Influence of Natural Dissolved Organic Matter, Temperature, and Mixing on the Abiotic Hydrolysis of Triazine and Organophosphate Pesticides

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Abiotic hydrolysis of simazine, atrazine, diazinon, methylparathion, and chlorpyrifos was studied in three different natural waters and buffered Milli-Q water. The triazines showed no detectable decrease in concentration in any of the waters over 43 days at pH 8.0 and 40 °C. The rates of hydrolysis for diazinon and methylparathion were statistically similar in all waters tested. Chlorpyrifos exhibited a ~32% decrease in hydrolysis rate in the presence of a high concentration of dissolved organic matter (DOM) (34.5 mg/L dissolved organic carbon). The activation energies are larger, and thus the predicted hydrolysis rates are significantly slower than those previously reported. The effect of continuous vigorous mixing on hydrolysis rates was investigated and found to have only a minor effect. The results suggest that uncatalyzed abiotic hydrolysis is very slow for these compounds at the temperatures and pH's typical of most natural waters and affirm the need for a greater understanding of the relative influence of DOM, catalysis, and biodegradation on the fate of organophosphate and triazine pesticides.

Keywords: *Pesticides; organophosphates; triazines; hydrolysis; abiotic; DOM*

INTRODUCTION

This study was performed as part of an effort to provide site-specific input data for environmental models used to predict the fate of pesticides from selected watersheds contributing to the San Joaquin River, CA. Pesticides are used extensively in agricultural and urban environments and become pollutants when they are transported beyond their intended area of influence. In order to predict the environmental fate of a pesticide, it is necessary to understand its mobility and rate of degradation under typical environmental conditions. Degradation processes are generally divided into biodegradation (i.e., mediated by microorganisms) and abiotic chemical transformations (Schwarzenbach et al., 1993). Hydrolysis is an important abiotic degradation process for many pesticides in aquatic environments. Although a plethora of hydrolysis rate data are available for many common pesticides (Howard, 1991), much of the data has been obtained under experimental conditions uncharacteristic of the field. For example, most hydrolysis experiments have been performed at, or above, room temperature, whereas water temperatures in the field are typically below 25 °C. In addition, all natural surface waters contain at least some dissolved organic matter (DOM) (Thurman, 1985), and there is experimental evidence that humic substances may significantly affect hydrolysis rates (Macalady et al., 1989). Lastly, changes in hydrolysis rates due to the presence of certain inorganic species (e.g., Cu(II)) have also been observed (Mortland and Raman, 1967; Meikle and Youngston, 1978; Blanchet and St. George, 1982; Chapman and Harris, 1984). These factors, as well as other experimental variables taken collectively, may account for the wide range of reported hydrolysis rates for these compounds in the literature.

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Five pesticides were chosen for this study based upon their abundant use in the northern San Joaquin Valley, CA, and included the triazines simazine and atrazine and three organophosphate insecticides, diazinon, methylparathion, and chlorpyrifos. The San Joaquin Valley accounts for about 10% of the total pesticide use in the United States (Domagalski and Dubrovsky, 1992) and thus represents a significant source of organic pollution to the major waterways of the region.

It is important to understand the relative influence of various environmental and experimental factors which can affect the observed empirical pesticide degradation rates. In this study, we focused on three factors: (1) the effect of DOM in different natural waters, (2) the effect of temperature, and (3) the effect of mixing. First, experiments were performed in actual field waters to investigate the possibility of intersite variation in hydrolysis rates due to differences in the overall nature of waters emanating from different watersheds within the region. The use of different waters evaluates the effect of DOM as well as the collective effects of pH, ionic strength, and inorganic species.

Great care was taken to ensure the sterility of the waters used for these experiments so that only nonbiologically mediated effects would be observed. Sterilization methods are an important consideration when performing experiments to determine abiotic degradation rates. Heat sterilization (autoclave) and chemical sterilizing agents and preservatives can produce experimental artifacts. Autoclaving has been shown to cause pH changes (Sharom et al., 1980), and the heat may alter the character of dissolved organic matter. Sterilization methods utilizing reactive chemicals and/or radiation, such as ozonation and UV, were excluded because of their potential to degrade or alter the nature of the DOM. Moreover, chemicals which remain in the solution during experiments can affect degradation rates. The chemical sterilant sodium azide (NaN_3) has

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been suspected of reacting with diazinon to cause anomalously fast degradation (Sharom et al., 1980; Lichtenstien et al., 1968). In addition, mercuric chloride ($HgCl_2$) has been observed to catalyze the degradation of some organophosphates (Munch and Frebis, 1992). Filtration through 0.2 μm membrane filters is commonly used when the other sterilization methods are unavailable or unsuitable (Ingraham and Ingraham, 1995). Although somewhat less reliable, filtration was selected as the sterilization method for the natural waters so as to minimize any alteration of their original composition or "character."

Second, the natural waters used in this study were found to exhibit consistent pH values. Therefore, effort was concentrated on understanding the temperature dependence of the hydrolysis rates. Many simple reactions are empirically observed to follow the Arrhenius law, and therefore it is common practice to characterize the temperature dependence of first- and pseudo-first-order reaction rates by making Arrhenius plots (Atkins, 1986). Hydrolysis rates at a minimum of two different temperatures are required to produce an Arrhenius plot and thus determine the parameters necessary for estimation of hydrolysis rates at other temperatures.

Last, in some studies described in the literature, the pesticide solutions were continuously mixed during the course of the experiment, while in other studies they were not. Still other investigators did not clearly specify whether the solutions were mixed or not. Therefore, the effect of continuous vigorous mixing was studied to estimate the impact of this variable relative to the overall experimental methodology and so that the results from studies with and without continuous mixing could be properly interpreted and compared. Furthermore, the information obtained could help to understand the influence of naturally varying hydrologic conditions on hydrolysis rates. To the authors' knowledge, the effect of mixing on pesticide hydrolysis rates has not been previously reported.

EXPERIMENTAL PROCEDURES

Sampling. Natural waters were collected from Orestimba Creek and Del Puerto Creek, two major waterways of the northern San Joaquin Valley. These two creeks drain intensively farmed watersheds and are conduits for large quantities of agricultural runoff to the San Joaquin River. Water was also collected from a third location, referred to herein as Eucalyptus Ave Drain, a small agricultural drain which also empties into the San Joaquin River. Water from this location was collected because it was found to have a high dissolved organic carbon (DOC) content of 34.5 mg/L (~70 mg/L DOM).

Natural waters were sampled at each site by wading into the waterway and dipping an 8 L stainless steel bucket upstream into the water and transferring the contents into 37.5 L stainless steel milk cans (Domagalski and Kuivila, 1993). This process was repeated until approximately 32 L of water was collected from each of both Orestimba Creek and Del Puerto Creek. Water from Eucalyptus Ave Drain was collected with the stainless steel bucket and transferred directly into 4 L amber bottles with Teflon-lined closures. Smaller samples were collected in 1 L amber bottles with Teflon closures for later determination of suspended solids concentrations. Dissolved oxygen at each location was measured using a colorimetric field test kit (CHEMetrics, Inc., Calverton, VA). Dissolved oxygen concentrations were consistently between 8 and 10 mg/L, suggesting that the waters as collected were well mixed and in near equilibrium with the atmosphere.

The waters from Orestimba and Del Puerto Creeks were subsequently transported back to a USGS facility in Sacramento, CA. Each of the waters were pumped through Teflon tubing into a Westfalia high-speed continuous flow centrifuge equipped with a stainless steel bowl (Horowitz et al., 1989). The centrifuge was spun at 9800 rpm (9500*g*), and the supernatant water flowed through Teflon tubing into 4 L amber bottles with Teflon-lined closures. The centrifuged creek waters and the Eucalyptus Ave Drain whole water were transported back to UCLA in large coolers covered with ice. The Eucalyptus Ave Drain whole water was subsequently filtered through 0.45 μm polysulfone membrane filters to removed suspended particulates. All waters were stored at 4 °C until needed.

Chemicals and Standard Solutions. The atrazine, simazine, diazinon, methylparathion, chlorpyrifos, and their respective hydrolysis products, hydroxyatrazine, hydroxysimazine, 2-isopropyl-4-methyl-6-hydroxypyrimidine (IMHP), *p*-nitrophenol, and 3,5,6-trichloro-2-pyridinol were purchased from Chem Service, Inc., and used without further purification. Stock solutions of the individual pesticides were prepared at ~1200 ppm for the organophosphates and at ~750 and ~450 ppm for atrazine and simazine, respectively. A mixed organophosphate solution and a mixed triazine solution were prepared from the stock solutions at approximately 400 and 250 ppm, respectively. A third spiking solution was prepared which contained all five pesticides with nominal concentrations of 165 and 135 ppm for the triazines and organophosphates, respectively. The internal standard, 2-nitro-*m*-xylene, was purchased from Aldrich Chemical Co. All stock solutions were prepared in Fisher Optima grade methanol. Standard solutions of the five pesticides were prepared in ethyl acetate at nominal concentrations of 0.5, 3, 6, 10, 15, and 20 mg/L and used for the preparation of standard curves.

Hydrolysis Experiments in Natural Waters (40 °C). Eight 4 L amber bottles and 32 1 L Boston round amber bottles were sterilized in an autoclave at 121 °C, 22 psig, for 30 min. A 90 mm Millipore stainless steel filter holder (with the legs removed) containing a Gelman Supor 0.2 μm polysulfone membrane was similarly sterilized by autoclaving. A filter sterilization apparatus was assembled which consisted of a Millipore 142 mm hazardous waste extractor containing a 0.45 μm Gelman Supor polysulfone membrane, connected by Teflon tubing to the sterilized 90 mm filter holder with the 0.2 μm membrane, which then was connected by Teflon tubing to a sterile 4 L amber bottle sealed by a cap with two fittings. One fitting served as inlet for the sterile filtrate, and the other was used for an exhaust outlet. The outlet was fitted with a 47 mm Teflon filter holder containing a presterilized 0.2 μm Gelman Supor membrane in order to prevent introduction of microbes through the exhaust port. Eight liters of each natural water was run through this filtration system. The entire setup was taken apart and cleaned and membranes were replaced and sterilized between each of the natural waters. After sterilization, the waters were stored at 4 °C until needed. Several small aliquots of water were taken under flame with a sterile pipet and plated on agar media. Three Petri dishes for each bottle were incubated at 37 °C for 72 h. An aliquot of each of the unsterilized waters was plated on two Petri dishes and incubated along with the others to test the ability of the media to support microbial growth. The appearance of colonies with the unsterilized water, and the absence of growth with the filtered water, was taken as confirmation of sterility.

Experimental samples were prepared by filling each of 24 1 L presterilized amber bottles to the same level, 950 mL, with the appropriate natural water. Eight bottles were prepared for each different field water. After each bottle was filled to the appropriate level, the water was quickly spiked with 350 μL of the five-pesticide methanol solution and the bottle sealed with a Teflon-lined closure which had just been immersed in ethanol. The starting concentrations were therefore approximately 60 and 50 μg/L for the triazines and organophosphates, respectively. The closures were further sealed with Teflon tape around the edge of the caps. All transfer of water and spiking was carried out under the flames of two large Bunsen burners. The 24 bottles were then stored at 4 °C while the Milli-Q water samples were prepared. The remaining amounts of each water, ~400 mL, were used for pH, TOC, and conductivity. The pH, TOC, conductivity, and suspended solids

Table 1. Summary of Water Quality Parameters for the 40 °C Hydrolysis Experiment

water quality parameter	Milli-Q water	Orestimba Creek	Del Puerto Creek	Eucalyptus Ave Drain
pH	8.0	8.0	8.0	7.9
DOC (mg/L)	0.4	3.7	6.5	34.5
conductivity (μmhos/cm)	1300[a]	1350	1600	1050
suspended solids[b] (mg/L)	N/A	121	394	702

[a] The conductivity of the Milli-Q water is due to the 0.02 M ionic strength, pH 8.0, phosphate buffer; the original resistance was 18 MΩ. [b] Suspended solids concentration of whole water as collected before centrifugation and/or filtration.

data for the waters used in this experiment are summarized in Table 1.

Based on the pH and conductivity data, the Milli-Q water samples were prepared at pH 8.0 with a 0.02 M ionic strength phosphate buffer. The water was then sterilized by filtration as previously described. The eight Milli-Q water samples were prepared and spiked as previously described. All 32 samples were then placed into two large water baths and maintained at 40 ± 0.5 °C for the duration of the experiment (43 days). One bottle from each of the waters was extracted and analyzed after about 24 h. Thereafter, one bottle of each water was analyzed at approximately 1 week intervals. Bottles were inspected frequently for any signs of microbial growth. Any bottles exhibiting cloudiness, or unusual odors upon opening, were discarded.

Extraction and Sample Preparation. The pesticides were extracted from the water phase by liquid−liquid extraction using ethyl acetate as described by Suffet and Faust (1972). In contrast to other solvents tested, ethyl acetate allowed for the extraction of the triazines as well as the organophosphates in a single step with adequate recovery. A 225 mL aliquot of water sample was measured in a graduated cylinder and poured into a 250 mL volumetric flask, containing a Teflon-coated stir bar, followed by the addition of 25.0 mL of Fisher Optima grade ethyl acetate to the flask with a volumetric pipet. The flask was placed on a magnetic stirrer and mixed vigorously for 5 min. The stirring was vigorous enough so as to produce a large vortex encompassing the entire contents of the flask. After 5 min, the flask was removed from the stirrer, and the two phases were allowed to separate. All extractions were performed in triplicate and the results averaged.

The extraction procedure produced an upper layer of about 5 mL, which was about 97% ethyl acetate and 3% water. The upper layer was pipetted off and dried by passing it through an 8 mm × 5 in. Pasteur pipet containing a small plug of pesticide grade glass wool and about 2.0 g of granular ACS reagent grade anhydrous sodium sulfate. The sodium sulfate column was first cleaned with about 3 mL of dry ethyl acetate and the eluate discarded. The extract was then applied to the column with a Pasteur pipet and allowed to percolate through the column into a 10 mL glass vial. The column was then rinsed with about 3 mL of ethyl acetate which drained into the vial for a total extract volume of about 8 mL. The extract was then stored in a freezer until analyzed (≤1 day).

Immediately prior to analysis the extracts were concentrated from ~8 mL ~0.5 mL in a heated 10 mL Kuderna−Danish concentrator with a 2.5 cc/s nitrogen blow-down. The samples were spiked with internal standard (2-nitro-*m*-xylene) and then diluted with ethyl acetate to a final volume of exactly 0.75 mL and finally transferred to 2 mL screw capped vials with Teflon-lined closures for analysis. Example recoveries for the extraction−concentration procedure are given in Table 2. During the recovery experiments, the empty bottles were extracted with 10 mL of ethyl acetate to determine whether there had been significant sorption by any of the analytes to the container walls. None of the analytes were detected in the concentrated extract, and thus it was concluded that sorption to the container walls was insignificant.

Analytical Methods. All pesticide analyses were performed on a Perkin-Elmer 8500 gas chromatograph equipped with a nitrogen−phosphorus detector (Detector Engineering Technology, Inc., TID-2), using splitless 1.25 μL injection on a 60 m × 0.32 mm i.d. SPB-1 Column (Supelco, Inc.) and He as carrier gas. The injector and detector temperatures were 250 and 350 °C, respectively. The temperature program used was as follows: initial temperature 40 °C, 1 min hold; ramp to 180 °C at 30 °C/min, hold for 5 min; ramp to 220 °C at 5 °C/min, hold for 3 min; for a total run time of 21.6 min. The response of the detector was found to be linear in the concentration range of 0.5−25 ppm. Because of the detector sensitivity to H_2 flow, standard curves were prepared each day that samples were analyzed. The identity of each of the compounds was initially confirmed by GC/MS, and all compounds were identified by retention time thereafter. Organic carbon measurements were performed on a Dohrmann DC-80 TOC analyzer, using aqueous UV−persulfate oxidation. Conductivity measurements were performed with a Horizon Ecology Co. Model 1484 conductivity meter, and pH was measured with a Fisher Accumet 925 pH meter. Metal analyses were performed on an ARL ICP/AES instrument equipped with a 1.5 m grating.

Table 2. Average Recoveries of Pesticides from Buffered Milli-Q Water and Del Puerto Creek Water for Triplicate Ethyl Acetate Extractions Followed by Heated Kuderna−Danish Tube Concentration with Nitrogen Blow-Down[a]

	buffered Milli-Q water		Del Puerto Creek water	
pesticide	% recovery	CV	% recovery	CV
simazine	59.1	2.9	65.2	1.9
atrazine	69.0	2.1	73.9	3.8
diazinon	74.6	2.7	86.5	4.8
methylparathion	76.3	5.4	90.4	2.8
chlorpyrifos	75.1	6.0	90.9	4.1

[a] CV, coefficient of variation, percent relative standard deviation.

Hydrolysis Experiments in Buffered Milli-Q Water (32 and 24 °C). Twenty 1 L amber bottles were filled with 950 mL of 0.02 M ionic strength, pH 8.0, phosphate-buffered Milli-Q water, sterilized by autoclave, and spiked with the three organophosphate pesticides as described above. Simazine and atrazine were omitted since no degradation was observed in the previous experiments. The 32 °C samples (10 bottles) were maintained at 32 ± 0.5 °C in a water bath. The 24 °C samples (10 bottles) were placed in a cabinet near the floor at ambient temperature. A thermometer was placed in the cabinet to monitor the temperature. The temperature of the cabinet was observed to be at 24 ± 1 °C for the duration of the experiment. As before, the bottles were inspected frequently for any signs of microbial growth. Samples were taken at 10−15 day intervals.

Hydrolysis Products. The base-hydrolysis products for all of the pesticides used in this study are well-known (Howard, 1991). Standard solutions of these compounds were prepared and then analyzed using the same analytical procedures as for the parent pesticides. This was done in order to confirm that these compounds would not interfere with the analyses in any way. All five base-hydrolysis products were found to elute prior to the analytes of interest. The retention times for all analytes are given in Table 3. In addition, the response of the nitrogen−phosphorus detector was found to be approximately 3 times lower for the organophosphate base-hydrolysis products due to the loss of the phosphorothioate group. Therefore, these compounds did not affect the results of the pesticide analyses.

Mixing Experiment. Eight 500 mL Boston round amber bottles with Teflon-lined closures were prepared with 450 mL of pH 8.0 buffered Milli-Q water, 0.02 M ionic strength, and then sterilized by autoclave. The solutions were spiked under sterile conditions with the three organophosphates to give a nominal starting concentration of 50 μg/L. The bottles were subsequently placed on a Eberbach Corp. 2-speed shaker at the low speed (~120 oscillations/min). After 1 h, one bottle was removed, and the contents were divided into two 225 mL

Table 3. Retention Times of the Pesticides and Their Respective Base-Catalyzed Hydrolysis Products Using the Capillary GC−NPD Analytical Method Employed in This Study

pesticide	retention time (min)	base-hydrolysis product	retention time (min)
simazine	14.09	hydroxysimazine	4.65
atrazine	14.33	hydroxyatrazine	4.72
diazinon	15.55	2-isopropyl-4-methyl-6-hydroxypyrimidine	9.33
methylparathion	17.19	4-nitrophenol	10.29
chlorpyrifos	19.40	3,5,6-trichloropyridinol	10.50

Table 4. Summary of Results from the 40 °C Hydrolysis Experiments[a]

	observed pseudo-first-order rate constants, k_{obs} (day^{-1}), in natural and buffered Milli-Q water at pH 8.0 and 40 ± 0.5 °C (r^2 values)			
pesticide	Milli-Q	Orestimba Creek	Del Puerto Creek	Eucalyptus Ave Drain
diazinon	0.0411 (0.976)	0.0360 (0.938)	0.0363 (0.982)	0.0360 (0.919)
methylparathion	0.0680 (0.989)	0.0584 (0.981)	0.0592 (0.995)	0.0540 (0.989)
chlorpyrifos	0.0619 (0.992)	0.0571 (0.976)	0.0572 (0.991)	0.0417 (0.969)

[a] Atrazine and simazine are excluded as they showed no detectable decrease in concentration for the duration of the experiment.

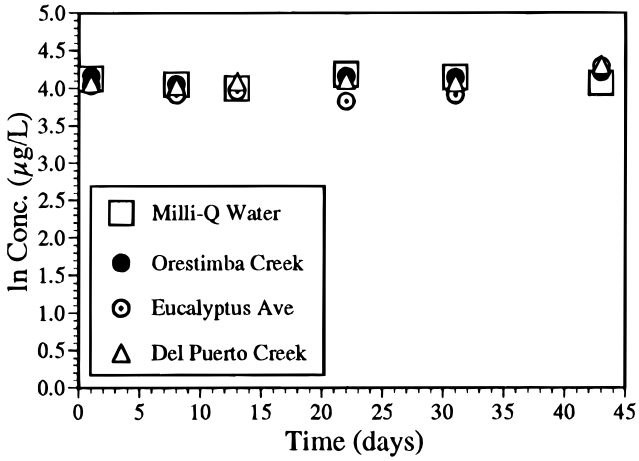

Figure 1. Observed concentration vs time data for simazine in sterile natural and pH 8.0 phosphate-buffered Milli-Q waters at 40 °C.

aliquots, extracted, and analyzed as previously described. The shaker remained on continuously, one bottle was removed each week for 7 weeks, and the residual concentration of the pesticides was determined in duplicate as previously described.

RESULTS AND DISCUSSION

Hydrolysis Experiments in Natural Waters. The results of the 40 °C hydrolysis experiments are summarized in Table 4. Simazine and atrazine showed no detectable decrease in concentration in any of the waters for the 43 day duration of the experiment. This result is consistent with other studies which have found that atrazine and simazine should hydrolyze extremely slow at pH 8.0 (Howard, 1991; Erickson and Lee, 1989). Plots of the experimental data for simazine and atrazine was shown in Figures 1 and 2, respectively. Because there was no observed change in concentration, the triazines inadvertently acted as recovery surrogates and reflect the consistency of the extraction−concentration procedure.

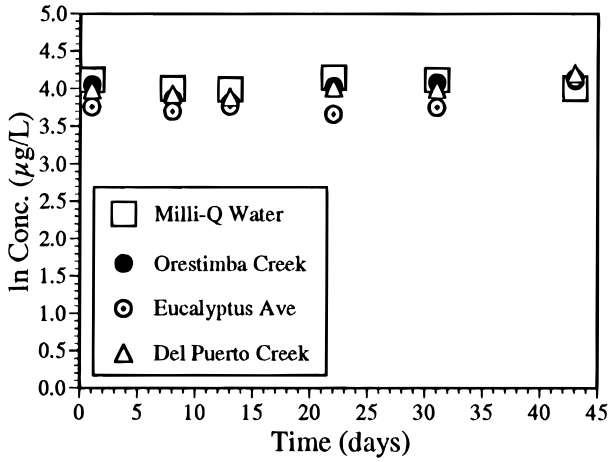

Figure 2. Observed concentration vs time data for atrazine in sterile natural and pH 8.0 phosphate-buffered Milli-Q waters at 40 °C.

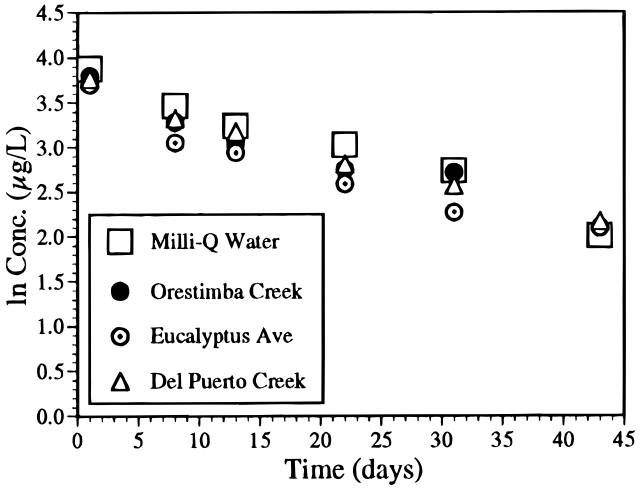

Figure 3. Observed concentration vs time data for diazinon in sterile natural and pH 8.0 phosphate-buffered Milli-Q waters at 40 °C.

It is noteworthy, however, that the presence of ~70 mg/L DOM had no catalytic effect on the transformation of the triazines. This is in contrast to the catalytic effect of humic substances that has been observed in the presence of 2% DOM (Li and Feldbeck, 1972) and in soils (Stevenson, 1994). These data suggest that abiotic hydrolysis is insignificant for atrazine and simazine at the pH's and DOM concentrations typical of most natural waters.

The hydrolysis data for diazinon, methylparathion, and chlorpyrifos are shown in Figures 3−5, respectively. Linear regression of these data reveals that the hydrolysis rates are faster in the buffered Milli-Q water in comparison to all three of the natural waters. Figure 6 shows a comparison of the pseudo-first-order half-lives for the three pesticides in the four different waters and the estimated 95% confidence limits. Although the error bars imply that the differences between the rate constants may not be statistically significant, the fact that the trend is consistent among the three pesticides suggests some validity. Two aspects of the data shown in Figure 6 are particularly important. First, the rates of hydrolysis appears to be most decreased in the water with the highest DOC concentration. Second, the decrease in hydrolysis rates is most pronounced for chlorpyrifos, the most hydrophobic of the three compounds with a log K_{ow} of 4.96 as compared to 3.81 and 2.86 for diazinon and methylparathion, respectively

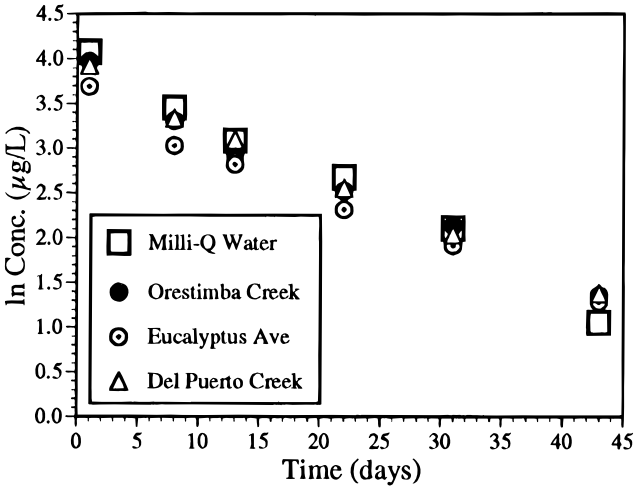

Figure 4. Observed concentration vs time data for methyl-parathion in sterile natural and pH 8.0 phosphate-buffered Milli-Q waters at 40 °C.

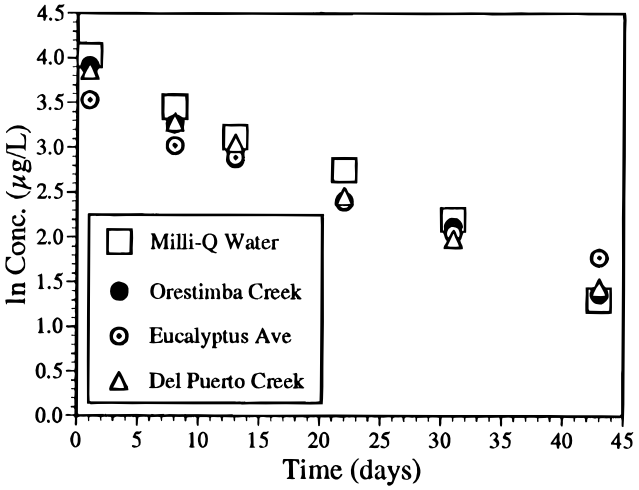

Figure 5. Observed concentration vs time data for chlorpyrifos in sterile natural and pH 8.0 phosphate-buffered Milli-Q waters at 40 °C.

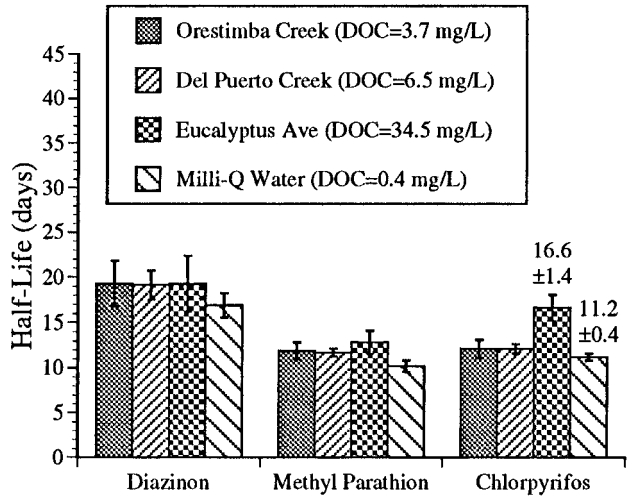

Figure 6. Comparison of the half-lives in the different waters for the three organophosphate pesticides at 40 °C and pH 8.0. The error bars represent the estimated 95% confidence limits.

(Howard, 1991). These two observations suggest that the slowing of hydrolysis rates may be related to the degree of association or "binding" of the pesticide to the DOM. This may be analogous to the observations of Macalady and Wolfe (1985), who found that the rate of alkaline hydrolysis was slowed by a factor of 7−11 for chlorpyrifos that was sorbed to sediments. Although the effect is not as profound in this study, the mechanism may be analogous. A few examples of an inhibitory effect on hydrolysis rates by humic substances have been previously reported (Macalady et al., 1989; Perdue and Wolfe, 1983).

The results of the natural water hydrolysis experiments are in contrast to the results of several other studies which found that chlorpyrifos hydrolyzed faster in natural waters relative to buffered distilled water (Racke, 1993). There is evidence to suggest that the increased hydrolysis rates may be due to the catalytic effect of certain chelate-forming metal species, such as Cu^{2+} (Blanchet and St. George, 1982; Chapman and Harris, 1984; Meikle and Youngston, 1978). Still, Macalady and Wolfe (1985) were unable to explain up to a 7-fold increase in the observed hydrolysis rate for chlorpyrifos in natural water as compared to buffered distilled water at pH 7.0 and 25 °C, on the basis of metal catalysis, biodegradation, sterilization method, oxidation, or sorption effects.

Effect of DOM on Pesticide Hydrolysis. The experiments reported herein were run at pH 8.0; thus, base hydrolysis would be expected to predominate. At this pH, the DOM would be negatively charged, due to deprotonation of the acidic functional groups. Thus, the ability of a nucleophile (e.g., OH^-) to react with DOM-bound organic compounds might be greatly diminished or even eliminated due to electrostatic repulsion and/or steric hindrance.

To test this hypothesis, we used the following kinetic approach for evaluation of the hydrolysis data:

$$\frac{dC_T}{dt} = -k_f C_{aq} - k_b C_b \quad (1)$$

where C_T is the total concentration of pesticide in the system, C_{aq} is μg of freely dissolved chemical/L of solution, C_b is μg of DOM-bound chemical/L of solution, and k_f and k_b are the freely dissolved and DOM-bound pseudo-first-order hydrolysis rate constants, respectively. Now define that

$$C_T = C_{aq} + C_b \quad (2)$$

and

$$K_B = \frac{C_b}{C_{aq}} = \frac{\mu\text{g of DOM-bound chemical}}{\mu\text{g of freely dissolved chemical}} \quad (3)$$

Now, substituting eqs 2 and 3 into eq 1:

$$\frac{d(C_{aq} + K_B C_{aq})}{dt} = -k_f C_{aq} - k_b K_B C_{aq} \quad (4)$$

which can be rearranged to

$$\frac{dC_{aq}}{C_{aq}} = \frac{-(k_f + k_b K_B)}{(1 + K_B)} \quad (5)$$

and integrated to

$$\ln C_{aq} = \frac{-(k_f + k_b K_B)}{(1 + K_B)} t + \ln C_{aq,o} \quad (6)$$

If it is assumed that no hydrolysis occurs in the DOM-bound state, then $k_b \rightarrow 0$ and eq 6 reduces to

$$\ln C_{aq} = \frac{-k_f}{(1 + K_B)}t + \ln C_{aq,o} \quad (7)$$

Now, since the most profound and statistically significant difference in hydrolysis rates was observed for chlorpyrifos in the Eucalyptus Ave water, these data will be used for evaluation. The observed rate constants for chlorpyrifos in Milli-Q water and Eucalyptus Ave drain water at 40 °C are $k_{obs} = k_f = 0.0619$ day^{-1} and $k'_{obs} = 0.0417$ day^{-1}, respectively (Table 4). Since the slope of the line described by eq 7 is the observed pseudo-first-order hydrolysis rate constant, we obtain

$$\frac{k_f}{1 + K_B} = k'_{obs} \quad (8)$$

and inserting the corresponding experimental data:

$$\frac{0.0619}{1 + K_B} = 0.0417 \quad (9)$$

Therefore, $K_B = 0.484$.

Thus, in order to explain the observed effect, about 32% of the total chlorpyrifos in the system must be bound to DOM at any given time and the rate of hydrolysis in the DOM-bound phase must be negligible. To evaluate the validity of this result, an implicit organic carbon-normalized partition coefficient for the binding of chemical to the DOM can be calculated. Recalling that

$$K_B = \frac{C_b}{C_{aq}} = \frac{C_{doc}[\text{DOC}] \times 10^{-6}}{C_{aq}} \quad (10)$$

where C_{doc} (μg of chemical/kg of DOC) is the organic carbon-normalized concentration of chemical in the DOM and [DOC] is the dissolved organic carbon concentration in mg/L. The factor of 10^{-6} is needed to convert the sorbent mass units from milligram to the more conventional kilogram. Now defining

$$K_{doc} = \frac{\mu\text{g of chemical/kg of DOC}}{\mu\text{g of chemical/L of solution}} = \frac{C_{doc}}{C_{aq}} \quad (11)$$

Therefore, combining eqs 10 and 11, we get

$$K_{doc} = \frac{K_B}{[\text{DOC}] \times 10^{-6}} = \frac{0.484}{3.45 \times 10^{-5}} = 14\,029 \text{ L/kg} \quad (12)$$

This result is well within the range of sediment and soil K_{oc} values for chlorpyrifos reported in the literature, i.e., 995−31000 L/kg (Racke, 1993). Furthermore, this result is reasonable based on the authors' own data for chlorpyrifos sorption to Orestimba and Del Puerto Creek sediments which are in the range of about 15000−30000 L/kg (Noblet and Suffet, 1996). Additional support for the feasibility of the implicit K_{doc} can be obtained by comparison to the DOM-binding behavior of other compounds reported in the literature. If it is assumed that the extent of binding to DOM is related primarily to the hydrophobicity of the compound, then compounds of similar hydrophobicity should exhibit similar DOM-binding behavior. In one such example, McCarthy and Jimenez (1985) determined the DOM-binding behavior of anthracene (log K_{ow}= 4.45) to Aldrich humic acid (MW ≥ 1000) using equilibrium dialysis and fluorescence techniques. They observed that at [DOC] = ∼35 mg/L, the K_{doc} for anthracene was about 14 000. This is identical with the value implied herein for chlorpyrifos (log $K_{ow} = 4.96$).

The lower degree of DOM binding for chlorpyrifos relative to anthracene based on the K_{ow}'s can easily be explained by the differences in the nature of the DOM used in the experiments. Another consideration is the effect of temperature, since sorption tends to decrease as temperature increases (Schwarzenbach et al., 1993). The experiments in this study were conducted at 40 °C, and therefore the observed effects could be exacerbated by a greater degree of DOM binding at lower experimental and typical field temperatures.

Determination of Arrhenius Parameters. The similarities and differences in hydrolysis rates among the natural and buffered Milli-Q waters observed in these experiments are important in terms of understanding hydrolysis mechanisms and the relative impact of DOM on the fate of pesticides in natural waters. However, the most profound decreases in hydrolysis rate were observed in water from Eucalyptus Ave drain, which at ∼70 mg/L DOM clearly represents an extreme case. Orestimba and Del Puerto Creeks are more representative of agricultural drainage in the region, and Figure 6 shows that the corresponding decreases in hydrolysis rates (as increases in half-lives) for these waters relative to buffered Milli-Q water (12%, 14%, and 8% for diazinon, methylparathion, and chlorpyrifos, respectively) were within the 95% confidence limits. Given these caveats on the natural water data, it seemed appropriate to perform subsequent experiments for the determination of Arrhenius parameters in buffered Milli-Q water. In addition to the resulting Arrhenius data being more generally applicable to all waters, the use of buffered Milli-Q water would allow for sterilization by autoclave, thus eliminating the difficulties associated with the filter sterilization of large volumes of natural water.

The temperature dependence of many reactions can be described by the empirical Arrhenius equation (Schwarzenbach et al., 1993). The equation can be written in log-linear form as

$$\ln k_{obs} = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right) \quad (13)$$

where A is the pre-exponential or frequency factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. For a reaction that exhibits Arrhenius temperature dependence, a plot of ln k_{obs} vs $1/T$ will give a straight line with a slope of E_a/R and the intercept equal to ln A. Arrhenius plots of the hydrolysis data for the three organophosphates are shown in Figures 7−9. The data do appear to exhibit an Arrhenius dependence on temperature, and therefore the parameters derived by linear regression can be used to predict hydrolysis rates at any temperature of interest. The Arrhenius data obtained are summarized in Table 5. These Arrhenius parameters can in turn be used to estimate the hydrolysis rates at the lower temperatures more characteristic of field conditions. These results show the importance of performing hydrolysis experiments at multiple temperatures. In the absence of Arrhenius data, there would have been no way to predict the approximately 7-, 6-, and 5-fold decreases in hydrolysis rates for the 10 °C drop from 25 °C to the field temperature of 15 °C for diazinon, methylparathion, and chlorpyrifos, respectively.

Although it is difficult to compare hydrolysis rates directly because of small differences in experimental

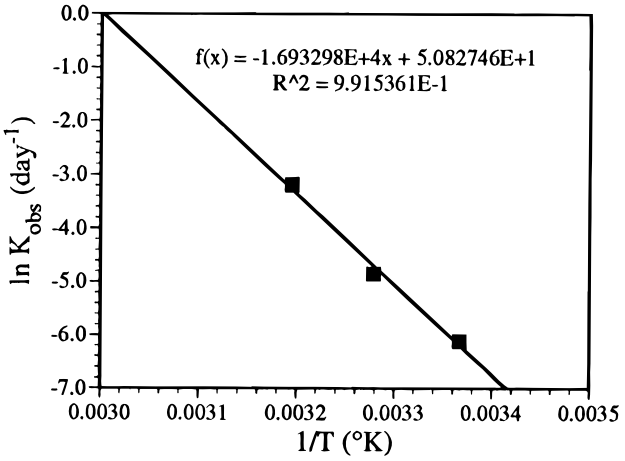

Figure 7. Arrhenius plot of the abiotic hydrolysis rate data for diazinon in pH 8.0 phosphate-buffered Milli-Q water.

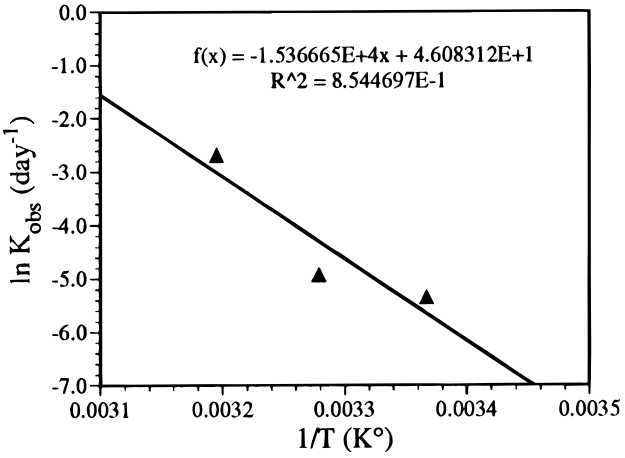

Figure 8. Arrhenius plot of the abiotic hydrolysis rate data for methylparathion in pH 8.0 phosphate-buffered Milli-Q water.

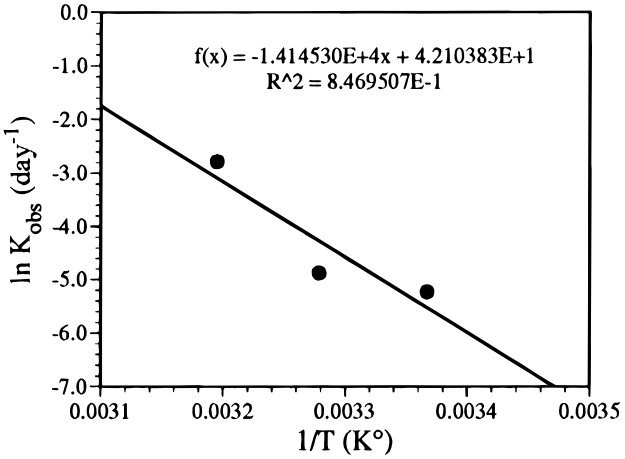

Figure 9. Arrhenius plot of the abiotic hydrolysis rate data for chlorpyrifos in pH 8.0 phosphate-buffered Milli-Q water.

conditions, the Arrhenius data from this study predict hydrolysis rates for these pesticides that are much slower than those previously reported (Howard, 1991; Racke, 1993; LaCorte et al., 1995; Lartiges and Garrigues, 1995). Indeed, the calculated hydrolysis half-lives for diazinon, methylparathion, and chlorpyrifos at a nominal field temperature of 15 °C are 1988, 1000, and 769 days, or 5.4, 2.7, and 2.1 years, respectively. These results are particularly interesting inasmuch as most of the discussion of these compounds in the literature has focused on explaining the enhancement of hydrolysis rates due to a variety of factors such as biodegradation and the presence of certain metal species. Most of the reported half-lives for diazinon range from 54 days at pH 8.0 and 25 °C (Chapman and Cole, 1982) to 185 days at pH 7.4 and 20 °C. Half-lives for methylparathion range from 16 days at 25 °C and pH 8.5 in fresh water to 231 days at 25 °C and pH 7.0 in sea water (Badawy and El-Dib, 1984; Howard, 1991). Chlorpyrifos has been reported to have hydrolysis half-lives of 23 and 54 days, at pH 8.1, for 25 and 15 °C, respectively (Meikle and Youngston, 1978). Walker et al. (1988), reported half-lives of 14−24 days for chlorpyrifos in estuarine water, nonsterile and sterilized with formaldehyde, at 25 °C. Macalady and Wolfe (1983) offered a rate constant of 6.22×10^{-6} min^{-1} as their "best estimate" for neutral hydrolysis at 25 °C in buffered distilled water; which corresponds to a half-life of ∼77 days. Although not explicitly reported, Sharom et al. (1980) show a plot of diazinon hydrolysis in unsterilized distilled water at 21 ± 1 °C and pH ∼7, wherein the half-life appears to be about 70 days. The same study found that chlorpyrifos and parathion exhibited half-lives of ∼12 and ≫16 weeks, respectively. Only about 10% of the parathion had hydrolyzed after 16 weeks. A comparison between methylparathion and parathion is probably valid since methyl analogs have been shown to hydrolyze at similar, but somewhat faster, rates (Gomaa et al., 1969; Freed et al., 1979). Fewer studies have determined the Arrhenius parameters for these compounds. A comparison of the activation energies determined in this study to those previously reported is presented in Table 5. Again, the results from this study show activation energies significantly higher than those previously reported.

Table 5. Hydrolysis Rate Constants and the Resulting Arrhenius Data for the Three Organophosphate Pesticides in pH 8.0 Phosphate-Buffered Milli-Q Water

	k_{obs} (day^{-1})			Arrhenius parameters	
pesticide	40 °C	32 °C	24 °C	E_a (kcal/mol)	ln A
diazinon	0.041 1	0.007 86	0.002 22	33.7	50.83
methylparathion	0.068 0	0.007 23	0.004 75	30.5	46.08
chlorpyrifos	0.061 9	0.007 66	0.005 34	28.1	42.10

The interpretation of the hydrolysis data is complicated by several factors. First, these compounds are known to undergo both neutral and acid- and/or base-catalyzed hydrolysis (Freed et al., 1979). At pH 8.0, it is reasonable to suspect a significant contribution from both hydrolytic mechanisms. Thus, the observed hydrolysis rates are most likely the result of two competing hydrolysis mechanisms, each with their own activation energies. Thus, it would be more appropriate to refer to the activation energies determined as "apparent activation energies" since the specific mechanisms are not known (Brezonik, 1994).

Metals. Each of the natural waters used in this study were analyzed by ICP/AE for the following elements: P, Na, K, Ca, Mg, Zn, Cu, Fe, Mn, B, Mo, Al, Si, Ti, V, Co, Ni, Cr, Pb, Sr, Ba, Li, As, Se, Cd, Ag, and Sn. The results from ICP/AE analyses showed low levels (<5 ppb; Sn < 15 ppb) of heavy metals in the natural waters used in this experiment. This result is consistent with the fact that no increase in hydrolysis rates was observed in the natural waters relative to Milli-Q water. Therefore, it seems safe to infer that dissolved inorganic species had little or no influence on the hydrolysis rates observed in this study, save for their effect on pH and ionic strength.

Table 6. Comparison of Apparent Hydrolysis Activation Energies Determined in This Study to Selected Values Reported in the Literature

pesticide and water type	pH	activation energy, E_a (kcal/mol)[a]	reference
diazinon			
buff Milli-Q	8.0	33.7	this study
buff distilled	3.1	13.15	Gomaa et al., 1969
buff distilled	10.4	14.29	Gomaa et al., 1969
Milli-Q	6.1	3.1	Lartiges and Garrigues,[a] 1995
river	7.3	3.5	Lartiges and Garrigues,[a] 1995
filtered river	7.3	7.6	Lartiges and Garrigues,[a] 1995
seawater	8.1	3.9	Lartiges and Garrigues,[a] 1995
methylparathion			
buff Milli-Q	8.0	30.5	this study
buff distilled	11.0	9.9	Badawy and El-Dib, 1984
Milli-Q	6.1	7.0	Lartiges and Garrigues,[a] 1995
river	7.3	6.1	Lartiges and Garrigues,[a] 1995
filtered river	7.3	9.7	Lartiges and Garrigues,[a] 1995
seawater	8.1	8.8	Lartiges and Garrigues,[a] 1995
chlorpyrifos			
buff Milli-Q	8.0	28.1	this study
buff distilled	7.4	14.0	Freed et al., 1979
buff distilled	4.7	22.8	Meikle and Youngston, 1978
buff distilled	6.9	19.0	Meikle and Youngston, 1978
buff distilled	8.1	21.8	Meikle and Youngston, 1978
pond water	8.0	17.5	Macalady and Wolfe, 1983
buff distilled	4.5−7.5	22.1 ± 0.8	Macalady and Wolfe, 1983
buff distilled	11.25	13.0 ±1.5	Macalady and Wolfe, 1983

[a] The reported data therein are for nonsterile waters and therefore may include a biodegradation component.

Table 7. Effect of Continuous Shaking on the Observed Pseudo-First-Order Hydrolysis Rates of the Three Organophosphate Pesticides

	$T_{1/2}$ at 29 °C (days)			
pesticide	with shaking[a]	without shaking[b]	apparent temp (°C)[c]	effective ΔT (°C)[d]
diazinon	108.9	130	30.0	+1.0
methylparathion	63.4	84	30.7	+1.7
chlorpyrifos	62.2	79	30.5	+1.5

[a] Elevated temperature due to heat from shaker motor; stable at 29 ± 0.5 °C. [b] Hydrolysis rate at 29 °C estimated using the Arrhenius parameters determined herein. [c] Apparent temperature to account for observed shaking hydrolysis rates estimated from Arrhenius data. [d] Effective ΔT, estimated equivalent temperature change necessary to account for the observed hydrolysis rate increase due to shaking.

Possible Experimental Artifacts. It is evident that experimental errors such as losses due to volatilization, biodegradation, pH changes, etc., would cause results opposite in the sense to those observed. The erroneous lowering of observed hydrolysis rates could stem from several possible causes: (1) contamination of glassware used for extraction, (2) changing of extraction efficiency as a function of analyte concentration, (3) degradation of pesticide standards and/or internal standard, (4) degradation products or other compounds coeluting with analytes, and/or (5) sorption−desorption to container walls. After careful consideration and investigation of each of the above factors, the authors concluded that the experimental controls were sufficient to preclude these processes from having a significant effect on the experimental observations. Thus, the authors firmly believe the data obtained in this study are valid and not the result of experimental artifacts.

Effect of Mixing on Hydrolysis Rates. The results of the continuous shaking hydrolysis experiment are summarized in Table 7. Due to heat emanating from the shaker motor, the ambient temperature of the water was consistently 29 ± 0.5 °C during the course of the experiment (50 days). In order to evaluate the effect of continuous mixing, the Arrhenius parameters were used to estimate the nonshaking hydrolysis rates at 29 °C. The hydrolysis rates measured for the shaking experiment were faster than the predicted nonshaking rates for all three pesticides. Presumably, vigorous mixing is analogous to increasing temperature in that the primary effect is to increase the kinetic energy of the molecules in solution and thus increase the number of molecular collisions per unit time. The hydrolysis mechanism is governed primarily by the pH (Freed et al., 1979) and thus should not be directly affected by temperature or mixing. Therefore, to quantify the effect of shaking on hydrolysis rates, the notion of an "effective temperature" was employed. Using the Arrhenius data for nonshaking conditions, the temperature necessary to produce the observed shaking hydrolysis rates was estimated and compared to the actual temperature of the experiment. Thus, an effective temperature change, ΔT_{eff}, due to mixing alone can be determined, and the relative impact of mixing on the observed hydrolysis rates can be estimated. These data are shown in Table 6. The estimated effective temperature changes of ∼1−2 °C clearly show that the relative impact of vigorous mixing on the observed hydrolysis rates is minimal. Therefore, the absence of mixing cannot explain the slow hydrolysis rates observed in this study. In addition, this result has important implication for environmental modeling, in that the energetics of an aquatic system need not be considered as an additional parameter for the accurate prediction of abiotic transformation rates.

Conclusions. The results of this study have important implications for pesticide fate modeling in aquatic systems. For the triazines, the results suggest that dissolved humic substances alone are not sufficient to catalyze transformations and that a solid substrate, i.e., sediment or soil, may play an important role.

The data for the organophosphates suggest that in addition to facilitating transport, DOM may also impede the abiotic hydrolytic degradation of these pesticides. The Arrhenius data derived in this study emphasize the importance of understanding the temperature dependence of environmental fate processes. The effect of vigorous mixing on the observed hydrolysis rates of the organophosphates was found to be minimal, equivalent to only a 1−2 °C increase in temperature. Thus, the

lack of continuous mixing cannot explain the slow hydrolysis rates observed. These results suggest that in the absence of catalytic effects, abiotic hydrolysis is very slow for these pesticides under typical field conditions and may be insignificant relative to other fate processes. Moreover, the results underscore the need for developing a greater understanding of the relative impact of processes such as catalysis, biodegradation, and DOM association on the fate of organophosphate pesticides.

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