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# Degradation of Chlorothalonil in Irradiated Water/Sediment Systems

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Water/sediment systems were used to investigate partitioning behavior between waters and sediments, as well as the degradation of the fungicide chlorothalonil (CHT) in each matrix. Experiments were run in the light and dark simultaneously for 30 days in both creek and pond sediment systems. Of the total applied CHT, 87−88% dissipated from the water phase in both water/sediment systems within 1 day when irradiated by simulated sunlight. In contrast, 60−68% remained in the water at day 1 in the dark. Approximately 3−6 and 10−16% of the applied CHT was found in sediments under light conditions at day 1 and in the dark at day 3, respectively which are the highest amounts observed during the experimental period. CHT similarly behaved in irradiated water/sediments and sediment-free aqueous solutions, indicating that CHT primarily degraded by photodegradation rather than adsorption to sediment in the early stages of the experiment. 4-Hydroxychlorothalonil was detected only in water in the dark systems. Trichloro-1,3-dicyanobenzene and 3-cyano-2,4,5,6-tetrachlorobenzamide were also detected and identified with liquid chromatography−electrospray ionization−mass spectrometry. These results suggest that photodegradation is likely to be important to the dissipation of CHT in aqueous solutions and microbial degradation plays an important role for residues that would ultimately reside in sediment.

**KEYWORDS: Water/sediment systems; chlorothalonil; simulated sunlight; photodegradation; microbial degradation**

## INTRODUCTION

Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile, CHT) is a nonsystemic foliar fungicide used to control many fungal diseases in a wide range of crops, especially vegetables and fruits. Also, it is the most common pesticide used to control fungal disease in turf, and turf application rates are among the highest of all labeled use patterns. It affects enzymatic functions via interaction with protein sulfhydryl groups and glutathione (*1*). It is extensively metabolized to the more toxic and persistent 4-hydroxychlorothalonil (4-OH-CHT), many dechlorinated degradation products by reductive dechlorination, and other degradation products by oxidation/hydrolyzation in soil (*1*). Chlorothalonil is classified as "highly toxic to fish", with 96 h $LC_{50}$ values ranging from 10 to 30 $\mu$g/L for fish species (*2*). Some investigations have shown it to be stable to UV light in aqueous media and in its crystalline state (*3*). However, Peñuela et al. (*4*) has reported that CHT degraded in deionized water with half-lives of 101.17 and 36.86 h when exposed to sunlight and simulated sunlight in a Suntest apparatus, respectively. In groundwater (*4*), CHT degraded more quickly (half-life of 0.71 h) than in deionized water (half-life of 36.86 h). Also, Sakkas et al. (*5*) has reported that CHT degraded rapidly when exposed to sunlight or artificial light with half-lives of 1−48 h depending upon the light source, water composition, and dissolved organic matter concentration. CHT adsorbs strongly to soil, with a reported sorption coefficient ($K_{om}$) of 1030 $dm^3$/kg (*6*).

Many pollutants in aquatic systems associate with sediment. Their fate in such systems is likely to be different than in terrestrial soil systems. It is important to assess the persistence and fate of chemicals in these systems to most accurately assess potential biological impacts. Many water bodies such as creeks, drainage ditches, or ponds receiving runoff water that contains pesticide residues are shallow and may have biotic and abiotic degradation processes driven by sunlight. These processes include degradation by algae or phototropic aquatic bacteria and redox reactions occurring on water/sediment interfaces initiated by sunlight (*13, 14*). However, many researchers have conducted degradation experiments on chlorothalonil in aqueous solutions or solvents (*4*, *5*, *7*−*9*) or soils (*10*−*12*) separately. This investigation was conducted in small-scale water/sediment systems under light conditions and in the dark to determine the persistence and behavior of CHT between two different types of sediments and to identify degradation products that are formed in the systems.

## EXPERIMENTAL PROCEDURES

**Chemicals.** CHT standard was obtained from Ricerca Inc., and 4-OH-CHT standard was a gift from Zeneca. Their purities were 99.6 and 97.6%, respectively, and structures are presented in **Figure 1**. All solvents were of high-performance liquid chromatography (HPLC) grade, and all reagents were of reagent grade. CHT and 4-OH-CHT

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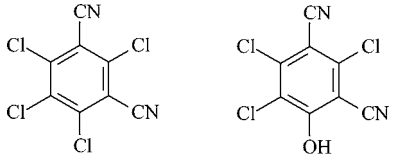


**Figure 1.** Structural formulas of chlorothalonil (CHT) and 4-hydroxychlorothalonil (4-OH-CHT).

**Table 1.** Physicochemical Properties of the Two Sediments

| sediment | texture | clay (%) | silt (%) | sand (%) | OM[a] (%) | pH | CEC[b] (mequiv/100 g) |
|---|---|---|---|---|---|---|---|
| creek | silt | 0.00 | 92.75 | 7.25 | 0.16 | 6.7 | 0.90 |
| pond | silt loam | 7.50 | 66.25 | 26.25 | 0.65 | 5.6 | 7.73 |

[a] Organic matter. [b] Cation exchange capacity.

standard stock solutions were prepared in ethyl acetate and in acetonitrile at a concentration of 1000 mg/L, respectively.

**Sediment and Water Sampling.** Sediment and water were collected from a local pond (Mississippi State, MS) and creek (Mathison, MS). Water was collected close to the two sediment sampling sites. Water and sediments were passed through a 2 mm sieve, and then water was passed through a 212 $\mu$m sieve within 1 h of collection. The water content of the wet sediment was ~22%, and the pH values of the creek and pond water were 7.55 and 6.89, respectively. Preliminary analysis of water and sediment indicated that both CHT and 4-OH-CHT were not above detectable levels (<2 $\mu$g/L). The physicochemical properties of the two sediments were determined by the Soil Testing Laboratory Extension Service at the Mississippi State University and are presented in **Table 1**.

**Preparation of Water/Sediment Systems.** Water/sediment systems were prepared by adding 50 g (dry weight basis) of sediment and 175 mL of water to Teflon containers (8.2 cm depth, 6.0 cm i.d.) and incubated in a growth chamber at 20 °C for ~2 weeks to allow microbial communities to acclimate to the experimental conditions. The sediment depth was ~1.2 cm deep, and the water was ~6.4 cm deep in each system. These small (150−3000 mL of water and 25−600 g of sediment) laboratory water/sediment systems have been used to elucidate the fate of various pesticides (*15*−*19*). Following the acclimatization period, CHT in ethyl acetate (87.5 $\mu$L) was added onto the water surface to obtain an aqueous concentration of 0.5 mg/L, which is less than the reported water solubility of 0.6−1.2 mg/L (*1*), and the water phase was gently stirred for ~1 min. Ethyl acetate has been used as a cosolvent in photodegradation experiments in water (*4*), and it was shown in preliminary experiments that it did not influence the experimental results. The containers were incubated in a temperature-controlled growth chamber equipped with four UV fluorescent bulbs (Light Sources FL40T12-/BL, Milford, MA) to simulate the UV output of sunlight at 20 °C. The distance from the light source to sample was 50 cm. The output of the lamps between 290 and 400 nm was measured using an EPP2000 Miniature Fiber Optic Spectrometer and SpectraWiz (Ver 2.1) software (StellarNet, Tampa, FL) and had a maximum intensity at 340 nm. These lamps have been used in other published experiments (*20*−*23*). **Figure 2** illustrates the UV absorption spectra of CHT and 4-OH-CHT ($2 \times 10^{-6}$ M) in water and the outputs of simulated sunlight and natural sunlight measured in June in Mississippi State, MS, where extinction coefficients were 2000 $M^{-1}$/cm at 314 nm and 1950 $M^{-1}$/cm at 325 nm for CHT and 15350 $M^{-1}$/cm at 290 nm and 6085 $M^{-1}$/cm at 340 nm for 4-OH-CHT.

Dark control samples at the same initial concentration were kept in the dark at the same temperature as the growth chamber. All experiments were conducted in duplicate. Water and sediment samples were withdrawn at days 0, 1, 3, 7, 14, 22, and 30 after the application of CHT. During the experimental period, distilled water was added daily to compensate for the loss of evaporated water, which was similar between both light and dark systems (~8−10 mL of distilled water was added daily). Two containers were withdrawn from every treatment at each sampling time. The water was pipetted from the container, and

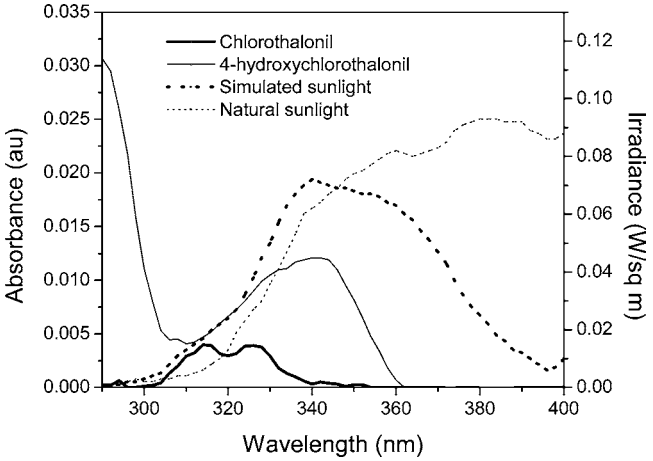


**Figure 2.** UV absorption spectra of CHT and 4-OH-CHT ($2 \times 10^{-6}$ M) in water and outputs of simulated sunlight and natural sunlight measured in June in Mississippi State, MS.

the volumes of water and the weights of sediments were recorded to calculate the concentrations of analyte in each matrix.

**Hydrolysis and Photolysis in Sediment-Free Water.** Photolysis and hydrolysis experiments were conducted in distilled−deionized water, in pH 9 buffer, and in two natural waters used in water/sediment systems at a concentration of 0.5 mg/L CHT for 7 days to compare with the results of water/sediment degradation experiments. For photolysis, a 87.5 $\mu$L aliquot of the stock solution was added to a 200 mL amber bottle, and the ethyl acetate was gently evaporated with the aid of a nitrogen stream. The residue was redissolved in 175 mL of each solution. Samples were poured into the same Teflon container used in the water/sediment system and irradiated in a temperature-controlled growth chamber outfitted with fluorescent lamps under the same conditions as the water/sediment experiment. Samples prepared for hydrolysis at the same initial concentration as photolysis samples were kept in the dark at the same temperature.

**Sample Extractions.** At each time point, water was pipetted from the surface of the system, centrifuged at 3500 rpm for 20 min to remove suspended solids, and then directly injected onto an HPLC system. In the case of samples having concentrations too low to quantify (>10 $\mu$g/L), 30 mL of water sample was extracted with 20 mL of dichloromethane after acidification with 3 mL of concentrated HCl. The dichloromethane layer was evaporated, and the residue was taken up in HPLC water (detection limit = 2 $\mu$g/L).

Extraction methods for CHT and 4-OH-CHT from sediment were based upon those reported by Van der Pas et al. (*10*). CHT was extracted from sediments by adding 30 mL of a mixture of water and dichloromethane (1:3, v/v) to 10 g of moist sediment (water contents ranged from 7.7 to 8.0%), followed by shaking on a wrist action shaker (Pittsburgh, PA) for 1 h. After shaking, the sample was centrifuged on an HNSII centrifuge (Thermo Inc., Needham Heights, MA) for 20 min at 4000 rpm. The dichloromethane layer was removed and reduced in volume under nitrogen, and the residue was taken up in acetone. For 4-OH-CHT, 10 g of moist sediment was extracted by adding 30 mL of a mixture of water and acetone (1:2, v/v), followed by shaking and centrifuging. The acetone in the extract was removed under a stream of nitrogen. The remaining aqueous solution was acidified with HCl below pH 2 and then extracted with 20 mL of dichloromethane. The dichloromethane layer was evaporated, and the residue was taken up in a mixture of water and acetonitrile (1:1, v/v). The detection limit for both CHT and 4-OH-CHT was 2 $\mu$g/L. Measured CHT in the sediment was contained both in pore water and on sediment.

**HPLC and LC-ESI-MS Analysis.** The amount of CHT and 4-OH-CHT remaining in water and sediment was measured on a Waters 2695 HPLC with UV detection using a Waters (model 996, Milford, MA) photodiode array detector at 232 nm for CHT and at 243 nm for 4-OH-CHT. Data were processed using MassLynx (version 3.4) software. The degradation products were separated from the parent compound

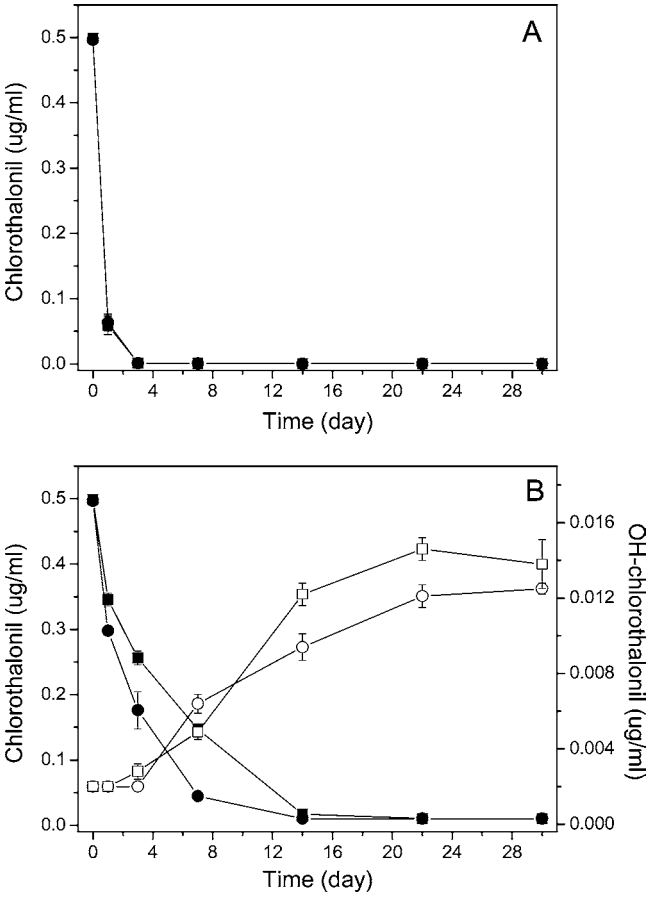


**Figure 3.** Changes in CHT and 4-OH-CHT concentrations in water phase under light (**A**) and in the dark (**B**) with time: (■) CHT in creek water; (●) CHT in pond water; (□) 4-OH-CHT in creek water; (○) 4-OH-CHT in pond water. No 4-OH-CHT was detected in either creek or pond water under light condition.

using a Spherisorb 5 $\mu$m C8 (Waters, Milford, MA; 150 × 4.6 mm i.d.) analytical column. Mobile phase A consisted of acetonitrile, and mobile phase B was 0.5% phosphoric acid in water. The gradient elution started with 10% A for 2 min, linearly increased to 90% A within 25 min, and then remained at 90% A for an additional 5 min. The flow rate was 1.0 mL/min. Liquid chromatography−electrospray ionization−mass spectrometry (LC-ESI-MS) in negative ion mode was performed on a Micromass Quattro Micro triple-quadrupole mass spectrometer (Micromass, Manchester, U.K.) to identify the formation of 4-OH-CHT and other degradation products/metabolites, operating at a capillary voltage of 3.05 kV, a cone voltage of 40 kV, a source temperature of 80 °C, a desolvation temperature of 140 °C, a cone gas flow of 60 L/h, and a desolvation gas flow of 609 L/h. The MS scan range was *m*/*z* 90−400, with a Waters Alliance 2695 system (Milford, MA) and a Waters 2487 UV detector (Milford, MA). A Phenomenex column Luna 5 $\mu$m phenyl-hexyl (Torrance, CA; 250 × 2 mm i.d.) was used to separate the analytes. Elution was carried out with acetonitrile (A) and 10 mM ammonium acetate containing 0.1% formic acid (B). The solvent gradient began at A:B (10:90, v/v) for 2 min and proceeded to A:B (90:10, v/v) over 40 min. The mobile phase flow rate was 0.2 mL/min. MS data acquisition and analysis were performed using MassLynx version 3.5 software.

## RESULTS AND DISCUSSION

**Fate of CHT in Water/Sediment System.** Both CHT and 4-OH-CHT were recovered with >greater than 90% efficiency from water. Recoveries from sediment were >75% using the stated methods.

Changes in the concentrations of CHT and 4-OH-CHT in water/sediment systems for 30 days are shown in **Figures 3** and **4**. After CHT was treated to the water, 87−88% of the applied CHT in both water/sediment systems dissipated within 1 day from water under light conditions with nearly identical dissipation rates (see **Figure 3A**). The estimated half-life is <1 day. CHT is reported to degrade relatively quickly when exposed to natural/artificial sunlight with half-lives ranging from 0.7 to 101 h (*4*, *8*). CHT has two bands of absorption at 314 and 326 nm in acetone and at 314 and 325 nm in water, which are almost the same values as those (313 nm and 325 nm) measured in ethanol (*7*), indicating that CHT would be capable of absorbing the UV energy of sunlight and should be susceptible to direct photolysis in aquatic systems. However, in the dark, 68 and 60% of the applied CHT remained in the water phase at day 1 in creek and pond water systems, respectively, suggesting that photodegradation strongly affects the degradation of CHT in water and that its rapid loss is not due solely to absorption to sediments (see **Figure 3B**). The half-lives calculated in creek and pond water in the dark were 3.0 days ($r^2 = 0.9730$) and 2.1 days ($r^2 = 0.9945$), respectively, showing faster dissipation from pond water (see **Figure 3B**). It is likely that the faster dissipation in the pond water system resulted from higher organic matter content (0.65%) in pond sediment than in creek sediment (0.16%) and higher adsorption to sediment in the pond water/sediment system. Patakioutas et al. (*24*) have reported that

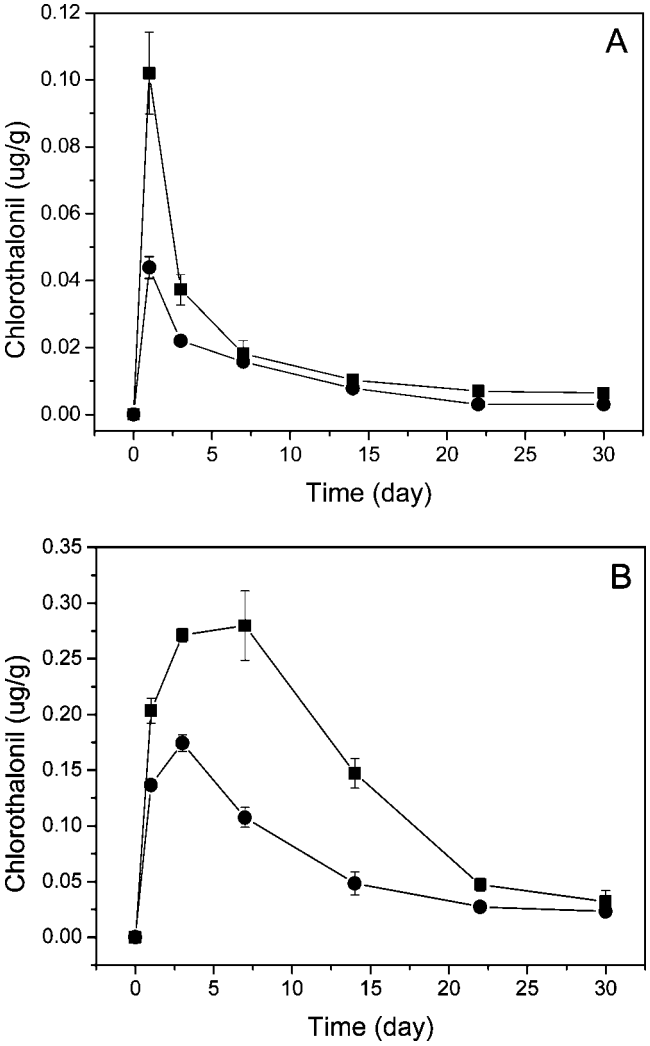


**Figure 4.** Changes in CHT concentrations in sediment under light (**A**) and in the dark (**B**) with time: (■) creek sediment; (●) pond sediment. No 4-OH-CHT was detected in either creek or pond sediment in both conditions.

**Table 2.** Behavior of CHT in Water/Sediment Systems both under Illumination and in the Dark[a]

| | day 0 | | day 1 | | day 7 | | day 14 | | day 30 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | μg | % | μg | % | μg | % | μg | % | μg | % |
| creek–light | | | | | | | | | | |
| water | 87.5 | 100.00 | 10.15 | 11.60 | 0.08 | 0.09 | 0.00 | 0.00 | 0.00 | 0.00 |
| sediment | 0.00 | 0.00 | 5.09 | 5.82 | 0.91 | 1.04 | 0.51 | 0.58 | 0.34 | 0.39 |
| system | 87.5 | 100.00 | 15.24 | 17.42 | 0.99 | 1.13 | 0.51 | 0.58 | 0.34 | 0.39 |
| pond–light | | | | | | | | | | |
| water | 87.5 | 100.00 | 11.09 | 12.68 | 0.10 | 0.11 | 0.00 | 0.00 | 0.00 | 0.00 |
| sediment | 0.00 | 0.00 | 2.25 | 2.57 | 0.80 | 0.91 | 0.39 | 0.45 | 0.00 | 0.00 |
| system | 87.5 | 100.00 | 13.34 | 15.25 | 0.90 | 1.03 | 0.39 | 0.45 | 0.00 | 0.00 |
| creek–dark | | | | | | | | | | |
| water | 87.5 | 100.00 | 59.23 | 67.69 | 26.02 | 29.74 | 5.17 | 5.91 | 2.60 | 3.00 |
| sediment | 0.00 | 0.00 | 10.19 | 11.65 | 13.99 | 15.99 | 7.32 | 8.36 | 1.64 | 1.88 |
| system | 87.5 | 100.00 | 69.42 | 79.34 | 40.01 | 45.73 | 12.49 | 14.27 | 4.24 | 4.85 |
| pond–dark | | | | | | | | | | |
| water | 87.5 | 100.00 | 52.67 | 60.19 | 9.03 | 10.32 | 1.97 | 2.25 | 2.35 | 2.69 |
| sediment | 0.00 | 0.00 | 6.97 | 7.97 | 5.51 | 6.30 | 2.32 | 2.65 | 0.53 | 0.60 |
| system | 87.5 | 100.00 | 59.64 | 68.16 | 14.54 | 16.62 | 4.29 | 4.90 | 2.88 | 0.29 |

[a] Amounts of CHT were calculated as the sum of the parent and the calculated 4-OH-CHT, corrected for the difference in molecular mass; 87.5 μg of chlorothalonil was initially applied to the system, which corresponds to 0.5 mg/kg chlorothalonil in the water/sediment systems. These data are averages of duplicate experiments, showing standard deviations of <5%.

the $K_f$ value of CHT in five soils increased with increasing soil organic matter content. Also, it is possible that this result came from increased microbial and biotic degradation as a result of increased levels of organic matter. Takayama et al. (*25*) have reported that chlorothalonil residues in soils amended with farmyard manure decreased both in the presence and in the absence (autoclaved) of microorganisms, indicating that chlorothalonil degrades by both biotic and abiotic processes. There are also other investigations suggesting that microbial cometabolism of CHT in soil and water is the major process responsible for degradation (*9*, *11*, *12*, *26*). Experiments with $^{14}$C-labeled CHT would be needed to fully explain its processes. It appears that the effect of pH on the degradation of CHT in water is negligible as the pH is close to pH 7.0, and it has been reported that no degradation of CHT was observed in the dark in pH 5 and 7 buffers (*8*). However, CHT has been reported to degrade by ~80% in 89 days at pH 9, yielding degradation products such as 4-hydroxy-2,5,6-trichloroisophthalonitrile and 3-cyano-2,4,5,6-tetrachlorobenzamide (*8*).

Hydrolysis contributed to the degradation of CHT. Therefore, the photolysis contribution (net photolysis) was calculated by adding the quantity $(C_0 - C_t)_{dark}$, which dissipated in a certain time in the dark, to the remaining $(C_t)_{light}$ concentration detected in the irradiated solution at the same time, where $C_0$ represents the initial concentration of the fungicide and $C_t$ represents the concentration at a point in time (*27*). The half-lives by hydrolysis and photolysis (net) were 17.0 days ($r^2 = 0.9969$) and 1.2 days ($r^2 = 0.9644$) in distilled−deionized water and 1.9 days ($r^2 = 0.9985$) and 2.1 days ($r^2 = 0.9313$) in pH 9 buffer solution, respectively. Degradation appeared to follow a pseudo-first-order kinetic model, and a faster dissipation (3.0 and 2.1 days) from the water phase in water/sediment systems was observed than in distilled−deionized water (17.0 days).

Approximately 3−6 and 10−16% of the applied CHT were found in sediments of irradiated systems at day 1 and in the dark at day 3, respectively, which are the highest amounts observed during the experimental period (see **Figure 4**). These levels declined to 0−0.39 and 3.28−4.78% in the light and dark, respectively, at day 30, indicating that sediment is not a major sink for CHT in aqueous systems. In the early stages of the

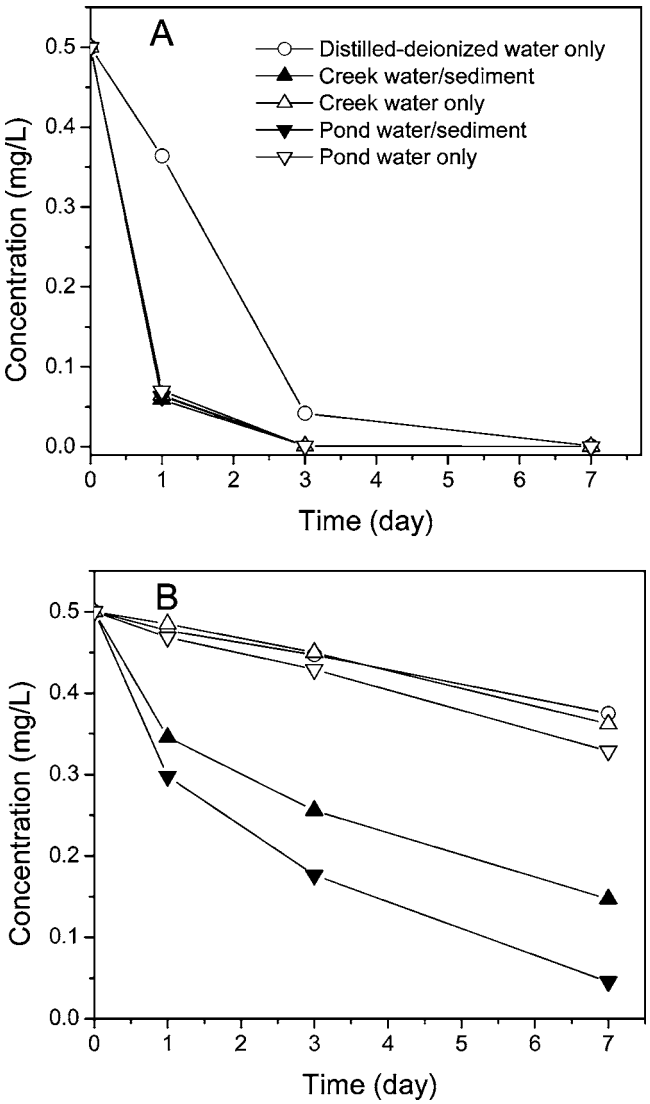


**Figure 5.** Comparison of CHT dissipation from the water phase among five systems under simulated sunlight (**A**) and in the dark (**B**) at 20 °C.

experiment in irradiated samples, CHT concentrations in the creek sediment rapidly increased, then rapidly decreased with a corresponding decrease of CHT concentration in the water phase. In the dark control samples, the CHT concentration rapidly increased and then gradually decreased at a slower rate.

The mass balances were calculated for the 1st, 7th, 14th, and 30th days to show the fate of CHT/4-OH-CHT in water/sediment systems (see **Table 2**). Interestingly, the system recoveries (water + sediment) under light conditions at day 1 were just 15−17% versus 68−79% in the dark, respectively, suggesting that photodegradation is highly important to the dissipation of CHT in aqueous environments in the early stages of the experiment. However, the system recoveries of CHT in the dark at 14 days ranged from 5 to 14%, suggesting that microbial and chemical degradations other than photodegradation also play important roles in the dissipation of CHT in water/sediment systems.

Hydrolysis and photolysis of CHT in sediment-free creek and pond waters treated with CHT at a concentration of 0.5 mg/L were also conducted in Teflon containers and compared with the results obtained from water/sediment experiments (**Figure 5**). CHT behaves similarly in all systems under simulated light conditions, dissipating from the water phase by >86% of the initially applied within 1 day. These results indicate that CHT

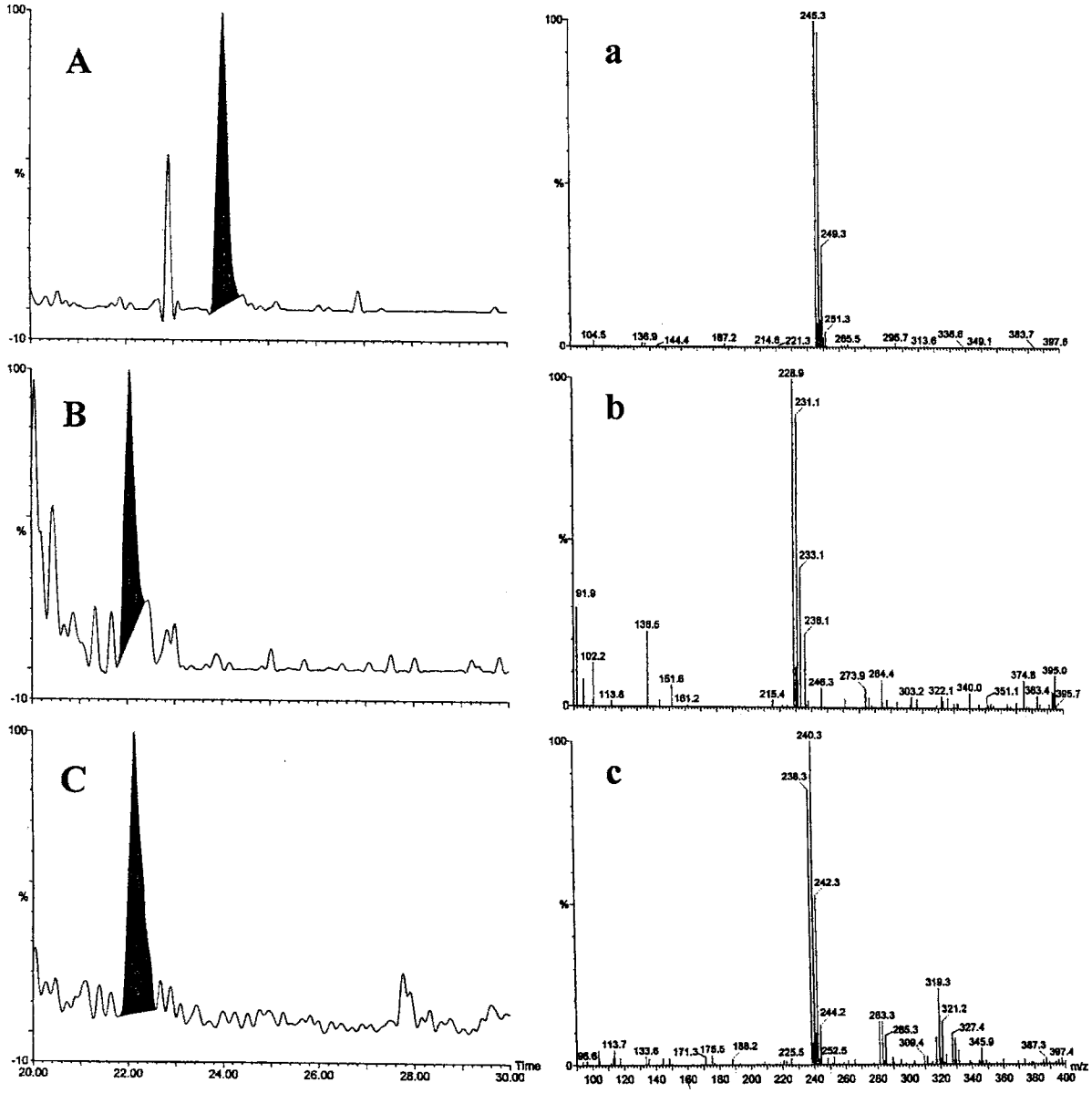


**Figure 6.** Trace chromatograms and their mass spectra of *m*/*z* 245 $[M - H]^-$ (**A** and **a**), *m*/*z* 229 $[M - H]^-$ (**B** and **b**), and *m*/*z* 281 $[M - H]^-$ (**C** and **c**), respectively, detected in this experiment.

is primarily degraded by photodegradation rather than adsorption to sediment in the early stage of experiments despite the strong adsorption to sediment of CHT (*6*). These results also indicate that photodegradation is faster in natural water than in pure water. **Figure 5B** shows the differences in dissipation rates from the water phase in the presence and absence of sediment in the dark. The dissipation rates were higher in water/sediment systems (half-lives = 2.1−3.0 days) than in sediment-free natural water (half-lives = 11.6−14.4 days; $r^2$ = 0.9885−0.9943) and in distilled−deionized water (half-life = 17.0) and illustrate the importance of sediment to the dissipation of CHT from aqueous systems.

**Degradation Products/Metabolites.** Trace chromatograms and their mass spectra of three degradation products/metabolites are presented in **Figure 6**. During the experimental period, 4-OH-CHT, a major degradation product/metabolite of CHT, was detected only in the water in the dark system and identified by LC-ESI-MS. This mass spectrum shows characteristics isotope clusters for three chlorine atoms at *m*/*z* 247 $[M - H + 2]^-$, *m*/*z* 249 $[M - H + 4]^-$, and *m*/*z* 251 $[M - H + 6]^-$ (see **Figure 6a**), which were identical to that of the 4-OH-CHT standard. It ranged in concentration from 3 to 16 $\mu$g/L (see **Figure 3B**), accounting for as much as 3.4% of the applied mass of degraded CHT, indicating that it probably resulted from hydrolysis and/or microbial degradation in the system. It is possible that 4-OH-CHT may be produced in irradiated samples as well and then degraded at a rate exceeding its rate of production because it was not detected in irradiated samples in this investigation. It has been reported that irradiation with simulated sunlight degraded 4-OH-CHT in distilled−deionized water, phosphate buffer, and pond water with half-lives of ∼30 min (*28*). As can be seen in **Figure 3B**, during the experimental period, the decline of 4-OH-CHT concentrations was very slow, indicating that 4-OH-CHT is resilient against degradation mechanisms occurring in the dark in water. This result is consistent with existing published literature reporting the degradation of CHT to 4-OH-CHT in low-humic sandy soils (*10*). The authors of this paper report the rate of decline of 4-OH-CHT from the maximum amount detected to be very slow over a 6-month experimental period. 4-Hydroxychlorothalonil has also been detected in other media including soils (*9*, *10*,

*12*), cranberries (*29*), pH 9 buffer (*8*), and leachate from golf course greens (*30*), and surface water in suburban streams (*31*).

4-OH-CHT was also present at concentrations of 7 $\mu$g/L in distilled−deionized water and 86 $\mu$g/L in pH 9 buffer at day 7 in the dark. Similar to water/sediment experiments, no 4-OH-CHT was observed under light conditions in distilled−deionized water samples (detection limit = 0.5 $\mu$g/L ) at day 7. However, it was detected in the initial samples of pH 9 buffer under light conditions at 6 $\mu$g/L at 3 h and at 2 $\mu$g/L at 7 h of the treatment: 4-OH-CHT was not detected after 7 h of treatment under light conditions. These results indicate that 4-OH-CHT was formed by both hydrolysis and photolysis (likely via photonucleophilic substitutions) and suggest that 4-OH-CHT was very quickly degraded by light at a rate exceeding its rate of production.

Also, another degradation product/metabolite was detected at trace levels at day 30 in waters in the dark in water/sediment experiments and was identified as trichloro-1,3-dicyanobenzene, exhibiting parent ions at *m*/*z* 229 $[M - H]^-$ in the correct ratio for $Cl_3$ (see **Figure 6b**), leading to a molecular mass of 230. This product was formed by dechlorination of the benzene ring. We could not distinguish between the four possible isomers of this product with LC-MS. However, it is possible that this product may be 2,4,5-trichlorodicyanobenzene because this product and 4-OH-CHT were simultaneously detected in soil under laboratory conditions and both are known products of microbial metabolism (*1*). It could not be quantified, as a standard for this product was not available. The same product was detected in water irradiated using a xenon arc lamp (*4*) and in cranberry bogs at relatively low concentrations (*29*). The mass spectrum of this product detected in this study was compared to that obtained by GC-MS in the electron impact mode (*4*), showing almost the same patterns, but some minor ion peaks exist due to the low levels. However, this product was not formed in distilled−deionizd water in our experiments.

One more degradation product/metabolite was detected, only in pH 9 buffer. The mass spectrum showed ion clusters characteristic for four chlorine atoms at *m*/*z* 283 $[M - H + 2]^-$, *m*/*z* 285 $[M - H + 4]^-$, *m*/*z* 287 $[M - H + 6]^-$, and *m*/*z* 289 $[M - H + 8]^-$, leading to a molecular mass of 282 (see **Figure 6c**). It is likely that CHT was base-hydrolyzed by oxidation/hydrolyzation of one of the nitrile groups to yield 3-cyano-2,4,5,6-tetrachlorobenzamide. Like 4-OH-CHT formation in pH 9 buffer, low amounts were detected under light conditions. HPLC peak areas of 874, 850, and 818 at 3, 7, and 15 h after treatment were measured in irradiated solutions. Peak areas of 3467, 4571, and 8976 at 15, 48, and 384 h were measured in the dark. The amounts of product are presented as peak areas because a standard for this product was not available. This product was not detected after 15 h of treatment under light conditions, indicating that it was also unstable to light. Szalkowski and Stallard (*8*) have previously reported this product by hydrolysis in pH 9 buffer, and this mechanism has been explained in their paper and is that the −OH nucleophile adds to the triple bond of the C≡N group, with subsequent interaction of imino acid with water and −OH to form the amide. These authors have determined that this product is formed in only basic conditions. A significant ion peak was detected at *m*/*z* 238 $[M - H - CHNO]^-$, and some minor ion peaks were formed at *m*/*z* 317 $[M - H + 2H_2O]^-$, *m*/*z* 327 $[M - H + CH_2O_2]^-$, and *m*/*z* 344 $[M - H + CH_2O_2 + NH_3]^-$. The *m*/*z* 327 $[M - H + 46]^-$ ion appears to be an adduct from *m*/*z* 281 due to the presence of formic acid in the mobile phase.

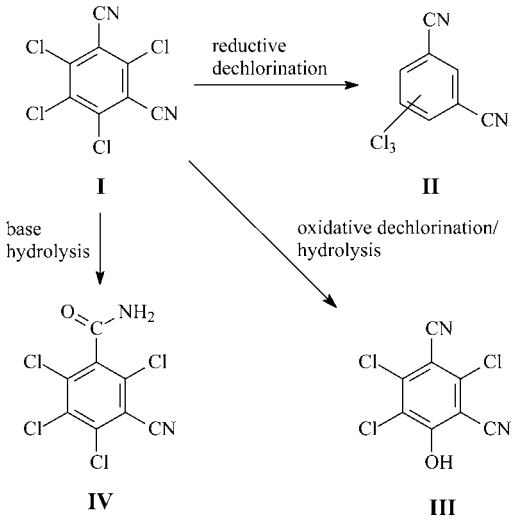


**Figure 7.** Possible degradation pathway of CHT in aquatic systems: **I**, CHT; **II**, trichloro-1,3-dicyanobenzene; **III**, 4-OH-CHT; **IV**, 3-cyano-2,4,5,6-tetrachlorobenzamide.

An overall degradation pathway in aquatic systems is presented in **Figure 7**, and each pathway is depicted as follows: **I** → **II**, reductive dechlorination; **I** → **III**, oxidative dechlorination/hydrolysis; **I** → **IV**, base hydrolysis

**Conclusions.** This investigation showed the fate of the fungicide CHT in irradiated water/sediment systems. The conditions in those systems may be similar to shallow water conditions that would typically be found in drainage basins receiving runoff from treated terrestrial areas. This laboratory water/sediment system is a small system (~250 mL) with aerobic conditions in the water phase and partly anaerobic conditions in the sediments. Chlorothaonil appears to behave in dark controls of this system similarly to the behavior reported in the U.S. EPA Aerobic Aquatic Metabolism Study (http://cfpub.epa.gov/oppref/rereg). Once CHT was introduced to water, it would rapidly dissipate from water and sediment by hydrolysis/microbial degradation as well as photolysis. Chlorothalonil was mainly removed from the water column at the early stages under light conditions. 4-Hydroxychlorothalonil was detected in all media tested, and it appears to be stable in dark conditions in these media, indicating that 4-OH-CHT can possibly remain and affect aquatic organisms in water that is shielded from sunlight. Sediment was not a major sink for CHT or 4-OH-CHT in aquatic systems.

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