## Organophosphate Pesticide Degradation Under Drinking Water Treatment Conditions: Modeling Perspectives

by

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#### Abstract

The oxidation rate of chlorpyrifos was examined in the pH range of 6-11 in the presence of free chlorine. As pH decreased, the observed rate of chlorpyrifos oxidation increased. Hypochlorous acid appears to be the primary oxidant responsible for chlorpyrifos oxidation. The reaction order with respect to both free chlorine and chlorpyrifos was found to be first order. A simple model was developed to predict the apparent second order rate coefficient over the pH range examined. The objectives of this work were to develop experimental approaches and a modeling philosophy to study degradation of organophosphate pesticides as a class under drinking water treatment conditions.

#### Introduction

The Food Quality Protection Act of 1996 (FQPA) requires that all tolerances for pesticide chemical residuals in or on food be considered; this includes all other potential exposures where there is reliable occurrence information. Drinking water is considered a potential pathway for dietary exposure due to pesticide contamination of drinking water sources. The United States Geological Survey (USGS) completed a national reconnaissance, the National Water Quality Assessment (NAWQA), to help define human exposure to mixtures of contaminants [1-3]. For this assessment the USGS analyzed for 76 pesticides and 7 selected metabolites in US drinking water sources. The most commonly occurring pesticides were atrazine, metolachlor, diazinon, chlorpyrifos, and carbaryl. Pesticides residuals were monitored in source and finished drinking water for several community water systems [4, 5]. Since neither study reported the concentration of pesticides at different stages of treatment on a single slug of water, the effects of various treatment processes cannot be assessed. Only the influent and effluent of each treatment facility could be qualitatively discussed with respect to overall removal efficacy.

Ultimately, pesticide regulators need the ability to forecast the effects of drinking water treatment on pesticides. In addition to understanding the individual effects of various stages of treatment, the effect of these processes on the removal/transformation pathways of entire pesticide classes must be addressed to achieve a predictive modeling capability. However, most

of the work to date has generally focused on the removal or transformation of one pesticide due to one specific treatment process. For example, physical surface water treatment (coagulation/flocculation, sedimentation, and filtration) does not appear to remove or transform hydrophilic chemicals [6]. However, certain chemicals have been shown to be oxidized by oxidants commonly used in drinking water disinfection or hydrolyze during water softening. Over 90% of all community water systems use free chlorine as both a primary and secondary disinfectant, and over 30% of community water systems (primarily groundwater sources) use upflow lime softening to remove excess calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>). About 95% of the US population obtains potable water from a community water system [7]. Therefore, softening (base assisted hydrolysis) and disinfection (chemical oxidation) could potentially transform toxic `parent compounds to either a benign or more toxic and stable end-product.

Hydrolysis has been identified, in general, as an important transformation process for pesticides in various aqueous systems. The half-lives for certain chemicals under conditions similar to drinking water treatment have been known to increase or decrease compared to pure water experiments [8-11]. Processes other than hydrolysis, such as adsorption to particles, photolysis, redox processes, and microbial degradation all contribute to the fate of pesticides in the environment. In water treatment, two of the most relevant pesticide removal processes are adsorption and hydrolysis. Adsorption of atrazine has been observed in the presence of activated carbon [12]. Some of the organophosphate and s-triazine pesticides have been shown to adsorb to inorganic surfaces such as diatomaceous earth or glass filters [8, 13]. During water softening processes, additional removal could be associated with adsorption to calcium carbonate precipitates as well as alkaline hydrolysis.

Oxidation of some pesticides is known to occur under conditions similar to drinking water treatment with chemical disinfectants used in the industry. For example, atrazine, aldicarb, methomyl, carbaryl, propoxur, and diazinon were found to quickly degrade in the presence of ozone [5, 14-16]. However, ozone is not commonly used as a primary disinfectant opposed to free chlorine, [HOCl]<sub>T</sub>. Ozone can reduce the concentration of parent compound but may not mitigate the potential toxicity [15, 16].

Little work to date has solely investigated the kinetics and mechanism of pesticide transformations due to reaction with free chlorine. Chlorine is not as strong an oxidant as ozone [17] and it is less reactive with common aqueous constituents in drinking water sources. Therefore, this makes it a good oxidant to use as a secondary disinfectant in drinking water distributions systems. However, free chlorine has been found to react with s-triazine, organophosphate, and carbamate pesticides [5, 15, 16, 18-22]. Four s-triazines were found to degrade in the presence of free chlorine [19, 20]. The proposed reaction center and pathway for each s-triazine was oxidation of the sulfur resulting in the formation of sulfoxide and sulfone degradation products. Atrazine was found to be significantly degraded by ozone [14]; however, subsequent chlorination of ozonated effluent had very little effect on residual atrazine or its degradation products [5]. Carbamate pesticides, as a class, appear to vary in their reactivity with free chlorine. Carbaryl and propoxur do not react with chlorine; however, aldicarb, methomyl, and thiobencarb do exhibit reactivity with free chlorine [16, 18, 23]. This demonstrates that reactivity of different members of a specific class of pesticides with aqueous chlorine may vary

significantly due to structural variations; this reinforces the need for predictive methods that can account for these variations.

When chlorine reacts with the phosphorothioate subgroup of organophosphate (OP) pesticides, the thiophosphate functionality (P=S) is rapidly oxidized, resulting in the formation of oxons (P=O) [15, 21, 22]. The oxons are more potent than the parent pesticide as inhibitors of acetlycholinesterase, an enzyme necessary for proper function of the nervous system [22]. Coupe and Blomquist, [4] frequently found diazinon, chlorpyrifos, and malathion in surface waters prior to treatment. However, the parent was not detected in the finished drinking water. Chlorpyrifos and diazinon have been found to be oxidized to their corresponding oxon forms in the presence of free chlorine [15, 21, 22]. Diazoxon has also been found to be resistant to further oxidation by free chlorine [15]. Since the corresponding oxons were not analyzed in this study [4], their presence or fate in the distribution system is still uncertain.

The objective of this research was to develop experimental protocols, elucidate the OP reaction pathways, and derive a modeling philosophy to predict the fate of OP pesticides under drinking water treatment conditions for the entire pesticide class. Chlorpyrifos (CP) was chosen as a model OP because it is frequently detected in drinking water sources. The rate of CP loss in the presence of free chlorine was examined under simulated drinking water conditions. A model was developed to predict the apparent second order loss of CP based on the intrinsic rate coefficients for both hypochlorous acid (HOCI) and hypochlorite (OCI<sup>-</sup>). This was achieved by determining the reaction order for both CP and total free chlorine,  $[HOCI]_T = [HOCI] + [OCI<sup>-</sup>]$ , over the pH range of 6-11. The apparent second order rate coefficient ( $k_{app}$ ) at each pH was determined from the first order observed rates as a function of increasing free chlorine concentration. Using a simple kinetic model, the intrinsic rate coefficients for both hypochlorous acid ( $k_0$ ) and hypochlorite ( $k_1$ ) were determined from the experimental approach and modeling philosophy developed here can be applied to studying the reaction of other OP pesticides with free chlorine.

## **Materials and Methods**

## Materials

Chlorpyrifos (99.5%) was purchased from ChemService (West Chester, PA). Commercial sodium hypochlorite (NaOCl) was purchased from Aldrich (Milwaukee, WI). The 10-13% NaOCl solution contained equimolar amounts of OCl<sup>-</sup> and Cl<sup>-</sup>. Aqueous stock solutions and experiments utilized laboratory prepared deionized water (18 M $\Omega$  cm<sup>-1</sup>) from a Barnstead ROPure Infinity<sup>TM</sup>/NANOPure <sup>TM</sup> system (Barnstead-Thermolyne Corp., Dubuque, IA). Phosphate and carbonate salts for buffer solutions were dissolved in deionized water and filtered through a 0.45 µm filter, which was pre-rinsed with deionized water. All other organic and inorganic chemicals were certified ACS reagent grade and used without further purification.

# Methods

The glassware and polytetrafluoroethylene (PTFE) septa used in this study were soaked in a concentrated free chlorine solution for 24 hours, rinsed with deionized water, and dried at 105 °C prior to use. All pH measurements were obtained with an Orion 940 pH meter with a Ross combination electrode from Fisher Scientific (Pittsburgh, PA). All chlorination experiments were conducted at constant temperature (25±1°C). The kinetic experiments used to estimate rate coefficients measured at least 87% or greater loss in parent compound.

The following approaches were followed for each experiment. CP was spiked by adding 1 mL of a 4 mM stock in ethyl acetate into an empty 4-L borosilicate glass Erlenmeyer flask. A gentle flow of nitrogen gas was used to evaporate the ethyl acetate and 4 L of deionized water was then added to the flask. The solution was slowly stirred and allowed to dissolve for 12 hours resulting in a concentration of 1  $\mu$ M. CP chlorination kinetic experiments were conducted under pseudo-first-order conditions with chlorpyrifos to total free chlorine molar ratios of 20, 100, and 200. At each discrete sampling interval, two reaction vessels were sacrificed in their entirety. One vessel was used to determine total free chlorine concentration via Standard Method 4500-Cl F DPD-FAS titrimetric method [24]. Residual free chlorine in the other vessel was quenched with sodium sulfite in 20% stoichiometric excess of the initial free chlorine concentration. The pH of a 100-mL sample was then adjusted to 2 for analysis of CP [11]; the acid assisted hydrolysis of CP was shown to be negligible [25].

In the pH range above 8, 10 mM carbonate  $[CO_3]_T$  buffer was used to maintain the pH. The free chlorine solution was first diluted to 18,000 mg Cl<sub>2</sub>/L. This diluted solution was added to the aqueous solution containing 0.5  $\mu$ M chlorpyrifos and carbonate buffer in a 2-L Erlenmeyer flask under rapid mix conditions. Aliquots of the 2-L reactor were then placed into small 128mL amber reaction vessels and stored in a dark water bath at 25±1°C.

In the pH range of 6.0-7.5, the rate of CP oxidation by free chlorine was very fast. Therefore, 100 mL of the 2-L aqueous system buffered with 10 mM phosphate buffer,  $[PO_4]_T$ , was placed in a 250-mL amber Erlenmeyer flask. Chlorine was added to it while rapidly mixing with a magnetic stir plate and stir bar with a non-reactive coating. The time frame of these experiments was under 20 minutes, and parallel experiments were conducted to determine free chlorine concentrations.

For all experiments, CP was extracted from the aqueous solution using C-18 solid phase extraction (SPE) cartridges purchased from Supleco (Bellefonte, PA). The sample was spiked with 1  $\mu$ M of phenthorate (internal standard), mixed thoroughly by hand for two minutes, passed through the SPE cartridge, and eluted with 3 mL of ethyl acetate. Quantification of CP was by comparison with eight SPE extracted standards over the concentration range of 0.01 to 1  $\mu$ M. A Hewlett-Packard 6890 GC equipped with a 5973 MSD was used to analyze CP concentrations. GC conditions were as follows: 30-m Restek Rtx-200 column with a 0.25-mm ID and 0.5- $\mu$ m film thickness. The temperature profile was: 100 °C for 5 minutes, 100 to 250 °C at 10 °C/minute, and then held at 250 °C for 25 minutes.

### **Results and Discussion**

The reaction order for both free chlorine and CP were determined in the presence of excess chlorine. The reaction order of CP in the presence of free chlorine,  $[HOC1]_T$ , was determined by plotting  $ln([CP]/[CP]_o)$  versus time for each experiment. If linearity exists, the

slope of the regression line represents the observed first order rate coefficient  $(k_{obs})$  for CP disappearance.

$$\ln \frac{[CP]}{[CP]_{o}} = -k_{obs}t$$
(1)

The reaction was found to be first order with respect to CP in the presence of free chlorine. Figure 1 shows the first order observed loss of CP at pH 8.75 and  $[HOC1]_T = 10$ , 50, and 100  $\mu$ M. At each chlorine concentration linearity exists, indicating that the loss of CP is first order with respect to itself in the presence of free chlorine. The reaction order for free chlorine was determined by plotting the log(k<sub>obs</sub>) versus the log of the initial free chlorine concentration (Figure 2). The slope of the line indicates the reaction order of free chlorine. At pH 9 and over the entire pH range, the slope of the line was approximately 1. Thus, the reaction order for oxidation is first order with respect to both CP and free chlorine.

The second order apparent rate coefficient  $(k_{app})$  at each pH was determined by plotting the  $k_{obs}$  versus the initial free chlorine concentration. Since both species of free chlorine are present (HOCl + OCl<sup>-</sup>), the apparent loss of CP in the presence of both oxidants can be described as

$$\frac{d[CP]}{dt} = -k_{app}[HOCl]_{T}[CP]$$
(2)

$$\mathbf{k}_{obs} = \mathbf{k}_{app} [HOC1]_{T}$$
(3)

Figure 3 shows that  $k_{obs}$  increased linearly with increasing chlorine concentration for pH 6.36-8.5. This figure illustrates that the pseudo-first order rate coefficients for CP are proportional to initial total free chlorine concentration. Also,  $k_{app}$  increased significantly as pH decreased,  $k_{app}$ values at pH 8.5 and 6.36 were  $1.08 \times 10^5 \text{ M}^{-1}\text{h}^{-1}$  and  $1.52 \times 10^6 \text{ M}^{-1}\text{h}^{-1}$  respectively. The pK<sub>a</sub> of hypochlorous acid (HOCl) is 7.5 [26]. If the dominate reacting species is HOCl, then the apparent rate coefficient at each pH should increase as pH decreases from 11 to 6.36, the pH range over which  $k_{app}$  values were determined.

The intrinsic rate coefficient for hypochlorite ( $k_1$ ) was approximated by plotting  $k_{app}$  versus the hydrogen ion activity over the pH range of 8.5-11.0 (Figure 4). The intercept of the regression line approximates  $k_1$  for the reaction rate coefficient of OCl<sup>-</sup> with CP at zero hydrogen ion activity,  $k_1 = 1470.93 \text{ M}^{-1}\text{h}^{-1}$ . The loss of CP in the presence of free chlorine can be describes as

$$\frac{d[CP]}{dt} = -k_0[HOC1][CP] - k_1[OC1^-][CP]$$
(4)

where  $k_0$  is the intrinsic rate coefficient for hypochlorous reacting with CP. The concentrations of both hypochlorous acid and hypochlorite can be represented as

$$[HOC1]_{T} = \alpha_{0}[HOC1]_{T} + \alpha_{1}[HOC1]_{T}$$
(5)

where  $\alpha_0$  and  $\alpha_1$  are the speciation coefficients for hypochlorous acid and hypochlorite. Combining equations 4 and 5, the rate of CP loss is

$$\frac{d[CP]}{dt} = -(\alpha_0 k_0 + \alpha_1 k_1)[CP][HOC1]_T$$
(6)

The  $k_{app}$  can then be described as

$$\mathbf{k}_{\mathrm{app}} = \alpha_0 \mathbf{k}_0 + \alpha_1 \mathbf{k}_1 \tag{7}$$

The intrinsic rate coefficients  $k_0$  and  $k_1$  were calculated by multiple regression analysis for the experimentally determined  $k_{app}$ . Values of the intrinsic rate coefficients were obtained for the lowest quadratic mean derivation, defined as  $\sum ((k_{app,experimental} - k_{app,theoretical})^2/(k_{app,experimental})^2$ . Approximate starting values for the intrinsic rate coefficients were  $k_0 = 1.52 \times 10^6 \text{ M}^{-1}\text{h}^{-1}$  and  $k_1 = 1470.93 \text{ M}^{-1}\text{h}^{-1}$ . The value of  $k_1$  was estimated from the intercept in Figure 4, and the  $k_0$  value was the  $k_{app}$  at pH 6.36 where HOCl constitutes approximately 93% of the total free chlorine concentration.

As determined from regression analysis, the intrinsic rate coefficients for hypochlorous acid and hypochlorite are  $1.72 \times 10^{6} \text{ M}^{-1}\text{h}^{-1}$  and 990 M<sup>-1</sup>h<sup>-1</sup> respectively. These values were then used to calculate  $k_{app}$  values using equation 7. Figure 5 shows the experimental and model results for the  $k_{app}$  as a function of pH. A good correlation between the model and experimental values was obtained. The reaction rate coefficient for hypochlorous acid was found to be approximately 2000 times greater than hypochlorite. This demonstrates that HOCl is the dominate oxidant responsible for the loss of CP. The model does slightly over-predict the apparent rate coefficient in the pH range of 6-9. However, the predicted apparent rate coefficient still falls within the 95% confidence interval of the experimentally observed value. Half-lives for CP loss in the presence of 14.1  $\mu$ M (1.0 mg-Cl<sub>2</sub>/L) free chlorine concentration for pH 6,7,8, and 9 are 1.8, 2.3, 7.6 and 59.4 minutes respectively. These half-life predictions are representative of drinking water pH and chlorine concentration.

### Conclusions

A model was presented that predicts the apparent rate of CP loss in the presence of free chlorine. Hypochlorous acid reacts much more rapidly with CP than hypochlorite. The model predictions correlated well with the experimentally observed apparent second order rate coefficients for CP degradation in the presence of aqueous chlorine. This shows that CP degradation can be predicted using a relatively simple model and that the experimental approaches appear to be appropriate to examine OP reactions with free chlorine. Future work will examine chlorpyrifos oxon formation due to CP reaction with free chlorine, as well as complete degradation pathways (i.e. reaction with chlorine and hydrolysis). These degradation pathways will then be used to construct a more complicated model with the potential to predict the concentrations of OP pesticides and their oxons. Models like the one proposed here will aid

the water treatment industry in assessing whether or not chlorination mitigates the potential toxicity of potable water from source waters contaminated with pesticides.

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Figure 1 First order observed loss of CP at pH 8.75 as a function of increasing chlorine concentration.  $[CP]_0 = 0.5 \ \mu\text{M}, [CO_3]_T = 10 \ \text{mM}, \text{Temperature} = 25\pm1^\circ\text{C}, \text{ and } [HOCl]_T = 10, 50, \text{ and } 100 \ \mu\text{M}.$ 



Figure 2 Reaction order of free chlorine at pH 9.0.  $[CP]_o = 0.5 \ \mu M$ ,  $[CO_3]_T = 10 \ mM$ , Temperature =  $25\pm1^{\circ}C$ , and  $[HOC1]_T = 10$ , 50, and 100  $\mu M$ .



Figure 3 Apparent second order rate coefficient for free chlorine reacting with CP over the pH range of 6.36-8.5.  $[CP]_o = 0.5 \ \mu\text{M}$ ,  $[Buffer]_T = 10 \ \text{mM}$ , Temperature =  $25\pm1^\circ\text{C}$ , and  $[HOCl]_T = 10$ , 50, and 100  $\mu\text{M}$ .



Figure 4 Approximation of the intrinsic second order rate coefficient for hypochlorite ion reacting with CP over the pH range of 8.5-11.  $[CP]_0 = 0.5 \ \mu\text{M}, [CO_3]_T = 10 \ \text{mM},$ Temperature =  $25\pm1^\circ\text{C}$ , and  $[HOC1]_T = 10$ , 50, and 100  $\mu\text{M}$ .



Figure 5 Model results for  $k_{app}$  over the pH range of 6-11.  $[CP]_o = 0.5 \ \mu M$ ,  $[Buffer]_T = 10$  mM, Temperature =  $25\pm1^{\circ}$ C, and  $[HOCI]_T = 10$ , 50, and 100  $\mu$ M. Line represents model results.