Free Chlorine Estimator for Dichlor and Trichlor Systems (V 1.0)

INTRODUCTION

A web–based application (WBA) has been developed to estimate the free chlorine (hypochlorous acid plus hypochlorite ion, TOTFree) concentration in drinking water samples when cyanuric acid (CYA) is present as is the case when adding chlorine–containing chemicals commonly referred to as Dichlor (anhydrous sodium dichloroisocyanurate or sodium dichloroisocyanurate dihydrate) or Trichlor (trichloroisocyanuric acid) to drinking water systems. The WBA implements the equilibrium Simple Model presented by Wahman and Alexander (2019) to estimate TOTFree concentrations.

FREE CHLORINE ESTIMATOR APPLICATION

The WBA consists of three areas described below in detail: (i) *Header*, (ii) *Inputs for free chlorine estimate*, and (iii) *Estimated free chlorine concentration*.

Header area. The top of the WBA's web page contains a *Header* area (Figure 1) where general information about the WBA is presented along with hyperlinks to the main research article used in creating the WBA (Wahman and Alexander, 2019) and the Application Documentation (i.e., this document).

Free Chlorine Estimator for Dichlor and Trichlor Systems

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The provided application allows the user to estimate the free chlorine concentration when cyanuric acid is present as is the case when adding chlorine-containing chemicals commonly referred to as Dichlor (anhydrous sodium dichloroisocyanurate or sodium dichloroisocyanurate dihydrate) or Trichlor (trichloroisocyanuric acid) to water. The equilibrium equations and associated temperature dependent constants used for the free chlorine estimation are for the Simple Model developed by Wahman and Alexander (2018) and references therein. To open a document describing the application in a new window, click on the following link: Application Documentation.

The application was developed by the United States Environmental Protection Agency (EPA). No warranty expressed or implied is made regarding the accuracy or utility of the system, nor shall the act of distribution constitute any such warranty. Any reference to specific commercial products, processes, or services by service mark, trademark, manufacturer, or otherwise, does not constitute or imply their endorsement, recommendation, or favoring by EPA. The EPA seal and logo shall not be used in any manner to imply endorsement of any commercial product or activity by EPA or the United States Government. The views expressed in this application do not necessarily represent the views or policies of the EPA. Although a reasonable effort has been made to assure that the results obtained are correct, this application is experimental. Therefore, the author and the EPA are not responsible and assume no liability whatsoever for any results or any use made of the results obtained from this application, nor for any damages or litigation that result from the use of the application for any purpose.

Figure 1 – Header area

Inputs for free chlorine estimate area. Below the *Header* area is the *Inputs for free chlorine estimate* area where the user selects values for the required inputs obtained from a drinking water sample for which a TOTFree estimate is desired (Figure 2).

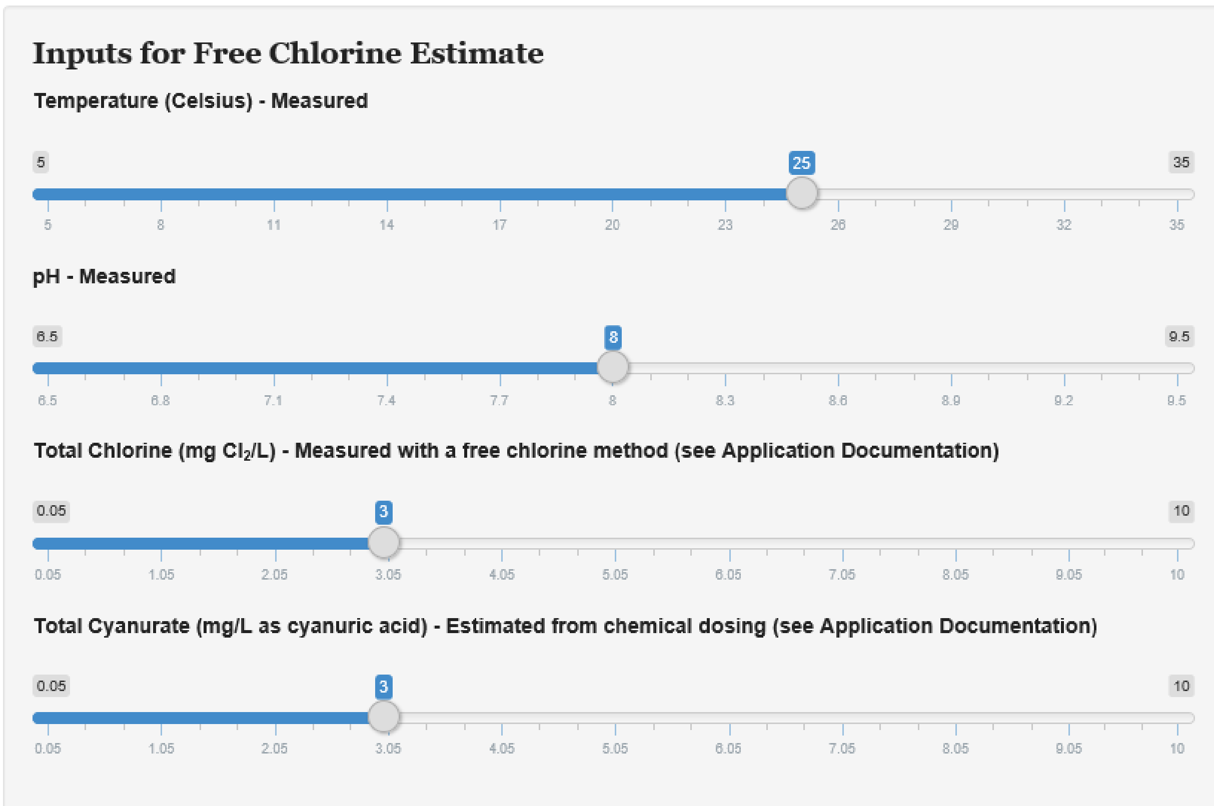

Figure 2 – Inputs for free chlorine estimate area

The user must provide four pieces of information about the water sample to allow estimation of the TOTFree concentration: (i) temperature (°C), (ii) pH, (iii) total chlorine concentration (TOTCl, mg Cl_2/L), and (iv) total cyanurate concentration (TOTCy, mg/L as itself).

The water sample's temperature and pH are obtained by direct measurement at the time of sample collection. The sample's TOTCl concentration is also obtained by direct measurement at the time of sample collection, but **TOTCl must be determined using a free chlorine DPD (e.g., Hach Company, 2014a) or amperometric titration (APHA et al., 2005) method which will actually provide the TOTCl concentration in the water sample because of known method interferences (Wahman et al., 2019)**.

In addition to the three directly measured parameters at the time of water sample collection, the user needs to provide the TOTCy concentration of the water sample. In drinking water, TOTCy concentrations are generally less than the available method detection limit of simple field kits (approximately 5 mg/L) which rely on melamine precipitation chemistry (Hach Company, 2014b). 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 (Briggle et al., 1981; Downes et al., 1984; Hou and Ding, 2011; Sun et al., 2011), differential pulse polarography (Struys and Wolfs, 1987), and ultraviolet detection (Downes et al., 1984). Therefore, the TOTCy concentration cannot be measured currently at concentrations expected in typical drinking water samples in the field.

As opposed to the TOTCl concentration which will decrease due to the water's chlorine demand and must be measured directly in water samples, the TOTCy concentration should be relatively stable in drinking water. Therefore, the TOTCy concentration may be estimated conservatively by the user from the total dosage of cyanurate containing chemicals added to the water, requiring the user to know the total dosage and appropriately calculate the added TOTCy concentration based on the specific chemical added and the amount of chemical added. To serve as a guide, the TOTCy added as CYA for each 1 mg/L of the three chemicals approved for use in drinking water as well as CYA is summarized in Table 1, assuming 100% chemical purity.

Table 1 – Total cyanurate (TOTCy) addition for each 1 mg/L of chemical addition as itself

Chemical Added	Molecular Weight	Total Cyanuric (TOTCy) Addition as Cyanuric Acid (mg/L) for each mg/L of Chemical Added as Itself
Cyanuric Acid	129.07	1.000
Anhydrous Sodium Dichloroisocyanurate	219.95	0.587
Sodium Dichloroisocyanurate Dihydrate	255.98	0.504
Trichloroisocyanuric Acid	232.41	0.555

For example, if a plant is adding 4.0 mg/L of sodium dichloroisocyanurate dihydrate (SDD) chemical that has a 98% purity, the TOTCy concentration is calculated as shown by Equation 1.

$$\text{TOTCy as CYA} = (0.98)\left(4.0\,\frac{\text{mg SDD}}{\text{L}}\right)\left(0.504\,\frac{\text{mg TOTCy}}{\text{mg SDD}}\right) = 2.0\,\frac{\text{mg}}{\text{L}}\,\text{TOTCy as CYA} \quad (1)$$

Estimated free chlorine concentration area. Located below the *Inputs for free chlorine estimate* area is the *Estimated free chlorine concentration* area. For the inputted water sample conditions, the corresponding WBA estimated TOTFree in mg Cl_2/L is calculated and displayed (Figure 3). The estimated TOTFree concentration dynamically changes based on changes in the selected inputs located in the *Inputs for free chlorine estimate* area.

Estimated free chlorine concentration = 1.44 mg/L as chlorine

Figure 3 – Estimated free chlorine concentration area

SIMPLE MODEL IMPLEMENTATION

The Simple Model equilibrium expressions and associated constants that the WBA uses to estimate the TOTFree concentration are presented in Table 2.

Table 2 – Simple model equilibrium expressions and associated constants [a]

Equilibrium Expression	Equilibrium Constant	pK
$H_3Cy \rightleftharpoons H_2Cy^- + H^+$	K_6	$\frac{1{,}743}{T_K} + 1.12$ [b]
$Cl_2Cy^- + H_2O \rightleftharpoons HClCy^- + HOCl$	K_{7a}	$\frac{2{,}028}{T_K} - 2.15$ [c]
$HClCy^- + H_2O \rightleftharpoons H_2Cy^- + HOCl$	K_{9a}	$\frac{2{,}229}{T_K} - 1.65$ [c]
$HOCl \rightleftharpoons OCl^- + H^+$	K	$\frac{3{,}000}{T_K} - 10.0686 + 0.0253T_K$ [d]

[a] T_K is temperature in Kelvin; [b] Wahman (2018); [c] Wahman and Alexander (2019); [d] Morris (1966)

Equation 2 represents a third–order polynomial equation derived from the Simple Model in terms of the TOTFree concentration.

$$\left(\frac{K_6{\propto_0}^2}{K_{7a}K_{9a}\{H^+\}}\right)\mathrm{TOTFree}^3 + \left(2\mathrm{TOTCy}\frac{K_6{\propto_0}^2}{K_{7a}K_{9a}\{H^+\}} + \frac{K_6\propto_0}{K_{9a}\{H^+\}} - \mathrm{TOTCl}\frac{K_6{\propto_0}^2}{K_{7a}K_{9a}\{H^+\}}\right)\mathrm{TOTFree}^2 + \left(\mathrm{TOTCy}\frac{K_6\propto_0}{K_{9a}\{H^+\}} + 1 + \frac{K_6}{\{H^+\}} - \mathrm{TOTCl}\frac{K_6\propto_0}{K_{9a}\{H^+\}}\right)\mathrm{TOTFree} - \mathrm{TOTCl}\left(1 + \frac{K_{6c}}{\{H^+\}}\right) = 0 \qquad (2)$$

In Equation 2, α_o is the fraction of TOTFree that is hypochlorous acid (HOCl); $\{H^+\}$ is hydrogen ion activity which equals 10^{-pH}; K_6 is the CYA first equilibrium constant (Table 2); and K_{7a} and K_{9a} are chlorinated cyanurate equilibrium constants (Table 2). With the required inputs, only TOTFree is unknown in Equation 2. Solution of Equation 2 for TOTFree is accomplished in R, a freeware language and environment for statistical computing and graphics available for download at http://www.r-project.org/ (R Core Team, 2017). R's capabilities were extended through the use of the polynom package, a free user–contributed package downloaded through the R software, to numerically solve Equation 2 for the TOTFree concentration (Venables et al., 2016).

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