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The effect of adjuvant on pesticides behaviour in soil.

Diploma Thesis

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Summary

The increasing use of pesticides in the soil is presents a serious environmental problem with soil contamination in the world. Many recent studies have shown significant effect of adjuvant on pesticide persistence and their degradation behavior in the soil using different type of adjuvants.

The aim of this work was to evaluate the influence of an adjuvant addition on Pendimethalin and Dimethenamid-p degradation rate in soil. The experiment was carried out under field conditions with 8 different treatments. Pendimethalin and Dimethenamid-p were applied alone and in a mixture with adjuvant, pesticide + adjuvant with irrigation and pesticide + irrigation without adjuvant. We have used two type of herbicides, which are Stomp 400 SC (containing 400 g/L pendimethalin) and Outlook (containing 720 g/L dimethenamid-p, which is a resolved isomer of dimethenamid). Each pesticide treatments received different amount of pesticide and different amount of adjuvant but using same amount of irrigation water at the same day of the experiment. Pesticides residue was analyzed using HPLS instrument.

The main conclusions can be summarized behaviour of Pendimethalin and Dimethenamid-p are quite different. The dissipation of average half-life of Pendimethalin was found 43.7 days, and for Dimethenamid-p was 10.9 days respectively.

The hypothesis was not confirmed because the ANNOVA did not find significant effect of adjuvant and irrigation for both Pendimethalin and Dimethenamid-p. In addition, there was almost practically no difference between the treatments were pesticide mixing with adjuvant and without adjuvant, also were using irrigation and non-irrigation treatments.

The half-life of Dimethenamid-p showed slightly small difference between irrigation and adjuvant treatments. Irrigation for Dimethenamid-p has shown shorter half-life than treatment with adjuvant. However, if we see half-life and leaching behaviour Pendimethalin there was no difference between treatments of irrigation and adjuvant.

Key words: Pendimethalin, Dimethenamid, Grounded, Adjuvant, Pesticide behavior, Pesticide half-life

Declaration

I declare that the Diploma Thesis The effect of adjuvant on pesticides behaviour in soil is my own work and all the sources I cited in it are listed in Bibliography.

Prague, _____   Signature _____

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Table of contents

List of Tables

List of figures

Appendices

1. Introduction

The use of pesticides in the world has continued to increase, particularly in large-scale commercial farming enterprises due to increases in acreage and need to intensify agricultural production. The first synthetic pesticides became available during the 1940s, generating large benefits in increased food production. Concern about the adverse impacts of pesticides on the environment and on animal and human health started in the early 1960s. Furthermore, application of pesticides can lead to environmental damage, injury non-target plants and animals, soil microorganisms, reduced control of a target pest due to adaptation and can move to ground water. Since then, debate on the risks and benefits of pesticides has not ceased and a huge number of research had conducted on the impact of pesticides on the environment (Van der Werf, 1996).

The processes, as degradation by soil microorganisms, chemical degradation, sorption and binding by organic and mineral components, uptake by plant roots, and volatilization determine pesticide behaviour in soil. Modelling of field behaviour of pesticides started around 1970 (Leistra, 1971). Different kinetic model were used in describing dissipation of herbicide in soil. The models most often used in similar studies were single first order, single second order and biexpotential kinetics such as Gustafson and Holden or first order multi-compartment (Vink et al., 1994). The modelling plays a major role in the assessment of pesticide behaviour in the environment, for registration at the EU level (Boesten, 2000).

Performance of pesticides is highly affected by a group of products called adjuvants. Their influence by changing the physical properties, the efficacy and the chemical losses of the pesticides. The adjuvant properties can be chemical, physical or biological in nature and that properties of adjuvants increased herbicide activity through mechanisms such as droplet adhesion, retention, spreading, deposit formation, uptake and translocation (Sharma, S. D. et al., 1996). Adjuvants strongly influence pesticide delivery, uptake, redistribution, persistence and thus the final biological performance (Krogh, K. A et al., 2003).

Pendimethalin [N- (1- ethylpropyl)-3,4-dimethyl- 2, 6- dinitrobenzenamine] is a pre-emergence dinitroaniline herbicide, which is commonly used for selective weed control in the world agricultural practises (Robert L. Zimdahl et al., 1984).

Dimethenamid-p   S-2-chloro   -N-(2,4-dimethyl-3-thienyl)   -N-(2-methoxy-1-methylethyl)-acetamide. This compound belongs to the chemical family of chloroacetamides and is used as a pre-emergent or early post-emergent herbicide with a broad spectrum of activity against most annual grasses and some important broad leaf weeds (McGregor, D.B. and Roland Solecki 2005).

2. Scientific hypothesis and objectives

2.1. Scientific hypothesis

Addition of adjuvant improves the half-life of the pesticides and reduce the leaching of the pesticides in soil.

2.2. Objectives

The objective of this study is to evaluate the effect of an adjuvant addition on the Pendimethalin and Dimethenamid-p pesticides degradation rate, half-life and leaching in soil.

3. Literature review

3.1. Behaviour of pesticides in soil.

Pesticides may use in controlling insect pests, diseases and weeds in agriculture. The range of chemicals in this category includes insecticides and fungicides for controlling soil-borne pests and pathogens, systemic insecticides and fungicides intended for uptake by the underground parts of plants, herbicides, nematicides, and general soil sterilants. They increase agricultural production tremendously as these chemicals act on pests that destroy agricultural product (Dingham, 2005).

When pesticides applied on the field, only a certain percentage of the applied dose will reach the target crop. The remaining fraction will enter the soil, air, surface and ground waters through different pathways. In the different compartments of the ecosystem, pesticides are then -to a smaller or larger extent- available for organisms. Depending on the exposure concentration and the mode of action, pesticides can be harmful to humans, animals and the ecosystem. Therefore, public authorities and industry tried to minimise the negative consequences of pesticide use. The use of certain highly toxic pesticides has been banned and the use of triazine herbicides, organophosphate and carbamate insecticide has been restricted (Dingham, 2005). The behavior of a pesticide in the environment depends on its stability, physico-chemical properties, physical properties include molecular surface area, molar volume, molecular weight, polarity and density, and chemical properties are solubility of pesticides and BCF (bioconcentration factor) (Clark D . Linde 1994). The nature of the medium into which it is applied, the organisms present in the soil, and the prevailing climatic conditions (Graham-Bryce, 1981). In spite that pesticides are probably the class of organic contaminants most studied in the aquatic environment, their occurrence and behavior in wastewater treatment plants (WWTPs) has been very seldom studied, perhaps because these substances have been typically considered of agricultural rather than of urban origin (Marianne Kock-Schulmeyer et al.,2013). The increasing use of agrochemicals may result in serious potential human health and environmental problems, which must be addressed to minimize harmful effects. When chemicals such as acidic herbicides were applied to soil, only a small portion reaches the target site (Kalkhoff et al., 1998). Most of the pesticide is subject to processes such as sorption, degradation, run off, and leaching and evaporation. Transport by run off and leaching, can result in contamination of surface and ground waters (Kolpin et al., 1998).

Herbicide behavior in soils greatly depends on adsorption–desorption phenomena and knowledge of these processes is important to predict their mobility in soil (Gao et al., 1998).

For better understanding of pesticide behavior in soil and other chemical compounds in soil, it is necessary to consider at least the main factors, which is influencing of migration, decomposition, activity and persistence of above-mentioned compounds. These main factors include adsorption and desorption, volatilization, leaching, uptakes by plants as well as chemical and microbial degradation (Flury, 1996; Lennartz, 1999).

According to Gevao B, et al., (1999) assumed that adsorption process is probably the most important mode of interaction between soil and pesticides and controls the concentration of the latter in the soil liquid phase. From the physical-chemical data of adsorption, mobility and degradation obtained in the laboratory, it is possible to predict with a high degree of reliability the behaviour of pesticide in the soil (Navarro et al., 1992; Navarro and Barba, 1996). Most of pesticides in soil do not leach after they enter the soil, because they may adsorbed or tightly held by soil particle. Adsorption depends not only on the chemical, but also on the soil type and amount of soil organic matter present (Jesse C. and LaPrade, 1992). Adsorption processes may vary from complete reversibility to total irreversibility. The extent 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 acidbase nature of the pesticide molecule (Senesi, 1992; Pignatello and Xing, 1996).

Interaction between soil and pesticide is quite complex, as is shown (Fig.1). Pesticides after their usage can be confronted by inevitable chemical, physical and microbiological processes, which are responsible for inactivation, loss and transformations of pesticides in soil (S.Navarro et al. 2007). The leaching of pesticides receives particular attention, because it directly influences the extent of surface water and groundwater pollution. A number of pesticides has recently been detected in groundwaters in Western Europe and in the USA in the past years (R. Calvet., 1995). Leaching is the downward movement of pesticides through the soil (Watschke, T.L et al., 1988).

There are numerous factors that influence leaching, but the most important are the nature of the soil (clay and organic matter content), irrigation water flow, and temperature (Vighi and Funari, 1995). The extent of leaching and the resulting alteration in water quality depend on soil and pesticide properties, climatic conditions, crop type and cropping practices, and water management methods.

Considering the need of pesticide use in agriculture, the only acceptable solution for the prevention of groundwater contamination is improved pesticide management, leading to acceptable and safe application rates (R. Calvet., 1995).

Adsorption processes also one of important factors on behavior of pesticides in soil. The term "adsorption" is used to refer to processes in which pesticides or other molecules accumulate at the solid-water interface. The process of adsorption results in the formation of molecular layer on the soil particle surface and is reversible. The more generalized term, "sorption", is often used to indicate retention processes where there is no distinction between adsorption, absorption and precipitation. Absorption, unlike adsorption, involves the movement of the compound of interest "into" soil particles or organisms and precipitation involves the formation of a separate solid phase on solid surfaces (Koskinen and Harper, 1990)
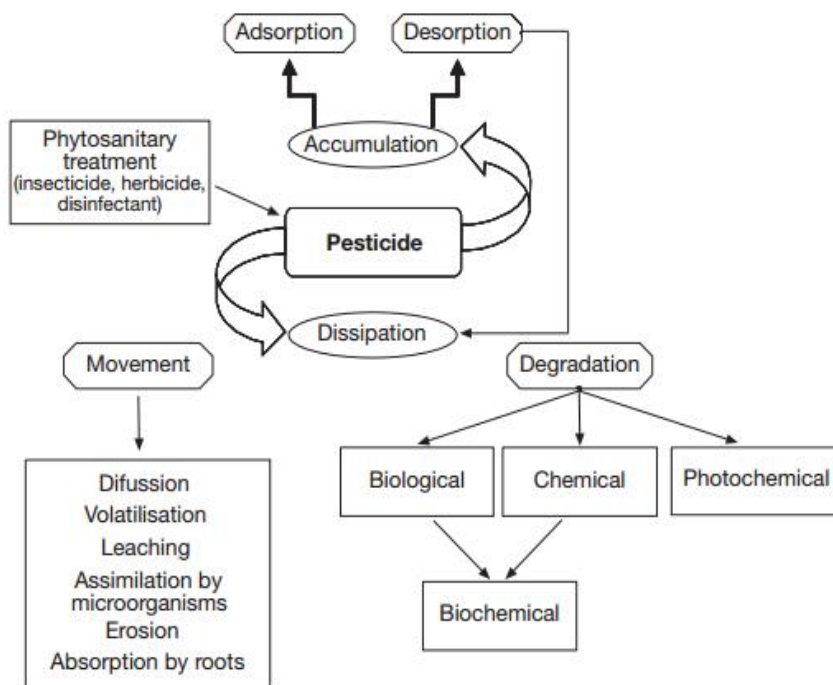
Figure 1. Schematic representation of pesticide dynamics in soil. (S. Navarro et al. 2007)

The principal of pesticides accumulation in soil is adsorption, which may be chemical in nature (as with electrostatic interactions) or purely physical (as with van der Waals forces). Adsorption takes place between charged pesticides molecules (sorbate) and soil particles (adsorbant), including clay minerals, sesquioxides, and humus. Positively charged pesticide molecules can bind to negatively

charged particles of clay 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 (Senesi 1992; Pignatello and Xing 1996).

Adsorption in soil can result in inactivation of pesticides to the point where pesticidal properties are virtually negated. In addition, adsorption can slow degradation by rendering pesticides unavailable for both biotic and abiotic reactions or it can speed degradation by allowing surface catalyzed reactions to take place. Finally, and perhaps most importantly, adsorption reactions, by removing the pesticide from mobile phases in the soil, can play a key role in determining the amount of leaching which a pesticide will undergo (Saltzman and Yaron, 1986; Scheunert, 1992).

Adsorption depends on three factors which often interact in a complicated way: the molecular properties of the solute, soil constitution and the experimental conditions under which the adsorption is studied (R.Calvet., 1980). According to Kodešová et al., (2011) evaluated of pesticide adsorption in soils, as one of the parameters, which are necessary to know when assessing possible groundwater contamination caused by pesticides commonly used in agriculture. For this purpose, batch sorption tests were performed for 11 selected pesticides and 13 representative soils. As a result, the K_F values for various pesticides and different soils show that there is no general trend of pesticide sorption in soils, which can be applied for all pesticides. It is evident that the largest adsorption (the largest K_F value) was observed either in soil sample from Stagnic Chernozem Siltic (the soil with the largest organic matter content) or in Dystric Cambisol and Haplic Cambisol on syenite (higher OM and low pH). The lowest pesticide adsorption (the lowest K_F value) was measured either in sand or loess (as expected due to very low OM content) (Kodešová et al., 2011).

Many recent studies have focused on organic matter content in soil, which is important, adsorption of pesticides in soil. The organic matter content is usually suggested to have a greatest effect on the pesticide adsorption in natural soils. Pesticide partition (distribution) coefficient (K_D) is usually calculated (based on the positive correlation between the organic carbon content and the K_D coefficient) assuming the organic carbon fraction in soil and the organic carbon partition coefficient (K_{OC}) (S.E. Jorgensen and G. Bendorichio 2001).

However, also other factors may play an important role. Richter et al. (1996) summarized various equations relating the K_D coefficient to organic carbon (OC) and pH. O.Richard (2002) studied organic matter is important because, with most pesticides, it is a main factor determining adsorption and hence availability in the soil solution.

Adsorption and desorption of pesticides on soils are the main retention phenomena that determine their transport, transformation, and biological effects in soil environments (Barriuso et al., 1994). For example, atrazine is moderately up to highly mobile in soils, especially where soils have low clay or organic matter content (Barriuso and Calvet, 1992). Atrazine is primarily retained on silicate clays by physical adsorption but both physical adsorption and chemisorption contribute to the retention of atrazine by soil organic matter (Laird et al, 1994). Rama and Ligy (2008) evaluated adsorption and desorption characteristics of lindane, methyl parathion and carbofuran in soil and they reported that clay content and organic matter played a significant role in pesticide adsorption and desorption processes.

According to Taylor and Spencer (1990), the two main environmental factors that affect pesticide behavior in soil are moisture and temperature, with moisture having a more significant relative weight than soil temperature. However, Bromilow et al. (1999) observed that soil moisture did not influence the degradation rate of flutriafol, epoxiconazole, propiconazole, triadimefon and triadimenol fungicides. With their experiments, the authorsidentified an opposite relationship between soil temperature and the degradation rate of these five fungicides. Awasthi and Prakash (1997) evaluated the fate of chlorpyrifos in soils under different moisture regimes. The major environmental factors that influenced chlorpyrifos loss in soil were moisture, pH, organic matter and clay content. Chlorpyrifos was degraded rapidly in all air-dry soils and slightly more slowly in soils at field capacity and/or under submerged conditions.

3.2.   Properties of pesticides affecting their behavior in soil.

There is no clear relationship between the chemical properties of pesticides and their rates of degradation because several phenomena are simultaneously involved in the degradation and because of the high variety of structures of pesticides (Calvet et al., 2005). Nevertheless, some atoms (halogens, and chlorine in particular) are known to be toxic to microorganisms (therefore a decrease of biodegradation is observed), but there is no general rule (Naumann, 2000).. For example, there is almost no biodegradation of chlordecone (organochlorine insecticide) because of its highly chlorinated cage-like structure that makes chlordecone a poor carbon source for bacteria (Cabidoche et al., 2009).

3.2.1. Solubility

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 solubilities will remain in water and tend to not be adsorbed on soil and living organisms. Solubility is 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 liter) (Clark D. Linde 1994). Feza Geyikci (2011) assumed that the tendency of a pesticide to dissolve in water affects its leaching potential. As water seeps downward through soil, it carries with it water-soluble chemicals. This process is called leaching. Water solubility greater than 30 mg/L has been identified as the flag for a potential leached. Highly soluble pesticides have a tendency to be carried in surface runoff and to be leached from the soil to groundwater. Poorly soluble pesticides applied to soil but not incorporated have a high potential for loss through runoff or erosion. In general, pesticide solubility in water inversely related to adsorption of pesticides in soil. Highly soluble pesticides are weakly adsorbed and pose a greater threat of groundwater contamination (Feza Geyikci 2011).

3.2.2. Persistence and mobility

Persistence may be defined as the tendency of a given compound, a pesticide in this case, to conserve its molecular integrity and chemical, physical and functional characteristics in medium through which it is transported and distributed after being released into the environment. Many organic compounds persist for long periods in soils, subsoil, aquifers, surface waters, and aquatic sediment. The low and high-molecular weight compounds that resist biodegradation are known as recalcitrant molecules. Many pesticides, mainly herbicides, have these characteristics (Navarro et al., 2007). Pesticide persistence and mobility are influenced by the properties of the pesticide. The properties of a pesticide are, in turn, influenced by the soil environment, site conditions, weather, and application method (E.A. Kerle, et al., 2007).

The importance of this process described in several studies E.A. Kerle et al (2007) was estimated pesticide persistence often is expressed in terms of half-life. This is the length of time required for one-half of the original quantity to break down. For example, if a pesticide has a half-life of 15 days, 50 percent of the pesticide applied will still be present 15 days after application and half of that amount (25 percent of the original) will be present after 30 days. Pesticides can be divided into three categories based on half-lives: *no persistent* pesticides with a typical soil half-life of less than 30

days, *moderately persistent* pesticides with a typical soil half-life of 30 to 100 days, or *persistent* pesticides with a typical soil half-life of more than 100 days (E.A. Kerle et al., 2007). The properties of some pesticides are given in (Table 1). Degradation of some pesticides in soil is primarily microbial, pesticide disappearance usually appears to follow first-order reaction kinetics, since the quantity of pesticide in soil is very small in relation to the other components (Blair et al., S2-1990). Use of first-order kinetics simplifies equations for estimating pesticide loss from soil. Degradation rates and determination coefficients can be calculated by fitting data of concentration in soil at different times to the following: (Tadeo, J.L. et al.,2000).

$$LnC = LnC_0 - K.t \qquad (1)$$

Where C (μg/g) is the pesticide concentration after time t (days), C_0 (μg/g) is the initial concentration and K (days $^{-1}$) is the rate constant.

If the pesticide half-life ($t_{1/2}$) is defined as the time required for the pesticide to undergo degradation and /or dissipation to half its initial concentration, then

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

Where the rate constant K is calculated by the equation 1. (Tadeo, J.L. et al., 2000).

Table 1. The properties of some pesticides useful for predicting environmental fate.
(E.A. Kerle et al., 2007)

Pesticide	Haf-life (days)	Sorbtion coefficient K_{oc}	Movement rating	Water Solubility mg/l[*]	Vapor pressure index	Henry's Law Index K_{h**}
Malathion	1	1800	extremly low	130	80	1000
1,3-dichloro-propene	10	32	moderate	2250	290 billion	77 billion
Dicamba	14	2	very high	400 000	0	0
Benomyl	67	1900	low	2	0.001	0.78
Diuron	90	480	moderate	42	0.69	21
Bensulide	120	1000	moderate	5.6	8	3058
Prometon	500	150	very high	720	77.3	130

*Multiplied 10^7 **Multiplied 10^9

Persistence is affected by photodegradation, chemical degradation and microbial degradation. All three processes may participate in the breakdown of a single pesticide. The rate of degradation depends on pesticide chemistry, as well as on environmental conditions.

Distribution between foliage and soil, as well as temperature, soil and water pH, microbial activity, and other soil characteristics may affect pesticide persistence (E.A. Kerle, et al., 2007). Among the many pesticides pendimethalin is a dinitroaniline herbicide used for selective control of weeds in crops such as corn (Zea mays L.), soybeans (Glycine max L. Merr.), peas (Pisum sativum L.), and several vegetable crops (Ndon, B. A. 1978). Persistence of pendimethalin is influenced by cultivation practices, soil temperature and moisture conditions, and soil type. Pendimethalin can be applied preplant incorporated, preemergence, or postemergence with or without in-corporation because it has a relatively low volatility (vapor pressure 3.0 x 10' mm Hg at 25 C) (Savage, K. E. 1978). Evidence from many studies as Flom, D. G. and S. D. Miller (1978) their studied pendimethalin applied under no-tillage conditions in North Dakota was found to be most persistent in a silty clay and least persistent in a sandy loam.

Mobility is one of the most important factors in determining bioavailability and efficacy of a soil treatment. If a pesticide is too mobile, it fails to protect the structure, while increasing risk of groundwater contamination. However, if the chemical is too tightly bound to soil particles, bioavailability is limited. Mobility is affected by the pesticide's sorption, water solubility, and vapor pressure and by external influences that include soil properties, weather, topography, and vegetation. Sorption describes the attraction between a chemical and soil, vegetation, or other surfaces. However, the term most often refers to the binding of a chemical to soil particles. Sorption is defined as the attraction of an aqueous species to the surface of a solid (Alley, 1993). Pesticide mobility may result in redistribution within the application site or movement of some amount of pesticide off site.

After application, a pesticide may:
- Attach (sorb) to soil particles, vegetation, or other surfaces and remain near the site of deposition
- Attach (sorb) to soil particles and move with eroded soil in runoff or wind;
- Dissolve in water and be taken up by plants, move in runoff, or leach;
- Volatilize or erode from foliage or soil with wind and become airborne;

Organic amendments are being promoted to enhance the sustainability of agricultural systems, especially in arid and semi-arid zones where the soils are frequently very poor in organic matter content. The addition of organic amendments leads to significant changes in the biological, chemical, and physical properties of the soil, and these changes may influence the mobility and persistence of herbicides and thus modify their environmental fate. Consequently, this practice is regarded as one of

the most efficient strategies for reducing herbicide leaching. Although, increasing organic matter content in a soil generally results in greater herbicide sorption and reduced water contamination (Majumdar and Singh, 2007;Delgado-Moreno et al., 2010).

3.3. Soil properties affecting pesticide behavior in soil

Soil properties vary from place to place with differences in bedrock composition, climate, and other factors. At times, the amounts of some soil elements and other substances may exceed levels recommended for the health of humans, animals, or plants. Certain chemical elements occur naturally in soils as components of minerals, yet may be toxic at some concentrations. Other potentially harmful substances may end up in soils through human activities (H.Shayler et al., 2009). The physicochemical properties of the pesticide used, as well as soil properties (texture, clay content, organic matter and permeability) play important roles in determining leaching. Soil organic carbon (OC) content is the single largest soil factor influencing pesticide sorption and mobility (Wauchope et al., 2002).

3.3.1. Clay

The mineral adsorbents involved in the adsorption of pesticides are clays (as silicate minerals), oxides and hydroxides (Calvet, 1989). Their surfaces are mainly hydrophilic because of hydroxyl groups and exchangeable cations. The adsorption of pesticides on clay minerals is likely to occur on external surfaces of clay particles rather than in interlamellar space and increases with the specific surface of clays (Barriuso et al., 1994). Oxides and hydroxides are frequently associated to clays, they have a high surface activity and their charge depends on the soil pH (Calvet, 1989). For example, the adsorption of glyphosate increases as follows: kaolinite < illite < montmorillonite < nontronite (Mc Connell & Hossner, 1985). The adsorption of glyphosate on iron and aluminium oxides and hydroxides is high at intermediate pH and driven by ionic bindings between the positive surface sites of minerals and the negative acid groups of glyphosate (Morillo et al., 2000). However, sorption is much lower at very acid or very alkaline pH because oxides will bear the same charge as glyphosate.

The clay fraction of the soil is composed of both crystalline and amorphous minerals. Most of the charged and polar sorption sites are on the secondary minerals, the layer silicates. Amorphous minerals can also provide some hydrophobic sorption sites. In contrast, crystalline minerals such as

quartz and feldspar typically contribute little to the sorption capacity of a soil (Harper, 1994). Clay or organic soils are more adsorptive than coarse, sandy soil due in part to their increased surface areas (Johnson et al., 2007).

3.3.2. Organic mater

Soil organic matter originates from crop residues, microbial biomass and organic amendments. It has very heterogeneous composition and contains both hydrophilic and hydrophobic groups (Calvet et al., 2005). Even if organic matter only represents few percents of the total dried material in soil, it is a major sorbent of pesticides in soil (Calvet, 1989). This is attributed to its high chemical reactivity towards both mineral surfaces and organic molecules, allowing various types of interaction with pesticides. The sorption capacities of organic matter are not only controlled by their chemical composition, but also by their size, due to a greater number of sorptive sites related to a greater surface area with decreasing particle-size (Benoit et al., 2008). In general, the adsorption of pesticides increases with organic matter, except for ionic molecules. The addition of organic amendments leads to significant changes in the biological, chemical, and physical properties of the soil, and these changes may influence the mobility and persistence of herbicides and thus modify their environmental fate. Consequently, this practice is regarded as one of the most efficient strategies for reducing herbicide leaching (Majumdar and Singh, 2007; Fernández-Bayo et al., 2009).

The soil organic matter has a polydisperse nature with polyelectrolytic character, surface activity properties and various chemically-reactive functional groups, hydrophilic and hydrophobic sites, which qualify these substances as privileged in the interaction with organic pesticides (Senesi 1992). All pesticides and their transformation products (TPs) are retained by soils to different degrees, depending on the interactions between soil and pesticide properties.

Most influential soil characteristic is the organic matter content (Doong, R.A. et al., 2001). The larger the organic matter content, the greater is the adsorption of pesticides and transformation products (C. Crescenzi, et al., 2004). Soil organic matter is considered to be the single most important soil constituent influencing pesticide sorption in soils (Farenhorst, 2006). In soils, pesticides are initially and predominately sorbed to organic matter that coats soil particles (Park et al., 2003). Generally, the lower the water solubility of a chemical and the higher the amount of organic carbon in the soil, the greater the sorption of a hydrophobic compound (Alexander, 1999). In addition, organic matter plays

an important role for the retention of pesticides in soil. It is, therefore, not surprising that organic soil amendments like manure, compost and biosolids used primarily to increase agricultural productivity also have effects on pesticide sorption and leaching (Larsbo et al., 2008).

3.3.3. pH

The soil pH plays an important role in particular for the adsorption of ionic pesticides like glyphosate or sulcotrione. Indeed, Mamy and Barriuso, (2005) observed that depending on the charge of the pesticide, the adsorption will increase (or decrease) with pH. For example, the retention of glyphosate increases when the soil pH decreases because the number of negative charges of the molecule decreases, allowing the adsorption on negatively charged adsorbents like clay or organic matter.

Soil pH influence the rate of pesticide breakdown due to reaction with water and influence of degradation pesticides in the soil. A relationship between soil pH and rate of degradation has been demonstrated for many ionisable pesticides, although there are exceptions. No influence of pH on degradation was found for atrazine (Hance 1979), 2,4-D (Picton and Farenhorst 2004), and rimsulfuron (Vicari et al. 1996). Soil pH may influence the degradation of a pesticide directly if its stability is pH dependent (chemical hydrolysis) or indirectly via changes in soil microbial biomass/activity, or pesticide sorption. If degradation is influenced indirectly by pH, it tends to proceed faster at high pH. Soil pH can affect the equilibrium between undissociated pesticide molecules and the anion molecules of the pesticide. Such an equilibrium shifts as soil pH changes in relation to pKa value of the pesticide. The herbicide 2,4-dichlorophenoxyacetic acid, for example, has a pKa of 2.8 (Wauchope et al., 1992).

When soil pH goes above 2, 8 - 2, 4 - dichlorophenoxyacetic acid would exist primarily in its dissociated, negatively charged form. As soil pH increases, adsorption will decrease because the 2,4-D molecules are more repelled from the overall negative charges of soil colloids (McCarty et al., 2003). For ionizable pesticides such as 2,4-D, 2,4,5-T, picloram, and atrazine adsorption process will increases with decreasing soil pH (Z.Y. Li, et al., 2002).

The effect of pH on binding has been reported for less basic pesticides such as the triazine herbicides (Weber et al., 1969), amitrole (Senesi et al., 1986), and dimefox (Grice et al., 1973), which become cationic depending on their basicity and the pH of the system, and also governs the degree of ionization of acidic groups of the humic substances.

3.4. Transport of pesticide in soil

The transport of pesticides in soil, and their rate of disappearance from soil, is of considerable importance, yet so complex that the composite behavior of pesticides in the sub-surface is almost impossible to determine accurately. Although individual modes of disappearance have been extensively studies in isolation, it is of particular importance to develop predictive capabilities of their overall behavior (G.Singh , W.F.Spencer et al., 1992). The transport and destination of pesticides involves complex mechanisms that are influenced by many processes, including volatilization, leaching, adsorption, and chemical and biological decomposition. By diffusion process pesticide transfer through the soil profile from one point to where it's concentrated more to another where its concentration less (Gao et al.,1998).

Two processes primarily govern the movement of chemicals in soil – mass flow (advection) and dispersion. Mass flow, or advection, refers to the movement of dissolved materials or fine particulates with the water current in the soil while dispersion refers to the mixing of materials within the water column (Schnoor, 1992). The mass flux of water, and thus mass flow, in soil controlled primarily by gravitational and capillary forces acting on the water. The maximum hydraulic conductivity of a soil is observed to occur at saturation when all of the soil pores are water filled (Enfield and Yates, 1990). As a soil dries the proportion of air filled pores increases. As such, conductivity is decreased upon drying since the ability to conduct water is greatly reduced in air-filled pores. Thus, any factors, which affect the soil moisture and movement of water within soils, will also affect mass flow. These factors include climate, soil hydraulic characteristics, and plant uptake of water along with the associated evapotranspiration losses (Saltzman and Yaron, 1986). The various transport phenomena, leaching in soil, volatilization to the atmosphere and runoff to untreated fields, are important factors determining both the efficacy of a pesticide at the target site and its potential contamination of nearby surface and groundwater (G.Singh , W.F.Spencer et al., 1992).

In several studies it has been found that proportionally higher amounts of pesticide transport occur at higher water flux velocities than at lower water flux velocities. These findings may be explained by the fact that at lower water fluxes there is a greater amount of time provide for molecules to diffuse into aggregates as well as for adsorption or perhaps degradation reactions to take place (Davidson and McDougal, 1973; Saltzman and Yaron, 1986). The greater movement of pesticides at higher water flux velocities is especially important in areas where preferential flow paths

have been provided by fissures and cracs in the soil. Fissures and cracks may occur as a result of pedogenic processes or as a result of the activity of plant root systems or soil organisms, such as insects and worms, within the soil (DeMartinis and Cooper, 1994).

3.5. Degradation of pesticides in soil
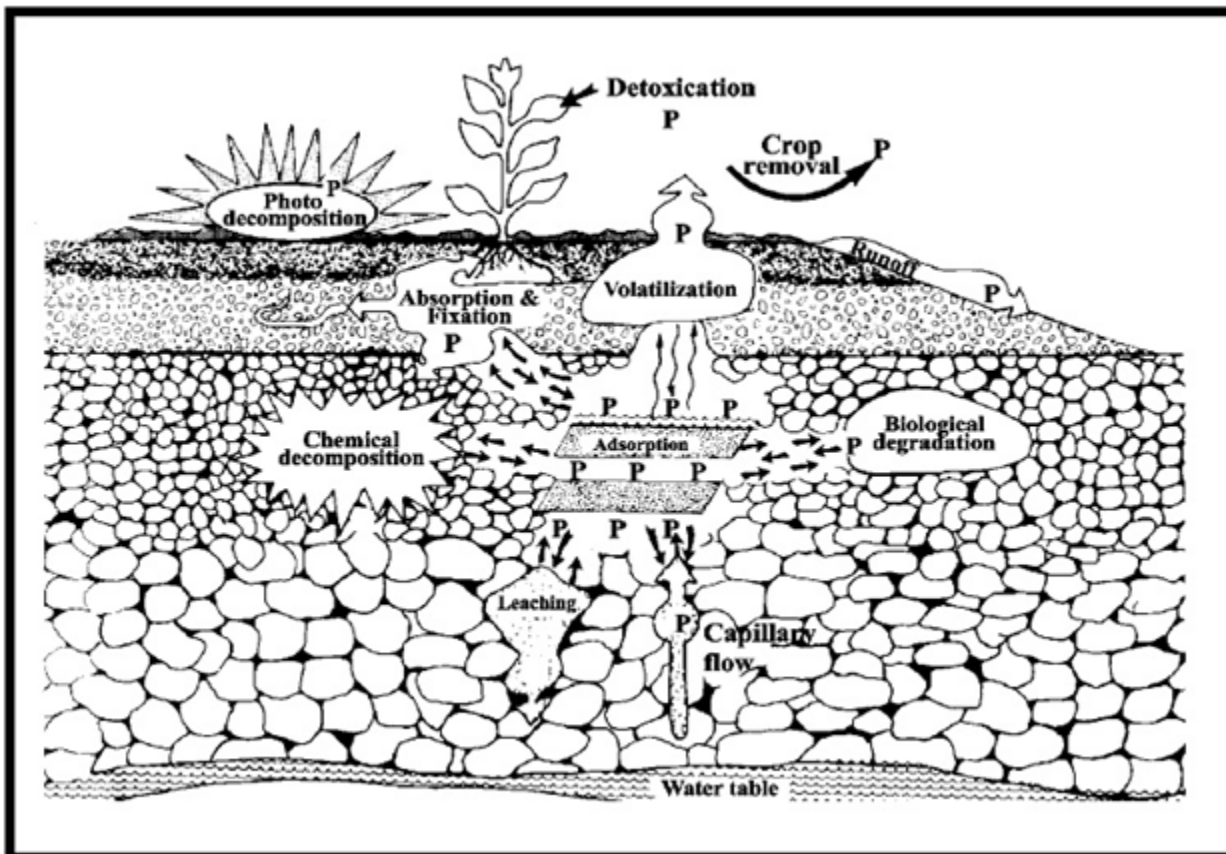
Figure: 2. Pathways of pesticide loss. (Skrotch, W.A. and Sheet, T.J, 1981)

Note: P = Adapted from Herbicide Injury Symptoms and Diagnosis

Degradation is the process of pesticide breakdown after application and it is a very important route of pesticide dissipation. As pesticides are broken down, the possibility of the pesticide chemicals reaching ground or surface water and thus creating environmental or health related concerns is generally minimized. Pesticides can be broken down by microbes, chemical reactions, and light; these processes are known as biodegradation, chemical degradation, and photodegradation, respectively (Wheeler, 2002).

The degradation processes described in the literature demonstrate a great efficiency in the decontamination of systems contaminated by pesticides. Several factors influence the rate of degradation, such as the chemical structure of the pollutants, pH, iron concentration, hydrogen peroxide and the organic load. Because of the great potential of contamination by pesticide residues and the variation in the time necessary for natural degradation, it is necessary to discover those processes that accelerate the decontamination of the affected environment. Thus, several degradation processes such as photocatalytic degradation, advanced oxidative processes, phytoremediation, bioremediation, ozonation and photoFenton reactions have been proposed. All these systems are considered to be efficient for pesticide degradation (Zenilda L. et al., 2011).

As shown (Fig.2.) advanced pesticide removal methods are typically needed to meet environmental quality requirements and improve the ecological system. These include combinations of biological, chemical, and physical processes. Adsorption has evolved into one of the most effective physical processes for pesticide removal, because the technique uses equipment that is readily available, easy-to-use, and not energy-intensive, and also because the treatment is cost-effective (Aslan and Turkman, 2004; Carrizosa et al., 2000).

Adsorption and degradation are often correlated with each other because sorption processes affect biodegradation by modifying the chemical bioavailability of the adsorbed species (Kah et al., 2007; Villaverde et al., 2008). Degradation rates are affected by environmental factors. Therefore, a particular pesticide can have variable rates of degradation.

3.5.1. Biodegradation in soil

Biological decomposition of pesticides is most important and effective way to remove these compounds from the environment (Dabrowska et al., 2004). The microorganisms have the ability to interact, both chemically and physically, with substances, leading to structural change or the complete degradation of the target molecule (Wiren-Lehr et al., 2002). Among the microbial communities, bacteria, fungi, and actinomycetes are the main transformers and pesticides degraders (De Schrijver and De Mot, 1999).

Pesticide biodegradation is inanimately tied to the activity of specific microorganisms. Soil temperature and moisture are important factors that influence the activity of soil microorganisms. Numerous studies have examined the effects of soil temperature and moisture on the biodegradation of agrochemicals in soils (Choi et al., 1988; Veeh et al., 1996).

Generally, faster pesticide degradation rates occur with increasing soil temperature up to a temperature that corresponds to the maximal activity of the microorganisms that use the pesticide as a substrate (Choi et al., 1988; Ma et al., 2001). Once temperature goes beyond an optimum level, degradation rates decline (Veeh et al., 1996). Degradation by microorganisms is desirable because it usually results in the detoxification of the pesticide. In soil the microorganisms metabolize organic pesticides either aerobically or anaerobically. In most cases, the microorganisms degrade the molecules and utilize them as a source of energy and nutrients (Getenga, 2003; Boivin et al., 2005), or use them through cometobolism, which occur when an organic compound is not used by the microorganism for growth, but is metabolized in conjunction with another substrate used for growth (Kumar et al., 1996; Sanchez ae al., 2004).

According to Van Eerd et al. (2003), the microbial metabolism of pesticides may involve a three-phase process. In phase I, the initial properties of a parent compound are transformed through oxidation, reduction, or hydrolysis to generally produce a more water-soluble and usually a less toxic product than the parent. In phase II, the conjugation of pesticides often involves utilization of existing enzymatic machinery and is therefore called a cometabolic process. Microbial pesticide conjugation reaction include xylosylation, alkylation, acylation and nitrosation and can occur intra-or extracellularly. Phase III, involves conversion of phase II metabolites into secondary conjugates, which are also nontoxic (Van Eerd et al., 2003). Following studies is about microbial degradation of pesticides in soil, which is most common means of pesticide degradation. Microorganisms are extremely efficient at degrading a wide variety of organic compounds. Microorganisms degrade pesticides by two different processes. Microorganisms, which can use a pesticide as a food source, and they have a ability to metabolize the pesticide. This method of degradation leads to a fairly rapid disappearance of the pesticide. Some microorganisms will alter the structure of the pesticide but are unable to gain any energy from the reaction.

This process is called cometabolism. A pesticide degraded by a cometabolic process would tend to persist in the soil for a longer period of time (Watschke, T.L et al., 1988).

3.5.2. Chemical degradation

Chemical degradation occurs when a pesticide reacts with water, oxygen, or other chemicals in the soil. As soil pH becomes extremely acidic or alkaline, microbial activity usually decreases. However, these conditions may favor rapid chemical degradation. Chemical breakdown is the

breakdown of pesticides by chemical reactions in the soil. The rate and type of chemical reactions that occur are influenced by the binding of pesticides to the soil, soil temperatures, pH levels (Kerle et al. 2007). Wise and Trantolo (1994) chemical degradation is the breakdown of pesticides by processes where living organisms are not involved. Major chemical reactions such as hydrolysis, oxidation, and reduction, without the influence of microbial activity, are processes involved in chemical degradation.

Chemical reactions between pesticides and their metabolites often lead to the formation of strong bonds (chemisorption), which increase in persistence of the residues in the soil, but decrease their bioavilability and toxicity (Dec and Bollag 1997). It also reduces leaching and transport properties. The nature of the binding forces involved and the types of mechanism operating in the adsorption processes of pesticides onto the soil include ionic, hydrogen, and covalent bonding; charge transfer or pesticides electron donor-acceptor mechanisms; van der Walls forces; ligand exchange; and hydrophobic bonding or partitioning (Gevao et al. 2000)

3.6.   Effect of adjuvants degradation of pesticides in soil

Adjuvants and surfactants are spray solution additives, and are considered to be any product added to a pesticide solution to improve the performance of the spray mixture (Wilfarm, L.L.C and Gladstone, M.O 1998). The five surfactant classes are: nonionic surfactants, crop oil concentrates, nitrogen-surfactant blends, esterified seed oils and organo-solicone surfactants. (Miller, P and Westra, P. 1998).

Surfactants are frequently added to pesticide and herbicide formulations as adjuvants to improve handling, delivery and effectiveness. From a regulatory perspective such additives are generally considered to be inert, and their influence on co-contaminant fate and transport processes has been largely ignored. Although the addition of surfactants at concentrations above the critical micelle concentration (CMC) is shown to enhance the total aqueous-phase concentration of hydrophobic organic compounds (HOCs), the free (non-micellar) aqueous phase HOC concentration decreases with increasing surfactant concentration (Pennell, KD et al., 2004).

Properties of adjuvant increased herbicide activity through mechanisms such as droplet adhesion, retention, spreading, deposit formation, uptake and translocation. These adjuvant properties can be chemical, physical or biological in nature (Sharma, S. D et al., 1996). The listed properties of adjuvants can influence the concentration of herbicide residues in soil. Adjuvants strongly influence pesticide delivery, uptake, redistribution, persistence and thus the final biological performance

(Krogh, K. A et al., 2003). The evidence from several studies indicates that surfactant could either reduce pesticide leaching by increasing the sorption or it could increase leaching potential by increasing mobility of pesticide. The experiment was done by authors in the laboratory using high ranges (500-20,000 mg L-1) of anionic and non-ionic surfactant concentrations. However, the hydro-physical properties of soil as well as on the leaching and adsorption of pesticides are depended upon the type of surfactants and the amount used (Abu-Zreig et al., 2000). The ability of the surfactants to enhance the water solubility of hydrophobic organic compounds (HOCs) or to lower interfacial tension has led to many applications in environmental remediation. For example, surfactant-aided soil washing (SASW) has been used for years to remediate HOC contaminated soil and sediment ex situ (Sun et al., 1995).

4. Materials and Methods

4.1. Experimental design

The study area have a size of 0.015 ha (aprox. 15×10 m). Then this plot was partiotioned in to 12 section with size of 2,5m $\times$ 5m; 12,5 m^2 each for first sampling and then further divided in to 24 section with size of 1,25m $\times$ 2,5m 6,25 m^2 each for the remaining sampling time. For our study, we used complete randomized design consisting of 24 sections and 8 treatments. Each treatment received three replication. See the Figure 3 and Appendix. 1-2. pp 57
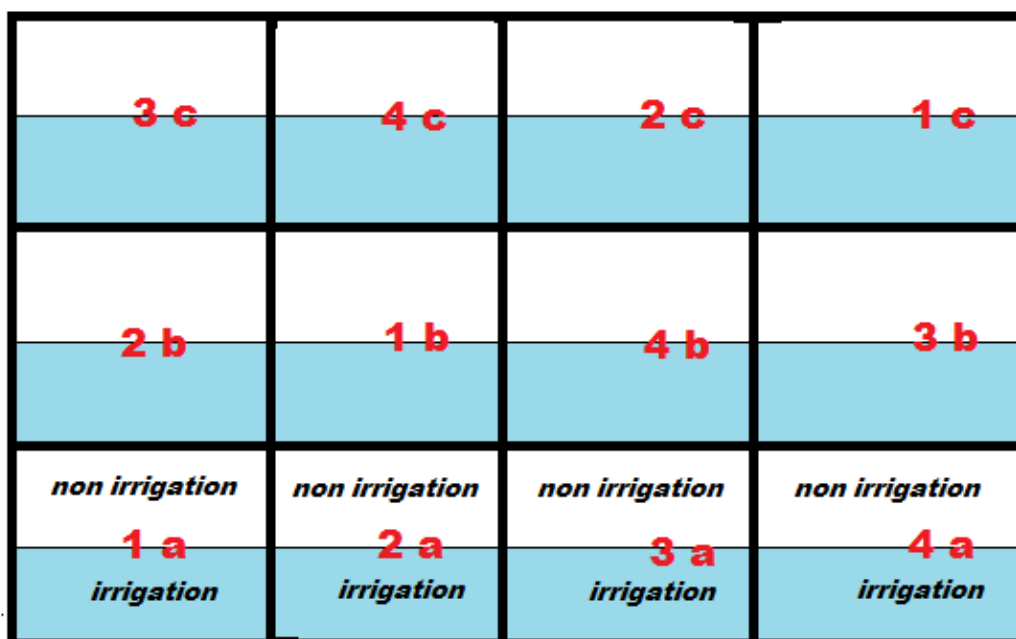
Figure 3. Experimental design

4.2. Soil characteristics

The experiment was conducted from July to October 2014 in field condition which is located in Praha Suchdol belonging to the Czech University of Life Science Prague. The elevation of the study area is 275 m above the sea level and the soil type is Haplic Chernozem and the parent material is loess. The main chemical and physical soil properties of Ap horizon determined as shown in Tab.2.

Table 2. Chemical and physical soil properties

| Soil type	Haplic Chernozem	pH KCl	pH H_2O	CEC mmol(+)/100 g	HA mmol(+)/100 g
Location	Praha Suchdol	7,33	7,76	23,5	0,99
Parent material	Loess	OM (%)	Sand (%)	Silt (%)	Clay (%)
		2,25	23,3	56,5	20,2

4.3.   Pesticide characteristic.

For our study purpose, we used two most common pesticides in agricultural practices; these are Pendimethalin and Dimethenamid-p. Pendimethalin-is yellow crystalline solid, mp 56-57 ℃. Solubility in water (20℃ - 0.3 mg /L) is readily soluble in aromatic hydrocarbons and their halogen derivatives. Very stable in alkaline and acidic condition. 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. PDM is characterized by low water solubility, moderate to high vapor pressure, strong adsorption to soil, and high octanol–water partition coefficients (Swarcewicz, M. K. and Gregorczyk, A. 2012). Pendimethalin [N- (1- ethylpropyl)-3,4-dimethyl- 2, 6- dinitrobenzenamine] (Fig.4) is a pre-emergence dinitroaniline herbicide, which is commonly used for selective weed control European terrestrial field dissipation studies show moderate persistence of pendimethalin in soil with half-lives ranging from 27 to 155 days depend of environmental conditions (Robert L. Zimdahl et al., 1984).

Dimethenamid is a yellow liquid and it is water solubility (1174 mg L-1, 25 °C), moderately sorptive (*K*OC, 155 for nonaged residue, in soil with 0.5-4.9% OC and 12-36% clay), and is not particularly vulnerable to photodecomposition or volatilization (Weed Science Society of America 1994). The aerobic half-life varies from 20 days to 5-6 weeks in the field and 38 days in vitro. Although dimethenamid has been registered since 1992, information concerning biodegradability and dissipation mechanisms is limited. (Weed Science Society of America 1994)

Dimethenamid-P is the International Standardization Organization (ISO) approved common name for S-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)-acetamide (Fig.4).

This compound belongs to the chemical family of chloroacetamides and is used as a pre-emergent or early post-emergent herbicide with a broad spectrum of activity against most annual grasses and some important broad leaf weeds. It is taken up through the coleoptiles (grass seedlings) or the roots and emerging shoots (dicotyledonous seedlings) and reduces cell division and plant growth (McGregor, D.B. and Roland Solecki 2005). These two pesticide Pendimethalin and Dimethenamid-p are approved for a variety of crops in a large number of countries, in Czech Republic also used for selective controls of in crops such us corn, dry beans, peanuts, soybeans, potatoes, horseradish and several vegetable crops.
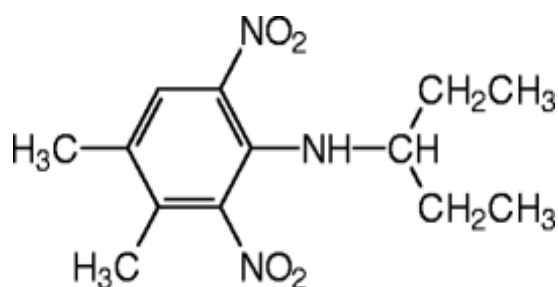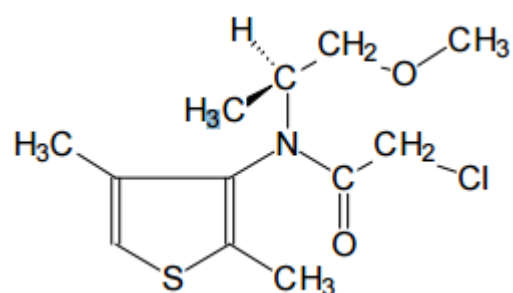
Pendimethalin   Dimethenamid-p

Figure 4. Chemical structure of Pendimethalin and Dimethenamid-p

4.4.   Climatic condition

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. The date of pesticide application was start at 16.07. 2014 and the experiment was end 3.10.2014. Weather condition of area at the date of experiment is shown in Table 3.

Table 3. Weather condition during the pesticides application.

Date	Weather during the application			
	Cloud (%)	Temperature (°C)	Soil moisture	Wind (m/s)
16.07.2014	0	21,6	moist	1,50

Table 4. Climatological data during the experiment period (rainfall, average, minimal, maximal temperature and global radiation), (meteostanice.agrobiologie.cz, Meteostation of the CULS)

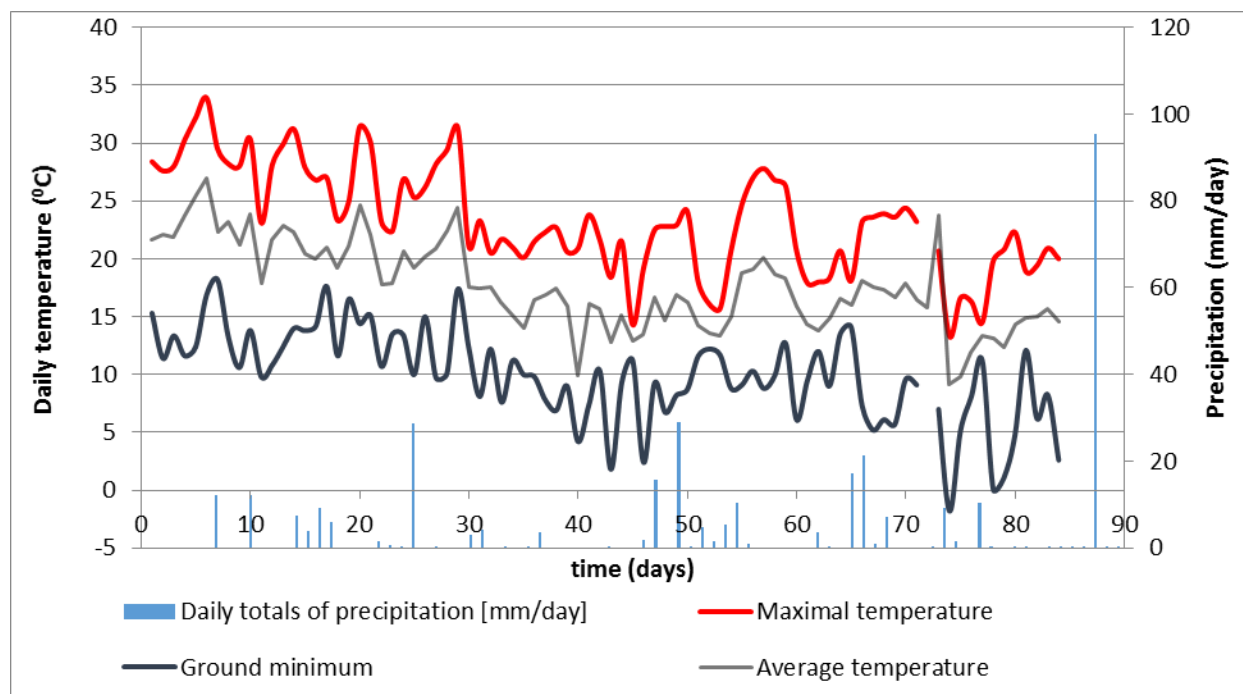| Day	sum of rainfall (mm)	Average Values			
		day temperature (^{O}C)	Maximal temperature (^{O}C)	Minimal temperature (^{O}C)	Global radiation (kJ m^{-2} day^{-1})
0-2	0 (30)	21.9	28.0	16.7	18166.0
3-9	12.1	23.8	30.4	16.9	22546.8
10-21	28.7	20.7	26.9	15.8	17309.2
22-44	28.9	16.7	22.5	11.9	14551.6
45-89	95.5	15.7	20.9	11.1	10823.2

Figure 5. Climatological data for the experiment period, from 16.07.2014 to 03.10.2014, Rainfall in (mm), Maximal and average temperature in (^{0}C), Ground minimum.

The table 4 and fig. 5 shows necessary climatological data during our experiment period and it is observed that there was relatively enough rainfall and the average maximum temperature was 28 ^{0}C, minimum temperature 11.1 ^{0}C, not less than 10 ^{0}C which was suitable condition for all the processes.

4.5. Pesticide application and irrigation

For our experiment, we have used herbicides, which are Stomp 400 SC (containing 400 g/L pendimethalin) and Outlook (containing 720 g/L dimethenamid-p, which is a resolved isomer of dimethenamid). Each treatment received 4 l/ha Stomp 400 SC and 1.4 l/ha Outlook depending on category of the treatments at the first day of our study. In addition, for the remaining treatments both of our herbicide were mixed up with Grounded (0.4 l/ha), which is Adjuvant. The herbicide was applied on the field using special self-propelled pesticide sprayer, (Schachtner jets 015F110, 0.25 MPa pressure application, amount of water 300 l/ha). (See Appendix. 5-6, pp. 58) Irrigation applied for all treatments one day after application of herbicide using special quadrate sprinkler device with a size of (2 m × 2 m; 4 m^2). The amount of water applied for each treatments was 30 mm per the quadrate area.

4.6. Sampling method

For determination of the applied doses of the pesticides, the first sampling was process during the pesticides application using the Petri dishes. Mixed soil sample from three point of each treatments were taken. Soil samples were taken from three soil depths (0-5cm; 5-10cm; and 10-15cm) See Appendix. 3-4, pp. 57. Soil samples were taken 5 times from each treatments with three replicates. One day after application of herbicide all 8 variants divided two part and was irrigated half part of the plot. The first sampling was a day after pesticide application 17 of July, 2014 and before irrigation, using only soil cylinder, from the top layer. The next sampling were 9th, 22nd, 44th and 79th day after herbicide application and samples were taken with both soil sampler and cylinder at the same time. Control samples were also taken before application of herbicide to determine the soil bulk density and to know pesticide residues in experimental area. Soil samples were frozen and stored until their analysis.

4.7. Soil Analysis for the determination of Pendimethalin and Dimethenamid-p

Soil samples were frozen and dried using lyophilization, grinded and sieved through 2 mm sieves and pooled. Then 10 g of soil was weighed and determined by using a balance scale and transferred into the one use 50 ml of plastic cuvette. Then 10 mL of methanol were added to the plastic cuvette containing the 10g of soil and the mixture was shaked together for 20 hours using the automatic shaker. Then the mixture were centrifuged for 10 min at 13000 rpm. The suspended soil extract were filtered by using 0.7 μm glass syringe filter and putted the filtered extract into vials.

After the preparation of methanol extract, the concentration of pendimethalin and dimethenamid in the soil samples were determined by using HPLC. The HPLC consists of the following parts: P680 HPLC Pump, ASI-100 Automated Sample Injector. Separation took place in Kinetex 2.6μ, C18, 100 A column, 50×4.6 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 550ml of acetonitril, 450 ml of redistilled water and 1 mL L^{-1} of formic acid. 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 signal from the detector was stored and processed using the chromatographic software Chromeleon version 6.70 (Dionex). The wavelength for pendimethalin and dimethenamid-P detection was 235 and 254 nm respectively. The pendimethalin retention time was 6.4 min. and the detection limit was 0.03 μg ml^{-1}. The Dimethenamid-p retention time was 1.4 min. and the detection limit was 0.03 μg ml^{-1}. Soil extraction data were fitted to first-order kinetics, and the half-lives (t1/2) of the herbicides were calculated in the top soil (0–15cm).

4.8. Stastiscal analysis

The effect of treatment, sampling term and soil depth factors was investigate among the experimental results for pendimethalin and dimethenamid-p was performed using analysis of variance (Multifactor ANOVA).

5. Results

5.1. Pendimethalin

5.1.1. Distribution of Pendimethalin in soil profile

The following figures shows the distribution of Pendimethalin in soil profile (0-15 cm), after 9, 22, 44 and 79 days pesticide application. See Fig. 6, 7, 8, 9.

Figure 6. Distribution of Pendimethalin in soil profile (0-15 cm), after 9 days pesticide application (P00-Pendimethalin, without adjuvant and irrigation; P0I- Pendimethalin, without adjuvant, with irrigation; PG0- Pendimethalin with adjuvant and without irrigation; PGI- Pendimethalin with adjuvant and irrigation)

When we see distribution of the Pendimethalin it was behaving similarly in treatments of PGI and PG0 in which their concentration was decreased dramatically between the 5-10 cm and then their concentration was decreased from detection limit. When we compare all treatments in this figure, Pendimethalin was deep leached only in treatments of P0I. There was slight amount of this pesticide up to depth of 10-15 centimeter which then disappeared below this depth.
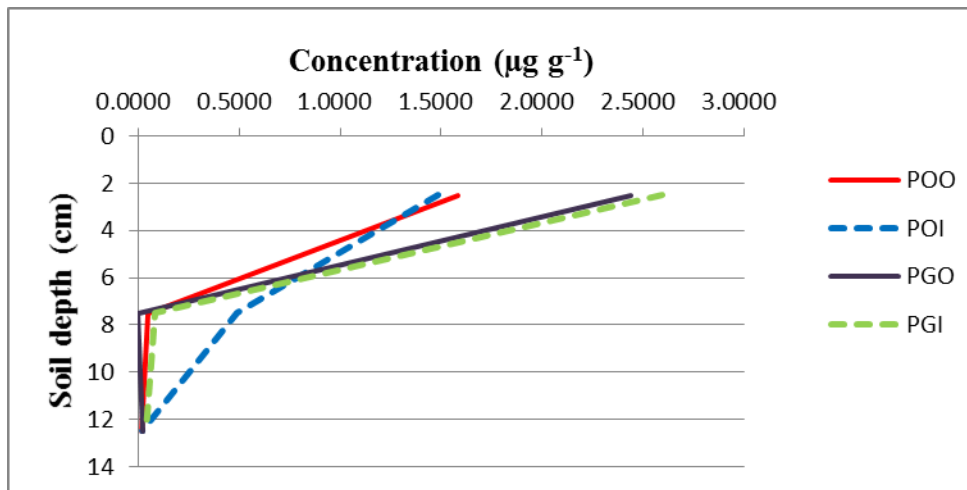
Figure 7. Distribution of Pendimethalin in soil profile (0-15 cm), after 22 days pesticide application (P00-Pendimethalin without adjuvant, without irrigation; P0I- Pendimethalin, without adjuvant, with irrigation; PG0-Pendimethalin with adjuvant and without irrigation; PGI- Pendimethalin with adjuvant and irrigation)

Behavior of Pendimethalin was almost similar in all treatments in which its concentration was below the detection limit 10 cm but when we see their concentration at shallower depth P0I and PGI was slightly higher at shallower depth of soil profile as compared to P00 and PG0.

Figure 8. Distribution of Pendimethalin in soil profile (0-15 cm), after 44 days pesticide application (P00-Pendimethalin, without adjuvant, without irrigation; P0I- Pendimethalin, without adjuvant, with irrigation; PG0- Pendimethalin with adjuvant, without irrigation; PGI- Pendimethalin with adjuvant and irrigation)

There was almost no difference in leaching of Pendimethalin 22 days after pesticide application and 44 days after pesticide application. It was behaving similarly in all treatments except presence of comparatively high amount Pendimethalin at shallower depth in treatments of P0I and PGI as compared to its concentration in treatments of P00 and PG0.
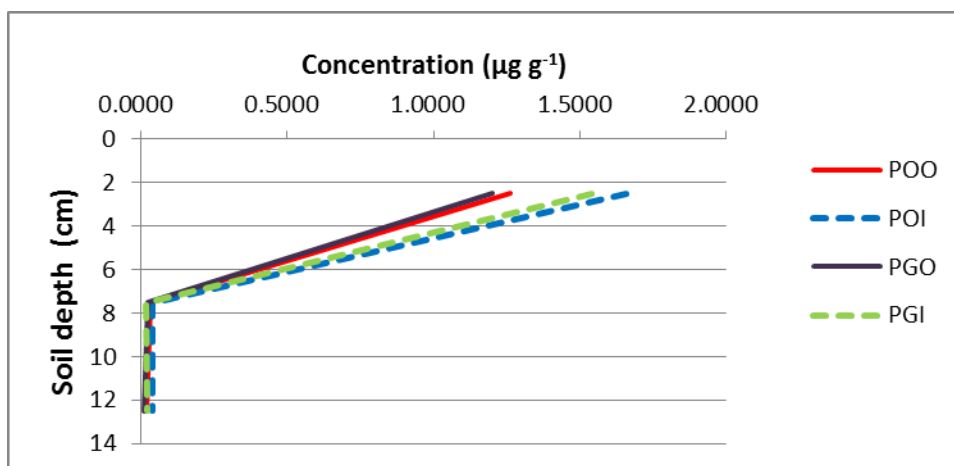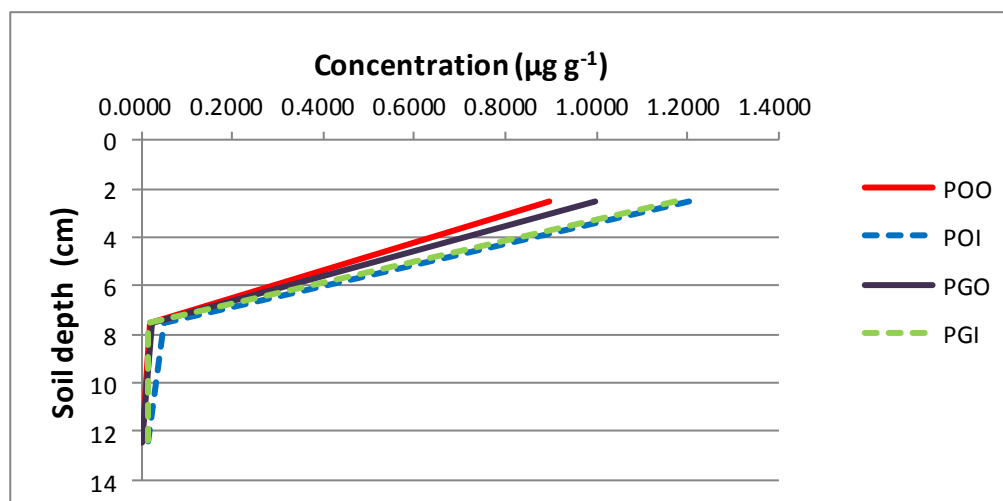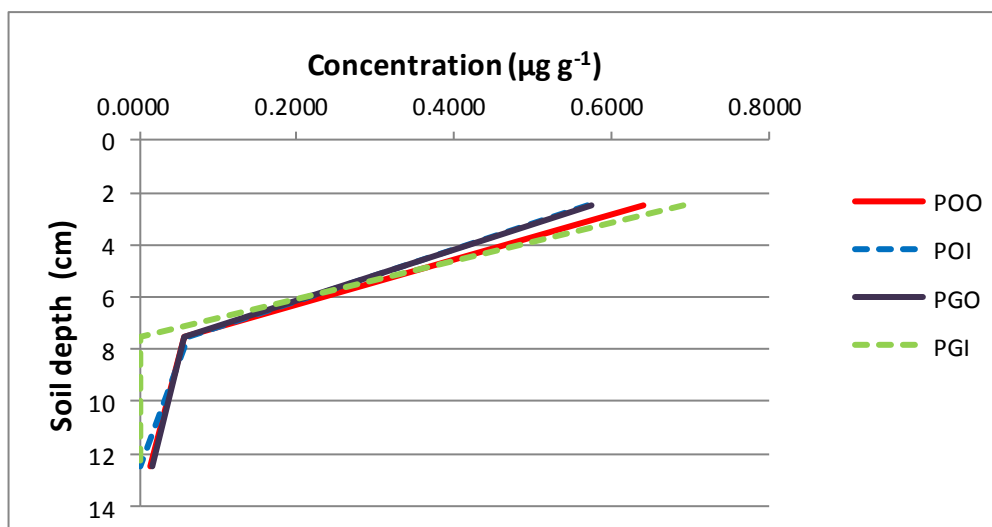

Figure 9. Distribution of Pendimethalin in soil profile (0-15 cm), after 79 days pesticide application, (P00-Pendimethalin, without adjuvant and irrigation; P0I- Pendimethalin, without adjuvant, with irrigation; PG0- Pendimethalin with adjuvant and without irrigation; PGI- Pendimethalin with adjuvant and irrigation)

79 days after pecticide application distribution of Pendimethalin was slightly different in PGI treatment as compared to other treatments. Based on the result amount of Pendimethalin was slightly higher in shallower depth of PGI treatments than other treatments and also Pendimethalin was disappeared below 10 cm in PGI but there was slight amount of Pendimethalin in other treatments up to 12 cm deep in to the soil.

5.1.2. Measured and calculated concentration of Pendimethalin.

The residual concentrations of Pendimethalin for the sampling depth of 0-15 cm; for all tested treatments are presented by following figures. These results suggested that both Pendimethalin curves shows for all tested treatments relatively similar. The calculated average half-life of Pendimethalin was 43.7 days and it has a longer half-life and then Dimethenamid-p. See. Fig. 10, 11, 12, 13.

Figure 10. Measured and calculated concentration of Pendimethalin without adjuvant and without irrigation in soil layer 0-15 cm.

The results obtained dissipation of Pendimethalin was decreased continuously with time in soil depth with 0-15 cm; for treatment-A (Fig.10). The initial concentration of pesticide was 12.98 µg g^{-1} for all Pendimethalin treatments and in this treatment residual concentration of pesticide 3.40 µg g^{-1} (+-9.58) were detected 79 days after application of single pesticide. The calculated half-life of Pendimethalin in soil for this treatment is 44 days.

Figure 11. Measured and calculated concentration of Pendimethalin without adjuvant and with irrigation in soil layer 0-15 cm.

30

The results obtained dissipation of Pendimethalin was decreased continuously with time in soil depth with 0-15 cm; for treatment-B (Fig.11). The residual concentration of Pendimethalin in this treatment 3.22 µg g^{-1}, (+-9.76) were detected 79 days after pesticide application using only irrigation. The calculated half-life of Pendimethalin in soil for this treatment is 43 days. If we compare the treatment with treatment-A there was no significant differences between without irrigation treatment.
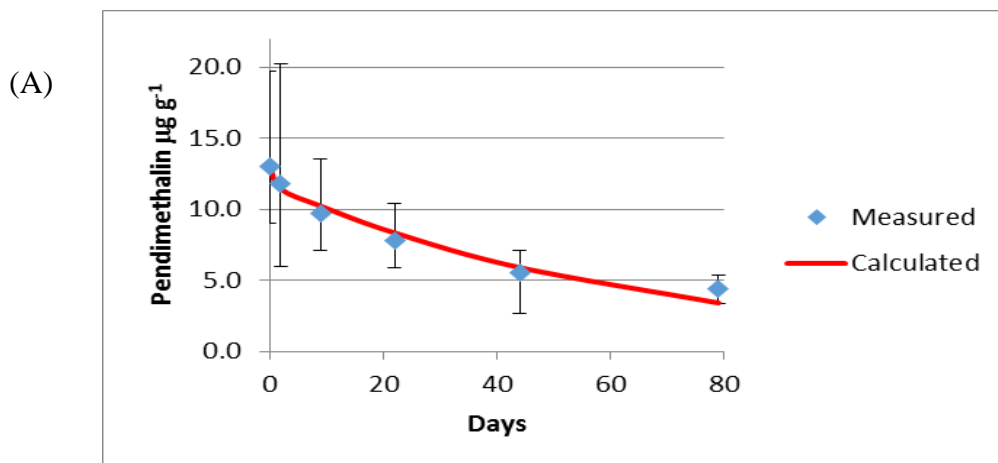
(C)

Figure 12. Measured and calculated concentration of Pendimethalin with adjuvant and without irrigation in soil layer 0-15 cm.

The results obtained dissipation of Pendimethalin was decreased continuously with time in soil depth with 0-15 cm; for treatment-C (Fig.12). The residual concentration of Pendimethalin in this treatment 3.41 µg g^{-1} (+-9.57) were detected 79 days after application of pesticide mixing with adjuvant. The calculated half-life of Pendimethalin in soil for this treatment is 43 days. We can assume that there is no significant effect of adjuvant on Pendimethalin half-life in soil.

(D)
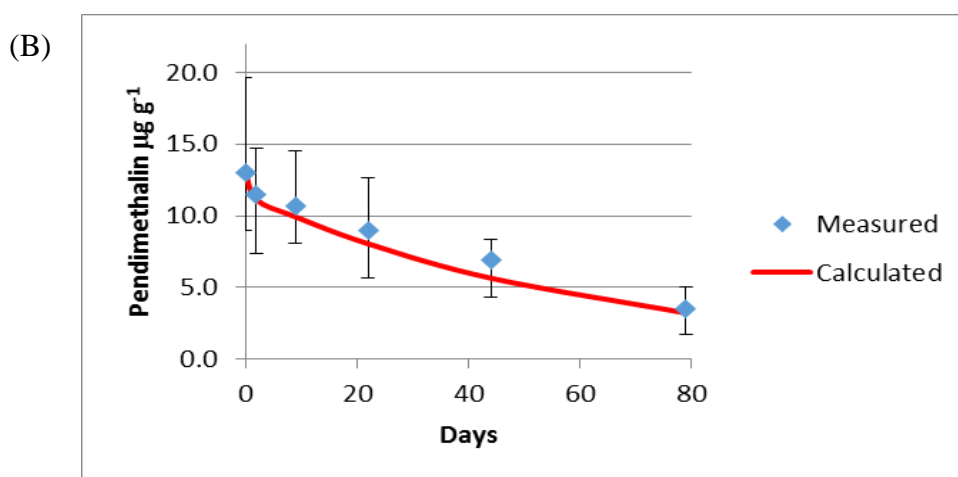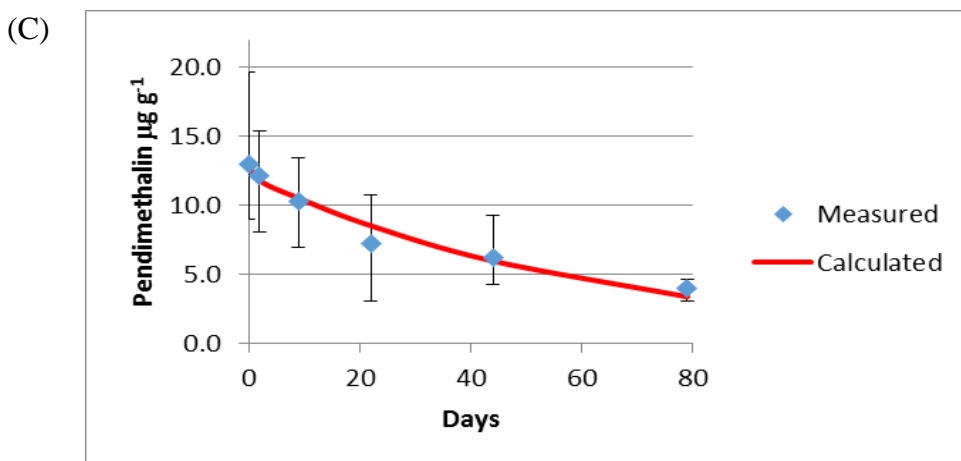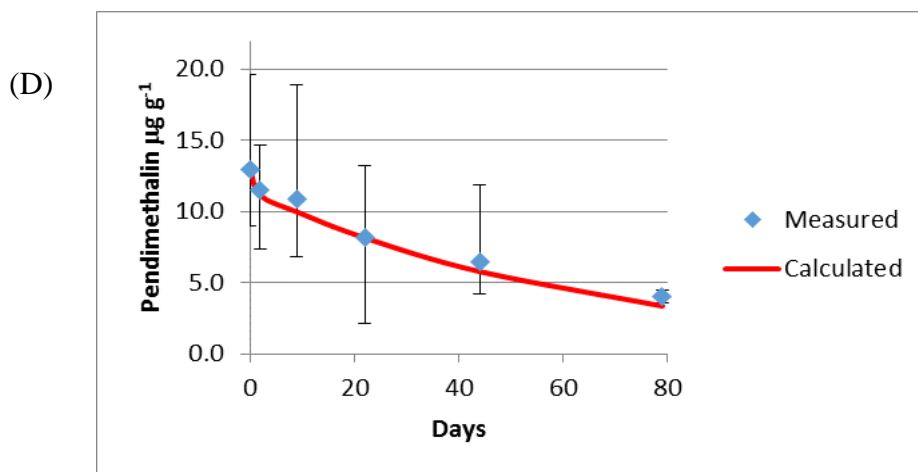

Figure 13. Measured and calculated concentration of Pendimethalin with adjuvant and irrigation in soil layer 0-15 cm.

31

The results obtained dissipation of Pendimethalin was decreased continuously with time in soil depth with 0-15 cm; for treatment-D (Fig.13). The residual concentration of Pendimethalin in this treatment 3.35 µg g^{-1} (+-9.63) were detected 79 days after application of pesticide mixing with adjuvant and using irrigation. The calculated half-life of Pendimethalin in soil for this treatment is 43 days. Comparison the treatment were pesticide applied with addition of adjuvant, and pesticide applied using irrigation treatments. We did not find relatively effect on Pendimethalin half-life in soil were applied pesticide addition of adjuvant and using irrigation all together.

The half-life ($t_{1/2}$) of Pendimethalin was calculated using first-order kinetics, which is model that is usually used to evaluate persistence of pesticide (Tadeo, J.L. et al., 2000). The first-order constant *k* was calculated using equation (1).

The calculated values for half-life of Pendimethalin presented in Table.5

Table 5. The calculated half-life of Pendimethalin

Treatments	Adjuvant	Irrigation	Half- life (DT 50)
P00	no	no	44.1
P0I	no	yes	43.1
PG0	yes	no	43.0
PGI	yes	yes	44.6

These results suggested that the half-life of Pendimethalin in soil, which were calculated for all treatments of Pendimethalin are relatively similar as shown (Tab.5). In that case, we did not identify influence of adjuvant and irrigation the half-life of Pendimethalin in the soil.

5.2.   Dimethenamid-p.

5.2.1. Distribution of Dimethenamid-p in soil profile

The distribution of Dimethenamid-p shown for soil profile (0-15 cm), after 9, 22,44 and 79 days pesticide application. See Fig. 14, 15, 16, 17.

Figure 14. Distribution of Dimethenamid-p in soil profile (0-15 cm), after 9 days pesticide application (D00- Dimethenamid-p without adjuvant, without irrigation; D0I- Dimethenamid-p, without adjuvant, with irrigation; DG0- Dimethenamid-p with adjuvant and without irrigation; DGI- Dimethenamid-p with adjuvant and irrigation)

The 9 day after concentration of Dimethenamid-p was slightly at shallow depth of DG0 and DGI as compared to D00 and D0I, and their concentration of line was almost zero below 8 cm in all treatments.

Figure 15. Distribution of Dimethenamid-p in soil profile (0-15 cm), after 22 days pesticide application, (D00- Dimethenamid-p without adjuvant, without irrigation; D0I- Dimethenamid-p, without adjuvant, with irrigation; DG0- Dimethenamid-p with adjuvant and without irrigation; DGI- Dimethenamid-p with adjuvant and irrigation)

22 days after pesticide application, distribution of Dimethenamid-p in soil profile was different in DGI than other treatments. In which it is concentration was higher at shallow depth, also leached deep to the soil profile. In case of other treatments Dimethenamid-p was almost lower the detection limit below the 10 cm in soil profile.

Figure 16. Distribution of Dimethenamid-p in soil profile (0-15 cm), after 44 days pesticide application, (D00- Dimethenamid-p without adjuvant, without irrigation; D0I- Dimethenamid-p, without adjuvant, with irrigation; DG0- Dimethenamid-p with adjuvant and without irrigation; DGI- Dimethenamid-p with adjuvant and irrigation)

When we see Dimethenamid-p, it was leached deep to the soil, in case of D0I up to 10 cm and in the other treatments concentration of Dimethenamid-p between the 5-10 cm soil profiles was slightly higher. D00 as compared to other treatment and D0I had smaller concentration of Dimethenamid-p at shallower depth than all treatments
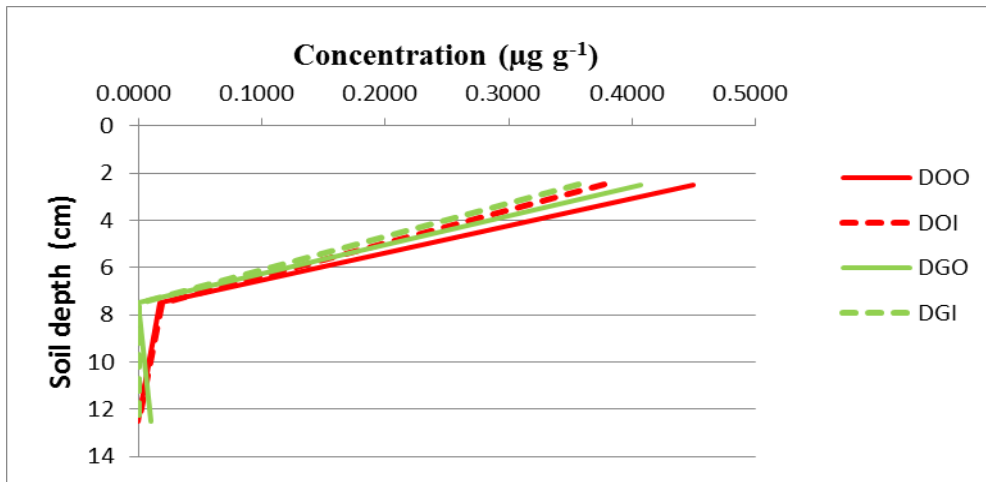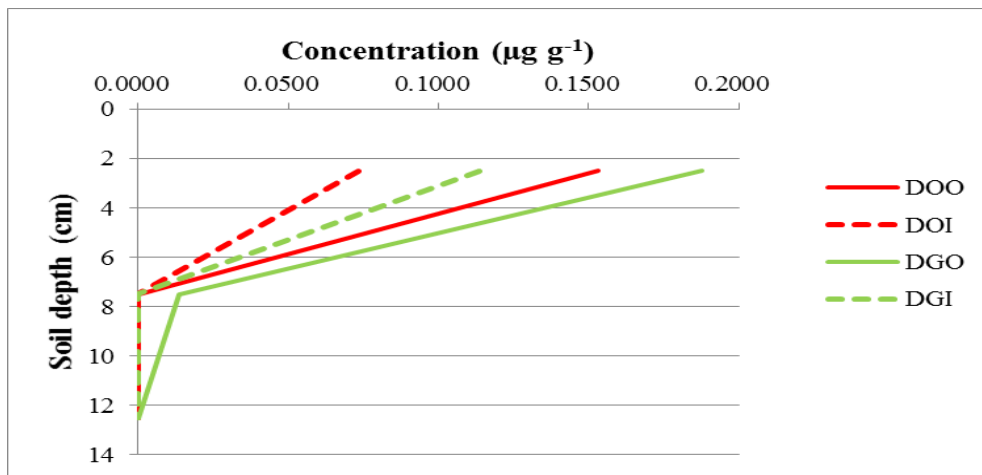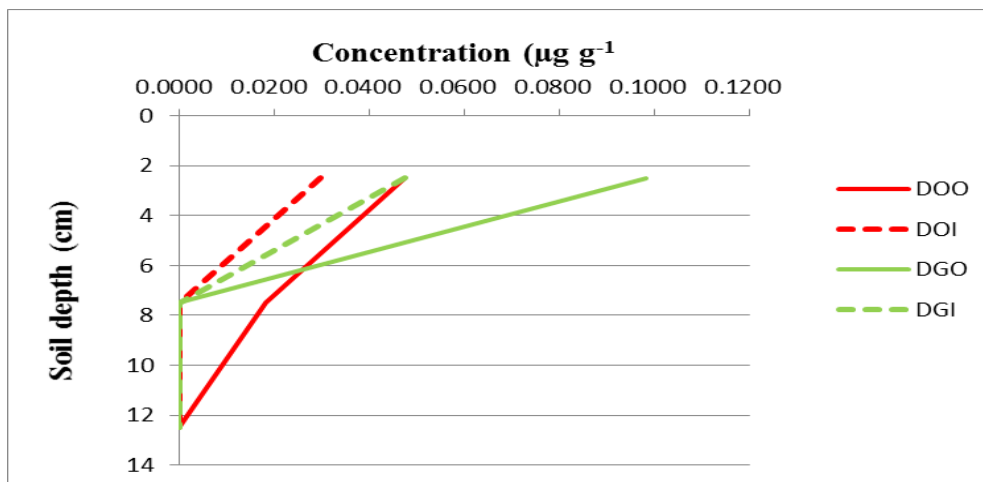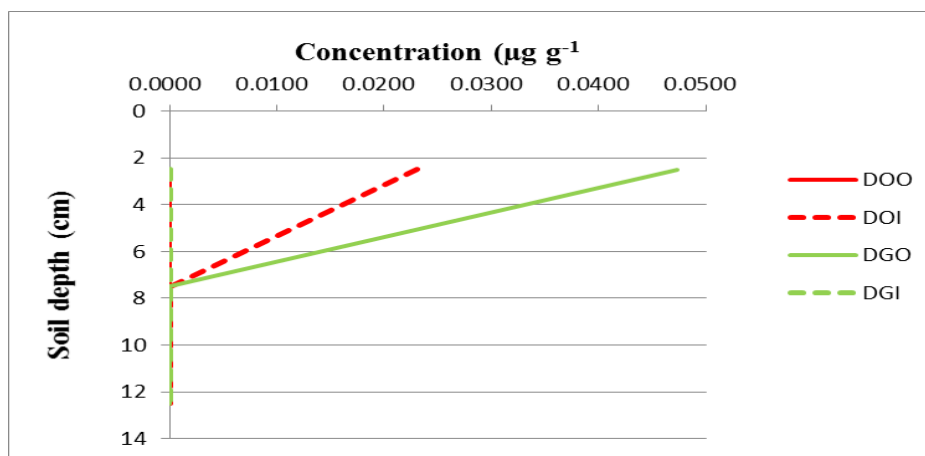
Figure 17. Distribution of Dimethenamid-p in soil profile (0-15 cm), after 79 days pesticide application, (D00- Dimethenamid-p without adjuvant, without irrigation; D0I- Dimethenamid-p, without adjuvant, with irrigation; DG0- Dimethenamid-p with adjuvant and without irrigation; DGI-Dimethenamid-p with adjuvant and irrigation)

Distribution of Dimethenamid-p 79 day after pesticide application in DGI and D00 treatments was completely lower than detection limit for all soil depth. Concentration of Dimethenamid-p in DG0 and D0I treatments below the 10 cm pesticide was already leached up and up to 5 cm we can see slightly less concentration of Dimethenamid-p.

5.2.2. Measured and calculated concentration of Dimethenamid-p

The residual concentrations of Dimethenamid-p for the sampling depth of 0-15 cm; for all tested treatments are presented by following figures. These results suggested that the Dimethenamid-p curves shows slightly difference for all the treatments of Dimethenamid-p. The average calculated half-life of Dimethenamid-p has showed 10.9 days. See.Fig.19, 20, 21, 22.

(A)

Figure 18. Measured and calculated concentration of Dimethenamid-p without adjuvant and without irrigation in soil layer 0-15 cm.

The results obtained dissipation of Dimethenamid-p was decreased continuously with time in soil depth with 0-15 cm; for treatment-A (Fig.18). The initial concentration of pesticide was 6.605 µg g^{-1} were Dimethenamid-p applied without adjuvant which are A and B treatments, and residual concentration of pesticide in this treatment 0.03 µg g^{-1}, (+-6.57) were detected 79 days after application of single pesticide. The calculated half-life of Dimethenamid-p in soil for this treatment was 11 days.

(B)
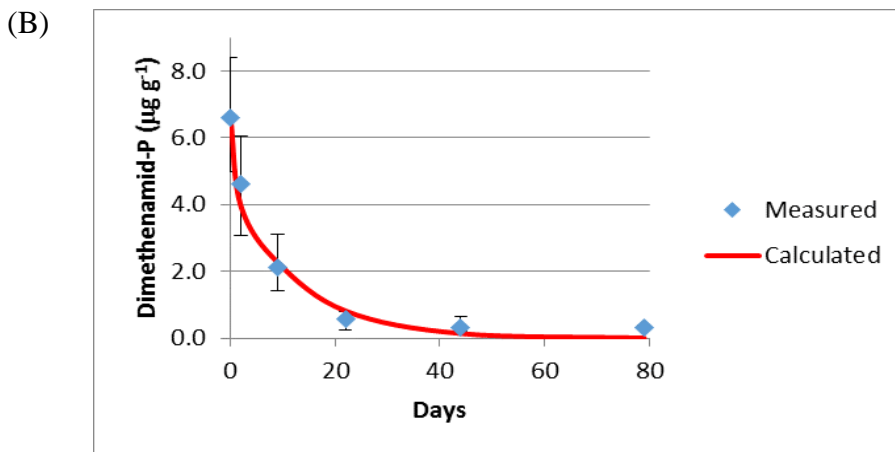
Figure 19. Measured and calculated concentration of Dimethenamid-p without adjuvant and with irrigation in soil layer 0-15 cm.

The results obtained dissipation of Dimethenamid-p was decreased continuously with time in soil depth with 0-15 cm; for treatment-B (Fig.19). The residual concentration of Dimethenamid-p in this treatment 0.009 µg g^{-1}, (+-6.596) were detected the same day after pesticide application using only irrigation. The calculated half-life of Dimethenamid-p in soil for this treatment was 8.8 days.

(C)
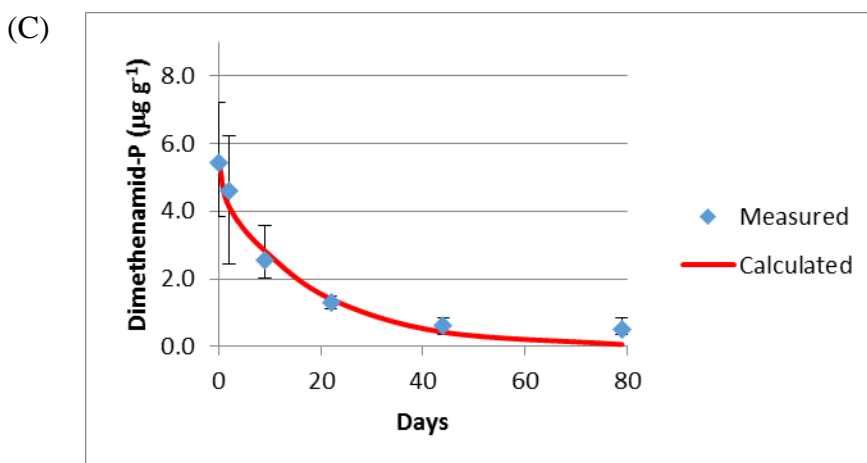
Figure 20. Measured and calculated concentration of Dimethenamid-p with adjuvant and without irrigation in soil layer 0-15 cm.

The results obtained dissipation of Dimethenamid-p was decreased continuously with time in soil depth with 0-15 cm; for treatment-C (Fig.20). The initial concentration of pesticide was 5.43 µg g^{-1} were Dimethenamid-p mixing with adjuvant which are C and D treatments, and residual concentration of pesticide in this treatment 0.065 µg g^{-1}, (+-5.37) were detected same day after application of pesticide applied only with adjuvant. The calculated half-life of Dimethenamid-p in soil for this treatment was 13 days.

(D)

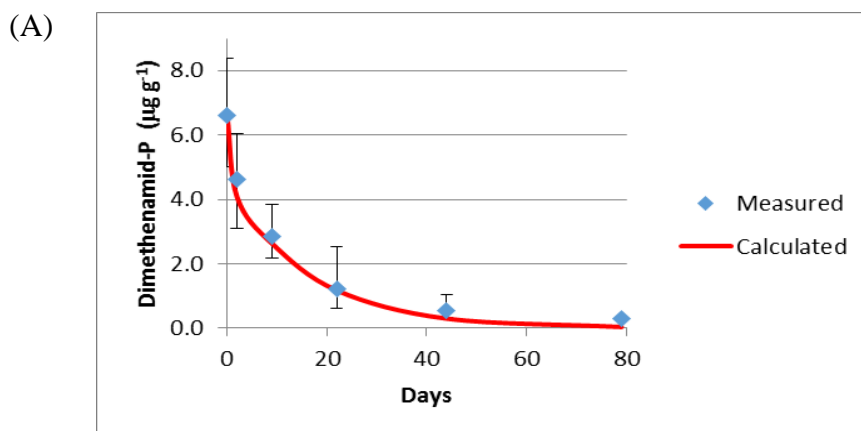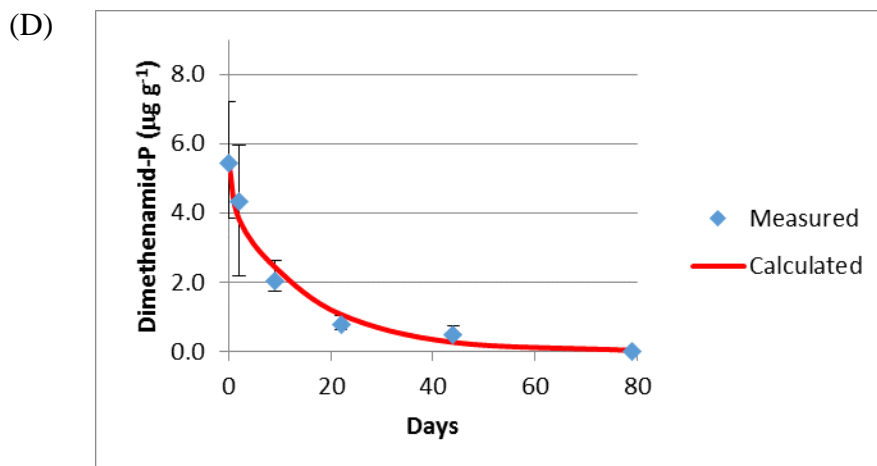
Figure 21. Measured and calculated concentration of Dimethenamid-p with adjuvant and irrigation in soil layer 0-15 cm.

The results obtained dissipation of Dimethenamid-p was decreased continuously with time in soil depth with 0-15 cm; for treatment-D (Fig.21). The residual concentration of Dimethenamid-p in this treatment 0.03 µg g^{-1} (+-5.40) were detected same day after application of pesticide mixing with adjuvant and using irrigation. The calculated half-life of Dimethenamid-p in soil for this treatment was 11 days.

Table 6. The calculated half-life of Dimethenamid-p

Treatment	Adjuvant	Irrigation	Half- life (DT 50)
D00	no	no	11.1
D0I	no	yes	8.8
DG0	yes	no	12.9
DGI	yes	yes	10.9

The evidence from obtained results that Dimethenamid-p has shorter half-life than Dimethenamid-p respectively. As above mentioned they have different chemical properties and solubility. However, the effect of adjuvant have observed half-life of the Dimethenamid-p were the treatment pesticide applied mixing with adjuvant. In this case, half-life of Dimethenamid-p is slightly different were treatment pesticide applied without adjuvant. See (Tab.6).

5.3.   Comparison of Pendimethalin and Dimethenamid-P

Table 7. Analysis of variance for concentration of Pendimethalin and Dimethenamid-p for all experiment days after herbicide application.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS					
A:Term	1.00556	3	0.335188	12.03	0.0000
B:Irrigation	0.000737856	1	0.000737856	0.03	0.8708
C:Adjuvant	0.0136125	1	0.0136125	0.49	0.4851
D:Depth	4.95268	3	1.65089	59.25	0.0000
E:Pesticide	1.46071	1	1.46071	52.42	0.0000
RESIDUAL	9.41773	338	0.0278631		
TOTAL (CORRECTED)	17.5807	347			

The effect of sampling term, irrigation, adjuvant, soil depth and pesticide factors on the Pendimethalin and Dimethenamid-p concentration for all experiment results. The obtained results suggested that there is 3 factors have statistically significant on Pendimethalin and Dimethenamid-p concentration in soil which are sampling term, soil depth and pesticide. We can clearly understand the significant difference of these two pesticides from comparison of means. Table 7.

The P-values test the statistical significance of each of the factors. In our statistical result shows that P-values are less than 0.05, for 3 various factors. Which means these three factors have a statistically significant effect on Pendimethalin and Dimethenamid-p concentration.

5.4.   Statistical evaluation of Pendimethalin

Table 8. Analysis of Variance for Concentration of Pendimethalin for all experiment days after herbicide application.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS					
A:treatment	0.957192	3	0.319064	0.92	0.4338
B:Term	11.3622	4	2.84056	8.16	0.0000
C:Depth	46.2602	2	23.1301	66.48	0.0000
RESIDUAL	63.3267	182	0.347949		
TOTAL (CORRECTED)	146.801	191			

The (Tab.8) shows separately the effect of treatment, sampling term and soil depth factors on Pendimethalin concentration for all experiment results after pesticide spraying. The multifactor ANOVA results shows there is two sampling term and soil depth factors have a statistically significant effect on Pendimethalin concentration at the 95.0% confidence level.

Table 9. Multiple Range Tests for Concentration Pendimethalin (0-15 cm)

Treatment	Count	LS Mean	LS Sigma	Homogeneous Groups
P00	55	0.460679	0.0828155	X
P01	38	0.489821	0.105134	X
PG0	54	0.604495	0.0832685	X
PG1	45	0.621701	0.0954953	X

At the Table 9, the one homogenous groups was identified using columns of X's. The levels containing X's mark shows that there are no statistically significant differences. Because each column, the levels containing X's form. There was no statistically significant differences between any pair of means at the 95.0% confidence level.

5.5. Statistical evaluation of Dimethenamid-p

Table 10. Analysis of Variance for Concentration of Dimethenamid-p for all experiment days after herbicide application.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS					
A:treatment	0.0336663	3	0.0112221	0.28	0.8402
B:Term	5.0318	4	1.25795	31.32	0.0000
C:Depth	0.357258	2	0.178629	4.45	0.0130
RESIDUAL	7.31015	182	0.0401657		
TOTAL (CORRECTED)	14.9927	191			

The (Tab.10) shows separately the effect of treatment, sampling term and soil depth factors on Dimethenamid-p concentration for all experiment results after pesticide spraying. The multifactor ANOVA results shows there is two sampling term and soil depth factors have a statistically significant effect on Dimethenamid-p concentration at the 95.0% confidence level.

Table 11. Multiple Range Tests for Concentration Dimethenamid-p (0-15 cm)

Treatment	Count	LS Mean	LS Sigma	Homogeneous Groups
DG1	45	0.1791	0.0324453	X
D00	55	0.197105	0.0281372	X
D01	38	0.205203	0.0357203	X
DG0	54	0.215792	0.0282911	X

At the Table 11, the one homogenous groups was identified using columns of X's. The levels containing X's mark shows that there was no statistically significant differences. Because each column, the levels containing X's form.

6. Discussion

Experiments were carried out to evaluate the behaviour of the two pesticides in soil were used: Pendimethalin and Dimethenamid-p in different treatments. Pendimethalin behavior, used with adjuvant, irrigation and non-irrigation treatment, those are the relatively same result and calculated average half-life was 43.7 days, average residual concentration was observed 3.3494 µg g^{-1} after 79 DAA (day after application). The pesticide Dimethenamid-p with same treatment and calculated average half-life was 10.9 days, average residual concentration was observed 0.0340 µg g^{-1} 79 DAA. The results presented that the degradation of the two pesticides half-life influenced by their behaviour in soil and can effect chemical properties due to solubility in water.

This result is in accordance with Vassilios et al., (2012) studied the mefenoxam, a systemic fungicide, and pendimethalin herbicide were determined in bare and tabacco tilled soil in field condition for over 125 days. The dissipation half-lives of mefenoxam from the top soil layer in tilled and bare soil columns were observed at 10.3 and 13.1 days, while the half-lives for pendimethalin dissipation were 26.7 to 27.5 days, respectively. Vassilios et al., (2012) observed maximum concentrations of mefenoxam and pendimethalin were observed 15th and 33rd DAA, with soil layer (5-10 cm) and for mefenoxam in tilled soil (0.523±0.053 mg kg^{-1}), for pendimethalin, in bare soil (0.718±0.040 mg kg^{-1}). In the third soil layer (10-15 cm), residues of maxima concentrations for mefenoxam appeared about 30 DAA in tilled and bare soil (0.648±0.039 and 0.734± 0.031 mg kg^{-1}), for pendimethalin, about 63 DAA in tilled and bare soil (0.386±0.151and 0.511±0.098 mg kg^{-1}).

Furthermore, the study soils, which were used by Vassilios et al., (2012) physical properties are significantly similar with our study soil. In addition, Vassilios et al., (2012) were distinguished two important factors - solubility and adsorption - can be used to explain the behavior of mefenoxam and pendimenthalin herbicides. Comparing the two herbicides, mefenoxam presents a high water solubility (26 g l^{-1} at 20°C) and low adsorptivity (mean K_{oc}=660 ml g^{-1}) in contrast with pendimethalin, which presents very low water solubility (0.33 mg l^{-1} at 20°C) and high adsorptivity (mean $K_{oc=}$18,050 ml g^{-1}). The high water solubility of mefenoxam results in an easier transfer of the pesticide through the soil mass preferentially following the water flow; therefore, the maxima in the second and third soil layers should appear earlier than those of pendimethalin.

Jennifer J. Crawford et al., (2002) was investigate significantly differences in the dissipation of ^{14}C-dimethenamidin under anaerobic redox conditions with different treatments glucose pretreatment, $NO^{3-} + SO_4^{2-}$ amendment, unamended, and autoclaved. Soil may be related to the fact that ^{14}C-dimethenamidin dissipation is often times dominated by anaerobic processes. Jennifer J. Crawford et al., (2002) examined ^{14}C-dimethenamidin dissipation volatile, aqueous, extractable, and bound (unextractable) ^{14}C-residues were quantified and characterized. The redox potential decreased over time, and evidence of denitrifying, iron-reducing, sulfate-reducing, and methanogenic conditions was observed, dependently on the amendments. Anaerobic degradation of ^{14}C-dimethenamid occurred in all treatments, and the time observed for 50% disappearance (DT_{50}) was 13-14 days for non-autoclaved treatments half-life in another condition. ^{14}C-metabolites accumulated to up to 20% of applied ^{14}C. At least two major metabolites were observed in non-autoclaved treatments, whereas only one was observed in autoclaved microcosms. More than 50% of the applied ^{14}C was eventually incorporated into soil-bound residue.

The degradation of Pendimethalin obviously depend on moisture content and temperature in soil as Robert L. Zimdahl et al., (1984) described by a quadratic model degradation of Pendimethalin on different moisture content and temperature using three type of soils; a clay (Typic, Ultic, Aquic Palexeralf) from Italy and a clay loam (Aridic Argiustoll; fine, Mont-morillonitic mesic) and sandy loam (coarse-loamy, mixed, mesic, Aridic Argiustoll) from Colorado. Degradation increased as soil temperature increased in the order 10, 20, 35, and 30C. The rate was the same as 75 and 100% field capacity but slower at 50%. At the same temperature and soil moisture the influence of soil type was small. Based on chemical analysis of soil from field and laboratory studies, the half-life was approximately 47 days. Based on biological analyses of soil, the half- life was 78 to 111 days.

Good linearity was found by Mariusz et al., (2011) in this study between logarithmic concentration of chloridazon residues and time. They were applied chloridazon alone and in a mixture with three different adjuvants: oil, surfactant and multicomponent (used for preemergence application). The addition of oil and surfactant adjuvants slowed down the degradation of chloridazon in soil. The DT_{50} values for the mixture of chloridazon + oil and surfactant adjuvants was about 8−14 days higher in comparison with the DT_{50} for chloridazon applied alone (43 days). No significant differences were observed between degradation rates and the DT_{50} for chloridazon applied alone and with a multicomponent adjuvant.

When compare to effect of irrigation on pesticide degradation in soil, following study related to our study which was done by Jursík et al. (2013) using irrigation after application of pesticide. The study was in field condition and physical properties of soil also similar which is Haplic Chernozem soil, only they were used different pesticides (acetochlor, metolachlor and pethoxamid) instead of Pendimethalin and Dimethenamid-p. Jursík et al. (2013) observed higher leaching of metolachlor and pethoxamid was recorded in irrigated plots. No leaching was found in the case of acetochlor. The highest leaching was found for metolachlor (9.2–25.5% in soil layer 5–10 cm). The highest phytotoxicity was found for acetochlor (9.8%) > pethoxamid (4.6%) > metolachlor (1.8%).

Influence of adjuvants on pesticide residues in soil, degradation and leaching depend on the kind of adjuvant. Mariusz Kucharski and Jerzy Sadowski (2009) determined the influence of an addition of adjuvants on behaviour of phenmedipham as a degradation rate and leaching into the soil profile. The herbicide was applied alone and in mixture with adjuvants (oil and surfactant). Mariusz Kucharski and Jerzy Sadowski (2009) was observed the addition of oil adjuvant reduced the degradation rate of phenmedipham in soil. The authors did not find no significant differences between degradation rates for phenmedipham applied alone and with surfactant adjuvant. The DT_{50} value for mixture phenmedipham + oil adjuvant was about 11 days higher in comparison with DT_{50} for phenmedipham applied alone and amounted 32.1 ($\pm$2.1) days. Mariusz Kucharski and Jerzy Sadowski (2009) evaluated the addition of adjuvants, especially oil adjuvant, to herbicide caused the slowdown of phenmedipham leaching into soil profile.

7. Conclusion

1. Behavior of Pendimethalin and Dimethenamid-p are quite different. Average half-life of Pendamethalin was 43.7 days and this value for Dimethenamid-p 10.9 days.

2. That the hypothesis was not confirmed because the ANNOVA did not find significantly effect between the treatments with adjuvant and without adjuvant and were using irrigation and non-irrigation treatments for both Pendimethalin and Dimethenamid-p.

3. The half-life of Dimethenamid-p showed slightly small difference between irrigation and adjuvant treatments. Irrigation for Dimethenamid-p has shown shorter half-life than treatment with adjuvant. However, if we see half-life and leaching behavior Pendimethalin there was no difference between treatments of irrigation and adjuvant.

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9. Appendices

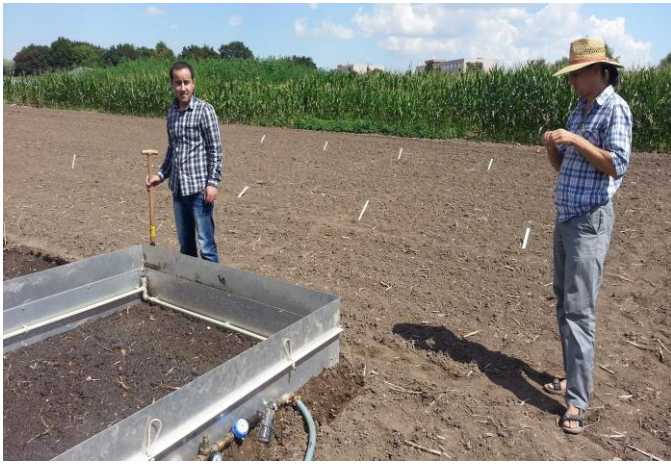Some pictures from experimntal field.

Pictures. 1 and 2 Preparation of the field for experiment.

Picture 3. Soil sampling with soil sampler.

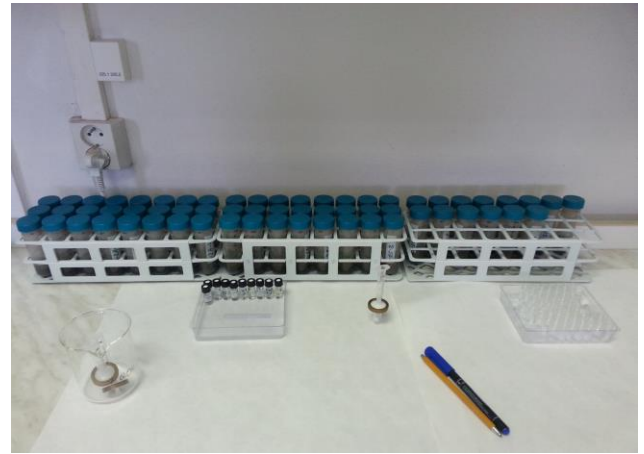Picture 4. Soil sampling with soil cylinder.

Picture 5. Irrigation of experiment field.

Picture 6. Treatment after the irrigation

Pic.7. Drying the soil samples using lyophilization

Pic.8. Prepare the methanol extraction for analysis

Picture 9. Determine the pesticide concentration by HPLC