

## Sorption of Chlorpyrifos to Selected Minerals and the Effect of Humic Acid

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Sorption of chlorpyrifos (CPF) from 2.85  $\mu\text{M}$  (1 mg/L) aqueous solutions in 0.01 M NaCl to montmorillonite, kaolinite, and gibbsite was investigated at 25 °C. Uptake of CPF by kaolinite and gibbsite was generally <10%, with pH having at most a small effect. Sorption to montmorillonite was significantly greater, with approximately 50% of the initial CPF being removed from solution below pH 5. Above pH 5 the sorption decreased to about 30%. About 70% of CPF was sorbed to kaolinite and gibbsite after 30 min, whereas on montmorillonite only 50% sorbed in an initial rapid uptake (~30 min) followed by slower sorption, with a maximum achieved by 24 h. Although CPF desorbed completely from kaolinite in methanol, only about two-thirds was desorbed from montmorillonite. CPF has only a weak affinity for the surfaces of kaolinite and gibbsite. In the case of montmorillonite, sorption is significantly stronger and may involve a combination of sorption to external surfaces and diffusion into microporous regions. At pH >6 increased negative surface charge results in a lower affinity of CPF for the external surface. In the presence of 50 mg/L humic acid (HA) the amount of CPF sorbed on gibbsite and kaolinite was 3–4 times greater than that in the binary systems. The HA forms an organic coating on the mineral surface, providing a more hydrophobic environment, leading to enhanced CPF uptake. The HA coating on montmorillonite may reduce access of CPF to microporous regions, with CPF tending to accumulate within the HA coating.

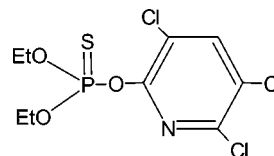
**KEYWORDS:** Chlorpyrifos; sorption; montmorillonite; kaolinite; gibbsite; humic acid

### INTRODUCTION

Chlorpyrifos [*O,O*-diethyl-*O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate; **Figure 1**] is a phosphorothioate ester, introduced as a pesticide more than 40 years ago. It is extensively used worldwide in domestic and agricultural pest control against a wide variety of pest species, including termites, cockroaches, fleas, and many soil and foliar crop pests (1). The U.S. Environmental Protection Agency recently eliminated nonagricultural uses of chlorpyrifos to reduce exposure to children (2).

The primary degradation pathway of CPF in both soil and water environments is hydrolysis, with the major metabolite formed being 3,5,6-trichloro-2-pyridinol (TCP) (1). A number of factors have been found to increase the rate of CPF hydrolysis, such as increasing pH and temperature and the presence of copper(II) (1, 3–7).

Because of its low aqueous solubility (1–1.4 mg/L at 25 °C) and relatively high log  $K_{ow}$  (4.7–5.3) (1), the sorption of CPF will play a crucial role in determining its fate and transport in



**Figure 1.** Structure of chlorpyrifos (CPF).

the environment. Bondarenko and Gan (8) investigated the sorption of CPF to a variety of sediments and speculated that, because it was preferentially partitioned into the sediment phase, it may be transported via attachment to suspended particles. Thus, it is thought that the binding to sediments plays an important role in the runoff of CPF into water bodies (1, 8).

Wu and Laird (9) investigated the interaction of CPF with smectite clays, calcium-saturated humic acid, and natural sediment. They found little correlation between the sorption to the smectites and cation exchange capacity, surface area, or surface charge. This led the authors to conclude that the surface chemistry of the clays did not play an important role in the uptake of CPF. Chlorpyrifos was found to sorb strongly to calcium-saturated humic acid, with no desorption. The sorption of CPF to the natural sediment more closely resembled the adsorption–desorption behavior of CPF to the smectites rather than its interactions with calcium-saturated humic acid.

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Because of its hydrophobicity, it is not surprising that CPF is frequently found associated with colloidal fractions in the environment. This behavior may also limit the bioconcentration of CPF. For example, Smith et al. (10) proposed that the bioconcentration of CPF in goldfish was limited because of sorption to sediment materials. Phillips et al. (11) studied the toxicity of CPF–humic acid (HA) complexes to the larval walleye fish. They found that walleye exposed to CPF–HA complexes had a lower survival rate than those exposed to HA or CPF alone. The CPF may be transferred from the HA directly to the fish, which provides an additional exposure route for CPF from suspended solids to fish and other aquatic organisms. In contrast, Jones and Huang (12) suggested that interaction of pesticides with humic substances could potentially reduce their toxicity. At a humic concentration of 4.2 mg/L the toxicity of CPF was decreased by 100% according to the Microtox bioassay. Lower (2.1 mg/L) and higher (42 mg/L) concentrations of humic substances were not as effective at reducing CPF toxicity. The reasons for this apparent nonlinear response are not known.

Baskaran et al. (13) studied the relationship between the sorption and degradation behavior of CPF with depth in two Australian soil profiles. A significant correlation was found between the sorption of CPF and organic carbon content, whereas the degradation of CPF was found to increase with increasing soil depth. Felsot and Dahm (14) also found a positive correlation between the sorption of CPF and organic matter content in five soils.

In many environmental studies and simulations (1, 13, 15, 16),  $K_d$  and  $K_{oc}$  values are provided. These parameters are usually measured using empirical modeling of sorption data, and although they are important predictive tools for modeling environmental transport and mobility, they do not provide a thorough understanding of the chemical processes that occur at surfaces. It is the goal of this work, then, to improve our chemical understanding and elucidate the fundamental interaction mechanisms that are responsible for the retention of CPF in soil systems. At this stage, these mechanisms are poorly understood. Our study reports on the sorption of CPF by two clay minerals, kaolinite and montmorillonite, and the aluminum hydroxide gibbsite. We also carried out experiments in which CPF was sorbed to the surfaces in the presence of a humic acid in order to investigate the potential impact of organic matter.

## MATERIALS AND METHODS

**Materials.** Chlorpyrifos, with a certified purity of 99.2% (Supelco, Melbourne, Australia), was stored in the dark at 4 °C. Analytical reagent grade NaCl,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{KNO}_3$ , HCl, glacial acetic acid, NaOH, KOH, 25%  $\text{NH}_4\text{OH}$ , and HPLC grade methanol and acetonitrile were purchased from Merck (Melbourne, Australia). Milli-Q reagent grade water (Millipore) was used for all experimental work and glassware cleaning.

**Clay Mineral Preparation.** Wyoming montmorillonite (SWy-2) and high-defect kaolinite (KGa-2) were obtained from the Clay Mineral Society Source Clay Repository (Purdue University). Wyoming montmorillonite (SWy-2) was prepared by stirring 250 g of the SWy-2 in 0.2 M  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  for 48 h. Two hundred and fifty grams of KGa-2 kaolinite was first washed in Milli-Q water and then stirred for 48 h in 0.2 M  $\text{KNO}_3$ . The resulting slurries were then dialyzed against Milli-Q water for 6 weeks with the water changed at least twice daily. Samples were then freeze-dried. The BET surface areas of the montmorillonite and kaolinite samples provided by the Clay Minerals Society were  $31.82 \pm 0.22$  and  $23.50 \pm 0.06$  m<sup>2</sup>/g, respectively (17).

Gibbsite was prepared using a method adapted from that of Gastuche and Herbillon (18). Nine hundred grams of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 2.5 L of Milli-Q water. Approximately 1.5 L of 4 M KOH

was added to this solution in increments over a period of 2–3 h, with constant stirring using a Teflon-coated magnetic stirrer, until the pH of the slurry was 3.4. The slurry was then aged at 40–45 °C for 24 h before being dialyzed against Milli-Q water at 50–55 °C for 6 weeks, with the water refreshed daily. The slurry was then freeze-dried. The BET surface area was measured with a Micromeritics ASAP 2000 instrument after the sample was dried in a desiccator for 48 h and further degassed at 25 °C for 24 h and was found to be  $50.10 \pm 0.07$  m<sup>2</sup>/g.

**Purification of Aldrich Humic Acid.** Aldrich humic acid was purified in a manner similar to that used by Marshall et al. (19). Approximately 10 g of the humic acid was mixed with 100 mL of concentrated HCl and allowed to stand for 24 h at room temperature. The mixture was centrifuged at 16000g for 30 min, and the resulting pellet washed several times with Milli-Q water. The humic acid was dissolved in Milli-Q water to which 25% aqueous  $\text{NH}_4\text{OH}$  had been added to adjust the pH to approximately 10, the supernatant solution decanted, and the humic acid precipitated by the addition of concentrated HCl. The resulting suspension was then filtered (Whatman no. 542 filter paper) and air-dried at room temperature for 24 h before being oven-dried at 80 °C for 48 h.

**Standard Solution Preparation.** A stock solution of CPF was prepared weekly at a concentration of 285  $\mu\text{M}$  (100 mg/L) in HPLC grade methanol and stored at 4 °C in the dark. A calibration curve was prepared fresh for HPLC analysis by first making a working standard at a concentration of 2.85  $\mu\text{M}$  (1 mg/L) and then undertaking serial dilutions.

A humic acid stock solution at a concentration of 5.0 g/L was prepared by dissolving purified Aldrich humic acid (HA) in Milli-Q water with a few drops of 25%  $\text{NH}_4\text{OH}$  to ensure the humic acid was completely dissolved. Standard solutions were prepared by serial dilution.

**High-Performance Liquid Chromatography (HPLC) Assay Methods.** Chlorpyrifos and its major metabolite TCP were analyzed according to a HPLC method similar to that of Baskaran et al. (13) to determine if any degradation occurred during sorption experiments. The Shimadzu LC-10Ai chromatograph consisted of a solvent delivery unit, a degassing unit, an autosampler, and a UV–vis detector set at 280 nm (20). A Synergy Hydro-RP column (Phenomenex, Australia), protected by a guard column of matching stationary phase (Phenomenex, Australia), was used at a flow rate of 1.5 mL/min. The analysis was conducted under gradient elution conditions, with the mobile phase composition changing from 44:56 acetonitrile/1% glacial acetic acid v/v % to 80:20 acetonitrile/1% glacial acetic acid v/v % over a period of 25 min.

Humic acid was analyzed using a method modified from that of Susic and Boto (21), with a Shimadzu HPLC system, LC-10Ai, consisting of a solvent delivery system, a degassing unit, an autosampler, and a fluorescence detector with an excitation wavelength of 340 nm and an emission wavelength of 455 nm. The mobile phase was 0.003%  $\text{NH}_4\text{OH}$  at pH 10, with a flow rate of 1.0 mL/min. A Synergy Fusion-RP column (Phenomenex, Australia), protected by a guard column of the same packing material (Phenomenex, Australia), was used for separation of the humic acid.

**Kinetic Experiments.** Kinetic experiments were conducted in batch and continuous modes at pH 3 and 6. Both batch and continuous experiments were conducted for periods of up to 7 days from the initial addition of the sorbate. Initial experiments were conducted under both light and dark conditions. As no photolytic degradation of CPF was observed, all subsequent experiments were conducted in the light. In the absence of any mineral approximately 14% of the CPF adsorbed onto the glass centrifuge tubes, which is consistent with previous work (22). This sorption was subtracted from the total amount sorbed to determine the amount on the mineral surface.

**Batch Sorption Experiments.** Sufficient solid clay mineral was added to 200 mL of 0.01 M NaCl background electrolyte to give a BET surface area of 100 m<sup>2</sup>/L. The suspension was allowed to equilibrate with constant stirring with a Teflon-coated stir bar for 16 h, under an atmosphere of nitrogen, in a temperature-controlled room ( $25 \pm 1$  °C). Metrohm 691 pH-meters with Orion Ross ‘Sure Flow’ or Metrohm combined pH-glass microelectrodes were used for the measurement of pH. Prior to the commencement of each experiment,

the electrodes were calibrated with NBS standard buffers at pH 4.01 and 6.86 (23). The pH of the suspension was then lowered to approximately 3 using HCl, and CPF stock solution was added to give a concentration of 2.85  $\mu\text{M}$  (1 mg/L). In all cases the concentration of methanol in the final suspensions was <1% (v/v). After the pH had stabilized, a 3 mL portion of suspension was transferred to a glass culture tube, which was purged with nitrogen and securely capped. The pH of the remaining suspension was then adjusted about 0.5 unit by the addition of NaOH, and a 3 mL portion was taken, purged with nitrogen, and capped. This process was repeated to obtain a series of samples with pH in the range from 3 to 7. Above pH 7 CPF degrades rapidly by alkaline hydrolysis (1). Tubes were then tumbled for 24 h. The pH of each sample was remeasured after equilibration, and the samples were centrifuged (Jouan CR 412) for 30 min at 1000g. The supernatant solutions were analyzed for residual CPF and TCP by HPLC. To see if dissolution of the mineral substrates was significant, supernatant concentrations of Al, Si, and Ca were analyzed by ICPOES at pH 3 and 7. The solution concentration of these species at pH 3 was about 10% higher than their concentration at pH 7. We do not expect that this would have a significant impact on the pH dependence of the sorption.

Batch sorption experiments for the ternary CPF–HA–mineral systems were conducted using the general method outlined above. After the clay mineral suspension had been equilibrated for 16 h, HA was added to give a total concentration of 50 mg/L. The suspensions were equilibrated for a further 2 h, before the addition of 2.85  $\mu\text{M}$  CPF. The tubes were tumbled for 24 h, and the pH was remeasured. Samples were centrifuged (Jouan CR 412) at 1000g for 30 min, and the supernatants were transferred to vials for HPLC analysis. Separate analyses were conducted for CPF and TCP and then for residual humic acid.

Sorption isotherms for CPF were measured at constant pH in batch experiments similar to those described above. Here the pH of the suspension was held constant while the amounts of CPF were increased to a final solution concentration of 2.85  $\mu\text{M}$ . After each CPF addition, the pH was readjusted to the chosen value and a 3 mL portion of suspension transferred to a glass culture tube, which was flushed with  $\text{N}_2$ , capped, and placed on an end-on-end shaker.

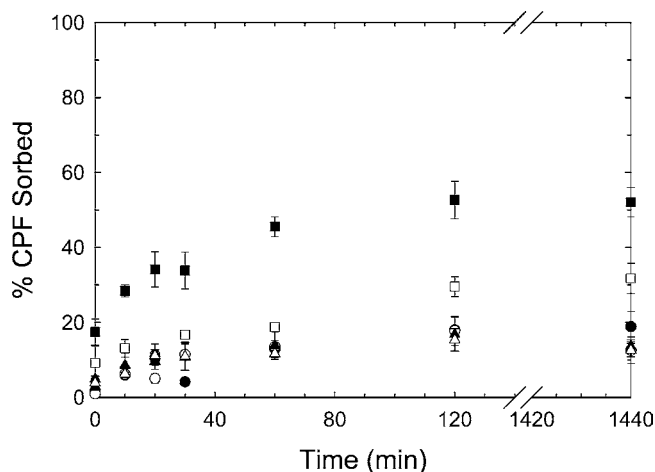
For desorption of CPF from montmorillonite and kaolinite in both the presence and absence of HA an initial batch sorption experiment was undertaken. After 24 h of equilibration, the samples were centrifuged (Jouan CR 412) for 30 min at 1000g and the supernatants removed for HPLC analysis. Three milliliters of HPLC grade methanol was added to each tube, and the tubes were purged with  $\text{N}_2$  and shaken to resuspend the mineral before being tumbled for a further 24 h. Samples were then centrifuged at 1000g for 30 min and the supernatants analyzed for CPF and TCP by HPLC.

## RESULTS

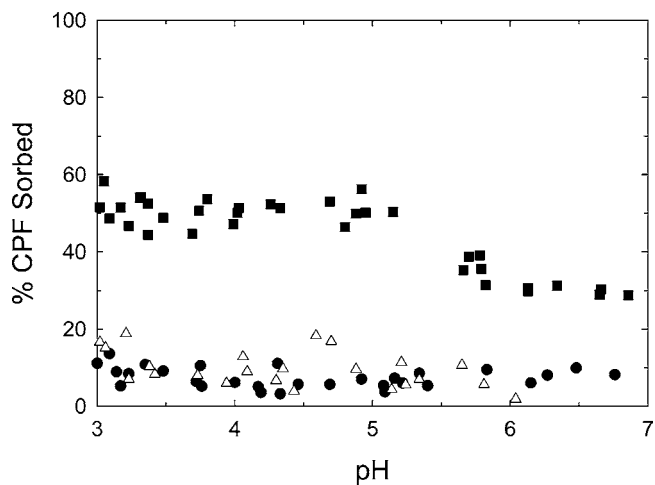
**Degradation.** It is known that CPF undergoes degradation by a number of mechanisms (1) to form TCP, the major degradation product, and TMP, a minor product. To check that degradation was not significant in our study, identical solutions containing only CPF (2.85  $\mu\text{M}$ ) that had been kept under both light and dark conditions, respectively, for 7 days were analyzed for CPF and TCP by HPLC. No TCP was detected, and the CPF concentrations differed by <2%.

**Kinetics.** Sorption of CPF to montmorillonite (Figure 2) was characterized by a rapid initial process (occurring within about the first 30 min), followed by a slower stage, with maximum sorption reached within 24 h. Although not shown in Figure 2, sorption was measured after 48 h and then at 7 days—there was no further increase in uptake on any substrate after the initial 24 h. In montmorillonite systems the initial fast sorption accounted for 50–55% of the sorption maximum at both pH 3 and 6. For gibbsite and kaolinite the initial (fast) sorption accounted for approximately 75% of the total at pH 3 and 6.

**Sorption Edges.** The sorption of CPF as a function of pH (Figure 3) was investigated by batch-mode experiments. The



**Figure 2.** Time course of the sorption of 2.85  $\mu\text{M}$  CPF at 25 °C to 100  $\text{m}^2/\text{L}$  montmorillonite (■), kaolinite (●), and gibbsite (Δ) at pH 3 (solid symbols) and pH 6 (open symbols). Background electrolyte was 0.01 M NaCl.

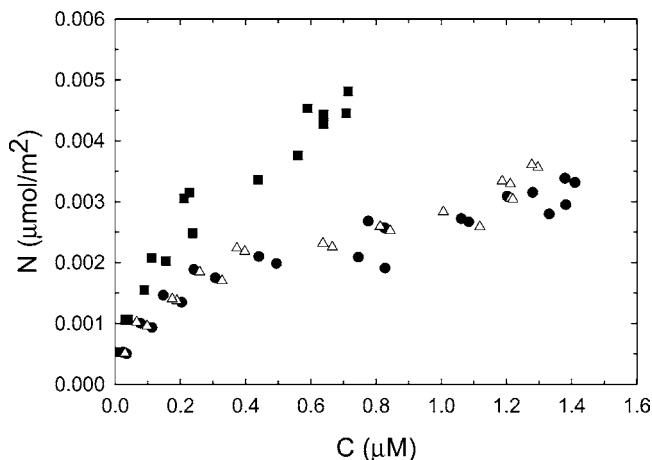


**Figure 3.** Sorption of 2.85  $\mu\text{M}$  CPF at 25 °C to 100  $\text{m}^2/\text{L}$  montmorillonite (■), kaolinite (●), and gibbsite (Δ) at 25 °C. Background electrolyte was 0.01 M NaCl.

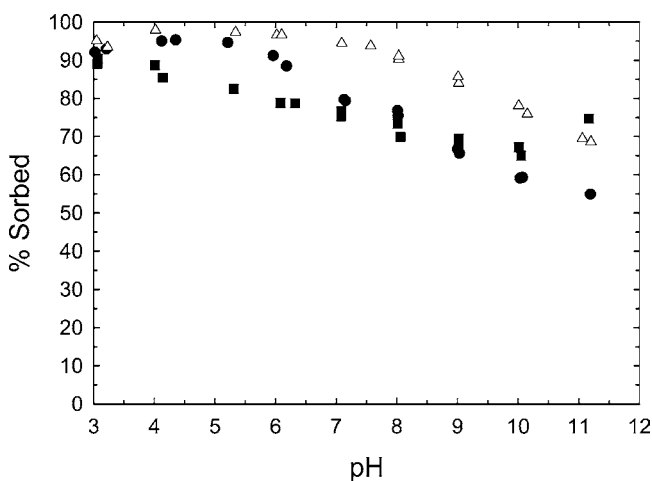
total concentration of CPF in these experiments was 2.85  $\mu\text{M}$ , and sufficient mineral was added to give a total BET surface area of 100  $\text{m}^2/\text{L}$ . Figure 3 shows that the magnitude of the sorption was significantly greater for montmorillonite than for the other two minerals. The effect of pH is also interesting. In montmorillonite systems, sorption decreased sharply by about 20% between pH 5 and 6. However, although there was a small decrease in sorption on gibbsite, pH had little effect on CPF uptake by kaolinite.

**Isotherms.** Sorption isotherms for CPF were measured at pH 3 (Figure 4). The stronger sorption of CPF to montmorillonite observed in the sorption edge (Figure 3) was reflected in the isotherms, where the uptake by montmorillonite was significantly greater than sorption to the other two minerals. The gibbsite and kaolinite isotherms were virtually indistinguishable.

**Humic Acid Sorption.** Figure 5 shows the uptake of HA in binary systems containing mineral and aqueous 50 mg/L HA. The data for the three minerals are similar—humic uptake was strongest for each of the minerals at low pH, with sorption gradually decreasing as pH increased. Slightly more HA was sorbed to gibbsite than to kaolinite or montmorillonite at all pH values.



**Figure 4.** CPF sorption isotherms at 25 °C for 100 m<sup>2</sup>/L montmorillonite (■), kaolinite (●), and gibbsite (△) at pH 3. Background electrolyte was 0.01 M NaCl.



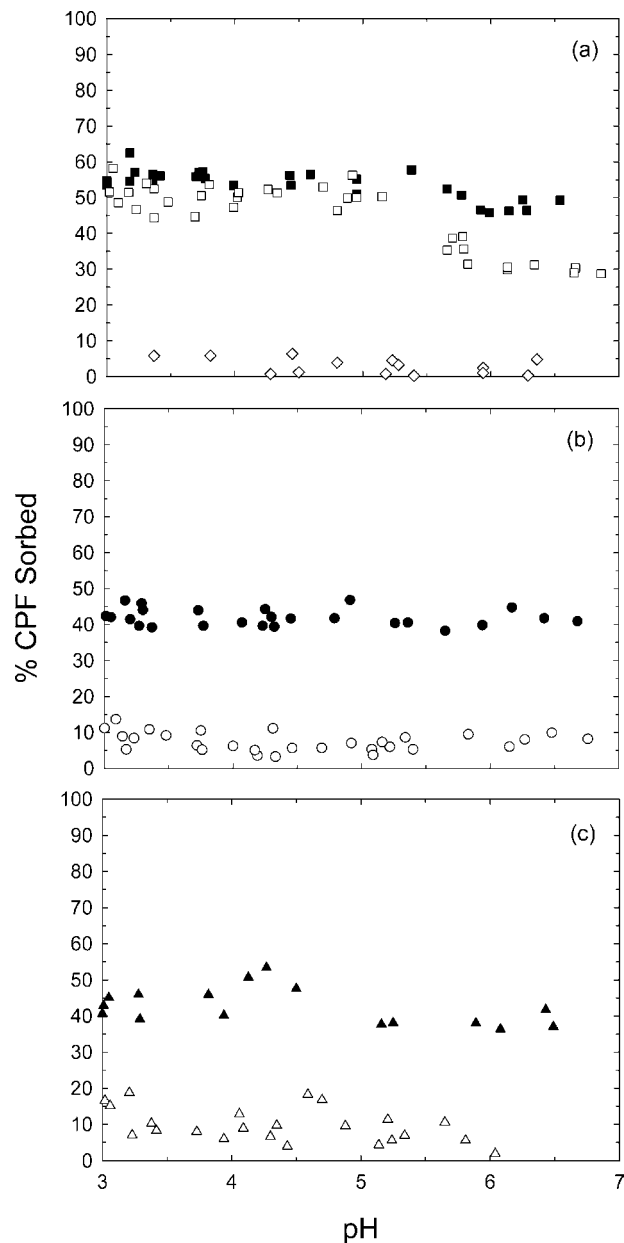
**Figure 5.** Sorption of 50 mg/L humic acid at 25 °C to montmorillonite (■), kaolinite (●), and gibbsite (△). BET surface area of all substrates was 100 m<sup>2</sup>/L. Background electrolyte was 0.01 M NaCl.

**Ternary Humic Systems.** In experiments on the ternary systems the mineral component was first suspended and equilibrated in a solution containing 50 mg/L HA. Then CPF was added, and sorption was measured with the results given in **Figure 6**. In the presence of HA the amount of CPF sorbed to gibbsite and kaolinite increased approximately 4-fold. However, in the montmorillonite system HA did not appear to significantly change the amount of CPF sorbed below pH 5. Above pH 5, the amount of CPF sorbed remained approximately constant, in contrast to the marked decrease observed in the absence of humic acid.

Because the solubility of HA tends to decrease with decreasing pH, it is possible, particularly at lower pH values, that colloidal HA was present. To test whether colloidal HA had an effect on CPF uptake, an experiment was conducted in which CPF was added to a solution containing 50 mg/L HA but no mineral phase. The solution was equilibrated at several pH values, and the samples were centrifuged to remove any colloidal material. CPF was then measured in the supernatant solutions.

**Figure 6a** (diamond symbols) shows that very little CPF was removed, which indicates that any colloidal HA could not have removed significant amounts of CPF during the sorption experiments in the ternary systems.

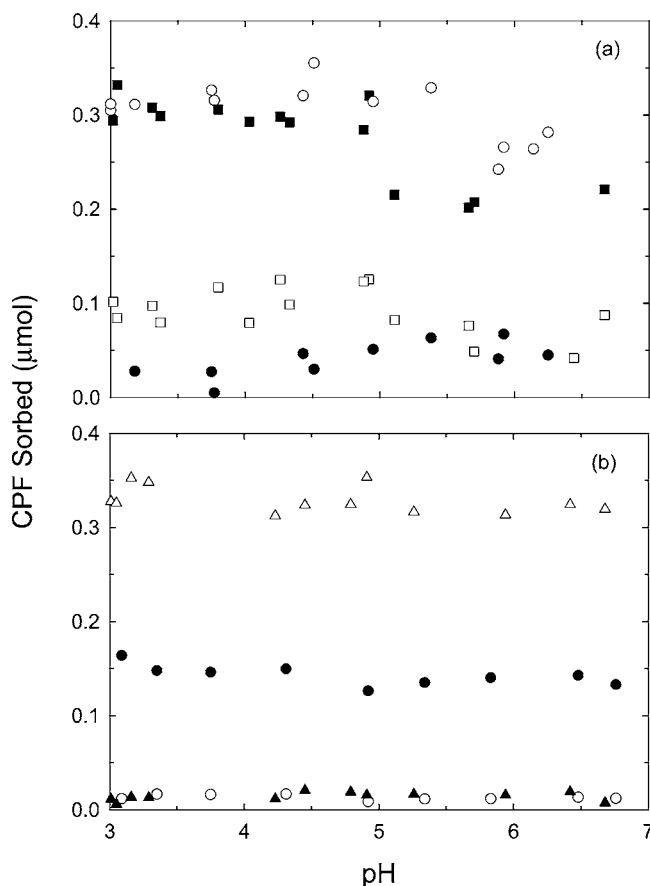
**Desorption.** The strength of the binding of CPF to the mineral surfaces was tested in desorption experiments. CPF was first



**Figure 6.** Sorption of 2.85 µM CPF at 25 °C on 100 m<sup>2</sup>/L (a) montmorillonite (■), (b) kaolinite (●), and (c) gibbsite (▲). Solid symbols represent sorption in the presence of 50 mg/L humic acid, and open symbols represent sorption to the minerals alone. Also shown in (a) is the sorption of 2.85 µM CPF in the presence of humic acid without any mineral present (◇). Background electrolyte was 0.01 M NaCl.

sorbed to montmorillonite or kaolinite in aqueous suspensions, and then the solid phase was resuspended in methanol and the recovery of CPF determined. It is important to note that methanol was used as the desorbing solvent, not to mimic any environmental conditions but to test if the more hydrophobic solvent could remove significant amounts of CPF. The data plotted in **Figure 7** show the amount of CPF sorbed to the surface before and after the desorption step. The pH refers to the pH at which the initial sorption took place.

**Figure 7** shows that approximately two-thirds of the sorbed CPF was readily desorbed from the montmorillonite surface by methanol. Perhaps of more interest is the fact that greater recoveries of CPF were possible in the ternary system containing humic acid. Recoveries of CPF sorbed to kaolinite were virtually 100% whether or not humic acid was present.



**Figure 7.** (a) Sorption of CPF at 25 °C to montmorillonite in 0.01 M NaCl (■) and residual sorption after resuspension in methanol (□) and in 0.01 M NaCl with humic acid (○) and residual sorption after resuspension in methanol (●). (b) Sorption of CPF to kaolinite in 0.01 M NaCl (●) and residual sorption after resuspension in methanol (○) and in 0.01 M NaCl with humic acid (△) and residual sorption after resuspension in methanol (▲). BET surface area was 100 m<sup>2</sup>/L, and initial CPF concentration was 2.85 μM.

## DISCUSSION

**CPF Sorption.** The sorption edges and isotherms (Figures 3 and 4) clearly demonstrate that sorption to montmorillonite is significantly different from sorption to the other two substrates. For montmorillonite, not only is the magnitude of the sorption significantly greater, but it is also characterized by a pH dependence not observed in the other mineral systems. The kinetic data (Figure 2) also indicate somewhat different sorption behaviors; in montmorillonite systems, particularly at pH 3, maximum uptake occurs after about 24 h, whereas for gibbsite and kaolinite systems little additional sorption occurs after 2 h. We can rule out degradation as a significant contributor to the disappearance of CPF from solution, because the primary CPF degradation product, TCP, was not detected in any experiments.

The differences in sorption behavior between substrates can be accounted for by considering the nature of the mineral substrates. Gibbsite and kaolinite are both nonswelling and do not contain the microporous structure that is present in montmorillonite (24). It has been argued previously that BET surface areas significantly underestimate the total available surface area of montmorillonites (25), and so the BET surface area does not truly represent the environmental situation. Thus, the increased sorption to montmorillonite in our experiments is probably

because of the availability of surfaces not structurally present on the other minerals. The slower kinetics observed for sorption to montmorillonite also suggests a diffusion-controlled process. The initial sorption phase probably reflects sorption at external surfaces, whereas the slower process that occurs over 24 h results from diffusion into microporous structures of the clay.

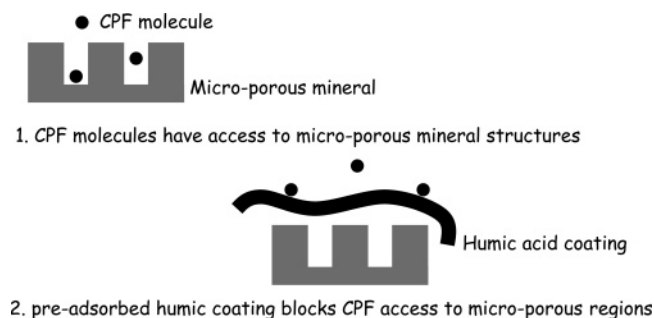
The argument presented above is not new, having been suggested by previous authors for a range of hydrophobic organic compounds. Wu and Laird (9), for example, suggested that the sorption of CPF to a variety of Ca-substituted smectites occurred via condensation into a network of nano- and microporous regions of the clays. Hundal et al. (26) proposed a similar mechanism to explain the uptake of phenanthrene by a number of smectites including Wyoming montmorillonite. Diffusion-controlled migration into interlayers and micropores has also been used to explain the sorption behavior of hormones and phenols to swelling clays (27, 28).

Perhaps the most interesting aspect of the current study is the pH dependence of CPF uptake by montmorillonite. Wu and Laird (9) measured sorption only at pH 6. Figure 3 shows that CPF sorption falls by approximately one-third in the pH range from 5 to 6. This reduction is also evident in the kinetic data given in Figure 2, where greater sorption is observed at pH 3 than at pH 6. We postulate that this reduction in sorption is because of an increase in negative surface charge at the edges of montmorillonite crystals across the pH range from 5 to 6. Studies of the surface properties of montmorillonites (29–31) suggest that the point of zero charge for the edges is in the range of 5–6.5. As the pH increases, the variable charged edges of the clay become progressively more ionized, yielding a more polar surface that results in a reduction in the affinity of the hydrophobic CPF.

The results of desorption experiments also illuminate the process. CPF desorbed almost completely from kaolinite into methanol, suggesting that surface binding is probably weak and that hydrophobic and/or van der Waals forces were responsible for CPF retention. For montmorillonite, however, only about two-thirds of the CPF desorbed into methanol; the CPF molecules that remained were most probably strongly retained by, or diffused into, the montmorillonite structure, preventing their easy removal.

To summarize, CPF sorption to montmorillonite is a two-stage process. The initial rapid sorption is probably to external surfaces. Sorption increases slowly over time as CPF molecules diffuse into microporous regions of the clay structure (including interlayer regions). Below pH 5 sorption to readily accessible external surfaces accounts for about two-thirds of the total amount sorbed, as reflected by the amount sorbed rapidly at pH 3 (Figure 2), and the amount readily recovered from the surface by methanol in the desorption experiments (Figure 7). At pH > 5 less CPF is sorbed to the more highly charged external surfaces, reflected by the lower initial sorption at pH 6 (Figure 2), and the decreased fraction of sorbed CPF recovered into methanol in desorption experiments (Figure 7).

**Humic Acid.** The presence of HA greatly increases CPF uptake by gibbsite and kaolinite (Figure 6) but has comparatively little impact on CPF uptake by montmorillonite below pH 5. A simple explanation for the increase in CPF uptake in the gibbsite and kaolinite systems is that the mineral surface is coated by sorbed HA, which makes the surface more hydrophobic and encourages increased uptake of CPF. CPF–HA complexes have been documented previously (11, 12), so it is not surprising that complexes would form with HA sorbed to a mineral surface.



**Figure 8.** Pictorial representation of the effect of a humic acid coating on the uptake of CPF by montmorillonite.

The data for the montmorillonite ternary system are, at first sight, surprising. Most of the HA is sorbed to the montmorillonite (**Figure 5**), yet, unlike the other mineral systems, there is little increase in the amount of CPF sorbed below pH 5 when HA is present. To explain this, we must consider the mode of CPF uptake on montmorillonite and also recall that in our experiments on the ternary systems the minerals were first equilibrated in the presence of HA. Therefore, before CPF was added, most of the HA was sorbed to the mineral surfaces. If the montmorillonite surface is precoated with HA, access of CPF to the micropore regions of the clay structure sites will be denied because of the HA coating. A cartoon representation of this idea is given in **Figure 8**. It is also possible that some HA molecules block access to interstices within the montmorillonite by occupying these spaces themselves. Thus, when montmorillonite is pre-equilibrated with sufficient HA, the micropores do not play a significant role in the uptake of CPF. However, the increased hydrophobicity of the external surface due to sorbed HA compensates for the lack of uptake by micropores. This is also reflected in desorption experiments, where a greater fraction of sorbed CPF was recovered in methanol when HA was present than when there was no HA, indicating that much of the sorbed CPF was weakly held at the surface with HA and is therefore readily removed by methanol extraction. Furthermore, both **Figures 5** and **7** show that in the presence of HA the sorption of CPF to montmorillonite changes little above pH 5, whereas in the montmorillonite–CPF only system much less CPF sorbs above pH 5. This increase in CPF uptake is likely caused by increased hydrophobicity of the surface resulting from sorbed HA, which interacts strongly with the montmorillonite surface across the pH region investigated. These HA–surface interactions may occur directly or, as has been previously suggested, through the formation of Ca bridges (32) at higher pH values. This supports the view that CPF is largely associated with a HA coating as changes in the surface charge of the underlying montmorillonite with pH do not affect CPF uptake.

**Conclusion.** There is a large difference in the sorption of CPF to montmorillonite compared with that to kaolinite and gibbsite. In the montmorillonite system, not only is a significantly greater amount of CPF sorbed, but sorption is also pH-dependent. At low pH, sorption involves initial and rapid uptake of CPF onto external surfaces, followed by diffusion into microporous regions, whereas at pH > 6 CPF has a lower affinity for the external surface because of increased surface charge, so the microporous regions become relatively more important for sorption. In the case of gibbsite and kaolinite, CPF sorbs more rapidly, and all of the sorbed CPF is recovered after desorption in methanol, suggesting only weak interaction with the surface.

The amount of CPF sorbed on gibbsite and kaolinite is substantially enhanced in the presence of humic acid. Sorbed HA provides a more hydrophobic surface environment and

facilitates CPF uptake. On montmorillonite the HA also coats the mineral particles, reducing CPF access to microporous surfaces; CPF, therefore, tends to accumulate on the HA coating rather than at the mineral surface.

The results from this study demonstrate the importance of both swelling clays and humic acid on the sorption of CPF and, hence, its fate, transport, and bioavailability in the environment. The results demonstrate that swelling clays will be important sinks for immobilizing CPF in the environment, whereas the presence of HA can markedly increase CPF partitioning to some nonswelling mineral phases.

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