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Impacts of Salinity on the Hydrolysis of Chlorpyrifos

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ABSTRACT: The organophosphate insecticide, chlorpyrifos, was used as a probe to assess the individual effects of salinity and trace metals in seawater on its hydrolysis rate as their influence on organic chemicals remains poorly characterized. This investigation measured the hydrolytic degradation of chlorpyrifos to its transformation product, 3,5,6-trichloro-2-pyridinol (TCP), in five sterilized/buffered media: 25 parts per thousand (ppt) artificial seawater, 25 ppt sodium chloride (NaCl), 10 parts per billion (ppb) copper, 0.5 ppb copper, and buffered deionized water (0 ppt). Chlorpyrifos hydrolyzed 21, 62, and 13% faster in 25 ppt seawater, 10 ppb copper, and 0.5 ppb copper, respectively, and 40% slower in 25 ppt NaCl compared to 0 ppt. The formation of TCP in each medium was consistent with the observed degradation of chlorpyrifos. Trace amounts of copper at concentrations similar to those observed in freshwater environments and seawater accelerated the hydrolytic rate, while NaCl significantly inhibited it. This research illustrates the importance of considering the combined influences of trace metals as well as salinity when evaluating the environmental fate of hydrophobic organic compounds in aquatic ecosystems.

KEYWORDS: *hydrolysis, chlorpyrifos, salinity, seawater, copper, sodium chloride, organic contaminant, pesticide, degradation, surface water*

INTRODUCTION

Water quality issues have long been recognized as one of the major byproducts of agricultural practices. This includes pesticide inputs to streams, lakes, and groundwater associated with agricultural watersheds. Once applied, pesticides have the potential to contaminate not only surface waters directly adjacent to agricultural activities but also those located significantly farther downstream including estuarine and marine ecosystems. The chemical composition of the water changes as these systems transition from freshwater to estuarine, potentially influencing the persistence of pesticides and other water contaminants. Consequently, assessing the occurrence and behavior of pesticides in these dynamic systems is critical for evaluating their potential to harm aquatic ecosystems and contaminate natural resources. Chlorpyrifos is an organophosphate insecticide used on agricultural food and feed crops, cattle ear tags, golf course turf, industrial plants, and treated wood products.[1] With a K_{oc} of 360−31,000, it is classified as having low mobility in soils.[2] However, it may be still susceptible to transport to surface waters in areas where it is applied close to aquatic environments.[2] This is problematic as chlorpyrifos is highly toxic to aquatic organisms and birds at trace levels.[3,4] Furthermore, residues of chlorpyrifos in food have been reported to be linked with a range of human health problems including loss of working memory, reduced IQ, delayed motor development, seizures, tremors, blurred vision, and weight loss.[2,5] Therefore, understanding how changing water conditions affect the degradation of chlorpyrifos in aquatic environments is critical for evaluating its potential to harm such organisms.

Hydrolytic degradation is a major removal process of chlorpyrifos in aquatic systems.[6] This typically involves the breakdown of one of its phosphoric or thiophosphoric esters which can be initiated by either a nucleophilic or electrophilic attack and is strongly dependent on pH and other solution constituents.[7,8] Water and hydroxide ions are generally presumed to be the primary nucleophiles in an aquatic system.[8] However, previous research reveals that the presence of metal ions must be considered as possible electrophiles.[8] When present at concentrations higher than what is typically found in environmental systems, dissolved copper, Cu(II), has been reported to accelerate the hydrolysis of organophosphate pesticides.[9,10] However, the individual effects of natural water constituents such as salinity and seawater ions including Cu(II) (at environmentally relevant concentrations) and sodium chloride (NaCl) on the hydrolysis of chlorpyrifos remain poorly characterized. For instance, previous studies that investigated the hydrolysis of chlorpyrifos either excluded the effects of salinity or used field samples containing multiple other constituents (e.g., dissolved organic matter, particulate carbon, and other dissolved solids) that were unable to isolate individual component effects.[7,11] This is important to address as the hydrolysis of chlorpyrifos is reported to be significantly accelerated by multiple factors such as a basic pH, Cu(II), and other natural water constituents.[7,8,11] Without investigating the effects of these parameters individually, it is difficult to determine whether its hydrolytic rate is enhanced primarily by

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an elevated pH, Cu(II) concentration, salinity, or a combination thereof in surface waters. Therefore, the extent that salinity contributes to accelerating the hydrolytic rate, if at all, remains unclear.

In addition, the majority of studies that have investigated the impact of Cu(II) on the hydrolysis of chlorpyrifos used Cu(II) concentrations significantly higher than the average concentration in inland freshwaters, 10 parts per billion (ppb), and seawater, <1 ppb, or used field water samples that did not isolate its effects.[10,12] For example, Meikle and Youngson used 0.953 parts per million (ppm) and Blanchet and St-George used 36.86 ppm as the lowest Cu(II) concentration to evaluate its impact on the hydrolysis of chlorpyrifos which are considerably higher than what is found in the environmental systems.[9,10] Additionally, other experiments that investigated the catalytic mechanism of Cu(II) on chlorpyrifos hydrolysis were conducted in solvent−water mixtures instead of pure water.[13] Last, many studies have solely used NaCl to evaluate the impacts of salinity on both the toxicity and abiotic degradation of hydrophobic organic compounds in the environment.[14−16] While NaCl is the most abundant salt in seawater, using it to characterize chemical degradation mechanisms in marine environments neglects to account for the potential effects of multiple other metals found in seawater, including but not limited to Cu(II).[17,18] Since it is hypothesized that salinity based upon artificial seawater (ASW) will accelerate the hydrolysis of chlorpyrifos due to the presence of Cu(II), the influence of salinity based upon NaCl was also investigated to evaluate the influence of ionic strength.

A knowledge gap exists in defining the effects of salinity and environmentally relevant concentrations of Cu(II) on the hydrolysis of chlorpyrifos. The primary objective of this research was to use chlorpyrifos and 3,5,6-trichloro-2-pyridinol (TCP) as probes to help characterize the potential impacts of salinity (based upon NaCl and ASW) and environmental Cu(II) on the hydrolysis of organic contaminants. This was conducted by isolating the influence of each medium on the hydrolysis of chlorpyrifos under constant pH and temperature conditions in sterilized, buffered deionized (DI) water. Specifically, this research strives to answer whether salinity alone is capable of accelerating its hydrolysis. It also aims to determine whether the trace amount of Cu(II) common in seawater and freshwater environments can catalyze its hydrolysis. Last, it attempts to establish the different effects (if any) of using NaCl as a salinity source versus seawater.

MATERIALS/METHODS

Reagents and Solvents. Chlorpyrifos and TCP were purchased from Chem Service (West Chester, PA). NaCl and sodium borate ($Na_2B_4O_7$) were from Fisher Scientific (Pittsburgh, PA), and copper (II) chloride ($CuCl_2$) was from Sigma-Aldrich (St. Louis, MO). Hydrochloric acid (1 M) was obtained from Mallinckrodt Chemical Company (Paric, KY). All solvents were of high-performance liquid chromatography (HPLC) grade and were used without further purification. Acetonitrile (ACN) and water were from Fisher Scientific, and methanol was from VWR (Radnor, PA). Instant Ocean (Blacksburg, VA) was used as ASW and mixed in sterilized DI water according to directions on the package.

Hydrolysis Experiments. Samples of chlorpyrifos were prepared from a 1000 ppm stock solution in ACN that was later diluted for analysis in each medium. The stock solution was diluted to 35 ppb in various solutions, including sterilized DI water, 25 parts per thousand (ppt) ASW, 25 ppt NaCl, 10 ppb $CuCl_2$, and 0.5 ppb $CuCl_2$. To determine if Cu(II) may enhance the hydrolysis of chlorpyrifos in seawater, the hydrolysis rate was analyzed in 10 ppb Cu(II) and 0.5 ppb Cu(II) solutions which are similar to the average Cu(II) concentrations in inland freshwaters and natural seawater, respectively.[7,12] Natural seawater is known to contain dissolved organic matter and other constituents in varying amounts which could also impact rates, and as the scope of this work was limited to isolating the impacts of salinity from trace Cu(II) concentrations, hydrolysis experiments in natural seawater were not conducted. 35 ppb is well below the reported aqueous solubility of chlorpyrifos of 1.39 ppm in DI water or that of 73 ppb in seawater.[19] The cosolvent was less than 0.25% of the total volume for all solutions. All samples were sterilized and buffered to a pH of 8.15 using a 0.01 M sodium borate buffer (with the exception of the ASW which already had a pH of 8.15) adjusted with hydrochloric acid. This value represents the approximate pH of seawater.[20] The pH of each sample was measured using a Mettler Toledo S220 Seven Compact pH meter, and the salinity of each sample was confirmed using a YSI Model 85. Sterilization was conducted using a Steris Amsco Century SG-120 Scientific Gravity Sterilizer. For each medium, two replicate 900 mL samples were made and stored in capped, 950 mL Trace Clean amber glass bottles (VWR). During each sampling event, two 60 mL aliquots were taken from each 900 mL sample for a total of four aliquots per media type ($n = 4$ for each sampling point). All samples were kept in a dark incubator (Forma Scientific Model 3932) set at 20 °C throughout the entirety of the experiment. Sampling of each bottle was conducted every 2 weeks over a 12 week period with the exception of the 10 ppb Cu(II) solution as it degraded by over two half-lives by the end of week 8. The pH of each sample was remeasured during every sampling event to ensure that the hydrolysis reactions were not affecting the buffered pH value. The pH for all samples remained between 8.15 ± 0.03 throughout the 12 week period.

Sample Preparation and Extraction. Each 60 mL aliquot was acidified to a pH of 1.5 to improve the recovery of TCP (a pK_a of 4.55) using 20−25 drops of 1 M hydrochloric acid.[19] Once acidified, the chlorpyrifos and TCP residues were extracted from 60 mL aliquots using C18 solid-phase extraction (SPE) cartridges (100 mg of sorbent, 3 mL of reservoir volume) from Thermo Fisher (Waltham, MA) placed on a vacuum manifold to capture the analytes. Cartridges were preconditioned with 3 mL of methanol and 3 mL of DI water prior to adding the sample. Residual pesticide was eluted from the cartridge with 2 mL of methanol for both compounds. The extracts were transferred into 2 mL borosilicate amber glass vials obtained from Agilent (Santa Clara, CA) and immediately analyzed by HPLC. Recoveries of chlorpyrifos and TCP averaged 85 ± 5% and 90 ± 4%, respectively, for all media types ($n = 8$).

HPLC Analysis. An Agilent 1260 Infinity high performance liquid chromatograph equipped with a diode array detector was used to analyze chlorpyrifos and TCP in the SPE extracts. Both compounds were separated on an Agilent Zorbax Eclipse C18 column using a gradient mobile phase consisting of ACN and water with a flow rate of 0.7 mL/min and an injection volume of 40 μL. Chlorpyrifos and TCP were detected at 288 and 300 nm, respectively. External standards were used to quantify the concentrations of both analytes. Limits of detection were 20 and 15 ppb for chlorpyrifos and TCP, respectively. At each sampling point ($t = 0$, 2, 4, 6, 8, 10, and 12 weeks), the concentration of TCP and percent residual chlorpyrifos remaining in solution was averaged across aliquots ($n = 4$) for each medium and plotted as a function of time. The pseudo-first-order rate constant was calculated from the plot of the $\ln C/C_0$, where $\ln C/C_0 = -kt$ (k = the pseudo-first-order rate constant in days and t = time). The half-life was calculated from the rate constant, where $t_{1/2} = (\ln 2)/k$. The formation rate of TCP was calculated using the formula rate = $\Delta[C]/\Delta[t]$, where $\Delta[C]$ is the change in TCP concentration during time period $\Delta[t]$. The hydrolysis rate of chlorpyrifos and the formation rate of TCP in the five different media types were analyzed relative to those in buffered DI water using one-way analysis of variance and the Games−Howell post-hoc test at $\alpha = 0.05$. IBM SPSS Statistics was used for the statistical analysis.

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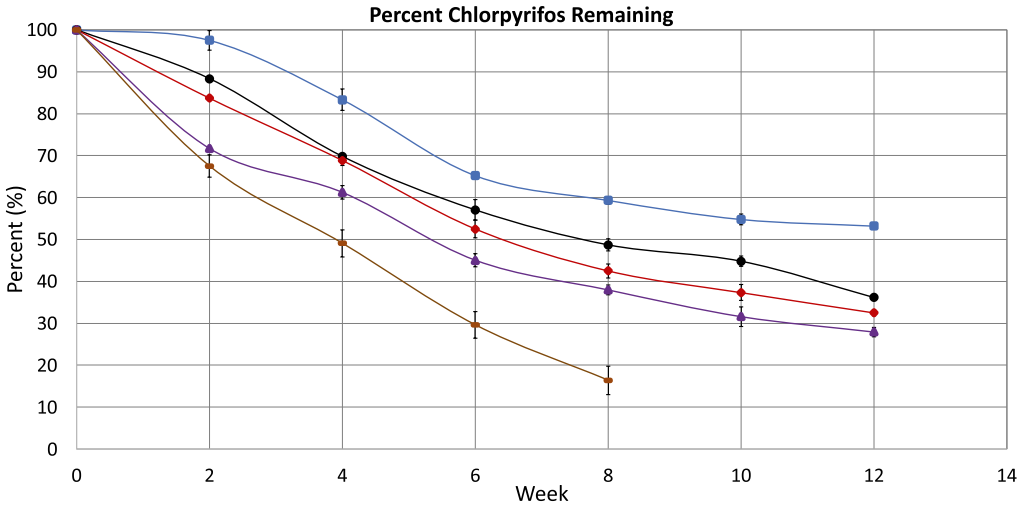

Figure 1. Percent of chlorpyrifos remaining in various media over the 12 week period. ● = buffered DI water, violet ▲ = 25 ppt ASW, blue ■ = 25 ppt NaCl, brown − = 10 ppb Cu(II), red ◆ = 0.5 ppb Cu(II). Error bars indicate standard error (n = 4).

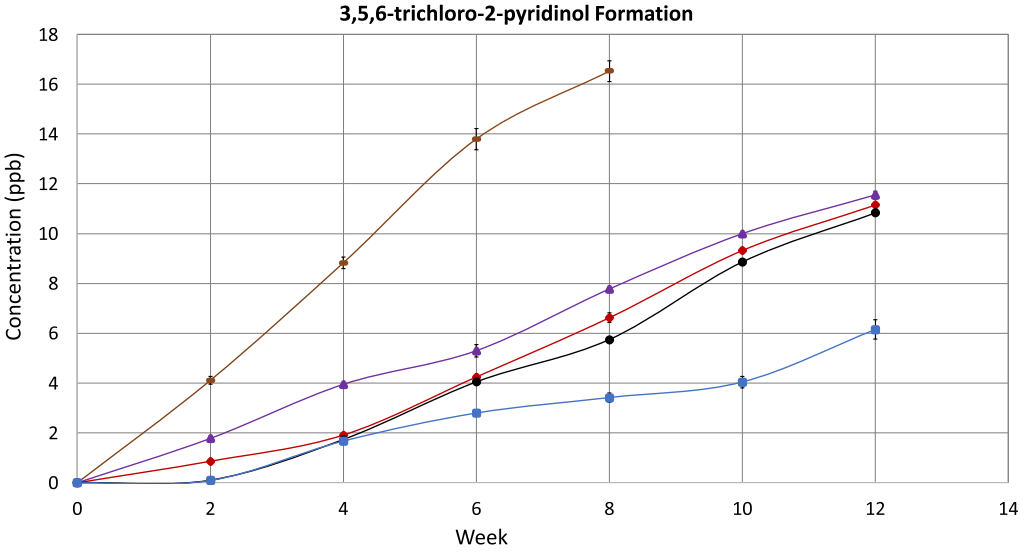

Figure 2. Formation of TCP in various media over the 12 week period. ● = buffered DI water, violet ▲ = 25 ppt ASW, blue ■ = 25 ppt NaCl, brown − = 10 ppb Cu(II), red ◆ = 0.5 ppb Cu(II). Error bars indicate standard error (n = 4).

RESULTS AND DISCUSSION

Degradation Rates and Half-Lives. Chlorpyrifos was degraded quantitatively by hydrolysis to form one major product, TCP, in all solutions (Figures 1 and 2). The hydrolysis rate followed apparent pseudo-first-order kinetics (Figure 3), and the rate constant and estimated half-life were dependent on media type (Table 1). With the exception of 25 ppt NaCl, chlorpyrifos degraded by more than one half-life over the 12 week period in all solutions. Hydrolysis rate constants ranged from 0.0087 ± 0.0002 to 0.0319 ± 0.0029 day^{-1} (over a 3.5-fold range) which correspond to half-lives of 79.67 and 21.73 days, respectively. The hydrolysis half-life was 56.82 ± 0.64 days in buffered DI water, 44.86 ± 2.69 days in 25 ppt ASW, 79.67 ± 4.10 days in 25 ppt NaCl, 21.73 ± 2.33 days in 10 ppb Cu(II), and 49.69 ± 1.56 days in 0.5 ppb Cu(II). These values fall within the range of recently reported half-lives for other organophosphate pesticides.[21] There was a significant difference between hydrolysis rates among each of the five media types (p < 0.001) relative to buffered DI water. These differences became more apparent when these rates were extrapolated to times required for 90% dissipation. Based upon pseudo-first-order kinetics, the time for 90% dissipation was also calculated for each media type to be 188.7, 148.6, 264.7, 72.23, and 164.5 days in buffered DI water, 25 ppt ASW, 25 ppt NaCl, 10 ppb Cu(II), and 0.5 ppb Cu(II), respectively.

Influence of ASW and Cu(II) on the Degradation of Chlorpyrifos. Chlorpyrifos degraded more rapidly in 25 ppt ASW ($t_{1/2}$ = 44.86 ± 2.69 days) compared to that in buffered DI water ($t_{1/2}$ = 56.82 ± 0.64 days) with a 21% shorter half-life (Figure 1 and Table 1). Instant Ocean ASW has been reported to have a slightly higher concentration (11 ppb) of Cu(II) compared to natural seawater (<1 ppb).[12,22,23] Therefore, the 10 ppb Cu(II) solution reflects both the average concentration in most inland freshwater systems and approximate concentration in an ASW solution.[12] Chlorpyrifos hydrolyzed significantly faster in both the 0.5 ppb Cu(II) and 10 ppb Cu(II) solutions compared to that in buffered DI water with 13 and 62% shorter half-lives, respectively. The increased rate in 0.5 and 10 ppb Cu(II) suggests that the average concentration of Cu(II) in natural seawater as well as in

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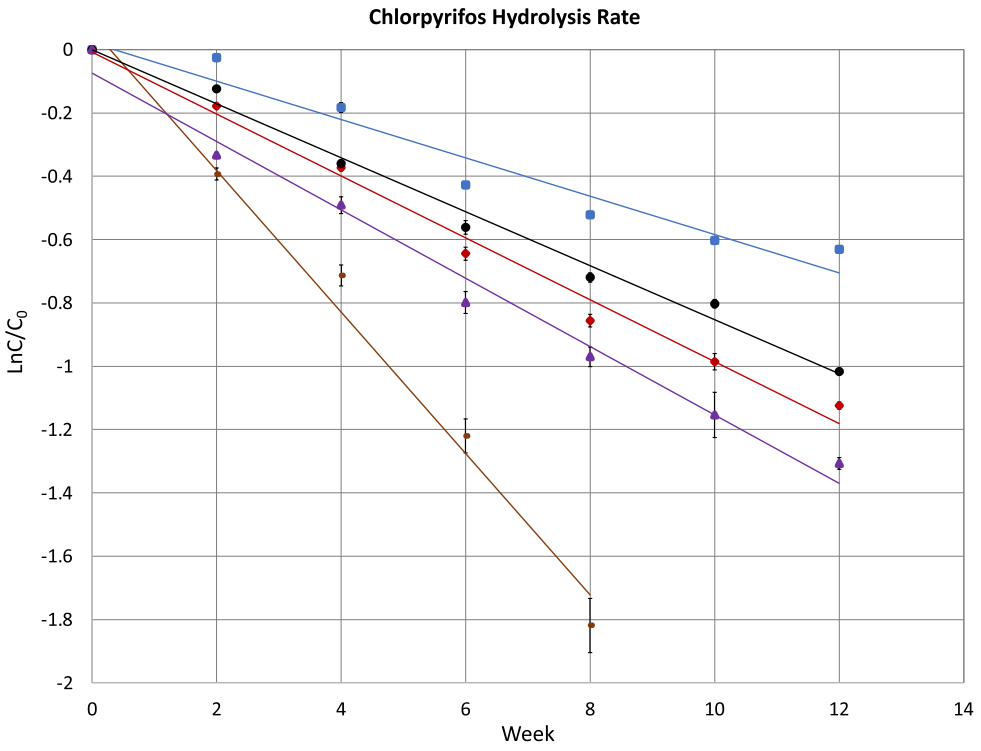

Figure 3. Chlorpyrifos hydrolysis rate in various media over the 12 week period. ● = buffered DI water, violet ▲ = 25 ppt ASW, blue ■ = 25 ppt NaCl, brown − = 10 ppb Cu(II), red ◆ = 0.5 ppb Cu(II). Error bars indicate standard error (n = 4).

Table 1. Hydrolysis Rate Constants and Half-Lives of Chlorpyrifos for Each Medium[a]

solution	rate constant (day^{-1})	r^2	$t_{1/2}$ (days)
0 ppt	0.0122 ± 0.0003	0.99	56.82 ± 0.64
25 ppt ASW	0.0155 ± 0.0009	0.99	44.86 ± 2.69
25 ppt NaCl	0.0087 ± 0.0002	0.94	79.67 ± 4.10
10 ppb Cu(II)	0.0319 ± 0.0029	0.99	21.73 ± 2.33
0.5 ppb Cu(II)	0.0140 ± 0.0005	0.99	49.69 ± 1.56

[a]Values after ± indicate standard deviation (n = 4).

most freshwater systems can accelerate its hydrolysis. This suggests that Cu(II) could be a contributing cause of the accelerated hydrolysis rate in ASW compared to that in buffered DI water or in NaCl solution. Overall, chlorpyrifos appears to be very sensitive to trace Cu(II) concentrations representative of those found in environmental systems as its half-life in 10 ppb Cu(II) was roughly 28 days shorter than in 0.5 ppb Cu(II) or 56% shorter. The mechanism by which Cu(II) catalyzes chlorpyrifos hydrolysis has been described in prior research as the formation of a Cu(II) chelate with nitrogen in the ring structure and the phosphate side chain of chlorpyrifos.[10] These authors suggest that this six-membered ring weakens bonding of the side chain to the 2-pyridinol moiety because of electron shifts in the cyclic resonance structure, thereby promoting hydrolysis.[10] However, the environmental relevance of this catalyzing mechanism has remained questionable due to the low concentration of Cu(II) in surface waters. The catalyzing mechanism of Cu(II) could remain effective even at trace Cu(II) concentrations similar to those found in the environment. Both ASW and Cu(II) enhanced chlorpyrifos hydrolysis when isolated from the influence of other parameters that impact hydrolysis rates (e.g., pH, other dissolved solids, and dissolved organic matter content).[11]

Influence of NaCl on the Degradation of Chlorpyrifos. In contrast to the effects of Cu(II) and ASW, NaCl considerably inhibited the hydrolysis rate of chlorpyrifos compared to the rate in buffered DI water. The hydrolysis half-life was 79.67 ± 4.10 in 25 ppt NaCl and 56.82 ± 0.64 in buffered DI water or 40% longer (Figure 1 and Table 1). In addition, despite being used as a source of salinity in multiple degradation studies, the half-life of chlorpyrifos in 25 ppt NaCl was significantly longer than its half-life in 25 ppt ASW, 44.86 ± 2.69 (Figure 1 and Table 1).[14−16] Previous research suggests that the suppression of hydrolysis in the presence of NaCl may be due to the associated increase in solution ionic strength presumably through ionic shielding of hydroxide ions from the electrophilic phosphorus center by chloride ions.[24] This shielding would lower the energy of the nucleophile (hydroxide) relative to the energy of the reaction transition state resulting in an overall increase in activation energy and decrease in rate for the reaction.[25]

In relation to NaCl, the complex composition of ASW appears to initiate multiple mechanisms with competing effects such as the accelerative impact of Cu(II) and suppressive impact of NaCl on chlorpyrifos hydrolysis. Considering that ASW contains both Cu(II) (approximately 11 ppb) and NaCl (approximately 10.8 ppt), the overall increased hydrolysis rate in ASW suggests that the accelerative effects of ions such as Cu(II) outweigh the inhibitive effects of NaCl.[22,26] Despite being present in ASW only at trace levels, the effects of Cu(II) (in addition to any other trace constituents that may have contributed to accelerating the hydrolysis rate) appear to offset those of NaCl.[22,26] This suggests that differences in degradation rates observed in seawater vs freshwater systems should be interpreted cautiously before directly attributing

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them to salinity alone as trace constituents in seawater such as Cu(II) could substantially alter overall degradation processes impacting the fate of hydrophobic organic compounds.

Influence of Media Type on the Formation of TCP. As expected, TCP formed significantly faster ($p < 0.001$) in solutions that yielded faster degradation rates of chlorpyrifos among the five media types (Figure 2 and Table 2). Consistent with the degradation of chlorpyrifos, the formation rate of TCP in the 25 ppt ASW, 25 ppt NaCl, 10 ppb Cu(II), and 0.5 ppb Cu(II) solutions was all statistically significantly different from that of buffered DI water. The largest deviations from the rate of buffered DI water were in 25 ppt NaCl and 10 ppb Cu(II). In 10 ppb Cu(II), the rate of formation (0.2876 ± 0.0207 ppb day^{-1}) was over 2 times greater than that of buffered DI water (0.1290 ± 0.0006 ppb day^{-1}). This suggests that concentrations of Cu(II) representative of those found in ASW and inland freshwater environments may enhance the generation of TCP due to hydrolysis (Table 2). This agrees with the decreased half-life of chlorpyrifos in 10 ppb Cu(II); as the parent degrades faster, the degradation product forms more rapidly. Conversely, the rate of formation in NaCl (0.0738 ± 0.0081 ppb day^{-1}) was roughly half that of buffered DI water (0.1290 ± 0.0006 ppb day^{-1}). Considering the half-life of chlorpyrifos in NaCl was 40% longer than that in buffered DI water, it follows the hydrolysis product formed more slowly (Figure 2). In addition to impacting the rate of formation of TCP, notable differences in the distribution of TCP were also observed in ASW over the 12 week period. For example, the concentration of TCP in ASW at the end of week 4 was 3.94 ± 0.230 ppb, which was more than 2 times greater than the concentration in buffered DI water, 1.738 ± 0.302 ppb (Figure 2).

Table 2. Formation Rate of TCP in Each Medium

solution	rate of formation (ppb day^{-1})[a]
0 ppt	0.1290 ± 0.0006
25 ppt ASW	0.1373 ± 0.0021
25 ppt NaCl	0.0738 ± 0.0081
10 ppb Cu(II)	0.2876 ± 0.0207
0.5 ppb Cu(II)	0.1327 ± 0.0003

[a]Rates are in ppb per day ± the standard deviation ($n = 4$).

While the goal of this study was to use chlorpyrifos and TCP as probes to help elucidate the potential impacts of salinity and environmental Cu(II) on the hydrolysis of organic contaminants, the impacts of media type in prior works have been shown to alter the toxicities of chlorpyrifos and TCP.[27,28] For example, in 5 and 15 ppt salinity, chlorpyrifos was notably more toxic to the euryhaline shrimp *Litopenaeus vannamei* compared to 25 ppt.[28] However, few studies have focused on the impacts of media type on the relative toxicities of chlorpyrifos versus TCP. This warrants further research as the coexistence of chlorpyrifos and TCP can result in a synergistic interaction involving high risk to aquatic ecosystems.[27] Moreover, as with many hydrophobic organic compounds, the degradation product, TCP, has been found to be substantially more toxic than the parent, chlorpyrifos, in certain cases.[27] In particular, the impacts of salinity on the toxicity of chlorpyrifos and TCP to aquatic organisms should be further evaluated as it impacts the rate of degradation of chlorpyrifos as well as the formation and distribution of TCP over time.

ASW did appear to increase the rate at which chlorpyrifos hydrolyzes with a 21% shorter half-life in 25 ppt ASW (44.86 ± 2.69 days) than that in buffered DI water (56.82 ± 0.64 days). In addition, the formation of its hydrolysis product, TCP, was also significantly impacted by ASW. However, the individual seawater constituents, Cu(II) and NaCl, had opposing effects. While the approximate concentration of Cu(II) in ASW (10 ppb) yielded a half-life (21.73 ± 2.33 days) that was 62% shorter than that in buffered DI water, the half-life in 25 ppt NaCl (79.67 ± 4.10 days) was 40% longer, suggesting that Cu(II) could be a contributing cause of the accelerated hydrolysis rate in ASW. These data indicate that chlorpyrifos may hydrolyze more rapidly in alkaline freshwater environments having a higher average Cu(II) content (10 ppb) than natural seawater (<1 ppb). Future research could evaluate the impact of other trace metals found in seawater and determine how the altered degradation of chlorpyrifos and formation of TCP from salinity impact their relative toxicity to aquatic organisms. When investigating salinity effects based upon NaCl on chemical degradation mechanisms, caution should be exercised in extrapolating the results to the broader marine and estuarine system. This work suggests that trace constituents in seawater can play a larger role in the degradation of hydrophobic organic compounds than major constituents in seawater and need to be taken into account in assessments evaluating chemical risk to aquatic organisms.

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Notes

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■ ABBREVIATIONS

ACN, acetonitrile; ASW, artificial seawater; TCP, 3,5,6-trichloro-2-pyridinol

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