INVESTIGATION OF SORPTION BEHAVIOR OF ORGANIC PESTICIDES ON SOIL

Theses of the Ph.D. Dissertation

Lívia Németh Konda

Gödöllő
2002
Szent István University
Doctoral Program in Environmental Science

Head of Doctoral School
Zoltán Menyhért, DSc
Professor
Szent István University, Gödöllő
Faculty of Agricultural and Environmental Science
Department for Agricultural Ecology

Supervisor:
György Füleky, CSc
Professor
Szent István University, Gödöllő
Faculty of Agricultural and Environmental Science
Department for Soil Science and Agricultural Chemistry

.............................. ..............................
Dr. Zoltán Menyhért        Dr. György Füleky
1. ANTECEDENTS AND OBJECTIVES

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 progressive increase of production and application of agrochemicals also causes negative environmental effects. The presence of pesticides in soil, ground- and surface water and air may constitute considerable effects to ecosystems and human health. Human health may be affected by pesticide residues in food and drinking water, while ecosystems may be affected by loss of biodiversity and decrease in population of sensitive living system. The assessment of effects on the environment is a integral part of the process of product development, 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. The ecological approach requires an adequate knowledge of the presence and fate of the agrochemicals in the different environmental compartment and clarifying interaction with ecosystem to reduce risk. 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 the behavior of organic chemicals in the soil environment. 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 the 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.

The objectives of this work were to investigate the sorption
characteristic and environmental fate and behavior of some commonly used
organic pesticides on representative Hungarian agricultural soil. The
purposes of the experiments involved in thesis:

1. To study of the adsorption processes and binding mechanisms of
acetochlor, atrazine, carbendazim, diazinon, imidacloprid and
isoproturon to soil colloids.
2. 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. 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.
3. To validate the computer estimated octanol-water partition
coefficients ($P_{ow}$) of these chemicals as compared to the
experimentally determined values. To get information about the
usability of HPLC parameters for determination of adsorption
coefficient ($K_{oc}$) values of pesticides on soil.
4. To investigate the desorption behavior of the selected chemicals on soil. To develop a rapid soil extraction method suitable for routine analyses of organic pesticides in soil.

5. To obtain information on the environmental behavior of acetochlor, atrazine, chlorpyrifos and propisichlor under field condition.

2. METHODS

2.1. Laboratory experiments

2.1.1. 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. Pesticide Analysis

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 liquide phase of the soil solution during the laboratory sorption experiments. Sample preparation was achieved by solid phase extraction method.
2.3. Adsorption – Desorption of Pesticides

To establish the sorption isotherms of acetochlor, atrazine, diazinon, carbendazim, imidacloprid and isoproturon laboratory equilibrium studies were performed at 0.4 – 5 mg/L and 1 – 15 mg/L concentration ranges on soil using the batch equilibrium technique. The sorption experiments were performed according OECD Guideline 106.

Desorption of pesticides from equilibrated soil was investigated by subcritical water extraction method at 105 °C and 120 kPa pressure. The method developed was compared to traditional batch equilibrium method in terms of desorbed amount of pesticides from soil and extraction time.

2.1.3. Evaluation of Estimation Methods

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. Partition coefficients ($P_{ow}$) and adsorption coefficients ($K_{oc}$) of the pesticides were determined experimentally using high performance liquid chromatography. The $P_{ow}$ and $K_{oc}$ values were calculated by interpolation based on retention factor determined for the compound. The log $P_{ow}$ and $K_{oc}$ values of the reference compounds used for calculation were based on literature values and data obtained by Shake Flask Method (OECD Guideline for Testing of Chemicals 117) and Batch Equilibrium Method (OECD Guideline for Testing of Chemicals 127, draft document, August 1999).
2.2. Field Experiment

2.2.1. Experimental Plot and Soil

The field experiment was conducted on a plot plowed to a depth of 25 cm sown with maize. Crop characteristics were as follows: sowing depth 5 cm, 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 2100 g a.i./ha dose of acetochlor, atrazine, chlorpyrifos and propisochlor respectively.

2.2.2. 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.

2.2.3. 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.

2.2.4. Pesticide Analysis

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 during field experiment. Sample preparation of soil and sediment samples was organic solvent extraction and liquid-liquid partitioning. Extraction of pesticides from water samples was performed with C18 solid phase extraction method.

3. RESULTS AND CONCLUSIONS

3.1. Adsorption – Desorption of Pesticides

The determined sorption isotherms at 0.4 – 5 mg/L initial pesticide concentration 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 log Koc values calculated from Freundlich equation 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 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”.

The adsorption processes at extended concentration ranges 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. The new 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. 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.
The hot water percolation apparatus was successfully applied to desorption of the pesticides from soil. The results of hot water percolation experiment were 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 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 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. Compounds having high kinetic constant are probably faster desorb and may exhibit pronounced leaching. The developed method can be a valuable supplement to conventional analytical methods.

3.2. Evaluation of Estimation Methods

Good agreement was observed between experimental and the computer expert system estimated log $P_{ow}$ 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 atrazine, 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.

3.3. Field Experiment

The field study was 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. There was a consistent decrease in pesticide residues in the 0-5 cm soil layer with time after spraying. 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 rainfall volume and intensity 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. 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. According the literature data 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. 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 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.

4. 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.
5. PUBLICATION LIST

Publications on the Subject of the Dissertation


