CZECH UNIVERSITY OF LIFE SCIENCES, PRAGUE

Faculty of Agrobiology, Food and Natural Resources

Department of Soil Science and Soil Protection

The behavior of herbicides in soil under sunflower growth

Chování herbicidů v půdě pod porostem slunečnice

Ph.D. Thesis

Author: Ing. Umrbek Sharipov ABDULLAYEVICH

Supervisor: Prof. Dr. Ing. Luboš Borůvka

Co-Supervisor: Ing. Martin Kočárek, Ph.D.

Declaration

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Umrbek Sharipov Abdullayevich

Abstract

The behavior of six herbicides (pendimethalin, aclonifen, flurochloridone, S-metholachlor, pethoxamid and dimethenamid-P) in three soil type (Haplic Chernozem, Haplic Fluvisol, and Arenic Regozem) was studied under field and laboratory conditions.

The field experiments were conducted from 2015 to 2017 in sunflower growth. Herbicides were applied to the established plots at two rates (×1 and ×2) of the application dose of each herbicide. Soil samples were collected during the sunflower vegetation period from the two-soil layer (0-5 and 5-10 cm). The residual herbicide concentration in soil was determined by (HPLC-UV). Herbicide's (DT_{50}) half-life was calculated and its distribution in soil layers was used to evaluate herbicides' mobility. Pendimethalin and aclonifen were found to be moderately persistent in 48-75 % of the applied rates, with the highest DT_{50} values for both application rates (×1 and ×2). In contrast, dimethenamid-P and pethoxamid were found to be non-persistent in 15-45 % of the applied rate detectable 30 days after application, with shortest DT_{50} values in all three tested soils. The longest DT_{50} value for herbicides was observed in Haplic Fluvisol, while the fastest degradation and shortest DT_{50} value was observed in Haplic Chernozem for both application rates ($\times 1$ and $\times 2$). The highest concentrations of herbicides in the 5-10 cm soil layer were found in Arenic Regozem (Volárna), and the order of herbicides differed every year.

The laboratory degradation and sorption experiment were carried out in accordance with standard procedures (OECD, 2000). The half-life of herbicides in laboratory conditions differed from the half-life in the field and increased as follows: aclonifen 18 < pethoxamid 20 < dimethenamid-P 25 < pendimethalin 30 < flurochloridone 45 < S-metolachlor 47 days. The shortest dissipation half-life was found in Haplic Chernozem (14-38 days), while the longest was found in Haplic Fluvisol (20-57 days). The degradation of herbicides in the laboratory was mainly controlled by clay and (OM) organic matter content. Freundlich sorption coefficient (K_F, $cm^{3/n}$ $\mu g^{1-1/n}$ g^{-1}) was determined for each herbicide and soil type. The mean K_F, values (across soil types) increased as follows: dimethenamid-P 1.7 < pethoxamid 3.5 < S-metolachlor 3.7 < flurochloridone 17.6 < aclonifen 50.3 < pendimethalin 97.0 ($cm^{3/n}$ $\mu g^{1-1/n}$ g^{-1}). The highest K_F values for all herbicides were obtained in Haplic Fluvisol with higher OM (> 3.45%), while Arenic Regozem showed the lowest K_F values. The findings reached the conclusion that OM was the most important factor influencing herbicide sorption.

Key words: Degradation, Herbicide behavior, Sorption, Mobility, Herbicide half-life

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List of abbreviations

WRB	World Reference Base
FAO	Food and Agriculture Organization of the United Nations
OECD	Organization for Economic Co-operation and Development
PPDB	Pesticide Properties Data Base
EFSA	European Food Safety Authority
PRE	pre-emergent herbicide
DDT	dichloro-diphenyl-trichloroethane
GUS	groundwater ubiquity score
CEC	cation exchange capacity
OM	organic matter
OC	organic carbon
SOM	soil organic matter
DOC	dissolved organic carbon
DT_{50}	half-life
K_F	Freundlich adsorption coefficient
K_{OC}	organic carbon sorption coefficients
TPs	transformation products
EC	emulsifiable concentrate
HPLC	high performance liquid chromatography
UV	ultraviolet
LOD	limit of detection
LOQ	limits of quantification
STD	standard deviation
SDS	safety data sheets

1. Introduction

The increasing world population demands a continually growing supply of food and food products. Because of relative lack of new areas suitable for agriculture, the performance of the existing areas is enhanced by using herbicides (Cherhati et al., 2004). Herbicides are one of the crucial factors in a worldwide increase in agricultural production. Herbicides contribute effectively and profitably to weed control and benefit society as a whole. Hovever, use of herbicides has created considerable concern for human health and environmental risk associated with herbicides use (Giuseppe et al., 1998). Despite the benefits, the use of these kinds of chemicals must be controlled because an important fraction of these pesticides is released into the environment presenting a potential hazard risk (Bermúdez-Saldaña et al., 2005). As a direct consequence of their industrial, agricultural, or domestic use, and occasionally as a result of accidents or negligence, increasing amounts of these chemicals are released into the environment. They pose risks to ecosystems and human health since many organic pollutants are toxic to living organisms even in trace amounts. Therefore, organic chemical pollution in the atmosphere, soil, surface waters, and subsurface porous formations (aquifers) has become a major societal concern in industrialized countries over the last forty years (Šašek et al., 2000).

The agricultural soil is the final destination of a large number of herbicides, either when they are applied directly to the soil or on the shoots of plants (Walker, 1987). When the herbicides, reach the ground, interacting with the environment, their fate is governed by three general types of processes: i) physical (sorption-desorption, volatilization, leaching by water, and transportation along the ground by wind and water); ii) chemicals (photodecomposition, sorption, chemical reactions with the soil constituents); iii) biological (represented by the microbial decomposition of the molecules and removal from soil by plants) (Martins et al., 2012). For sustainable agriculture and to meet the growing demand for food, use of chemicals is imminent to achieve the desired targets. Due to more awareness, the consumer has a strong interest to know all aspects of improved technologies including herbicide use, which is growing year by year, with special emphasis on residues in food chain and environment (Channabasave et al., 2008).

Sunflower (*Helianthus annuus* L.) is one of the four most important annual crops in the world grown primarily for edible oil (De la Vega and Hall, 2002) and second important oil crop grown in the Czech Republic. It is considered an economic and nutritious crop containing oils, which are very essential in human diet (Lehoczky and Reisinger, 2003). Sunflower is an oilseed whose chances of wider adoption have improved with the availability of high-quality hybrid genetic material with a short vegetation period, which is more suitable for the typical temperate

zone of Czech agriculture. According to a report published by the Czech Ministry of Agriculture (2013), the annual sunflower grown area is approximately 25 000 ha, with the main growing areas located in the country's warmest regions, and 90 percent of the sunflower area in the Czech Republic is treated with pre-emergence (PRE) soil herbicides (Jursk et al., 2015). Domestic production is far insufficient to meet the needs of domestic crushers and other users, and the government was taking steps to increase imports to 25 000 tons in 1998 (Csaki et al., 1999).

The major function of PRE herbicides is to prevent early-stage weed control in the field and to make sunflower production sustainable and unfavorable for weeds (Preston et al., 2019). Sunflower is a good competitor with weeds. However, this competitive advantage occurs only after the plants are well-established. Weed competition damage is most severe during the first four weeks after emergence, so early weed control is essential. Weeds that compete for more than four weeks cause significant yield loss even if they are removed (Zollinger, 2007). PRE herbicide application in herbicide-tolerant sunflowers would protect the crop for the first four to five weeks of growth and should allow for greater flexibility in post-emergent herbicide application timing (Malidza et al., 2016). Along with stated above knowledge, there is little known about several herbicide behavior under sunflower plants and their adsorption and degradation relationships with various soil types and their characteristics especially stressing on SOM, pH and soil texture (Wauchope et al., 2002; Coquet et al., 2004), and comprehensive knowledge is of importance to accurately predict their environmental persistece and behavior to prevent further concerns (Boivin et al., 2005).

The main objectives of the present study were a) to determine the mobility and dissipation of the six pre-emergence herbicides applied to soil at different dose rates under field conditions (×1 and ×2 the recommended dose rate), b) to investigate herbicide adsorption and degradation in three soils under laboratory conditions, and to identify the main soil parameters that influence herbicide adsorption and degradation. This will provide a comprehensive view of the studied herbicides' soil persistence, as well as their soil adsorption affinity and mobility, which will define the scenario of exposure dissipation in field conditions.

2. Scientific Hypotheses and Objectives

2.1 Scientific hypotheses

Sorption and degradation of herbicides in soil is affected by organic matter content (OM), soil pH, soil texture, and CEC. Herbicide degradation is faster in Chernozem than in soils that are more acid.

- soil pH affects herbicide sorption into soil, persistence, and mobility because ionizable chemicals may protonate at low pH (e.g., weakly basic amines), or conversely, become anions at neutral or alkaline conditions, such as the weak acid herbicides.

- in general, microbial activity is higher in soils with high soil OM content, so herbicide degradation is expected to be faster, and persistence shorter as soil OM increases.

- the degradation is governed by both abiotic and biotic processes (e.g., chemical hydrolysis and microbial breakdown) and faster degradation occurs in Chernozem soils because of suitable conditions for both abiotic and biotic degradation processes due to higher OM content and other physicochemical properties.

- Increasing the application rate (×1 and ×2) of the recommended dose could effect of herbicide leaching in the soil profile and increase the soil dissipation and half-life.

2.2 Objectives

This study aims to evaluate the half-life and mobility of six herbicides in soil under sunflower (*Helianthus annuus*) growth at three locations (Suchdol, Dobroměřice, and Volárna) as well as to compare the effect of soil properties on herbicide behavior.

- To determine and compare the effects of soil types (Haplic Chernozem, Haplic Fluvisol, and Arenic Regozem) differences and properties on herbicide behavior in soil.

- To identify main soil parameters that influence the adsorption and degradation of herbicides employing the correlation analysis.

- To investigate the effect of application rate on herbicide distribution in soil profiles (0-5 and 5-10 cm) and dissipation half-life.

3. Literature review

3.1 Behavior of herbicides in soil

The fate and behavior of herbicides in the soil environment involve several different and often simultaneous phenomena including chemical, biological and photochemical degradation, transport and accumulation, volatilization, and leaching that are influenced to various extents by several factors such as physicochemical, biochemical, pedological, climatic and management practices (Gevao et al., 2000; Navarro et al., 2007). Sorption is the crucial phenomenon determining the behavior of organic chemicals in the soil environment. The herbicide concentration in the solid, aqueous and gaseous phases and the living part of the soil is determined by sorption and has influences on transportation and transformation processes. Leaching in soil and volatilization from wet soil surfaces are directly influenced by the adsorption-desorption equilibrium in the soil-water system as this can define the extent to which a chemical is available for degradation. The availability of a chemical to organisms is primarily related to its concentration in the aqueous and gaseous phases. Thus, sorption processes can have a major effect on the availability of the chemical by reducing its amount accessible to plants and other soil and aquatic organisms. Desorption of a chemical is also critical in assessing its behavior in runoff streams, in surface and ground water pollution (Navarro et al., 2007; Kodešová et al., 2011). Most of the pesticides are subject to processes such as sorption, degradation, runoff, and leaching and evaporation. Transport by runoff and leaching can result in contamination of surface and ground waters (Kolpin et al., 1998).

When pesticides are 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 try to minimize the negative consequences of pesticide use (Dingham, 2005).

3.2 Transport of herbicides in the soil

Surface-applied or soil-incorporated pesticides and other agricultural chemicals, after entering the agricultural system, may be translocated into plants, volatilized into the atmosphere,

leached downward below the root zone, sorbed onto soil constituents, transported while being adsorbed on soil particles, or degraded to nontoxic molecules. They also may affect the next crop, as well as non-target species (Singh et al., 1992). 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. The transport of pesticides in soil, and their rate of disappearance from the 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 studied in isolation, it is of particular importance to developing predictive capabilities of their overall behavior (Helling, 1971). 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).

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 provided 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 cracks 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 (De Martinis and Cooper, 1994).

3.3 Adsorption and desorption

Adsorption to soil is of critical importance for the regulation of herbicide persistence and mobility throughout the environment because sorption processes control the amount of herbicide present in the soil solution. These processes are dependent on several factors related to soil characteristics such as mineral composition, organic matter content, soil solution chemistry, and chemical characteristics of the herbicide (Ainsworth et al., 1993). 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). Sorption influences pesticide leaching in the subsurface and must be taken into account when predicting pesticide transport (Shalit and

Steenhuis, 1996). Kinetic studies have revealed several interactions between sorption and degradation (Gevao et al., 2000; Guo et al., 2000;) It is commonly accepted that sorbed chemicals are less accessible to microorganisms, and that sorption accordingly limits their degradation as well as their transport (Selim et al., 1999; Koskinen et al., 2001). Soil sorption of neutral compounds has been widely assessed. Soil organic matter content appears to be a predominant factor influencing their retention (Johnson and Sims, 1993; Coquet, 2002). Many studies have verified that soil parameters (organic matter content, pH) significantly affect the sorption processes of herbicides in the soil. Adsorption on soil is one of the most important factors controlling pesticide movement toward groundwater (Koskinen and Haper, 1990). Organic matter content in soil has been shown to be the most important fraction for the adsorption of non-ionic herbicides (Chiou et al., 1989). Thus, high organic matter content in soil may result in a decreased mobility into the soil profile and consequently more persistence on the topsoil.

Adsorption depends on three factors that often interact in a complicated way: the molecular properties of the solute, soil constitution, and the experimental conditions under which the adsorption is studied (Calvet, 1995). Adsorption and desorption behavior of s-metolachlor, glyphosate, and epoxiconazole was investigated on maize mulch residues decomposed under laboratory and field conditions. The conceptual approach in this investigation included the characterization of chemical composition and hydrophobicity of mulch residues to generate parameters to predict sorption behavior. Adsorption of s-metolachlor and epoxiconazole greatly increased with mulch decomposition, whereas glyphosate adsorption was less affected, but its desorption was increased (Aslam et al., 2013).

The sorption of pesticides is generally evaluated by using sorption isotherms (Sadegh-Zadeh et al., 2011; Celis et al., 1997). Batch equilibrium is a common technique used to determine soil sorption of pesticides. In a batch equilibrium technique, a series of solutions containing the pesticide to be tested at different concentrations are prepared. The solutions are then mixed with a known amount of soil and shaken until equilibrium is achieved. The concentration of the chemical in the solutions is then measured and a difference in the mass of the pesticide between at the start and equilibrium is assumed to be due to adsorption by the soil particles. Then, the amount of pesticide adsorbed per unit weight of soil is calculated for each initial concentration of the pesticide. A relationship is then established between the pesticide concentration at equilibrium and the sorbed concentration of the pesticide by the soil (Von Oepen et al., 1991).

3.4 Leaching and volatilization

The leaching of herbicides receives particular attention because it directly influences the extent of surface water and groundwater pollution. Several herbicides have recently been detected in groundwaters in Western Europe and the USA in the past years (Calvet, 1995). The efficacy of pre-emergent herbicides is significantly affected by soil moisture; under dry conditions, their efficacy usually decreases. However, intense precipitation after the application of these herbicides can cause the transport of active ingredients in the soil profile, crop injury, and/or leaching. Sandy soils, which usually have a lower sorption capacity, have a higher risk of herbicide leaching. However, clay soils are more vulnerable to erosion and runoff (Soukup et al., 2004). Funari et al. (1998) investigated the leaching behavior of metolachlor, alachlor, atrazine, cyanazine, simazine, and terbuthylazine herbicides which are widely used in agriculture, and properties of studied soil were 29% clay, 49% silt, 22% sand with 1% organic carbon content and a pH of 7.6. The results indicated that all these herbicides disappeared substantially in the soil surface layer and half-life (DT$_{50}$) of the studied herbicides were terbuthylazine 44, atrazine 35, metolachlor 34, - cyanazine 28, simazine 28, and alachlor 20 days, respectively, and all herbicides leached about 90 cm in the soil depth. Jursík et al. (2013) compared the efficacy, selectivity to sunflower, and dissipation of three chloracetamide herbicides (acetochlor, metolachlor, and pethoxamid) in relation to precipitation after application. The experiments were conducted using a silty loam soil with 19.3% clay, 56.3% silt, 24.4% sand, and a pH 7.5, sorption capacity was 209 mmol+/kg. The leaching (vertical transport) of the studied herbicides was noticed from irrigated plots. The highest leaching was found for metolachlor (9.2-25.5 % in soil layer 5-10 cm), while acetochlor showed no leaching. The mean phytotoxicity in the irrigated plots was 6.9%, compared to 3.9% in the non-irrigated plots, and the efficacy of the tested herbicide was affected by wet conditions, and the highest phytotoxicity was found for acetochlor (9.8%) > pethoxamid (4.6%) > metolachlor (1,8%). Therefore, we can assume that the leaching behavior of herbicide metolachlor is higher than other herbicides due to its water solubility, and phytotoxicity of pethoxamid was respectively higher than among the other studied herbicides (Jursík et al., 2013).

Volatilization is characterized by a change of herbicide's state from a solid or liquid phase to a gaseous phase and subsequent dissipation to the atmosphere. Volatilization increases with air and soil temperature, and wind speed. In contrast, when the relative humidity is high, volatilization will decrease. Air currents can carry away volatilized herbicides from the treated area, and this invisible vapor drift may cause crop injury for long distances downwind (Menalled

and Dyer, 2004). Volatilization, on the other hand, reduces the amount of a pesticide available for pest control and the potential for ground water contamination while increasing the potential for contaminating the atmosphere and surface water (Doull, 1989). In recent years, growing concerns about the risks of pesticide exposure from airborne pesticides has accelerated the development of numerous laboratory and field methods to characterize the most important factors influencing volatilization (Taylor & Spencer, 1990; Stork et al., 1994). Pesticide volatilization from soil is primarily controlled by the pesticide's intrinsic properties (e.g., vapor pressure, water solubility), followed by the method of application (soil surface versus incorporation), and soil physical factors (e.g., moisture distribution, soil organic matter content, soil temperature, and soil transport properties). The most significant physical property in terms of pesticide losses to the air is its vapor pressure (Farmer et al., 1972; Glotfelty et al., 1984). Volatile herbicides (those with higher vapor pressures) generally dissipate more rapidly than herbicides with lower vapor pressures. The volatility of a herbicide is determined primarily by its molecular weight. Most herbicides are relatively nonvolatile under normal field conditions. The more volatile herbicides are generally incorporated into the soil to avoid gaseous losses and highly volatile herbicides are no longer used (William and Curran, 2001). Besides, the volatility generally increases with decreasing clay and organic matter content in soil (Helling et al., 1971).

3.5 Properties of pesticides affecting their behavior in soil

Currently, in use, there is a large number of pesticides, with a wide range of physicochemical properties and belonging to a variety of chemical classes. The physicochemical properties of a given pesticide decide on its behavior in soil and its biological activity. Pesticides' key properties include molecular size, ionizability, lipophilicity, polarizability, and volatility, but one or two of these properties have a significant influence on their soil behavior (Bailey and White, 1970). In soil, due to the organic characteristics of pesticides, they are involved in several processes that may affect their potential activity. In general, the fate of pesticides in the soil ecosystem depends on the abiotic transformation related to physical, chemical, and photochemical processes as well as the biological transformation related to the activity of alive organisms, particularly microorganisms (Różański, 1992).

3.5.1 Persistence and mobility

Persistence refers to how long a pesticide [or its metabolite(s)] remains detectable in the environmental compartment of interest (Vencill 2002). Persistence is characterized as the ability of a given compound, in this case, a pesticide, to retain its molecular integrity as well as its chemical, physical, and functional properties in the medium by which it is transported and distributed after being released into the environment. Many organic compounds, mainly herbicides persist for long periods in soils, subsoil, aquifers, surface waters, and aquatic sediment (Navarro et al., 2007). Nevertheless, another common expression of herbicide persistence is the field dissipation half-life, or simply "half-life" ($t_{0.5}$, $t_{½}$, or DT_{50}). This is the length of time required for one-half of the original quantity to break down. 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 (Kerle et al., 2007). Pesticide persistence and mobility are influenced by the properties of the pesticide and the properties of a pesticide are, in turn, influenced by the soil environment, site conditions, weather, and application method. In several studies it has been found that the persistence of pendimethalin is influenced by cultivation practices, soil temperature and moisture conditions, and soil type (Savage, 1978). Flom and Miller (1978) investigated the persistence of pendimethalin applied under no-tillage conditions in North Dakota; it was found to be most persistent in silty clay and least persistent in sandy loam. The half-life gives only a rough estimate of the persistence of a herbicide since the half-life of a herbicide can vary significantly depending on soil characteristics, weather (especially temperature and soil moisture), and the vegetation at the site. Dissipation rates often change with time (Parker and Doxtader 1983). For example, McCall et al. (1981) found that the rate of dissipation increased until approximately 20% of the applied herbicide remained, and then declined. Several mathematical models have been proposed to represent the herbicide dissipation and kinetics of degradation in soils. These included zero-order, half-order, first-order, second-order, and mixed-order models (Hamaker et al.,1968; Hance et al.,1971). The models commonly used to fit data from an evaluation of degradation in soil are, in essence, either empirical or theoretical. An example of an empirical approach is the power rate model

$$\frac{-dC}{dt} = kC^n \qquad\qquad\qquad [1]$$

where *C* is pesticide concentration, *t* is the time, *k* is the rate constant for pesticide disappearance, and *n* is the fitting parameter. This model can fit pesticide-disappearance curves by varying *n* and

k until a good fit is achieved. From this equation, it is evident that the rate is proportional to the power of the pesticide concentration. When *n* = 1, the model is equivalent to the first-order kinetics, and it has often been used in this form. When *n* = 0, the model reduces to zero-order kinetics, and when *n* = 2, it is presented by the second-order kinetics. A plot of the logarithm of the pesticide concentration remaining against time gives either a straight, concave down, or concave up for first-, zero-, or second orders of reaction, respectively (Hamaker and Thompson, 1972). Pesticide half-life is calculated using the following equation:

$$t_{1/2} = \frac{\ln 2}{k}$$ [2]

where $t_{1/2}$ is the pesticide half-life.

The mobility of pesticides in soil, and hence their bioavailability and transfer to other environmental compartments (atmosphere, water bodies), depend on the mechanisms and kinetics of their sorption on and desorption from soil particles (Moorman et al., 2001). If a pesticide is too mobile, it fails to protect the structure, while increasing the 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).

3.5.2   Water solubility

Water solubility is a measurement of how much of a chemical will dissolve in water. In the safety data sheets (SDS), manufacturers use relative terms – such as miscible, dispersible, suspension, emulsifiable, and water solubility – to describe their product's solubility. Some manufacturers will use a numerical value for this description, such as 2.9 mg/L or ppm. Pesticides with a value of 100 ppm or less are considered relatively insoluble, while pesticides with values greater than 1,000 ppm are considered extremely soluble (Fishel, 2014). If a chemical 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 the water and tend to not be adsorbed on soil and living organisms (Linde, 1994). The tendency of a pesticide to dissolve in water affects its leaching potential. As water seeps down through the soil profile, it carries with it water-soluble chemicals and 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 tend 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 is inversely related to the adsorption of pesticides in soil. Highly soluble pesticides are weakly adsorbed and pose a greater threat of groundwater contamination (Geyikci, 2011).

3.6 Degradation behavior of herbicides in the soil

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 (Guo et al., 2000).

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, and ozonation reactions have been proposed. All these systems and processes are considered to be efficient for pesticide degradation (Zenilda et al., 2011).

3.6.1 Microbial degradation

Degradation processes by soil microorganisms are desirable because they usually result in detoxification and essential pathways for pesticide breakdown. Therefore, microorganisms are extremely efficient at degrading a wide variety of organic compounds and degrade pesticides by two different processes. The first degradation leads to the relatively rapid disappearance of the pesticide in the soil. In this case, the microorganisms degrade the molecules and utilize them as a source of energy and nutrients (Getenga, 2003; Boivin et al., 2005). The microorganisms can interact, both chemically and physically, with substances, leading to structural change or complete

degradation of the target molecule. Among the microbial communities, bacteria, fungi and actinomycetes are the are the main transformers and pesticide degraders and their relative numbers determine how quickly decomposition occurs (Wiren-Lehr et al., 2002; De Schrijver and De Mot, 1999). Senthilkumar et al. (2011), studied three species of Pseudomonas for the biodegradation of the herbicide aroclor 1242 and found that these bacteria have a high ability to degrade it, with degradation percentages of 99.8, 89.4, and 98.4 respectively. Kafilzadeh et al. (2015) separated bacteria from sediments and water samples from high agricultural activity areas to detect endosulfan degradation and observed that the five bacteria species klebsiella, acinetobacter, alcaligenes, flavobacterium, and bacillus could effectively degrade endosulfan.

Microorganisms require certain environmental conditions for optimal growth and utilization of any pesticide. Factors that affect microbial activity are moisture, temperature, pH, oxygen, and mineral nutrient supply. Usually, a warm, well-aerated, fertile soil with a near-neutral pH is most favorable for microbial growth and, hence, for herbicide breakdown (William, 2001). Soil temperature and moisture are important factors that influence the activity of soil microorganisms. Once the temperature goes beyond an optimum level, degradation rates decline (Bolan and Baskaran, 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 (Ma et al., 2006). As previously stated, pesticides are degraded by microorganisms through two different processes: metabolism and cometabolism. Pesticides are metabolized as a food source by microorganisms, and this process is known as metabolism. However, some microorganisms will alter the structure of the pesticide while gaining no energy from the reaction, a process known as cometabolism. A pesticide degraded by a cometabolic process would tend to persist in the soil for a longer period (Kumar et al., 1996; Sanchez et al., 2004; Watschke et al., 1988).

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 the utilization of existing enzymatic machinery and is therefore called a cometabolic process. Microbial pesticide conjugation reaction includes xylosylation, alkylation, acylation, and nitrosation and can occur intra or extracellularly. Phase III involves the conversion of phase II metabolites into secondary conjugates, which are also nontoxic (Van Eerd et al., 2003).

Furthermore, Doelman et al. (1994) stated, that there is a correlation between the number of biomass microorganisms and the rate of biological pesticide degradation in soil. Moreover, there are also many pesticides, which may be resistant to the enzymes produced by soil microorganisms (Monkiedje et al., 2002). The reason for this fact may be: (1) the lack of sufficient ability to degrade some pesticides in the population of soil microorganisms; (2) the impossibility of the penetration of pesticides through the cell membrane; (3) the repressing of enzyme activity and (4) the properties of pesticides (Somerville et al., 1987). Moreover, metabolites, which are the products of pesticide transformation process, may be more toxic than the parent substances resulting in the limitation of the activity of microbial group responsible for the degradation of pesticides introduced into the soil (Różański, 1992).

3.6.2 Chemical degradation

Chemical degradation is the breakdown of pesticides by chemical reactions and 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 (Kerle et al., 2007). Chemical degradation (decomposition) is driven by chemical reactions, including hydrolyzation (reaction with hydrogen, usually in the form of water), oxidation (reaction with oxygen), and disassociation (loss of ammonium or another chemical group from the parent molecule) (Helling et al., 1971).

The chemical degradation processes are described in some literature as an abiotic reaction which is the nonbiological degradation of pesticides in soil and water. The principal abiotic reactions that occur in water are hydrolysis, oxidation-reduction, and photolysis; in sediments, hydrolysis and redox reactions may prevail. Redox reactions in aquatic environments can be mediated by direct or indirect photolysis or catalyzed by metal species. In soil, abiotic reactions occur in the liquid phase (i.e. soil solution) and at the solid-liquid interface. In soil solution, hydrolysis and redox reactions are the most common abiotic transformations; these reactions are catalyzed by clays, organic matter, and metal oxides. The result of hydrolysis reaction is the formation of ions and a breakdown of the pesticide into a simpler structure (Bollag and Liu, 1990).

3.6.3 Photodegradation

Photodegradation refers to decomposition by sunlight. Sunlight intensity varies with numerous factors including latitude, season, time of day, weather, pollution, and shading by soil,

plants, etc. Studies of the photodegradation of herbicides are often conducted using ultraviolet (UV) light exclusively, but there is some debate as to whether most UV light reaches the surface of the earth. Therefore, photodegradation rates determined in the laboratory may overestimate the importance of this process in the field (Helling et al.1971). Degradation can occur by direct and indirect photolysis. In direct photolysis, the pesticide absorbs UV light and afterward reacts with substances in the environment or decomposes by itself. However, indirect photolysis is more common. This is caused by oxygen and hydroxy or peroxy radicals, which are produced by photolysis in humic or inorganic compounds (Pehkonen and Zhang 2002). Photochemical reactions are one of the most frequent transformations of pesticides in the environment. Therefore, investigations of photodegradation processes can provide better knowledge on transformations and degradation processes of organophosphate (OP) pesticides in the environment and their oxidation/degradation rate (Meijers et al.,1995; Roche and Prados, 2012). The effects of soil properties such as moisture content, clay content, organic matter content, and soil depth have been investigated in several studies. Sukul and Spiteller (2001) found slow degradation in high clay content soil in the case of Metalxyl fungicide, they assumed that degradation was controlled by either microbial degradation or abiotic factors other than light. The slower rate of degradation was observed for a soil having a larger clay content, and light screening by adsorption into the interlayer of clay might reduce the effect of irradiation (Saha and Sukul 1997).

3.7 Factors affecting herbicide activity in the soil

The term of herbicide activity in soil is used once herbicides are applied in the environment (soil, plant) and considered to discuss concerning the uptake by target weeds, their selectivity, and mode of action. The herbicidal efficacy (or effectiveness) is greatly affected by the timing and environmental conditions and improper herbicide application may lead to herbicide loss from the targeted area, increased crop injury, and reduced weed control. Therefore, complete weed control is not always possible, even slight reductions in weed populations can greatly enhance the productivity of crops. As a result, always consult the label for any questions regarding proper placement, stage of crop growth, or mixing restrictions before any chemical application (Rouse and Dittmar, 2008). Several factors, including plant, soil, and climatic factors affect both the selectivity and activity of herbicides (Cudney, 1996). Herbicide selectivity is a phenomenon where a chemical kills the target plant species in mixed plant populations without harming or only slightly affecting the other plant, while herbicide activity is related to the phytotoxic effect that the

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herbicide has on plant growth and development. These two concepts are closely related to each other (Rao, 2000).

3.7.1   Climatic factors

Climatic factors such as temperature, rainfall, air movement, humidity, and radiation influence the processes that affect the herbicide activity. The influence of climatic factors has a severe consequence on crop weed competition. Temperature, for example, affects the physical and chemical properties of the herbicide (Koskinen and Harper, 1987), as well as plant processes (Coelho and Dale, 1980). Rainfall, on the other hand, is required to leach pre-emergence herbicides such as acetochlor into the soil (Rao, 2000).

3.7.2   Temperature

Temperature affects the leaching and vapor pressure of herbicides, as well as the processes through which herbicides may be lost from the soil. High temperatures, for example, can lead to increased herbicide losses through faster chemical and microbial degradation and volatilization (Rao, 2000). According to Kozlowski et al. (1967), high temperatures have been found to greatly increase herbicide toxicity, mainly due to an increase in absorption and translocation rate of the herbicide. Crop injury is sometimes increased by extremely high temperatures as the plant is placed under multiple stresses, so making it more susceptible to herbicide injury (Peterson et al., 2001).

Temperature also affects the activity of soil-applied herbicides through its influence on the rate of seed germination, seedling emergence, and growth. Seedlings tend to be more susceptible to soil-applied herbicides under cool conditions than under warm temperatures as plant emergence is delayed and metabolism is slowed (Wolfe, 1991; Peterson et al., 2001). The uptake and translocation of most herbicides by both roots and leaves increase with increasing temperature, while low temperatures decrease absorption of water and solutes by roots although species differences occur (Lambrev and Goltsev, 1999). Therefore, temperature plays an important role in the rate of herbicide uptake. High temperatures favor rapid uptake and good weed control generally results when the temperature at the time of herbicide application was high (Mathers, 2006).

3.7.3   Rainfall

Precipitation after application of herbicides can wash out the herbicides and reduce efficiency. Moisture is needed for weed seed germination. So weed adaptation to these stresses has more competitive advantages over crops. Increased rainfall frequency and intensity will have an adverse effect on uptake, retention, and activity of soil-applied herbicides (Bailey, 2004; Rodenburg et al., 2011). The amount, intensity, and frequency of rainfall or irrigation will affect the movement of herbicides to and away from target plants, as well as the ability of the herbicide to go into solution. Under dry conditions, some precipitation is necessary to activate soil-applied herbicides by moving the chemical into the rooting zone, where the herbicide can readily be absorbed and easily translocated throughout the plant (Rao, 2000). Heavy rains immediately after herbicide application can lead to surface runoff, removing some of the applied herbicide, and so decreasing herbicide effectiveness (Koskinen and Harper, 1987).

There are relatively small differences among soil-applied herbicides in the amount of rain needed to mobilize them within the profile. Hartzler (1997) studied the effect of rainfall on the activity of acetochlor, dimethenamid, and metolachlor applied in preemergence and discovered that 6 mm of rain significantly increased the activity of dimethenamid and acetochlor compared to metolachlor. The authors also stated that in most cases, soil type and soil moisture condition will impact herbicide activity more than herbicide characteristics. In order to obtain good weed control, at least 10 - 15 mm of continual rainfall or sprinkler irrigation is essential after acetochlor application to leach the product into the soil zone where weed seeds germinate before their emergence (Monsanto, 2002).

3.8 Soil factors

As previously discussed, pesticide persistence and efficacy in soil are controlled by various soil processes including adsorption, decomposition, and movement. These processes are directly or indirectly affected by soil properties such as soil moisture, temperature, pH, organic matter, and microbial population. Tillage systems affect these same soil properties (Philips and Philips, 1984; Koskien and McWhorter, 1986). 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 (Shayler et al., 2009). The physicochemical properties of the pesticide used, as well as soil

properties (texture, clay composition, organic matter, and permeability), are critical in assessing leaching (Wauchope et al., 2002).

3.8.1 Soil texture and clay content

Soil texture is determined by the relative proportions of sand, silt, and clay. Texture affects the movement of water through soil and, therefore, affects the movement of dissolved chemicals, such as pesticides. The coarser soil, the faster movement of the percolating water, and the less opportunity for adsorption of dissolved chemicals. Soils with more clay and organic matter tend to hold water and dissolved chemicals longer. These soils also have a far larger surface area on which pesticides can be adsorbed. The coarser texture of the soil, the greater the chance of the pesticide to reach groundwater (LaPrade, 1992).

The mineral adsorbents involved in the adsorption of pesticides are clays (as silicate minerals), oxides, and hydroxides (Calvet, 1980). 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 with clays, they have a high surface activity and their charge depends on the soil pH (Calvet, 1980). For example, the adsorption of glyphosate increases as follows: kaolinite < illite < montmorillonite < nontronite (Mc Connell and Hossner, 1985). 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 the 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).

3.8.2 Organic matter

Soil organic matter (SOM) originates from crop residues, microbial biomass, and organic amendments. It has a very heterogeneous composition and contains both hydrophilic and hydrophobic groups. Even if organic matter only represents a few percent of the total dried material in soil, it is a major sorbent of pesticides in soil (Calvet et al., 2005). 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 its size and chemical composition, due to a greater number of sorptive sites related

to a greater surface area (Cox et al., 1998). In general, herbicide sorption increses with increasing soil organic matter content (Walker, 1991; Benoit et al., 1999). 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).

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. All pesticides and their transformation products (TPs) are retained by soils to different degrees, depending on the interactions between soil and pesticide properties (Senesi, 1992). Soil organic matter is considered to be the single most important soil constituent influencing pesticide sorption in soils. The larger the organic matter content, the greater is the adsorption of pesticides and transformation products. In soils, pesticides are initially and predominately sorbed to organic matter that coats soil particles (Farenhorst, 2006; Crescenzi et al., 2000; Park et al., 2003). Generally, the lower water solubility of a chemical and the higher amount of organic carbon in the soil, the greater the sorption of a hydrophobic compound (Alexander, 1999). Besides, organic matter plays an important role in 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).

The influence of soil organic matter (OM) needs to be considered as one of the main factors that directly affect the degradation of pesticides in soil. Many studies have been conducted to determine the influence of organic matter added to soils on the degradation of pesticides (Fernandes et al., 2006; Kot-Wasik et al., 2004; Antonious et al., 2005). The addition of an organic amendment to soil normally results in an increase in the microbiological activity due to the availability of simple organic molecules such as sugars and amino-acids to the microbes (Iglesias-Jiménez et al., 1997), and herbicide degradation is expected to be faster, and persistence shorter as soil OM increases (Walker, 1991).

Dolaptsoglou et al. (2007) reported that the addition of urban sewage sludge, corn straw, and poultry compost in agricultural soil reduced the degradation rate of terbuthylazine. On the other hand, other studies have demonstrated that organic matter amendment has no effect on pesticide degradation. Getenga and Kengara (2004) reported that there was no effect of compost amendment on the degradation of glyphosate in soils. However, in his earlier study Getenga (2003)

found that compost added to the same soil increased atrazine degradation. The incorporation of organic amendments to soil may decrease mineralization of pesticides by increasing pesticide sorption (Senesi et al., 2001). However, amendments can also accelerate or enhance biodegradation by stimulating microbial growth due to nutrient incorporation into the soils (Abdelhafid et al., 2000; Sanchez et al., 2004).

3.8.3   Soil pH

The stability of some herbicides is pH-dependent and plays an important role in particular for the adsorption of ionic herbicides like glyphosate and sulcotrione. Even if the pesticide itself does not become charged, soil pH may affect the soil surface characteristics, potentially strengthening or weakening the binding of certain herbicides (Bending et al., 2003). Indeed, Mamy and Barriuso (2005) observed that depending on the charge of the pesticide, the adsorption will increase (or decrease) with soil 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 influences the rate of pesticide breakdown due to water reaction and the influence of pesticide degradation in the soil. The acidic soils may enhance the degradation of the phytotoxic portion of some herbicide molecules (Joshi et al., 1985). For example, sulfonylurea herbicides are reported to be increasingly persistent with increasing soil pH (Beckie and McKercher, 1989). A relationship between soil pH and rate of degradation has been demonstrated for many ionizable 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 the dissociation constant value (pKa) 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 increase with decreasing soil pH (Li et al., 2002).

Moreover, 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 also governs the degree of ionization of acidic groups of the humic substances. Also, herbicides that exist in soil solution in an anionic form will tend to be more strongly adsorbed at lower pH with potentially less availability to plants. However, lower pH can also increase the number of uncharged herbicide molecules which may increase plant availability due to increased lipophilicity and root affinity for the compound (Stougaard et al., 1990).

4. Materials and Methods

4.1 Study areas

The study experiments were performed at three locations in the Czech Republic, namely Suchdol, Dobroměřice, and Volárna. Suchdol is an experimental field of the Czech University of Life Sciences Prague, located in the western part of the capital city of Prague. Dobroměřice is a municipality village 1 km north of town Louny in Ústecký kraj, and Volárna is a village situated about 8 km north of town Kolín in Středočeský kraj. The three sites have relatively different weather condition as well as soil types and soil chemical and physical characteristics.

4.1.1 Climate conditions

According to a report from the Czech Hydrometeorological Institute, the weather in Dobroměřice is warm and dry, with an average annual temperature of around 8°C. The village is surrounded mainly by agricultural land and producing high-quality hops, sunflower, wheat, and other crops. The average annual rainfall is around 520 mm. Volárna is classified as humid continental climate (humid with severe winter, no dry season with a cool temperate) and characterized by cold winters and warm summers. The average annual temperature is around 9°C, and winter has prolonged freezing periods, with the coldest month most often being in December and August is on average the month with the most sunshine. The land area is mostly agricultural cropland. About 560 mm of precipitation falls annually. The climatic data from the Meteorological station of the Czech University of Life Sciences Prague suggest that Suchdol is moderately continental, and the average annual temperature is around 9°C and average annual precipitation about 500 mm. Table 1. shows weather conditions during the three years experiment.

Table 1. Weather conditions during the three years experiment (period from April to October) (monthly average precipitation and mean air temperature). (https://www.chmi.cz).

Weather conditions	Year	Locations		
		Suchdol	Dobroměřice	Volárna
Precipitation (mm)	2015	40.8	55.1	44.0
	2016	54.5	50.6	50.3
	2017	64.3	63.1	76.0
Mean air temperature (^{0}C)	2015	15.8	13.7	15.2
	2016	15.7	15.0	15.0
	2017	15.3	14.6	14.6

4.1.2 Soils

The basic chemical and physical soil properties were obtained using standard laboratory procedures under constant laboratory temperature of 20 °C: the soil pH_{H2O} and pH_{KCl} (ISO, 1994), the effective cation exchange capacity (CEC) (Bower et al., 1966), the organic carbon content (Cox), the organic matter content (OM) (TC multiplied by 1.724), the $CaCO_3$ content (Looppert and Suarez, 1996), the humic substances (Pospíšil, 1981), the bulk density (ρ_d) of undisturbed soil samples taken by soil cylinders (100 cm³) was determined (ISO, 2017), and the particle size distribution was determined by sieving and sedimentation, applying the hydrometer method based on Stoke's law, and have been grouped in three textural classes (clay, silt, and sand) (Gee et al., 2002). The measured physical and chemical properties of the soils are presented in Table 2.

4.1.3 Soil profile descriptions

The general site description of studied soils was described based on the internationally accepted Guidelines for Soil Description (FAO, 1990) and soil profiles were classified using the Czech Taxonomic Classification of Soils (Němeček et al., 2011). Soil diagnostic horizons were determined in each profile, which was divided into horizontal layers based on color, texture, structure, and material composition. In a few instances, the tentative *soil classification* conducted in the field was revised according to the results of the laboratory analyses and were classified as Haplic Chernozem with silty clay loam in Suchdol, Haplic Fluvisol with loam in Dobroměřice and Arenic Regozem with sandy loam in Volárna. Soil profile pictures with descriptions are depicted in Pictures 1, 2 and 3.

4.1.4 Herbicides and used products

The six herbicides representative of different groups with contrasting physicochemical properties were used (Table 3). The herbicides pendimethalin (Stomp 400 SC; 400 g L^{-1}), aclonifen (Bandur; 600 g L^{-1}), flurochloridone (Racer 25 EC; 250 g L^{-1}), S-metolachlor (Dual Gold 960 EC; 960 g L^{-1}), pethoxamid (Successor 600; 600 g L^{-1}) and dimethenamid-p (Outlook; 720 g L^{-1}) with analytical standard purity 95-99 % were purchased from Sigma-Aldrich. Acetonitrile (HPLC Supra-Gradient, purity 99.97%) and methanol (for pesticide residue analysis, purity 99.9%) were purchased from Lach-Ner. Distilled water for (HPLC) was further purified using a Milli-Q RG apparatus (Millipore, Bedford, MA, USA). The herbicide aqueous solutions were used in sorption and degradation experiments in the laboratory as well as on the field experiments.

Table 2. Physical and chemical properties of studied soils in different horizons: pH_{H2O}, pH_{KCl}, OC (organic carbon content), humic substances, $CaCO_3$ content, cation exchange capacity (CEC), bulk density (ρ_d), clay, silt, and sand contents.

Horizon	Depth (cm)	pH_{H2O}	pH_{KCl}	OC (%)	Humic substances A400/A600	$CaCO_3$ (%)	CEC (mmol+g^{-1})	ρ_d (cm^{-3})	Clay (%)	Silt (%)	Sand (%)
Suchdol											
Ap	0-30	7.91	7.13	2.63	3.895	0.57	118.99	1.72	22.49	68.57	8.94
Ac	30-62	7.97	7.37	1.80	3.774	1.0	118.21	1.38	27.92	60.10	11.98
A/C	62-75	7.93	7.41	0.89	4.147	1.4	122.04	1.77	31.27	60.79	7.94
Ck	75-95	8.22	7.73	0.76	4.182	22.5	94.94	1.74	31.13	57.83	11.04
Dobroměřice											
Ap	0-30	7.80	7.32	3.45	4.342	0.93	145.62	1.71	18.50	48.90	32.60
Ap/Mg	30-45	7.62	6.97	2.96	4.287	0.37	163.60	1.67	17.26	51.31	31.43
Mg	45-85	7.79	7.21	0.70	3.643	0.35	85.71	1.63	16.14	52.18	31.68
MgC	85-115	7.78	7.55	0.60	3.817	0.79	94.97	1.42	15.81	55.76	28.43
Volárna											
Ap1	0-10	8.15	7.52	2.26	3.097	3.51	105.01	1.74	16.14	12.31	71.55
Ap2	10-34	6.04	5.04	1.35	3.808	0.28	22.73	1.94	6.17	3.79	90.04
C	34-92	6.85	6.58	0.37	3.131	0.23	11.37	1.88	5.58	3.00	91.42
Cg	92-115	7.44	6.35	0.59	3.066	0.23	34.74	1.82	6.18	2.63	91.19
Gro	115-135	7.61	6.70	0.22	4.406	0.25	20.87	1.76	6.54	0.98	92.56

Suchdol

Location: Suchdol

District: Praha-Suchdol

Region: Praha 6

GPS coordinates 50°8′8"N, 14°22′43"E

Elevation: 280 m. above sea level.

Picture 1. Suchdol – Haplic Chernozem
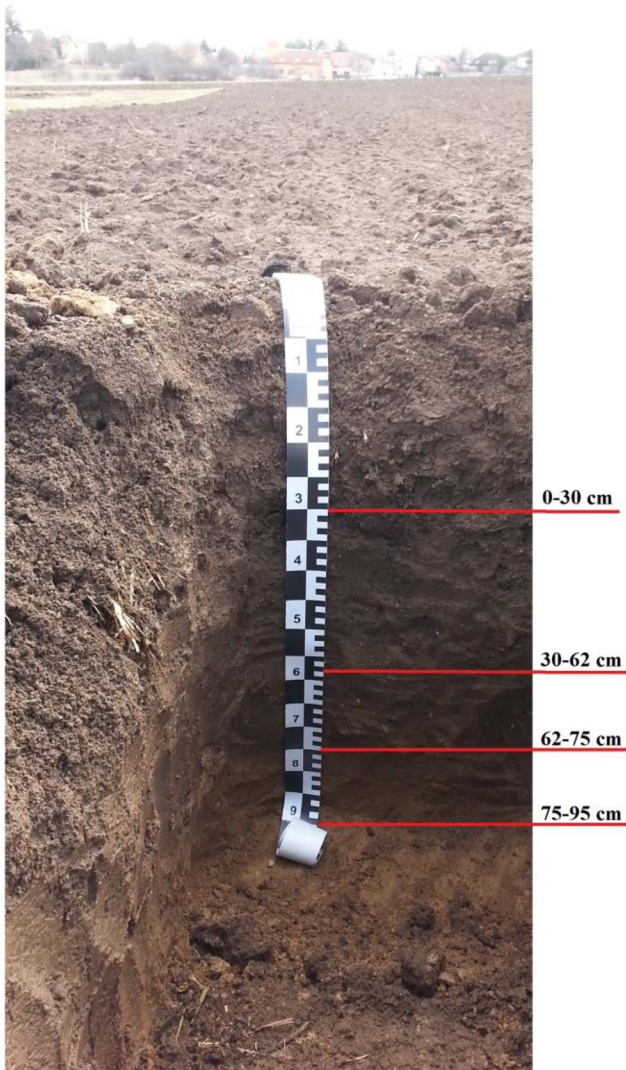
Ap 0-30 cm; dark reddish brown (7,5YR 2/3) silty loam; medium granular structure; 10% gravel; plant residues and roots; moderately decomposed; weakly alkaline; abrupt irregular boundary.

Ac 30-62 cm; dark brown (7,5YR 3/2) silty clay loam; subangular blocky structure; compacted layer; 15% gravel; weakly alkaline; abrupt irregular boundary.

A/C 62-75 cm; grayish brown (7,5YR 3/3) silty clay loam; subangular blocky structure; 5% gravel; weakly alkaline; abrupt irregular boundary.

Ck 75-95 cm; dull brown (7,5YR 5/4) silty clay loam; layer rich in $CaCO_3$; weakly alkaline; groundwater was not detected.

Dobroměřice

Location: Dobroměřice

District: Louny

Region: Ústecký kraj, (Region Ústí)

GPS coordinates 50°22′13″N, 13°47′41″E

Elevation: 185 m. above sea level.

Ap   0-30 cm; very dark gray (7,5YR 3/1) loam; medium granular structure; 15% gravel; plant roots; moderately decomposed; weakly alkaline; abrupt irregular boundary.

Ap/Mg 30-45 cm; dark gray 75%, and dark grayish brown 25% (7,5YR 3/2) +(10YR 3/2) loam; granular structure; 10% gravel; few plant roots; weakly alkaline; abrupt irregular boundary.

Mg 45-85 cm; dark yellowish-brown (10YR 4/4) loam; weak fine granular structure; weakly alkaline; abrupt irregular boundary.

MgC 85-115 cm; very dark brown (10YR 2/2) loam; weak fine granular structure; weakly alkaline; groundwater was not detected.

Picture 2. Dobroměřice – Haplic Fluvisol

Volárna

Location: Volárna

District: Kolín

Region: Středočeský kraj, (Central Bohemian Region)

GPS coordinates 50°09′18″N, 15°24′04″E

Elevation: 196 m. above sea level.

Picture 3. Volárna – Arenic Regozem
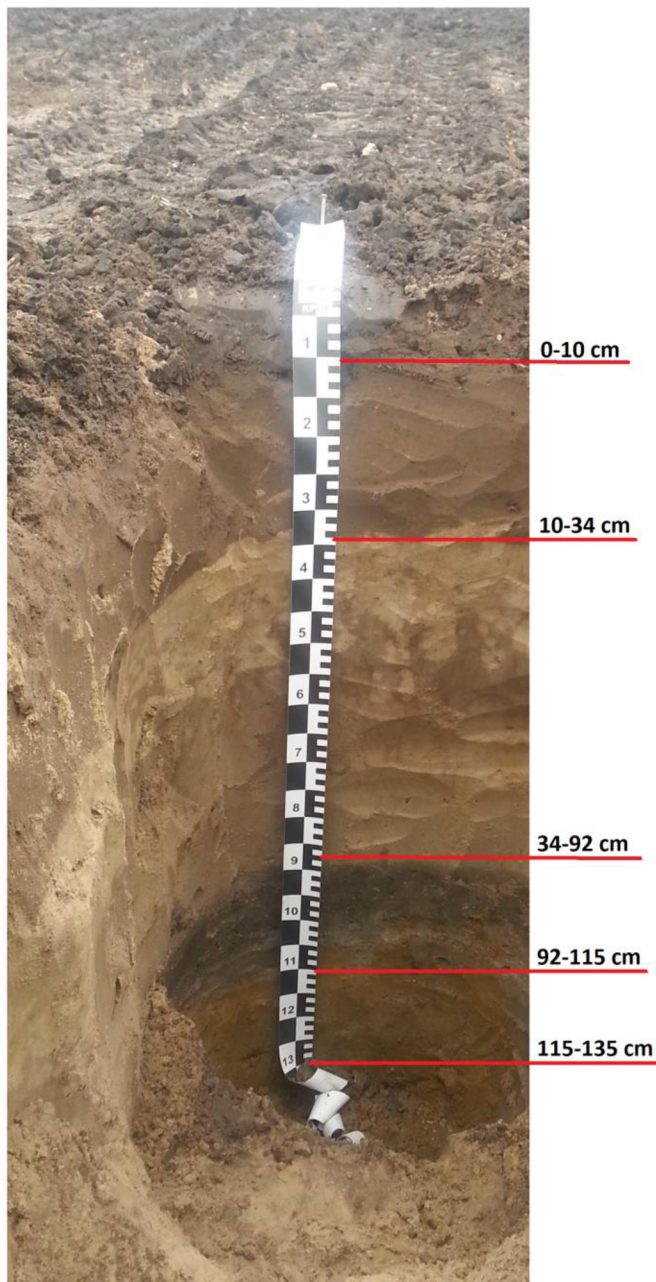
Ap1 0-10 cm; dark grayish (10YR 2/1) sandy loam; layer dominated by organic matter, clay and $CaCO_3$; medium fine granular structure; moderately decomposed; weakly alkaline; plant residues; abrupt irregular boundary.

Ap2 10-34 cm; brownish black (10YR 3/2) loamy sand; weak granular structure; weakly acidic; low organic matter and carbonate; few fine roots; clear boundary.
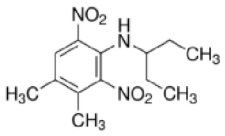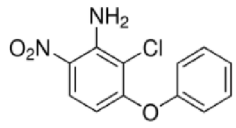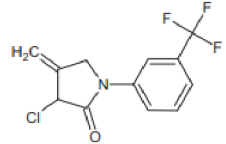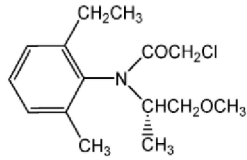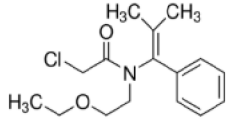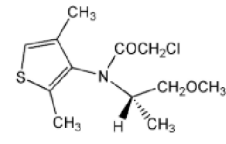
C 34-92 cm; dominated color is yellowish-brown (10YR 4/2) fine sand; single grained structure; weakly acidic; clear boundary.

Cg 92-115 cm; brownish-black (10YR 3/1) very fine sand; single grained structure; weakly alkaline; abrupt irregular boundary.

Gro 115-135 cm; dark yellowish-brown (10YR 4/1) very fine sand; oxidized layer; high iron oxides; single-grained structure; weakly alkaline; groundwater detected.

Table 3. Herbicides' solubility in water, Freundlich sorption coefficient K_F and K_{FOC}, groundwater ubiquity score (GUS), half-life in the soil in laboratory condition, dissociation constant (pKa).

Properties	Pendimethalin	Aclonifen	Flurochloridone	S-Metolachlor	Pethoxamid	Dimethenamid-P
CAS number [c]	40487-42-1	74070-46-5	61213-25-0	87392-12-9	106700-29-2	163515-14-8
Molecular structure [a, b]						
Molecular formula [c]	$C_{13}H_{19}N_3O_4$	$C_{12}H_9ClN_2O_3$	$C_{12}H_{10}Cl_2F_3NO$	$C_{15}H_{22}ClNO_2$	$C_{16}H_{22}ClNO_2$	$C_{12}H_{18}ClNO_2S$
Molecular weight (g mol^{-1}) [c]	281.31	264.66	312.12	283.79	295.81	275.79
Solubility in water at 20ºC (mg L^{-1}) [c]	0.33	1.4	21.9	480	400	1499
K_F (cm$^{3/n}$ μg$^{1-1/n}$ g^{-1}) [c]	220.1	138.1	9.4	1.88	4.4	3.69
K_{FOC} (cm$^{3/n}$ μg$^{1-1/n}$ g^{-1}) [c]	13792	7126	700	226.1	211	227
GUS [c]	-0.41	0.28	1.99	1.91	1.34	2.24
DT$_{50}$ (lab at 20°C), (days) [c]	182.3	62.3	53	14.5	6.3	23
(pKa) at 25 °C	2.8[c] (strong acid) 10.94[d] (strongest acidic) −1[d] (strongest basic)	-3.15[c] (very strong acid)	No dissociation [c]	No dissociation [c]	No dissociation [c]	No dissociation [c]
H-bond donors [e]	1	1	0	0	0	0
H-bond acceptors [e]	7	4	4	2	2	3
Polar surface area (Å^2) [e]	104	81.1	20.3	29.5	29.5	58

[a] Sigma-Aldrich web page
[b] Chem Service inc. web page.
[c] Pesticide Properties DataBase (PPDB) web page.
[d] Toxin and Toxin Target Database (T3DB) web page.
[e] PubChem open chemistry database web page.

4.2 Field experiments

4.2.1 Experiment design and herbicide application

The field experiments were conducted in the years 2015, 2016, and 2017 during the vegetation period and every year initiated during the 2nd or 3rd week of April. The experiments were set up in the same design in all three locations and each plot size was (2.25 x 7 m). The experiments were organized in a randomized block with three replicates containing 13 treatments including the control treatment. One (1) day after sowing the sunflower, herbicides were applied to the established plots at two rates of single and double application of the recommended dose (×1 and ×2) of each herbicide as a water emulsion of the commercial EC (emulsifiable concentrate) formulation. A small-plot sprayer was used to apply the herbicides (application volume 300 L/ha, nozzle Lurmark 015 F 80, application pressure 0.3 MPa). The application rates were 5 L ha^{-1} of pendimethalin (2000 g ha^{-1} a.i); 4 L ha^{-1} of aclonifen (2400 g ha^{-1} a.i); 3 L ha^{-1} of flurochloridone (750 g ha^{-1} a.i); 1.2 L ha^{-1} of S-metolachlor (1152 g ha^{-1} a.i); 2 L ha^{-1} of pethoxamid (1200 g ha^{-1} a.i) and 1.4 L ha^{-1} of dimethenamid-P (1008 g ha^{-1} a.i), respectively. To determine the actual amount of herbicide used, three Petri dishes were placed on the ground of each plot and the dishes were immediately washed with methanol into a 50 mL flask after the herbicide application.

4.2.2 Sampling method

According to the experiment plan and weather conditions in sites, soil samples were collected five (5) times, starting the day after herbicide application and continuing throughout the vegetation period, from two soil layers (0-5 and 5-10 cm) of each treatment in triplicate using the soil cylinders. Furthermore, control samples were taken from each plot prior to the herbicide application (day 0). Detailed information of sampling time for each location is presented in (Table 4). In addition, undisturbed soil samples were also taken to obtain the basic information about the physical properties of studied soils such as soil water content and bulk density. Soil bulk density was used to calculate the remaining concentration of herbicides in soil per unit area (g/cm^{3}). Soil samples collected were frozen and stored until their analysis.

4.2.3 Sample preparation for analyses

The soil samples were dried using lyophilization immediately after collection, ground, and sieved through a 2 mm sieve. Then 10 g of soil was weighed and transferred into 50 mL plastic cuvette, and 10 mL of methanol was added to each plastic cuvette containing the 10 g of soil. The

soil suspension was shaken for 20 h, centrifuged in a refrigerated centrifuge at 5 °C and 13,000 rpm for 10 min, then suspended soil extract was filtered using a 0.7 μm glass syringe filter and the filtered extract was put into vials. The herbicide concentrations in soil extract were determined using the HPLC-UV method (Dionex, USA). The amount of solute per mass unit of dry soil (μg g^{-1}) was then calculated.

Table 4. Soil sampling days for the field locations.

Locations	Sampling time 2015	Time after application (days)	Sampling time 2016	Time after application (days)	Sampling time 2017	Time after application (days)
Suchdol	30-Apr-15	6	14-Apr-16	2	21-Apr-17	2
	13-May-15	19	27-Apr-16	15	28-Apr-17	9
	27-May-15	33	13-May-16	31	11-May-17	22
	26-Jun-15	63	16-Jun-16	65	2-Jun-17	44
	7-Aug-15	105	18-Jul-16	97	3-Aug-17	106
Dobroměřice	5-May-15	7	29-Apr-16	4	27-Apr-17	2
	15-May-15	17	6-May-16	11	4-May-17	9
	1-Jun-15	34	26-May-16	31	18-May-17	23
	1-Jul-15	64	21-Jun-16	57	8-Jun-17	44
	6-Aug-15	100	11-Aug-16	108	4-Aug-17	101
Volárna	16-Apr-15	7	21-Apr-16	6	12-Apr-17	2
	26-Apr-15	17	19-May-16	34	19-Apr-17	9
	12-May-15	33	30-May-16	45	2-May-17	22
	12-Jun-15	64	17-Jun-16	63	25-May-17	45
	10-Aug-15	123	19-Aug-16	126	9-Aug-17	121

4.3 Laboratory experiments

Sorption is always taken into account when assessing the environmental fates of herbicides, such as leaching, plant uptake, surface runoff, and degradation in field conditions. Furthermore, herbicide degradation varies significantly between field and laboratory studies, thus comparing results always contributes to the understanding of herbicide behavior in soil. Therefore, laboratory experiments were proposed for study, and the results were used to "predict" the sorption and degradation behavior of herbicides in soil. Procedures for both experiments are presented in the following sections. There were two separate experiments carried out in the laboratory: the sorption and degradation experiment. For both experiments, disturbed soil samples were taken only from the top Ap horizon (thickness of 30 cm) from three locations (Suchdol, Dobroměřice and Volárna).

4.3.1 Sorption experiment

The sorption experiment was carried out using a standard batch equilibrium method according to guidelines of the Organization for Economic Co-operation and Development (OECD, 2000). Herbicide solutions were prepared in 0.01M $CaCl_2$ (excluding aclonifen) with five different concentrations containing (c_{ini} = 1; 2.5; 5; 10 and 25 µg cm^{-3}) in (active substances in the herbicide products). The five initial herbicide concentrations (plus a control with no herbicide addition) and three replicates of each concentration were applied for each soil. The solutions were added to 10 g of air-dried, ground, and sieved (2 mm sieve) soils and placed into the 50 cm^3 glass bottles. 20 mL of known herbicide concentration solution was added to the glass bottle, and the bottles were shaken for 24 hours at 20 °C using the shaking apparatus. After shaking, the suspensions were transfered to a centrifuge tubes and centrifuged for 10 minutes at 4700 rotations per minute. The suspended soil extract was filtered using 0.7 µm glass syringe filter and the filtered extract was put into vials. According Humburg (1989), the fast biodegradability screening test, water/sediment simulation test, and soil, aclonifen is susceptible to primary degradation (>70 %), but not to ultimate mineralization. Therefore, in the case of aclonifen, 0.1g L^{-1} of NaN_3 (sodium azide) solution was used to reduce microbial activity in the soil, and the suspension was shaken 2 hours rather than 24 hours. The rest of the procedures was done according to the above-mentioned methodology. The initial (c_{ini}) and final equilibrium herbicide concentrations (c_{eq}) in solutions (µg cm^{-3}) of all studied herbicides were measured using the HPLC technique (Dionex, USA). The Freundlich equation was used to describe the sorption isotherms:

$$s = K_F C^{\frac{1}{n}}$$
[3]

where C (µg cm^{-3}) and s (µg g^{-1}) are equilibrium concentrations in solution and soil, respectively, while K_F ($cm^{3/n}$ µg$^{1-1/n}$ g^{-1}) and n are empirical coefficients.

4.3.2 Degradation experiment

The degradation experiments of herbicides were performed according to OECD, (2002). Fresh soil samples were collected from the three experimental fields and prepared immediately after bringing it to the laboratory to avoid changes in soil water content and plant parts, larger soil fauna and stones were removed prior to passing the soil through a 2 mm sieve and 50 g of soil samples were placed into the 250cm^3 glass bottles. The studied herbicides flurochloridone, pendimethalin, aclonifen, dimethenamid-p, s-metolachlor and pethoxamid solutions were

prepared using 0.01M CaCl$_2$ aqueous solution in order to minimize soil mineral balance disruption. First, the herbicide solubility was improved using the methanol and prepared solutions were separately applied into the glass bottles in two different doses with triplicates. Suchdol and Dobroměřice soils were characterized by silty loam and loamy soil which retain better soil moisture and nutrients. In contrast, the soil from Volárna was characterized as sandy loam soil with low organic matter and lower water holding capacity. Therefore, based on the soil properties a different amount of solution was added to the soil samples from Suchdol and Dobroměřice (12.5 mL) than to those from Volárna (8 mL). The treated soil samples were thoroughly mixed and incubated in a thermostat at 20°C constant temperature. During the incubation, moisture content (w/w) was maintained by adding some amount of water once a week and lids were not tightly closed to avoid the creation of anaerobic conditions and suitable flow-through for soil incubation. The duration of incubation was 120 days, samples were taken at appropriate time intervals (0; 1; 2; 5; 12; 23; 46; 80; 120 days) after herbicide application, and bottles were immediately frozen after collection until to proceed the soil extraction. When the incubation period was finished (120 days after), samples were processed to prepare for soil extracts. The sample extracts were prepared using 50 mL of methanol to each bottle and put to shaking for 24 hours; after shaking, the analyzed soil suspension was placed into the centrifuge tube and centrifuged for 10 min at 4700 rotations per minute. The suspended soil extracts were filtered using 0.7 μm glass syringe filter and transferred into vials. The final pesticide concentrations (c$_{eq}$) remaining in soil solutes (μg cm^{-3}) were measured using the HPLC technique (Dionex; USA). Herbicides' half-life was calculated using the first-order kinetics simplified equations for estimating pesticide loss from the soil. According to Tadeo et al. (2000), degradation rates and determination coefficients were calculated by fitting data of concentration in soil at different times as follows:

$$LnC = \ln C_0 - K.t \qquad [4]$$

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

$$t_{1/2} = \frac{\ln 2}{k} \qquad [5]$$

where t$_{1/2}$ is the herbicide half-life (days) and k (day^{-1}) is the dissipation rate constant calculated by equation 4 (Tadeo et al., 2000).

4.3.3 HPLC conditions and herbicides' calibration lines

The samples from adsorption and degradation studies were analyzed by HPLC (Dionex, USA), using a PDA-100 photodiode array detector equipped with a P680 HPLC pump and ASI-100 automated sample injector. The guard columns (Security Guard Cartridge AQ C18 4 x 2.00 mm) pre-column, connected to a Kinetex 2.6μ, C18, 100 A column, 50 × 4.6 mm (Phenomex), were used for separation of the studied herbicides. The detection wavelengths (nm), retention time (min), injection volume (μL), and detection limit (μg/mL) for each herbicide are shown in Table 5. The flow rate of the mobile phase was 1 mL min^{-1} and the column temperature was set at 25°C. The mobile phase was prepared separately for each herbicide by mixing acetonitrile, redistilled water, and formic acid. For pendimethalin, 700 mL of acetonitrile, 300 mL of water and 1 mL L^{-1} of formic acid was used, for aclonifen 850 mL of acetonitrile, 150 mL of water and 1 mL L^{-1} of formic acid, for flurochloridone 800 mL of acetonitrile, 200 mL of water and 1 mL L^{-1} of formic acid, for s-metolachlor 500 mL of acetonitrile, 500 mL of water and 1 mL L^{-1} of formic acid, for pethoxamid 900 mL of acetonitrile, 100 mL of water and 1 mL L^{-1} of formic acid, for dimethenamid-P 525 mL of acetonitrile, 475 mL of water and 1 mL L^{-1} of formic acid. The herbicides' limits of detection (LOD) were determined as the lowest injected concentrations of the pesticides yielding signal to noise ratios of 3. The herbicides' limits of quantification (LOQ) were determined based on the standard deviation (STD) of the UV detector response and the slope of the calibration line (s) (LOQ = 10 STD/s). The tested herbicides' recovery ranged from 84.9% to 118.1.6% for all herbicides, respectively.

Table 5. Parameters from the HPLC reading for the herbicides; wavelength, (nm), retention time (min), injection volume (μL), and detection limit (μg/mL).

Herbicides	Parameters			
	Wavelength	Retention time	Injection volume	Detection limit
Flurochloridone	252	2.13	10	0.015
Pendimethalin	240	2.39	10	0.01
Aclonifen	225	1.90	10	0.02
Dimethenamid-P	210	1.88	10	0.05
S-Metolachlor	220	1.59	10	0.03
Pethoxamid	245	1.97	10	0.025

4.4 Statistical analysis

Statistical analysis was carried out for data from the laboratory experiments to analyze the relationships between treatment variables. A simple and multiple correlation analysis between soil properties and absorption coefficients and degradation experiment results were evaluated using the Pearson correlation coefficient and p-value. The soil properties (Table 2) were the main predictors of correlation analysis and the statistically significant level was always 0.05 or lower. A Shapiro-Wilk test was used to test data from the laboratory degradation experiment for normality (soil type and type of herbicide).

Data obtained from the field experiment were statistically analyzed and significance levels were set at $p < 0.05$. The leaching of herbicides under different conditions was assessed using the total amounts of herbicides in soil layers 5-10 cm ($f_{M,5-10,t}$, [%]). The effect of soil type, application rate, sampling term, and type of herbicide in the total of all soil layers 5-10 cm ($f_{M,5-10,t}$, [%]) was studied using the nonparametric Kruskal–Wallis test. Next, the effects of soil type, application rate, sampling term, and type of herbicide on herbicides' half-lives were studied using multifactor ANOVA, because the half-life values showed a normal distribution. All statistical analyses were performed using the Statistica® 13 (StatSoft, Inc. Oklahoma, USA).

5. Results and Discussion

5.1 Sorption parameters of herbicides

The Freundlich sorption isotherms of herbicides are shown in Figure 1, and sorption parameters (K_F and n) together with the regression coefficients and R^2 values calculated for herbicides with three soils are provided in Table 6. The K_F values ranged from 1.07 to 135.37 $cm^{3/n}$ $\mu g^{1-1/n}$ g^{-1} and sorption of herbicides increased in the order dimethenamid-p < pethoxamid < s-metolachlor < flurochloridone < aclonifen < pendimethalin. The slopes (n>1) of isotherm of herbicides calculated for three soils indicated a high level of linearity as n values were higher than 1, excluding flurochloridone (Table 6). Among the six herbicides, the highest K_F value reported was systematically observed in Haplic Fluvisol of Dobroměřice (a loam with high organic matter content and lower pH, Table 1). In this soil, K_F values ranged from 2.41 for dimethenamid-p to 135.37 $cm^{3/n}$ $\mu g^{1-1/n}$ g^{-1} for pendimethalin. In contrast, lowest K_F values were found in the Arenic Regozem of Volárna (a sandy loam with low organic matter content and higher pH) for dimethenamid-p and pethoxamid. It should be noted that pendimethalin displayed highest K_F values and was more strongly adsorbed on all three soils than any of the other herbicides (Table 6).
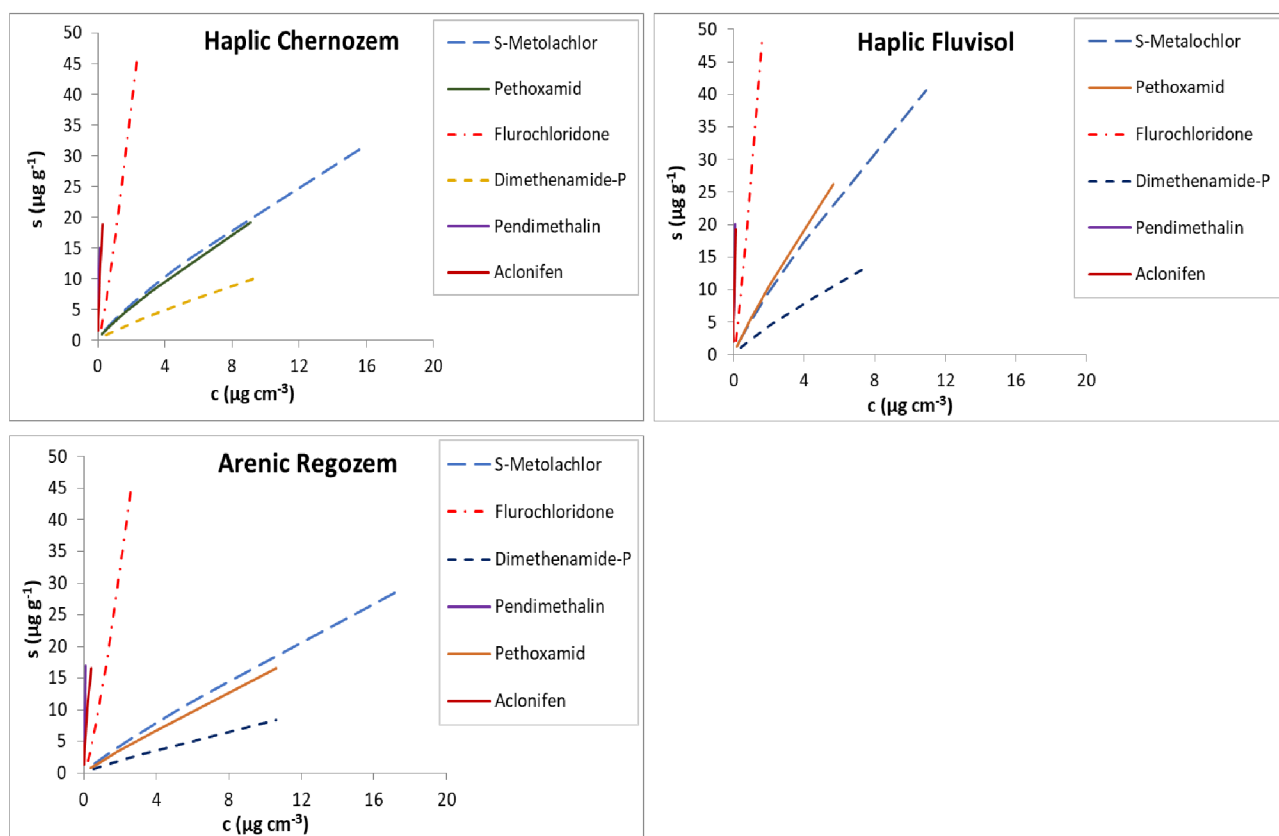
Figure 1. Adsorption isotherms of six studied herbicides in three soils: Suchdol – Haplic Chernozem; Dobroměřice – Haplic Fluvisol and Volárna – Arenic Regozem.

Concerning the K_F parameter values, our results are consistent with those shown by Wauchope et al. (1992), and Rytwo et al. (2005) who discussed the strong affinity of pendimethalin to the solid phases due to its hydrophobic nature. Kočárek et al. (2018) studied sorption isotherms of pendimethalin under laboratory conditions and obtained a higher K_F value (270.1 $cm^{3/n}$ $\mu g^{1-1/n}$ g^{-1}) in a silt loam soil. The aclonifen K_F values (Table 6) were lower than the value (K_F=138.1 $cm^{3/n}$ $\mu g^{1-1/n}$ g^{-1}) presented in PPDB (2019). On the other hand, aclonifen sorption was studied by Trevisan et al. (1999) in 9 different soil types where, corresponding to our soil characteristics, they determined significantly higher K_D values between 8.54 and 602.60 mL g^{-1}.

As mentioned above, the Freundlich isotherm for the flurochloridone adsorption is described by an S-type curve, since n values were < 1 in the three soils and ranged from 0.76 to 0.85 respectively. These values for flurochloridone indicate a relatively higher affinity for all three soils at a low concentration, and a reduction in adsorption at a higher concentration (Pinna et al., 2014). Sorption coefficient (K_F) values (Table 3) for s-metolachlor, pethoxamid and dimethenamid-p show that they have a considerably lower sorption behavior compared to the other three herbicides. This was probably due to their physicochemical properties such as a smaller polar surface area ($Å^2$) and high-water solubility (Table 2).

Nevertheless, the K_D values for s-metolachlor were within the range of previously published results for soils with similar properties, e.g., 0.51-3.40 cm^3 g^{-1} (Si et al., 2009), 0.76-16.67 cm^3 g^{-1} (Westra et al., 2015), and 0.6 – 5.7 cm^3 g^{-1} (Weber et al., 2003). The K_F values of pethoxamid for our three soils are within the range of 1.88 - 5.61 $cm^{3/n}$ $\mu g^{1-1/n}$ g^{-1}, while its highest sorption was indicated in Haplic Fluvisol. Pose-Juan et al. (2018) recently studied the adsorption of pethoxamid in a sandy loam soil that was amended with green compost (S+GC), sewage sludge (S+SS), and unamended (S); they obtained significantly smaller K_F values of 0.20 $cm^{3/n}$ $\mu g^{1-1/n}$ g^{-1} for the unamended soil. Furthermore, the adsorption curve of pethoxamid showed a high level of linearity (n_f =1.68) in the unamended soil, while its adsorption by S+SS and S+GC was close to linearity (C-type) (n_f=1.16 and 0.96) (Pose-Juan et al., 2018). The dimethenamid-p K_F values (Table 3) were lower than the value (K_F=3.69 $cm^{3/n}$ $\mu g^{1-1/n}$ g^{-1}) presented in PPDB (2019). Kočárek et al. (2018) reported a low K_F value 2.12 $cm^{3/n}$ $\mu g^{1-1/n}$ g^{-1} of dimethenamid-p sorption on a silt loam soil. Westra et al. (2015) also observed low dimethenamid-p K_D values. The mean of dimethenamid-p K_D values determined in 25 soil types was 2.3 cm^3 g^{-1}.

The substantial variability in the behavior of the three soils toward herbicides sorption, evidenced by the differences in K_F values, implies that the soil properties affect the sorption. In order to understand properly which soil property influences the sorption of herbicides in the studied soils, simple and multiple linear regressions were conducted.

Table 6. The Freundlich adsorption parameters, K_F, $(cm^{3/n}\ \mu g^{1-1/n}\ g^{-1})$ for the studied herbicides and n values for three soils.

Location/Soil type	Dimethenamid-p			Pethoxamid			S-Metolachlor			Flurochloridone			Aclonifen			Pendimethalin		
	K_F	n	R^2	K_F	n	R^2	K_F	n	R^2	K_F	n	R^2	K_F	n	R^2	K_F	n	R^2
Suchdol - Haplic Chernozem	1.57	1.20	0.998	3.07	1.21	0.998	3.30	1.23	0.998	15.83	0.80	0.996	42.56	1.53	0.991	82.31	1.58	0.988
Dobroměřice - Haplic Fluvisol	2.41	1.17	0.999	5.61	1.12	0.999	5.32	1.18	0.998	27.32	0.85	0.997	81.42	1.43	0.972	135.37	1.36	0.995
Volárna - Arenic Regozem	1.07	1.15	0.999	1.88	1.09	0.999	2.31	1.13	0.999	12.77	0.76	0.993	27.02	1.68	0.983	73.33	1.57	0.988
Average K_F value	1.68			3.52			3.65			18.64			50.33			97.00		
Standard deviation	0.7			1.9			1.5			7.7			28.0			33.5		
Range	1.33			3.73			3.01			14.55			54.39			62.04		

5.1.1 Effect of soil properties on the sorption of herbicides

The statistical correlation between the herbicides K_F coefficients and soil properties is given in Table 7. Consistent with the herbicide's properties and pKa values (Table 3), their molecules are in neutral form and behave as non-ionic organic compounds. Consequently, the sorption of non-ionic molecules onto soils is mainly driven by hydrophobic partitioning to the soil organic matter via van der Waals forces and electron donor - acceptor interactions and by hydrogen bonding with hydroxyl groups on the solid surfaces. Numerous studies have established an effect of soil organic matter upon the sorption of non-ionic herbicides in different soil conditions. Our findings for the compounds flurochloridone, s-metolachlor, dimethenamid-p, and pethoxamid confirm research findings that suggested a hydrophobic interaction plays a critical role in controlling their sorption on soil with higher OM content (Weber et al., 2000; 2004; Pinna et al., 2014; Pose-Juan et al., 2018).

Table 7. Statistical correlations between the K_F coefficients and soil properties: pH_{KCl}, pH_{H2O}, organic matter content (OM), $CaCO_3$ content, cation exchange capacity (CEC), sand, silt and clay content.

	pH_{KCl}	pH_{H2O}	OM	$CaCO_3$	CEC	Sand	Silt	Clay
Pendimethalin	-0.147	-0.829[***]	0.981[***]	-0.513[*]	0.974[***]	-0.095	0.108	-0.013
Aclonifen	-0.286	-0.899[***]	0.996[***]	-0.633[*]	0.995[***]	-0.240	0.252	0.133
Flurochloridone	-0.210	-0.863[***]	0.990[***]	-0.569[*]	0.986[***]	-0.161	0.173	0.053
S-metolachlor	-0.332	-0.919[***]	0.996[***]	-0.669[*]	0.996[***]	-0.286	0.297	0.180
Pethoxamid	-0.320	-0.914[***]	0.995[***]	-0.661[*]	0.996[***]	-0.275	0.287	0.169
Dimethenamid-p	-0.378	-0.933[***]	0.992[***]	-0.705[**]	0.997[***]	-0.333	0.344	0.228

Correlation significant at: [*] $p < 0.05$; [**] $p < 0.01$; [***] $p < 0.001$.

The results show strong positive correlation between the K_F coefficient and organic matter content (OM) and cation exchange capacity (CEC) for the studied herbicides (at $p < 0.001$). This confirms them being the major predictors in describing the sorption of studied herbicides, and supports the findings of Trevisan et al. (1999); Weber et al. (2004); and Westra et al. (2015). Moreover, the OM correlated strongly with CEC ($r \geq 0.989$, $p < 0.001$), while no correlation was observed between the clay content and CEC (Table 8). This suggest that the impact of CEC in soil solution is mainly due to the OM content.

Generally, compounds with lower water solubility are adsorbed to a greater extent by organic matter (Carringer et al., 1975), the structure of the pendimethalin and aclonifen molecules have considerably low water solubility (0.33 and 1.4 mg L^{-1}) and high K_{FOC} values (13,792 and 7,126 $cm^{3/n}$ $\mu g^{1-1/n}$ g^{-1}) (Table 3). However, the results indicated that adsorption was highly correlated to OM ($r \geq 0.981$, $p < 0.001$ for all six herbicides) regardless of differences in their water solubility and K_{FOC} values.

Table 8. The correlation coefficients describing relationship between the studied soil properties: pH_{KCl}, pH_{H2O}, organic matter content (OM %), $CaCO_3$ content (%), cation exchange capacity (CEC mmol+ kg^{-1}), sand, silt and clay contents (%).

	pH_{KCl}	pH_{H2O}	OM	$CaCO_3$	CEC	Sand	Silt	Clay
pH_{KCl}	1							
pH_{H2O}	0.660[*]	1						
OM	-0.305	-0.905[***]	1					
$CaCO_3$	0.907[***]	0.895[**]	-0.647[*]	1				
CEC	-0.346	-0.919[***]	0.989[***]	-0.680[*]	1			
Sand	0.976[***]	0.622[*]	-0.262	0.903[***]	-0.301	1		
Silt	-0.976[***]	-0.631[*]	0.274	-0.908[***]	0.313	-1.000[***]	1	
Clay	-0.964[***]	-0.535[*]	0.155	-0.851[**]	0.196	-0.994[***]	0.992[***]	1

Correlation significant at: [*] $p < 0.05$; [**] $p < 0.01$; [***] $p < 0.001$.

The adsorption coefficient normalized to organic carbon content (K_{OC}) can be used as a measure of the influence of hydrophobic bonds on the adsorption of non-polar hydrophobic pesticides on OM. However, even when hydrophobic bonds dominate adsorption, the use of K_{OC} may result in deviation from reality because the sorption capacity of a natural particle is highly dependent on the nature and amount of surface exposed, which in turn is determined by the degree of inter-association of the individual constituents. K_{OC} values are usually used to compare the behavior of nonionizable pesticides; while OM has been broadly reported as one of the main soil properties determining adsorption for this type of pesticide, other soil characteristics have to be taken into account, including the clay fraction, pH, ionic strength and cation exchange capacity (Spongberg and Ganliang, 2000; Ferreira et al., 2001). It should be noted that mobility of some hydrophobic pesticides can be increased in soil with high organic matter due to an increase of water solubility of such substances in the presence of dissolved organic carbon (DOC), as evidenced by Kodešová et al. (2012) for chlorotoluron and Haarstad and Fresvig, (2000) in the case of DDT.

Bailey and White (1970), previously explained the ability of pure minerals to effectively bind organic molecules with experimental evidence. Based on the hypothesis of mineral blockage by OM, clay mineral (e.g., kaolinite and montmorillonite) contribution is expected to be at a maximum when the ratio of clay minerals to OC fractions is more than 30, regardless of the mineral content; a small ratio was observed only for one soil investigated in this study (35 for Haplic Fluvisol) (Table 2). Sorption of herbicides, however, was not affected by clay content in all studied soils, since relationships between the K_F values and clay content were not found to be significant ($r \leq 0.228$) (Table 7). Barriuso et al. (1994) concluded that the contribution of clay constituents to pesticide retention can be dominant in low-OM soils. For instance, Harper. (1988) studied the behavior of metribuzin down a silty clay loam profile and found that clay content was the single best predictor of adsorption. On the other hand, the determination of the effect of a single soil variable on adsorption is always difficult because soil properties are often correlated with each other. Table 8 shows correlations between soil properties where soil pH_{H2O} was negatively correlated with OM ($r \geq 0.905$, $p < 0.001$), and CEC ($r \geq -0.919$, $p < 0.001$).

The K_F was negatively correlated to soil pH_{H2O} ($r \geq -0.829$, $p < 0.001$). A negative, but not significant correlation between K_F and pH_{KCL} was also observed for all herbicides (Table 7). Weber et al. (1989) suggested that adsorption of pesticides by hydrophobic bonding is pH independent. According to Ahmad et al., (2014), the acid ionization constant (pKa) of herbicides and the pH of the soil solution influence the sorption behavior of the molecule. Since, soil pH changes have only minor effects on the adsorption of non-ionic molecules (Kan and Tomson, 1990). In the case of the pendimethalin and aclonifen, these also behaved similarly on the pH of the soil solution. However, it should be noted that the information available about pendimethalin dissociation is quite inconsistent (Kočárek et al., 2018), and it is stable in the pH range 4-9 (Sakaliene et al., 2007), and aclonifen, which has a pKa of -3.15 (PPDB 2019), was neutral in the current experiments, as the studied soil solutions pH ranged from 7.8 to 8.2 (Table 2). So, the herbicides cannot be in their fully dissociated forms (Sakaliene et al., 2007). Herbicide sorption may therefore not have occurred by the independent mechanisms of anionic-cation interaction, but rather involved hydrogen bonds, van der Waals forces or hydrophobic partitioning (Trevisan et al., 1999; Shetti et al., 2019).

A negative correlation was found between the K_F coefficient and $CaCO_3$ content ($r \geq -0.513$, $p < 0.05$) for all herbicides. Content of CO_3^{2-} in soil has previously been reported by Rodriguez-Rubio et al. (2006) as fundamental for 2,4-D sorption in soil with a very large content of calcium carbonate. The authors found a drastic decrease in 2,4-D adsorption in the absence of

carbonates and suggested that the herbicide also adsorbed on the soil carbonates. However, in our case the opposite trend occurred, and it should be expected that adsorption of herbicides would not be favored by $CaCO_3$ content. In addition, Kodešová et al. (2011) suggest that $CaCO_3$ content is not suitable for estimating the sorption coefficient because the obtained correlation is based on extreme values of $CaCO_3$ content (i.e., either very high or very low values).

Table 9. Correlation matrix between the K_F coefficients of different herbicides.

	Pendimethalin	Aclonifen	Flurochloridone	S-metolachlor	Pethoxamid	Dimethenamid-p
Pendimethalin	1					
Aclonifen	0.998***	1				
Flurochloridone	0.999***	1.000***	1			
S-metolachlor	0.985***	0.993***	0.992***	1		
Pethoxamid	0.996***	0.999***	0.999***	0.997***	1	
Dimethenamid-p	0.972***	0.983***	0.981***	0.998***	0.989***	1

Correlation significant at: * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

As indicated previously, the sorption coefficient was not correlated with clay and silt content, and slightly negative but not significant correlation was observed with sand content (Table 7). This suggests that they were not the major predictors describing the sorption of the studied herbicides, and supports the findings of Weber et al. (2004); Alletto et al. (2013); and Westra et al. (2015), but opposes the findings of Peter and Weber, (1985) who reported a direct effect of clay content to adsorption of herbicides alachlor and metolachlor.

Table 9 summarizes the correlations between the K_F values of all six herbicides. A strong positive correlation was found between the sorption coefficient of all the studied herbicides. As discussed above, this could be because the same prevailing sorption mechanism and herbicides were present mainly in their neutral form, and behave as non-ionizable compounds. In addition, similarities in their behavior under the same soil conditions could be expected.

5.2 Degradation experiments in laboratory

Degradation curves for six herbicides in three soils are presented in Fig. 2. The degradation of herbicides in soils followed first-order kinetics and the values for degradation rate and half-lives (DT_{50}) are shown in Table 10. In general, the rate of degradation decreased in the order aclonifen > pethoxamid > dimethenamid-p > pendimethalin > flurochloridone > s-metolachlor. Degradation rate constants of herbicides were in the range of 0.012 - 0.048 d^{-1}, which corresponds to half-lives between 14 and 57 days. The longest DT_{50} values for herbicides were observed in Haplic Fluvisol, while the shortest values were in Haplic Chernozem (Table 10). The DT_{50} values in these cases were likely due to the higher organic matter content in the soil (Table 2). Additionally, the high DT_{50} values could be explained by the sorption coefficients (K_F) of herbicides. The adsorption of herbicides by Haplic Fluvisol was significantly higher than in the other two soils (Table 6). It has been demonstrated that sorbed chemicals are less accessible to microorganisms (Selim et al., 1999), and that sorption limits their degradation as well as their transport (Koskinen et al., 2001). Also, the DT_{50} values could increase if microbiological degradation is the main dissipation mechanism (Felsot and Dzantor, 1995; Munoz-Leoz et al., 2013).

Degradation of herbicides in soil initially depends on the intrinsic properties of the herbicides, and secondly on the soil properties (Singh et al., 1992). Table 11 gives correlation coefficients between degradation rates and soil properties and adsorption coefficients for each herbicide. Overall, a positive correlation was observed for degradation rate with clay content, and a negative correlation was observed with OM content and CEC. The degradation rate of two herbicides correlated significantly only with soil pH; positive correlation for pethoxamid, and negative but not significant correlation for flurochloridone. For other herbicides, weak positive correlations were observed between soil pH and degradation rate.

Aclonifen and pethoxamid showed faster degradation and shorter dissipation half-lives in the studied soils. The average values were 18 days for aclonifen and 20 days for pethoxamid. Shortest values were found in Haplic Chernozem and Arenic Regozem (Table 10). The obtained half-life for aclonifen was much shorter than the value presented (62.3 days) in PPDB (2019) and for pethoxamid, it is somewhat higher than those reported in the literature (Pose-Juan et al., 2018; Rodriguez-Cruz et al., 2019). Vischetti et al. (2002) also observed a high aclonifen half-life (40.3 to 49.1 days) in the laboratory under different temperature and soil moisture conditions in a sandy clay loam soil.

Table 10. The dissipation half-lives, DT_{50} (day), and kinetic rate constants, k_R (day^{-1}), of herbicides in soil.

Soil	Pendimethalin		Aclonifen		Flurochloridone		S-metolachlor		Pethoxamid		Dimethenamide-P	
	k_R	DT_{50}	k_R	DT_{50}	k_R	DT_{50}	k_R	DT_{50}	k_R	DT_{50}	k_R	DT_{50}
Suchdol	0.040	17	0.048	14	0.018	38	0.019	37	0.040	17	0.037	19
Dobroměřice	0.014	51	0.035	20	0.015	46	0.012	57	0.027	26	0.020	34
Volárna	0.030	23	0.037	19	0.014	51	0.015	47	0.040	17	0.032	21
Average k_R and DT_{50}	0.028	30	0.040	18	0.016	45	0.015	47	0.036	20	0.030	25

Table 11. Statistical correlations between degradation rate k_R and selected soil properties plus K_F.

	K_F	pH_{H2O}	OM	$CaCO_3$	CEC	Clay
Pendimethalin	-0.865[**]	0.405	-0.741[**]	-0.003	-0.737[**]	0.536[*]
Aclonifen	-0.377	0.092	-0.319	-0.491	-0.314	0.880[***]
Flurochloridone	-0.082	-0.461	0.061	-0.783[**]	0.067	0.994[***]
S-metolachlor	-0.595[*]	0.204	-0.583[*]	-0.214	-0.579[*]	0.702[**]
Pethoxamid	-0.950[***]	0.725[**]	-0.942[***]	0.381	-0.940[***]	0.171
Dimethenamid-p	-0.788[**]	0.498	-0.807[***]	0.100	-0.803[***]	0.446

Correlation significant at: [*] $p < 0.05$; [**] $p < 0.01$; [***] $p < 0.001$.

As Table 11 shows, the degradation rate of aclonifen was positively correlated with clay content ($r \geq 0.880$, $p < 0.001$), positively but not significantly correlated with soil pH, and negative but not significant correlation was observed with OM, $CaCO_3$, and CEC when evaluated for all three soils. Based on the Pesticide Properties DataBase (PPDB) data, aclonifen is hydrolysis stable between pH 5 to 9 at 22-70 °C, and photolysis is not a major route of degradation (PPDB, 2019). It is known that microbial degradation takes more time and the results suggest that degradation of aclonifen was mainly caused by chemical hydrolysis and/or oxidation due to its shortest half-life among the herbicides.
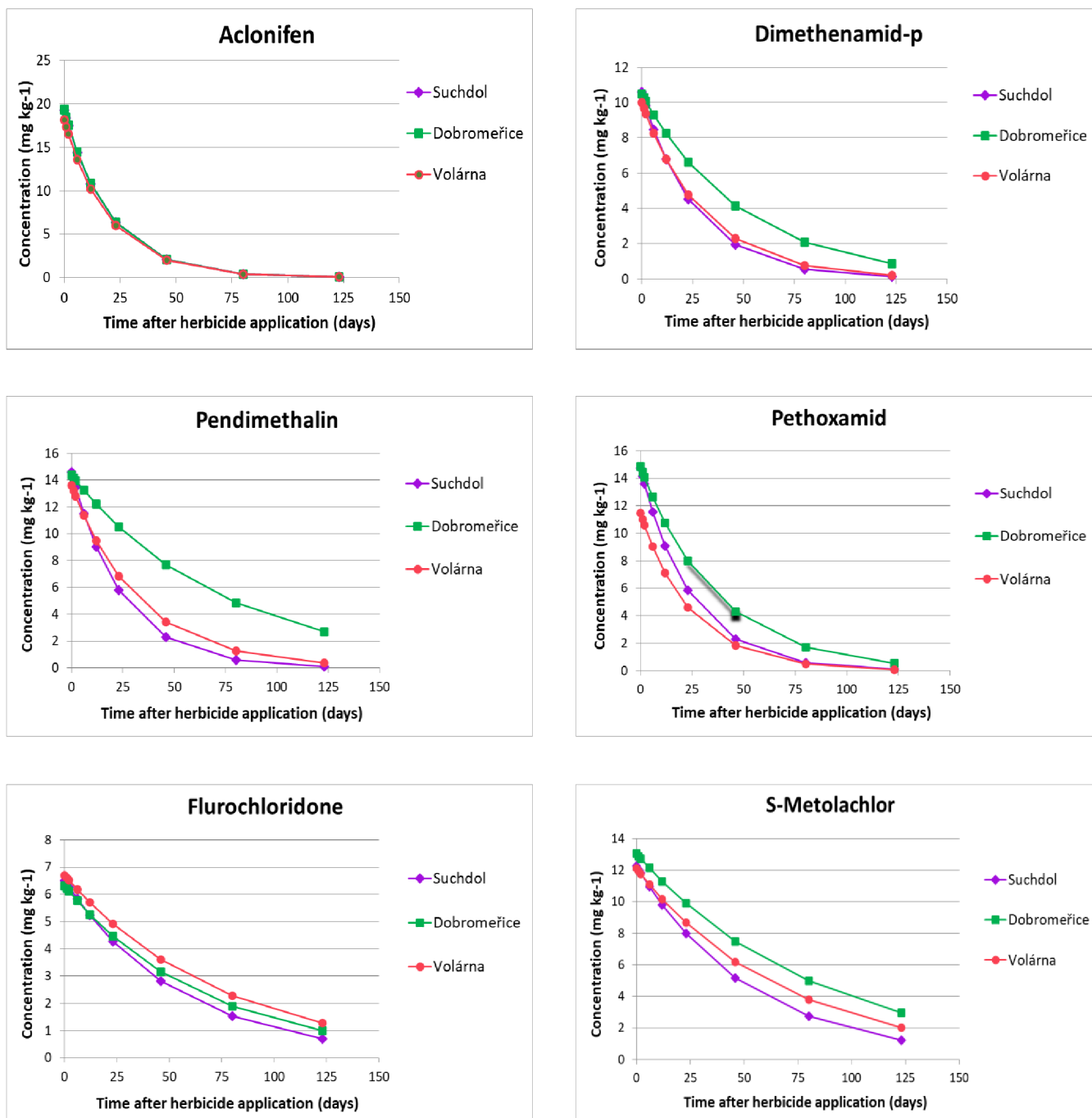
Figure 2. Decreasing concentration of six herbicides with time in three soils: Suchdol – Haplic Chernozem; Dobroměřice – Haplic Fluvisol and Volárna – Arenic Regozem.

The faster degradation rate and shorter DT_{50} values obtained for pethoxamid could be explained by its lower sorption ability to soil (Table 3), and its high content in dissolved organic carbon (DOC). The herbicide could be adsorbed by DOC, and the bioavailability for degradation could be enhanced if it remains adsorbed in solution, as indicated for other herbicides (Marín-

Benito et al., 2012). However, Dhareesank et al. (2005) also demonstrated that relatively rapid dissipation of pethoxamid in soil could be explained by its adsorption in a more irreversible form over time after the application due to its hydrophobic character. Rodriguez-Cruz et al. (2019) investigated the rate of dissipation of pethoxamid in soil amended with green compost and sewage sludge, and in unamended soils, with initial concentrations of 2, 10, and 50 mg kg^{-1}. The results indicated that organic residues may only contribute to the decrease in the dissipation rate of pethoxamid when applied at the lowest rates of 2 mg kg^{-1}. In addition, the rate of degradation was positively correlated with soil pH (r $\geq$ 0.725, p < 0.01), positively, but not significantly correlated with clay content and CaCO$_3$, and negatively correlated with OM (r $\geq$ - 0.942, p < 0.001), and CEC (r $\geq$ - 0.940, p < 0.001) for all three soils (Table 11).

The dissipation half-lives for dimethenamid-p in the three soils varied from 19 to 34 days (Table 10), which almost fall within the range of the DT$_{50}$ values calculated in laboratory studies at 20 °C (7.7-31.5 days) (EFSA, 2018). A longer dissipation half-life value of 34 days was found in Haplic Fluvisol, and significantly lower values were observed in Haplic Chernozem and Arenic Regozem (Table 10). The degradation rate was negatively correlated with OM (r $\geq$ - 0.807, p < 0.001), and CEC (r $\geq$ - 0.803, p < 0.001), positively, but not significantly correlated with clay content, as well as soil pH and CaCO$_3$ for all three soils (Table 8). Furthermore, dimethenamid-p is stable to hydrolysis, but photolysis is relatively quick (3-5 weeks) in water and in soil (EFSA, 2018). In this study, an increase of dissipation half-life of herbicides was observed mainly in soils with higher OM content, and this has also been observed for dimethenamid-p in similar conditions, even though dimethenamid-p has higher water solubility and lower K$_{FOC}$ values (Table 2) in comparison with other herbicides. Our finding is in line with previous studies, suggesting that dimethenamid-p is initially dissolved in soil solution or bound onto soil constituents and then desorbed into the soil solution, where it is likely degraded quickly by microbes (Kočárek et al., 2018).

The pendimethalin's half-life reported here was shorter than the value of 182.3 days as presented in PPDB (2019). The calculated half-life values were extremely short, especially in Haplic Chernozem (more than 10 times) and Arenic Regozem (around 8 times) (Table 10). Despite this, the average pendimethalin half-life value was in the same range (24.4–34.4 days) as those determined by Kočárek et al. (2016) in a Haplic Chernozem soil under greenhouse conditions. These results indicate that pendimethalin was rapidly degraded in the studied soils; hence, dissipation rates were not related with the hydrophobicity and the extent of adsorption,

even though the pendimethalin was strongly adsorbed by all three soils (Table 3). A positive correlation was observed between degradation rate and clay content ($r \geq 0.536$, $p < 0.05$) and, negative correlation with OM ($r \geq -0.741$, $p < 0.01$), and CEC ($r \geq -0.737$, $p < 0.01$), and, a negative but not significant correlation was observed with $CaCO_3$ (Table 11).

The observed dissipation half-lives (from 38 to 51 days) for flurochloridone in three soils were matching those previously reported, varying from 9 to 66 days (EFSA 2010). A longer dissipation half-life (51 days) was found in Arenic Regozem (Table 10). Available data on flurochloridone soil persistence under laboratory conditions is scarce. Walker (1987) demonstrated a similar result after incorporation of flurochloridone in a sandy loam soil incubated in the laboratory at 20 and 10° C. Flurochloridone soil half-lives were 40 and 90 days, respectively. According to information presented in PPDB. (2019), flurochloridone is moderately persistent and its main degradation pathway is by chemical hydrolysis. The degradation rate of flurochloridone positively correlated with clay content ($r \geq 0.994$, $p < 0.001$), and negatively with $CaCO_3$ ($r \geq -0.783$, $p < 0.05$), and a positive but not significant correlation was observed with OM and CEC. A slightly negative correlation was found with soil pH when evaluated for all three soils (Table 11). A strong positive correlation between clay content and degradation rate suggests that clay content would be the predominant factor to determine the dissipation of flurochloridone in soil. In fact, a non-significant relationship was found between degradation rate and the OM content for all three soils. In addition, it could also be hypothesized that degradation of flurochloridone may decrease (longer half-life) in soils with lower pH.

The observed half-life values ranged from 37 to 57 days for s-metolachlor and the highest value was found in Haplic Fluvisol (Table 10). The degradation of s-metolachlor has been previously evaluated in many studies. Our results showed similar dissipation half-lives (9.6 – 81 days) to those published by Rice et al. (2002) and were slightly higher than the dissipation half-lives evaluated in five different soils by Wu et al. (2011) (37.9 – 49.5 days). Assuming that s-metolachlor was more persistent in soil with higher OM content, compared to soils with lower OM content (Table 10). Therefore, degradation rate was negatively correlated with OM content ($r \geq -0.583$, $p < 0.05$), and CEC ($r \geq -0.579$, $p < 0.05$), whereas a significant positive correlation was found with clay content ($r \geq 0.702$, $p < 0.01$) for all the evaluated soils (Table 11). Accordingly, decreasing soil OM content and increasing clay content results in a decreased dissipation half-life of s-metolachlor in soils. Statistically significant negative correlation with OM content has been observed previously by Wu et al. (2011), who studied degradation of s-

metolachlor in soils collected from five agricultural fields in China with varying OM content (1.22 - 3.94%); it was concluded that s-metolachlor degraded faster in soils with a higher OM content.

In summary, it seems likely that the degradation of herbicides in soils was affected by several parameters, including OM content, clay content, CEC and soil pH. However, in most cases, OM content showed a statistically significant relationship with the herbicide's adsorption coefficient and the rate of degradation. This suggests that they may be inversely related. It should also be noted that sorption was negatively correlated with pH (Table 7), and it is frequently assumed that degradation is promoted by having a greater proportion of the chemical available in solution (Villaverde et al., 2008). As expected, there was a negative correlation between the adsorption coefficient (K_F) and degradation rate, based on the result provided by linear regression analysis (Table 11). It seems that the use of the adsorption coefficient would be useful in predicting the corresponding degradation or persistence for the studied herbicides in soil.

5.3 Dissipation of herbicides in the soil

The dissipation of herbicides in soil includes degradation processes: chemical, photochemical, and biological processes as well as sorption to soil solid phases, surface runoff, downwards and capillary movement in the soil solution, and volatilization (Gluhar et al., 2019). Dissipation of herbicides in soil was calculated as the percentage amounts of herbicides remaining in comparison to the applied rate in both soil layers (0-5 cm and 5-10 cm) since herbicides were applied at different application rates. Herbicide concentrations for both application rates (×1 and ×2) significantly declined from 6 days after the application of herbicides in all three experimental years. In most cases, 30 days after herbicide applications, 20-70 % of the applied herbicide was almost similar for both application rates (×1 and ×2), and still detected in the 0-5 cm soil layer. Figures 4, 5, and 6 shows the dissipation of herbicides in 0-5 cm soil layer at the recommended application dose (×1) for each experimental year.

Figure 3. Herbicide dissipation (% of the applied rate in soil layer 0-5 cm) at recommended dose (×1), after herbicide application in 2015, at three locations: (Suchdol – Haplic Chernozem; Dobroměřice – Haplic Fluvisol and Volárna – Arenic Regozem).

The duration of the field experiments were 95-130 days, however certain herbicides dissipated earlier, within 30 days. Dimethenamid-P and pethoxamid were found to be non-persistent in all three studied soils. In the case of dimethenamid-P there was shown that 20-45 % of the applied rate was detected 30 days after application. Pethoxamid showed that 15-45 % of the applied rate was detected 30 days after application. Other tested herbicides were found moderately persistent in soils and showed significantly longer persistence, 48-75 % of the applied rate was detected after 30 days of application.

Herbicide persistence was much higher in Haplic Fluvisol than in Arenic Regozem and Haplic Chernozem. The findings suggest that weather conditions, especially rainfall, have an important influence on herbicide behavior and might have a greater impact than soil properties.

Figure 4. Herbicide dissipation (% of the applied rate in soil layer 0-5 cm) at recommended dose (×1), after herbicide application in 2016, at three locations: (Suchdol - Haplic Chernozem; Dobroměřice - Haplic Fluvisol and Volárna - Arenic Regozem).

Several studies have demonstrated the different dissipation of herbicides in different experimental years (Jursík et al., 2013, 2016, Andr et al., 2017). In our study, herbicides persistence was substantially lower (shorter half-life) at the ×1 rate compared to the ×2 rate (Table 13-14). According to Kočárek et al. (2016), increasing the application rate twice reduced the half-life of pendimethalin. Lin et al. (2007), found that doubling the application rate resulted in a longer pendimethalin half-life. In contrast, several researchers found that doubling the application rate did not affect herbicide dissipation (Tsiropoulos and Miliadis, 1998; Kewat et al., 2001; Jursík et al., 2016).

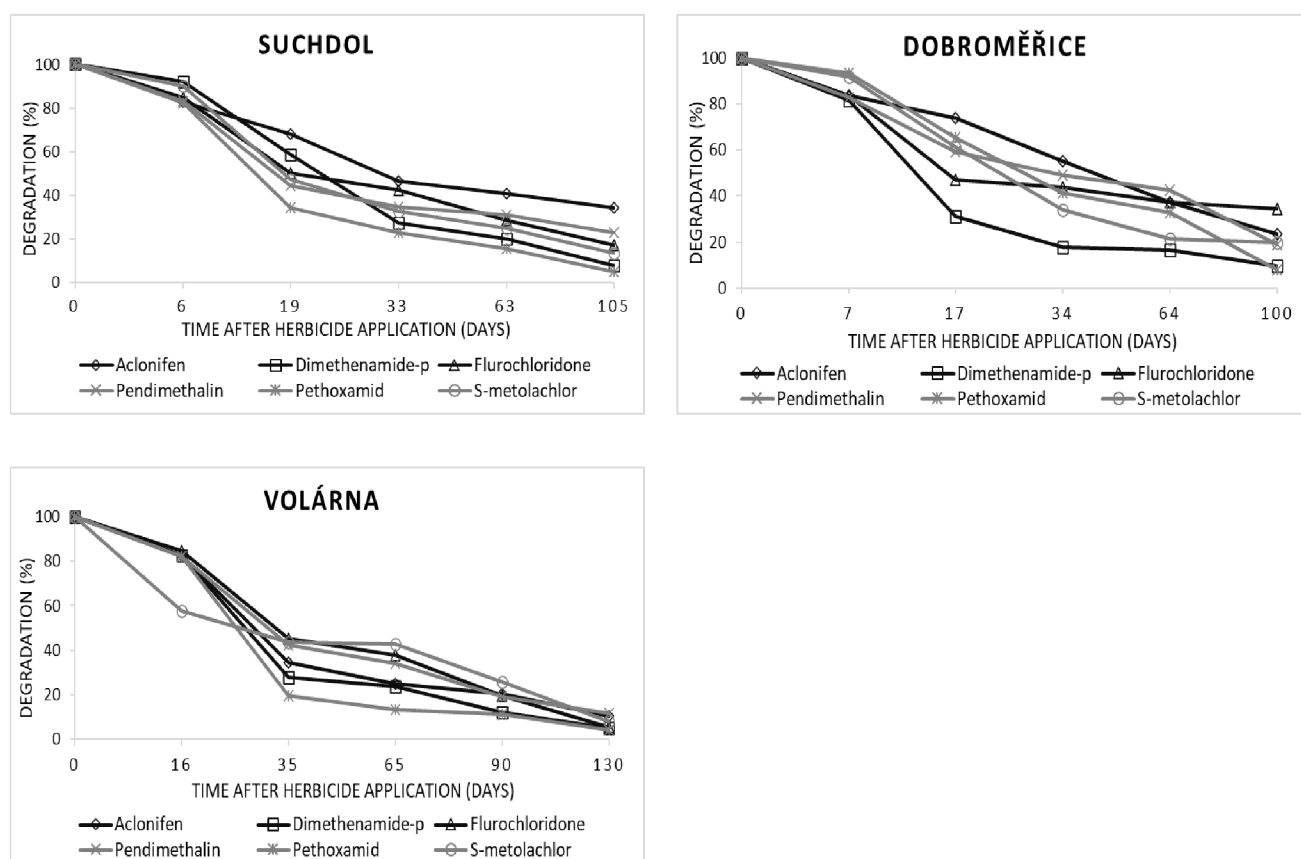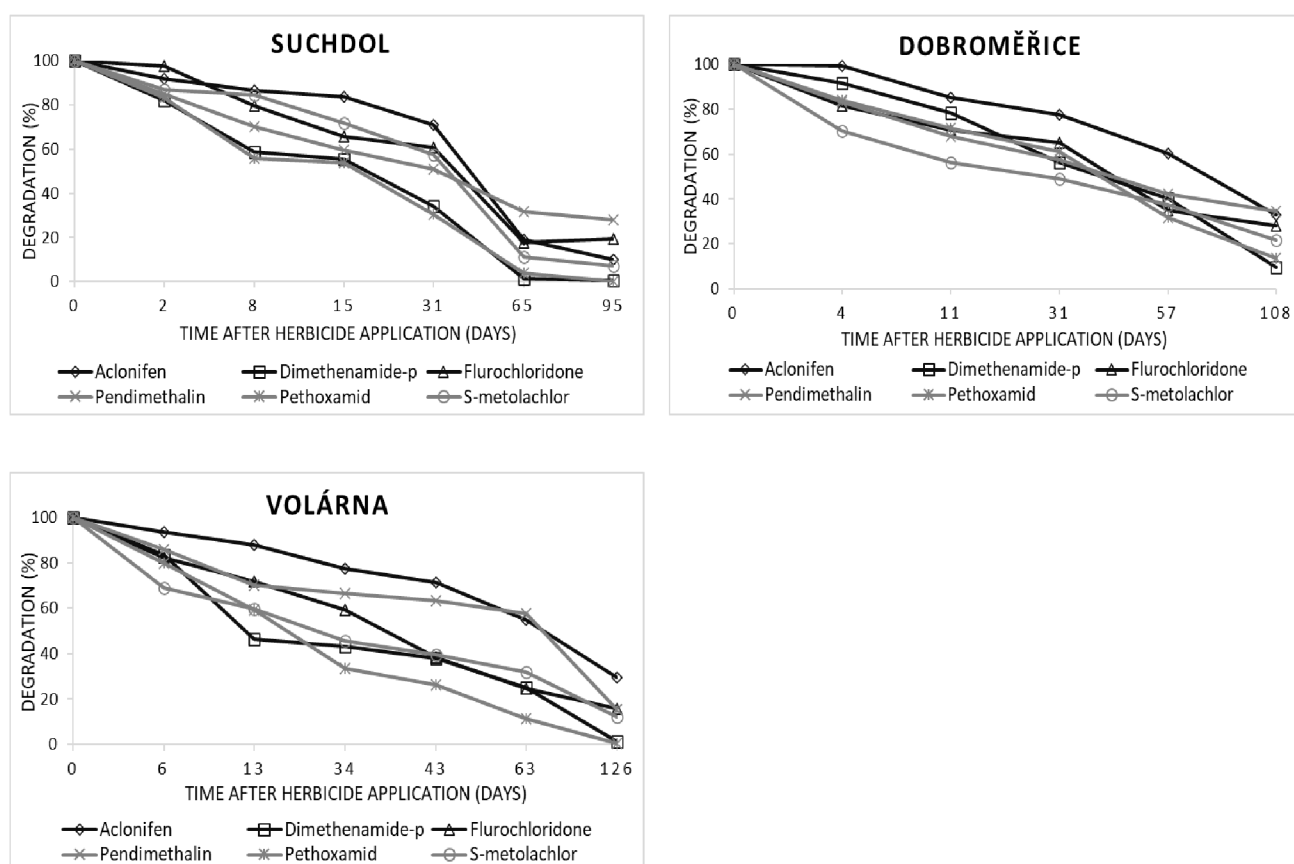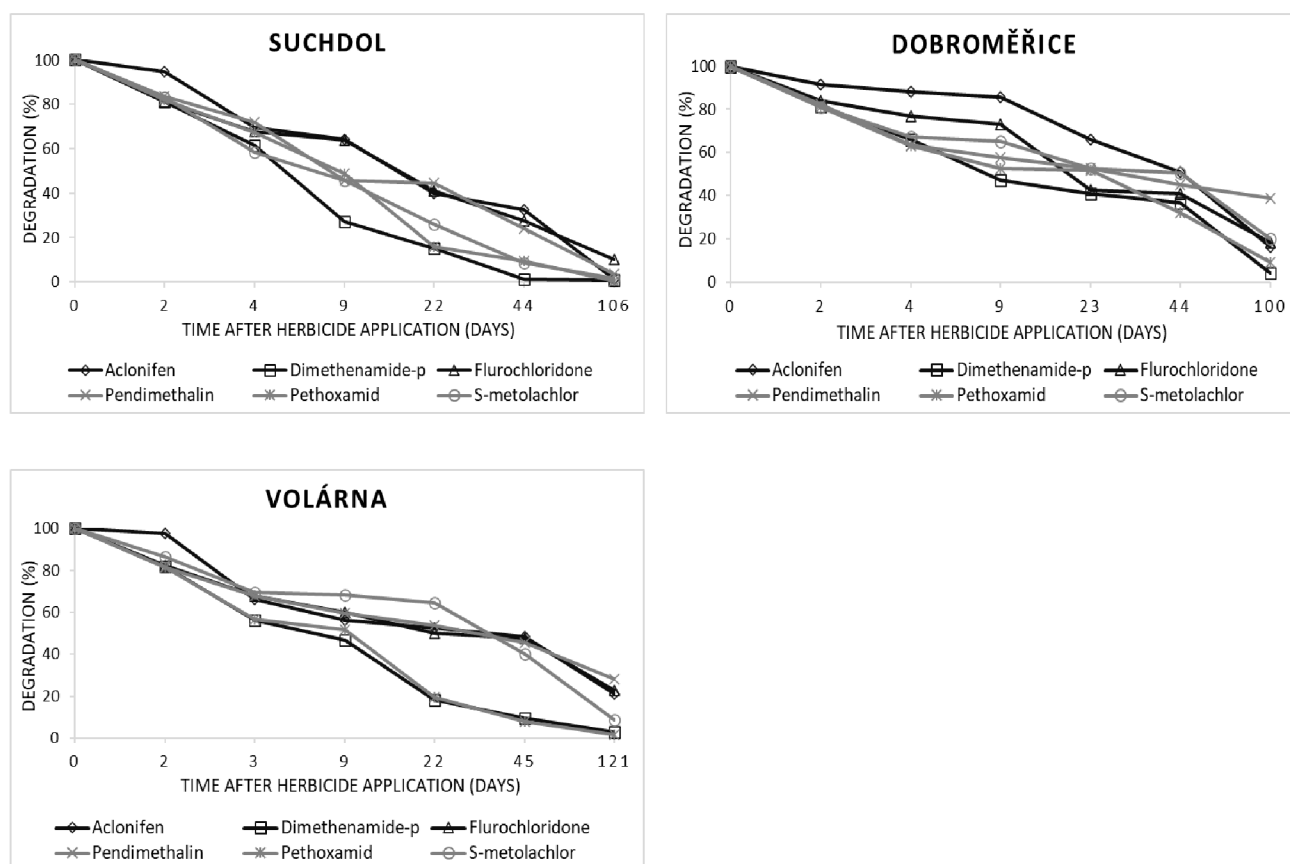**Figure 5.** Herbicide dissipation (% of the applied rate in soil layer 0-5 cm) at recommended dose (×1), after herbicide application in 2017, at three locations: (Suchdol - Haplic Chernozem; Dobroměřice - Haplic Fluvisol and Volárna - Arenic Regozem).

5.4 Vertical transport of herbicides in the soil profile

The degree of herbicide vertical transport (leaching) in the soil profile is depicted in Figure 3. The highest concentrations of herbicides were detected in the 0–5 cm soil layer in all tested soils. This was done by measuring the percentage of herbicide detected in the 5 – 10 cm of the soil layer. The vertical transport of herbicides was affected by soil type, the herbicide properties, and weather conditions in experimental years. In 2015 and 2016, rather low amounts of herbicides (up to 2% of applied rate) except dimethenamid-p and aclonifen were found in the 5–10 cm soil layer. In 2017 the greatest vertical transport was observed for dimethenamid-p and pethoxamid (7% and 8% of the applied rate, respectively) in Arenic Regozem. Among the investigated soils, Arenic Regozem (Volárna) had the highest leaching in the 5 - 10 cm soil layer, particularly in 2017. Herbicides transport through the soil profile has the potential risk to contaminate groundwater resources (Mueller et al., 1999; Si et al., 2009). Herbicide transport and dissipation are strongly affected by herbicide physical and chemical characteristics, soil properties (Kočárek et al., 2010), and weather conditions (Jursík et al., 2013; Andr et al., 2017). Sigua et al. (1993) and Jursík et al. (2013), examined the effect of rainfall on herbicide leaching and found that herbicide behavior in the soil is influenced by immediate rainfall after herbicide application.

Several models are available to evaluate the environmental pollution risk of pesticides and take into account the adsorption and degradation characteristics. Groundwater Ubiquity Score (GUS) (Gustafson, 1989) is one of the most commonly used models:

$$GUS = \log DT_{50} \times \left(4 - \log K_{OC}\right) \qquad [6]$$

With GUS, pesticides can be classified as "leachers" (GUS > 2.8), "transition" (2.8 < GUS < 1.8) and "non-leachers" (GUS < 1.8). In this study, dimethenamid-P, S-metolachlor, and pethoxamid showed the highest GUS values calculated for the three studied soils (Table 12).

Dimethenamid-P residual concentrations in the 5-10 cm soil layer were found to be substantially higher in 2016 and 2017. In 2015, however, extremely low dimethenamid-P concentrations were detected in almost all sampling terms (0,6,9,33 and 105 days). Dimethenamid-P leaching in a soil layer was investigated by Kočárek et al. (2018), who discovered that dimethenamid-P was detected mostly in the top layer (0-5 cm) until 44 days after herbicide application. According to our findings, pethoxamid and S-metolachlor leaching may

occur only on sandy soil with a poor sorption capacity (Arenic Regozem). Dhareesank et al. (2006), reported that pethoxamid has a relatively good environmental profile.
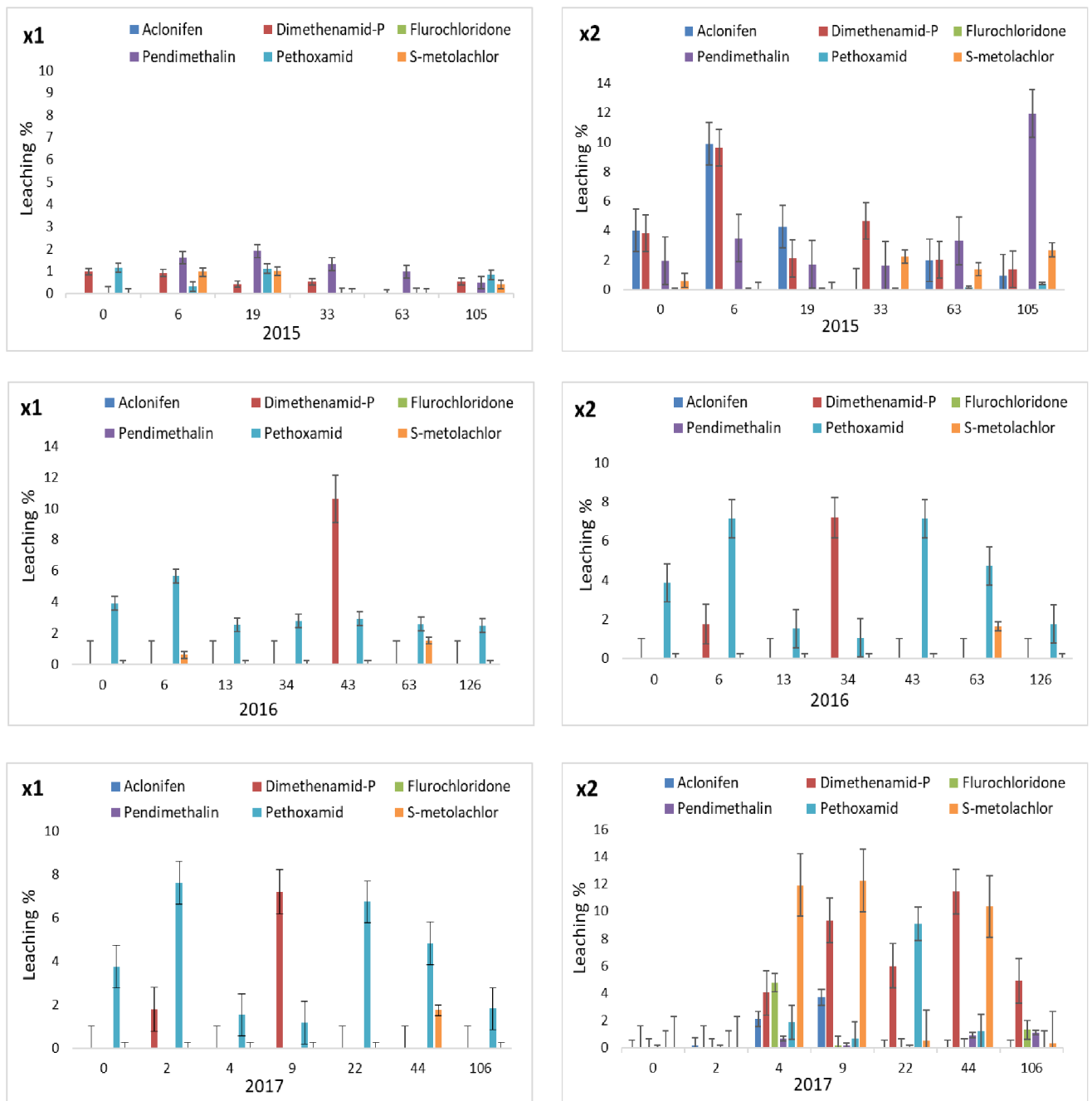
Figure 6. Vertical transport (% of the applied rate in soil layer 5-10 cm) of tested herbicides at two rates (×1 and ×2) of recommended dose in three soils: Haplic Chernozem, Haplic Fluvisol and Arenic Regozem.

Table 12. Groundwater Ubiquity Score (GUS), determined for each herbicide in the three soils (Haplic Chernozem, Haplic Fluvisol and Arenic Regozem) for three experimental years.

		Experimental years			
2015		**2016**		**2017**	
Herbicides	GUS	Herbicides	GUS	Herbicides	GUS
Haplic Chernozem					
Pendimethalin	0,42	Pendimethalin	0,44	Pendimethalin	0,36
Aclonifen	0,93	Aclonifen	0,80	Aclonifen	0,69
Flurochloridone	1,52	Flurochloridone	1,50	Flurochloridone	1,44
S-Metolachlor	2,53	S-Metolachlor	2,31	S-Metolachlor	2,03
Pethoxamid	2,27	Pethoxamid	1,79	Pethoxamid	1,88
Dimethenamide-P	2,85	Dimethenamide-P	2,13	Dimethenamide-P	2,16
Haplic Fluvisol					
Pendimethalin	0,27	Pendimethalin	0,30	Pendimethalin	0,29
Aclonifen	0,65	Aclonifen	0,70	Aclonifen	0,61
Flurochloridone	1,48	Flurochloridone	1,45	Flurochloridone	1,23
S-Metolachlor	2,44	S-Metolachlor	2,54	S-Metolachlor	2,44
Pethoxamid	2,26	Pethoxamid	2,39	Pethoxamid	2,23
Dimethenamide-P	2,71	Dimethenamide-P	2,94	Dimethenamide-P	2,54
Arenic Regozem					
Pendimethalin	0,40	Pendimethalin	0,42	Pendimethalin	0,43
Aclonifen	0,99	Aclonifen	1,19	Aclonifen	1,12
Flurochloridone	1,51	Flurochloridone	1,57	Flurochloridone	1,55
S-Metolachlor	2,74	S-Metolachlor	2,69	S-Metolachlor	2,58
Pethoxamid	2,62	Pethoxamid	2,19	Pethoxamid	2,22
Dimethenamide-P	3,02	Dimethenamide-P	2,76	Dimethenamide-P	2,63

According to Inoue et al. (2010), S-metolachlor leaching was significantly affected by rainfall up to the 20 cm soil layer when rainfall was 80 mm. Moreover, S-metolachlor leaching into groundwater is predominantly caused by macropore flow, which is higher in clay soil than in sandy soil and occurs mostly during long dry seasons in the spring and summer (Inoue et al., 2010). Our results, on the other hand, are consistent with those of Si et al. (2009), who observed that S-metolachlor leaches more intensely in sandy soils than in clay soils. Pendimethalin, aclonifen, and flurochloridone had the lowest percentage of leaching since they were not detected in the 5-10 cm of the soil layer. Only in the case of aclonifen a low amount of leaching (up to 2% of applied rates) was found in the 5-10 cm soil layer in 2015.

5.5 Herbicides half-life

Tables 13 and 14 indicate the determined first-order rate constants, coefficients of determination (R^2), and dissipation half-life (DT_{50}) for each herbicide at both (×1 and ×2) application rates. The R^2 values demonstrate that the first-order kinetic equations are well-fitted to the obtained data for herbicide dissipation in all three soils. In a three-year experiment, the herbicides' field DT_{50} values for ×1 application rate ranged from 21.1 to 55.4 days for pendimethalin, 17.1 to 61.2 days for aclonifen, 26.3 to 50.4 days for flurochloridone, 16.6 to 40.8 days for S-metolachlor, 11.3 to 34.7 days for pethoxamid, and 11.8 to 34.05 days for dimethenamid-P, respectively. The field DT_{50} values for ×2 application rate ranged from 20.7 to 69.1 days for pendimethalin, 21.7 to 68.1 days for aclonifen, 27.9 to 51.9 days for flurochloridone, 18 to 44.9 days for S-metolachlor, 12.7 to 36.1 days for pethoxamid, and 13.1 to 42.6 days for dimethenamid-P, respectively. It is well known that the degradation of herbicide in field and laboratory conditions are not the same. Several factors may have an impact on the degradation in field conditions. For instance, herbicide properties, soil characteristics, especially physiochemical properties, and weather conditions (Kočárek et al., 2018; Jursík et al., 2013; 2016; 2020). In our case, the DT_{50} values of pendimethalin and aclonifen in field conditions were quite long for both application rates.

The pendimethalin half-lives were in the same range as those reported by Kočárek et al. (2018) with half-lives ranging from 43 to 44.6 days in Haplic Fluvisol under field conditions. However, the DT_{50} values for pendimethalin were significantly higher than previously reported findings 14 and 21 days (Lin et al., 2007), and 20.9 to 31.3 days (Pervinder et al., 2017) in sandy loam and loamy sand soils.

Flurochloridone, S-metolachlor, pethoxamid, and dimethenamid-P had significantly shorter DT_{50} values when compared to laboratory conditions (Table 10). The flurochloridone DT_{50} values were considerably lower than those reported by Rouchaud et al. (1997), who found flurochloridone half-lives of 41 to 80 days repeatedly applied on preemergence in potato crops under field conditions over two years. Pethoxamid DT_{50} values were somewhat higher at both application rates (×1 and ×2) than those reported by the PPDB (2019), (14.8 days), mainly in Haplic Fluvisol during a three-year experiment. Kočárek et al. (2018), obtained extremely low half-life values (8.8 days) for dimethenamid-P in field conditions.

According to the obtained results, the longest DT_{50} values for herbicides were observed in Haplic Fluvisol in all three years of the experiment. In 2017, however, all herbicides had much

lower DT_{50} values. We can assume that this is due to higher precipitation (63.1-76.0 mm), which may impact herbicide disappearance from the soil through processes such as biodegradation, leaching and surface run-off. Gluhar et al. (2019) investigated herbicide dissipation and its environmental impacts on leaching and run-off. They discovered the non-significant effect of rainfall on S-metolachlor leaching and obtained a DT_{50} value of 12.3 days. Among the three soils, Haplic Chernozem demonstrated the fastest degradation and the shortest half-life values for both application rates ($\times 1$ and $\times 2$), supporting the study's hypothesis.

Table 13. The first-order rate constants, k_R (day^{-1}), coefficients of determination, R^2, and dissipation half-lives, DT$_{50}$ (day), of the herbicides in field conditions for ×1 application rate.

Soils and experimental years	Pendimethalin			Aclonifen			Flurochloridone			S-Metolachlor			Pethoxamid			Dimethenamide-P		
	k_R	R^2	DT$_{50}$	k_R	R^2	DT$_{50}$	k_R	R^2	DT$_{50}$	k_R	R^2	DT$_{50}$	k_R	R^2	DT$_{50}$	k_R	R^2	DT$_{50}$
2015																		
Suchdol	0.019	0.809	36.9	0.015	0.899	47.4	0.020	0.941	34.9	0.021	0.960	32.8	0.032	0.924	21.7	0.026	0.983	26.9
Dobroměřice	0.019	0.938	36.9	0.015	0.996	46.2	0.014	0.757	50.4	0.020	0.967	35.3	0.024	0.987	28.3	0.027	0.800	25.8
Volárna	0.018	0.912	39.3	0.024	0.912	28.2	0.022	0.946	31.4	0.019	0.893	36.7	0.026	0.953	26.5	0.025	0.896	27.9
Average DT$_{50}$ value			**37.7**			**40.6**			**38.9**			**34.9**			**25.5**			**26.9**
Standard deviation			1.4			10.8			10.1			2.0			3.4			1.1
Range			2.4			19.2			19			3.9			6.6			2.1
2016																		
Suchdol	0.016	0.938	43.4	0.025	0.968	27.6	0.021	0.949	33	0.028	0.971	24.5	0.061	0.970	11.3	0.059	0.962	11.8
Dobroměřice	0.012	0.884	55.4	0.011	0.967	61.2	0.015	0.929	46.5	0.017	0.889	40.8	0.020	0.947	34.7	0.020	0.994	34.05
Volárna	0.015	0.946	47.3	0.013	0.982	54.8	0.019	0.952	35.9	0.020	0.913	34.1	0.045	0.977	15.5	0.033	0.817	21.1
Average DT$_{50}$ value			**48.7**			**47.9**			**38.5**			**33.1**			**20.5**			**22.3**
Standard deviation			6.1			17.8			7.1			8.2			12.5			11.2
Range			12			33.6			13.5			16.3			23.4			22.25
2017																		
Suchdol	0.033	0.946	21.1	0.040	0.979	17.1	0.024	0.920	29.1	0.042	0.969	16.6	0.054	0.963	12.8	0.057	0.942	12.2
Dobroměřice	0.014	0.740	48.3	0.019	0.989	36.7	0.026	0.823	26.3	0.020	0.866	35.2	0.025	0.864	27.3	0.033	0.906	21
Volárna	0.013	0.827	52.02	0.016	0.833	42.8	0.020	0.685	33.8	0.023	0.889	29.6	0.043	0.875	16.1	0.038	0.846	18.3
Average DT$_{50}$ value			**40.5**			**32.2**			**29.7**			**27.1**			**18.7**			**17.2**
Standard deviation			16.9			13.4			3.8			9.5			7.6			4.5
Range			30.92			25.7			7.5			18.6			14.5			8.8

Table 14. The first-order rate constants, k_R (day^{-1}), coefficients of determination, R^2, and dissipation half-lives, DT_{50} (day), of the herbicides in field conditions for ×2 application rate.

Soils and experimental years	Pendimethalin			Aclonifen			Flurochloridone			S-Metolachlor			Pethoxamid			Dimethenamide-P		
	k_R	R^2	DT_{50}	k_R	R^2	DT_{50}	k_R	R^2	DT_{50}	k_R	R^2	DT_{50}	k_R	R^2	DT_{50}	k_R	R^2	DT_{50}
2015																		
Suchdol	0.019	0.978	35.9	0.010	0.905	68.1	0.019	0.915	36.2	0.022	0.906	31.7	0.033	0.975	20.9	0.028	0.933	24.9
Dobroměřice	0.013	0.955	51.5	0.022	0.990	31.9	0.022	0.927	31.4	0.027	0.969	25.9	0.026	0.956	26.1	0.031	0.976	22.3
Volárna	0.013	0.939	53.8	0.021	0.960	32.7	0.016	0.916	42.3	0.021	0.990	32.2	0.021	0.952	32.3	0.039	0.990	17.7
Average DT_{50} value			**47.1**			**44.2**			**36.6**			**29.9**			**26.4**			**21.6**
Standard deviation			9.7			20.7			5.5			3.5			5.7			3.6
Range			17.9			36.2			10.9			6.3			11.4			7.2
2016																		
Suchdol	0.017	0.949	41.2	0.032	0.924	21.7	0.017	0.939	40.1	0.026	0.992	26.4	0.042	0.952	16.5	0.051	0.981	13.6
Dobroměřice	0.010	0.973	69.1	0.017	0.893	39.8	0.016	0.920	42.6	0.015	0.929	44.9	0.019	0.986	36.1	0.016	0.992	42.6
Volárna	0.019	0.943	36.1	0.021	0.924	33.2	0.013	0.985	51.9	0.036	0.917	19.3	0.032	0.937	21.9	0.028	0.924	24.6
Average DT_{50} value			**48.8**			**31.6**			**44.9**			**30.2**			**24.8**			**26.9**
Standard deviation			17.8			9.2			6.2			13.2			10.1			14.6
Range			33			18.1			11.8			25.6			19.6			29
2017																		
Suchdol	0.033	0.899	20.7	0.031	0.963	22.1	0.025	0.935	27.9	0.038	0.954	18	0.055	0.990	12.7	0.053	0.970	13.1
Dobroměřice	0.018	0.920	39.4	0.019	0.981	35.9	0.016	0.952	44.2	0.018	0.922	39.4	0.030	0.961	22.8	0.025	0.931	28.1
Volárna	0.012	0.795	57.3	0.029	0.915	23.4	0.013	0.864	51.1	0.023	0.963	30.3	0.040	0.978	17.3	0.038	0.956	18.3
Average DT_{50} value			**39.1**			**27.1**			**41.1**			**29.2**			**17.6**			**19.8**
Standard deviation			18.3			7.6			11.9			10.7			5.1			7.6
Range			36.6			13.8			23.2			21.4			10.1			15

6. Conclusion

The research in this thesis focused on dissipation half-life and mobility of studied herbicides and to evaluate the effect of soil properties on herbicide behavior. Furthermore, to assess the implications of the results in terms of soils sorption and degradation.

For laboratory study: The sorption of herbicides increased in the order dimethenamid-P < pethoxamid < S-metolachlor < flurochloridone < aclonifen < pendimethalin. The largest K_F values for all herbicides were obtained in Haplic Fluvisol with higher SOM (> 3.45%). Furthermore, herbicides, particularly pendimethalin and aclonifen, have a greater affinity for soil with higher SOM. The results concluded that the presence of a greater concentration of SOM may increase the adsorption of these herbicides. Therefore, it can be concluded that the SOM was the most important factor influencing herbicide sorption. Linear regressions for pesticide sorption prediction might be a valuable tool for avoiding groundwater pollution and optimizing field application management.

Degradation of herbicides was followed by first-order kinetics and increased in the order aclonifen < pethoxamid < dimethenamid-P < pendimethalin < flurochloridone < S-metolachlor. The dissipation half-lives of herbicides were significantly longer in Haplic Fluvisol (20-57 days) compared to Arenic Regozem (17-51 days) and Haplic Chernozem (14-38 days). The degradation of herbicides is mainly controlled by clay and SOM content. The longer half-lives were mainly found in soils with higher SOM content. The influence of clay contents upon degradation was verified for pendimethalin, aclonifen, flurochloridone and S-metolachlor. The multiple linear regressions showed that degradation rate of herbicides pendimethalin, S-metolachlor, pethoxamid, and dimethenamid-P were negatively effected by CEC and SOM content. No correlation was found between the soil pH and studied herbicides, except for pethoxamid. The linear regression and Pearson correlation test showed that the adsorption coefficient is most likely to play a significant role in predicting soil degradation of the studied herbicides.

For field study: According to laboratory experiments, the degradation rate was very slow, with higher DT_{50} values in the field experiment for the herbicides pendimethalin and aclonifen. In contrast, the herbicides flurochloridone and S-metolachlor showed faster degradation rate, with shorter DT_{50} values in the field experiment. Pethoxamid and dimethenamid-P showed faster degradation in the field, with shorter DT_{50} values, corresponding to laboratory results.

Field dissipation half-life findings were considerably different at each site over the three-year studies, and herbicide concentrations for both application rates (×1 and ×2), were dramatically decreased from 6 days after herbicide application in all three experimental years. Dimethenamid-P and pethoxamid were found to be non-persistent in all three tested soils, with only 20-45 % and 15-45 % of the applied rate detectable 30 days after application, respectively. Other herbicides were found to be moderately persistent showing 48-75 % of the applied rates after 30 days, with significantly longer persistence.

In 2015 and 2016, rather low amounts of herbicides (up to 2% of applied rate) except dimethenamid-p and aclonifen were found in the 5-10 cm soil layer. In 2017, the greatest vertical transport was observed for dimethenamid-p and pethoxamid (7% and 8% of the applied rate, respectively, in the layer 5-10 cm) in Arenic Regozem. Among the investigated soils, Arenic Regozem (Volárna) had the highest leaching in the 5-10 cm soil layer, particularly in 2017. Dimethenamid-P, S-metolachlor, and pethoxamid had the highest GUS leaching values, with (GUS > 2.13) for dimethenamid-P, GUS > 2.31 for S-metolachlor, and GUS > 1.79 for pethoxamid, and were classified as "leachers" and "transition". Pendimethalin, aclonifen, and flurochloridone had the lowest percentage of leaching since they were not identified in the 5-10 cm of the soil layer.

The herbicides' field DT_{50} values for ×1 application rate ranged from 21.1 to 55.4 days for pendimethalin, 17.1 to 61.2 days for aclonifen, 26.3 to 50.4 days for flurochloridone, 16.6 to 40.8 days for S-metolachlor, 11.3 to 34.7 days for pethoxamid, and 11.8 to 34.05 days for dimethenamid-P, respectively. The field DT_{50} values for ×2 application rate ranged from 20.7 to 69.1 days for pendimethalin, 21.7 to 68.1 days for aclonifen, 27.9 to 51.9 days for flurochloridone, 18 to 44.9 days for S-metolachlor, 12.7 to 36.1 days for pethoxamid, and 13.1 to 42.6 days for dimethenamid-P, respectively. According to the obtained results, the longest DT_{50} values for herbicides were observed in Haplic Fluvisol in all three years of the experiment. In 2017, however, all herbicides had much lower DT_{50} values. Among the three soils, Haplic Chernozem demonstrated the fastest degradation and the shortest half-life values for both application rates (×1 and ×2), supporting the study's hypothesis.

Based on the findings, the herbicides' half-life values (field experiment) were significantly increased at doubled (×2) application rate in all studied soils. Shorter DT_{50} values and faster herbicide degradation at application rate (×1) could be attributed primarily to soil type, pH, organic matter content and environmental conditions. Since the herbicides were applied as a spray to the bare soil, the degradation could be due to photochemical process as well as

volatilization. On the other hand, soil binding and microbial degradation should be considered when considering the environmental implications of preemergence herbicides. Further laboratory and field investigations need to be carried out to accurately characterize the degradation pathway of studied herbicides and determine the effect of each factor (e.g., microbial decomposition, photochemical reactions, and volatilization) on degradation.

The following suggestions can be made based on the results of laboratory and field experiments about the usage of the investigated herbicides in agricultural practice for preemergence purposes.

When applying herbicides with high water solubility, such as pethoxamid, S-metolachlor, and dimethenamid-P, it is recommended to follow the application dose of each herbicide to avoid potential groundwater pollution. Furthermore, herbicide sorption behavior should be considered when applying herbicides to soils, particularly those with high organic matter content, because all herbicides demonstrated the highest adsorption values in soils with high organic matter content.

Finally, important recommendations to know for herbicide application include soil water content and field surface preparation, application time, application dose, and meteorological conditions at the field site.

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