

Estimation of water utility compliance with trihalomethane regulations using a modelling approach

Manuel J. Rodriguez, Jean Sérodes and Michel Morin

ABSTRACT

Over the last few years, the presence of chlorination by-products (CBP) in drinking water has become an issue of particular concern for utility managers. As regulations about CBP (in particular trihalomethanes – THM), are becoming more strict, water utilities will have to adjust their operation strategies to comply with new standards while maintaining a residual chlorine which ensures an acceptable microbiological quality. Complying with stricter THM standards is particularly difficult for utilities which use surface raw water and practice chlorination as the unique treatment process. In this paper, the authors explore the usefulness of predictive models as decision-making tools for drinking water managers in dealing with the THM issue. In the first part of the paper, the process of developing models of THM formation in chlorinated surface waters using two different sources of data (from bench-scale and from field-scale studies) is described. The second part of the paper focuses on the application of such models to the analysis of the feasibility of updating THM regulations in the province of Quebec (Canada). Simulations allow the estimation of the percentage of utilities, currently using chlorination as the unique treatment, which would have to upgrade treatment to comply with a new THM standard.

Key words | distribution systems, drinking water quality, modelling, Quebec, regulations, trihalomethanes

Manuel J. Rodriguez (corresponding author)

Michel Morin

Département d'aménagement,
Université Laval,
1624 Pavillon Savard,
Quebec, G1K-7P4
Canada,

Telephone: +1 418 656 2131 ext. 8933

Fax: +1 418 656 2018

E-mail: manuel.rodriguez@ame.ulaval.ca

Jean Sérodes

Département de Génie civil,
Université Laval,
1624 Pavillon Savard,
Quebec, G1K-7P4
Canada

INTRODUCTION

Chlorine is a widely used disinfectant in the treatment of drinking water around the world because of its relatively low cost and its ability to inactivate micro-organisms and prevent their regrowth within the distribution system. Since research undertaken by Rook (1974), which enabled detection of the presence of chlorination by-products (CBP) in water distribution systems, the focus on drinking water chlorination and the risk associated with it has increased enormously. It is well known that the reaction of chlorine with organic compounds present in raw waters (from natural and anthropogenic origins) generates CBP. Among these, trihalomethanes (THM: chloroform, bromodichloromethane, chlorodibromomethane and bromoform) have been the focus of special attention. Epidemiological and toxicological studies have suggested some of them are carcinogenic (Levallois 1997). More

recently another group of CBP, the haloacetic acids (HAA: principally monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic and dibromoacetic), has also become a focus of concern.

Due to the health risk associated with the presence of THM in drinking water, several industrialized countries have included maximum acceptable THM concentrations in their water regulations. Health Canada recently set out drinking water guidelines stating a maximum acceptable level of 100 µg/l for total trihalomethanes (TTHM) (the sum of the four THM) (Health Canada 1996). Quebec's Environment Ministry is currently considering lowering the maximum TTHM concentration specified in its drinking water standards from 350 µg/l to 100 µg/l (annual average of four seasonal samples). Standards for HAA are currently proposed by the US EPA's Disinfectant/DBP

rule, and maximum levels will probably figure in the next update of the Canadian guidelines. To comply with new guidelines and regulations, many utilities will, in years to come, need to adapt their treatment strategies. This is an issue of particular concern in Quebec because about 300 municipal distribution systems supply surface water which has been chlorinated without any previous treatment (Gouvernement du Quebec 1997).

When proposing new rules or updating existing rules for CBP, regulatory agencies must not only consider the reduction of health risks (associated with the reduction of potentially carcinogenic CBP in water), but also the economic costs to municipalities wanting to comply with new regulations. The process of evaluating the feasibility of updating CBP regulations could be made more effective through the use of predictive models (Morin 1999).

This paper presents the development of THM predictive models and their applications in estimating the potential impacts of updating THM regulations, with a particular focus on Quebec water utilities. First, a general description of the THM modelling concept is presented. There follows a detailed description of the process of developing two models, using data from the US and Quebec. The paper then presents the combination of these models with the EPA-water treatment cost model (WTP) in the analysis of the implications of THM regulations for Quebec water utilities which use chlorine as the unique treatment process. Finally, the usefulness, and limitations of, the results of the analysis are discussed.

MODELLING TRIHALOMETHANE FORMATION

Characteristics and benefits of models

The modelling of THM consists of establishing empirical or mechanistic relationships between THM levels in treated water, and the parameters of water quality and of operational control which can be linked to their formation. Past research has shown that the most important factors for THM formation are: the levels of organic matter in water (generally designated by total or dissolved organic carbon and by 254 nm UV-absorbance); the

applied chlorine dose; the pH of water; water temperature; and the reaction time of residual chlorine in water (USEPA 1992). The concentrations of bromides are also usually considered because of their influence on the distribution of the four THM compounds. The chlorination of waters with low bromide concentrations generally leads to higher proportions of chloroform in comparison with the other three THM compounds.

Models for THM may be useful in different ways. They can be used routinely by utility operators to control their operational parameters (for example, pH and chlorine dose) or in pilot trials to evaluate the effects of upgrading physico-chemical treatment (to increase organic matter removal) on THM levels. Models can also be used by environmental health researchers to undertake epidemiological studies by generating, from operational and water quality predictors, past data about THM in water utilities. Finally, models can be used by regulatory agencies to estimate, on a national or a regional basis, requirements for infrastructure updating at utilities faced with complying with proposed regulations. The latter is the application which is presented in this paper.

Modelling methodology

Models for THM can be developed from data generated through different approaches. On one hand, data may be generated from field sampling at the treatment plant and along distribution systems. In this case, the measured THM can be related to water quality and operational data corresponding to actual treatment operations at the utility. On the other hand, THM data may be generated at laboratory-scale by carrying out batch chlorination tests of raw or treated water samples. This is the approach currently used to evaluate THM formation potential tests (APHA, AWWA & WPCF 1992). The advantages with models developed from laboratory-scale data are that operational conditions can be controlled, and that the effect of contact time on THM levels can be assessed. The main drawback of this approach to data generation is that the effects of the distribution system on residual chlorine depletion and on THM formation cannot be quantified. THM models from data generated through sampling at

representative points of the distribution system have the advantage that THM concentrations are close to those to which humans are actually exposed in their tap water. However, the difficulty of estimating travel times of water within the system is generally a major limitation of models developed with this type of data.

A survey of existing literature demonstrates that both approaches to data generation have been used for developing THM predictive models, most of them empirical. Table 1 presents the models which have been developed using both data generation approaches. It must be noted that models developed from field-scale data are all for specific distribution systems. An overview of the structure and results for these models suggests that prediction capabilities are significantly higher for models generated from bench-scale data. This is due mainly to the difficulty of adequately estimating the time water takes to travel along the distribution system when developing models from field-scale data. For the same reason, and because the effects of biofilm and pipe material are not considered, the applicability of models from bench-scale data in predicting THM in real distribution systems is difficult to assess. As for field-scale data models, their applicability is sometimes limited to the specific system from which the data is gathered.

The methodology for a feasibility analysis of updating THM regulations in Quebec is based on the approach used by the EPA in establishing the US disinfectant/DBP rule (Roberson *et al.* 1995). The proposed approach consists of two steps. The first is the development of two empirical THM predictive models applicable in the context of Quebec's water quality and treatment. One model is developed from bench-scale data while the other is elaborated from data from Quebec water distribution systems. The second step is the combination of these models with the EPA-WTP model. This latter model allows for the estimation of removal of organic matter through different treatment configurations (Malcolm Pirnie, Inc. 1992). This approach thus permits an estimation of THM amounts in distribution systems based on information about raw water quality and different operational strategies. It also permits one to estimate what water treatment strategy is required to comply with a specific THM standard. The application presented herein focuses on the formation of

total THM (TTHM) which is the parameter considered in drinking water regulations (not individual THM).

Model development from bench-scale data

As robust bench-scale data are currently not available for Quebec raw waters, three databases developed by others have been used. Two of these databases were developed by authors mentioned in Table 1 (Amy *et al.* 1987; Rathbun 1996), and the third was developed by Montgomery Watson for the American Water Works Association (Montgomery Watson/AWWA 1991). These are the most complete databases which have been published; they contain sufficient information about all the important parameters which influence THM formation.

In order to create a robust database which allows the development of a model with more widespread applicability, we combined these three sources of data. This strategy was considered to be reasonable because bench-scale tests and laboratory methods for the measurement of water quality parameters were comparable for the three studies (Table 2). The only significant difference is in the measurement of organic carbon. Amy *et al.* (1987) and Montgomery/AWWA (1991) considered total organic carbon (TOC) whereas Rathbun (1996) considered dissolved organic carbon (DOC). In order to be able to combine the databases, values of TOC were converted to values of DOC using a linear relationship developed from a database of 90 raw waters of the province of Quebec for which data on these two parameters were available.

The result of data combination was a unique database, comprised of about 1800 observations, which considers wider ranges of water quality and operational parameters. However, to take into account the specific water quality conditions of Quebec water utilities which use chlorination as the unique treatment process, only observations corresponding to concentrations of dissolved organic carbon (DOC) between 1.0 and 8.0 mg/l were considered. This led to a database of 1483 observations. Distributions of water quality and operational conditions of this database are presented in Table 3.

Working from this database, a multivariate regression model for TTHM formation was created, using a step-by-step (*stepwise*) procedure with Statview (Abacus

Table 1 | Overview of different THM models from literature.

Author	Source of data	Data generation approach for THM	Model equation*	<i>n</i>	<i>r</i> ²
Urano <i>et al.</i> (1983)	Water collected from the Sagami river (Japan) combined with a solution of humic acid	Laboratory scale with variable chlorine dose and contact time	$TTHM = 8.2 \times 10^{-4} (pH - 2.8)(TOC)(D)^{0.25}(t)^{0.36}$	NP	NP
Arizona State University (Amy <i>et al.</i> 1987)	Raw waters from different utilities across the US	Laboratory scale with variable chlorine dose, temperature and contact time	$TTHM^{**} = 0.0031(UV \times TOC)^{0.440}(D)^{0.409}(t)^{0.265}(T)^{1.06}(pH - 2.6)^{0.715}(Br + 1)^{0.036}$	995	0.90
Lou & Chiang (1994)	Water from the Taipei (Taiwan) distribution system	Eighteen points sampled twice over a 6 month period	$TTHM = (TTHM_0) + 7.01(pH - 2.3)^{0.11}(NVTOC)^{1.06}(t)^{0.748}(D)^{0.764}(\beta)$	16	NP
Ibarluzea <i>et al.</i> (1994)	Water from the treatment plant of San Sebastian (Spain)	Sampling at the treatment plant and the finished water	$CHCl_3 = 10.8 + 0.04(Flu) + 1.16(pH) + 0.12(T) + 1.91(C_0)$	12	0.82
US Geological Survey (Rathbun 1996)	Waters collected at different locations along the Mississippi river and two affluents	Laboratory scale with variable chlorine doses, pH and contact time. Temperature kept constant	$TTHM = 14.6(pH - 3.8)^{1.01}(D)^{0.206}(UV)^{0.849}(t)^{0.306}$	669	0.98
Chang <i>et al.</i> (1996)	Water samples from raw water intake at a utility in Taiwan	Laboratory scale with variable chlorine dose and contact time	$TTHM = 12.7(TOC)^{0.291}(t)^{0.271}(D)^{-0.072}$	120	0.94
Garcia-Villanova <i>et al.</i> (1997)	Water from the distribution system of the city of Salamanca (Spain)	Sampling at six points on eleven different dates	$Ln(CHCl_3) = 0.81 + 0.63Y + 6.02 \times 10^{-4}(T)^3 - 2.41(T)^4 + 0.029(pH)^2 + \alpha + \varepsilon$	66	0.86
Clark & Sivaganesan (1998)	Prepared synthetic waters with solution of humic acid	Laboratory scale with variable chlorine dose, temperature, pH and contact time	$TTHM = A \left(C_1 - \left(\frac{C_1(1-K)}{1 - Ke^{ut}} \right) \right)$	42 (for calculation of <i>A</i> and <i>K</i>)	0.71 and 0.78 respectively for <i>A</i> and <i>K</i>
Golfinopoulos <i>et al.</i> (1998)	Water from the utility of Athens (Greece)	Sampling at four points in the treatment plant (one at the finished water outlet)	$TTHM = 13.5 \ln(Chla) - 14.5(pH) + 230(Br) - 140(Br)^2 - 25.3(S) + 110.6(Sp) - 6.6(T \times Sp) + 1.48(T \times D)$	88	0.98

NP: value not presented by authors.

*Some authors proposed more than one model equation. In such cases, only the most representative equation is shown.

In $\mu\text{mol/l}$.Nomenclature**

TTHM: total trihalomethanes ($\mu\text{g/l}$); *TTHM₀*: *TTHM* at the finished water before chlorination ($\mu\text{g/l}$); *CHCl₃*: chloroform ($\mu\text{g/l}$); *UV*: absorbance UV at 254 nm (cm^{-1}); *TOC*: total organic carbon (mg/l); *Br*: bromide ($\mu\text{g/l}$); *Chla*: chlorophyll *a* (mg/m^3); *T*: water temperature ($^{\circ}\text{C}$); *Flu*: fluorescence of the raw water (%); *D*: chlorine dose (mg/l); *t*: contact time (h); *C₀*: residual chlorine at the treatment plant after chlorination (mg/l); *C_i*: initial residual chlorine (mg/l); *Y*: dummy variable indicating year of sampling; *x*: parameter depending on water dispersion within the distribution system; *α*: parameter depending on the location at which CHCl_3 is predicted; *ε*: random error; *A*: dimensionless parameter; *K*: dimensionless parameter; *u*: reaction rate constant (min); *S*: dummy variable indicating summer season; *Sp*: dummy variable indicating spring season.

Table 2 | Laboratory methods for generation of the three bench-scale databases.

Database	Strategy for laboratory chlorination tests	Methods for measurement of water quality parameters	Median TTHM concentrations (µg/l) (range in parentheses)	
			Number of observations	
		TOC or DOC	Bromide	THM
Amy <i>et al.</i> (1987)	Nine different waters.	TOC analyser (Xertex Corp., model DC-80)	Ion chromatography (Dionex, model 10)	Gas chromatography with liquid-liquid extraction (Hewlett Packard, model 5794)
	One chlorine dose (proportional to TOC), three different temperatures, natural pH. Samples taken at ten different contact times over a seven-day incubation period.			
Montgomery/AWWA (1991)	Eight different waters.	TOC analyser (Shimadzu, model 500)	Ion chromatography (model not specified)	Gas chromatography with liquid-liquid extraction (Varian, model 3400)
	Two different chlorine doses (proportional to TOC), two different temperatures, three different pH levels (natural and two adjusted). Samples taken at ten different contact times over a four-day incubation period.			
Rathbun (1996)	Fourteen different waters. Three different chlorine doses, one single temperature, three different adjusted pHs. Samples taken at nine different contact times over a seven-day incubation period.	DOC measured using the wet oxidation method	Segmented flow automated colorimetry	Gas chromatography with liquid-liquid extraction (Hewlett Packard, model 5880)

Table 3 | Distribution of water quality parameters for the combined bench-scale database.

	Percentile				
	Minimum	25th	50th (median)	75th	Maximum
Bromide (mg/l)	0.01	0.02	0.06	0.11	0.42
DOC (mg/l)	2.2	3.5	5.0	5.9	7.7
pH	4.6	6.6	7.5	7.7	10.0
Temperature (°C)	10	20	20	25	30
Chlorine dose (mg/l)	1.5	15.0	18.8	30.0	50.0
Contact time (h)	0	2	24	126	168
TTHM (µg/l)	1.0	88.6	184.5	334.0	1360.0

Concepts Inc. 1996). The method consists of first classifying the predictor variables according to their statistical significance and then including one variable at a time at different steps. During the process of model development, several linear and non-linear regression structures were considered. To assess the quality of data used for analysis, the database was randomly separated into two data sets. One data set was used to estimate the statistical parameters of the model, while the other served to evaluate the model's prediction performance. It was noted that prediction capabilities for the regressions were practically identical when the evaluation was carried out using one or other of the data sets. Thus, the decision was made to estimate the statistical parameters of the definitive model using the entire database. The form of the model is that recently proposed by Rathbun (1996) with five variable predictors as follows:

$$TTHM = a(DOC)^b(t)^c(pH)^d(D)^e(T)^f \quad (1)$$

where *DOC* is expressed in mg/l and *t*, *D*, and *T* denote respectively contact time (h), chlorine dose (mg/l) and water temperature (°C). Estimated values of statistical coefficients (*a*, *b*, *c*, *d*, *e*, *f*) and model accuracy are shown in Table 4. This model was found to be statistically

Table 4 | Results of statistical regressions with both databases.

	Bench-scale data	Field-scale data	
		Site 2	Site 3
Coefficient of determination (r^2)	0.90	0.34	0.57
Absolute average error	46 µg/l	32 µg/l	38 µg/l
Model significance	$p < 0.0001$	$p = 0.0019$	$p < 0.0001$
Statistical coefficients:			
<i>a</i>	0.044	1.392	− 132.2
<i>b</i>	1.030	1.092	7.5
<i>c</i>	0.262	—	—
<i>d</i>	1.149	0.531	14.5
<i>e</i>	0.277	—	—
<i>f</i>	0.968	0.255	2.0
<i>g</i>	—	—	48.4

significant as all of its variables, except bromide, are statistically significant at level 0.05. It is understandable that the consideration of bromide does not improve the model predictive capacity because the dependent variable is total THM concentration rather than the concentration of specific THM species (chloroform and brominated compounds). The analysis of exponential coefficients in models suggests that the effects of chlorine dose and contact time on TTHM formation are more non-linear than the effect of DOC, pH and water temperature. In general terms, results were comparable to those obtained by other researchers who have used bench-scale data for modelling (Table 1). The determination coefficient (r^2) was similar to that obtained by Amy *et al.* (1987) but lower than that obtained by Rathbun *et al.* (1996). This is understandable because the combined database considers larger ranges of operational conditions during chlorination (temperature, pH and chlorine dose). Also, for the same reason, the developed model has a greater applicability than the others. A detailed analysis of the model showed that prediction errors were more marked for the higher observed TTHM concentrations. Predictions for TTHM concentrations below 150 $\mu\text{g/l}$ appeared to be very accurate (Figure 1a). A sensitivity analysis of the model allowed us to establish that such a range of TTHM is generally associated with DOC concentrations below 6.0 mg/l (Figure 1b). These are typical DOC values encountered in surface waters of about 80% of Quebec distribution systems which use chlorination as a unique treatment practice.

Model development from field-scale data

Alternative regression models were developed using field data from distribution systems of Quebec. Information about water quality and operational parameters, as well as about THM formation, was compiled from recent water utility surveys performed by Quebec's Ministry of Environment (MEF). In this investigation, only information about utilities using surface water (lakes or rivers) and direct chlorination is considered. Drinking water from these utilities is especially susceptible to the formation of high concentrations of THM. In these utilities, water quality has been monitored at three sites—the raw water uptake (site 1), in treated water following chlori-

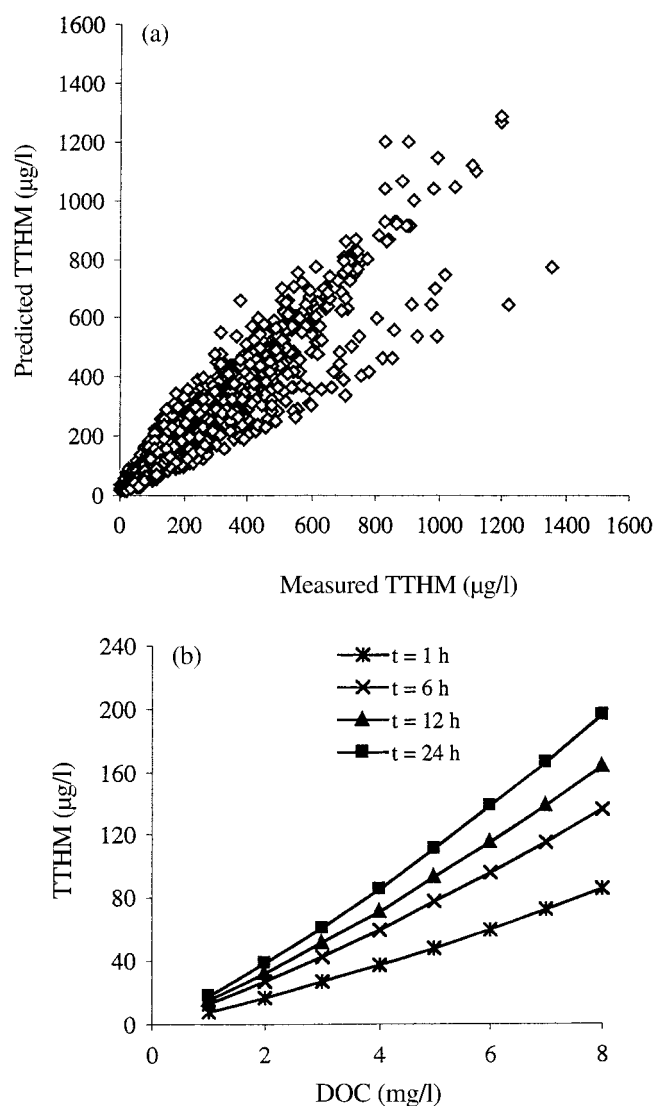


Figure 1 | Results and application of model developed from combined bench-scale data; (a) model accuracy; (b) sensitivity analysis of model (conditions: chlorine dose ensuring a residual of 0.2 mg/l after 1 h, $\text{pH}=7$, temperature of water= 20°C).

nation (site 2), and in the distribution system about 1.5 km from the treatment plant (site 3). Table 5 presents a statistical distribution of water quality and operational parameters in these utilities. All water quality parameters were measured using standard methods by the MEF laboratory (APHA, AWWA, WPCF 1992). It is especially interesting to note that TTHM levels are significantly higher at site 3 than at site 2. This suggests that compliance with current and future TTHM regulations cannot

Table 5 | Distribution of water quality parameters for the field-scale database.

	<i>n</i>	Percentile				
		10th	25th	50th (median)	75th	90th
DOC (1)	237	1.2	2.1	4.0	6.0	7.7
pH (1)	246	6.4	6.8	7.1	7.5	8.0
Temperature (1)	230	6	10	14	18.0	20.0
Free residual chlorine (2)	261	0.1	0.4	0.9	1.5	2.9
TTHM (2)	174	5.2	19.9	47.7	79.1	135.0
Free residual chlorine (3)	800	0.0	0.2	0.4	0.9	1.1
TTHM (3)	186	9.1	28.5	76.9	117.1	173.5

(1): site 1.

(2): site 2.

(3): site 3.

be limited to the treatment plant, but must also be extended to the extremities of the distribution system, where the consumers' tap water can have even greater THM concentrations.

Using a statistical *stepwise* procedure identical to that mentioned previously, models for TTHM were developed for both site 2 and site 3. TTHM at site 2 was predicted from raw water DOC (DOC_{rw}), raw water pH (pH_{rw}) and water temperature using a non-linear regression. TTHM at site 3 was predicted from the same variables, but also from free residual chlorine at site 2 (FC) using a linear regression. The regression models thus obtained are as follows:

$$TTHM_{(2)} = a(DOC_{rw})^b(pH_{rw})^d(T)^f \quad (2)$$

and:

$$TTHM_{(3)} = a + b(DOC) + d(pH) + f(T) + g(FC) \quad (3)$$

Models were developed with a relatively small data sample because not all values of predictive parameters were available for the entire database ($n = 113$ for site 2 and $n = 91$ for site 3). Results for these models are also shown

in Table 4. All of their variables are statistically significant but, as expected, the determination coefficients and the predictive performances of these models are less impressive in comparison with the performance of the model created from bench-scale data (Figures 2a and 2b). This is mainly due to improper consideration of critical variables such as the chlorine dose and the reaction time. Information about chlorine dose was not available for sampling days on which THM was measured. This specifically affects TTHM predictions at site 2. However, residual chlorine at site 2 constitutes a significant predictor for TTHM at site 3. Additionally, it is not possible to estimate the reaction time of chlorine in these utilities because each system may have specific hydraulic and flow rate conditions (presence or absence of storage tank, water demand patterns, etc.). Figure 2c illustrates the application of the model to evaluate the effect of DOC on TTHM. For the range of DOC typical of Quebec surface waters, estimated values for TTHM were lower but comparable with those predicted by the model from bench-scale data. They vary from 8 to 80 $\mu\text{g/l}$ at site 2 and from 38 to 170 $\mu\text{g/l}$ at site 3.

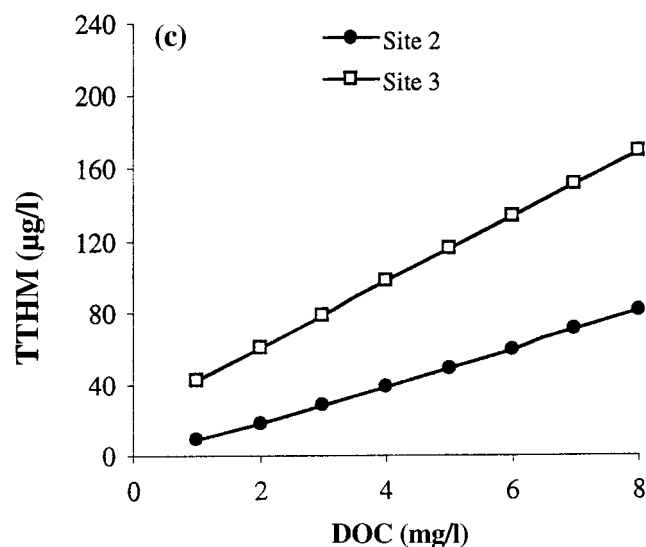
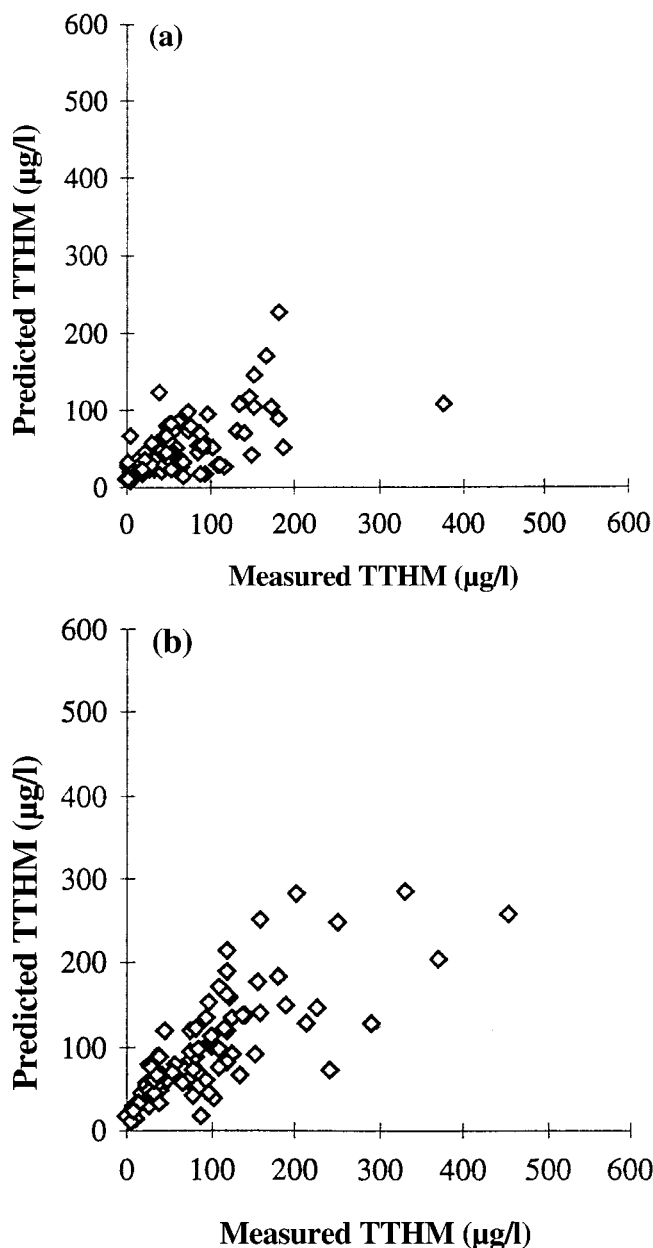


Figure 2 | Results and application of models developed from Quebec field-scale data; (a) model accuracy for site 2; (b) model accuracy for site 3; (c) sensitivity analysis of models (conditions: chlorine dose ensuring a residual of 0.2 mg/l after 1 h, pH=7, temperature of water=20°C).

FEASIBILITY ANALYSIS OF UPDATING QUEBEC THM REGULATIONS

The models described herein can be used to estimate TTHM concentrations for different water quality and operational conditions in distribution systems where chlorination is the only treatment process. By combining

TTHM models with empirical predictive equations contained in the EPA-WTP model, it is possible to estimate the additional treatment processes which would be required for compliance with selected TTHM standards. Such treatment processes are aimed at removing THM precursors and, hence, reducing the level of THM in the distribution system. In this investigation the analysis is focused on the effect of three treatment strategies on THM precursor removal. They are: conventional water treatment (flocculation, sedimentation and filtration), conventional treatment with enhanced coagulation, and conventional treatment with additional granular activated carbon (GAC) filtration. The variations in two important parameters, TOC and pH, with the application of each treatment strategy are considered in this analysis. As mentioned earlier, these are parameters which greatly influence THM formation in chlorinated waters. Empirical equations predicting TOC removal and pH changes during alum coagulation have been developed by others (Table 6). Equations 4 and 5 of Table 6 are respectively applied to simulate TOC removal and pH changes by alum coagulation (standard coagulation or enhanced coagulation) and Equation 6 is used to estimate

Table 6 | Model equations used for treatment and chlorination simulations.

Type of models	Equations	Source
Models within EPA-WTP to simulate water quality changes	<ul style="list-style-type: none"> • TOC removal by alum coagulation $\ln(TOC_f) = -0.16 + 1.16\ln(TOC_0) - 0.45\ln(AL) - 0.07\ln(TOC_0) \times \ln(AL) + 0.06pH \times \ln(AL) \quad (4)$	<ul style="list-style-type: none"> • Alum coagulation model was developed for EPA-WTP (Malcolm Pirnie 1992) based on data from 17 water utilities across the US, generated in three full-scale studies (Edzwald 1984; Singer 1988; Montgomery & Metropolitan 1989).
	<ul style="list-style-type: none"> • Alkalinity and pH changes $Alk = I_b - I_a = [HCO_3^-] + 2[CO_3^{2-}] + [H^+] \quad (5)$	
	<ul style="list-style-type: none"> • TOC removal by GAC filtration $TOC_f = \left[\frac{(TOC_0)^{0.16}}{1 + 0.09(ET)^{0.54} \times e^{-0.095(ET)^{-0.57}} \times R} \right]^{6.1} \quad (6)$	
Models for alum and chlorine doses	<ul style="list-style-type: none"> • Enhanced coagulation alum dose $AL = 10.9 + 2.63(DOC) + 0.17(Alk) + 0.74(pH) \quad (7)$ <p>($n = 25$; $r^2 = 0.59$; $p < 0.001$)</p>	<ul style="list-style-type: none"> • GAC model proposed by Clark <i>et al.</i> (1986) and Clark (1987). • Equation 7 was developed by Morin (1999) from data generated by White <i>et al.</i> (1997).
	<ul style="list-style-type: none"> • Models for simulations with TTHM model developed from bench-scale data <p><i>Chlorine dose (D) as function of total residual chlorine (TC): contact time of 1 h</i></p> $D = 1.99 + 0.23(TOC) + 1.13(TC) - 0.17(pH) \quad (8)$ <p>($n = 37$; $r^2 = 0.97$; $p < 0.001$)</p>	
	<ul style="list-style-type: none"> • <i>Chlorine dose as function of free residual chlorine (FC): contact time of 1 h</i> $D = 1.24 + 0.23(TOC) + 1.12(FC) - 0.03(pH) \quad (9)$ <p>($n = 36$; $r^2 = 0.96$; $p < 0.001$)</p>	
	<ul style="list-style-type: none"> • <i>Chlorine dose as function of free residual chlorine: contact time of 24 h</i> $D = -2.12 + 0.54(TOC) + 1.41(FC) + 0.42(pH) \quad (10)$ <p>($n = 18$; $r^2 = 0.94$; $p < 0.001$)</p>	
	<ul style="list-style-type: none"> • Model for simulations with TTHM model developed from field-scale data $FC_{tp} = -0.06 + 0.21(TOC) + 1.56(FC_{ext}) \quad (11)$ <p>($n = 47$; $r^2 = 0.96$; $p < 0.001$)</p>	

Nomenclature

TOC_f : concentration of TOC after treatment (mg/l); TOC_0 : concentration of TOC before treatment (mg/l); AL : coagulation alum dose (mg/l); ET : empty bed contact time for GAC filtration (min); R : regeneration frequency of the activated carbon (d); I_b : equivalent concentration of all positively charged ions except hydrogen; I_a : equivalent concentration of all negatively charged ions except hydroxide, bicarbonate and carbonate; $[HCO_3^-]$: molar concentration of the bicarbonate ion; $[CO_3^{2-}]$: molar concentration of the carbonate ion; $[OH^-]$: molar concentration of the hydroxide ion; $[H^+]$: molar concentration of the hydrogen ion; Alk : water alkalinity (mg/l $CaCO_3$); D : chlorine dose (mg/l); TC : total residual chlorine (mg/l); FC : free residual chlorine (mg/l); FC_{tp} : free residual chlorine at the treatment plant (mg/l); FC_{ext} : free residual chlorine at the system extremity (mg/l).

additional TOC removal when using GAC filtration. More detailed description of other algorithms within the EPA-WTP model as well as their development methodology are found elsewhere (Malcolm Pirnie, Inc. 1992).

Treatment conditions for simulation

A set of raw surface waters from Quebec utilities which currently apply only chlorine as a treatment process were randomly selected in order to generate a sample of representative water quality conditions. This sample ($n = 89$)

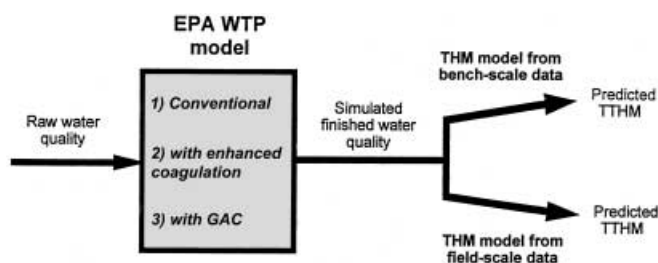


Figure 3 | Procedure for predicting TTHM resulting from different treatment configurations with chlorination.

contains information about parameters of raw water that affect, or are influenced by, any of the three proposed treatment configurations, as well as by chlorination. Parameters considered herein are pH, alkalinity, DOC and TOC. Raw water quality samples were simulated by the

EPA-WTP model using each of the treatment configurations. Outputs of these simulations were next used to predict TTHM with the two models presented previously (from bench-scale and field-scale data) (Figure 3). This approach allows for an analysis of different water treatment configurations with variable operational conditions, and thus permits an evaluation of their role in complying with different assumed THM standards.

In this investigation, several operational conditions were considered (Tables 7 and 8). Three different alum doses were used for conventional coagulation; they are within a range of doses frequently applied during surface water treatment. Doses for enhanced coagulation were estimated from required percentages of THM precursor removal (TOC) using a linear regression developed by Morin (1999) from field data recently generated by others (Equation 7 of Table 6). Different conditions for GAC

Table 7 | Operational conditions used for the analysis with the TTHM model from bench-scale data.

Treatment process	Alum dose (mg/l)	Bed regeneration frequency (d)	Chlorine dose ensuring the following residual objectives (mg/l)	Contact time (h)
Chlorination alone			0.2 after 1 h	
			0.5 after 1 h	6, 12, 24, 36, 48
			0.2 after 24 h	
Conventional	10, 20, 30		0.2 after 1 h	
			0.5 after 1 h	6, 12, 24, 36, 48
			0.2 after 24 h	
Conventional with GAC	20	100, 200, 300	0.2 after 1 h	
			0.5 after 1 h	6, 12, 24, 36, 48
			0.2 after 24 h	
Conventional with enhanced coagulation	Variable		0.2 after 1 h	
			0.5 after 1 h	6, 12, 24, 36, 48
			0.2 after 24 h	

Table 8 | Operational conditions used for the analysis with the TTHM model from field-scale data.

Treatment process	Site 2		Site 3		Objective of residual chlorine in system extremities (mg/l)
	Alum dose (mg/l)	Bed regeneration frequency (d)	Alum dose (mg/l)	Bed regeneration frequency (d)	
Chlorination alone					0.1, 0.2
Conventional	10, 20, 30		10, 20, 30		0.1, 0.2
Conventional with GAC	20	100, 200, 300	20	100, 200, 300	0.1, 0.2
Conventional with enhanced coagulation	Variable		Variable		0.1, 0.2

filtration were established by varying the filter bed regeneration frequency, whereas bed contact time was considered to be constant (20 min) (Lykins *et al.* 1988). Chlorination conditions were established on the basis that they must ensure minimum residual chlorine levels at the treatment plant and within the distribution system, that is, after a considerable contact time. The level for total residual chlorine of 0.2 mg/l after a contact time of 1 h corresponds to current Quebec drinking water regulations (Gouvernement du Québec 1984). The other two objectives for free residual chlorine, 0.5 mg/l after 1 h and 0.2 mg/l after 24 h, correspond to desired levels at, respectively, the treatment plant and extremities of the system. According to the literature, such levels would ensure an acceptable disinfection level and would minimize bacterial regrowth within the system (Haas 1999; Van der Kooji *et al.* 1999). Chlorine doses for simulations were estimated in accordance with these objectives for residual chlorine using Equations 8 to 11 in Table 6. Such estimations allowed us to take into consideration the fact that removal of THM precursors through treatment simultaneously reduces water chlorine demand. This led to more adequate chlorine doses than those actually observed during routine operations in plants (Sérodes & Rodriguez 1996; Rodriguez & Sérodes 1999). Finally, in all cases, temperature was set to 20°C which corresponds to average summer conditions. Because THM continue

to form within the distribution system when residual chlorine is present, the analysis also considers variable reaction times from the treatment plant (water travel time within the distribution system).

Analysis for future THM regulations

As mentioned previously, it is expected that the next update of Quebec drinking water regulations will require compliance with an annual average of TTHM of 100 µg/l based on four seasonal samples. In a recent investigation conducted by the Quebec Ministry of the Environment, it was established that in order to comply with such an annual standard, utilities would have to comply with a maximum TTHM level of 140 µg/l in summer conditions (Tremblay & Trinh Viet 1995). We validated this finding using the THM data available for the 89 utilities considered previously. We found small differences (about 10 µg/l). However, because both analyses were carried out with very little seasonal data, we tried to establish the same estimation using the TTHM model developed from bench-scale US data. This effort produced much less conservative results, and suggests that to comply with the proposed annual regulation, it would be necessary to comply with a standard of 250 µg/l in summer conditions. The same estimation was carried out for an annual average standard

Table 9 | Distribution of TTHM concentrations ($\mu\text{g/l}$) simulated from 89 raw waters, according to different treatment strategies.

	Model from bench-scale data			Model from field-scale data					
				Site 2			Site 3		
	10th percentile	Median	90th percentile	10th Percentile	Median	90th percentile	10th percentile	Median	90th percentile
Chlorination alone:									
Less favourable condition	14	43	155	9	36	91	43	85	179
More favourable condition	28	101	317	9	36	91	51	92	187
Conventional treatment:									
Less favourable condition	3	17	51	4	13	36	1	23	73
More favourable condition	17	68	180	7	23	58	30	68	129
Conventional treatment with enhanced coagulation:									
Less favourable condition	4	15	34	1	4	11	1	15	34
More favourable condition	11	29	62	3	10	24	1	34	67
Conventional treatment with GAC:									
Less favourable condition	1	6	16	5	13	24	1	22	55
More favourable condition	7	25	71	5	13	24	2	29	63

Note: *Less favourable condition* means the operational condition during treatment and distribution which generates the lowest simulated value of TTHM for a single raw water.

More favourable condition means the operational condition during treatment and distribution which generates the higher simulated value of TTHM for a single raw water.

of $40 \mu\text{g/l}$, which is significantly more restrictive, and corresponds to the EPA's second stage Disinfectant/DBP proposed rule. The results suggest that to comply with a standard of $40 \mu\text{g/l}$ annually, maximum THM concentrations in summer conditions must be $55 \mu\text{g/l}$ (using the Quebec field data) or $95 \mu\text{g/l}$ (using the model from bench-scale data).

Modelling results

Carrying out simulations by combining EPA-WTP and TTHM models applying variable operational conditions

allowed us to estimate TTHM levels in distribution systems and thus the prediction of the water treatment needed to comply with TTHM regulations. Such analyses were undertaken using the conservative values of maximum acceptable TTHM levels presented earlier (i.e. $140 \mu\text{g/l}$ and $55 \mu\text{g/l}$, corresponding respectively to the proposed $100 \mu\text{g/l}$ and hypothetical $40 \mu\text{g/l}$ standards).

Independent simulations were carried out using THM models from bench-scale data and field-scale data. All possible combinations of operational conditions presented in Tables 7 and 8 were evaluated (144 model simulations). Table 9 presents the results of these simulations. Predicted values of TTHM for different treatment

strategies are evidently very variable and they strongly depend on assumed operational conditions. The interpretation of results was carried out on the supposition that a future TTHM rule will aim to be applied at any location along the distribution system (thus also taking into consideration long water travel times).

For raw water which is directly chlorinated, assuming both high free residual chlorine objectives in the distribution system extremities (0.2 mg/l after 24 h—thus high chlorine dose) and high contact time (48 h), the median value of estimated TTHM given by the model from bench-scale data is 101 $\mu\text{g/l}$. When applying the field-data model for site 3 with the same raw water quality and operational conditions, the median of estimated TTHM is 92 $\mu\text{g/l}$. It is understandable that maximum TTHM simulated values are higher in the case of the model from bench-scale data because the likely water travel times at site 3 are much less than 48 h. However, both estimations are significantly lower than the maximum acceptable level of 140 $\mu\text{g/l}$ for summer conditions. Based on results from both models, such levels would be exceeded only when raw waters with high organic content are considered ($\text{DOC} > 4 \text{ mg/l}$). TTHM estimations exceed the hypothetical maximum acceptable level of 55 $\mu\text{g/l}$ when operational conditions are extreme (very high chlorine doses) even for low values of DOC and short travel times.

When a conventional treatment prior to chlorination is considered, both TTHM models predict median values of TTHM lower than 70 $\mu\text{g/l}$. Only in cases involving extreme operational conditions (very high chlorine dose, long travel time, insufficient coagulant dose), and very high raw water organic content ($\text{DOC} > 6 \text{ mg/l}$), would the 140 $\mu\text{g/l}$ -level be exceeded.

Finally, predicted median values of TTHM are very low when a more elaborate treatment prior to chlorination treatment is considered. In such cases, maximum estimated values of TTHM were found to be 75 $\mu\text{g/l}$ and 71 $\mu\text{g/l}$ when applying, respectively, the bench-scale data and the field-scale data models. However, these latter values correspond to very high values of DOC and very extreme operational conditions (relatively low removal of COD by enhanced coagulation or relatively low maintenance of GAC filters, as well as high values of chlorine dose and contact time).

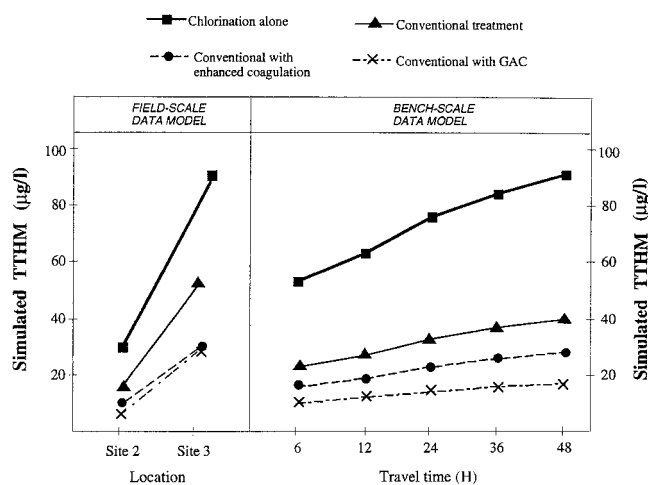


Figure 4 | Effect of travel time on median values of TTHM simulated by both models, according to different treatment strategies (conditions: chlorine dose ensuring a residual of 0.2 mg/l after 1 h, alum dose=20 mg/l, regeneration bed frequency for GAC=200 days).

Significance of the reference point in the distribution system

It would appear to be important to analyse the estimated TTHM values according to the location along the distribution system. As mentioned earlier, longer travel times (contact times) will favour higher THM formation. Figure 4 presents median values of estimated TTHM according to the water travel time from the chlorination point. Simulation results when applying the model from bench-scale data show that the influence of travel time on TTHM concentration is greater when assuming chlorination treatment alone than when assuming any other treatment configuration prior to chlorination. Such results could not be validated with the model from field-scale data because travel times are very likely not comparable. Water travel times within distribution systems of utilities supplying larger populations are generally higher than those within systems supplying small populations. However, in Québec, most utilities which actually use chlorination alone supply small populations (Gouvernement du Québec 1997). It is highly unlikely that maximum travel time of water in utilities which use chlorine alone will exceed 12 h. For that level of contact time, estimated median values for TTHM are considerably lower than the 140 $\mu\text{g/l}$ -level but slightly higher than the 55 $\mu\text{g/l}$ -level.

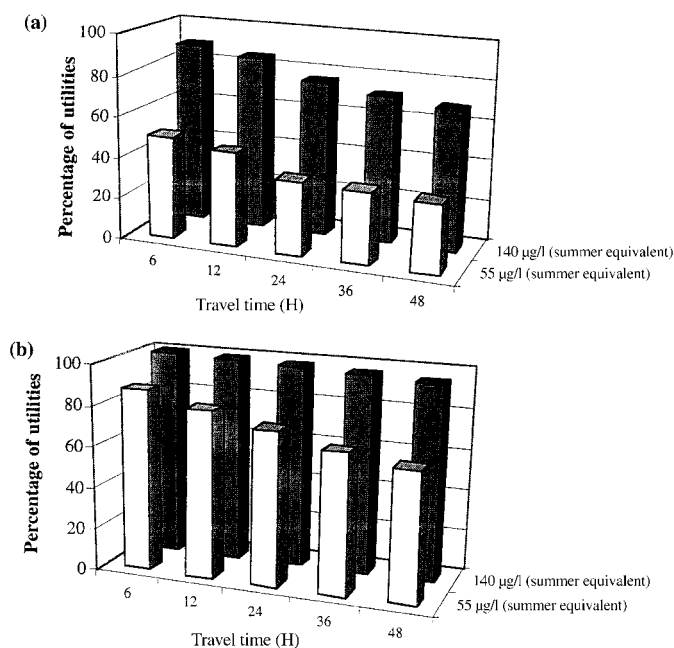


Figure 5 | Percentage of utilities which would comply with the proposed and a hypothetical TTHM standard at different travel times according to the bench-scale data model: (a) chlorination alone; (b) conventional treatment.

Utility compliance with future TTHM standards

Analysing median values for TTHM estimation, considering different water quality and operational conditions, makes it possible to estimate the proportion of Québec water utilities (using chlorination alone) which comply with proposed and hypothetical TTHM standards. As shown in Figures 5 and 6, utility compliance capacity decreases according to the reference point in the distribution system. Results of simulations using the bench-scale data models suggest that, for the proposed standard of 100 µg/l (140 µg/l for summer conditions), few small systems (maximum travel time within 12 h) would not comply (about 20% of utilities). When using the field-scale model (site 3), the results are comparable. However, if travel times were higher than 24 h (medium-size and larger distribution systems), about a quarter of utilities would not be able to comply with the 100 µg/l standard.

Finally, results confirm the difficulty of utilities faced with complying with a hypothetical standard much stricter than 100 µg/l. When considering the TTHM standard proposed by the US EPA in its D/DBP rule second stage

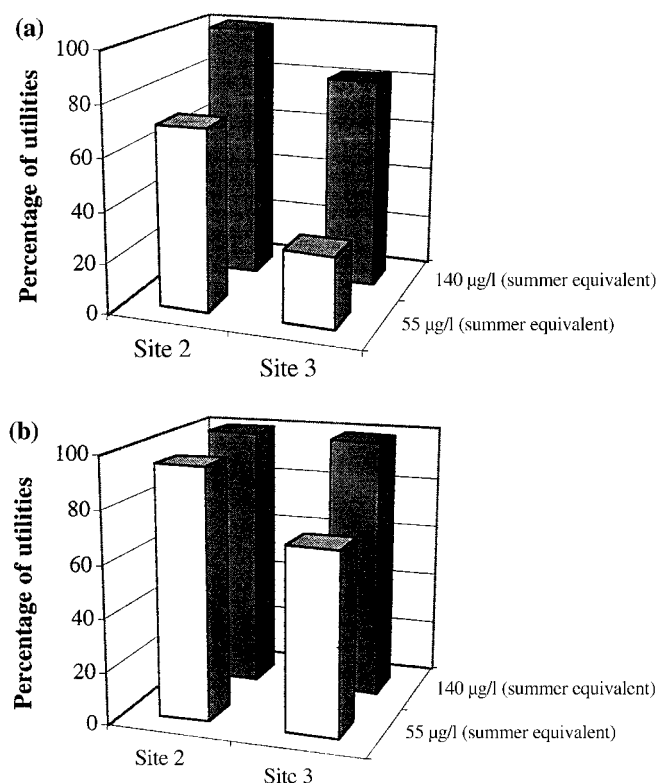


Figure 6 | Percentage of utilities which would comply with the proposed and a hypothetical TTHM standard at different locations according to the field-scale data model: (a) chlorination alone; (b) conventional treatment.

(40 µg/l for quarterly seasonal samples, that is 55 µg/l for Quebec summer conditions), many more systems which use chlorination alone (more than two-thirds, according to both models) would have to update their treatment process to a conventional one, or to an even more sophisticated one (for example with enhanced coagulation or with GAC) in order to comply with standards.

DISCUSSION AND CONCLUSIONS

A modelling approach designed to permit an evaluation of the feasibility of updating TTHM regulations in Quebec is presented. The methodology consists of combining two models, one for the estimation of removal of THM precursors and the other for predicting THM formation following chlorination. The methodology as presented requires several assumptions which lead to results which are more or less accurate. These assumptions are related, on one

hand, to the operational conditions used during the application of the EPA-WTP to estimate DOC removal with different treatment processes and, on the other hand, to the application of THM predictive models. We developed two TTHM predictive models from databases generated using different strategies. The results obtained by applying the two models are different but comparable. Our assumptions were based on common sense, literature statements and on complementary models we developed from data generated by others (particularly for estimated chlorine and enhanced coagulation doses). Given the complexity of water quality evolution in distribution systems, modelling results must be interpreted with caution. TTHM prediction must be viewed from a qualitative perspective and not a quantitative one.

Due to the fact that very little data about disinfection by-products are currently available for distribution systems in Quebec, or for other regions or countries, the generation of data using a modelling approach is extremely useful. Estimating how utilities will deal with future THM regulations would require extensive sampling programmes in distribution systems. Determining which treatment process would be required to allow utilities to comply with those regulations would require costly pilot projects within each utility. The modelling approach developed herein would probably not be useful to a single utility in determining the specific treatment necessary for its compliance with eventual future regulations. However it may be favourably used to evaluate—on a regional basis—whether proposed regulations are realistic, given the economic repercussions for municipalities and governments which may be related to the upgrading of drinking water infrastructures.

ACKNOWLEDGEMENTS

The authors would particularly like to thank Mrs H  l  ne Tremblay and Mr Alain Riopel of the Quebec Environment Ministry, for technical assistance and for supplying data. We also thank Dr G. Amy, Dr R. Rathbun and Ms K. Mallon, respectively from University of Colorado, US Geological Survey and Montgomery Watson, for provid-

ing bench-scale THM data. We are grateful to Mr Luc Bouchard, graduate student, for database management. Financial support for this research has been assured through a grant from the Natural Science and Engineering Research Council of Canada (NSERC).

REFERENCES

- Abacus Concepts Inc. 1996 *Using Statview*. Berkeley, California.
- Amy, G. L., Chadik, P. A. & Chowdhury, Z. K. 1987 Developing models for predicting trihalomethane formation potential and kinetics. *J. Am. Wat. Wks. Ass.* **79**(7), 89–96.
- APHA, AWWA & WPCF 1992 *Standard Methods for the Examination of Water and Wastewater*. 18th Edition, Washington, DC.
- Clark, R. M. & Sivaganesan, M. 1998 Predicting chlorine residuals and formation of TTHMs in drinking water. *J. Environ. Engng* **124**(12), 1203–1210.
- Clark, R. M. 1987 Modeling TOC removal by GAC: the general logistic function. *J. Am. Wat. Wks. Ass.* **79**(1), 50.
- Clark, R. M., Symons, J. M. & Ireland, J. C. 1986 Evaluating field-scale GAC systems for drinking water. *J. Environ. Engng* **112**(4), 744.
- Chang, E. E., Chao, S., Chiang, P. & Lee, J. 1996 Effects of chlorination on THM formation in raw water. *Toxicol. Environ. Chem.* **56**, 211–225.
- Edzwald, J. K. 1984 *Removal of THM Precursors by Direct Filtration and Conventional Treatment*. Report # 600/2-84/068, USEPA, Cincinnati, OH.
- Garcia-Villanova, J., Garcia, C., Gomez, J. A., Garcia, M. P. & Ardanuy, R. 1997 Formation, evolution and modeling of trihalomethanes in the drinking water of a town: I. At the municipal treatment utilities. *Wat. Res.* **31**(6), 1299–1308.
- Golfinopoulos, S. K., Xilourgidis, N. K., Kostopoulou, M. N. & Lekkas, T. D. 1998 Use of a multiple regression for predicting trihalomethane formation. *Wat. Res.* **32**(9), 2821–2829.
- Gouvernement du Qu  bec 1984 R  glement sur l’eau potable. *Gazette officielle du Qu  bec*, 7 pp.
- Gouvernement du Qu  bec 1997 *L’eau potable au Qu  bec: un second bilan de sa qualit  *. Biblioth  que Nationale du Qu  bec.
- Haas, C. N. 1999 Benefits of employing a disinfection residual. *J. Wat. Supply Res. Technol.-Aqua.* **48**(1), 11–15.
- Health Canada 1996 *Guidelines for Canadian Drinking Water Quality*. 6th Edition.
- Ibarluzea, J. M., Go  ni, F. & Santamaria, J. 1994 Trihalomethanes in water supplies in the San Sebastian area, Spain. *Bull. Environ. Contam. Toxicol.* **52**, 411–418.
- Levallois, P. 1997 Qualit   de l’eau potable et trihalom  thanes. *BISE* **8**(6), 1–4.
- Lou, J. C. & Chiang, P. C. 1994 A study of trihalomethanes formation in a water distribution system. *Hazard. Waste Hazard. Materials* **11**(2), 333–343.

- Lykins, B. W., Clark, R. M. & Adams, J. Q. 1988 Granular activated carbon for controlling THMs. *J. Am. Wat. Wks. Ass.* **80**(5), 85–92.
- Malcolm Pirnie, Inc. 1992 *Water Treatment Plant Simulation Program, Version 1.21, User Manual*. United States Environmental Protection Agency (USEPA), Washington, D.C.
- Montgomery Consulting Engineers and Metropolitan Water District of Southern California 1989 *Disinfection By-products in U.S. Drinking Waters*. USEPA and AAMW, Cincinnati, OH and Washington, DC.
- Montgomery Watson & AWWA 1991 *Disinfection/Disinfection By-products Database and ModelPproject*. American Water Works Association (AWWA), Denver, Colorado.
- Morin, M. 1999 *Analyse de la faisabilité technique d'un abaissement de la norme relative aux trihalométhanes dans l'eau potable à l'aide de modèles empiriques*. Masters Thesis, Université Laval, Quebec, Canada.
- Rathbun, R. E. 1996 Regression equations for disinfection by-products for the Mississippi, Ohio and Missouri rivers. *Sci. Total Environ.* **191**, 235–244.
- Roberson, J. A., Cromwell, J. E., Krasner, S. W., McGuire, M. J., Owen, D. M., Regli, S. & Summers, R. S. 1995 The D/DBP rule: Where did the numbers come from? *J. Am. Wat. Wks. Ass.* **87**(10), 46–57.
- Rook, J. J. 1974 Formation of haloforms during chlorination of natural waters. *Wat. Treat. Examin.* **23**, 234–243.
- Rodriguez, M. J. & Sérodes, J. B. 1999 Assessing empirical linear and non-linear modelling of residual chlorine in urban drinking water systems. *Environ. Modelling Software* **14**, 93–102.
- Sérodes, J. B. & Rodriguez, M. J. 1996 Predicting residual chlorine evolution in storage tanks within distribution systems: Application of a neural-network approach. *J. Wat. Supply Res. Technol.-Aqua.* **45**(2), 57–66.
- Singer, P. C. 1988 *Alternative Oxidant and Disinfectant Treatment Strategies for Controlling THM Formation*. Report # 600/2-88/044, USEPA, Cincinnati, OH.
- Stumm, W. & Morgan, J. J. 1981 *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*. John Wiley & Sons, New York.
- Tremblay, H. & Trinh Viet, H. 1995 *Réseaux municipaux visés par le règlement sur l'eau potable susceptibles de présenter une concentration annuelle moyenne de THM supérieure à 100 mg/L. Estimation des coûts de réalisation des ouvrages*. Ministère de l'Environnement et de la Faune.
- Urano, K., Wada, H. & Takemasa, T. 1983 Empirical rate equation for trihalomethane formation with chlorination of humic substances in water. *Wat. Res.* **17**(12), 1797–1802.
- USEPA 1992 *Analysis of Potential Trade-Offs in Regulation of Disinfection By-products*. Office of Water.
- Van der Kooij, D., Lieverloo, J. H. M., Schellart, J. A. & Hiemstra, P. 1999 Distributing drinking water without disinfectant: highest achievement or height of folly? *J. Wat. Supply Res. Technol.-Aqua.* **48**(1), 31–37.
- White, M. C., Thompson, J.D., Harrington, G.W. & Singer, P. C. 1997 Evaluating criteria for enhanced coagulation compliance. *J. Am. Wat. Wks. Ass.* **89**(5), 64–77.