

Adsorption – desorption studies : introduction

J. Cornejo

During the last years it has been reported that pesticides have been found in groundwater, surface waters, foods and even in animal and human tissues. The movement of these chemicals through the soil profile governs their potential to be transferred into waterbodies and foodchains.

The management and research models in describing the movement and fate of pesticides in the soil ecosystem is largely dependent on the diverse processes that include leaching, volatilisation, chemical, biological and photochemical degradation and sorption-desorption on soil particles. Adsorption is probably the controlling step in the transport of chemicals along the soil profile and should not be underestimated. Biodegradation, for example, is generally more pronounced for molecules in the solution phase than when they are sorbed.

On the other hand, sorption of organic chemicals to soil and soil colloids is an important interface mass-transfer process. The description of such a process needs of information on the equilibrium achieved between phases and the rate on which equilibrium is approached. In any case this process may be affected by physicochemical properties of the pesticide, solid and liquid phase properties and climatic conditions. On the basis of the above considerations their relative partitioning between the solid and solution phase can also determine the behaviour of pesticides in soils.

In order to understand the sorption-desorption processes and to obtain the parameters needed for their quantification several recommendations, guidelines, etc. have been developed. In this section some methods have been presented taking into account the existing guidelines. However, new methods dealing with specific problems are presented.

In the section 3.1. two contributions are presented related with the fractionation and characterisation of the humic substances and methods to study the pesticide stabilisation and bound residues formation in soils. In section 3.2. methods presented are related to the adsorption capacity of soils and soil components by means of adsorption-desorption isotherms obtained in static or dynamic systems and by calculation of adsorption coefficients K_{clay} and K_{oc} . Methods presented in section 3.3. dealing with the procedures to establish the operating mechanism during the sorption process of pesticides on soil and soil components.

Preparation and characterization of samples

The retention of pesticides by soil particles has been extensively studied. However, many papers are published every year because is still necessary to obtain a better knowledge of sorption phenomena. Sorption on soil colloids depends of several factors but undoubtedly is dependent on the nature and properties of the surfaces available for interaction with molecules present in the interface (Cornejo and Hermosín 1996). It is generally recognised

that limited attention has been paid to relate the properties of the soil organic matter with the sorption of pesticides in soil as compared to similar studies with inorganic soil colloids. This fact must be attributed to the complexity of the structure of soil organic matter that has not been totally elucidated so far (Saiz Jimenez, 1996).

In Section 3.1. Piccolo *et al.* provide several methods to qualitatively isolate humic, fulvic acids and humin from soils. Extraction procedure is very detailed explained and later on procedures to purify humic extracts from silicate and metal contaminants are also reported. In order to assess the molecular dimensions of humic extracts from soils, the Soil Exclusion Chromatography (SEC) is widely used. This method is quite useful to determine the weight-average molecular weight (M_w) and the number-average molecular weight (M_n). On the other hand, these authors also show the advantages of Nuclear Magnetic Resonance Spectroscopy (NMR) for assessing the structural features of soil organic matter, indicating the difference between liquid and solid-state NMR spectroscopies. Another technique recommended for analysis of natural organic matter is the Infrared Spectroscopy, in the modern version of Fourier Transform IR (FTIR), performed by either the KBr pellet technique in the transmittance mode or by KBr mixtures on the diffuse reflectance mode (DRIFT).

Sorption-desorption of many pesticides by soils are usually not completely reversible and the reversibility often decreases when the chemical residence time in soil increases. This behaviour is leading to the stabilization of the pesticide under less available and less biodegradable forms. Barriuso *et al.* present a methodology for the application of soil fractionation techniques and to isolate soil organic constituents of different properties to determine their capacity to establish interactions with pesticides and to stabilize them as bound residues. Methods for preparation clays and soil clay minerals for pesticide sorption studies are presented in Section 3.3, where they are also shown from a mechanistic point of view.

Sorption of pesticides on soil

From a broad point of view adsorption describes the process of enrichment (positive adsorption) or depletion (negative adsorption) of one or more chemical species in an interface region. However, it is the free energy balance $G = H - TS$ of the adsorption process which finally determines the relative bonding (H) of the sorbate and sorbent and the order of the system (S). Although it is generally accepted the importance of sorption-desorption process, considerable controversy exists to explain the behaviour of organic compounds in soils. On the other hand, it is necessary to have the reliable parameters to make the proper prediction of sorption behaviour of these chemicals in soils. Most of these predictions techniques are related to estimate K_{oc} , assuming the organic carbon content (OC) as the single best soil characteristic determining the pesticide adsorption. The use of the octanol-water partition coefficient (K_{ow}) of a given compound and its water solubility has been proposed by Chiou *et al.* (1979) to explain the behaviour of nonionic organic compound in soils. However, these parameters have been considered of limited use even for nonionic organic chemicals (Schwartzbach and Westall, 1981, Weber 1986, Weidenhaupt *et al.* – 1997). Further difficulties exist when the partition theory is tried to be applied to the sorption in low organic matter soils. Many papers have demonstrated very good correlations between sorption of pesticides and soil mineral components content. Evenmore, the association between organic matter and clay minerals, especially in low organic matter soils and most of subsoils change drastically its behaviour on organic chemicals sorption

(Cornejo and Hermosin, 1996). In many cases the pesticides whose sorption capacity has been related to soil clay content were polar, ionic or ionizable characters.

Two methods are presented in section 3.2 in connection with the determination of adsorption coefficient K_{oc} by Kördel and the introduction by Hermosin *et al.* of an organic chemical adsorption coefficient on a clay fraction basis, K_{clay} , defined in a similar way that K_{oc} is. The authors present a detailed review of several cases described in the literature where the soil clay fraction acts as determining factor in pesticides-soil sorption process. The validation of the method was made using two herbicides and several soil clay fractions separated from soils used in previously pesticides sorption studies. On the other hand, Kördel presents an HPLC screening method for the determination of the adsorption-coefficient K_{oc} . This method is very simple serving as a reasonable compromise between batch equilibrium in soil column experiments and estimations of K_{oc} from the octanol/water partition coefficient K_{ow} . The values obtained are good enough compared with the corresponding results from batch equilibrium studies.

Batch experiments used in the literature to determine sorption of pesticides by soils and soil components generally follow the OECD Guideline for Testing of Chemicals, 106: Adsorption-Desorption (OECD, 1981) and OECD Guidelines for Testing of Chemicals: Adsorption/desorption using a batch equilibrium method. Guideline 106 (OECD, 1996). This technique is widely used to obtain the sorption parameters after application the appropriated mechanism equation, either for soils or its constituents. Drevnkar *et al.* describe a method to obtain the sorption coefficient of several sorbents with different type of organic matter content.

Molinari *et al.* describe a simplified and fast method for the screening of chemical substances on the basis of their kinetics and isotherms of adsorption-desorption process on dry soil. This method is suggested when a small volume of liquid phase is used in final analysis.

A flow equilibration method is described by Garcia-Valcarcel *et al.* in which a pesticide solution of known concentration is passed through a column of soil until the effluent reaches the same concentration as the input solution. This method is quite simple and unexpensive not requiring especial equipment simulating field conditions. From another point of view, Walker has developed a method to measure sorption of pesticides by soils in a static system at realistic soil: solution ratio. As the Garcia-Valcarcel method, this is a very simple and unexpensive one. This method consists in the use of a centrifugation technique combined with a filtration system in order to obtain the soil solution and the corresponding pesticide concentration.

A different technique is proposed by Deleu and Copin being designated by the authors as "Availability Test". The aim of this test is to estimate the pesticide concentration of the soil solution in situation close to field conditions. The test is based on the determination of the amount of compound, which is soluble in different volumes of $CaCl_2$ after adsorption of the pesticide on identical weights of soil.

Mechanisms of adsorption

It is not really easy to determine the adsorption mechanism of pesticides by soil particles in fate and transport models. Several mechanisms may operate during the interaction between given pesticide and soil particles depending on the nature of the organo-mineral association. The overall sorption process is often observed to be initially fast, but then to

decrease to a slower sustained rate that may require long periods of time to reach the equilibrium. The low rate of adsorption is attributed to interparticle diffusion of solute to internal surface of soil components and to diffusion of solute through their matrices. Slow kinetic studies can help to understand the true extension of sorption. It is necessary to point out that most studies have approached the sorption-desorption problem from the sorption step alone. When desorption studies have been undertaken hysteresis effects have often been observed. This phenomenon is sometimes described as nonequilibrium, nonsingularity, slowly reversible or irreversible or resistant sorption. Many discussions have appeared in the last years on this process based on nonequilibrium sorption behaviour and slow kinetics of several chemicals in soils.

After the above considerations it is clear that very careful kinetic studies must be undertaken together with sorption isotherms in static or dynamic systems as previous steps to describe the proper mechanism.

Two contributions included in section 3.3. are based on the description of sample preparation and techniques used for sorption mechanisms studied. Fusi *et al.* present methods to study pesticide interaction with clays in water and organic solvents. Quantitative measurements are conducted in water and qualitative studies by FT-IR in organic solvents in order to identify the functional groups and type of bonds involved. The authors describe procedures for determination of kinetic and adsorption isotherms and the ways to fit data so obtained to adsorption models. They also indicate the calculation method of thermodynamic parameters from the above mentioned experimental measurements.

Romero Taboada *et al.* indicate similar methods than Fusi *et al.*, applied to the study of cyanazine, carbendazime and ethirimol adsorption on soil, peat and montmorillonite.

Further research needs

The sorption of pesticides by soils has been shown to generally involve multiple reactivity located on organic and inorganic surfaces and matrices of different size particles or aggregates. Most of the expressions used are considered under equilibrium conditions but very often slow kinetics occur. It should be convenient to take into account the mechanisms of diffusion through the organic matter matrices and that occurring through the interparticle pores. The methods given in section 3 (Adsorption – desorption studies) show a wide spectrum of procedures to understand the sorption-desorption process of pesticides in soils and soil components. Most of these methods are new approaches or modified methodologies to help to understand the sorption process in situations as close as possible to the field conditions. However, there are some gaps in the actual methodologies that need to be improved. Sorption shows sometimes anomalous behaviour that are not yet satisfactory explained. Furthermore, there are questions on relationship between soil properties and sorption-desorption process that need appropriated answers.

Some areas where we need more research and new methods on sorption of pesticides in the soil environment are suggested:

- Procedures to determine the association degree of inorganic and organic colloids in soil versus pesticides sorption.

- Determination of reactivity of adsorption sites both in inorganic and organic colloids surface and their corresponding matrices especially when they are associated as micro-aggregates.
- Studies are needed to understand the mechanisms of slow adsorption and desorption kinetics.
- Satisfactory methods for study bound or recalcitrant residues.

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