

Mathematical models for prediction of trihalomethanes in drinking water

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Abstract: Use of chlorine for disinfection of water for potable supply is commonly practiced in Australia and elsewhere. Chlorine (Cl_2) is an inexpensive and effective disinfectant but will decay in the distribution system due to its reaction with natural organic matter remaining in water after the water has been treated, normally by coagulation and flocculation. The decay kinetics of chlorine is a function of several physico-chemical factors of water quality, including organic content, temperature and pH.

In the reaction of chlorine with organic matter, halogenated disinfection by-products (DBPs) can form including trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs). These are considered important compounds from adverse human health perspectives with total and individual compound concentrations being regulated in many countries. Because of the importance of halogenated DBPs in drinking water, they have been the subject of much research over recent decades, including modelling of their formation for prediction purposes. Models developed have included statistically fitted ones, incorporating a range of key variables known to affect their formation. However, the mechanisms involved in formation of DBP appear to be numerous, making the development of a model for both total and individual compound formation that can be applied practically, a significant challenge.

In this paper, we report a modelling approach to describe the formation of THMs, for total and for the four compound species, chloroform, bromodichloromethane, chlorodibromomethane and bromoform. Data available from chlorine decay experiments that had been conducted on several Australian waters with temperature and pH controlled and at various bromide (Br) concentrations to ~ 0.7 mg/L were used with for model development.

In contrast to models generally reported in the literature where models relate absolute THM values to water quality parameters, here model development is based on standardization of the formation of THM at a nominal set of water quality conditions, i.e. formation of total THMs at 0.1 mg L^{-1} Br, pH 7 and temperature at 15°C assigned as 100% formation. The impacts of different pH and temperature levels and bromide concentrations on the % formation of total THM (TTHM) were determined. This was done with aim to enable assessment of the impacts of each influencing parameter on total THM formation. From this information, the impacts of these parameters may be evaluated for other waters with different water quality conditions (pH, temperature, Br concentration) in context of chlorine decay following disinfection by chlorination.

For modelling of the formation of individual THM compounds, mathematical functions were determined for relationships between Br/ Cl_2 decay ratios with the percentage formations of chloroform and bromoform, and with the ratios of formation of chlorodibromomethane to bromodichloromethane. From these functions, the absolute formations of each of the four THM species can be estimated from the predicted total THM formed, based on chlorine decay, bromide concentration, temperature and pH of the water. Bromide was found to have a key role in both TTHM and the individual species formed. In this study few data points of controlled temperature and pH were available and consequently simple linear relationships for these were assumed. Future improved model development would require higher resolution data for these parameters.

Keywords: Disinfection by-product, THMs, Chlorine decay.

1. INTRODUCTION

The formation of disinfection by products (DBP) is an important issue to the water industry as these compounds may be of health concern to the community (ADWG, 2004). The concentrations of key DBP compounds in drinking water are regulated in many countries while in others such as Australia, guideline levels have been set by national health authorities, with some states moving to regulation. The type of compounds formed is a function of the disinfection process used, particularly when chemical disinfection is applied such as chlorine and chloramine. Chlorine is the most widely applied chemical disinfectant in the supply of drinking water based on its efficiency and low cost. Nonetheless, it has significant drawbacks including its rapid decline in concentration in the water distribution system through rapid and slow reactions with organics present in the water, and consequential formation of DBP in this process (Fisher *et al.* 2004). Other physical and chemical factors also affect DBP formation including pH and temperature (Sohn *et al.* 2004). The presence of bromide further impacts on DBPs in the presence of free chlorine, as it is oxidized to bromine which then oxidizes organics producing brominated DBPs. Key DBPs formed from the use of chlorine include trihalomethanes (THM), haloacetic acids (HAA) and haloacetonitriles (HAN). There have been numerous efforts reported in the literature to develop models for the prediction of THMs in drinking waters, as totals (Sohn *et al.* 2004; Uyak *et al.* 2005; Sun *et al.* 2009) but much less for models of individual compounds that comprise the group. Here we report a novel modelling approach to describe the total formation of trihalomethanes in surface water before and after blending with reverse-osmosis treated seawater. Also reported is the modelling of the formation of individual THM compounds, chloroform, bromodichloromethane, chlorodibromomethane and bromoform.

2. MATERIALS AND METHODS

Data used for development of models of total trihalomethane (TTHM) formation and the abundances of the four compound species, chloroform, bromoform, chlorodibromomethane and bromodichloromethane were acquired from laboratory investigation. These data were obtained from controlled experiments where surface waters from several locations in Victoria and South Australia were tested as collected or spiked with bromide (to 0.5 mg L^{-1}), temperatures controlled at 15°C , 25°C and 30°C and pH controlled at 7, 8.5 and 10. Under these conditions, chlorine decay tests were performed as described by Eaton *et al.* (1998) and Daly *et al.* (2007) and at various times up to 10 days of chlorine decay, the concentrations of the four THM compounds were determined. THM species were determined using an automated headspace sampler (Perkin Elmer, TurboMatrix 110) followed by gas-chromatography with electron-capture detection (Perkin Elmer Clarus® 500 GC).

In the attempt to develop a more generic model as opposed to site-specific one, data were standardised to percentages based on a nominal set of test conditions (i.e. formation of TTHM at Br, 0.1 mg L^{-1} , pH 7, temperature 15°C was assigned 100% formation) and from this, % THM formations for other test conditions were assigned.

Treated water samples from a water treatment plant (WTP) in South Australia that uses a conventional treatment process (coagulation, flocculation, sedimentation, filtration) were collected, blended with reverse-osmosis treated seawater (using second pass permeate of a reverse osmosis pilot plant) and then analysed for a range of water quality parameters including bromide, pH and natural organic concentration. These samples provided waters with a wide range of qualities that were then used in chlorine decay tests and THM formation at various reaction times up to 10 days.

Data of water samples that had been spiked with bromide and where the pH and temperatures were controlled were used firstly to determine the effects of bromide with chlorine consumption on TTHM formation at controlled pH and temperature. The aim in this approach was to develop models of the trend effects of each water quality parameter, as opposed to grouping of the three parameters through statistical methods, such as multivariate or polynomial techniques. Following this, trend analyses were conducted of THM specie formation based on temperature, pH and bromide concentration.

Mathematical relationships were established between the relative abundances of the four species, as percentages, with the ratio of the concentrations of Br to Cl_2 reacted.

3. RESULTS AND DISCUSSION

The impact of bromide (Br) concentration on the formation of TTHM was investigated from data acquired of several surface waters spiked with bromide at concentrations ranging between 0 and 0.5 mg L⁻¹. These waters had been tested at controlled pH (7 and 8.5) and temperature (15°C and 30°C), set chlorine doses and reaction times, where TTHMs were subsequently quantified. For this data set, formations of TTHM under the various conditions of Br, pH and temperature were all standardized to percentages based on the TTHM formed at pH 7, Br at 0.1 mg L⁻¹ and 15°C being assigned 100%. Limitation in data availability led to an assumption being made that trends between data points, e.g. between pH 7 and 8.5, and between 15°C and 30°C were of straight lines ($Y=M.X + C$, where Y is the output parameter e.g. %TTHM, M is gradient, X is input parameter e.g. bromide concentration and C is Y intercept).

The following equations were determined to describe relationships between TTHM formation (as % of standardized formation, detailed above) and Br (mg/L) concentration at pH and temperature (T, °C) conditions tested and for set Cl₂ addition and reaction time (shown in Figure 1).

$$\text{For } 15^{\circ}\text{C, pH } 7, \%TTHM = 249.4 \times Br + 74.2, \text{ where Br is bromide concentration (mg L}^{-1}\text{)} \quad (1)$$

$$\text{For } 15^{\circ}\text{C, pH } 8.5, \%TTHM = 257.0 \times Br + 103.8 \quad (2)$$

$$\text{For } 30^{\circ}\text{C, pH } 7, \%TTHM = 199.7 \times Br + 77.1 \quad (3)$$

$$\text{For } 30^{\circ}\text{C, pH } 8.5, \%TTHM = 208.7 \times Br + 82.5 \quad (4)$$

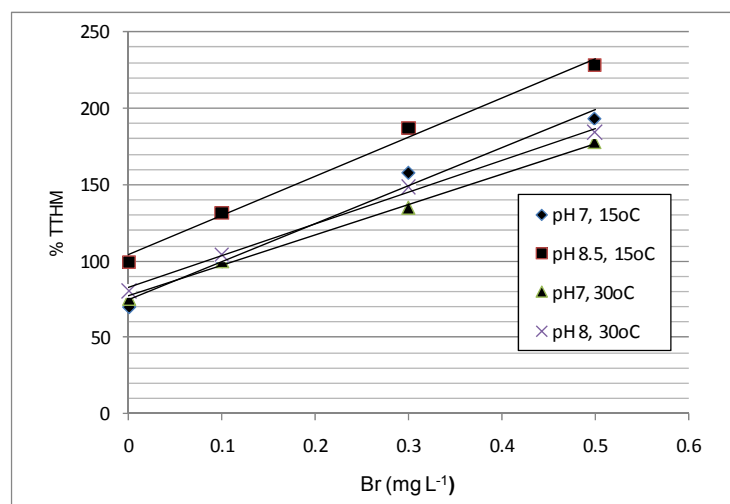


Figure 1. Relationships between bromide concentrations and %TTHM formation relative to standardized conditions (pH 7, Br at 0.1 mg L⁻¹ and 15°C, 100%TTHM).

From the above, further equations were established to relate pH between 7 and 8.5 with %TTHM, at 15°C and 30°C, as follows,

$$\text{For pH between 7 and 8.5, at } 15^{\circ}\text{C, the relationship of the gradients, M, of equations (1) and (2) was determined as follows, } M = 5.02 \times \text{pH} + 214.3, \quad (5)$$

$$\text{For pH between 7 to 8.5, at } 15^{\circ}\text{C, the relationship of the Y intercept value, C, of equations (1) and (2) was determined as follows, } C = 11.1 \times \text{pH} + 0.992, \quad (6)$$

$$\text{For pH between 7 and 8.5 at } 30^{\circ}\text{C, the relationship of the gradients, M, of equations (3) and (4) was determined as follows, } M = 5.98 \times \text{pH} + 157.8, \quad (7)$$

$$\text{For pH between 7 to 8.5 at } 30^{\circ}\text{C, the relationship of the Y intercept value, C, of equations (1) and (2) was determined as follows, } C = 77.9$$

For model development that describes TTHM μg/L formation, the following steps were carried out:

Step 1. For pH_i value over the range 7 to 8.5 and for 15°C, Equation 5 is used to calculate M_(pHi,15) and for 30°C, Equation 7 is used to calculate M_(pHi,30).

Step 2. For pH_i over the range 7 to 8.5 and for 30°C, Equation 6 is used to calculate C_(pHi,15) and for 30°C, C = 77.9 was used.

Step 3. The effects of temperature (T_j) were determined over the range of 15°C to 30°C, as follows,

$$M(T_j) = [(M_{(pHi,15)} - M_{(pHi,30)})/15] + [M_{(pHi,15)} - 15 + (M_{(pHi,15)} - M_{(pHi,30)})/15] \quad (8)$$

$$C(T_j) = [(C_{(pHi,15)} - 77.9)/15] + [C_{(pHi,15)} - 15 + (C_{(pHi,15)} - 77.9)/15] \quad (9)$$

Step 4. For bromide ion concentration, Br_k , $\%TTHM_x = M(T_j) \cdot Br_k \cdot Br_{IMF} + C(T_j)$, (10)
 where $\%TTHM_x$ is the % THM formation of a water sample, Br_{IMF} is an impact factor of Br on TTHM formation for a specific water.

Step 5. From TTHM vs Cl_2 dose (to 6 mg/L) and Cl_2 reacted data of a surface water sample (collected from South Australia) with average Br, 0.157 mg L⁻¹, pH 7.74 and temperature, 21.9°C, the $\%TTHM_D$ was calculated to be 124.4%, compared with the standardized conditions (Br, 0.1 mg L⁻¹, pH 7 and temperature, 15°C, being 100%).

Step 6. The ratio of $\%TTHM_x$ to $\%TTHM_D$ is used as a multiplication factor (R_1) for THM formation at pH_i , T_j and Br_k .

Step 7. The TTHM formation of a water where the Cl_2 consumed, pH (7 to 8.5), temperature (15°C to 30°C) and Br concentration (to ~0.7 mg L⁻¹), are known, is calculated from the following equation,

$$TTHM_x = R_1 \times [(C_{THM}, \mu g \text{ THM @ } 1 \text{ mg } Cl_2 \text{ consumed}) \times \text{Total } Cl_2 \text{ mg consumed}]^{R_{THM}}, \quad (11)$$

where R_{THM} = THM formation rate variable, C_{THM} = THM formation constant, C_{THM} and R_{THM} are determined from model fitting of data of a specific water. In the model developed, the C_{THM} and R_{THM} are applied as input variables that can be adjusted for different waters if required. For the samples of the South Australian water source tested, values determined were as follows: $C_{THM} = 32 \mu g \cdot L^{-1}$, and $R_{THM} = 0.844$.

A flow diagram of the steps taken in the development of the TTHM model is shown in Figure 2.

There are four THM compounds, chloroform, bromodichloromethane, chlorodibromomethane and bromoform. The distribution of these is a function of the ratio of bromide concentration and the chlorine reacted (or consumed). With a higher ratio of chlorine, more chloroform is formed while a higher ratio of bromide leads to higher formation of bromoform. The relative distributions of bromodichloromethane and chlorodibromomethane are also a function of relative concentrations of bromide to chlorine reacted.

For model development for prediction of the relative abundances of the four THM compounds, the following steps were carried out from data of compounds obtained at 15°C and 25°C.

Step 8. From data of $Br/Cl_{2(reacted)}$ and % $CHCl_3$ formed, a relationship was established for 25°C, (12)
 i.e. $\%CHCl_3 = EXP(A_1 - B_1 \times (Br/Cl_2)^{0.5})$, where $A_1 = 4.61$; $B_1 = 9.53$

and for 15°C, $\%CHCl_3 = EXP(A_2 - B_2 \times (Br/Cl_2)^{0.5})$, $A_2 = 4.61$, $B_2 = 10.28$

(13)

Step 9. Similarly, from data of $Br/Cl_{2(reacted)}$ and % $CHBr_3$ formed, a relationship was established for 25°C, (14)
 i.e. $\%CHBr_3 = A_3 \times (1 - EXP(-B_3 \times Br/Cl_2))$, where $A_3 = 99.4$, $B_3 = 5.47$

and for 15°C, $\%CHBr_3 = A_4 \times (1 - EXP(-B_4 \times Br/Cl_2))$, $A_4 = 100.0$, $B_4 = 7.64$ (15)

Step 10. To account for temperature effects and based on the available data above,

for a temperature, T°C, between 15°C to 25°C,

$$\%CHCl_3 = EXP(A_i - B_i \times (Br/Cl_2)^{0.5}), \text{ where } A_i = 4.605 \text{ and } B_i = -0.075 \times T^\circ C + 11.4 \quad (16)$$

$$\text{and } \%CHBr_3 = A_j \times (1 - EXP(-B_j \times Br/Cl_2)), \text{ where } A_j = 99.7 \text{ and } B_j = -0.217 \times T^\circ C + 10.9 \quad (17)$$

Step 11. For determination of the relative abundances of chlorodibromomethane and bromodichloromethane, the relation between the ratio $Br/Cl_{2(reacted)}$ with the ratio of $CHBr_2Cl/CHBrCl_2$ was determined for 25°C data only (the 15°C data was too variable and limited in range to be useful).

$$\text{i.e. } CHBr_2Cl/CHBrCl_2 = -0.021732 + 7.39589 \times Br/Cl_2^{0.5} \quad (18)$$

From steps 8 and 9, the percentage abundances of chloroform and bromoform are determined, respectively. From the calculated ratio of chlorodibromomethane to bromodichloromethane, their individual percentage abundances were calculated from their total percentage abundance, i.e. $\% (CHBr_2Cl + CHBrCl_2) = (100\% - \%CHCl_3 - \%CHBr_3)$. From the model percentages of the four compounds and the TTHM, the concentrations of the four compounds can then be calculated (see Figure 3).

Comparison of model fitted data with laboratory data for water samples of the South Australian water source with and without Br being spiked are shown in Table 1 (unblended) and Table 2 (blended, 75% to 25%). Of the 32 laboratory data sets, about 75% of the modelled data were similar to actual data. For TTHMs, R^2 values for the relationship between actual versus model fitted data were 0.62 (unblended waters) and 0.75 (blended waters). Mean percentage differences between actual and model fitted THM species were less than +/-3%.

Variance of model output data to laboratory measured data may be attributable to errors in the model design but may also be due to errors in the chlorine decay test and analyses of THM compounds.

The approach in model development was to not limit applicability to any specific water and for this, key factors such as the formation of TTHM per chlorine reacted and the impact of Br on TTHM formation, were incorporated as input variables, along with key influencing water quality parameters (pH, temperature, bromide). The aim in this approach is to account for waters 'behaving differently' than those waters used for model development, where it is possible that other impacting factors exist but are as yet not identified.

Models reported in the literature for total THM include those that are of single fitted functions (e.g. kinetic, empirical power (Sohn *et al.* 2004), multivariate regression, artificial neural networks and physically based reaction models (e.g. first order) that incorporate parallel and/or consecutive reactions (Sun *et al.* 2009).

Although these models can match well the data used for model development, their applicability to full scale water works remains to be established. This may be a result of variance caused by the quality and reactivity of different waters and of the same water changing in quality over time and season, in the formation of TTHM and relative abundances of THM species. The model approach used in this study was of integration of consecutive and parallel reaction models (component models), that also include input factors that attempt to account for variance in reactivities from parameters such as bromide and organics present. This is to lower reliance on the need to update fixed model constants and reaction co-efficients, by having those of key reaction component models as input variables. The aim in this approach is to allow an operator at a water treatment plant or others not familiar with the model components and its function, to be able to calibrate its operation to mirror acquired laboratory data of TTHM and THM species formation for a selected water type. Once calibrated, the model may then be used to estimate TTHM and THM specie formation for waters blended as previously described or otherwise treated by conventional treatment processing for drinking water supply.

4. CONCLUSIONS

From data available to this study, relationships were established between the relative concentrations of bromide and the chlorine reacted with TTHM formation and the abundances of THM species. Affecting the formation of TTHM and the four THM species are also the parameters of temperature and pH. The relationships of these on TTHM and THM specie formation were modelled as individual parameters following standardization of formations based on a selected set of nominal test conditions. Some relationships reported here are based on low resolution data, i.e. two values of each of temperature and pH within their impacting ranges were available. Greater resolution of data should allow for improved relationships being developed that describe trends of the effects of pH and temperature. Application of temperature and pH values beyond those used to develop the model (temperature 15°C - 30°C and pH 7- 8.5) is not justified. The modelling approach described in this paper is proposed as a concept that may be applied for estimation of the concentrations of TTHM and THM species for specific treated and chlorinated drinking waters.

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Table 1. Comparison of laboratory data with model fitted data of THM species and TTHM of a conventionally treated South Australian water source without blending.

Data	Temp °C	Br (mg/L)	pH	Cl ₂ Dose (mg/L)	Cl ₂ Residual (mg/L)	CHCl ₃ (µg/L)	CHBrCl ₂ (µg/L)	CHBr ₂ Cl (µg/L)	CHBr ₃ (µg/L)	Total (µg/L)
Lab Data 1	25	0.2	7.5	6	2.42	12	31	27	12	82
Model						16	24	33	15	88
Lab Data 2	25	0.2	7.5	6	1.61	22	34	35	15	106
Model						18	30	39	18	105
Lab Data 3	25	0.2	7.5	6	0.04	38	45	51	14	148
Model						24	38	51	23	136
Lab Data 4	25	0.2	7.5	5.5	1.74	13	28	37	19	97
Model						15	25	35	17	92
Lab Data 5	25	0.2	7.5	5.5	1.11	21	35	39	17	112
Model						17	29	40	19	105
Lab Data 6	25	0.2	7.5	5.5	0.06	23	54	59	22	158
Model						21	35	48	23	126
Lab Data 7	25	0.2	7.5	5	2.07	5	10	11	6	32
Model						11	20	29	15	75
Lab Data 8	25	0.2	7.5	5	1.15	12	26	37	20	95
Model						14	25	37	18	94
Lab Data 9	25	0.2	7.5	5	0.06	16	36	44	18	114
Model						17	31	45	23	116
Lab Data 10	25	0.4	7.5	5	2.3	4	11	27	23	65
Model						8	21	42	34	106
Lab Data 11	25	0.4	7.5	5	1.14	7	22	40	26	95
Model						11	28	54	45	138
Lab Data 12	25	0.4	7.5	5	0.01	11	42	64	39	156
Model						13	33	66	54	167
Lab Data 13	15	0.2	7.5	4.5	1.14	7	18	29	18	72
Model						10	21	33	26	91
Lab Data 14	15	0.2	7.5	4.5	0.08	14	37	48	22	121
Model						13	27	42	32	114
Lab Data 15	15	0.2	7.5	5	1.57	9	22	36	22	89
Model						12	23	33	24	92
Lab Data 16	15	0.2	7.5	5	0.41	19	37	36	13	105
Model						15	42	29	15	118

1	Standardization of the effect of Br on %TTHM formation at pH (7 and 8.5) and temperature (15°C and 30°C)
2	Relationships established between pH and temperature with %TTHM formation, %TTHM = M x Br + C, for 15°C and 30°C at pH 7 and 8.5
3	Integration of pH vs Br and temperature vs Br standardized models
4	Using the above, determine the %TTHM _x percentage for a test water with pH _i , T _j and Br _k
5	Using a known data set of TTHMs, chlorine consumptions (various), Br (constant), pH (constant) and temperature (constant), calculate equivalent %TTHM _D (based on above) and develop model of TTHM formation per chlorine consumed
6	Calculate $R_1 = \%TTHM_x / \%TTHM_D$, and $TTHM_x = R_1 \times [(C_{THM}, \mu g\ THM @ 1\ mg\ Cl_2\ consumed) \times Total\ Cl_2\ mg\ consumed]^{R_{THM}}$

Figure 2. Develop steps of the TTHM model, incorporating the effects of bromide, temperature and pH.

Table 2. Comparison of laboratory data with model fitted data of THM species and TTHM of a conventionally treated South Australian water source, following blending (75% to 25%).

Data	Surface Water %	Temp °C	Br (mg/L)	pH	Cl ₂ Dose (mg/L)	Cl ₂ Residual (mg/L)	CHCl ₃ (µg/L)	CHBrCl ₂ (µg/L)	CHBr ₂ Cl (µg/L)	CHBr ₃ (µg/L)	Total (µg/L)
Lab Data 17	75%	25	0.17	7.8	4.5	1.46	9	20	31	18	78
Model							12	20	29	14	74
Lab Data 18	75%	25	0.17	7.8	4.5	0.04	20	38	38	13	109
Model							16	27	38	19	100
Lab Data 19	75%	15	0.17	7.8	3.7	1.07	6	15	29	20	70
Model							8	17	26	21	72
Lab Data 20	75%	15	0.17	7.8	3.7	0.19	12	33	40	18	103
Model							10	21	33	27	92
Lab Data 21	50%	25	0.12	7.8	3.1	1.09	5	12	21	16	54
Model							7	12	18	9	48
Lab Data 22	50%	25	0.12	7.8	3.1	0.05	10	31	33	15	89
Model							12	18	26	12	68
Lab Data 23	50%	25	0.72	7.8	3.1	0.94	2	6	24	48	80
Model							1	7	23	77	107
Lab Data 24	50%	25	0.72	7.8	3.1	<0.1	2	12	39	119	172
Model							2	9	31	103	144
Lab Data 25	50%	15	0.12	7.8	3.6	1.36	6	14	28	21	69
Model							9	15	20	9	53
Lab Data 26	50%	15	0.12	7.8	3.6	0.12	10	32	40	19	101
Model							13	22	29	13	76
Lab Data 27	50%	15	0.12	7.8	2.5	0.74	2	8	19	19	48
Model							5	11	17	14	47
Lab Data 28	50%	15	0.12	7.8	2.5	0.11	4	17	25	14	60
Model							6	14	22	19	61
Lab Data 29	25%	25	0.06	7.9	1.8	0.56	3	8	15	16	42
Model							5	8	11	5	29
Lab Data 30	25%	25	0.06	7.9	1.8	0.11	2	14	36	37	89
Model							7	11	14	6	37
Lab Data 31	25%	15	0.06	7.9	1.5	0.53	1	4	9	14	28
Model							3	6	9	7	25
Lab Data 32	25%	15	0.06	7.9	1.5	0.18	1	7	22	26	56
Model							4	8	12	9	33

1	Establishment of relationship between Br/Cl ₂ (reacted) and % chloroform abundance, at known temperatures
2	Establishment of relationship between Br/Cl ₂ (reacted) and % bromoform abundance, at known temperatures
3	Temperature effects for each of the above determined and integrated into model
4	Establishment of relationship between Br/Cl ₂ (reacted) and ratio of CHBr ₂ Cl/CHBrCl ₂
5	For an input of Br/Cl ₂ reacted and using the above relationships, the percentages of the four THM species can be calculated. From these percentages, the concentrations of each THM specie (µg.L ⁻¹) is calculated from the TTHMx (µg.L ⁻¹), previously determined

Figure 3. Development steps of the THM specie abundance model.