

**EXTRACTION OF PESTICIDE RESIDUES IN SOILS
USING MULTIVARIATE OPTIMIZATION AND
SUPERCRITICAL FLUID EXTRACTION**

by

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ABSTRACT

Modern pesticides are generally recognized as significantly benefiting our ability to satisfy the world's need for abundant, safe, affordable food and fiber. Pesticides reach the soil environment by direct or indirect applications from aerial and ground sprays. The main processes affecting the ultimate fate of pesticides in soil are retention by soil materials (adsorption/desorption processes), transformation processes (biological and chemical degradation), and transport into soil, to the atmosphere, and to surface or groundwater.

Sorption/desorption equilibria and kinetics of atrazine, diuron, and bensulfuron methyl were conducted using a batch technique on several selected soils. The sorption/desorption distribution coefficients (K_a/K_d) of diuron and bensulfuron methyl were calculated using the Freundlich equation. Results indicated that the content of organic matter was the major variable contributing to diuron and bensulfuron methyl sorption. The low $1/n_d$ (isotherm slope for desorption) values showed that both pesticides were not readily desorbed from the soils tested. The rates of sorption were more rapid than those of desorption for atrazine and bensulfuron methyl, especially in the case of bensulfuron methyl on the soil containing a high level of organic matter (57.5%). In this soil sorption was extremely fast, compared to the other soils that contained high clay (56.4%) or high sand (91.6%). The slow rates of

desorption were presumably associated with the heterogeneous nature of the soil, and potential hysteresis phenomena. Hysteresis was observed, at various degrees, depending on the pesticides and soils tested. The energy of activation values for both sorption ($E_a = 11-25$ kJ/mol) and desorption ($E_d = 18-38$ kJ/mol) suggested that transport or diffusion control is rate-limiting for both processes. This study also showed that the desorption of bensulfuron methyl was almost irreversible, particularly with high contents of soil organic matter. This was correlated to the K_d values obtained from the isotherm equilibrium experiments. The stronger sorption of bensulfuron methyl than diuron suggested a potential different sorption mechanism.

A multivariate optimization scheme (MOS) was used to investigate the effects of environmental variables [i.e., soil organic matter %, clay minerals %, various pesticides, residence time of pesticide (aging), etc.] and supercritical fluid extraction (SFE) parameters (i.e., pressure, temperature, extraction duration, extraction mode, etc.) on the extractability of pesticide residues from soil samples. MOS offered the opportunity to systematically and simultaneously examine the interaction and effects among important soil variables and extraction parameters. MOS is a highly efficient technique for studying a large number of variables and identifying optimal extraction conditions.

Pesticide residence time had a major influence on binding processes for all tested pesticides. Extractability as a function of soil composition was greatly dependent on the particular pesticide examined. Bensulfuron methyl was extracted with the greatest difficulty from soils containing both high

levels of organic matter and clay. Atrazine was extracted more easily than diuron. High organic matter and high clay content led to strong binding for diuron and atrazine, respectively.

Effects of SFE parameters on extractability were apparently related to the nature of residues (e.g., freshly fortified versus aged residues). For freshly fortified samples, analyte solubility in supercritical fluid and/or modified supercritical fluid was the critical factor as indicated by the strong influence of pressure on extraction efficiency. For aged samples, temperature was an important determinant of extraction efficiency, indicating that mass transfer or diffusion processes were rate-limiting. The presence of modifier and extraction duration also significantly impacted extractability of aged pesticides.

Several aged soil samples (with atrazine, diuron, bensulfuron methyl) were extracted by Soxhlet, sonication, surfactant extraction, accelerated solvent extraction (ASE), and supercritical fluid extraction (SFE) for comparison. Among solvent extraction, ASE provided better extraction efficiency than the conventional methods. This is probably due to the elevation of temperature and pressure that create a subcritical phase for the extraction. This results in an increase of solvating power and solubility of analyte into the extraction liquid. Surfactant extraction yielded better extractability, particularly in the case of diuron and atrazine, than other solvent extractions (i.e., Soxhlet).

SFE was the best approach to recover aged residues from the soils. With the aid of a surfactant as a modifier, additional bound residues can be extracted using the optimal SFE method, especially for aged atrazine and diuron. Prewetting of aged samples was found to be effective in accelerating the extraction rate.

For aged atrazine and diuron extraction, elevated temperature appeared to be a significant element in effectively recovering or extracting the analytes from the soils. However, it seemed to be detrimental in recovering bensulfuron methyl, which was presumably associated with thermal degradation that occurred in the extraction. To optimize the SFE procedures, characteristics of the analyte(s) should be also carefully taken into account. Analytical results suggested that interaction time was important to the extraction, but fresh supercritical fluid using a dynamic mode may cause better extraction rate and efficiency of the aged residues. The combination of an initial static followed by a dynamic mode extraction apparently enhanced extraction rate and efficiency.

Pesticide degradation occurred mostly in the environment (i.e, soil system), but in some cases, it was also observed under laboratory conditions (i.e., during sorption/desorption experiments, sample aging, analytical procedure, etc.). The rate and extent of the degradation basically depended on the characteristics of the pesticide and the nature of the soil conditions/ composition. Identification and semiquantification were conducted using TLC-Bioassay, LC-RadioChem, LC-UV-DAD, and LC or GC/MS techniques. In general, bensulfuron methyl degraded very rapidly even in the soil-

aqueous system (during sorption/desorption isotherms and sample aging). Major transformation compounds were identified as sulfonamide, O-desmethyl-bensulfuron methyl (ODM-DPX-F5384), and homosaccharin. There was also thermal degradation during the SFE process at an elevated temperature ($> 80^{\circ}\text{C}$). Diuron degradation was observed in the field studies (degradation and lysimeter studies). 3,4-Dichlorophenylurea (DCPU) and N-(3,4-dichlorophenyl)-N'-methylurea (DCPMU) were present to a various extent, depending on the length in the field. The percent of DCPU and DCPMU detected increased with the increase in sampling intervals. It was surprising that diuron was decomposed to dichloroaniline (DCA) with the presence of either Celite® 545 or silica homogeneous material during the SFE extraction at above 120°C . Atrazine was considered to be the most stable compound, compared to bensulfuron methyl and diuron. No degradation took place under any laboratory conditions (sorption/desorption experiments, sample aging, and SFE procedures at elevated temperature, i.e., 150°C). Atrazine showed some degree of transformation after an extended period of time (aging) in the field, resulting in dealkylation and/or hydroxylation.