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Chlorinated Cyanurates: Review of Water Chemistry and Associated Drinking Water Implications

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Abstract

Since 1958, cyanuric acid and two chlorinated cyanurates, commonly referred to as dichlor (anhydrous sodium dichloroisocyanurate or sodium dichloroisocyanurate dihydrate) or trichlor (trichloroisocyanuric acid), have been added to outdoor swimming pools to stabilize chlorine residual by minimizing sunlight related degradation. Subsequently in July 2001, dichlor and trichlor were approved for routine drinking water treatment under the United States' Federal Insecticide, Fungicide, and Rodenticide Registration Act, and manufacturers have achieved NSF 60 certification for dichlor or trichlor addition to drinking water. Currently in the United States, dichlor or trichlor drinking water use may be approved by states, tribes, or territories. One complicating factor with dichlor or trichlor is that the actual free chlorine concentration in these systems cannot be measured accurately by currently approved methods. This review summarizes the existing water chemistry associated with dichlor and trichlor use as a chlorine source in drinking water along with the associated implications.

INTRODUCTION

Outdoor swimming pools.

Since 1958, cyanuric acid and two of the chlorinated cyanurates, commonly referred to as dichlor (anhydrous sodium dichloroisocyanurate or sodium dichloroisocyanurate dihydrate) or trichlor (trichloroisocyanuric acid), have been added to outdoor swimming pools to help stabilize chlorine residual by minimizing sunlight related degradation (Canelli 1974). Although parts of dichlor and trichlor's chemical names resemble cyanide, the chemicals do not contain cyanide. In outdoor swimming pools, two general approaches are taken: (1) cyanuric acid is added in conjunction with free chlorine or (2) dichlor or trichlor are added alone because they add both cyanuric acid and free chlorine from a single chemical.

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Regardless of how cyanuric acid and free chlorine get into the water, a rapid equilibrium is obtained between cyanuric acid and its dissociation products, free chlorine, and chlorinated cyanurates (O'Brien et al. 1974, O'Brien 1972). Recommended levels of free chlorine and cyanuric acid are summarized in Table 1 for public pools.

Under typical outdoor swimming pool conditions, free chlorine consists of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) which absorb light maximally at 235 (Silverman & Gordon 1980) and 292 nm (Furman & Margerum 1998), respectively. Because wavelengths that reach the Earth's surface are greater than approximately 280 nm (Zayat et al. 2007), OCl^- is sensitive to sunlight, leading to free chlorine loss. Conversely, cyanuric acid and its dissociation products and chlorinated cyanurates exhibit maximum absorbance values less than 230 nm and are therefore not as impacted by sunlight (O'Brien et al. 1974).

Figure 1 highlights the impact of cyanuric acid on the stability of total chlorine (free chlorine plus the chlorine bound in chlorinated cyanurates) in the presence of sunlight. Without cyanuric acid addition, the total chlorine concentration decreases by half within 30 minutes, but with cyanuric acid addition, a more stable solution is created. For example, 70% of the total chlorine remained after 3 hours when 25 mg/L of cyanuric acid was added. Furthermore, O'Brien (1972) illustrated pH's impact during sunlight exposure where an accelerated total chlorine loss occurred as pH increased, highlighting that OCl^- is more susceptible to sunlight degradation compared to HOCl.

Drinking water.

Even though sunlight related degradation of free chlorine is not a major concern in drinking water systems, use of dichlor or trichlor as an alternative free chlorine source in drinking water has been pursued. Under the United States' Federal Insecticide, Fungicide, and Rodenticide Registration Act (FIFRA), the use of dichlor or trichlor for the routine treatment of drinking water was first approved in July 2001 (Kuechler 2009). Subsequently, several manufacturers have achieved NSF 60 certification for the addition of dichlor or trichlor to drinking water. As of January 2018, NSF 60 certification had been obtained by six and seven manufacturers for dichlor and trichlor, respectively (NSF International 2018). The NSF 60 certification lists a 30 mg/L maximum concentration with disinfection and oxidation as the product function. The World Health Organization (WHO) also provides guidelines for the addition of dichlor and cyanuric acid to drinking water where WHO specifies maximum concentrations of 50 and 40 mg/L, respectively (World Health Organization 2011, 2007). Overall, in the United States, dichlor or trichlor may be approved for use by states, tribes, or territories for use in drinking water.

One complicating factor with the use of dichlor or trichlor is that the actual free chlorine concentration cannot be measured accurately by typical methods in these systems. Because of the fast equilibrium between cyanuric acid and its dissociation products, free chlorine, and chlorinated cyanurates; free chlorine N,N-diethyl-p-phenylenediamine (DPD) and amperometric titration based methods actually measure the total chlorine (i.e., free chlorine plus the chlorine bound in the chlorinated cyanurates) in systems using dichlor or trichlor and therefore overestimate the actual free chlorine residual in water samples (Wajon & Morris 1980, Whittle 1970). The current review seeks to summarize the existing water

chemistry and corresponding implications associated with using dichlor or trichlor as a chlorine source in drinking water.

FREE CHLORINE AND CYANURIC ACID SYSTEM WATER CHEMISTRY

Cyanuric acid.

Cyanuric acid's properties are summarized in Table 2. It has both an enol and keto form (Figure 2). The keto form is present in solids or acidic solution while the enol form is present in basic solutions (Kuechler 1997). The cyanurate moiety ($C_3N_3O_3$) is typically denoted as Cy; therefore, cyanuric acid is represented by H_3Cy . Depending on pH, cyanuric acid can dissociate into three dissociation products (H_2Cy^- , HCy^{2-} , Cy^{3-}) as depicted in Figure 3. Under a typical drinking water pH range (i.e., 6.5–9.5), only H_3Cy and its first dissociation product (H_2Cy^-) exist at any meaningful concentration.

Chlorinated cyanurates (dichlor and trichlor).

Dichlor (Cl_2Cy) and trichlor (Cl_3Cy) are chemicals that provide both cyanuric acid and free chlorine to water from a single chemical, and their properties are summarized in Table 2. For drinking water, dichlor is produced as a sodium anhydrous or a sodium dihydrate solid or granule, and trichlor is also produced as a solid or granule (Table 2, Figure 2) (Wojtowicz 2000). As stated previously and as opposed to outdoor swimming pools, their use in drinking water is not related to providing chlorine residual stability in the presence of sunlight. Rather, stated advantages for dichlor and trichlor as chlorine sources are that they are solid forms of chlorine, require simpler handling than liquid and gas chlorine forms, have stabilities on the order of years, do not add calcium to water when dissolved, and are high percent chlorine chemicals (55–92%, Table 2) (Kuechler 2009). Additional advantages of dichlor over trichlor are that dichlor is more soluble in water and produces a solution with a pH near neutral (Table 2).

Kuechler (2009) notes some general safety considerations when using dichlor or trichlor. Specifically, dichlor or trichlor is not compatible with calcium hypochlorite; therefore, the chemicals should not be used in the same chemical feeder. In addition, wet trichlor tablets produce a strong chlorinous odor; therefore, tablet feeders should be in well ventilated areas.

Equilibrium water chemistry model.

Regardless of how cyanuric acid becomes present in water with free chlorine (i.e., separate addition of cyanuric acid and free chlorine or addition of dichlor or trichlor), a rapid equilibrium is obtained between cyanuric acid and its three dissociation products, free chlorine, and chlorinated cyanurates (Figure 4). As an example of the equilibrium speed, the hydrolysis rate constant for the release of HOCl from one of the important chlorinated cyanurates present under drinking water conditions ($HClCy^-$, Figure 4, K9) is 0.17 s^{-1} (Matte et al. 1990). For comparison, monochloramine's hydrolysis rate constant for HOCl release is $2.1 \times 10^{-5}\text{ s}^{-1}$ (Morris & Isaac 1983). Using these hydrolysis constants, the time required to release 50% of the HOCl present in the parent compound (reaction half-time, $t_{1/2}$) is 4.1 seconds for $HClCy^-$ and 9.2 hours for monochloramine, illustrating that redistribution of chemical species in systems using dichlor or trichlor should occur on the

order of seconds when perturbations occur. Furthermore, Jensen and Johnson (1990) used stopped-flow spectroscopy to determine that a chlorinated cyanuric solution and a free chlorine only solution had the same $t_{1/2}$ (0.4 seconds) when reacting with DPD, suggesting an extremely fast release of HOCl from chlorinated cyanurates.

The complete water chemistry model for the free chlorine and cyanuric acid system has been established at 25 °C by O'Brien (1972) and O'Brien et al. (1974), requiring ten independent equilibrium reactions and associated temperature dependent equilibrium constants along with two mass balance equations. The model allows simulation of the concentrations of cyanuric acid and its three dissociation products, free chlorine, and chlorinated cyanurates.

Other researchers have proposed similar estimates for some of the equilibrium constants (Gardiner 1973, Brady et al. 1963), but in the case of research conducted by Pinsky and Hu (1981), substantially different estimates for some equilibrium constants were proposed. Subsequently, the results of Pinsky and Hu (1981) have been called into question because their free chlorine measurement method overestimated the free chlorine concentration in their experiments (Wojtowicz 1996a, Jensen et al. 1990). Overall, the model proposed by O'Brien et al. (1974) remains the established one for the free chlorine and cyanuric acid system at 25 °C.

One set of equilibrium reactions and constants to simulate the water chemistry of the free chlorine and cyanuric acid system are presented in Table 3 and are shown schematically in Figure 4. To simulate the water chemistry at 25 °C (note that temperature dependence of the equilibrium constants has not been determined), three concentrations must be known or assumed:

1. The total chlorine (TOTCl) concentration, consisting of the free chlorine plus the chlorine bound in chlorinated cyanurates. Note that in addition to total chlorine other terms have been used in the literature to describe the concentration of free chlorine plus the chlorine bound in the chlorinated cyanurates such as “reservoir chlorine” (O'Brien et al. 1974) or “available chlorine” (Kuechler 2009);
2. The total cyanurate (TOTCy) concentration, consisting of the cyanurate present in cyanuric acid and its three dissociation products along with that bound in the chlorinated cyanurates; and
3. pH which provides the hydrogen ion (H^+) concentration, assuming a low ionic strength solution where activity is approximately equal to concentration as is typically the case in drinking water.

With these three known or assumed concentrations, there are twelve remaining unknown concentrations, which require twelve independent equations (Eq 1 through Eq 12, Figure 5) to provide a unique solution for the system:

- One mass balance equation for TOTCl (Eq 1, Figure 5),
- One mass balance equation for TOTCy (Eq 2, Figure 5), and
- Ten temperature dependent equilibrium equations (Eq 3 through Eq 12, Figure 5)

Using the twelve equations (Eqs 1 through 12, Figure 5), a single working equation where only the HOCl concentration is unknown can be derived (Eq 15, Figure 5). For each pH, a solution involves (i) solving Eq 15 (Figure 5) for the HOCl concentration, (ii) using the determined HOCl concentration to solve Eq 12 and Eq 13 (Figure 5) for the OCl^- and cyanurate ion (Cy^{3-}) concentrations, and (iii) using the determined Cy^{3-} concentration to solve Eqs 3 through 11 (Figure 5) for the remaining nine unknown chemical concentrations.

PERCENT FREE CHLORINE VARIATION

Using the equilibrium chemistry model and solution methodology previously described, operational impacts of dichlor and trichlor use can be evaluated. Specifically, determination of the percent of TOTCl that is present as free chlorine can be evaluated for various conditions of interest, including pH, chemical source, chemical dose, and chlorine demand.

pH.

The general pH impact on free chlorine is illustrated in Figure 6 for 1 mg Cl_2/L TOTCl solutions. The percent free chlorine reaches a minimum around pH 7.0 (72% for trichlor and 61% for dichlor) and approaches 100% when the pH approaches 10 for either dichlor or trichlor addition. The increasing free chlorine as pH increases is a result of viewing HOCl as the form of chlorine in equilibrium with chlorinated cyanurates rather than OCl^- (K_{1a} , K_{7a} , and K_{11a} in Table 3). Overall and for the same TOTCl, the operational pH of a drinking water system can have a substantial impact on the free chlorine concentration when using dichlor or trichlor.

Chemical source.

Figure 6 also illustrates that the chemical source of chlorine impacts the percent free chlorine. For the same target TOTCl (1 mg Cl_2/L in Figure 6), using dichlor over trichlor for chlorine addition leads to a lower percent free chlorine because on a per chlorine basis, dichlor adds more TOTCy to the water (Table 2). A comparison to typical outdoor pool addition conditions is also shown in Figure 6 to highlight that a much larger percentage of TOTCl is present as free chlorine under typical drinking water conditions because a much lower TOTCy concentration is used compared to outdoor pools (e.g., < 5 mg/L versus 50–100 mg/L).

Chemical dose.

The free chlorine percent also depends on the amount of dichlor or trichlor added. Figure 7 highlights the impact of adding two different TOTCl concentrations of dichlor. At pH 7.0, 61% and 41% of TOTCl is free chlorine for 1 and 4 mg Cl_2/L TOTCl, respectively. Therefore, even though the TOTCl concentration increased 3 mg Cl_2/L (1 to 4 mg Cl_2/L TOTCl), the free chlorine concentration only increased 1 mg Cl_2/L (0.61 to 1.6 mg Cl_2/L free chlorine). Increasing dichlor or trichlor chemical dosage results in increasing both the TOTCl and TOTCy concentrations at a fixed ratio (Table 2). On the surface, a dosage increase would appear to not lead to an impact in the percent free chlorine, but as previously mentioned, HOCl is viewed as the form of free chlorine bound in chlorinated cyanurates. Therefore, as dichlor or trichlor dosing increases, the ratio of HOCl to TOTCy is effectively

decreasing because only a portion of the free chlorine is HOCl at a given pH, resulting in a smaller percentage of TOTCl present as free chlorine.

Chlorine demand.

Thus far, the discussion has assumed that there was no chlorine demand occurring when adding dichlor or trichlor to water. In real waters, there will exist a chlorine demand to some extent, resulting from natural organic matter (NOM) or reduced species (e.g., iron or manganese). Chlorine demand's impact on the water chemistry is effectively to decrease TOTCl while not impacting TOTCy, decreasing the TOTCl to TOTCy ratio. The impact of chlorine demand is illustrated in Figure 7 for initial dichlor additions of 1 and 4 mg Cl₂/L TOTCl. If chlorine demand occurs such that the TOTCl is subsequently reduced to 0.2 mg Cl₂/L in either case, the percent free chlorine is reduced from 61% to 48% (0.61 to 0.10 mg Cl₂/L free chlorine) and 41% to 17% (1.6 to 0.03 mg Cl₂/L free chlorine) for the initial 1 and 4 mg Cl₂/L dichlor doses, respectively. As chlorine demand occurs in systems using dichlor or trichlor, both the TOTCl and percent free chlorine decreases.

DISINFECTION AND STABILITY

Disinfection efficacy.

For the same TOTCl, the literature supports that chlorinated cyanurate presence reduces disinfection efficacy compared to free chlorine only, and the effective disinfectant in systems where chlorinated cyanurates are present is free chlorine, specifically HOCl (e.g., Murphy et al. 2015, Wojtowicz 1996b, Yamashita et al. 1988, Engel et al. 1983, Canelli 1974). Figure 8 presents the impact of increasing TOTCy concentrations for a fixed TOTCl concentration on the inactivation of *Cryptosporidium parvum* where increasing the TOTCy concentration leads to reduced log inactivation, indicating a deleterious impact with increasing TOTCy concentrations. Although Figure 8 shows a negative impact from increasing TOTCy concentrations, it does not specifically show that HOCl is the true disinfectant in the system.

A convincing case for HOCl being the true disinfectant in systems where chlorinated cyanurates are present is shown in Figure 9 where the inactivation of *Streptococcus faecalis* was studied. When plotting the 99% kill time versus the TOTCl concentration for various experimental conditions, no correlation is seen between TOTCl concentration and 99% kill time. A different picture emerges when plotting the same data but now accounting for the actual HOCl concentration present for the experiments. In this case, a clear linear trend is seen where 99% kill time decreases with increasing HOCl concentration, providing evidence that HOCl is the true disinfectant in these systems and that chlorinated cyanurates have minimal disinfecting capability when compared to HOCl. For drinking water, assuming the free chlorine concentration determines disinfection efficacy results in a conservative assumption.

Stability and disinfection by-product formation.

Based on the water chemistry in a dichlor or trichlor system, one logical extension is that these systems may have a more stable chlorine residual compared to a free chlorine only system. As a first estimate, one may simply view chlorine residual loss as a second-order

reaction between HOCl and a generic reacting species (X) such as NOM, and a general rate equation (Eq 16) can be written where k_X represents a generic second-order rate constant:

$$r = k_X[\text{HOCl}][X] \quad 16$$

For the same equivalent TOTCl addition and compared to a free chlorine only system, dichlor or trichlor use would result in a lower HOCl concentration as shown previously, reducing the reaction rate (r) represented by Eq 16 and slowing the loss of TOTCl. Slowing the TOTCl residual loss may also delay disinfection by-product (DBP) formation if one assumes that DBP formation would be proportional to chlorine demand, but if TOTCl is completely consumed, similar DBP formation would be expected.

Figure 10 (Panel A) shows a simulation where only HOCl is assumed to react with NOM when dosing free chlorine only, dichlor, or trichlor. As expected, the simulation shows that based on TOTCl concentrations both dichlor and trichlor are simulated to be more stable than an equivalent free chlorine only dose. In addition, dichlor is expected to be slightly more stable than trichlor because for equivalent TOTCl doses, dichlor's percent free chlorine is lower than trichlor's as previously discussed.

On a TOTCl concentration basis, it takes approximately 5, 12, or 16 days for the TOTCl residual to decrease to 0.2 mg CB/L TOTCl when using free chlorine only, trichlor, or dichlor, respectively (Figure 10, Panel A), but a different picture emerges if the free chlorine concentration is the basis. On a free chlorine concentration basis, it takes approximately 5 days in either case for the free chlorine concentration to decrease to 0.2 mg Cl_2/L (Figure 10, Panel A). Furthermore, during these 5 days, the free chlorine concentration present when using free chlorine only is greater than the free chlorine concentration with either dichlor or trichlor. Figure 10 (Panel B) summarizes the free chlorine concentration * time (CT) values for each simulated condition, demonstrating that using free chlorine only produces greater free chlorine CT values than using either dichlor or trichlor. Overall, the CT values (Figure 10, Panel B) support the previous discussion that dichlor or trichlor are less effective disinfectants compared to free chlorine only.

Regarding DBP formation, a preliminary evaluation was conducted on the impact of cyanuric acid addition to free chlorine on trihalomethane formation by Feldstein et al. (1984). A limitation of this study was that chemical doses used were more representative of pool conditions than are currently being used for drinking water. Overall, evaluation of the presented hypotheses related to residual stability and DBP formation when cyanuric acid is present remains an avenue for future research.

FREE CHLORINE DETERMINATION

Analytical measurement.

One complicating factor with the use of dichlor or trichlor in US drinking water systems is that the free chlorine concentration cannot be measured accurately by currently approved methods. Because of the fast equilibrium between cyanuric acid and its three dissociation

products, free chlorine, and chlorinated cyanurates (Figure 4), any analysis method that directly reacts with free chlorine will effectively measure the TOTCl concentration in the water. In addition, any change in pH by a measurement method will change the free chlorine concentration from that present in the original sample (Figures 6 and 7). Therefore, free chlorine concentrations cannot currently be directly measured, impacting verification of compliance with US primary disinfection requirements or states that require numeric disinfectant residual requirements in the distribution system.

Based on utility surveys (AWWA Water Quality and Technology Division Disinfection Systems Committee 2000), DPD (Standard Methods 4500-Cl G and F) and amperometric titration (Standard Methods 4500-Cl D and E) based methods are the two most used methods to measure chlorine residuals in the plant and distribution system (DS) (APHA et al. 2005). DPD is the first (62% plant, 87% DS) and amperometric titration (31% plant, 10% DS) is the second most utilized method for measuring the chlorine residual. Because DPD and amperometric titration based methods directly react with free chlorine and change the sample's pH, they measure the TOTCl in the water and overestimate the actual free chlorine residual present in systems using dichlor or trichlor (Jensen & Johnson 1990, Canelli 1980, Wajon & Morris 1980, Whittle 1970).

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

Amperometric electrodes have been shown to measure a partial bias from chlorinated cyanurates and overestimate the free chlorine concentration (Jensen et al. 1990, Jensen & Johnson 1989, Canelli 1980). Specifically, Canelli (1980) found a partial bias by chlorinated cyanurates and indicated that the response from monochloroisocyanurate species were 50% that of HOCl. The impact was that the amperometric electrode measured a value between the free chlorine and TOTCl concentration.

Direct measurement of chemical concentrations using molar absorptivity (ultraviolet spectroscopy) at wavelengths between 196 and 292 nm was used by O'Brien et al. (1974) to determine the water chemistry of the free chlorine and cyanurate system in buffered laboratory waters. Extension of the spectroscopy method to actual drinking waters is improbable because of limitations resulting from interferences at relevant wavelengths (i.e., 200–300 nm) in drinking water from constituents such as NOM (e.g., Sohn et al. 2007).

Water chemistry estimate.

To overcome the limitation of being unable to measure free chlorine directly in systems using dichlor or trichlor, one option is to use the established water chemistry to estimate the free chlorine concentration with the knowledge that the water chemistry is only known for 25 °C.

As mentioned previously, three concentrations are required to estimate the free chlorine concentration for dichlor or trichlor system water samples: TOTCl, TOTCy, and H⁺ (i.e., pH). Two of these (TOTCl and pH) are easily obtained through direct measurement. In water samples from dichlor or trichlor systems, pH can be directly measured, and TOTCl can be

acquired from free chlorine DPD or amperometric titration methods because, as previously discussed, these methods measure TOTCl.

TOTCy determination poses an issue that can be overcome by a conservative assumption. In drinking water, TOTCy concentrations are generally less than the available method detection limit of simple field kits designed for outdoor pools (approximately 5 mg/L TOTCy) which rely on melamine precipitation chemistry (Hach Company 2014). Currently, other methods exist that could be used to measure TOTCy concentrations at drinking water relevant concentrations, but they are complex and include silver nanoparticles (Kappi et al. 2014), high performance liquid chromatography (Hou & Ding 2011, Sun et al. 2011, Downes et al. 1984, Briggles et al. 1981), differential pulse polarography (Strays & Wolfs 1987), and ultraviolet detection (Downes et al. 1984). Therefore, TOTCy concentrations cannot be measured currently at concentrations expected in typical drinking water samples in the field.

As opposed to TOTCl which will decrease due to the water's chlorine demand and must be measured directly, TOTCy should be relatively stable in drinking water. Therefore, the TOTCy concentration may be estimated conservatively from the original dosage of cyanurate containing chemicals added to the water (i.e., dichlor or trichlor dosing), requiring one to know the dosage and appropriately calculate the added TOTCy.

Overall, estimation of free chlorine concentrations is possible from drinking water samples using two measurements, one assumption, and the known equilibrium chemistry. For instance, Wahman (2017) has recently developed a web-based application to assist in free chlorine's estimation using the established chemistry from O'Brien et al. (1974) that be accessed at <https://usepaord.shinvapps.io/cvanuric/>. The web-based application requires three inputs for estimating free chlorine in water samples: TOTCl, TOTCy, and pH, but as noted previously, the web-based application is only currently applicable to 25 °C.

WATER CHEMISTRY IMPLICATIONS AND FUTURE NEEDS

Water chemistry temperature dependence.

Based on the previous discussion and known water chemistry, the major implication with regards to using dichlor or trichlor in drinking water systems is the current inability to directly measure the free chlorine concentration in these systems. Using the existing water chemistry (e.g., the existing web-based application), one can estimate the free chlorine concentration at 25 °C, but estimates at other temperatures are currently not possible, limiting the usefulness of the water chemistry estimate in actual drinking water systems where temperature may vary over a wide range (e.g., 5 to 35 °C).

Therefore, there exists an immediate need to expand the water chemistry model to include temperatures from 5 to 35 °C which is the focus of ongoing research. Once determined, the existing water chemistry model and associated web-based application could be updated to include temperature, providing the ability to determine free chlorine concentrations in actual water samples for conditions commonly found in practice. The ability to determine actual free chlorine concentrations in water samples would allow evaluation of compliance with

primary disinfection requirements as well as distribution system residual requirements for systems using dichlor or trichlor as their chlorine source.

Total cyanuric acid method.

Supplementing the expansion of the water chemistry to include temperature dependence, a field based method to measure TOTCy would be desirable to avoid assumptions on TOTCy concentrations from chemical dosing. Specifically, the method needs to measure TOTCy in the range relevant to drinking water practice (e.g., 0.1 to 5 mg/L). Because TOTCy should be relatively stable, laboratory based analytical methods could also be developed for samples transported from the field.

Additional implications.

The known water chemistry of dichlor and trichlor leads to several additional practical questions to consider and possible avenues of future research, including, but not limited to, the following:

- How prevalent is the use of dichlor or trichlor in drinking water systems in the United States? Inclusion of questions specific to dichlor or trichlor use on disinfectant related surveys would provide information on their use.
- For states that require maintenance of a numeric secondary disinfectant residual in distribution systems in lieu of “detectable” (Wahman & Pressman 2015), how is or will compliance with the numeric requirement be based? For example, with the understanding that chlorinated cyanurates are ineffective disinfectants compared with free chlorine, will total chlorine or the actual free chlorine concentration present in samples be the basis for compliance?
- Compared to an equivalent dose of free chlorine only, does the use of dichlor or trichlor increase residual stability? Similarly, does the use of dichlor or trichlor delay and possibly reduce regulated DBP formation, and are there unregulated DBPs specific with their use? Understanding residual stability and associated DBP formation compared to using free chlorine only would provide necessary information to understand the potential benefits or unintended consequences of dichlor or trichlor use.
- Because only a portion of the TOTCl is present as free chlorine, does the use of dichlor or trichlor or the addition of cyanuric acid provide any benefits in terms of a reduction in chlorate formation during storage of concentrated chlorine feed solutions?
- Is or will dichlor or trichlor be considered for use in disinfecting water storage facilities (ANSI & AWWA 2011) or water mains (ANSI & AWWA 2015), and if so, are considerations being made to account for the actual free chlorine concentration present during the various disinfection scenarios allowed under these standards so that an equivalent free chlorine exposure is achieved?
- For dichlor and trichlor systems, what is the chemistry associated with
 - blending with chloraminated waters,

- breakpoint chlorinating,
- bromide presence, or
- other common oxidants (e.g., chlorine dioxide, ozone, permanganate)?

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FIGURE 1. Cyanuric acid addition impact on total chlorine stability for outdoor pool conditions (i.e., sunlight exposed).

5 and 10 mg/L cyanuric acid addition data from Canelli (1974) and 0, 25, 50, and 100 mg/L cyanuric acid addition data from Wojtowicz (2004)

FIGURE 2.
Chemical structures of cyanuric acid, dichlor, and trichlor

FIGURE 3. Cyanuric acid dissociation based on pH.

Generated using the equilibrium constants (K_6 , K_{10} , and K_{12}) in Table 3.

FIGURE 4. Free chlorine, cyanuric acid, and chlorinated cyanurate equilibria.

Grey highlighted chemicals are the major cyanurate containing species expected under drinking water conditions and chemical dosages. Hydrogen ion for dissociation reactions and water and hypochlorous acid for hydrolysis reactions are not shown for clarity. Adapted with permission from Brady et al. (1963). Copyright 1963 American Chemical Society.

Assumed Knowns (3)

$$TOTCl, TOTCy, [H^+]$$

Remaining Unknowns (12)

$$[Cl_3Cy], [HCl_2Cy], [H_2ClCy], [Cl_2Cy^-], [HClCy^-], [ClCy^{2-}], [H_3Cy], [H_2Cy^-], [HCy^{2-}], [Cy^{3-}], [HOCl], [OCl^-]$$

Required Equations (12)

$$TOTCl = 3[Cl_3Cy] + 2[HCl_2Cy] + [H_2ClCy] + 2[Cl_2Cy^-] + [HClCy^-] + [ClCy^{2-}] + [HOCl] + [OCl^-] \quad (1)$$

$$TOTCy = [Cl_3Cy] + [HCl_2Cy] + [H_2ClCy] + [Cl_2Cy^-] + [HClCy^-] + [ClCy^{2-}] + [H_3Cy] + [H_2Cy^-] + [HCy^{2-}] + [Cy^{3-}] \quad (2)$$

$$[HCy^{2-}] = \frac{[H^+][Cy^{3-}]}{K_{12}} \quad (3)$$

$$[H_2Cy^-] = \frac{[H^+]^2[Cy^{3-}]}{K_{12}K_{10}} \quad (4)$$

$$[H_3Cy] = \frac{[H^+]^3[Cy^{3-}]}{K_{12}K_{10}K_6} \quad (5)$$

$$[ClCy^{2-}] = \frac{[H^+][HOCl][Cy^{3-}]}{K_{12}K_{11a}} \quad (6)$$

$$[HClCy^-] = \frac{[H^+]^2[HOCl][Cy^{3-}]}{K_{12}K_{11a}K_8} \quad (7)$$

$$[H_2ClCy] = \frac{[H^+]^3[HOCl][Cy^{3-}]}{K_{12}K_{11a}K_8K_4} \quad (8)$$

$$[Cl_2Cy^-] = \frac{[H^+]^2[HOCl]^2[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}} \quad (9)$$

$$[HCl_2Cy] = \frac{[H^+]^3[HOCl]^2[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}K_2} \quad (10)$$

$$[Cl_3Cy] = \frac{[H^+]^3[HOCl]^3[Cy^{3-}]}{K_{12}K_{11a}K_8K_{7a}K_{21a}} \quad (11)$$

$$[OCl^-] = \frac{K[HOCl]}{[H^+]} \quad (12)$$

Derivation of working equation

Solution of TOTCl (Eq. 1) in terms of Cy^{3-}

$$[Cy^{3-}] = \frac{TOTCl - [HOCl] \left(1 + \frac{K}{[H^+]}\right)}{3 \frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_{21a}} + 2 \frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + 2 \frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}}} \quad (13)$$

Solution of TOTCy (Eq. 2) in terms of Cy^{3-}

$$[Cy^{3-}] = \frac{TOTCy}{\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_{21a}} + \frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + \frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}} + \frac{[H^+]}{K_{12}K_{10}K_6} + \frac{[H^+]}{K_{12}K_{10}} + 1} \quad (14)$$

Solution of working equation by setting Eq. 13 equal to Eq. 14

$$0 = TOTCy \frac{3 \frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_{21a}} + 2 \frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + 2 \frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}}}{\frac{[H^+]^3[HOCl]^3}{K_{12}K_{11a}K_8K_{7a}K_{21a}} + \frac{[H^+]^3[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}K_2} + \frac{[H^+]^3[HOCl]}{K_{12}K_{11a}K_8K_4} + \frac{[H^+]^2[HOCl]^2}{K_{12}K_{11a}K_8K_{7a}} + \frac{[H^+]^2[HOCl]}{K_{12}K_{11a}K_8} + \frac{[H^+][HOCl]}{K_{12}K_{11a}} + \frac{[H^+]}{K_{12}K_{10}K_6} + \frac{[H^+]}{K_{12}K_{10}} + 1} + [HOCl] \left(1 + \frac{K}{[H^+]}\right) - TOTCl \quad (15)$$

FIGURE 5. Summary of equations for solution of chlorinated cyanurate water chemistry. System of twelve equations consisting of total chlorine (TOTCl) and total cyanurate (TOTCy) mass balances (Eqs. 1 and 2) and related equilibria (Eqs. 3 through 12) shown in Table 3

FIGURE 6. Percent free chlorine based on chemical source.

Generated using all the equilibrium constants in Table 3. All simulations have a 1 mg Cl_2/L total chlorine concentration.

FIGURE 7. Free chlorine demand impact on percent free chlorine (dichlor dosed).
Generated using all the equilibrium constants in Table 3.

FIGURE 8. Impact of cyanuric acid addition on inactivation of *Cryptosporidium parvum*.
Adapted with permission from Murphy et al. (2015). Copyright 2015 American Chemical Society.

FIGURE 9. 99% kill time for *Streptococcus faecalis* for various cyanuric acid concentrations and chlorine concentrations.

The same experiments are presented on either a (1) total chlorine (cross, triangle, diamond, and square symbols) or (2) hypochlorous acid (open and closed circle symbols) concentration basis. Hypochlorous acid concentrations were generated using all the equilibrium constants in Table 3 (Wojtowicz 1996b), and total chlorine concentrations are from Anderson (1965).

FIGURE 10.

Simulated residual stability (A) and concentration * time values (B) for equivalent total chlorine additions

TABLE 1

Public pool concentrations for use of cyanuric acid per ANSI/APSP (2009)

Parameter	Minimum	Ideal	Maximum
Total (Available) Chlorine (mg Cl ₂ /L)	1	2–4	4
Cyanuric Acid (mg/L)	Not Applicable	30–50	100

TABLE 2

Summary of chlorinated cyanurate related chemical properties

Property	Cyanuric Acid	Sodium Dichloroisocyanurate	Sodium Dichloroisocyanurate Dihydrate	Trichloroisocyanuric Acid
CAS Number	108–80–5	2893–78–9	51580–86–0	87–90–1
Chemical Formula	$C_3H_3N_3O_3$	$C_3Cl_2N_3NaO_3$	$C_3Cl_2N_3NaO_3 \cdot 2H_2O$	$C_3Cl_3N_3O_3$
Molecular Weight	129.07	219.95	255.98	232.41
% Available Chlorine (Theoretical)	0	65	55	92
% Cyanuric Acid (Theoretical)	100	59	50	56
pH, 1% solution unless otherwise noted	4.8 ^a (saturated solution)	6.0 ^b	6.0 ^b	2.8 ^b
Solubility (mg/L H ₂ O)	2,010 ^a (25°C)	24,000 ^b (20°C)	28,000 ^b (20°C)	1,400 ^b (20°C)
Total Chlorine (mg Cl ₂ /L) per FIFRA Label (Theoretical)	Not Applicable	0.81	0.69	0.76
Total Cyanurate (mg/L) per FIFRA Label (Theoretical)	Not Applicable	0.73	0.63	0.46

^aKuechler (1997)^bKuechler (2009)

TABLE 3

Summary of required equilibrium constants to simulate chlorinated cyanurate water chemistry

Reaction	Constant	pK ^a
$\text{Cl}_3\text{Cy} + \text{H}_2\text{O} \rightleftharpoons \text{HCl}_2\text{Cy} + \text{HOCl}$	K_{1a}	1.8
$\text{HCl}_2\text{Cy} \rightleftharpoons \text{Cl}_2\text{Cy}^- + \text{H}^+$	K_2	3.75
$\text{H}_2\text{ClCy} \rightleftharpoons \text{HClCy}^- + \text{H}^+$	K_4	5.33
$\text{H}_3\text{Cy} \rightleftharpoons \text{H}_2\text{Cy}^- + \text{H}^+$	K_6	6.88
$\text{Cl}_2\text{Cy}^- + \text{H}_2\text{O} \rightleftharpoons \text{HClCy}^- + \text{HOCl}$	K_{7a}	4.51
$\text{HClCy}^- \rightleftharpoons \text{ClCy}^{2-} + \text{H}^+$	K_8	10.12
$\text{H}_2\text{Cy}^- \rightleftharpoons \text{HCy}^{2-} + \text{H}^+$	K_{10}	11.40
$\text{ClCy}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCy}^{2-} + \text{HOCl}$	K_{11a}	6.90
$\text{HCy}^{2-} \rightleftharpoons \text{Cy}^{3-} + \text{H}^+$	K_{12}	13.5
$\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+$	K	7.54 ^b

^aO'Brien et al. (1974) at 20 mM ionic strength and 25 °C unless otherwise noted^bMorris (1966) at 0 mM ionic strength and 25 °C