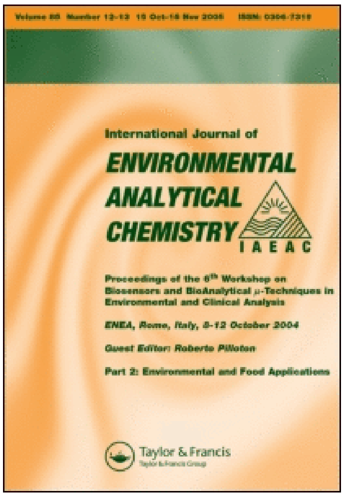

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Koskinen, W. C. and Rochette, E. A.(1996) 'Atrazine Sorption-Desorption In Field-Moist Soils', International Journal of Environmental Analytical Chemistry, 65: 1, 223 — 230
To link to this Article: DOI: 10.1080/03067319608045557
URL: http://dx.doi.org/10.1080/03067319608045557

Intern. J. Environ. Anal. Chem., Vol. 65, pp. 223–230
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ATRAZINE SORPTION-DESORPTION IN FIELD-MOIST SOILS

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(Received, 14 October 1995; in final form, 7 June 1996)

Methods commonly used to obtain sorption coefficients require that the soils be above field capacity moisture so that the aqueous phase containing the pesticide to be quantified can be separated from the soil. We have developed a system using supercritical CO_2 that can remove the pesticide from soil solution of unsaturated soil without first requiring the separation of the solution from soil. Sorption coefficients increased with soil organic carbon and clay contents for three field-moist soils. Also, sorption significantly increased in a sand as moisture content increased from 4.0 to 16% and in a silt loam as moisture increased from 9.6 to 27%. Isosteric heats of sorption were easily determined with the supercritical fluid system and ranged from −10 to −12 kcal mol^{-1} and were correlated to organic carbon and clay contents of the soils. Sorption coefficients in field-moist soils were much greater than are typically obtained with the batch slurry system, while heats of sorption were much more negative, indicating greater sorption at low moisture contents.

KEY WORDS: SFE, water content, water potential.

INTRODUCTION

Sorption is one of the key processes controlling the fate of pesticides in the soil water environment. Sorption controls the availability of the pesticide to the target organism in the soil and to degrading microorganisms. Sorption also strongly influences chemical transport to the atmosphere, ground water and surface water. Not surprisingly, there is a great amount of literature on characterization and quantification of pesticide sorption-desorption in soil.

Most commonly the batch equilibration method has been used to quantify pesticide sorption-desorption. However, there has been concern that quantification under slurry conditions may not adequately reflect conditions in the field. A slurry is used to facilitate separation of water from the soil to allow determination of the aqueous concentration before and after equilibration. The use of a slurry may also result in artifacts in the quantification of sorption. For instance, repeated shaking of the soil and centrifugation may cause abrasion of the soil particle surfaces resulting in changes in binding sites as a function of time.

Few attempts have been made to address these problems. For instance, a centrifugation technique has been utilized to allow removal of water for analysis from soils at or near field-capacity[1,2]. Headspace techniques can be used to quantify sorption of volatile pesticides in field-moist soils[3,4]. But until recently, there have been no techniques to determine sorption coefficients for nonvolatile pesticides in soil at water contents typically encountered in the field (i.e. below field capacity). Rochette and Koskinen[5] developed a technique that uses supercritical fluid CO_2 ($SF\text{-}CO_2$) to extract herbicides from the soil water without extracting them from the soil, which in turn allows quantification of pesticide sorption-desorption at very low water contents. They were able to quantify atrazine sorption-desorption in a soil at water contents ranging from 4 to 16%.

Research was conducted using the $SF\text{-}CO_2$ technique to expand our knowledge of the effects of soil water on pesticide sorption-desorption. Specifically, the objective of this study was to determine the effect of water content and water potential on atrazine sorption-desorption in soils with different physical and chemical properties.

MATERIALS AND METHODS

Chemicals

Atrazine (> 99% purity) was obtained from Chem Service (West Chester, PA 19381). ^{14}C-uniformly-ring-labeled atrazine (0.38 Gbq $mmol^{-1}$ was purchased from Pathfinder Laboratories (St. Louis, MO). SFC/SFE-grade carbon dioxide 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 $SF\text{-}CO_2$ extracts for ^{14}C quantification by liquid scintillation counting.

Soils

Soils used included the surface soil (0–15 cm) of a Zimmerman fine sand (Alfic Udipsamment), a Verndale sandy loam (coarse loamy over sandy, mixed frigid Udic Argiboroll), and a Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed mesic Typic Hapludoll). Selected physical and chemical properties are listed in Table 1.

Sorption experiment

Subsamples of field-moist soils (6 g) were weighed into aluminum weighing boats and treated with 1 ml atrazine solution (46.8 nmol atrazine ml^{-1} methanol to obtain 4.68 nmol atrazine g^{-1} soil. The soils were mixed with the spike solution and approximately 0.5 ml water and allowed to dry to their original weights to ensure removal of methanol. To

Table 1 Physical and chemical properties of soils.

Soil	*Clay (%)*	*Silt (%)*	*Organic Carbon (%)*	*pH*[†]
Zimmerman	3	2	0.5	5.8
Verndale	7	13	1.6	6.2
Waukegan	22	63	2.2	5.8

[†] determined in 0.01 M $CaCl_2$

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 thimbles and equilibrated 24 h before extraction.

SF-CO_2 sorption experiments were conducted using a HP7680A supercritical fluid extractor (Hewlett Packard, Little Falls, DE) The extractor is equipped for 7-ml extraction thimbles and C18-bonded silica was used as trapping material.

The soil in the extraction thimble was swept with 18.4 ml CO_2 at 0.25 g ml^{-1} density. Six to eight 2-min sequential sweep periods were utilized for each sample. Between sequential sweep periods, 7 min elapsed during depressurization, rinsing of the cryotrap, and weighing of the sample vessel to determine water loss. It should be noted that at a SF-CO_2 density of 0.25 g ml^{-1}, there was no water lost from any of the samples during the course of the experiment. The 7-min periods are considered desorption equilibrations. Trap and nozzle temperature were 10 and 55°C, respectively. The trap rinse solvent was 1.5 ml methanol.

Extracts were combined with scintillation cocktail and counted with a Packard 1500 Tri-carb Liquid Scintillation Analyzer (Downers Grove, IL). Mass balances of ^{14}C were completed by combusting 0.3-g subsamples of soil, which had been mixed with equal volume of microcrystalline cellulose powder, using a Packard 306 sample oxidizer (Downers Grove, IL) and quantifying liberated $^{14}CO_2$ by liquid scintillation counting. Mass balances of atrazine for soils before and after SF-CO_2 extraction were 108 ± 6%, indicating that all the atrazine applied to soil was recovered from the trap or was still sorbed to the soil.

Isosteric heat (ΔH_i) were calculated using the equation $\Delta H_i = R\ \delta \ln C/\delta(1/T)$, where R is the gas constant (1.987 cal K^{-1} $mole^{-1}$), and T is temperature (°K). In this study three temperatures were used: 40.0, 50.0 and 60.0°C. The extractor maintains the extraction thimble at the specified temperature (± 2%). The ΔH_i values were not corrected for changes in the solubility of atrazine in water or supercritical CO_2 that arise due to changing temperatures.

Soil moisture potentials

Soil moisture potentials were determined using a modified method of Klute[7] and Soilmoisture Equipment Co. (Santa Barbara, CA) moisture potential apparatus. Approximately 50 g of each of the three soils were placed in glass beakers, saturated with deionized water, and allowed to stand overnight. The saturated samples were transferred to 7.5-cm i.d., 7.5-cm long metal cylinders having cheesecloth bottoms, placed on a 3-bar ceramic plate in a pressure chamber, and equilibrated in the pressure chamber with tensions of 0.1, 0.3, 1, and 3 bars (potentials of –0.1, –0.3, –1.0, and –3.0 bars). At each tension duplicate subsamples of approximately 3 g were taken, using a l-cm i.d. brass coring tool, from each sample for moisture determination. Soil moisture contents were determined after 24 h at 105°C. Water potentials were calculated using the respective linear regression equations of the natural log of the water content (expressed as a fraction) against the natural log of the water potential. Water content did not change during the experiment.

RESULTS AND DISCUSSION

In the experiments, a low density of SF-CO_2 (0.25 g ml^{-1}) was used to avoid extraction of soil-sorbed atrazine. At higher densities, it appears that supercritical CO_2 actually extracts soil-sorbed atrazine as well as aqueous-phase atrazine. The short time period of the sorption-desorption (< 2 hr) experiment after the initial 24 hr equilibration precludes potential effects of atrazine decomposition during desorption equilibrations.

Effect of water content

The sorption-desorption coefficient profile obtained for the Zimmerman soil at 10% soil moisture is shown in Figure 1. Relatively constant Kds were obtained for the sorption equilibration (SE) through eight desorption equilibrations (D1–D9) indicating the desorption-equilibrium was re-established very rapidly, within 7 min. For discussion of effects of water content on sorption-desorption, we will compare Kd values for the first desorption equilibration (Kd, D1) as a function of water content (Table 2). Small changes in water content, when soils are below field capacity, significantly affect

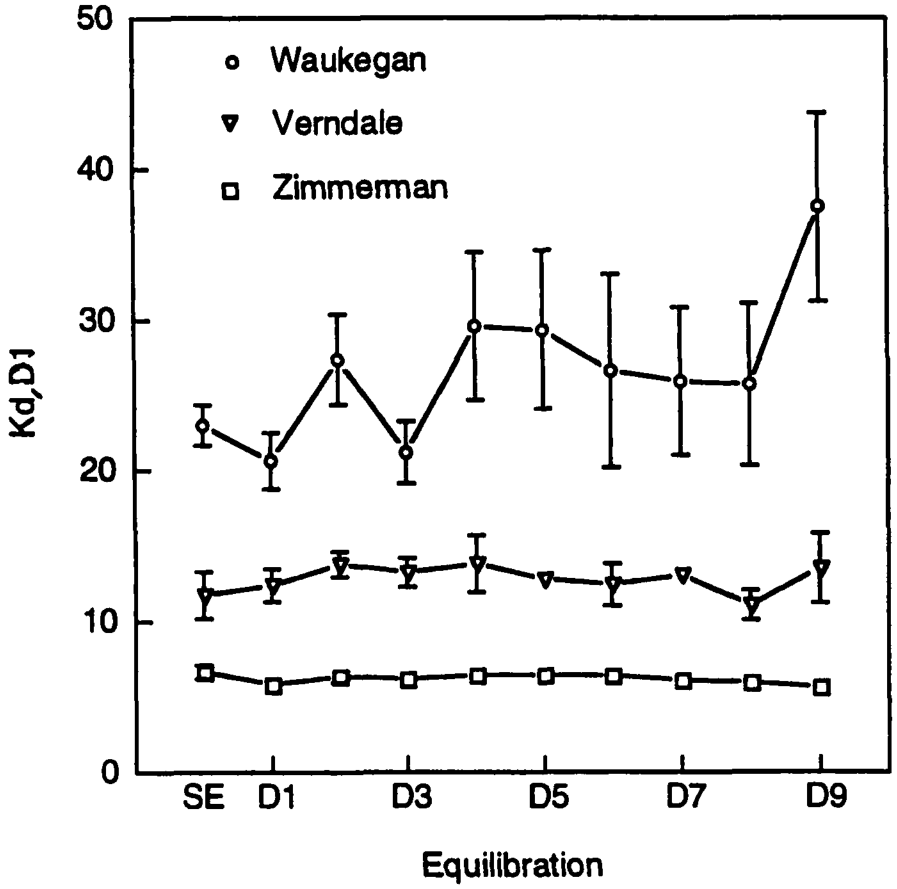

Figure 1 Sorption coefficient (Kd) values resulting from atrazine sorption equilibrations (SE) and desorption equilibrations (D1 through D9) for the Verndale, Waukegan, and Zimmerman soils at 9.6% soil moisture contents. Error bars represent absolute standard deviations; points without error bars have errors smaller than the symbols.

Table 2 Effect of water content and potential on atrazine sorption-desorption.

Soil	*Water content (%)*	*Water potential (bars)*	*Kd, D1 (L kg^{-1})*
Zimmerman	16[†]	0.025[†]	7.67 ± 0.08[†]
	9.6	0.15	5.82 ± 0.07
	5.6	0.95	2.92 ± 0.03
	4.0[†]	2.94[†]	1.21 ± 0.04[†]
Verndale	9.6	0.95	12.4 ± 1.1
Waukegan	26.7	0.95	53.3 ± 1.4
	9.6	3600	20.6 ± 1.9

[†]from Rochette and Koskinen[5]

sorption. For instance, in the Zimmerman soil, Kd, D1 increased with increased water content. We had initially expected that Kd values might remain constant or decrease as water content increased as has been observed for volatile compounds determined using headspace techniques[4]. On the other hand, atrazine SF-CO_2 Kd values of soils having essentially no water (dried over P_2O_5) were extremely high[5]; this is consistent with the high initial sorption values obtained in vapor sorption studies[4]. The reason for the increase in Kd, D1 with increased water content from 4 to 16% is unknown. A similar effect occurs with the Waukegan soil (Table 2).

Effect of soil properties

The sorption-desorption profiles obtained for the Verndale and Waukegan soils at 10% soil moisture are also shown in Figure 1. Relatively constant Kd values were obtained for the sorption equilibration (SE) through eight desorption equilibrations (D1–D9), similar to the Zimmerman soil.

Sorption increased with increased organic carbon and clay contents; sorption was in the order Waukegan > Verndale > Zimmerman. As the sorption increased, the standard deviations for Kd values increased. Also, as the number of equilibrations increased, the standard deviations for Kd values also increased, especially for the Waukegan soil. The greater error in Kd is due to decreased precision in measuring the small changes in the amounts of atrazine in solution[7].

Isosteric heats of sorption for herbicide-soil systems have been used in the past as indicators of strengths of bonds between herbicides and soils[8,9]. The relationship between ln C and 1/T is extremely linear for all soils (Figure 2). The absolute values of the relative atrazine ΔH_i values for the soils also increased as the soil clay and organic carbon contents increased in the order Zimmerman < Verndale < Waukegan, −10.3, −11.0, and −12.2 kcal mol^{-1}, respectively. The more negative the ΔH_i value, the stronger the atrazine-soil bond and these values are much more negative than previously reported in batch slurry experiments. It should be pointed out that the ΔH_i values were calculated using desorption (D1) data, rather than sorption data as is commonly done.

Because the same water content for different soils are at different potentials, the question arises whether to compare sorption-desorption of different soils at the same water content or potential. Experiments were conducted to compare atrazine sorption-desorption in different soils at the same water potential and the results are in Table 2.

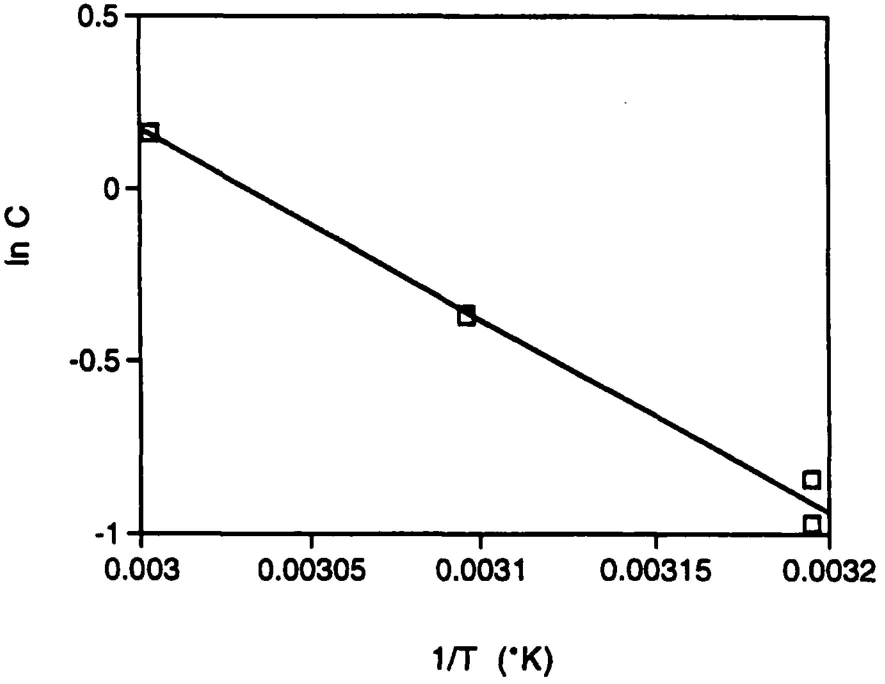

Figure 2 Plot of ln C against 1/T for the Verndale soil, where C is the concentration of atrazine in the soil water (μmol L^{-1}) and T is temperature in °K. The slope (Table 3) is used for calculating ΔH_i.

If we compare Kd, D1 at 10% moisture for Zimmerman, Verndale, and Waukegan soils (potential varies by 4 orders of magnitude), the ratio of Kd, D1 is 1.0 : 2.1 : 3.5. In contrast, at 1.0 bar potential (water contents vary by a factor > 4), the same ratio is 1.0 : 4.3 : 18. This means that different soils having the same water potential have greater differences in Kd values than soils having the same water content. This is important since plant roots may be exposed to water at potentials greater than the water present at the plant wilting point.

For many years, atrazine has arguably been most correlated to organic carbon content in normal agricultural soils. To normalize atrazine sorption between soils of different organic carbon contents, K_{oc} has been calculated (K_{oc} = (Kd/%OC) × 100). K_{oc} values for atrazine sorption on the 3 soils are shown in Table 3. K_{oc} at constant water content is less variable than K_{oc} at constant potential. The high K_{oc} for the Waukegan soil indicates that

Table 3 Effect of calculation of water content on K_{oc} (Kd normalized for soil organic carbon content).

Soil	*Water content, 9.6%*	*Water content, 0.95 bars*
Zimmerman	1164 ± 14	584 ± 6
Verndale	775 ± 69	775 ± 69
Waukegan	936 ± 86	2423 ± 64

there may be different processes occurring when there is clay in the system. The problem in trying to correlate atrazine sorption to soil organic carbon is that it can also be sorbed onto clays. More work is needed in the area of clay-atrazine interactions at low water contents.

A reasonably linear relationship between water contents and Kd values obtained for the Zimmerman soil (Kd, D1 = 0.522 wc – 0.185, r^2 = 0.930) might suggest that the desorption equilibrium was not reached. The resulting dilution, decrease in solution concentration, would then account for the increase in sorption coefficients. However this does not appear to be the case. A better fit to the data would be a curvi-linear line (Figure 3). Also, at all water contents for all soils, Kd, D1 through Kd, D9 were constant indicating that after a number of desorption steps the equilibrium was reattained within a given system.

It may be that greater water contents facilitate greater accessibility to more strongly sorbing sites. Another possibility is that changes in solution chemistry may have occurred as the soil water content increased. For instance, a decrease in solution ionic strength or a change in solution pH may have favored sorption of the herbicide by the soil.

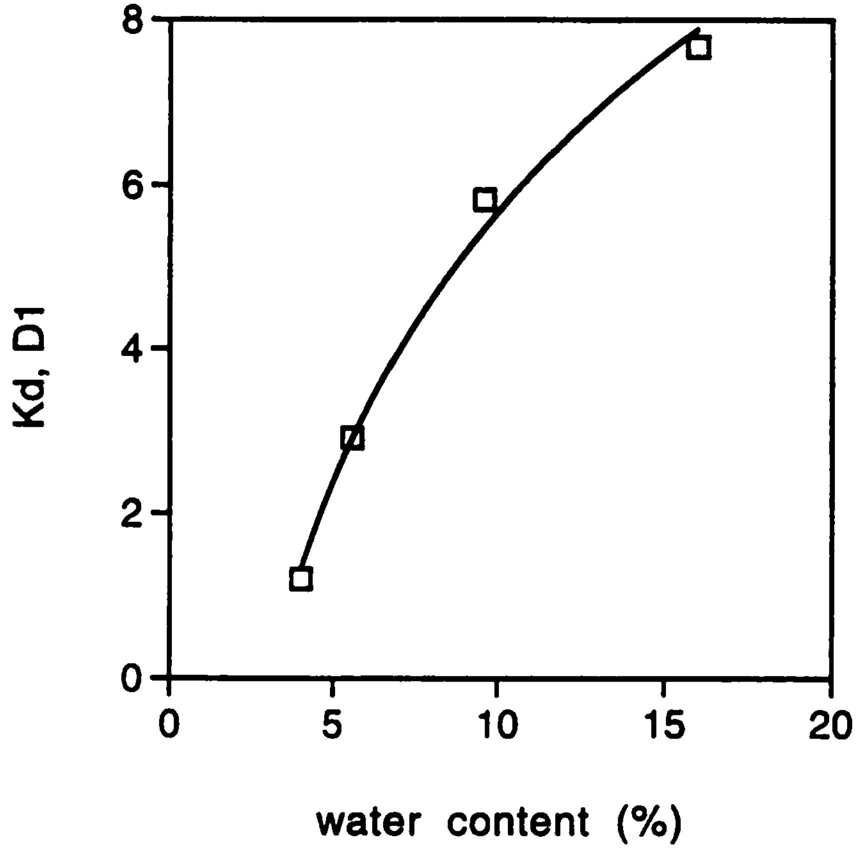

Figure 3 The relationship between water contents and Kd values for the Zimmerman soil.

CONCLUSION

At this point is unclear how to best characterize soil water in relation to sorption. However, since sorption-desorption controls pesticides availability to plant and soil microorganisms, which in turn are affected by water potential, more research should be done on the effects of potential on sorption-desorption.

It appears that differences in water content may have a greater effect on isosteric heats of sorption than differences in soils. The difference in ΔH_i for the Zimmerman soil between 4%[5] and 10% (present research) water content was 2.9 kcal mol^{-1} compared to 1.9 kcal mol^{-1} for the difference between a loamy sand and silt loam. Additional research in this area is also needed.

In spite of the above questions, we have shown that we have developed a technique to determine sorption-desorption in field-moist soils. Sorption-desorption experiments can be conducted in time period that precludes effects due to pesticide decomposition. Atrazine Kd values obtained with SF-CO_2 increased as the content of soil clay and organic carbon increased, which was an expected relationship between Kds and soil properties. Values for isosteric heats of sorption decreased as Kd values increased, which suggests that soil-atrazine interactions were strongest for the soil with the largest atrazine sorption capacity as would be expected.

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