

**CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE**

**Faculty of Agrobiolgy, Food and Natural Resources**

**Department of Soil Science and Soil Protection**



**Impact of Compost Addition on Chlorotoluron  
Sorption in Soil**

Diploma Thesis

Author: Martina Hýbler

Advisor: Ing. Martin Kočárek, Ph.D.

Co-supervisor: Prof. Dipl.-Ing. Dr. Walter W. Wenzel

2012

## **Declaration**

I declare that the diploma thesis on the theme Impact of Compost Addition on Chlorotoluron Sorption in Soil was worked out separately. Only quoted sources mentioned in references were used.

Prague, 19.3.2012

## **Acknowledgements:**

I would like to thank very much to Ing. Martin Kočárek, Ph.D. for giving me valuable advices, guidance of my diploma thesis and help during the laboratory work. I also thank to Prof. Dipl.-Ing. Dr. Walter W. Wenzel for consultations. I thank to Ing. Ondřej Drabek, Ph.D. for CEC determination, Ing. Antonín Nikodem and Ing. Josef Kratina for help in laboratory. I also would like to thank to Monica Ortiz and Tim Cassidy for correction of the text, Denise Thiel for technical support and to my family for overall support and understanding.

## Summary

For a long time society has given increased attention to the possible negative effects of pesticides on the environment and human health. In particular the aquatic environment, which is especially sensitive to pesticide pollution. Consequently before pesticides are released for use, it is necessary to minimise risks by investigating both their properties and potential negative impacts on different components of the environment.

Although pesticides use provides certain benefits associated with preventing the emergence and spread of plant pest populations, there are significant potential risks. For example, the main risks include soil contamination at the site of use, or pesticide movement through the soil profile into groundwater.

This diploma thesis specifically focused on exploring rates of pesticide chlorotoluron sorption in soil. The objective was to determine which soil characteristics influence the parameters of the Freundlich ( $K_F$  a  $1/n$ ) and Langmuir ( $K_L$  a  $s_{max}$ ) equations. Subsequently the experiment was undertaken in two stages: the first stage involved the determination of chlorotoluron sorption in soil samples and the second stage assessed the soil characteristics.

At first, a simple linear regression was used for testing dependency of soil properties on the parameters of Freundlich and Langmuir equations. Subsequently, Freundlich adsorption coefficient  $K_F$  (for the fixed  $n$  value) was tested, it was found that the coefficient  $K_F$  was affected by organic matter content ( $C_{OX}$ ) and salinity. Also the dependency of soil properties on  $K_F$  (for the fixed  $n$  value) was examined by using multiple linear regression. Furthermore, by using this method the possibility of applying pedotransfer rules according to Kozák and Vacek (2000) and Kodešová et al. (2011) was verified. In applying these pedotransfer rules on examined soil samples were not found statistically significant relationships among soil characteristics and Freundlich adsorption coefficient  $K_F$ , and therefore was sought in this part of the thesis a new pedotransfer rule.

*Keywords:* Chlorotoluron, Luvic Chernozem, Sorption, Adsorption Isotherm, Pedotransfer Rules

## Souhrn

Společností je dlouhodobě věnována zvýšená pozornost možným negativním vlivům pesticidů na životní prostředí a lidské zdraví. Zejména vodní prostředí je na znečištění pesticidy obzvláště citlivé. Proto je před použitím pesticidů třeba znát nejen jejich vlastnosti, ale také jejich negativní působení na jednotlivé složky životního prostředí, tak aby bylo možné tyto vlivy minimalizovat.

Je zřejmé, že používání pesticidů má svůj účel, který přináší společnosti na jednu stranu výhody (zabránění vzniku a šíření populací plevelů, škůdců), avšak na druhou stranu, má také negativní účinky. Těmi hlavními jsou například kontaminace půdy v místě jejich použití anebo jejich pohyb půdním profilem do spodních vod.

Tato diplomová práce byla zaměřena především na zkoumání míry sorpce pesticidu chlorotoluronu v půdě. Cílem bylo provést pokus, který se skládal ze dvou částí, přičemž první jeho část se týkala stanovení sorpce chlorotoluronu v půdních vzorcích a druhá pak, z určení jejich půdních vlastností. V souvislosti s tím bylo posuzováno, které půdní vlastnosti ovlivňují parametry Freundlichovy ( $K_F$  a  $1/n$ ) a Langmuirovy ( $K_L$  a  $s_{max}$ ) rovnice.

Nejprve byla za pomoci jednoduché lineární regrese testována závislost jednotlivých půdních vlastností na parametrech Freundlichovy a Langmuirovy rovnice. Následně byl testován Freundlichův adsorpční koeficient  $K_F$  (za podmínek konstantního  $n$ ), čímž bylo zjištěno, že tento koeficient  $K_F$  byl ovlivněn obsahem organické hmoty ( $C_{OX}$ ) a salinitou. Taktéž byla zkoumána závislost půdních vlastností na  $K_F$  (za podmínek konstantního  $n$ ) metodou vícenásobné lineární regrese. Dále byla pomocí této metody ověřována možnost aplikace pedotransferových pravidel dle Kozáka a Vacka (2000) a Kodešové et al. (2011). Při aplikaci těchto pedotransferových pravidel na zkoumaných půdních vzorcích nebyla zjištěna statistická závislost mezi půdními vlastnostmi a Freundlichovým adsorpčním koeficientem  $K_F$ , a proto bylo v rámci této části práce hledáno nové pedotransferové pravidlo.

*Klíčová slova:* Chlorotoluron, sorpce, černozem luvická, adsorpční izoterma, pedotransferové pravidlo

## Content:

1.	Introduction .....	1
2.	Hypothesis and Aim of the Diploma Thesis .....	3
3.	Literature Review .....	4
3.1	Pesticides and Soil .....	4
3.1.1	Classification of Pesticides, Technique and Time of Application .....	5
3.1.2	Alternatives to Pesticides .....	6
3.2	The Fate of Pesticides in the Soil and in the Environment .....	7
3.2.1	Characteristics Governing the Fate of Pesticides.....	8
3.2.2	Negative Impacts of Pesticides throughout their Lifecycle.....	10
3.3	Physical-chemical Properties of Pesticides .....	12
3.3.1	Solubility.....	13
3.3.2	Octanol/Water Partition Coefficient ( $K_{ow}$ ).....	14
3.3.3	Distribution Coefficient ( $K_d$ ) .....	15
3.3.4	Organic Carbon Partition Coefficient ( $K_{oc}$ ).....	15
3.3.5	Vapour Pressure ( $P_{vp}$ ) .....	17
3.3.6	Henry's Law Constant ( $H'$ ) .....	17
3.3.7	Bioconcentration Factor (BCF) .....	18
3.4	Physical-chemical Properties of Soil .....	19
3.4.1	Soil Organic Matter Content .....	19
3.4.2	Dissolved Organic Carbon (DOC).....	20
3.4.3	Clay Content.....	21
3.4.4	Particle Density ( $\rho_z$ ) .....	22
3.4.5	Porosity .....	23
3.4.6	pH .....	24
3.5	Sorption.....	25
3.5.1	Factors Governing Sorption .....	26
3.5.2	Adsorption Isotherm .....	27
3.6	Degradation.....	31
3.6.1	Biotic Degradation.....	32
3.6.2	Abiotic Degradation .....	33
3.6.3	Degradation of Chlorotoluron in Soils.....	36
3.7	Transport.....	36
3.7.1	Volatilization .....	37
3.7.2	Runoff and Leaching.....	38
3.8	Pesticide Bioavailability.....	39
3.9	Pedotransfer Rules.....	40

4.	Materials and Methods.....	42
4.1	Description of Chlorotoluron .....	42
4.2	Soil.....	42
4.3	Determination of Adsorption Isotherms.....	43
4.3.1	Determination of Adsorption Isotherm in Laboratory.....	43
4.3.2	Calculation of Adsorption Isotherms .....	45
4.3.3	Interlay of Measured Points with Freundlich and Langmuir Adsorption Isotherms.....	46
4.4	Determination of Chlorotoluron in Solution.....	48
4.5	Determination of Soil Characteristics .....	49
4.5.1	Determination of Soil Texture and Particle Density $\rho_2$ .....	49
4.5.2	Soil Active pH Determination.....	50
4.5.3	Soil Exchangeable pH Determination.....	50
4.5.4	Spectrophotometric Determination of Humus Quality .....	50
4.5.5	Determination of Hydrolytic Acidity .....	51
4.5.6	Determination of Cation Exchange Capacity according to Bower .....	51
4.5.7	Determination of Humus Content by Tjurin Method .....	52
4.5.8	Determination of Carbonates .....	52
4.5.9	Salinity .....	52
5.	Results.....	54
5.1	Behaviour of Adsorption Isotherms for Chlorotoluron.....	54
5.2	Statistical Outcomes .....	56
5.2.1	Application of Linear Regression to Examine the Dependence of Freundlich and Langmuir Parameters on Soil Characteristics .....	56
5.2.2	Adsorption Coefficient $K_F$ (for the fixed $n$ value) .....	59
5.2.3	Testing for an Alternative Pedotransfer Rule .....	60
6.	Discussion.....	65
7.	Conclusion.....	67
8.	References.....	68
9.	List of used abbreviations .....	75
10.	Appendix.....	76

## List of Figures:

Figure 1:	Integrated pest management (IPM)/integrated crop management (ICM) the need to integrate different techniques (Matthews, 2000) .....	7
Figure 2:	Interactions influencing the fate of the pesticide (Hutson and Roberts, 1990) .....	8
Figure 3:	Factors governing the fate of pesticides in soil (Hutson and Roberts, 1990) .....	9
Figure 4:	Types of adsorption isotherm (Sposito, 1984 in Sparks, 1995) .....	28
Figure 5:	Adsorption isotherms of chlorotoluron for soil sample A (A) and soil sample B (B).....	54
Figure 6:	Adsorption isotherms of chlorotoluon for soil sample C (A) and soil sample D (B) .....	54
Figure 7:	Adsorption isotherms of chlorotoluron for soil sample E (A) and soil sample F (B) .....	55
Figure 8:	Adsorption isotherms of chlorotoluon for soil sample G (A) and soil sample H (B).....	55
Figure 9:	Graph of correlation between $1/n$ and $C_{ox}$ ; P-value = 0.0088, $R^2 = 0.707974$ .....	56
Figure 10:	Graph of correlation between $K_L$ and $C_{ox}$ ; P-value = 0.0135, $R^2 = 0.665547$ .....	57
Figure 11:	Graph of correlation between $K_L$ and $V_d$ ; P-value = 0.0068, $R^2 = 0.730697$ .....	57
Figure 12:	Graph of correlation between $S_{max}$ and $C_{ox}$ ; P-value = 0.0101, $R^2 = 0.694999$ .....	57
Figure 13:	Adsorption isotherms of soil sample A (A) and soil sample B (B) .....	58
Figure 14:	Adsorption isotherms of soil sample C (A) and soil sample D (B) .....	58
Figure 15:	Adsorption isotherms of soil sample E (A) and soil sample F (B) .....	58
Figure 16:	Adsorption isotherms of soil sample G (A) and soil sample H (B).....	59
Figure 17:	Graph of Freundlich adsorption coefficient $K_F$ and its dependence on observed soil characteristics ( $C_{ox}$ and salinity); P-value = 0.0284, $R^2$ value = 0.76.....	61
Figure 18:	Graph of Freundlich adsorption coefficient $K_F$ and its dependence on observed soil characteristics ( $C_{ox}$ , salinity and particle density); P-value = 0.0304, $R^2$ value = 0.87 .....	62
Figure 19:	Graph of Freundlich adsorption coefficient $K_F$ and its dependence on observed soil characteristics (sand, $C_{ox}$ and salinity); P-value = 0.0276, $R^2$ value = 0.876 .....	63
Figure 20:	Graph of Freundlich adsorption coefficient $K_F$ and its dependence on observed soil characteristics (silt, $C_{ox}$ and salinity); P-value = 0.0374, $R^2$ value = 0.855 .....	64



## List of Tables:

Table 1:	Solubility of pesticides and their distribution in environment (Linde, 1994) .....	13
Table 2:	Mobility classification based on $K_{OC}$ (McCall et al., 1981 in Roberts and Kearney, 1995)..	16
Table 3:	Characteristics of some common clay minerals (Tarasevich et al, 1975 in Morrill et al., 1982) .....	22
Table 4:	Chemical properties of chlorotoluron (IUPAC global availability of information on agrochemicals, 2011) .....	42
Table 5:	The amounts of Syncuran used for the attainment of required concentration of chlorotoluron in a solution and measured concentration of chlorotoluron in solutions ..	44
Table 6:	Soil characteristics.....	53
Table 7:	Parameters of Freundlich and Langmuir adsorption isotherm.....	55

## 1. Introduction

During the past, several decades, increasingly more chemicals have been manufactured for use in the everyday activities of mankind. These range from ordinary cleaning agents, detergents, industrial chemicals, biocidal products to agricultural chemicals. Their negative impact on human health and environment has been recognised and are considered to be organic pollutants.

The increasing demand for producing food for the continuously growing human population is provided by the intensification of agriculture, and therefore the agrochemicals are used in spite of their side effects. The utilisation of pesticides is needed for optimizing the yield or quality crops and it is a cost effective and rapid way of removing the undesirable pests, weeds and diseases.

The usage of pesticides on agricultural areas is one of the sources of chemical contamination of our environment, especially of soil and water. The magnitude of negative effects caused by pesticides to our environment is influenced by both chemical-physical properties of a soil and a pesticide, but also by weather conditions. The main chemical-physical properties of the pesticide influencing its behaviour in environment are: solubility, octanol/water partition coefficient, vapor pressure, organic carbon partition coefficient or distribution coefficient. On the other hand, the pesticide's behaviour is also affected by the chemical-physical properties of the soil. The main soil properties influencing pesticide behaviour in soil are: content of soil organic matter, clay content, porosity or pH.

Once the pesticide is applied on crops, it starts to move throughout the environment. Before the pesticide penetrates into the soil, it is partly absorbed by plants, degraded by light or it volatilizes into the atmosphere and it might be transported faraway from its original source. When it enters the soil, it begins to move through the soil profile, but it is also degraded by microorganisms. It depends very much on the pesticide's sorption how the pesticide will be transported. Sorption is an important process in determination of the pesticide's fate in the environment and therefore it is examined. When the pesticide is strongly bonded to soil particles, the groundwater sources are less endangered by the pesticide's contamination. On the other hand, when the pesticide is not sorbed on soil particles and remains in the soil solution, there is a great danger of leaching.

Pesticides pose a danger not only to our environment, but also to the living organisms, including humans. Throughout the pesticide's lifecycle it is absorbed by crops and animals and it occurs in water, so it can be accumulated in food chains and be transferred with food or water into the human's body.

## 2. Hypothesis and Aim of the Diploma Thesis

### Hypothesis

The higher the content of humus is the higher is the chlortoluron sorption on soil.

The main objectives of this diploma thesis are following:

- to become familiar with properties of pesticides and soil which influence their behaviour in environment,
- to carry out an experiment for the determination of the soil properties,
- to carry out an experiment for defining the soil sorption,
- to assess which soil properties influence sorption of chlorotoluron in soil,
- to find pedotransfer rule for prediction of chlorotoluron  $K_F$  in soil.

### 3. Literature Review

#### 3.1 Pesticides and Soil

According to Kutilek and Nielsen (1994) without soil, our planet would not be green and all life would be restricted to the oceans. They defined soil as a very thin layer of the earth when its thickness is compared to the dimensions of the atmosphere or geosphere. Even the average depth of water in the oceans is orders of magnitude greater than that of soil. In spite of its slim dimension, soil is indispensable for life on continents.

A pesticide can be defined as any substance or mixture of substances intended for preventing, destroying or repelling any insect, nematode, fungus, insect, weed or any other form of terrestrial or aquatic plant or animal or microbiological life, and for use as a plant regulator, defoliant or desiccant (Khan, 1980).

The principles of seed treatment, fumigation and the use of certain preparations to kill unwanted pests were known to the ancient agriculturalists (Khan, 1980). Pesticides were first used in agricultural production in the second half of the 19<sup>th</sup> century. Examples included lead, arsenic, copper, and zinc salts, and naturally produced plant compounds such as nicotine. These were used for insect and disease control on crops. In the 1930s and 1940s 2,4-D, an herbicide, and DDT, an insecticide, were introduced; subsequently, increasing amounts of pesticides were used in agricultural production worldwide (Sparks, 1995).

Linde (1994) reported that pesticides are distributed in the environment by physical processes such as sedimentation, adsorption, and volatilization. Also transport processes (runoff and leaching) are involved (Khan 1980; Calvet and Barriuso, 1994).

Pesticides can then be degraded by chemical and/ or biological processes. Chemical processes generally occur in water or the atmosphere and follow one of four reactions: oxidation, reduction, hydrolysis, and photolysis. Biological mechanisms in soil and living organisms utilize oxidation, reduction, hydrolysis and conjugation to degrade chemicals (Linde, 1994).

Chlorotoluron belongs to a group of phenylurea herbicides together with isoproturon, metobromuron, chloroxuron and difenoxuron (Fouqué-Brouard and Fournier, 1996). Today about 25 phenylurea herbicides are marketed. They are used as pre or post

emergence herbicides for the control of annual grasses and broad leafed weeds, for example in cereals (Vroumsia et al., 1996).

The total chlorotoluron consumption in the Czech Republic in 2009 was 148 064.8 kg according to the State Phytosanitary Administration (2009). Chlorotoluron was the seventh most frequently used herbicide in the Czech Republic used to control cereals weeds (Chlormequat-chlorid, 636 958.0 kg; Glyphosate-IPA, 410 755.1 kg; Acetochlor, 291 999.4 kg; Glyphosate, 263 907.8 kg; Metazachlor, 180 863.6 kg; Glyphosate-potassium, 161 678.1 kg).

### 3.1.1 Classification of Pesticides, Technique and Time of Application

Pesticides can be classified in many different ways: according to the target pest, as herbicides, those are used to control weeds, insecticides, to control insects, fungicides, to control fungi, and others such as nematicides and rodenticides (Sparks, 1995), the chemical structure of the compound used, or the degree or type of health hazard involved (Gevao et al., 2000).

The mode of action of a pesticide can influence the selection of an application technique and timing of application. An insecticide may be effective by contact, by ingestion (stomach poison) or by inhalation (fumigant effect). Similarly, fungicides and herbicides may have contact activity, or be effective within a plant by systematic activity upwards, or be translocated across leaves and in some cases, e.g. glyphosate, downwards into the rhizomes of grasses. Some pesticides have sufficient persistence that timing is less critical compared with other chemicals, which break down very rapidly; however, the latter characteristic allows a pesticide to be applied closer to the time of harvesting a crop (Matthews, 2000).

Systematic chemicals are redistributed in plants by upward movement, so ideally they are applied as granules in the soil or as a seed treatment. A major advantage of a seed treatment is that very little of the pesticide is applied, and being localised it is less disruptive of non-target organisms. Treatments at planting will often protect young seedlings for up to six weeks, depending on the insecticide used and dosage applied (Matthews, 2000).

### 3.1.2 Alternatives to Pesticides

Several alternative approaches to crop protection and pest control have been used with varying degrees of success. Prior to the development of modern pesticides, man had widely used cultivation practices and plant breeding as traditional methods (Khan, 1980).

Farmers had to rely first and foremost on the selection of cultivars resistant to pests and diseases. Unfortunately, not all resistant cultivars were acceptable in terms of the harvested produce due to bitter taste, poor yield or some other negative factor. Farmers therefore adopted various cultural techniques, including crop rotation, closed seasons with destruction of crop residues, intercropping (Matthews, 2000), timing of sowing dates, timing of harvesting (Khan, 1980) and other practices, to mitigate pest damage (Matthews, 2000). Biological control was also an important factor in suppressing pest populations, but many of these basic techniques were forgotten due to the perceived convenience of applying chemical controls. The use of modern methods of manipulating genes in transgenic crops merely speeds up the process of selection of new crop cultivars. Whether they will provide a sustainable system of crop production has yet to be demonstrated (Matthews, 2000).

In integrated pest management programmes (Figure 1), instead of application of conventional insecticides, there is an increasingly important role for pheromones, which can be used in mass disruption programmes or in combination with insecticides as a “lure and kill” strategy. Various techniques are used to deploy the pheromone or other form of attractant, but it is often incorporated with the insecticide inside a trap or on a surface on which the attracted insects will walk (Matthews, 2000).

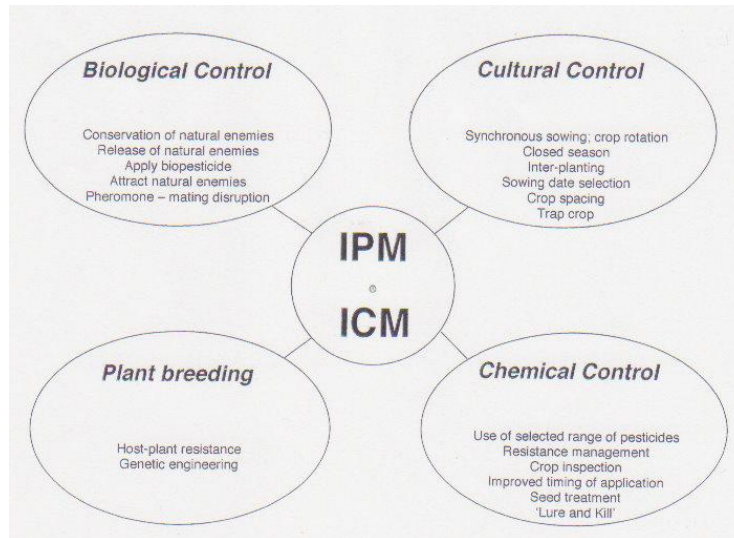


Figure 1: Integrated pest management (IPM)/integrated crop management (ICM) the need to integrate different techniques (Matthews, 2000)

### 3.2 The Fate of Pesticides in the Soil and in the Environment

Once they reach the soil, organic chemicals, such pesticides or hydrocarbons, according to Brady and Weil (1999) move in one or more of seven directions:

1. they may vaporize into the atmosphere without chemical change;
2. they may be absorbed by soils;
3. they may move downward through the soil in liquid or solution form and be lost from the soil by leaching;
4. they undergo chemical reactions within or on the surface of the soil;
5. they may be broken down by soil microorganisms;
6. they may wash into streams and rivers in surface runoff; and
7. they may be taken up by plants or soil animals and move up the food chain.

It is the combination of events whether climatic, soil-derived or the inherent properties of the chemical itself that determines what will happen to that compound. The complexities of the interactions are indicated in Figure 2.

The fate of a chemical will be substantially influenced by events:

1. a compound applied to dry soil with no rainfall will not leach, irrespective of its relative persistence,



2. a short - lived compound applied under cool, wet conditions may leach to lower soil horizons where microbial activity is reduced and thereby its persistence increased,
3. a relatively non-mobile parent compound may rapidly hydrolyze in wet conditions to a more mobile metabolite which, in turn, is rapidly degraded during its path down the soil profile (Hutson and Roberts, 1990).

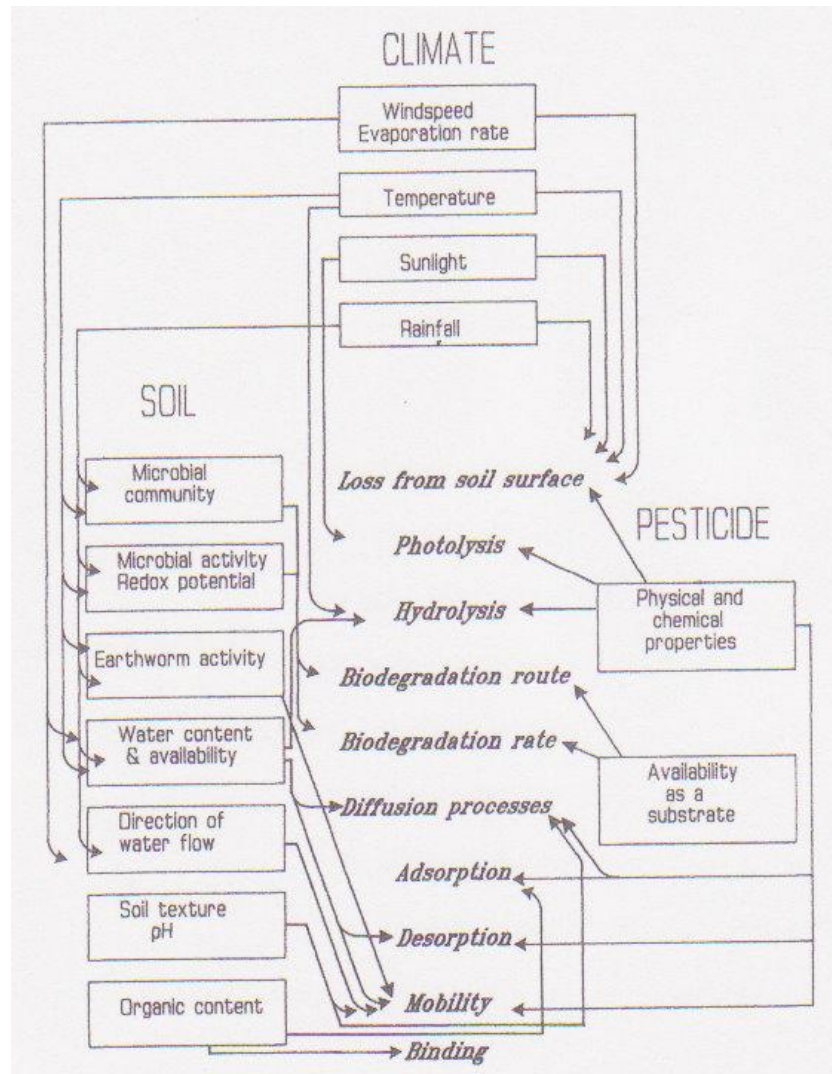


Figure 2: Interactions influencing the fate of the pesticide (Hutson and Roberts, 1990)

### 3.2.1 Characteristics Governing the Fate of Pesticides

The principal factors governing the fate of a chemical, be it xenobiotic or natural, in the field are given in Figure 3. The chemical structure defines the intrinsic properties of the compound, the soil defines the properties of the medium containing it and the climate

defines the temperature, water and air fluxes. Fate is determined by the complex interactions of all three (Hutson and Roberts, 1990).

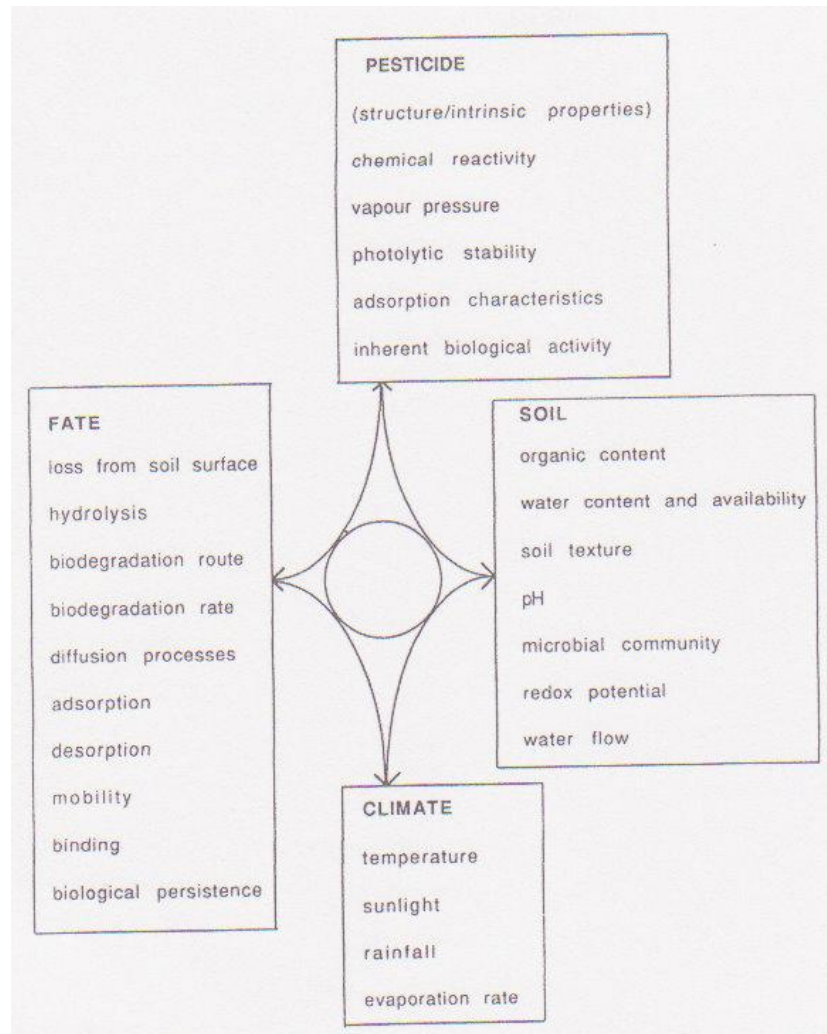


Figure 3: Factors governing the fate of pesticides in soil (Hutson and Roberts, 1990)

According to Linde (1994), octanol/water partition coefficient is also an indicator of the environmental fate of a chemical since it gives a general idea of how the chemical will be distributed in the environment. Khan (1980), Fushiwaki and Urano (2001) stated another important physicochemical characteristic governing the fate of pesticides in the environment - adsorption on soil. Guo et al. (2000) mentioned that sorption and degradation are the two most important processes governing fate and transport of chemical contaminants in the environment and the understanding of their relationship would help in the management of pesticides in agricultural fields and in the assessment of their potential to contaminate

ground water. In addition, Fouqué-Brouard and Fournier (1996) reported that an understanding of the sorption mechanism is fundamental for predicting the fate and distribution of many organic contaminants. Brady and Weil (1999) added that the specific fate of chemicals will be determined at least in part by their chemical structures, which are very variable. Khan (1980) suggested that movement and decomposition are also the factors, which influence the fate of pesticides in soil.

### 3.2.2 Negative Impacts of Pesticides throughout their Lifecycle

#### 3.2.2.1 Soil Contamination

Soil is one of the most important parts of the natural environment and largely non-renewable. Soils as a natural resource perform a number of key environmental, social and economic functions (Blum, 2005). Direct application of pesticides may result in an accumulation of their residues in soil. Another source of pesticides in soil is the residues of these chemicals in the atmosphere, either in dust or in rainwater, which can be washed out by precipitation and fall onto the soil (Khan, 1980).

Agriculture and forestry do not only produce biomass above the ground but also influence the quality and quantity of the ground water production underneath, because each drop of rain falling on the land has to pass the soil before it becomes ground water (Blum, 2005). The potential pathways, which water and soluble pesticide may follow in soil, can determine the ultimate fate and degree of water source contamination (Roberts and Kearney, 1995). It is almost impossible to apply pesticides in such a way that only the target pest is exposed. It is natural that chemicals applied almost anywhere in the environment will tend to be distributed to all of the surrounding environment (Kennedy et al., 2000). On the other hand, soil acts like an active filter, where chemical compounds are degraded by physical, chemical and biological processes. It is also a selective filter because of its capacity to retain chemicals and avoid their seepage into aquifers (Cornejo et al., 2000).

Both the accumulation of pesticides in the soil and their dispersion in the environment depend chiefly on the characteristics and overall functioning of the ecosystem. Among the most important factors to consider are the physico-chemical and biological properties of the soil (texture, structure, pH, organic matter content and microbiological

activity), environmental conditions (mainly temperature and humidity) and the characteristics of the pesticide itself (Sánchez et al., 2004).

#### 3.2.2.2 Water Contamination

It is known that chemicals reach bodies of water by transportation through soil after generic manmade operation of land “disposal” of liquids. Examples of this include: irrigation with low quality waters, groundwater recharge operations involving partially treated wastewaters, and excessive fertilization and pesticide practices (Petruzzelli et al., 1991).

Persistence and leaching of pesticides determine the possible contamination of groundwater (Fouqué-Brouard and Fournier, 1996). The harmful impact of pesticides on groundwater in Japan was described by Fushiwaki and Urano (2001). They also suggested that pesticides in river water are biodegraded by microorganisms, although some are adsorbed on suspended solids and accumulate in sediment. Hutson and Roberts (1990) added that there is a general belief that the biological activity in underground waters is so low that the pesticides will remain there and possibly accumulate over many years.

Cohen et al. (1984, in Hutson and Roberts, 1990) proposed a set of environmental fate criteria which would indicate whether particular pesticides have the potential to reach ground water in hydrogeologically sensitive areas, having 25 cm/yr of recharge to ground water, “porous soil” and unconfined ground water (i.e., not artesian) and following leaching criteria:

- Pesticide mobility:
  - Water solubility – greater than about 30 ppm (this is not always reliable prediction criteria);
  - $K_d$  – less than 5, and usually less than 1 to 2 (where  $K_d$  = soil/water distribution coefficient);
  - $K_{oc}$  - less than 300 - 500 ( $K_d$  divided by organic carbon content);
  - Henry’s Law constant – less than  $10^{-2}$  atm - m<sup>3</sup>/mol;
  - Speciation – negatively charged (either fully or partially) at ambient pH;
  - GUS (Gustafson, 1989).

- Pesticide persistence:
  - Hydrolysis half-life – greater than about 25 weeks;
  - Photolysis half-life – greater than about 1 week (but this criteria is only important while the pesticide is on the surface);
  - Soil half-life – greater than about 2 - 3 weeks (Cohen et al., 1984 in Hutson and Roberts, 1990).

### 3.2.2.3 Atmosphere Contamination

The primary source of pesticides is its application in agriculture. A pesticide applied in the soil can be released to the atmosphere through diffusive fluxes as well as through evaporation of water contaminated by pesticides. The latter represents non-diffusive sources (emission). From the atmosphere, a pesticide can enter the underlying surface in two ways through, again, diffusive fluxes and through precipitation (removal, sinks). Such a secondary contamination of the underlying surface leads to similar exchange processes between the surface and the atmosphere as those concerning the primary contamination, and so on (Koziol and Pudykiewicz, 2000).

Volatile pesticides are transported all over the globe mainly through the motion of the atmosphere with other compartments playing an important role as the complicated system of sources and sinks (Koziol and Pudykiewicz, 2000).

## 3.3 Physical-chemical Properties of Pesticides

When a pesticide is used in the environment, it becomes distributed among four major compartments: water, air, soil, and biota (living organisms). The fraction of the chemical that will move into each compartment is governed by the physico-chemical properties of that chemical (Linde, 1994).

There is a large number of pesticides currently in use, with a wide range of physico-chemical properties and belonging to a wide variety of chemical classes. Clearly, the physico-chemical properties of a given pesticide will govern its behaviour in the soil and its biological activity (Gevao et al., 2000). Moreover, Gevao et al. (2000) described molecular

size, ionisability, water solubility, lipophilicity and volatility as key properties of a pesticide, but generally, one or two properties have a dominating influence.

### 3.3.1 Solubility

The water solubility is according to Linde (1994) a measure of the amount of chemical that can dissolve in water. The units of solubility are generally in ppm (parts per - million) which is mg/ L (milligrams per litre). Agrochemicals display a wide range of solubilities in different solvents or phases in the environment (Kennedy et al., 2000). Solubility of a pesticide in water is sometimes considered as an approximate indicator of its adsorption (Khan, 1980).

If a chemical's water solubility is known, the distribution of that chemical in the environment and possible degradation pathways can be determined. For example, chemicals that have high water solubilities will remain in water and tend to not be adsorbed on soil and living organisms (Linde, 1994).

A chemical with a high water solubility and vapor pressure generally will vaporize and be transported by air. Table 1 shows how solubility can indicate where a chemical will be distributed. Percentages are shown for distribution in soil sediments, water, and biota. The table shows that chemicals that are not very soluble tend to be adsorbed in soil sediments or biota (Linde, 1994).

Table 1: Solubility of pesticides and their distribution in environment (Linde, 1994)

<b>Distribution in Environment (%)</b>				
<b>Chemical</b>	<b>Solubility ppm</b>	<b>% in Soil Sediment</b>	<b>% in Water</b>	<b>% in Biota</b>
DDT	0.003	98.6	1.31	0.081
Chlorpyrifos	0.3	75.3	24.7	0.020
Lindane	10	39.4	60.6	0.011
2,4 D	900	3.16	96.8	0.0003

Linde (1994) stated following factors affecting water solubility: polarity, hydrogen bonding, molecular size, temperature of soil and pH of soil.

### 3.3.2 Octanol/Water Partition Coefficient ( $K_{OW}$ )

$K_{OW}$ , the octanol/ water partition coefficient measures the ratio of the equilibrium concentrations in octanol and water (Tomlin, 1997 in Kennedy et al., 2000) and it can be used to predict the likelihood of persistence of chemicals in produce or the environment (Kennedy et al., 2000). Linde (1994) stated that  $K_{OW}$  can be calculated by using the following equation (1):

$$K_{OW} = \frac{\text{Concentration in Octanol Phase}}{\text{Concentration in Water Phase}} \quad (1)$$

In this equation, the units of concentration cancel so values of  $K_{OW}$  are unitless.

Values for organic chemicals can be quite large so  $K_{OW}$  is generally expressed in “log  $K_{OW}$ ” and the values range from -3 to 7. Low values are easily measured since the chemical stays in water. Log  $K_{OW}$  values larger than four must be estimated because they cannot be easily measured. Chemical’s with large  $K_{OW}$  values are of great concern since they can be adsorbed in soils and living organisms. In general, a large  $K_{OW}$  value means that a chemical tends to be in an organic (non-polar) environment and not in water (polar). This means that it will have low water solubility. Most pesticides are less polar than water so they tend to accumulate in soil or living organisms, which contain organic matter. So one can see that  $K_{OW}$  values give an overall estimate as to where a chemical will be distributed in the environment (Linde, 1994).

Factors influencing  $K_{OW}$  are according to Linde (1994) polarity and general physical factors.

Hutdon and Roberts (1990) stated that a variety of relationships has been developed between  $K_{OC}$  and various physicochemical parameters, the most useful being with the octanol/ water partition coefficient  $K_{OW}$ . Furthermore, octanol/ water partition coefficient  $K_{OW}$ , is used to approximate  $K_p$  (the partition coefficient) between the soil and aqueous phases, (grams of sorbed solute per gram of soil/ concentration of solute in the aqueous phase).

### 3.3.3 Distribution Coefficient ( $K_d$ )

Distribution Coefficient ( $K_d$ ) is the ratio of the amount of chemical sorbed by the soil to that remaining in solution (Brady and Weil, 1999). It predicts the tendency of pesticide or other organic compound to leach into the groundwater. It is given in units of  $\text{cm}^3 \cdot \mu\text{g}^{-1} \cdot \text{g}^{-1}$  (Kodešová et al., 2012).

According to Linde (1994) it is expressed as (2):

$$K_d = \frac{\text{Concentration of chemicals in soil}}{\text{Concentration of chemical in water}} \quad (2)$$

Distribution coefficient is one of the parameters of Freundlich equation (Sparks, 1995).

According to Hutson and Roberts (1990) computer models are now being increasingly used to predict a measure of the likely fate of a compound under defined conditions. Predictions are generally based upon a combination of simple physical and chemical characteristics of the molecule such as vapor pressure,  $K_d$ ,  $t_{1/2}$  - the amount of time it takes for half of an amount of a chemical to be hydrolyzed (Linde, 1994), and more complex inputs which are required to assess accurately soil wetting and drying and water flow (Hutson and Roberts, 1990). According to Del Re et al. (1994) is important that only inputs which previous sensitivity tests have identified as being those with the greatest effect on model outputs be valid; often these are half-life,  $K_d$ , hydraulic properties and rainfall amount.

$K_d$  coefficient serves as an input value for different prediction models, for example it is use in EXAMS model (Gouy and Bélamie, 1994), EXAMS and PRZM2 models (Keller et al., 1994), VARLEACH model (Trevisan et al., 1994), WAVE model (Vancloster et al., 1994) or HYDRUS-1D used by Kodešová et al. (2004, 2005b) to simulate water flow in unsaturated soil.

### 3.3.4 Organic Carbon Partition Coefficient ( $K_{OC}$ )

The soil organic matter is generally the main factor explaining the adsorption of pesticides onto the soil solid phase, therefore it is common to characterise adsorption of pesticides by another partition coefficient,  $K_{OC}$  (in L/ kg). Values for  $K_d$  vary greatly because



the organic content of soil is not considered in the equation (2). The preferred value for determining a soil's ability to adsorb is  $K_{OC}$ , since it considers the organic content of the soil and therefore it is valid for soils with high amount of organic matter (Linde, 1994).

Higher coefficient numbers suggest that much of the chemical is bound by soil colloids and is less apparent to appear in the groundwater (the mobility classification based on  $K_{OC}$  is summed up in Table 2). If, however, the management objective is to remove the organic chemical from the soil, low coefficient numbers are more desirable (Brady and Weil, 1999). Barriuso et al. (1994) reported that  $K_{OC}$  values allow to point out that less humified organic matter in the coarsest soil size fractions had higher adsorption capacity than humified organic matter in the finest fractions.

Table 2: Mobility classification based on  $K_{OC}$  (McCall et al., 1981 in Roberts and Kearney, 1995)

<b><math>K_{OC}</math></b>	<b>Mobility class</b>
0 – 50	Very high
50 – 150	High
150 – 500	Medium
500 – 2000	Low
2000 – 5000	Slight
> 5000	Immobile

Jones et al. (2000) reported that most pesticides are sorbed in soil by partitioning onto soil organic matter, and this can be generalised across soils by defining a sorption coefficient ( $K_{OC}$ ) to soil organic carbon.  $K_{OC}$ , corresponds to the ratio of  $K_d$  to the organic carbon content of the soil (Coquet, 2002). Linde (1994) expressed the equation as following (3):

$$K_{OC} = \frac{K_d \cdot 100}{\% \text{ organic carbon}} \quad (3)$$

An example of relationship between  $K_{OC}$  values and application rate of pesticide was introduced by Jones et al. (2000). To reduce concentrations in surface water, the farmer should use the product with the highest  $K_{OC}$  and lowest application rate that would control the specific pest or weed. However, this may not be best from an environmental viewpoint since a lower concentration of one pesticide can have a greater environmental effect than a higher concentration of another. Also higher  $K_{OC}$  compounds tend to sorb more strongly to sediment and therefore remain longer in streams near the treated fields than more weakly adsorbed compounds that move with the water phase.

### 3.3.5 Vapour Pressure ( $P_{vp}$ )

Vapour pressure is often used as an indicator of the rate at which a chemical will evaporate. Another feature of vapor pressure is that it will indicate whether a chemical will stay in one area or volatilize and disperse over a large area. Vapour pressure ( $P_{vp}$ ) is a measure of the pressure that a chemical in air exerts on the surface below.  $P_{vp}$  is an integral part in calculating the volatility and Henry's Law constant for a chemical. This surface can be water or dry soil (Linde, 1994).

Pesticides with high vapour pressures may become environmental problems because they can volatilize and disperse over a large area. Chemicals with a high vapor pressure need to be handled in such a way so that the vapours do not escape into the atmosphere. A chemical with a low vapour pressure does not move into air so there is a potential for accumulation in water if it is water-soluble. If it is not water-soluble, the chemical may accumulate in soil or biota (Linde, 1994).

### 3.3.6 Henry's Law Constant ( $H'$ )

Henry's law constant is a measure of the concentration of a chemical in air over its concentration in water. A pesticide with a high Henry's law constant will volatilize from water into air and be distributed over a large area. Chemicals with a low Henry's law constant tend to persist in water and may be adsorbed onto soil. The Henry's law constant value is an integral part in calculating the volatility of a chemical (Linde, 1994).

Henry's Law constant for a chemical is according to Linde (1994) generally expressed in one of two ways (4) or (5):

$$H' = \frac{\text{concentration in gas phase}}{\text{concentration in liquid phase}} \quad (4)$$

$$H = \frac{\text{liquid vapor pressure}}{\text{chemical solubility}} \quad (5)$$

The first quantity, represented by  $H'$ , is dimensionless since the units for concentrations cancel out. This Henry's law constant variable has a hyphen after it to help distinguish it from the second Henry's law constant value. The second quantity, represented by  $H$ , is usually in units of Pa - m<sup>3</sup>/ mol or atm - m<sup>3</sup>/ mol (Linde, 1994).

Chemicals in the air can partition (move) into water droplets in clouds and fog. If the Henry's law constant is low, substantial amounts of the volatilized chemical will dissolve in the water droplets and be transported back to the earth's surface by rain. This process of a chemical moving from the gas phase into water droplets and being deposited onto the earth's surface is called wet deposition. Dry deposition is another process that occurs when the chemical is adsorbed onto soil particles in air, which is deposited on the earth's surface (Linde, 1994).

### 3.3.7 Bioconcentration Factor (BCF)

Bioconcentration factor is an indicator of how much a chemical will accumulate in living organisms. Chemicals that have high BCF values are generally no longer used because of possible hazards to living organisms. Once absorbed into an organism, chemicals can move through the food chain (Linde, 1994).

BCF is the accumulation of a chemical in living organisms (biota) compared to the concentration in water (6).

$$BCF = \frac{\text{Concentration in Biota}}{\text{Concentration in Water}} \quad (6)$$

BCF values are unitless and generally range from one to a million.

Factors that influence bioconcentration factor are polarity, solubility, lipid content, metabolism and habitat (Linde, 1994).

BCF can be an indicator of a chemical's tendency to accumulate in the food chain. The main purpose for metabolism is not to detoxify, but to make the chemical more polar so that the chemical will be more water soluble and then be excreted in the urine. BCF is also a good indicator of where a chemical will be distributed. If BCF is high, the chemical will generally have a low water solubility, a large  $K_{OW}$  (octanol/ water partition coefficient), and a large  $K_{OC}$  (soil adsorption coefficient) (Linde, 1994).

### 3.4 Physical-chemical Properties of Soil

Kutílek and Nielsen (1994) divided soil properties into two groups: static soil properties (e.g. organic matter, texture, mineralogy, soil depth and soil colour) and dynamic soil properties (e.g. hydraulic conductivity, soil water content, salt content, microorganisms, exchangeable cations and redox conditions).

Soil physical properties profoundly influence how soils function in an ecosystem and how they can best be managed. Based upon a large number of studies conducted during the last decade regarding spatial variability, it appears more appropriate to group soil physical properties into two classes 1) capacity parameters and 2) transport parameters. Capacity parameters include the content of sand, silt, or clay particles, organic matter content, porosity and soil water content. Such parameters usually denote static soil properties. Transport or dynamic parameters comprise hydraulic conductivity, soil water diffusivity and fluxes of water and solutes (Kutílek and Nielsen, 1994).

#### 3.4.1 Soil Organic Matter Content

Pesticides have a strong affinity for soil organic matter. Soil organic matter has an important effect on the bioactivity, persistence, biodegradability, leachability, and volatility of pesticides (Sparks, 1995).

Kodešová et al. (2011) pointed out that the organic matter content is usually suggested to have a greatest effect on the pesticide adsorption in natural soils. Furthermore,

Spark and Swift (2002) suggested that the sorption interactions of pesticides in the soil environment might involve either the mineral or organic components, or both. For soils that have higher organic matter levels (5 %), the mobility of the pesticides has been related to the total organic matter content, with the nature of the organic matter having little apparent influence on sorption processes.

According to Calvet and Barriuso (1994) addition of organic matter to a soil may also affect the sorption of pesticide. They also stated that the rate of application must be increased as the soil organic matter content increases. Sparks (1995) specified that the amount of pesticide that must be added to soils is strongly affected by the quantity of soil organic matter.

Soil amendments with organic materials like straw and cow manure have been reported to alter the fate and kinetics of chemicals added to soils. Several workers have observed enhanced dissipation and formation of bound residues of organic chemicals in soil after amendment with organic matter. Increasing temperatures and the amendment of maize straw both promote the microbial activity in the soil (Gevao et al., 2000). Calvet and Barriuso (1994) also suggested that another way to study the effect of sorption on microbial degradation is to run experiments with amended media with organic matter.

Pesticides which interact with organic matter will react with both the soluble and solid phase fractions, therefore, competitive effects, the reversibility of these two types of interaction, and mass action effects will govern the distribution of the pesticides between the solid and soluble phases of the organic matter (Spark and Swift, 2002).

#### 3.4.2 Dissolved Organic Carbon (DOC)

The dissolved organic carbon fraction of the total organic carbon in the soil and the ionic strength of the soil solution appear to have little or no effect on the sorption/transport characteristics of these pesticides over the range of concentrations studied by Spark and Swift (2002).

Total organic matter includes both the soluble and insoluble fraction of organic matter, although the proportion of soluble organic matter in a soil is usually very small. For soils, which have low organic matter contents, the mobility of the pesticide is often related

to the active components of the inorganic fraction, which is predominantly the clay-sized fraction. An increase in the clay content results in decreasing mobility of the pesticide, with the composition of the clay and the identity of the major cations in the soil solution also being important. There is considerable evidence that pesticides can interact with the soluble form of soil organic matter in the absence of the solid components of the soil. The extent and nature of this interaction depends on factors such as molecular weight and polarity of the pesticide (Spark and Swift, 2002).

Soluble humic substances can enhance the transport of pesticides in soils and into groundwater. Fulvic acids, which have low molecular weight and high acidities and are more soluble than humic acids, can transport pesticides and other organic materials quite effectively. For example, the downward movement of the insecticide DDT in the organic layers of some forest soils has been ascribed to water-soluble, humic substances (Sparks, 1995).

Humic substances can also serve as reducing agents and chemically alter pesticides. The alteration is enhanced by the presence of reactive groups such as phenolic, carboxyl, enolic, heterocyclic, aliphatic-OH, and semiquinone like those contained in fulvic acids and humic acids. The presence of stable free radicals in humic substances would also indicate that they can effect chemical alterations of pesticides. The hydroxylation of the chloro-s-triazines is an example of nonbiological transformation of a pesticide by humic substances (Sparks, 1995).

### 3.4.3 Clay Content

Clay is a general term for inorganic material that is  $< 2 \mu\text{m}$  in size (Sparks, 1995) and occurs in soils in hydrated forms and is made up of sheets of silica tetrahedral and alumina octahedral (Morrill et al., 1982). The importance of clay minerals on sorption of pesticides is determined by their active surface and CEC and it varies with the type of clay minerals. The various clay minerals described for example Sparks (1995). The characteristics of some common clay minerals are summed up in Table 3.

Table 3: Characteristics of some common clay minerals (Tarasevich et al, 1975 in Morrill et al., 1982)

Characteristics	Montmorillonite	Vermiculite	Illite	Kaolinite
Types of Layering	2:1	2:1	2:1	1:1
Type of Swelling	Expanding	Limited expanding	Non-expanding	Non-expanding
CEC (meq/100 g)	80 – 120	120 – 200	15 - 40	2 - 10
Specific surface (m <sup>2</sup> /g)	700 – 800	500 – 700	75 - 125	25 - 50

Historically, it has been assumed that most pollutants do not move through soils containing substantial amount of clay (Nash et al., 2002). Hutson and Roberts (1990) described that sorption onto clay minerals is an ionic process dependant mainly upon the cation exchange capacity (CEC) of the clay. Morrill et al. (1982) furthermore added that adsorption of organic compounds by clay minerals differ because of the strength of the negative charge, the specificity of adsorption sites and the nature of the cation on the exchange complex. An organic compound must have some polarity in order to “penetrate” into the basal surfaces of montmorillonite. Many organic pesticides are polar in nature and are subject to adsorption between two ditetrahedral sheeds. Hutson and Roberts (1990) specified that sorption onto clay minerals increases from non-ionic through polar to cationic compounds. The adsorption capacity of clays for some herbicides followed the order montmorillonite > illite > kaolinite (Bailey and White, 1970 in Hutson and Roberts, 1990).

Sparks (1995) reported that recently, there has been much interest in using clays, particularly smectites, because of their high surface areas, for removal of organic pollutants from water.

#### 3.4.4 Particle Density ( $\rho_z$ )

In most mineral soils, the mean mass per unit volume of solids is about 2600 - 2700 kg/m<sup>3</sup>. This is close to the density of quartz, which is generally the most prevalent mineral in the coarsest fraction of the soil. Some of the minerals composing the finest fraction of the soil have a similar density. However, the presence of iron oxides and of various other “heavy” minerals (generally defined as those having a density exceeding

2900 kg/m<sup>3</sup>) increases the average value of  $\rho_z$ , whereas the presence of low - density organic matter generally lowers the mean density of the solids (Hillel, 1998).

The particle density among other parameters (organic matter content,  $\text{pH}_{\text{KCl}}$ , cation exchange capacity, sorption complex saturation,  $\text{CaCO}_3$  content and salinity) was used by Kodešová et al. (2011) for determination of pedotransfer rules for the prediction of the  $K_F$  coefficients.

### 3.4.5 Porosity

Porosity is an index of the relative pore space in a soil. Its value generally ranges from 0.3 to 0.6 (30 – 60 %) (Hillel, 1998).

According to Hillel (1998) the simplest classification scheme recognizes three categories of soil pores: micropores, capillary pores and macropores. Brady and Weil (1999) grouped the pores by size into macropores (0.08 - 5+ mm), mesopores (0.03 – 0.08 mm), micropores (0.005 – 0.03 mm), ultramicropores (0.0001 – 0.005 mm) and cryptopores (< 0.0001 mm).

Micropores occur typically in clayey soils. The water held in such narrow pores is subject to adsorptive force fields, water retained in micropores is often discontinuous and does not participate in ordinary liquid flow phenomena. Such water is sometimes referred to as “adsorbed” water, “bound” water, or “residual” water (Hillel, 1998).

On the other hand, capillary pores, are the typical pores in a medium - textured soil. They range in width from several micrometers to a few millimetres. The fluid permeating them generally obeys the laws of capillarity and of Darcy (Hillel, 1998).

Macropores occur as cracks or fissures in clayey soils upon drying, as well as in all types of soils as a result of biological activity – for example, burrowing animals, including earthworms, and the presence of decayed roots. When empty of water, macropores constitute barriers to capillary flow. When filled with water, however, macropores permit very rapid flow (Hillel, 1998).

Where water moves slowly through the soil matrix (matrix flow) many pollutants, especially particulate materials and those that sorb to soil, are removed. However, where water moves quickly into and through soils via stable macropores, large quantities of water



and contaminants can be rapidly transported downslope. Many studies have demonstrated the ability of macropore flow to transport pollutants rapidly through soil (Nash et al., 2002).

Brady and Weil (1999) pointed out that chemicals may be washed from the soil surface into large pores and once they are carried below the zone of greatest root and microbial activity, they are less likely to be removed or degraded before being carried further down to the groundwater.

#### 3.4.6 pH

Soil pH has often been called the master variable of soils and greatly affects numerous soil chemical reactions and processes. It is an important measurement in deciding how acid the soil is, and can be expressed as  $\text{pH} = -\log(\text{H}^+)$ . Soils that have a  $\text{pH} < 7$  are acid, those with a  $\text{pH} > 7$  are considered alkaline, and those with a  $\text{pH}$  of 7 are assumed to be neutral (Sparks, 1995).

Adsorption by clays of some pesticides tends to be pH - dependent, with maximum adsorption occurring at low pH level. For example, at pH values above 5.7 the adsorption on soil colloids is greatly reduced and the tendency for the herbicide to move downward in the soil is increased. Of course, the adsorption in acidic soils also reduces the availability of herbicide atrazine to weed roots, thus reducing its effectiveness as a weed killer (Brady and Weil, 1999). Dependency of pH on adsorption was also described by Feldkamp and White (1979 in Calvet and Barriuso, 1994). For ionizable compounds, pH is of primary importance. Adsorption increases with decreasing pH for weak acids and weak bases showing a maximum for some compounds. Adsorption of neutral molecules is little affected by soil pH but this is not true for weak acids and bases where the ionized and unionized forms behave differently (Hutson and Roberts, 1990).

An example how pH influences degradation of a pesticide was introduced by Kennedy et al. (2000). Chemicals subject to alkaline hydrolysis will degrade ten times faster for each increase in the pH value of one unit. Endosulfan is also subject to alkaline hydrolysis and degrades to non-toxic endosulfan diol as the pH value is raised. The effect of soil pH on adsorption of pesticides was also studied by Kodešová et al. (2011).

### 3.5 Sorption

The term sorption is more appropriately used in environmental situations to denote the uptake of a solute by a solid (soil or sediment or component of soil) without reference to a specific mechanism, or when the mechanism is uncertain (Doucette, 2003). Sorption determines the chemical concentration in solution, which controls transport and degradation processes (Altfelder, 1999). According to Calvet and Barriuso (1994) sorption can be chronologically divided in two steps. The first step is an interface phenomenon, that is, adsorption on colloidal surfaces. In the upper layer of the soil, the adsorbing surface is essentially organic due to coating of mineral surface by organic polymers. The second step is diffusion into organic molecular aggregates and into the more or less altered plant tissues. Consequently, sorption of non-ionic molecules (adsorption and intra-particle diffusion) can be mainly described on the basis of interactions with the organic matter but has nothing to do with a water organic/solvent partition.

The term “sorption” was introduced in 1909 by McBain (in Morrill et al., 1982) and it includes:

1. adsorption, i.e., the condensation of gases on free surfaces, or the fixation of solutes from a solution on the surface of a solid; and
2. absorption, i.e., the uptake of molecules or ions from a solution within the mass of an adsorbing phase.

According to Coquet (2002) sorption processes play an important role in determining the fate of pesticides in soil. By setting the partition of the pesticide between the solid and the liquid phases, they control its availability for absorption by weed or crop roots or undesirable soil biota, and its availability for transport via movement of the soil solution and groundwater recharge. Therefore, sorption is a major factor in the balance that exists between the efficacy of a pesticide and its potential to be leached to groundwater. Sorption must always be considered when the behaviour of organic chemicals is investigated in soil (Altfelder, 1999).

According to Hamaker and Thompson (1972 in Coquet, 2002) a classical way to quantify the sorption of a pesticide in soil is through the measurement of its distribution coefficient ( $K_d$ ) which relates linearly the sorbed concentration ( $S$ ), of the pesticide to its concentration in solution ( $C$ ) at equilibrium (7):

$$S = K_d C \quad (7)$$

It was noted early on the difficulty in predicting sorptive behaviour for pesticides that dissociate to form an ion. Several factors, such as dissociation, soil solution pH, ionic strength and composition, and surface charge, may have to be considered to successfully predict sorption of acidic compounds by soils. Furthermore, sorption of ionizable organic compounds can occur through various mechanisms, such as ion exchange, charge - transfer interaction, hydrogen bonding, and van der Waals forces (Spadotto and Hornsby, 2003). The behaviour of pesticide residues in soils mainly depends on the amount of water moving through the soil and to the extent to which pesticides are retained in soils, which in turn depends on the sorption properties of the soil (Fouqué-Brouard and Fournier, 1996).

### 3.5.1 Factors Governing Sorption

Many soil characteristics are related to pesticide sorption and their relative importance depends on the polarity of molecules. Clay and organic matter contents are two important factors. However, if clay is mainly responsible of cation adsorption and may play a role in clay rich soils and subsoils, the soil organic matter is essential for sorption of non-ionic organic compounds. Sorption coefficient values are generally correlated with the soil organic carbon content essentially when a large domain of organic carbon content is considered. This correlation is not so well defined when the organic carbon content is less than 3 %, which corresponds to the majority of cropped soils (Calvet and Barriuso, 1994). Sorption of pesticides also depends on the electrical charge and the ionizability, on the hydrophobicity and the polarity and on the geometrical and topological characteristic of the molecules. So very broad relations may be suggested between these coefficients and pesticides bioavailability in soils. It has been observed that molecule affinity for water has a deep influence on sorption of non-ionic molecules (Jones et al., 2000). According to Riise and Pettersen (1994) soil organic carbon is often considered to be one of the single most important factors for the sorption of several pesticides in soil. Regardless of the source of organic carbon, partitioning coefficients for non-ionic pesticides are often converted to  $K_{oc}$  values based on the percentage weight of organic carbon in soil. It was documented in many

studies that sorption processes of organic compounds depend on the sorbent physicochemical properties as pH, cation exchange capacity, ionic strength, surface area, etc (Kodešová et al., 2011).

### 3.5.2 Adsorption Isotherm

Adsorption of pesticides is generally evaluated by the use of adsorption isotherms. An isotherm represents a relation between the amount of pesticide adsorbed per unit weight of adsorbent and the pesticide concentration in the solution at equilibrium (Khan, 1980). An adsorption isotherm, which describes the relation between the activity or equilibrium concentration of the adsorptive and the quantity of adsorbate on the surface at constant temperature, is usually employed to describe adsorption (Sparks, 1995). An adsorption isotherm is obtained by plotting the amount of substance (adsorbate) adsorbed on a solid (adsorbent) against the amount remaining in solution at constant temperature, and the graph represents equilibrium conditions. The differences in time required to reach equilibrium reflect molecular complexities of the adsorbates and adsorption surfaces. Adsorption varies widely as the soil-to-solution ration is altered. The adsorption isotherm can be often described by the Langmuir or Freundlich equations or modifications thereof (Morrill et al., 1982).

Adsorption isotherms can be classified into four major types based on the shape of the plot of adsorption vs. equilibrium concentration (Morrill et al., 1982).

With an S-type (S = "cooperative adsorption") isotherm the slope initially increases with adsorptive concentration, but eventually decreases and becomes zero as vacant adsorbent sites are filled. This type of isotherm indicates that at low concentrations the surface has a low affinity for the adsorptive which increased at higher concentrations (Sparks, 1995). This type of curve is obtained if the solute molecule is monofunctional, or has strong intermolecular attraction within the adsorbed layers, and/or the solvent is strongly adsorbed (Morrill et al., 1982).

The L-shaped (Langmuir) isotherm is characterized by a decreasing slope as concentration increases since vacant adsorption sites decrease as the adsorbent becomes covered. Such adsorption behaviour could be explained by the high affinity of the adsorbent

for the adsorptive at low concentrations, which then decreases as concentration increases (Sparks, 1995). This kind of isotherm is found when there is no strong competition from the solvent for sorption sites on the solid surface, or if the adsorbate has linear or planar molecules and the major axis is parallel to the adsorbent surface (Morrill et al., 1982).

The H-type (high affinity) isotherm is indicative of strong adsorbate-adsorptive interactions such as inner-sphere complexes (Sparks, 1995). This type of curve is obtained in systems with a high affinity between the adsorbate and adsorbent. Such a curve can result from chemisorption, or adsorption of ionic micelles or polymeric molecules (Morrill et al., 1982).

The C-type (C = "constant partition") isotherm is indicative of a partitioning mechanism whereby adsorptive ions or molecules are distributed or partitioned between the interfacial phase and the bulk solution phase without any specific bonding between the adsorbent and adsorbate (Sparks, 1995). This type of curve is characterized by constant partition of adsorbate between solution and adsorbent (Morrill et al., 1982).

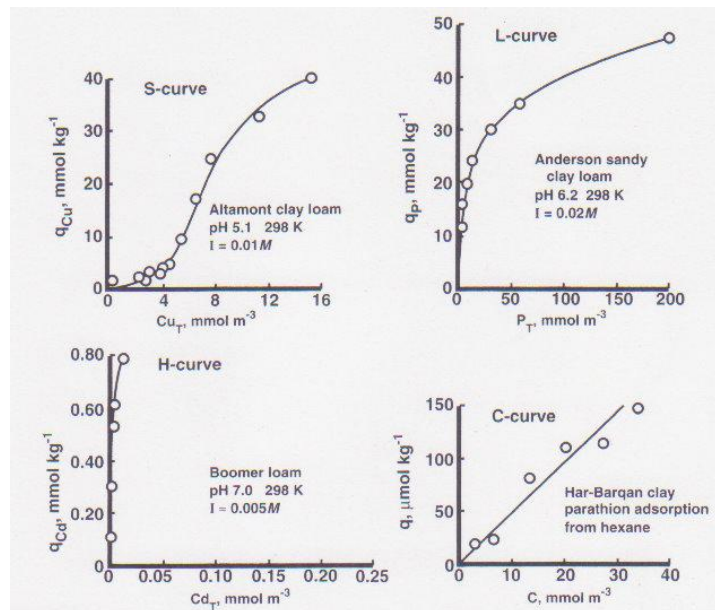


Figure 4: Types of adsorption isotherm (Sposito, 1984 in Sparks, 1995)

The Freundlich and Langmuir equations can be related mathematically, but adherence to the Freundlich equation by a particular system does not ensure conformance with the Langmuir equation. Neither the Freundlich nor the Langmuir equation provides for a within-

curve maximum and both break down at high solute concentrations. In field conditions, the heterogeneity of adsorbents may reduce the usefulness of Freundlich and Langmuir equation to merely empirical descriptions (Morrill et al., 1982).

### 3.5.2.1 Freundlich Equation

Pesticide sorption isotherms in soils were found to be well described by the Freundlich equation (Coquet, 2002). The Freundlich equation, which was first used to describe gas phase adsorption and solute adsorption, is an empirical adsorption model that has been widely used in environmental soil chemistry. The equation (8) can be expressed as:

$$q = K_d C^{1/n} \quad (8)$$

where  $q$  is the amount of adsorption and  $C$  is the equilibrium concentration of the adsorptive,  $K_d$  is the distribution coefficient, and  $n$  is a correlation factor. By plotting the linear form of equation (9),

$$\log q \text{ vs. } 1/n \log C + \log K_d, \quad (9)$$

the slope is the value of  $1/n$  and the intercept is equal to (10):

$$\log K_d \text{ if } 1/n = 1, \quad (10)$$

equation (9) becomes equal to equation (11):

$$q = K_d C \quad (11)$$

and  $K_d$  is a partition coefficient. One of the major disadvantages of the Freundlich equation is that it does not predict an adsorption maximum. The single  $K_d$  term in the Freundlich equation implies that the energy of adsorption on a homogeneous surface is independent of surface coverage. While researches have often used the  $K_d$  and  $1/n$  parameters to make conclusions concerning mechanisms of adsorption, and have interpreted multiple slopes

from Freundlich isotherms as evidence of different binding sites, such interpretations are speculative (Sparks, 1995).

### 3.5.2.2 Langmuir Equation

Another widely used sorption model is the Langmuir equation. It was developed by Irving Langmuir (1918, in Sparks 1995) to describe adsorption of gases on solids (Morrill et al., 1982). It was first applied to soils by Fried and Shapiro (1956) and Olsen and Watanabe (1957 in Sparks, 1995) to describe phosphate sorption on soils. Since that time, it has been heavily employed in many fields to describe sorption on colloidal surfaces. As with the Freundlich equation, it best describes sorption at low sorptive concentrations. However, even here, failure occurs (Sparks, 1995).

The derivation is according to Morrill et al. (1982) based on three assumptions:

1. energy of adsorption is constant and independent of surface coverage;
2. adsorption is on localized sites with an interaction between adsorbate molecules; and
3. the maximum adsorption possible is a complete monolayer.

The Langmuir adsorption equation can be expressed as (12):

$$q = kCb/(1+kC) \quad (12)$$

where  $q$  and  $C$  were defined previously,  $k$  is a constant related to the binding strength, and  $b$  is the maximum amount of adsorptive that can be adsorbed (monolayer coverage). In some of the literature  $x/m$ , the weight of the adsorbate/unit weight of adsorbent, is plotted in lieu of  $q$ . Rearranging to a linear form, becomes (13)

$$C/q = 1/kb + C/b \quad (13)$$

Plotting  $C/q$  vs  $C$ , the slope is  $1/b$  and the intercept is  $1/kb$  (Sparks, 1995).

The Langmuir equation is not successful in prediction adsorption from liquid solution as for gases on surfaces, and is useful only when multilayer adsorption is not involved. When

the Langmuir equation fails to explain adequately the experimental data, the Freundlich equation might be used (Morrill et al., 1982).

#### 3.5.2.3 Brunauer, Emmet and Teller (BET) Equation

As the assumptions in the development of the Langmuir equation are restricted to monomolecular layer adsorption, more complicated theories and isotherms have been developed for explaining multilayer adsorption, including the BET equation. The BET equation was further modified. The BET equation has been used for studying the adsorption of pesticides with high vapor pressures, such as ethylene dibromide (Morrill et al., 1982).

### 3.6 Degradation

Chemical conversion and degradation of pesticides in soil is a widespread phenomena that plays an important role in the dissipation of many pesticides in soil (Khan, 1980). Degradation is generally a combination of both abiotic and biotic processes (Hutson and Roberts, 1990). According to Linde (1994) the process of degradation will largely be governed by the compartment (water, soil, atmosphere, biota) in which the pesticide is distributed. Degradation process is affected by many factors involved in the interactions among microorganisms, chemical and soil constituents. For example, sorption limits the degradation of pesticides by reducing their partitioning into the soil liquid phase (Guo et al., 2000). Furthermore, in intensively used agricultural soils the tillage layer has a predominant influence on the transport and degradation of pesticides. This is due to the high carbon content and biomass of the upper soil layer resulting in an increased sorption capacity and increased mineralization rates. In deeper soil layers, the degradation rate normally significantly decreases with decreasing biomass (Fomsgaard, 1993 in Kördel et al., 1995).

Morrill et al. (1982) summed up several items, which influence the degradation of pesticides and other organic compounds in soils. The items that chemically influence organic compound degradation in soils include:

- chemical structure of the compound;
- organic matter content of the soil;
- soil pH;



- other compounds or ions present;
- concentration of the added compound and previous applications;
- amount and kind of clay minerals in the soil;
- formulation of the compound; and
- application methods.

Water although not mentioned as a chemical agent, affects degradation of organic compounds, is usually the most critical factor in their degradation and transformation. Since most pesticides decomposition is hydrolytic, water must be present as a chemical agent. Water is present in soil systems, and its various effects are usually related to physical transport; hence, water is treated with the environmental factors (Morrill et al., 1982).

Furthermore, Morrill et al. (1982) stated that the environmental components that affect pesticide degradation in soils: moisture, temperature, aeration, and depth of application.

There are variations in the rates of pesticide degradation within and between classes of pesticides, and there is some evidence that rates of biodegradation are affected by the application of mixtures of insecticides. It was produced the following general rates of degradation from least to greatest persistence: organophosphates > carbamates > and aliphatic acid herbicides > phenoxy, toluidine and nitrile herbicides > benzoic acids and amides > ureas and triazines >> chlorinated hydrocarbons (Hutson and Roberts, 1990).

### 3.6.1 Biotic Degradation

#### 3.6.1.1 Microbial Metabolism

According to Linde (1994) biodegradation is not the only degradation process in soil, but it is the main one.

Microbial metabolism of pesticides is an important degradation process in water and soil. The process can take several steps (e.g. the chemical is absorbed into the cell membrane of the microbe, and enzymes within microbe break down the chemical into smaller fragments) and the end goal is to mineralize the chemical (changing it into the basic components of CO<sub>2</sub>, H<sub>2</sub>O, and mineral salts). Higher organisms are able to metabolize chemicals but they are not able to mineralize them (Linde, 1994).

There are four types of microbes: bacteria, fungi, protozoa, and algae. Bacteria (65 % of the total biomass in soil) and fungi are the most abundant in nature so they are the most important in biological transformation processes. Bacteria dominate the degradation process in alkaline soils and water. Fungi dominate the degradation process in acidic soils. The surrounding conditions will determine whether aerobic or anaerobic metabolism will occur in the degradation of a pesticide (Linde, 1994).

Rouchaud et al. (2000) stated that high herbicide doses and repeated applications over a long period are favourable for generating accelerated biodegradation. On the other hand, crop rotation and low herbicide doses in agriculture (cereals, sugar beet, corn) usually limit the occurrence of accelerated biodegradation. Morrill et al. (1982) added that soil organic matter might also facilitate decomposition of pesticides by supplying a nutrient source or an energy source for microbes, or acting as a cometabolite.

In general, if a pesticide is tightly adsorbed to soil, it is not available for biodegradation. Thus, the amount of pesticide in the soil solution determines its availability for biodegradation (Anderson, 1994). However, decreases in degradation are often found not to be proportional to increases in adsorption (Guo et al., 2000). A pesticide that is unable to be degraded by microbes is likely to accumulate in soils and contaminate ground water (Linde, 1994). Factors affecting the microbial degradation of pesticides in soil include pH, time, temperature, adsorption, moisture and soil type (Khan, 1980).

### 3.6.2 Abiotic Degradation

#### 3.6.2.1 Photolysis

Solar radiation is responsible for many chemical changes of pesticides in the environment. Within the range of ultraviolet (UV) sunlight wavelength (290 to 450 nm), sufficient energy exists to bring about many chemical transformation of pesticides (Khan, 1980). Photochemical reactions can take place in air or water (Linde, 1994) or very near the surface (Khan, 1980) when sunlight is present (Linde, 1994), because the penetration of UV light into solid matter is limited (Khan, 1980). Light from the Sun can be defined as bundles of energy called photons that move in a wave-like manner (Linde, 1994).

Molecules can absorb waves as energy, which can cause chemical bonds to be broken. The wavelengths of concern for pesticide degradation are between 290 - 400 nm, which comprises about 4 % of the wavelengths emitted from the Sun. Wavelengths < 290 nm are filtered out by ozone in the atmosphere and wavelengths > 400 nm do not have sufficient energy to break chemical bonds (Linde, 1994).

Chemicals according to Linde (1994) can be degraded directly or indirectly:

- 1) a pesticide can react directly with sunlight, breaking its bonds;
- 2) light can photolyze (break chemical bonds) other molecules in air, which can then in turn react with pesticides.

The first reaction occurs when photons from sunlight cause the breaking of chemicals bonds. The total decomposition of a pesticide in air can take several steps.

The second type of photolysis occurs when sunlight reacts with various molecules present in air. These include: O<sub>3</sub> (ozone), NO<sub>2</sub>, OH, and O<sub>2</sub> (Linde, 1994).

The extent of photodecomposition depends on the duration of exposure, the intensity and wavelength of the light, the state of the chemicals, the nature of the supporting medium or solvent, pH of the solution and the presence of water, air, and photosensitizers (Khan, 1980).

#### 3.6.2.2 Hydrolysis

Hydrolysis is an important process in environmental fate (Hutson and Roberts, 1990) and it is also an important reaction that takes place in water for pesticide degradation. A pesticide reacts with water to form degradation products that can be distributed in the environment (Linde, 1994).

Hydrolysis means that a chemical has reacted with water to form a new product. Pesticide hydrolysis rates are generally described in half-lives. A general reaction format for hydrolysis is that the molecule R-X reacts with water to form R-OH and H-X (Linde, 1994).

Factors influencing hydrolysis are: substituents, temperature and pH (Linde, 1994).

Hydrolysis half-life ( $t_{1/2}$ ) is according to Linde (1994) determined by adding a known amount of chemical into a solution and then measuring the amount of the original chemical present at various time intervals. Then a graph of the natural log of chemical present vs.

time is plotted. The slope of the line will equal the value  $K_T$  (hydrolysis rate constant).  $t_{1/2}$  can then be determined by using  $K_T$  in the equation (14):

$$t_{1/2} = 0.693 / K_T \quad (14)$$

Hydrolysis is very temperature sensitive because an increase of 1 °C can increase the rate by 10 % and a difference of 10 °C can affect the rate by as much as a factor of 2.5 (Linde, 1994). It has been suggested that the hydrolyses is accelerated by metal ions such as copper and manganese, or by inorganic or organic species like phosphate, carbonate, etc. However, these processes are generally likely to be of minor importance because of their extremely low concentrations under field conditions (Hutson and Roberts, 1990).

Hydrolysis half-life values will help one to estimate how long a chemical will persist in an aqueous environment. If the chemical resists hydrolysis then it may degrade via some other pathway such as microbial metabolism (Linde, 1994).

### 3.6.2.3 Oxidation – Reduction Reactions

Chemical degradation of pesticides by hydrolysis and oxidation is quite a common process. Other reaction including chemical reduction or isomerization are important for certain compounds (Khan, 1980). Soil chemical reactions involve some combination of proton and electron transfer. Oxidation occurs if there is a loss of electrons in the transfer process while reduction occurs if there is a gain of electrons. The oxidized component or oxidant is the electron acceptor and the reduced component or reductant is the electron donor. The electrons are not free in the soil solution, thus the oxidant must be in close contact with the reductant (Barlett, 1993; Patrick et al., 1995 in Sparks, 1995). In soils, soil organic matter is the primary source of electrons. Thus, to completely describe a redox reaction, an oxidation reaction must balance the reduction reaction (Sparks, 1995).

For example, many sulphur containing pesticides are modified in soils by oxidation (Khan, 1980).

### 3.6.3 Degradation of Chlorotoluron in Soils

Chlorotoluron degradation starts with two parallel pathways, namely, chlorination and hydroxylation of the aromatic ring, which are then followed by consecutive chlorination reactions and after almost two weeks by ring opening and partial mineralisation (Losito et al., 2000). The estimated half-life in loamy sand and organic and peat soil is several months. Rates of degradation were nearly tripled by raising the temperature from 25 °C to 35 °C. Under field conditions, chlorotoluron appears to degrade at a higher rate. When applied in the spring on bare soil, it disappeared from the 0 – 5 cm soil layer with a half-life of 30 – 40 days; dissipation was slower in autumn (Lund et al., 1996). Jones et al. (2000) reported that the breakdown of chlorotoluron, was about four times slower than that of isoproturon; however, soils able to degrade isoproturon rapidly also gave the most rapid degradation of chlorotoluron.

Chlorotoluron is slowly degraded in water and is quite persistent. Chemical hydrolysis is not a significant degradation mechanism. However, it is degraded by photolysis in water and under laboratory conditions; the half-lives at pH 5.7, and 9 at 22 °C were over 200 days. In another study, half-lives of approximately 120 and 80 days were reported for river and pond water (containing 1 % sediment), respectively. Degradation proceeded via N-demethylation, yielding 3-(3-chloro-*p*-tolyl)-1-methylurea as the major metabolite and some minor polar metabolites (Lund et al., 1996).

## 3.7 Transport

The pesticide may be associated with water as a solution, suspension, or emulsion (Khan, 1980). Transport processes are first, those that carry the pesticide away from the point of entry and disperse it. This movement is governed by the diffusion of the chemical in water and by bulk water properties such as the rate of flow and the degree of mixing and by thermal effects. Second, transport processes operate to distribute the chemical from water into the other compartments of the aquatic environment such as sediment and biota. (Roberts and Kearney, 1995).

According to Morrill et al. (1982) the transport mediums for pollutants are air, rain, surface - and groundwater, sediment, and organisms. Use of pesticides in agriculture has,

occasioned dispersal of toxic compounds on a global scale, and many pesticides, especially the chlorinated forms, persist in soils for number of years. About 50 % of the pesticides applied to crops may volatilize and be transported by air. As many of pesticides are found in groundwater, it is apparent that there is significant transport of these chemicals through the soil profile (Spark and Swift, 2002). Water as a solvent can hold or carry pesticides in solution and can also transport soil particles to which pesticides have sorbed (Roberts and Kearney, 1995).

Pesticide applied for agricultural purposes on the soil sphere is transported to the aquatic environment through atmospheric transport as well as via soil runoff, erosion and leaching, and that the sediment in the hydrosphere plays an important role in storage of such chemicals. In the aqueous phase, the pesticide attains an equilibrium concentration with the sediment by adsorption and desorption, and may also be concentrated in aquatic organisms (Hutson and Roberts, 1990).

### 3.7.1 Volatilization

Volatilization is a process where a chemical is transported from a wet or dry surface into the atmosphere. There is no set variable that defines volatilization, however, it can be described by: flux (the amount of chemical that flows from a unit surface area into the air), or half-life (how long it takes for half of the chemical to volatilize) (Linde, 1994).

The rate of disappearance by this pathway is often greater than or equal to that due to chemical degradation. Volatilization losses can sometimes exceed 90 % of the application within 48 hours or less when residues of volatile pesticides are exposed on moist soil or plant surface (Roberts and Kearney, 1995). Some pesticides are more volatile than others, so they will differ in the amount that is transported. A chemical that is extremely volatile is of concern since an airborne pesticide can be quickly spread over a large area by wind. A chemical that is not volatile can accumulate on the soil or water surface and be transported down through the soil layer to ground water (Linde, 1994).

Factors influencing volatilization are wind, terrain/ fetch, temperature, chemical properties, solubility, soil, molecular properties, concentration and vapour pressure (Linde,

1994), also the location of the chemical in the soil (Hutson and Roberts, 1990) and the moisture status of the soil or plant surface (Roberts and Kearney, 1995).

It was showed that volatilization was enhanced by high solute concentration, soil moisture content, temperature and air flux and was reduced in favour of sorption by dry conditions and high clay or organic matter content. The increase in volatilization with soil moisture content is due to successful competition for sorption sites by water molecules; in wet soils, however, dissolution of the compounds in the pore water may reduce volatilization (Hutson and Roberts, 1990).

### 3.7.2 Runoff and Leaching

There are two major ways that pesticides can reach surface and ground waters: runoff and leaching. Runoff will occur if the chemical does not adsorb onto soil. Leaching occurs when the chemical is weakly adsorbed by soil and can easily move through the soil (Linde, 1994). The greatest leaching hazard occurs in highly permeable, sandy soils that are also low in organic content (Brady and Weil, 1999). Weak acid pesticides are bound weakly to soil so they can easily move downward to ground waters (Linde, 1994).

Surface run-off or overland flow occurs when the surface storage capacity is exceeded and flow is generated. It can be a critical process, since water is in direct contact with the immediate soil surface which contains the largest portion of applied pesticide and this is particularly true where flow and/ or sediments are transported directly into surface water sources (Roberts and Kearney, 1995).

Through run-off from fields, pesticides make their way into ditches, rivers, lakes. Ultimately, they reach the oceans through the water cycle. They may also leach into groundwater, which is then discharged into streams or is subsequently used for irrigation. Drift, evaporation and precipitation carry pesticides into both, nearby and far habitats via the foodchain accumulated in animal tissue, they can travel far distances and arrive at places in which they were never applied. Entire ecosystems are effected by the use of pesticide (Neumeister et al., 2003).

Factors that influenced pesticide concentrations in run – off are for example storm timing, site hydrology, formulation, pesticide physical and chemical properties (Roberts and Kearney, 1995).

Brady and Weil (1999) noted that the tendency of organic chemicals to leach from soils is closely related to their solubility in water and their potential for adsorption. The degree of pesticides losses varies from soil to soil, depending on the structure quality and organic carbon content. Many authors reported that the amount of rainfall immediately after the pesticide application is the most important for pesticide leaching. The pesticide movement is affected by the soil hydraulic properties (the soil texture, structure, and occurrence of preferential flow), the interaction between the sorption capacity of the solute and soil properties, degree of degradation of bulk residues in soil, and chemical specific process reducing the relative availability of chlorotoluron for leaching over time (Kočárek et al., 2010).

### 3.8 Pesticide Bioavailability

A compound is bioavailable when it can be absorbed by a living organism in a given medium. This is property, which represents a potential to be absorbed, that is, to be easily transported to an organism or to be in its immediate vicinity. Pesticides bioavailability is strongly dependant on retention/ release phenomena (Calvet, 1989 in Calvet and Barriuso, 1994) and on molecular mechanisms of interactions between molecules and the soil solid phase. Basically, it is assumed that bioavailability is a decreasing function of the sorption coefficient. Consequently, any factor having an influence on sorption may have an influence on bioavailability (Calvet and Barriuso, 1994).

Taking into account energetic characteristics of sorption isotherms, one can suggest that bioavailability may decrease according to the following order of isotherm shapes: S - isotherms > C - isotherms > L - isotherms > H - isotherms (Calvet and Barriuso, 1994).

To be bioavailable, sorbet molecules must be released at a rate, which allows a sufficient amount to be absorbed. Sorbed molecules in the soil constituents (essentially the organic matter) are less available than the sorbet molecules on the surface of constituents



(that is adsorbed molecules) because they have to diffuse out the solid phase before being able to desorb (Calvet and Barriuso, 1994).

### 3.9 Pedotransfer Rules

Normalisation of the  $K_d$  adsorption coefficient by the soil organic carbon content (i.e.  $K_{OC}$  calculation) may be viewed according to Coquet and Barriuso (2002) as a pedotransfer function (PTF) development process, whereby pesticide adsorption behaviour is being predicted from a soil constitution parameter.

The different regressions, or PTFs that were obtained by Coquet and Barriuso (2002) for the four pesticides they studied showed that the soil constitution parameters to implement in such PTFs will necessarily be dependent on the specific physicochemical properties of each pesticide, as well as on the range of variation of each soil constitutive variable considered in the PTF development process.

For instance, Kozák and Vacek (2000) the effect of soil properties on atrazine adsorption which was described by means of multivariate statistical methods (correlation and regression analyses). The values of the calculated regression coefficients were used for the following equation (15):

$$E(Y/X_1, X_2, X_3, X_4) = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 \quad (15)$$

The  $b_0$  value is called the absolute term,  $b_1$  represents the regression coefficient for clay content,  $b_2$  for CEC,  $b_3$  for  $\text{pH}_{\text{KCl}}$  and  $b_4$  for  $C_{\text{org}}$  content,  $E$  represents the estimation of the value under study, i.e.  $K_f$  value.

Kodešová et al. (2011) determined the pedotransfer rules for the  $K_f$  coefficient prediction. First of all the simple regression was used to relate the  $K_f$  coefficients and various soil properties. Then the multiple linear regressions were used to define pedotransfer rules for the prediction of the  $K_f$  coefficient (for the fixed  $n$  value) from the other measured physical and chemical soil properties.

Other examples of an application of the pedotransfer rules were introduced by Kočárek et al. (2010). It was used for predicting the adsorption coefficients (for

chlorotoluron) in the subsurface horizons by using the pedotransfer rules from the CEC,  $\text{pH}_{\text{KCl}}$ ,  $\text{C}_{\text{ox}}$  and clay content. Also in Kočárek et al. (2005) were used the pedotransfer functions and rules according to Kozák and Vacek (2000) for estimating the soil hydraulic properties, sorption and half-time degradation of chlorotoluron. Furthermore, Coquet (2002) concluded that from the results, it is thought that the organic carbon content would be the main soil variable on which to build catchment-scale pedotransfer functions for the prediction of the sorption isotherm parameters in the topsoil of the Bruyères-et-Montbérault catchment.

## 4. Materials and Methods

For the diploma thesis purposes were necessary to carry out two different experiments. The first experiment involved the determination of soil sorption and the second experiment consisted of assessing the soil characteristics.

### 4.1 Description of Chlorotoluron

For the sorption experiment a herbicide Sincuran 80 DP was used. Sincuran 80 DP contained 80 % of active substance - chlorotoluron.

Chlorotoluron 3-(3-chloro-p-tolyl)-1,1-dimethylurea chlorotoluron is a pre- or early post-emergence herbicide widely used to control annual grasses and broad-leaved weeds in winter cereals (Lund et al., 1996) and it is also an environmental pollutant (Mehmood et al., 1995). The chemical properties of chlorotoluron are summed up in Table 4.

Table 4: Chemical properties of chlorotoluron (IUPAC global availability of information on agrochemicals, 2011)

Molecular formula	C <sub>10</sub> H <sub>13</sub> ClN <sub>2</sub> O
Molecular weight	212.68
Water solubility in water	74 mg · l <sup>-1</sup> (20 °C)
Bulk density	1.34 g · ml <sup>-1</sup>
GUS leaching potential index	2.79
K <sub>oc</sub>	205
Vapour pressure	0.005 mPa (25 °C)
Log K <sub>ow</sub>	2,5 (20 °C, pH 7)
Soil degradation DT50 (typical)	45 days

### 4.2 Soil

For the experiments a soil from an area of Crop Research Institute in Prague – Ruzyně was chosen. The soil was classified as Luvic Chernozem. The Soil - forming process is loess on

the sandy marlite. The climatic region of selected experimental plot can be described as slightly warm, dry, with mild winters and the altitude of experimental plot is 330 m.

The soil was mixed with compost at the Crop Research Institute in Prague – Ruzyně. The mixture was mixed by a tumble mixer for 3 minutes and 8 variants were created (in variation A was added 1 %, in variation B 2 %, in variation C 3 %, in variation D 4 %, in variation E 5 %, in variation F 6 %, in variation G 7 % and in variation H 8 % of compost from total weight of mixture). Production of compost was performed on experimental composting plant in the Crop Research Institute in Prague – Ruzyně. In the composting plant to process the residual biomass, respectively biowaste, the technology used is belt-driven composting piles on the open area. In the composting plant was produced a compost of satisfactory quality usable in experiments aimed at improving the physical and hydrophysical properties of selected soils. The main raw materials for the creation of compost are: fresh grass from the lawn maintenance area of the Crop Research Institute in Prague – Ruzyně, leaves, wooden chips, oversize fraction and a limited amount of straw.

### 4.3 Determination of Adsorption Isotherms

#### 4.3.1 Determination of Adsorption Isotherm in Laboratory

Adsorption isotherms were determined in a laboratory of Department of Soil Science and Soil Protection using the standard batch procedure, which is described below.

Utilities:

- Analytical scales by Sartorius with accuracy  $\pm 0,0001$  g
- An volumetric flasks
- An automatic dispenser
- Pipetes
- Glass filters (Cronus Syringe Filter GF 25 mm, 0.7  $\mu$ m, Gold)
- Centrifuge and centrifuge cuvettes
- Shaking apparatus
- vials with volume 2 ml for HPLC
- HPLC equipment (Dionex)

Reagents:

- Solution of CaCl<sub>2</sub> 0.02 M
- Chlorotoluron, concentration of 1, 2.5, 5, 10 and 25 [μg . cm<sup>-3</sup>]
- Distilled water
- Methanol

Calculation and preparation of solutions:

0.02 M CaCl<sub>2</sub>: calculation 1 M ..... 111 g/l (table)  $\implies$  0.2 M = 111.2/100 = 2.22 g CaCl<sub>2</sub>/l  
2.22 g of CaCl<sub>2</sub> was quantitatively transferred into 1 l volumetric flask, it was dissolved in distilled water and filled up to the measuring line. The concentrations of chlorotoluron were 1, 2.5, 5, 10 and 25 [μg . cm<sup>-3</sup>]. Because for the determination of adsorption isotherms was used Syncuran, which contains 80 % of chlorotoluron, the amounts of Syncuran were calculated by using this equation (16):

$$n = \frac{100 \cdot y}{80 \cdot 1000} \quad (16)$$

Where  $n$  is the amount of Syncuran [g . l<sup>-1</sup>] and  $y$  is the required concentration of chlorotoluron [ppm].

The amounts of Syncuran used for attainment of required concentration of chlorotoluron in a solution and measured average concentrations of chlorotoluron in solutions (three measurements were done in case of each concentration of chlorotoluron) are showed in Table 5.

Table 5: The amounts of Syncuran used for the attainment of required concentration of chlorotoluron in a solution and measured concentration of chlorotoluron in solutions

Chlorotoluron [μg . cm <sup>-3</sup> ]	Amount of Syncuran for 1 l [g]	Measured concentration[μg . cm <sup>-3</sup> ]
1	0.00125	1.07
2.5	0.003125	2.79
5	0.00625	5.27
10	0.01250	10.21
25	0.03125	25.58

The amounts of Syncuran were weighted and quantitatively transferred into 1 l volumetric flask. Syncuran was dissolved and filled by 0.02 M CaCl<sub>2</sub> up to the measuring line. From each concentration was taken a reference sample into a vial for determination of starting concentration of the chlorotoluron in the solution.

Before the experiments the soil was dried, ground and sieved through 2 mm sieve. 10 g of dry soil was placed into a glass bottles and to each soil sample was add 10 ml of chlorotoluron solution with known concentration. Glass bottles were shaken on the shaking apparatus for 24 hours. After that, the content of the glass bottles was transferred into centrifuge cuvettes. Soil samples in cuvettes were centrifuged for 30 min at 12 000 rotations per min. During the centrifugation the firm particles sticked to the wall of cuvettes and pure solution was carefully filtrated into vials. The concentrations of pesticides in the solution were determined by using High Performance Liquid Chromatography (HPLC) (Kočárek et al., 2005).

#### 4.3.2 Calculation of Adsorption Isotherms

The points of adsorption isotherms were calculated by using following equations:

Calculation of  $m_0$  ( $\mu\text{g}$ ) – the initial total mass of chlorotoluron in the solution (soil and water) (17):

$$m_0 = c_d V_w \quad (17)$$

where  $c_p$  ( $\mu\text{g}\cdot\text{cm}^{-3}$ ) is an initial concentration of chlorotoluron in the solution and  $V_w$  ( $\text{cm}^3$ ) is a volume of chlorotoluron solution.

Calculation of  $m_1$  ( $\mu\text{g}$ ) – a final mass of chlorotoluron in the solution (18):

$$m_1 = c_k V_w \quad (18)$$

where  $c_K$  ( $\mu\text{g} \cdot \text{cm}^{-3}$ ) is a final concentration of chlorotoluron in the solution after 24 hours and  $V_w$  ( $\text{cm}^3$ ) is a volume of chlorotoluron solution.

Calculation of  $m$  ( $\mu\text{g}$ ) - a total weight of chlorotoluron adsorbed on soil particles (19):

$$m = m_0 - m_1 \quad (19)$$

where  $m_0$  ( $\mu\text{g}$ ) is the initial total mass of chlorotoluron in the solution and  $m_1$  ( $\mu\text{g}$ ) is the final mass of chlorotoluron in the solution.

Calculation of  $s$  ( $\mu\text{g} \cdot \text{g}^{-1}$ ) – an amount of chlorotoluron adsorbed on soil particles (20):

$$s = \frac{m_0 - m_1}{n} \quad (20)$$

where  $m_0$  ( $\mu\text{g}$ ) is the initial total mass of chlorotoluron in the solution and  $m_1$  ( $\mu\text{g}$ ) is the final mass of chlorotoluron in the solution and  $n$  is a mass of soil sample (g).

On the graph,  $c_K$  values are depicted on the x axis and  $s$  values on the y axis.

#### 4.3.3 Interlay of Measured Points with Freundlich and Langmuir Adsorption Isotherms

The determined points of adsorption isotherms were interlayed by Freundlich and Langmuir function. The method of least squares was used for interlay of measured points. At first, both equations had to be transferred into a linear form.

Freundlich equation in the linear form (21):

$$s = k_F c^{\frac{1}{n}} \quad \Longrightarrow \quad \log s = \log k_F + \frac{1}{n} \log c \quad (21)$$

Afterwards was defined (22):

$$x = \log c \quad \text{and} \quad y = \log s \quad (22)$$

And thus is valid (23) and (24):

$$b_0 = \frac{\sum_i x_i^2 \sum_i y_i - \sum_i x_i \sum_i x_i y_i}{N \sum_i x_i^2 - \left( \sum_i x_i \right)^2} = \log k_F \quad (23)$$

$$b_1 = \frac{N \sum_i x_i y_i - \sum_i x_i \sum_i y_i}{N \sum_i x_i^2 - \left( \sum_i x_i \right)^2} = \frac{1}{n} \quad (24)$$

where  $N$  is an amount of soil samples, in this case it is 15.

The values of Freundlich equation parameters were obtained by substitution, calculation of  $b_0$ ,  $b_1$  and their putting into the equations (25):

$$k_F = 10^{b_0} \text{ and } n = \frac{1}{b_1} \quad (25)$$

The  $s$  values were obtained by reverse putting of  $k_F$  and  $n$  coefficients into Freundlich equation. The  $s$  values expressed in dependence on  $c$  values were used for a construction of graphs with the adsorption isotherms.

Langmuir equation in the linear form (26):

$$s = \frac{s_{\max} k_L c}{1 + k_L c} \implies \frac{1}{s} = \frac{1 + k_L c}{s_{\max} k_L c} \implies \frac{c}{s} = \frac{1}{s_{\max} k_L} + \frac{c}{s_{\max}} \quad (26)$$

Afterwards was defined (27):

$$x = c \text{ and } y = \frac{c}{s} \quad (27)$$



And thus is valid (28) and (29):

$$b_0 = \frac{\sum_i x_i^2 \sum_i y_i - \sum_i x_i \sum_i x_i y_i}{N \sum_i x_i^2 - \left( \sum_i x_i \right)^2} = \frac{1}{s_{\max} k_L} \quad (28)$$

$$b_1 = \frac{N \sum_i x_i y_i - \sum_i x_i \sum_i y_i}{N \sum_i x_i^2 - \left( \sum_i x_i \right)^2} = \frac{1}{s_{\max}} \quad (29)$$

The values of Langmuir equation were obtained by the substitution, calculation  $b_0$  and  $b_1$  and by putting them into the equations (30):

$$k_L = \frac{b_1}{b_0} \text{ and } s_{\max} = \frac{1}{b_1} \quad (30)$$

The  $s$  values were obtained by their reverse putting into Langmuir equation. From  $s$  and  $c$  values were constructed the graphs which express adsorption isotherms.

All the calculations were done in the computer program MS Excel.

#### 4.4 Determination of Chlorotoluron in Solution

The determination of chlorotoluron in solution was done by using HPLC instrument. This instrument consists of the following parts: P680 HPLC Pump, ASI-100 Automated Sample Injector. Separation took place in Nucleosil 120-5, C18 column, 125 × 4 mm (Watrex). The guard column (Security Guard Cartridge AQ C18 4 × 2.00 mm) was used to prolong the lifetime of the column. Mobile phase was prepared by mixing 600 ml of methanol, 400 ml of redistilled water and 6 ml of NH<sub>4</sub>OH. The columns were placed in the Thermostatted Column Compartment TCC-100 set to a constant temperature of 25 °C. Detection of pesticides was performed by PDA-100 Photodiode Array Detector. The wavelength for the

detection 310 nm. The signal from the detector was stored and processed using the chromatographic software Chromeleon version 6.70 (Dionex) (Kočárek et al., 2005).

#### 4.5 Determination of Soil Characteristics

In case of soil characteristic determination (except determination of soil texture) three repetitions from each soil sample were done. The average was calculated from the obtained values (the outliers were canceled out).

##### 4.5.1 Determination of Soil Texture and Particle Density $\rho_z$

###### Determination of Soil Texture by using hydrometric method

The soil texture was determined in accordance with Gee and Or (2002 in Dane and Topp, 2002) methodology. Soil samples were prepared as follows: 45 g of soil was weighted and 45 ml of sodium hexametaphosphate and 45 ml of distilled water were added. The mixture was boiled and mixed by a glass straw. It was let to cool and afterwards it was replaced into a sedimentation cylinder and filled by water up to 1000 ml.

Density of soil suspension measured in each times (1, 2, 5, 15, 45 minutes, 2, 5 and 24 hours) was used to construct the curves of grain size and soil types determined of used soil.

###### Determination of Particle Density $\rho_z$

10 g of dry soil was weighed and heated in a ceramic bowl for 5 minutes. Initially the pycnometer filled with distilled water and placed into a water bath (20 °C) for 20 minutes. Afterwards it was weighed, before pouring out the distilled water. Next the soil suspension was measured into the pycnometer, which was then filled with distilled water to displace any remaining air. The pycnometer was then left for another 20 minutes in the water bath (20 °C) and weighed. Afterwards the recorded values were used to calculate particle density according to the following equation (31):

$$\rho_z = \frac{N_z \cdot \rho_v}{(N_z + P_{H2O} - P_z)} \quad (31)$$

where  $\rho_z$  is particle density ( $\text{g}\cdot\text{cm}^{-3}$ ),  $\rho_v$  is density of water at 20 °C ( $= 1 \text{ g} \cdot \text{cm}^{-3}$ ),  $N_z$  is amount of soil (g),  $P_{H_2O}$  is weight of the pycnometer with water (g),  $P_z$  is weight of pycnometer with the mixture (g) (Flint, A.L. and Flint, L.E., 2002 in Dane and Topp, 2002).

#### 4.5.2 Soil Active pH Determination

10 g of soil was weighed into a 50 ml beaker and 20 ml boiled distilled water was added. The soil suspension was mixed for 5 minutes with a glass rod, then the pH was measured by combined glass electrode (ISO 10390, 1994).

#### 4.5.3 Soil Exchangeable pH Determination

40 g of soil was weighed into a 250 ml plastic bottle and 100 ml of 1 M KCl was added. This was shaken by the shaking apparatus for 45 minutes, followed by filtration into a beaker and measurement of the pH using the glass electrode (exchangeable pH).

From the obtained filtrate 50 ml was pipetted into an Erlenmeyer flask, adding 3 drops of phenolphthalein and 0.02 M NaOH was titrated to first faint pink colour. Afterwards the consumption of hydroxide a (ml) was subtracted and the values were used to calculate exchangeable acidity. The exchangeable acidity determination according to Hendershot et al. (1993). The remaining of filtrate was used for measuring the  $\text{pH}_{\text{KCl}}$  value by glass electrode (ISO 10390, 1994).

#### 4.5.4 Spectrophotometric Determination of Humus Quality

The extraction of humin substances was done by weighing 2 g of soil sample (three repeats from each sample) into 100 ml PE bottle and adding 40 ml of 0.05 M  $\text{Na}_4\text{P}_2\text{O}_7$ . It was left to shake on a shaking apparatus for 45 minutes and afterwards overfilled into a centrifuge cuvette and centrifuged. Next, the supernatant was overfilled into a tube. For the spectrophotometric measurement, a comparative solution was prepared from a pure solution of 0.05 M  $\text{Na}_4\text{P}_2\text{O}_7$ . It was measured before the samples were measured to obtain a baseline. A small portion of solution was overfilled into a spectrophotometer cuvette, the

cuvette walls were cleaned and the sample placed into spectrophotometer. An absorption curve was created from absorbances between 400 and 600 nm and to calculate  $Q_{4/6}$  values.

#### 4.5.5 Determination of Hydrolytic Acidity

40 g of soil was placed into 250 ml plastic bottle and 100 ml of 1 M  $\text{CH}_3\text{COONa}$  was added. After shaking for 45 minutes in the shaking apparatus, it was filtered into a beaker. Then 50 ml of filtrate was pipetted into an Erlenmeyer flask, adding 3 drops of phenolphthalein and 0.1 M NaOH was titrated to first faint pink colour. The consumption of hydroxide a (ml) was subtracted and the values were used to calculate hydrolytic acidity (Klute, 1996).

#### 4.5.6 Determination of Cation Exchange Capacity according to Bower

2 g of soil was weighed and placed into a 30 ml centrifuge cuvette. Initially the soil sample was saturated with sodium by adding 10 ml of 1 M  $\text{CH}_3\text{COONa}$  into the centrifuge cuvette. It was vigorously shaken by the centrifuge cuvette for 3 minutes and centrifuged for 3 min at 8000 rotations per min. The supernatant was then emptied and 10 ml of 1 M  $\text{CH}_3\text{COONa}$  was added to the sediment in the centrifuge cuvette. The whole procedure was repeated 3 times in total.

The soil was saturated with sodium and the excess salt was washed out. Then 10 ml of 96 % ethanol was added to the sediment. Shaken for 3 minutes, centrifuged for 3 minutes at 8000 rotations per min. and then the supernatant was emptied. The entire procedure was repeated three times in total.

The third step was to displace sodium in the solution by adding 10 ml of 1 M  $\text{CH}_3\text{COONH}_4$  to the sediment in the centrifuge cuvette. This was shaken by hand for three minutes and centrifuged for 3 min at 8000 rotations per min. Next the contents of the centrifuge cuvette was filtrated into a volumetric flask. This procedure was repeated three times. The filtrate in the volumetric flask was refilled by 1 M  $\text{CH}_3\text{COONH}_4$  up risk. The sodium concentration was measured in solution. The sodium concentration values are required for the CEC calculation (Bower and Hatcher, 1966).

#### 4.5.7 Determination of Humus Content by Tjurin Method

0.2 g of soil was weighed into a 100 ml beaker with 10 ml mixture of chromium sulphate. The beaker was covered by a shallow bowl and mixed. Next, it was placed into an oven for 45 minutes at a temperature of 125 °C, along with four breakers containing a pure mixture of chromium sulphate (10 ml) (blind samples) for the assessment of Mohr salt factor. After 45 minutes all the beakers were taken out of the oven. The beaker containing the soil sample was centred on a magnetic stirrer and mixed. Platinic electrodes were immersed into the mixture and Mohr salt was titrated into the beaker until the permanent deviation was revealed (the process indicated by a change of colour). The consumption of Mohr salt was noted and used for calculating the  $C_{OX}$  values (Skjemstad and Baldock, 2008 in Carter and Gregorich, 2008).

#### 4.5.8 Determination of Carbonates

The determination followed the method of Looppert et al. (1996), where 20 g of soil was weighted, added to a generated bottle and 10 % HCl added to fill a 10 ml reversible bottle. The generated bottle was closed and HCl was decanted stepwise into the generated bottle containing the soil. After each overspill the bottle was shaken. When the level of fluid in both tubes was even, the production of  $CO_2$  (%) was detected and recorded. The production of  $CO_2$  corresponds to the content of carbonates in the sample.

#### 4.5.9 Salinity

10 g soil sample was weighed into a PE bottle and 50 ml of 50 % ethanol was added. The suspension was left to shake for 45 minutes in the shaking apparatus and then filtered into the beaker. The specific conductivity of the filtrate was measured by a conductometer (Rhoades, 1996).

The soil characteristics are summed up in Table 6.

Table 6: Soil characteristics

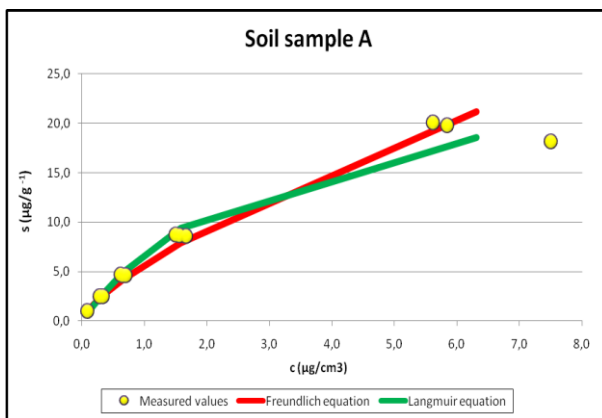
Soil Sample	Q <sub>4/6</sub>	HK/FK	CEC (meq+)/100 g)	S (meq/100 g)	V (%)	salinity (μS . cm <sup>-1</sup> )	C <sub>ox</sub>	V <sub>a</sub> (meq/100 g)	H <sub>a</sub> (meq/100 g)
A	3.49	0.39	26.75	25.628	96.01	39.0	1.82	0.221	1.068
B	3.54	0.39	27.50	26.319	95.71	46.3	2.11	0.151	1.181
C	3.52	0.39	24.75	23.682	95.68	38.0	2.05	0.146	1.068
D	3.38	0.38	32.17	31.061	96.56	39.6	2.14	0.157	1.106
E	3.54	0.39	32.08	31.166	97.14	43.1	2.36	0.108	0.917
F	3.74	0.42	27.08	25.883	95.57	51.5	2.26	0.164	1.2
G	3.59	0.40	26.25	25.088	95.57	45.7	2.42	0.146	1.162
H	3.53	0.39	33.42	32.377	96.89	40.6	2.40	0.127	1.04
Soil Sample	pH <sub>H2O</sub>	pH <sub>KCl</sub>	CaCO <sub>3</sub> (%)	ρ <sub>z</sub> (g . cm <sup>-3</sup> )	Clay (%)	Silt (%)	Very fine sand (%)	Sand (%)	
A	6.77	6.41	0.12	2.59	37	40	5	17	
B	6.83	6.32	0.02	2.60	40	37	7	16	
C	6.75	6.44	0.04	2.61	40	40	4	16	
D	6.80	6.41	0.12	2.55	38	38	3	21	
E	6.67	6.42	0.25	2.59	38	42	5	15	
F	6.66	6.36	0.15	2.58	39	38	5	19	
G	6.68	6.57	0.09	2.54	39	41	6	14	
H	6.70	6.59	0.08	2.56	39	41	7	13	

## 5. Results

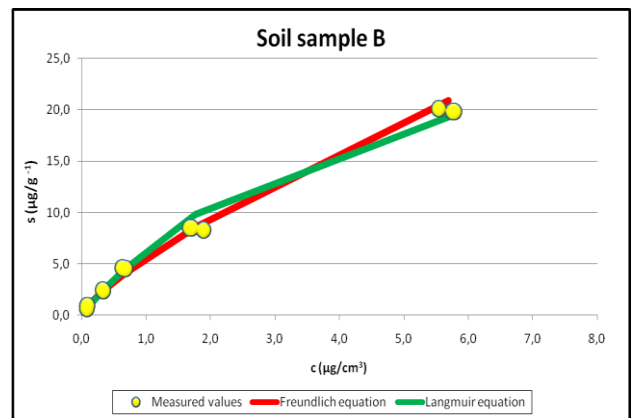
### 5.1 Behaviour of Adsorption Isotherms for Chlorotoluron

Although chlorotoluron was absorbed similarly in all eight soil samples, a slight decline of adsorbed chlorotoluron can be observed in the following order: Sample F (Figure 7) > Sample A (Figure 5) > Sample D (Figure 6) > Sample B (Figure 5) > Sample E (Figure 7) > sample H (Figure 8) > sample C (Figure 6) > sample G (Figure 8).

Table 7 summarises the resulting parameters of Freundlich and Langmuir adsorption isotherms for the sampled soils.

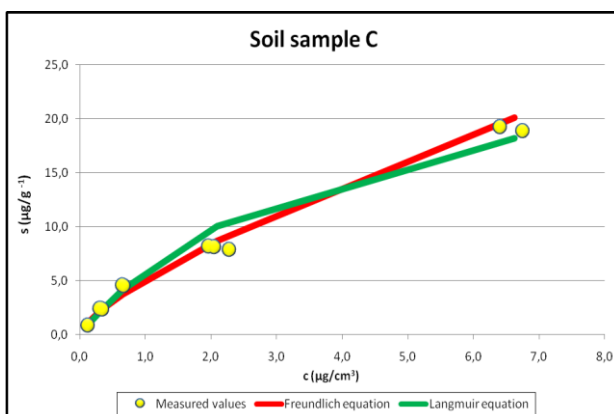


A)

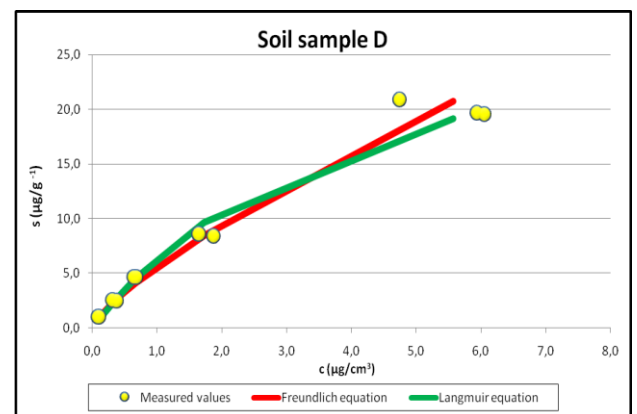


B)

Figure 5: Adsorption isotherms of chlorotoluron for soil sample A (A) and soil sample B (B)

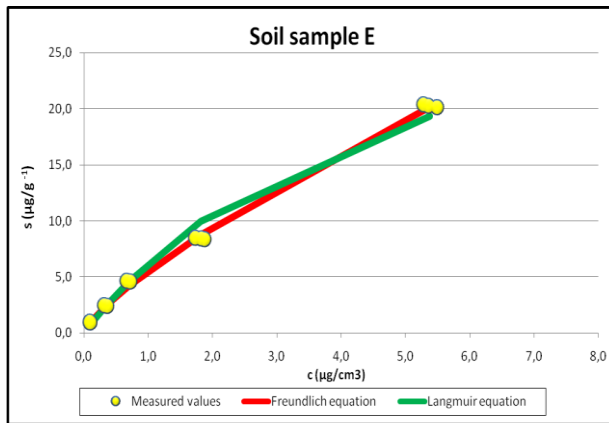


A)

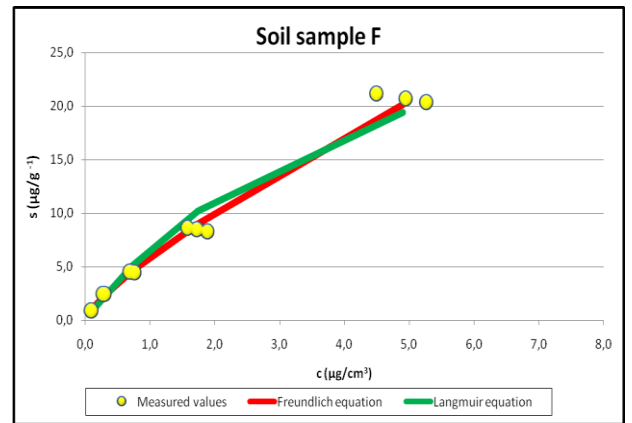


B)

Figure 6: Adsorption isotherms of chlorotoluron for soil sample C (A) and soil sample D (B)

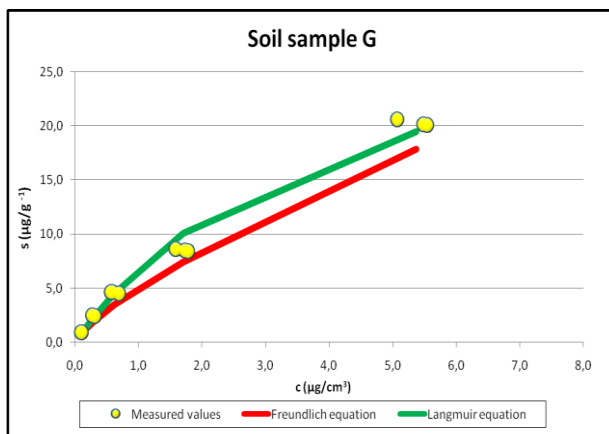


A)

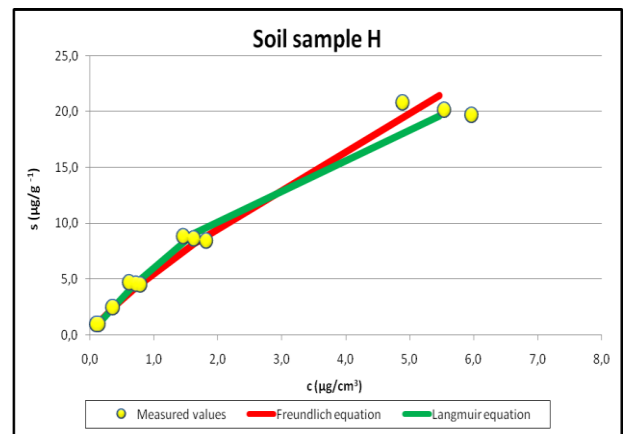


B)

Figure 7: Adsorption isotherms of chlorotoluron for soil sample E (A) and soil sample F (B)



A)



B)

Figure 8: Adsorption isotherms of chlorotoluron for soil sample G (A) and soil sample H (B)

Table 7: Parameters of Freundlich and Langmuir adsorption isotherm

Soil sample	$K_F$	$1/n$	$K_L$	$S_{max}$
sample A	5.70	0.71	0.32	27.73
sample B	5.61	0.74	0.23	34.14
sample C	5.08	0.73	0.26	28.97
sample D	5.59	0.76	0.23	34.51
sample E	5.52	0.77	0.20	37.55
sample F	5.91	0.77	0.21	38.34
sample G	5.89	0.76	0.24	34.33
sample H	5.52	0.80	0.19	38.59



## 5.2 Statistical Outcomes

### 5.2.1 Application of Linear Regression to Examine the Dependence of Freundlich and Langmuir Parameters on Soil Characteristics

The statistical software Statgraphic Centurion XV was used for all calculations. In this case the dependent variables were the Freundlich parameters ( $K_F$  and  $1/n$ ) and Langmuir parameters ( $K_L$  and  $s_{max}$ ). The independent variables were the soil characteristics ( $\text{pH}_{\text{H}_2\text{O}}$ ,  $\text{pH}_{\text{KCl}}$ ,  $V_a$ ,  $H_a$ ,  $Q_{4/6}$ ,  $\text{CaCO}_3$ , CEC, S, V,  $C_{ox}$ , salinity, particle density, content of clay, silt, very fine sand and sand). The relationship between parameters and soil characteristics was tested by simple linear regressions.

Most of the values did not show any correlation with Freundlich and Langmuir parameters (Appendix 5). Conversely, some P-values were under the value 0.05. This means that there were statistically significant relationships in case of  $1/n$  and  $C_{ox}$  (P-value = 0.0088 and  $R^2 = 0.707974$ ) (Figure 9),  $K_L$  and  $C_{ox}$  (P-value = 0.0135 and  $R^2 = 0.665547$ ) (Figure 10),  $K_L$  and  $V_a$  (P-value = 0.0068 and  $R^2 = 0.730697$ ) (Figure 11),  $s_{max}$  and  $C_{ox}$  (P-value = 0.0101 and  $R^2 = 0.694999$ ) (Figure 12) at the 95.0 % confidence level.

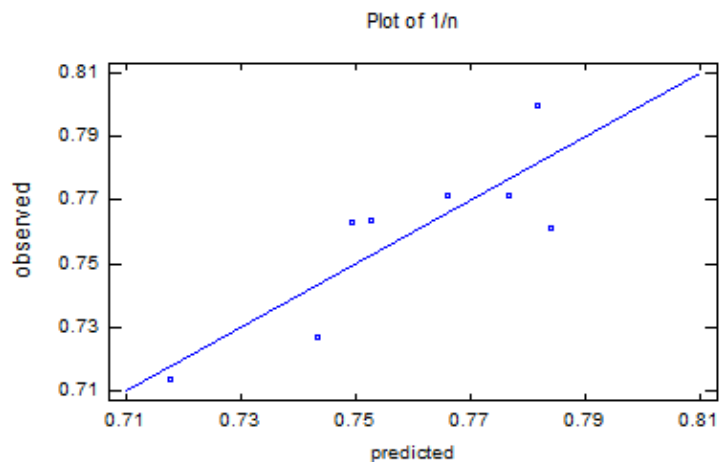


Figure 9: Graph of correlation between  $1/n$  and  $C_{ox}$ ; P-value = 0.0088,  $R^2 = 0.707974$

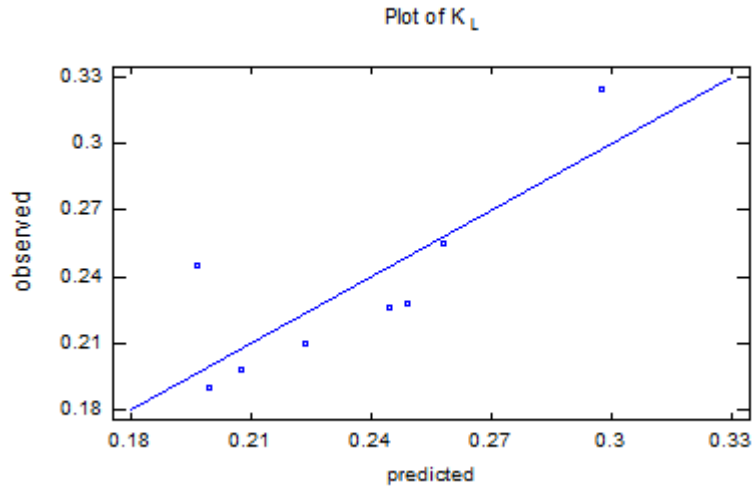


Figure 10: Graph of correlation between  $K_L$  and  $C_{ox}$ ; P-value = 0.0135,  $R^2 = 0.665547$

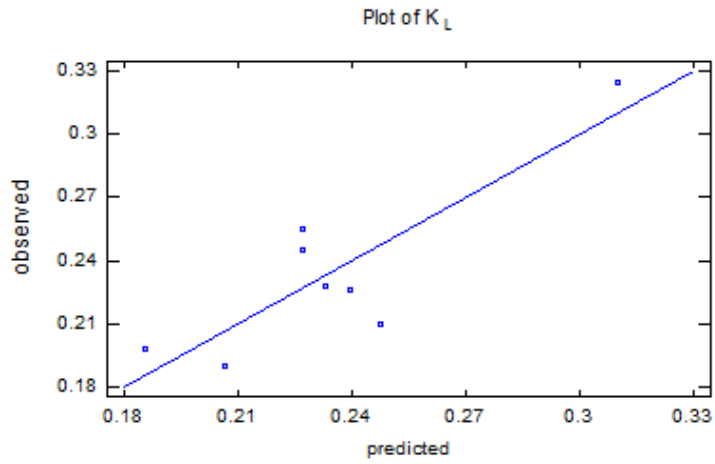


Figure 11: Graph of correlation between  $K_L$  and  $V_a$ ; P-value = 0.0068,  $R^2 = 0.730697$

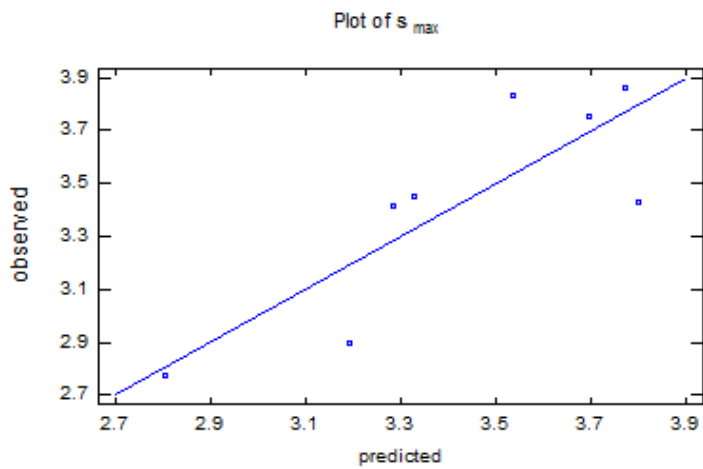
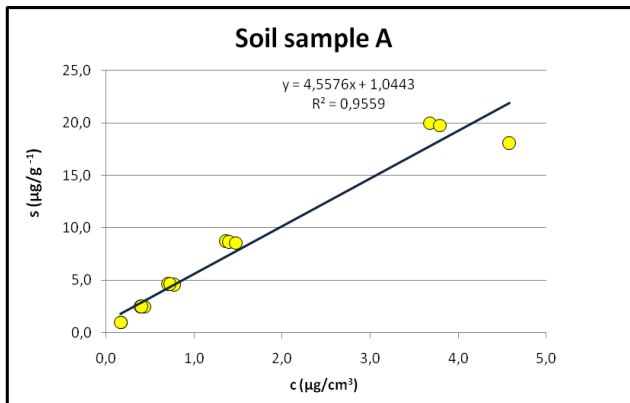
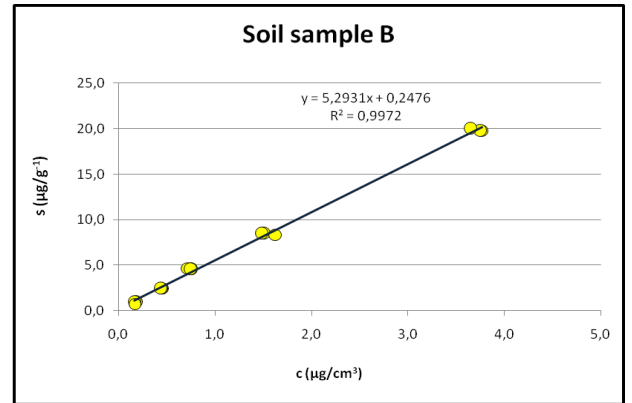


Figure 12: Graph of correlation between  $S_{max}$  and  $C_{ox}$ ; P-value = 0.0101,  $R^2 = 0.694999$

Adsorption isotherms expressed for the fixed  $n$  value of all soil samples are in Figures 13, 14, 15 and 16.

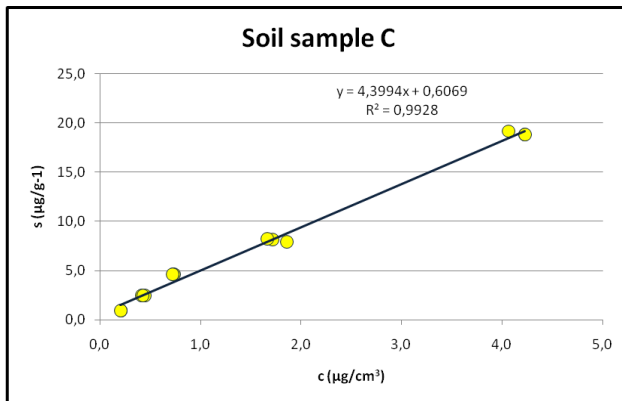


A)

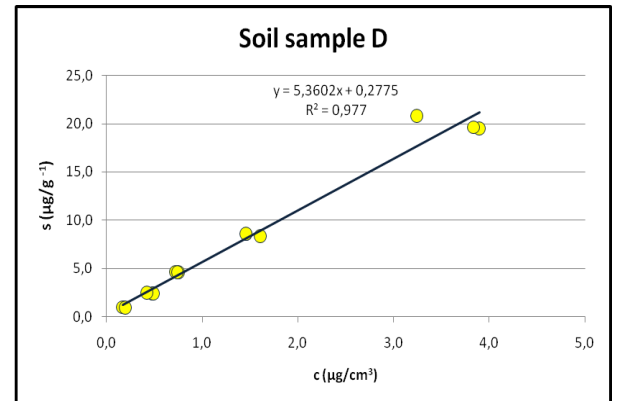


B)

Figure 13: Adsorption isotherms of soil sample A (A) and soil sample B (B)

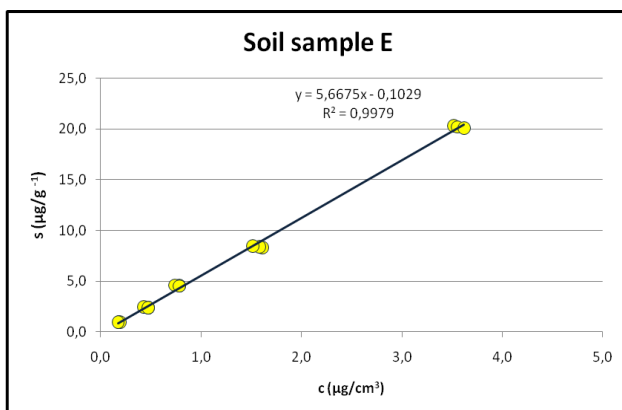


A)

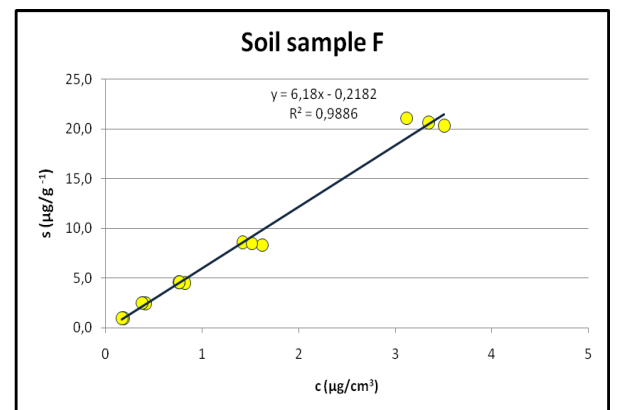


B)

Figure 14: Adsorption isotherms of soil sample C (A) and soil sample D (B)



A)



B)

Figure 15: Adsorption isotherms of soil sample E (A) and soil sample F (B)

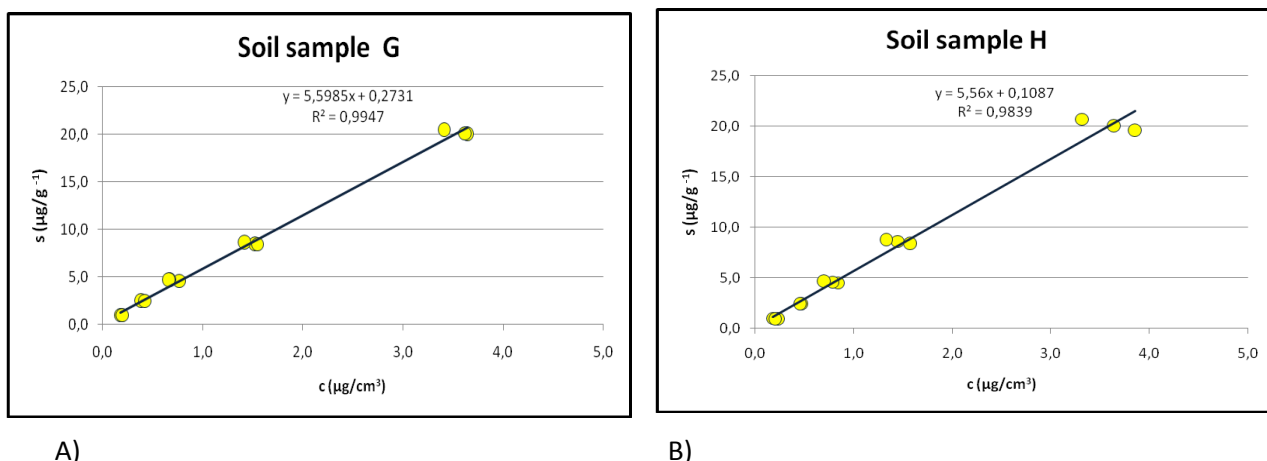


Figure 16: Adsorption isotherms of soil sample G (A) and soil sample H (B)

In the preceding tested values, there were no statistically significant dependences of  $K_F$  coefficient on soil characteristics. Therefore the  $K_F$  coefficient (for the fixed  $n$  value, where  $n = 0.7554$ ) was used for further testing.

As explained by Kodešová et al. (2011), the  $K_F$  coefficient is commonly used to assess pesticide sorption in various soils. The large  $K_F$  value indicates large pesticide sorption. When fitting the same experimental data, however, the  $K_F$  value depends on the  $n$  coefficient (the lower  $K_F$  values are obtained for lower  $n$  values, e.g. higher  $1/n$  values). Therefore, the average  $n$  coefficient for each pesticide was used to refit the experimental data points to obtain  $K_F$  values. These values may be used to assess impact of soil properties on the pesticide adsorption on soil particles. For this diploma thesis purposes, the fixed  $n$  value was calculated as an average of  $1/n$  values showed in Table 7.

### 5.2.2 Adsorption Coefficient $K_F$ (for the fixed $n$ value)

The dependant variable in this case was the adsorption coefficient  $K_F$  (for the fixed  $n$  value, where  $n = 0.7554$ ). The independent variables were the soil characteristics ( $\text{pH}_{\text{H}_2\text{O}}$ ,  $\text{pH}_{\text{KCl}}$ ,  $V_a$ ,  $H_a$ ,  $Q_{4/6}$ ,  $\text{CaCO}_3$ , CEC, S, V,  $C_{\text{ox}}$ , salinity, particle density, content of clay, silt, very fine sand and sand). The relationship was tested by using a simple linear regression.

Although most values did not show any correlation with the adsorption coefficient, some P-values were under the value 0.05. This means that there were statistically significant

relationships between  $K_F$  and  $C_{ox}$  (P-value = 0.0390 and  $R^2 = 0.535617$ ),  $K_F$  and salinity (P-value = 0.0209 and  $R^2 = 0.616891$ ) at the 95.0 % confidence level.

Appendix 6 shows the simple regression of  $K_F$  (for the fixed  $n$  value) and soil characteristics.

### 5.2.3 Testing for an Alternative Pedotransfer Rule

In this section are the results for testing of an alternative pedotransfer rules for chlorotoluron. The dependent variable in this case was the calculated Freundlich parameter,  $K_F$  (for the fixed  $n$  value, where  $n = 0.7554$ ). The independent variables were the soil characteristics.

At first  $K_F$  was tested by multiple linear regression for  $C_{ox}$  and salinity, because both soil characteristics were statistically dependent on  $K_F$  when they were tested by simple regression. Afterwards other soil characteristics (even if they were not statistically dependant) were added to the test to see if the results could be improved.

The results obtained are presented below, note that the P-values and  $R^2$  values are summed up in Appendix 5.

Dependent variable:  $K_F$  (for the fixed  $n$  value) and independent variables:  $C_{ox}$  and salinity

The output shows the results fitting a multiple linear regression model to describe the relationship between  $K_F$  and two independent variables ( $C_{ox}$  and salinity). The equation of the fitted model is (32):

$$K_F = 2.29939 + 0.000820962 * C_{ox} (\%) + 0.0558176 * salinity (\mu S \cdot cm^{-1}) \quad (32)$$

The P-value was less than 0.05, and there is a statistically significant relationship between the variables at the 95.0 % confidence level (P-value = 0.0284,  $R^2$  value = 0.76).

The obtained correlations are shown as a graph in Figure 17.

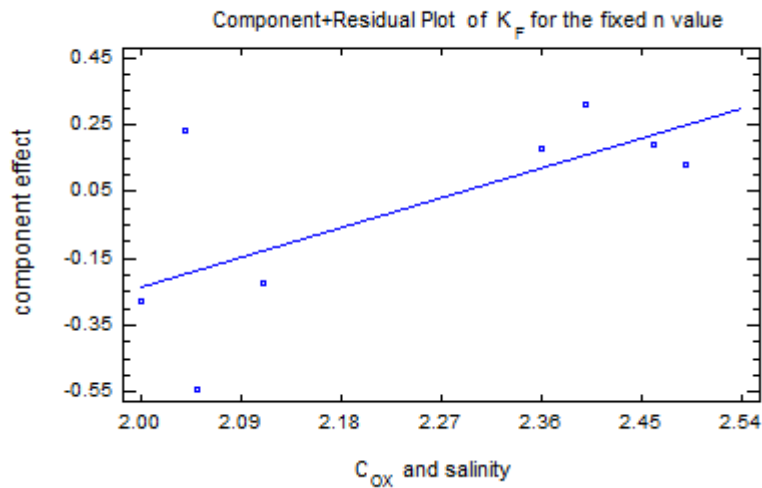


Figure 17: Graph of Freundlich adsorption coefficient  $K_F$  and its dependence on observed soil characteristics ( $C_{OX}$  and salinity); P-value = 0.0284,  $R^2$  value = 0.76

Dependent variable:  $K_F$  (for the fixed  $n$  value) and independent variables:  $C_{OX}$ , salinity and particle density

The output shows the results of fitting a multiple linear regression model to describe the relationship between  $K_F$  constant and three independent variables ( $C_{OX}$ , salinity and particle density). The equation of the fitted model is (33):

$$K_F = 18.9678 + 0.000460461 * C_{OX} (\%) + 0.0614541 * salinity (\mu S \cdot cm^{-1}) - 6.4383 * \rho_z (g \cdot cm^{-3}) \quad (33)$$

The P-value was less than 0.05, meaning a statistically significant relationship between the variables at the 95.0 % confidence level (P-value = 0.0304,  $R^2$  value = 0.87).

The obtained correlations are shown as a graph in Figure 18.

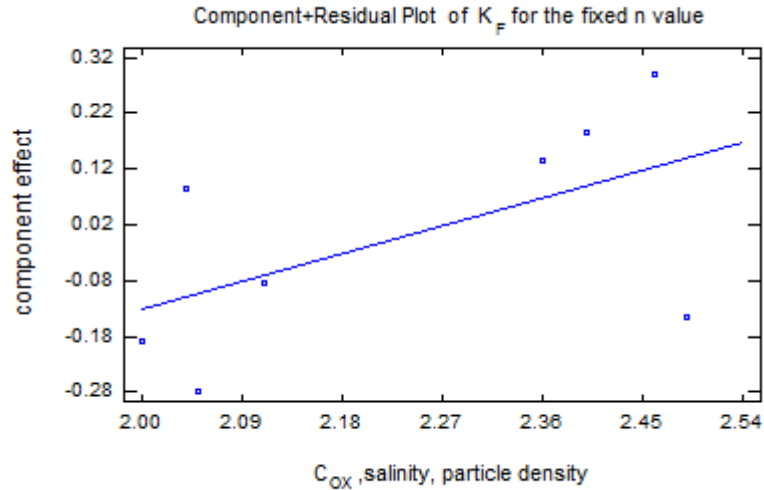


Figure 18: Graph of Freundlich adsorption coefficient  $K_F$  and its dependence on observed soil characteristics ( $C_{OX}$ , salinity and particle density); P-value = 0.0304,  $R^2$  value = 0.87

Dependent variable:  $K_F$  (for the fixed  $n$  value) and independent variables: sand,  $C_{OX}$  and salinity

The output shows the results of fitting a multiple linear regression model to describe the relationship between  $K_F$  and three independent variables (sand,  $C_{OX}$  and salinity). The equation of the fitted model is (34):

$$K_F = 1.3195 + 0.0833261 * sand(\%) + 0.00152513 * C_{OX}(\%) + 0.0323033 * salinity(\mu S \cdot cm^{-1}) \quad (34)$$

The P-value in this case was less than 0.05, there was a statistically significant relationship between the variables at the 95.0 % confidence level (P-value = 0.0276,  $R^2$  value = 0.876).

The obtained correlations are shown as a graph in Figure 19.

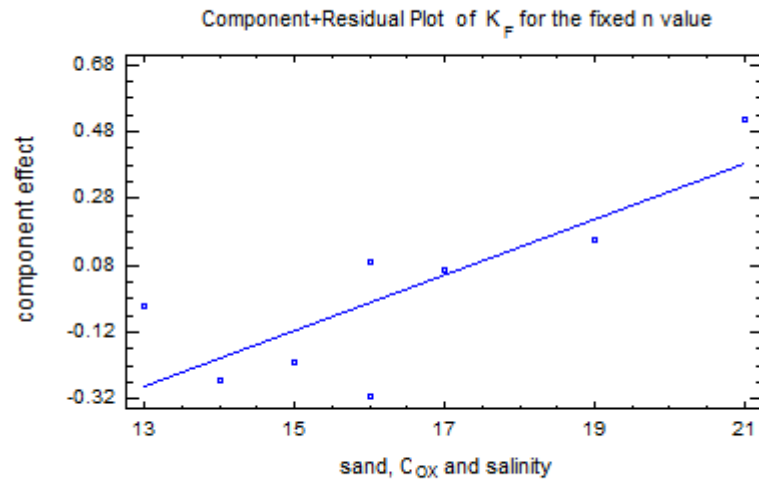


Figure 19: Graph of Freundlich adsorption coefficient  $K_F$  and its dependence on observed soil characteristics (sand,  $C_{OX}$  and salinity); P-value = 0.0276,  $R^2$  value = 0.876

Dependent variable:  $K_F$  (for the fixed  $n$  value) and independent variables: silt,  $C_{OX}$  and salinity

The output shows the results of fitting a multiple linear regression model to describe the relationship between  $K_F$  and three independent variables (silt,  $C_{OX}$  and salinity). The equation of the fitted model is (35):

$$K_F = 11.8067 - 0.199634 * \text{silt}(\%) + 0.00222827 * C_{OX}(\%) - 0.0104542 * \text{salinity}(\mu S \cdot cm^{-1}) \quad (35)$$

The P-value was less than 0.05 and it means that there was a statistically significant relationship between the variables at the 95.0 % confidence level (P-value = 0.0374,  $R^2$  value = 0.855).

The obtained correlations are shown as a graph in Figure 20.



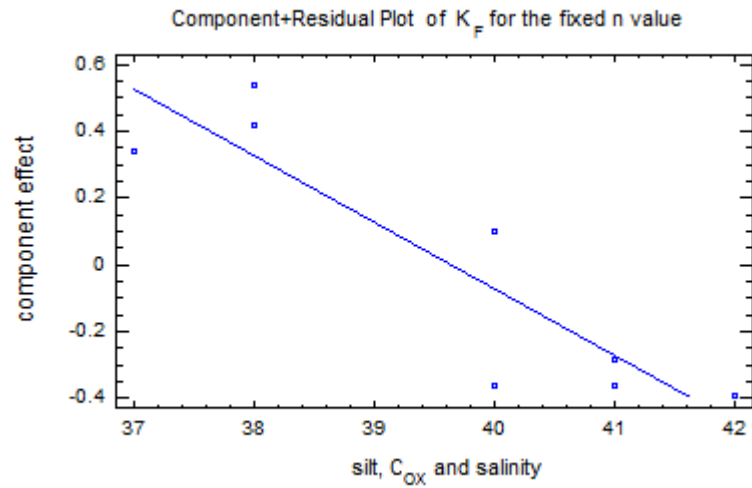


Figure 20: Graph of Freundlich adsorption coefficient  $K_F$  and its dependence on observed soil characteristics (silt,  $C_{ox}$  and salinity); P-value = 0.0374,  $R^2$  value = 0.855

## 6. Discussion

As part of this thesis, an experiment was carried out to explore the rates of pesticide chlorotoluron sorption in specific soil samples. For all soil samples the calculated values of Freundlich adsorption coefficients  $K_F$  were similar, ranging from 5.08 (soil sample C) to 5.91 (soil sample F). The narrow range of  $K_F$  coefficients might have been caused by similar soil characteristics of the soil samples (see Table 6). The  $K_F$  coefficients determined in this diploma thesis for Luvic Chernozem were similar to  $K_F$  coefficients that were determined by Kodešová et al. (2011) for Harpic Chernozem ( $K_F = 4.07$  and  $4.64$ ), higher than for loess ( $K_F = 0.85$ ) and sand ( $K_F = 0.46$ ).

In this diploma thesis the sorption of chlorotoluron was found to be influenced by organic matter content ( $C_{OX}$ ) and salinity (Appendix 6). By this testing, the conclusion made by Kodešová et al. (2011) was verified. Kodešová et al. (2011) studied chlorotoluron sorption in soil and stated that the adsorption of non-ionic pesticides was closely correlated with organic matter content. But in some cases a variety of additional soil properties improved the regressions, i.e. enhanced pesticide sorption.

Furthermore, the multiple linear regression used in this thesis has shown that the  $K_F$  coefficient (for the fixed  $n$  value) depended on a combination of either:  $C_{OX}$ , sand and salinity, or  $C_{OX}$ , salinity and particle density, or  $C_{OX}$ , salinity and silt, or  $C_{OX}$  and salinity (Appendix 5). Conversely, there are documented results by Kodešová et al. (2011) that differ, where the  $K_F$  coefficient depended on a combination of either organic matter content and  $pH_{KCl}$ , or organic matter content and sorption complex saturation. Moreover, Kodešová et al. (2005a), based on their study, proposed that multiple regression analysis indicated the impact of  $pH_{KCl}$ , clay content and cation exchange capacity to be not significant.

In next section of this thesis, a pedotransfer rule according to Kozák and Vacek (2000) was verified. These authors reported the pedotransfer rule for the prediction of  $K_F$  coefficients from  $pH_{KCl}$ , CEC, content of organic matter ( $C_{OX}$ ) and clay content for pesticide atrazine. By using multivariate statistical methods, they obtained a regression equation (15) of the fitted model. Based on the experiment carried for this thesis, it was demonstrated that the  $K_F$  coefficient was influenced from 75.9333 % by  $pH_{KCl}$ , CEC, content of organic matter ( $C_{OX}$ ) and clay content, but the result was not statistically significant.

The equation of the fitted model is (36):

$$K_F = 20.1791 + 0.00141762 * C_{ox} (\%) + 0.0352162 * CEC - 2.27534 * pH_{KCl} - 0.0606887 * clay(\%) \quad (36)$$

Subsequently, a pedotransfer rule reported by Kodešová et al. (2011) was verified. Kodešová et al. (2011) stated the pedotransfer rule for the prediction of the  $K_F$  coefficient from organic matter content ( $C_{ox}$ ) and  $CaCO_3$  for pesticide chlorotoluron. The  $K_F$  coefficient was influenced from 92.4 % on above mentioned soil characteristics (P-value = 0.0000) and this regression equation was obtained (37):

$$K_F = -0.68 + 1.74 OM(\%) + 0.11 CaCO_3(\%). \quad (37)$$

When applying this pedotransfer rule on soil samples used in this thesis, the following results were obtained. The  $R^2$  value indicated that  $K_F$  was influenced by  $C_{ox}$  and  $CaCO_3$  only from 28.9 % and the P-value (0.4263) indicated that the relationship between  $K_F$  and  $C_{ox}$  and  $CaCO_3$  was not statistically significant at the 95.0 % or higher confidence level. The equation of the fitted model is (38):

$$K_F = 0.811698 - 0.141746 * C_{ox}(\%) + 0.323736 * CaCO_3(\%). \quad (38)$$

Application of pedotransfer rules according to Kozák and Vacek (2000) and Kodešová et al. (2011) were not verified, but on the other hand it was found the alternative pedotransfer rules for the behaviour of chlorotoluron in Luvic Chernozem. Three soil characteristics had the greatest influence on the  $K_F$  coefficient:  $C_{ox}$ , sand and salinity. The coefficient of determination in this case was  $R^2 = 0.876$ , P-value = 0.0276 and a regression equation (34) of the fitted model was obtained.

## 7. Conclusion

The conclusion of this diploma thesis can be summarised as four main points:

- the initial experimental hypothesis has been confirmed. Organic matter influences the sorption of chlorotoluron in soil. The range of organic matter content values ( $C_{OX}$ ), which were from 1.82 to 2.42, allowed to develop dependency of chlorotoluron sorption on organic matter in soil samples,
- the pedotransfer rule according to Kozák and Vacek (2000) was not verified for the behaviour of chlorotoluron in Luvic Chernozem,
- the pedotransfer rule proposed by Kodešová et al. (2011) was not proved for the behaviour of chlorotoluron in Luvic Chernozem,
- the alternative pedotransfer rule was found for the behaviour of chlorotoluron in Luvic Chernozem with different organic matter content. The soil characteristics that most influenced the Freundlich adsorption coefficient  $K_F$  (for the fixed  $n$  value) were:  $C_{OX}$ , sand and salinity.

## 8. References

- Altfelder, S. 1999. Nonequilibrium Sorption of Nonionic Organic Chemicals in Soils: Experiments and Modeling, Dissertation. Technischen Universität Carolo – Wilhelmina.
- Anderson, J.P.E. 1994. Kinetics of Pesticide Biodegradation in Soils? Principles and Applications. Environmental Behaviour of Pesticides and regulatory Aspects, ISBN 2-930119-03-9, 211 – 221.
- Barriuso, E., Benoit, P., Bergheaud, V. 1994. Role of Soil Fractions in Retention and Stabilisation of Pesticides in Soils. Environmental Behaviour of Pesticides and regulatory Aspects, ISBN 2-930119-03-9, 138 – 143.
- Blum, W.E.H. 2005. Functions of Soil for Society and the Environment. Reviews in Environmental Science and Bio/ Technology, 4, 75 – 79.
- Bower, C. A., Hatcher, J.T. 1966. Simultaneous determination of surface area and cation-exchange capacity. Soil Sci. Soc. Am. Proc., 30, 525 – 527.
- Brady, N.C., Weil, R.R. 1999. The Nature and Properties of Soils. Twelfth edition. Prentice-Hall, New Jersey, ISBN 0-13-852444-0, p. 881.
- Calvet, R., Barriuso, E. 1994. Retention and Bioavailability of Pesticides in Soil; Environmental Behaviour of Pesticides and regulatory Aspects, ISBN 2-930119-03-9, 63 – 71.
- Carter, M.R, Gregorich, E.G. (Eds.). 2008. Soil Sampling and Method of Analysis, Canadian Society of Soil Science, Taylor and Francis Group, USA, p. 225–237.
- Carter, M.R. (Ed.). 1993. Soil Reaction and Exchangeable acidity, in Soil Sampling and Method of Analysis, Canadian Society of Soil Science, Lewis Publisher, USA, 141 – 185.

Coquet, Y. 2002. Variation of Pesticide Sorption Isotherm in Soil at the Catchment Scale, *Pest Management Science*, 58, 69 – 78.

Coquet, Y., Barriuso, E. 2002. Spatial variability of Pesticide Adsorption within the Topsoil of a small agricultural Catchment. *Agronomie*, 22, 389 – 398.

Dane, J.H., Topp, G.C. (Eds.). 2002. *Methods of Soil Analysis. Part 4. Physical Methods*, Soil Science Society of America, Inc., Madison, USA, 229–240.

Del Re, A.A.M., Trevisan, M., Capri, E., Evans, S.P., Brasa, E. 1994. Criteria of existing Pesticide Models Evaluation. *Environmental Behaviour of Pesticides and regulatory Aspects*, ISBN 2-930119-03-9, 476 – 482.

Doucette, W.J., 2003. Quantitative Structure – activity Relationships for predicting Soil-sediment Sorption Coefficient for organic Chemicals. *Environmental Toxicology and Chemistry*, 22 (8), 1771 – 1788.

Fouqué-Brouard, Ch.M., Fournier, J.M. 1996. Adsorption-desorption and leaching of phenylurea Herbicides on Soils. *Talanta*, 43, 1793 – 1802.

Fushiwaki, Y., Urano, K. 2001. Adsorption of Pesticides and their Biodegraded Products on Clay Minerals and Soils. *Journal of Health Science*, 47 (4), 429 – 432.

Gevao, B., Semple, K.T., Jones, K.C. 2000. Bound Pesticide Residues in Soils: a Review. *Environmental Pollution*, 108, 3 – 14.

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, 45 – 62.

Gustafson, D.I., 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. *Environ. Toxicol. Chem.* 8, 339–537.

Hillel, D. 1998. *Environmental Soil Physics*, Academic Press, San Diego, ISBN-13: 978-0-12-348525-0, ISBN-10: 0-12-348525-8, p. 771.

Hutson, D.H., Roberts, T.R. 1990. *Environmental Fate of Pesticides*, John Wiley & Sons Ltd, Chichester, ISBN 0-471-91711-7, p. 286.

ISO 10390. 1994. International Organization of Standardization, Standard of Soil quality – Determination of pH.

Jones, R.L., Arnold, D.J.S., Harris, G.L., Bailey, S.W., Pepper, T.J., Mason, D.J., Brown, C.D., Leeds-Harrison, P.B., Walker, A., Bromilow, R.H., Brockie, D., Nicholls, P.H., Craven, A.C.C., Lythgo, C.M. 2000. Processes affecting Movement of Pesticides to Drainage in cracking Clay coils. *The Royal Society of Chemistry, Pesticide Outlook – October 2000*, 174 – 178.

Keller, L., Carbone, J., Hamilton, J., Hurt, S., Gocha, N., Ollinger, J. 1994. Use of USEPA Computer models to Predict Mencozeb Concentration in Surface Water Following its Use in Potato Fields. *Environmental Behaviour of Pesticides and regulatory Aspects*, ISBN 2-930119-03-9, 483 – 490.

Kennedy, I.R., Sanchez-Bayo, F., Lee, N., Shivaramaiah, M.H., Crossan, A., Baskaran, S., Hill, A. S. 2000. Protection of the Environment and Produce from Contamination with Pesticide Residues. *Quality assurance in agricultural produce, ACIAR Proceedings 100*, 206 – 215.

Khan, S.U. 1980. *Pesticides in the Soil Environment*, Elsevier Scientific Publishing Company, Amsterdam, ISBN 0-444-41873-3, p. 223.

Klute, A. 1996. *Methods of Soil Analysis. Agronomy Monograph 9*, American Society of Agronomy, Madison, WI, USA.

Kočárek, M., Kodešová, R., Kozák, J., Drábek, O. 2010. Field Study of Chlorotoluron Transport and its Prediction by the BPS Mathematical Model. *Soil & Water Res.*, 5 (4), 153 – 160.

Kočárek, M., Kodešová R., Kozák, J., Drábek, O. and Vacek, O. 2005. Chlorotoluron Behaviour in Five different Soil Types. *Plant, Soil and Environment*, 51 (7), 304 – 309.

Kodešová, R., Kočárek, M., Hájková, T., Hýbler, M., Drábek, O. and Kodeš, V. 2012. Chlorotoluron mobility in compost amended soil. *Soil & Tillage Research* 118 (2012), 88-96.

Kodešová, R., Kočárek, M., Kodeš, V., Drábek, O., Kozák, J., Hejtmánková, K. 2011. Pesticide adsorption in relation to soil properties and soil type distribution in regional scale. *Journal of Hazardous Materials* 186 (1), 540–550.

Kodešová, R., Kočárek, M., Kozák, J. and Pijálková, H. 2005a. Estimation of Parameters Describing Freundlich and Langmuir Adsorption Isotherms, 13th International Poster Day, Transport of Water, Chemicals and Energy in the System Soil-Crop Canopy-Atmosphere System, Čelkova, A., Matějka, F. (Eds.), Institute of Hydrology SAS, Bratislava, Slovak Republic, Proceedings CD, ISBN 80-885754-13-4, p. 273 - 281.

Kodešová, R., Kozák, J., Šimůnek, J. and Vacek, O. 2005b. Single and Dual – Permeability Models of Chlorotoluron Transport in the Soil Profile. *Plant Soil Environ.*, 51 (7), 310 – 315.

Kodešová R., Kozák J. and Vacek, O. 2004. Field and Numerical Study of Chlorotoluron Transport in the Soil Profile. *Plant Soil Environ.*, 50 (8), 333 - 338.

Kozák, J. and Vacek, O. (2000). Pedotransfer Functions as a Tool for Estimation of Pesticides Behavior in Soils. *Rostlinná výroba.*, 46, 69 - 76.

Koziol, A.S., Pudykiewicz, J.A. 2000. Global-scale environmental Transport of persistent organic Pollutants. *Chemosphere*, 45, 1181 – 1200.



Kördel, W., Wahle, U., Knoche, H., Hund, K. 1995. Degradation capacities of Chlorotoluron and Simazine in Subsoil Horizons. *The Science of the Total Environment*, 171, 43 – 50.

Kutílek, M., Nielsen, D.R. 1994. *Soil Hydrology*, Catena Verlag, Cremlingen - Destedt, ISBN 3-923381-26-3, p. 370.

Linde, C.D. 1994. *Physico-Chemical Properties and Environmental Fate of Pesticides*. Environmental hazards assessment Program. Sacramento, p. 53.

Losito, H., Zambonin, C.G., Palmisano, F. 2000. Degradation of Chlortoluron in Water disinfections Processes. *Journal of Environmental Monitoring*, 2, 582 – 586.

Lund, U., Mintz, B., Galal-Gorchev, H., Helmer, R., Bonnefoy, X., Espinoza, O. 1996. Chlorotoluron in Drinking-water. *Guidelines for drinking-water quality*. 2<sup>nd</sup> ed. Vol.2. World Health Organization, Geneva, 1 – 4.

Matthews, G.A. 2000. *Pesticide Application Methods*. Third edition. Blackwell Science Ltd, London, ISBN 0-632-05473-5, p. 432.

Mehmood, Z., Kelly, D.E., Kelly, S.L. 1995. Metabolism of the Herbicide Chlorotoluron by Human. *Chemosphere*, 31 (11/12), 4515 – 4529.

Morrill, L.G., Mahilum, B.C., Mohiuddin, S.H. 1982. *Organic Compounds in Soils: Sorption, Degradation and Persistence*, Ann Arbor Science Publishers, Inc., Michigan, ISBN 0-250-40514-8, p. 326.

Nash, D., Halliwell, D., Cox, J. 2002. Hydrological Mobilization of Pollutants at the Field/Slope Scale. *CAB International 2002. Agriculture Hydrology and Water Quality*, 225 – 237.

Neumeister, L., Sarapatka, B., Kuzma, S., Samsonova, P., Urban, J., Bubenikova, I., Sweeney, S. 2003. *Pesticides in Central and Eastern European Countries Usage, Registration,*

Identification and Evaluation, Part 3: Czech Republic, Pesticide Action Network Germany, Germany, p. 120.

Petruzzelli, D., Helfferich, F.G., Liberti, L. 1991. Ion-Exchange Kinetics on Reactive Polymers and Inorganic Soil Constituents. Rates of Soil Chemical Processes, Soil Science Society of America, Inc., Madison, ISBN 0-89118-795-2, 95 – 118.

Riise, G., Pettersen, M.N. 1994. Association of Dichlorprop and Atrazine with Soil Organic Carbon. Environmental Behaviour of Pesticides and regulatory Aspects, ISBN 2-930119-03-9, 73 – 78.

Roberts, T.R., Kearney, P.C. 1995. Environmental Behaviour of Agrochemicals, John Wiley & Sons Ltd, Chichester, ISBN 0-471-95301-6, p. 407.

Rouchaud, J., Neus, O., Bulcke, R., Cools, K., Eelen, H., Dekkers, T. 2000. Soil Dissipation of Diuron, Chlorotoluron, Simazine, Propyzamide, and Diflufenican Herbicides After Repeated Applications in Fruit Tree Orchards. Archives of Environmental Contamination and Toxicology, 39, 60 – 65.

Sánchez, M.E., Estrada I.B., Martínez, O., Martín-Villacorta, J., Aller, A., Morán, A. 2004. Influence of the Application of Sewage Sludge on the Degradation of Pesticides in the Soil. Chemosphere, 57, 673 – 679.

Spadotto, C.A., Hornsby, A.G. 2003. Organic Compounds in the Environment. Soil Sorption of Acidic Pesticides: Modeling pH Effects. J. Environ. Qual., 32, 949 – 956.

Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E. (Eds.). 1996. Methods of Soil Analysis. Part 3. Chemical Methods, Soil Science Society of America, Inc., Madison, WI, USA, 437 – 474.

Sparks, D.L. 1995. Environmental soil chemistry, Academic Press, Inc., San Diego, ISBN 0-12-656445-0, p. 267.

Spark, K.M., Swift, R.S. 2002. Effect of Soil Composition and dissolved organic Matter on Pesticide Sorption. *The Science of the Total Environment*, 298, 147 – 161.

Trevisan, M., Capri, E., Evans, S.P., Del Re, A.A.M. 1994. Validation and Comparison of Pesticide Soil Transport Models for Field Dissipation of Metamitron. *Environmental Behaviour of Pesticides and regulatory Aspects*, ISBN 2-930119-03-9, 501 – 508.

Vanclooster, M., Diels, J., Mallants, D., Feyen, J., Dust, M., Vereecken, H. 1994. Characterizing the Impact of Uncertain Soil Properties on Simulated Pesticide Leaching. *Environmental Behaviour of Pesticides and regulatory Aspects*, ISBN 2-930119-03-9, 470 – 475.

Vroumsia, T., Steiman, R., Seigle-Murandi, F., Benoit-Guyod, J.-L., Khadrani, A. 1996. Biodegradation of three Substituted Phenylurea Herbicides (Chlortoluron, Diuron, And Isoproturon) by Soil Fungi. A Comparative Study. *Chemosphere*, 33 (10), 2045 – 2056.

IUPAC global availability of Information on Agrochemicals [online]. 5.3.2011 [11.3.2011]. Available: <<http://sitem.herts.ac.uk/aeru/iupac/151.htm>>.

State Phytosanitary Administration [online]. 1.3.2011 [9.3.2011]. Available: <[http://eagri.cz/public/web/file/100356/Spotreba\\_ucinnych\\_latek\\_kg\\_l.htm](http://eagri.cz/public/web/file/100356/Spotreba_ucinnych_latek_kg_l.htm)>.

## 9. List of used abbreviations

DDT	Dichlorodiphenyltrichloroethane
IPM	Integrated Pest Management
ICM	Integrated Crop Management
H'	Henry's Law constant
GUS	Groundwater ubiquity score
BCF	Bioconcentration factor
DOC	Dissolved organic carbon
CEC	Cation exchange capacity
BET	Brunauer, Emmet and Teller equation
$P_{vp}$	Vapor pressure
$K_d$	Distribution coefficient
$K_{OC}$	Organic carbon partition coefficient
$K_{OW}$	Octanol/water partition coefficient
$K_p$	Partition coefficient between soil and aqueous phases
$\rho_z$	Particle density
S	Sorbed concentration
C	Concentration in solution
q	Amount of adsorption
n	Correlation factor
HPLC	High performance liquid chromatography
EXAMS	Exposure analysis modeling system
PRZM2	Pesticide root zone model
WAVE	Water and agrochemicals in soil and vadose environment

## 10. Appendix

### List of Appendixes:

Appendix 1: Measured values ( $c$ ) and amounts of chlorotoluron adsorbed on soil particles ( $s$ ) .....	77
Appendix 2: Calculation of Freundlich equation for sample A.....	79
Appendix 3: Calculation of Langmuir equation for sample A.....	79
Appendix 4: Simple regression .....	80
Appendix 5: Multiple regression where dependent variable $K_F$ (for the fixed $n$ value).....	81
Appendix 6: Simple regression of $K_F$ (for the fixed $n$ value).....	81
Appendix 7: Soil & Tillage Research - Chlorotoluron mobility in compost amended soil.....	82

Appendix 1: Measured values (c) and amounts of chlorotoluron adsorbed on soil particles (s)

Soil Sample	c ( $\mu\text{g}\cdot\text{cm}^{-3}$ )	s ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Soil sample	c ( $\mu\text{g}\cdot\text{cm}^{-3}$ )	s ( $\mu\text{g}\cdot\text{g}^{-1}$ )
A 1/1	0.10	0.97	C 1/1	0.13	0.94
A 1/2	0.09	0.97	C 1/2	0.12	0.94
A 1/3	0.09	0.98	C 1/3	0.12	0.94
A 2/1	0.29	2.50	C 2/1	0.35	2.45
A 2/2	0.34	2.46	C 2/2	0.31	2.48
A 2/3	0.30	2.59	C 2/3	0.32	2.47
A 3/1	0.63	4.64	C 3/1	0.67	4.60
A 3/2	0.71	4.56	C 3/2	0.66	4.62
A 3/3	0.65	4.62	C 3/3	0.65	4.62
A 4/1	1.50	8.71	C 4/1	2.04	8.17
A 4/2	1.56	8.65	C 4/2	2.27	7.94
A 4/3	1.67	8.54	C 4/3	1.96	8.25
A 5/1	7.50	18.08	C 5/1	6.40	19.18
A 5/2	5.61	19.97	C 5/2	6.74	18.84
A 5/3	5.84	19.74	C 5/3	6.74	18.84
B 1/1	0.11	0.98	D 1/1	0.11	0.96
B 1/2	0.09	0.98	D 1/2	0.09	0.97
B 1/3	0.10	0.72	D 1/3	0.12	0.95
B 2/1	0.35	2.45	D 2/1	0.38	2.42
B 2/2	0.35	2.45	D 2/2	0.39	2.41
B 2/3	0.33	2.46	D 2/3	0.32	2.47
B 3/1	0.69	4.58	D 3/1	0.69	4.58
B 3/2	0.64	4.63	D 3/2	0.65	4.62
B 3/3	0.68	4.59	D 3/3	0.67	4.60
B 4/1	1.72	8.49	D 4/1	1.87	8.34
B 4/2	1.69	8.52	D 4/2	1.65	8.56
B 4/3	1.90	8.31	D 4/3	1.64	8.57
B 5/1	5.79	19.79	D 5/1	6.05	19.53
B 5/2	5.75	19.83	D 5/2	5.93	19.65
B 5/3	5.54	20.04	D 5/3	4.74	20.84

Measured values (c) and amounts of chlorotoluron adsorbed on soil particles (s) - continuation

Soil Sample	c ( $\mu\text{g}\cdot\text{cm}^{-3}$ )	s ( $\mu\text{g}\cdot\text{cm}^{-3}$ )	Soil Sample	c ( $\mu\text{g}\cdot\text{cm}^{-3}$ )	s ( $\mu\text{g}\cdot\text{cm}^{-3}$ )
E 1/1	0.11	0.96	G 1/1	0.11	0.96
E 1/2	0.11	0.95	G 1/2	0.10	0.97
E 1/3	0.10	0.97	G 1/3	0.11	0.95
E 2/1	0.33	2.47	G 2/1	0.28	2.51
E 2/2	0.37	2.42	G 2/2	0.28	2.51
E 2/3	0.37	2.42	G 2/3	0.32	2.48
E 3/1	0.72	4.55	G 3/1	0.70	4.57
E 3/2	0.67	4.60	G 3/2	0.59	4.68
E 3/3	0.73	4.55	G 3/3	0.57	4.70
E 4/1	1.88	8.33	G 4/1	1.74	8.47
E 4/2	1.83	8.38	G 4/2	1.78	8.43
E 4/3	1.73	8.48	G 4/3	1.59	8.62
E 5/1	5.28	20.30	G 5/1	5.08	20.50
E 5/2	5.36	20.22	G 5/2	5.54	20.04
E 5/3	5.49	20.09	G 5/3	5.49	20.09
F 1/1	0.11	0.96	H 1/1	0.14	0.96
F 1/2	0.11	0.96	H 1/2	0.10	0.97
F 1/3	0.10	0.97	H 1/3	0.12	0.95
F 2/1	0.31	2.48	H 2/1	0.36	2.51
F 2/2	0.28	2.52	H 2/2	0.36	2.51
F 2/3	0.28	2.52	H 2/3	0.35	2.48
F 3/1	0.77	4.50	H 3/1	0.80	4.57
F 3/2	0.70	4.57	H 3/2	0.73	4.68
F 3/3	0.70	4.57	H 3/3	0.62	4.70
F 4/1	1.89	8.32	H 4/1	1.63	8.47
F 4/2	1.59	8.62	H 4/2	1.82	8.43
F 4/3	1.73	8.48	H 4/3	1.46	8.62
F 5/1	5.26	20.32	H 5/1	5.97	20.50
F 5/2	4.50	21.08	H 5/2	4.89	20.04
F 5/3	4.94	20.64	H 5/3	5.53	20.09

Appendix 2: Calculation of Freundlich equation for sample A

			x	y					
Sample A	c ( $\mu\text{g}\cdot\text{cm}^{-3}$ )	s ( $\mu\text{g}\cdot\text{g}^{-1}$ )	log c	log s	x <sup>2</sup>	x · y	s'	N	15,00
A 1/1	0.10	0.97	-1.01	-0.01	1.03	0.01	1.08	<b>b<sub>0</sub></b>	0.76
A 1/2	0.09	0.97	-1.03	-0.01	1.05	0.01	1.05	<b>b<sub>1</sub></b>	0,71
A 1/3	0.09	0.98	-1.03	-0.01	1.07	0.01	1.04	<b>k<sub>F</sub></b>	5.70
A 2/1	0.29	2.50	-0.54	0.40	0.29	-0.21	2.36	<b>n</b>	1,40
A 2/2	0.34	2.46	-0.47	0.39	0.22	-0.18	2.62	<b>1/n</b>	0,71
A 2/3	0.30	2.59	-0.52	0.40	0.27	-0.21	2.42		
A 3/1	0.63	4.64	-0.20	0.67	0.04	-0.13	4.10		
A 3/2	0.71	4.56	-0.15	0.66	0.02	-0.10	4.46		
A 3/3	0.65	4.62	-0.18	0.66	0.03	-0.12	4.21		
A 4/1	1.50	8.71	0.18	0.94	0.03	0.17	7.62		
A 4/2	1.56	8.65	0.19	0.94	0.04	0.18	7.83		
A 4/3	1.67	8.54	0.22	0.93	0.05	0.21	8.23		
A 5/1	7.50	18.08	0.87	1.26	0.77	1.10	24.02		
A 5/2	5.61	19.97	0.75	1.30	0.56	0.97	19.53		
A 5/3	5.84	19.74	0.77	1.30	0.59	0.99	20.10		
<b>Σ</b>			-2.15	9.80	6.06	2.70			

Appendix 3: Calculation of Langmuir equation for sample A

			x	y					
Sample A	c ( $\mu\text{g}\cdot\text{cm}^{-3}$ )	s ( $\mu\text{g}\cdot\text{g}^{-1}$ )	c	c/s	x <sup>2</sup>	x · y	s''	N	15,00
A 1/1	0.10	0.97	0.10	0.10	0.01	0.01	0.84	<b>b<sub>0</sub></b>	0.11
A 1/2	0.09	0.97	0.09	0.10	0.01	0.01	0.82	<b>b<sub>1</sub></b>	0.04
A 1/3	0.09	0.98	0.09	0.09	0.01	0.01	0.81	<b>k<sub>L</sub></b>	0.32
A 2/1	0.29	2.50	0.29	0.12	0.08	0.03	2.39	<b>s<sub>max</sub></b>	27.37
A 2/2	0.34	2.46	0.34	0.14	0.11	0.05	2.73		
A 2/3	0.30	2.59	0.30	0.12	0.09	0.04	2.46		
A 3/1	0.63	4.64	0.63	0.14	0.40	0.09	4.71		
A 3/2	0.71	4.56	0.71	0.16	0.50	0.11	5.19		
A 3/3	0.65	4.62	0.65	0.14	0.43	0.09	4.84		
A 4/1	1.50	8.71	1.50	0.17	2.26	0.26	9.08		
A 4/2	1.56	8.65	1.56	0.18	2.43	0.28	9.31		
A 4/3	1.67	8.54	1.67	0.20	2.80	0.33	9.75		
A 5/1	7.50	18.08	7.50	0.41	56.22	3.11	19.64		
A 5/2	5.61	19.97	5.61	0.28	31.48	1.58	17.89		
A 5/3	5.84	19.74	5.84	0.30	34.13	1.73	18.14		
<b>Σ</b>			26.89	2.64	130.96	7.72			



#### Appendix 4: Simple regression

Simple regression	P – value	R <sup>2</sup> value	Simple regression	P – value	R <sup>2</sup> value
K <sub>F</sub> vs. pH <sub>H2O</sub>	0.6142	0.0450	K <sub>L</sub> vs. pH <sub>H2O</sub>	0.3387	0.1525
K <sub>F</sub> vs. pH <sub>KCl</sub>	0.1115	0.3668	K <sub>L</sub> vs. pH <sub>KCl</sub>	0.7193	0.0231
K <sub>F</sub> vs. V <sub>a</sub>	0.5931	0.0504	K <sub>L</sub> vs. V <sub>a</sub>	0.0068	0.7307
K <sub>F</sub> vs. H <sub>a</sub>	0.7317	0.0211	K <sub>L</sub> vs. H <sub>a</sub>	0.7697	0.0154
K <sub>F</sub> vs. Q <sub>4/6</sub>	0.9660	0.0003	K <sub>L</sub> vs. Q <sub>4/6</sub>	0.5524	0.0619
K <sub>F</sub> vs. CaCO <sub>3</sub>	0.5386	0.0662	K <sub>L</sub> vs. CaCO <sub>3</sub>	0.5761	0.0550
K <sub>F</sub> vs. CEC	0.3983	0.1211	K <sub>L</sub> vs. CEC	0.1053	0.3771
K <sub>F</sub> vs. S	0.4000	0.1203	K <sub>L</sub> vs. S	0.1094	0.3703
K <sub>F</sub> vs. V	0.4424	0.1013	K <sub>L</sub> vs. V	0.2690	0.1982
K <sub>F</sub> vs. C <sub>ox</sub>	0.3464	0.1482	K <sub>L</sub> vs. C <sub>ox</sub>	0.0135	0.6655
K <sub>F</sub> vs. Salinity	0.9551	0.0000	K <sub>L</sub> vs. Salinity	0.3421	0.1506
K <sub>F</sub> vs. Particle density	0.3073	0.1718	K <sub>L</sub> vs. Particle density	0.6315	0.0408
K <sub>F</sub> vs. Clay	0.3355	0.1544	K <sub>L</sub> vs. Clay	0.4646	0.0922
K <sub>F</sub> vs. Silt	0.3226	0.1622	K <sub>L</sub> vs. Silt	0.9285	0.0015
K <sub>F</sub> vs. Very fine sand	0.8338	0.0079	K <sub>L</sub> vs. Very fine sand	0.9752	0.0002
K <sub>F</sub> vs. Sand	0.2292	0.2300	K <sub>L</sub> vs. Sand	0.7120	0.0244
1/n vs. pH <sub>H2O</sub>	0.3484	0.1470	s <sub>max</sub> vs. pH <sub>H2O</sub>	0.1736	0.2843
1/n vs. pH <sub>KCl</sub>	0.4214	0.1104	s <sub>max</sub> vs. pH <sub>KCl</sub>	0.6813	0.0301
1/n vs. V <sub>a</sub>	0.0552	0.4845	s <sub>max</sub> vs. V <sub>a</sub>	0.0766	0.4319
1/n vs. H <sub>a</sub>	0.9423	0.0009	s <sub>max</sub> vs. H <sub>a</sub>	0.9434	0.0009
1/n vs. Q <sub>4/6</sub>	0.5928	0.0505	s <sub>max</sub> vs. Q <sub>4/6</sub>	0.3193	0.1642
1/n vs. CaCO <sub>3</sub>	0.6680	0.0327	s <sub>max</sub> vs. CaCO <sub>3</sub>	0.3305	0.1574
1/n vs. CEC	0.0507	0.4974	s <sub>max</sub> vs. CEC	0.0915	0.4018
1/n vs. S	0.0553	0.4840	s <sub>max</sub> vs. S	0.0973	0.3911
1/n vs. V	0.2452	0.2166	s <sub>max</sub> vs. V	0.3007	0.1761
1/n vs C <sub>ox</sub>	0.0088	0.7080	s <sub>max</sub> vs. C <sub>ox</sub>	0.0101	0.6950
1/n vs. Salinity	0.3229	0.1620	s <sub>max</sub> vs. Salinity	0.1349	0.3320
1/n vs. Particle density	0.2374	0.2230	s <sub>max</sub> vs. Particle density	0.3294	0.1580
1/n vs. Clay	0.7011	0.0263	s <sub>max</sub> vs. Clay	0.9957	0.0000
1/n vs. Silt	0.8798	0.0041	s <sub>max</sub> vs. Silt	0.9003	0.0028
1/n vs. Very fine sand	0.5291	0.0692	s <sub>max</sub> vs. Very fine sand	0.6934	0.0278
1/n vs. Sand	0.5490	0.0629	s <sub>max</sub> vs. Sand	0.7651	0.0160

Appendix 5: Multiple regression where dependent variable  $K_F$  (for the fixed  $n$  value)

Multiple regression	P - value	R <sup>2</sup> value
$K_F$ vs. $C_{OX}$ , pH <sub>HCL</sub> , CEC	0.1138	0.742
$K_F$ vs. $C_{OX}$ , CaCO <sub>3</sub>	0.0843	0.628
$K_F$ vs. $C_{OX}$ , salinity, particle density	0.0304	0.870
$K_F$ vs. $C_{OX}$ , salinity	0.0284	0.760
$K_F$ vs. sand, $C_{OX}$ , salinity	0.0276	0.876
$K_F$ vs. silt, $C_{OX}$ , salinity	0.0374	0.855

Appendix 6: Simple regression of  $K_F$  (for the fixed  $n$  value)

Simple regression	P - values	R <sup>2</sup> value
$K_F$ vs. pH <sub>KCl</sub>	0.6853	0.0293
$K_F$ vs. pH <sub>H2O</sub>	0.8967	0.0030
$K_F$ vs. $V_a$	0.2809	0.1896
$K_F$ vs. $Q_{4/6}$	0.6155	0.0446
$K_F$ vs. Carbonates	0.3617	0.1397
$K_F$ vs. $H_a$	0.5435	0.0646
$K_F$ vs. CEC	0.3401	0.1517
$K_F$ vs. $C_{ox}$	0.0390	0.5356
$K_F$ vs. Salinity	0.0209	0.6169
$K_F$ vs. Particle density	0.1509	0.3110
$K_F$ vs. Clay	0.6007	0.0484
$K_F$ vs. Silt	0.8597	0.0056
$K_F$ vs. Very fine sand	0.6813	0.0301
$K_F$ vs. Sand	0.9127	0.0022