STUDY OF THE SORPTION OF HERBICIDES IN DIFFERENT SOIL – SOLUTION SYSTEMS

Ph.D. Theses

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2005.
INTRODUCTION

The clarification of the environmental impact of pesticides is an important and urgent task due to their soil and water contamination. Their fate is influenced by many biotic and abiotic factors like the adsorption on the soils. The adsorption of isoproturon and prometryn being weakly polar and moderately soluble herbicides was studied in different soil – solution systems.

Static equilibrium experiments were carried out on three soils with different organic matter content (chernozem, brown forest and sandy soil) and in the present of soil constituents (quartz and extra humic substance content). The variable factors of the experiments were the quality of electrolytes, the pH (pH=5, pH=7, pH=8) and the dissolved organic matter (DOM) content. To get to know the role of the additives in the process the adsorption experiments were carried out at neutral pH with the herbicide Glean® 75DF with its active ingredient chlorsulfuron and with mixtures made of chlorsulfuron and two different additives (Supragil and Borresperse).

The analytic methods used were mainly liquid chromatography (HPLC) and in certain cases total organic carbon determination and UV-spectrophotometry. The adsorption isotherms were fitted with a special equation which represents the steps very well. The parameters of this equation having exact physicochemical meaning were used for the interpretation of the adsorption. Special attention was paid to the role of the dissolved organic matter.

The degradation of isoproturon was studied, too. It was investigated by GC-MS whether the different conditions lead to different degradation products.
NEW SCIENTIFIC RESULTS

1. Measuring the specific adsorbed amount of the same samples by different analytical techniques (i.e. high-pressure liquid chromatography, UV spectrophotometry and total organic carbon determination) resulted in remarkable difference. This is caused not simply by the methods but also by the disturbing effects of the humic substances as well as of the associates between the solute and the dissolved humic substances. In the case of soil adsorbents the higher is the equilibrium concentration the more remarkable is this difference. Despite the altering results of the analytical methods it’s worth to use more of them since they show different sides of the mechanisms of the processes.

2. The adsorption and the mobility of the investigated herbicides (isoproturon, prometryn) are pH-dependent. The measure of this dependency is the function of the properties of the sorbent (soil, quartz), the changes of the surface as well as of the solute molecules.

3. In acidic solutions the specific adsorbed amount of isoproturon and prometryn is generally higher than in alkaline solutions. It is caused by the protonation of the solute molecules at low pH and this can result in H-bonding and electrostatic interactions. In environmental systems the temporary acidification of the soils or the acid rain can fix the herbicide on the soils but later it can be released as the buffer capacity of the soils acts. In the adsorption of isoproturon and prometryn the hydrophobic interaction plays the major role. If the insoluble organic content of the soils is high the immobilization of these compounds is more likely.

4. The dissolved organic matter (DOM) whose concentration is the function of pH form a colloid system helping the solubilization and the association of slightly polar organic pollutants. The mobilization of the herbicides isoproturon and prometryn plays a special role in their distribution between the sorbent and the liquid phase.
5. The adsorption of chlorsulfuron is independent or slightly dependent on the organic matter content of the soils and its specific adsorbed amount is very similar to that of its formed herbicide Glean\textsuperscript{®} 75DF. The additives (wetting agent and dispersant) having various role resulted in different adsorbed amounts of chlorsulfuron: the dispersant led to the lowest adsorbed amounts.

6. The isotherms fitted by the special equation which describes consecutive adsorption of the herbicides consist of at least two steps. The diffuse environmental pollution whose concentration range can be modelled with the first step of the adsorption isotherms is weakly influenced by the pH. In case of higher concentrations (point-like pollutions) pH plays the main role in the processes of the adsorption. The higher steps can be interpreted with the effect of binding places with the another kind of interaction or with the effect of surface complexes with different association degree which appear in the parameters of the equation. The dissolving humic substances play an important role in the determination of the shape of the higher steps.

7. The degradation experiment of isoproturon showed that on soils having higher organic matter content the rate of the degradation is faster but it was independent from pH. On chernozem which had the highest degradation rate two metabolites of isoproturon (N-methyl-N’-(4-i-propyl-phenyl)urea and N-(4-i-propyl-phenyl)acetanilide) were identified by GC-MS which were only known before as degradation products formed during UV irradiation.


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