microbial growth (Gaultier *et al.*, 2008a; Vinther *et al.*, 2008; Jensen *et al.*, 2004; Fomsgaard & Kristensen, 1999; Walker *et al.*, 1992; McCormick & Hiltbold, 1966). On the other hand, pesticide sorption in soil, which is often positively related to SOC (Kah *et al.*, 2007; Boivin *et al.*, 2005b), strongly reduces the bioavailability of pesticides (Kah *et al.*, 2007; Sorensen *et al.*, 2006; Boivin *et al.*, 2005a; Thorstensen & Lode, 2001; Guo *et al.*, 2000; Ogram *et al.*, 1985). In an attempt to improve our understanding of this complexity, degradation of the same three test compounds used in the sorption studies (Paper III) was studied in topsoil samples taken from the same sixteen locations in the E21 catchment.

Incubation experiments for each soil/pesticide combination were carried out on two replicate samples for 64 days using standard procedures. The data from the incubation study were fitted to first-order degradation kinetics using non-linear regression in equation (7) and degradation half-lives ( $DT_{50}$ , days) were calculated using equation (6). Various indicators of microbial activity (e.g. the lignolytic enzymes manganese peroxidase (MnP) and laccase,

mineralization of  $^{14}\text{C}$  dehydrogenation polymer (DHP) of coniferyl alcohol, basic respiration and substrate-induced respiration (SIR), with the latter partitioned into  $\text{CO}_2$  production from actively growing and dormant microorganisms) were also measured on soil samples from the same 16 locations. These methods are described in detail in paper I.

The degradation rate constants for bentazone, glyphosate and isoproturon showed considerable differences between soils with coefficients of variation ranging from 42 to 64% for the three compounds (Table 3, Paper I). Degradation rate constants for bentazone were in the range  $0.005\text{--}0.034 \text{ day}^{-1}$  which corresponds to half-lives of 20 to 139 days. Our data are consistent with those (8-133 days) reported by others (Rodriguez-Cruz *et al.*, 2006; Thorstensen & Lode, 2001). Degradation rate constants for isoproturon were in the range  $0.011\text{--}0.104 \text{ day}^{-1}$  which corresponds to half-lives of 7–63 days. Again, this degree of variation is similar to that reported in the literature for isoproturon, with values ranging from 1.4 to 40 days (Larsbo *et al.*, 2009; Rodriguez-Cruz *et al.*, 2006; Walker *et al.*, 2001). The degradation rates of glyphosate ( $0.006\text{--}0.05 \text{ day}^{-1}$ , which correspond to half-lives of 14–116 days) are also consistent with other studies where the  $\text{DT}_{50}$  values in a variety of different soil types have been reported in the range of 1.7 to 197 days (Sorensen *et al.*, 2006; Giesy *et al.*, 2000).

The results in Paper I showed that  $k$  for glyphosate and isoproturon was smaller for soils with high SOC. These soils also have stronger sorption (Paper III), which reduces the availability of the pesticide for degradation (see Figure 4). In contrast, bentazone degradation rate was significantly positively correlated with SOC, SIR, and active microorganisms ( $r$ ), which clearly reflect a strong control of microbial activity on bentazone degradation.

To investigate and better understand these complex relationships between soil properties and degradation rates of pesticides, a simple multiplicative model was developed and tested in Paper I:

*Equation 8*

$$k = k_{ref} \cdot (B)^m \cdot (A)^n$$

where  $k_{ref}$  is a pesticide-specific reference rate coefficient which, in addition to the influence of variables not included in the model, should be related to the inherent degradability of the compound as determined by its molecular structure,  $m$  and  $n$  are constants,  $A$  is some measure of microbial activity and  $B$  is some measure of bioavailability. Six different forms of equation 8 were tested, combining three potential descriptors of microbial

activity (laccase activity, SIR, and SOC) with two for bioavailability,  $K_f$  or the calculated fraction of pesticide in soil solution. Although pH could also have been considered, SOC was chosen as a surrogate variable for microbial activity, since it was strongly correlated to the microbial parameters MnP, SIR and r (Paper I, Table 5). Details of the model fitting procedures are reported in Paper I. Several of the models fitted the data well (see Table 7, Paper I), with  $R^2$  values ranging up to 50% and regression co-efficients significant at  $p < 0.1$ . Figure 5 shows measured and predicted degradation rate coefficients for a model based on  $K_f$  and SIR (model 1 in Table 7, Paper I).

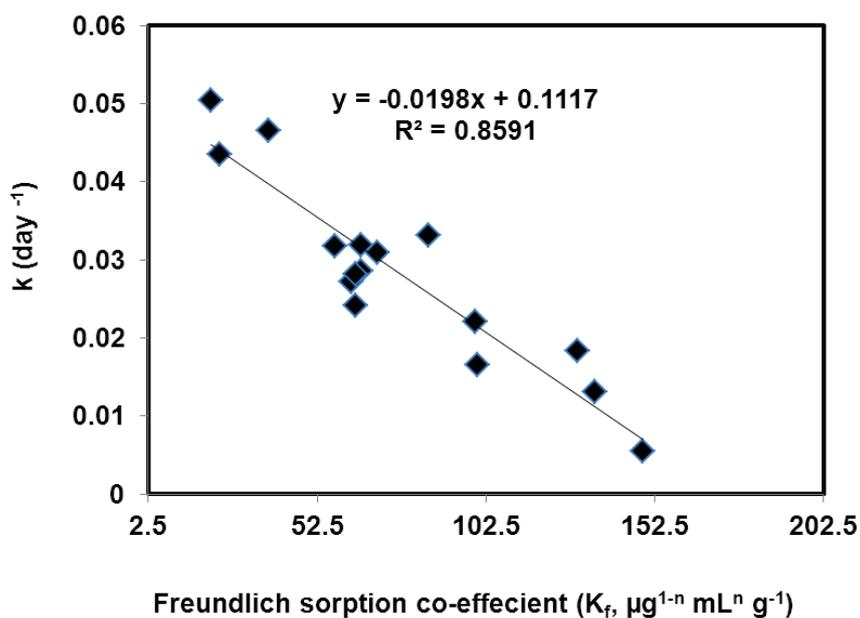


Figure 4. Relationship between the degradation rate constant  $k$  (day<sup>-1</sup>) for glyphosate and the Freundlich sorption coefficient ( $K_f$ ,  $\mu\text{g}^{1-n} \text{mL}^n \text{g}^{-1}$ ).

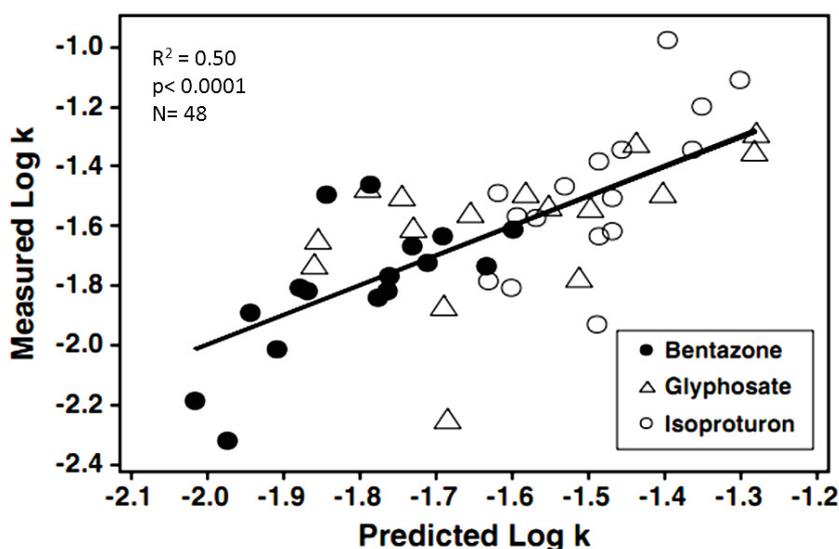


Figure 5. Comparison of measured degradation rate constants with those predicted using model 1 (Table 7, Paper I)  $\text{Log}k = -2.27\text{Log}k_{\text{ref}(B)} - 0.89\text{Log}k_{\text{ref}(G)} - 1.47\text{Log}k_{\text{ref}(I)} - 0.50\text{Log}K_f + 0.37\text{Log}SIR$ . Here subscripts B, I and G represent bentazone, isoproturon and glyphosate, respectively.

### *Modelling variation in pesticide degradation: a meta-analysis*

Based on the findings in Paper I and a further review of the literature, the modelling approach was further refined and tested on larger data set collated from the published literature, which included a wider range of pesticides and soil types (Paper II). A mechanistic basis for the multiplicative model was also derived from a consideration of Michaelis-Menten kinetics. Details of this are presented in Paper II. In practice, measurements of enzyme activities or microbial biomass like those obtained in Paper I will not be available as input to large-scale modelling exercises. Instead, only data widely available from soil surveys would be useful. Several soil properties have been shown to be strongly correlated to measured microbial activity (e.g. basic respiration) and biomass (e.g. substrate-induced respiration), especially soil organic carbon content, pH, clay content, and total nitrogen (Wichern & Joergensen, 2009; Lentzsch *et al.*, 2005; Anderson & Domsch, 1989). Other site factors such as land use and climate also significantly affect microbial biomass (Wichern & Joergensen, 2009; Lentzsch *et al.*, 2005; Hofman *et al.*, 2004; Emmerling & Udelhoven, 2002; Oberholzer *et al.*, 1999). Although specific groups of microbes are generally responsible for degradation, rather than the total

biomass (Bending & Rodriguez-Cruz, 2007; Aislabie & Lloyd-Jones, 1995), significant relationships are often found between the total biomass and pesticide degradation, which suggests that the amount of such pesticide-degrading microbial groups is often roughly proportional to the total biomass (Torstensson & Stenström, 1986).

Thus, it was tested whether microbial biomass can be replaced by proxy soil variables in a multiplicative model of the form:

*Equation 10*

$$k = k_{ref} F_L x_1^{n_1} x_2^{n_2} \dots x_i^{n_i}$$

where  $x_1 \dots x_i$  are one or more proxy variables for microbial biomass (e.g. pH, clay and organic carbon contents) and  $n_1 \dots n_i$  are empirical exponents.  $F_L$ , the bioavailability factor, was defined in this analysis as  $1/(m_g + K_d)$  where  $m_g$  is the gravimetric water content. As noted above, soil organic carbon and microbial biomass are often strongly correlated. Thus, one plausible form of equation (10) can be written as:

*Equation 11*

$$k = k_{ref} \left( \frac{1}{m_g + f_{oc} k_{oc}} \right) f_{oc}^n$$

where it has been assumed that  $K_d$  is perfectly correlated with  $f_{oc}$  (i.e.  $K_d = f_{oc} k_{oc}$ ). Figure 6 shows example calculations with equation 11 for three hypothetical organic substances of varying  $k_{oc}$  values. It suggests that the competing effects of  $f_{oc}$  on bioavailability and microbial activity may result in an optimum soil organic carbon content for degradation. This optimum,  $f_{oc(max)}$ , can be derived by setting the derivative of equation (11) to zero. Assuming that the remaining parameters (e.g.  $m_g$ ) are independent of  $f_{oc}$  gives:

*Equation 12*

$$f_{oc(max)} = \frac{m_g n}{(1 - n)k_{oc}}$$

If  $n < 1$ , which should be expected based on the non-linear relationship between soil organic carbon content and microbial biomass (Anderson & Domsch, 1989), then equation (12) shows that the optimum  $f_{oc}$  for degradation

shifts as  $k_{oc}$  changes, with  $f_{oc(max)}$  increasing as  $k_{oc}$  decreases. For the example illustrated in figure 6,  $f_{oc(max)}$  takes values of 0.03, 0.3 and 3% for the three hypothetical compounds with  $k_{oc}$  values of 1000, 100 and 10  $\text{cm}^3 \text{g}^{-1}$ , respectively. In most cases, only a small number of soils covering a limited range of organic carbon contents (predominantly agricultural topsoil with  $f_{oc}$  varying from perhaps ca. 1 to 3%) have been studied, which implies that an optimum  $f_{oc}$  content for degradation rate constant may not be apparent in any one study. This is probably the reason why some studies have reported that degradation rate is positively correlated to  $f_{oc}$  whereas others reported that they are negatively correlated. In principle, the model should also be able to describe how  $k$  varies vertically within a soil profile, as a function of  $f_{oc}$  and  $K_d$ . In a comparative study of vertical variations of  $k$  for eight pesticides of contrasting properties, Di *et al.* (1998) found that degradation decreased with depth (and decreasing  $f_{oc}$ ), except for the most strongly sorbing compounds where  $k$  actually increased with depth, a trend which is in qualitative agreement with the behavior predicted by the model, as illustrated in Figure 6 for compounds of low and high  $k_{oc}$  values.

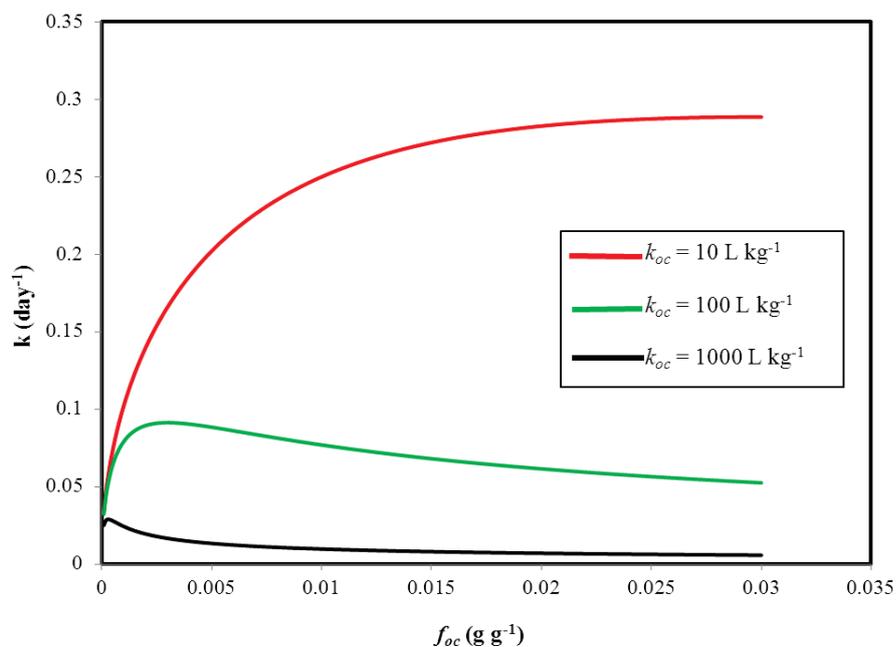


Figure 6. The degradation rate constant predicted as a function of soil organic carbon content for pesticides of contrasting  $k_{oc}$  values, calculated with equation 11, for  $m_g = 0.3 \text{ g g}^{-1}$ ,  $n = 0.5$  and  $k_{ref} = 1 \text{ L kg}^{-1} \text{ day}^{-1}$ .

The model approach was tested on data collected from literature. The criteria for data inclusion were presented in Paper II. A search on ISI Web of Science, yielded 11 different studies that fulfilled our criteria ( Paper II, Table 1), comprising in total 230  $k$  values measured for 21 different pesticides. The characteristic spatial scale of the studies also varied greatly, from soil profiles (Si *et al.*, 2009; Mueller *et al.*, 1992), through field (Walker *et al.*, 2001) and small catchment scales (Ghafoor *et al.*, 2011) up to regional (Gaultier *et al.*, 2008a; Kah *et al.*, 2007) and continental scales (Dyson *et al.*, 2002). Five out of the 21 studies also measured microbial biomass by three different techniques (see Table 1 in Paper II). We tested the model on this limited subset of data using biomass directly as a predictor rather than surrogate variables, including an empirical exponent for additional model flexibility. Soil organic matter is known to be more stable in the subsoil, caused by the combined effects of poorer quality and better physical protection against degradation (Gillabel *et al.*, 2010). This means that the easily available substrate is a smaller fraction of the total soil organic carbon, which leads to a smaller fraction of active microbial biomass (Stenström *et al.*, 2001). In addition, nutrient availability and oxygen supply may also be more limited in subsoil. Thus, we included soil depth as an additional variable into the models. We tested two ways of doing this, treating it either as a continuous variable (normalized to a reference depth,  $z_r$ , which we set to 10 cm) or as a binary variable which takes a value of 1 for topsoil ( $\leq 30$ cm) and 2 for subsoil ( $\geq 30$ cm). Both approaches improved model performance, but models with depth defined as a continuous variable performed slightly better and were therefore retained.

Two basic models were therefore tested:

*Equation 13*

$$k = k_{ref} F_L^m M_b^n \left(\frac{z_r}{z}\right)^q$$

*Equation 14*

$$k = k_{ref} F_L^m f_{oc}^n f_{clay}^p \left(\frac{z_r}{z}\right)^q$$

where an additional empirical exponent,  $m$ , was included as a modifier to the bioavailability factor. The linearized form of equations 13 and 14 was fitted to the data using partial least-squares regression (PLSR). The main advantage of PLSR over simple multiple linear regression is that it explicitly handles

multi-collinearity in the predictors. We assumed that the exponents in equations 13 and 14 were identical for all pesticides and that only the reference degradation rate constants  $k_{ref}$  are pesticide and study specific. All statistical analyses were performed with R (R Development Core Team, 2011) and are described in detail in Paper II.

Results showed that including depth as an additional predictor variable gave a significant improvement (Figure 7), which supports the idea that the activity or efficiency of the microbial biomass decreases with depth in the soil profile. Validation statistics for selected models with different predictor combinations based on equations 13 and 14 are presented in Paper II. The performance of the model based on  $F_L$  and  $f_{oc}$  for 21 pesticide-combinations is illustrated in Figure 8.

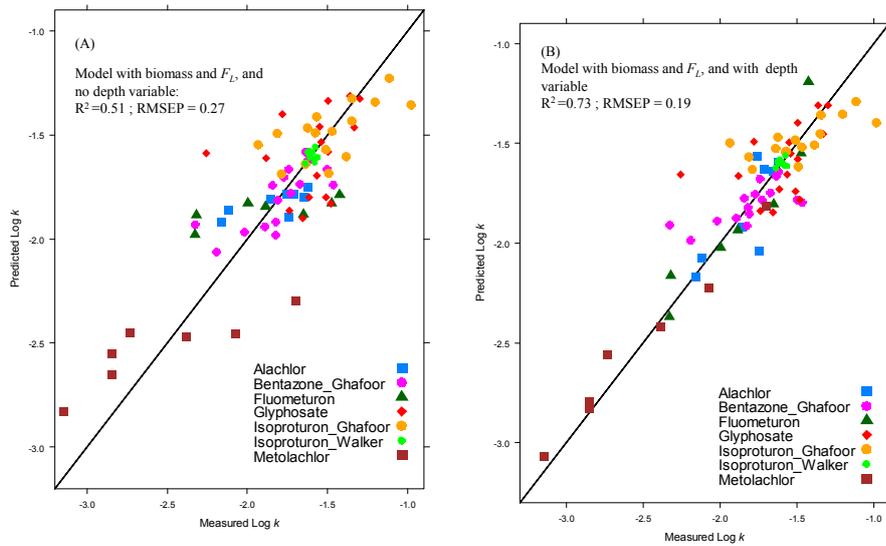


Figure 7. Comparison of measured and predicted degradation of 7 pesticide-study combinations for a model without depth (A)  $Logk = Logk_{ref} + 0.343 Log F_L + 0.546 Log Biomass$  and for a model which includes depth as a predictor (B)  $Logk = Logk_{ref} + 0.441 Log F_L + 0.385 Log Biomass - 0.727 Log Depth_{continuous}$

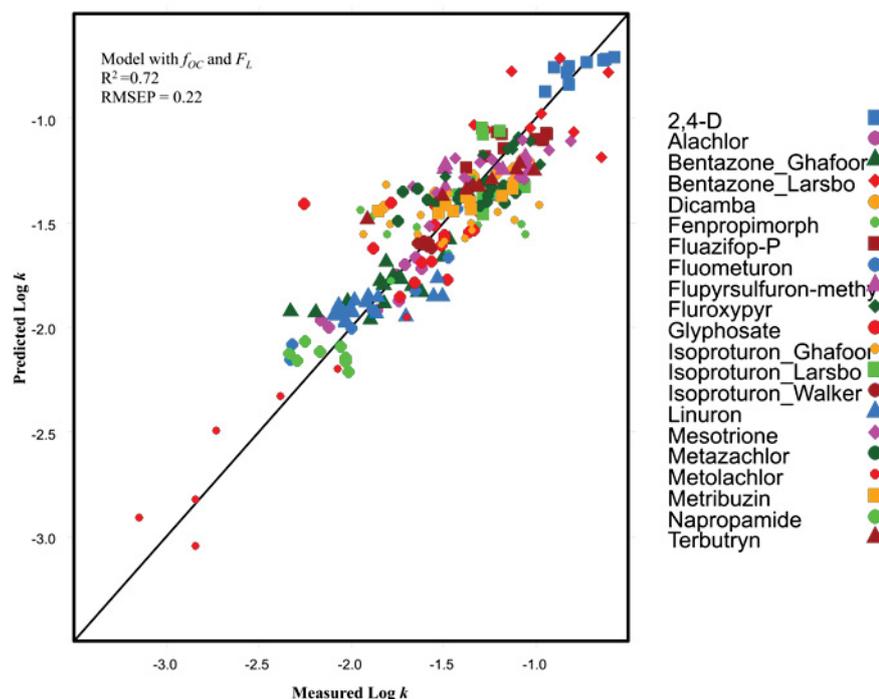


Figure 8. Comparison of measured and predicted degradation of 21 pesticide-study combinations with the model  $\text{Log}k = \text{Log}k_{ref} + 0.252 \text{Log}F_L + 0.315 \text{Log}f_{oc} - 0.415 \text{Log}Depth_{continuous}$

In the paper II, the model was benchmarked for individual substances by analyzing whether it gave improved predictions compared to just taking the mean of the measurements (a ‘pure intercept’ model based only on  $k_{ref}$ ), and showed that it did so for all except four of the pesticide-study combinations in the database. This is, by itself, sufficient justification for claiming that the approach is promising and clearly represents an improvement over current practice in spatial modelling, which is to use average values for  $k$ . Further, for the 15 compounds for which the model is found to work, the model reduced the RMSE from 0.26 for the pure intercept model to 0.20 (i.e. by 23%). For the limited dataset for which microbial biomass was measured (6 substances), the model reduced the overall RMSE by 31% (from 0.29 to 0.20). The equivalent figures for the  $R^2$  values are increased by 25% and 83% respectively (from 0.64 to 0.80 and 0.41 to 0.75 respectively). These results may appear to represent modest gains compared with the use of average values for  $k$ , but this

is not too surprising considering the many sources of uncertainty, especially the fact that the relationships between the active degrading biomass, total biomass and proxy variables such as clay content and organic matter content are likely to be quite variable.



## 5 Conclusions, recommendations and future research

### 5.1 Application of the new modelling approaches in practice

The results show that the  $k_{oc}$  concept is inadequate to describe sorption in soils with organic carbon contents less than ca. 2% and that a simple empirical extended partitioning model which also accounts for the effects of inorganic sorbents shows great promise. The choice of predictors may be based on mechanistic reasoning and the physico-chemical characteristics of the compound under consideration. The partitioning coefficients for individual compounds on inorganic sorbents could be estimated from literature meta-analyses but their accurate determination probably requires sorption measurements made in subsoil, and these are less often reported. For spatial modelling applications, the predictor variables  $f_{oc}$ ,  $f_{clay}$  and pH are widely available in soil survey databases, while measurements of oxides of Al and Fe are not always reported. This emphasizes the need to measure and report contents of oxides of Al and Fe in soil surveys because my results show that small variations in the contents of oxides of Al and Fe can contribute to significant variations in pesticide sorption, especially for ionizable compounds.

From the meta-analysis of a literature data set comprising degradation rates measured for a wide range of substances in strongly contrasting soils, we can conclude that a general multiplicative model (equation 14) shows promise as an effective approach to predict degradation. Better models could probably be obtained by applying equation 14 to data on individual compounds, so that the exponents in the equation would then become compound-specific. This might be possible for a few widely studied pesticides (e.g. Fenner *et al.*, 2007), but for many compounds the extensive literature data required to obtain statistically robust models will not be available. In the absence of such data, a general approach described in paper II (model 10 in Table 2) seems preferable

to the use of single database values of  $k$  for large-scale modelling applications at catchment or regional scales. In this case,  $k_{ref}$  for any given compound could be estimated from existing databases if the values of the proxy variables for the soil samples on which the degradation rates were measured are either known or can be estimated within reasonable bounds. This should at least be the case for studies performed according to the regulatory guidelines devised by regulatory bodies such as OECD, SETAC or US-EPA that specify acceptable ranges for texture and organic carbon content of the test soils. The main uncertainty with this approach is likely to be the fact that  $k$  is only reported for a few soils.

## 5.2 Recommendations for future research

The following aspects need to be further investigated and resolved in order to improve pesticide risk assessment and management, especially at large scales:

1. The models presented in this thesis can be further improved and tested. Specifically, the models were primarily based on measurements made on only three test compounds in the soils of one catchment. The general applicability of this modelling approach should be further evaluated for other classes of compounds in soils of other catchments under different agro-climatic conditions.
2. Combining probabilistic modelling approaches (Lindahl *et al.*, 2005; Beulke *et al.*, 2004) with the sorption and degradation pedotransfer functions described in this thesis may provide a promising approach to incorporate spatial variability and uncertainty in the environmental risk assessment of pesticides.
3. The spatial variability of pesticide fate as influenced by the effects of land management practices and topography on soil properties should be further studied in the context of large-scale modelling applications. For example Farenhorst *et al.* (2009) demonstrated that in an extreme scenario of replacing the 2,4-D  $K_d$  values of toeslope profiles (ranging from 0.16 to 1.77 L kg<sup>-1</sup>) by those measured in knoll profiles (ranging from 0.12 to 0.50 L kg<sup>-1</sup>) — the amount of herbicide leached to a 15 cm depth increased by 29.1% under an actual rainfall scenario.
4. Subsoil is an important part of the pedosphere. For example, in clayey soils pesticides can leach quickly through the surface soil in macropores (Kjaer *et al.*, 2005) and thus the sorption and degradation capacity in the subsurface soil layers becomes more important. Simulation studies suggest that risk assessments of pesticide leaching to depth require accurate data on sorption and degradation parameters

throughout the entire soil profile (Farenhorst *et al.*, 2009). In principle, the modelling approach developed in this thesis can also explain how sorption and degradation vary vertically within a soil profile, as a function of organic and inorganic soil constituents,  $F_L$  and soil microbial biomass (or proxy variables such as  $f_{oc}$ ). However, in field studies the sampling intensity is limited by financial resources so that pesticide sorption and degradation processes are much more frequently studied in surface soils than in subsurface soils. This was also true in my study. More work is therefore required to test the models in this respect. The issue of higher spatial variability of sorption and degradation in subsoil than that in surface soils was not tackled in this thesis and still needs further investigation. With respect to degradation, studies at the micro-scale in soil have revealed that the spatial distribution of microbial communities in subsoil is more variable than in surface soil (Nunan *et al.*, 2001).

5. Generally speaking, most sorption and degradation studies are conducted under laboratory conditions. Such studies measured on disturbed soil samples may poorly reflect the local environmental conditions experienced in undisturbed soil in the field. There is need to conduct more studies under field conditions.
6. There exists a large discrepancy between the relatively small, “millimeter” scale at which environmental conditions directly influence microbial activity and pesticide fate, and the much larger field, catchment, or regional scales at which management decisions are usually made by regulatory authorities or agencies. The scale of interest depends on the responsible authority or the end user. For example, most public authorities are interested in regional and national scales and others may even be interested in continental scale risk assessment (e.g. in the EU). Farmers and extension advisors are interested in the fate of pesticides at the field and farm scales. There is therefore a need to develop risk assessment modelling tools that can account for larger scale variations occurring due to soil horizonation vertically (decimeter to meter scale) and between soil mapping units laterally (meter and even larger scale).



## References

- Abernath, J.R. & Wax, L.M. (1973). Bentazone mobility and adsorption in 12 Illinois soils. *Weed Science* 21(3), 224-227.
- Ahmad, R., Kookana, R.S., Alston, A.M. & Bromilow, R.H. (2001). Differences in sorption behaviour of carbaryl and phosalone in soils from Australia, Pakistan, and the United Kingdom. *Australian Journal of Soil Research* 39(4), 893-908.
- Aislabie, J. & Lloyd-Jones, G. (1995). A review of bacterial-degradation of pesticides. *Australian Journal of Soil Research* 33(6), 925-942.
- Akaike, H. (1974). A new look at the statistical model identification. *IEEE Transactions on Automatic Control* 16(6), 716-723.
- Alexander, M. (1999). *Biodegradation and bioremediation*. 2nd. ed. San Diego: Academic Press. ISBN 0120498618.
- Allen, R. & Walker, A. (1987). The influence of soil properties on the rates of degradation of metamitron, metazachlor and metribuzin. *Pesticide Science* 18(2), 95-111.
- Anderson, T.H. & Domsch, K.H. (1989). Ratios of microbial biomass carbon to total organic carbon in arable soils. *Soil Biology & Biochemistry* 21(4), 471-479.
- Bailey, G.W. & White, J.L. (1964). Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity. *Journal of Agricultural and Food Chemistry* 12(4), 324-332.
- Barr, D.P. & Aust, S.D. (1994). Pollutant degradation by white rot fungi. *Reviews of Environmental Contamination and Toxicology* 138, 49-72.
- Barriuso, E., Laird, D.A., Koskinen, W.C. & Dowdy, R.H. (1994). Atrazine desorption from smectites. *Soil Science Society of America Journal* 58(6), 1632-1638.
- Bending, G.D., Lincoln, S.D. & Edmondson, R.N. (2006). Spatial variation in the degradation rate of the pesticides isoproturon, azoxystrobin and diflufenican in soil and its relationship with chemical and microbial properties. *Environmental Pollution* 139(2), 279-287.

- Bending, G.D., Lincoln, S.D., Sorensen, S.R., Morgan, J.A.W., Aamand, J. & Walker, A. (2003). In-field spatial variability in the degradation of the phenyl-urea herbicide isoproturon is the result of interactions between degradative *Sphingomonas spp.* and soil pH. *Applied and Environmental Microbiology* 69(2), 827-834.
- Bending, G.D. & Rodriguez-Cruz, M.S. (2007). Microbial aspects of the interaction between soil depth and biodegradation of the herbicide isoproturon. *Chemosphere* 66(4), 664-671.
- Bergström, L. & Stenström, J. (1998). Environmental fate of chemicals in soil. *Ambio* 27(1), 16-23.
- Beulke, S. & Brown, C.D. (2001). Evaluation of methods to derive pesticide degradation parameters for regulatory modelling. *Biology and Fertility of Soils* 33(6), 558-564.
- Beulke, S., Brown, C.D., Dubus, I.G., Fryer, C.J. & Walker, A. (2004). Evaluation of probabilistic modelling approaches against data on leaching of isoproturon through undisturbed lysimeters. *Ecological Modelling* 179(1), 131-144.
- Blume, E., Bischoff, M., Moorman, T.B. & Turco, R.F. (2004). Degradation and binding of atrazine in surface and subsurface soils. *Journal of Agricultural and Food Chemistry* 52(24), 7382-7388.
- Boesten, J.J.T.I. (2000). From laboratory to field: uses and limitations of pesticide behaviour models for the soil/plant system. *Weed Research* 40(1), 123-138.
- Boesten, J.J.T.I. & Van der Linden, A.M.A. (1991). Modelling the influence of sorption and transformation on pesticide leaching and persistence. *Journal of Environmental Quality* 20(2), 425-435.
- Bogan, B.W. & Lamar, R.T. (1995). One electron oxidation in the degradation of creosote polycyclic aromatic hydrocarbons by *Phanerochaete chrysosporium*. *Applied and Environmental Microbiology* 61(7), 2631-2635.
- Boivin, A., Amellal, S., Schiavon, M. & van Genuchten, M.T. (2005a). 2,4-dichlorophenoxyacetic acid (2,4-D) sorption and degradation dynamics in three agricultural soils. *Environmental Pollution* 138(1), 92-99.
- Boivin, A., Cherrier, R. & Schiavon, M. (2005b). A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere* 61(5), 668-676.
- Bollag, J.M. (1992). Decontaminating soil with enzymes. *Environmental Science & Technology* 26(10), 1876-1881.
- Borggaard, O.K. & Gimsing, A.L. (2008). Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review. *Pest Management Science* 64(4), 441-456.
- Boyle, D., Wiesner, C. & Richardson, A. (1998). Factors affecting the degradation of polyaromatic hydrocarbons in soil by white-rot fungi. *Soil Biology & Biochemistry* 30(7), 873-882.
- Calvet, R. (1989). Adsorption of organic chemicals in soils. *Environmental Health Perspectives* 83, 145-177.

- Carrizosa, M.J., Calderon, M.J., Hermosin, M.C. & Cornejo, J. (2000). Organosmectites as sorbent and carrier of the herbicide bentazone. *Science of the Total Environment* 247(2-3), 285-293.
- Carsel, R.F., Mulkey, L.A., Lorber, M.N. & Baskin, L.B. (1985). The Pesticide Root Zone Model (PRZM) - a procedure for evaluating pesticide leaching threats to groundwater. *Ecological Modelling* 30(1-2), 49-69.
- Castillo, M.D., Ander, P., Stenström, J. & Torstensson, L. (2000). Degradation of the herbicide bentazone as related to enzyme production by *Phanerochaete chrysosporium* in two solid substrate fermentation systems. *World Journal of Microbiology & Biotechnology* 16(3), 289-295.
- Cederlund, H., Börjesson, E., Öneby, K. & Stenström, J. (2007). Metabolic and cometabolic degradation of herbicides in the fine material of railway ballast. *Soil Biology & Biochemistry* 39(2), 473-484.
- Charnay, M.P., Tuis, S., Coquet, Y. & Barriuso, E. (2005). Spatial variability in <sup>14</sup>C-herbicide degradation in surface and subsurface soils. *Pest Management Science* 61(9), 845-855.
- Coquet, Y. (2003a). Sorption of pesticides atrazine, isoproturon, and metamitron in the vadose zone. *Vadose Zone Journal* 2(1), 40-51.
- Coquet, Y. (2003b). Variation of pesticide sorption isotherm in soil at the catchment scale. *Pest Management Science* 59(1), 69-78.
- Coquet, Y., Ribiere, C. & Vachier, P. (2004). Pesticide adsorption in the vadose zone: a case study on Eocene and Quaternary materials in Northern France. *Pest Management Science* 60(10), 992-1000.
- Criquet, S., Farnet, A.M., Tagger, S. & Le Petit, J. (2000). Annual variations of phenoloxidase activities in an evergreen oak litter: influence of certain biotic and abiotic factors. *Soil Biology & Biochemistry* 32(11-12), 1505-1513.
- Dakhel, N., Barriuso, E., Charnay, M.P., Touratier, C. & Ambrosi, D. (2001). Amitrole degradation in vineyard soils in relation to pedo-climatic conditions. *Biology and Fertility of Soils* 33(6), 490-494.
- de Jonge, H. & de Jonge, L.W. (1999). Influence of pH and solution composition on the sorption of glyphosate and prochloraz to a sandy loam soil. *Chemosphere* 39(5), 753-763.
- Di, H.J., Aylmore, L.A.G. & Kookana, R.S. (1998). Degradation rates of eight pesticides in surface and subsurface soils under laboratory and field conditions. *Soil Science* 163(5), 404-411.
- Dubus, I.G. & Brown, C.D. (2002). Sensitivity and first-step uncertainty analyses for the preferential flow model MACRO. *Journal of Environmental Quality* 31(1), 227-240.
- Dyson, J.S., Beulke, S., Brown, C.D. & Lane, M.C.G. (2002). Adsorption and degradation of the weak acid mesotrione in soil and environmental fate implications. *Journal of Environmental Quality* 31(2), 613-618.
- Emmerling, C. & Udelhoven, T. (2002). Discriminating factors of the spatial variability of soil quality parameters at landscape-scale. *Journal of Plant Nutrition and Soil Science-Zeitschrift Für Pflanzenernahrung und Bodenkunde* 165(6), 706-712.

- Eriksson, J., Mattson, L. & Söderström, M. (2010). *Tillståndet i svensk åkermark och gröda. Data från 2001-2007. Naturvårdsverket Rapport 6349, p.129*
- Ertli, T., Marton, A. & Foldenyi, R. (2004). Effect of pH and the role of organic matter in the adsorption of isoproturon on soils. *Chemosphere* 57(8), 771-779.
- FAOSTAT *Pesticides Use Data*. <http://faostat.fao.org/site/424/default.aspx#ancor>. [online] [Accessed October 19, 2012].
- FAOSTAT *Population Data*. <http://faostat.fao.org/site/550/default.aspx#ancor>. [online] [Accessed October 19, 2012].
- Farenhorst, A., McQueen, D.A.R., Saiyed, I., Hilderbrand, C., Li, S., Lobb, D.A., Messing, P., Schumacher, T.E., Papiernik, S.K. & Lindstrom, M.J. (2009). Variations in soil properties and herbicide sorption coefficients with depth in relation to PRZM (pesticide root zone model) calculations. *Geoderma* 150(3-4), 267-277.
- Felding, G. (1997). Pesticide adsorption as a function of depth below surface. *Pesticide Science* 50(1), 64-66.
- Fenner, K., Lanz, V.A., Scheringer, M. & Borsuk, M.E. (2007). Relating atrazine degradation rate in soil to environmental conditions: Implications for global fate modelling. *Environmental Science & Technology* 41(8), 2840-2846.
- Finzi, A.C., Sinsabaugh, R.L., Long, T.M. & Osgood, M.P. (2006). Microbial community responses to atmospheric carbon dioxide enrichment in a warm-temperate forest. *Ecosystems* 9(2), 215-226.
- FOCUS (2006). Guidance document on estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. *The Final Report of the Work Group on Degradation Kinetics of Focus. Sanco/10058/2005, version 2.0, FOCUS: Brussels, Belgium, .*
- Foley, J.A., Ramankutty, N., Brauman, K.A., Cassidy, E.S., Gerber, J.S., Johnston, M., Mueller, N.D., O'Connell, C., Ray, D.K., West, P.C., Balzer, C., Bennett, E.M., Carpenter, S.R., Hill, J., Monfreda, C., Polasky, S., Rockstrom, J., Sheehan, J., Siebert, S., Tilman, D. & Zaks, D.P.M. (2011). Solutions for a cultivated planet. *Nature* 478(7369), 337-342.
- Fomsgaard, I.S. & Kristensen, K. (1999). Influence of microbial activity, organic carbon content, soil texture and soil depth on mineralisation rates of low concentrations of <sup>14</sup>C-mecoprop - development of a predictive model. *Ecological Modelling* 122(1-2), 45-68.
- Forouzangohar, M., Haghnia, G.H. & Koocheki, A. (2005). Organic amendments to enhance atrazine and metolachlor degradation in two contaminated soils with contrasting textures. *Soil & Sediment Contamination* 14(4), 345-355.
- Fox, J. (2002). Appendix to An R and S-PLUS. Companion to Applied Regression. Nonlinear regression and nonlinear least squares. (<http://cran.r-project.org/doc/contrib/Fox-Companion/appendix-nonlinear-regression.pdf>).
- Fredslund, L., Vinther, F.P., Brinch, U.C., Elsgaard, L., Rosenberg, P. & Jacobsen, C.S. (2008). Spatial variation in 2-methyl-4-chlorophenoxyacetic acid mineralization and sorption in a sandy soil at field level. *Journal of Environmental Quality* 37(5), 1918-1928.

- Gaultier, J., Farenhorst, A., Cathcart, J. & Goddard, T. (2008a). Degradation of [carboxyl-<sup>14</sup>C] 2,4-D and [ring-U-<sup>14</sup>C] 2,4-D in 114 agricultural soils as affected by soil organic carbon content. *Soil Biology & Biochemistry* 40(1), 217-227.
- Gaultier, J., Farenhorst, A., Cathcart, J. & Goddard, T. (2008b). Regional assessment of herbicide sorption and degradation in two sampling years. *Journal of Environmental Quality* 37(5), 1825-1836.
- Ghafoor, A., Jarvis, N., Thierfelder, T. & Stenström, J. (2011). Measurements and modelling of pesticide persistence in soil at the catchment scale. *Science of the Total Environment* 409(10), 1900-1908.
- Giesy, J.P., Dobson, S. & Solomon, K.R. (2000). Ecotoxicological risk assessment for Roundup (R) Herbicide. *Reviews of Environmental Contamination and Toxicology* 167, 35-120.
- Gillabel, J., Cebrian-Lopez, B., Six, J. & Merckx, R. (2010). Experimental evidence for the attenuating effect of SOM protection on temperature sensitivity of SOM decomposition. *Global Change Biology* 16(10), 2789-2798.
- Gimsing, A.L., Borggaard, O.K. & Bang, M. (2004). Influence of soil composition on adsorption of glyphosate and phosphate by contrasting Danish surface soils. *European Journal of Soil Science* 55(1), 183-191.
- Glass, R.L. (1987). Adsorption of glyphosate by soils and clay minerals. *Journal of Agricultural and Food Chemistry* 35(4), 497-500.
- Goetz, A.J., Walker, R.H., Wehtje, G. & Hajek, B.F. (1989). Sorption and mobility of chlorimuron in Alabama soils. *Weed Science* 37(3), 428-433.
- Grathwohl, P. (1990). Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons : Implications on  $K_{oc}$  correlations. *Environmental Science & Technology* 24(11), 1687-1693.
- Grey, T.L., Walker, R.H., Wehtje, G.R. & Hancock, H.G. (1997). Sulfentrazone adsorption and mobility as affected by soil and pH. *Weed Science* 45(5), 733-738.
- Guo, L., Jury, W.A., Wagenet, R.J. & Flury, M. (2000). Dependence of pesticide degradation on sorption: nonequilibrium model and application to soil reactors. *Journal of Contaminant Hydrology* 43(1), 45-62.
- Harper, S.S. (1988). Sorption of metribuzin in surface and subsurface soils of the Mississippi delta region. *Weed Science* 36(1), 84-89.
- Hofman, J., Dusek, L., Klanova, J., Bezchlebova, J. & Holoubek, I. (2004). Monitoring microbial biomass and respiration in different soils from the Czech Republic - a summary of results. *Environment International* 30(1), 19-30.
- Houot, S., Topp, E., Yassir, A. & Soulas, G. (2000). Dependence of accelerated degradation of atrazine on soil pH in French and Canadian soils. *Soil Biology & Biochemistry* 32(5), 615-625.
- Hultgren, R.P., Hudson, R.J.M. & Sims, G.K. (2002). Effects of soil pH and soil water content on prosulfuron dissipation. *Journal of Agricultural and Food Chemistry* 50(11), 3236-3243.

- Hurvich, C.M. & Tsai, C.L. (1989). Regression and time-series model selection in small samples. *Biometrika* 76(2), 297-307.
- Jackson, C.R., Liew, K.C. & Yule, C.M. (2009). Structural and functional changes with depth in microbial communities in a tropical Malaysian peat swamp forest. *Microbial Ecology* 57(3), 402-412.
- Jacobsen, C.S., van der Keur, P., Iversen, B.V., Rosenberg, P., Barlebo, H.C., Torp, S., Vosgerau, H., Juhler, R.K., Ernstsén, V., Rasmussen, J., Brinch, U.C. & Jacobsen, O.H. (2008). Variation of MCPA, metribuzine, methyltriazine-amine and glyphosate degradation, sorption, mineralization and leaching in different soil horizons. *Environmental Pollution* 156(3), 794-802.
- Jarvis, N.J. (1994). *The MACRO model. Reports and Dissertations 19*. Uppsala, Sweden: Department of soil sciences, Swedish University of Agricultural Sciences.
- Jensen, P.H., Hansen, H.C.B., Rasmussen, J. & Jacobsen, O.S. (2004). Sorption-controlled degradation kinetics of MCPA in soil. *Environmental Science & Technology* 38(24), 6662-6668.
- Jurado-Exposito, M. & Walker, A. (1998). Degradation of isoproturon, propanil and alachlor in soil with constant and variable incubation conditions. *Weed Research* 38(4), 309-318.
- Kah, M., Beulke, S. & Brown, C.D. (2007). Factors influencing degradation of pesticides in soil. *Journal of Agricultural and Food Chemistry* 55(11), 4487-4492.
- Kah, M. & Brown, C.D. (2006). Adsorption of ionisable pesticides in soils. *Reviews of Environmental Contamination and Toxicology, Vol 188* 188, 149-217.
- Keeler, B.L., Hobbie, S.E. & Kellogg, L.E. (2009). Effects of long term nitrogen addition on microbial enzyme activity in eight forested and grassland sites: Implications for litter and soil organic matter decomposition. *Ecosystems* 12(1), 1-15.
- Kim, J.E., Wang, C.J. & Bollag, J.M. (1997). Interaction of reactive and inert chemicals in the presence of oxidoreductases: Reaction of the herbicide bentazon and its metabolites with humic monomers. *Biodegradation* 8(6), 387-392.
- Kjaer, J., Olsen, P., Henriksen, T. & Ullum, M. (2005). Leaching of metribuzin metabolites and the associated contamination of a sandy Danish aquifer. *Environmental Science & Technology* 39(21), 8374-8381.
- Klein, M. (1991). *PELMO: Pesticide leaching model*. Schmallenberg-Germany: Fraunhofer-Institut für Umweltchemie und Ökotoxikologie.
- Larsbo, M., Stenström, J., Etana, A., Börjesson, E. & Jarvis, N.J. (2009). Herbicide sorption, degradation, and leaching in three Swedish soils under long-term conventional and reduced tillage. *Soil & Tillage Research* 105(2), 200-208.
- Lentzsch, P., Wieland, R. & Wirth, S. (2005). Application of multiple regression and neural network approaches for landscape-scale assessment of soil microbial biomass. *Soil Biology & Biochemistry* 37(9), 1577-1580.

- Li, H., Sheng, G.Y., Teppen, B.J., Johnston, C.T. & Boyd, S.A. (2003). Sorption and desorption of pesticides by clay minerals and humic acid-clay complexes. *Soil Science Society of America Journal* 67(1), 122-131.
- Lindahl, A.M.L., Kreuger, J., Stenström, J., Gårdenäs, A.I., Alavi, G., Roulier, S. & Jarvis, N.J. (2005). Stochastic modelling of diffuse pesticide losses from a small agricultural catchment. *Journal of Environmental Quality* 34(4), 1174-1185.
- Liu, Z.Z., He, Y., Xu, J.M., Huang, P.M. & Jilani, G. (2008). The ratio of clay content to total organic carbon content is a useful parameter to predict adsorption of the herbicide butachlor in soils. *Environmental Pollution* 152(1), 163-171.
- Lopez, A., Mascolo, G., Foldenyi, R. & Passino, R. (1996). Disinfection by-products formation during hypochlorination of isoproturon contaminated groundwater. *Water Science and Technology* 34(7-8), 351-358.
- Mamy, L. & Barriuso, E. (2005). Glyphosate adsorption in soils compared to herbicides replaced with the introduction of glyphosate resistant crops. *Chemosphere* 61(6), 844-855.
- McConnell, J.S. & Hossner, L.R. (1985). pH-dependent adsorption isotherms of glyphosate. *Journal of Agricultural and Food Chemistry* 33(6), 1075-1078.
- McCormick, L.L. & Hiltbold, A.E. (1966). Microbiological decomposition of atrazine and diuron in soil. *Weeds* 14, 77-82.
- McKinlay, R., Plant, J.A., Bell, J.N.B. & Voulvoulis, N. (2008). Endocrine disrupting pesticides: implications for risk assessment. *Environment International* 34(2), 168-183.
- Mermoud, A., Martins, J.M.F., Zhang, D. & Favre, A.C. (2008). Small-scale spatial variability of atrazine and dinoseb adsorption parameters in an alluvial soil. *Journal of Environmental Quality* 37(5), 1929-1936.
- Moeys, J., Bergheaud, V. & Coquet, Y. (2011). Pedotransfer functions for isoproturon sorption on soils and vadose zone materials. *Pest Management Science* DOI: 10.1002/ps.2187.
- Mueller, T.C., Moorman, T.B. & Snipes, C.E. (1992). Effect of concentration, sorption, and microbial biomass on degradation of the herbicide fluometuron in surface and subsurface soils. *Journal of Agricultural and Food Chemistry* 40(12), 2517-2522.
- Muyzer, G., Dewaal, E.C. & Uitterlinden, A.G. (1993). Profiling of complex microbial populations by denaturing gradient gel electrophoresis analysis of polymerase chain reaction-amplified genes coding for 16S rRNA. *Applied and Environmental Microbiology* 59(3), 695-700.
- Nearpass, D.C. (1976). Adsorption of picloram by humic acids and humin. *Soil Science* 121(5), 272-277.
- Nunan, N., Ritz, K., Crabb, D., Harris, K., Wu, K.J., Crawford, J.W. & Young, I.M. (2001). Quantification of the in situ distribution of soil bacteria by large-scale imaging of thin sections of undisturbed soil. *Fems Microbiology Ecology* 37(1), 67-77.
- Oades, J.M. (1988). The retention of organic matter in soils. *Biogeochemistry* 5(1), 35-70.

- Oberholzer, H.R., Rek, J., Weisskopf, P. & Walther, U. (1999). Evaluation of soil quality by means of microbiological parameters related to the characteristics of individual arable sites. *Agribiological Research-Zeitschrift Für Agrarbiologie Agrikulturchemie Okologie* 52(2), 113-125.
- OECD (2000). OECD guideline for the testing of chemicals, Test No. 106: adsorption-desorption using a batch equilibrium method. *OECD Paris, France*, .
- Ogram, A.V., Jessup, R.E., Ou, L.T. & Rao, P.S.C. (1985). Effects of sorption on biological degradation rates of (2,4-Dichlorophenoxy)acetic acid in soils. *Applied and Environmental Microbiology* 49(3), 582-587.
- Oliveira, R.S., Koskinen, W.C., Ferreira, F.A., Khakural, B.R., Mulla, D.J. & Robert, P.J. (1999). Spatial variability of imazethapyr sorption in soil. *Weed Science* 47(2), 243-248.
- Peng, R.H., Xiong, A.S., Xue, Y., Fu, X.Y., Gao, F., Zhao, W., Tian, Y.S. & Yao, Q.H. (2008). Microbial biodegradation of polyaromatic hydrocarbons. *Fems Microbiology Reviews* 32(6), 927-955.
- Pignatello, J.J. & Xing, B.S. (1996). Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science & Technology* 30(1), 1-11.
- Pizzul, L., Castillo, M.D. & Stenström, J. (2009). Degradation of glyphosate and other pesticides by ligninolytic enzymes. *Biodegradation* 20(6), 751-759.
- Pusino, A., Liu, W.P. & Gessa, C. (1992). Influence of organic matter and its clay complexes on metolachlor adsorption on soil. *Pesticide Science* 36(3), 283-286.
- R Development Core Team. (2011). R: A language and environment for statistical computing. R foundation for statistical computing, Vienna, Austria. ISBN 3-900051-07-0, URL <http://www.r-project.org/> Accessed [28 Nov 2012]. In.
- Rodriguez-Cruz, M.S., Jones, J.E. & Bending, G.D. (2006). Field-scale study of the variability in pesticide biodegradation with soil depth and its relationship with soil characteristics. *Soil Biology & Biochemistry* 38(9), 2910-2918.
- Rodriguez-Cruz, M.S., Jones, J.E. & Bending, G.D. (2008). Study of the spatial variation of the biodegradation rate of the herbicide bentazone with soil depth using contrasting incubation methods. *Chemosphere* 73(8), 1211-1215.
- Sarmah, A.K. & Sabadie, J. (2002). Hydrolysis of sulfonylurea herbicides in soils and aqueous solutions: A review. *Journal of Agricultural and Food Chemistry* 50(22), 6253-6265.
- Schnitzer, M. & Kodama, H. (1992). Interactions between Organic and Inorganic Components in Particle-Size Fractions Separated from 4 Soils. *Soil Science Society of America Journal* 56(4), 1099-1105.
- Sheng, G.Y., Johnston, C.T., Teppen, B.J. & Boyd, S.A. (2001). Potential contributions of smectite clays and organic matter to pesticide retention in soils. *Journal of Agricultural and Food Chemistry* 49(6), 2899-2907.

- Si, Y.B., Takagi, K., Iwasaki, A. & Zhou, D.M. (2009). Adsorption, desorption and dissipation of metolachlor in surface and subsurface soils. *Pest Management Science* 65(9), 956-962.
- Sinsabaugh, R.L. (2010). Phenol oxidase, peroxidase and organic matter dynamics of soil. *Soil Biology & Biochemistry* 42(3), 391-404.
- Sinsabaugh, R.L., Lauber, C.L., Weintraub, M.N., Ahmed, B., Allison, S.D., Crenshaw, C., Contosta, A.R., Cusack, D., Frey, S., Gallo, M.E., Gartner, T.B., Hobbie, S.E., Holland, K., Keeler, B.L., Powers, J.S., Stursova, M., Takacs-Vesbach, C., Waldrop, M.P., Wallenstein, M.D., Zak, D.R. & Zeglin, L.H. (2008). Stoichiometry of soil enzyme activity at global scale. *Ecology Letters* 11(11), 1252-1264.
- Sonon, L.S. & Schwab, A.P. (1995). Adsorption characteristics of atrazine and alachlor in Kansas soils. *Weed Science* 43(3), 461-466.
- Sorensen, S.R., Schultz, A., Jacobsen, O.S. & Aamand, J. (2006). Sorption, desorption and mineralisation of the herbicides glyphosate and MCPA in samples from two Danish soil and subsurface profiles. *Environmental Pollution* 141(1), 184-194.
- Spadotto, C.A. & Hornsby, A.G. (2003). Soil sorption of acidic pesticides: Modelling pH effects. *Journal of Environmental Quality* 32(3), 949-956.
- Spark, K.M. & Swift, R.S. (2002). Effect of soil composition and dissolved organic matter on pesticide sorption. *Science of the Total Environment* 298(1-3), 147-161.
- Sprankle, P., Meggitt, W.F. & Penner, D. (1975). Adsorption, mobility, and microbial degradation of glyphosate in soil. *Weed Science* 23(3), 229-234.
- Steffen, K.T., Hatakka, A. & Hofrichter, M. (2003). Degradation of benzo[a]pyrene by the litter decomposing basidiomycete *Stropharia coronilla*: Role of manganese peroxidase. *Applied and Environmental Microbiology* 69(7), 3957-3964.
- Stenström, J., Svensson, K. & Johansson, M. (2001). Reversible transition between active and dormant microbial states in soil. *FEMS Microbiology Ecology* 36(2-3), 93-104.
- Thorstensen, C.W. & Lode, O. (2001). Laboratory degradation studies of bentazone, dichlorprop, MCPA, and propiconazole in Norwegian soils. *Journal of Environmental Quality* 30(3), 947-953.
- Thorstensen, C.W., Lode, O., Eklo, O.M. & Christiansen, A. (2001). Sorption of bentazone, dichlorprop, MCPA, and propiconazole in reference soils from Norway. *Journal of Environmental Quality* 30(6), 2046-2052.
- Tiktak, A., de Nie, D., van der Linden, T. & Kruijne, R. (2002). Modelling the leaching and drainage of pesticides in the Netherlands: the GeoPEARL model. *Agronomie* 22(4), 373-387.
- Tiktak, A., Hendriks, R.F.A. & Boesten, J.J.T.I. (2012). Simulation of movement of pesticides towards drains with a preferential flow version of PEARL. *Pest Management Science* 68(2), 290-302.
- Torstensson, L. & Stenström, J. (1986). 'Basic' respiration rate as a tool for prediction of pesticide persistence in soil. *Toxicity Assessment* 1, 57-72.

- Vanderheyden, V., Debongnie, P. & Pussemier, L. (1997). Accelerated degradation and mineralization of atrazine in surface and subsurface soil materials. *Pesticide Science* 49(3), 237-242.
- Villaverde, J., Kahl, M. & Brown, C.D. (2008). Adsorption and degradation of four acidic herbicides in soils from southern Spain. *Pest Management Science* 64(7), 703-710.
- Vink, J.P.M. & van der Zee, S.E.A.T.M. (1997). Effect of oxygen status on pesticide transformation and sorption in undisturbed soil and lake sediment. *Environmental Toxicology and Chemistry* 16(4), 608-616.
- Vinther, F.P., Brinch, U.C., Elsgaard, L., Fredslund, L., Iversen, B.V., Torp, S. & Jacobsen, C.S. (2008). Field-scale variation in microbial activity and soil properties in relation to mineralization and sorption of pesticides in a sandy soil. *Journal of Environmental Quality* 37(5), 1710-1718.
- von Gotz, N. & Richter, O. (1999). Simulation of herbicide degradation in different soils by use of pedo-transfer functions (PTF) and non-linear kinetics. *Chemosphere* 38(6), 1401-1407.
- Walker, A., Brown, P.A. & Mathews, P.R. (1985). Persistence and phytotoxicity of napropamide residues in soil. *Annals of Applied Biology* 106(2), 323-333.
- Walker, A., Cotterill, E.G. & Welch, S.J. (1989). Adsorption and degradation of chlorsulfuron and metsulfuron-methyl in soils from different depths. *Weed Research* 29(4), 281-287.
- Walker, A., Jurado-Exposito, M., Bending, G.D. & Smith, V.J.R. (2001). Spatial variability in the degradation rate of isoproturon in soil. *Environmental Pollution* 111(3), 407-415.
- Walker, A., Moon, Y.H. & Welch, S.J. (1992). Influence of temperature, soil moisture and soil characteristics on the persistence of alachlor. *Pesticide Science* 35(2), 109-116.
- Walker, A. & Thompson, J.A. (1977). Degradation of simazine, linuron and propyzamide in different soils. *Weed Research* 17(6), 399-405.
- Walker, A., Turner, I.J., Cullington, J.E. & Welch, S.J. (1999). Aspects of the adsorption and degradation of isoproturon in a heavy clay soil. *Soil Use and Management* 15(1), 9-13.
- Wang, Y.J., Zhou, D.M. & Sun, R.J. (2005). Effects of phosphate on the adsorption of glyphosate on three different types of Chinese soils. *Journal of Environmental Sciences-China* 17(5), 711-715.
- Wauchope, R.D., Yeh, S., Linders, J.B.H.J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kordel, W., Gerstl, Z., Lane, M. & Unsworth, J.B. (2002). Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. *Pest Management Science* 58(5), 419-445.
- Weber, J.B., Wilkerson, G.G. & Reinhardt, C.F. (2004). Calculating pesticide sorption coefficients ( $K_d$ ) using selected soil properties. *Chemosphere* 55(2), 157-166.
- Weber, W.J., Mcginley, P.M. & Katz, L.E. (1992). A distributed reactivity model for sorption by soils and sediments .1. conceptual basis and equilibrium assessments. *Environmental Science & Technology* 26(10), 1955-1962.

- Whelan, M.J., Davenport, E.J. & Smith, B.G. (2007). A globally applicable location-specific screening model for assessing the relative risk of pesticide leaching. *Science of the Total Environment* 377(2-3), 192-206.
- Wichern, F. & Joergensen, R.G. (2009). Soil microbial properties along a precipitation transect in Southern Africa. *Arid Land Research and Management* 23(2), 115-126.
- Worrall, F., Parker, A., Rae, J.E. & Johnson, A.C. (1996). Equilibrium adsorption of isoproturon on soil and pure clays. *European Journal of Soil Science* 47(2), 265-272.
- Xing, B.S., Pignatello, J.J. & Gigliotti, B. (1996). Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environmental Science & Technology* 30(8), 2432-2440.
- Xu, D.P., Xu, Z.H., Zhu, S.Q., Cao, Y.Z., Wang, Y., Du, X.M., Go, Q.B. & Li, F.S. (2005). Adsorption behavior of herbicide butachlor on typical soils in China and humic acids from the soil samples. *Journal of Colloid and Interface Science* 285(1), 27-32.



## Acknowledgements

I feel proud to express thanks to many visible and invisible people whose enthusiastic encouragement and untiring support deserve due recognition.

Nick, it is my luck to find you. Your keen interest and encouraging behaviour, sympathetic attitudes, animate directions, observant pursuit, scholarly criticism, invaluable suggestions and corrections, masterly advice and indefatigable assistance at all times during the entire study programme are commendable. Thanks for interesting discussions about the project, manuscripts and all the help with writing. I would never be able to finish this doctoral thesis without your immense patience, ever-inspiring guidance and encouragements. I am very grateful to you.

John, until I had my first few interactions with you, I never imagined that you could be so supportive and friendly. My stay at microbiological lab was tremendous experience of learning in your guidance. You always motivated and guided me in lab work. I express great appreciation and sincerest gratitude for your constructive criticism, friendly behaviour, technical advice and candour during my research work.

Julien, I am extremely thankful to you. You helped me to increase my expertise in R programming language. You were always being there when I needed some talk about R codes. Always, I would remember your friendly and soft behaviour.

Mats and Johannes: I am very thankful to you for your helping hands during soil column sampling, in the lab and making sure everything was up and running.

Jenny and Lars: thank you very much for providing me such a nice working environment, invaluable advice on many occasions and help to arrange financial assistance for research.

I am very grateful to Sarah and Simon (Mälardalens University) for their assistance during my early days in Sweden.

My thanks also go to my colleagues at the Department of Soil and Environment, and Department of Microbiology for creating a friendly work environment and for giving help when it was needed: Elisabet Börjesson, Leticia Pizzul, Harald Cederlund, Karin Öneby, Elisabet Lewan, Anna Lindahl, Grant Tranter, Karin Steffens, Jian Liu, Anders Lindsjö, Kristina Mårtensson, Katarina Kyllmar, Karin Blombäck, Dennis Collentine, Ararso Etana, Stefan Andersson, Ingmar Messing, Barbro Ulén, Helena Aronsson, Helena Andersson, Annika Svanbäck, Pia Kynkäänniemi, Maria Sandin, Frank Schmieder, Kristian Persson, Masud Parvage, Lovisa Forsberg, Gunnel Alvenäs, Gunnar Torstensson, Göran Johansson, Ing-Marie Bringholm, Ragnar Persson, Anne Olsson.

Special thanks to my Pakistani friends in Uppsala, without whom I might find myself a fish out of water. Dr. Abro, Dr. Naeem, Dr. Munir, Dr. Rakha, Mazhar, Khuram, Goraya, Usman, Shezi, Rehmat, Nadeem, Imran, Asif, Rizwan, Aqib, Ramzan, Akhtar, Alvi and all others: thanks for all the good memories of rowing together in the open and fairly deep river of Uppsala and then in open and wide lake Mälaren, grill parties during summer days and indoor parties when Sweden turns to its habitual lengthy, white and frozen winters.

I am grateful to my Swedish family friends: Abdul Ghafoor (Stockholm), Syed Shah (Eskilstuna), and Björn, Mery and Martin, Sabine, and Nargis from Uppsala for their friendly discussions and kindness shown to my family.

Last but not the least, many thanks to my beloved Family for their understanding and endless love, support, and prayers. I ♥ you. My grandfather, who is the role model in my whole life. His encouragement to be hard worker in every walk of life was started long ago when I turned eight. My late grandmother, whose love and affection I could never forget. My father and late mother, who always fulfilled my wish lists and prayed tirelessly for me. Mom, you left me so early but I always feel your love and affections you had given to me only for five years. I am highly grateful to my Uncle Nisar Awan and Aunt Irshad Alvi for their words of advice and their help during my studies. Their kindness is blessing for me. Words fail me to express my appreciation to my better half for her support, encouragement and persistence confidence in me to pursue this degree. I ♥ you.