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DESORPTION AND BIOAVAILABILITY OF RESIDUAL SIMAZINE IN SOIL FROM A CONTINUOUS CORN FIELD

By

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ABSTRACT

DESORPTION AND BIOAVAILABILITY OF RESIDUAL SIMAZINE IN SOIL FROM A CONTINUOUS CORN FIELD

By

Steven Loren Scribner

The desorption kinetics and bioavailability of aged simazine residues present in an agricultural soil were evaluated. Sorption of spiked ^{14}C-simazine was measured on these soils to establish the soil-water simazine concentration at equilibrium, Ce. Desorption rates of native simazine were found to be extremely slow, indicating a highly retarded diffusion process. Simazine concentration (C) in soil-water from the corn field was monitored for four months following simazine application. The fractional equilibrium (C/Ce) of simazine was approximately 1.0 immediately after application indicating that the soil-water distribution of simazine was near equilibrium. The soil-water concentration steadily decreased below the predicted equilibrium levels as the amount of time following simazine application increased. Two months following simazine application the C/Ce was approximately 0.1 (10% of the predicted equilibrium concentration). The slow desorption of soil-bound simazine rendered it unavailable for plant uptake and microbial degradation.

TO

My father, Dr. Loren M. Scribner.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LITERATURE REVIEW

Sorption and Persistence of Nonionic Organic Compounds

Nonionic organic compounds (NOC) may cause complex environmental problems. These chemicals include herbicides, pesticides, polychlorinated biphenyls and other industrial solvents. Sorption by soil is a key mechanism in determining the fate of these organic contaminants (Pignatello, 1989). A compound's mobility and bioavailability are highly dependent on the soil's sorptive character. Compounds strongly sorbed to soil may become unavailable for microbial degradation and plant uptake resulting in increased persistence in soils (Ogram et al., 1985; Saltzman et al., 1972). To control or prevent environmental problems associated with the industrial or agricultural uses of organic compounds (including pesticides), a fundamental understanding of their interactions in soil is necessary.

There are two major theories about the nature of sorptive interactions of NOC in soil (Pignatello, 1989). One is adsorption, the other is partitioning. These two processes play a major role in determining the fate of organic contaminants and are dependent on soil characteristics such as soil organic matter content, moisture content and mineral content.

Adsorption is the traditional theory used to explain the interaction of chemicals and soil (Mingelgrin and Gerstl, 1983). It is a process of molecular condensation on a soil surface where compounds are held at specific sites. The sites are formed by such forces as hydrogen bonding, Van der Waal, charge transfer and electrostatic-columbic interactions (Khan, 1973). For example, isomorphous substitution in the mineral lattice of a clay creates electrostatic sites that may attract positively charged organic compounds, such as paraquat or diquat. (Hassett and Banwart, 1989). The polar and ionic functional groups of soil organic matter (e.g. COO^-, OH) may also interact with charged species or polar organic compounds with reactive functional groups (e.g. NH_2, -OH). In contrast, most NOC are unable to compete with water or other highly polar or charged species for these binding sites. Therefore, adsorption does not give a complete description of the system.

Solute partitioning is mechanistically distinct from adsorption. Solute partitioning as a mechanism refers to the dissolution of a solute into an organic phase (e.g. soil organic matter) analogous to the partitioning of solutes from water into a bulk organic phase like hexane. Compounds do not interact with specific sites, but rather nonpolar interactions occur between the solute and the partition phase. Hydrophobic bonding is a somewhat poorly defined mechanism involving weak solute/solvent interactions instead of a strong sorbate/sorbent interaction (Means et al., 1985). It is not clear, however, whether hydrophobic bonding implies a surface interaction or a process of dissolution, and thus partitioning is a preferable mechanistic description for NOC and pesticides. Although organic matter is hydrophobic in nature, it also contains a high percentage of polar functional groups such as -OH and COOH. As mentioned above, these polar groups may interact via specific mechanisms with certain polar organic molecules. An example of this chemistry is the 1,4-addition of aromatic amines to the quinone groups of soil humics. Alternatively, the soil organic matter phase may act as a partition medium for the dissolution of organic solutes with the primary polar-polar group interactions involving water. Solute partitioning is characterized by (Chiou, 1989):

1) linear isotherms, extending to high relative solute concentration,
2) lack of competitive effects in multisolute systems,
3) low heat effects, and
4) inverse dependence of the sorption coefficient, K, on the organic matter content of the sorbent.

Adsorptive mechanisms are characterized by (Chiou, 1989):

1) nonlinear isotherms,
2) competitive effects in multisolute systems, and
3) high equilibrium heats of adsorption.

These characteristics can be used to experimentally distinguish surface adsorption and partitioning mechanisms.

Recent evidence (Chiou, 1990) strongly suggests partitioning as the major mechanism of uptake of NOC in soil-water systems. Linear isotherms are commonly observed for the sorptive uptake of NOC by soils and can be described by a linear equation:

$$X/M = K * C \qquad [1]$$

Where X/M is the amount of solute sorbed to the soil, K is the sorption coefficient and C is the equilibrium concentration. The sorption coefficient corresponds to the slope of the linear isotherm and is the ratio of the concentration of the sorbed compound in soil to the concentration of the compound in water in contact with the soil at equilibrium. The partition coefficient, K, can be normalized for organic matter content (f_{om}) of a soil to define a new constant:

$$K_{om} = K / f_{om} \qquad [2]$$

It has been observed that K_{om} remains relatively constant across most soils for a particular compound. It can therefore be utilized to predict sorption of a particular compound on various soils if the organic matter content is known. These relationships are now used routinely in environmental fate and transport models to predict pesticide mobility in soils. Although there is overwhelming evidence that soil organic matter content and NOC sorption in soil-water systems are correlated (Gschwend and Wu, 1986; Khan et al., 1979; Karrickhoff, 1984; Chiou et al., 1979), there is still active debate on the mechanistic basis for this relationship. Many have questioned whether there is sufficient evidence to prove the partitioning model (Mingelgrin and Gerstl, 1983). This is particularly the case for polar compounds, which might effectively compete with water for polar binding sites in soils (Hassett and Banwort, 1989), and in soils with low organic matter contents (<.1%) where the mineral fraction may dominate the sorptive interactions. In certain cases linear isotherms and failure to observe competitive adsorption effects may not contradict a physical adsorption model. MacIntyre and Smith (1984) observed noncompetitive sorption for components of hydrocarbon mixtures on clays and sediments with low organic matter content.

The distribution of sorbed and aqueous phase NOC in soils at equilibrium is defined by the sorption or partition coefficient, K. If degradation, plant uptake, or leaching decrease the amount of NOC in solution, desorption from the sorbed state occurs to reestablish equilibrium. This process occurs in a predictable manner that is defined by K. Theoretically this system should produce a desorption isotherm identical to the sorption isotherm. However, it is not uncommon to find nonsingular (or hysteric) isotherms (Saltzam et al., 1972; McCall and Agin, 1985; Di Toro and Horzempa, 1982), indicating that desorption does not follow the same equilibrium as the sorption pathway. Several reasons have been proposed to explain this hysteresis (Rao and Davidson, 1980):

1. Artifact due to analytical method
2. Chemisorption or transformation of the solute
3. Formation of a resistant fraction
4. Failure to establish equilibrium in method

Artifacts have been identified (Karrickhoff and Brown, 1978; Gschwend and Wu, 1985), along with certain chemical transformation reactions (Koskinen et al., 1979). These generally play a minor role. The resistant fraction appears to be the major cause of nonequilibrium and isotherm non-singularity (Pignatello, 1989).

Extremely slow desorption defines this "resistant fraction." Parathion was found to desorb very slowly (Wolfe et al., 1973) and to persist in soil sixteen years after the last application (Stewart et al., 1970). Ethylene dibromide (EDB), a volatile pesticide having a low affinity for soil, is easily degraded by bacteria common to soil and was present in soil nineteen years after application (Steinberg et al., 1987). The soil fumigant, DBCP, was also found in Hawaiian soils nineteen years after the last application (Buxton and Green, 1987). Atrazine was bound very strongly (considered nonextractable) to soil nine years after herbicide application, as over 50% of the initially applied atrazine or it's degradation products were found bound to mineral or organic matter (Capriel et al., 1985).

The previous experiments were conducted on field soils in which the pesticide was applied for several years, resulting in the apparent development of a native (resistent) fraction of the compound. The pesticide residues in these soils are somewhat unusual in that they have been aged for an extended period of time (years). Laboratory studies utilize soils treated with a specific compound and uptake and desorption rates are subsequently measured over a relatively short time scale (hour, days). For example, 2,4-D and picloram were added to soils and found to have biphasic sorption. The biphasic sorption consisted of initially rapid uptake followed by very slow uptake (McCall and Agin, 1985). Rates of sorption and desorption decreased as the time the NOC remained in soil increased. Similar results for several nonionic low molecular weight organic compounds (e.g. chlorobenzenes, pyrene) are known (Karrickhoff and Morris, 1985; Wu and Gschwend 1986; Khan, 1973). This is consistent with the development in the field of a resistant fraction in natural soils, resulting in compounds becoming inaccessible over time, but on a shorter time scale.

Intraparticle entrapment has been suggested as a mechanism for slow desorption of EDB in field soil (Steinberg et al., 1987). Micropores in the soil matrix may trap the compound and this concept is supported by increased release of EDB from soil when pulverized. The use of different aggregate size fractions (2 to 53μm, 53 to 100μm, etc.) in EDB desorption studies showed that release kinetics were only weakly dependent on aggregate size. This suggests that the EDB residues were entrapped in small, remote micropores that were disrupted only by pulverization.

The humic and fulvic acid components of organic matter coat various size aggregates and soil particles. When the organic matter coating of a soil aggregate surface is exposed to the bulk solution, sorption and desorption of a NOC should occur quickly (minutes). Over time, however, a molecule may diffuse into or through aggregate channels. A compounds diffusion rate could be limited by several factors (Wu and Gschwend, 1986): Diffusion path length, tortuosity of path, microscale partitioning between soil organic matter and the aqueous phase along the diffusion path, and diffusion through organic matter. This would suggest desorption equilibration from hours to days (Wu and Gschwend, 1986). Faster desorption would be expected for smaller aggregates since the diffusion path would be shorter. An even more restricted particle sorption or entrapment must be envisioned and developed to understand NOC desorption from months to years, as observed for pesticide residues in field soils. This could include diffusion into sterically restricted hydrophobic pores or mineral grains.

Wu and Gschwend (1986) use a retarded/diffusion model to describe intraparticle diffusion through natural soil aggregates. Effective diffusion coefficients (D_{eff}) for various chlorobenzenes added to soils were on the order of $1x10^{-11}$. These studies demonstrate an inverse relationship between K and $D_{eff.}$ Longer sorption and desorption times were measured for larger aggregates. In contrast to the studies of Wu and Gschwend (1986), which involved spiked soils, the measured diffusion coefficient of EDB from field soils was approximately 10^{-17} (Steinberg et al., 1987), resulting in desorption equilibration times of 10^9 times slower than predicted from correlations between K and D_{eff}. This translates into 50% equilibration times of two to three decades. As mentioned earlier, the desorption kinetics of EDB was only weakly dependent on the particle size fraction (Steinberg et al., 1987). These results suggest that EDB residues were entrapped in soil micropores where release was retarded by extreme tortuosity and steric restriction.

Extremely slow desorption of NOC held as a resistant fraction in field soils appear to exist. A major problem in studying this phenomenon is reproducing what happens in soils over decades in the laboratory environment. Thus, it is important to study the behavior of pesticide residues that have long residence times in soils. The models for diffusion from intraparticle micropores start to explain the system, but more research is needed to evaluate how effective these models describe the effects of long-term contaminant aging in actual field soils.

Another problem arises in analytical measurements of residual NOC. The resistent fraction is difficult to extract. It requires exhaustive measures including hot solvents, aggregate pulverization and long extraction times (Sawhney et al., 1988). A significant fraction (50%) of atrazine residues and degradation products were found to remain in soil after a 2 hour methanol soxhlet extraction (Capriel et al., 1985). Without harsh procedures, the resistent fraction is not observed and the actual concentration in soil may be higher than what was measured in the conventional manner. This may result in a masking of environmental problems because of ineffective analytical techniques.

The process of contaminant aging in soil may exert an important influence on the environmental behavior of NOC. A compound may sorb into increasingly remote sites over time, thus taking years to decades to desorb. This may be a source of continual ground water contamination long after application has ceased. Slow desorption kinetics may control the bioavailability of a NOC and cause an unexpected persistence. However, persistent herbicides such as atrazine have been found to be potentially available to plants and microbes (Capriel et al., 1985). A residual herbicide may be continually available to future sensitive crops or completely protected and unavailable to microbial degradation. It is important to understand the interaction between NOC and soil in order to: (1) make accurate predictions of contaminant fate and transport, (2) avoid the misinterpretation of environmental fate data obtained in laboratory studies using spiked soils, (3) make environmentally sound pesticide management decisions in agricultural systems, and (4) develop effective soil restoration technologies such as soil washing and in-situ bioremediation.

DESORPTION AND BIOAVAILABILITY OF SIMAZINE

INTRODUCTION

Simazine (2-chloro-4,6-bis(ethylamino)-s-triazine) is a widely used triazine herbicide for broadleaf and grassy weed control in several crops. It has a pK_a of 1.65, a water solubility of 3.5 ppm and a vapor pressure of 6.1×10^{-9} mm Hg (Gunther, 1970). The persistence of triazine herbicides in soil may result in injury to crops planted in rotation. This carryover potential was recognized shortly after development (Sheets, 1970). Triazine persistence in soil is affected by several factors, including microbial degradation, leaching, and sorption to organic and mineral fractions. Meggitt (1962) reported atrazine and simazine carryover from the previous year sufficient to injure sensitive crops including oats and sugarbeets. The greatest fraction of herbicide was also found in the upper two inches of the soil profile, suggesting minimal leaching. Complete mineralization to CO_2 by microbial degradation of triazine herbicides is low (0.5 to 5%) in soil (Dao et al., 1979; Kauffman and Kearney, 1970). Capriel et al. (1985) reported over 50% of atrazine and dealkylated atrazine metabolites remained in soil after nine years. The repeated use of simazine, for example as in a continuous corn rotation, may result in the development of a stable, persistent fraction of the herbicide in soil.

Several organic compounds and pesticides, such as parathion, EDB, DBCP, have been reported to persist in soils for over ten years despite being easily degraded by bacteria found in soils (Buxton and Green, 1987; Steinberg et al., 1987; Wolfe, 1973). Recent research (Ogram et al., 1985) has suggested that contaminants in the soil-bound state are biologically unavailable. It follows that desorption is a prerequisite for biodegradation and that if desorption is sufficiently slow it may limit biodegradation. Steinberg et al. (1987) used a radial diffusion model to describe the desorption kinetics of residual EDB from agricultural soils. Diffusion from a porous spherical particle (aggregate) was described using the general equation (Crank, 1975):

$$C/Ce = f(D_{eff} * t / r^2)^{1/2} \qquad [3]$$

where D_{eff} is the effective diffusion coefficient (cm^2/sec), r(cm) is the mean particle radius, t is the diffusion time, C is the measured aqueous phase concentration at time t, and Ce is the predicted equilibrium solution concentration. The measured value of D_{eff} reported by Steinberg et al. (1987) is approximately 10^{-17} cm^2/sec. This corresponds to 50%

equilibrium solution concentrations of 23 to 31 years. Wu and Gschwend (1986) reported D_{eff} values between the range of 10^{-9} and 10^{-12} cm^2/sec for various chlorobenzenes from recently spiked laboratory soil samples. The fundamental difference between these two experiments that appears to account for the much slower diffusion of EDB, is that EDB had residence times of years in the soil. Steinberg et al. (1987) concluded that the aging of residues was extremely important in determining the kinetics of desorption and suggested that with time these residues occupy increasingly remote sites in aggregates accounting for their extremely slow release times, and possibly for their increased persistence. To determine a compounds fate, bioavailability and transport, a clear understanding of desorption processes and the factors affecting desorption kinetics is required.

The objective of this study was to compare the bioavailability and desorption kinetics of aged simazine from a continuous corn field to simazine recently applied to soil. The bioavailability of aged and recently added simazine was compared to their desorption kinetic behavior to test the hypothesis that desorption into the aqueous phase is a prerequisite for plant uptake and microbial availability, and that contaminant aging results in slower desorption kinetics. Laboratory desorption experiments of simazine directly compared the kinetics of native and recently added ^{14}C-simazine. Simazine concentration in field soil-water was measured throughout a growing season to evaluate the existence of nonequilibrium conditions for field soils resulting from increasingly slow simazine desorption from the sorbed state. A bioassay using (1) field soil containing aged simazine residues and (2) a soil with no history of triazine use spiked with approximately the same simazine concentration as the native (aged) fraction, evaluated the effect of contaminant aging on bioactivity in sugarbeet. The microbial degradation of each fraction was compared by a microbial incubation of field soil containing both the native fraction and recently added ^{14}C-simazine in approximately equal concentrations.

EXPERIMENTAL SECTION

Soil

A fine-loamy, mixed mesic, Aeric Ochraqualf (capac series) soil was obtained from the Crop and Soil Science Farm at Michigan State University. The soil contained 76% sand, 15% silt, 9% clay and an organic carbon content ranging from 1.25 to 2.00 percent. Soil was sampled from a corn field with over twenty years of annual simazine application. Soil samples were collected from the upper 20 cm, air-dried at room temperature, ground and passed through a 2.0 mm screen. The organic carbon content of the soil was determined commercially by microcombustion and trapping evolved CO_2 (Huffman Laboratories, Boulder, Colorado).

Simazine Determination in Soil

Twenty grams soil was extracted by refluxing 150 ml methanol/water (9:1) solution for 24 hours. The solution was filtered, rotoevaporated to partial dryness, extracted with methylene chloride, and rotoevaporated to complete dryness. The sample was brought to volume in methylene chloride and injected into a Hewlett/Packard 5890A Gas Chromatograph (GC). An oven temperature program from 100 to 240 °C was used for the determination of simazine. The GC was equipped with a nitrogen/phosphorous detector (250°C) and a Supelco SPB-5 wide bore column. The recovery of a standard simazine solution yielded results greater than 98% efficiency. This extraction method resulted in a 41% higher recovery for total simazine than a standard determination for triazine herbicides in soil (Leavitt, 1988).

Sorption Coefficient (K, K_{oc}) Determination for Simazine

Ten grams of air-dried sieved soil and 20 ml of water were placed in a 25 ml Corex centrifuge tube. A 5.55 mg/ml solution of ^{14}C-simazine dissolved in DMSO was added in the amounts of 2, 5, 10, 15, and 25 µl, corresponding to 1.11, 2.75, 5.50, 8.25 and 13.75 µg/gram soil. ^{14}C-simazine material was obtained from Ciba-geigy, had a radiochemical purity of 97.8%, a specific activity of 1.8 µCi/µmole and was labelled on one of the carbon atoms in the aromatic ring. Samples were mechanically shaken for 0.5 hours and then gently agitated by hand occasionally over the next 24 hours. The experiment was also conducted for 48 hours. Tubes were centrifuged and 1.0 ml of the supernatant was pipetted into 10 ml scintillation cocktail and analyzed on a Packard Tri-Carb 1500 liquid scintillation analyzer (LSA). Ten µl of the labelled solution was added to 20 ml distilled water as a standard. The standard was treated identical to the samples. The equilibrium concentration, Ce (mg/L), was plotted against the amount sorbed, x/m (mg/Kg). The amount sorbed was calculated from the difference between the initial and final simazine concentrations in the aqueous phase. The slope, K, was determined by linear regression according the equation:

$$X/M = K * Ce. \qquad [1]$$

All samples were carried out in duplicate.

Desorption Experiments

A portion of the air-dried soil prepared as described above was suspended in water for two days. It was then wet-sieved to give aggregate size fractions of 2 to 53, 53 to 106, and 106 to 250 μm. These were analyzed as above to determine total simazine concentration. The 2 to 53 μm particle size fraction had the greatest simazine concentration and was therefore used in the following experiments. Five grams of soil and 20 ml water containing 0.01 M $CaCl_2$ and 500 mg/L NaN_3 (to prevent microbial degradation) were placed in 25 ml Corex centrifuge tube and shaken gently. At intervals spanning several days duplicate samples were centrifuged, the supernatant pipetted from the tube and weighed. The aqueous phase was then extracted with methylene chloride, rotoevaporated, brought to volume in methylene chloride and analyzed as previously described. All samples were carried out in duplicate. A sequential desorption procedure was also conducted. The initial supernatant was removed after 24 hours, weighed and analyzed as previously described. The soil was then resuspended with the same amount of water that was removed. This was repeated five times at 24 hour intervals.

Desorption was also measured for recently added simazine. As in the previous desorption experiments, 5 gm soil and 20 ml of water were placed in a Corex centrifuge tube. The tubes were spiked with 10 μl of a 5.55 mg/ml ^{14}C-simazine solution in DMSO and shaken gently for 24 hours. To determine the amount of simazine sorbed, samples were centrifuged, the supernatant removed, and the amount of simazine in the aqueous phase determined by LSA. The centrifuged soil was resuspended in water and at intervals of 1, 2, 4 and 24 hours tubes were sacrificed and analyzed for ^{14}C-simazine in the aqueous phase.

Determination of Simazine in Field Soil Water

Soil was collected from the corn field periodically just prior to and for four months following simazine application of two lb/acre. Simazine concentration was determined. The soil moisture content was determined by oven drying 50 grams of field soil at 110 C for 24 hours. The organic carbon content of the soil was determined commercially (Huffman Laboratories, Boulder, Colorado). The field soil samples (approximately 400 gm) were placed in a plexiglass cylinder with a perforated bottom plate which held a number 1 Whatman filter paper. Soil water was collected in a cup (attached to the bottom of the apparatus) after centrifugation of the soil sample at 1800 RPM for 2 hours (a more complete description of the apparatus is given by Adams, 1980). The collected water was weighed, extracted with methylene chloride, and rotoevaporated. The sample was redissolved in 5.0 ml methylene chloride and analyzed by GC. The measured simazine concentration in soil water was compared to the predicted equilibrium simazine concentration that was calculated from the sorption coefficient, K, and the measured masses of simazine, water and soil in the sample. The sorption coefficient K was calculated from the measured K_{oc} value and the carbon content of the individual soil samples.

Sugarbeet Bioassay for Simazine

Soil was collected in mid-July from the corn field (referred to as native soil) and passed through a 1 inch sieve. Soil from an adjacent soybean field that had not received simazine application was collected as a control. Simazine concentration in soil and water concentrations were measured for each soil. Simazine was aspirated onto the control soil (referred to as clean since it contained no Simazine), while mixing, to an equivalent concentration as the aged soil. The soils were then analyzed for simazine again to ensure similar concentrations of native and spiked simazine in the two soils. To evaluate differences in the bioavailability of aged (native) and recently added (spiked) simazine residues, a bioassay was conducted with sugarbeet. Native, spiked and clean soils were placed in 500 ml pots. Eight sugarbeet seeds were planted in each pot, watered daily and fertilized weekly with 50 ml of a 2 g/L Peters solution. The plants were observed for simazine damage (chlorosis or death) for four weeks.

Microbial Degradation of Simazine

Soil was collected in mid-August and prepared as previously described. Total simazine and simazine soil water concentration were measured. A ^{14}C-simazine water solution, with a concentration of 0.555 ppm, was added to 500 grams air-dried soil using an aspirator, and mixed thoroughly. The final moisture content corresponded to approximately 75% field capacity. The total simazine concentration in soil was determined as described above. The final ^{14}C-simazine concentration was approximately equal to the native simazine concentration. Thirty gram portions of the soil were then placed in 250 ml Erlenmeyer flasks. A vial containing 2.0 ml 1N KOH was placed in the flask which was then stoppered. At intervals of several days, duplicate flasks were sacrificed for total simazine and ^{14}C-simazine determination. Total simazine (^{14}C-labelled plus native) was determined by GC, as described previously. Labelled simazine was determined by analyzing 2 ml of the 5 ml Simazine extract using LSA. Native simazine was determined by subtracting the labelled simazine from the total simazine.

At three day intervals 2 ml of 1N KOH were placed in scintillation cocktail and analyzed to determine $^{14}C-CO_2$ production. The KOH was immediately replaced. A portion of the extracted soil was combusted in a biological oxidizer and the $^{14}C-CO_2$ released was trapped and analyzed by LSA. A 90.2% recovery of the labelled simazine was observed (11.0% converted to CO_2, 48.5% was extracted from soil and 30.7% recovered from combustion of the soil).

RESULTS AND DISCUSSION

Determination and Comparison of Apparent Sorption Coefficients

Partition coefficients for the sorption of ^{14}C-simazine by the capac soil are given in Table 1. The ^{14}C-simazine sorption isotherm is shown in Figure 1. The isotherm is linear, consistent with the concept of solute partitioning. The partition coefficient, K, calculated by linear regression was 1.5 for 24 hour equilibration and 1.6 for the 48 hour equilibration, suggesting equilibrium after 24 hours.

The partition coefficient can be normalized for organic carbon content (f_{oc}) of a soil to define a new constant, K_{oc}:

$$K_{oc} = K / f_{oc} \qquad [4]$$

Previous studies have established that K_{oc} values remain relatively constant among soils (Choiu, 1983). This result demonstrates the predominant role of organic matter in the sorption of NOC and pesticides, and that in general, the sorptive characteristics of soil organic matter for NOC's is similar for different soils. The K_{oc} for simazine (78) measured in this study was compared with previous K_{oc} values

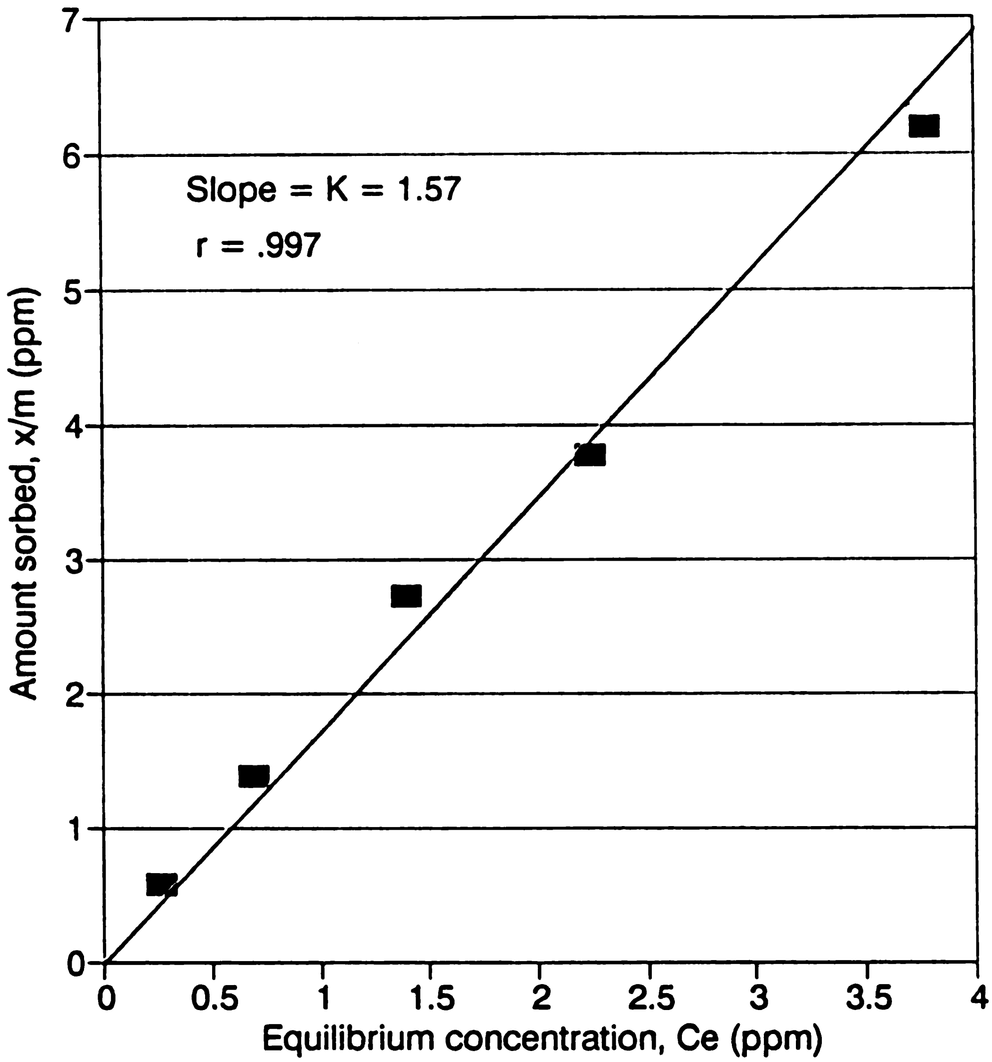

Figure 1. Sorption isotherm for [14C]-simazine on a capac soil.

Table 1. Comparison of K values for native Simazine (from desorption) and added Simazine (from labelled sorption isotherm).

Equilibration time	Simazine type	Apparent K value	Koc
24	labelled	1.5	78
48	labelled	1.6	80
24	native	26	1340
48	native	23	1182

(135-138) from different soils (Karickhoff, 1981). The partition coefficient determined by adding ^{14}C-simazine to soil can be used to establish the soil-water distribution of simazine at equilibrium. The distribution coefficient or "apparent" K values for 24 and 48 hour equilibrations of native simazine residues in the field soil are given in Table 1. These data show that the apparent K values for simazine desorption were over 15 times the K value obtained for the sorption of ^{14}C-simazine by the same soil. It is apparent from this comparison that the native simazine residues are far from equilibrium with the aqueous phase after a 24 to 48 hour desorption period.

The apparent slow desorption of native simazine residues observed in laboratory experiments, suggests the possibility that simazine concentrations in water contacting field soils may be significantly lower than that predicted based on the assumption of equilibrium conditions. The simazine concentration at equilibrium can be predicted by knowing the value of K and the masses of simazine, soil and water in the system:

$$\text{Total simazine} = \text{simazine in water} + \text{simazine in soil} \quad [5]$$

$$\text{Total simazine}(\mu g) = Ce(\mu g/ml) * \text{volume of water}(ml) + Ce(\mu g/ml) * K_{oc} * f_{oc} * \text{soil}(g). \quad [6]$$

The predicted equilibrium concentration, Ce, can be compared to the actual measured simazine concentration in the soil water to evaluate the existence of nonequilibrium conditions in the distribution of simazine between soil and water. Table 2 lists the data needed to predict the equilibrium simazine concentration (Ce). The fractional equilibrium, C/Ce (measured simazine concentration/predicted simazine concentration at equilibrium) is plotted vs. time in Figure 2. The plot clearly demonstrates that equilibrium conditions existed only shortly after simazine application in the field. The April samples that contained simazine residues from the previous year's application had the lowest fractional equilibrium values, 0.01 to 0.02, showing the simazine concentrations in water to be 1 to 2% of the predicted equilibrium values. However, immediately following simazine application in May the measured simazine concentration in water approaches the predicted equilibrium concentration, ie. C/Ce is approximately equal to one. The value of C/Ce steadily decreased during the month following application to a value of about 0.1 to 0.2. Thus, one month after application the simazine water concentration was approximately 10 percent of the predicted solution phase concentration at equilibrium, i.e. the fractional equilibrium fell from approximately 1 to 0.1 in just over a month. During the next two months (July and August) C/Ce decreased to approximately 0.05 showing the simazine concentration in soil water to be about 5% of the predicted

Table 2. Data collected for the determination of the fractional equilibrium of simazine in soil water from a continuous corn field (average field capacity of soil was 90%).

Date sampled	Percent organic carbon	Percent moisture	Total simazine (ppm)	Simazine water (ppb)	C/Ce
4-4	1.76	16.0	0.18	3.3	.0242
4-18	1.11	15.1	0.23	3.4	.013
4-25	1.31	13.6	0.20	4.4	.022
5-3	1.50	14.1	0.25	259	1.2
5-10	1.73	16.4	0.20	121	.79
5-17	1.56	17.1	0.17	92.0	.63
5-24	1.44	16.1	0.31	148	.54
5-31	1.55	15.4	0.16	8.1	.059
6-6	1.38	13.3	0.25	38.0	.17
6-20	1.62	15.2	0.18	17.9	.12
7-17	1.75	15.8	0.20	8.2	.055
8-15	1.81	16.3	0.25	13.1	.066

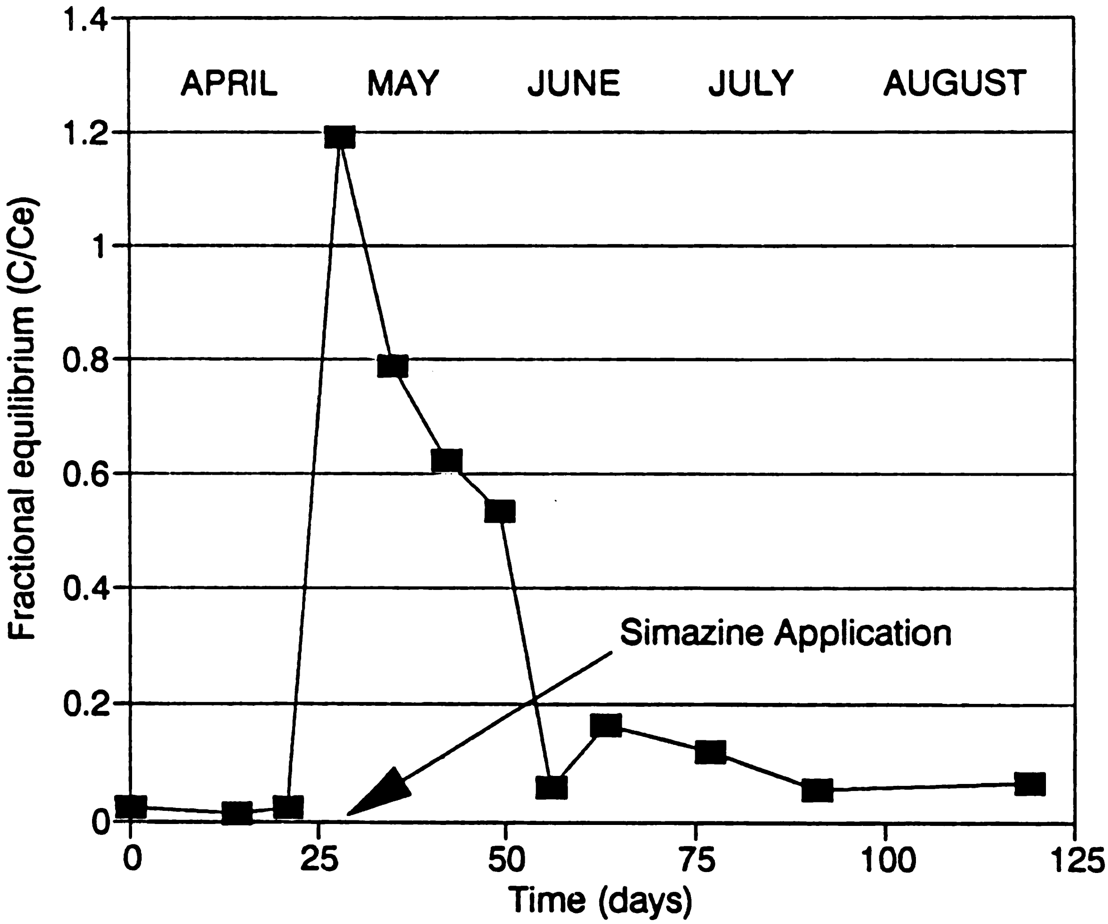

Figure 2. Seasonal variation of the fraction equilibrium of simazine in soil water from a continuous corn field.

equilibrium value. A residual simazine fraction developed over time which had slower desorption properties than freshly added simazine.

Native Simazine Desorption

The desorption of native simazine from unfractionated field soil is shown by plotting the fractional equilibrium, C/Ce, against desorption time (Figure 3). The total release after sixteen days was only 32% of the predicted equilibrium concentration. Desorption of added simazine was rapid and within 90% of the calculated equilibrium concentration within 1 to 24 hours (Figure 4). The data in Figures 3 and 4 clearly show that the desorption kinetics of aged simazine residues to be extremely slow compared to that of the recently added simazine.

A second experiment was performed to evaluate desorption of native simazine residues. A series of sequential desorption steps were evaluated by replacing the aqueous phase every 24 hours. This procedure should allow more simazine to desorb from the soil. For the first three days the fractional equilibrium was from 0.2 to 0.24 (21 to 24%) (Figure 5). The total simazine concentration was reduced in the system each time the aqueous phase was removed. Therefore, Ce was recalculated using the new total simazine value after each sampling and the added fractional equilibrium value exceeded 1. After the fourth day there

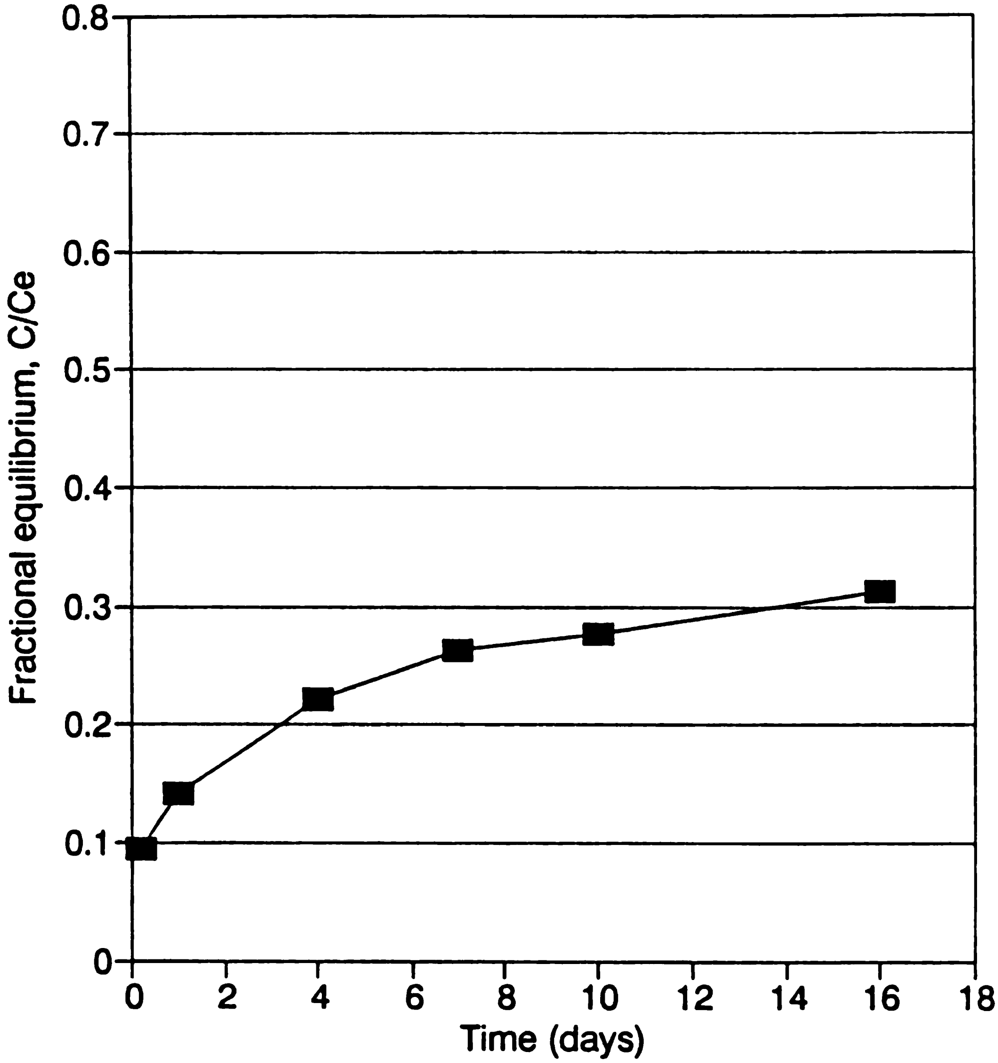

Figure 3. Desorption of native simazine from capac soil.

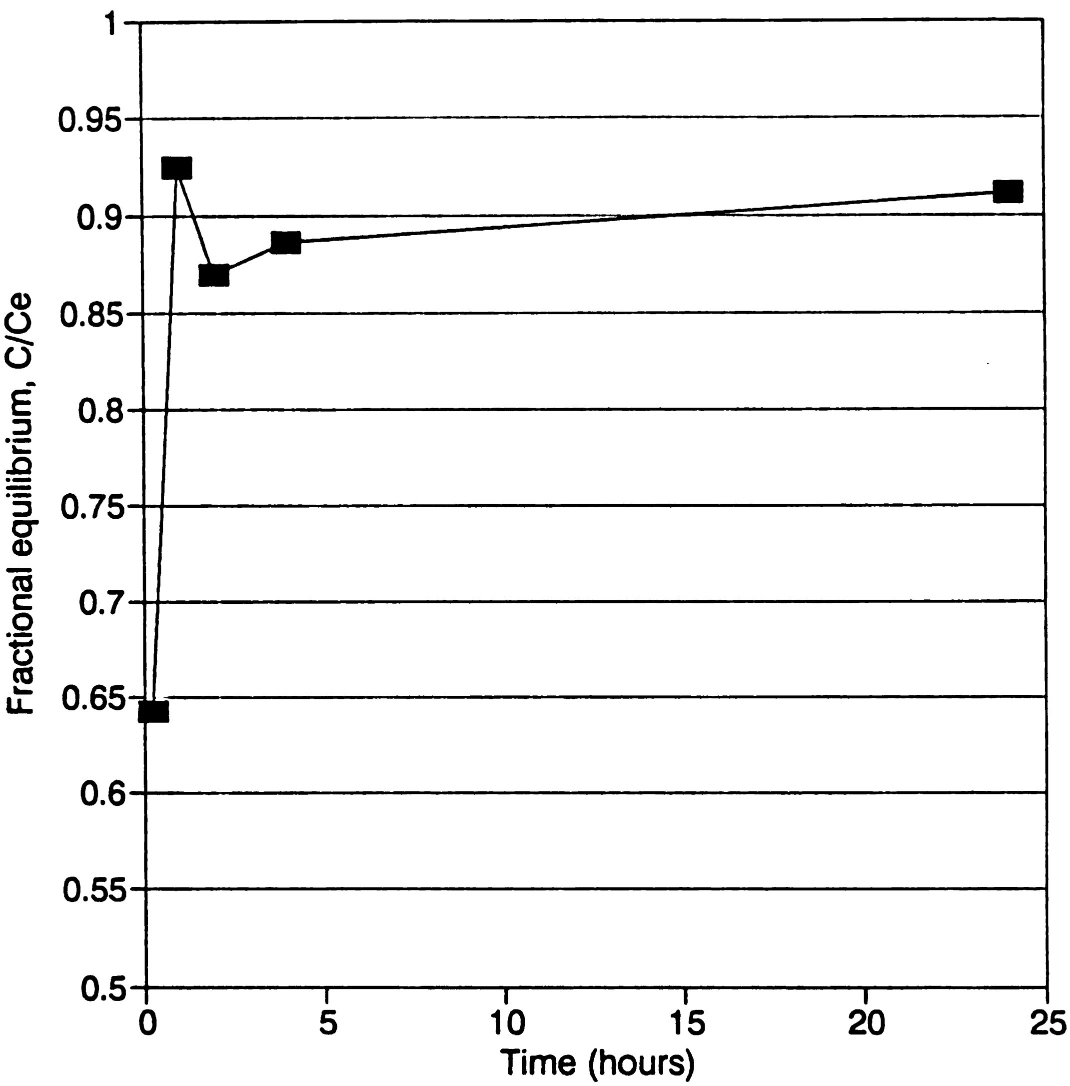

Figure 4. Desorption of simazine recently added to capac soil.

was a sharp decline in fractional equilibrium, suggesting that the native fraction became increasingly more resistent to release as the mass of Simazine desorbed increased. This is more clearly demonstrated by Figure 6 where the fraction of native simazine remaining in soil is plotted vs. the expected simazine remaining. After six days the expected soil concentration is less than two percent of the original amount of sorbed simazine; however the actual measured concentration is above 45 percent.

The release of native simazine from soil organic matter into the aqueous solution may be treated as diffusion from a spherical particle (aggregate). Recently, Steinberg et al (1987) used a radial diffusion model to describe the desorption of native EDB residues from field soils. This approach allowed estimation of an effective diffusion coefficient (D_{eff}) to quantitate the kinetics of EDB desorption. An analytical solution to the equation describing the diffusion from spheres of known radius (Crank, 1975) is of the general form (Steinberg, 1987):

$$C/Ce = f(D_{eff} * t / r^2)^{1/2} \qquad [7]$$

where C/Ce is the fractional equilibrium at time t, D_{eff} is the effective diffusion coefficient and r is the aggregate radius. This equation treats desorption as a diffusion process from uniform spheres of equal radius into a well

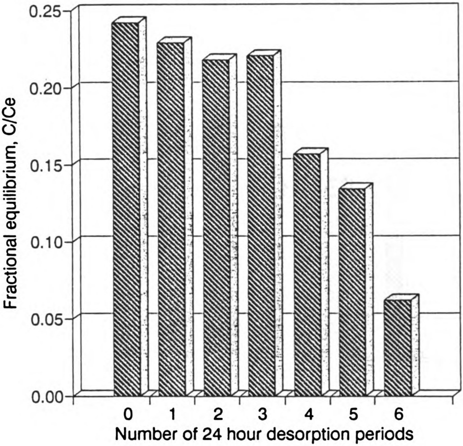

Figure 5. Fractional equilibrium in the aqueous phase attained for 24 hour desorption periods for native simazine in soil. The aqueous phase was removed and replaced with distilled water after each 24 hour time period.

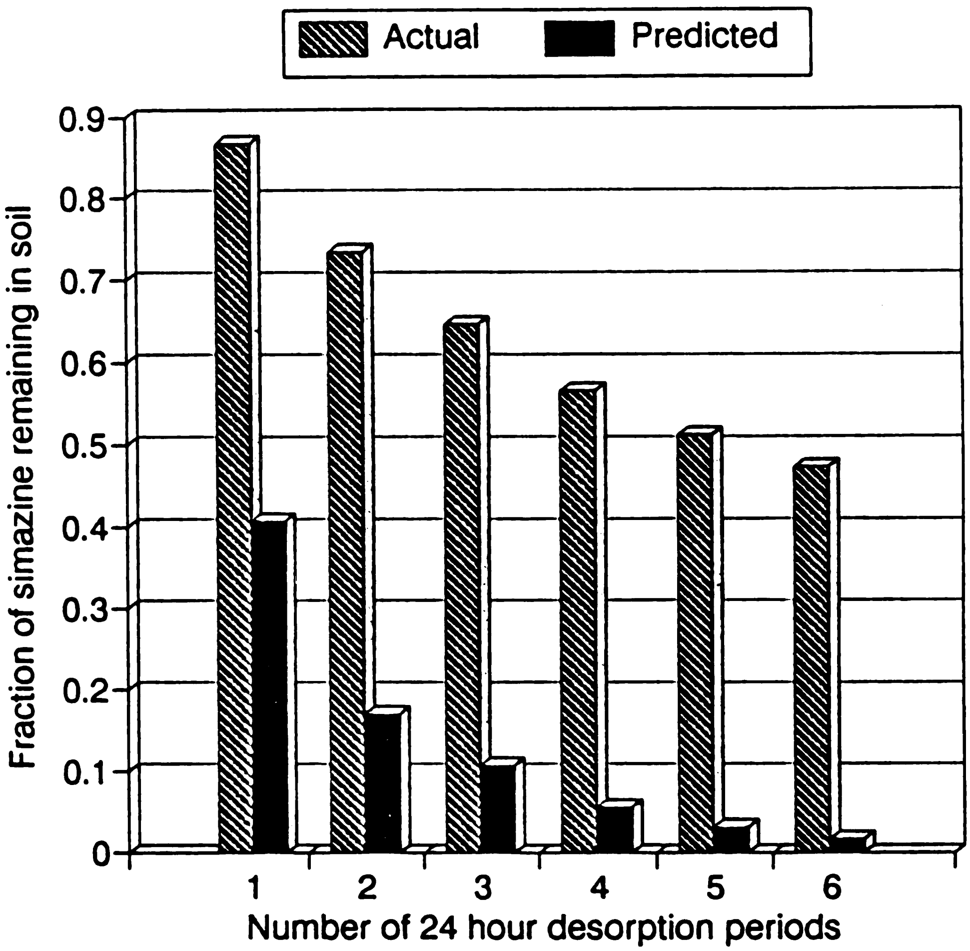

Figure 6. Fraction of native simazine remaining in soil after 24 hour desorption periods compared to predicted values. The aqueous phase was removed and replaced after each 24 hour time period.

stirred solution of limited volume. The model assumes simazine is evenly distributed and will diffuse into the aqueous phase until equilibrium is attained. The desorption of native simazine from the 2 to 53 μm aggregate fraction is given in Figure 7. A series of theoretical curves relating the fractional equilibrium vs. $t^{1/2}$ can be generated from eq. 5 assuming an average particle size of 26μm (Figure 8). The desorption data were visually matched to the theoretical curves to estimate an effective diffusion coefficient. The native simazine fraction exhibited extremely slow approach to equilibrium with an effective diffusion coefficient in the range of 5.0×10^{-16} (cm^2/sec). The diffusion coefficients of organic solutes in water are typically on the order of 1×10^{-6} cm^2/sec. Assuming a D_{eff} value of 5×10^{-16} the time required to reach 50% equilibrium solution concentration of simazine is 0.5 years. The time required to reach 90 and 100% equilibrium solution concentration is 4.5 and 18 years, respectively. Figure 9, a plot of the diffusion coefficients vs. fractional equilibrium for each time point reveals that the approach to equilibrium is retarded, indicating an increased resistance to desorption as this process continues with time.

Sugarbeet Bioassay

The herbicidal activity of native (aged) simazine residues was compared to that of recently added simazine using

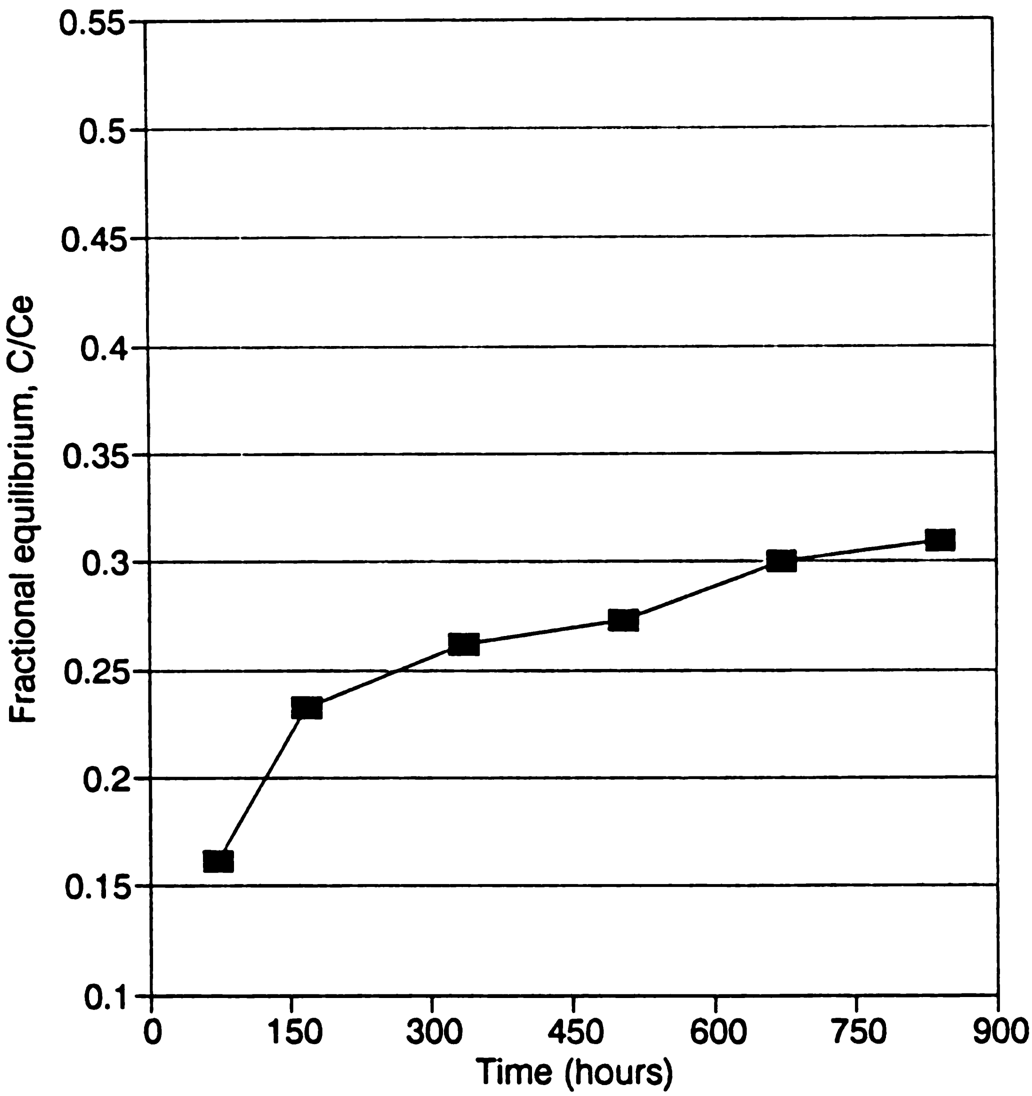

Figure 7. Desorption of native simazine from the 2 to 53 micron aggregate soil size fraction.

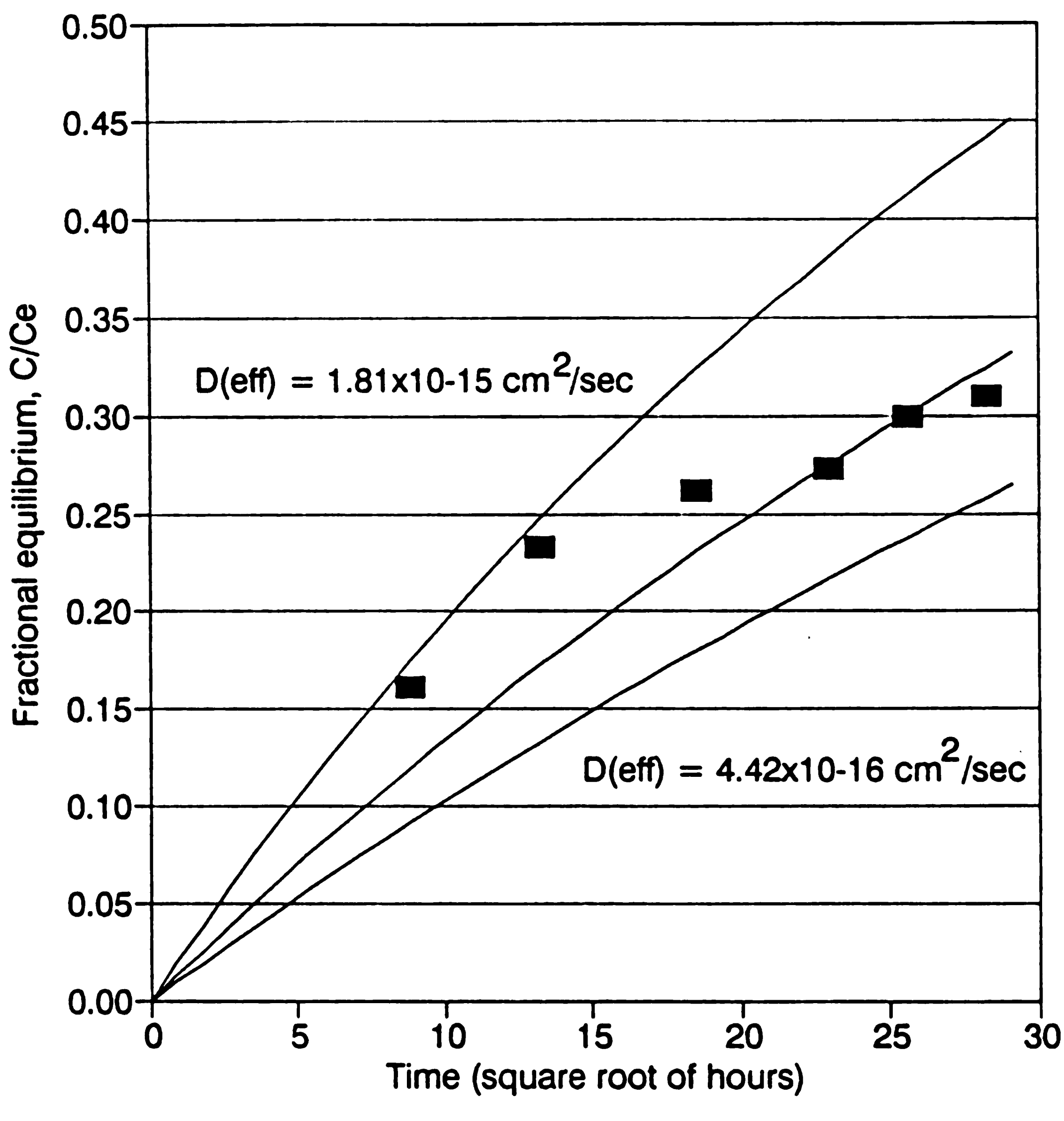

Figure 8. Desorption of native simazine from the 2 to 53 micron size fraction of soil. Measured data are matched to theoretical diffusion curves for different effective diffusion coefficients, D(eff), that describe diffusion from a spherical particle.

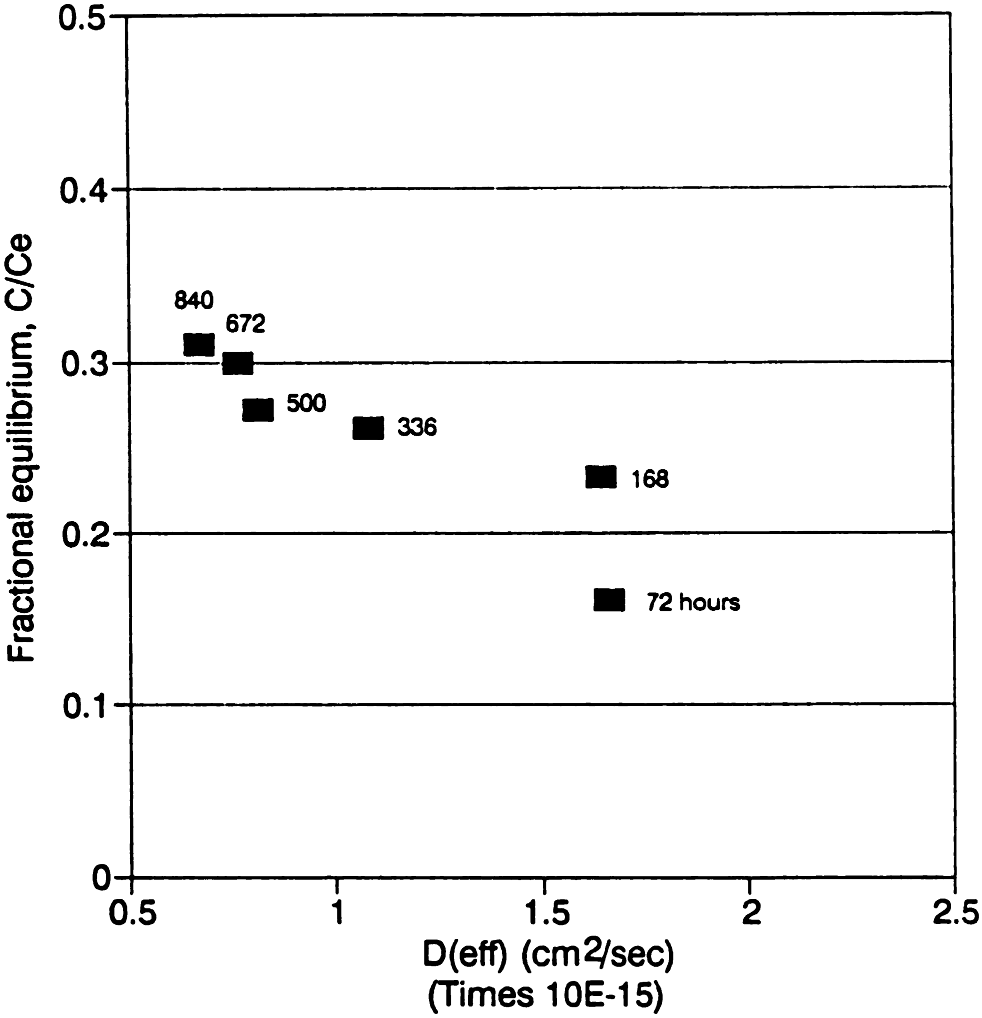

Figure 9. Estimated effective diffusion coefficient, D(eff), for each desorption time point plotted against the fractional equilibrium. The plot shows a progressive decrease in D(eff) as the desorption process continues.

sugarbeet as an indicator plant. Simazine was added to soil with no residual simazine (clean soil) at a level approximately equal to the native simazine concentrations (200 ppb) found in the study soil in August. The measured simazine concentration for clean, native and spiked soils, along with the percentage of sugarbeets affected by chlorosis is listed in Table 3. Over 50% of the sugarbeet plants (Figure 10) developed chlorosis when grown on soils where simazine was added to clean soil compared to 0% chlorosis for plants grown in soil with the same concentration of native simazine. The native concentration is 3 to 4 times greater than the standard allowable limit (50 to 75 ppb) to grow sugarbeets, yet no visible effect was apparent. This suggests that the native simazine is not desorbing to the aqueous phase and as a result is unavailable to the plants.

Microbial Degradation

Figures 11 and 12 compare the degradation of total, added and native simazine over time. These data show that the total simazine (native plus added) concentration decreased from about 200 ppm to 152 ppm over a 34 day incubation. When the native and added simazine pools are examined individually, it is apparent that the decrease in total simazine is due entirely to biodegradation of the added simazine and that the native simazine is resistent to

Table 3. Number of sugarbeet seedlings showing simazine herbicidal damage when grown in clean soil, soil spiked with simazine and soil containing aged simazine residues.

Soil type	Simazine concentration	No. of plants	No. plants sensitive	% plants affected
Clean	0 ppm	48	0	0
Spiked	0.20 ppm	51	26	51
Aged	0.22 ppm	42	0	0

Figure 10. Photograph showing chlorosis (brown and yellow areas at leaf tips) of sugarbeet seedlings grown in soil spiked with simazine (simazine concentration in soil was 0.20 ppm).

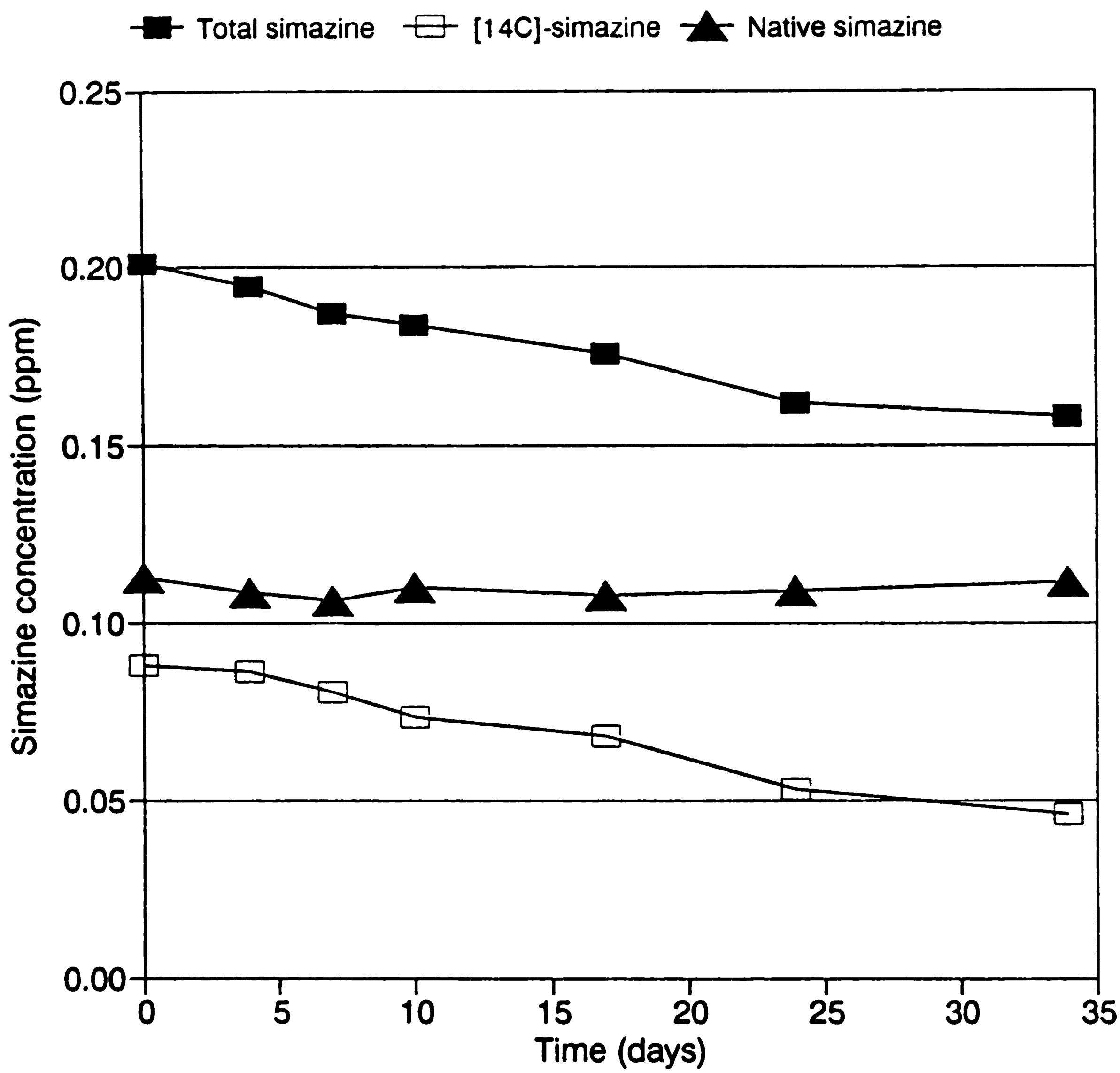

Figure 11. Degradation of the total, native and added [14C]-simazine over a 34 day incubation in soil.

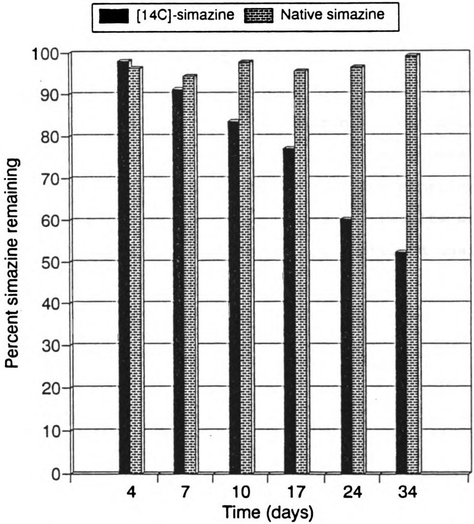

Figure 12. Degradation of native simazine compared to the degradation of added [14C]-simazine during a 34 day soil incubation.

biodegradation. Thus 48% of the added simazine is biodegraded in the 34 day incubation, whereas, no biodegradation of native simazine occurred. It is apparent from these results that the native simazine is unavailable for microbial degradation. The lack of bioavailability is likely a manifestation of the fact that the native simazine is not desorbing into the aqueous phase where it would be more available for microbial degradation. Recent studies by Ogram et al (1985) have shown that soil-bound organic contaminants are unavailable to microbial degraders. It logically follows that desorption into the aqueous phase is a prerequisite for biodegradation. If the kinetics of desorption are sufficiently slow, as our results clearly show, then the simazine residues are protected against microbial degradation.

CONCLUSION

Simazine in the contaminated soil is resistant to desorption into the aqueous solution, degradation to indigenous soil microbes and plant (sugarbeet) uptake. This is in sharp contrast to added simazine which was desorbed rapidly, degraded by indigenous microbes and available for plant uptake. This suggests that the native simazine is entrapped in soil micropores.

The conceptual picture of soil micropores is presently obscure, however, the release of simazine entrapped in pores of soil aggregates can be viewed mathematically as a diffusion controlled process (Steinberg, 1987). The spherical diffusion model that was employed gave effective diffusion coefficients in the range of $5.0x10^{-16}$ cm^2/second. This very slow effective diffusion results in calculated time required to reach equilibrium concentration in water of 18 years. The effective diffusion coefficients decreased as the desorption continued over time, suggesting that times to reach equilibrium would be even longer.

Examination of the concentrations of simazine soil water showed that the fractional equilibrium values decreased from approximately one at the time of field application of simazine to less than 0.1 at the end of August. These field experiments demonstrate that the desorption of simazine becomes increasingly slower resulting in higher ratios of soil-bound to aqueous phase simazine concentrations than expected at equilibrium. Our results are consistent with previous studies on aged EDB residues in agricultural soils. Apparently, for these pesticides increasingly remote sites in soils become populated over time leading to the formation of a residual pesticide fraction that desorbs very slowly and is biologically unavailable. As the desorption process continues, the diffusion coefficients of these residues decrease because the compounds are held in more remote sites of the soil aggregates.

The bioavailability of simazine appears to be related to its desorption from soil. Our results suggest that if simazine does not desorb into the aqueous phase it will be unavailable to plant uptake. The native simazine residues with slow desorption kinetics show no herbicidal activity whereas recently added simazine residues that desorb rapidly produce chlorosis in sugarbeet plants. The results in this study also suggests that the native simazine was almost completely protected against biodegradation by indigenous soil microbes. If simazine is partitioned or entrapped in soil pores that are inaccessible to microbial degraders, and desorb very slowly from these sites, it would follow that such residues would be protected against microbial attack.

The residual simazine reported is probably a small fraction of the annually added simazine that diffuses into remote micropore sites in the soil. It is most likely a consequence of the continuous use of the herbicide and the relatively high initial applied concentration. The bulk of the added simazine follows predicted equilibrium conditions, plant uptake and microbial degradation. However, over time a residual fraction develops that behaves differently than added herbicide. The presence of a persistent residual fraction of pesticides in agricultural soil is cause for concern. This residual fraction could (1) be a source of slow and continuous leaching of a NOC to groundwater for decades after the NOC use has been discontinued, (2) require predictions of contaminant fate and transport to account for persistent fractions, (3) result in the misinterpretation of environmental fate data obtained in laboratory studies using spiked soils, and (4) inhibit effective use of soil restoration technologies such as soil washing and in-situ bioremediation due to an unavailable resistent fraction.

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