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Doctoral Program in Environmental Science

**INVESTIGATION OF SORPTION BEHAVIOR OF ORGANIC
PESTICIDES ON SOIL**

Ph.D. Dissertation

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LIST OF ABBREVIATIONS

a.i.	Active Ingredient
ASTM :	American Society for Testing Methods
CCPR	Codex Committee on Pesticide Residues
DTA	Differential Thermal Analysis
FAO	Food and Agriculture Organization of the United Nations
FDA	Food and Drug Administration
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
IR	Infrared Spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
K _{clay}	Adsorption coefficient related to the soil clay content
K _d	Distribution coefficient
K _f	Freundlich sorption coefficient
K _{oc}	Adsorption coefficient related to the soil organic carbon content
MRL	Maximum Residue Level
MS	Mass Spectrometry
MW	Molecule Weight
NPD	Nitrogen-Phosphorous selective Detector
OECD	Organization for Economic Co-operation and Development
pKa	Logarithm of dissociation constant
P _{ow}	Octanol-water partition coefficient
RSD	Relative Standard Deviation
US EPA	US Environmental Protection Agency
UV	Ultraviolet Spectroscopy
VIS	Visible Spectroscopy
WHO	World Health Organization

1. INTRODUCTION

1.1. THE ROLE OF AGROCHEMICALS IN MODERN ECONOMY

It is generally acknowledged that the application of chemicals for agriculture as well as plant protection and animal health has large benefits to society. Pesticide use has been one of the major factors in improving efficiency in agriculture. Notwithstanding the positive qualities, the present use of pesticides also causes negative environmental effects. In general, during and after application of pesticides a substantial amount of it ends up in soil, ground- and surface water and air. The presence of pesticides in these domains may constitute considerable negative effects to ecosystems and human health. Human health may be affected by pesticide residues in food and drinking water and by direct exposure due to application, while ecosystems may be affected by loss of biodiversity and decrease in population of sensitive living system. In fact, the use of pesticides in agriculture can affect wildlife both directly, through accidental poisoning, and indirectly, by depleting the food chains. In many respects, the greatest potential for unintended effects of pesticides is through contamination of the soil and the hydrologic system. The potential pollution and environmental risk resulting from the use of pesticides have been discussed in details in the literature (BARBAS and RESEK 1996, CLAPP et al. 1993, COOPER 1993, EAGLE 1988). On the other hand, the assessment of effects on the environment is an integral part of the process of product development, and official authorization and registration. Environmental risk assessment of pesticides as well as veterinary medicinal products, their ingredients and relevant metabolites are strictly regulated and detailed in the European Union by the directives 91/414/EEC and 81/852/EEC. This assessment should be designed to identify potential hazards, and thus adverse effects on the environment to be quantified and evaluated in relation to benefits. Considerable efforts have been taken by international organizations e.g. WHO, FAO, OECD, FDA, US EPA to clarify interaction of agrochemicals with the environment and ecosystems to reduce risk. Concern of national authorities regarding the pesticides as potential environmental risk sources is reflected well in the law establishing maximum residue limits (MRLs) for drinking water, crops, and certain animal products, and in the fact that use of pesticides is prohibited in the surrounding of water resources, surface water and national parks.

1.1.1. Interactions Between Organic Pesticides and Soil

Following application, a xenobiotic moves between different parts of the environment mainly by mass flow in water, and diffusion\mass flow in the gaseous phase. This reduces the concentration in the treated compartment and transports residues to untreated compartments, e.g. from plant surface to soil or from soil to water. The fate and behavior of pesticides 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 a number of physical, physico-chemical, biochemical, pedological and climatic factors and management practices. The sorption is the crucial phenomenon determining behavior of organic chemicals in the soil environment. The pesticides concentration in the solid, aqueous and gaseous phases and in 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 stream, in surface and ground water pollution.

1.1.1.1. Role of the Organic Matter in the Soil Sorption Processes

The adsorption rate is affected by the properties of the pesticide and the soil characteristics as well. It is rather difficult, if not impossible, to know the sorption mechanism for most soil-pesticide combinations because of the complexity of the solid matrix of soils. Several mechanisms may operate during the interaction between a given pesticide and soil particles, depending of nature of the organo-mineral association.

Several studies have shown that, with respect to mineral components, the content and nature of organic matter in the soil play a key role in the performance of applied pesticides (STEVENSON 1972, HAMEKER and THOMSON 1972, SENESI and CHEN 1989, SENESI 1992, DAWIS 1993, BORGGAARD and STREIBIG 1989, JOHNSON and SIMS 1993, BOLLAG et al. 1992, SHENG et al. 2001, RAMOS et al. 2000). KOZAK at al. (1992, 1994) investigated the effect of soil properties on herbicide adsorption by means of multivariate statistical methods, i.e. regression and

correlation analyses. The organic carbon content and pH only showed substantial contribution to the adsorption of the majority of herbicides under study.

Conventional classification of humic substances divides them into three principal fractions according to the corresponding solubilities at different pH values: fulvic acids which are soluble in both acid and alkali, humic acids which are soluble in alkali, and humin which is not soluble in either medium. These fractions are normally present at equilibrium under natural soil conditions and as soil clays, humic substances in the environment are almost certainly different from those isolated after several treatments (SCHNITZER 1991, SAIZ-JIMENEZ 1996). 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. The natures of the binding forces are determined by the type of mechanisms that operate often simultaneously. These include ionic, hydrogen and covalent bonding, charge-transfer and electron donor-acceptor mechanisms, Van der Waals forces, ligand exchange and hydrophobic bonding or partitioning (SENESI 1992).

Nature of the binding forces and type of mechanisms existing in a pesticide-soil interaction are dependent on chemical characteristic of pesticide as well. Adsorption via ionic bonding, or cation exchange, applies only to those pesticides, which are in the cationic form in solution or can accept a proton and become cationic. Basic pesticides such as s-triazines may become cationic through protonation depending on their basicity and the pH of the system that also governs the degree of ionization of acidic groups of the humic substances. Maximum adsorption of s-triazines on organic soils occurs at pH levels close to the dissociation constant (pK_a) of the herbicide is indicative of ion exchange. However, the pH at the surface of humic substances may be lower than that of the liquid phase, thus protonation of a basic molecule may occur even though the measured pH of the medium is grater than the pK_a of the adsorbate. IR studies of s-triazin-humic acids system showed that ionic bonding can occur between a protonated secondary amino-group of s-triazine and a carboxylate anion, and possibly, a phenolate group of the humic acids (SENESI et al. 1987,a). The presence of numerous oxygen- and hydroxyl-containing functional groups on humic substances renders the formation of H-bonding for pesticides containing suitable complementary groups highly probable, although a strong competition with water molecules may be expected for such site on humic substances. IR and DTA data suggest the occurrence of one or more H-bonds, possibly involving C=O groups of humic substance and secondary amino-groups of the s-triazines. Acidic pesticides, such as chlorophenoxyalkanoic acids, can also be adsorbed by H-bonding onto humic substance at pH values below their pK_a in non-ionized forms through their COOH groups (SENESI et al. 1987,b). Hydrogen bonding is suggested to play an important role in the adsorption onto humic substance of several non-ionic polar pesticides including substituted ureas and

phenylcarbamates. (SENESI and TESTINI 1983). The presence in humic substances of both electron-deficient structures, such as quinones, and electron-rich moieties, such as diphenols, suggest the possible formation of charge-transfer complex, via electron donor-acceptor mechanisms, with pesticides possessing electron donor or electron acceptor properties. The electron-deficient structures in the humic substance remove electrons from the electron-rich donating amine and/or heterocyclic nitrogen atoms of the triazine molecule via single-electron donor-acceptor processes. Substituted ureas also posses electron donor capacity (SENESI and TESTINI 1983, MELCER et al. 1987). Similar electron donor-acceptor mechanisms exist in their herbicidal action in plants, when the photosynthesis inhibition takes place by interference with single-electron transfer in the Hill reaction in chloroplasts. Formation of covalent bond is mostly irreversible incorporation into humic substances of pesticides. Phenylcarbamates, phenylureas, dinitroaniline herbicides and organophosphate insecticides are biodegraded in soil into aromatic amines, such as chloroanilines. These residues can be chemically bound to soil organic matter. Several study confirm the formation of covalent binding of amino groups of the s-triazines to carbonyl and quinone groups of the humic acids. (HAYES 1970, SENESEI and TESTINI 1982, 1983) Van der Waals forces consist of week, short-range dipolar or induced-dipolar attractions, which operate in all adsorbent-adsorbate interactions. These forces are produced from temporary dipoles caused by small perturbation of electronic motion of atoms or molecules. They assume particular importance in the adsorption of non-ionic and non-polar pesticides on suitable sites of humic acids molecules. Since these forces are additive, their contribution increases with the size of the interacting molecule and with its capacity to adapt to the humic acids surface. Adsorption by ligand exchange mechanism involves the replacement of water in the humic substance-cation-water bridge enrichment by suitable adsorbent molecules such as s-triazines and anionic pesticides (NEARPASS 1976). Hydrophobic adsorption is proposed as a pH-independent mechanism for retention by hydrophobic active sites of humic substances of non-polar pesticides. Hydrophobic adsorption is suggested in case of organochlorine insecticides, phenylcarbamates and substituted anilines (BRIGGS 1969). It is considered a possible, additional interaction mechanism for s-triazines and phenylureas (GEVAO et al. 2000). The separated and purified humic substances are often used to study their interaction with organic chemicals in great detail and recognize the binding mechanisms (PICCOLO and CELANO 1994, RICHNOW et al. 1994). The environmental aspects of the interaction between humic substances and pesticides were summarized by SENESEI (1992) and by PICCOLO (1994). The authors concluded that as a result of the irreversibility or reversibility of the adsorption processes, the bound residues can be considered either definitely inactivated, when they become incorporated in the humic polymer, or only momentarily inactivated in bound forms, and they still represent a possible future source of contamination.

1.1.1.2. Role of the Inorganic Colloids in the Soil Sorption Processes

As above mentioned many soils pesticides have a greater affinity for organic surface than for mineral surface. Nevertheless, natural soil colloids are heterogeneous association of inorganic and organic colloid soil constituents. In some cases, up to 90% of the soil organic matter was found to be associated with the mineral fraction of soil and the strong clay-bound fraction of humic acid – fulvic acid does not behave as a separate entity in the interaction of soil constituents with pesticides. On the other hand, in arid zones and those regions, in which contribute low organic matter content of soil and long period of dryness, the mineral surface is the main active sites to adsorb pesticides (HERMOSIN and CORNEJO 1989). Similar condition exists at depths below the root zone, where abiotic interactions of organic pesticides take place on mineral soil colloid surface. The inorganic surface functional group most abundant and with higher reactivity in the soil clay fraction is the hydroxyl group located on the external periphery of a mineral. This kind of hydroxy group is found in silicates and metal oxides and oxyhydroxides. Normally, more than one type of surface hydroxy group can be distinguished on the basis of stereochemical reason. The reactivity of siloxan surface in a 2:1 layer aluminiumsilicate can be originated by isomorphic substitution of Al^{3+} by Fe^{2+} or Mg^{2+} , and Si^{4+} by Al^{3+} resulting in strong complexes with cations and dipolar molecules because of the localization of negative charge. Description of surface functional groups has been given by SPOSITO (1989). The possible mechanisms of interaction between organic pesticides and toxic organic chemicals with clay minerals are partly similar to that are exist in organic matter- organic chemicals interaction. These mechanisms have been reviewed by MINGELGRIN and PROST (1989). The sorption potential of mineral surface in natural soils is blocked by organic matter and hence the contribution of clay minerals to the sorption is depend on both the ratio of clay mineral to organic carbon fractions of the soil and on the nature of the pesticides (PUSINO et al. 1992). The type of soil clay becomes increasingly important when the soil organic carbon content is low. Same studies were shown the cationic pesticide and the basic herbicides are adsorbed by organic and clay soil colloids as well (HERMOSIN et al. 1985, MAQUEDA et al. 1993). The results of study of SANCHEZ-MARTIN and SANCEZ-CAMAZANO (1991) on organophosphorous pesticide adsorption on soil showed that phosphate derivative adsorption is related to clay content. The FT-IR differential spectra of chloroacetanilide herbicides-clay system showed possible formation of hydrogen bonds and charge-transfer bonds between herbicides and clay adsorbents (LIU et al. 2000). MURPHY et al. (1994) have found the K_{oc} adsorption coefficient may influenced by the nature of mineral-organic association. HERMOSIN and CORNEJO (1994) have proposed the use of a K_{clay} instead of a K_{oc} for adsorption studies of polar or ionizable organic molecules in poor organic matter content soils.

1.1.1.3. Affect of the pH on Sorption Processes

As it was mentioned formally, the pH is the other one factor, which has significant influence on adsorption-desorption of pesticides in soils in particular for polar substances. In the case of acidic organic compounds, during the process of protonation-deprotonation, they become either noncharged or negatively charged. Pesticide containing carboxylic acid (COOH) groups or OH groups exhibits certain dissociation constant (pK_a). The pK_a associated with the carboxylic acid is commonly less than 5 (e.g. phenoxyacetic acid), whereas the OH group, if present, most likely exhibits a pK_a of 9 or higher. At pH values approximately two units below the pK_a , the carboxylate group is fully protonated, therefore, the compound's charge is zero. When the pH equal its pK_a , 50% of the carboxylic acid group will be protonated, thus contributing zero charge, while the other 50% will be deprotonated, thus contributing negative charge, When pH is approximately two pH units above the pK_a , 100% of the functional groups will be fully deprotonated. When the pesticide contains amino group (e.g. s-triazines), such a compound is referred to as "basic". When fully deprotonated, its charge would be zero. When its pH equal its pK_a , half of its functional sites will be positively charged and the other half will carry no charge. When its pH is two units below its pK_a , all its functional sites will be positively charged because of protonation. On the other hand, similarly to surface of humic substance, the mineral surface appears to be more acid than the bulk solution. The surface of clay minerals would be 1.5 -3.3 units lower than bulk solution pH, depending on mineralogy. Because of this lower pH at the surface, basic organic compounds would adsorb at the surface via hydrogen bonding at bulk pH values higher than expected. Hydrophobic-hydrophobic interactions responsible for adsorption of organic pesticides by organic surfaces are related to the solubility of the compounds in question and are independent of pH (EVANGELOU 1998).

1.1.2. Physicochemical Interpretation of the Sorption Processes

As with all mass transfer processes at interphases, the description of the sorption-desorption process requires information about the equilibrium reached between phases and the rate of which equilibrium is approached. The equilibrium sorption of both non-ionic and ionic chemicals is commonly described by adsorption isotherms. An important parameter is the adsorption coefficient, which is defined as the ratio between the concentration of the substance in the soil and the concentration of the substance in the aqueous phase at adsorption equilibrium.

Very often, the adsorption isotherms are well fitted to the Freundlich model:

$$q = K_f \cdot C_e^n \quad (\text{Eq. 1. 1. 1.})$$

where:

q is the amount of adsorbed pesticide per unit mass of soil,

C_e is the equilibrium pesticide concentration in solution,

K_f is Freundlich sorption coefficient

n is empirical constants.

The Freundlich equation was successfully applied for the description of soil adsorption data by many authors (SANCHEZ-CAMAZANO et al. 2000, RAMOS et al. 2000, ADHIKARI et al. 1991, KOOKANA and AYLMORE 1993, ARANZAZA et al 1991, DUSSET et al. 1994). However some authors pointed out possible disadvantages of applying this equation. The main objections were summarized by NICHOLLS (1992). Despite the drawbacks of the Freundlich equation, its great advantage lies in its flexibility, which allows comparison of the extent of pesticide adsorption in different soils. In the case where the equilibrium concentration is $C_e=1$, the isotherm becomes a straight line and K_f represents the distribution coefficient K_d . This coefficient is widely used to compare sorption in different soils.

The Langmuir adsorption isotherm is also used to describe the sorption processes:

$$q = \frac{a \cdot k \cdot c}{1 + k \cdot c} \quad (\text{Eq. 1. 1. 2.})$$

where:

q is the amount of adsorbed pesticide per unit mass of soil,

c is the equilibrium pesticide concentration in solution,

a represents the adsorption capacity and k is the adsorption equilibrium constant.

The main reason for application of Langmuir equation lies in its ability to give an estimation of the adsorption maximum (a) for the chemical studied. The application of other adsorption isotherms having less importance in describing the sorption agrochemicals have been summarized by TRAVIS and ETNIER 1981.

The important role of soil organic matter in the adsorption of many pesticides is widely recognized, it follows from this, variability in K_d (distribution coefficient) among soils can be reduced by correcting for differences in organic carbon content.

$$K_{oc} = K_d \cdot 100 / OC \quad (\text{Eq. 1. 1. 3.})$$

where: OC is the soil organic carbon content in %.

The adsorption coefficient normalized to the organic carbon content is a useful indicator of the binding capacity of a chemical on organic matter of soil and allows comparison to be made between different chemicals. However, the use of K_{oc} to predict adsorption implies that adsorption occurs only on the hydrophobic organic component, and disregards the influence of the composition of both soil organic matter and soil minerals, and the effects of pH, ionic strength, temperature, and other variables.

Many authors have related the extent of adsorption with the physico-chemical characteristics of the sorbent. For non-ionic organic chemicals, adsorption has been directly related to the hydrophobicity of the materials. Organic chemicals with low aqueous solubility and high octanol/water partition coefficients (P_{ow}) are considered to be more strongly adsorbed by soil than compounds that are more water-soluble and have a lower P_{ow} . K_{oc} can be estimated through correlations with the water solubility and the n-octanol-water partition coefficient. Many different equations for prediction of adsorption, using K_{oc} have been published. (KARICKHOFF 1981, TORRENTS et al. 1997). BRIGGS (1981) derived the following relationships for the adsorption of 105 pesticides belonging to more than 12 different chemical groups:

$$\log K_{oc} = 0.52 \log P_{ow} + 0.88 \quad (\text{Eq.1. 1. 4.)}$$

Nevertheless if the solute and/or the organic sorbent are more polar, the interactions are other than hydrophobic will contribute to sorption, causing the K_{oc} – P_{ow} correlations to fail. Podoll et al. (1987) mentioned that the correlation between hydrophobicity and adsorption may not hold true for all organic chemicals. In fact, for the more polar or water-soluble compounds, the electrostatic interaction between the chemical and the charged soil surface can bee the predominant mechanism influencing adsorption. (TORRENTS et al. 1997). Extensive reviews on the use of K_{oc} have been published by SHEA (1989) and GERSTL (1990).

It is also possible to predict the value of K_{oc} from the molar water solubility (HASSET et al. 1983). A main limitation to use of K_{oc} – P_{ow} or K_{oc} – solubility relationships is that these do not include the potential contribution of the soil minerals to sorption, particularly in low organic matter – high clay soils. In fact, for any given combination of soils and compounds, a variety of sorption forces are possible. Thus the above-mentioned relationships cannot provide an accurate prediction of sorption.

Another approach was chosen by PUSSMIER et al. (1994). The authors successfully used high performance liquid chromatographic (HPLC) columns, packed with either immobilized humic acid or with octadecylsilica, for the prediction of the soil organic matter adsorption coefficient K_{oc} of 14 triazole fungicides. The retention data on the humic acid HPLC column were found to be suitable for prediction purposes. However, the authors reported that prediction in some cases might

not be consistent for chemicals of similar chemical nature, due to differences in adsorption mechanisms.

Recently analytical methods were published to determine the P_{ow} and K_{oc} from HPLC parameters (HODSON and WILLIAMS 1988, KÖRDEL et al. 1997, MUELLER and KÖRDEL 1996, KÖRDEL et al. 1993, KÖRDEL et al 1995, KONDA et al. 2002)

1.1.3. Analytical Chemical Aspects

Adsorption of pesticides onto soil or sediment particles gives rise to a problem in the analytical, qualitative and quantitative, determination of pesticides residues in soil and water. The European Union (EU) provides directives and regulations on the maximum residue levels (MRL) for residues of pesticides in water in accordance with the recommendations of Codex Committee on Pesticide Residues (CCPR). The levels are based on scientific evaluations estimating the acceptable daily intake and the expected residue level in food when a pesticide is used according to good agricultural practice. As a result, for a single pesticide MRL ranges can be encountered which comprise several orders of magnitude. For most environmental samples and drinking water, the MRLs generally are much lower than for food samples. The EC directive for drinking water states that the concentration should not exceed the level of 0.1 µg/L for individual compounds and 0.5 µg/L for total pesticides (80/778/EEC 1980). This essentially means that methods for water analysis must exhibit 1000 times lower detection limits than those for foodstuffs and drug analysis.

The major task of the analytical discipline pesticide residue analysis is to provide reliable and cost-effective methods for the identification and quantification of more than 400 trace analytes that can be present in a variety of matrices. Before 1960, most analyses were carried out for individual pesticides using relatively non-specific methods such as UV-VIS spectrophotometry, total-halogen methods (for chlorinated pesticides) and biochemical techniques which involved inhibition of the enzyme cholinesterase (organophosphorus insecticides) or the fungus *Penicillium cyclopium* (fungicides) on thin layer plates. The use of biological techniques based on immunoassays obviously has a long history. The field of pesticide residue analysis was revolutionized in the late 1960s by the introduction of gas chromatography (GC). The introduction of capillary GC in the late 1970s, combined with the commercial of several sensitive and selective GC-detectors (electron capture, nitrogen-phosphorous selective and mass spectrometric detectors), contributed heavily to the rapidly increasing popularity of GC-based procedures for pesticide residue analysis. The favorable aspects of GC and the fact that most pesticide residue analysis laboratories are generously provided with GC equipment, makes capillary GC, today, the major analytical technique for this

type of analysis (GREVE 1996, KOK et al. 1984, RAMOS et al. 1999, Ramos et al. 2000). Since the introduction of column liquid chromatography (LC) in the field of pesticide residue analysis – which occurred 1980 – its application has expanded considerably. In case of pesticides with low volatility, high polarity and/or thermal instability the chemical derivatization is necessary prior to GC analysis. Typical examples are chlorophenoxy acids, carbamates and phenylureas. These analytes can be separated and efficiently detected by LC-UV, while GC analysis requires an often complicated derivatisation procedure prior to separation. It makes the methods more laborious and time consuming (apart from the possible sample loss due to excessive manipulations or uncompleted reactions). For all these reasons, techniques capable of performing the separation in the liquid phase are preferred. The availability of more selective fluorescence and electrochemical detectors for LC further enhances the practical value of this separation technique. Today the HPLC is widely employed technique for the quantitative analysis of pesticides in different biological and environmental matrices (SCHULTEN 1982, BALINOVA 1993, MOLINA et al. 1995, TROCEWICZ 1996, GIRAUD et al. 1997, BARCELO et al. 1991, HOGENDOOM et al. 1991, KONDA et al. 1999). Additionally various coupled chromatographic techniques (GC-GC, LC-GC, LC-LC) have been introduced to increase selectivity of the methods. The GC-MS, LC-MS techniques give an important contribution in the field of new multi-method development. Recently the application of capillary electrophoresis to separation and quantitative determination of pesticides have been published (BARROSO et al. 1998, SONG et al 1995, DINELLI et al. 1994).

1.2. SCOPE OF THE STUDY

The ecological approach requires an adequate knowledge of the presence and fate of the pesticide in the environment. The sorption processes of pesticides in soil have been studied extensively. The complexity of the phenomena and the variety of soils and types of chemicals has resulted in a great deal of work, not only experimental but also theoretical. However due to the great differences in methodological approaches, the complexity of experimental and numerical techniques and the measurement uncertainty the comparison and assessment of the results are sometime difficult. Despite of the great progress in recognition of the principles that govern the partition of organic chemicals between solid and liquid phases, because of the complexity and diversity of existing processes, much research is still necessary to obtain a better understanding of sorption phenomena. On the other hand a product's hazard cannot sufficiently be assessed from laboratory studies only due to different environmental, agricultural and socio-economic conditions of each country and the large number of interacting environmental and anthropogenic factors. Most

pesticides are widely used and experiences from other countries can greatly help to identify possible hazards under comparable conditions, however a separate evaluation is recommended to confirm or refute specific risks for a particular country or region. Thus, it appears necessary to develop new procedures and methods to get additional data and extended information about nature of the pesticide-soil environmental system under laboratory and field condition as well.

This study presents the results of investigations on sorption characteristic and environmental fate and behavior of some representative organic pesticides on Hungarian agricultural soil. The investigations were carried out at the Analytical Chemistry Department of the Institute for Veterinary Medicinal Products, Budapest, and at the Department for Soil Science and Agricultural Chemistry of the Szent Istvan University, Gödöllő. The results of the studies have been published in international scientific journals or submitted for publication. Wishing to save the original text, I did not change the articles already published dramatically, I simply standardized their format. I have compiled the references in a chronological and logical order in this dissertation, which presentation has advantages and disadvantages as well. One of the main handicaps is, that some parts (i.e. introduction, materials and methods) unavoidably contain repetitions. The four chapters of the “Investigations, Results and Discussion” part represent four independent series of investigations, even if based on the results of the previous ones. I hope, that the general introduction part and the final summary help to integrate the chapters into a coherent work in the readers’ mind.

2. INVESTIGATIONS, RESULTS AND DISCUSSION

2.1. SORPTION BEHAVIOR OF ACETOCHLOR, ATRAZINE, CARBENDAZIM, IMIDACLOPRID AND ISOPROTURON ON HUNGARIAN AGRICULTURAL SOIL

The results of the study were published in Chemosphere (KONDA et al. 2002 a).

2.1.1. INTRODUCTION

Progressive increase of production and application of chemicals for agriculture as well as for plant protection and animal health has converted the problem of environmental pollution into national and international issues. The pollution of soil, ground and surface water involves a serious risk to the environment and also to the human health due to direct exposure or through residues in food and drinking water (PLIMMER 1990, RISEBROUGH 1990, MATHYS 1994, CAPEL et al. 1995, MAJEWSKI and CAPEL 1995, WANIA and MACKAY 1996, LARSON et al. 1997).

Acetochlor is a selective herbicide used as a pre-emerge or pre-plant treatment. It is adsorbed mainly by the shoots and secondarily by the roots and acts by inhibition of protein synthesis. Atrazine and isoproturon are selective systematic herbicides which are applied to the soil as a pre-emerge or post-emerge treatment. They are principally absorbed by the roots but also by the leaves, with translocation and inhibition of the photosynthetic electron transport. Carbendazim is a systemic fungicide, acts by inhibiting development of the germ tubes, the formation of appressoria, and the growth of mycelia. It is used as anthelmintic in the veterinary practice. Diazinon is a non-systemic insecticide and acaricide with contact, stomach and respiratory action, with cholinesterase inhibitor activity. It is used as control of sucking and chewing insects and mites on a very wide range of crops. Diazinon is an active ingredient of some veterinary ectoparasiticides to control mange mites, ticks, lice, keds, biting flies, blowflies on sheeps, cows, pigs, goats and horses as well. Imidacloprid is a systemic insecticide with contact and stomach action. This chemical is effective against sucking insects and soil insects, and is contained in some veterinary drug formulations as active ingredient for the treatment of cats and dogs against parasites as well (BUDAVÁRI 1989, TOMLIN 1994). The above mentioned chemicals have been used in plant production and animal health intensively for the last several years, so the soil and water contamination by them is more and more of a public concern.

While various physico-chemical processes affect the fate of agrochemicals contacted with soil, the adsorption-desorption is one of the most important processes which controls all other processes such as their movement, persistence, and degradation (KOLPIN et al. 1998, GREENLAND and HAYES 1981). Desorption of chemicals is also critical in determining the availability to the target species, their behavior in runoff stream and in ground water pollution. The objective of this study was to investigate the sorption behavior of the six above mentioned biocids belonging to different class of pesticides in Hungarian agricultural soil. Our secondary aim was to evaluate the mathematical models describing sorption referred in the literature with respect to their particular fit to the experimental data of the set of pesticides studied. Furthermore we intended to validate the computer estimated (theoretical) octanol-water partition coefficients (P_{ow}) of these chemicals as compared to the experimentally determined values and getting information about the usability of HPLC parameters for determination of K_{oc} values of pesticides on soil.

2.1.2. MATERIALS AND METHODS

2.1.2.1. *Chemicals, Reagents and Standards*

Acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon all with purity higher than 99% were obtained from Sigma Aldrich Kft. (Hungary, Budapest). The structures of these chemicals are shown in Figure 1. HPLC-grade methanol, acetone, tetrahydrofuran, acetonitrile and analytical-grade citric acid monohydrate, calcium chloride dihydrate, phenol, naphthalene, toluene and phenanthrene were purchased from Merck (Darmstadt, Germany). Extraction cartridges used were Waters Sep-Pak octadecyl (C_{18} , 500 mg) columns (Waters Corp., Milford, MA, USA). HPLC disposable membrane filters (0.45 μm) were purchased from Millipore (Bedford, MA, USA). HPLC grade water was obtained using a Milli-Q system (Millipore Corp., Bedford, MA, USA). Stock standard solutions of each pesticide (1000 $\mu\text{g/mL}$) were prepared by dissolving the required amount in acetonitrile and were stored under refrigeration. Dilutions were made with 0.01 M calcium chloride solution to the desired final concentrations.

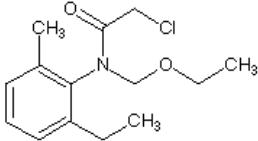
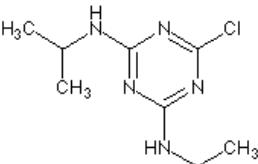
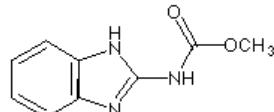
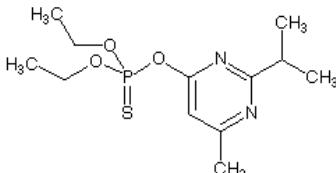
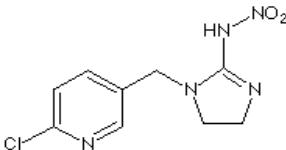
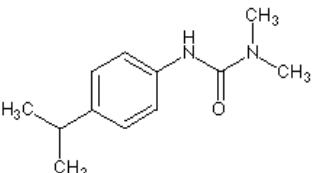
Common name	Molecular structure	IUPAC name	MW
ACETOCHLOR		2'-ethyl-6'-methyl-N-(ethoxymethyl)-2-chloroacetanilide	269.77
ATRAZINE		2-chloro-4-ethylamino-6-isopropylamino-s-triazine	215.69
CARBENDAZIM		1H-Benzimidazol-2-ylcarbamic acid methyl ester	191.19
DIAZINON		Phosphorothioic acid O,O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl]ester	304.35
IMIDACLOPRID		1-[(6-Chloro-3-pyridinyl)methyl]-4,5-dihydro-N-nitro-1H-imidazol-2-amine	255.66
ISOPROTURON		N,N-Dimethyl-N'-(4-(1-methylethyl)-phenyl) urea	206.29

Figure 1. Chemical structure of the six pesticides studied.

2.1.2.2. Experimental Soil

All sorption experiments were conducted on representative Hungarian brown forest soil with clay alluviation (Luvisol according to classification of Food and Agriculture Organization of the United Nations), which has the following composition and characteristic: 1.16 % organic matter

(0.68% organic carbon), 21.8 % silt, 15.4 % clay and 62.8 % sand, with cation-exchange capacity of 16.8 mequiv / 100 g of soil and pH 6.1 (measured in distilled water). X-ray diffraction determined mineralogical composition of the soil was the following: 59 % quartz, 12 % plagioclase, 11 % phyllo silicate, 6 % chlorite, 4 % potash feldspar, 3 % kaolinite, 3 % pyroxene, 1 % smectite and 1 % siderite.

2.1.2.3. Adsorption-Desorption of Pesticides

The soil was air-dried, homogenized and passed through a 2.0 mm sieve. Pesticide dilutions were prepared in 0.01 M calcium chloride to maintain constant ionic strength. Concentrations ranged between 0.04-5.00 mg/L for all compounds. Each sample consisted of 5 g of soil mixed with 25 mL of the pesticide solution in 50 mL polypropylene centrifuge tube sealed with screw caps. The tubes were agitated on a rotary shaker for 24 hours at 20 ± 1 °C to achieve equilibrium. Blanks without soil prepared in the same way showed no adsorption of pesticides on the tube wall except for diazinon, in which case the loss was significant. Therefore the diazinon sorption experiment was made using glass tubes and screw caps with teflon lining. The amount of pesticide adsorbed by the soil was calculated from the difference between the initial and equilibrium pesticide concentrations in solution. The adsorption equilibration process was made in three replicates.

Desorption of pesticides was determined on triplicate soil samples equilibrated with 1.0mg/L and 5.0 mg/L diazinon solution, and 0.2 mg/L, 1.0 mg/L and 5.0 mg/L pesticide concentration in case of atrazine, acetochlor, carbendazim, isoproturon and imidacloprid. After equilibration the suspension was centrifuged at 3600 rpm for 30 min (Jouan, CP422 model maintained at 20 ± 1 °C). The supernatant was poured off and replaced by the same volume of 0.01 M calcium chloride solution. The tube was shaken as previously described and centrifuged. The desorption equilibration process was repeated three times. The amount of pesticide remaining adsorbed by the soil was calculated as the difference between the initial adsorbed amount and the desorbed amount.

The adsorption isotherms were described for each compound using the Freundlich equation

$$q = K_f C_e^n \quad (\text{Eq. 2. 1. 1.})$$

where:

q is the amount of adsorbed pesticide per unit mass of soil (mg/kg),

C_e is the equilibrium pesticide concentration in solution (mg/L),

K_f and n are empirical constants.

2.1.2.4. Pesticides Analysis

Sample Preparation

After equilibration 15 mL aliquots of centrifuged suspension were recentrifuged at 8000 rpm for 20 min. SPE cartridges were activated by washing once with 2 mL methanol and 2 mL 0.01 M calcium chloride solution. 10 mL supernatant was loaded into the reservoir of the extraction cartridge and drawn slowly through the column. After sample addition, the stationary phase with the retained pesticide was dried for 5 min with air. Elution was performed with 2 mL acetone. The organic solvent was evaporated to dryness under a gentle stream of nitrogen and the residue was dissolved in 0.5 mL mixture of acetonitrile-water (1:1 v/v). Prepared samples were passed through disposable membrane filters and analysed with high performance liquid chromatography with UV detection.

Instrumentation and Operating Conditions

The HPLC system was a JASCO liquid chromatograph (JASCO, Kyoto, Japan) equipped with two JASCO PU-850 pumps, an AS-950 autosampler and a UV-975 UV-VIS detector. Data acquisition and processing were accomplished by means of a Waters Maxima 820 data station running on an IBM PC/AT 486 computer. Symmetry C18 column (75×3.9 mm i.d., 4 μm particle size, Waters, Milford, MA, USA) preceded by a guard column (BST C18 20 \times 4 mm, Budapest, Hungary) was used as stationary phase.

Samples were eluted and analyzed using the following two mobile phases: for imidacloprid, carbendazim, isoproturon and atrazine 10:20:70 (v/v/v) tetrahydrofuran - methanol - 0.1% (m/v) citrate buffer (pH 5.8); for acetochlor and diazinon 40:60 (v/v) acetonitrile - 0.1 % (m/v) citric acid solution respectively. The flow rate was 1 mL/min and the injected volume was 50 μL in all cases. The analytes were quantitatively determined by UV detection at 220 nm wavelength.

Method Characteristics

Calibration curves for each of the compounds were linear up to 5 mg/L with regression coefficients of 0.999. Detection limits were 0.2 $\mu\text{g}/\text{L}$ for atrazine, acetochlor, carbendazim, and imidacloprid, while 0.4 $\mu\text{g}/\text{L}$ for isoproturon and diazinon as determined according to the American Society of Testing and Materials ASTM D4210 standard. Repeatabilities were appropriate with

relative standard deviation lower than 5% in all cases and recoveries ranging from 92.9-101.7%. Typical chromatograms of investigated pesticides are shown in Figure 2 and 3.

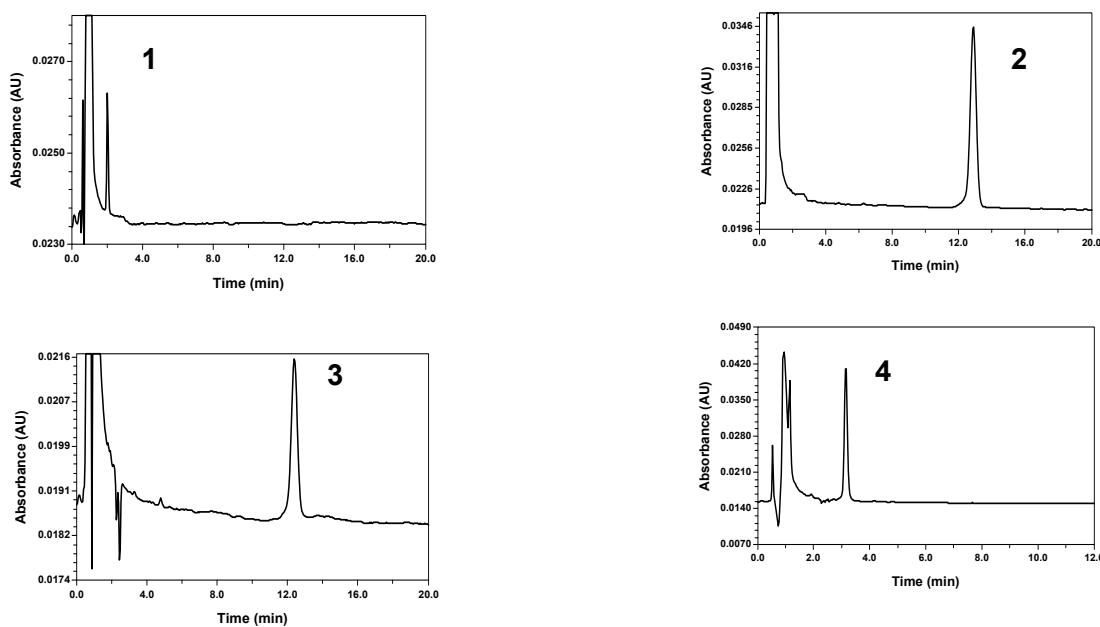


Figure 2. Typical chromatograms of imidacloprid (1), carbendazim (2), isoproturon (3) and atrazine (4) in soil solution.

Conditions: Symmetry C18 column, 75 x 3.9 mm i.d., 4 μ m particle size; mobile phase, 10:20:70 (v/v/v) tetrahydrofuran - methanol - 0.1% (m/v) citrate buffer (pH 5.8); flow rate, 1 mL/min; UV detection, 220 nm; injection volume, 50 μ L; concentration, 0.64-0.82 μ g/mL.

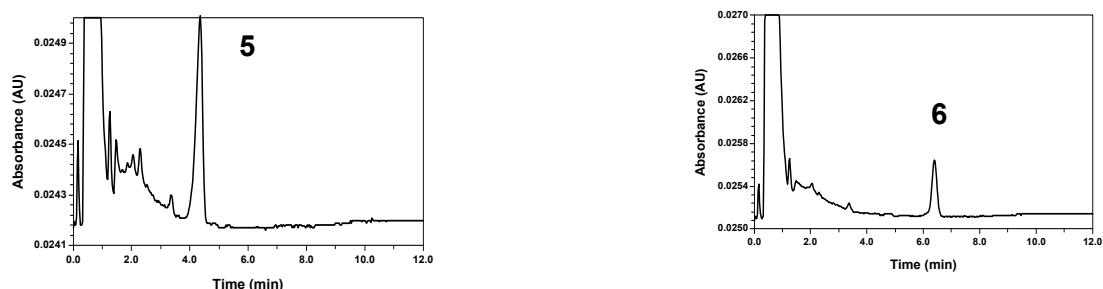


Figure 3. Typical chromatograms of acetochlor (5) and diazinon (6) in soil solution.

Conditions: Symmetry C₁₈ column, 75 x 3.9 mm i.d., 4 μ m particle size; mobile phase, 40:60 (v/v) acetonitrile - 0.1 % (m/v) citric acid; flow rate, 1 mL/min; UV detection, 220 nm; injection volume, 50 μ L; concentration, 0.50-0.55 μ g/mL.

2.1.2.5. Determination of Octanol-Water Partition Coefficients

The n-octanol/water partition coefficient (P_{ow}) is a key parameter in the studies of the environmental fate of chemical substances. It is a useful parameter in the prediction of adsorption on soil (BRIGGS 1981, CHIOU et al. 1983, TORRENTS et al. 1997). The P_{ow} value is defined as the ratio of the equilibrium concentration of a dissolved substance in a two-phase system consisting of two immiscible solvents as n-octanol and water.

Preliminary estimation of the logarithm of the partition coefficients ($\log P_{ow}$) and prediction of dissociation coefficients of the six pesticides examined were made based on the chemical structure using Environmental Science Centre Estimation Software (U.S. EPA's Office of Pollution and Toxics) and Pallas 2.0 expert system (Compu Drug, Budapest, Hungary) respectively. P_{ow} partition coefficients of the pesticides were determined experimentally using high performance liquid chromatography. Instrumentation was the same as described above. The system was equipped with Waters Symmetry C18 column (75x 4.6mm i.d., 3.5 μ m particle size, Milford, MA, USA). The detection wavelength was 220 nm. 60:40 (v/v) methanol – 0.1% citrate buffer (pH 6) was used as mobile phase at 1 mL/min flow rate. Concentrations of standard pesticide solutions were 0.1 mg/mL for all compounds.

The P_{ow} is can be determined from the retention factor given by the expression:

$$k = (t_R - t_0)/t_0 \quad (\text{Eq. 2. 1. 2.})$$

where:

k is the retention factor,

t_R is the retention time of the substance,

t_0 is the dead-time, i.e. the average time, an unretained solute needs to pass the column.

In order to correlate the measured retention factors of pesticides with their P_{ow} , a calibration graph was constructed from four points. Four reference compounds - phenol, naphthalene, toluene and phenanthrene selected according to the computer-estimated $\log P_{ow}$ of pesticides - were injected in triplicate at 0.1 mg/mL concentration. The $\log P_{ow}$ values of the reference compounds used for calculation was based on literature values and data obtained by Shake Flask Method (OECD Guideline for Testing of Chemicals 117). The corresponding logarithms of retention factors, $\log k$, are calculated and plotted as a function of $\log P_{ow}$. The partition coefficients of the pesticides were obtained by interpolation of the calculated retention factor on the calibration graph.

2.1.2.6. Estimation of the Adsorption Coefficient (K_{oc}) from HPLC Parameters.

The principle of the method is similar to that was described in the 2.1.2.5. Section. While passing through the HPLC column along with the mobile phase the examined test substance interacts with the stationary phase. As a result of partitioning between mobile and stationary phases the test substance is retarded. A suitable stationary phase having polar and non-polar sites allows for interaction of polar and non-polar groups of a molecule in a similar way, as is the case for organic matter in soil matrices. The adsorption coefficient is deduced from the retention factor (k) using a calibration plot of $\log k$ versus $\log K_{oc}$ of the selected reference compounds.

The HPLC system was the same as was used in the previously study. BST LiChrosorb 5 CN-W column (200x4 mm id. 5 μm particle size) was used as stationary phase. Methanol – 0.01 M citrate buffer (pH 6), 40:60 (v/v) was used as mobile phase at 1 mL/min flow rate. Concentrations of standard pesticide solutions were 1 mg/mL for all compounds. The detection wavelength was 220 nm. Phenol, naphthalene and phenanthrene were used as reference compound. The $\log K_{oc}$ values of the reference compounds used for calculation were based on literature values and data obtained by batch equilibrium data (OECD Guideline for Testing of Chemicals 127, draft document, August 1999). The K_{oc} values of the pesticides were obtained by interpolation of the calculated retention factor on the calibration graph.

2.1.3. RESULTS AND DISCUSSION

The adsorption isotherms of the six pesticides studied are shown in Figure 4 and 5. The calculated values of K_f , n and K_{oc} (K_f related to the soil organic carbon content) are given in Table 1. The experimental data showed that the rate of adsorption have decreased in order of carbendazim, diazinon, acetochlor, imidacloprid, isoproturon and atrazine. The slopes ($n < 1$) of isotherms indicated that as the initial concentrations of pesticides increased, the percentage adsorbed by the soil decreased. This correlation was more pronounced in case of carbendazim, atrazin and isoproturon. This might be explained by an increased difficulty to access the adsorption sites when pesticide concentrations are elevated.

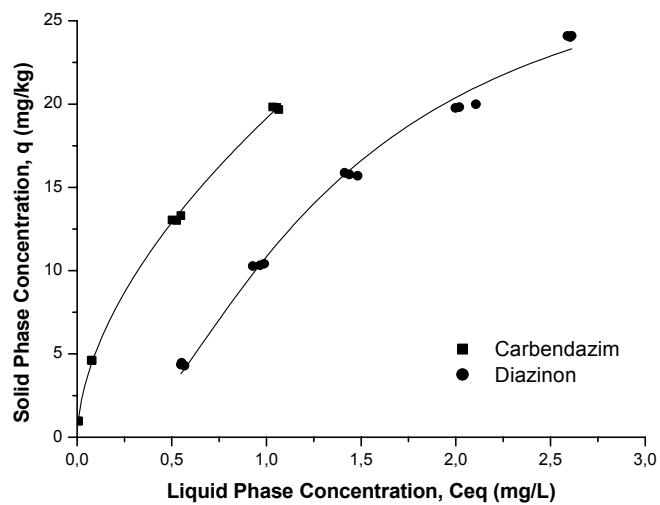


Figure 4. Adsorption isotherms for carbendazim and diazinon.

The amount of diazinon in the liquid phase was not detectable following equilibration process at 0.04 mg/L initial concentration level.

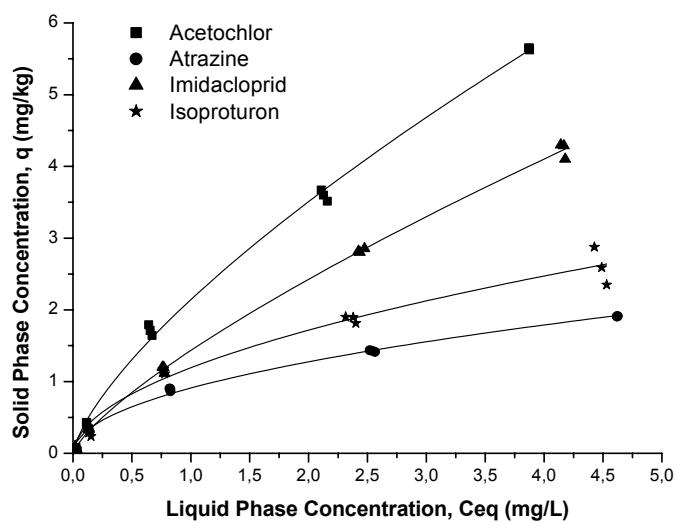


Figure 5. Adsorption isotherms for acetochlor, atrazine, imidacloprid and isoproturon.

Table 1. Parameters of the Freundlich equation describing the adsorption isotherms of the six pesticides examined.

Pesticide	K_f	K_{oc}^*	n	r
ACETOCHLOR	2.14	313.6	0.71	0.997
ATRAZINE	0.91	133.4	0.49	0.994
CARBENDAZIM	19.14	2805	0.57	0.999
DIAZINON	10.19 10.84 ^a	1493 1589	0.98 b = 1.29 ^a c = 0.5 ^a	0.969 0.993 ^a
IMIDACLOPRID	1.43	209.6	0.76	0.999
ISOPROTURON	1.19	174.4	0.53	0.990

* $K_{oc} = 100 \times K_f / OC$, where OC is the soil organic carbon content in %.

^a Parameters are calculated from the extended Freundlich model:

$$q = K_f C_e^n, \quad \text{and} \quad n = b C_{eq}^{-c}$$

where q is the amount of adsorbed pesticide per unit mass of soil (mg/kg), C_e is the equilibrium pesticide concentration in solution (mg/L), K_f , b and c are empirical constants.

In addition to adsorption isotherms which give information about the quantity adsorbed in a soil, desorption experiments are required to study the intensity of soil-pesticide interaction involved. The cumulative non-desorbable amounts of chemicals are given in Table 2. Sorption of pesticides by soil was not completely reversible although desorption was attempted immediately after adsorption. The amounts of non-desorbed pesticide were extremely high in case of carbendazim. This could be due to bonding between the chemical and the soil, which is stronger and therefore more stable than for the other four pesticides. The percentage of desorbed amounts of imidacloprid and diazinon were decreased while those of atrazine and carbendazim were increased with the increase of the initial adsorbed concentration. Based on the experimental data no such correlation could be observed in case of acetochlor and isoproturon.

Table 2. Experimental data of desorption process of six pesticides on the soil.

Pesticide	adsorbed amount ^a (mg/kg)	desorbed amount ^b (mg/kg)	non-desorbable amount ^c (%)
ACETOCHLOR	0.42	0.15	63.8
	1.79	0.96	46.6
	5.65	2.79	50.6
ATRAZINE	0.33	0.13	60.4
	0.90	0.73	18.6
	1.91	1.78	6.7
CARBENDAZIM	0.96	0.03	97.1
	4.62	0.25	94.6
	19.68	1.66	91.5
DIAZINON	4.47	2.97	33.6
	24.10	14.33	40.5
IMIDACLOPRID	0.34	0.26	23.2
	1.20	0.73	39.2
	4.30	2.02	53.0
ISOPROTURON	0.30	0.15	47.8
	1.17	0.65	44.3
	2.35	1.27	46.0

^a Initial adsorbed amount (q)

^b Average values of cumulative data obtained from three times repeated desorption equilibration process in triplicates.

^c Average cumulative non desorbable amount in percentage of the initial adsorbed amount

Good agreement was experienced between the computer expert system estimated data and the experimentally determined octanol-water partition coefficients of investigated chemicals. Data and the most important physicochemical properties of solutes are explained in Table 3. Plot of experimental log P_{ow} values vs. log k values are shown on Figure 6. Based on the results of the study it can be concluded that the Freundlich adsorption constants (K_f) are slightly related to the physicochemical properties of the selected pesticides, nevertheless no close correlation could be established.

The K_{oc} values calculated from HPLC parameters were significantly lower than were determined from batch equilibrium experiments (see 2.1.2.3. Section). The HPLC retention data estimated log K_{oc} values were 2.32 for acetochlor, 1.70 for atrazin, 1.87 for carbendazim, 2.74 for diazinon, 1.79 for imidacloprid and 1.99 for isoproturon while 2.49, 2.12, 3.45, 3.17, 2.32 and 2.24

were calculated from Freundlich equation respectively. However, the estimated K_{oc} may be useful for choosing appropriate test parameters for adsorption/desorption studies according to the batch equilibrium method. Plot of experimental $\log K_{oc}$ values vs. $\log k$ values are shown on Figure 7.

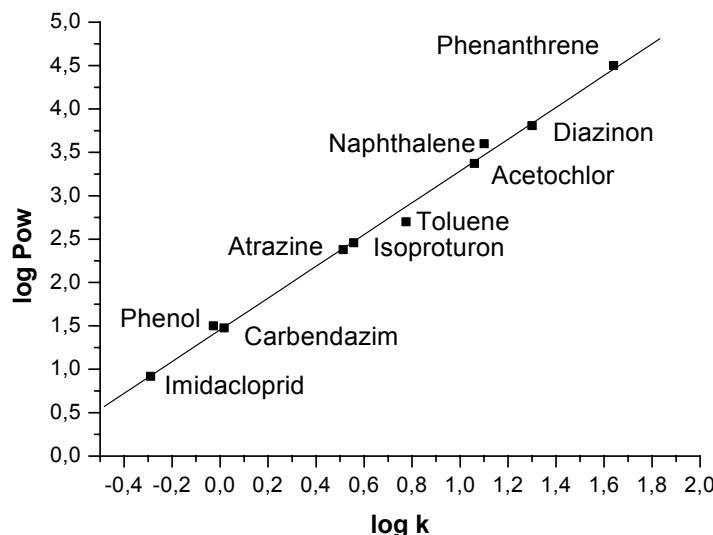


Figure 6. Plot of experimental $\log P_{ow}$ values vs. $\log k$ values of selected organic solutes

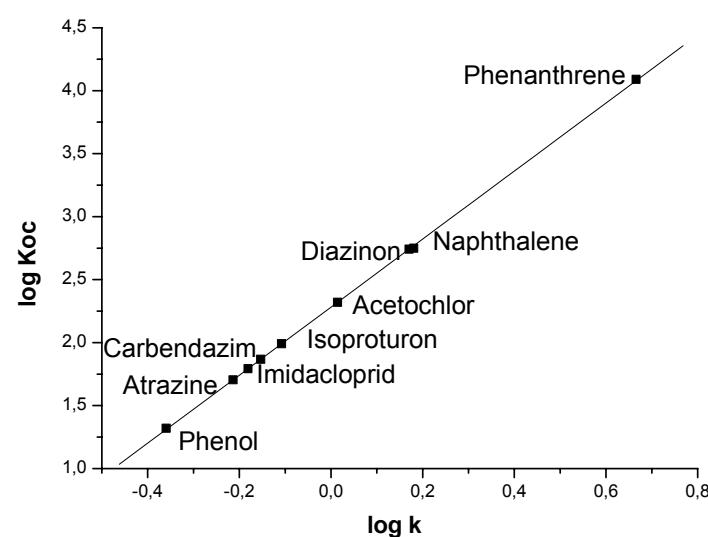


Figure 7. Plot of experimental $\log K_{oc}$ values vs. $\log k$ values of selected organic solutes

Table 3. Predicted and experimental properties of pesticides investigated

Pesticide	logP _{ow} ^a	logP _{ow} ^b	water solubility ^c mg/L	Dissociation coefficient ^d
ACETOCHLOR	3.37	3.37	223 (25°C)	-
ATRAZIN	2.82	2.38	33 (20°C)	2.75
CARBENDAZIM	1.55	1.48	8 (24°C, pH7)	5.52
DIAZINON	3.86	3.81	60 (20°C)	1.64
IMIDACLOPRID	0.56	0.92	510 (20°C)	5.94
ISOPROTURON	2.84	2.46	65 (22°C)	-

^a Logarithm of estimated octanol-water partition coefficients based on chemical structure using Environmental Science Centre Estimation Software.

^b Logarithm of octanol-water partition coefficients obtained by calculation from HPLC retention factor k. Correlation coefficient: 0.999.

^c The listed solubility values are citated in Pesticide Manual, 10th ed.

^d Predicted dissociation coefficients using Pallas 2.0 expert system.

2.1.5. CONCLUSIONS

The difference in the soil sorption process of these six chemicals may be explained by several factors. The extent of adsorption depends on the amount of the pesticide and properties both of the soil and the pesticide. Carbendazim and diazinon were more strongly and extensively adsorbed in the soil, than acetochlor, imidacloprid, isoproturon and atrazine. A magnitude higher absorption capacity of carbendazim and diazinon might be explained in part by their water solubilities and hidrophobicities. The strong adsorption and low desorption characteristics of these chemicals suggest that for the soil studied, migration to the groundwater should be lower than for the other four chemicals examined. At the same time the bound residues can be considered only momentarily

inactivated, which represents a possible source of contamination by a time-delayed release of toxic units as chemical “timed-bombs”.

Further research will be undertaken to investigate the sorption behavior at higher concentration ranges and the binding mechanisms of these pesticides to understand more clearly the causes for hysteresis and estimate the potential migration to the groundwater.

2.2 MODELING OF SINGLE- AND MULTI-STEP ADSORPTION ISOTHERMS OF ORGANIC PESTICIDES ON SOIL

Submitted for publication to J. Agric. Food Chem. (KONDA et al. 2002 b)

2.2.1. INTRODUCTION

With progressive increase of production and application of chemicals for agricultural activities, the contamination of soil, ground and surface water has converted a problem throughout the world (LARSON at al. 1997, MATHYS 1994, KOLPIN et al. 1998, RISENBROUGH 1990). Efforts to preserve the environment and to reduce the risk of contamination have established the need to understand the behavior of pesticides in the natural environment. The fate and behavior of pesticides in the environment involve several different and often simultaneous phenomena, such as chemical and biological transformation processes, runoff, leaching, volatilization and wind erosion. While various physico-chemical processes affect the fate of agrochemical contacted with soil, the sorption to the solid matrix of soil is one of the most important phenomena, which controls other processes such as pesticide transport, persistence, bioavailability and degradation (GREENLAND and HAYES 1981, WOLFE and SEIBER 1993, HAROLD 1998, ROMBKE et al. 1996, HORNSBY et al. 1996, KOOKANA and AYLMORE 1994, KAWAMOTO and URANO 1989, EAGLE 1988).

Many theories and models have been presented in the literature to simulate the sorption processes (SPOSITO 1984, SPARKS 1999, DEFAY and PRIGOGINE 1966, WEBWR et al. 1991, LASTOSKIE 1997). Derivation of a scientifically based adsorption isotherm was first achieved by Langmuir. The Langmuir model assumes monolayer adsorption on an energetically homogeneous surface, where the adsorption takes place only at specific localized sites and the saturation coverage corresponds to complete occupancy of these sites. Each site can accommodate one and only one molecule or atom and there is no interaction between neighboring adsorbed molecules or atoms (GILES et al. 1974). Nevertheless the soil has a polydisperse nature with polyelectrolytic character, surface activity properties and various chemically reactive functional groups, hydrophilic and hydrophobic sites, which is possibly reflected in great differences in adsorption energy. The nature of the binding forces in soil are determined by the different type of mechanisms as ionic, hydrogen and covalent bonding, charge-transfer and electron donor-acceptor mechanisms, van der Waals forces, ligand exchange and hydrophobic bonding or partitioning (GOPAL et al. 1994, PARLAR 1992, SENESI 1992). In some instances, especially when organic

compounds are adsorbed, the S-shaped isotherms are the results of cooperative interactions among the adsorbed molecules. These interactions (e.g., surface polymerization, multi-layer sorption or stereochemical interactions) cause the adsorbate to become stabilized on a solid surface, and thus they produce an enhanced affinity of the surface for the adsorbate as its surface excess increases (SPOSITO 1989). The variety of chemical heterogeneity of soil components are further complicated by the colloidal structure of soil, such as its micro- or mesoporous heterogeneity besides the existence of macropores.

Using more realistic assumptions, modifications have been made to the Langmuir isotherm, which are summarized in the monographs of RUTHVEN (1984), YANG (1987), ADAMSON (1990), RUDZINSKI and EVERETT (1992). Another concept derived from the models for saturated media takes into account the chemical heterogeneity of the soil by considering two (or possibly more) sites of different adsorption capacities (EVANGELOU 1998). Several more complex equations such as that of Brunauer, Emmett, and Teller have been proposed to describe multi-layer adsorption (ANDERSON 1946, GREGG and JACOBS 1949, VARSÁNYI 1987). GREGG and SING (1982) have given a detailed discussion of the various models used to interpret each type of the isotherms. Numerical methods presented during the last years, however, could not be easily handled because of the large number of parameters required, which make the model too complex for practical calculation from reasonable number of experiments (CULVER et al. 1991, LICK et al. 1997, ARDIZZONE et al. 1993, DO and DO 2002, TEPPEN et al. 1998).

The most commonly used adsorption isotherm equations for organic contaminant on soil are the Langmuir and the Freundlich isotherm. In many cases, the sorption of pesticides has been well described using these empirical models (SPARKS et al. 1993, GRABER and BORISOVER 1998, GAO et al. 1998, BUCHTER et al. 1989). These commonly used equations have the advantage of the possibility of linearization yielding the adsorption parameters by the slope and intercept of the fitted line. These equations have been found to fit some pesticide adsorption results moderately well and have occasionally been used to estimate the capacity for adsorption.

The objective of the present work was to investigate the sorption behavior of organic pesticides atrazine, acetochlor, carbendazim, diazinon, imidacloprid and isoproturon at extended concentration ranges to understand their binding mechanisms to soil colloids. These chemicals have been used in plant production and animal health intensively for the last several years. Their biological effects and utilization are detailed in the literature (BUDA VÁRI 1989, TOMLIN 1994). They represent a wide range of chemical and functional classes capable for the investigation of the behavior of organic pesticides in soil environment. Our secondary aim was to develop a valid mathematical model to allow the description of the adsorption processes of the investigated

compounds and to calculate physicochemical parameters of equilibrium derived from adsorption isotherms as well.

2.2.2. MATERIALS AND METHODS

2.2.2.1. *Chemicals, Reagents and Standards*

Chemicals, reagents and standards used for this experiment were the same as were used in the previously study. They were identified in detail in the section 2.1.2.1. The chemical structure of the studied pesticides was presented in the Figure 1.

2.2.2.2. *Experimental Soil*

All sorption experiments were conducted on the same soil as which was used in the previously study (Luvisol according to classification of Food and Agriculture Organization of the United Nations). The characteristics of soil were detailed in the section 2.1.2.2.

2.2.2.3. *Adsorption of Pesticides*

All experiments have been performed under isotherm condition at 20 ± 1 °C. The soil was air-dried, homogenized and sieved to a grain size fraction < 2 mm. Pesticide solutions were prepared in 0.01 M calcium chloride to maintain constant ionic strength. Concentration ranged between 1.0-15.0 mg/L for atrazine, acetochlor, diazinon, imidacloprid and isoproturon, and 1.0-8.0 mg/L for carbendazim because of its limited solubility. Each sample consisted of 2.5 g of soil mixed with 25 mL of the pesticide solution in 50 mL polypropylene centrifuge tube sealed with screw caps, except for diazinon, in which case adsorption was found to the plastic. Because of that, the diazinon sorption experiment was performed using glass tubes and screw caps with teflon lining. The tubes were agitated on a rotary shaker for 24 hours to achieve equilibrium. The amount of pesticide adsorbed by the soil was calculated from the difference between the initial and equilibrium pesticide concentrations in solution. The adsorption equilibration process was made in three replicates for each concentration.

2.2.2.4. Pesticide Analysis

After equilibration, 15 mL aliquots of suspension were centrifuged at 6000 rpm for 20 min. Clean up of the supernatant was performed with C18 solid phase extraction method. 10 mL supernatant was loaded to the previously activated extraction column and was washed subsequently with 2 mL water. Elution was performed with 2 mL acetone. The organic solvent was evaporated to dryness under a gentle stream of nitrogen and the residue was dissolved in 1.0 mL mixture of acetonitrile-water (1:1 v/v). Prepared samples were passed through disposable membrane filters and analyzed with high performance liquid chromatograph and UV detector. Above 5 mg/L initial pesticide concentration no SPE was used. Soil supernatants were centrifuged as described above, filtered, diluted if necessary, and injected to the HPLC.

The HPLC system, analytical column, guard column and mobile phases were the same as were used in the previously study. Instrumentation and operating condition were detailed in the section 2.1.2.4.

2.2.2.5. Method Characteristic

Linearity (regression coefficients 0.978 – 0.999 up to 5 mg/L) and repeatability (2.1-4.9%) of the methods were appropriate in all cases. Recoveries ranged 92.9-101.7%. Detection limits were 0.2 µg/L for atrazine, acetochlor, carbendazim, and imidacloprid, while 0.4 µg/L for isoproturon and diazinon. Typical chromatograms of investigated pesticides are shown in Figure 2. and 3.

2.2.3. RESULTS AND DISCUSSION

The sorption isotherms for acetochlor and carbendazim obtained from our experimental equilibrium data have been found to fit well to the Langmuir equation. By visual inspection of the isotherms obtained for atrazine, diazinon, imidacloprid and isoproturon similarities were observed to the characteristic types IV. described by Brunauer, Deming and Teller (GREGG and JACOBS 1949). Nevertheless we have not found adequate mathematical description in the reviewed literature, which could represent well the multi-step-shaped plot measured in case of them. Hence we derived a non-linear mathematical model - obtained from the sum of Langmuir type isotherms with the additional assumption that sterically or energetically heterogeneous adsorption sites exist in the soil and there are potential interactions among the adsorbed molecules. Each step on the

curve thus represents different existing specific type of adsorption mechanisms, which could be described by Langmuir equation:

$$q = \frac{a \cdot k \cdot c}{1 + k \cdot c} \quad (\text{Eq. 2. 2. 1.})$$

where:

q is the amount of adsorbed pesticide per unit mass of soil (mg/kg),

c is the equilibrium pesticide concentration in solution (mg/L),

a represents the adsorption capacity (mg/kg),

k is the adsorption equilibrium constant (mg^{-1}).

Furthermore, a critical concentration of the substance on the sorbent depending on the adsorbate-sorbent interaction has been introduced. Above this concentration, the next, new adsorption mechanism becomes effective. Using the limit concentration, the equation (Eq. 2. 2. 1.) can be modified in the following way:

$$q = \frac{a \cdot k \cdot (c - b)}{1 + k \cdot (c - b)} \quad (\text{Eq. 2. 2. 2.})$$

where: b is the concentration limit of the adsorption mechanism in question [mg/L].

In a physical and mathematical approach, the function can be used only if $c > b$. Thus the equation must be modified using the function below:

$$\left[\frac{(c - b) + \text{abs}(c - b)}{2} \right] = c - b, \quad \text{if } c - b > 0 \quad (\text{Eq. 2. 2. 3.})$$

$$\left[\frac{(c - b) + \text{abs}(c - b)}{2} \right] = 0, \quad \text{if } c - b < 0$$

Thus the (Eq. 2. 2. 2..) could be rearranged:

$$q = \frac{a \cdot k \cdot \left[\frac{(c - b) + \text{abs}(c - b)}{2} \right]}{1 + k \cdot \left[\frac{(c - b) + \text{abs}(c - b)}{2} \right]} \quad (\text{Eq. 2. 2. 4.})$$

After transformation (Eq. 2. 2. 4.) yields:

$$q = \frac{a \cdot k \cdot [(c - b) + \text{abs}(c - b)]}{2 + k \cdot [(c - b) + \text{abs}(c - b)]} \quad (\text{Eq. 2. 2. 5.})$$

This mathematical formula describes the model of one step for one type of adsorption mechanism.

For calculating the second and further steps, it is assumed that, the total adsorption capacity is the sum of the adsorption capacities of the effective adsorption sites above the critical concentration. The common features of this theory are the adsorption equilibrium constant (k), and the adsorption capacity (a) provided by the adsorption mechanism in question and the limit concentration (b). The mathematical expression is the same in all cases. The i^{th} step can be calculated from Eq. 2. 2. 5. using the next formula:

$$q = \frac{a_i \cdot k_i \cdot [(c - b_i) + abs(c - b_i)]}{2 + k_i \cdot [(c - b_i) + abs(c - b_i)]} \quad (\text{Eq. 2. 2. 6.})$$

where: i the index of a given step.

Multi step isotherms can be calculated additively from the adsorption isotherms of the individual “steps” (Eq. 2. 2. 6.)

$$q = \sum_{i=1}^s \left\{ \frac{a_i \cdot k_i \cdot [(c - b_i) + abs(c - b_i)]}{2 + k_i \cdot [(c - b_i) + abs(c - b_i)]} \right\} \quad (\text{Eq. 2. 2. 7.})$$

where s the total number of steps on isotherms.

The two steps isotherm is as follows:

$$q = \frac{a_1 \cdot k_1 \cdot c}{1 + k_1 \cdot c} + \frac{a_2 \cdot k_2 \cdot [(c - b_2) + abs(c - b_2)]}{2 + k_2 \cdot [(c - b_2) + abs(c - b_2)]} \quad (\text{Eq. 2. 2. 8.})$$

The parameter b is implicitly equal zero in the first step.

The three steps isotherm is:

$$q = \frac{a_1 \cdot k_1 \cdot c}{1 + k_1 \cdot c} + \frac{a_2 \cdot k_2 \cdot [(c - b_2) + abs(c - b_2)]}{2 + k_2 \cdot [(c - b_2) + abs(c - b_2)]} + \frac{a_3 \cdot k_3 \cdot [(c - b_3) + abs(c - b_3)]}{2 + k_3 \cdot [(c - b_3) + abs(c - b_3)]} \quad (\text{Eq. 2. 2. 9.})$$

Using the derived function, the parameters of a given isotherm can be calculated by non-linear curve fitting. Modifying Eq. 2. 2. 7. by an empirical power constant ($n > 0$), the error of fitting could be significantly decreased.

$$q = \sum_{i=1}^s \left\{ \frac{a_i \cdot k_i \cdot [(c - b_i) + abs(c - b_i)]^n}{2^n + k_i \cdot [(c - b_i) + abs(c - b_i)]^n} \right\} \quad (\text{Eq. 2. 2. 10.})$$

Unfortunately no evident physical explanation could be attributed to n. For calculations presented in this study Eq. 2. 2. 9. was used.

The mathematical equation detailed above has been applied to describe absorption isotherms for all the examined compounds. We found that the experimental adsorption data could be simulated with single-step (Langmuir) model for acetochlor and carbendazim, two-step model for diazinon, isoproturon, and atrazine, and three-step model for imidacloprid. The adsorption isotherms of the six pesticides studied are shown in Figure 8-13.

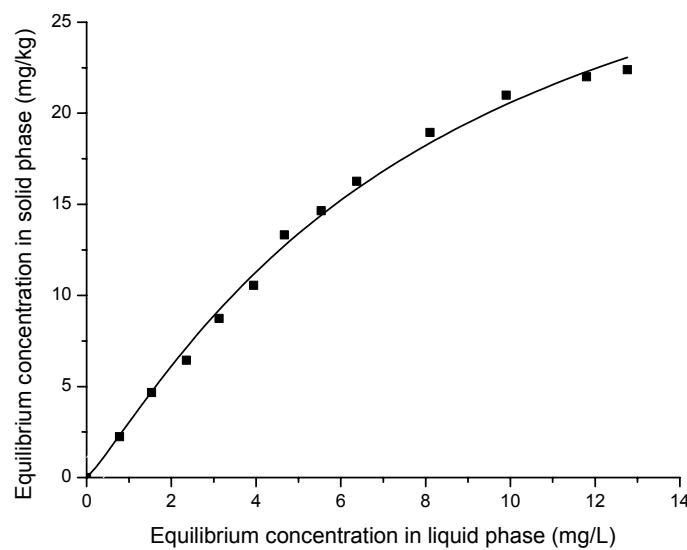


Figure 8. Adsorption isotherm of acetochlor

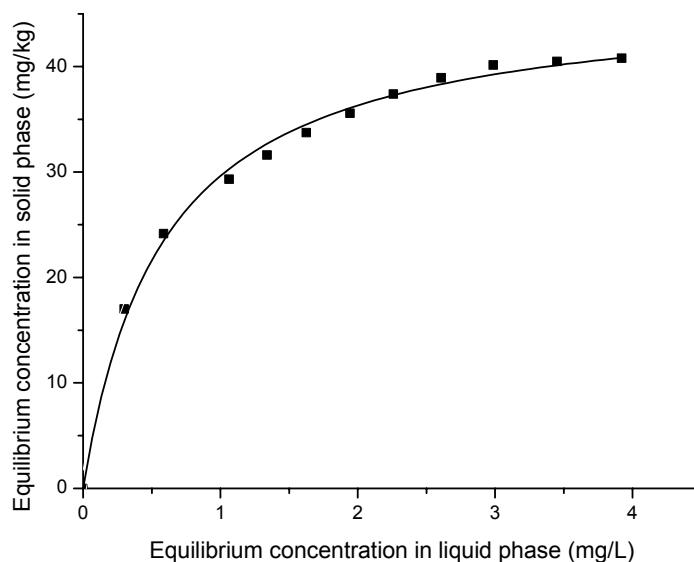


Figure 9. Adsorption isotherm of carbendazim

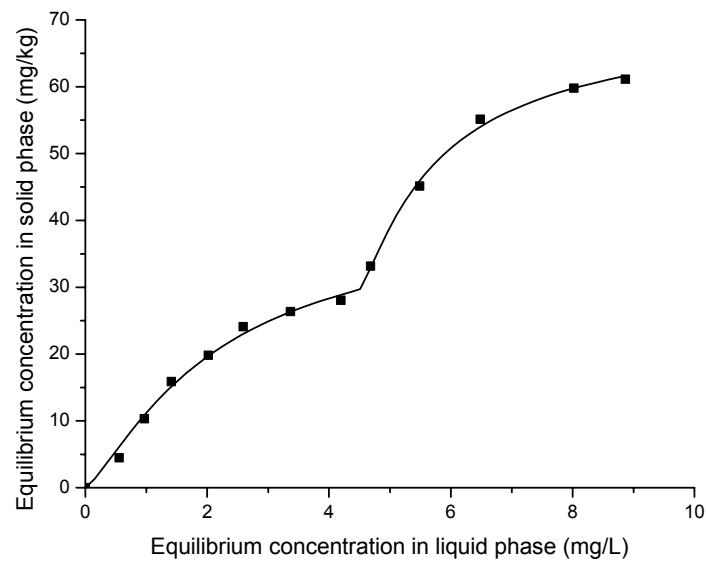


Figure 10. Adsorption isotherm of diazinon

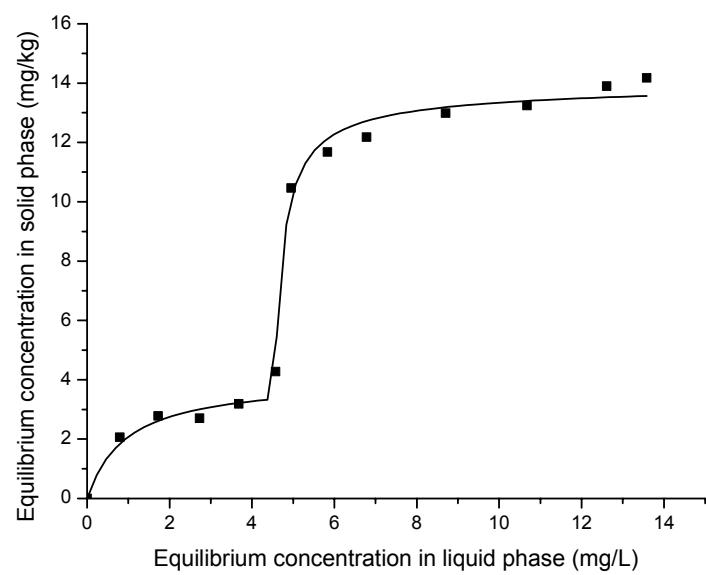


Figure 11. Adsorption isotherm of isoproturon

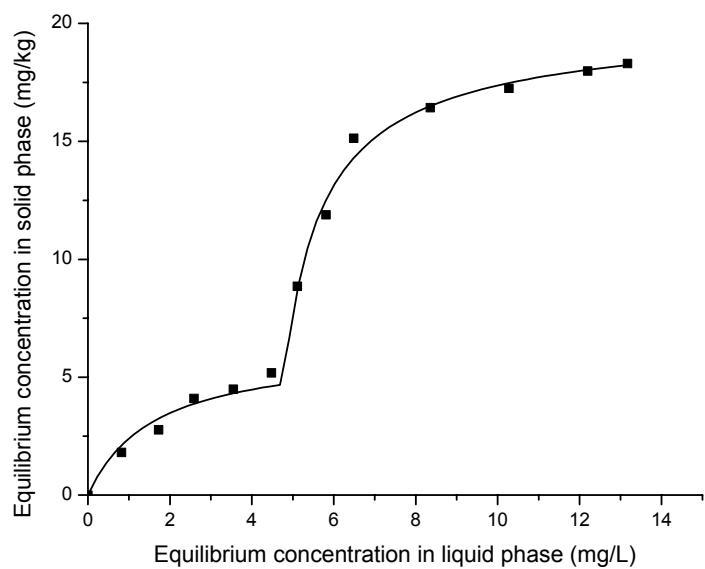


Figure 12. Adsorption isotherm of atrazine

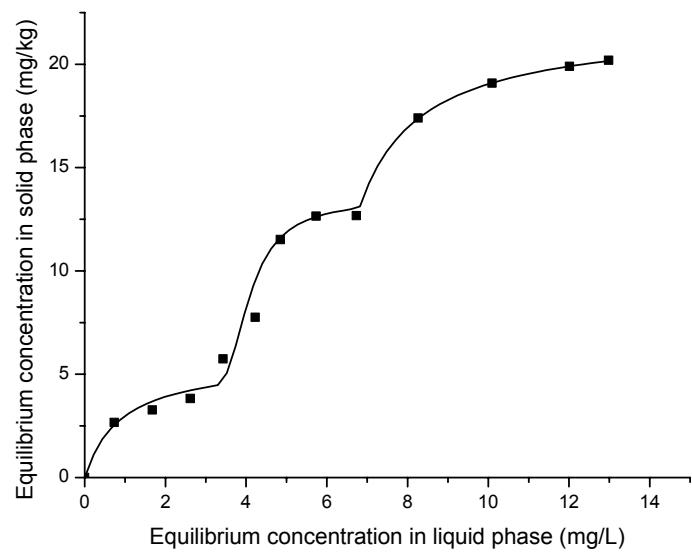


Figure 13. Adsorption isotherm of imidacloprid

The shape of sorption isotherm line suggests but does not confirm information about the sorbate-sorbent interaction. We assume that the steps arising on the isotherms indicate the inhomogeneity of adsorbent surface activity. A smaller part of the active site may have increased activity and they have been saturated at relatively low concentration. Additionally interactions between the pesticide molecules may occur on the surface or in the solution as well, since most of the pesticides consist of functional groups with different chemical and hydrophobic character.

Table 4. Calculated Parameters from Adsorption Isotherms of the Selected Pesticides

Pesticides	a_1	a_2	a_3	k_1	k_2	k_3	b_2	b_3
ACETOCHLOR	36.78 (1.46)			0.09 (0.01)				
CARBENDAZIM	46.91 (0.74)			1.71 (0.11)				
ATRAZINE	6.28 (1.27)	13.93 (1.11)		0.41 (0.18)	1.16 (0.29)		4.77 (0.11)	
DIAZINON	41.19 (2.61)	30.71 (2.60)		0.37 (0.05)	0.88 (0.22)		4.49 (0.08)	
ISOPROTURON	4.06 (0.88)	9.99 (0.66)		1.04 (0.73)	4.95 (1.15)		4.55 (0.01)	
IMIDACLOPRID	5.64 (1.27)	9.36 (0.81)	7.79 (0.86)	0.87 (0.28)	1.22 (0.31)	0.73 (0.17)	3.43 (0.18)	6.70 (0.84)

a_i represent the adsorption capacity provided by the adsorption mechanism in question,

k_i is the equilibrium constant and b_i is the limit concentration in the i^{th} step.

Standard deviations are given in parentheses.

Regression coefficients were 0.991-0.999.

The cumulated adsorption capacities (sum of the each steps) were decreased in order of diazinon (77.67 mg/kg), carbendazim (46.91 mg/kg), acetochlor (36.78 mg/kg), imidacloprid (22.79 mg/kg) and isoproturon (14.05 mg/kg). The adsorption capacities calculated for the first step (a_1) are about two times lower than for the second (a_2) in case of atrazine, isoproturon and imidacloprid, while approximately equal in case of diazinon. The similarity of the b_2 parameters determined for atrazine, diazinon and isoproturon might indicate that the first interactions between soil and pesticides are closely similar to each other. The k constant dependent on temperature

characterizes the adsorption equilibrium. Interpretation of individual k_i values is rather difficult without information regarding the energetic background of the adsorption processes. In case of isoproturon the explanation of k_i is further complicated by the relatively larger errors of estimation due to limited number of experiments. The calculated parameters from the isotherms are given in Table 4.

2.2.4. CONCLUSIONS

Based on the results obtained from the present study it can be concluded that the developed mathematical model described the measured experimental adsorption data well. The model gives an exact implementation of the description of adsorption processes for those compounds, which provide plots with one or multi steps shape. It also gives the possibility to extend the description of the adsorption processes with great precision. The parameters calculated from the new equation provide to estimate for the absorption constant, adsorption capacity and concentration limit for different adsorption mechanism which existing often simultaneously in soil-pesticides environmental system. Determination of the sorption isotherm type, and characteristics adsorption parameters provide information about solute mobility in soil, and allows to prediction of environmental behavior such as runoff and leaching properties of the pesticide.

Examination of desorption feature of these pesticides may provide additional information concerning the intensity of soil-pesticide interaction involved. However, further experiments have been initiated to study the energetic background of the multi-step adsorption nature of the studied pesticides on soil.

2.3. SUBCRITICAL WATER EXTRACTION TO EVALUATE DESORPTION BEHAVIOR OF ORGANIC PESTICIDES IN SOIL

The results of the study were published in J. Agric. Food Chem. (KONDA et al. 2002 c).

2.3.1. INTRODUCTION

Agricultural consumption of chemicals is a matter of environmental concern because they are recognized as a source of potential adverse environmental impact and their presence in surface and ground water have grown considerably (BARBAS and RESEK 1996, KOLPIN et al. 1998, LEISTRA and BOESTEN 1989, RITTER et al. 1994, TEMPLETON et al. 1998, COOPER 1993, HALLBERG 1989). To address this problem adequately, knowledge of the presence and fate of xenobiotics in the natural environment is required. Fate and behavior of chemicals in the environment involve several different and often simultaneous phenomena. Among these sorption to the soil is the most important process, which controls other physico-chemical and biological processes (GREENLAND and HAYES 1981, SCHNOOR 1992). Understanding the key factors affecting adsorption and desorption characteristics of a pesticide in soil contribute to the prediction of its mobility and environmental distribution between different environmental compartments as air, water, soil and sediment. The complexity of the phenomena and the variety of soils and types of chemicals has resulted in a great deal of work, not only experimental but also theoretical (HAYES 1970, DEC et al. 1997, COX et al. 1997, SPARKS 1999, GREG and SING 1982, SPARKS et al. 1993, HUANG et al. 1989, FRENCEL 1974, CLAPP et al. 1993, GOUY et al. 1999, OI 1999, CELLIS and KOSKINEN 1999).

Usually, residues of pesticides are extracted from soil with organic solvents such as acetone, ethyl acetate or methanol. In some cases for the investigation of the water-soluble compounds, extraction with water is sufficient. The use of supercritical fluids, most commonly carbon dioxide for soil extraction is becoming increasingly popular (WONG et al. 1991, STEARMAN 1995). The low critical temperature of carbon dioxide (31 °C) means that low extraction temperature can be used to recover thermally unstable solutes. Nevertheless, organic solvents and the supercritical carbon dioxide are not adequate to solubilize humate matter, and this fact results in failure to extract chemicals in soil quantitatively (DEAN 1996, LERCH et al. 1997, CHUNG and ALEXANDER 1998). However, the organic solvent and supercritical carbon dioxide extraction cannot provide information regarding the sorption characteristics of the pesticide in the soil-water system.

The most widely used experimental procedure for screening the sorption behavior of chemicals in soil uses 0.01 M CaCl₂ as aqueous solution at room temperature (OECD 1981). The low solvent power of water regarding non-polar pesticides having limited solubility and long extraction time made the method tedious and time-consuming. Over the last few decades several methods have been introduced to increase the efficiency of aqueous extraction, mainly for the determination of the available nutrient contents of soil. NÉMETH (1976) developed an electric field regulated water extraction system which operated between 20-80 °C. KÖRSCHENS et al. (1984) used hot water in a Soxhlet extraction apparatus to measure the available carbon and nitrogen contents of soil. SUNTHEIM and MATZEL (1985) used continuous water extraction method for determining phosphorus in soil. FÜLEKY and CZINKOTA (1993) developed a hot water percolation method using a “coffee percolator”-like apparatus to determine macro and micro-elements in soil. Recently many extraction studies have been performed using subcritical water as an effective extractant for a number of organic compounds in soil having a broad spectrum of polarity and hydrophobicity (YANG et al. 1997, FIELD et al. 1998, 1999, CRESCENZI et al. 1999, HAGEMAN et al. 1996, HARTONEN et al. 1997, JIMÉNEZ-CARMONA et al. 1997, DI CORCIA et al. 1999). Subcritical water extraction coupled off-line to a liquid chromatography system using octadecyl modified silica gel trap devised by YANG (1999) has shown to be an efficient device for analysing aromatic hydrocarbons in soil. CRESCENZI et.al. (2000) developed an effective analytical method for the determination of polar and medium polar contaminants in soil, by coupling a hot phosphate-buffered water extraction apparatus to a liquid chromatograph/mass spectrometer system on-line. They evaluated efficiency of device by extracting 13 selected pesticides.

The purpose of present work was to develop a rapid soil extraction method suitable for routine analyses of organic pesticides in soil by setting a hot water extraction device to exploit high temperature and pressure to increase the speed and efficiency of the extraction procedure. In terms of desorbed amount of pesticides from soil and time of extraction process the efficiency of the procedure developed by us has been evaluated and compared to that of a traditional reference procedure, the batch equilibrium soil-desorption method (OECD 1981). The selected model compounds, acetochlor, atrazine, diazinon, carbendazim, imidacloprid and isoproturon have been used in plant production and animal health intensively for the last several years and represent a wide range of chemical and functional classes. They comprise a good test set for evaluation of the new extraction method.

2.3.2. MATERIALS AND METHODS

2.3.2.1. Chemicals, Reagents and Standards

Chemicals, reagents and standards used for this experiment were the same as were used in the first study. They were identified in detail in the section 2.1.2.1. Sand (silicium dioxide) used in the recovery studies was purchased from Merck (Darmstadt, Germany). The physicochemical properties of the studied pesticides are presented in the Table 5. The chemical structure of the compounds was presented in the Figure 1.

Table 5. Physicochemical Properties of the Six Pesticides Investigated

Pesticide	K _{oc} ^a	logP _{ow} ^b	water solubility ^c (mg/L)
ACETOCHLOR	313.6	3.37	223 (25°C)
ATRAZIN	133.4	2.82	33 (20°C)
CARBENDAZIM	2805	1.55	8 (24°C, pH7)
DIAZINON	1589	3.86	60 (20°C)
IMIDACLOPRID	209.6	0.56	510 (20°C)
ISOPROTURON	174.4	2.84	65 (22°C)

^a Adsorption constants related to the soil organic carbon content (0.68% for the experimental soil) are calculated from the Freundlich equation. Adsorption experiments were performed in our preliminary studies according to OECD Test Guideline 106 (1981).

^b Logarithm of estimated octanol-water partition coefficients based on chemical structure using Environmental Science Centre Estimation Software.

^c The listed solubility values are cited in Pesticide Manual (1994).

2.3.2.2. Experimental Soil

For sorption experiments, analyte-free soil sample from location Bak in Hungary was used. This soil represents well the soil relations for remarkable part of the agricultural area of the country without any extremity in its characteristic. The type of the soil was Luvisol according to classification of Food and Agriculture Organization of the United Nations. The typical properties of soil were presented in the section 2.1.2.2.

2.3.2.3. Sorption Experiments

Stock standard solutions of each pesticide (1.0 mg/mL) were prepared by dissolving the required amount in acetonitrile and were kept under refrigeration. Dilutions were made with 0.01 M calcium chloride solution to the desired final concentrations. Aqueous solutions of pesticides at 15 mg/L concentration (8 mg/L for carbendazim because of its limited solubility) were shaken in 450 mL Erlenmeyer flask with air-dried and sieved (<2 mm) soil (30 grams soil/300 mL of solution) for 16 hours at 20 ± 1 °C to achieve equilibrium. Blank samples were prepared without soil in the same way to achieve recovery values to confirm that no significant degradation of the chemical or sorption on the glass wall occurred during equilibration time. Equilibrium concentrations were determined in supernatants by high performance liquid chromatography with UV detection. The amount of pesticide adsorbed by the soil was calculated from the difference between the initial and equilibrium pesticide concentrations in the liquid phase. The adsorption equilibration process was made in three replicates for each chemical. For comparative purpose, desorption was conducted by replacing supernatant with 0.01 M calcium chloride solution. Suspensions were shaken for 16 h, centrifuged, and supernatants were analyzed. The desorption-equilibration process was repeated six times.

2.3.2.4. Hot Water Extraction Procedure

Extraction was performed with a high performance hot water percolation instrument developed by FÜLEKY and CZINKOTA (1993) for the determination of the available nutrient contents of soil. Twenty-five grams (dry weight) of each pesticide-equilibrated soil was mixed with 10 g of sand to provide adequate flow rate and filled to the replaceable sample holder. Water preheated to 105°C in the container was passed through the sample at a pressure of 120 kPa and

collected in six 100 mL aliquots. The percolation time was measured. The pesticide contents of the effluents were determined. The extractions were carried out on three replications per chemical. To evaluate the effect of the high temperature on analyte recovery, six-step experiment was performed in three parallels by extracting 10 gram of each pesticide-spiked sand under the same conditions described above.

2.3.2.5. Pesticide Analysis

Supernatant was separated from soil by sedimentation. 15 mL aliquots of liquid phase from sorption experiment or effluents from the hot water extraction were centrifuged at 8000 rpm for 20 min. SPE cartridges were activated by washing once with 2 mL methanol and 2 mL 0.01 M calcium chloride solution. 10 mL supernatant was drawn through the extraction column. After sample addition, the stationary phase with the retained pesticide was dried for 5 min with air. Elution was performed with 2 mL acetone. The organic solvent was evaporated to dryness under a gentle stream of nitrogen and the residue was dissolved in 1.0 mL volume of acetonitrile-water mixture (1:1 v/v). Prepared samples were passed through disposable membrane filters and analyzed by high performance liquid chromatography with UV detection.

The HPLC system, analytical column, guard column and mobile phases were the same as were used in the previously study. Instrumentation and operating condition were detailed in the chapter 2.1.2.4. Typical chromatograms of investigated pesticides are shown in Figure 2. and 3.

External calibration curves with standard solution at five concentration levels were used in the calculations. Calibration curves for each of the compounds were linear up to 5 mg/L with regression coefficients of 0.999. Detection limits were 0.2 µg/L for atrazine, acetochlor, carbendazim, and imidacloprid, while 0.4 µg/L for isoproturon and diazinon as determined according to the American Society of Testing and Materials ASTM D4210 standard.

2.3.3. RESULTS AND DISCUSSION

2.3.3.1. Effect of the Temperature on Analyte Recoveries

High-temperature water has decreased surface tension, viscosity and polarity, which make it an efficient solvent for extracting poorly water-soluble organics from soil matrixes. Elevated temperature is also advantageous in increasing the rate of mass transfer between liquid and soil by

increasing diffusion coefficients (YANG et al. 1998). Additionally the boiling temperature of water at standard pressure allows the precise control of temperature, thus enhances the repeatability of the method. On the other hand, use of hot water as extractant poses a risk inherent to decompose thermolabile compounds or those that prone to hydrolytic attack. Therefore we evaluated the temperature effect on stability of selected pesticides by performing recovery studies using pesticide-spiked sand without soil. Except for acetochlor and carbendazim, heat load during the extraction period of pesticides adsorbed on soil did not significantly differ from that of the reference (pesticide spiked sand without soil), because 60 – 82 % of the desorbed pesticide amount from soil was recovered in the first portion of the extract. Heat exposure was identical for all pesticides during the period when samples were left to cool at room temperature (approx. 45 min). Good recovery of the pesticides considered were obtained from the method (84.6 % - 91.1 %) with appropriate repeatability (7.9 % - 10.2 %), except for diazinon, when recovery was 59.4 % with 14.4 % relative standard deviation by the reason that conceivable decomposition occurred at 105°C water temperature.

2.3.3.2. Extraction of Pesticides in Soil and Method Comparison

The performance of the hot water extraction method was compared to batch equilibrium method (see the experimental section). The average values and variation coefficients for desorption experiments for the investigated pesticides in three replicates are presented in Table 6.

The pesticide contents determined by the two methods are generally of the same magnitude: the hot water extraction method gives higher amount of imidacloprid and smaller amount of acetochlor than the 0.01 M calcium chloride solution method, and approximately the same carbendazim, isoproturon and atrazine contents. The diazinon content of the hot water extract was higher than that in the reference procedure, possibly resulted from the higher efficiency of the hot water extraction although decomposition of the chemical occurred as well. Desorbed quantities were 85 % of acetochlor, 62 % of atrazine, 65 % of carbendazim, 44 % of diazinon, 95 % of imidacloprid and 84 % of isoproturon in percentage of the adsorbed amount of pesticide on soil following equilibration process.

The 6x100 mL volume of percolated hot water were sufficient to release the amount of isoproturon and atrazin available for desorption from the soil samples: they were not detected in the fifth and sixth 100 mL aliquots of effluents. Amount of hot water was not enough in case of acetochlor and carbendazim: there were remarkable amount of residues in the last aliquots, 41 µg/100mL and 64 µg/100mL respectively. It was presumably adequate for imidacloprid when the

pesticide concentration of the sixth aliquot was 8 µg/100mL. The average time for one extraction step was 34.5 second. The repeatability of the method can be considered to be good since relative standard deviation ranges from 6.0 % to 9.4 %. The RSD % value is highest for the diazinon (17.1 %) due to uncontrolled chemical reactions resulting from thermolability of the compound.

Table 6. Experimental Data of Sorption Processes of the Six Pesticides Investigated.

Pesticide	Adsorbed amount (mg/kg)	Desorbed amount (mg/kg)	
		Batch equilibrium method^a	Hot water percolation^b
ACETOCHLOR	24.98 (4.2)	25.47 (4.9)	21.17 (7.9)
ATRAZINE	16.89 (3.4)	11.20 (4.2)	10.38 (8.1)
CARBENDAZIM	42.87 (4.8)	27.39 (5.0)	27.86 (8.6)
DIAZINON	65.84 (4.2)	24.19 (4.8)	29.02 (17.1)
IMIDACLOPRID	23.96 (3.8)	19.40 (5.5)	22.79 (9.4)
ISOPROTURON	13.65 (4.1)	12.33 (4.7)	11.52 (6.0)

^a Average values of cumulative data in mg/kg obtained from six times repeated desorption equilibration process in triplicates.

^b Average cumulative extracted amount in mg/kg obtained from six-step percolation experiment in triplicates. Relative standard deviations are given in parentheses.

2.3.3.3. Mathematical Modeling of Hot Water Percolation Processes.

The possibility of mathematical presentation of the result obtained by hot water percolation method has been explored. For each pesticide there was close correlation between the amount of water percolated and the quantity of pesticides extracted.

This relationship is described in satisfactory manner in each case by the equation:

$$y = A \cdot (1 - e^{-b \cdot V}) \quad (\text{Eq. 2. 3. 1.})$$

where:

y is the amount of the pesticide extracted per unit mass of soil [mg/kg],

V is the amount of water percolated [mL],

A and b are empirical constants, representing the maximum amount of pesticide available for desorption [mg/kg], and volume constant [mL^{-1}] respectively.

The first order kinetic equation is suitable for the formal kinetic description of the processes by which pesticides are released during percolation:

$$y = A \cdot (1 - e^{-k \cdot t}), \quad (\text{Eq. 2. 3. 2.})$$

where:

t is the time of percolation [s],

k is the kinetic constant [s^{-1}].

All percolation experiments were achieved under constant volumetric flow-rate condition (average value 3.3 mL/s), therefore: $k = u \cdot b$, where u is the volumetric flow-rate [mL/s]. Using the above described kinetic equation the rate of the desorption can be calculated at any time during the percolation. The kinetic profiles of the investigated compounds are shown in Figure 14. The calculated parameters from the equation are given in the Table 7.

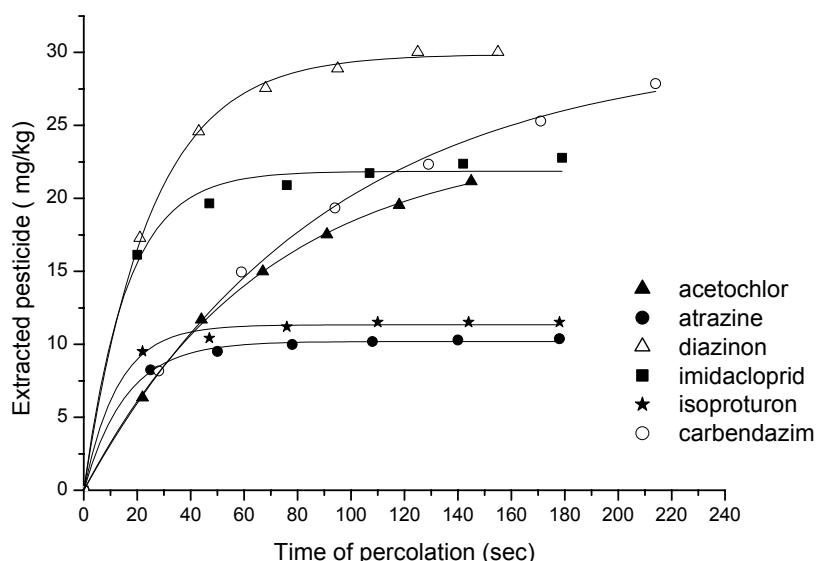


Figure 14. Cumulative amount of extracted pesticides as a function of percolation time.

Table 7. Calculated Parameters from the Kinetic Equation Describing the Percolation Processes for the Six Pesticides Examined

Pesticide	A	k	r
ACETOCHLOR	23.87 (0.38)	0.0147 (0.0005)	0.999
ATRAZINE	10.20 (0.09)	0.0639 (0.0036)	0.999
CARBENDAZIM	30.17 (0.74)	0.0110 (0.0006)	0.999
DIAZINON	29.87 (0.18)	0.0403 (0.0011)	0.999
IMIDACLOPRID	21.85 (0.39)	0.0626 (0.0066)	0.996
ISOPROTURON	11.34 (0.16)	0.0787 (0.0081)	0.997

A represent the maximum amount of pesticide available for desorption in mg/kg,

k is the kinetic constant in s⁻¹.

Standard deviations are given in parentheses.

2.3.4. CONCLUSIONS

The hot water percolation apparatus was successfully applied to desorption of the pesticides from soil. Results are in close correlation with the pesticide contents extracted with traditional batch method. The strength of the method lies in the possibility screening of a large number of samples within a short period of time at low cost. Nevertheless neither the percolation method nor batch method considers soil structure. However parameters obtained from kinetic measurements provide information about the system. Parameters calculated from kinetic equation provide an opportunity to estimate the amount of chemical available for desorption, the rate of the processes in the studied soil-pesticide-water system, and modeling the leaching process to obtain additional information on the environmental behavior of the examined pesticide. Determining the kinetic constant (*k*) of the test substance and comparing it to the *k* values of a set of substances with known leaching characteristics on the same soil type may provide useful information regarding the leaching characteristic of the test substance. Compounds having high *k* values are probably faster

desorb and may exhibit pronounced leaching. The developed method can be a valuable supplement to conventional analytical methods.

The only limitation of the hot water percolation method is that it could fail to recover compounds that are both poorly hydrophilic in nature and thermolabile or prone to hydrolytic attack. Thus, evaluation of thermal and hydrolytic stability of the pesticide, as well as its susceptibility to the catalytic activity of soil colloids should be carefully assessed.

2.4. ENVIRONMENTAL DISTRIBUTION OF ACETOCHLOR, ATRAZINE, CHLORPYRIFOS AND PROPISOCHLOR UNDER FIELD CONDITIONS

The results of the study were published in J. Agric. Food Chem. (KONDA and PÁSZTOR 2001).

2.4.1. INTRODUCTION

The progressive increase of production and application of chemicals for agricultural activities has converted the problem of environmental contamination into a national and international issue. A number of pesticides have been detected in ground water and surface water in the United States and in Europe in the past years. In 43 states of USA, at least 143 pesticides and 21 transformation products have been detected, including compounds in every major chemical class (MEYER and THURMAN 1996, BARBAS and RESEC 1996, CLARC and GOOLSBY 1999). The most frequently detected pesticides were those that have been used extensively, such as triazines (atrazine, cyanazine and simazine), acetanilide herbicides (metolachlor, acetoxychlor and alachlor) and 2,4-D. The most frequently detected insecticides that are currently used were carbofuran and diazinon (LARSON et al. 1995, SCREBER et al. 1996, KOLPIN et al. 1998). German researchers detected 145 organic polluting chemicals in the river Elbe among others triazines, dimethoate and their metabolites (GRIFFINI et al. 1997). In the Italian river Arno and in Greek natural surface water several pesticides have been measured as well (GÖTZ et al. 1998, MILIADIS and MALATOUD 1997). According to the survey of the Hungarian Environmental Information and Monitoring System phenoxyacetic acid derivates (2,4-D and MCPA), triazine compounds (atrazine, terbutryn and terbumeton) and chlorinated hydrocarbons (DDE, DDT, DDD, lindane, endosulfan) could be detected in 4,6 % of the soil samples taken in agricultural areas in 1997-1998. Analysis of drinking and ground water samples originated from different parts of Hungary has shown that 21 pesticides of different types were determined in 62 samples from 28 sampling points in the same time period. The concentration of pesticide exceeded the level of 0.1 µg/L in 8 cases for diazinon, atrazine, prometryn, 2,4-D and MCPA (KÁRPÁTI et al. 1998).

As the need for water increases and the amount of potable water in the world is limited, people are increasingly conscious of the need to protect water resources. To reduce the risk of contamination, it is essential to understand the factors that affect the behavior of pesticides in the natural environment. The fate and behavior of pesticides in the soil environment involve several different and often simultaneous phenomena. The pesticides may be transformed by chemical and

biological processes or transported from the site of application by runoff, leaching, volatilization, and wind erosion. Attention should be focused on behavior within the soil environment (GREENLAND and HAYES 1981, WOLFE and SEIBER 1993, MOOMAW et al. 1996, vanES 1998). The behavior of a pesticide in soil depends on its physicochemical properties, the nature of the soil and the organisms it contains, climatic conditions, crop type, cropping practices, and water management methods. All of these properties and processes determine the biological availability of pesticides and their redistribution from the point of application (GOPAL et al. 1994, HORNSBY et al. 1996, JAMET 1996). In practice, these various factors all interact and ideally should be considered together. In recent years there have been several works on the behavior of pesticides in soil. Many laboratory studies (ALBANIS et al. 1991, BROUWER et al. 1994, dousset ET AL. 1994, XIONGWU et al. 1996, KAUNE et al. 1998, GRABER and BORISIVER 1998) and field experiments (FLURY 1996, MATHYS 1994) have been made. However, laboratory studies were mainly aimed to clarify individual effects of the above-mentioned factors on pesticide-environment interaction. Such laboratory studies cannot be easily interpreted under real field conditions. A product's hazard cannot sufficiently be assessed exclusively from laboratory studies due to different environmental and socio-economic conditions of each country and the large number of interacting environmental and anthropogenic factors. In the present study we describe the fate and transport of four commonly used pesticides in Hungary. Three herbicides - acetochlor, atrazine and propisochlor - and an insecticide - chlorpyrifos – were investigated to obtain information on the environmental behavior of these chemicals under field conditions.

2.4.2. MATERIALS AND METHODS

2.4.2.1. *Chemicals, Reagents and Standards*

Acetochlor, atrazine, chlorpyrifos and propisochlor all with purity higher than 99%, were obtained from Sigma Aldrich Kft. (Hungary, Budapest). The structure of chemicals is shown in Figure 15. Chromatographic-grade acetone, methanol, methylene chloride, n- hexane and analytical-grade ammonium acetate, sodium sulfate (anhydrous) and acetic acid were purchased from Merck (Darmstadt, Germany). Stock standard solutions of each pesticide (1mg/mL) were prepared by dissolving the required amount in acetone and were kept under refrigeration. Dilutions were made daily with n-hexane to the desired final concentration before gas chromatographic analysis. Extraction cartridges used were Waters Sep-Pak octadecyl (C_{18} 500 mg) columns (Waters Corp., Milford, MA, USA).

Common name	Molecular structure	IUPAC name	MW
ACETOCHLOR		2-chloro-N-ethoxymethyl)-6'-ethylacet-o-toluidide	269,77
ATRAZINE		6-chloro-N ² -ethyl-N ⁴ -isopropyl-1,3,5-triazine-2,4-diamine	215,69
CHLORPYRIFOS		O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate	350,59
PROPIOCHLOR		2-chloro-6'-ethyl-N-isopropoxy-methyl-aceto-o-toluidide	283,77

Figure 15. Chemical structure of the four pesticides studied.

2.4.2.2. Experimental Plot and Soil

The experiment was conducted on a plot plowed to a depth of 25 cm sown with maize. Crop characteristics were as follows: sowing depth 5cm, row width 74 cm, plant spacing 20 cm. Average slope of land was 2%. Type of soil was sandy loam (Luvisol according to classification of Food and Agriculture Organization of the United Nations), which has the following composition and characteristic: 1.26 % organic matter, 23.7 % silt, 14.6 % clay, 60.7 % sand and 0.9 % calcium

carbonate. Formulations of commercial preparation were emulsified concentrate for propisochlor and chlorpyrifos, and aqueous suspension in case of acetochlor and atrazine. Content of active ingredients (a.i.) of test substance were 480 g/L chlorpyrifos, 300 g/L acetochlor, 200 g/L atrazine and 840 g/L propisochlor. The field was sprayed as pre-emerge treatment at the recommended application rate: 1500 g a.i./ha, 1000 g a.i./ha, 720 g a.i./ha and 2100g a.i./ha dose of acetochlor, atrazine, chlorpyrifos and propisochlor respectively.

2.4.2.3. Weather Condition

The meteorological conditions (daily minimum/maximum air temperature and precipitation) were recorded at the experimental site. The quantity of rainfall was recorded by a portable liquid-level recorder attached to an artificial reservoir. Precipitation and rainfall data are summarized in Table 8.

2.4.2.4. Sampling Method

An H-type flume (60 cm deep) was built in the lower part of experimental plot to collect runoff water and sediment. The stream flowed along the lowest side of experimental plot. Mixed soil sample was taken from a depth of 0-20 cm before spraying as an untreated control sample. Composite soil samples were taken from 12 predetermined positions of the experimental plot from depths of 0-5 cm and 5-20 cm, immediately after application and on the 14th, 28th, 42nd, 56th, 98th, 126th and 140th days after application. The sampling was carried out with a special drilling device to obtain undisturbed soil cores in order to avoid contamination of the lower soil layers by soil particles from the upper layers. Water samples were collected from the stream additionally at the same time. The runoff water and sediment samples were collected from the artificial reservoir after every runoff event during the experimental interval. The flume and the approach box were cleaned (sediment and collected water were removed) after each runoff events. Soil samples were collected in polyethylene bags. Water and sediment samples were collected after sedimentation on site, in amber glass flasks and polyethylene bags respectively. The samples were placed in cool boxes and transported to the laboratory and stored at -18°C until preparation.

Table 8. Precipitation during the experiment and the amount of rain during the runoff events recorded at the experimental plot.

Time interval (DAT)	Precipitation (mm)	Date of runoff event (DAT)	Rainfall ^a (mm)
0-6	29.8		
6-13	20.3	13	17.2
13-23	28.6	23	17.5
23-25	21.0		
25-26	49.7	26	43.7
26-46	20.2		
46-52	19.6		
52-54	41.3	54	40.3
54-62	4.9		
62-67	34.0	67	29.4
67-68	21.0		
68-69	24.1	69	23.5
69-86	46.2		
86-89	15.1	89	14.1
89-101	27.3	101	25.4
101-105	3.2		
105-116	35.0	116	31.2
116-129	20.4		
129-137	33.6	137	30.6

^a: Amount of rain recorded at the experimental plot during the runoff events.

DAT: days after treatment

2.4.2.5. Sample Preparation

After removal of pieces of stones and plants, the soil or sediment samples were homogenized. Portions (50g) were weighed and extracted with 100 mL of acetone (containing 2 ml 2 M ammonium-acetate) on a flask shaker for 30 min. The extract was filtered and the extraction was repeated two more times. Clean up of sample extract was carried out by liquid-liquid partitioning. 450 mL of 2 % sodium sulfate solution was added to the combined filtrate and it was extracted with 3×100 mL methylene chloride. Methylene chloride phase was drained through 30 g anhydrous

sodium sulfate, and rotary evaporated. The residue was dissolved in 5 mL n-hexane and analyzed. At the time of analysis 50 g of soil or sediment was dried on 105°C till constant weight in order to determine the moisture content of samples.

Extraction of pesticides from water samples was performed with C₁₈ solid phase extraction method. The collected water sample was equilibrated to room temperature, filtered through filter paper and the pH was adjusted to pH 7.2-7.4 with acetic acid. SPE cartridges were activated by washing once with 2 mL methanol and 2 mL distilled water. 100 mL supernatant was loaded into the reservoir of the extraction cartridge and drawn slowly through the column. After sample addition, the stationary phase with the retained pesticides was dried for 5 min with air. Elution was performed with 10 mL methylene chloride. The organic solvent was drained through anhydrous sodium sulfate and evaporated to dryness under a gentle stream of nitrogen. The residue was dissolved in 0.5 mL n-hexane and analyzed.

2.4.2.6. Capillary Gas Chromatography Analysis

A Chrompack 9000 gas chromatograph equipped with nitrogen phosphorous selective detector was used for simultaneous identification and quantification of acetochlor, atrazine, chlorpyrifos and propisochlor. Chromatographic separation was achieved on a CP-SIL 8CB capillary column, length 25 m, column i.d. 0.53 mm, film thickness 1 µm (Chrompack International B. V., Middelburg, The Netherlands). The GC operating conditions were as follows. The injector port temperature was 230°C, the detector temperature was 270°C. The oven temperature was 140°C for 1 min, 140-180°C at 12 °C/min, 180°C for 10 min, 180-250°C at 30°C/min, and isothermal hold at 250°C for 10 min. Nitrogen was used as the carrier gas at a flow rate of 9.6 mL/min; hydrogen and air flow rate were 3.6 mL/min and 55 mL/min respectively. Injection volume was 1µL. Data acquisition and processing were accomplished by means of a Waters Maxima 820 data station running on an IBM PC/AT 486 computer.

2.4.2.7. Method Characteristics

The calibration curves were linear up to 20.0 ng/µL (regression coefficients 0.999). The limit of detection was 0.05-0.2 µg/L in water and 0.02-0.001 mg/kg in soil for each compound as determined according to the American Society of Testing and Materials ASTM D4210 standard. The analytical method was validated by analyzing two series (n=5) of water samples spiked with

the four pesticides at 0.5 µg/L and 10.0 µg/L concentration levels, and two series (n=5) of soil samples spiked at 0.05mg/kg, 0.10 mg/kg and 0.5 mg/kg concentration levels. Repeatability was appropriate with relative standard deviations lower than 5% in all cases and recoveries ranging from 87.4-96.7% for soil and 84.7-89.6% for water samples. Retention times of the compounds were: atrazine 7.4 min, acetochlor 10.5 min, propisochlor 11.3 min and chlorpyrifos 13.7 min. The typical chromatograms of the soil, sediment and runoff water samples are shown on the Figure 16-18.

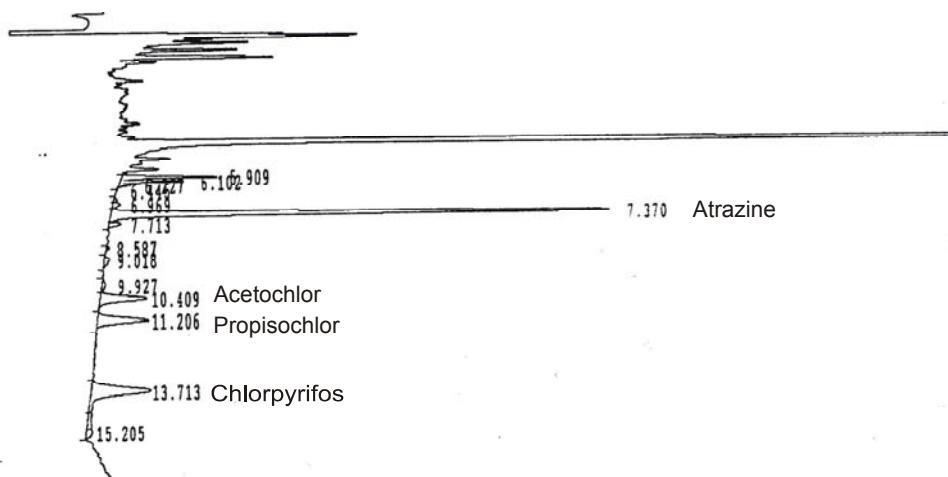


Figure 16. Typical chromatogram of soil sample

Conditions: column CP-SIL 8CB (25 m x 0.53 mm i.d, 1 µm df); injector 230°C; detector NPD, 270°C.; oven 140°C for 1 min, 140-180°C at 12 °C/min, 180°C for 10 min, 180-250°C at 30°C/min, 250°C for 10 min; carrier gas N₂ 9.6 mL/min; injection volume 1µL. Concentrations: atrazine 0.247 mg/kg, acetochlor 0.211 mg/kg, propisochlor 0.315 mg/kg, chlorpyrifos 0.01 mg/kg. The results of analysis were expressed on dry material basis.

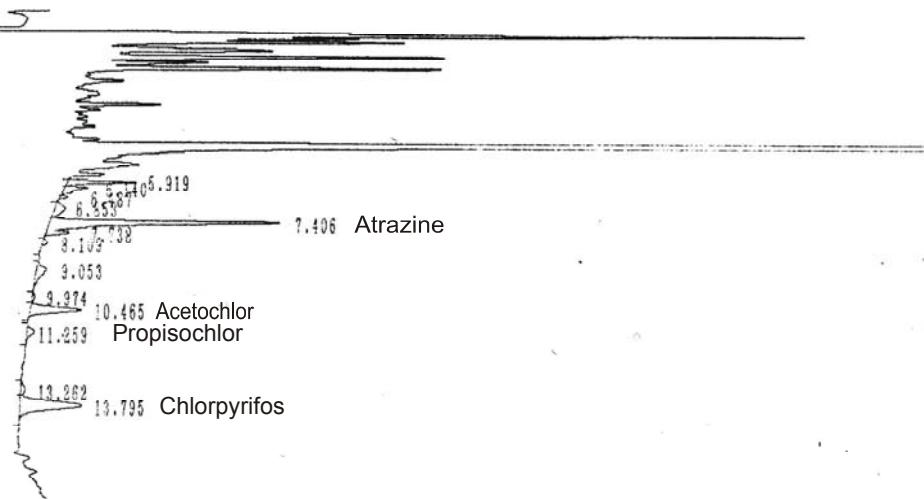


Figure 17. Typical chromatogram of sediment sample

Conditions were the same as in Figure 16. Concentrations: atrazine 0.128 mg/kg, acetochlor 0.194 mg/kg, propisochlor 0.056 mg/kg, chlorpyrifos 0.06 mg/kg. The results of analysis were expressed on dry material basis.

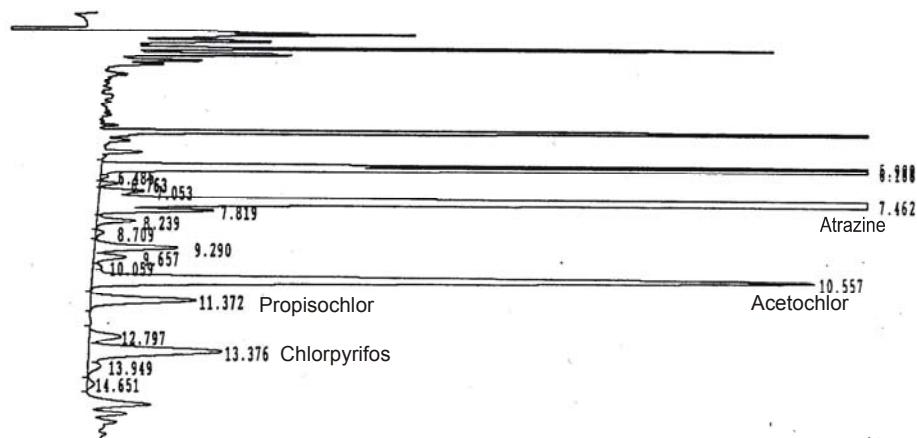


Figure 18. Typical chromatogram of runoff water sample

Conditions were the same as in Figure 16. Concentrations: atrazine 154 µg/L, acetochlor 89.1 µg/L, propisochlor 47.4 µg/L, chlorpyrifos 0.139 µg/L.

2.4.3. RESULTS

2.4.3.1. Pesticide Distribution and Persistence in Soil

The initial concentrations of acetochlor, atrazine, chlorpyrifos and propisochlor in soil were 0.740 mg/kg, 0.670 mg/kg, 0.298 mg/kg and 1.105 mg/kg immediately after application. There was a consistent decrease in pesticide residue concentration in the 0-5 cm soil layer with increasing time after spraying. The residues of compounds decreased to 0.462 mg/kg (62.5% of the initial), 0.376 mg/kg (56.2%), 0.098 mg/kg (33.0%) and 0.672 mg/kg (60.8%) at the 14th day, and 0.217 mg/kg (29.3%), 0.242 mg/kg (36.1%), 0.010 mg/kg (3.5%) and 0.309 mg/kg (28%) respectively at the 28th day. By 140 days after treatment only 1.37% atrazine and 0.69% chlorpyrifos of the initial concentration were measured and acetochlor and propisochlor were not detected (Figure 19).

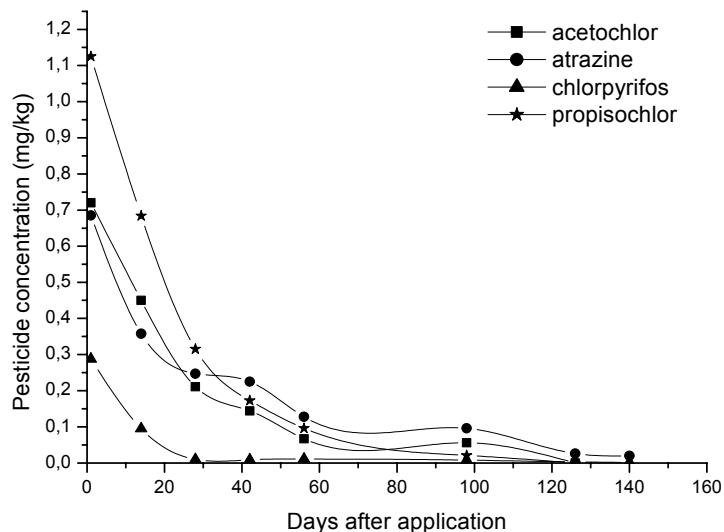


Figure 19. The change of the amounts of pesticides in soil depth of 0-5 cm layer for the experimental interval.

The results of analysis of soil samples were expressed on dry material basis.

A significant vertical downward movement could be observed in case of atrazine and chlorpyrifos. It took place intermittently during and immediately after periods of rainfall. The leaching was more pronounced during the first four weeks after application. This assumption is based on the concentrations of atrazine and chlorpyrifos in the 5-20 cm soil layer, which were 0.029 mg/kg and 0.030 mg/kg at 28th day respectively. No significant change could be observed

from 42th day to 140th day. Acetochlor and propisochlor were not detected in the 5-20 cm soil layer; presumably they remained in the surface 5 cm of the soil and dissipated (Figure 20).

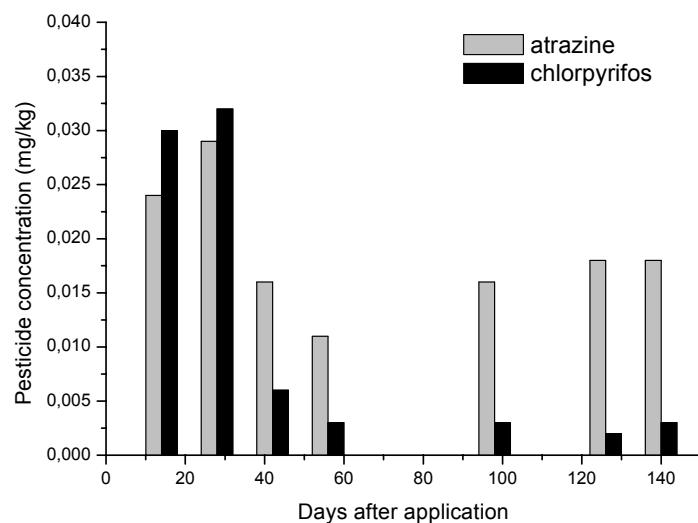


Figure 20. The change of the amounts of pesticides in soil depth of 5-20 cm layer for the experimental interval.

The results of analysis of soil samples were expressed on dry material basis.

2.4.3.2. Runoff of Pesticides

Runoff had enough velocity and transport capacity to carry soil particles during rainfall. The highest pesticide concentrations of runoff water were detected following the 3rd rainfall event, at 28th day after application: 89.1 µg/L acetochlor, 154 µg/L atrazine, 0.139 µg/L chlorpyrifos and 47.4 µg/L propisochlor were detected. The maximum concentration of pesticides in sediment was detected at the same time: 0.198 mg/kg acetochlor, 0.128 mg/kg atrazine, 0.007 mg/kg chlorpyrifos and 0.056 mg/kg propisochlor were detected. The concentrations of pesticides in the sediment and surface runoff water are presented in the Figure 21 and 22. The maximum detected residues of atrazine and acetochlor in stream water were 6.12 µg/L and 1.47 µg/L respectively, while chlorpyrifos and propisochlor were not detected.

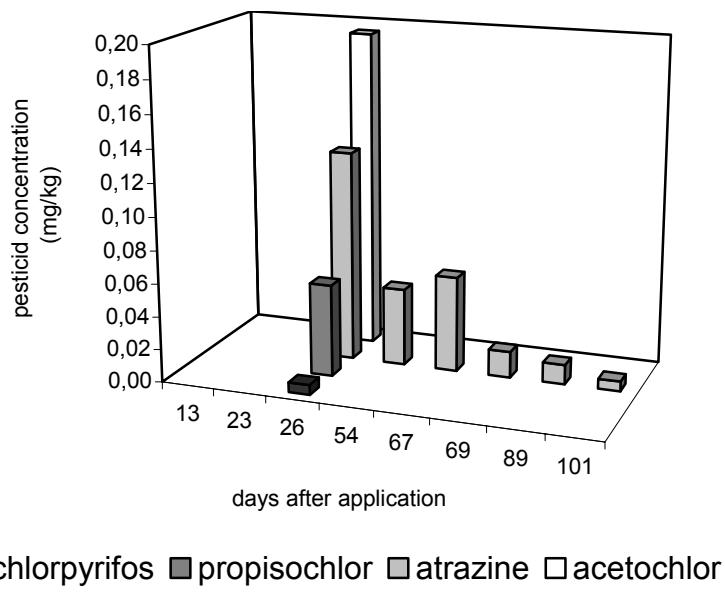


Figure 21. Acetochlor, atrazin, chlorpyrifos and propisochlor concentration in sediment samples.

The results of analysis of sediment samples were expressed on dry material basis.

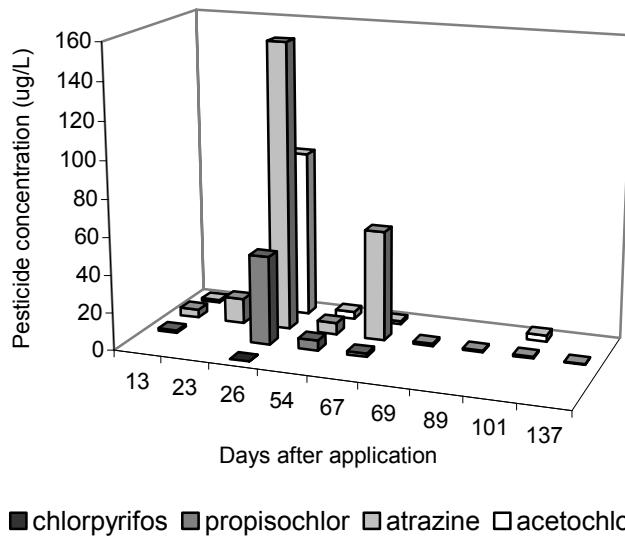


Figure 22. Acetochlor, atrazin, chlorpyrifos and propisochlor concentration in runoff water samples.

2.4.4. DISCUSSION

Based on the results of the study it can be concluded that the pesticide downward movement, losses by the surface runoff process and the contamination of stream are closely related to time of rainfall elapsed after treatment and amount of rain at the experimental plots.

The initial higher leaching of pesticides is explainable with the higher surface concentration and the rudimentary roots of plants - which could not decrease water percolation to deeper zone - at the beginning of experiment.

The runoff caused losses primarily depending on rainfall volume and intensity. In addition, runoff and erosion were aggravated by the lack of crop canopy during the first part of experiment, which could protect the soil from direct raindrop impact. The detected maximum concentrations of atrazine and acetochlor in sediment and runoff water were about 2-3 times higher than those of propisochlor and two orders of magnitude higher than chlorpyrifos concentrations. Downward movement of chlorpyrifos was more pronounced than those of the others. These phenomena might be explained only partly with the different physicochemical properties of the compounds. Atrazine, acetochlor and propisochlor are characterized by relatively high water solubility and low soil sorption coefficient, whereas chlorpyrifos has low water solubility and high sorption coefficient (Table 9.)

Table 9. Physicochemical properties of the four pesticides investigated

Pesticide	$\log P_{ow}$	K_{oc}	water solubility mg/L
ACETOCHLOR	3,03	313	223 (25°C)
ATRAZIN	2,50	39-155	33 (20°C)
CHLORPYRIFOS	4,70	8498 ^b	1,4 (25°C)
PROPISOCHLOR	3,50	-	184 (20°C)

The logarithm of octanol-water partition coefficients ($\log P_{ow}$), soil sorption coefficients (K_{oc}) and water solubility values are from The Pesticide Manual (TOMLIN 1994).

^b data is from study of RACKE (1993).

The typical field dissipation half-lives of chlorpyrifos for soil-surface and soil-incorporated applications at agricultural use rates range from 1 - 2 weeks and 4 - 8 weeks, respectively (RACKE 1993). Our results are in good agreement with these observations. The first runoff event happened at 26th days after application, and it is assumed there wasn't considerable chlorpyrifos amount any more in the upper soil layer at that time. The half life of other three pesticides was approximately 3 weeks.

The pesticide contamination of the stream was significant following the first rainfall. The European Union (EU) provides directives and regulations about the maximum residue levels (MRL) of pesticides in foodstuffs as well as in water, in accordance with the recommendations of the Codex Committee on Pesticide Residues (CCPR). In the case of environmental and drinking water, the EU directive declares that the concentration should not exceed the level of 0.1 µg/L for individual compounds and 0.5 µg/L for total pesticides (80/778/ECC). The detected residues of atrazine and acetochlor in stream water were one order of magnitude higher than the MRL at the end of the second week after application.

Knowledge of the fate of pesticides in soil, in terms of basic phenomena such as transport, retention and transformation, is essential to the development of predictive tools for the prevention of surface and groundwater contamination. Dissolved pesticides or those adsorbed to eroding soil particles can result in contamination of surface water resources (SCHNOOR 1992, PARLAR 1992, KOOKANA and AYLMORE 1994, MULLER et al. 1994, DI and AYLMORE 1997).

3. SUMMARY AND NEW RESULTS

3.1. SUMMARY OF THE THESIS

This general Introduction chapter (1.) briefly discusses the main aspects of sorption phenomena and reviews the relevant sorption processes and interactions between organic pesticides and soil, which affect on their environment behavior. Furthermore the chapter summarizes the significance and actuality of the subject, the analytical aspect of the problem and closes with a short summary of the scope of the study.

The first experimental chapter (2.1.) reports the result of laboratory studies performed to investigate the sorption behavior of six commonly used pesticides (acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon) on Hungarian brown forest soil with clay alluviation (Luvisol). The batch equilibrium technique was used to achieve sorption isotherms. The determined sorption isotherms could be described by the Freundlich equation in non-linear form ($n < 1$) for all compounds, however in case of diazinon using the extended Freundlich equation proved to be a better approach. The adsorption constants related soil organic carbon content (K_{oc}) calculated from Freundlich equation were presented. The $\log K_{oc}$ values were 2.47 for acetochlor, 2.12 for atrazine, 3.45 for carbendazim, 3.17 for diazinon, 2.32 for imidacloprid and 2.24 for isoproturon. The octanol-water partition coefficients (P_{ow}), which can be a useful parameter to predict of adsorption behavior of a chemical on soil, and dissociation coefficients of these pesticides were calculated based on the chemical structure of them using a computerized expert system. The P_{ow} and K_{oc} were determined experimentally from High Performance Liquid Chromatographic (HPLC) parameters as well. Good agreement was observed between experimental and the computer expert system estimated P_{ow} data. Computer estimated $\log P_{ow}$ values ranged 0.5 and 3.86 for the examined pesticides, with imidacloprid and diazinon being the least and most hydrophobic respectively. Experimentally determined $\log P_{ow}$ ranged between 0.92 and 3.81 with the same tendency. It can be concluded that the Freundlich adsorption constants (K_f) are slightly related to the octanol-water partition coefficients of investigated chemicals, nevertheless no close correlation could be established because of the influence of further characteristics of solutes and soil. The K_{oc} values calculated from HPLC parameters were significantly lower than were determined from batch equilibrium experiments. The retention data estimated $\log K_{oc}$ values were 2.32 for acetochlor, 1.70 for atrazin, 1.87 for carbendazim, 2.74 for

diazinon, 1.79 for imidacloprid and 1.99 for isoproturon. It is assumed that the HPLC estimation method cannot replace the batch equilibrium experiments for calculating adsorption coefficient (K_f), however the HPLC estimated K_{oc} may be useful for choosing appropriate test parameters for adsorption/desorption studies.

The aim of the second study (2.2.) was to investigate the sorption behavior and binding mechanisms of the organic pesticides on soil. To establish the sorption isotherms of acetochlor, atrazine, diazinon, carbendazim, imidacloprid and isoproturon laboratory equilibrium studies were performed at extended concentration ranges on brown forest soil using the batch equilibrium technique. The pesticide concentrations in the equilibrated liquid phase were quantified with high performance liquid chromatograph by UV detection. The adsorption processes could be described by single-step (Langmuir) isotherm for acetochlor and carbendazim, two-step curve for diazinon, isoproturon, and atrazine, and three-step curve for imidacloprid. A non-linear mathematical model - derived from the Langmuir equation - has been developed which represent well the detected single and multi step shaped adsorption isotherms. The interpreted model was found to fit the experimental data well and allows the description of the adsorption profile with great precision. The altered adsorption activity, which indicated by the step arising on the plot, may represent the existence/occurrence of a different specific type of adsorption mechanism. This binding force starts to operate simultaneously at a critical concentration of solute in the studied soil-pesticide system. The parameters calculated from the equation provide an opportunity to estimate the extent of absorption constant, adsorption capacity and concentration limit characteristic to the measured stepwise isotherms.

In the third study (2.3.) the feasibility of extracting organic pesticides in soil was evaluated using a hot water percolation apparatus at 105 °C and 120 kPa pressure. Efficiency of the method was assessed by extracting six selected pesticides, acetochlor, atrazine, diazinon, carbendazim, imidacloprid and isoproturon from previously equilibrated soil at 13.6 - 65.8 mg/kg concentration range. Studies were performed on brown forest soil with clay alluviation (Luvisol). The method developed was compared to traditional batch equilibrium method in terms of desorbed amount of pesticides from soil and extraction time. Pesticides in the liquid phase from batch sorption experiment and in the effluent from the hot water percolation were quantified by high performance liquid chromatography with UV detection. The results of percolation experiment are in close correlation with those of conventional soil testing method. Desorbed quantities by hot water percolation were 85 % acetochlor, 62 % atrazine, 65 % carbendazim, 44 % diazinon, 95 % imidacloprid and 84 % isoproturon, while using batch equilibrium method 101 %, 66 %, 64 %, 37

%, 81 % and 90 % were desorbed expressed in the percentage of the adsorbed amount of pesticide on soil following equilibration. The average time for hot water extraction was 3.45 min, in contrast to the 16 h time consumption of the traditional batch method. The effect of temperature on stability of selected compounds was also evaluated using pesticide-spiked sand without soil. Recoveries of analytes ranged between 84.6 % and 91.1 % with reproducibility 7.9 %-10.2 %, except for diazinon, for which recovery was 59.4 % with 14.4 % relative standard deviation since decomposition occurred at elevated temperature. The percolation process has been described by first order kinetic equation. The parameters calculated from the equation provide an opportunity to estimate the amount of compound available for desorption, the rate of desorption processes in the studied soil-pesticide-water system, and modelling the leaching process to obtain additional information on the environmental behavior of the examined pesticide.

The last chapter of the experimental part (2.4.) reports the results of a field study performed to investigate the environmental behavior, movement, distribution, persistence and runoff by rainfall of the pesticides acetochlor, atrazine, chlorpyrifos and propisochlor under field conditions during a five-month period at normal weather conditions. The pesticide concentrations in soil depths of 0-5 and 5-20 cm, and in sediment and runoff water samples - collected from an artificial reservoir built in the lower part of the experimental plot - were measured every second week and following every runoff event. The contamination of a stream running across the lowest part of the plot was also monitored. The weather conditions were recorded at the experimental site. The pesticide residues were quantified by a capillary gas chromatograph equipped with a nitrogen phosphorus selective detector (GC-NPD). There was a consistent decrease in pesticide residues in the 0-5 cm soil layer with time after spaying. After 140 days after treatment only atrazine and chlorpyrifos were present; acetochlor and propisochlor were not detected in this soil layer. Atrazine and chlorpyrifos in the soil at a depth of 5-20 cm were detectable during the whole experimental interval, while acetochlor and propisochlor concentrations were below the limit of detection. Pesticide losses by the surface runoff process and the contamination of the stream were closely related to the time of rainfall elapsed after treatment and amount of rain at the experimental plots. Losses were primarily dependent on surface rainfall volume and intensity. The maximum detected residues of atrazine and acetochlor in stream water were one order of magnitude higher than the maximum residue limit specified by the European Union (EU) for environmental and drinking water (0.1 µg/L for individual compounds and 0.5 µg/L for total pesticides). Chlorpyrifos and propisochlor were not detected in this matrix.

3.2. NEW SCIENTIFIC RESULTS

This work represents the results of four years long work on the investigation of sorption behavior of some commonly used organic pesticides on representative Hungarian agricultural soil.

The investigations resulted the following new results:

- A sensitive and selective high performance liquid chromatographic method has been developed for quantitative and qualitative determination of the acetochlor, atrazine, diazinon, carbendazim, imidacloprid and isoproturon from liquid phase of the soil solution. The method is suitable to adsorption-desorption experiments and meets the requirement of good laboratory practice. With slight modification, due to its low cost and high throughput, it is applicable for screening pesticide-containing environmental samples.
- A validated capillary gas chromatography method has been developed for the multi-residue analysis of acetochlor, atrazine, chlorpyrifos and propisochlor from environmental matrixes, soil, sediment and water samples. The limit of detection of the methods is allows the determination of pesticide residue in water samples at European Union declared concentration level, and adequate to environmental monitoring and screening purpose.
- The feasibility of the computer and chromatographic estimation methods has been verified to predict those physicochemical data of the investigated organic pesticides, which have the significant effect on soil sorption processes (octanol-water partition coefficient, dissociation coefficients, adsorption coefficient). The estimated parameters are useful to specify appropriate test conditions to adsorption-desorption experiments.
- The characteristic adsorption parameters (adsorption constant, adsorption capacity) of the selected pesticides have been determined on the experimental soil at two different concentration ranges. The obtained adsorption isotherms were presented. Furthermore a new nonlinear mathematical model has been developed, which gives an exact implementation of the description of adsorption processes for all the examined compounds. The multi shaped sorption isotherm lines detected for atrazine, diazinon, imidacloprid and isoproturon confirm theory of inhomogeneity of the soil surface activity and different binding forces, which existing simultaneously in sorption processes.

- A rapid and sensitive subcritical water extraction method has been developed, which suitable to investigate of desorption behavior of organic pesticides on soil. The acceptability of the new method has been demonstrated. Both equilibrium and kinetic approaches were presented. Nevertheless the limitations of the method were discussed.
- The behavior, movement, distribution, persistence and runoff by rainfall of acetochlor, atrazine, chlorpyrifos and propisochlor have been investigated under field condition. It has been shown that there is a correlation between adsorption and leaching and thus the adsorption constants can be used to estimate the mobility of pesticides. The experimental results of the presented study have demonstrated the applicability of the laboratory-determined parameter to predict the environmental behavior of an organic chemical; nevertheless it is considerably dependent on the application and environmental conditions. Our results confirm the theory that following laboratory studies further field studies might be necessary, particularly for chemicals, which are relatively persistent or exhibit high mobility.

Further Objectives

In the last few year remarkable international scientific development could be observed in the field of environmental evaluation of pesticides. Because of the great environmental importance of the subject, further research is expected in this area in the near future. Since all of our results raise several further questions, we intend to carry on the research on sorption mechanisms of pesticides on specified soil compounds as clay minerals and humic substances to understand more clearly the pesticide-soil interactions. We hope the results of our studies contribute to increasing of the scientific knowledge in the field of environmental risk assessment of pesticides.

ÖSSZEFOGLALÁS

A növényvédő szerekkel szemben támasztott alapkötetelmény a hatékonyság és gazdaságosság mellett, hogy felhasználásuk során a lehető legkisebb mértékben terheljék a környezetet. A mezőgazdaságban növényvédelmi és állategészségügyi célra alkalmazott készítmények társadalmi és gazdasági előnyei egyértelműen igazoltak. A jelenlegi felhasználás mellett napjainkban előtérbe került az alkalmazás során fellépő környezeti hatások vizsgálatának és értékelésének szükségesége. A talajban zajló szorciós folyamat a kijuttatott növényvédő szer környezeti viselkedését meghatározó fontos tényező. A hatóanyag és a talaj adszorciós/deszorciós folyamatainak vizsgálata fontos adatokat szolgáltat a vegyület környezeti megoszlásának előrejelzéséhez. Munkám célja néhány, a mezőgazdaságban széleskörűen alkalmazott szerves növényvédő szer adszorciós és deszorciós tulajdonságainak vizsgálta volt hazai mezőgazdasági művelés alatt álló talajon.

A disszertáció bevezető fejezete bemutatja a téma jelentőségét, összefoglalja és értékeli a vonatkozó szakirodalmat. Röviden ismerteti az adszorció elméletét, a talajra jutó szerves növényvédő szerek környezeti viselkedését befolyásoló legfontosabb fizikai és kémiai folyamatokat és kölcsönhatásokat, a növényvédő szerek talajon végbemenő szorcióját befolyásoló tényezőket és az ezek vizsgálata során elért tudományos eredményeket. Áttekinti a pesztticidek környezettel való kölcsönhatásának vizsgálatára és analitikai meghatározásukra kidolgozott kísérleti módszereket.

A kísérleti rész első három fejezete hat, a növényvédelemben és állatgyógyászatban széleskörűen alkalmazott eltérő kémiai szerkezetű és fizikai kémiai tulajdonságú szerves növényvédő szer (acetoklór, atrazin, karbendazim, diazinon, imidakloprid és izoproturon) adszorciós és deszorciós tulajdonságainak laboratóriumi vizsgáltát ismerteti agyagbemosódásos barna erdő talajon (FAO talajosztájozási rendszere alapján Luvisol). Az alkalmazott vizsgálati módszer az OECD ajánlása szerinti szakaszos egyensúlyi adszorciós módszer volt két eltérő koncentráció-tartományban (0.4 - 5 mg/l és 1 - 15 mg/l). Karbendazim esetén a vegyület alacsonyabb vízoldhatósága miatt a legnagyobb kiindulási oldatkonzentráció 8 mg/l volt. A növényvédőszerek talajról való visszányerhetőségének vizsgálata szakaszos deszorciós módszerrel és szubkritikus forróvizes extrakciós módszerrel történt. A vizsgált vegyületek minőségi és mennyiségi meghatározása nagyhatékonyságú folyadékkromatográfiás módszerrel UV detektálással, a mintaelőkészítés szilárd fázisú extrakciójával történt.

A kísérletileg meghatározott izotermák kezdeti szakasza (az alacsonyabb koncentráció-tartományban) Fraundlich típusú összefüggéssel volt modellezhető. A Freundlich összefüggésből számított, a talaj szerves szén-tartalmára vonatkoztatott adszorpciós állandó (K_{oc}) értékek a vizsgált vegyületekre a következők voltak: acetoklór 2.47, atrazin 2.12, karbendazim 3.45, diazinon 3.17, imidakloprid 2.32, isoproturon 2.24. A szorciós kísérleteket megelőzően a vizsgált vegyületekre jellemző fizikai-kémiai paramétereket, a disszociációs állandót (pKa) és a vegyületek hidrofóbicitására jellemző oktanol-víz megoszlási állandót (P_{ow}) számítógépes szakértői rendszerek segítségével a kémiai szerkezet alapján becsülttem. A P_{ow} és K_{oc} állandók értékét folyadékkromatográfiás paraméterektől is meghatároztam. A kémiai szerkezet alapján becsült és a kromatográfiás retenciós faktorból meghatározott P_{ow} értékek jó egyezést mutattak. A legalacsonyabb értékek az imidaklopridra (0.5 és 0.9), a legnagyobb értékek a diazinonra (3.86 és 3.81) adódtak. A K_{oc} adszorciós állandó esetében a folyadékkromatográfiás adatokból becsült értékek minden vizsgált vegyületre kisebbnek adódtak a szakaszos adszorciós kísérletekből meghatározott értékeknél: acetoklór 2.32, atrazin 1.70, karbendazim 1.87, diazinon 2.74, imidakloprid 1.79, izoproturon 1.99. Az eredmények alapján megállapítható, hogy a kromatográfiás módszer nem helyettesítheti a szakaszos egyensúlyi szorciós módszert. A kromatográfiás retenciós faktor alapján meghatározott adszorciós értékek azonban felhasználhatók az adszorciós/deszorciós vizsgálatok kísérleti körülményeinek megválasztásához.

A szorciós folyamatok további tanulmányozásához és a lehetséges megkötődési mechanizmusok jobb megértéséhez a szakaszos szorciós kísérleteket kiterjesztett kezdeti peszticid-konzentráció tartományban is elvégeztem. A kísérleti adatokból meghatározott izotermák az acetoklór és a karbendazim esetén Langmuir egyenettel voltak leírhatók. Az atrazin, diazinon és izoproturon esetében kapott két-lépcsős izotermák, valamint az imidakloprid esetén kapott háromlépcsős izotermák matematikai leírásához a szakirodalomban nem találtam megfelelően jól illeszkedő modellt. A többlépcsős izotermák matematikai leírásához a talaj-adszorció leírására általánosan alkalmazott Langmuir összefüggésen alapuló új matematikai modellt vezetünk be. Az új modell bevezetéséhez feltételeztük, hogy az izotermákon jelentkező lépcsők eltérő típusú adszorciós mechanizmusok működését reprezentálják, melyek egy adott határkoncentráció fölött lépnek életbe és válnak meghatározóvá. Az adott adszorciós mechanizmust reprezentáló lépcső Langmuir összefüggéssel írható le. A teljes adszorciós kapacitás az egyes lépcsőket leíró egyenletek összegzésével kapott összefüggésből számítható. A bevezetett modell a kapott egy- és több-lépcsős izotermákra egyaránt jól illeszkedett. A modell előnye, hogy alkalmazásával lehetővé válik a teljes szorciós folyamatra, valamint a részfolyamatokra jellemző adszorciós kapacitás érték és a határkoncentráció meghatározása.

A vizsgált peszticidek deszorpciós vizsgálatához az előző kísérletekkel azonos módon a kísérleti talaj ismert koncentrációjú peszticid oldattal való kezelése után (adszorpciós gyensúlyi koncentráció tartomány: 13.6-65.8 mg/kg), a deszorbeálható peszticid mennyiség meghatározását szakaszos deszorpciós módszerrel (OECD Test Guideline 106) és szubkritikus forróvizes extrakciós módszerrel (105°C , 120k Pa) végezem. Mindkét módszert értékeltem a hatékonyság (visszanyerhetőség) és a reprodukálhatóság szempontjából. A két módszerrel kapott deszorpciós eredmények jó egyezést mutattak. A deszorbeált peszticid mennyiség a forró vizes extrakciós módszerrel: 85 % acetoklór, 62 % atrazin, 65 % karbendazim, 44 % diazinon, 95 % imidakloprid és 84 % izoproturon volt, az OECD test módszerrel 101 %, 66 %, 64 %, 37 % 81 % és 90 % volt. A forróvizes perkolációs módszer átlagos ideje 3.45 perc volt, szemben a hagyományos rázatásos módszer 16 óra időszükségletével. A szubkritikus forróvizes extrakciós módszer értékeléséhez vizsgáltam a hőmérséklet hatását a vegyületek stabilitására. Az extrakciót az előzőekkel azonos körülmények között, ismert koncentrációjú peszticid oldattal addicionált kvarchomok mintákkal megismételve, az átlagos visszanyerési értékek a vizsgált vegyületekre 84,6 % és 91,1 % (relatív standard eltérés 7,9 % - 10.2 %), diazinonra 59.4 % (relatív standard eltérés 14.4%) volt. Diazinon esetében az alacsonyabb visszanyerési érték és a magasabb relatív standard eltérés érték a vegyület hőbomlásának a következménye. Az extrakciós folyamat matematikailag elsőrendű kinetikai egyenlettel volt modellezhető. A kinetikai összefüggésből a taljról maximálisan deszorbeálhtó fajlagos anyagmennyiség és a folyamatok sebességére jellemző kinetikus állandó az adott peszticid-talaj rendszerre számítható és felhasználható a vizsgált növényvédő szerek környezeti hatásvizsgálatához.

A kísérleti rész negyedik fejezete négy formulázott növényvédőszer-készítmény (acetoklór, atrazin, klópirifosz és propizoklór) környezeti viselkedésének, elmozdulásának és perzisztenciájának valós szántóföldi körülmények között végzett vizsgálatának eredményeit ismerteti. Talajmintavétel 12 előre meghatározott pontból a kezelés előtt, a kezelést követően, majd 5 hónapon keresztül kéthetente és minden felszíni lefolyást okozó esőzést követően történt a talaj 0-5 cm-es és 5-20 cm-es rétegeiből. Az üledék és a felszíni lefolyó víz mintavétele a kísérleti parcella legalsó részén kiépített beton minta-gyűjtőből történt, minden runoff eseményt eredményező esőzés után. Ezzel egyidőben a parcella alsó részénél folyó patak vízéből is történt mintavétel. A hőmérséklet és a csapadék-mennyiség mérése a helyszínen történt. A peszticid szermadarék értékek minőségi és mennyiségi meghatározása kapilláris gázkromatográfiás módszerrel, nitrogén-foszfor-szelektív detektorral (GC-NPD) történt. A talaj 0-5 cm rétegében a kezelést követően a szermadarék értékek monoton csökkenése volt megfigyelhető, a kezelést követő 140. napon csak atrazin és klópirifosz volt kimutatható. Az 5-20 cm talajrétegből vett minták analízise alapján az atrazin és a klópirifosz szignifikáns vertikális irányú elmozdulása volt megfigyelhető. Acetoklór és

propizoklór az alsó talajrétegben nem volt kimutatható. A patak vízéből kímutatott legnagyobb atrazin és acetoklór szermadarék értékek egy nagyságrenddel meghaladták az Európai Unió által meghatározott maximális szermadarék határértéket ($0.1 \mu\text{g/l}$ egyedi növényvédő szer, $0.5 \mu\text{g/l}$ az összes peszticid mennyisége). Klórpírifosz és propizoklór a patak-vízben nem volt detektálható. A kísérleti eredmények alapján szoros összefüggés volt a vizsgált növényvédő szerek bemosódása, a felszínről való lemosódásának mértéke, a patak szennyeződése és az esőzés időpontja, mennyisége és intenzitása között.

Új tudományos eredmények

A disszertáció a szerves növényvédő szerek talajon való szorciós folyamatainak vizsgálatára irányuló négy éves kísérleti munka eredményeit ismerteti. Kísérleti munkám eredményeit az alábbiakban foglalom össze.

- Szelektív, alacsony kímutatási határral rendelkező nagyhatékonyságú folyadékkromatográfiás módszert dolgoztam ki atrazin, acetoklór, diazinon, karbendazim, imidakloprid és izoproturon meghatározására talajoldatban. A módszer kielégíti a jó laboratóriumi gyakorlat követelményeit, alkalmas szorciós/deszorciós vizsgálatokhoz és kevés módosítással alkalmassá tehető környezeti minták peszticid-szennyezettségének szűrővizsgálatához.
- Validált kapilláris gázkromatográfiás módszert dolgoztam ki acetoklór, atrazin, klórpírifosz és propizoklór egymás melletti meghatározására környezeti mintákból. A módszer alkalmas vízminták szermadarék értékének meghatározására az Európai Unió által meghatározott koncentráció szinten és felhasználható környezeti minták monitoring vizsgálataihoz.
- Igazoltam a számítógépes és kromatográfiás becslési módszerek alkalmazhatóságát a vizsgált pesztticidek talajon zajló szorciós folyamatait befolyásoló fizikai-kémiai paraméterek (oktanol-víz megoszlási hanyados, disszociációs állandó, adszorciós állandó) meghatározására. A becsült paraméterek felhasználhatók az adszorciós-deszorciós vizsgálatok kísérleti körülményeinek megválasztásához és optimalizálásához.
- Meghatáztam a vizsgált növényvédő szerek jellemző adszorciós paramétereit (adszorciós állandó, adszorciós kapacitás) hazai mezőgazdasági talajon, két eltérő koncentrációtartományban. Az egy és többlépcsős izotermák leírására alkalmas matematikai modellt

vezettem be a talaj-peszticid adszorpciós kölcsönhatások vizsgálatához. Új adatokat szolgáltattam az inhomogén felületi aktivitásra, az egyidejűleg zajló szorciós folyamatokra és eltérő kötődési mechanizmusokra vonatkozó elmélethez.

- Szubkritikus forróvizes extrakciós módszert dolgoztam ki a talajon megkötött szerves növényvédő szerek deszorciós tulajdonságainak vizsgálához. A módszert értékeltem minden egyensúlyi minden kinetikus szempontból. A bevezetett új módszer alkalmazhatóságát igazoltam.
- Az acetoklór, atrazin, klórpirifosz és propizoklór környezetben való megoszlását, elmozdulását és perzisztenciáját vizsgáltam valós szántóföldi körülmények között. A szántóföldi kísérlet eredményei alapján igazoltam, hogy a laboratóriumi kísérletek során meghatározott paraméterek alkalmasak a szerves növényvédő szerek környezeti viselkedésének felbecsüléséhez. Ugyanakkor a földrajzi elhelyezkedéstől függő eltérő klimatikus-, talaj-, geológiai- és mezőgazdasági művelési viszonyok miatt, a laboratóriumi vizsgálatokat követően fontos szerepe lehet szántóföldi kísérleteknek, különösen perzisztens, nagy mobilitással rendelkező vegyületek esetén.

További javaslatok

Az elmúlt években jelentős nemzetközi tudományos fejlődés volt megfigyelhető a pesztticidek környezeti értékelésének területén. A téma kiemelt fontossága miatt további tudományos kutatások várhatók a szakterületen. Kísérleteink során számos kérdés nyitva maradt. A szorciós mechanizmusok jobb megismerése céljából további vizsgálatokat tervezünk talajkomponenseken, agyagásványokon és humuszanyagokon. A kidolgozott új mérési módszerek és az elvégzett vizsgálatok eredményei várhatóan felhasználhatók a gyakorlati növényvédőszer-alkalmazás, a rövid- és hosszútávú környezeti kockázatbecslés és a növényvédő szerek környezeti viselkedésének további vizsgálatainak során.

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