

Web-Based Applications to Simulate Drinking Water Inorganic Chloramine Chemistry

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Two web-based applications (WBAs) relevant to drinking water practice are presented to simulate (1) inorganic chloramine formation and stability, including an example inorganic chloramine demand reaction for organic matter, and (2) breakpoint curves. The model underlying both WBAs is a well-established inorganic chloramine formation-and-decay model. The WBAs were developed to be freely accessible over the Internet as web pages (<https://usepaord.shinyapps.io/Unified-Combo/> and <https://usepaord.shinyapps.io/Breakpoint-Curve/>), providing drinking water practitioners (e.g., operators, regulators, engineers, professors,

students) with learning tools to explore inorganic chloramine chemistry in an interactive manner without requiring proprietary software or user modeling expertise. The WBAs allow the user to specify two side-by-side simulations, providing a direct comparison of impacts associated with changing simulation conditions (e.g., free chlorine, free ammonia, and total organic carbon concentrations; pH; total alkalinity; and temperature). Once completed, the user may download simulation data to use offline. The WBAs' implementation, validation, and example simulations are described.

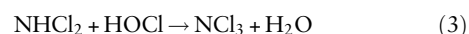
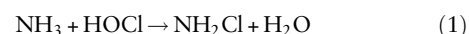
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Chlorine disinfection remains quite popular in the United States (AWWA Water Quality and Technology Division Disinfection Systems Committee 2008a, 2008b), but because of the Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules (USEPA 2006, 1998), many US utilities now use combinations of chlorine and chloramines to avoid excessive regulated trihalomethane and haloacetic acid formation. In addition, the presence of raw-water ammonia and its potential impacts on disinfectant efficacy are becoming increasingly understood (AWWA 2013). Therefore, an understanding of chloramine chemistry is of practical importance.

When free ammonia (consisting of ammonium [NH_4^+] and ammonia [NH_3]) and free chlorine (consisting of hypochlorous acid [HOCl] and hypochlorite ion [OCl^-]) are added to water, three inorganic chloramine chemical species may form: monochloramine (NH_2Cl), dichloramine (NHCl_2), and trichloramine (NCl_3). The inorganic chloramines formed, and their subsequent stability, largely depend on the initially added free ammonia and free chlorine concentrations and the water's pH. In addition, chloramine demand reactions

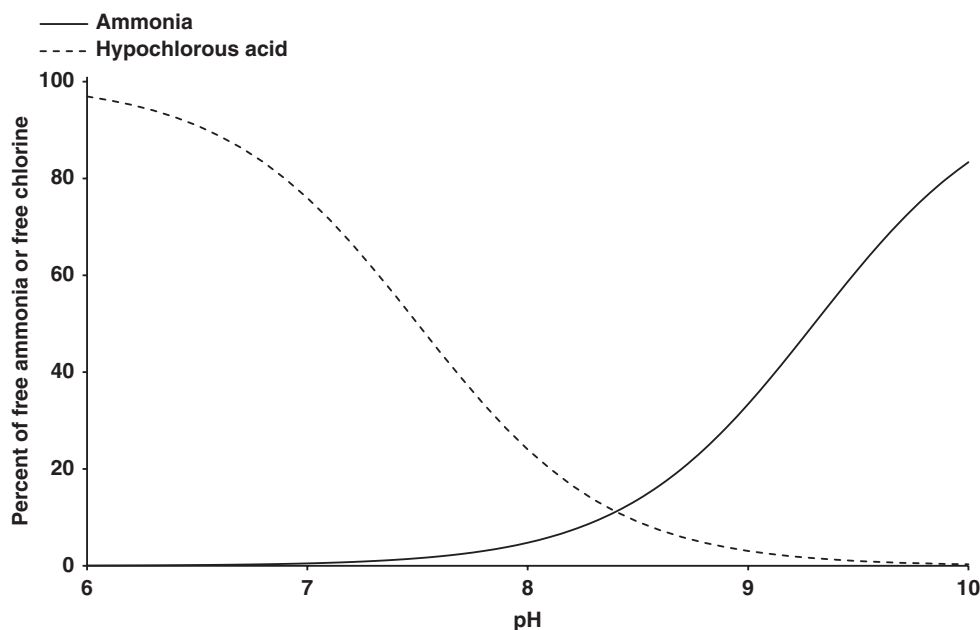
(e.g., natural organic matter [NOM]) and the degree of chemical mixing will also affect inorganic chloramine formation.

If one ignores chloramine demand reactions, has a water with low bromide (e.g., <0.1 mg/L), and assumes perfect chemical mixing, Eqs 1–3 represent a simplified set of reactions typically presented (e.g., Crittenden et al. 2005) to explain inorganic chloramine formation, highlighting (1) the importance of pH resulting from free chlorine and free ammonia being acid–base chemicals, (2) free chlorine and free ammonia's concentration importance, and (3) the sequential nature of inorganic chloramine formation (i.e., monochloramine must form before any dichloramine formation).



As shown in Eqs 1–3, the reacting free chlorine and free ammonia chemical species in inorganic chloramine formation are HOCl and NH_3 , respectively, and their respective percentages of free chlorine and free

FIGURE 1 pH-based percentage of free ammonia or free chlorine that is ammonia or hypochlorous acid

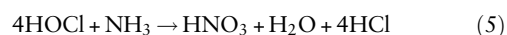
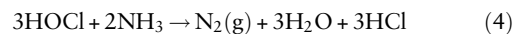


ammonia are pH dependent (Figure 1). As pH decreases, the HOCl fraction of free chlorine increases ($pK_a = 7.5$, 25°C), and the NH_3 fraction of free ammonia decreases ($pK_a = 9.3$, 25°C), leading to the increased formation of dichloramine, and possibly trichloramine, in relation to monochloramine.

The other major consideration for inorganic chloramine formation is the added free chlorine and free ammonia concentrations. The ratio of added free chlorine to free ammonia (i.e., mg of free chlorine as chlorine $[\text{Cl}_2]$ to mg of free ammonia as nitrogen $[\text{N}]$) is referred to as the chlorine-to-ammonia-nitrogen ($\text{Cl}_2:\text{N}$) mass ratio. If a water has a given free ammonia concentration, increasing the $\text{Cl}_2:\text{N}$ mass ratio translates into increasing the free chlorine added to the water. A common method to concisely illustrate the impact of $\text{Cl}_2:\text{N}$ mass ratio on resulting chemical (e.g., free ammonia, free chlorine, and inorganic chloramines) concentrations is a chlorine breakpoint curve (Figure 2), where the chemical species are plotted against the applied $\text{Cl}_2:\text{N}$ mass ratio (or increasing free chlorine dose). In Figure 2, total chlorine represents the sum of free chlorine and the inorganic chloramines, and 1 mg N/L of ammonia is present initially.

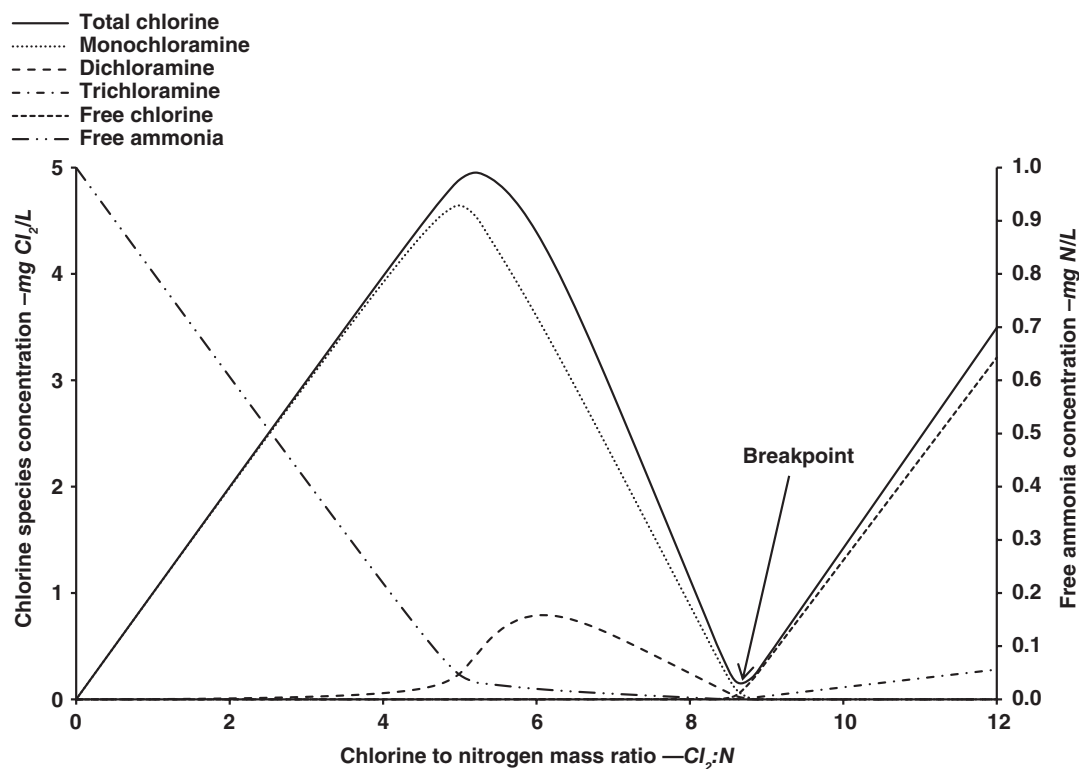
In practice, using less than a 5.07:1 $\text{Cl}_2:\text{N}$ mass ratio (1:1 molar ratio) and at pHs commonly found in drinking water (i.e., pH 7–9), monochloramine is the predominant and desired inorganic chloramine formed (AWWA 2013). For $\text{Cl}_2:\text{N}$ mass ratios greater than 5.07:1, enough free chlorine has been added to combine

essentially all the free ammonia into inorganic chloramines. Therefore, additionally added free chlorine reacts with the formed inorganic chloramines, leading to total chlorine residual loss (where chlorine degrades to chloride and cannot recombine to reform chloramines) for $\text{Cl}_2:\text{N}$ mass ratios up until the breakpoint. If nitrogen gas (N_2) is assumed to be the only nitrogen product (Eq 4), the breakpoint theoretically occurs at a 7.6:1 $\text{Cl}_2:\text{N}$ mass ratio (1.5:1 molar ratio), but the actual ratio is likely higher as some nitrate will form as well (Eq 5). For example, the breakpoint occurs at an approximate 8.6:1 $\text{Cl}_2:\text{N}$ mass ratio for the breakpoint curve in Figure 2 that was generated using the kinetic model described in the “Model Development” section. A ratio of 8.6:1 is not unexpected as, in pure solutions or relatively clean waters, the breakpoint occurs at reported $\text{Cl}_2:\text{N}$ mass ratios ranging from 7.8:1 to 9.5:1, which is consistent with a mixture of N_2 and nitrate formation (Black & Veatch Corporation 2010). The breakpoint represents the point of lowest total chlorine residual. Further increasing the $\text{Cl}_2:\text{N}$ mass ratio past the breakpoint leads to an increase in the total chlorine residual, primarily in the form of free chlorine, but some trichloramine may also form (Figure 2).



Every chlorine breakpoint curve is generated on the basis of the initial free ammonia concentration,

FIGURE 2 Chlorine breakpoint curve: 120 min reaction, pH 7.5, 150 mg CaCO₃/L total alkalinity, 1 mg N/L initial free ammonia, and 25°C

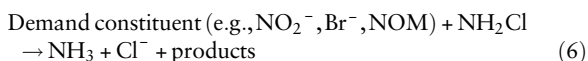


temperature, pH, and a specific reaction time. Therefore, chlorine breakpoint curves are a snapshot at a given reaction time after chemical addition. Depending on the chosen conditions, chlorine breakpoint curves may look substantially different from the one presented in Figure 2 but will, in general, possess a similar shape.

Once formed, inorganic chloramines react (i.e., are lost) through two general pathways that are also pH and $Cl_2:N$ mass ratio dependent: (1) decay and (2) demand. For discussion purposes herein, inorganic chloramine decay refers to inherent inorganic chloramine instability that results in decreasing inorganic chloramine concentrations over time (Jafvert & Valentine 1992), and inorganic chloramine demand refers to water constituents or surfaces in contact with the water that react with and decrease inorganic chloramines over time, including reactions with nitrite (Wahman & Speitel 2012, Vikesland et al. 2001, Margerum et al. 1994, Johnson & Margerum 1991), bromide (Wahman et al. 2017, Luh & Mariñas 2014, Vikesland et al. 2001), NOM (Duirk 2006, 2003; Duirk et al. 2005, 2002; Vikesland et al. 1998), microorganisms and their soluble products (e.g., Maestre

et al. 2013), and pipe surfaces (Vikesland & Valentine 2002a, 2002b, 2000). In addition, nitrification and monochloramine cometabolism are pathways to accelerate chloramine residual loss that become more prevalent at lower $Cl_2:N$ ratios (i.e., greater free ammonia concentrations) (Wahman et al. 2016).

The demand reactions may be generalized by the reaction shown in Eq 6, indicating that any demand reaction decreases chloramine stability. In a practical sense, only considering inorganic chloramine decay reactions results in a best-case scenario for maintaining inorganic chloramine residuals for a given set of environmental parameters (e.g., pH, temperature, and total alkalinity), and inorganic chloramine demand represents additional reaction mechanisms that may accelerate inorganic chloramine residual loss in actual drinking water systems. Therefore, inorganic chloramine decay represents the baseline inorganic chloramine stability that one can hope to obtain for a given set of conditions. As with initial inorganic chloramine formation, inorganic chloramine stability is also affected by pH and $Cl_2:N$ mass ratio. Inorganic chloramines are more stable as pH increases and the $Cl_2:N$ mass ratio decreases (Vikesland et al. 2001, Jafvert & Valentine 1992).



Although useful for providing a basic conceptual understanding, simplifying inorganic chloramine chemistry formation and stability to discussions centered on recommended ranges of $\text{Cl}_2\text{:N}$ mass ratios and pHs hides the underlying complexities of inorganic chloramine formation and their subsequent stability because the chloramine system is kinetically controlled. The simplification limits one's ability to fundamentally understand the implication of deviating from typical conditions and to possibly troubleshoot inorganic chloramine issues in practice. In addition, simply knowing trends does not allow one to quantify how a process change may affect inorganic chloramine formation or stability. For example, should one expect a pH increase from 7 to 8 to increase inorganic chloramine stability by 10 or 100%?

Fortunately, for almost 30 years, an experimentally validated reaction scheme, typically termed the unified model (Table 1, reactions 1–14), has existed that describes inorganic chloramine formation and decay (CFD) over a range of conditions applicable to drinking water (Jafvert & Valentine 1992, Jafvert 1985). The unified model was further experimentally validated and updated by Vikesland et al. (2001) to include temperature dependence of important reactions (Tables 1 and 2, reactions 1–3 and 5) and carbonate general acid catalysis of monochloramine disproportionation (i.e., monochloramine reacting with itself to form dichloramine; Tables 1 and 2, reaction 5).

Even though a reasonable reaction scheme has existed, a widely and freely accessible implementation of the unified model has not. This is largely because of the requirement to program and solve the reaction scheme, which prevented model implementation in a user-friendly environment where proprietary software or user modeling experience was not required.

Recognizing some of these limitations, Ozekin et al. (1996) made several simplifying assumptions to describe chloramine decay by a simple second-order relationship (Eq 7) with a single coefficient they termed the Valentine stability coefficient (k_{VSC}). The major assumptions were that (1) only reactions 1–3, 5, and 7 in Table 1 were considered; (2) the rate of monochloramine loss is governed by the rate of dichloramine formation (Table 1, reactions 3 and 5); (3) monochloramine and free chlorine are in equilibrium (Table 1, reactions 1 and 2); and (4) any formed dichloramine is rapidly lost through reaction 7 in Table 1. Although adequate to simulate chloramine decay of already-formed chloramines, the VSC concept was not envisioned to simulate the range of conditions that a completely implemented unified model would simulate.

$$\text{Rate of monochloramine loss} = k_{\text{VSC}}[\text{NH}_2\text{Cl}]^2 \quad (7)$$

To address the limited access and accelerate the learning curve associated with simulating inorganic chloramine chemistry formation and stability, two web-based applications (WBAs) relevant to drinking water practice were developed to simulate (1) inorganic chloramine formation and subsequent stability, including an example inorganic chloramine demand reaction for organic matter, and (2) breakpoint curves. The intent is for the two WBAs to serve as learning tools for drinking water operators, engineers, researchers, and students, but the WBAs also are applicable to actual practice. The WBAs provide a free, interactive environment for the user to explore and understand fundamental inorganic chloramine chemistry where the only requirement is a web browser and Internet connection to access the WBAs' web pages. Although not intended to simulate specific real-life situations, the WBAs may be used to evaluate and understand the implications of possible operational changes (e.g., $\text{Cl}_2\text{:N}$ mass ratios, target inorganic chloramine residual, booster chlorination, and pH) and their possible impacts on inorganic chloramine formation and subsequent stability. Recent developments in freely available software allowed a web-based interface to be developed, overlaying a robust statistical software package. The result is a unified model implementation accessible over the Internet.

MODEL DEVELOPMENT

Model reactions and hydraulics. Table 1 provides a summary of the implemented reaction scheme process matrix underlying both WBAs, whereas Table 2 provides the associated reaction rate constants. As pH is set to a fixed user-entered parameter, the model's final aspect is the required acid-base equilibrium chemistry for the free chlorine, free ammonia, and carbonate systems (Table 3).

The inorganic chloramine reaction scheme (Table 1, reactions 1–14) developed by Jafvert and Valentine (1992) served as the model basis. The model also includes extensions made by Vikesland et al. (2001) for temperature dependence of important reactions and the carbonate general acid catalysis of monochloramine disproportionation (Tables 1 and 2, reactions 1–3 and 5). To provide the ability to simulate the impact of an example demand reaction for illustrative purposes, a basic implementation of reactions with NOM (Duirk et al. 2005) was also incorporated, providing the user with the ability to investigate this common and important inorganic chloramine demand reaction (Tables 1 and 2, reactions 15 and 16). Organic chloramine formation is not included in the reaction scheme. In addition, because the currently implemented model does not include bromide reactions, the model is most applicable

TABLE 1 Chloramine reactions, rate expressions, and associated stoichiometry

Reaction Number	Reaction	Reaction Rate Expression	Process Matrix Stoichiometry							
			NH ₃	HOCl	NH ₂ Cl	NHCl ₂	NCl ₃	I	DOC ₁	DOC ₂
1	HOCl + NH ₃ → NH ₂ Cl + H ₂ O	$k_1[\text{HOCl}][\text{NH}_3]$	-1	-1	1					
2	NH ₂ Cl + H ₂ O → HOCl + NH ₃	$k_2[\text{NH}_2\text{Cl}]$	1	1	-1					
3	HOCl + NH ₂ Cl → NHCl ₂ + H ₂ O	$k_3[\text{HOCl}][\text{NH}_2\text{Cl}]$		-1	-1	1				
4	NHCl ₂ + H ₂ O → HOCl + NH ₂ Cl	$k_4[\text{NHCl}_2]$		1	1	-1				
5	NH ₂ Cl + NH ₂ Cl → NHCl ₂ + NH ₃	$k_5[\text{NH}_2\text{Cl}]^2$	1		-2	1				
6	NHCl ₂ + NH ₃ → NH ₂ Cl + NH ₂ Cl	$k_6[\text{NHCl}_2][\text{NH}_3][\text{H}^+]$	-1		2	-1				
7	NHCl ₂ + H ₂ O → I	$k_7[\text{NHCl}_2][\text{OH}^-]$				-1		1		
8	I + NHCl ₂ → HOCl + N ₂ + 3H ⁺ + 3Cl ⁻	$k_8[\text{I}][\text{NHCl}_2]$		1		-1		-1		
9	I + NH ₂ Cl → N ₂ + 3H ⁺ + 3Cl ⁻	$k_9[\text{I}][\text{NH}_2\text{Cl}]$			-1			-1		
10	NH ₂ Cl + NHCl ₂ → N ₂ + 3H ⁺ + 3Cl ⁻	$k_{10}[\text{NH}_2\text{Cl}][\text{NHCl}_2]$			-1	-1				
11	HOCl + NHCl ₂ → NCl ₃ + H ₂ O	$k_{11}[\text{HOCl}][\text{NHCl}_2]$		-1		-1	1			
12	NHCl ₂ + NCl ₃ + 2H ₂ O → N ₂ + 2HOCl + 3HCl	$k_{12}[\text{NHCl}_2][\text{NCl}_3][\text{OH}^-]$		2		-1	-1			
13	NHCl ₂ + NCl ₃ + H ₂ O → N ₂ + HOCl + 3HCl	$k_{13}[\text{NH}_2\text{Cl}][\text{NCl}_3][\text{OH}^-]$		1	-1		-1			
14	NHCl ₂ + 2HOCl + H ₂ O → NO ₃ ⁻ + 5H ⁺ + 4Cl ⁻	$k_{14}[\text{NHCl}_2][\text{OCl}^-]$		-2		-1				
15 ^a	NH ₂ Cl + DOC ₁ → NH ₃ + Products	$k_{15}[\text{NH}_2\text{Cl}][\text{DOC}_1]$	1		-1				-1	
16 ^a	HOCl + DOC ₂ → Products	$k_{16}[\text{HOCl}][\text{DOC}_2]$		-1						-1

Sources: Duijk et al. 2005, Jafvert & Valentine 1992

DOC₁—fast-reacting organic matter, DOC₂—slow-reacting organic matter, I—unidentified monochloramine autodecomposition intermediate

pH is set and maintained at a user-defined value in the web-based applications; therefore, OH⁻ and H⁺ have been omitted from the process matrix stoichiometry to simplify presentation.

^aOnly included in the chloramine formation and decay web-based application.

TABLE 2 Kinetic rate constants (25°C unless temperature dependency provided)

Reaction Number	Rate Constant	Value or Equation (Temperature (T) is in Kelvin)	Source(s)
1	k_1	$6.6 \times 10^8 e^{-1,510/T} \text{ s}^{-1}$	Morris & Isaac 1983
2	k_2	$1.38 \times 10^8 e^{-8,800/T} \text{ s}^{-1}$	Morris & Isaac 1983
3	k_3	$3.0 \times 10^5 e^{-2,010/T} \text{ s}^{-1}$	Morris & Isaac 1983
4	k_4	$6.5 \times 10^{-7} \text{ s}^{-1}$	Margerum et al. 1978
5	k_5	$k_{5H}[H^+] + k_{5HCO_3}[HCO_3^-] + k_{5H_2CO_3}[H_2CO_3]$ where $k_{5H} = 1.05 \times 10^7 e^{-2,169/T} \text{ M}^{-2} \text{ s}^{-1}$ $k_{5HCO_3} = 4.2 \times 10^{31} e^{-22,144/T} \text{ M}^{-2} \text{ s}^{-1}$ $k_{5H_2CO_3} = 8.19 \times 10^6 e^{-4,026/T} \text{ M}^{-2} \text{ s}^{-1}$ $6.0 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$	Granstrom 1955 Vikesland et al. 2001 Vikesland et al. 2001
6	k_6	$6.0 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$	Hand & Margerum 1983
7	k_7	$1.1 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$	Jafvert & Valentine 1987, Jafvert 1985
8	k_8	$2.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Leao 1981
9	k_9	$8.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	Leao 1981
10	k_{10}	$1.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$	Leao 1981
11	k_{11}	$k_{CO_3}[CO_3^{2-}] + k_{OCl}[OCl^-] + k_{OH}[OH^-]$ where $k_{CO_3} = 6.0 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ $k_{OCl} = 9.0 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ $k_{OH} = 3.28 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$	Hand & Margerum 1983
12	k_{12}	$5.56 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$	Jafvert & Valentine 1992
13	k_{13}	$1.39 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$	Jafvert & Valentine 1992
14	k_{14}	$2.31 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$	Jafvert & Valentine 1992
15	k_{15}	$5.4 \text{ M}^{-1} \text{ s}^{-1}$	Average from Duirk et al. 2005
16	k_{16}	$1.8 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$	Average from Duirk et al. 2005

TABLE 3 Equilibrium reactions and associated temperature-dependent rate constants

Equilibrium Reaction	Equilibrium Constant (Temperature (T) is in Kelvin)	Source
$HOCl \rightleftharpoons H^+ + OCl^-$	$K_{HOCl} = 10^{-(1.18 \times 10^{-4}T^2 - 7.86 \times 10^{-2}T + 20.5)}$	Morris 1966
$NH_4^+ \rightleftharpoons NH_3 + H^+$	$K_{NH_4^+} = 10^{-(1.03 \times 10^{-4}T^2 - 9.21 \times 10^{-2}T + 27.6)}$	Bates & Pinching 1950
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$	$K_{H_2CO_3} = 10^{-(1.48 \times 10^{-4}T^2 - 9.39 \times 10^{-2}T + 21.2)}$	Snoeyink & Jenkins 1980
$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	$K_{HCO_3^-} = 10^{-(1.19 \times 10^{-4}T^2 - 7.99 \times 10^{-2}T + 23.6)}$	Snoeyink & Jenkins 1980
$H_2O \rightleftharpoons OH^- + H^+$	$K_w = 10^{-(1.5 \times 10^{-4}T^2 - 1.23 \times 10^{-1}T + 37.3)}$	Snoeyink & Jenkins 1980

to waters containing no or low (e.g., <0.1 mg/L) bromide concentrations (Vikesland et al. 2001). For context, 0.115 mg/L bromide represented the 90th-percentile value among large (serving more than 10,000 customers) surface water plants (USEPA 2005). The incorporation of bromide chemistry is a future research need as bromide sources include brackish water, desalination sources, and upstream bromide-laden discharges (Regli et al. 2015).

For simplicity, the model uses batch (equivalent to ideal plug flow) hydraulics, assumes chemical additions

are immediately and completely mixed with no localized concentration gradients, and ignores wall reactions. The model hydraulics translate into several scenarios in practice that can be simulated, including (1) chemical injections into continuously flowing water pipelines where the added chemicals are immediately and completely mixed with the flowing bulk water, and pipe wall reactions do not affect the bulk water chemical concentrations; (2) sampling of water from a point in a distribution system and holding that water over time in batch to assess chloramine stability; and (3) preparing

TABLE 4 Additional R software packages used for web-based application development

Name	Purpose	Source
deSolve	Solves systems of ordinary differential equations representing the implement model	Soetaert et al. 2010
ggplot2	Generates output plots for simulation data	Wickham 2009
reshape2	Restructures and aggregates simulation data for output plots	Wickham 2007
scales	Provides methods to modify scales and legends in graphics	Wickham 2014
shiny	Creates interactive web-based applications with R	RStudio Inc. 2014
shinyBS	Extends the shiny package by adding Twitter Bootstrap components, including generation of pop-up boxes upon screen-pointer hovering	Bailey 2014

inorganic chloramines in the laboratory in a beaker and then holding that water over time in batch. As a first estimate and if plug-flow conditions are maintained and wall reactions are negligible in an actual drinking water distribution system, simulation times are equivalent to water age. The assumed hydraulics are a simplification of actual drinking water systems but provide a relevant hydraulic condition found in practice, allowing a first estimate of expected inorganic chloramine formation and subsequent stability.

The current model allows the user to investigate inorganic chloramine formation and stability over a variety of conditions, and additional model extensions may be included in the future (e.g., nitrite or bromide impacts) to further expand the possible simulation conditions. Conceptually, and when ignoring the NOM chloramine demand reactions, the model represents a first estimate for inorganic chloramine stability based on water age because only the inherent inorganic chloramine instability is included (i.e., inorganic chloramine decay). In practice, non-ideal mixing and flow, localized pH, pipe-wall reactions, nitrification, and presence of other inorganic chloramine demand reactions would serve to decrease inorganic chloramine stability.

Model implementation. The model (Tables 1–3) was implemented using R (R Core Team 2017), a freeware language and environment for statistical computing and graphics available for download (www.r-project.org/). R's capabilities were extended using free user-contributed packages downloaded through the R software (Table 4).

The recent development making WBA creation possible with R was the release of the Shiny package (RStudio Inc. 2014), providing the ability to create a web-based user interface to interact with the underlying model calculations being performed by R, removing the need for the WBA end user to become familiar with and learn the R language (or any other model implementation language) and providing a platform to access the WBAs (e.g., an Internet web page). Because the WBAs are hosted on a server, no special software is required

by the user. The server computer also provides the necessary computing resources, avoiding consumption of the user's resources, and any future WBA updates are immediately available.

Model validation. The unified model is well established, but the WBAs required validation with other unified model implementations to ensure no programming errors had occurred in WBA development. To accomplish this, WBA simulations were compared with simulations generated using the unified model implemented in Aquasim (Reichert 1994) by Wahman and Speitel (2012). Aquasim is a freely available computer program designed to simulate aquatic systems (www.eawag.ch/en/departement/siam/software/). Figure 3, part A, displays an example simulation comparing both model implementations. The current WBA implementation provides the same results as the published implementation, providing evidence that the WBA model implementation is working as expected. In addition to a numerical check on model implementation, an example of the WBA simulations compared with published experimental data (Vikesland et al. 2001) is provided in Figure 3, part B, detailing the WBA representing the published experimental data as well.

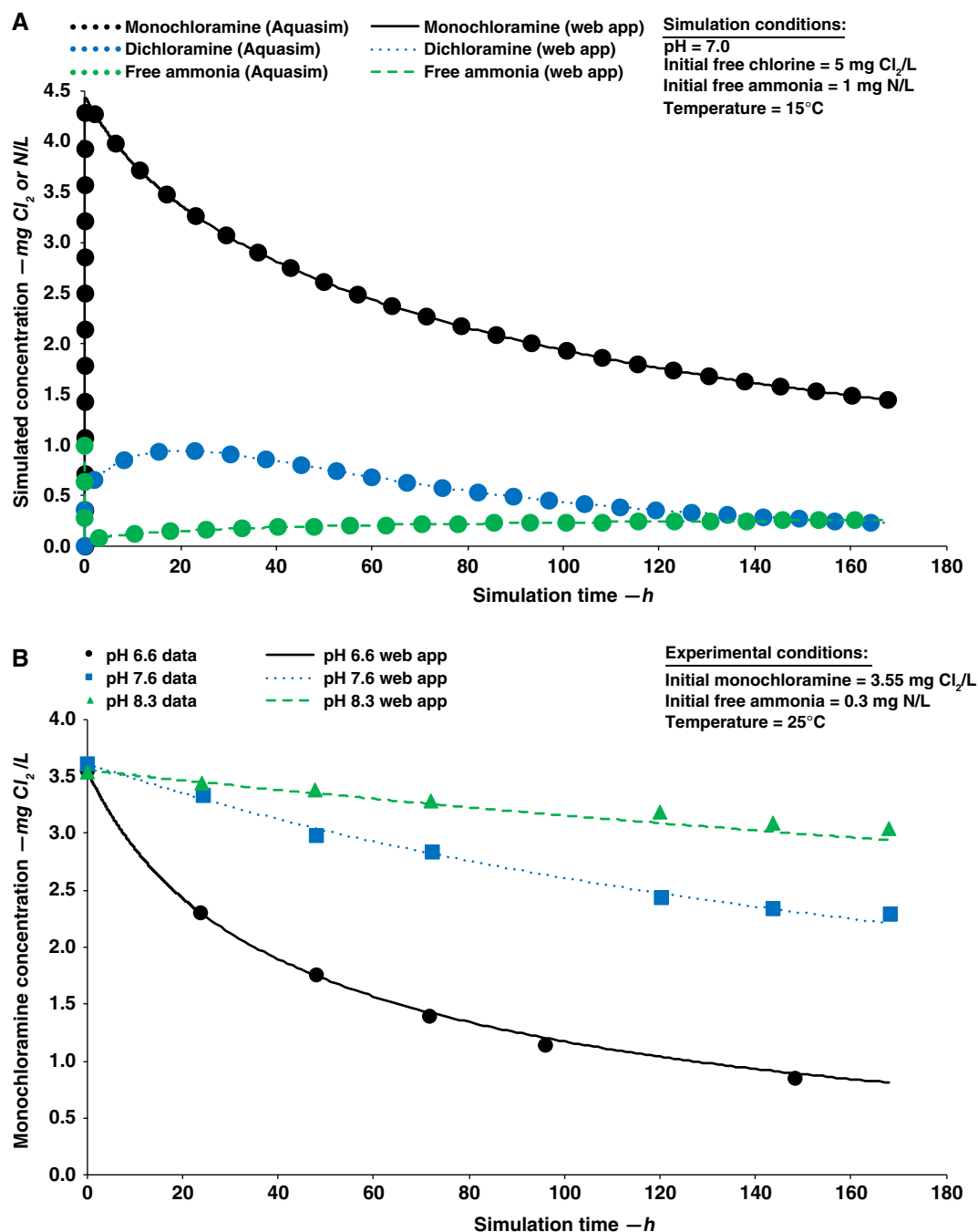
INORGANIC CFD APPLICATION

The inorganic CFD-WBA may be accessed at <https://usepaord.shinyapps.io/Unified-Combo/>. The CFD-WBA's web page areas are discussed next.

Header and simulation input areas. The top of the CFD-WBA's web page contains a header area (Figure 4, part A), where general information about the CFD-WBA is presented, along with hyperlinks to the three main research articles used in creating the CFD-WBA.

Below the header area is the simulation input area, where the user selects and inputs the desired variables (Figure 4, part B). In the simulation input area, the user selects from three general chemical addition scenarios: (1) "Simultaneous Addition" (selected in Figure 4, part B), in which free chlorine and free ammonia are present simultaneously from either free chlorine addition to a

FIGURE 3 Validation examples: numeric comparison with published model^a (A) and comparison with published data^b (B)



^a Web-based application simulation compared with Wahman and Speitel's (2012) Aquasim model simulation

^b Web-based application simulations compared with experimental data from Vikesland et al. (2001)

water containing free ammonia or free ammonia addition to a water containing free chlorine, and the user wishes to simulate inorganic chloramine formation and subsequent decay (e.g., drinking water treatment plant inorganic chloramine formation); (2) “Preformed Chloramines,” in which known concentrations of

inorganic chloramines and free ammonia already exist, and the user wishes to simulate inorganic chloramine decay (e.g., drinking water distribution system samples); or (3) “Booster Chlorination,” in which known concentrations of inorganic chloramines and free ammonia already exist, and the user wishes to simulate adding

FIGURE 4 Chloramine formation-and-decay application screenshot: header (A) and simulation input (B) areas

A

Batch (Plug Flow) Reactor Simulation of Drinking Water Chloramine Formation and Decay (Version 0.52, Updated 02/16/2016)

Created by David G. Wahman, United States Environmental Protection Agency, Office of Research & Development.

Chloramine kinetic model implementation from Jafvert & Valentine (*Environ. Sci. Technol.*, 1992, 26 (3), pp 577-586) and Vikesland et al. (*Water Res.*, 2001, 35 (7), pp 1766-1776).

Natural organic matter reaction implementation from Duirk et al. (*Water Res.*, 2005, 39 (14), pp 3418-3431), using their average fast and slow organic reaction rate constants.

The provided application provides two side-by-side simulations (A and B) and associated graphs to allow comparison of input choices on chloramine formation and decay.

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. EPA has relinquished control of the information and no longer has responsibility to protect the integrity, confidentiality or availability of the information. 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. This application has been reviewed in accordance with EPA policy and has been approved for external and free use. The views expressed in this application do not necessarily represent the views or policies of the Agency. 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.

B

Simulation A Inputs

Copy Simulation A's Inputs to Simulation B's Inputs

Update Simulation A and Plots (Press after Finished Changing Simulation Inputs)

Chemical Addition Scenarios

Simultaneous Addition

Free Chlorine Addition Method

Known Concentration

Free Chlorine Concentration (mg Cl₂/L)

4

Free Ammonia Addition Method

Chlorine to Nitrogen Ratio

Mass Ratio (Cl₂:N)

4.75

Total Organic Carbon (TOC)

TOC Concentration (mg C/L)

0

TOC Fast Reactive Fraction

0.02

TOC Slow Reactive Fraction

0.65

Simulation Time Unit Selection

Days

Simulation Time (days)

10

Simulation A Chemical Concentration Data Download (.csv file)

Simulation B Inputs

Copy Simulation B's Inputs to Simulation A's Inputs

Update Simulation B and Plots (Press after Finished Changing Simulation Inputs)

Chemical Addition Scenarios

Simultaneous Addition

Free Chlorine Addition Method

Known Concentration

Free Chlorine Concentration (mg Cl₂/L)

4

Free Ammonia Addition Method

Chlorine to Nitrogen Ratio

Mass Ratio (Cl₂:N)

4.75

Total Organic Carbon (TOC)

TOC Concentration (mg C/L)

0

TOC Fast Reactive Fraction

0.02

TOC Slow Reactive Fraction

0.65

Simulation Time Unit Selection

Days

Simulation Time (days)

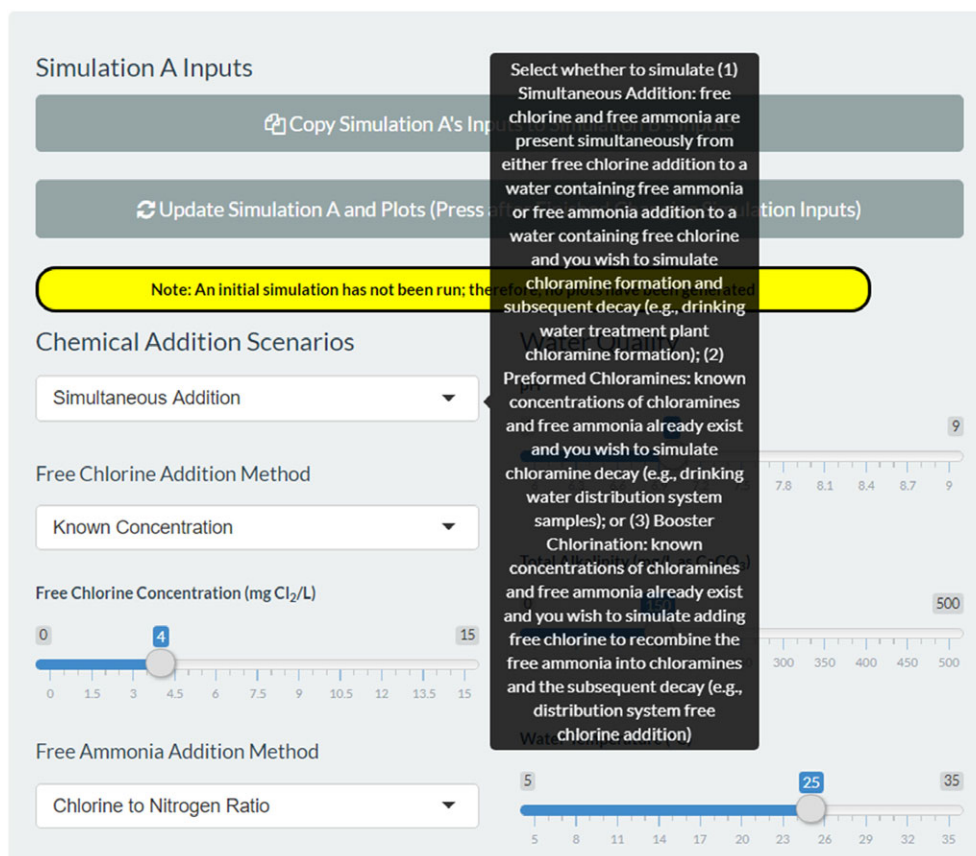
10

Simulation B Chemical Concentration Data Download (.csv file)

free chlorine to recombine the free ammonia into inorganic chloramines and then the subsequent inorganic chloramine decay (e.g., distribution system free chlorine addition). The “Booster Chlorination” scenario would also represent blending free chlorine and chloraminated waters. The CFD-WBA is self-contained and provides

the necessary information to direct the user on how to conduct a simulation, providing guidance through pop-up boxes that appear when hovering a screen pointer over a required input or possible selection (Figure 5). For each chemical addition scenario, the user selects the free chlorine and free ammonia addition methods. In

FIGURE 5 Chloramine formation-and-decay application screenshot: example pop-up box describing possible chemical addition scenario selections



addition, the user enters general water quality parameters (e.g., pH, alkalinity, temperature).

If desired, the user may also simulate organic matter demand by entering a total organic carbon (TOC) concentration and then selecting the TOC fraction associated with the fast and slow reactive fractions defined by Duirk et al. (2005). Because organic carbon reactions are likely source water dependent, implementation of the organic matter reactions is provided in a simplistic manner to illustrate an example of how chloramine demand reactions affect inorganic chloramine stability. The current implementation uses the average reaction rate constants for the fast (Table 2, reaction 15) and slow (Table 2, reaction 16) reactive TOC fractions determined by Duirk et al. (2005), and the fast and slow TOC rate constants are not currently user adjustable. The CFD-WBA does allow users to change the TOC fraction associated with the fast and slow reactions if they want to investigate the impact of having more or less reactive TOC. For reference, Duirk et al. (2005) determined fast and slow TOC reactive site fractions for six NOM sources, ranging from 0.010 to 0.023 and 0.42 to 0.68, respectively.

Because inorganic chloramine reactions may occur on varying time scales, the CFD-WBA allows the user to select time frames in minutes, hours, and days, ranging from 1 min to 60 days. The time selection will affect the (1) simulation run length and (2) abscissa scale on generated plots.

The general input area also contains three buttons that allow the user to (1) copy the current simulation's input conditions directly to the other simulation ("Copy Simulation A's Inputs to Simulation B's Inputs"), (2) run the simulation with the provided input conditions and generate output plots ("Update Simulation A and Plots (Press after Finishing Changing Simulation Inputs)"), and (3) export the finished simulation data to a comma-separated variable (.csv) file for use in external programs ("Simulation A Chemical Concentration Data Download (.csv file)").

Plot preferences and initial conditions summary table area. After entering the conditions and running a simulation, the CFD-WBA's next area controls which chemicals are displayed on generated output plots and provides a summary table of the simulation initial conditions (Figure 6). In the left side of this area, the user may toggle on and off the chemicals (total chlorine,

FIGURE 6 Chloramine formation-and-decay application screenshot: plot preferences and initial conditions summary table areas

Simulation A Plot Preferences

Update Plots for Simulation A

Chemicals to Plot

- ☒ Total Chlorine
- ☒ Monochloramine
- ☒ Dichloramine
- ☒ Trichloramine
- ☒ Free Chlorine
- ☒ Free Ammonia

Simulation A Initial Conditions

Parameter	Value
Free Chlorine (mg Cl ₂ /L) =	4
Free Ammonia (mg N/L) =	0.84
Monochloramine (mg Cl ₂ /L) =	0
Dichloramine (mg Cl ₂ /L) =	0
Chlorine:Nitrogen Ratio (X:1) =	4.75
Chlorine:Ammonia Ratio (X:1) =	3.91
pH =	7
Total Alkalinity (mg CaCO ₃ /L) =	150
Temperature (Celsius) =	25
Total Organic Carbon (mg C/L) =	0
TOC Fast Site Fraction =	0.02
TOC Slow Site Fraction =	0.65

Simulation B Plot Preferences

Update Plots for Simulation B

Chemicals to Plot

- ☒ Total Chlorine
- ☒ Monochloramine
- ☒ Dichloramine
- ☒ Trichloramine
- ☒ Free Chlorine
- ☒ Free Ammonia

Simulation B Initial Conditions

Parameter	Value
Free Chlorine (mg Cl ₂ /L) =	4
Free Ammonia (mg N/L) =	0.84
Monochloramine (mg Cl ₂ /L) =	0
Dichloramine (mg Cl ₂ /L) =	0
Chlorine:Nitrogen Ratio (X:1) =	4.75
Chlorine:Ammonia Ratio (X:1) =	3.91
pH =	9
Total Alkalinity (mg CaCO ₃ /L) =	150
Temperature (Celsius) =	25
Total Organic Carbon (mg C/L) =	0
TOC Fast Site Fraction =	0.02
TOC Slow Site Fraction =	0.65

monochloramine, dichloramine, trichloramine, free chlorine, and free ammonia) to display through the provided checkboxes. Once the user's selection is made, the "Update Plots for Simulation A" button can be pressed to immediately update the plots. After a simulation is completed, a summary of the initial conditions used in the simulation is also created in the right side of this area for reference.

Output plot area. The CFD-WBA generates three plot types for each simulation that can be selected from the tabs associated with each plot type (Figures 7 and 8). The first tab ("Individual Chemicals," Figure 7) displays a series of plots showing single chemical concentrations over time; the second tab ("Composite Chemicals," Figure 8, part A) displays a composite plot of all selected chemicals on the same plot over time; and the third tab ("Chlorine to Nitrogen Ratios," Figure 8, part B) displays a plot showing the Cl₂:N and Cl₂:NH₃ mass ratios over time.

CHLORINE BREAKPOINT CURVE APPLICATION

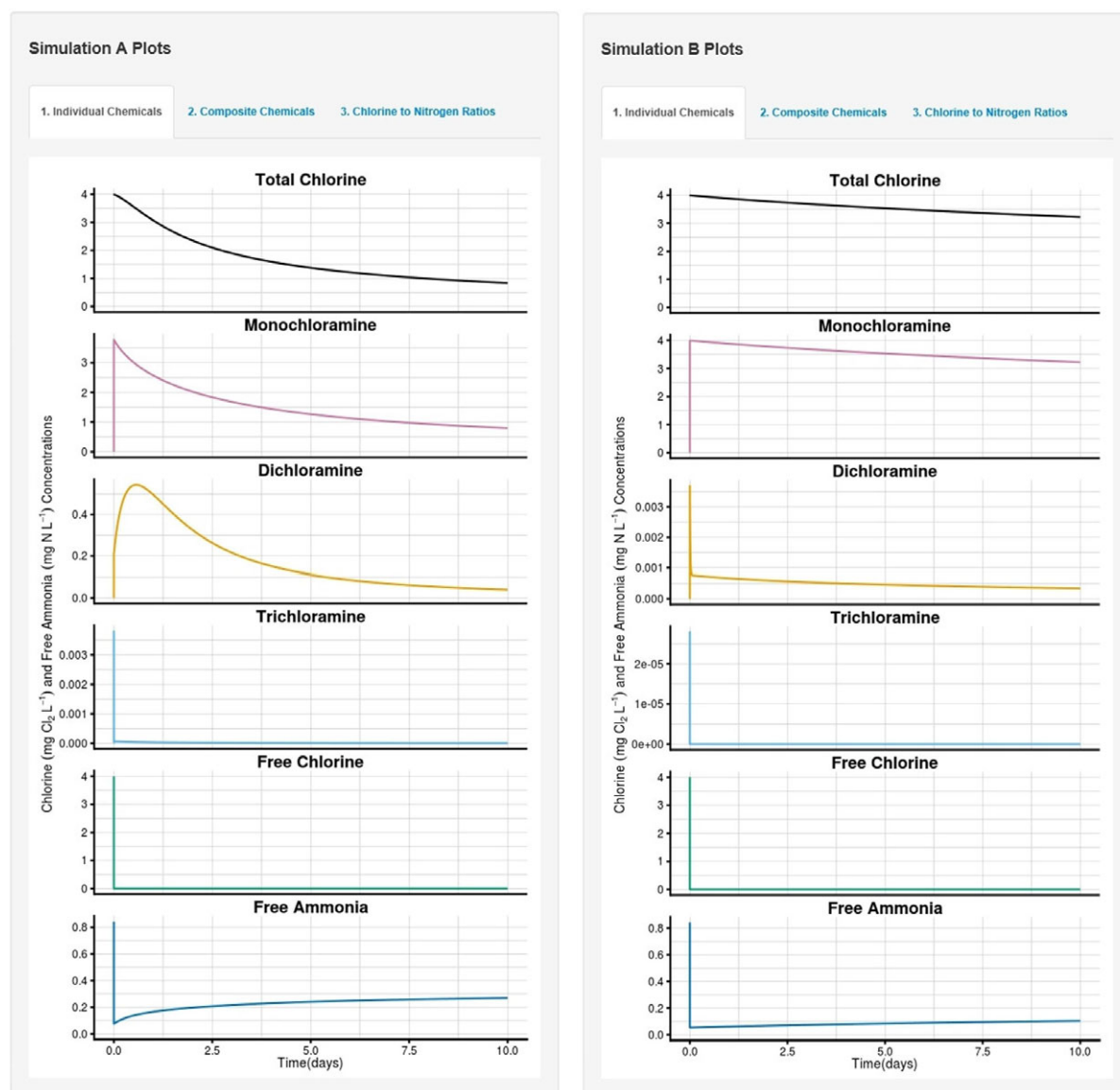
In addition to the CFD-WBA, a second WBA was specifically developed to simulate and generate chlorine breakpoint curves under various conditions. The chlorine breakpoint curve web-based application (BP-WBA) is based on the same underlying model implementation as the CFD-WBA but has three main differences: the BP-WBA (1) does not include the organic matter demand reactions of Duirk et al. (2005), (2) provides a different user interface (i.e., Internet web page) specific for the generation of chlorine breakpoint curves (<https://usepaord.shinyapps.io/Breakpoint-Curve/>), and (3) has only two chemical addition scenarios in which the water is assumed to contain either (a) an initial free ammonia concentration and then free chlorine is added in various concentrations or (b) an initial free chlorine concentration and then free ammonia is added in various concentrations. In

either scenario, no inorganic chloramine concentrations initially exist. The first scenario is a typical implementation of breakpoint chlorination in which a water initially contains free ammonia. The second scenario represents a chloramination situation by adding free ammonia into a water already containing free chlorine to show the impact of Cl₂:N mass ratio selection, illustrating the impact of over- or underfeeding ammonia. The BP-WBA's web page areas are subsequently discussed.

Header and simulation input areas. The BP-WBA contains a header describing the WBA and provides hyperlinks to source articles (Figure 9, part A). Below the header area is a simulation input area (Figure 9, part B), allowing the user to specify the initial free ammonia or free chlorine concentration, total alkalinity, pH, and temperature. The BP-WBA input area also contains the three buttons found in the CFD-WBA input area, allowing the user to copy inputs from one simulation to the other, run the simulation, and download simulation concentration data. When a BP-WBA simulation is initiated, the BP-WBA uses the simulation inputs and conducts a series of simulations for Cl₂:N mass ratios from 0 to 15 in increments of 0.2 (76 total simulations). Each simulation is run for a fixed 240 min reaction time.

Output plot area. The BP-WBA output plot area produces a chlorine breakpoint curve based on the user-selected reaction time with the provided slider (0–240 min; Figure 10). The ability to generate chlorine breakpoint curves associated with various reaction times is important, as any chlorine breakpoint curve has an associated reaction time, whether or not it is explicitly stated. The user may also animate the chlorine breakpoint curve by pressing the provided play button, causing the chlorine breakpoint curve to step between 0 and 240 min reaction times in 1 min increments, thus allowing the user to visualize the impact of reaction time on the corresponding chlorine breakpoint curve. As

FIGURE 7 Chloramine formation-and-decay application screenshot: output plot area with “Individual Chemicals” tab selected^a



^a Simulation A is pH 7 and simulation B is pH 9. All other initial conditions are the same (4 mg Cl₂/L free chlorine, 4.75:1 Cl₂:N mass ratio, 150 mg/L as CaCO₃ total alkalinity, 25°C, and 0 mg C/L total organic carbon).

with the CFD-WBA, the user may also select which chemicals to show on the chlorine breakpoint curve plot using the provided checkboxes.

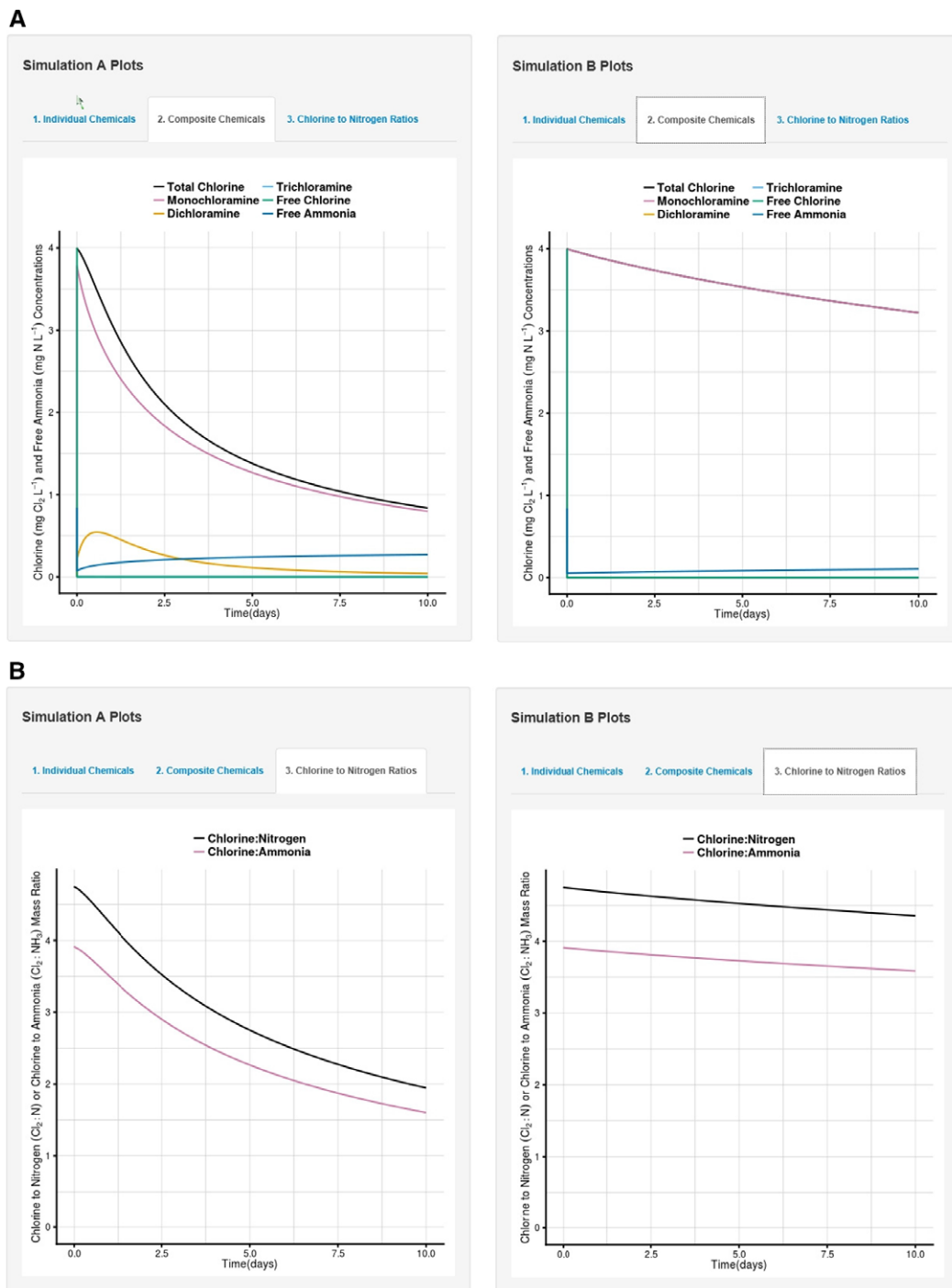
EXAMPLE SIMULATIONS

To provide an example of both the CFD-WBA and BP-WBA, example simulations were conducted with each WBA.

Inorganic CFD application. For the CFD-WBA, the chemical addition scenario of simultaneously adding free

chlorine and free ammonia is presented in Figures 4 and 6–8. The initial conditions (4 mg Cl₂/L free chlorine, 4.75:1 Cl₂:N mass ratio, 150 mg/L as calcium carbonate (CaCO₃) total alkalinity, 25°C, 0 mg/L TOC, and 10 day simulation time) of simulations A and B are identical, except pH (pH 7 in simulation A and pH 9 in simulation B; Figure 5). To assist in simulation input entry, the user may input simulation A’s conditions, press the provided “Copy Simulation A’s Inputs to Simulation B’s Inputs” button, and then change simulation B’s pH from 7 to

FIGURE 8 Chloramine formation-and-decay application screenshot^a: output plot area with “Composite Chemicals” (A) or “Chlorine to Nitrogen Ratios” tab (B) selected



^a Simulation A is pH 7 and simulation B is pH 9. All other initial conditions are the same (4 mg Cl_2/L free chlorine, 4.75:1 $\text{Cl}_2:\text{N}$ mass ratio, 150 mg/L as CaCO_3 total alkalinity, 25°C, and 0 mg C/L total organic carbon).

9 with the provided slider. Entering simulation inputs in this manner allows the user to enter and compare the impact of changing a single variable (e.g., pH in this instance) on inorganic CFD.

For simulation A (pH 7; Figure 7), initial inorganic chloramine formation (Table 1, reactions 1 and 3) is complete within 1 min, leading to initial concentrations of 4.0 mg Cl_2/L total chlorine, 3.8 mg Cl_2/L

FIGURE 9 Chlorine breakpoint curve application screenshot: header (A) and simulation input (B) areas

A

Chlorine Breakpoint Curve Simulator (Version 0.25, Updated 12/18/2017)

Created by David G. Wahman, United States Environmental Protection Agency, Office of Research & Development.

Model implementation from Jafvert & Valentine (*Environ. Sci. Technol.*, 1992, 26 (3), pp 577-586) and Vikesland et al. (*Water Res.*, 2001, 35 (7), pp 1766-1776).

The provided application generates two side-by-side breakpoint curves (A and B) for comparison purposes with user defined conditions. Because several simulations are conducted to generate a breakpoint curve, simulation updates may take approximately a minute to complete.

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B

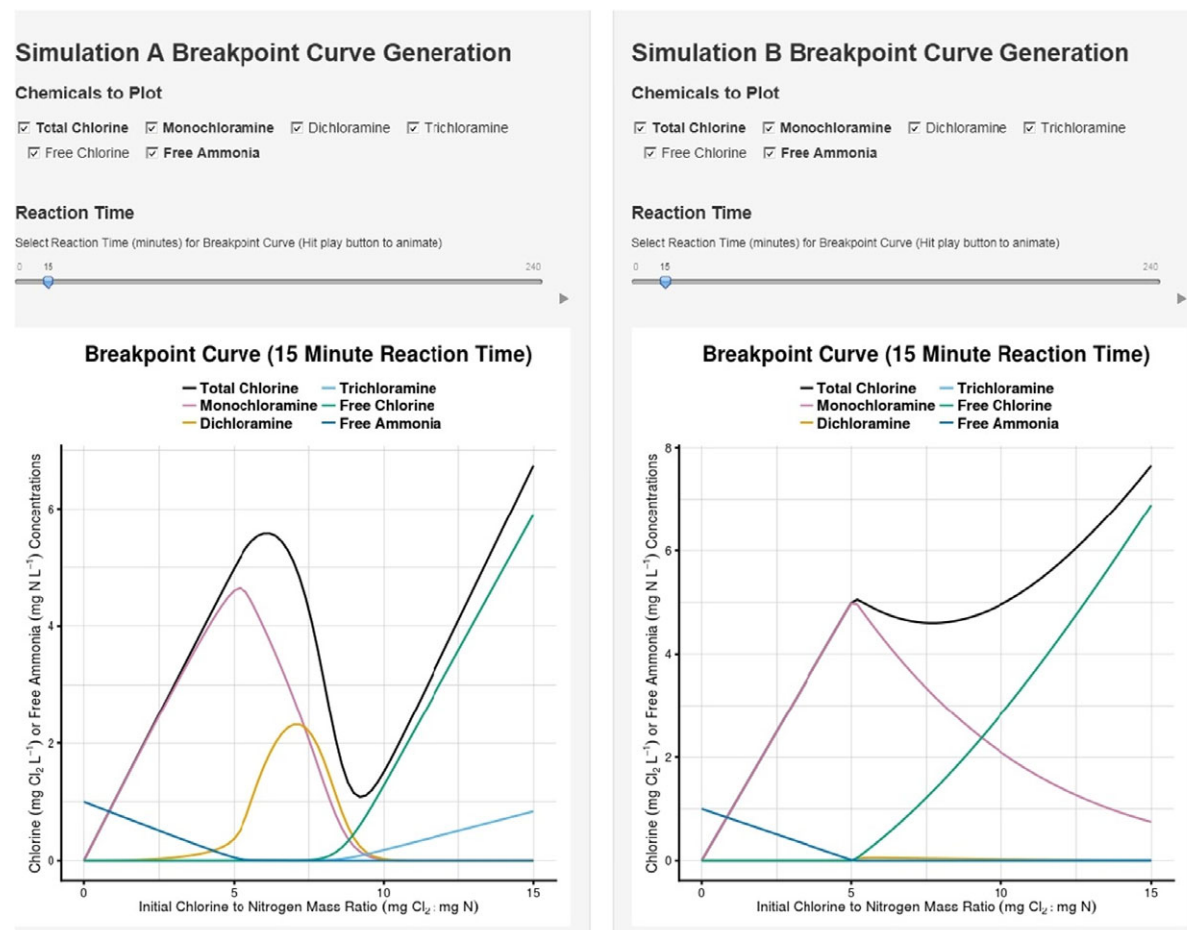
The screenshot displays two side-by-side input panels for the Chlorine Breakpoint Curve Simulator.
Simulation A Inputs:
- Initial Conditions: Select Chemical with Initial Fixed Concentration (Free Ammonia).
- Initial Free Ammonia Concentration (mg N/L): Slider set to 1.
- Total Alkalinity (mg/L as CaCO₃): Slider set to 150.
- pH: Slider set to 7.
- Water Temperature (°C): Slider set to 25.
- Buttons: Copy Simulation A's Inputs to Simulation B's Inputs, Update Simulation A (Press after Finished Changing Simulation Inputs), Simulation A Chemical Concentration Data Download (.csv file).
Simulation B Inputs:
- Initial Conditions: Select Chemical with Initial Fixed Concentration (Free Ammonia).
- Initial Free Ammonia Concentration (mg N/L): Slider set to 1.
- Total Alkalinity (mg/L as CaCO₃): Slider set to 150.
- pH: Slider set to 9.
- Water Temperature (°C): Slider set to 25.
- Buttons: Copy Simulation B's Inputs to Simulation A's Inputs, Update Simulation B (Press after Finished Changing Simulation Inputs), Simulation B Chemical Concentration Data Download (.csv file).

monochloramine (95% of total chlorine), and 0.2 mg Cl₂/L dichloramine (5% of total chlorine). After this initial formation, the monochloramine concentration decreases as it converts to dichloramine (Table 1, reaction 2 and then 3 or reaction 5), but because dichloramine is somewhat stable at pH 7 (Table 1, reaction 7), dichloramine concentration initially increases, resulting in a 0.51 mg Cl₂/L maximum dichloramine concentration (15% of total chlorine) at 13 h and eventually reaching dichloramine's maximum percentage of total chlorine (16%) at 22 h. One practical aspect of this simulation is that the peak dichloramine concentration would not occur until several hours after initial inorganic chloramine formation. Depending on system hydraulics and the presence of inorganic chloramine demand reactions in an actual system, a drinking water utility operating under these conditions and sampling shortly after inorganic chloramine formation may believe that dichloramine formation is relatively minor, but the peak dichloramine concentration may occur in the drinking water distribution system.

Simulation B (pH 9; Figure 7) shows a different behavior for inorganic chloramine formation and stability. At pH 9, initial dichloramine formation is relatively slow (Table 1, reaction 3), and any dichloramine that forms quickly decays (Table 1, reaction 7); therefore, monochloramine initially represents the entire 4 mg Cl₂/L total chlorine concentration. Because monochloramine must still pass through dichloramine to decay, and dichloramine forms slowly at pH 9 (Table 1, reaction 2 and then 3 or reaction 5), total chlorine is more stable at pH 9 than at pH 7. After 10 days, the simulated total chlorine residual is 0.84 (79% loss) and 3.2 (20% loss) mg Cl₂/L for simulations A and B, respectively.

Another practical example of these kinetic-based simulations is how they differ from calculations made if one assumes that inorganic chloramine chemistry is an equilibrium rather than a kinetically controlled system. For example, Oldenburg et al. (2002) used an equilibrium assumption for inorganic chloramine chemistry while interpreting pH's impact on chloramine inactivation of the pure culture ammonia-oxidizing bacteria *Nitrosomonas europaea* during batch experiments.

FIGURE 10 Chlorine breakpoint curve application screenshot: output plot area displaying 15 min reaction chlorine breakpoint curves^a



^a Simulation A is pH 7 and simulation B is pH 9. All other initial conditions are the same (1 mg N/L free ammonia, 150 mg/L as CaCO₃ total alkalinity, and 25°C).

Specifically, dichloramine was proposed to be responsible for the increased inactivation rate as pH decreased. On the basis of the assumption that the three inorganic chloramine species were in equilibrium with each other, Oldenburg et al. (2002) estimated that 58 and 5% of their chloramine was present as dichloramine at pH 7 and 9, respectively. On the basis of the previous simulations, this equilibrium assumption does not appear to be appropriate and highlights the importance of considering the kinetics of inorganic chloramines versus making equilibrium assumptions, as one may greatly overestimate the anticipated dichloramine concentration (e.g., 58 versus 5% initially, with a maximum of 16% for pH 7) when interpreting the results.

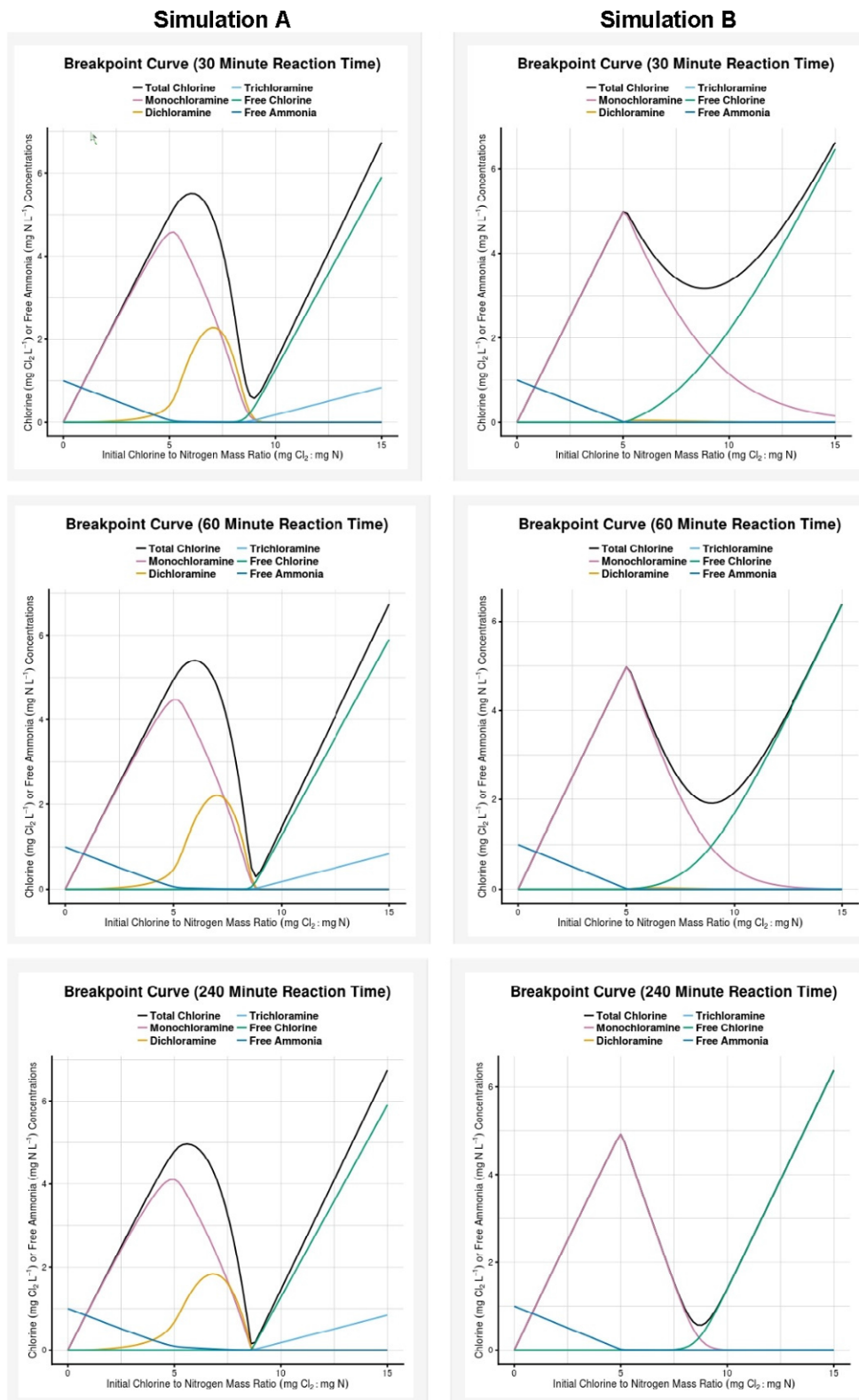
Chlorine breakpoint curve application. For the BP-WBA, simulation A and B's initial conditions (1 mg N/L initial free ammonia concentration, 150 mg/L as

CaCO₃ total alkalinity, and 25°C) are once again set identically, except pH (pH 7 in simulation A and pH 9 in simulation B; Figure 9, part B).

For simulation A (pH 7), the chlorine breakpoint curves for 15, 30, 60, and 240 min reaction times (Figures 10 and 11) have the characteristic breakpoint curve shape, with the curves changing slightly with time. After 240 min, the breakpoint occurs at an approximate 8.6:1 Cl₂:N mass ratio, where a 0.15 mg Cl₂/L total chlorine residual remains. For Cl₂:N ratios between 5:1 and 8.6:1, there is a noticeable dichloramine concentration as dichloramine formation exceeds dichloramine loss, allowing dichloramine to accumulate. Beyond the breakpoint, trichloramine concentration is simulated to increase as the applied Cl₂:N mass ratio increases.

Compared with simulation A (pH 7), simulation B (pH 9) shows a much slower breakpoint reaction

FIGURE 11 Chlorine breakpoint curve application screenshots: chlorine breakpoint curves for various reaction times^a



^a Simulation A is pH 7 and simulation B is pH 9. All other initial conditions are the same (1 mg N/L free ammonia, 150 mg/L as CaCO₃ total alkalinity, and 25°C).

occurring and essentially no measurable dichloramine or trichloramine concentrations. At pH 9, dichloramine formation is relatively slow, while dichloramine loss is relatively fast, causing any formed dichloramine to be immediately lost and unable to accumulate to a noticeable concentration. Simulation B also shows that monochloramine and free chlorine are both at measurable concentrations above approximately a 5:1 $\text{Cl}_2\text{:N}$ mass ratio after 60 min of reaction. After 240 min, the breakpoint for simulation B again occurs at an approximate 8.6:1 $\text{Cl}_2\text{:N}$ mass ratio, where a 0.57 mg $\text{Cl}_2\text{/L}$ total chlorine residual remains (0.33 mg $\text{Cl}_2\text{/L}$ monochloramine and 0.24 mg $\text{Cl}_2\text{/L}$ free chlorine). The changing breakpoint curve with time and slower breakpoint reactions at high pH are well documented in the literature (Black & Veatch Corporation 2010).

SUMMARY

Two WBAs for simulating inorganic chloramine chemistry were developed to provide drinking water practitioners (e.g., water treatment operators, engineers, students, and regulators) with a learning tool to explore inorganic chloramine chemistry. The major assumptions made in developing the WBAs include the following: (1) inorganic CFD is simulated by reaction schemes presented by Jafvert and Valentine (1992) and Vikesland et al. (2001); (2) for the CFD-WBA, the NOM reactions of Duirk et al. (2005) were implemented in a simplistic manner to illustrate an example chloramine demand reaction, and no other chloramine demand reactions are included; (3) batch (equivalent to plug flow) hydraulics; (4) chemical additions are immediately and completely mixed with no localized concentration gradients; (5) wall reactions are ignored; and (6) pH is held constant at the user-supplied value. Recognizing these assumptions and setting the TOC concentration to zero, simulations represent a best-case scenario for inorganic chloramine stability in the distribution system.

The user requires no modeling or software experience to use the WBAs. Rather, the user proceeds to the respective web page link, selects the desired simulation conditions, and presses a button to initiate simulations and produce output plots showing chemical concentrations over time or generating a chlorine breakpoint curve. When completed, the simulation data may be exported and used offline as the user requires.

Because the WBAs are provided as web pages, future updates can be immediately applied and distributed as the WBAs only require program updates on the web server. The WBAs may be expanded and updated in the future to incorporate additional chemistries (e.g., nitrite and bromide).

List of chemical abbreviations

Br^- : bromide
 CaCO_3 : calcium carbonate
 Cl^- : chloride
 Cl_2 : chlorine
 CO_3^{2-} : carbonate
 DOC_1 : fast reacting organic matter
 DOC_2 : slow reacting organic matter
 H^+ : hydrogen ion
 H_2CO_3 : carbonic acid
 HCl : hydrochloric acid
 HCO_3^- : bicarbonate
 HNO_3 : nitric acid
 H_2O : water
 HOCl : hypochlorous acid
 I : unidentified monochloramine auto-decomposition intermediate
 N_2 : nitrogen gas
 NCl_3 : trichloramine
 NH_3 : ammonia
 NH_4^+ : ammonium
 NH_2Cl : monochloramine
 NHCl_2 : dichloramine
 NO_2^- : nitrite
 NO_3^- : nitrate
 OCl^- : hypochlorite ion
 OH^- : hydroxide

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PEER REVIEW

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