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Fate of a Highly Strained Hydrocarbon in Aqueous Soil Environment

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Quadricyclane, a highly strained hydrocarbon, is currently being evaluated by the U.S. Air Force as a possible high-performance aviation fuel. It is therefore important to discover how it would interact with the environment in the event of a spill. The reactions of quadricyclane were investigated in water, 50/50 wt % water/2-propanol and pure 2-propanol, and in abiotic aqueous soil environments consisting of four different naturally occurring soils. The reaction products were *exo*-5-norbornen-2-ol and nortricyclyl alcohol. The reactions in the three solvent systems were pseudo-first-order in quadricyclane. Second-order rate constants were determined from plots of the pseudo-first-order rate constants versus [H^+] and were found to be 26.0 L mol^{-1} min^{-1} in water, 0.195 L mol^{-1}min^{-1} in 50/50 water/2-propanol, and 0.099 L mol^{-1}min^{-1} in 2-propanol, all at 25 °C. The soil experiments were run for periods of up to 9 months. The most important factor affecting the reactivity of quadricyclane in the soils was pH, while organic matter content was not important. In soils of high pH, quadricyclane behaved as a light nonaqueous phase liquid except that it had a propensity to form microemulsions. In soils of low pH, the reactions producing the alcohols and their subsequent dissolution in the groundwater became significant.

Introduction

The behavior of light nonaqueous phase liquids (LNAPLs) in porous media has been the subject of a large amount of research. These liquids include saturated and unsaturated hydrocarbons that have densities less than that of water. Most saturated hydrocarbons of the LNAPL type have very low solubilities in water (ppb range), whereas unsaturated hydrocarbons, such as benzene and toluene, have higher solubilities (1000−2000 ppm range) (*1*).

LNAPLs spilled at the soil surface migrate downward in the unsaturated zone due to the effects of gravity and capillarity (surface tension effects). As the LNAPL continues through the unsaturated zone, some of the organic LNAPL will be trapped in the pore spaces of the soil. If the spill is large enough in size, some of the LNAPL will eventually reach the capillary fringe where it accumulates near the water table (*2, 3*). Further movement occurs as the LNAPL dissolves in the groundwater; the higher the solubility of the LNAPL, the greater the contamination of the groundwater.

Highly strained cyclic hydrocarbons constitute an interesting class of LNAPLs. These hydrocarbons are of interest because of their high heats of formation and relatively high densities, and they are currently under consideration by the U.S. Air Force for possible use as high-performance aviation fuels. Since spills are inevitable once highly strained cyclic hydrocarbons start to be used in large quantities, their fate in the environment needs to be examined. They are reactive and have densities closer to that of water than their straight or branched chain analogs. Quadricyclane [quadricyclo-(2.2.1.0^{2,6}.0^{3,5})heptane], C_7H_8, is an example of this class of hydrocarbons. It is a relatively stable organic liquid with a boiling point of 108 °C and a density of 0.982 g/cm^3.

Quadricyclane is known to be stable in slightly alkaline or neutral solutions (*4*); however, it is attacked by electrophiles (*5−7*) and dienophiles (*8−10*) to give very stereospecific *exo* products. It also undergoes redox reactions (*11*) and metal-catalyzed isomerizations to norbornadiene (C_7H_8) (*12, 13*). The oxidation potential of quadricyclane in acetonitrile is +0.91 V versus a saturated calomel electrode (*14*). This is an entire unit lower than for most other saturated hydrocarbons. Quadricyclane is more easily oxidized than its isomer norbornadiene, which has an oxidation potential of +1.56V.

This study focuses on the behavior of quadricyclane in aqueous solutions and in aqueous soil environments consisting of four different soil types varying in pH and organic matter content.

Experimental Section

Reagents. Quadricyclane, norbornadiene, and 5-norbornen-2-ol ($C_7H_{10}O$) were obtained from Aldrich Chemical Company and used without further purification. Nortricyclyl alcohol ($C_7H_{10}O$) was prepared by treating quadricyclane in water with aqueous HBF_4. Identification and purities of the compounds were determined by gas chromatography, gas chromatography/mass spectrometry, and ^1H and ^{13}C NMR.

Soils. The soils used in this study were selected to give combinations of high organic matter content−low pH (ALOHPL), low organic matter content−high pH (TNOLPH), high organic matter content−high pH (TNOHPH), and low organic matter content−low pH (ALOLPL). The AL and TN refer to soils collected in Alabama and Tennessee, respectively. Only topsoil was collected. All four soil types had similar clay fractions. Table 1 lists the important data characterizing the soils. Particle size fractions of sand, silt, and clay were determined by the pipette method (*15*) and were used to classify the soil texture according to the USDA classification scheme. The mineralogical composition of the clay fractions was analyzed by X-ray diffraction on a Siemens D5000 X-ray spectrometer in conjunction with thermal gravimetric analysis using a DuPont thermogravimetric analyzer (*16*). Exchangeable Mg^{2+}, Ca^{2+}, K^+, and Na^+ were determined by leaching the soil with a 1 M ammonium acetate solution (*17*). The exchangeable Al^{3+} was determined by shaking the samples with 1 M KCl solutions. Atomic absorption analysis of the leachate was carried out on an Instrumental Laboratory Model 251 spectrophotometer. The soils were treated with trace amounts of thymol and mercuric chloride to exclude biological activity.

Chemical Analyses. Analyses were carried out on a Shimadzu GC14 gas chromatograph equipped with a flame ionization detector (FID), an AOC-17 autoinjector, and a CR501 computing integrator/data processor. The FID was coupled to a Restek RTX-1 capillary column (30 m, 0.25 mm i.d.). For the quantitative measurements, in which the absolute values of the quadricyclane and its products in the soils needed to be found, 0.4−1.0 g of a standard solution (for

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TABLE 1. Description of Four Soils Used in This Experiment

	soil acronym			
	ALOLPL	**ALOHPL**	**TNOLPH**	**TNOHPH**
family description	Typic Kanhaplaquults	Plintic Kandiudults	Cumilic Hapdudolls	Typic Eutrochepts
pH	5.12	4.60	5.93	6.35
% organic matter	1.0	6.0	2.2	2.8
% sand	77.8	70.2	57.5	48.0
% clay	11.2	11.4	12.3	14.4
texture	sandy loam	sandy loam	sandy loam	loam
mineralogical Composition of clay fraction[a]	interlayered vermiculite (5), kaolinite (4) quartz (1), and goethite (trace)	interlayered vermiculite (5), kaolinite (4), gibbsite (2), quartz (2), and goethite (1)	illite (4), vermiculite (3), kaolinite (2), mica/interstratified vermiculite (1), and quartz (1)	illite (4), vermiculite (4), kaolinite (2), mica/interstratified vermiculite (1), and quartz (1)
exchangeable cations[b] Ca^{2+}	3.0	3.4	29.2	46.3
Mg^{2+}	1.6	1.3	8.3	15.2
K^+	0.8	0.5	0.7	0.8
Al^{3+}	3.9	35.0	0.6	0.9
Na^+	1.3	1.2	1.2	1.2

[a] The numbers in parentheses denote a semi-quantitative rank based on interpretation of the X-ray diffraction pattern; (5) is dominant (>50%), (4) is about 30–40%, (3) is about 20–30%, and (1) is less than 10% of the clay fraction. [b] In mmol/kg of soil.

example, 881.8 ppm of decane in 2-propanol) was added as an internal standard to a weighed amount of the aqueous solution (typically 0.4–0.8 g). Multiple injections at 40 °C were made over the range of 0.2–1.0 μL. After 4 min at 40 °C, the temperature was raised at a rate of 25 °C min^{-1} to 200 °C and held there for 10 min. The areas of the components of the solutions were plotted against the areas of the decane standard for each injection, and the data were fitted to linear relations that all had correlation coefficients greater than 0.99.

For product identification, mass spectral analyses were carried out on a VG 7070 EHF mass spectrometer equipped with a Varian 3700 gas chromatograph and a data station. Aqueous injections of 1 μL were made at 40 °C. After holding for 4 min, the temperature was raised at a rate of 25 °C/min to 200 °C and held at that temperature for 10 min. Ionization was carried out in the electron impact mode.

Solubility. Attempts were made to measure the solubility of quadricyclane and norbornadiene at room temperature in water at neutral pH by using settling and ultrafiltration techniques, but due to the formation of microemulsions, which are visible under high magnification, artificially high values were obtained. Etzweiler et al. (*18*) have suggested a method especially suitable for such a system, which produced much better results. An apparatus was therefore built using Spectra/por membrane tubing with a molecular weight cutoff of 12 000–14 000. As a control, the solubility of benzene was checked and found to be 1788 ppm [cf. the accepted value of 1760 ppm (*1*)].

Aqueous Experiments. Kinetic data were collected from mixtures of aqueous quadricyclane solutions (ca. 200 ppm) and from quadricyclane in a 50/50% by weight solution of water and 2-propanol, and quadricyclane in pure 2-propanol (both ca. 5,000 ppm) for comparison as the low solubility of quadricyclane in water and its tendency to form emulsions was expected to be a problem. HBF_4 was used in all the mixtures as the H^+ source. This acid is a strong monoprotic acid, and the BF_4^- anion is a very poor nucleophile, which is therefore unlikely to be involved in further reactions. Samples in water were prepared by vigorously shaking a mixture of 0.5 cm^3 of quadricyclane and 5.0 cm^3 of deionized water for 15 min, centrifuging for 5 min, and carefully extracting ca 1.5 cm^3 of the lower layer. This extract was placed in a vial and weighed, and a known quantity of a standard aqueous solution of 0.0846 mol/L HBF_4 was added. Samples in the 50/50 water/2-propanol solution were prepared by taking an 2-propanol solution containing known amounts of quadricyclane (11 314 ppm) and dodecane (2 030 ppm) and combining this with weighed amounts of an aqueous solution of 0.24 M HBF_4. Deionized water was then added to make the aqueous portion 50% by weight. Samples in 2-propanol were prepared by adding a known quantity of a 2-propanol solution containing 0.62 mol/L HBF_4 into an 2-propanol solution containing the same known concentrations of quadricyclane and dodecane as previously used. The dodecane was used as an internal standard to which the quadricyclane and product GC area readings were normalized to correct for shot-to-shot variability. The temperature was maintained at 25 °C and samples were withdrawn and analyzed by gas chromatography. Injections were made at 40 °C, held at that temperature for 4 min, and then raised at a rate of 25 °C/min to 250 °C. The autoinjector was used to repeat the injections at regular intervals between 30 min and 2 h.

An experiment was also performed in which 1 cm^3 of quadricyclane was added to 100 cm^3 of strongly acidic water, and the pH was monitored while the reaction progressed. No change over the course of the reaction was observed.

Soil Experiments. A total of 12 g of the less porous ALOLPL soil and 10 g of each of the other three soils were placed into different vials, and 2 cm^3 of deionized water and 3 cm^3 of quadricyclane were added. The vials were tightly closed and subjected to rotation in a jar mill for various periods of time, ranging from 2 weeks to 9 months. The samples were subsequently removed from the vials and placed in 250 cm^3 centrifuge bottles, and 75 cm^3 of dodecane and 30 cm^3 of saturated NaCl solution were added. The bottles were then shaken for about 12 h with a mechanical shaker, after which time they were centrifuged to separate the soil, aqueous extract, and dodecane extractant. Next, the liquids were decanted into a separation funnel, and the two immiscible liquids were separated. This extraction procedure was conducted twice on each soil sample.

For both the $t = 0$ samples and those that were rotated for 2 weeks, an attempt was made to further extract reactants and products by the use of a pH swing. The samples were taken to pH 12 using NaOH and a further extraction with dodecane was carried out, and the process was repeated at pH 2 using HCl. No additional products were found, and as no significant improvement in recovery was observed, these steps were discontinued.

The same extraction proceedure was also carried out on samples of three of the soils (ALOHPL, ALOLPL, and TNOLPH) that had been doped with a mixture of 5-norbornen-2-ol and nortricyclyl alcohol and rolled for 2 weeks, and the amounts

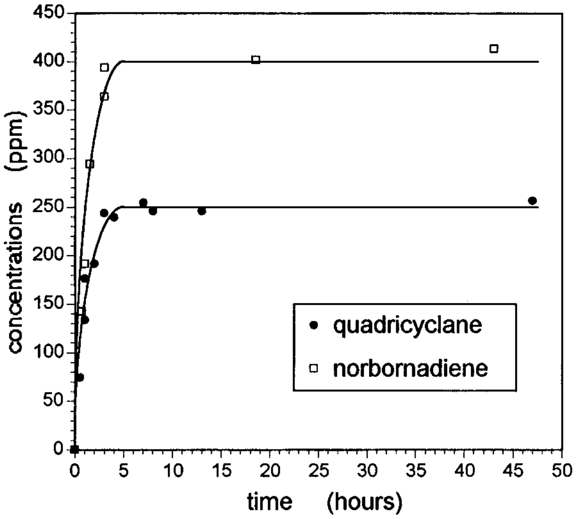

FIGURE 1. Solubility of quadricyclane and norbornadiene in water, according to the method of Etzweiler et al. (*18*).

recovered were measured. Loss of mass due to leakage from the vials was investigated by measuring the weight loss as a function of time of two closed vials containing deionized water.

Results and Discussion

Quadricyclane has a high propensity to form micro-emulsions in aqueous solutions that are visible under high magnification. Early attempts to determine its solubility by batch methods involving shaking the hydrocarbon with water, drawing off the water layer, and subjecting the aqueous solution to centrifugation or microfiltration with 0.1-μm filters before analysis gave values in excess of 300 ppm. Similar results were obtained from settling experiments done over several days. Figure 1 displays the data collected by the Etzweiler method, from which the solubility of quadricyclane was determined to be 245 ppm and that of norbornadiene to be 410 ppm. Thus, the solubility of quadricyclane is much higher than that of most saturated hydrocarbons.

The disappearance of quadricyclane, Q, follows pseudo-first-order kinetics and has been analyzed using the kinetic model:

$$Q + H^+ \xrightarrow{k_1} QH^+$$

$$QH^+ + H_2O \xrightarrow{k_2} A + H^+$$

$$QH^+ + H_2O \xrightarrow{k_3} B + H^+$$

where A represents *exo*-5-norbornen-2-ol and B represents nortricyclyl alcohol, both of which have the formula $C_7H_{10}O$. Thus

$$\text{rate} = -d[Q]/dt = k_1[Q]\,[H^+] \qquad (1)$$

When the pH in aqueous solution was monitored, no change was observed; therefore, the equation can be simplified to

$$-d[Q]/dt = k'_1\,[Q] \qquad (2)$$

where

$$k'_1 = k_1[H^+] \qquad (3)$$

Kinetic data were collected on samples with initial quadricyclane concentrations in the 200 ppm range. Plots of ln $[\text{quadricyclane}]_0/[\text{quadricyclane}]_t$ vs time in aqueous solution, 50/50 wt% water/2-propanol and pure 2-propanol are given in Figure 2. Table 2 gives the values for k'_1 and k_1 in 2-propanol, 50/50 wt % water/2-propanol, and water, all at 25 °C.

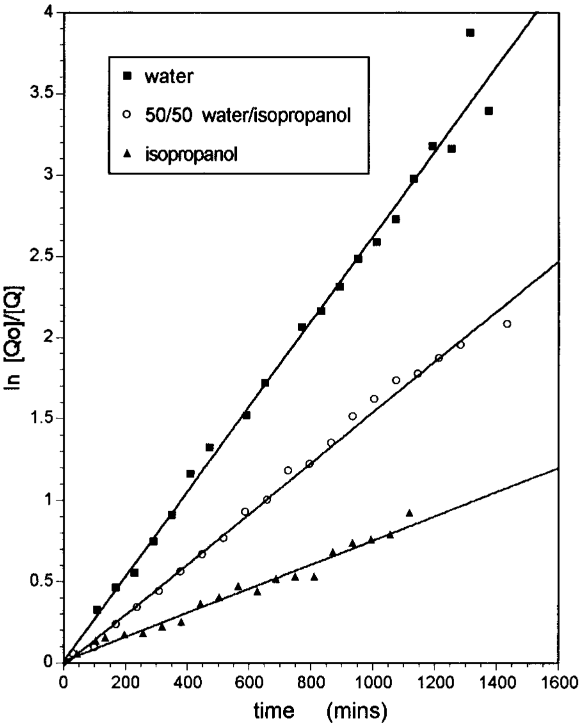

FIGURE 2. Kinetic plots of the disappearance of quadricyclane with time in three different solvent systems: water, with $[H^+] = 0.000135$ mol/L and $R^2 = 0.956$; 50/50 wt % water/2-propanol, with $[H^+] = 0.0109$ mol/L and $R^2 = 0.990$; and 2-propanol, with $[H^+] = 0.0097$ mol/L and $R^2 = 0.977$. $T = 25$ °C.

TABLE 2. Rate of Quadricyclane Disappearance as a Function of pH for Solvent Systems of Water, 50/50% by Weight Water/2-Propanol, and 2-Propanol

solvent	$[H^+]$, mol/L	K'_1, min^{-1}	$t_{1/2}$, min	k_1, L mol^{-1} min^{-1}
water	10.00×10^{-4}	2.68×10^{-2}	25.9	
	7.56×10^{-4}	2.03×10^{-2}	34.2	
	6.61×10^{-4}	1.45×10^{-2}	47.8	
	3.16×10^{-4}	6.00×10^{-3}	115.5	
	2.63×10^{-4}	7.55×10^{-3}	91.8	
	1.35×10^{-4}	2.58×10^{-3}	268.6	
	1.00×10^{-4}	1.00×10^{-3}	690.7	26.0[a]
50/50	10.62×10^{-2}	2.05×10^{-2}	33.8	
	3.53×10^{-2}	6.87×10^{-3}	100.9	
	1.09×10^{-2}	1.52×10^{-3}	455.9	
	0.31×10^{-2}	4.71×10^{-4}	1471.3	0.195[b]
2-propanol	11.79×10^{-2}	1.14×10^{-2}	60.8	
	5.23×10^{-2}	4.64×10^{-3}	149.4	
	2.58×10^{-2}	9.84×10^{-4}	704.4	
	0.97×10^{-2}	7.58×10^{-4}	914.2	0.099[c]

[a] From 23 runs ($R^2 = 0.869$). [b] From 16 runs ($R^2 = 0.9990$). [c] From 8 runs ($R^2 = 0.9986$). K'_1 was obtained by plotting ln $\{[\text{quadricyclane}]_o/[\text{quadricyclane}]_t\}$ vs t in minutes; and k_1 was obtained by plotting K'_1 vs $[H^+]$. Temperature is 25 °C for all runs.

As can be seen from the k_1 values in Table 2, the reactivity in water is much higher than in 2-propanol or 50/50 wt % water/2-propanol. The value of k'_1 for the disappearance of quadricyclane in water at pH = 5.0 and 25 °C can be calculated from the data given in Table 2, using eq 3, to be 2.6×10^{-4} min^{-1} with a corresponding half-life of 1.85 days. Similarly, the k'_1 value for 50/50 wt % water/2-propanol at pH 5.0 is 1.95×10^{-6} min^{-1}, and the half-life is 0.68 years. In 2-propanol,

TABLE 3. Molar Ratios of the Product Distributions in the Various Solvent Systems Utilized

solvent	B/A	D/C	B/D	A/C	(A + B)/(C + D)
H_2O	15.4 (± 3.0)	no	no	no	no
50/50	3.8 (± 0.5)	3.8 (± 0.5)	3.3 (± 0.5)	3.3 (± 0.5)	3.3 (± 0.5)
2-propanol	no	2.4 (± 0.5)	no	no	no

[a] A, *exo*-5-norbornen-2-ol; B, nortricyclyl alcohol; C, *exo*-5-norbornen-2-isopropoxide; D, nortricyclyl isopropoxide; no, not observed.

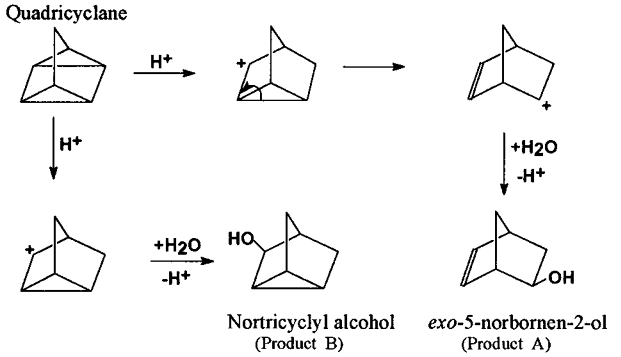

FIGURE 3. Reaction scheme for the acid-catalyzed reaction of quadricyclane with water.

k'_1 is 9.9 × 10^{-7} min^{-1}, and the corresponding half-life is 1.33 years. These results mirror those previously observed for the reactions of norbornadiene with acetic acid in various solvents (*19, 20*) and those reported for the reaction of quadricyclane with acetic acid (*7*).

The proposed reaction mechanism for the breakdown of quadricyclane in acidic aqueous solutions is shown in Figure 3. An equivalent reaction occurs in 2-propanol, with the reaction products being the ethers *exo*-5-norbornen-2-isopropoxide (product C) and nortricyclyl isopropoxide (product D). Table 3 shows that, as the solvent polarity increases from 50/50 wt % water/2-propanol to pure water, the nortricyclyl alcohol (product B) is increasingly favored over *exo*-5-norbornen-2-ol (product A), with the ratio of B/A increasing from 3.8 to 15.4. Furthermore, examination of the product distribution in the 50/50 solvent system reveals that the formation of the alcohols (products A + B) occurs preferentially to the formation of the ethers (products C + D) by a ratio of 3.3, in keeping with the higher nucleophilicity of water as compared to 2-propanol.

The results of the chemical analyses of dodecane extracts of the soils are shown in Figure 4. The data of the immediate extraction (t = 0) indicate that the quadricyclane is stable during the procedure of shaking and centrifuging with an aqueous NaCl solution and dodecane. Only the extract of the ALOHPL soil showed traces of decomposition products.

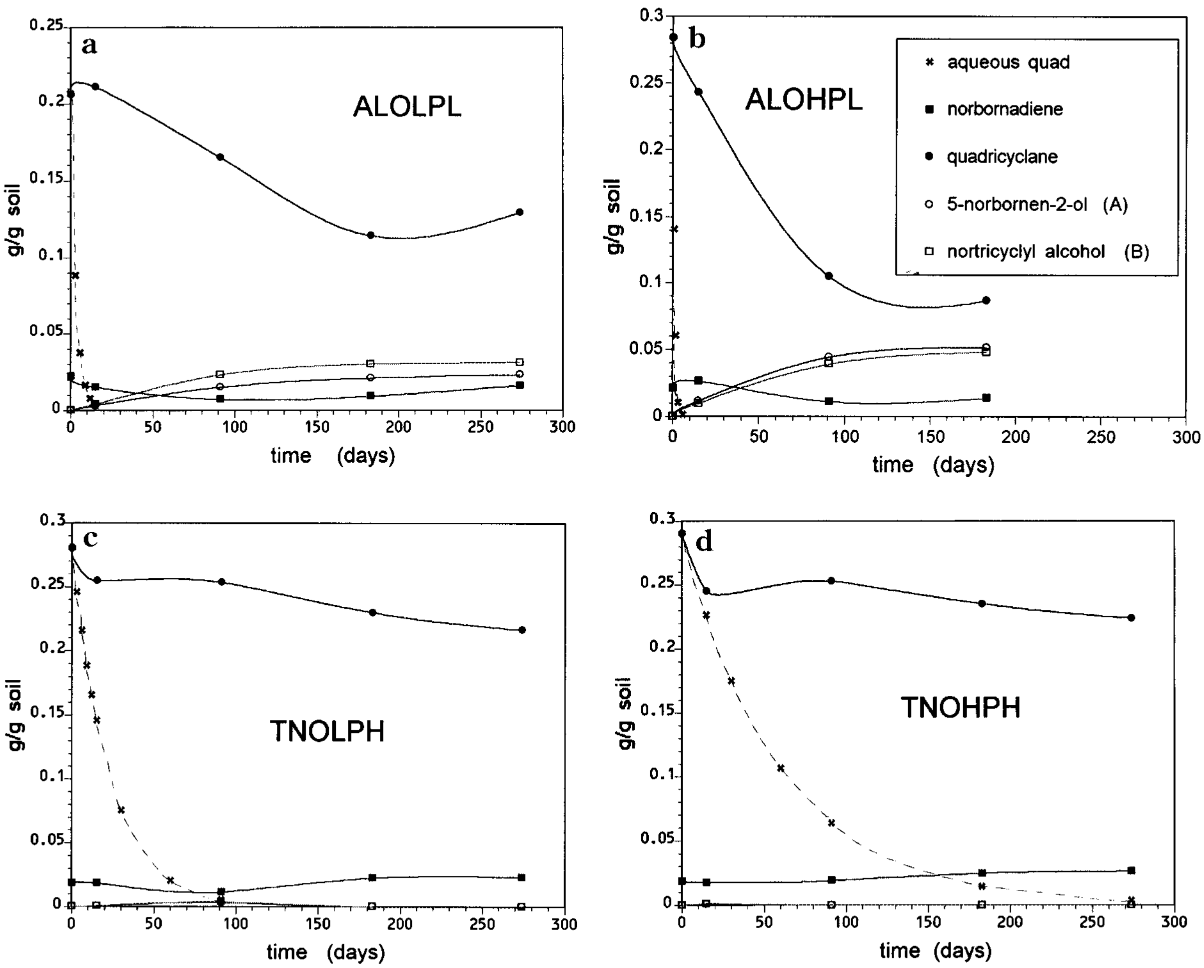

FIGURE 4. Amounts of quadricyclane, norbornadiene, *exo*-5-norbornen-2-ol, and nortricyclyl alcohol recovered from the batch experiments (in g). The dotted lines represent what would happen to quadricyclane in an aqueous solution of the same pH as the soils: (a) ALOLPL, (b) ALOHPL, (c) TNOLPH, and (d) TNOHPH.

Furthermore, the amount of norbornadiene (present as an impurity in the quadricyclane) in the soil extracts did not change significantly, indicating that no isomerization of quadricyclane into norbornadiene had occurred during the 9 months of the experiment in any of the samples.

Overall the pH of the soil is by far the most important factor in determining the stability of quadricyclane in the porous media. Significant amounts of the quadricyclane reacted to give *exo*-5-norbornen-2-ol and nortricyclyl alcohol with the ALOLPL soil (Figure 4a), which has the lowest level of organic matter of any of the soils used, while even greater amounts of products were observed in the ALOHPL soil (Figure 4b). The reactions were much slower in soil, however, than in aqueous solutions, and the ratio of nortricyclyl alcohol to *exo*-5-norbornen-2-ol was much smaller than for the aqueous samples, being in the region of 1.5 for the ALOLPL soil and 0.9 for the ALOHPL soil. The slower reactions in soils thus appear to favor the formation of *exo*-5-norbornen-2-ol over the formation of nortricyclyl alcohol. There was a small dip in the total amount of reactants and products recovered from the 180-day ALOLPL sample due to extraction problems caused by gel formation in the rolled sample. After 6 months, the batch experiment with the ALOHPL soil was aborted because the concentration of the two alcohols became very high. In the less acidic TNOLPH and TNOHPH soils (Figure 4c,d, respectively), the quadricyclane appeared stable. After 9 months, only trace amounts of nortricyclyl alcohol were detected.

Quadricyclane and norbornadiene can be extracted from the soils very efficiently. For the $t = 0$ samples, close to 100% was recovered for all the soils using the techniques described. The actual amounts of reactants and products recovered in each case are shown in Figure 4. The extraction was not so effective, however, for the two alcohol products. The results from the three soils that were doped with the alcohols showed that the amount of *exo*-5-norbornen-2-ol recovered ranges from 56.6% in the ALOHPL soil to 68.8% in the TNOLPH soil. The extraction of nortricyclyl alcohol was more efficient, ranging from 71.4% in the ALOHPL soil to 84.7% in the TNOLPL soil.

No other products were observed in measurable quantities, even when the pH swing was performed, leading us to conclude that the mass imbalance in the longer term rolled Alabama soils is most likely due to to the less efficient extraction of the alcohol products. The losses in the two Tennessee soils, where the alcohols were not involved, can be explained by losses through the caps of the vials where quadricyclane is the most volatile component present. Measurements on the two water-filled vials showed a weight loss of the order of 0.6% over 9 months.

In a homogeneous acidic aqueous solution, dissolved quadricyclane has a short half-life and reacts rapidly to form the two reaction products; however, the breakdown rates of quadricyclane in the four natural soils were observed to be much slower, and quadricyclane was found to be chemically stable in soils at pH 6.0 and higher. Since 3 cm^3 of quadricyclane and 2 cm^3 of water were added to each vial containing the soil, there is a large excess of quadricyclane over the solubility limit, and we physically observed a separate non-aqueous phase. The rate of quadricyclane reaction therefore depends on the surface area of the quadricyclane–water interface(s). If we assume that these interfacial areas are the same for all soils, we would expect that the change of rates of reaction with pH would be similar to those observed in the homogeneous aqueous solutions. This is not the case, so some other process must be occurring, although it is not possible to draw any definite conclusions from the existing data. The composition of the soil solution, soil particles, and organic matter did not seem to induce any additional reactions of quadricyclane or its reaction products.

The abiotic breakdown of quadricyclane in natural soils is slow compared to the time scales associated with its migration in the vadose zone of porous media. Consequently, after a spill, quadricyclane can be expected to migrate as an LNAPL. In low pH soils, the quadricyclane will then gradually react to form compounds that are soluble in water. Most of the migration in the second stage after a spill in these soils will therefore take place as organic solutes in the aqueous phase. In soils with near-neutral pH, however, the conversion to reaction products and their subsequent movement will be of little importance.

Quadricyclane has a propensity to form microemulsions that are long-lived due to its density being very close to that of water. This could play a role in the aqueous migration of quadricyclane, especially in areas with significant groundwater flow. Chemical reactions play an important role in predicting the fate of quadricyclane when exposed to a subsurface environment. The reaction rates are strongly soil dependent. This will highly complicate any efforts to simulate the environmental behavior of quadricyclane.

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