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ARTICLE

Oxidative Removal and Kinetics of Fipronil in Various Oxidation Systems for Drinking Water Treatment

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Fipronil, a pesticide gaining wide usage, was oxidized with common drinking water treatment disinfectants and oxidants; with a degradate identified using liquid chromatography−mass spectrometry. Oxidants investigated were free chlorine (HOCl/OCl⁻), monochloramine (ClNH$_2$), chlorine dioxide (ClO$_2$), and permanganate (MnO$_4^-$) at pH 6.6 and 8.6. Free chlorine, chlorine dioxide, and permanganate were reactive with fipronil to various degrees, whereas monochloramine was only marginally reactive. No oxidation products were observed for free chlorine, monochloramine, or chlorine dioxide. Oxidation by permanganate produced an identifiable degradate, fipronil sulfone, which was recalcitrant to further oxidation by permanganate. Fipronil sulfone could, however, be further degraded by free chlorine. Under typical conditions of water treatment, free chlorine was an effective oxidant for fipronil and fipronil sulfone, achieving partial removal at typical conditions. pH effects were observed for free chlorine, chlorine dioxide, and permanganate with more rapid oxidation occurring at pH 8.6 than at pH 6.6.

KEYWORDS: Fipronil; oxidation removal; degradation products; kinetic rate

INTRODUCTION

Fipronil (5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)]-phenyl-4-((trifluoromethyl)sulfinyl)pyrazole) (CAS Registry No. 120068-37-3) is a phenylpyrazole insecticide developed by Rhône-Poulenc Agro (now Bayer CropScience) in 1987. It was approved in 1996 for crop usage in the United States and is mainly used for soil and foliar insect control, including rice pests, vine weevils, termites, blank ants (*1*), wireworms (*2*), click beetles (*3*), and locusts (*4*). Fipronil is being used increasingly in place of organophosphates, pyrethroids, carbamates, and many cyclodienes, possibly due to the lack of resistances (*5*). Fipronil is also used on a wide variety of urban pests, including cockroaches, mosquitoes, ticks, and fleas (*6*, *7*). Fipronil is the active ingredient for many common domestic insecticides including Icon, Front-line, Termidor, and Top Spot (*8*).

Fipronil disrupts central nervous system activity by interfering with or blocking the passage of chloride ions through the γ-aminobutyric acid (GABA) regulated chloride channel and, at sufficient dosages, causes paralysis and death (*9*). Subsequent activity is much more potent to insects and other invertebrates as compared to mammals (*10*, *11*). Known degradation products (i.e., fipronil sulfone, fipronil sulfide, and fipronil desulfinyl) were suggested to have similar toxicity potentials (*12*, *13*) but were more environmentally stable (*12*). Fipronil is stable under acidic

(pH 5.5) and neutral conditions (*3*) but can undergo degradation through photolysis (*13*, *14*), hydrolysis at alkaline conditions (*3*, *15*), and some oxidation and reduction processes (*1*) in soil. Bobe et al. (*3*) identified two degradates from photo-oxidation (fipronil desulfinyl and fipronil sulfonate) and one formed during alkaline hydrolysis (fipronil amide). Ngim et al. (*14*) confirmed these photo-oxidation degradates and found an intermediate in the mechanism (fipronil sulfone). Bobe et al. (*1*) identified four degradates in the environment (two degradates formed by reduction/oxidation in soil, two degradates formed by hydrolysis or photolysis in water or soil); fipronil sulfide is formed in relatively high moisture and less aerated environment, and fipronil sulfone is formed in aerobic environment.

Fipronil and some degradates of fipronil (fipronil sulfide, fipronil sulfone, and fipronil desulfinyl) have been detected in several U.S. states at low parts per billion (μg/L) concentrations, particularly in urban creeks and water systems (*16*). Concentrations for fipronil and the degradates fipronil sulfide, fipronil sulfone, and fipronil desulfinyl ranged from 0.001 to 0.117 μg/L, from 0.003 to 0.015 μg/L, from 0.002 to 0.038 μg/L, and from 0.002 to 0.158 μg/L, respectively. The highest concentrations (5.29 μg/L) for fipronil have been reported in Louisiana surface waters in agricultural areas (*8*), with spikes occurring during the months of March and April when rice fields are drained. Although primarily used for agricultural purposes, the number of fipronil detections in urban settings is comparable to those in agricultural settings (*8*).

Because fipronil is widely used and residues have been detected in many surface waters, it can potentially be transported to

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drinking water. Currently, little information is available regarding the oxidation and transformation of fipronil during drinking water treatment. The aim of this study was to investigate the oxidative removal and kinetic rate of fipronil by free chlorine (FC), monochloramine (MCA), chlorine dioxide (ClO_2), and permanganate (MnO_4^-) under exposures and typical conditions of drinking water treatment. Additionally, rate constants were calculated for fipronil and fipronil sulfone to provide a better understanding of treatment effectiveness.

EXPERIMENTAL PROCEDURES

Materials. Fipronil was obtained from AccuStandard, Inc. (New Haven, CT). Fipronil sulfone, fipronil sulfide, and fipronil desulfinyl were obtained from USGS (Sacramento, CA). All treatment chemicals (sodium hypochlorite, ammonium chloride, and potassium permanganate) were certified ACS and were obtained from Fisher Scientific (Fair Lawn, NJ). Working solutions utilized buffered laboratory water (18.2 MΩ·cm) prepared from distilled water using a Simplicity model 185 Milli-Q (MQ) water purification system (Millipore Co., Bedford, MA).

Oxidation Reactions. Experiments were conducted on volumes of working pesticide solutions at an initial concentration of 25 μg/L in 30 mL amber glass reactors (Fisher Scientific). Working pesticide solutions were prepared by diluting aqueous stock solutions in 5 mM phosphate-buffered laboratory water at pH 6.6 or 8.6. Solution pH was measured using an Orion combination pH probe. Reactions were initiated by spiking aliquots of aqueous oxidant stock solution to the working pesticide solution (fipronil or fipronil sulfone) in molarity excess. A sample was taken and immediately injected into the LC-MS for 7−10 repeated injections with the injection time serving as the reaction time. Oxidant concentrations were continuously monitored during injections via the described below.

Four oxidants found in water treatment processes were evaluated in this study based upon preliminary screening studies: free chlorine, monochloramine, chlorine dioxide, and permanganate. Free chlorine, chlorine dioxide, and permanganate (in particular) showed very high reactivities and, thus, the highest potential for degradate production as well as the highest need for kinetic data. Monochloramine did not indicate high reactivity but was included due to its wide usage in water treatment.

Free chlorine stock solutions were prepared by dilution from a 5% NaOCl solution. Free chlorine concentrations were calculated as the difference between the total chlorine (determined with the Hach DPD method 8167 using Accuvacs; Hach Co., Loveland, CO) and monochloramine concentrations (determined with the Hach Nitrogen, Free Ammonia, and Chloramine (Mono) Indophenol method 10200).

Monochloramine stock solutions were prepared from stable high concentration substock solutions of NaOCl and NH_4Cl at a molar ratio of 1.05:1 at pH 11 (*17*). During MCA formation, the pH was precisely controlled to never fall below 9.0 by utilizing buffered source water, pH probe monitoring, and additions of sodium hydroxide, as needed. An excess of 5% ammonia was accurately determined in the MCA stock solution using an Orion model 9512 ammonia probe (Thermo-Electron Corp., Waltham, MA) ensuring no free chlorine in the stock solution. Additionally, absorbance scans from 200 to 400 nm on the MCA stock solution at pH 9.0 produced no peak at 294 nm (wavelength commonly associated with OCl^-), confirming the absence of free chlorine. MCA concentrations during experiments were determined with Hach method 10200 using chemicals obtained from the Hach Co.

Permanganate stock solutions were prepared by dissolving potassium permanganate crystals in buffered deionized water. Permanganate concentrations were determined with Hach DPD method 8167 using Accuvacs obtained from the Hach Co. Gaseous chlorine dioxide was produced using a CDG bench scale ClO_2 generator (CDG, Bethlehem, PA) utilizing thermally stable solid sodium chlorite. The gaseous chlorine dioxide stream was bubbled through a stone diffuser into a receiving solution of pH preadjusted buffered laboratory water. Chlorine dioxide concentrations were monitored with a conventional spectrophotometer (Cary 50 Conc., Varian) at 359 nm.

LC-MS Analysis. Fipronil, fipronil sulfone, fipronil sulfide, and fipronil desulfinyl were chromatographically separated using an Agilent 1100 series LC-MSD system (G1946D), which included a solvent degassing unit, a binary high-pressure gradient pump, an automatic sample injector, a column thermostat and unit, and a 1946D SL model mass spectrometer. A sample volume of 20 μL was injected into a 150 × 3.0 mm Phenomenex Synergi Fusion-RP 80A 4 μm column preceded by a SecurityGuard C-18 guard column. The column was maintained at 25 °C at a flow rate of 0.3 mL/min. A binary gradient of solvent A (MQ water with 0.04% acetic acid) and solvent B (methanol) was used. The solvent gradient profile was as follows: 70% B for 3 min, ramp from 70 to 100% over 6 min, and held at 100% B for 8 min, followed by return to initial mixture and equilibration. The mass spectrometry utilized a negative ion electrospray mode in selected ion monitoring (SIM) mode with the nebulizer pressure set at 35 psig, the capillary set at 3500 V, a drying temperature of 300 °C, a drying gas flow of 12 L/min, and the fragmentor set at 80 V.

All standard curves were at least six-point linear curves with an average regression coefficient (R^2) of 0.998, indicating good linearity over the range of concentrations investigated. Retention times for fipronil, fipronil sulfone, fipronil sulfide, and fipronil desulfinyl were 9.74, 10.59, 10.2, and 9.30 min, respectively. The method detection limits (MDLs defined as a signal-to-noise ratio of 3 to 1) were determined via standard methods (Title 40 − Electronic code of federal regulations, EPA) by injecting seven separate samples, at concentrations estimated at 3 times the anticipated MDL, and multiplying the standard deviation of the resulting concentration by 3.14. The MDLs for fipronil, fipronil sulfone, fipronil sulfide, and fipronil desulfinyl were 0.49 ± 0.16, 0.23 ± 0.07, 0.30 ± 0.10, and 0.17 ± 0.05 μg/L, respectively.

Kinetic Analysis. For kinetic analysis, pseudo-first-order rate coefficients (k_{obsd}) were determined experimentally under constant oxidant concentrations, from which the experimental second-order rate coefficients (k_{exptl}) were calculated. Oxidant concentrations were held nearly constant throughout a reaction by using a significant excess of oxidant relative to fipronil concentration. The average percent change of concentration over the experimental run time was 8 ± 7%.

The overall rate of reaction in a batch system for oxidant (C_{ox}) and fipronil (C_F) can be expressed generally by

$$\text{rate} = \frac{dC_F}{dt} = -kC_{OX}C_F \tag{1}$$

where k is the second-order rate constant ($M^{-1} s^{-1}$).

For a constant oxidant concentration, a pseudo-first-order rate constant (k', s^{-1}) can be used and

$$\text{rate} = \frac{dC_F}{dt} = -k'C_F \tag{2}$$

Integration yields the plotting equation used to determine the pseudo-first-order rate constant:

$$\ln\left(\frac{C_F}{C_{F0}}\right) = -k't \tag{3}$$

The assumption of first-order kinetics is valid if linearity is observed when eq 3 is plotted and oxidant concentrations are in sufficient excess. For each oxidant, free chlorine, monochloramine, chlorine dioxide, and permanganate, fipronil exhibited first-order behavior with regression coefficients (R^2) when plotted per eq 3 ranging from 0.933 to 1.00 (see **Figure 1** for a representative illustration for free chlorine). The resulting slope of the regression line yielded the observed pseudo-first-order rate coefficient (k').

Experimental second-order rate coefficients (k) were determined at each pH by plotting k' versus the constant oxidant concentration. The resulting slope of each regression line yields the experimental second-order rate coefficients (k) at that pH and are given in **Table 1** with regression coefficient (R^2) values ranging between 0.985 and 0.999.

RESULTS AND DISCUSSION

Byproduct Formation. The mass spectra for fipronil and fipronil sulfone standards are presented in **Figures 2** and **3**. Whereas fipronil was observed to degrade during oxidation with FC, MCA, and ClO_2, no degradates (including fipronil sulfone, fipronil sulfide, and fipronil desulfinyl) were observed via the LC-MS method used. With oxidation by MnO_4^-, however, one
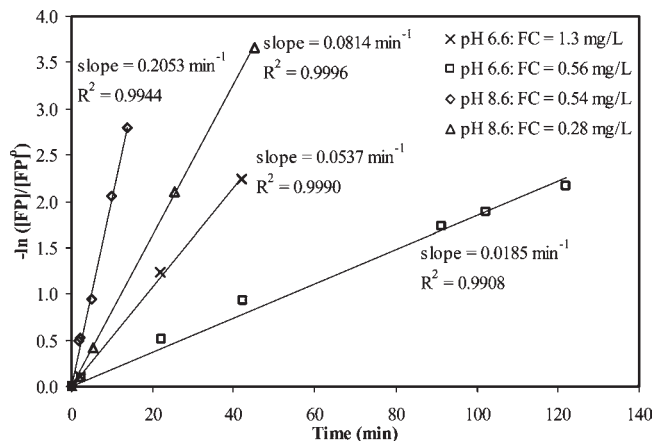
Figure 1. Pseudo-first-order plot of free chlorine fipronil oxidation kinetics in laboratory water at pH 6.6 and 8.6 and different constant FC concentrations.

Table 1. Half-Life of Fipronil and Second-Order Rate Constants Determined in This Study at pH 6.6 and 8.6 for Each Oxidant Studied[a]

	pH 6.6			pH 8.6		
	half-life (min)	k_F (M^{-1} s^{-1})	R^2	half-life (min)	k_F (M^{-1} s^{-1})	R^2
FC	37	60.4	0.9849	3.4	488	0.9971
ClO$_2$	7715	0.43	0.9976	42	48	0.9914
MnO$_4$	77	246	0.9997	5.5	370	1
MCA	3.1×10^5	0.0028		1.8×10^5	0.0062	

[a] Regression coefficients are for the corresponding pseudo-first-order rate regressions.

degradate peak corresponding to fipronil sulfone was observed via LC-MS using negative electrospray ionization over a range of 100−500 amu for both pH 6.6 and 8.6. Fipronil sulfone was not observed for any other oxidant (e.g., FC, MCA, or ClO$_2$), and no other byproduct peaks were observed in scan mode. Other work by Bobe et al. (*3*) on hydrolysis of fipronil reported only fipronil amide as a degradation product.

Free Chlorine Kinetics. Fipronil reactions with free chlorine were examined at pH 6.6 and 8.6 under pseudo-first-order conditions with free chlorine in excess. In the presence of free chlorine, fipronil decreased rapidly (and no degradation products were identified). Pseudo-first-order kinetic plots are presented in **Figure 1** for the chlorination of fipronil at pH 6.6 and 8.6 for two different FC concentrations each. On the basis of these data, second-order rate constants were then estimated as 60.4 M^{-1} s^{-1} at pH 6.6 and 488 M^{-1} s^{-1} at pH 8.6 (**Table 1**).

Fipronil appears to be more susceptible to oxidation at higher pH values, showing an order of magnitude increase in rate from pH 6.6 to 8.6. The reason would be that the hydrogen bonding between fipronil and water is weaker at higher pH, so the attack of oxidants to fipronil is facilitated. Free chlorine is composed of both hypochlorous acid and hypochlorite ($pK_a = 7.6$). Hypochlorous acid is typically a much stronger oxidant than the hypochlorite ion; thus, reactions at lower pH are generally faster (at least with compounds that do not speciate themselves). Although fipronil does not speciate with pH (SPARC software (*18*)), as the pH increases the functional moieties tend toward deprotonation, possibly allowing the hypochlorite ion to act as a nucleophile similar to the hydroxide ion. This has been observed for other pesticides, pharmaceuticals, and personal care compounds (*19−21*).

Hydrolysis (and other losses) was observed to be negligible at pH 6.6 and 8.6, consistent with results by Bobe et al. (*3*) for
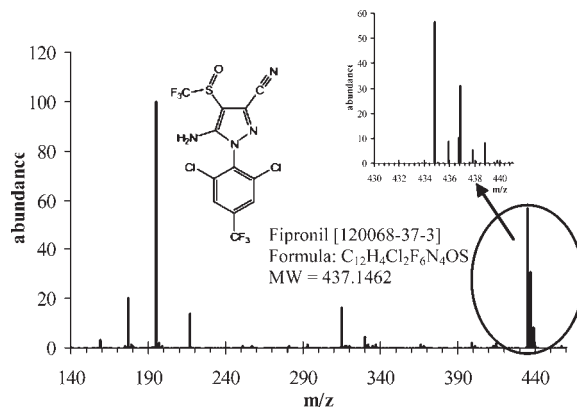

Figure 2. Mass spectra (and structure) of fipronil via LC-MS in ESI(−) mode.
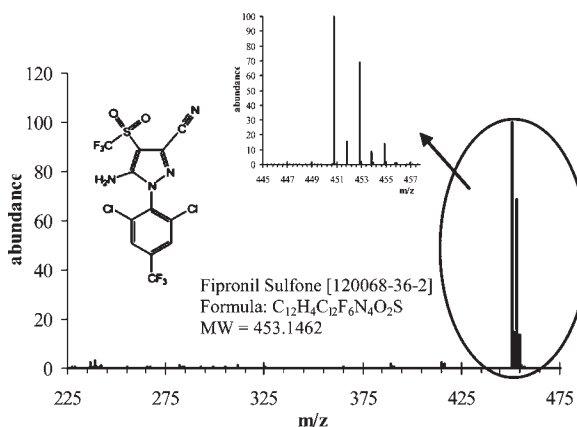

Figure 3. Mass spectra (and structure) of fipronil sulfone via LC-MS in ESI(−) mode.

fipronil. Specifically, utilizing the pseudo-first-order rate data from Bobe et al. (*3*) yields an estimated removal of <0.5% at either pH 6.6 or 8.6.

Chlorine Dioxide Oxidation Kinetics. Fipronil was also readily oxidized by ClO$_2$ (and no ClO$_2$ degradation products were identified in this study) with higher rates observed at higher pH (similar to the trend for FC). Specifically, the oxidation rate for ClO$_2$ was 2 orders of magnitude greater at pH 8.6 than at 6.6 or 0.43 and 48 M^{-1} s^{-1}, respectively (**Table 1**).

A possible explanation for the greater rate at high pH is that chlorine dioxide is a selective electrophilic oxidant with affinity for electron-rich carbon bonds or centers (e.g., phenols, sulfides, nitrate, tertiary amines, and thiols) (*22, 23*) and electrophilic abstractions (*24*). Under typical drinking water treatment conditions, chlorine dioxide is generally not reactive with primary or secondary amines, aldehydes, ketones, or aromatic hydrocarbons (*2*). The increased reactivity at higher pH values might be explained by the nature of chlorine dioxide reactions for electron-dense bonds or centers and the protonation state of fipronil.

At higher pH, the functional moieties (especially aniline and sulfoxide for fipronil) may be more amenable to electrophilic abstraction. This explanation is consistent with work by Huber et al. (*25*) on several pharmaceuticals, where greater oxidation rates were observed with ClO$_2$ at higher pH.

Chloramine Oxidation Kinetics. In contrast to FC and ClO$_2$, oxidation of fipronil by MCA was very slow (and no degrades were observed via LC-MS even though high exposures were used experimentally to allow partial parent removal). Experimental second-order rate constants were determined for MCA and

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fipronil to be only 0.0028 and 0.0062 $M^{-1} s^{-1}$, respectively (**Table 1**). Thus, little or no degradation of fipronil would be expected in drinking water treatment with MCA.

Permanganate Oxidation Kinetics. In the presence of permanganate, fipronil was oxidized rapidly and one degradation product was identified, fipronil sulfone (as discussed above). The apparent second-order reaction rates were of the same order of magnitude for pH 6.6 and 8.6, or 246 and 370 $M^{-1} s^{-1}$, respectively. Permanganate is known to be a fairly nonselective oxidant at most pH levels, and readily oxidizes sulfoxides to sulfones (26−28) with the sulfinyl functionality oxidized to a sulfonyl group (as shown in **Figures 2** and **3**). Thus, permanganate was the only oxidant found to readily oxidize fipronil to fipronil sulfone under typical water treatment conditions.

Fipronil Sulfone Kinetics. To assess whether fipronil sulfone would be recalcitrant or labile to further oxidation, kinetic studies were conducted for fipronil sulfone and both MnO_4^- and FC (the most common disinfectant used in water treatment). The experiments showed that fipronil sulfone was recalcitrant to oxidation by permanganate at pH 6.6 and only slightly reactive at 8.6 (suggesting the MnO_4^- reacts nearly exclusively with the sulfinyl functionality of the parent, fipronil). Specifically, at pH 6.6 and a permanganate concentration of 12.5 mg/L, the fipronil sulfone concentration remained unchanged over 100 min. At pH 8.6 and a permanganate concentration of 10.3 mg/L, a decrease of just 6% in the fipronil sulfone concentration was observed over 84 min (corresponding to a second-order rate constant of 0.14 $M^{-1} s^{-1}$). This would imply that fipronil sulfone would build up in a system utilizing only permanganate as the oxidant or disinfectant, because the reaction rate of the parent compound is essentially 3 orders of magnitude larger than for the degradate.

Oxidation rate constants for fipronil sulfone and FC were also determined and were 27.7 and 21.4 $M^{-1} s^{-1}$ at pH 6.6 and 8.6, respectively. Several facilities utilize permanganate as a preoxidant at their intakes to combat taste and odor problems, followed by FC as their primary disinfectant. In such a (common) scenario, fipronil would be partially oxidized to fipronil sulfone in the intakes, followed by partial removal of the degradate, fipronil sulfone, as well as the parent, during primary disinfection with free chlorine.

This scenario was quantitatively examined using the rate constants developed for MnO_4^- and FC for fipronil and fipronil sulfone. The removal of fipronil by both MnO_4^- and FC, as well as removal of fipronil sulfone, can be modeled using standard first-order kinetics:

$$\frac{C_F}{C_{F0}} = e^{-k't} \qquad (4)$$

where C_F and C_{F0} are the concentrations of fipronil at time t and initially, respectively, and k'_F is the pseudo-first-order rate constant for fipronil. Formation and concurrent removal of fipronil sulfone can be modeled by eq 1

$$rate = \frac{dC_F}{dt} = -kC_{OX}C_F \qquad (1)$$

$$\frac{C_{FS}}{C_{FS0}} = \frac{C_{F0}}{C_{FS0}}\left(\frac{k'_F}{k'_{FS} - k'_F}\right)(e^{-k'_F t} - e^{-k'_{FS} t}) + e^{-k'_{FS} t} \qquad (5)$$

where C_{FS} and C_{FS0} are the concentrations of fipronil sulfone at time t and initially, respectively, and k'_{FS} is the pseudo-first-order rate constant for fipronil sulfone. The modeling assumed MnO_4^- pre-oxidation with 1 mg/L of MnO_4^- for 5 min (i.e., a 5 mg·min/L exposure) followed by disinfection with FC at a concentration
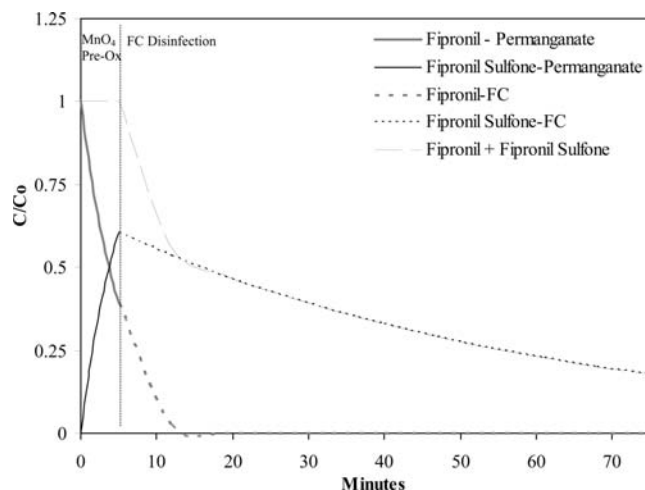

Figure 4. Modeled removal of fipronil and fipronil sulfone for a permanganate (MnO_4^-) (1 mg/L × 5 min) peroxidation followed by free chlorine (FC) disinfection (1 mg/L × 70 min).

of 1 mg/L (as Cl_2) for 70 min (i.e., a 70 mg·min/L exposure). The results are presented graphically in **Figure 4** and show that fipronil is partially removed with concurrent fipronil sulfone formation at the front of the treatment plant. After FC is added, FC continues to degrade the fipronil (albeit at a slower rate). Fipronil sulfone is degraded by FC at a slower rate than fipronil. On the basis of model assumptions, fipronil would be completely degraded (<1% remaining) within 10 min of FC. However, the model shows that up to 20% of the fipronil sulfone formed would remain in the system after 70 min of exposure. The modeling assumed that after the 5 mg·min/L exposure of MnO_4^-, no MnO_4^- remained in the system.

The results of this study indicate that fipronil may be partially removed from drinking water under most treatment disinfection conditions with free chlorine, chlorine dioxide, and permanganate, but will not be removed with monochloramine. The degradate, fipronil sulfone, was formed as the primary oxidation byproduct with MnO_4^- but was not formed with FC, ClO_2, or MCA. Faster oxidation with FC, ClO_2, and MnO_4^- was observed at pH 8.6 as compared with pH 6.6. More study is needed on fipronil sulfone with respect to occurrence in treated drinking water as well as its potential health effects.

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