EPA Public Access

Author manuscript

AWWA Water Sci. Author manuscript; available in PMC 2020 April 15.

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Published in final edited form as:

AWWA Water Sci. 2019 ; 1(2): . doi:10.1002/aws2.1133.

Chlorinated Cyanurates in Drinking Water: Measurement Bias, Stability, and Disinfectant Byproduct Formation

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Abstract

Two chlorinated cyanurates, commonly referred to as dichlor (anhydrous sodium dichloroisocyanurate or sodium dichloroisocyanurate dihydrate) and trichlor (trichloroisocyanuric acid) may be approved for use in United States drinking water systems as chlorine sources. One complication with dichlor or trichlor's application in drinking water is that the actual free chlorine concentration in these systems cannot be quantified accurately by currently approved methods. Based on known water chemistry, two hypothesized advantages of dichlor or trichlor use are potential increased residual chlorine stability and decreased regulated disinfectant byproduct (DBP) formation. To inform these practical considerations, the current research investigated measurement bias in N,N-diethyl-p-phenylenediamine (colorimetric and portable parallel analyzer), indophenol, amperometric titration, and amperometric electrode free chlorine methods. In addition, hold studies using a surface water and dosed with either free chlorine only, dichlor, or trichlor provided the first side-by-side comparisons of disinfectant residual stability and regulated DBP formation.

INTRODUCTION

In the United States (US), two chlorinated cyanurates commonly referred to as dichlor (anhydrous sodium dichloroisocyanurate or sodium dichloroisocyanurate dihydrate) and trichlor (trichloroisocyanuric acid) were first approved in July 2001 under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) for the routine treatment of drinking water (Kuechler 2009); therefore, their use as a free chlorine (hypochlorous acid, HOCl, plus hypochlorite ion, OCl⁻) source in drinking water is at the discretion of the relevant Safe Drinking Water Act (SDWA) primacy agency. Historically, dichlor and trichlor have been used in outdoor swimming pools to stabilize chlorine residual by minimizing sunlight related degradation (Canelli 1974). Even though sunlight related degradation of free chlorine (FreeCl) is not a major concern in drinking water systems, dichlor and trichlor use as alternative FreeCl sources in drinking water have several stated benefits, including that they

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(i) require simpler handling than liquid or gaseous chlorine forms because they are solids, (ii) have storage stabilities on the order of years, (iii) do not add calcium to water when dissolved, and (iv) have a high percent chlorine on a per mass basis (55–92%) (Kuechler 2009). Additional advantages of dichlor over trichlor when preparing concentrated dosing solutions are that dichlor has a greater water solubility (24,000 versus 1,400 mg/L) and produces a near neutral solution pH (Kuechler 2009).

Chemically, adding dichlor (Cl_2Cy^- , where Cy represents $\text{C}_3\text{N}_3\text{O}_3$) or trichlor (Cl_3Cy) to water is equivalent to adding both FreeCl and cyanuric acid (H_3Cy) to water at proportions based on the chemical structure of dichlor or trichlor. In either case, a rapid equilibrium (Figure 1A and Table 1, Full Model) is obtained between H_3Cy and its three dissociation products (H_2Cy^- , HCy^{2-} , and Cy^{3-}), FreeCl (HOCl and OCl^-), and six chlorinated cyanurates (Cl_3Cy , HCl_2Cy , H_2ClCy , Cl_2Cy^- , HClCy^- , and ClCy^{2-}). If no ammonia is present, a portion of the added total chlorine (FreeCl plus six chlorinated cyanurates, TOTCl) is present as FreeCl, and the remainder is bound in the six chlorinated cyanurates (O'Brien et al. 1974, O'Brien 1972). The equilibrium model presented in Figure 1A is termed herein as the Full Model and is valid for 25 °C. The sum of all the Cy containing chemicals is termed total cyanurate (TOTCy).

Recently, Wahman and Alexander (2018) reduced the Full Model by only including equilibrium expressions important under relevant drinking water conditions (i.e., 6.5 pH 9.5, TOTCl 10 mg Cl_2/L , and TOTCy 10 mg Cy/L). This model was termed the Simple Model (Figure 1B and Table 1, Simple Model) and included only four (K , K_6 , K_{7a} , and K_{9a}) temperature dependent equilibrium expressions, temperature dependence from 5 to 35 °C, and six chemical species: FreeCl (HOCl and OCl^-), cyanuric acid and its first dissociation product (H_3Cy and H_2Cy^- , respectively), and two chlorinated cyanurates (HClCy^- and Cl_2Cy^-). For a justification of the equilibrium assumption in the Simple Model, refer to the Supplementary Information (SI, Justification for Simple Model Equilibrium Assumption and Figures S1 and S2). The Simple Model is used herein for all simulations.

Using the Simple Model, the TOTCl portion that is FreeCl (assuming no ammonia is present) depends on (i) whether dichlor or trichlor was added which determines the ratio of TOTCl to TOTCy (TOTCl:TOTCy) added, (ii) the amount of dichlor or trichlor added which determines added TOTCl and TOTCy, (iii) pH, (iv) temperature, and (v) the extent of disinfectant demand that has occurred which reduces the added TOTCl. Changes to any of these items changes the TOTCl fraction present as FreeCl and therefore the FreeCl concentration. For the Simple Model, the difference between TOTCl and FreeCl is the chlorine bound in the two chlorinated cyanurates (HClCy^- and Cl_2Cy^-). For instance, a lower TOTCl fraction will be present as FreeCl if (i) dosing dichlor versus trichlor as the chlorine source, (ii) the amount of dichlor or trichlor dose increases, (iii) temperature decreases, or (iv) chlorine demand increases (Wahman 2018a, Wahman & Alexander 2018). For pH, the TOTCl fraction present as FreeCl varies with the lowest fraction (e.g., 0.6 and 0.7 for a 1 mg Cl_2/L TOTCl dose of dichlor or trichlor, respectively, SI Figure S3) occurring at approximately pH 7 and almost all TOTCl is FreeCl as the pH approaches 10 (SI Figure S3). Refer to Wahman (2018a) and Wahman and Alexander (2018) for a further discussion

of the water chemistry involved with using dichlor or trichlor in drinking water and the developed Simple Model.

Because of fast chlorinated cyanurate hydrolysis reactions releasing HOCl (e.g., Matte et al. 1990) and the possibility of direct reactions with method reagents (e.g., Jensen & Johnson 1990), one complicating factor with dichlor or trichlor use is that the FreeCl concentration cannot be measured accurately if the analysis method involves direct reactions with FreeCl or chlorinated cyanurates or the sample pH changes. In systems with FreeCl and chlorinated cyanurates and assuming no ammonia is present to form chloramines, any method with reagents reacting with FreeCl will actually measure TOTCl. Even if no FreeCl reactions occurred, pH changes resulting from the method would impact the measured FreeCl concentration compared to the FreeCl present in the original sample (SI Figure S3).

The inability to measure actual FreeCl concentrations in dichlor or trichlor systems is important and should be overcome to understand their use in water systems. For the same TOTCl concentration, the literature shows that chlorinated cyanurate presence reduces disinfection efficacy compared to a system with only FreeCl, and furthermore, HOCl is viewed as the effective disinfectant when chlorinated cyanurates are present because chlorinated cyanurates exhibit minimal disinfection efficacy compared to HOCl (Murphy et al. 2015, Wojtowicz 1996, Yamashita et al. 1988, Engel et al. 1983, Canelli 1974). Practically, assuming the actual FreeCl concentration solely determines disinfection efficacy, results in a conservative assumption as any contribution from chlorinated cyanurates would only increase efficacy.

If the actual FreeCl concentration cannot be determined, verification of compliance with US primary disinfection requirements (e.g., calculation of concentration times time, $C \times T$) or compliance in states that require a numeric versus detectable disinfectant residual in the distribution system (Wahman & Pressman 2015) may not be possible. The current issue with FreeCl measurement was recently highlighted by the State of Utah (Utah Division of Drinking Water 2017) and US Environmental Protection Agency (USEPA 2018).

Utility surveys (AWWA Water Quality and Technology Division Disinfection Systems Committee 2000) indicate that N,N-diethyl-p-phenylenediamine (DPD, Standard Methods 4500-Cl G and F) and amperometric titration (Standard Methods 4500-Cl D and E) methods are the two most commonly used to measure chlorine residuals in the plant and distribution system (DS) (APHA et al. 2005), representing over 90% of this usage. Because the reagents used in DPD and amperometric titration methods directly react with FreeCl and possibly chlorinated cyanurates, the methods measure TOTCl and overestimate (i.e., positive bias) the actual FreeCl residual present in systems using dichlor or trichlor (Jensen & Johnson 1990, Canelli 1980, Wajon & Morris 1980, Whittle 1970). Note that unlike monochloramine, HClCy^- hydrolysis is fast enough to completely release FreeCl during the recommended reaction timeframe (i.e., 20 to 60 s, SI Figure S2) of a FreeCl DPD test (Hach Company 2014a).

There are other possible methods to measure the FreeCl concentration directly in water samples from dichlor or trichlor systems, but they also suffer from limitations.

Amperometric electrodes measure a positive bias from chlorinated cyanurates and overestimate the FreeCl concentration with a measured value between the actual FreeCl and TOTCl concentrations (Jensen et al. 1990, Jensen & Johnson 1989, Canelli 1980). O'Brien et al. (1974) used spectroscopy at wavelengths between 196 and 292 nm to directly determine actual FreeCl concentrations, and more recently Wahman and Alexander (2018) used 292 nm absorbance to determine actual FreeCl concentrations when developing the Simple Model. Extension of the spectroscopy method to drinking waters is improbable because of limitations resulting from interferences at relevant wavelengths (i.e., 200–300 nm) from constituents such as natural organic matter (NOM) (e.g., Sohn et al. 2007, Korshin et al. 1997, Strickler & Kasha 1963) or nitrate (e.g., Bastian et al. 1957) and required detection limits for drinking water samples. In addition to reported FreeCl method measurement biases, newer approved FreeCl methods have yet to be evaluated with dichlor or trichlor, including (i) portable parallel analyzer DPD and (ii) indophenol methods.

Besides those previously mentioned, Wahman (2018a) hypothesized two possible advantages for systems using dichlor or trichlor instead of FreeCl only. For the same TOTCl dose and compared to FreeCl only, dichlor or trichlor systems may (i) achieve a more stable TOTCl residual and as a result (ii) possibly delay and even decrease regulated disinfectant byproduct (DBP) formation which could reduce regulated DBP exposure. As a first estimate, TOTCl residual loss can be represented as a second-order reaction between HOCl and a generic reacting species (X), where X could be NOM or another reduced species. NOM is typically quantified by the measurement of total organic carbon (TOC), and TOC is used herein as a NOM surrogate. Thus, Equation 1 represents a generic rate equation where k_x represents a generic second-order rate constant, and r_x is the overall reaction rate for constituent X. Brackets in Equation 1 represent molar concentrations.

$$r_x = k_x[\text{HOCl}][\text{X}] \quad (1)$$

Compared to a FreeCl only system and using the same equivalent TOTCl addition, dichlor or trichlor systems would have lower HOCl concentrations, as discussed previously, because a portion of the TOTCl would be present as chlorinated cyanurates, reducing r_x (Equation 1) and slowing TOTCl demand. This hypothesis requires evaluation as there are no drinking water studies that have directly compared the residual stability of using FreeCl only versus dichlor or trichlor.

Regarding DBP formation, slowing TOTCl demand may delay DBP formation if one assumes that DBP formation would be proportional to TOTCl demand. The only study that has investigated DBP formation related to the use of dichlor or trichlor in drinking water was Feldstein et al. (1984). This group conducted a preliminary evaluation of trihalomethane formation when adding H_3Cy to FreeCl, but they used chemical doses representative of outdoor swimming pool conditions rather than those typically used for drinking water. In addition, haloacetic acid formation was not studied. Therefore, there is a need for expanded DBP studies related to the use of dichlor and trichlor under realistic drinking water conditions.

The goals of the current research are to investigate three practical considerations when using dichlor or trichlor: (i) measurement bias of FreeCl methods, including verification of previously reported FreeCl method bias along with evaluation of additional approved FreeCl methods and provide the first direct comparison of using FreeCl only, dichlor, or trichlor on a surface water for (ii) residual stability and (iii) formation of regulated DBPs (four trihalomethanes, THM4, and five haloacetic acids, HAA5). Even though only a single surface water was explored in the current research, the results provide important baseline information that does not currently exist and highlights avenues of future research, including evidence for direct reactions of chlorinated cyanurates with NOM.

EXPERIMENTAL SECTION

Reagent and Glassware Preparation

All solutions were prepared in ultra-pure water (18.2 MΩ-cm)¹. Stock H₃Cy², sodium dichloroisocyanurate dihydrate², trichlor², and sodium hypochlorite³ solutions were prepared from reagent grade chemicals, accounting for reagent purity. Carbonate (4 mM) and phosphate (2 mM) buffers were made from sodium bicarbonate³ or sodium phosphate dibasic anhydrous³ and adjusted to the target pH with hydrochloric acid³ or sodium hydroxide³ as required. All glassware was treated to make chlorine demand free prior to use (Summers et al. 1996).

Analytical Methods

A summary of the analytical methods evaluated for FreeCl and TOTCl measurement methods used in the current research is provided in Table 2 alongside information regarding direct reactions with FreeCl or changes pH. The pH and temperature were measured by Standard Methods 4500-H⁺ and 2550, respectively (APHA et al. 2005)⁸. TOC was measured by EPA Method 415.3 (USEPA 2009b)⁹. THM4 and HAA5 were determined by a commercial laboratory¹⁰ using EPA Method 551.1 (USEPA 1995a) and EPA Method 552.2 (USEPA 1995b), respectively. Absorbance at 254 nm was determined by Standard Method 5910 (APHA et al. 2005)¹¹.

Measurement Bias Experiments

Simple Model simulated free chlorine concentrations.—As a basis for evaluating measured FreeCl concentrations in each measurement bias experiment, simulated FreeCl concentrations were determined using known chemical additions, pH, temperature, and the Simple Model (Figure 1B and Table 1, Simple Model). Bias presence was defined as having a statistical difference (t-test, $\alpha = 0.05$) between the Simple Model simulated and method measured FreeCl concentrations. Bias magnitude was quantified as the difference between the Simple Model simulated and method measured FreeCl concentrations. Initially, the

¹Barnstead NANOpure Diamond

²Acros Organics

³Fisher Chemical

⁸Orion pH electrode and Orion Star A211 pH meter

⁹Shimadzu TOC-L CPH/CPN

¹⁰Environmental Engineering & Technology, Inc.

¹¹Hach DR/4000U Spectrophotometer

validity of Simple Model simulated FreeCl concentrations was verified with absorbance derived actual FreeCl concentrations per the methodology of Wahman and Alexander (2018) and as subsequently discussed in *Amperometric electrode system experiment*.

Amperometric electrode system experiment.—A continuous online amperometric electrode system⁷ (AES) was used and compared with FreeCl and TOTCl colorimetric DPD methods (Table 2) and absorbance derived actual FreeCl concentrations (Wahman & Alexander 2018). Using a 2-mM phosphate buffer at a nominal pH 7.5 (7.5 ± 0.01), experimental waters were prepared with 3 mg Cl₂/L FreeCl and additions of either 0, 2, or 3 mg/L H₃Cy or 4 mg Cl₂/L FreeCl and additions of either 0, 2, or 4 mg/L H₃Cy. Experiments were conducted in triplicate. The AES was calibrated and maintained per manufacturer's instructions.

When not conducting experiments, the AES continuously received municipal tap water with a FreeCl residual (approximately 0.8 mg Cl₂/L). To conduct an experiment, the water source was changed from the municipal tap water to the experimental water. First, a gear pump¹² and controller¹³ connected to a 6 L Erlenmeyer flask covered in foil and containing the experimental water was used to flush tap water out of the AES and stabilize the measurement. During this phase (approximately 8 minutes), effluent from the AES was discharged to waste. Subsequently, a second 6 L Erlenmeyer flask covered in foil was used to recirculate the experimental water through the AES, and AES effluent was discharged back into the same 6 L Erlenmeyer flask. After allowing the measurement to stabilize (approximately 8 minutes), triplicate measurements were taken in succession where the total sample time was approximately 20 minutes. Experiments were conducted at room temperature (23 ± 0.83 °C).

AES experimental conditions were selected such that absorbance derived actual FreeCl concentration determination was possible to allow validation of Simple Model simulated FreeCl concentrations, following the methodology of Wahman and Alexander (2018). In this method, two solutions were required with the same TOTCl concentration, pH, and temperature. Solution 1 contained only FreeCl; therefore, the solution 1 FreeCl concentration, [FreeCl₁], equaled the TOTCl concentration, [TOTCl]. Solution 2 contained FreeCl and H₃Cy, making solution 2's FreeCl concentration, [FreeCl₂], less than [FreeCl₁] and [TOTCl].

Using Equation 2, the absorbance ratio of solution 2 to solution 1 at 292 nm (A_2/A_1) and the known [TOTCl] (which is the same for both solutions 1 and 2) was used to determine [FreeCl₂]. In Equation 2, brackets represent concentrations in mg Cl₂/L. Per Wahman and Alexander (2018), all spectrophotometric measurements were conducted with a 10-cm quartz cuvette using a spectrophotometer¹¹ set to read a single wavelength of 292 nm. The spectrophotometer was blanked with ultra-pure water prior to use. Triplicate absorbance measurements were taken and averaged for each measured triplicate sample.

⁷Hach CL10 sc Amperometric Chlorine Analyzer with Free Chlorine Sensor

¹²Micropump Model 070-000

¹³Cole-Parmer Model 75210-20

$$[\text{FreeCl}_2] = \frac{A_2}{A_1}[\text{TOTCl}] = \frac{A_2}{A_1}[\text{FreeCl}_1] \quad (2)$$

Colorimetric DPD, personal parallel analyzer (PPA) DPD, and indophenol

methods experiment.—Experiments were conducted to directly compare measurement of prepared FreeCl only, dichlor, and trichlor solutions using FreeCl and TOTCl colorimetric DPD, FreeCl and TOTCl personal parallel analyzer (PPA) DPD, and FreeCl and monochloramine indophenol methods (Table 2). Using a 4-mM carbonate buffer, triplicate solutions at nominal TOTCl concentrations of 0, 0.5, 1, 2, and 4 mg Cl₂/L were prepared, and each sample was measured in triplicate by each method at nominal pHs of 7 (7.1 ± 0.1) and 9 (9.0 ± 0.02). Experiments were conducted at room temperature (25 ± 0.71 °C).

Amperometric titration experiment.—FreeCl amperometric titration and FreeCl and TOTCl colorimetric DPD methods (Table 2) were compared for a series of solutions prepared in duplicate at nominal pH 7.5 (7.5 ± 0.03) and room temperature (22 ± 0.43 °C). Using a 4-mM carbonate buffer, seven different solutions were created at a nominal TOTCl concentration of 2 mg Cl₂/L. Five of the solutions were prepared by adding 2 mg Cl₂/L FreeCl and then various additions of H₃Cy (0, 1, 2, 3, or 4 mg/L) while the remaining two solutions were made directly from either dichlor or trichlor.

Hold Study

Water source and preparation.—Raw water (pH 7.6, 3.9 mg C/L TOC, and 0.113 cm⁻¹ UV₂₅₄) from a surface water treatment plant in Pennsylvania was collected and stored at 4 °C until use. Prior to the experiment, the raw water was equilibrated to room temperature over 24 hours. The raw water was subsequently treated using a jar test apparatus¹⁴ at conditions representative of that plant: (i) rapid mix: 100 rpm for 3 minutes and receiving 110 mg/L polyaluminum chloride (PACl)¹⁵ and 0.75 mg/L potassium permanganate³; (ii) slow mix: 20 rpm for 10 minutes; and (iii) settling: 0 rpm for 60 minutes. After settling, the supernatant was decanted (not filtered) from each jar. To generate enough water for the demand study, three rounds of water were treated and then combined to form a single water batch for the hold study. Prior to commencing the hold study, it was verified that no potassium permanganate remained in the water.

Hold study experiment.—The decanted supernatant (pH 7.3, 2.3 mg C/L TOC, and 0.057 cm⁻¹ UV₂₅₄) was adjusted to a nominal pH 7.5 (7.5 ± 0.07) and then dosed with either FreeCl only, dichlor, or trichlor at an initial TOTCl concentration of 4 mg Cl₂/L. The experiment was conducted in duplicate and at room temperature (22 ± 1.5 °C). The dosed water was subsequently divided into glass vials (40 mL) or bottles (250 mL) that were protected from light during storage and sacrificed at designated sampling times. Residual

¹⁴Phipps & Bird (7790–901B) with Six 2L Square Acrylic Jars (B–KER2)

¹⁵SternPAC

FreeCl and TOTCl, pH, and temperature were monitored periodically over 42 days and THM4 and HAA5 concentrations were monitored periodically over 24 days.

Residual model and parameter estimation.—To simulate the residual in the hold study, a batch reactor kinetic model was implemented using Aquasim (Reichert 1994), a computer program designed to simulate aquatic systems that is freely available at <http://www.eawag.ch/en/departement/siam/software/>, consisting of two parts. First, the Simple Model (Table 1, Simple Model) equilibrium chemistry was implemented for chemical speciation of chlorine and cyanurate containing chemicals. Second, to account for NOM reactions, a methodology similar to that of Duirk et al. (2005) was implemented where NOM was assumed to have both slow and fast reacting fractions that could be related to the TOC concentration. The implemented NOM reactions, rate expressions, and stoichiometry are summarized in Table 3.

NOM reaction related model parameters (k_{fast} , k_{slow} , $k_{\text{slow,bound}}$, and f_{fast} in Table 3) were estimated using the data fitting routine provided in Aquasim (Secant algorithm), which was configured to minimize the weighted residual sum of squares (WRSS) between measurements and simulated model results (Equation 3):

$$\text{WRSS} = \sum_{i=1}^n \left(\frac{y_{\text{meas},i} - y_i}{W} \right)^2 = \sum_{i=1}^n \left(\frac{y_{\text{meas},i} - y_i}{y_{\text{meas},i}} \right)^2 \quad (3)$$

In Equation 3, $y_{\text{meas},i}$ is the i -th measurement, W is the weighting factor, and y_i is the model simulated concentration corresponding to the i -th measurement. Because concentration measurements were changing over an order of magnitude, $y_{\text{meas},i}$ was implemented for W to prevent higher concentrations from biasing the fitting procedure, resulting in a dimensionless WRSS (Draper & Smith 1998, Robinson 1985).

RESULTS AND DISCUSSION

Measurement Bias Experiments

Amperometric electrode system experiment.—For the AES experiment, Figure 2 summarizes a comparison between Simple Model simulated, absorbance, AES, and colorimetric DPD FreeCl concentrations along with colorimetric DPD TOTCl concentrations. Including the uncertainty in the Simple Model equilibrium constants (Wahman 2018b, Wahman & Alexander 2018, Morris 1966), the absorbance determined actual FreeCl concentrations were not significantly different (t -test, $\alpha = 0.05$) than the Simple Model simulated actual FreeCl concentrations at cyanuric acid additions of 0, 2, 3, and 4 mg/L. Subsequently, Simple Model simulated FreeCl concentrations were used to interpret experiment results without further verification. As previously discussed, the absorbance FreeCl method is applicable for high purity waters absent of known interferences (e.g., NOM and nitrate). In addition and as discussed by Wahman and Alexander (2018), experimental conditions (e.g., pH and expected actual FreeCl concentrations) and equipment

(e.g., 10-cm absorbance cell pathlength) must be appropriately selected to determine actual FreeCl concentrations by the absorbance FreeCl method.

For the FreeCl colorimetric DPD method, the FreeCl concentrations for samples with H₃Cy addition were significantly greater (t-test, $\alpha = 0.05$) than the Simple Model simulated and effectively the same as the TOTCl colorimetric DPD measured concentrations. These results validate the reported positive measurement bias for the FreeCl colorimetric DPD method and that the magnitude of the bias is effectively the total chlorinated cyanurate concentration (mg Cl₂/L) and taken as the difference between the added TOTCl and simulated FreeCl concentration.

In contrast to the FreeCl colorimetric DPD method, the AES does not measure the TOTCl concentration with H₃Cy present. Rather, it appears to measure a concentration between the actual FreeCl and TOTCl concentrations, suggesting a response from the chlorinated cyanurates that is less than an equivalent FreeCl concentration. Specifically, the response was between 52 to 68% of the total chlorinated cyanurate concentration.

As mentioned previously, Canelli (1980) reported a positive bias using an amperometric electrode when measuring FreeCl with H₃Cy present and attributed the bias to a response resulting from chlorinated cyanurates where their response was 50% of an equivalent FreeCl concentration. Based on the Simple Model, four chemical species (HOCl, OCl⁻, HClCy⁻, and Cl₂Cy⁻) contain chlorine. At a fixed pH and temperature and assuming the AES response is a result of these four chlorine containing chemicals, Equation 4 and the experimental data (n = 36) can be used to estimate possible values for f_{HClCy} and $f_{\text{Cl}_2\text{Cy}}$ under various scenarios (Table 4).

$$[\text{AES}_p] = [\text{FreeCl}] + f_{\text{HClCy}}[\text{HClCy}^-] + f_{\text{Cl}_2\text{Cy}}[\text{Cl}_2\text{Cy}^-] \quad (4)$$

In Equation 4, brackets represent concentrations in mg Cl₂/L, [AES_p] is the predicted AES concentration, and f_{HClCy} and $f_{\text{Cl}_2\text{Cy}}$ are the fractions of HClCy⁻ and Cl₂Cy⁻ concentrations contributing to the AES_p concentration, respectively. FreeCl, HClCy⁻, and Cl₂Cy⁻ concentrations were determined from Simple Model simulations of the experimental conditions. The calculated AES_p concentration can be compared to the experimental AES concentration, [AES_E], by calculating a residual sum of squares (RSS) between the two concentrations (Equation 5, brackets represent concentrations in mg Cl₂/L). Using 0.5 for f_{HClCy} and $f_{\text{Cl}_2\text{Cy}}$ as Canelli (1980) reported as the Baseline Scenario, a relatively poor estimation of the AES_E concentration is obtained (1.8 RSS, Table 4, Baseline Scenario). Therefore, an analysis was conducted to evaluate if a combination of HClCy⁻ or Cl₂Cy⁻ concentrations and corresponding estimates of f_{HClCy} and $f_{\text{Cl}_2\text{Cy}}$ would better explain the AES_E concentrations under all conditions studied.

$$\text{RSS} = \sum ([\text{AES}_E] - [\text{AES}_p])^2 \quad (5)$$

Three scenarios were evaluated using Equation 4 and estimating f_{HClCy} and $f_{\text{Cl}_2\text{Cy}}$ by minimizing the RSS: (i) both HClCy^- or Cl_2Cy^- (f_{HClCy} and $f_{\text{Cl}_2\text{Cy}}$ estimated, Scenario 1), (ii) only HClCy^- (f_{HClCy} estimated, $f_{\text{Cl}_2\text{Cy}} = 0$, Scenario 2), or (iii) only Cl_2Cy^- ($f_{\text{Cl}_2\text{Cy}}$ estimated, $f_{\text{HClCy}} = 0$, Scenario 3) concentrations were included in Equation 4 (Table 4). All three scenarios provided reasonable estimations of the AES_E concentrations, but based on the RSS results, the scenario where both HClCy^- and Cl_2Cy^- concentrations are included (Scenario 1) provided the best explanation of AES_E concentrations ($f_{\text{HClCy}} = 0.68$ and $f_{\text{Cl}_2\text{Cy}} = 0.55$). Based on an analysis of variance analysis (ANOVA), Scenario 1 was significantly better (F-test, $\alpha = 0.05$) than either Scenario 2 or 3 and justified the addition of a second fitting parameter (i.e., either f_{HClCy} or $f_{\text{Cl}_2\text{Cy}}$).

A further justification for Scenario 1 results from a review of residuals. A plot of the residuals for each scenario (SI Figure S4) shows that only Scenario 1 produced no trend in the residuals, indicating a better representation of the experimental data. Because Equation 4 is a multiple linear regression for Scenario 1, the f_{HClCy} and $f_{\text{Cl}_2\text{Cy}}$ estimates are correlated. SI Figure S5 depicts this correlation by showing f_{HClCy} and $f_{\text{Cl}_2\text{Cy}}$'s joint 95% confidence region and illustrates that the current estimates are significantly different (SI Figure S5) than Canelli (1980). Further experiments should be conducted to determine whether this analysis holds over a wider range of conditions, but the current results suggest that both HClCy^- and Cl_2Cy^- are reactive towards the AES, but their response is less than an equivalent FreeCl concentration.

Colorimetric DPD, PPA DPD, and indophenol methods experiment.—For the experiment comparing FreeCl and TOTCl colorimetric and PPA DPD methods along with the FreeCl and monochloramine indophenol methods, Figure 3 summarizes the results at pH 7, where the greatest bias is expected (SI Figure S3), for dichlor (Figure 3A) and trichlor (Figure 3B). Results for the FreeCl only control experiments at pH 7 and 9 and the dichlor and trichlor experiments at pH 9 are presented in SI Figures S6 and S7, respectively. Ideally, the FreeCl methods would measure a value similar to the Simple Model simulated FreeCl concentrations (i.e., 1st bar in each bar set in Figure 3). For dichlor and trichlor at pH 7, all FreeCl methods measured concentrations significantly greater (t-test, $\alpha = 0.05$) than the simulated FreeCl concentrations. For the DPD methods where both a FreeCl and TOTCl method were used, the FreeCl measurements were not significantly different (t-test, $\alpha = 0.05$) than the TOTCl measurements. When using dichlor or trichlor, the difference between TOTCl and the actual FreeCl concentration is the total chlorinated cyanurate concentration; therefore, these results validated a positive bias equal to the total chlorinated cyanurate concentration. In addition, these results are the first showing that PPA DPD and indophenol FreeCl methods also exhibited the same positive measurement bias and actually measured TOTCl when using dichlor or trichlor.

Based on the Simple Model and as previously discussed, a lower TOTCl fraction is present as FreeCl with increasing dichlor or trichlor addition (i.e., increasing TOTCl concentrations) and at pH 7 compared to pH 9. These trends are seen in the simulated FreeCl concentrations in Figure 3 and SI Figure S7. For example, at pH 7 (Figure 3A), 2 and 4 mg Cl_2/L dichlor additions are simulated to have actual FreeCl concentrations of 0.9 (45% of TOTCl) and 1.4 (35% of TOTCl) mg Cl_2/L , respectively. In addition, a 2 mg Cl_2/L dichlor addition (Figure

3A and SI Figure S7A) is simulated to have an actual FreeCl concentration of 0.9 (45% of TOTCl) and 1.6 (80% of TOTCl) mg Cl₂/L at pHs 7 and 9, respectively. Overall, in this experiment, FreeCl and TOTCl methods measured the TOTCl present whether dichlor or trichlor was the chlorine source.

The current experimental result that the FreeCl indophenol method (Hach Company 2017a) measured the TOTCl in the sample provides supporting evidence for the fast hydrolysis of chlorinated cyanurates, which releases FreeCl. The first step in the FreeCl indophenol method is to add ammonia to specifically form monochloramine with any FreeCl in solution. The formed monochloramine is subsequently and specifically derivatized and measured colorimetrically as a green-colored indophenol (Hach Company 2008). If chlorinated cyanurate hydrolysis was slow, the FreeCl indophenol method would have only measured the actual FreeCl concentration in the sample because the remaining TOTCl would remain bound in the chlorinated cyanurates (i.e., HClCy⁻ and Cl₂Cy⁻). The result that the FreeCl indophenol method measured the TOTCl in solution supports the fast hydrolysis reported in the literature, requiring that FreeCl be released from the chlorinated cyanurates and subsequently reacted with ammonia to form monochloramine to be measured with this method. In addition, the monochloramine indophenol method (Hach Company 2015a) was also run in these experiments and did not show a response significantly greater (t-test, $\alpha = 0.05$) than the control (i.e., the 0 mg Cl₂/L added TOTCl condition), indicating that the direct reaction of FreeCl or chlorinated cyanurates with method reagents does not occur as the only difference between the FreeCl and monochloramine indophenol methods is that ammonia is first added in the FreeCl version to form monochloramine. The specificity of the monochloramine indophenol method for only monochloramine is expected (Hach Company 2015b, 2015a, Lee et al. 2007).

Overall, the inability for the FreeCl DPD and indophenol methods to measure only the actual FreeCl concentration present is a result of either fast chlorinated cyanurate hydrolysis or a direct reaction of the chlorinated cyanurates with method reagents. For the DPD based methods, hydrolysis alone would be fast enough to account for the positive bias (SI Figure S2), but a direct reaction cannot be ruled out based on the experiments conducted. For the FreeCl indophenol method, it appears that the measured bias is the sole result of chlorinated cyanurate hydrolysis, leading to release of FreeCl with its subsequent reaction with ammonia to form monochloramine. The direct reaction of chlorinated cyanurates and FreeCl was ruled out because no measurement significantly different (t-test, $\alpha = 0.05$) from the control was obtained with the monochloramine indophenol method.

Amperometric titration experiment.—Figure 4 summarizes the amperometric titration experiment and confirms that FreeCl amperometric titration measures the TOTCl concentration in the presence of H₃Cy, whether added separately or as part of dichlor or trichlor addition. The inability to accurately measure FreeCl is clearly shown where the successive increases in H₃Cy added to 2 mg Cl₂/L FreeCl (CYA 0 to CYA 4, 0 to 4 mg/L H₃Cy addition) do not change the measurement response from FreeCl amperometric titration or FreeCl colorimetric DPD methods. For CYA 4 (2 mg Cl₂/L FreeCl and 4 mg/L H₃Cy), only approximately 20% of the TOTCl is present as FreeCl (0.4 mg Cl₂/L) with the balance present as chlorinated cyanurates (1.6 mg Cl₂/L), but both FreeCl methods measure TOTCl,

illustrating the positive bias in these measurements. As with the FreeCl DPD methods, the measurement bias is a result of either fast chlorinated cyanurate hydrolysis or a direct reaction of the chlorinated cyanurates with method reagents.

Hold Study

Residual Demand.—Figure 5 shows the FreeCl (Figure 5A) and TOTCl (Figure 5B) colorimetric DPD measured concentrations over the 42-day hold study. For either colorimetric DPD method, dichlor showed the greatest residual stability followed by trichlor and then FreeCl. Based on the results from the previous measurement bias experiments, the FreeCl and TOTCl colorimetric DPD methods should result in similar measurements, but at all temporal observations, the TOTCl DPD colorimetric measurement was greater than the FreeCl DPD colorimetric measurement as indicated by the positive values in Figure 5C. This difference was not observed during the previous measurement bias experiments where a laboratory water was used and is likely attributed to positive interferences in the TOTCl DPD measurement associated with using a surface water source (e.g., organic chloramines). It is important to note that the interference represents approximately 10% of the TOTCl DPD measurement initially, but the percentage increases as the TOTCl DPD measurement decreases, indicating that the interfering substance is relatively more stable than the TOTCl in the water. At 42 days, approximately 82, 57, and 40% of the TOTCl DPD measurement is a result of interference for water initially dosed with FreeCl only, trichlor, or dichlor, respectively. Overall, the hold study supported the hypothesis that a more stable TOTCl residual, based on the FreeCl DPD measurement, was maintained when using dichlor or trichlor as opposed to FreeCl only. Furthermore, the observation that the TOTCl DPD method overestimated TOTCl and the relative overestimation increased with time is important because one of the inputs to simulate a FreeCl concentration from the Simple Model is the TOTCl concentration (Wahman & Alexander 2018). If an overestimated TOTCl is used in the Simple Model, the resulting Simple Model FreeCl estimate will also be overestimated, resulting in overestimation of compliance with residual or disinfection requirements.

Using the Aquasim model (Table 1, Simple Model and Table 3), a further investigation into the hold study data was conducted to evaluate the hypothesis that the increased stability observed with dichlor or trichlor was simply a result of having a lower actual FreeCl (specifically HOCl) concentration. Initially, the FreeCl only experiment data was used to estimate three NOM reaction parameters (Tables 3 and 5): (i) the fast reactive organic matter fraction of TOC (f_{fast}), (ii) FreeCl fast reaction rate constant (k_{fast}), and (iii) FreeCl slow reaction rate constant (k_{slow}). Subsequently, these values were used to simulate the dichlor and trichlor experiment data (Figure 6A). Even with the Simple Model equilibrium assumption, which does not limit HOCl release from the chlorinated cyanurates (Table 1, K_{7a} and K_{9a}), the simulations overestimated the dichlor and trichlor data, indicating that a chlorinated cyanurate species was also likely reacting with NOM in addition to FreeCl.

To account for possible chlorinated cyanurate reactivity with NOM, a revised parameter estimation was conducted by simultaneously using the FreeCl only, dichlor, and trichlor data and adding an additional reaction between NOM and HCICy^- (HCICy^- slow, Table 3) where

the HCICy^- slow reaction rate constant ($k_{\text{slow,bound}}$) was estimated in addition to f_{fast} , k_{fast} , and k_{slow} . In the Simple Model, HCICy^- and Cl_2Cy^- are the only two chlorinated cyanurates included, and HCICy^- is present at a greater concentration than Cl_2Cy^- (SI Figure S8). As this was an exploratory analysis and to limit the number of added reactions, only HCICy^- was chosen to react with NOM.

Estimated parameters are summarized in Table 5, and the model simulations compared to the experimental data are shown in Figure 6B. Inclusion of a NOM reaction with HCICy^- provided a more accurate simulation of the experimental data and did not significantly change (t -test, $\alpha = 0.05$) the estimates for the parameters associated with fast and slow FreeCl reactions (f_{fast} , k_{fast} , and k_{slow} ; Table 5). The parameter estimates indicated that HOCl reacted 3.5 times as fast with the slow NOM fraction than did HCICy^- (Table 5, k_{slow} versus $k_{\text{slow,bound}}$). Also, HOCl reacted over two orders of magnitude faster with the fast NOM fraction than it did with the slow NOM fraction (Table 5, k_{fast} versus k_{slow}).

The intent of including a NOM reaction with a chlorinated cyanurate was not to conclusively prove that HCICy^- was the only possible chlorinated cyanurate that could have reacted with NOM. Rather, the intent was to show that an additional reaction with a chlorinated cyanurate was required beyond HOCl to simulate the experimental data for all three conditions simultaneously (i.e., FreeCl only, dichlor, and trichlor). As the addition of this single NOM reaction with HCICy^- resulted in the experimental data being simulated extremely well, no other reactions were considered. Future validation of these observations with additional waters should be conducted to determine the importance of the proposed HCICy^- reaction with NOM and if a reaction with Cl_2Cy^- occurs.

To assess the possible impact of using dichlor or trichlor in terms of residual stability in practice, the time to reach 0.2 mg Cl_2/L for the TOTCl (based on FreeCl DPD measurements) and actual FreeCl (Simple Model simulated) concentrations were determined. Based on the FreeCl DPD measurement which quantifies TOTCl (assuming no ammonia is present to form chloramines), approximately 20, 35, and 37 days were required for the residual to decrease to 0.2 mg Cl_2/L for FreeCl only, trichlor, and dichlor, respectively (Figure 6B). When Simple Model simulated actual FreeCl concentrations are compared (SI Figures S8 and S9A), the trend is reversed as 20, 12, and 8 days for FreeCl, trichlor, and dichlor were required for the simulated actual FreeCl residual to decrease to 0.2 mg Cl_2/L . The trend was reversed because as TOTCl is consumed in the experiments with dichlor or trichlor, the TOTCl decreases but the TOTCy does not decrease (i.e., TOTCl:TOTCy decreases); therefore, a greater portion of the TOTCl is present as chlorinated cyanurates (specifically HCICy^-) with a lesser amount as FreeCl (SI Figure S8), illustrating that at least part of the increase in TOTCl residual stability with dichlor or trichlor is a result of lower FreeCl concentrations as hypothesized.

As mentioned previously, FreeCl is considered the actual disinfectant in systems using dichlor or trichlor as chlorinated cyanurates exhibit relatively minimal disinfection efficacy compared to FreeCl. Using the simulated FreeCl concentrations (SI Figure 9A), $C \times T$ values can be calculated for each hold study (SI Figure S9B). The FreeCl only experiment provided the greatest $C \times T$ value for any time point followed by the trichlor and dichlor

experiments whose $C \times T$ values after 42 days were 41% and 27% of the FreeCl only experiment, respectively.

DBPs.—Figure 7 presents a breakdown of the THM4 and HAA5 results over 24 days during the hold study. After 14–days, THM4 formation for FreeCl only, dichlor, and trichlor was similar (60 to 62 $\mu\text{g/L}$), and after 24–days, there is still little difference in THM4 reduction for dichlor (103 $\mu\text{g/L}$, 6% reduction) or trichlor (108 $\mu\text{g/L}$, 2% reduction) compared to FreeCl only (110 $\mu\text{g/L}$). After 24–days, a greater HAA5 reduction is seen for dichlor (74 $\mu\text{g/L}$, 24% reduction) or trichlor (80 $\mu\text{g/L}$, 18% reduction) compared to FreeCl only (97 $\mu\text{g/L}$). The HAA reduction is driven by a reduction in trichloroacetic acid (TCAA) and dichloroacetic acid (DCAA) formation. These results indicate that there may be reduced HAA5 formation for dichlor or trichlor use compared to FreeCl only. THM4 and HAA5 speciations were similar when using FreeCl only, dichlor, or trichlor. For example, at 24–days, trichloromethane (TCM) and DCAA represented 75–78% and 46–49% of the THM4 and HAA5 concentrations, respectively.

Another interesting result from the DBP data can be seen when plotting the FreeCl colorimetric DPD demand versus THM4 or HAA5 halogen micromolar concentrations (Figure 8). For the 24–day THM4 data, there appears to be an anomalous increase this far into the hold study. If the apparent anomalous 24–day THM4 data is excluded, a linear trend results for both the THM4 ($0.97 R^2$) and HAA5 ($0.95 R^2$) halogen concentrations versus FreeCl DPD demand, indicating that a more stable residual (based on FreeCl colorimetric DPD demand) should lead to lower THM4 and HAA5 concentrations whether FreeCl only, dichlor, or trichlor are used as the FreeCl source.

Because the main application for chlorinated cyanurates has historically been outdoor swimming pools, most published research has focused on outdoor swimming pool conditions which are not representative of drinking water; thus, conclusions cannot be drawn from most published studies to drinking water or the current hold study. For example, Yang et al. (2016) studied THM and HAA formation for FreeCl and trichlor, but the water conditions included (i) a simulated tropical temperature (26 to 40 $^{\circ}\text{C}$), (ii) supplementation with a body fluid analogue (1 to 5 mg C/L TOC) of urine and sweat (e.g., urea, creatine, uric acid, citric acid), and (iii) a 25 mM phosphate buffer.

To the authors' knowledge, only a single study (Feldstein et al. 1984) has investigated chlorinated cyanurate DBP formation relevant to a drinking water application, but this study was limited. Specifically, Feldstein et al. (1984) (i) used directly filtered Ohio River water, (ii) only monitored regulated THM formation, and (iii) dosed the water with 13 mg Cl_2/L of FreeCl and either 0, 2, 100, 175, or 350 mg/L of H_3Cy . Feldstein et al. (1984) did not investigate HAA formation and only used one H_3Cy dose representative of current drinking water practice (i.e., 2 mg/L H_3Cy) as the other H_3Cy doses were one to two orders of magnitude greater than anticipated concentrations in drinking water. For the 2 mg/L H_3Cy dose, Feldstein et al. (1984) reported a 7% decrease in THM formation which is similar to that seen in the current hold study when using dichlor versus FreeCl only at 24 days, and they did not investigate whether THM formation was a result of chlorinated cyanurates or FreeCl reacting with NOM. Rather, they assumed that based on the known and fast

equilibrium chemistry that THM formation was a result of a direct reaction of the FreeCl present and that FreeCl was released quickly through chlorinated cyanurate hydrolysis.

Assuming a linear relationship between DBP formation and chlorine demand (i.e., Figure 8) and using the NOM demand reactions for HOCl and HCICy^- , an estimate of the THM or HAA formation attributed to either HOCl or HCICy^- in the dichlor and trichlor experiments can be obtained. HOCl attributed FreeCl colorimetric DPD demand was 69% and 76% for the dichlor and trichlor hold studies, respectively, with the balance attributed to HCICy^- . Therefore, the current results support that the majority of DBP formation (assuming a linear relationship exists as shown in Figure 8) is a result of direct reactions with FreeCl, but the kinetic analysis also shows that a NOM reaction with chlorinated cyanurates is also important. Whether chlorinated cyanurate reactions with NOM produce THMs or HAAs or other unregulated DBPs under drinking water conditions remains an avenue of future research, but the data and analysis presented herein suggests that chlorinated cyanurate reactions with NOM produce regulated DBPs, and that there is a reduction in HAA5 formation with the use of dichlor or trichlor compared to FreeCl only.

Practical Implications

The results of the research presented herein have several practical implications. The inability to measure the actual FreeCl concentration with H_3Cy present, as would be the case when using dichlor or trichlor as a chlorine source, is clear for both previously reported and newer FreeCl methods when ammonia is not present, resulting in a positive measurement bias. In all cases except for the AES, the FreeCl methods actually measured the TOTCl concentration which is made up of FreeCl and chlorinated cyanurates; therefore, the magnitude of the bias was effectively the total chlorinated cyanurate concentration. For the AES, a positive bias was observed, and the measurement was between the actual FreeCl and TOTCl concentration. Using the Simple Model, the positive bias magnitude was determined to correlate to 68 and 55% of the HCICy^- and Cl_2Cy^- concentrations ($\text{mg Cl}_2/\text{L}$), respectively (Table 4). As FreeCl is considered the disinfectant in these systems, compliance with primary disinfection and secondary (FreeCl) residual requirements cannot currently be verified by direct measurement. This highlights the need to develop new methods to determine the actual FreeCl concentrations in systems using dichlor or trichlor or simulate FreeCl concentrations from the Simple Model.

A SDWA primacy agency's regulatory requirement to maintain a secondary disinfectant residual, as either detectable or a numeric value, may lead to different interpretations of whether dichlor or trichlor would provide a benefit over FreeCl for residual maintenance. If only a detectable residual is required and there are no concerns that some percentage of the TOTCl residual is actually FreeCl, then dichlor or trichlor use may provide better residual maintenance; however, if a numeric FreeCl residual is required (i.e., for FreeCl systems) then dichlor or trichlor may not be appropriate to use until an approach to accurately quantify FreeCl residual when using dichlor or trichlor is developed. In addition, the hold study results showed that when using DPD methods the TOTCl residual concentrations were consistently greater than the paired (i.e., same sample) FreeCl residual concentrations. Therefore, if a system's objective is to quantify FreeCl residual, then a FreeCl method

should be used in lieu of a TOTCl method which may result in an artificially greater measured concentration.

For hold studies using dichlor or trichlor, it was necessary to include another reactive chlorine species besides FreeCl to simulate residual loss. Because a chlorinated cyanurate is likely directly reacting with NOM, future experiments should be conducted to verify which chlorinated cyanurates are reacting with NOM and to ascertain if this reaction leads to any DBPs (regulated or unregulated) that may be of concern.

For the surface water studied in this research, a benefit was seen with dichlor (24% reduction) or trichlor (18% reduction) over FreeCl for HAA5 formation, but little benefit was seen for THM4 formation. Also, THM4 and HAA5 concentrations were linearly correlated with FreeCl DPD measured demand, indicating that a more stable residual may delay THM4 or HAA5 formation. Future research should expand to additional surface and groundwaters to evaluate whether these trends hold over a variety of source waters, but the current results provide an essential first set of experiments under drinking water relevant conditions that directly compared FreeCl only, dichlor, and trichlor.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENT

The authors acknowledge the review and helpful comments provided by Dr. Julian L. Fairey of the University of Arkansas. This work has been subjected to the United States Environmental Protection Agency's (Agency's) review and has been approved for publication. The views expressed in this manuscript are those of the author and do not necessarily represent the views or policies of the Agency. Any mention of trade names, products, or services does not imply an endorsement by the Agency. The Agency does not endorse any commercial products, services, or enterprises.

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REFERENCES

APHA, AWWA & WEF, 2005 (21st ed). Standard Methods for the Examination of Water and Wastewater. American Public Health Association : American Water Works Association : Water Environment Federation, Washington, D.C.

- AWWA Water Quality and Technology Division Disinfection Systems Committee, 2000 Committee Report: Disinfection at Large and Medium-Size Systems. Journal American Water Works Association, 92:5:32.
- Bastian R, Weberling R & Palilla F, 1957 Ultraviolet Spectrophotometric Determination of Nitrate... Application to Analysis of Alkaline Carbonates. Analytical Chemistry, 29:12:1795.
- Brady AP, Sancier KM & Sirine G, 1963 Equilibria in Solutions of Cyanuric Acid and Its Chlorinated Derivatives. Journal of the American Chemical Society, 85:20:3101.
- Canelli E, 1974 Chemical, Bacteriological, and Toxicological Properties of Cyanuric Acid and Chlorinated Isocyanurates as Applied to Swimming Pool Disinfection – a Review. American Journal of Public Health, 64:2:155. [PubMed: 4594286]
- Canelli E, 1980 Evaluation of a Portable Bare-Electrode Amperometric Analyzer for Determining Free Chlorine in Potable and Swimming-Pool Waters. Water Research, 14:10:1533.
- Draper NR & Smith H, 1998 Applied Regression Analysis. John Wiley & Sons, Inc, New York, NY.
- Duirk SE, Gombert B, Croue JP & Valentine RL, 2005 Modeling Monochloramine Loss in the Presence of Natural Organic Matter. Water Research, 39:14:3418. [PubMed: 16045963]
- Engel JP, Rubin AJ & Sproul OJ, 1983 Inactivation of *Naegleria Gruberi* Cysts by Chlorinated Cyanurates. Applied and Environmental Microbiology, 46:5:1157. [PubMed: 6316851]
- Feldstein CM, Rickabaugh J & Miltner RJ, 1984 Effect of Cyanuric Acid, a Chlorine Stabilizer, on Trihalomethane Formation – EPA/600/D-84/167. United States Environmental Protection Agency, Washington, DC.
- Company Hach, 2008 (5th Edition ed). Water Analysis Handbook, Loveland, CO.
- Company Hach, 2013 Method 10250, Chlorine, Total, MR. USEPA DPD Method, 0.05 to 4.00 mg/L Cl₂ (MR). Hach Company, Loveland, Colorado.
- Company Hach, 2014a Method 8021, Chlorine, Free. USEPA DPD Method, 0.02 to 2.00 mg/L Cl₂. Hach Company, Loveland, Colorado.
- Company Hach, 2014b Method 10245, Chlorine, Free. USEPA DPD Method, 0.05 to 4.00 mg/L Cl₂ (MR). Hach Company, Loveland, Colorado.
- Company Hach, 2015a Method 10171, Chloramine (Mono). Indophenol Method, 0.04 to 4.50 Mg Cl₂/L (LR). Hach Company, Loveland, Colorado.
- Company Hach, 2015b Method 10260, Free Chlorine. USEPA DPD Method, Chemkey Reagents, 0.12 to 4.6 mg/L as Cl₂. Hach Company, Loveland, Colorado.
- Company Hach, 2017a Method 10241, Free Chlorine USEPA Indophenol Method, 0.04 to 4.50 mg/L Cl₂. Hach Company, Loveland, Colorado.
- Company Hach, 2017b Method 10260, Total Chlorine. USEPA DPD Method, Chemkey Reagents, 0.04 to 10.0 mg/L as Cl₂. Hach Company, Loveland, Colorado.
- Company Hach, 2018 Method 8167, Chlorine, Total. USEPA DPD Method, 0.02 to 2.00 mg/L Cl₂. Hach Company, Loveland, Colorado.
- Jensen JN & Johnson JD, 1989 Quantitation of Interferences under Equilibrium Conditions with Application to Free Chlorine Analysis in the Presence of Organic Chloramines. Analytical Chemistry, 61:9:991.
- Jensen JN & Johnson JD, 1990 Interferences by Monochloramine and Organic Chloramines in Free Available Chlorine Methods. 2. N,N-Diethyl-P-Phenylenediamine. Environmental Science & Technology, 24:7:985.
- Jensen JN, Le Cloirec PL & Johnson JD, 1990 Chloramine Interference in the Measurement of Free Chlorine by the Amperometric Membrane Electrode Water Chlorination: Chemistry, Environmental Impact and Health Effects. Lewis Publishers, Inc, Chelsea, MI.
- Korshin GV, Li C-W & Benjamin MM, 1997 Monitoring the Properties of Natural Organic Matter through UV Spectroscopy: A Consistent Theory. Water Research, 31:7:1787.
- Kuechler TC, 2009 Use of Chlorinated Isocyanurates for Drinking Water Chlorination. Proceedings of the Water Environment Federation, 2009:1:799.
- Lee W, Westerhoff P, Yang X & Shang C, 2007 Comparison of Colorimetric and Membrane Introduction Mass Spectrometry Techniques for Chloramine Analysis. Water Research, 41:14:3097. [PubMed: 17544050]

- Matte D, Solastiouk B, Merlin A & Deglise X, 1990 Étude Cinétique De La N–Chloration De L’acide Cyanurique En Phase Aqueuse. *Canadian Journal of Chemistry*, 68:2:307.
- Morris JC, 1966 The Acid Ionization Constant of HOCl from 5 to 35°C. *Journal of Physical Chemistry*, 70:12:3798.
- Murphy JL, Arrowood MJ, Lu X, Hlavsa MC, Beach MJ & Hill VR, 2015 Effect of Cyanuric Acid on the Inactivation of *Cryptosporidium Parvum* under Hyperchlorination Conditions. *Environmental Science & Technology*, 49:12:7348. [PubMed: 26042636]
- O’Brien JE, 1972 Hydrolytic and Ionization Equilibria of Chlorinated Isocyanurate in Water. Dissertation. Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts.
- O’Brien JE, Morris JC & Butler JN, 1974 Equilibria in Aqueous Solutions of Chlorinated Isocyanurate Chemistry of Water Supply, Treatment, and Distribution. Ann Arbor Science Publishers, Inc, Ann Arbor, MI.
- Reichert P, 1994 Aquasim – a Tool for Simulation and Data Analysis of Aquatic Systems. *Water Science and Technology*, 30:2:21.
- Robinson JA, 1985 Determining Microbial Kinetic Parameters Using Nonlinear Regression Analysis: Advantages and Limitations in Microbial Ecology. *Advances in Microbial Ecology*, 8:61.
- Sohn J, Amy G & Yoon Y, 2007 Process–Train Profiles of NOM through a Drinking Water Treatment Plant. *Journal American Water Works Association*, 99:6:145.
- Strickler SJ & Kasha M, 1963 Solvent Effects on the Electronic Absorption Spectrum of Nitrite Ion. *Journal of the American Chemical Society*, 85:19:2899.
- Summers RS, Hooper SM, Shukairy HM, Solarik G & Owen D, 1996 Assessing the DBP Yield: Uniform Formation Conditions. *Journal American Water Works Association*, 88:6:80.
- USEPA, 1995a Method 551.1 Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid–Liquid Extraction and Gas Chromatography with Electron–Capture Detection (Revision 1.0). USEPA, Cincinnati, Ohio.
- USEPA, 1995b Method 552.2 Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid–Liquid Extraction, Derivatization and Gas Chromatography with Electron Capture Detection (Revision 1.0). USEPA, Cincinnati, Ohio.
- USEPA, 2009a Method 334.0 Determination of Residual Chlorine in Drinking Water Using an on–Line Chlorine Analyzer. USEPA, Cincinnati, Ohio.
- USEPA, 2009b Method 415.3, Rev. 1.2: Determination of Total Organic Carbon and Specific UV Absorbance at 254 Nm in Source Water and Drinking Water. USEPA, Cincinnati, Ohio.
- USEPA, 2018 Memorandum – Compliance Determination for Inactivation Requirements of the National Primary Drinking Water Regulations When a Public Water Systems Uses Dichlor and Trichlor for Primary Disinfection (April 18, 2018). <<https://asdwa.files.wordpress.com/2018/04/dichlor-trichlor-memo-2018-04-18.pdf>>, August 27, 2018.
- Utah Division of Drinking Water, 2017 Plan Review Policy for Dichlor and Trichlor Installations (Ddw–Eng–0032 April 27, 2017). <<https://documents.deq.utah.gov/drinking-water/engineering/new-facilities-new-public-water-systems/DDW-2017-001930.pdf>>, August 27, 2018.
- Wahman DG, 2018a Chlorinated Cyanurates: Review of Water Chemistry and Associated Drinking Water Implications. *Journal American Water Works Association*, 110:9:E1. [PubMed: 30319139]
- Wahman DG, 2018b First Acid Ionization Constant of the Drinking Water Relevant Chemical Cyanuric Acid from 5 to 35 °C. *Environmental Science: Water Research & Technology*, 4:1522. [PubMed: 30416738]
- Wahman DG & Alexander MT, 2018 A Drinking Water Relevant Water Chemistry Model for the Free Chlorine and Cyanuric Acid System from 5 to 35 °C. *Environmental Engineering Science*, 10.1089/ees.2018.0387.
- Wahman DG & Pressman JG, 2015 Distribution System Residuals–Is “Detectable” Still Acceptable for Chloramines? *Journal American Water Works Association*, 107:8:53.
- Wajon JE & Morris JC, 1980 The Analysis of Free Chlorine in the Presence of Nitrogenous Organic Compounds. *Environment International*, 3:1:41.

- Whittle GP, 1970 Recent Advances in Determining Free Chlorine. National Specialty Conference on Disinfection.
- Wojtowicz JA, 1996 Relative Bactericidal Effectiveness of Hypochlorous Acid and Chloroisocyanurates. *Journal of the Swimming Pool and Spa Industry*, 2:1:34.
- Yamashita T, Sakae K, Ishihara Y, Isomura S & Inoue H, 1988 Virucidal Effect of Chlorinated Water Containing Cyanuric Acid. *Epidemiology and Infection*, 101:3:631. [PubMed: 2850940]
- Yang L, Schmalz C, Zhou J, Zwiener C, Chang VWC, Ge L & Wan MP, 2016 An Insight of Disinfection by-Product (DBP) Formation by Alternative Disinfectants for Swimming Pool Disinfection under Tropical Conditions. *Water Research*, 101:535. [PubMed: 27300590]

FIGURE 1. Free chlorine, cyanuric acid, and chlorinated cyanurate equilibria ^a

A. Full Model schematic ^{b, c} B. Simple Model schematic ^c

^aAdapted with permission from Brady et al. (1963). Copyright 1963 American Chemical Society.

^b Grey highlighted chemicals are the major cyanurate containing species expected under drinking water conditions and chemical dosages and represent the Simple Model.

^c Hydrogen ion for dissociation reactions and water and hypochlorous acid for hydrolysis reactions are not shown for clarity. Refer to Table 1 for the full equilibrium expressions and constant values.

FIGURE 2. Amperometric electrode system (AES) experiment in 2 mM phosphate buffer at pH 7.5 for 3 (A) and 4 (B) mg Cl₂/L total chlorine^a

^a Bars represent 95% confidence intervals for each method

Free Sim – Free chlorine Simple Model simulated; Free Absorbance – Free chlorine absorbance; Free Electrode – Free chlorine amperometric electrode; Free DPD – Free chlorine colorimetric N,N-diethyl-p-phenylenediamine (DPD); Total DPD – Total chlorine colorimetric DPD

FIGURE 3. Dichlor (A) and trichlor (B) DPD and indophenol experiment in 4 mM carbonate buffer at pH 7^a

^a Bars represent 95% confidence intervals for each method. The measured values for the 0 mg Cl₂/L experiments were at or below the method detection limit for the methods.

Free Sim – Free chlorine Simple Model simulated; Free DPD – Free chlorine colorimetric N,N-diethyl-p-phenylenediamine (DPD); Total DPD – Total chlorine colorimetric DPD; Free PPA – Free chlorine personal parallel analyzer (PPA) DPD; Total PPA – Total chlorine PPA DPD; Free Indophenol – Free Chlorine Indophenol

FIGURE 4. Amperometric titration experiment in 4 mM carbonate buffer at pH 7.5 ^a

^a Bars represent 95% confidence intervals for each method

Free Sim – Free chlorine Simple Model simulated; Free Amperometric – Free chlorine amperometric titration; Free DPD – Free chlorine colorimetric N,N-diethyl-p-phenylenediamine (DPD); Total DPD – Total chlorine colorimetric DPD

FIGURE 5. Hold study free (A), total (B), and free minus total (C) chlorine residual stability^a

^a Experiment conditions: coagulated and settled water, pH 7.5, 2.3 mg C/L TOC, 0.057 cm⁻¹ UV₂₅₄, and 22 °C. All free chlorine and total chlorine DPD measured concentrations were above the method detection limit of 0.02 mg Cl₂/L.

FIGURE 6. Hold study simulations including an organic matter reaction with free chlorine (A) or free chlorine and chlorinated cyanurates (B)^a

^a For both panels, the equilibrium expressions presented in Table 1 (Simple Model) and the Free Chlorine Fast and Free Chlorine Slow reactions from Table 3 were included. For panel B, the HClCy⁻ Slow reaction from Table 3 was also included. In both panels, A and B represent duplicate experiments.

FIGURE 7. Hold study regulated trihalomethane (A) and haloacetic acid (B) summary^a

^a Experiment conditions: coagulated and settled water, pH 7.5, 2.3 mg C/L TOC, 0.057 cm^{-1} UV_{254} , and 22 °C

TBM – tribromomethane; DBCM – dibromochloromethane; BDCM – bromodichloromethane; TCM – trichloromethane; MCAA – monochloroacetic acid; DBAA – dibromoacetic acid; MBAA – monobromoacetic acid; TCAA – trichloroacetic acid; DCAA – dichloroacetic acid

FIGURE 8. Hold study free chlorine demand and trihalomethane and haloacetic formation ^a

^a Experiment conditions: coagulated and settled water, pH 7.5, 2.3 mg C/L TOC, 0.057 cm^{-1} UV_{254} , and 22 °C

HAA5 – five regulated haloacetic acids; THM4 – four regulated trihalomethanes

TABLE 1

Equilibrium expressions and constants for chlorinated cyanurate water chemistry models

Equilibrium Expression	Equilibrium Constant	Model Equilibrium Constant Values Included	
		Full Model 25 °C pK ^a	Simple Model 5–35 °C ; 25 °C pK ^{b, c}
$\text{Cl}_3\text{Cy} + \text{H}_2\text{O} \rightleftharpoons \text{HCl}_2\text{Cy} + \text{HOCl}$	K _{1a}	1.8	N/A
$\text{HCl}_2\text{Cy} \rightleftharpoons \text{Cl}_2\text{Cy}^- + \text{H}^+$	K ₂	3.75	N/A
$\text{H}_2\text{ClCy} \rightleftharpoons \text{HClCy}^- + \text{H}^+$	K ₄	5.33	N/A
$\text{H}_3\text{Cy} \rightleftharpoons \text{H}_2\text{Cy}^- + \text{H}^+$	K ₆	6.88	$\frac{1,743}{T_K} + 1.12 ; 6.97^d$
$\text{Cl}_2\text{Cy}^- + \text{H}_2\text{O} \rightleftharpoons \text{HClCy}^- + \text{HOCl}$	K _{7a}	4.51	$\frac{2,028}{T_K} - 2.15 ; 4.65$
$\text{HClCy}^- \rightleftharpoons \text{ClCy}^{2-} + \text{H}^+$	K ₈	10.12	N/A
$\text{HClCy}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{Cy}^- + \text{HOCl}$	K _{9a}	N/A	$\frac{2,229}{T_K} - 1.65 ; 5.83$
$\text{H}_2\text{Cy}^- \rightleftharpoons \text{HCy}^{2-} + \text{H}^+$	K ₁₀	11.40	N/A
$\text{ClCy}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCy}^{2-} + \text{HOCl}$	K _{11a}	6.90	N/A
$\text{HCy}^{2-} \rightleftharpoons \text{Cy}^{3-} + \text{H}^+$	K ₁₂	13.5	N/A
$\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+$	K	7.54 ^e	$\frac{3,000}{T_K} - 10.0686 + 0.0253T_K ; 7.54^e$

^aO'Brien *et al.* (1974) at 0.020 M ionic strength unless otherwise noted^bWahman and Alexander (2018) at 0 M ionic strength unless otherwise noted^cT_K is temperature in Kelvin^dWahman (2018b) at 0 M ionic strength^eMorris (1966) at 0 M ionic strength

N/A – Not applicable to model

TABLE 2

Method summary

Target Measurement	Chemistry	Reaction with Free Chlorine	pH Change	Reference
Free chlorine	DPD colorimetric ⁴	Yes	Yes	Method 8021 (Hach Company 2014a) Method 10245 (Hach Company 2014b)
Free chlorine	DPD portable parallel analyzer ⁵	Yes	Yes	Method 10260 (Hach Company 2015b)
Free chlorine	Indophenol ⁴	Yes	Yes	Method 10241 (Hach Company 2017a)
Free chlorine	Amperometric titration ⁶	Yes	Yes	Method 4500–Cl D (APHA et al. 2005)
Free chlorine	Amperometric electrode system (AES) ⁷	Yes ^a	No	Method 334.0 (USEPA 2009a)
Monochloramine	Indophenol ⁴	No	Yes	Method 10171 (Hach Company 2015a)
Total chlorine	DPD colorimetric ⁴	Yes	Yes	Method 8167 (Hach Company 2018) Method 10250 (Hach Company 2013)
Total chlorine	DPD portable parallel analyzer ⁵	Yes	Yes	Method 10260 (Hach Company 2017b)

^aThe nature of the reaction is not to completely consume the free chlorine in solution as in other methods

⁴Hach DR900 Colorimeter

⁵Hach SL100 Portable Parallel Analyzer

⁴Hach DR900 Colorimeter

⁶Wallace and Tiernan Series A790 Amperometric Titrator

⁴Hach DR900 Colorimeter

⁴Hach DR900 Colorimeter

⁵Hach SL100 Portable Parallel Analyzer

TABLE 3

Summary of rate expressions for reactions with natural organic matter

Natural Organic Matter Reaction Name	Natural Organic Matter Reaction ^a	Natural Organic Matter Reaction Rate Expression	Model Reaction Stoichiometry for Natural Organic Matter Reactions				
			[HOCl]	[TOC _{fast}] ^b	[TOC _{slow}] ^c	[HCICy ⁻]	[H ₃ Cy]
Free Chlorine Fast	HOCl + TOC _{fast} → Products	$k_{\text{fast}}[\text{HOCl}][\text{TOC}_{\text{fast}}]$	-1	-1			
Free Chlorine Slow	HOCl + TOC _{slow} → Products	$k_{\text{slow}}[\text{HOCl}][\text{TOC}_{\text{slow}}]$	-1		0		
HCICy-Slow	HCICy ⁻ + TOC _{slow} → H ₃ Cy + Products	$k_{\text{slow, bound}}[\text{HCICy}^-][\text{TOC}_{\text{slow}}]$			0	-1	+1

^a k_{fast} = free chlorine fast reaction rate constant, M⁻¹ d⁻¹^b k_{slow} = free chlorine slow reaction rate constant, M⁻¹ d⁻¹^c $k_{\text{slow, bound}}$ = HCICy⁻ slow reaction rate constant, M⁻¹ d⁻¹

[HOCl] = hypochlorous acid concentration, M

[TOC_{fast}] = fast reacting organic matter concentration, M (molecular weight of 12)[TOC_{slow}] = slow reacting organic matter concentration, M (molecular weight of 12)[HCICy⁻] = HCICy⁻ concentration, M[H₃Cy] = H₃Cy concentration, M^a Products may include chloride, hydrogen ion, water, and oxidized TOC fractions that are not relevant to model simulations^b The initial [TOC_{fast}] was set to $f_{\text{fast}} * [\text{TOC}]$ where f_{fast} = fast reactive organic matter fraction of initial total organic carbon concentration, M/M [TOC₀] = measured initial total organic carbon concentration, M^c The initial [TOC_{slow}] was set to [TOC₀] and assumed to be in great excess; therefore, [TOC_{slow}] is constant and the stoichiometry is set to zero in the model

TABLE 4

Amperometric electrode system (AES) experiment scenario summary

Amperometric Electrode System (AES) Concentration - $mg\ Cl_2/L$						
Added Free Chlorine $mg\ Cl_2/L$	Added Cyanuric Acid mg/L	[AES _E]	[AES _P] = [FreeCl] + $f_{HClCy}[HClCy^-]$ + $f_{Cl_2Cy}[Cl_2Cy^-]$			
			Baseline $f_{HClCy} = 0.5$ $f_{Cl_2Cy} = 0.5$ RSS = 1.8	Scenario 1 $f_{HClCy} = 0.68 \pm 0.079$ $f_{Cl_2Cy} = 0.55 \pm 0.073$ RSS = 0.092	Scenario 2 $f_{HClCy} = 1.3 \pm 0.053$ $f_{Cl_2Cy} = 0$ RSS = 0.74	Scenario 3 $f_{HClCy} = 0$ $f_{Cl_2Cy} = 1.2 \pm 0.054$ RSS = 0.92
3	2	2.55	2.31	2.46	2.41	2.49
3	2	2.54	2.31	2.46	2.41	2.49
3	2	2.54	2.31	2.46	2.41	2.49
3	2	2.46	2.31	2.46	2.41	2.49
3	2	2.46	2.31	2.46	2.41	2.49
3	2	2.46	2.31	2.46	2.41	2.49
3	2	2.46	2.31	2.46	2.41	2.49
3	2	2.46	2.31	2.46	2.41	2.49
3	2	2.45	2.31	2.46	2.41	2.49
3	3	2.30	2.07	2.29	2.41	2.12
3	3	2.31	2.07	2.29	2.41	2.12
3	3	2.31	2.07	2.29	2.41	2.12
3	3	2.29	2.07	2.29	2.41	2.12
3	3	2.28	2.07	2.29	2.41	2.12
3	3	2.28	2.07	2.29	2.41	2.12
3	3	2.29	2.07	2.29	2.41	2.12
3	3	2.28	2.07	2.29	2.41	2.12
3	3	2.27	2.07	2.29	2.41	2.12
4	2	3.26	3.23	3.38	3.14	3.61
4	2	3.29	3.23	3.38	3.14	3.61
4	2	3.31	3.23	3.38	3.14	3.61
4	2	3.44	3.23	3.38	3.14	3.61
4	2	3.44	3.23	3.38	3.14	3.61
4	2	3.45	3.23	3.38	3.14	3.61
4	2	3.37	3.23	3.38	3.14	3.61
4	2	3.38	3.23	3.38	3.14	3.61
4	2	3.38	3.23	3.38	3.14	3.61
4	4	2.91	2.68	2.99	3.02	2.90
4	4	2.92	2.68	2.99	3.02	2.90
4	4	2.91	2.68	2.99	3.02	2.90
4	4	3.05	2.68	2.99	3.02	2.90
4	4	3.05	2.68	2.99	3.02	2.90
4	4	3.05	2.68	2.99	3.02	2.90
4	4	3.01	2.68	2.99	3.02	2.90
4	4	2.97	2.68	2.99	3.02	2.90

Amperometric Electrode System (AES) Concentration - $mg\ Cl_2/L$						
Added Free Chlorine $mg\ Cl_2/L$	Added Cyanuric Acid mg/L	[AES _E]	[AES _P] = [FreeCl] + $f_{HClCy}[HCICy^-]$ + $f_{Cl_2Cy}[Cl_2Cy^-]$			
			Baseline $f_{HClCy} = 0.5$ $f_{Cl_2Cy} = 0.5$ RSS = 1.8	Scenario 1 $f_{HClCy} = 0.68 \pm 0.079$ $f_{Cl_2Cy} = 0.55 \pm 0.073$ RSS = 0.092	Scenario 2 $f_{HClCy} = 1.3 \pm 0.053$ $f_{Cl_2Cy} = 0$ RSS = 0.74	Scenario 3 $f_{HClCy} = 0$ $f_{Cl_2Cy} = 1.2 \pm 0.054$ RSS = 0.92
4	4	2.95	2.68	2.99	3.02	2.90

[AES_E] – experimental amperometric electrode system (AES) concentration; [AES_P] – predicted AES concentration from Equation 4; RSS – Equation 5 determined residual sum of squares difference between [AES_E] and [AES_P]

TABLE 5

Parameter estimates for hold study natural organic matter reactions

Free Chlorine Only Estimates (n = 26 samples)		
Parameter	Estimate $\pm$ 95% Confidence Interval	Units
f_{fast}	0.14 ± 0.013	mole/mole
k_{fast}	$(4.3 \pm 3.8) \times 10^5$	$\text{M}^{-1} \text{d}^{-1}$
k_{slow}	$(1.1 \pm 0.044) \times 10^3$	$\text{M}^{-1} \text{d}^{-1}$
$k_{\text{slow,bound}}$	Not Determined	$\text{M}^{-1} \text{d}^{-1}$
Simultaneous Free Chlorine Only, Dichlor, and Trichlor Estimates (n = 78 samples)		
Parameter	Estimate $\pm$ 95% Confidence Interval	Units
f_{fast}	0.14 ± 0.0066	mole/mole
k_{fast}	$(5.8 \pm 3.0) \times 10^5$	$\text{M}^{-1} \text{d}^{-1}$
k_{slow}	$(1.1 \pm 0.028) \times 10^3$	$\text{M}^{-1} \text{d}^{-1}$
$k_{\text{slow,bound}}$	310 ± 17	$\text{M}^{-1} \text{d}^{-1}$