

Slow Sorption Kinetics of Pentachlorophenol on Soil: Concentration Effects

JOHN P. DIVINCENZO*[†] AND DONALD L. SPARKS

Department of Plant and Soil Sciences, University of Delaware, Newark, Delaware 19717-1303

We investigated the sorption kinetics of pentachlorophenol (PCP) on soil at a pH of 4.1 using batch techniques. A multiple spiking methodology was employed to circumvent the solubility limitation of PCP. The ratio of sorbed PCP to solution-phase PCP (S/C) after 2–4 days of equilibration was concentration dependent. It decreased from 90 to 60 L/kg with a 4-fold increase in the total PCP concentration, from 5 to 20 mg/L. Increasing residence times resulted in slow increases in sorption. The onset of the slow sorption kinetics was also concentration dependent. At higher PCP concentrations, the slow sorption kinetics were much more pronounced. However, there was not a clear definable trend in which concentration could be correlated to S/C. A 2-day desorption study demonstrated that the extent of desorption was also concentration dependent. At higher PCP concentrations, a smaller percent of the sorbed PCP was available for desorption.

Introduction

The residence time of an organic chemical in the soil environment can greatly affect both the environmental fate and the removability of that compound from the soil. As the contact time increases, the organic compound could become more resistant to removal by a host of different soil remediation technologies. Bioremediation and soil washing may be much less effective for pollutants with long-term residence times in the field.

Hydrophobic organic compounds (HOCs) exhibit a slow sorption stage following an initial rapid sorption (1–3). Both intraorganic matter diffusion (4, 5) and intraparticle diffusion (6–8) have been postulated as the cause of this non-equilibrium sorption. This can often result in a slow or incomplete desorption (9–11).

Many diffusion models attempt to describe both the slow sorption and desorption stages (12–15). However, there is a lack of long-term sorption kinetic data and a void in the understanding of the factors that control the slow sorption stage. The concentration gradient is inherent to all diffusion models; still, its effect on the slow sorption stage remains virtually unexplored. A complete understanding of the mechanisms that control the slow sorption of organic chemicals on soil is paramount to developing a useful kinetic model.

The objectives of this research were to investigate the long-term sorption kinetics for the protonated form of pentachlorophenol (PCP) on a silt loam soil. PCP is a hydrophobic

ionizable organic compound (HIOC) with a pK_a of 4.75. In the protonated form, PCP can behave similarly to other hydrophobic non-ionizable organic compounds (HNOCs). The effect of the concentration gradient on the slow sorption stage was investigated. In addition, the effect of both residence time and PCP concentration on the desorption of PCP was explored.

Experimental Section

Materials. Pentachlorophenol was purchased from Sigma (purity >95%) and used as received. Hexane was HPLC grade. 2,4,5-Trichlorophenol was used as an internal standard for GC analysis (Sigma, purity >95%). All inorganic reagents used were analytical grade (Fisher Chemicals).

The soil used was a Matapeake silt loam (Typic Hapludult) from the A_p horizon (Delaware). Physicochemical and mineralogical properties of the soil are as follows: pH = 6.1; cation exchange capacity (CEC), 5.02 cmol/kg; 1.7% organic matter (measured by incineration); 29.6% sand; 58.6% silt; and 11.8% clay. The mineral suite of the <2- μ m clay fraction was kaolinite \approx chloritized vermiculite > quartz > mica. A standard N₂/BET analysis, using a Quantachrome Quantasorb QS-7 with an LMFC-4 flow control accessory, yielded a surface area of 5.52 m²/g.

Methods

(a) Preequilibration of Soil. The natural soil pH is 6.1. Due to the soil's high buffering capacity, it was necessary to preequilibrate the soil to the desired pH (4.0) of the experiment. This would allow for a constant pH over the course of the entire experiment. This was accomplished by washing the soil repeatedly. The soil (20 g) was washed three times with a 250-mL solution (pH 4.0) of 0.01 M CaCl₂ and 0.02% NaN₃ (bacteriological inhibitor) by shaking at 150 cycles/min in 250-mL plastic screw-capped bottles for 24, 48, and 48 h. The samples were spun down in between washes for 20 min at 514g. The soil was then oven-dried at 50 °C for approximately 48 h and screened to pass through a U.S. standard No. 10 mesh (2 mm).

(b) Sorption Studies. A solution of the same composition (to standardize pH and ionic strength) as used for the preequilibration of the soil was used for the sorption studies (0.01 M CaCl₂ and 0.02% NaN₃, pH 4.0). Samples of 1.00 g of soil (determined to be appropriate in previous experiments) and 24.9 mL of solution were used in all experiments. All samples were spiked with aqueous PCP stocks (pH \sim 11.0, 1.275 g/L) and then mixed on an orbital shaker at 50 rpm, in the dark (to prevent photolysis) at 25 \pm 1 °C, for a minimum of 48 h. Additional mixing beyond this point proved to have no effect on sorption. In all experiments there was a minimum of 20% of the samples used as controls (no soil or no PCP).

All sorption kinetic studies were mixed continuously at 50 rpm. Particle degradation was shown to be negligible as determined by N₂/BET analysis before and after mixing (before 5.52 \pm 0.41 m²/g, after 5.60 \pm 0.52 m²/g). Any percent change in surface area was less than the inherent error of the BET analysis. In these studies, 25-mL glass centrifuge tubes with Teflon-lined screw caps were placed in a test tube rack laid on its side so that the tubes were horizontal on the orbital shaker. This increased mixing efficiency and the contact area between the solution and solid phase. Samples were collected and centrifuged at 6315g for 15 min. A portion of the aqueous phase was then stored for analysis. Two replicates were used at each time interval, and at one random time in each experiment five–seven replicates were collected. The dual spike sorption kinetics used the multiple spiking methodology discussed below.

* Corresponding author.

[†] Present address: Middle Tennessee State University, MTSU Box X157, Murfreesboro, TN 37132. Phone: (615) 904–8251; fax: (615) 898–5182; e-mail: jdivince@mtsu.edu.

Additional sorption kinetic studies used 25-mL brown glass bottles with Teflon-lined screw caps. Samples were upright at all times. The bottles were removed from the shaker after 2 days of equilibrating and then allowed to incubate for additional times. Samples were collected, and a portion of the liquid phase was removed and saved for analysis. Five replicates were used at each time interval.

Sorption isotherms were carried out identical to the sorption kinetics described above (centrifuge tubes), with one exception. After 2 days of mixing, the samples were removed from the shaker and stood upright, in the same incubation chamber. Also, the multiple spiking method described below was employed. The five total concentrations (C_T) for the isotherms ranged from 4.5 to 21.4 mg/L. All samples were set up in triplicate.

(c) Multiple Spiking. The solubility of the protonated form of PCP at 25 °C is 28 μ M (7.46 mg/L) (16). In order to do sorption studies at higher concentrations than the solubility, we employed a multiple spiking approach. The samples for the *dual spike kinetics* were equilibrated for 3 days and then spiked again. The total concentration (C_T) of PCP added was 10.0 mg/L.

For sorption studies at even higher concentrations of PCP (~20 mg/L), the samples were spiked every 2 h after the initial spike, for a total of 10 h (six spikes). The concentrations of the spikes were calculated based on the kinetics, which showed substantial sorption after 2 h (~80% of the total amount sorbed). The aqueous PCP concentration never exceeded the solubility limit.

(d) Desorption studies. The desorption kinetic studies were conducted on samples that had sorbed PCP for 20 days. After 20 days, the samples were centrifuged as described above. A total of 80% of the sample solution volume was removed (20 mL) and replaced with PCP-free solution (0.01 M CaCl_2 and 0.02% NaN_3 , pH 4.0). Samples were then returned to the orbital shaker at 50 rpm and collected over time. Aqueous samples were separated and stored following centrifugation. Two replicates were used at each time interval, and at one random time six replicates were collected; 10% of all the samples were controls (no soil or no PCP).

Additional desorption studies were conducted on samples that had sorbed PCP for varying amounts of time. After sorption, 80% of the solution volume was removed (20 mL) and replaced with PCP-free solution. Samples were then placed back on the orbital shaker at 50 rpm for 2 days. The samples were then removed from the shaker and collected over time. Aqueous samples were separated and stored. Five replicates were used at each time interval; 17% of all the samples were controls (no soil or no PCP).

(e) Analysis. An internal standard was added to all samples (2,4,5-trichlorophenol), and the samples were then acidified with 3 M HCl. A volume of hexane was added to all samples for extraction. The observation was made that the mass spectrometer (MS) analysis was most consistent within the concentration range of 0.5–2.5 mg/L PCP. Therefore, the amount of hexane added varied depending on the predicted aqueous concentration of PCP. An attempt was made to have all the samples analyzed within this concentration range in order to reduce error. Hence, samples were often either diluted or concentrated in hexane as deemed necessary.

After the addition of hexane, the samples were vigorously vortexed. UV spectrophotometric analysis showed no detectable amount of PCP remaining in the aqueous phase. An aliquot of the hexane was then removed and filtered through a 0.2- μ m membrane filter. Each sample was then injected twice into a gas chromatograph equipped with an MS detector. Two qualifying ions for PCP were used in all cases. The integrity of the chromatography and the non-existence of any aberrant peaks suggested the absence of any degradation.

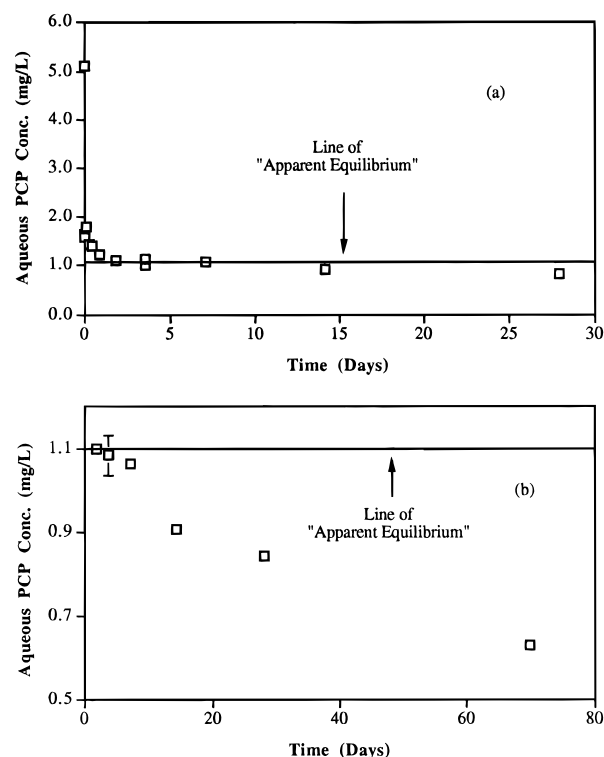


FIGURE 1. Sorption kinetics of pentachlorophenol on soil. The pH is 4.1 ± 0.1 . An "apparent equilibrium" occurs at about 42 h. A line of apparent equilibrium has been superimposed for visual aid. The K_d for PCP after 2 days of sorption was 90 L/kg. Each point is the average of two replicates. There are seven replicates at 3.6 days with a standard deviation for K_d of 7.60.

Results and Discussion

Studies demonstrated that the soil pre-equilibration procedure stabilized the pH of the soil at 4.1 ± 0.1 . This was the final pH in all studies. Soil washing also helps to remove nonsettling microparticles and dissolved organic matter that can cause unreal (artificial) hysteresis due to the solids concentration effect (17–19). That is, the K_d decreases with increasing solids concentration. Mixing at a faster speed (150 cycles/min) and centrifuging at a slower speed (514g) than was used for the sorption and desorption studies (50 rpm–6315g) helps to increase the washing efficiency (20).

The low solubility and high sorption potential of PCP presented a problem in using a broad range of different initial concentrations (C_0). A low initial PCP concentration would leave an undetectable amount of PCP in solution. The result is a very narrow working PCP concentration range. One way to circumvent this problem is to use a lower solids mass. However, desorption studies require that enough PCP be sorbed in order to detect the desorption of the compound. Therefore, it would be necessary to vary our solids mass between experiments. Since the soil was washed, the solids concentration effect may not be a problem. However, the decrease in K_d with increasing solids mass cannot always be accounted for by the solids concentration effect (21). For this reason, we chose to use the multiple spiking procedure rather than vary our solids mass. Furthermore, this might be indicative of a contaminated site that has repeated recharge of the pollutant.

Loss of PCP over the course of the experiments was negligible, with the controls containing 99% of the original PCP concentration. An experiment designed to study mixing showed that mixing beyond 2 days had no effect on sorption (results not shown).

Sorption Kinetics. Figure 1a shows the results of the sorption kinetics of PCP ($C_0 = 5.1$ mg/L) on soil at a pH of

4.1 ± 0.1. At this pH, 82% of the PCP is in the protonated form. Due to the low affinity of the charged (ionized) species for the surface, less than 4% of the sorbed PCP is in the charged form. Therefore, we are dealing predominantly with the protonated (neutral) species. However, important differences exist between the species, and this is currently in the process of being reported on (22).

An "apparent equilibrium" was reached in about 42 h (≈2 days). This was defined as the point at which 78% of the PCP was sorbed, and for the following 5 days there was no analytically measurable statistically significant change in the aqueous phase PCP concentration. A line of apparent equilibrium has been superimposed on the graph as a visual aid. The calculated distribution coefficient (K_d) for the time with seven replicates (3.6 days) is 90 L/kg with a standard deviation of 7.60. The K_d was calculated by the method of difference:

$$\frac{(C_o - C_e)V}{MC_e} \quad (1)$$

where C_o is the initial PCP concentration, C_e is the equilibrium aqueous PCP concentration, V is the total volume of solution, and M is the mass of soil.

It would be easy at this point to conclude that true equilibrium has been established. However, if the kinetics are followed for an extended amount of time, a slow sorption stage begins to manifest itself. The concentration at 14.1 days is statistically different than the concentration at 3.6 days (Figure 1a). This was determined by a comparison of means between the seven replicates at 3.6 days and the two replicates at 14.1 days. A 95% confidence interval was used. The experiment was carried out for 70 days and sorption continued to this time (Figure 1b). However, the change was less significant, as demonstrated by significance only occurring at 90% confidence between 14 and 70 days. This is analogous to the observation that the slow sorption stage is nonlinear. The rate of change in the aqueous PCP concentration is slowing down.

Sorption of HOCs is often biphasic; a slow sorption stage preceded by rapid sorption (1–3). The rapid sorption in this study would be sorption up to 2 days. An extremely rapid initial stage results in 68% of the PCP being sorbed at the first sampling point (20 min). An additional 10% (total 78%) is then sorbed by 2 days. Assuming that 2 days is the true equilibrium, these two phases could describe a biphasic relationship characterized by rapid and slow sorption. However, as the sorption continues, there is an additional 6% (total 84%) sorbed by 28 days and a total of 88% sorbed by 70 days. This is the true slow sorption stage, and the results suggest a biphasic relationship.

Figure 1b presents a different picture. The y-axis scale is expanded, and the data from 2 days out to 70 days is shown. The seven replicates at 3.6 days are now represented as an average with an error bar for the standard deviation. The apparent equilibrium previously defined is simply due to analytical limitations. Although not statistically different, there is clearly a slow continuous drop in the aqueous PCP concentration. The sorption of PCP is not biphasic. Most of the PCP crosses the soil–water interface in the first 2 days. However, there is simply a smooth continuous sorption that is non-linear. This will further be demonstrated later.

Sorption Isotherms. Three identical isotherms were set up, and each one was incubated for a different amount of time (2, 10, and 21 days). Due to the solubility limitations of PCP, it was necessary to utilize the multiple spike methodology discussed in the Experimental Section. This would allow for equilibrium aqueous concentrations (C_e) of PCP close to the solubility limit and would confirm a truly linear isotherm. If single spikes were used and all initial PCP concentrations were below the solubility limit, the highest

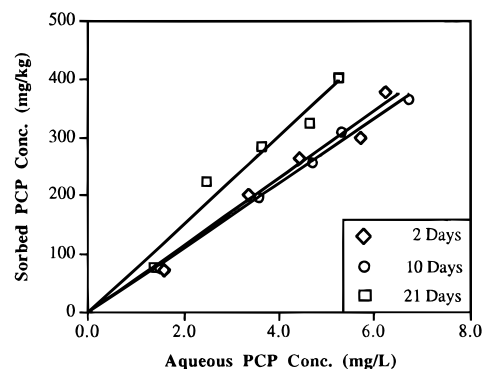


FIGURE 2. Sorption isotherms of pentachlorophenol with increasing residence time. There is no significant difference between 2 and 10 days of sorption. The significance between 2 and 21 days of sorption is only 80%. Each point is the average of three replicates. Error bars are too small to be seen.

attainable C_e for 1 g of soil (as mentioned previously, it is undesirable to vary the solids mass between experiments) would only be approximately 27% (2 mg/L) of the PCP solubility limit. In this case, the concentration range of C_e could represent the linear portion of a nonlinear isotherm.

The multiple spiking method employed (six spikes) resulted in compounded errors that added more scattering to the data. All the isotherms appeared linear out to C_e values greater than 6 mg/L (Figure 2). There is a trend of increasing slope (K_d) with increasing residence time. The K_d values in order of increasing residence time are 57.4, 55.3, and 75.5 L/kg. The difference between 2 and 10 days is not significant (95% CI). This is analogous to the kinetic study in which there was no significant change in the aqueous PCP concentration for a period of at least 5 days following 2 days of sorption (Figure 1a). The difference between 2 and 21 days is only significant at 80% confidence. The trend of increasing sorption with increasing residence time, analogous to the kinetic study, is less significant for the isotherm study due to the scattering of the data. The increase in K_d from 2 days out to 21 days for both experiments is approximately 1.3 times. However, it is clear that the K_d at 2 days is much less for the isotherm experiment (57.4 L/kg) than for the kinetic study (90 L/kg).

The only difference in the methodology for the two experiments, beside the multiple spiking used for the isotherms, was that in the kinetic studies the samples were mixed continuously and were laid on their side for the entire time. The samples for the sorption isotherm studies were mixed for 2 days on their side and then stood upright without any mixing for the remaining incubation. As mentioned previously, mixing beyond 2 days had no effect on sorption. Therefore, either the interfacial area between the aqueous and solid phases, which is greater in the kinetic study due to the tubes lying down, the spiking method and/or the concentration differences had some effect on the system. The initial concentration of PCP in the kinetic study was 5.1 mg/L. The final concentrations for the isotherms, after spiking, ranged from 4.5 to 21.4 mg/L. This point will be discussed further below.

Concentration Gradient. The occurrence of a slow sorption stage is not surprising as it has been demonstrated repeatedly in the literature for a host of HOCs (1, 3, 23–25). However, there is a deficiency in long-term sorption kinetic data. PCP in the protonated form would be expected to exhibit the same behavior as HNOCs. Diffusion into organic matter (4, 5) or intraparticle diffusion (6–8) have been the most common postulated mechanisms for the slow sorption stage. Since diffusion is in part controlled by a concentration gradient, one would expect the slow sorption stage to behave differently under different concentration gradients.

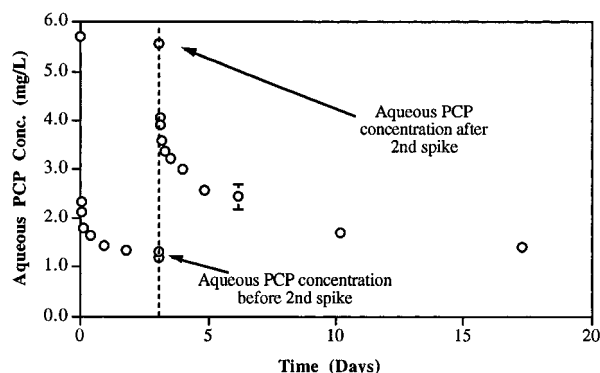


FIGURE 3. Dual spike kinetics of pentachlorophenol. The data closest to the y-axis represent samples collected after the first spike. At 3 days the remaining samples were removed from the incubator and spiked with additional PCP. This is represented by the dashed line. The second set of data represents the kinetics after the second spike. The first data point of the second spike represents the initial solution concentration of PCP for the second set of samples. The K_d for the samples at 3 days of the first spike is 88 L/kg. There are five replicates at 3 days with a standard deviation for K_d of 5.00.

The objective of the next experiment was to repeat the sorption kinetics at a much higher PCP concentration. Due to the solubility limitations of PCP, it was necessary to utilize the dual spike methodology discussed in the Experimental Section. After 3 days of equilibration, the samples were spiked a second time with PCP. The concentration in the aqueous phase was raised close to the initial concentration of the first spike, resulting in a total PCP concentration of 10.0 mg/L. The original sorption kinetic studies (Figure 1) used a total concentration of 5.1 mg/L.

The results are shown in Figure 3. The set of data points closest to the y-axis represents the kinetics of the initial spike. At a time of 3 days, the remaining samples were removed from the shaker and spiked again. This is represented by a dashed line on the figure. The aqueous concentration of the remaining samples at 3 days was now 5.56 mg/L. The kinetics of these samples were then followed and are represented by the second set of data in Figure 3.

The initial spike (Figure 3) follows closely the original kinetics (Figure 1) with 78% of the PCP sorbed by 2–3 days. The calculated K_d for the five replicates at 3 days is 88 L/kg. This agrees with the original kinetics whose K_d is 90 L/kg. The pooled standard deviation of these 12 samples is 4.55, and therefore this difference is not significant at 95% confidence. This demonstrates the reproducibility of our system.

Comparing the second spike (Figure 3) to the original kinetics (Figure 1), we see a significant change in the sorption profile. The data point that has the error bar (based on standard deviation of six replicates) is at 6 days, or 3 days from the time of the second spike (Figure 3). The preceding point is within 1 SD of the replicates and cannot be considered significantly different. However, beyond these points there is a significant change in the aqueous phase PCP concentration. The rate of change in the aqueous PCP concentration is much greater when compared to the original kinetics in Figure 1.

Figure 4 shows the above data transposed into changes in S/C with time, where S is the sorbed concentration (mg/kg) and C is the aqueous concentration (mg/L). This can be considered a measure of the relative attainment of equilibrium. If the true K_d was known, then $(S/C)/K_d$ would be the fractional approach to equilibrium.

As diffusion models would predict, the increase in S/C is much greater at higher PCP concentrations. Also evident is the depression in S/C at approximately 3 days for the higher concentration of PCP. This is similar to the effect seen for the isotherm experiments (depression in K_d) and will be

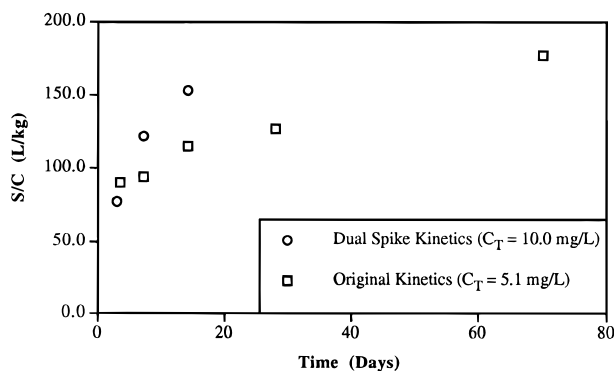


FIGURE 4. The results from Figures 1 and 3 transposed into the ratio of sorbed PCP to solution-phase PCP (S/C). The higher concentration kinetics show a much greater increase in S/C with time. S/C at 2–3 of equilibration, for the higher concentration samples, is depressed down to 78 L/kg from 90 L/kg.

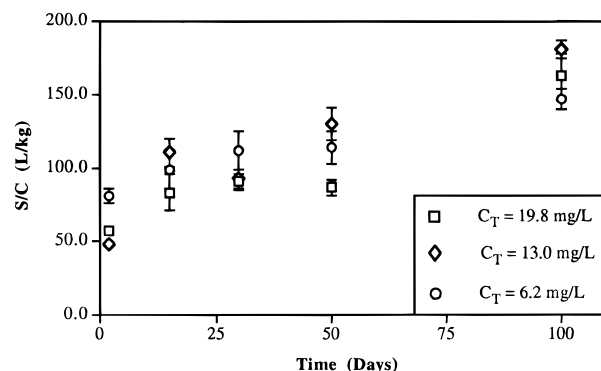


FIGURE 5. Effect of PCP concentration on the sorption kinetics. The multiple spiking methodology described in the Experimental Section was used. Each concentration had three–five replicates at each time. See text for discussion.

discussed further below. Since K_d is a measure of equilibrium partitioning, and it has been established that true equilibrium has not been attained, all references to K_d will now be redefined as S/C .

One concern was the dual spike methodology used for the higher concentration kinetics, whose results were compared to the original kinetics that were only spiked once. Perhaps the differences in the slow sorption rate were a result of the different methodologies. In order to address this, we compared the increase in S/C for three different concentrations. The multiple spiking methodology was used. Three different stock solutions were used so that the spiking volumes, number of spikes, and time of spikes would all be identical. The results are shown in Figure 5.

It is evident from these results that there is not a simple correlation between increasing concentration and the rate of increase in S/C . The intermediate concentration (13.0 mg/L) shows the greatest rate of increase in S/C between 2 and 15 days. It also has the largest S/C overall at 15, 50, and 100 days. The depression seen in S/C at 30 days is both surprising and unexplainable at this time. All three concentrations follow the same general sorption profile. As mentioned previously, the sorption is not biphasic but simply nonlinear. This is clearly demonstrated here. Furthermore, there appears to be a leveling off between 30 and 50 days, but then there is again an increase up to 100 days (Figure 5). Attempts are being made to model much of this kinetic data with a “new” two-site model.

It should be pointed out that only the aqueous phase is being measured. The apparently unusual jump from 50 to 100 days may be explainable by other reactions. Diffusion into common regions within the soil may result in localized

TABLE 1. Effect of Total PCP Concentration (C_T) on Ratio of Sorbed-Phase PCP to Solution-Phase PCP (S/C)

C_T (mg/L)	S/C (L/kg) ^a	SD
5.10	90.51	7.60
5.70	88.27	5.00
6.20	80.87	5.43
6.75	84.93	7.05
10.00	78.06	11.83
13.00	47.98	3.26
19.80	57.28	1.04
19.80	54.22	1.80
19.80	66.84	9.33
21.40	60.78	4.93

^a S/C is the ratio of sorbed-phase PCP (mg/kg) to solution-phase PCP (mg/L) at 2–4 days of equilibration.

concentrations above the solubility limit of PCP. Therefore, precipitation may explain this effect. Chemical or biological reactions are also a possibility. Sodium azide is used as a bacteriological inhibitor, but its effectiveness over long periods of time is unknown. Still, results within our lab have recovered greater than 90% of the PCP after 200 days (22). Analysis by mass spectrometry with two qualifying ions confirms that it is indeed PCP and not some degradation product. Sorption and precipitation would seem to be the most likely explanations for this observation.

The highest concentration samples (19.8 mg/L) have the lowest S/C at all time intervals except at 2 days (99% CI). This suggests that more than just diffusion is responsible for the increase in S/C during the slow sorption stage. There could be balancing factors in effect. Perhaps the samples with the highest concentration have a lower S/C due to a decrease in the polarity of the aqueous phase, which results in less favorable sorption.

This could explain the depression, observed here and previously, in S/C at 2–3 days of sorption for the higher concentration samples. Another possibility is that we are seeing the saturation of site 1 if one considers a simple two-site model. However, if partitioning is the mechanism of sorption on site 1, this seems less likely. One further explanation is that the PCP is inducing the release of soil organics and/or colloids. Galil and Novak (26) showed that as the initial PCP concentration is increased, the amount of total organic carbon (TOC) in solution increased. This would decrease S/C by increasing the amount of PCP associated with TOC in solution. However, this effect was minimal at pH values below 5.5. Still, the highest concentration used in their experiments was 10 mg/L.

Collective results from several different experiments are shown in Table 1. S/C values are the values after 2–4 days of equilibration. The trend of decreasing S/C with increasing C_T is very evident. The standard deviations for each set of data are also shown. The trend beyond $C_T = 10$ mg/L is unclear. A more realistic explanation might be that beyond this concentration the effect is no longer seen. That is, further increases in C_T have no effect on S/C . This would explain the apparent outlier at $C_T = 13.0$ mg/L.

In summary, it appears that, as the concentration of PCP is increased, S/C at short equilibration times (2–4 days) decreases. However, as the concentration increases, there is a greater rate of increase in S/C during the slow sorption stage (Figure 5). This trend reverses at some point beyond $C_T = 13.0$ mg/L (Figure 5). At these higher concentrations, the rate of increase in S/C is comparable to the rate at lower concentrations.

These results might explain why the isotherm at 21 days was still linear. If S/C increases faster for higher concentration samples, this would result in a nonlinear isotherm for longer incubated samples. However, the increase in S/C with increasing concentration is not a consistent trend. Some of

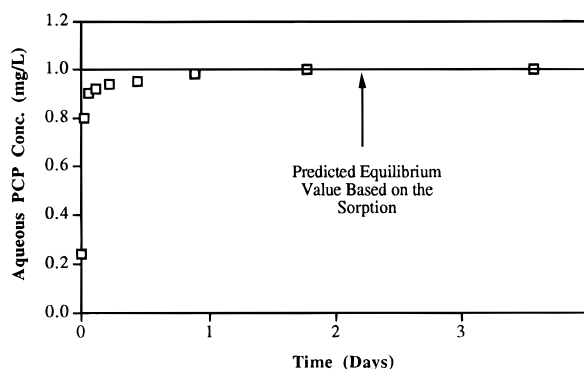


FIGURE 6. Desorption kinetics of PCP from soil. The samples were sorbed for 20 days and centrifuged, and then 80% of the solution (20 mL) was replaced with PCP-free solution. The pH was 4.1 ± 0.1 . The equilibrium aqueous PCP concentration was what would be predicted based on reversibility of linear sorption for 20 days.

the higher concentration samples have a slower rate of sorption than the intermediate concentration samples. If one compares the 13 and 19.8 mg/L samples in Figure 5 this becomes clear. Perhaps longer incubation times would result in nonlinear isotherms.

Additionally, the 2-day isotherm would be expected to be nonlinear with downward curvature. This is a result of the higher concentration samples having a lower S/C value (Table 1). However, all but the lowest concentration point on the isotherm had PCP concentrations greater than 10.0 mg/L. In this region there is no clear correlation of decreasing S/C with increasing C_T (Table 1). This might explain why S/C (previously defined as K_d) for the 2-day isotherm was so depressed.

Desorption Kinetics. The desorption kinetics of PCP are shown in Figure 6. These samples were initially sorbed with an initial PCP concentration of 6.12 mg/L for 20 days. The first sampling point (40 min) represents 74% of the total desorption. The aqueous concentration reached is what would be predicted from Eq 1 based on the linear sorption K_d at 20 days. No slow desorption stage is detectable due to the small concentration change between the first samples and the final samples. Only 15% of the total amount sorbed (123 mg/kg) is desorbed. Any change in the solution concentration would not be detectable by our analysis.

At this point, we will define apparent hysteresis as follows:

$$\frac{K_{d(\text{apparent})}}{K_{d(\text{desorbed})}} \quad (2)$$

where $K_{d(\text{apparent})}$ is the sorption distribution coefficient at 2 days of equilibration and $K_{d(\text{desorbed})}$ is the distribution coefficient for the 2-day desorption. This would be analogous to measuring the hysteresis of a field-contaminated soil, whose initial PCP concentration and actual K_d is unknown. The laboratory measured K_d for 2 days of sorption is assumed to be the true equilibrium K_d . That is, the kinetic experiment would not have been carried out sufficiently long enough to detect the slow sorption stage.

The bar graphs in Figure 7 show the results of a 2-day desorption study for three different concentrations. The samples were sorbed for varying amounts of time. The y-axis in Figure 7a represents the K_d at 2 days of sorption divided by the subsequent desorption K_d . Values of 1 indicate desorption to the point of equilibrium predicted by the 2-day sorption K_d . Values less than 1 can be considered hysteretic. Propagation of error results in significance (± 2 standard deviations, 95% confidence) occurring at ± 0.14 . Therefore, values of 0.86 or greater are non-hysteretic.

The only samples that are non-hysteretic are the 2-day samples for the lowest concentration (6.2 mg/L). There is a

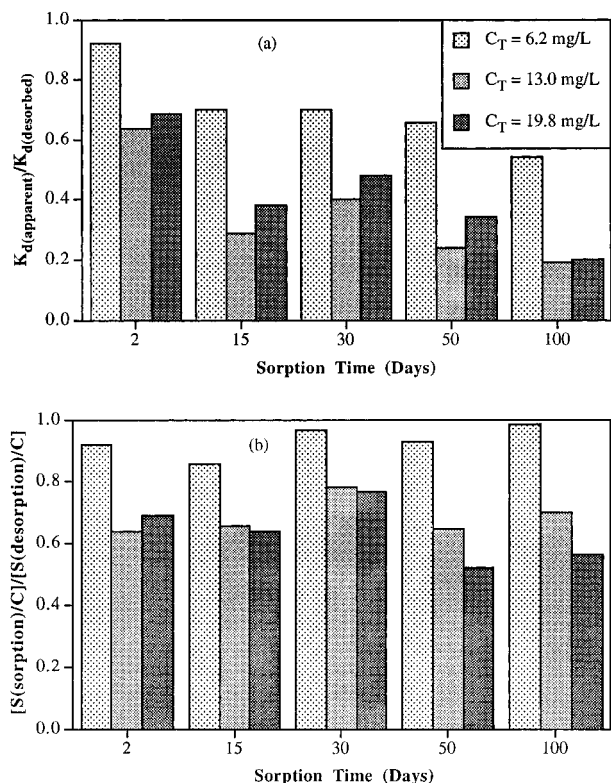


FIGURE 7. Summary of 2-day desorption data for varying sorption times: (a) apparent hysteresis (b) $[S(\text{sorption})/C]/[S(\text{desorption})/C]$. See text for description of terms.

clear concentration effect as was seen for the sorption studies (Figure 5). At each time interval, the apparent hysteresis for the 6.2 mg/L samples was the least and the intermediate concentration (13.0 mg/L) showed the most apparent hysteresis. Again, as with the sorption, there is no clear correlation between concentration and desorption. There is also a slight decrease in the apparent hysteresis (increase in ratio) from 15 to 30 days. This represents the same points in Figure 5 in which there was a drop in the K_d . All three concentrations show this effect, and it is outside of 2 SD from what can be considered a linear drop in the ratio (increase in apparent hysteresis) from 2 to 100 days. This might suggest that the effect is real and not an artifact. Comparing Figure 5, 2–15 days represents the region in which the rate of change in K_d is the greatest. Therefore, initiating desorption at a time in the sorption profile when the K_d is rapidly changing (15 days) might induce more apparent hysteresis.

Another trend is the increase in apparent hysteresis with increasing residence time. This is a common occurrence and has been reported extensively (27–30). However, it does not imply that the PCP is irreversibly bound. It is important to point out that the samples were only desorbed for 2 days and that true equilibrium has not been attained. Extended desorption times might result in a disappearance of the apparent hysteresis. Studies in our laboratory suggest this to be the case (22), but much more research is needed in this area.

One of the primary causes of unreal hysteresis is initiating desorption before sorption equilibrium is reached. This is in fact what is really happening. Therefore, the apparent hysteresis is not hysteresis at all but is an artifact. No real hysteresis has been demonstrated. The purpose of this exercise was to demonstrate the importance of knowing the sorption kinetics and the initial concentration. Field soils are often evaluated based on apparent equilibrium conditions since the long-term kinetics are not recognized. Desorption of freshly added compound is often compared to desorption of aged compound. Hysteresis of the aged compound is often

assumed to be the result of entrapment of the compound within the soil matrix. However, these results suggest that the sorption kinetics and the concentration are important in determining how much of the hysteresis is real and how much is apparent. Furthermore, when the actual amount of sorption is known, rather than assuming equilibrium after 2 days, the difference between the sorption and desorption will not be so profound. This is what is demonstrated in Figure 7b.

Figure 7b shows the ratio of $[S(\text{sorption})/C]/[S(\text{desorption})/C]$ versus sorption time for the same 2-day desorption study, where $S(\text{sorption})$ is the amount of PCP sorbed to the soil after the sorption step and $S(\text{desorption})$ is the amount of PCP still sorbed to the soil after the desorption step. This is equivalent to hysteresis values, but since we know that equilibrium has not been attained, the calculation of hysteresis is not valid. In the first case (Figure 7a), it was assumed that 2 days was the true equilibrium. Figure 7b takes into account the slow sorption stage and therefore the true amount of sorption. Once again values of 0.86 or greater can be considered to represent similar S/C values for sorption and desorption.

Figure 7b shows that much of the apparent hysteresis previously identified (Figure 7a) has been reduced by considering the actual amount of sorption. All values are greater than 0.86 for the low concentration samples. Furthermore, the values have increased substantially for the other two concentrations. The trend of increasing apparent hysteresis with increasing sorption time has also disappeared. This suggests that this effect was the result of not considering the slow sorption stage. Additionally, there now appears to be a correlation between concentration and the amount of PCP available for desorption. Since true equilibrium has not been reached, the gradient is still driving into the soil matrix. The higher concentration samples have a larger gradient inward and, therefore, might exhibit a greater resistance to desorption.

These results suggest that much of the hysteresis reported in the literature might at least be partially an artifact controlled by the sorption kinetics. The extent of artifactual hysteresis will probably depend on where the true sorption equilibrium lies. If the onset of desorption is initiated at a time in the sorption profile when sorption is rapidly occurring, then much of the hysteresis will be an artifact. A field-contaminated soil that shows substantial hysteresis might simply be the result of not knowing the true sorption profile. However, the authors are not suggesting that hysteresis of organics is not a true phenomenon. Field soils undergo changes that can result in entrapment of the contaminants within soil pores. We are simply suggesting that when determining hysteresis on lab or field soils that the concentration and particularly the slow sorption kinetics be fully considered.

Summary

The slow sorption kinetics of pentachlorophenol (PCP) were shown to be concentration dependent. However, there was not a clear correlation between concentration and the rate of sorption. Initially the rate of sorption increased with increasing PCP concentration, but this trend did not continue for concentrations beyond 13 mg/L. An opposite effect was seen at short equilibration times (2–4 days). The total sorption of PCP decreased with increasing PCP concentration but again reached a maximum effect. The slow sorption kinetics were shown to be important in determining how much PCP appeared to be available for desorption. Furthermore, the amount of PCP available for desorption was concentration dependent with the high concentration samples exhibiting the least amount of desorption.

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