Linuron Sorption−Desorption in Field-Moist Soils

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Pesticide sorption or binding to soil is traditionally characterized using batch slurry techniques. The objective of this study was to determine linuron sorption in field-moist or unsaturated soils. Experiments were performed using low-density (i.e., 0.25 g mL^{-1}) supercritical carbon dioxide to remove linuron from the soil water phase, thus allowing calculation of sorption coefficients (K_d) at low water contents. Both soil water content and temperature influenced sorption. K_d values increased with increased water content, if less than saturated. K_d values decreased with increased temperature. K_d values for linuron sorption on silty clay and sandy loam soils at 12% water content and 40 °C were 3.9 and 7.0 mL g^{-1}, respectively. Isosteric heats of sorption (ΔH_i) were −41 and −35 kJ mol^{-1} for the silty clay and sandy loam soils, respectively. The sorption coefficient obtained using the batch method was comparable (K_f for sandy loam soil = 7.9 $\mu g^{1-1/n}$ $mL^{1/n}$ g^{-1}) to that obtained using the SFE technique. On the basis of these results, pesticide sorption as a function of water content must be known to more accurately predict pesticide transport through soils.

Keywords: *Sorption; desorption; soil; linuron; SFE*

INTRODUCTION

To understand the behavior and environmental fate of organic pollutants, such as pesticides in the soil, it is important to accurately determine the magnitude and strength of sorption to the soil. Sorption traditionally has been characterized by determining the partitioning of the pollutant between soil and soil solution, resulting in a sorption coefficients (K_d). Pesticide sorption has been determined most commonly at room temperature using batch slurry techniques, which have a number of potential problems. For instance, they require soils to have water contents above field capacity, so that soil and soil solution can be separated before analysis; the experiments are usually carried out on air-dried soils that are rewetted before the experiment; and the extraction procedure, that is, shaking and centrifugation, usually alters the physical and chemical characteristics of the soil, resulting in changes in properties of the binding sites during the experiment. Also, temperature control during the experiment is problematic. Some alternative techniques for the determination of sorption, such as using HPLC retention times, and estimation methods based on chemical and physical parameters, which also have problems, have been reviewed by Gawlik et al. (1997).

Development of techniques whereby sorption−desorption can be characterized in field-moist or unsaturated soils is important. A technique that is promising in this respect is the use of supercritical fluid extraction (SFE) to selectively remove the pesticide from the soil solution surrounding the soil particle without extracting it from the soil itself. Above a certain temperature and pressure, the critical point, a substance will be in its supercritical state, where there is no difference between the gas and liquid states. For instance, for carbon dioxide the critical point is reached at a modest temperature (31.1 °C) and pressure (73.8 bar). The selectivity of the extraction by the supercritical fluid can be controlled by varying its density (i.e., temperature and pressure). Rochette and Koskinen have developed a technique that uses the selectivity of SFE to extract atrazine from the soil solution of field-moist soil without also extracting residues bound to the soil particles (Rochette and Koskinen, 1996, 1998; Koskinen and

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10.1021/jf990984f CCC: $19.00

Table 1. Physical and Chemical Properties of Soils Used in This Study

soil	texture	organic C (%)	clay (%)	silt (%)	pH[a]
Lanna	silty clay	2.6	46.5	46.2	7.2
Mellby	sandy loam	3.4	10.4	10.2	6.2

[a] Determined in 1 N KCl.

Rochette, 1996). This allowed characterization of sorption−desorption and calculation of sorption coefficients in field-moist soils.

The objective of this study was to further investigate the SFE technique and to determine sorption of other classes of herbicides such as substituted ureas, in field-moist or unsaturated soils. Experiments were performed with low-density (i.e., 0.25 g mL^{-1}) supercritical carbon dioxide (SF-CO$_2$) to remove linuron from the water phase only, without extracting it from soil, thus allowing calculation of sorption coefficients at low water contents.

EXPERIMENTAL PROCEDURES

Chemicals. Pure analytical linuron [*N*′-(3,4-dichlorophenyl)-*N*-methoxy-*N*-methylurea] (>99% purity) was obtained from Dr. Ehrenstorfer (GmbH), and ^{14}C-labeled linuron (1.1 × 10^9 Bq g^{-1}) was purchased from Izotop. SFC/SFE grade CO$_2$ was obtained from Air Products and Chemicals Inc. (Allentown, PA). Pesticide grade methanol and CaCl$_2$ were obtained from Fisher Scientific (Fair Lawn, NJ). Ecolite scintillation cocktail (ICN, Costa Mesa, CA) was combined with SF-CO$_2$ extracts for ^{14}C quantification by liquid scintillation counting.

Soils. Two Swedish topsoils (0−30 cm), a sandy loam soil (Mellby, Fluventic haplumbrept) and a silty clay soil (Lanna, Uderic haploboroll), were used in this study. Some physical and chemical characteristics of the soils are listed in Table 1.

Sample Preparation. Subsamples, 5 g, of field-moist soils were treated with 1 mL of a methanol solution containing analytical and ^{14}C-labeled linuron (final concentration = 10 μg g^{-1}), and the methanol was allowed to evaporate. To ensure removal of methanol from the soil, the soils were also mixed with ~0.5 mL of water and allowed to dry to their original weights. Original soil moisture contents were determined after 24 h at 105 °C. To obtain greater water contents, deionized water was added to the spiked soil in the weighing boats and mixed thoroughly. The soil was weighed into the extraction thimble and equilibrated for 24 h prior to extraction.

SFE Sorption Experiments. SF-CO$_2$ sorption experiments were performed using an HP 7680A supercritical fluid extractor (Hewlett-Packard, Little Falls, DE). The extractor, which was equipped for 7-mL extraction thimbles, had a variable-diaphragm nozzle preceding the cryotrapping system. Octadecylsilane bonded (C18, 5 μm) silica was used as trapping material. Soil in the extraction thimble was extracted with SF-CO$_2$ at densities from 0.25 to 0.90 g mL^{-1}.

Ten 5-min sequential extraction periods were used for each sample. Between sequential extraction periods, 7 min elapsed (desorption equilibrations) during depressurization, rinsing of the cryotrap, and weighing of the sample vessel to determine water losses. Extractions were performed at 40, 50, and 60 °C. Trap and nozzle temperatures were 10 and 55 °C, respectively, except for the extraction at 60 °C, when the nozzle temperature was 65 °C. The trap was warmed to 35 °C, and the nozzle temperature was lowered to 45 °C during the trap rinse substep. The trap was rinsed twice after extraction with 1.4 mL of methanol into two empty vials. Additional experiments were performed using an ISCO SFE 2200 system (Lincoln, NE).

SFE extract was combined with scintillation cocktail and the radioactivity in the solution, R_w (Bq), counted with a Packard 1500 Tri-carb liquid scintillation analyzer (LSC) (Downers Grove, IL). The radioactivity on soils, R_s (Bq), was calculated from the difference R_i (total initial radioactivity) − R_w. Mass balances of ^{14}C were determined by combusting triplicate subsamples of the extracted soil using a Packard 306 sample oxidizer and quantifying the released ^{14}CO$_2$ by LSC. Average mass balances of linuron for soils before and after SF-CO$_2$ extraction were 103 ± 3%, indicating that essentially all of the linuron applied to the soil was recovered from the trap or was still sorbed to the soil.

Sorption coefficients $K_d = ([C_s]/[C_w])$ were calculated by measuring the distribution of linuron between soil ($[C_s]$) and soil water phase ($[C_w]$, concentration in SFE extract after equilibration). $[C_s]$ and $[C_w]$ were calculated from R_s and R_w using the specific activity of the linuron. Sorption coefficients for K_d-SE (sorption equilibration) and K_d-(D1−D9) (nine desorption equilibrations) were calculated. Water contents at each equilibration were used in the calculations.

Batch Sorption Experiments. Batch sorption−desorption experiments were performed on the Mellby soil by weighing 10-g soil samples (air-dried) into 25-mL glass centrifuge tubes and adding 10 mL of [^{14}C]linuron solution prepared with 0.01 M CaCl$_2$. Initial [^{14}C]linuron solution concentrations were 2.5, 5.0, and 10 μg mL^{-1}. The soil slurries were sealed with Teflon-lined caps, shaken for 24 h, and then centrifuged at 1000 rpm for 30 min. The supernatant (5 mL) was removed and a 1-mL aliquot counted by LSC. Desorption experiments were performed using samples from the 5.0 and 10 μg mL^{-1} initial linuron solution. After removal of 5-mL supernatant solutions from sorption experiments, solutions of 0.01 M CaCl$_2$ without linuron were weighed into the tubes to obtain a slurry of 10 mL of solution to 10 g of soil. At each desorption step, the soil in the tubes was resuspended in solution using a vortex mixer. The tubes were capped and shaken for 24 h. A total of three 24-h desorption equilibration steps were performed.

Sorption Freundlich K_f and $1/n$ values were calculated using the Freundlich equation, which has the general formula $x/m = K_f C^{1/n}$, where x/m is the concentration of linuron on the soil (difference between initial linuron concentration and concentration after equilibration was assumed to sorbed on the soil, μg g^{-1}), K_f is the Freundlich sorption coefficient, C is the concentration of linuron in the soil solution after equilibration (μg mL^{-1}), and $1/n$ is the slope of the sorption isotherm. The equation, rewritten as $\log x/m = \log K_f + 1/n \log C$, was used for plotting isotherms.

RESULTS AND DISCUSSION

Effect of Density. The developed SFE technique to measure pesticide sorption in unsaturated soils is based on the assumption that the analyte is extracted from the soil water phase only and not from the soil and that this can be done by adjusting the SF-CO$_2$ density. The solvent strength of a supercritical fluid is directly related to its density (Giddings et al., 1968); thus, the solvent strength of the SF-CO$_2$ increases with density. SF-CO$_2$ extractions were performed at three densities, 0.25, 0.60, and 0.90 g mL^{-1}. The SF-CO$_2$ density significantly affected the sorption; increasing the density resulted in lower K_d values. For instance, average K_d values for the Mellby soil decreased from 7.5 to 0.4 mL g^{-1} when the density was increased from 0.25 to 0.90 g mL^{-1}.

The decrease in K_d is the result of greater extraction of linuron from the soil−water system at high densities. At higher densities, it appears that the solvent strength of the SF-CO$_2$ in relation to linuron solubility and extractability was too high, resulting in extraction of both soil-sorbed linuron as well as aqueous-phase linuron, which in turn resulted in low K_d values. Extractions of the soil performed at harsh conditions (density of 0.90 g mL^{-1}, 20-min extraction) gave quantitative recoveries of linuron (>90% of applied).

Because the described method is based on extraction of analytes from the soil water phase only and not from soil, mild extraction conditions (low SF-CO$_2$ density, 0.25 g mL^{-1}; short extractions times, 5 min) were used to extract linuron from the soil solution while avoiding extraction of soil-sorbed linuron. It is assumed that all of the linuron in the soil solution was extracted from

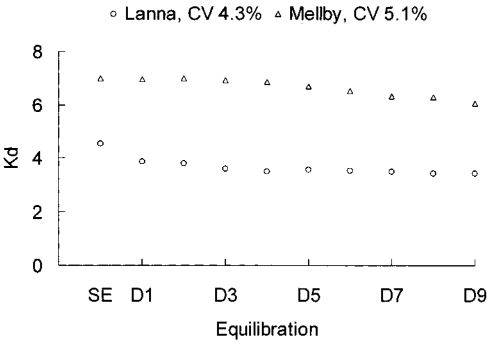

Figure 1. Sorption coefficient (K_d) values resulting from sorption equilibrations (SE) and desorption equilibrations (D1–D9) for Mellby and Lanna soils at 12% soil moisture contents (CV, coefficient of variation).

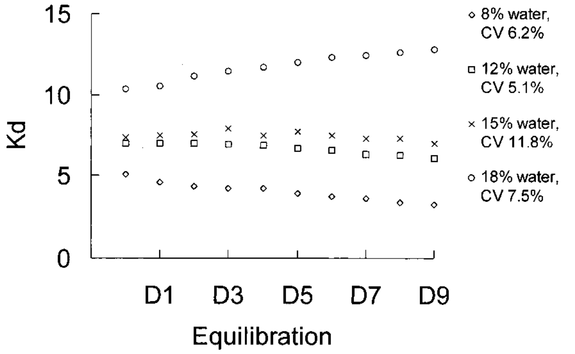

Figure 2. Effect of moisture on SFE K_d values for linuron on Mellby soil.

the soil water phase of the two soils. At low density, there is a potential concern that not all of the pesticide is extracted from the soil water solution due to low solubility of the pesticide in the SF-CO_2. In preliminary studies, extraction of a third soil, a loamy sand soil (0.5 OC%) at 0.25 g mL^{-1} yielded much higher concentrations of linuron in the SF-CO_2 than extractions of the Mellby and Lanna soils, indicating that the SF-CO_2 was not saturated with linuron during our experiments.

It also seems unlikely that the mild conditions used in this study could extract soil-bound linuron because much harsher conditions were necessary for quantitative extraction. Unfortunately, there is no suitable method to measure extraction of very small amounts of linuron from the soil. The constant K_d values for the desorption equilibria D1–D9 (Figure 1) also strongly suggest that linuron was not extracted from the soil. If linuron was extracted from the soil, the amounts attributed to the solution phase would decrease with an increased number of desorption equilibations as the linuron was removed from the more labile sites, which in turn would result in an increase in K_d, which was not the case.

Solubility of water in SF-CO_2 increases with increases in SF-CO_2 density; therefore, at high densities the soil moisture content would change during the experiment. However, solubility of water in low-density SF-CO_2 is minimal. At an SF-CO_2 density of 0.25 g mL^{-1}, there was a decrease in water content of ~2% from the samples during the course of the experiment. Thus, very little water entered the supercritical fluid, and both SF-CO_2 and liquid water were expected to be present during all experiments, hence maintaining equilibrium in the system. The SF-CO_2 extractions performed at different water contents gave constant K_d values for both soils, which further indicates that the soil/soil water equilibrium was reached after each desorption step.

Effect of Soil Properties. The 24-h period after spiking of the samples is considered the sorption equilibration (SE). The 7-min periods between the sequential sweep periods are the desorption equilibration periods (D1–D9). Linuron sorption (SE) and desorption (D1–D9) profiles obtained for the Mellby sandy loam and the Lanna silt clay soils at 12% soil moisture content and at 40 °C are shown in Figure 1. The K_d values were relatively constant through all desorption equilibrations (D1–D9). Therefore, K_d-D1 values were selected for the comparisons of effects of soil properties, water content, and temperature on linuron sorption in unsaturated soil. K_d-D1 values for Mellby and Lanna soils at 12% soil moisture and at 40 °C were 7.0 and 3.9 mL g^{-1}, respectively. Sorption of many pesticides to soil has been correlated to soil clay fraction and organic matter content (OC) [i.e., Torrents and Jayasundera (1997]. The Mellby soil had a greater OC than the Lanna soil, whereas the Lanna soil had much greater clay content. The greater sorption on Mellby soil as compared to that on the Lanna soil indicates that linuron sorption was more influenced by OC than clay content.

Effect of Water Content. Changes in water content, when soils were below field capacity, significantly affected sorption in both soils. The sorption–desorption coefficient profiles obtained at 40 °C for Mellby sandy loam soil at 8, 12, 15, and 18% soil moisture are shown in Figure 2. Average K_d increased from 4.0 to 11.7 when water content increased from 8 to 18%. A relative linear relationship between K_d-D1 for Mellby soil and water content [$K_d\text{-D1} = 0.527\ (\%\text{water}) + 0.353$, $R^2 = 0.946$] was obtained. In the Lanna soil, average K_d values increased from 3.7 to 4.0 when soil water content increased from 12 to 15%. Similar results have been obtained with atrazine (Rochette and Koskinen, 1996), triadimefon (Berglöf et al., 2000), and sulfonylurea herbicides (unpublished results).

The reason for the increase in K_d with increased water content, but below field capacity, is not entirely understood. One explanation may be that the greater amounts of water are in contact with greater amounts of surface area of the soil particles. Greater surface area would result in a greater number of sites on which the chemical can be sorbed. Another explanation could be that at high water contents water acts as a physical barrier, causing inefficient SF-CO_2 extraction of linuron from water in soil pores. Grover and Hance (1970) reported increased linuron batch sorption at greater water contents. Both greater and lower recoveries with increasing water contents have been reported earlier for SFE performed at harsher conditions (Burford et al., 1993; Snyder et al., 1993).

Regardless of the mechanisms involved, our results and those of others (Rochette and Koskinen, 1996; Berglof et al., 2000) show that even small changes in water contents below field capacity can greatly influence pesticide sorption and, consequently, its mobility in soil. For instance, it would appear that the amount of chemical immediately available for leaching through soil depends on the water content just prior to the leaching event. Therefore, the influence of water content on sorption behavior is one of the main factors that should be incorporated into pesticide transport models for an improved understanding and predictability of pesticide mobility in the environment.

Temperature Effects. Measured K_d values for linuron decreased with increased temperature. Desorption

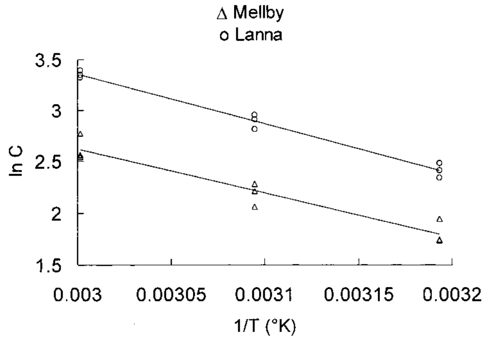

Figure 3. Plot of ln C against $1/T$ for the Mellby and Lanna soils. C is the concentration of linuron in the soil water (micromoles per liter), and T is the temperature in Kelvin. The slope is used for calculation of heat of sorption for D1.

coefficients K_d-D1 were used for thermodynamic calculations. K_d-D1 values for Lanna silty clay and Mellby sandy loam soils at 12% moisture and 40 °C were 3.9 and 7.0, respectively, at 50 °C, 2.5 and 5.3, respectively, and at 60 °C, 1.6 and 3.4 mL g^{-1}, respectively.

Calculated heats of sorption have been used to estimate the binding strength of pesticides in soil (Koskinen and Cheng, 1983). Soil solution concentrations (ln C) at D1 at constant linuron sorbed were linearly related to the inverse of the temperature (T, K) (Figure 3). The slope of the regression line was used for calculating the heat of sorption [$\Delta H_i = R(\delta \ln C/\delta(1/T))$]. The Lanna soil had a more negative ΔH_i (= −41 kJ mol^{-1}) than the Mellby soil (= −35 kJ mol^{-1}), indicating a stronger linuron−soil bond in the Lanna soil. Brücher and Bergström (1997) also reported batch K_f values for Lanna and Mellby soils to be temperature dependent, but they observed a nonlinear K_d and temperature relationship, which may have been due to inadequate temperature control. The SFE technique has excellent temperature control during the course of the experiment.

Using ln C versus $1/T$ plots, K_d values for Lanna and Mellby soils extrapolated to room temperature (23 °C) were 10 and 18 mL g^{-1}, respectively. K_{oc} SFE values (23 °C) [K_{oc}-D1 = (K_d-D1/%OC) × 100] for Lanna and Mellby soils were 390 and 530, respectively. These values correspond to K_{oc} values of 500−600 reported in the literature (Worthing and Hance, 1991).

Batch Equilibrium. The batch K_f value for Mellby soil was 7.9 $\mu g^{1-1/n}$ $mL^{1/n}$ g^{-1}. The batch K_{oc} value was 235 mL g^{-1}. The isotherm slope ($1/n$) was significantly lower than 1, indicating that sorption was concentration dependent. Desorption isotherms $1/n$ were lower than sorption $1/n$, indicating hysteresis. The batch K_d values obtained for the Mellby sandy loam soil at an initial concentration of 10 μg mL^{-1}, was 6.7 mL g^{-1}, significantly lower than the sorption coefficient obtained with the SFE method, extrapolated to 23 °C, 18 mL g^{-1}. Comparison of values between the two systems cannot be directly made because the systems are too different.

Conclusions. The SFE technique allowed studies of the effect of different soil moisture levels on sorption, studies that are impossible to perform with traditional batch techniques. The results obtained in this study showed that soil water content influenced the linuron sorption coefficients; K_d values increased with water content. The SFE technique also allows easy determination of the thermodynamics of sorption (i.e., isosteric heats of sorption) through determination of temperature effects on sorption. In the case of linuron, sorption was strong in both the sandy loam (ΔH_i = −35 kJ mol^{-1}) and silty clay (ΔH_i = −41 kJ mol^{-1}) soils.

It is necessary to broaden the scope of this technique by including soils from other climatic regimes and other pesticides and organic pollutants. Among parameters of interest are interactions between analyte concentration, water content and water potential, soil clay and organic carbon contents, and pH. In this technique**,** however**,** it is important to use an SFE system that can maintain high reproducibility, because varying flows of the supercritical fluid induced by inappropriate pumping or trapping of the analytes can cause problems, especially at the low densities used during our experiments. Experiments conducted on the HP 7680A supercritical fluid extractor did not suffer from these problems. Additional sorption experiments performed with an ISCO SFE 2200 system equipped with a different restrictor-trapping system using a fixed restrictor gave poor precision, probably due to the trapping step with partial plugging of the restrictor, causing irreproducible flow. Using a variable restrictor may solve the problem.

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Received for review September 1, 1999. Accepted May 28, 2000. T.B. gratefully acknowledges financial support from the Swedish Institute and MISTRA.

JF990984F