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Diploma thesis

**The Effect of Shading Geotextiles on Pendimethalin
Behavior in Soil**

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Declaration

I declare that the Diploma Thesis “The effect of shading geotextiles on pendimethalin behaviour in soil” is my own work and all the sources I cited in it are listed in Bibliography.

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Signature:

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SUMMARY

The goal of this study is to determine behavior of pendimethalin in soil. Pendimethalin- is selective herbicide which widely used in agriculture systems. Many factors have influence for degradation of pendimethalin. These factors include properties of soil and plants, environmental and climatic conditions. This study mainly focused for degradation of pendimethalin in soil which is covered with geotextiles. The influence of geotextiles for degradation of herbicide was measured three times in the soil. There were used four treatments 11-dose $1,5 \text{ l ha}^{-1}$ and 21-dose $3,00 \text{ l ha}^{-1}$ covered and treatments 12 - dose $1,5 \text{ l ha}^{-1}$ and 22- dose $3,00 \text{ l ha}^{-1}$ non covered by geotextile. For determination of pendimethalin concentration in soil were used HPLS- Dionex and for statistics Anova- multifactor. After evaluation of pendimethalin the calculated half-life time for all treatments has very similar results. For covered treatments, half life range from 80,4 to 80,2 days and lower dose one of treatments not has the effect for degradation of pendimethalin.

Also, we examined the influence of soil moisture and temperature for degradation of pendimethalin.

Keywords: Pesticides, geotextiles, pendimethalin, half- life, degradation

NOMENCLATURE

Abbreviations

°C	degree Celsius
cm	centimeter
g	gram
ha	hectare
hr	hour
kg	kilogram
L	liter
µm	micrometer
µL	microliter
M	molar
m	meter
ml	milliliter
mm	millimeter
mg	milligram
nm	nanometer
cm³	cubic santimeter
t	metric tonne (1,000 kg)
%	percent
w/w	weight in weight

1. INTRODUCTION

Pesticides – are mostly organic compounds with low molecular weight and different solubility in water. The chemical composition the acidity or alkalinity, water solubility, structure, polarity, size and polarization of molecules - all of these features together or individually affect the adsorption-desorption processes of pesticides to soil colloids. The soil is mainly serves as a successor of pesticides where they decomposed and constantly moving into plants or to the environment either as storage, where some of them can exist many years after the entering. Similar as the physic-chemical properties of pesticides, the soil physico-chemical properties (e.g., soil moisture, soil temperature) affected the pesticide behavior in soil too. Persistence of pesticides in the soil can vary from a few hours (e.g., fumigants) to decades (chlor organics). Persistence and mobility are the most important processes controlling the environmental fate of pesticides and both of these processes are strongly influenced by the weather (Walker, 1994). Now there are more than 1,055 active ingredients registered as pesticides (U.S. EPA) of which about 100 are insecticides and acaricides, 50 fungicides, 50 herbicides and 20 nematicides (Edwards). Herbicides constituting the biggest part of the world pesticide use at 40%, followed by insecticides 17% and fungicides 10% (U.S. EPA). For modern pesticide, to reduce their potential risks there were developed these requirements:

- a) low acute toxicity for human, animals and other objects of the environment;
- b) absence of negative effects in the long action of small doses, including mutagenic, carcinogenic and teratogenic effect (a teratogen - damaging the embryo);
- c) low persistence.

In addition, the recommended pesticides should include the following properties:

1. High efficiency in the fight against harmful organisms
2. The economic feasibility of use
3. The availability of raw materials and production.

In this study, we conducted field studies to determine the behavior of pendimethalin in soil. Pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine)- is a pre-emergence herbicide which is used against annual grasses and certain broadleaf weeds.

According to Weber et al., (1973) the main factors affecting the persistence of herbicides in the soil are degradation or transportation processes.

Persistence of pendimethalin (PDM) is influenced by cultivation practices, soil temperature and moisture conditions, as well as soil type (Smith et al. 1997; Lee et al. 2000; Stranberg and Scott- Fordsmand, 2004). The literature (Wauchope et al., 1992 and Weed Science Society of America, 1994) shows that since pendimethalin has very low solubility in water, it will not leach appreciably in most soils and it is considered to present a minimal risk of groundwater contamination. It is moderately persistent with a field half-life of approximately 90 days and does not undergo rapid microbial degradation (Wauchope et al., 1992). Pendimethalin was normally degraded through photo-degradation, volatilization or by biodegradation (WHO, 1993, Moza et al., 1992, Smith et al., 1979, Zhang et al., 2000 and Miller et al., 1996).

2. AIMS AND OBJECTIVES OF WORK

Hypothesis

The shading geotextiles will reduce the degradation of pendimethalin in soil.

The main objectives of this diploma thesis are following:

- to become familiar with soil properties, pesticide properties and climatic factors which affect the pesticide behaviour in soil
- to carry out an field experiment to evaluate the affect of shading geotextiles on pendimethalin behaviour in soil
- to determine the residues of pendimethalin in soil during the experiment
- to calculate the pendimethalin half life and evaluate the effect of shading geotextiles on pendimethalin half life

3. LITERATURE REVIEW

3.1 Behavior of pesticides in soil

The type and speed of transformations depends on chemical structure of active substances and its stability, mechanical structure and structure of soils, chemical properties of soils, structure of flora and fauna of soils, intensity of the effect of external influences and agricultural system. For better understanding of behavior of pesticides and any other chemical compounds in the soil, it is necessary to consider at least the main factors influencing migration, decomposition, activity and persistence. These main factors include adsorption and desorption, volatilization, leaching, uptakes by plants as well as chemical and microbial degradation.

Using of dispersion spraying of pesticides, substance can move into the air and can be transported by air currents defined as volatilization. Pesticides can release into the air from wet surfaces due to the sublimation of water vapor and by evaporation from the soil surface and plants. Once volatilized, a pesticide can move into air currents away from the treated surface, a phenomenon known as vapour drift (Navarro et al., 2007). Volatilization one of the important factors in the dispersion of pesticides. The importance of this process described in several studies conducted in recent years (Gan et al., 1998; Mayewski, 1999; Schroll et al., 1999; Neumans et al., 2000; Voutsas et al., 2005), in these scientific works been described that the potential volatility of pesticides depends on its vapor pressure, but it is closely depending also on soil temperature, porosity, structure, colloidal composition, water content and pH.

Adsorption is probably most important mode of interaction between soil and pesticides and controls the concentration of the pesticides in the soil liquid phase (Navarro et al., 1992). Adsorption of pesticides- in the soil is a complex process which depends on several factors. It plays an important role in movement of pesticides and serves for temporary maintenance in the vaporous or dissolved condition or in the form of suspension on a surface of soil particles.

The organic matter content has a greatest effect on the pesticide adsorption processes. Importance of organic matter, particle size and pH of the soil for sorption has been documented by many authors (Huang and Mckercher, 1984; Barriuso et al., 1992; Gao et al., 1998).

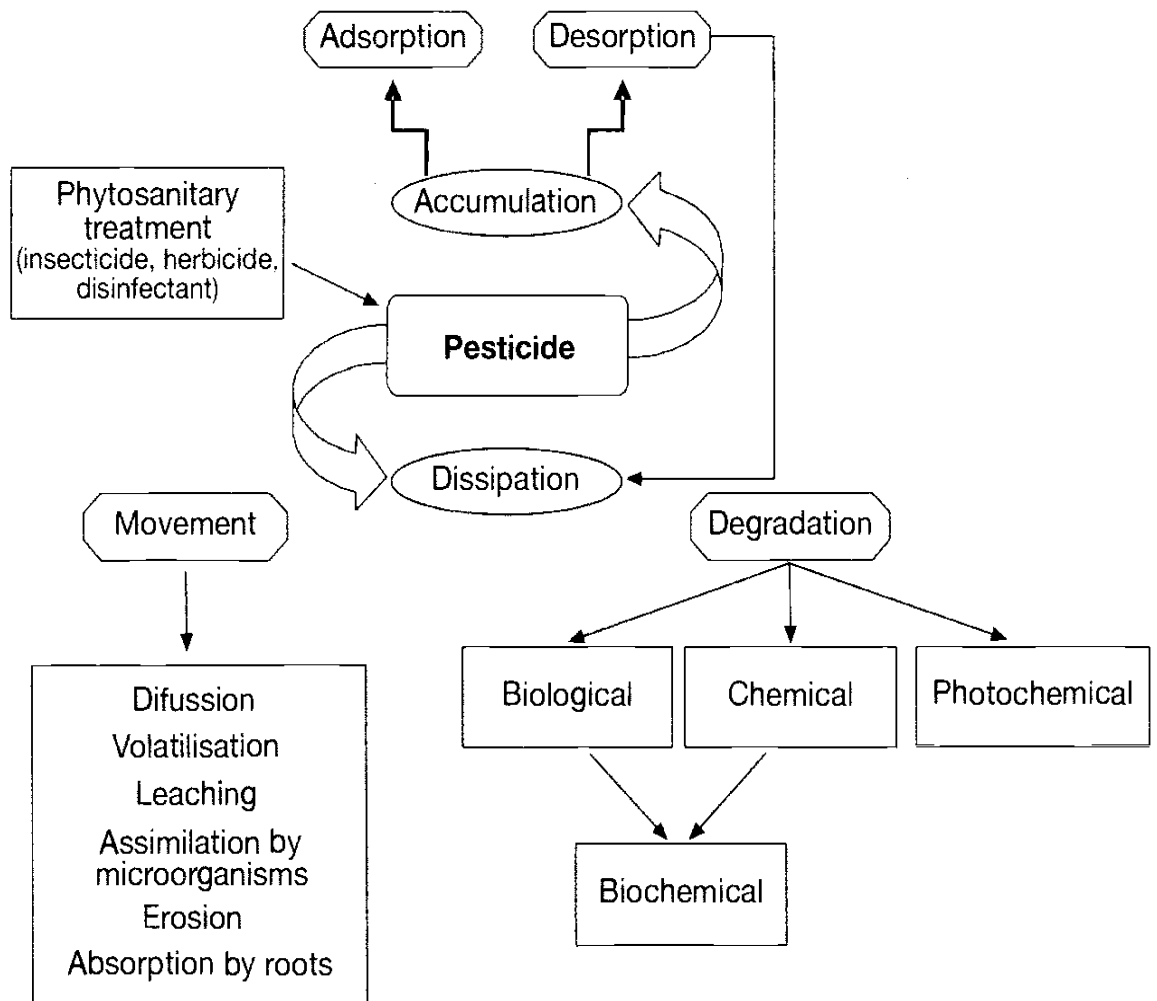


Figure 1. Schematic representation of pesticide dynamics in soil (S. Navarro et al., 2007)

Interaction between soil and pesticides is quite complex. In the Fig.1 we can see several chemical, physical and microbiological processes, which are responsible for inactivation, losses and transformations of pesticides.

According to Senesi (1992) the rate of adsorption depends on the properties of soil and the compound, which include size, shape configuration, molecular structure, chemical functions, solubility, polarity, polarizability and charge distribution of interacting species, and the acid base nature of the pesticide molecule. The speed and depth of vertical movement depends on pesticide water solubility, the characteristics of its adsorption and desorption, volatility, as well as the intensity of evaporation of soil water.

Leaching process is also one of main factors on behaviour of pesticide in soil. According to Spliid et al., use of pesticide in the field can be a risk of pollution surface and groundwater. During long time rainfall or an irrigation period, pesticides which have higher water solubility are moved down to the soil and through the root zone can leach up to groundwater. Some experimental works show that some pesticides, such as simazine, the addition of organic amendment to a soil reduce leaching considerably since the adsorption of herbicide increased (Cox et al., 1998). Also, leaching considered as the main cause of groundwater contamination by herbicides (Flury 1996), which is largely determined by physical and chemical properties of herbicides.

3.1.1 Pesticide properties affected their behavior in soil

The duration of preservation of pesticides in the soil depends on its chemical and physical properties, the dose and also forms of substance (powder, liquid, etc.). The chemical properties of pesticides determine their retention and transport in soils (Kearney, 1998).

Effects of pesticides on the activity of soil micro flora are hugely different; because of some pesticides can affect the development of microorganisms, and other pesticides have depression action or no effects on soil micro flora.

Nature and extent of the impact of pesticides on soil fauna and flora depend on the properties of pesticides, their content in the soil, the composition of the fauna, soil and climate conditions. The effects of pesticides on the soil micro flora are of importance because many microbial functions are critical to crop production, soil sustainability, and environmental quality (<http://newindianexpress.com>). Several works were described about effects of pesticides on soil micro- organisms (e.g. Digrak, Özçelik, 1998) and authors suggest that when pesticide applied at recommended doses have minor or transient effect on soil micro flora.

Aurelia measured (2009) behavior of microbial populations in soil after the application of different pesticides. Three pesticides were applied at recommended doses. The effects of these pesticides on total viable bacteria were investigated in laboratory experiments. Results of studies show that a normal dose of pesticides has insignificant effects on soil micro flora and microorganisms are able to recover rapidly.

Much attention was given to study about bound residues of pesticides, their concept and environmental significance in soil.

The number of metabolites or residual products that appear with photochemical and biochemical degradation is exceptionally high because of the large number of pesticides with different characteristics (Navarro et al., 2007).

The terms 'free' and 'bound' residues were coined to indicate that the former can be readily extracted from soil without altering their chemical structures, whereas the latter are resistant to such extraction (Gevao et al., 2000).

According assessment by Roberts (1984), bound residues are "chemical species originating from pesticides, used according to good agricultural practices that are unextracted by methods which do not significantly change the chemical nature of these residues". In 1998, according to IUPAC, Fuhr et al., (1998) suggested some modification for this definition: "compounds in soil, plants and animals which are stored in the matrix in the form of parent substance or its metabolites after extraction". Depending on the nature of binding, immobilized compounds may be released back to the soil solution or mineralized as a result of changing environmental conditions in the soil (Khan, 1982; Decand Bollag, 1988).

Persistence and mobility of pesticide are depending by the properties of the pesticide. The properties of a pesticide are influenced by the soil environment, site conditions, weather, and application method (Kerle, Jenkins and Vogue. 2007). The influence of the climatic factors - temperature, radiation, precipitation and wind on pesticide persistence are largely complex because not only do they affect most of the chemical, but they also interact with each other (Edwards 2002). Fig.5 shows this interaction.

Persistence and mobility are the most important processes controlling the environmental fate of pesticides and both of these processes are strongly influenced by weather (Walker, 1994).

Pesticide persistence often is express in terms of half-life. This is the time for the breakdown of pesticide for one- half of the original quantity. Kerle. Jenkins, and Vogue. (2007) divided pesticide into three group based on their half-life: a) non persistent pesticides, with a typical soil half-life of less than 30 days; b) moderately persistent pesticides, with a typical soil half-life of 30 to 100 days; c) persistent pesticides, with a typical soil half-life of more than 100 days.

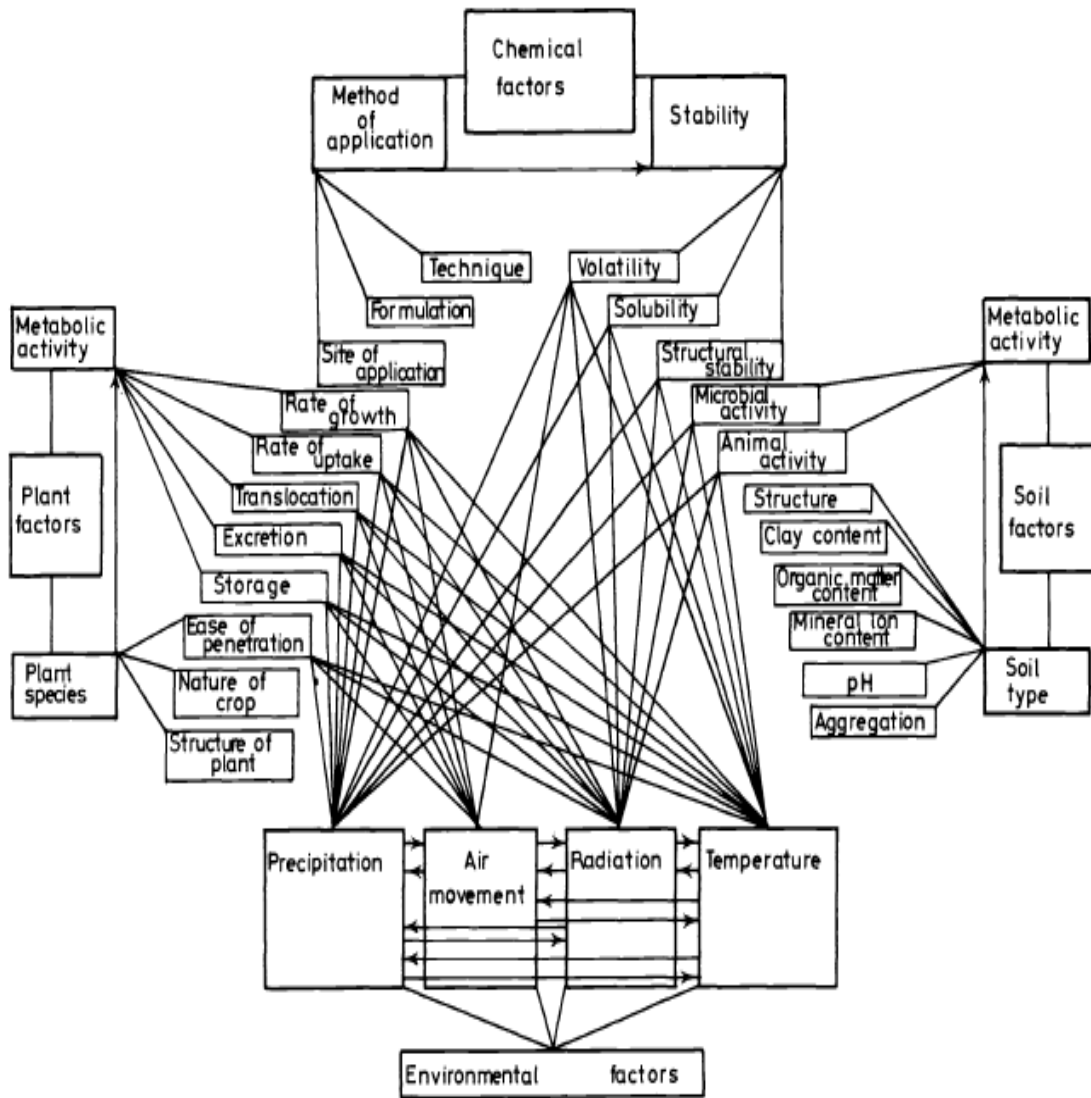


Figure 2. Interactions between factors that influence the persistence of pesticide in plants and soils (C.A Edwards)

3.1.2 Soil properties affected pesticide behavior in soil

Describing the possible situations associated with the use of pesticides, it should be remembered that they always have a negative impact on the living population in the soil, which activity underlies maintenance of soil fertility. In particular, pesticides cause depression in the nitrification process. The intensive use of pesticides can be cause of sterilization of the soil (<http://www.agroxxi.ru>). Pesticides, like other organic pollutants are retained in the soil according to their physico-chemical properties and to the soil nature and composition.

The physicochemical properties of soil and agro- climatic conditions regulate the movement and degradation of pesticides in agricultural lands (Archana, 2012). Knowledge of the movement of pesticides through the soil may help to protect chemical leaching to the surface and groundwater. Herbicide leaching through soil is particularly important in a number of environmental and agronomic problems (Costa et al. 1994).

Movement of pesticides in soil occurs with soil solution or simultaneously with the movement of colloidal particles, on which they adsorbed. It depends on processes of diffusion and mass current (dilution), which is the normal method of leaching. In surface runoff caused by rainfall or irrigation, pesticides move in solution or suspension and then accumulate in soil deepening. This form of movement of pesticides depends on terrain, erodibility of soil, intensity of a precipitation, degree of a covering of soils vegetation, from the period of time which has passed from the moment registration of pesticide. Soil moisture, temperature, organic matter, pH, texture, and rains are the main factors that determine mobility of herbicide (James et al. 1995; Walker et al. 1989; Lazic et al. 1997).

Edwards (2002) mentioned that particle size and structure of soil which influences persistence of pesticide is complex, because structure is also intimately linked with such features as hydrogen ion concentration, organic matter and clay content.

The organic matter content is usually suggested to have a greatest effect on the pesticide adsorption in natural soils (Kodešová et al., 2010). Organic matter is important because, with most pesticides, it is a main factor determining adsorption and hence availability in the soil solution (Richard. 2002). Pesticide distribution coefficient (K_d) directly proportional to the solubility of the pesticide in water and inversely proportional to the organic matter and clay content of the soil (Navarro et al., 2007).

According Walker and Thompson (1977) the linuron degradation positively correlated with soil organic carbon content due to increased microbial activity with increasing soil organic matter.

Several works have been studied about water flow and pesticide transport in soils (Köhne et al., 2005, Kodešová et al., 2005 and Dousset et al., 2007). These studies shows that pesticide application on the top of humic horizons, where pesticide adsorption and degradation are higher than in deeper horizons due to the presence of organic matter (Kodešová et al., 2009).

Kodešová et al., (2008) discusses about the influence of various soil structure to transport of pesticide. For this study were used chlortoluron and applied on soil taken from various horizons of three different types of soils. To evaluate the stability of the soil structure was used index of water-stable aggregates (Nimmo and Perkins, 2002). Aggregate stability measures the amount of stable aggregates against flowing water; it is recommended that aggregate stability be determined on the top three inches of surface soil (USDA, 2001). The research results showed that the concentration of chlortoluron was higher in the upper horizon *Ap* for each of the soil. A similar result was observed in the field by Kočárek et al. (2005). Authors explains this, with diffusion of the dissolved substance in the soil units right after the dissolved substance of the appendix and the subsequent slow release of the dissolved substance from units on preferential to a stream way.

3.1.3 Other factors affected pesticide behavior in soil

However, there is also other factors which has affect on interaction soil-pesticide. According to the results and discussions there are several factors influence to the fate and bounding of pesticides in soil.

These are the following factors:

1. Pesticide concentration; persistence of pesticides in soils has been found to increase with increasing concentration (Wolfe et al., 1973; Davidson et al., 1980; Racke and Lichtenstein, 1987; Gan et al., 1995).
2. Repeat applications; studies reported an increase in the formation of bound residues with repeated application (Katan et al., 1976; Fuhremann and Lichtenstein, 1978; Khan and Hamilton, 1980; Zhang et al., 1984).
3. Ageing is the result of either a redistribution of the chemical from weaker to stronger adsorption sites, slow chemisorption or covalent bond formation between the compounds and soil organic matter (Hatzinger and Alexander, 1995; White et al., 1997).
4. Mode of application to soil; The amount of bound residues formed in soils has been found to vary with the method of application of the compound, with a higher proportion of bound residues formed if the compounds were uniformly incorporated into the soil as opposed to surfacing application (Racke and Lichtenstein, 1985).
5. Addition of soil amendments; soil amendments with organic materials can alter the fate and kinetics of chemicals added to soils (Morillo et al., 2002; Navarro et al., 2003).

3.2 Sorption of pesticide in soil

Water solubility and adsorption processes are important properties of pesticides to move through the soil. Adsorption is defined as an accumulation of a pesticide or other chemical at either the soil-water or soil-gas interface (Koskinen and Harper, 1990). Pesticides which have low water solubility sorbs to soil more strongly, this process also depends on soil properties, as each soil has a characteristic ability to absorb pesticides. Soils with high organic matter and clay content sorbs pesticides better than sandy soils with low organic matter. Pesticide sorption in soil is a dissipation mechanism that is significantly influenced by soil organic matter (Locke and Bryson, 1997). Soil structure is also important because it determines infiltration rate.

According to Hassett and Banwart (1989) sorption processes could be driven by forces or combinations of forces “either related to the bonding of the sorbing species to the surfaces or to the lack of solvation of the sorbing in the solvent”.

The soil sorption coefficient K_d and soil organic carbon sorption coefficient KOC of pesticides are basic parameters, which use to describe behaviour of pesticides in soils. These parameters are specific for a given pesticide in a given soil, a selected horizon or at a soil depth and related to selected soil properties.

Herbicide sorption coefficients are most sensitive input parameters in herbicide fate models (Boesten and Van der Linden, 1991; Dubus et al., 2003). Symko and Farenhorst, 2008 described herbicide sorption coefficients change across small increments within soil profiles.

Authors Locke et al., 1995 evaluated that herbicide sorption in soils with management practices increased soil organic matter (OM). Sorption of weakly basic pesticides in soils been reported to be related to OM (Harris, 1966; Weber et al., 1969; Shea and Weber, 1980; Kozak et al., 1983; Nicholls and Evans, 1991) and inversely related to pH (McGlamery and Slife, 1966; Weber, 1966).

Some results show that pesticides interact with soluble variety of organic matter in the lack of solid components of the soil. The nature and extent of this interaction depends on molecular weight and polarity of the pesticide (Gamble et al., 1986, Kan and Tomson, 1990, Maquedo et al., 1993).

The sorption behaviour of metolachlor, isoproturon and terbuthylazine studied by authors Singh, Kloeppel and Klein, 2001. Authors compared sorption-desorption processes of three herbicides in two typical German soils: 1. Ebbinghof OM in 1,9%, 2. Soest OM in 1,0 %. All pesticides were analyzed using a Gynkotek HPLC with UV photometric detector.

Results show rapid sorption of these pesticides into soil colloids. The obtained sorption constant Koc obtained was in agreement with literature data (Kim et al., 1998; Benoit et al., 1999). Fig.3 shows that the sorption was highest for Ebbinghof soil which has higher organic content comparing to Soest soil with lower organic content. The present study confirms that the sorption of metolachlor, isoproturon and terbuthylazine is predominantly controlled by the organic matter content of the soils (Singh, Kloeppel and Klein, 2001).

Complete understanding of herbicide sorption processes in soils is essential to a more fundamental comprehension of the fate of herbicides in soils, and to further advance models for improving pesticide fate prediction in the field (Farenhorst et al., 2001).

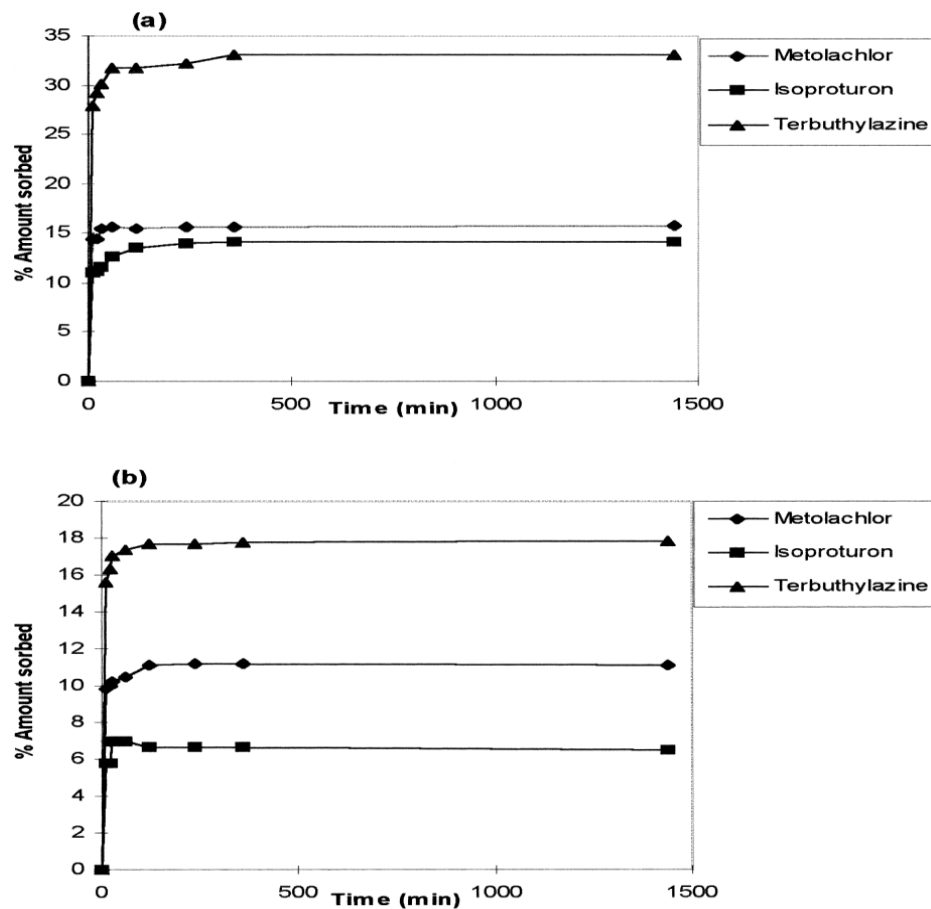


Figure 3. Sorption of three pesticides in (a) Ebbinghof and (b) Soest soils

3.2.1 Transport of pesticide in soil

Processes responsible for movement of pesticides are diffusion, volatilization, leaching, erosion and runoff. By diffusion process pesticide transfer through the soil profile from one point to where is concentrating more to another where its concentration less. This is according to Fick's Law, which describes the net number of particle that cross a given area per unit of time is proportional and has the opposite sign from the concentration gradient. The principal factors that influence this process are the coefficient of diffusion, solubility and steam pressure and particularly the temperature, moisture and porosity of soil and its degree of adsorption.

The significant process in terms of pesticide transport on soil is leaching. According to Flury (1996) leaching is the main cause of groundwater contamination by herbicides, which is determined by physical and chemical properties of herbicides. The main processes involved in herbicide transport in soils are sorption and solubility, the mobility of herbicides is regulated by the properties of the chemical and soil, hydro geological properties, application, and climatic conditions (Hartley and Graham Bryce 1980; Sawhney and Brown 1989). Mobility of pesticide may result in redistribution within the application position or movement of some amount of pesticide off site (Kerle, Jenkins and Vogue, 2007).

Directions for pesticide movement through soil include both macropore and micropore flow (Locke and Zablotowicz, 2004). "Macropore flow involves large pore sizes and consist of channels among soil aggregates, cracks caused by shrink-swell processes, voids left by decayed roots or tunnels created by fauna" (Locke and Bryson, 1997). According to Locke and Zablotowicz (2004) micropore flow includes inter and Intra- particle diffusion through small pores and rate of pesticide diffusion through micropores is dependent on the affinity of pesticide for sorbents on micropore surfaces and moisture gradients in the soil.

Erosion and run-off processes also play a role for transport of pesticides. Pesticide movement in run off occurs when pesticides applied to foliage or plant residues are washed of during precipitation (Locke and Zablotowicz, 2004). Runoff can carry pesticides dissolved in water and pesticides sorbed to eroding soil (Kerle, Jenkins and Vogue, 2007).

This process includes various factors among the most important being the soil slope, also the formulation of the pesticide and the time since its application, the soil's structural stability and the type of plant cover, rainfall intensity and physicochemical characteristics of pesticide and its degree of adsorption (Navarro et al, 2007). The movement of pendimethalin by surface runoff and leaching is expected to be low except where soil erosion results in sediment transport of the adsorbed herbicide (Stranberg and Scott-Fordsmand 2004).

3.2.2 Degradation of pesticide in soil

With transport process, degradation is the other action which responsible for disappearance of pesticides in soil. Pesticides in the soil are exposing to the decomposition caused by abiotic and biotic factors and processes. Not biotic decomposition of clay, oxides, hydroxides and ions of metals play a role of catalysts in reactions of decomposition of pesticides. Free radicals of humus substances alter the stability of the molecules of herbicides to degradation. Reutse (1984) identifies the following ways for abiotic degradation of pesticides:

1. Decomposition of pesticides by the hydrolysis, especially organochlorine insecticides, triazine herbicides is affected by temperature, humidity and pH. Hydrolysis proceeds faster in soils with strong acid reaction and in the presence of high organic content. Humidity of soils, structure of exchange cations and mineralogical structure influence decomposition of pesticides very significantly, but for different groups of pesticides established individual dependencies.
2. Decomposition reaction of oxidation-reduction type, to which sulfur-containing pesticides are exposing.
3. Decomposition due to the formation of nitroso compounds. The reactions occur at pH=3-4 and an excess of nitrates.
4. Decomposition reactions related to the presence of free radicals in the soil
5. Photochemical decomposition of pesticides under the influence of solar radiation.

There are also three degradation processes: photodecomposition or photochemical, chemical and biological degradation. Sunlight photo degradation is one of the most destructive pathways for pesticides after their release into the environment (Katagi, 2004). According to Navarro et al., (2007) the principal factors of this process are the presence of photo chemical catalysts, the intensity and length of exposure to radiation, soil pH and aeration, chemical structure and physical state of the pesticide and degree of colloid adsorption.

Biological degradation probably is the most important one. Biodegradation of pesticides happens by bacteria, actinomycetes, fungi and higher plants. Biodegradation, in general, is the breakdown of a chemical to various components (mainly CO₂, H₂O, NH₃, CH₄) by microorganisms or their enzymes (Atlas, 1988).

Biological transformations include oxidative reactions (hydroxylation, N-dealkylation, beta-oxidation, decarboxylation, cleavage of ether linkages, epoxidation, oxidative coupling, sulfoxidation), reductive reactions (e.g. reduction of nitro or alkene groups), hydrolytic reactions and synthetic reactions (conjugation or condensation reactions) (Bollag and Liu, 1990).

Ability to transform and detoxify pesticides is most expressed in bacteria and fungi. Esposito et al., (1998) showed that different actinomycetes were able to degrade diuron in soil, using manganese peroxidases. The duration of pesticide residues decomposition by microorganisms can range from several days to several months and sometimes decades, depending on the specific pesticide types of microorganisms, soil properties. Some pesticides decompose by certain groups of microorganisms.

Experiment to investigate the effect of herbicides on the changes of microbial biomass was conducted under laboratory conditions by authors Das et al., (2012). They suggested that application of herbicides significantly increased the microbial biomass carbon, nitrogen and phosphorus. Three herbicides were used fenoxaprop, pendimethalin and paraquat at their field application rates (50 g, 0 (kg) and 1,0 kg a.i ha, respectively). From studies shown in Fig.4, we can consider that the microbial biomass carbon was high comparing with control in the combined application of the herbicides of fenoxaprop and paraquat. Pendimethalin alone revealed maximal stimulation of microbial mass of nitrogen, comparing when it was in combination fenoxaprop.

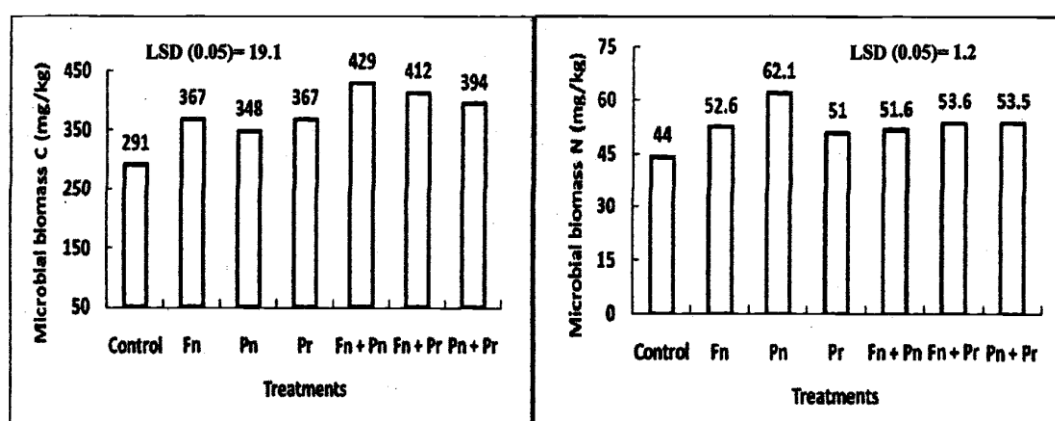


Figure 4. Effect of herbicides on microbial biomass carbon, nitrogen and phosphorus after 75 days incubation in soil. Treatments: Control (untreated); Fn, fenaxaprop; Pn, pendimethalin; Pr, paraquat

Pesticide degradation can be significantly depending by soil pH, cause of if the stability of the compound is pH dependent, or indirectly through changes in microbial populations, or in soil adsorption of the pesticide (Walker, 1989). Houot et al., (2000) measured that the degradation of atrazine was more rapid in soil with a pH greater than 7.0 than in soil with a pH less than 6.5.

Swarcewicz and Gregorczyk (2010) in controlled conditions measured influence of other pesticides on the rate of pendimethalin (PDM) degradation in soil. For the study used pendimethalin, mancozeb, thiamethoxan and metribuzin. The first aim was to determine which chemical mixtures influence for pendimethalin degradation. The second one of this work was to compare two equations: first order kinetic and non-linear empirical models. The degradation rate of an herbicide in soil is proportional to the difference of the measured concentration of herbicide in soil at the time and concentration of herbicide in the last day of measurement (Swarcewicz and Gregorczyk, 2012).

According to the results DT50 values increased when PDM was in the mixture of mancozeb DT50 46,1 and 63,9 days, but no significant effect found when substance was thiamethoxan DT50 and presence of metribuzin did not influence for PDM behaviour in soil.

The first order degradation is to be expected when the microorganisms are not in abundance in the soil, possibly because nutrient limitation (Navarro et al., 2000). Widely used way of presenting first-order kinetics is to plotting the logarithm of the pesticide concentration as a function of time, and if the reaction is first- order a straight line will obtained (Environmental Organic Chemistry, 2003). This can be expressed mathematically by a first-order rate law:

$$\frac{d[A]}{dt} = -k[A] \quad (1.1)$$

where k is referred to as the first-order rate constant and has the dimension $[T^{-1}]$. When constant k has been calculated, the half-life time can be calculated using the following equation:

$$t_{1/2} = \frac{\ln 2}{k} \quad (1.2)$$

If the water molecule were involved in the slowest step of the reaction, that is, in rate determining step, the reaction should be described by a second order rate law:

$$\frac{d[A]}{dt} = -k'[A][B] \quad (1.3)$$

where we have denoted H₂O as B, and k' is now referred as second order rate constant with dimension [M⁻¹L³T⁻¹]

Using these equations the persistence in the soil of different pesticides can be compared (Navarro et al., 2000).

4. MATERIALS AND METHODS

4.1. Description of pendimethalin

Pendimethalin- is yellow crystalline solid, mp 56 - 57 °C is readily soluble in aromatic hydrocarbons and their halogen derivatives. Pendimethalin is characterized by low water solubility (0.3 mg l⁻¹ at 20°C), moderate to high vapour pressure depending on temperature (4.0 mPa at 25°C), and strong adsorption to soil ($K_{oc} = 7,011 \text{ ml g}^{-1}$ in loamy sandy soil of 0.87% OC) (Tomlin 1997; U.S. Environmental Protection Agency 1997).

Highly effective broad-spectrum herbicide used against annual broadleaf and grain crops weeds in agricultural crops. It blocks a central process growth of weeds: cell division. Weeds immediately stop growing, wither and finally die. Pendimethalin is approved for a variety of crops in a large number of countries, in Czech Republic also used for selective controls of in crops such as corn (*Zea mays L.*), peas (*Pisum Sativum L.*) salad (*Lactuca cativa*) and several vegetable crops ((Royal Society of Chemistry 1987). PDM is characterized by low water solubility, moderate to high vapor pressure, strong adsorption to soil, and high octanol–water partition coefficients (Swarcewicz, and Gregorczyk, 2012).

Pendimethalin [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine] (Fig.5) is a pre-emergence dinitroaniline herbicide, which is commonly used for selective weed control (<http://sitem.herts.ac.uk>).

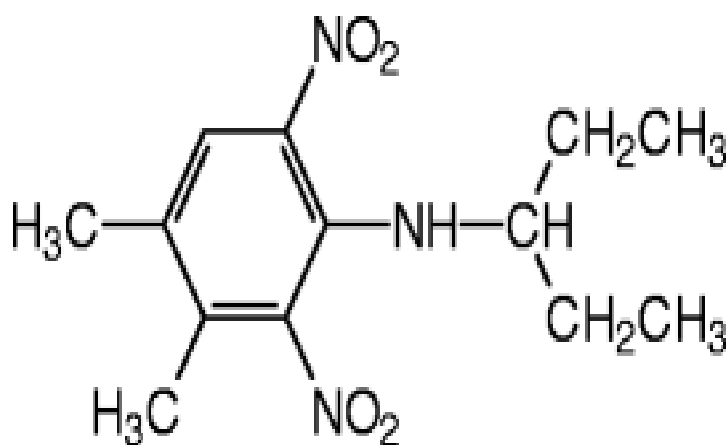


Figure 5. Chemical structure of pendimethalin

European terrestrial field dissipation studies show moderate persistence of pendimethalin in soil with half-lives ranging from 27 to 155 days (Rice et al. 2003). This thesis represents the results of a field study conducted in order to investigate the behavior of pendimethalin in soil, with a focus on the effect of shading geotextiles.

4.2 Description of soil

In the present study, we used soil from the field of Czech University of Life Sciences, which located in Praha Suchdol. For these purposes was performed on Haplic Chernozem soil (parent material loess), the elevation of soil location above sea level is 275 m. According to information (Kodešová et al., 2010) basic chemical and physical properties of soil is shown on Table.1

Table 1. Chemical and physical soil properties of Haplic Chernozem

Soil type	Location	Parent material	pHKCl	pHH ₂ O	EA (mmol+kg ⁻¹)	CEC (mmol+kg ⁻¹)	HA (mmol+kg ⁻¹)	BSC (mmol+kg ⁻¹)	SCS (%)
Haplic Chernozem	Praha Suchdol	Loess	7.21	7.69	0.72	263.8	4.20	259.60	98.4
			OM (%)	CaCO₃ (%)	Salinity μS cm ⁻¹	ρ_s (g cm ⁻³)	Sand (%)	Silt (%)	Clay (%)
			3.47	7.80	43.7	2.52	24.4	56.3	19.3

4.3 Description of climatic conditions

The field area is located at 50° 13' 60N and 14° 28' 0E. Climate is moderately continental, summer from +15 to +35, the winter from 5 to – 15. Date of covering by geotextile start at 28.03. 2012 end at 3.5.2012 when geotextiles removed. Weather condition of area at the date of experiment is shown in Table 2.

Table 2. Weather condition on date of experiment

Date	Weather during the application			
	Cloud (%)	Temperature (°C)	Soil moisture	Wind
28.3.2012 8.00 hod	0	10	dry	0

The climatological data, especially radiation and rainfall of area during the experimental period are given in Fig.6. and Fig.7.

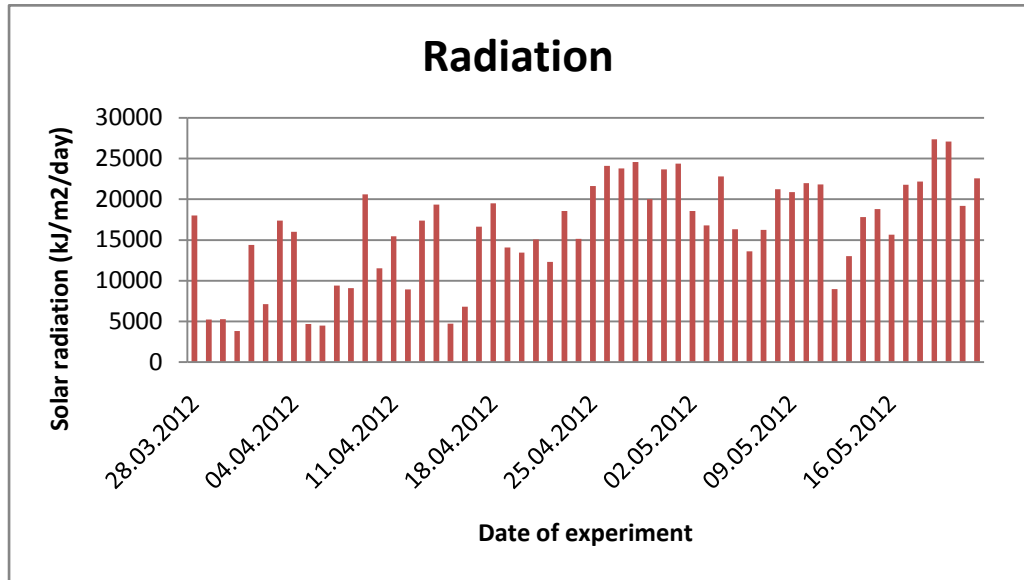


Figure 6. Daily solar radiation (kJ/m²/day)

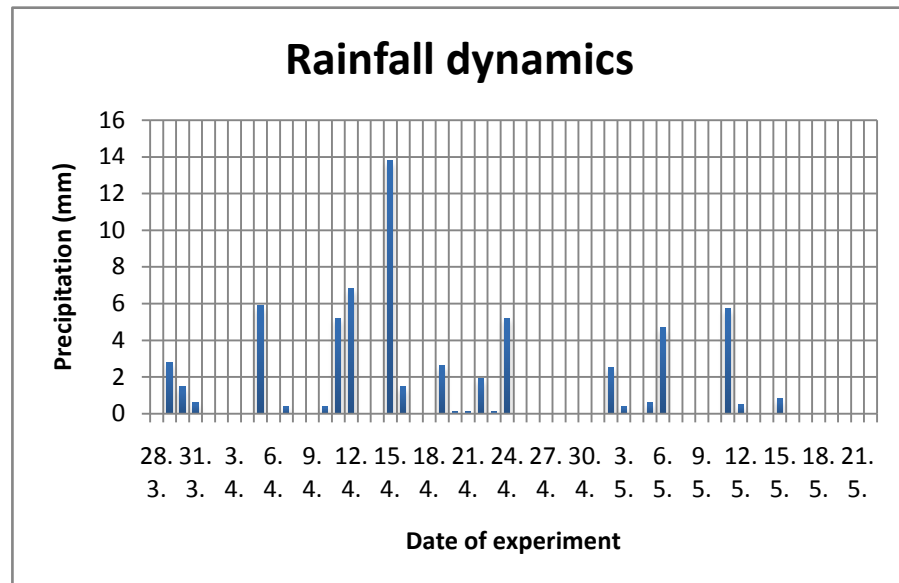


Figure 7. Rainfall dynamics (mm)

4.4 Description of soil sampling and sample preparation

The experimental field located in the area of Praha Suchdol. Soil type is Haplic Chernozem, covered by salad plant (*Lactuca cativa*). Diameters of trial field: 1,8 x 3 m (5,4 m²; 48 plants); (spon 30 x 30 cm). Pesticides are used in two doses, 1,5 l/ha and 3,00 l/ha (Tab.3).

Table 3. Tested variants in two doses

Var.	Textile	Pesticide	dose (l/ha)
01	yes	untreated control	-
02	no	untreated control	-
11	yes	Stomp 400 SC	1,50
12	no	Stomp 400 SC	1,50
21	yes	Stomp 400 SC	3,00
22	no	Stomp 400 SC	3,00

Soil samples were collected from two depths (0-5 cm and 5-10 cm), according to schematic attempt shown in Table 4. Soil samples were collected three times: the first sampling was after 30 days pesticide application 18.04.2012; the second one in 3.05.2012 and at that date geotextiles were removed; third sampling were at 21.05. 2012. The soil cylinders were used in the first and last sampling to determine the soil bulk density. Soil samples were frozen and dried using lyophilizator, grinded and screened through a 2 mm sieve. Ten grams of soil was placed into glass flasks and then 10 ml of methanol was added and shaken for 24 hours. After that, samples placed into plastic cylinders and then centrifuged for 30 min at 13000 rpm. Finally, the extracts were moved into vials with volume 1,5 ml and the pendimethalin concentration was determined by HPLC.

The amount of herbicides presented in soil extracts were expressed as the total amount of solute per mass unit ($\mu\text{g g}^{-1}$) and the total herbicide amount in both soil layers was calculated using the soil bulk density 1.2 and 1.6 g cm^{-3} in soil layer 0-0.05 and 0.05-0.1 m respectively.

Table 4. Schematic attempt of experiment

12	22	02
11	21	01
22	02	12
21	01	11
02	12	22
01	11	21

4.5 Determination of pendimethalin in methanol extract

The determination of pendimethalin in methanol extracts 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 Kinetex 2.6 μ , C18, 100 A column, 50 \times 4.6 mm (Phenomex). The guard columns (Security Guard Cartridge AQ C18 4 x 2.00 mm) were used to prolong the lifetime of the column. Mobile phase was prepared by mixing 800 ml of methanol, 200 ml of redistilled water. 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 pendimethalin detection was 240 nm. The signal from the detector was stored and processed using the chromatographic software Chromeleon version 6.70 (Dionex). The pendimethalin detection limits in methanol extracts was 0.008 $\mu\text{g ml}^{-1}$.

5. RESULTS

Concentration of pendimethalin in the soil methanol extract determined using HPLS. The residual concentrations of pendimethalin for the sampling depth of 0-5 cm and 5-10 cm for all tested variants are present in Figs. 8 and 9. There were found continuous decrease of pendimethalin concentration in top soil layer for all tested treatments. In both doses of herbicide ($1,51 \text{ ha}^{-1}$ and $3,00 \text{ l ha}^{-1}$) were measured low concentration in the case for non covered textile treatments.

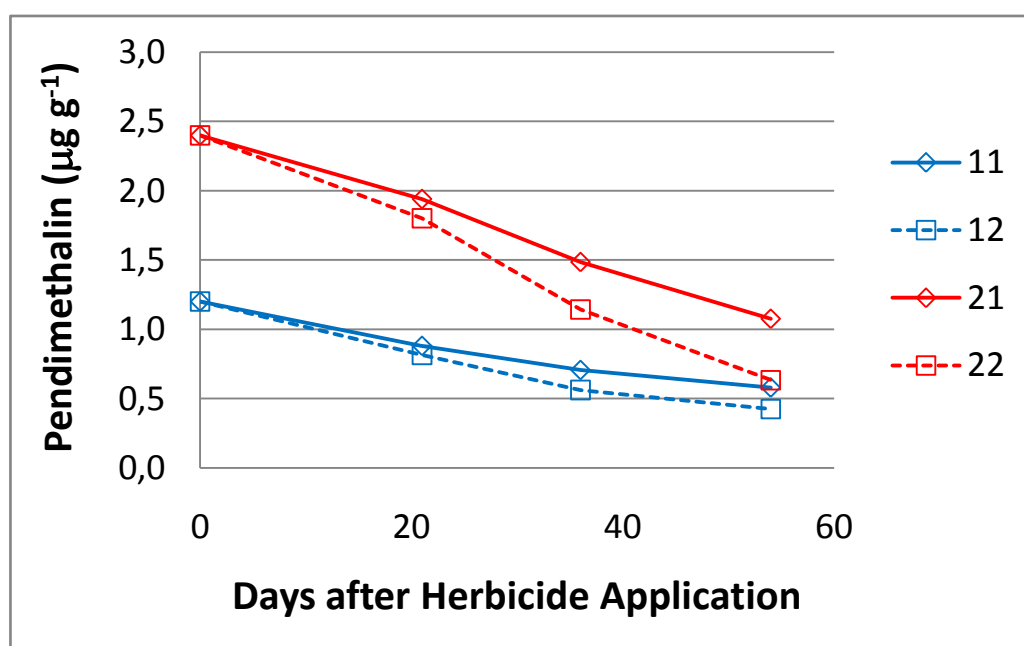


Figure 8. Concentration of pendimethalin after 21, 36 and 54 days (0-5 cm); Treatment: 11- dose $1,5 \text{ l ha}^{-1}$, textile; 12- $1,5 \text{ l ha}^{-1}$, no textile; 21- $3,00 \text{ l ha}^{-1}$, textile; 22- $3,00 \text{ l ha}^{-1}$, no textile

In Fig. 8, we can see a reduction of pendimethalin over time in the soil depth 0-5 cm as a function of time for all variants. The lowest levels of pendimethalin concentration for covered treatments 11 (dose $1,5 \text{ l ha}^{-1}$) and 21 (dose $3,00 \text{ l ha}^{-1}$) was detected in the range $0,57 \text{ mg g}^{-1}$ to $1,5 \text{ mg g}^{-1}$ respectively, after 54 DAA (days after application). For treatments, 12- dose $1,5 \text{ l ha}^{-1}$ and 22- dose $3,00 \text{ l ha}^{-1}$ not covered by geotextiles concentration of pesticide after 54 DAA were found in the range $0,42$ to $0,63$ respectively. According to this results we can suggest that there was significant differences between samples with geotextile and without geotextile.

On the other hand, we can see the difference for the soil depth 5-10 cm (Fig.9), concentration of pendimethalin increased in the second time sampling and it can be explained due to the time factor of sorption and transport properties of pesticides. At the third sampling period we can see a reduction of pendimethalin, that may be due to after some days pesticide absorbed on the soil colloids and degraded by micro organisms. Concentration of pesticide for all measured data (covered and non covered) was close to each other and detected in the range from 0,02 mg g⁻¹ to 0,01 mg g⁻¹ after 54 DAA.

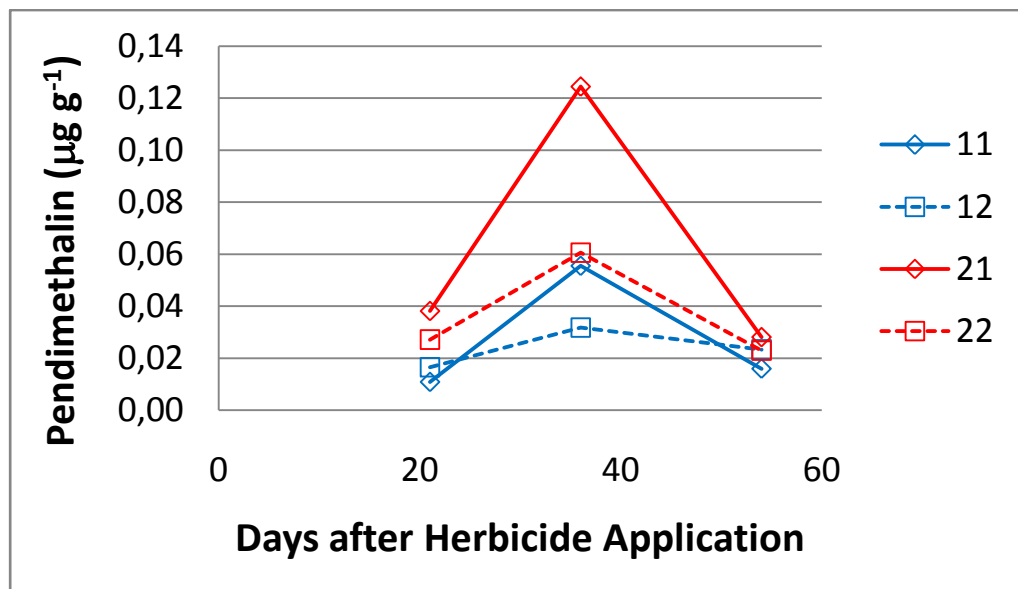


Figure 9. Concentration of pendimethalin after 21, 36 and 54 days (5-10 cm); Treatment: 11- dose 1,5 l ha⁻¹, textile; 12- 1,5 l ha⁻¹, no textile; 21-3,00 l ha⁻¹, textile; 22-3,00 l ha⁻¹, no textile

The half-life ($t_{1/2}$) of pendimethalin was calculated using equations 1.1 and 1.2 from first-order kinetics, which is model that is usually used to evaluate persistence of pesticide (Larson et al. 2000). We evaluate the pendimethalin concentration in the soil and then we calculate the herbicide concentration in both layers (0-5 and 5-10 cm).

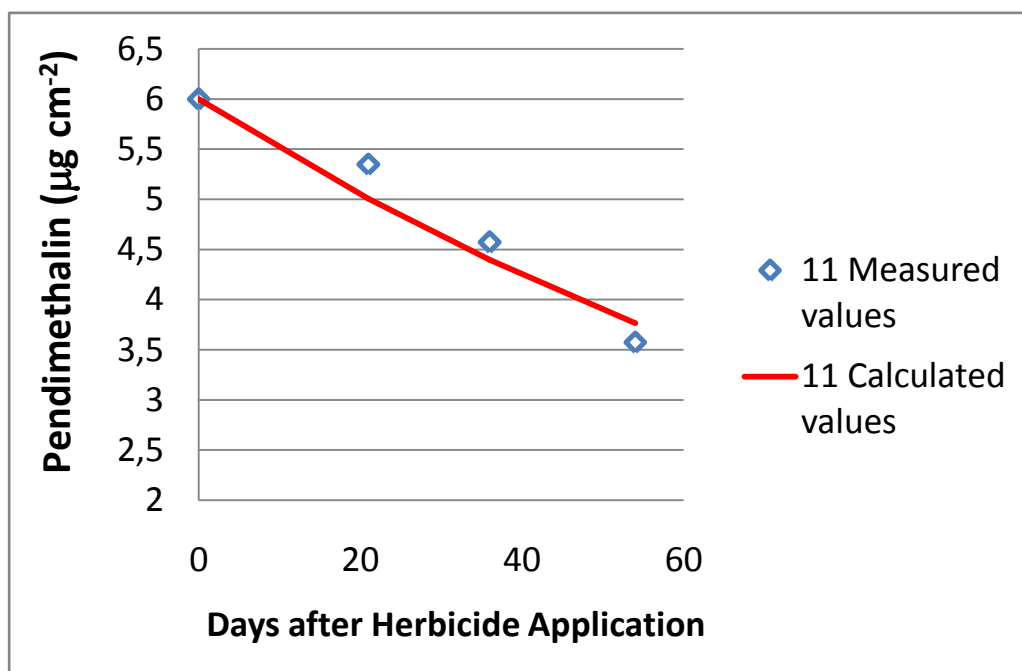


Figure 10. Measured and calculated values of pendimethalin concentration; Sample 11- dose $1,5 \text{ l ha}^{-1}$, textile

Measured and calculated values for treatment 11 (Fig 10) show continuous decrease of pendimethalin and calculated first order constant $k = 0,00864$.

For treatment 12- dose $1,5 \text{ l ha}^{-1}$ non covered by geotextiles the calculated values $k=0,014135$.

And there is also obtained linear function, and from this we calculate half life (Fig 11).

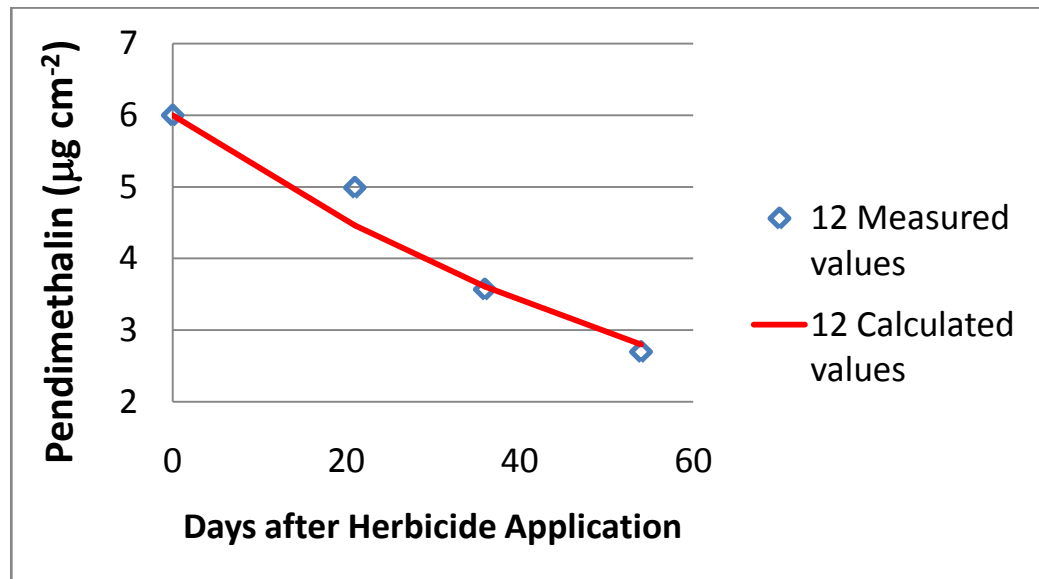


Figure 11. Measured and calculated values of pendimethalin concentration; Sample 12- dose $1,5 \text{ l ha}^{-1}$, no textile

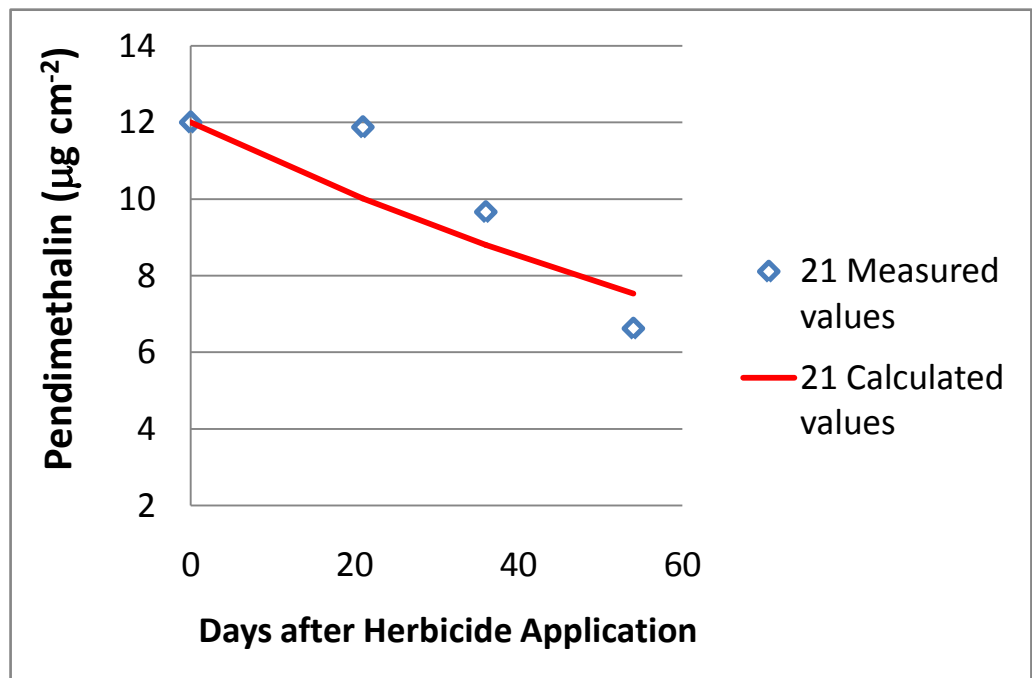


Figure 12. Measured and calculated values of pendimethalin concentration; Sample 21- dose $3,00 \text{ l ha}^{-1}$, textile

Calculated values for treatment 21-dose $3,00 \text{ l ha}^{-1}$ $k=0,008617$ is very similar with calculated k for treatments 11 dose $1,5 \text{ l ha}^{-1}$. Results also show very similar half life time for these two treatments.

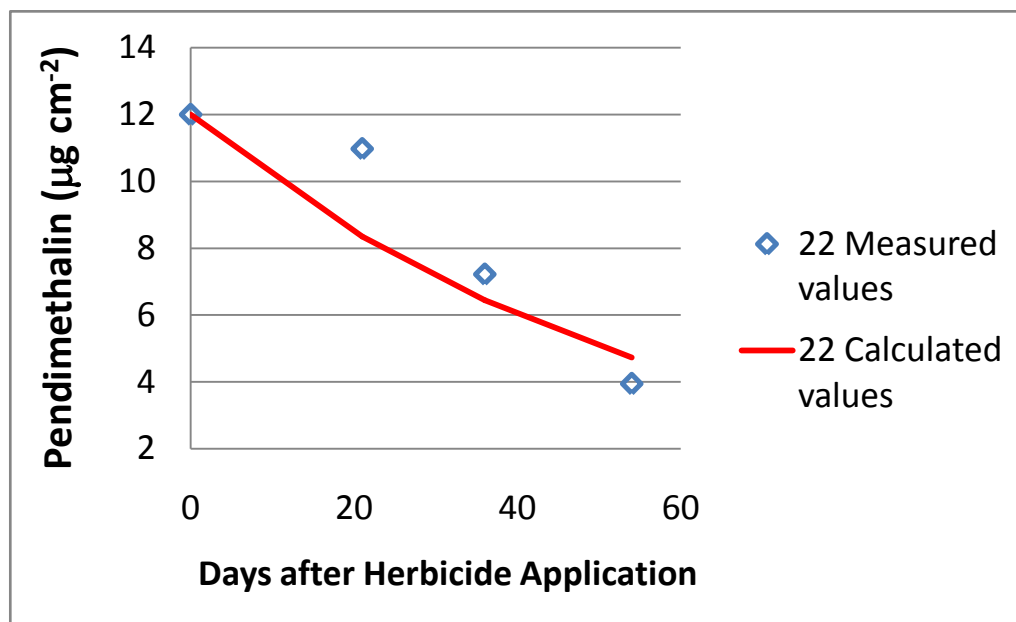


Figure 13. Measured and calculated values of pendimethalin concentration; Sample 22 - dose $3,00 \text{ l ha}^{-1}$, no textile

For this treatments presented in Fig.13 $k=0,017247$ and if we compare for other calculated values this value is more higher, half-life time also show some differences.

The calculated values of half-life of pendimethalin for treatments covered by geotextiles 11 with dose $1,5 \text{ l ha}^{-1}$ half life were 80,2 day and for 21with dose $3,00 \text{ l ha}^{-1}$ was 80,4 day, irrespective of a sample dose (Table 5). For treatments non covered by geotextiles 12- dose $1,5 \text{ l ha}^{-1}$ and 22- dose $3,00 \text{ l ha}^{-1}$ calculated half life was 49,0 and 40,2 respectively. According to results we can conclude, that for half-life of pendimethalin there was a significant effect of covering by textile.

Table 5. The calculated half-life of pendimethalin

Var.	Textile	dose (l/ha)	Half- life of pendimethalin in soil (days)
11	yes	1,50	80,2
12	no	1,50	49,0
21	yes	3,00	80,4
22	no	3,00	40,2

Temperature affects adsorption by altering the solubility and hydrolysis of pesticides in soil (Burns, 1975; Racke et al., 1997).

In Table 6 are presented measured average values of soil moisture and temperature from the beginning of experiment and three sampling dates. From the results we can see that for treatments not covered by geotextiles 12-dose 1,5 l ha⁻¹ and 22-dose 3,00 l ha⁻¹ the soil temperature was lower (8,47 C°) and this may have influence for lower degradation of the pendimethalin at the beginning of experiment. According to Weber (1990) favorable aerobic and warmer conditions might have influence for microbial activity to degrade pendimethalin. If we examine results for radiation and rainfall dynamics (Tab.7), results show lower amount of radiation 11250 kJ/m²/day at the first sampling period, and it has a significant effect for low temperature.

Table 6. Measured values of soil moisture and temperature at (0-5 cm) for three sampling data

Days	no textile		textile	
	moisture	temperature (C°)	moisture	Temperature (C°)
0-21	0,129	8,47	0,094	11,30
21-36	0,097	15,60	0,067	17,82
36-54	0,056	16,93	0,015	16,39

For treatments covered by geotextiles 11-dose 1,5 l ha⁻¹ and 21-dose 3,00 l ha⁻¹ the soil temperature was higher 11,3 C°. Because the rate of photo-degradation pendimethalin is quite high, we expect that shading by geotextiles will reduce radiation and degradation will be reduce. However, we reduced radiation but the temperature of soil increase because of covering by textile, and it has affected for more rapid degradation comparing with non covered treatments.

Table 7. Measured values of radiation and rainfall for three sampling data

Days	Radiation (kJ/m ² /day)	Rainfall (mm)
0-21	11250	1,10
21-36	19093	1,484
36-54	19128	0,668

To evaluate the statistical difference in soil moisture and temperature between two groups (with textile and no textile) were used Anova analysis.

The box plot first described by John Tukey (1977) and this is the effective method to display statistics. From the result presented in Fig 14, we can see that soil moisture for non covered treatment has statistically difference comparing with treatment covered by textile. Reject the null hypothesis for alpha =0,05

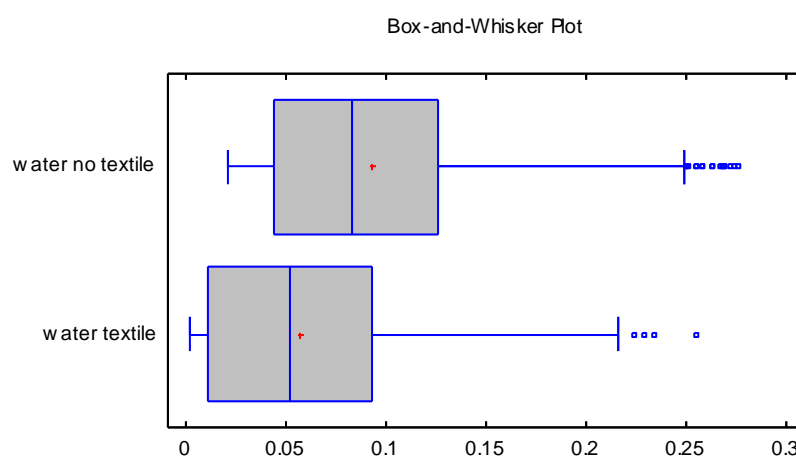


Figure 14. Box-and- Whisker Plot for soil moisture

Also, there was used t-test to compare means. From the comparison of means we have P-value=0. In this way, the test was used to determine whether the difference between the two means equals 0.0 versus the alternative hypothesis that the difference does not equal 0.0. Because the calculated P-value is less than 0.05, the null hypothesis can be rejected. The results show the significant difference of soil moisture between covered and not covered geotextiles.

The same analysis was done for soil temperature, again to compare two samples where will be differences with covered by geotextiles and without it. In this case, (Fig15) both samples have standardized skewness values outside the normal range. Both standardized kurtosis values are within the range expected. Calculated P-value= 0, 00000000328 and again are less than 0, 05, and we can reject the null hypothesis in favor of the alternative.

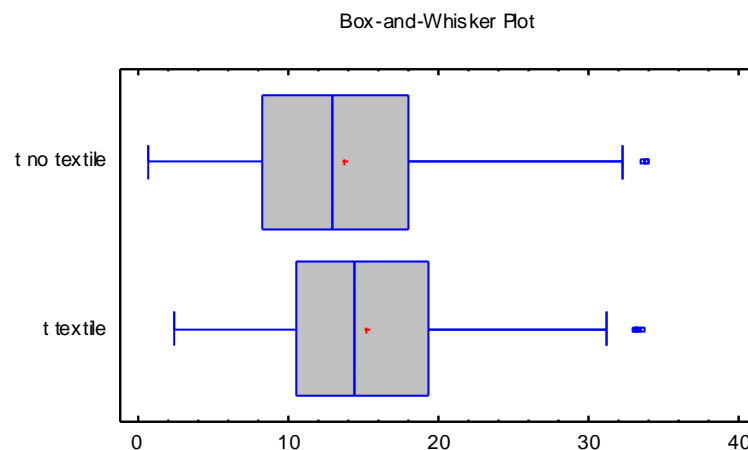


Figure 15. Box and Whisker plot for soil temperature

Evaluation of effect due to treatment, horizon and time factors of the pendimethalin concentration was done using Anova- Multifactor analysis. This procedure performed a multifactor analysis of variance for pendimethalin concentration in soil and time after pendimethalin application. The P-values test shows the statistical significance for each of the factors (Fig. 16). All three P-values are less than 0,05 these factors have a statistically significant effect on pendimethalin concentration in soil at the 95% confidence level.

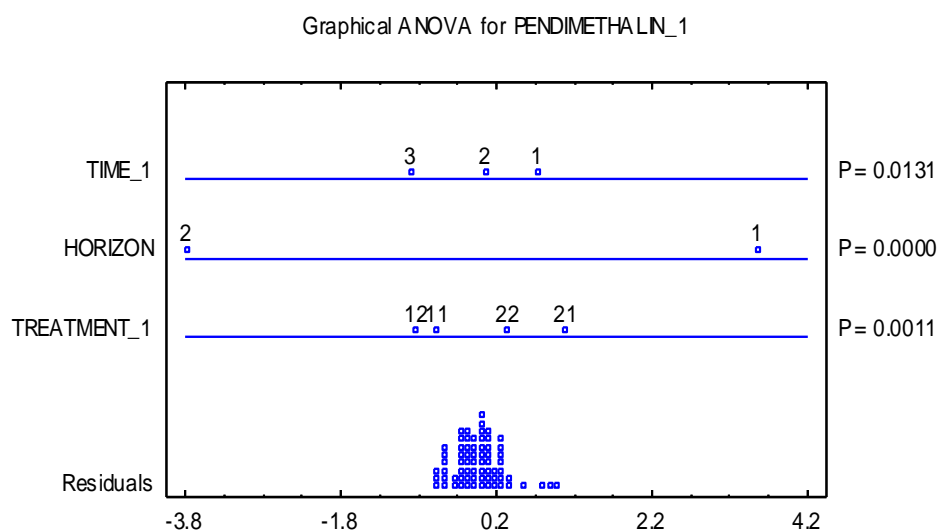


Figure 16. P-values of pendimethalin for 0-5 cm of soil

Table 8. Multiple Range Tests for pendimethalin (0-5 cm)

TREATMENT_1	Count	LS Mean	LS Sigma	Homogeneous Groups
12	17	0.319133	0.0796061	X
11	17	0.381117	0.0796061	XX
22	17	0.581367	0.0796061	XX
21	17	0.750221	0.0796061	X

In the Table 8, three homogenous groups are identified using columns of X's. The levels containing X's mark shows that there are no statistically significant differences. This method used to discriminate among the means is Fisher's significant difference (LSD) procedure. With this method, there is a 5.0% risk of calling each pair of means significantly different when the actual difference equals 0.

Dependent variable of pendimethalin in both layers due to treatment and time factors was calculated by Multifactor- Anova. The P- values shows the statistical significance difference for both of factors. From Fig. 17, we can see that P-values are less than 0,05, which means that these two factors has a statistically significant effect on pendimethalin at the 95% confidence level.

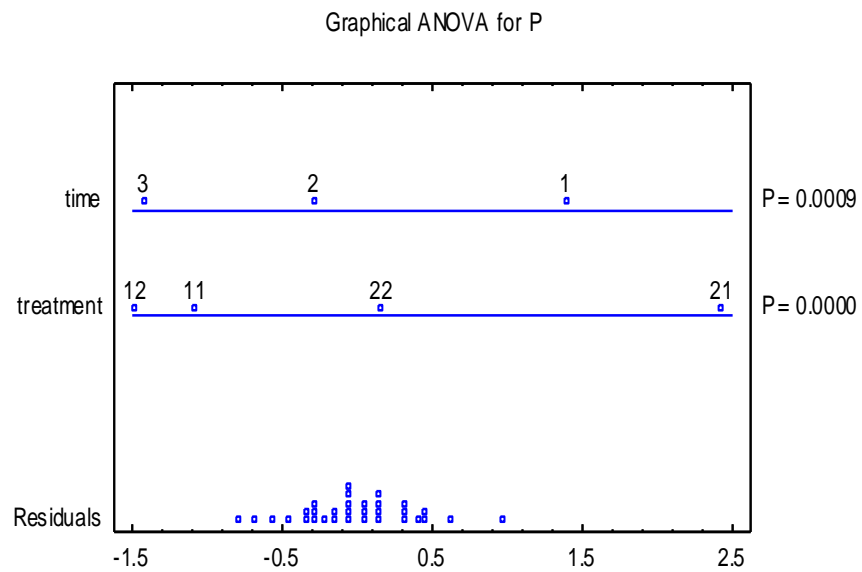


Figure 17. P-values of pendimethalin for both layers

Table 9. Multiple Range Tests for pendimethalin (both layers)

Treatment	Count	LS Mean	LS Sigma	Homogeneous Groups
12	8	0.653939	0.147328	X
11	8	0.787634	0.147328	XX
22	8	1.20837	0.147328	X
21	8	1.97805	0.147328	X

Results for LSD procedure (Tab.9), shown three homogenous groups are identified using columns of X's. There is difference between pesticide concentration which can be seen comparing of X's columns and this marks are not in the same column. According to this we conclude that treatments with higher dose have significant difference in comparison with a lower dose.

6. DISCUSSIONS

Kol et al. (2002), studies shows that pendimethalin is persistent, and its half life is 98 days at 30°C. It has potential to persist in the environment sufficient to affect small grain crops (Hermann et al., 2000).

Zimdahl et al. (1984) suggested that degradation of pendimethalin in soil proceeds more quickly under flooded, anaerobic conditions than under aerobic conditions. European terrestrial field dissipation studies have shown moderate persistence of pendimethalin in soil with half-life ranging from 27 to 155 days (Rice et al. 2003). In tobacco cultivation depending on fertilizers use half-lives of this herbicide were reported from 84 to 97 days (Albanis and Manos 1995). In cotton fields of Central Greece, the persistence of pendimethalin obtained half-life ranged between 42 to 63 days (Tsiropolus and Lolas 2004) and lower half-life of 39 days when pesticide was not incorporated in the soil in onion cultivation were reported by Tsiropolus and Milladis (1998).

If we compare calculated values of pendimethalin half-life, results are in the range of those previous reported works. Treatments covered by geotextiles 11 (1,5 l ha⁻¹) have half-life 80,2 day and 21 (3,00 l ha⁻¹) have 80,4. Next non covered treatments 12 (1,5 l ha⁻¹) show half-life 49,0 day and 22 (3,00 l ha⁻¹) have 40,2 day. We supposed that there will be the effect of different dose of pendimethalin. As we see from results the half-life for treatments with and without textile are similar, it means there was no significant effect of higher dose. On the other hand, comparison of covered and non covered treatments show the significant effect of geotextiles; e.g. treatment 11 with dose 1,50 l ha have half-life 80,2 days and treatment 12 with the same dose have 49,0 days.

It is one of the interesting results of the study because we expected in the treatment with a lower dose half-life of pendimethalin will be less.

The set of processes which play a role in the herbicide transport in soils are sorption and solubility, the mobility of herbicides is regulated by the properties of the chemical and soil, hydro geologic properties, application, and climatic conditions (Hartley and Graham Bryce 1980; Sawhney and Brown 1989). Soil moisture, temperature, organic matter, pH, texture, and rains are the main factors that determine mobility of herbicide (James et al. 1995; Walker et al. 1989; Lazic et al. 1997).

I. Chopra, B. Kumari (2010) studies, shows significant effect of these processes, mainly for transport of pendimethalin for deeper layer of soil. This research done under laboratory conditions in two soil columns 1,0 and 2,0 kg a.iha⁻¹ with simulated rainfall 300 mm. For the experiment was used: into collected sandy loam soils from some of the fields in India, with pH 7, 6 and organic content 0, 67% was added pendimethalin. For analysis was used method of Kumari et al. (2007). In conditions, 300 mm of precipitation pendimethalin found in 60 cm depth, and the highest concentration of pesticide found in the 0-10 cm depth.

In this study, regardless of soil depth residues of pendimethalin was higher in a higher dose 2 kg a.iha⁻¹ compare to a lower dose 1 kg a.iha⁻¹. From the result of studies we can summarize that in the continuous rainfall can influence leaching of pendimethalin up to 60 cm depth (Fig 18).

If we compare results of our experiment, were not significant differences between lower and higher dose of pendimethalin. The treatments with dose 1,5 l ha⁻¹ have half-life 80,2 day similar as treatments with higher dose 3,00 l ha⁻¹ has 80,4 day.

There was one more factor which influenced for degradation rate. Pendimethalin is a low volatile and low mobile herbicide which has low water solubility (Savage and Jordan 1980; Schleicher et al. 1995). In our experiment pendimethalin was less mobile, that may by the low amount of precipitation. Average of precipitation during the whole experiment was in the range 1,14 mm.

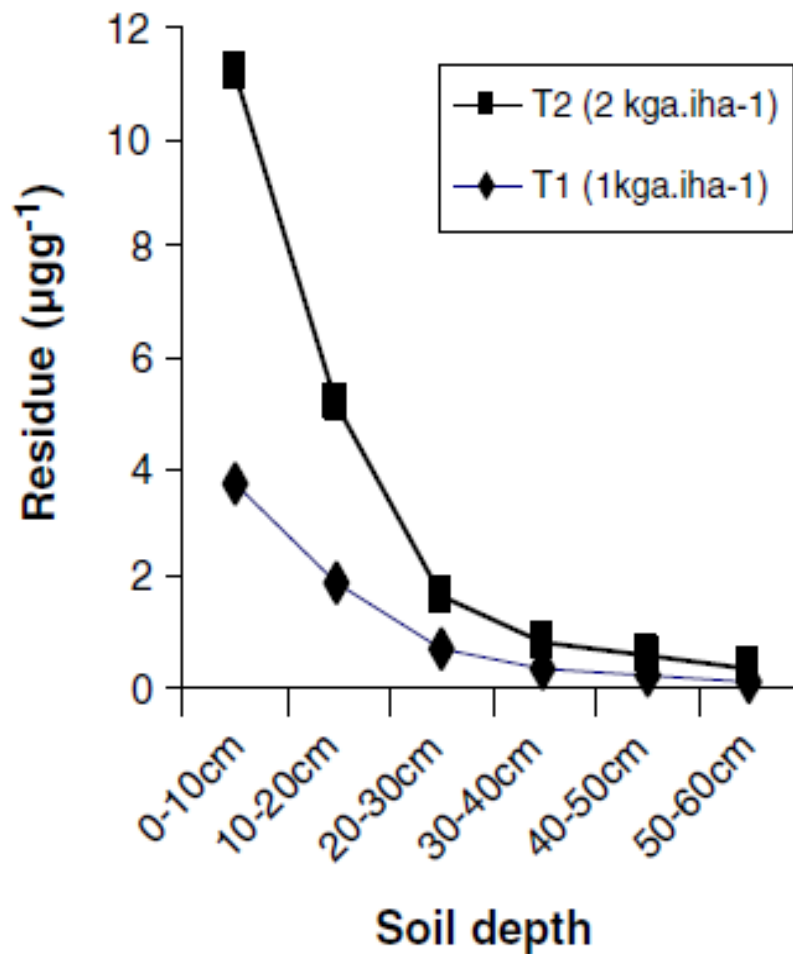


Figure 18. Distribution of pendimethalin at 0-60 cm depths at two application rates. (Chopra and Kumari, 2010)

Dissipation of pendimethalin proceeds faster under flooded, anaerobic conditions than cold and dry conditions (Stranberg and Scott-Fordsmand 2004; Kulshrestna and Singh 1992).

Since temperature and moisture can have a large effect on degradation rates, weather conditions following application in the field might be expected to have similar large effects on persistence. Walker (1989) suggested that temperature and moisture are more predictable than the effects of soil type: there are increased rates of pesticide dissipation with increases in temperature or soil moisture.

According to Walker and Allen (1984), for many pesticides there is a 2-to 2.5-fold increase in half-life with a 10C° decrease in temperature and a 1.5-to 2.5-fold increase in pesticide half-life if soil moisture is reduced by a factor of two.

In the study's authors Shereesha et al, explained that comparatively faster rate of degradation of pendimethalin was higher in summer time and this may be attributed by physical parameters like temperature, wind velocity, moisture level. Similar observations were also reported by Pandit and Choudhury (1994) for residue and persistence of pendimethalin on groundnut;

The studies of Archana and Prasad (2012) indicate that degradation rate of pendimethalin was rapid at 30% moisture and 40C°, due to better adaptability of micro organisms to degrade pesticide under aerobic and warmer conditions, compared to moist 80% and cooler 20C° temperature conditions.

By our results, we can agree with the previous authors that temperature and moisture have significant affect for pendimethalin degradation. At the beginning of the experiment, the soil temperature was low 8,47 C° for non covered treatment and due to this factor degradation of pendimethalin also was lower. Treatments covered by geotextiles show more rapid degradation at 11,3 C°. At the next sampling periods the temperature increased, and as we see from results degradation also increased. Of course, it is not explained only by soil temperature, moisture but mainly by time and adsorption processes.

7. CONCLUSIONS

The results obtained in this study summarized below:

1. From results, we can conclude that hypothesis was right for treatment with higher dose and for lower dose we have to reject the hypothesis because there were no significant differences.
2. In this study, observed half-life for covered and none covered by geotextiles has similar results. Treatment with geotextiles 11 ($1,5 \text{ l ha}^{-1}$) has 80,2 day in the range with treatment covered by geotextiles 21 ($3,00 \text{ l ha}^{-1}$) has 80,4 day. The calculated half life was 49,0 day for treatment without geotextiles 12 ($1,5 \text{ l ha}^{-1}$) and 40,2 day for treatment 22 ($3,00 \text{ l ha}^{-1}$) non covered by geotextiles. This results show us significant effect of geotextiles for degradation time of pendimethalin.
3. Pendimethalin has lower water solubility, and in our study herbicide was less mobile. The degradation of pendimethalin was slow at the beginning of the experiment, because of lower soil temperature and moisture. The climatic conditions, also has influence for this process. Measured values of radiation and rainfall dynamics at the first sampling period were lower.

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