

Subcritical Water Extraction to Evaluate Desorption Behavior of Organic Pesticides in Soil

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We evaluated the feasibility of extracting organic pesticides in soil 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 the traditional batch equilibrium method in terms of desorbed amount of pesticides from soil and extraction time. Pesticides in the liquid phase from the 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 the percolation experiment are in close correlation with those of the conventional soil testing method. Desorbed quantities by hot-water percolation were 85% acetochlor, 62% atrazine, 65% carbendazim, 44% diazinon, 95% imidacloprid, and 84% isoproturon, whereas using batch equilibrium method 101, 66, 64, 37, 81, and 90% were desorbed, expressed as 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 of 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 a 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 modeling the leaching process to obtain additional information on the environmental behavior of the examined pesticide.

KEYWORDS: Pesticides; soil; hot water; extraction; pesticide analysis

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 water and groundwater has grown considerably (1–7). 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 involves several different and often simultaneous phenomena. Among these, sorption to the soil is the most important process, as it controls other physicochemical and biological processes (8, 9). Understanding the key factors affecting adsorption and desorption characteristics of a pesticide in soil contribute to the prediction of its mobility and its environmental distribution between different environmental compartments such as air,

water, soil, and sediment. 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 (10). 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 streams, and in surface water and groundwater pollution. 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 (11–18) but also theoretical (19–29).

Usually, residues of pesticides are extracted from soil with organic solvents such as acetone, ethyl acetate, or methanol. In some cases, such as for the investigation of water-soluble compounds, extraction with water is sufficient. The use of supercritical fluids, most commonly carbon dioxide, for soil

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extraction is becoming increasingly popular (30, 31). The low critical temperature of carbon dioxide (31 °C) means that a 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 (32–34). 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 (35). The low solvent power of water regarding nonpolar 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 (36) developed an electric field regulated water extraction system which operated between 20 and 80 °C. Körschens (37) used hot water in a Soxhlet extraction apparatus to measure the available carbon and nitrogen contents of soil. Suntheim and Matzel (38) used a continuous water extraction method for determining phosphorus in soil. Füleky and Czinkota (39) 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 (40–47). Subcritical water extraction coupled off-line to a liquid chromatography system using octadecyl modified silica gel trap devised by Yang (48) has shown to be an efficient device for analyzing aromatic hydrocarbons in soil. Crescenzi et al. 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 the device by extracting 13 selected pesticides (49).

The purpose of the 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 (35). 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.

MATERIALS AND METHODS

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**, and their physicochemical properties are reported in **Table 1**. HPLC-grade methanol, acetone, tetrahydrofuran, acetonitrile, and analytical-grade calcium chloride dihydrate, citric acid monohydrate, and sand (silicium dioxide) were purchased from Merck (Darmstadt, Germany). Extraction cartridges used were Waters Sep-Pak octadecyl silica (C₁₈, 500 mg)

columns (Waters Corp., Milford, MA). HPLC disposable membrane filters (0.45 μm) were purchased from Millipore (Bedford, MA). Ultrapure water was obtained using a Milli-Q system (Millipore Corp., Bedford, MA).

Experimental Soil. For sorption experiments, an analyte-free soil sample from location Bak in Hungary was used. The type of soil was brown forest soil with clay alluviation (Luvisol, according to classification of Food and Agriculture Organization of the United Nations) with the following characteristics: 1.16% organic matter, 21.8% silt, 15.4% clay, and 62.8% sand, cation-exchange capacity 16.8 mequiv/100 g of soil, 0% calcium carbonate, and pH = 6.1. Mineralogical composition of the soil determined by X-ray diffraction was the following: 59% quartz, 12% plagioclase, 11% phyllo silicate, 6% chlorite, 4% potash feldspar, 3% kaolinite, 3% pyroxene, 1% smectite, and 1% siderite.

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 flasks with air-dried and sieved (<2 mm) soil (30 g soil/300 mL of solution) for 16 h 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 purposes, desorption was conducted by replacing supernatant with 0.01 M calcium chloride solution. Suspensions were shaken for 16 h, then centrifuged, and supernatants were analyzed. The desorption-equilibration process was repeated six times.

Hot-Water Extraction Procedure. Extraction was performed with a high-performance hot-water percolation instrument developed by Füleky and Cinkota (39) for the determination of the available nutrient contents of soil. A 25 g sample (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, a six-step experiment was performed in three parallels by extracting 10 g of each pesticide-spiked sand under the same conditions described above.

Pesticide Analysis. Supernatant was separated from the soil by sedimentation. Aliquots (15 mL) of liquid phase from the 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 of methanol and 2 mL of 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 of acetone. The organic solvent was evaporated to dryness under a gentle stream of nitrogen, and the residue was dissolved in a 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 was a JASCO liquid chromatograph (JASCO, Tokyo, 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. A symmetry C₁₈ column (75 × 3.9 mm i.d., 4 μm particle size, Waters, Milford, MA) preceded by a guard column (BST C₁₈ 20 × 4 mm, Budapest, Hungary) was used as stationary phase. Samples were eluted and analyzed using

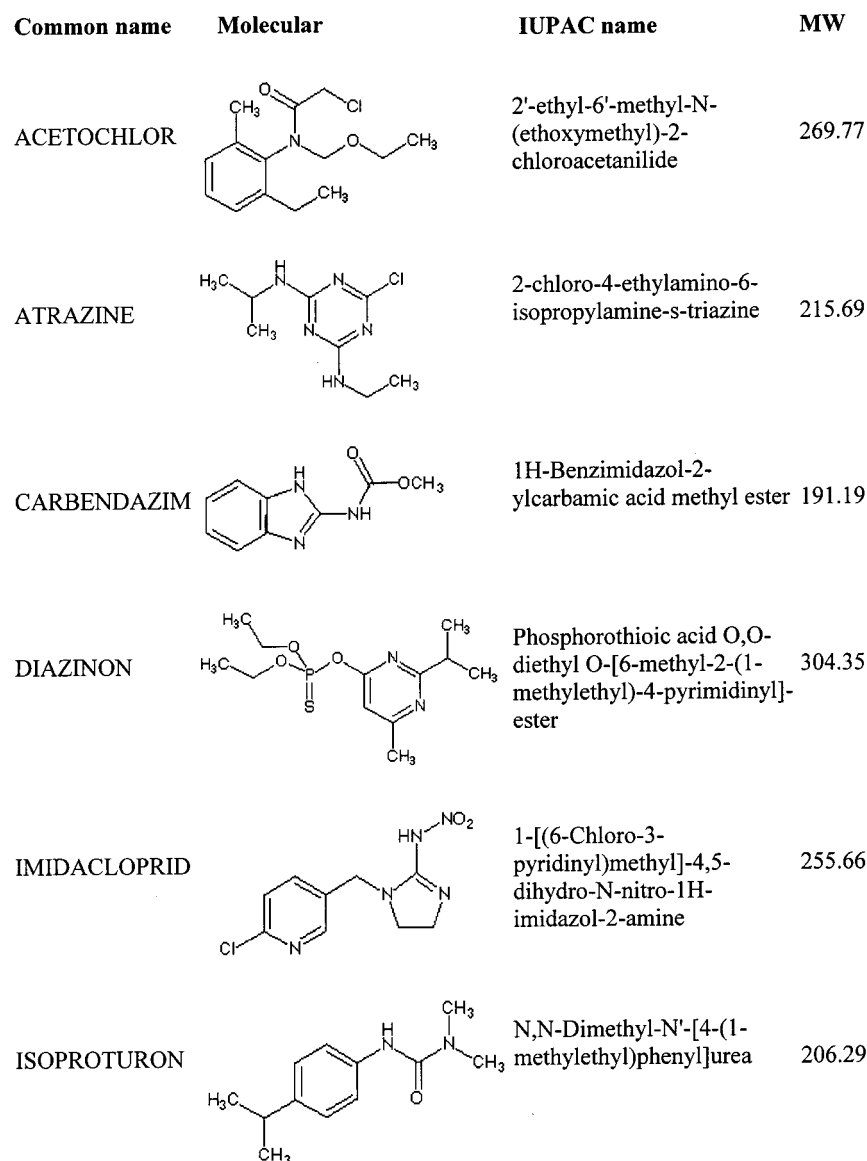


Figure 1. Chemical structures of the six pesticides studied.

Table 1. Physicochemical Properties of the Six Pesticides Investigated

pesticide	K_{oc}^a	$\log P_{ow}^b$	water solubility ^c (mg/L)
acetochlor	313.6	3.37	223 (25 °C)
atrazin	133.4	2.82	33 (20 °C)
carbenrazim	2805	1.55	8 (24 °C, pH 7)
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 (35). ^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 (57).

the following two mobile phases: for imidacloprid, carbenrazim, 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. The flow rate was 1 mL/min and the injected volume was 50 μ L in all cases. The analytes were quantitatively determined by UV detection at 220 nm wavelength. 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 μ g/L for atrazine, acetochlor, carbenrazim, and imidacloprid, and 0.4 μ g/L for isoproturon and diazinon, as determined according to the American Society of Testing and Materials (ASTM) D4210 standard.

RESULTS AND DISCUSSION

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 (50). Additionally, the boiling temperature of water at standard pressure allows the precise control of temperature, thus enhancing the repeatability of the method. On the other hand, use of hot water as extractant inherently poses a risk to decompose thermolabile compounds or those that are 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 carbenrazim, heat load during the extraction period of pesticides adsorbed on soil did not significantly differ from that

Table 2. 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 repeated (6×) 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.

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 (approximately 45 min). Good recovery of the pesticides considered were obtained from the method (84.6–91.1%) with appropriate reproducibility (7.9–10.2%), except for diazinon, for which recovery was 59.4% with 14.4% relative standard deviation because conceivable decomposition occurred at 105 °C water temperature.

Extraction of Pesticides in Soil and Method Comparison.

Performance of the hot-water extraction method was compared to that of the batch equilibrium method (see the Materials and Methods Section). The average values and variation coefficients for the desorption experiments for the investigated pesticides in three replicates are presented in **Table 2**. The pesticide contents determined by the two methods are generally of the same magnitude: the hot-water extraction method gives a higher amount of imidacloprid and a 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 a result of 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 the equilibration process.

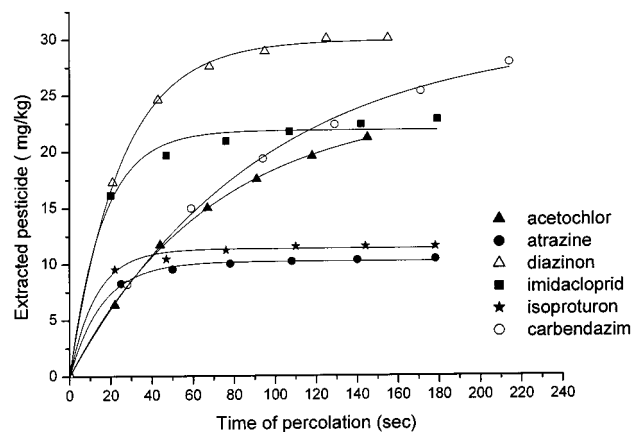
The 6 × 100 mL volume of percolated hot water was sufficient to release the amount of isoproturon and atrazine available for desorption from the soil samples: they were not detected in the fifth and sixth 100-mL aliquots of effluents. The amount of hot water was not enough in the case of acetochlor and carbendazim: there were remarkable amounts of residues in the last aliquots, 41 µg/100 mL and 64 µg/100 mL, respectively. It was presumably adequate for imidacloprid, for which the pesticide concentration of the sixth aliquot was 8 µg/100 mL. The average time for one extraction step was 34.5 s. The reproducibility of the method can be considered to be good because the relative standard deviations range from 6.0 to 9.4%. The RSD % value is highest for diazinon (17.1%) because of uncontrolled chemical reactions resulting from the thermolability of the compound.

Mathematical Modeling of the Hot-Water Percolation Processes. The possibility of mathematical presentation of the results obtained by the hot-water percolation method has been

Table 3. Calculated Parameters from the Kinetic Equation Describing the Percolation Processes for the Six Pesticides Examined^a

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 Standard deviations are given in parentheses.

**Figure 2.** Cumulative amount of extracted pesticides as a function of percolation time.

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 a satisfactory manner in each case by the following equation:

$$y = A(1 - e^{-b \cdot V}) \quad (1)$$

where y = the amount of the pesticide extracted per unit mass of soil [mg/kg], V = 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:

$$y = A(1 - e^{-k \cdot t}) \quad (2)$$

where t = time of percolation [s] and k = kinetic constant [s⁻¹].

All percolation experiments were achieved under constant volumetric flow-rate conditions (average value 3.3 mL/s), therefore: $k = u \cdot b$, where u = 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 2**. The calculated parameters from the equation are given in **Table 3**.

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 the traditional batch method. The strength of the method lies in the possible screening of a large number of samples within a short period of time at low cost. Nevertheless, neither the percolation

method nor the batch method consider soil structure. However, parameters obtained from kinetic measurements provide information about the system. Parameters calculated from kinetic equations 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 to 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.

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