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Sadiq, R.; Rodriguez, M. J.

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# Disinfection by-products (DBPs) in drinking water and the predictive models for their occurrence: a review

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# Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review

**[1]Rehan Sadiq and [2*]Manuel J. Rodriguez**

[1]Institute for Research in Construction, National Research Council, Ottawa, ON, Canada, K1A 0R6

[2] Département d'Aménagement, Université Laval, Québec City, QC, Canada, G1K7P4

**Abstract.** Disinfection for drinking water reduces the risk of pathogenic infection but may pose chemical threat to human health due to disinfection residues and their by-products (DBPs) when the organic and inorganic precursors are present in water. More than 250 DBPs have been identified, but the behavioral profile of only about 20 DBPs are adequately known. In the last two decades, many modelling attempts have been made to predict the occurrence of DBPs in drinking water. Models have been developed based on data generated in laboratory-scaled and field-scaled investigations. The objective of this paper is to review DBPs predictive models, identify their advantages and limitations, and examine their potential applications as decision-making tools for water treatment analysis, epidemiological studies and regulatory concerns. The paper concludes with a discussion about the future research needs in this area.

**Keywords:** Drinking water, disinfection, DBPs, predictive models, and human health risk.

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[*]Corresponding author:
Dr. Manuel J. Rodriguez
1624 Pavillon Savard, Université Laval,
Québec City, QC, Canada, G1K7P4
Tel (418) 656-2131 Ext. (8933)
Fax (418) 656-2018
Email: manuel.rodriguez@ame.ulaval.ca

## 1. Introduction

Since the 1970's, research in the drinking water field has significantly focused on documenting and understanding the occurrence of disinfection by-products (DBPs) in drinking water. In the recent years, a particular interest has been grown on the development of models to estimate the formation and the fate of DBPs. Several predictive models have been reported in the scientific literature. These models used different types of explanatory variables for variety of applications. Because, DBP modelling helps to guide decision-making in the drinking water industry, it emphasises the need for examining the state-of-the-art knowledge concerning this issue.

The main objective of this paper is to review DBP predictive models available in the scientific literature. A brief overview of disinfection and related human health concerns of DBP in drinking water is presented, which is then followed by the description of these models. Models are reviewed according to the characteristics of data used for the development, the methodology on which they are supported and their predictive capacity. The major benefits and outcomes of the reported models are also highlighted. In the second part of the paper, the potential applications of the models are discussed with the help of three hypothetical case studies. In accordance with the models' review, the critical research need for developing improved models to help in guide decision-making is identified.

## 2. Disinfection By-products (DBPs)

### 2.1. Disinfection for drinking water

The disinfection process has been routinely carried out since the dawn of the 20th century to eradicate and inactivate the pathogens from water used for drinking purpose. Disinfectants in addition to removing pathogens from drinking water serve as oxidants in water treatment. They are also used for (*a*) removing taste and colour; (*b*) oxidizing iron and manganese; (*c*) improving coagulation and filtration efficiency; (*d*) preventing algal growth in sedimentation basins and filters, and (*e*) preventing biological regrowth in the water distribution system (US EPA, 1999a). Chlorine and its compounds are the most commonly used disinfectants for water treatment. Chlorine's popularity is not only due to lower cost, but also to its higher oxidizing potential, which provides a minimum level of chlorine residual throughout the distribution system and protects against microbial recontamination.

The disinfection process is affected by different physico-chemical and biological factors and its efficiency can be characterised by dose and intensity (Gates, 1998). The disinfection efficiency (*Ct*) is a product of residual disinfectant and the contact time of chlorine in the water. This product is used as a design parameter for the disinfection facility. Disinfectants have varying capacities to inactivate or kill pathogens. The types and nature of organisms as well as the process conditions, including temperature and pH, also affect disinfection.  Table 1 compares the disinfection efficiency of three disinfectants under varying conditions of temperature, pH, contact time and dose. Generally, inactivation of organisms increases with increasing *Ct*. The pH has different effects on different disinfectants but in general at lower pH, chlorine is more effective against organisms than in alkaline conditions. Generally *Ct* required for inactivating microorganism is lower in warm water than in cold water. For a specific contact time, required chlorine doses for disinfection are consequently higher in winter than in summer conditions. However, in most drinking water utilities the application of a disinfectant (such as chlorine) in addition maintains adequate residuals to avoid the reappearance of microorganisms in the water distribution system. The disinfectant residuals deplete rapidly when the water temperature is high, which explains the difficulty of maintaining minimum residual level in the large distribution systems during summer. Also microbial activity within distribution systems is higher in warm than in cold waters (Arora *et al*., 1997). To maintain an adequate level of residual disinfectant in the distribution system, higher disinfectant doses are applied during the summer. Generally, the conditions affecting the disinfection efficiency and the requirements to maintain disinfectant residuals in the distribution systems simultaneously affect the formation of DBPs.

## 2.2. Occurrence of DBPs in drinking water

The application of disinfection agents to drinking water reduces the microbial risk but poses chemical risk in the form of their by-products. The DBPs are formed when the disinfectant reacts with natural organic matter (NOM) and/or inorganic substances present in water. More than 250 different types of DBPs have already been identified. Table 2 lists major classes of DBPs formed due to various disinfectants. The DBP concentrations may vary in orders of magnitude during different disinfection processes. Some DBPs reported in Table 2 have not been identified in field-scaled studies, however, they were observed in laboratory-scaled studies (Richardson, 1998). The formation of chlorinated DBPs in drinking water like trihalomethanes (THMs) has emphasized the need for exploring alternate disinfectants and new treatment technologies. Because organic/inorganic substances act as precursors for DBPs, their removal prior to disinfection has proven to be an effective method for reducing chlorinated DBP formation potential. The NOM can be partially removed using a conventional treatment (coagulation, flocculation, sedimentation and filtration) or by combining/replacing its components with more efficient processes such as granular activated carbon (GAC) filtration, enhanced coagulation and membrane filtration. Another effective method to control chlorinated DBPs in drinking water is the use of alternative disinfectants - ozone, chloramines, chlorine dioxide and more recently ultraviolet (UV) light - alone or in combination with chlorine. The use of various disinfectant alternatives to chlorination must be considered, however, they may form non-chlorinated DBPs. Finally, a better control of operational factors (e.g. control of pH or disinfection contact time) may contribute to a reduction in the formation of DBPs.

For chlorination, generally chlorine gas ($Cl_2$) is bubbled into pure water and rapid hydrolysis to hydrochloric (HCl) and hypochlorous acid (HOCl) takes place (Sadiq *et al*., 2002). The HOCl undergoes subsequent reactions resulting in the formation of THMs. HOCl oxidizes the bromide ($Br^-$) present in the water, which reacts readily with NOM to form brominated THMs (Stevens *et al*., 1976). Similar parameters that affect the disinfection efficiency (*Ct*) and residual depletion in the distribution system affect the rate and the degree of THM formation. THM occurrence is influenced by chlorine dose, concentration and nature of NOM (mainly humic substances), chlorine contact time (water residence time in distribution system), pH, temperature of water, and bromide ion (Amy *et al*., 1987a). In general, higher THM concentrations are expected at higher levels of the above-mentioned parameters.

In temperate environments, THM levels in drinking water are significantly affected by seasonal conditions (Singer *et al*., 1995; Health Canada, 1996; Arora *et al*., 1997; Chen and Weisel, 1998; Rodriguez and Sérodes, 2001; Sadiq *et al*., 2002). In the winter months and in some cases where the ice cover protects surface raw waters, the THM concentrations are lower due to lower water temperature and NOM. In these conditions, the chlorine demand is lower, therefore, the chlorine dose required to maintain adequate residual in the distribution system is also less important. Moreover, higher DBPs concentrations have been observed particularly in the extremities of water distribution systems, especially in the summer months (Health Canada, 1996; Sadiq *et al.*, 2002). The type of raw water also affects the THM levels. Generally, ground waters are naturally protected from runoff NOM, while the difference in occurrence of DBP precursors in river and lakes depends on geological, physical and environmental factors (trophic stage, watershed soil characteristics and land use, lake size, river flow rate, etc.).

For the DBPs associated to alternative disinfectant to chlorine (chloramines, chlorine dioxide, ozone), the similar operational factors influence the formation of the associated by-products (dose, pH, temperature, reaction time). Chloramines produce similar DBPs than chlorine but with much lower concentrations (Health Canada, 1996; US EPA, 2001b). For disinfection with chlorine dioxide (ClO2), there are no evidence of reactions with humic acids to form trihalomethanes (Lykins and Griese, 1986). However, the inorganic DBPs such as chlorite and chlorate are formed and they also have human health risk implications (Bercz, 1982; US EPA, 2001b). Finally, in ozonation, the most important by-product formed is bromate which depends on the presence of bromide and ammonia ion concentrations (von-Gunten *et al.*, 1995).

Because of major benefits of water disinfection and due to its outcomes associated with their DBPs a risk trade-off analysis between microbial and chemical risks becomes necessary (Figure 1). However in practice, this constitutes a major challenge because often the conditions leading to better disinfection efficiency also lead to higher occurrence of DBPs. The regulatory regime must establish the acceptable levels of risk for both microbial and chemical agents.

### 2.3. DBPs associated with human health adverse effects - guidelines

The Safe Drinking Water Act requires the US EPA to develop several new drinking water regulations. The regulations related to DBPs are the part of the Microbial-Disinfection by-products (M-DBPs) rule (US EPA, 1999b). The DBP regulations are based on evidence of their adverse human health effects, in particular cancer and reproductive disorders (Cantor *et al.*, 1998; Graves *et al.*, 2002). A considerably richer literature reporting adverse health effects through toxicological laboratory studies is available. Adverse effects of some of the important DBPs are summarised in Table 3.

The World health Organization (WHO, 1993) published drinking water guidelines for a few DBPs including THMs, haloacetic acids (HAAs), haloacetonitriles (HANs), chlorite, chloral hydrate, formaldehyde and cyanogen chloride. In addition to individual THM guidelines, the WHO has also suggested that the sum of the ratios of the THM levels to the guideline values should not exceed 1 (Table 4). Such guidelines have no official recognition in the US or Canada. The US EPA (2001a) has established the maximum allowable contaminant level of 0.08 mg/L for total THMs and of 0.06 mg/L for HAA5 (the sum of five HAAs, i.e. mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids). Compliance of these by-products is based on an annual running average of quarterly samples and since 2002 will be based on a locational running average (Sharfenaker, 2001). Bromate and chlorite are also regulated by US EPA (2001a). Health Canada (2001) has set 0.10 mg/L for total THM as an interim maximum acceptable concentration, which serves as a guideline for Provincial regulations. No Canadian drinking water quality guideline exists for other DBPs for the time being. The Australian-New-Zealand (2000) and UK (2000) drinking water standards are also summarized in Table 4 for comparison.

## 3. Predictive Models for DBPs

Models for DBPs have been developed for different purposes. In some cases, modelling is aimed at identifying the significance of diverse operational and water quality parameters controlling the formation of DBPs or at investigating the kinetics for their formation. In other cases, they are developed with predictive purposes as an alternative to monitoring in the field. In fact, measurement of DBP concentration in drinking water usually requires gas chromatography (GC) analysis, which is a time consuming and relatively expensive technique. Predictive modelling for DBPs consists of establishing empirical and mechanistic relationships of water quality and operational parameters with the prevailing levels of DBPs at various stages after the water treatment. The research in the last two decades has been aimed principally at linking DBP concentrations (mainly THMs) with total or dissolved organic matter (TOC or DOC), UV-absorbance at 254 nm (UV-254), pH, water temperature (T), concentration of bromide ion ($Br^-$), chlorine dose (D) and reaction time of residual chlorine (*t*). TOC (or DOC), UV-254 and specific UV absorbance, i.e., SUVA (specific ultraviolet absorbance, the ratio between UV-254 and TOC) are the common surrogates of NOM. TOC and DOC are indicators of mass of organic substance whereas UV-254 accounts for specific structure and functional groups (Edzwald *et al*., 1985; Croué *et al*., 1998; US EPA, 2001b). The SUVA is an indicator of NOM reactivity. Other NOM indicators that have been used are chlorophyll-*a* and fluorescence. The majority of chlorine demand is exhausted by the reaction with NOM but chlorine also reacts with various inorganic compounds (e.g., formation of chloramines in the presence of ammonia, formation of brominated compounds in the presence of $Br^-$, etc.). Studies have also shown that higher disinfectant dose increases the DBP formation potential in water (Montgomery Watson, 1993; Rathbun, 1996a). Longer reaction time generally leads to higher consumption of residual disinfectant and results in more formation of DBPs (Chen and Weisel, 1998; Rodriguez and Sérodes, 2001). This is one of the major reasons for the generally higher DBP concentrations observed in the extremities of water distribution systems compared to the finished water at treatment plants. However, recent research suggests that some chlorinated DBPs such as HAAs may degrade in extremities of distribution systems (Chen and Weisel, 1998; Rossman *et al*., 2001). The pH effects on DBP formation vary for different by-products (Singer *et al*., 1995). For example, in general THM formation increases with an increase in pH but the effects are reversed for HAA5. Temperature has a positive effect on DBP formation potential, and increases the rate of reaction (Amy *et al*., 1987a; US EPA, 2001b).

The modelling efforts in predicting DBP formation potential were started after the discovery of chloroform in chlorinated drinking waters in 1974 (Rook, 1974; Bellar *et al*., 1974). Considerable research has been focused on ascertaining the variables, which can significantly explain the DBP formation potential. Initial attempts included univariate analysis in which DBPs where correlated with TOC content in raw waters. For example, Singer and Chang (1989) developed linear relationships between TOX, THM, UV-254 and TOC. Other researchers have also investigated the relationships between precursor and operational indicators and DBPs as well as the relationships between different species of DBPs (e.g., Singer *et al*., 1995; Chen and Weisel, 1998; Arora *et al*., 1997; Gallard and von-Gunten, 2002; Gang *et al*., 2003).

Many other researchers have developed multivariate models to relate DBP concentrations to various combinations of explanatory variables, i.e., water quality and operational parameters associated with disinfection. The predictive models for DBPs are based on data obtained from field and laboratory-scaled studies. The field data are collected at different sampling points including raw water, finished water after disinfection and water distribution system. Laboratory-scaled studies have generally been based on batch sampling of raw and treated water samples. Laboratory studies have been found more reliable than field-scaled studies for developing empirical models because of controlled conditions. For example in laboratory studies, the effect of chlorine dose, pH and contact time on DBP formation can be easily investigated for the desired concentration of NOM in water. The major drawback of laboratory studies is that the effects of the distribution system on residual disinfectant concentration and DBP formation are not accounted for. In contrast, for models based on field data, human exposure can be measured or observed. However, some parameters affecting DBPs are difficult to estimate in the field-scaled studies. For example, estimating the actual contact time of disinfectants within the distribution system requires tracer studies and/or hydraulic simulation models, which are time consuming and not always very accurate. Another major drawback of field-scaled models is that they are generally site specific (Rodriguez *et al*., 2000). Table 5 lists a qualitative comparison of laboratory and field-scaled studies in the development of predictive models for DBP formation.

Since chlorine is the most popular and traditional disinfectant, most modelling efforts have been focused on THMs. A comprehensive literature review of existing predictive models for DBPs revealed that both laboratory-scaled and field-scaled studies are common practice. Most published models are empirically based, but some recent attempts have also been made to combine mechanistic and empirically based approaches. Some models have also been developed for individual THMs, especially for chloroform. Predictive models for DBPs associated to alternative disinfectants (ozone, chloramines, and chlorine dioxide) have also recently been developed. However the number of published models for non-chlorinated DBPs are much lower than those for chlorinated DBPs.

Table 6a and 6b summarize the predictive models for chlorinated and other DBPs, respectively. Tables 7a and 7b present brief description of these different models. Mostly these models are based on multivariate regression analyses in which explanatory variables were subjected to a logarithmic transformation. In few models, first and second order kinetic models are proposed with the kinetic coefficients, which are also estimated subsequently by multivariate regression. As observed, most models are associated to DBP data generated under laboratory-scaled conditions where operational factors and some water quality characteristics were controlled. Generally, laboratory-scaled models consider more explanatory/predictive variables than models based on field-scaled studies. The choice of explanatory variables in models is not motivated by mechanistic (physical) or statistical relationships alone, but rather by availability of reliable data. Also, the models based on laboratory-scaled data are generally developed with a higher number of observations. In fact, the logistics for laboratory-scaled experiments is generally less time-consuming than for field-scaled measurements and allows the investigation of variable chlorination conditions and investigating the formation of DBPs according to different contact times. This features the fact that reaction time of chlorine in water is precisely known in laboratory-scaled models, which makes the better statistical performance than the performance of field-scaled models.

Through this review, it appears difficult to make a precise judgement about the performance of the DBP models. In fact, models are often evaluated by means of classical statistical criteria alone (coefficient of determination, correlation coefficient, mean absolute errors between measured and predicted levels etc.). Authors often rely their judgement on model predictive ability according with such criteria without specifying the specific conditions (boundary conditions for predictors) or circumstances at with these models can be applied. In addition, most models are evaluated with the same data that have been used for their calibration and do not consider external databases for the model validation. It does not allow them to conclude the generalisation of these models. Another remark is that only few studies performed sensitivity analysis in the DBPs predictions with respect to selected explanatory variables. Finally, most studies do not include discussion on DBP model uncertainty.

Tables 7a and 7b present critical analyses of the models by describing their main advantages and their major outcomes. The common criticism over reported models based on laboratory-scaled data is that the experimental chlorination assays do not consider different water temperatures, and the chlorine doses are often much higher than those applied in real utilities. Because water temperature and disinfectant doses vary during the year in real utilities (as discussed in section

2.1) such outcome compromises the use of those models to predict field-scaled seasonal variation. The common criticism over reported models based on field-scaled data is that they are developed with a limited number of observations.

## 4. Potential Uses of Predictive Models

Classically, models are used to identify the relative significance of water quality (NOM indicators, bromine, pH, etc.) and operational variables (disinfectant dose, water temperature, contact time, etc.) responsible for the formation of DBPs. Sensitivity analyses of the models (Tables 6 and 7) can identify the contribution of each variable in DBP formation potential. Other potential benefits of developing predictive models for DBPs in drinking water are following:

*a-* *Water utility managers:* Models can be used to guide decision-making for operational control during the treatment process, e.g. for adjustment of pH and disinfectant dose or for controlling hydraulic residence time in reservoirs (contact time) to minimize DBP formation. In addition, DBP models can be used as a tool to select location for boosting chlorination residual levels to ensure complete removal of microbes and as well as minimization of DBPs formation. The DBP models can also be combined with residual disinfectant models to select the sampling points for water quality control within the distribution system.

*b-* *Environmental epidemiologists*: In some cases, models can be used for epidemiological studies (exposure assessment) and health risk assessment. They may be useful for estimating the human exposure to DBPs through drinking water by generating data for this purpose at desired locations. Regulations of DBPs are relatively recent and the sampling frequency required for compliance has been low. Consequently, current available data are not sufficient in the historical and geographical perspective to adequately conduct epidemiological studies relating to possible cancer and reproductive effects of these substances. By the use of surrogates, approximate estimations of temporal and geographical variability of DBPs can be investigated. In addition, these predictive models may also be combined with exposure assessment models for specific routes of DBPs’ exposure through drinking water.

c- *Regulatory agencies to estimate the need for infrastructure upgrading*: During regulations and standards updating, regulatory agencies evaluate the benefits of risk reduction associated with DBPs. In addition, agencies must evaluate the economic impacts in terms of upgrading treatment plants or changing raw water sources. In combination with the other models (e.g., the removal of organic precursors by different treatment processes), these predictive models can be used to evaluate the required reduction in precursors on a regional basis which allow compliance with DBP standards, and thus estimate the infrastructure needs for upgrading of treatment facilities.

Some potential applications of predictive models are illustrated with the help of hypothetical case studies in the following subsections.

## 4.1. Hypothetical case study 1

The assumption is that a municipality is currently using a conventional water treatment facility for supplying drinking water. Chlorination is the only disinfection method being employed for microbial inactivation and maintenance of residual disinfectant in the distribution system. The municipality is evaluating options for upgrading their facility through alternative disinfection or removing precursors (NOM) from the raw water to comply with the regulatory regime, i.e. total THM > 100 μg/L. The water managers decided to evaluate the second option using granular activated carbon (GAC) by taking into account the historical data distributed throughout the operational year of the water treatment facility.

Monte Carlo (MC) simulations are planned based on the uncertain nature of the data. The statistical distributions for these parameters are defined (Table 8). For example, the model proposed by Rodriguez *et al*. (2000) as given in Table 6a is used to estimate the required DOC concentration in the water to comply with the regulatory guidelines of 100 μg/L. Single values of total THM (e.g. one per season,) giving an annual average of 100 μg/L could also be used. A Latin Hypercube Sampling based on MC simulations is used to determine DOC levels.

The variability in existing (before treatment) and required DOC concentrations (to comply with 100 μg/L regulatory values) is shown by CDFs (cumulative distribution function) for comparison purposes (Figure 2a). Here it is assumed that the chlorine dose is maintained to ensure disinfection efficiency and acceptable residual chlorine in the distribution system (although chlorine demand would simultaneously be reduced). The removal efficiency (RE) of DOC required and complies with water quality guidelines is shown by the probability density function (PDF) in Figure 2b. Generally, empirical models containing design parameters are available to calculate removal efficiency of various water treatment options. The removal efficiency obtained from MC simulations can be related to those models to obtain design parameters. For example, the mean and standard deviation of PDF are also shown in Figure 2b which can help in modelling the design parameters of GAC, i.e., empty bed contact time (EBCT) and regeneration frequency. These removal efficiency results are equally applicable for other treatment options.

### 4.2. Hypothetical case study 2

The DBP models can also be used to estimate the human exposure to these compounds through various contact routes. The exposure assessment models for chloroform provided by Joe *et al.* (1990), shown in Table 9, are coupled with the total THM predictive model (Rodriguez *et al.*, 2000) to determine the exposure associated with the drinking water.

Three exposure routes – ingestion, inhalation and dermal contact – are considered in this analysis. Inhalation exposure through showers (baths) is considered. The other possible routes are through cooking and washing. To use the exposure assessment models, it is assumed that all 4 species of THMs behave like chloroform. The THM values are exposure concentrations, which are generated using the predictive model for treated levels of DOC as given in Case Study 1 and Figure 2a (Rodriguez *et al.*, 2000). The predicted THM concentrations are then used in exposure models given in Table 9 (Joe *et al.*, 1990).

The PDFs of exposure through ingestion, inhalation and dermal contact are shown in Figure 3. The uncertainties associated with DBP predictive and exposure assessment models, and the input parameters and scenarios contribute to the uncertainty in the actual exposure. These uncertainties can be reduced by the collection of more data. The exposure assessment results can be further used in human health risk assessment.

### 4.3. Hypothetical case study 3

As mentioned previously, the DBP models are useful for assessing human exposure in epidemiological studies. For example, the logistic-regression models developed by Milot *et al*. (2000) can be used to estimate the probability that utilities exceed specific values of THMs. These models have been developed with distribution system data for the province of Quebec (Canada).

Using the historical information (cancer studies require several years), the types of sources, treatment methods (and their modifications), and the information from geographical regions (soil properties and land use may vary), utilities can be classified in a retrospective way in accordance with their susceptibility of forming high THM concentrations. Such a classification can be done using probability thresholds to distinguish low, medium or high susceptibility (additional categories are possible). Using the complementary information required for epidemiological studies (consumption of tap water, control of socio-demographic factors, etc.), a historical and geographical assessment of exposure to THMs for populations served by the utilities of the area of interest can be undertaken.

Figure 4 illustrates the application of the logistic model (Milot *et al*., 2000) for a reference THM value of 100 μg/L. Figure 4 shows that probabilities of exceeding THM thresholds vary significantly across the categories of variables considered. Thus, in an epidemiological study, variability in exposures to THMs may play a key role.

## 5. Critical Research Needs

It appeared that a significant effort has been invested to develop predictive models for DBPs in drinking water. Models presented in this paper can be categorised based on methodology for data generation, the type of independent/explanatory variables and the model usefulness. According to the review, the main benefit for modelling appears to be their usefulness to identify factors influencing DBP formation and fate followed by chlorination of water. In fact, sensitivity analyses of these models will easily allow determining the relative contribution of water quality and operational parameters to the formation of DBPs. Some models can also be applied for predicting DBPs, but mainly subject to conditions (i.e., within the specific range of independent variables) and for the specific case that served for model development (experimental water or site-specific distribution system).

In the previous section, hypothetical case studies were presented in the manners that DBP models could be to guide decision-making. However, there is still lot of scope to improve the feasibility of using these models to predict DBPs for operational, epidemiological and regulatory purposes. To achieve this, it is important that future work must focus on multidisciplinary research related to chemistry, engineering, toxicology, epidemiology, statistics and governance. According to this review, the authors believe that in coming years the research efforts must focus on the following aspects:

- *The evaluation of laboratory-scaled models for predicting DBPs in field-scaled distribution system*: Research efforts must focus on investigating the capacity of models developed with laboratory-scaled data to estimate real seasonal and spatial variations of DBPs in the distribution systems. An important portion of this research must be the quantification of the distribution system contribution "pipe effect" on increasing or diminishing different DBP species. To achieve this goal, it is required that laboratory and field-scaled data be developed at the same utilities (simultaneous generation of data) or the laboratory-scaled models may be developed based on various sources of waters to generalise them for various scenarios.

- *The adaptation of laboratory-scaled models to be made useful for estimation of DBPs for field-scaled system*: A complementary research is required to develop strategies for simplification and adaptation of laboratory-scaled to field-scaled methods to generate DBP data. A significant challenge will be the better estimation of water residence time in distribution systems (through hydraulic models, tracer studies, flow rate correlations, etc.). Model adaptation could include the identification of conditions (seasons, water quality and operational ranges) at which laboratory-scaled models have better predictive capability within systems and the use of correction factors for other seasons. Such correction factors may vary according to the DBP specie. The application proposed by Westerhoff *et al*. (2000) is a preliminary attempt to achieve this.

- *The development of methods to estimate and reduce the uncertainties in the predictions of DBPs as well as to interpret them*: With all the reviewed models, it is possible to calculate DBP levels using explanatory variables. However, it is necessary to have more information about the confidence and certainty of these data in order to improve it. The use of fuzzy logic techniques (e.g., Sadiq and Rodriguez, 2003) may be an interesting alternative to accomplish this. This kind of research effort will simultaneously favour the applicability of the predictive modelling for operational, epidemiological and regulatory purposes.

- *Investigate the feasibility to integrate various modelling approaches to improve the predictive capacities of DBP models*: The majority of DBP models have been based on multivariate regression. Future research must experience alternative modelling techniques for DBPs predictions, such as artificial neural networks (Rumelhart *et al*., 1994; Milot *et al*., 2002), fuzzy rule-base modelling (e.g., Sadiq *et al*., 2003) which could improve DBP predictions. Robust database on DBPs has to be developed in order to adequately compare different techniques (with separation of calibration and validation data). The use of hybrid modelling methodologies may also be investigated, e.g. using different techniques to establish DBP kinetic coefficients and relate them to water quality and operational parameters, and then to reduce uncertainty in their predictions.

- *The development and application of DBP models that consider simultaneously the disinfection efficiency and residual disinfectant maintenance in distribution system*: Models have been reported in the scientific literature for each of these issues but no evident effort has been done to consider them simultaneously. As mentioned in the first section of this paper, parameters affecting these issues are similar (water temperature, organic content, chlorine dose, reaction time, etc.). Feasibility for integration of these issues in a multipurpose model has to be evaluated in the near future, particularly for treated water within the reservoir of treatment plants. To achieve this, robust data must be developed describing seasonal variations in water quality and operational changes.

- *Development of models for other DBPs*: Progress in toxicological research allows at identifying specific DBPs having potential implications for human health, but limited information is available about their presence and fate in drinking water. Mostly reported models are for THMs, it emphasises that research must focus on the generation of laboratory and field-scaled data of other DBPs. With these data, relationships between the different DBPs' species must be established and predictive models must be developed. Examples of species to favour in modelling are ozonation by-products and chlorinated DBPs (e.g. acetonitriles, chloropicrine and chloral hydrate) in addition to THMs and HAAs.

- *The development of criteria for assessment of the predictive capacity of DBP models*: It is important to develop criteria, which favour a uniform methodology for evaluating the predictive capacity of any DBP model. Such criteria may include the requirements for using minimum amount of external data for validation and for specific ranges of water quality and operational conditions within which models could be applied. Context in which DBP model can be applied (e.g. geographical features, type of water source, water utility types, etc.), boundary conditions for their application, as well as their specific potential usage (e.g., operational, epidemiological, regulatory) should be included in the criteria.

## 6. Summary and Conclusions

This paper has reviewed various models and approaches used for predicting DBPs' occurrence in drinking water. More particularly, the paper has focused, on one hand, on the disinfection practices and the formation of DBPs under varying water treatment conditions, and on other hand, on predictive models for DBPs and their potential use.

Based on literature reviewed, different modelling approaches have been used to relate water quality and operational parameters with DBP concentrations in water. Most of the models reported in the literature use DOC (or TOC), disinfectant dose, pH, temperature, and reaction time as explanatory variables. Some researchers used an entirely empirical approach and some introduced kinetics into the modelling process. Multiple linear and non-linear regression techniques are found to be the most common in developing DBP predictive models. Other methods like ridge, logistic regression and artificial neural networks have also been employed. Most of the predictive models are based on laboratory-scaled studies, but some models have been proposed based on actual water distribution sampling as well.

The DBP models can be useful for operational purposes during water treatment and water quality management, for the evaluation water treatment facilities, for exposure assessment in epidemiological studies and health risk assessment, and for estimating the benefits and impacts of DBP regulations. However, further research is necessary to evaluate the usefulness of DBP models and to adapt them for the purposes mentioned.

The use of alternative disinfectants and other treatment technologies have also increased the interest in developing predictive models for DBPs. By development of sophisticated analytical techniques (experimental), new DBPs have been discovered recently. More toxicological information on DBPs is available, therefore the development and use of models will be very helpful in the future to deal with these substances in drinking water.

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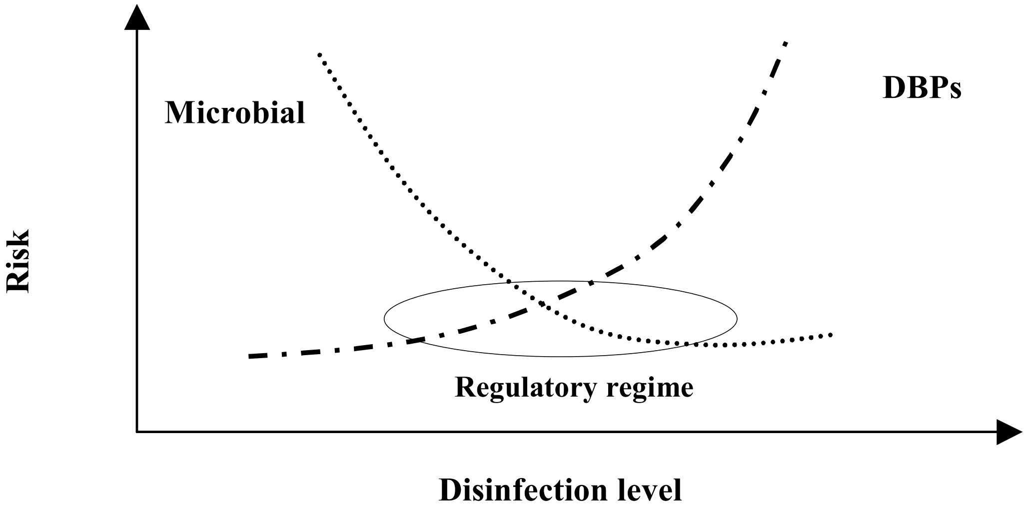
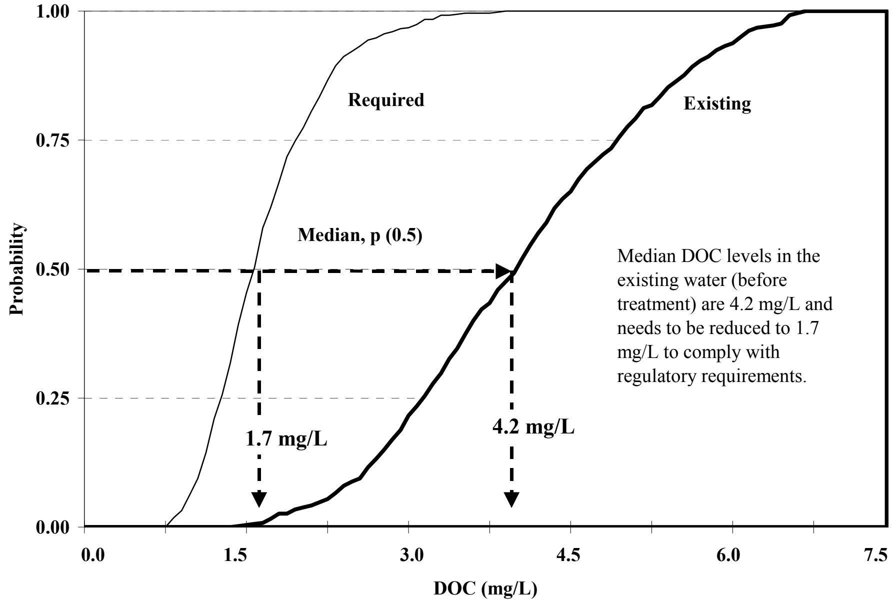
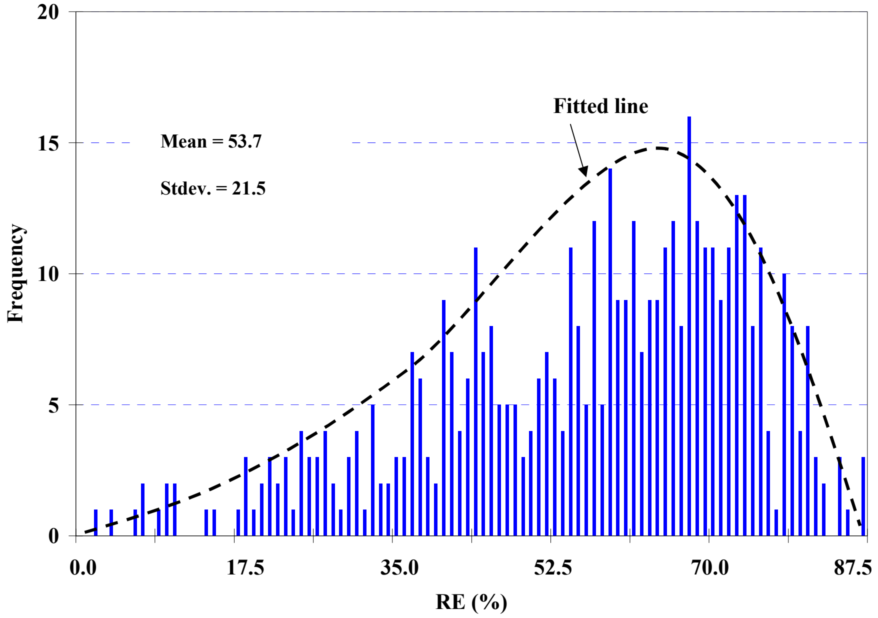


Figure 1. Microbial and chemical risk trade-off analysis for disinfection



Median DOC levels in the existing water (before treatment) are 4.2 mg/L and needs to be reduced to 1.7 mg/L to comply with regulatory requirements.

(a) CDFs of DOC concentrations in water for existing and required levels of total THM



(b) PDF of required DOC removal efficiency to comply with guideline of 100 μg/L total THM

Figure 2. Use of predictive models for DBPs in treatment process design (Case Study 1)

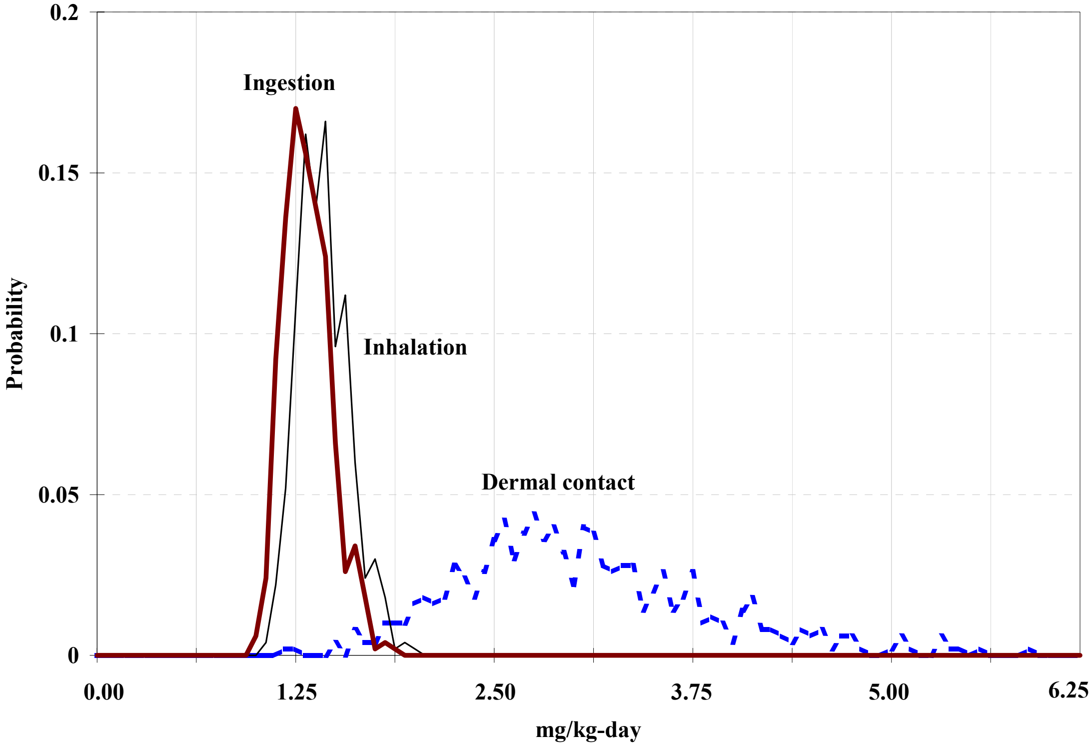
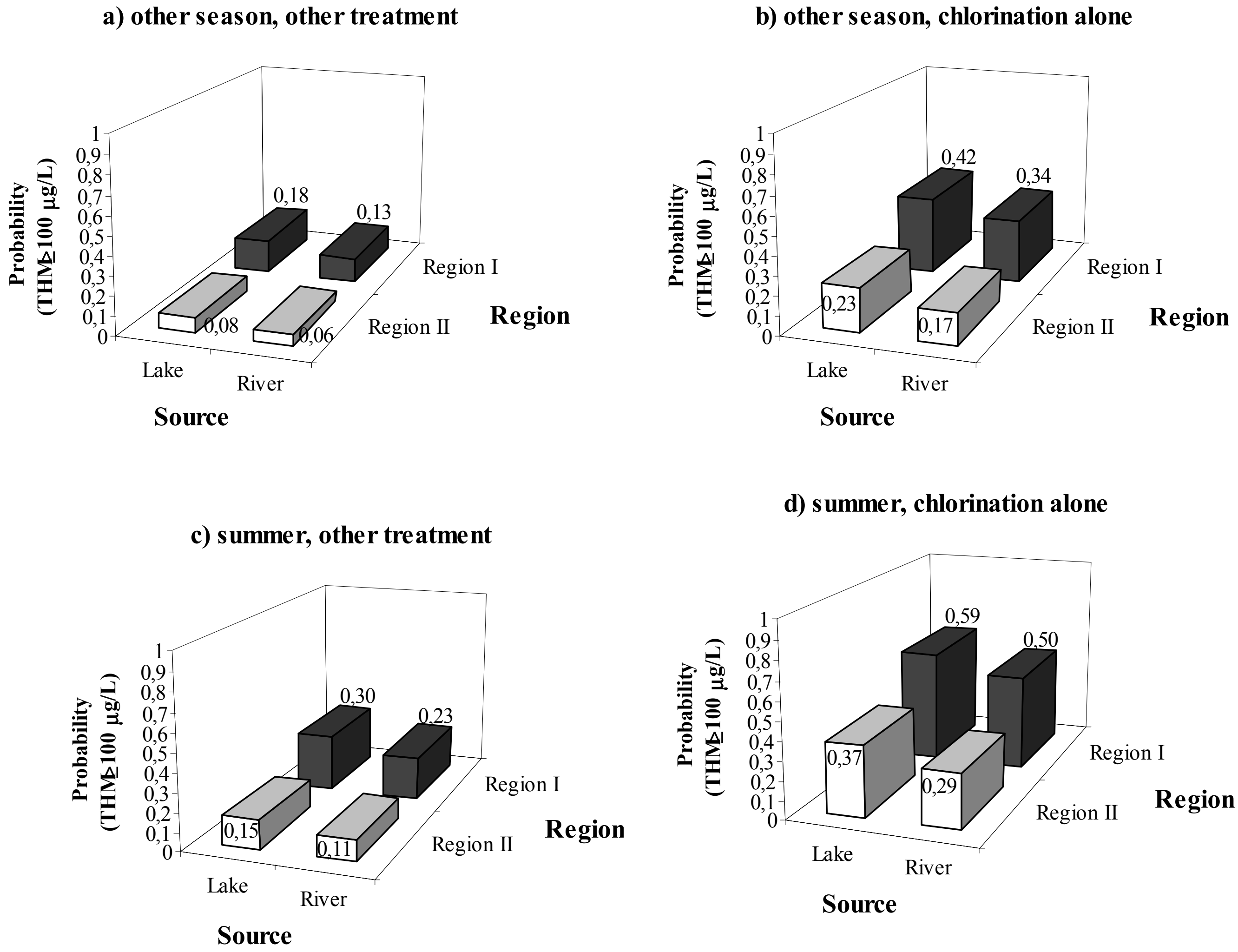


Figure 3. Results for model estimation of ingestion, inhalation and dermal exposure to total THMs (Case Study 2)



a) other season, other treatment

b) other season, chlorination alone

c) summer, other treatment

d) summer, chlorination alone

Figure 4. Model simulation of probability of THM levels being higher than 100 µg/L according to season, type of treatment, type of raw water and geographical location (Case Study 3)

Table 1. Percent of inactivation of various organisms under varying disinfection conditions

| Disinfectants | Conc. (mg/L) | Organism (*Group*) | Contact time (min) | pH | Temperature (°C) | % inactivation | References |
|---|---|---|---|---|---|---|---|
| Chlorine | 2.0 | *V. chloerae (B)* | 30 | 7.0 | 20 | >99.99 | Clark *et al.* (1994a, b) |
| | 0.5 | *Coliform (B)* | 2 | 7.0 | 5 | >99.99 | Berman *et al.* (1988) |
| | 1.1 | *E. coli (B)* | 2 | 7.0 | 5 | >99.999 | Rice *et al.* (1999a) |
| | 0.1 | *C. jejuni (B)* | 1 | 6.0 | 4 | >99.99 | Blaser *et al.* (1986) |
| | 0.61 | *A. butzleri (B)* | 1 | 7.1 | 5 | >99.999 | Rice *et al.* (1999b) |
| | 0.6-2.5 | *Polio virus (V)* | 0.7-2.4 | | 5 | >99 | Hoff (1986) |
| | 0.5 | *Rota virus (V)* | 0.25 | 6.0 | 5 | ≈99.99 | Berman and Hoff (1984) |
| | 0.5 | *Rota virus (V)* | 1.5 | 10.0 | 5 | ≈99 | |
| | 2.0 | *MS2 coliphage (V)* | 1 | 7.0 | 5 | ≈99.99 | Berman *et al.* (1992) |
| | 1.5 | *G. lamblia (P)* | 10 | 6-7 | 25 | ≈99 | Clark *et al.* (1989) |
| | 1.5 | *G. lamblia (P)* | 10 | 6.0 | 15 | ≈99 | |
| | 2.0 | *G. lamblia (P)* | 60 | 6-7 | 5 | >99 | |
| | 2.0 | *E. intestinalis (P)* | 8-16 | | | ≈99 | Rice *et al.* (1999c) |
| Mono-chloramines | 1.0 | *C. jejuni (B)* | 15 | 8.0 | 5 | >99 | Blaser *et al.* (1986) |
| | 10.0 | *Rota virus (V)* | >360 | 8.5 | 5 | ≈99 | Berman and Hoff (1984) |
| | 2.0 | *MS2 coliphage (V)* | 1 | 7.0 | 5 | ≈99 | Berman *et al.* (1992) |
| | 80.0 | *C. parvum (P)* | 90 | | 5 | ≈90 | Korich *et al.* (1990) |
| Chlorine-dioxide | 0.5 | *Rota virus (V)* | <1 | 6.0 | 5 | >99 | Berman and Hoff (1984) |
| | 0.5 | *Rota virus (V)* | <0.25 | 10.0 | 5 | >99 | |

*B*: Bacteria *V*: Viruses *P*: Protozoa

Table 2. Important groups of DBPs produced using different types of disinfectants

| Class of DBPs | Common example | Chlorine | Ozone | $ClO_2$ | Chloramines |
|---|---|---|---|---|---|
| **Trihalomethanes (THM)** | Chloroform | ✓[1] | ✓[2] | | ✓ |
| Other haloalkanes | | ✓ | | | |
| Haloalkenes | | ✓ | | | |
| **Haloacetic acids (HAA)** | Chloroacetic acid | ✓ | | | ✓ |
| Haloaromatic acids | | ✓ | | | |
| Other halomonocarboxylic acids | | ✓ | | | ✓ |
| Unsaturated halocarboxylic acids | | ✓ | | | ✓ |
| Halodicarboxylic acids | | ✓ | | | ✓ |
| Halotricarboxylic acids | | ✓ | | | |
| MX and analogues | | ✓ | | ✓ | ✓ |
| Other halofuranones | | ✓ | | | |
| Haloketones | | ✓ | ✓ | ✓ | |
| **Haloacetonitrile (HAN)** | Chloroacetonitrile | ✓ | ✓ | | |
| Other halonitrile | Cyanogen chloride | ✓ | | | ✓ |
| Haloaldehyde | Chloral hydrate | ✓ | | | ✓ |
| Haloalcohals | | ✓ | | | ✓ |
| Phenols | 2-Chlorophenol | ✓ | ✓ | | |
| Halonitromethane | Chloropicrin | ✓ | | | |
| **Inorganic compounds** | Bromate, Hypobromite, Chlorite & Chlorate etc. | | ✓ | ✓ | |
| Aliphatic aldehyde | Formaldehyde | ✓ | ✓ | ✓ | |
| Other aldehydes | | ✓ | ✓ | ✓ | |
| Ketones (aliphatic and aromatic) | Acetone | ✓ | ✓ | ✓ | |
| Carboxylic acids | Acetic acid | ✓ | ✓ | ✓ | |
| Aromatic acids | Benzoic acid | ✓ | ✓ | ✓ | |
| Aldo & Ketoacids | | | ✓ | ✓ | |
| Hydroxy acids | | ✓ | ✓ | | |
| Others | | ✓ | ✓ | ✓ | ✓ |

[1] There are four regulated THM compounds, but if iodomethanes are included in THMs then there will be 9 compounds

[2] Bromoform is produced if bromide ion is present

NB: Major classes of DBPs are shown in bold

Table 3. Toxicological information for DBPs (modified after US EPA, 1999b)

| Class of DBPs | Compound | [a]Rating | Detrimental effects |
|---|---|---|---|
| Trihalomethanes (THM) | Chloroform | B2 | Cancer, liver, kidney, and reproductive effects |
| | Dibromochloromethane | C | Nervous system, liver, kidney, and reproductive effects |
| | Bromodichloromethane | B2 | Cancer, liver, kidney, and reproductive effects |
| | Bromoform | B2 | Cancer, nervous system, liver and kidney effects |
| Haloacetonitrile (HAN) | Trichloroacetonitrile | C | Cancer, mutagenic and clastogenic effects |
| Halogenated aldehydes and ketones | Formaldehyde | B1 | [b]Mutagenic |
| Halophenol | 2-Chlorophenol | D | Cancer, tumour promoter |
| Haloacetic acids (HAA) | Dichloroacetic acid | B2 | Cancer, reproductive and developmental effects |
| | Trichloroacetic acid | C | Liver, kidney, spleen and developmental effects |
| Inorganic compounds | Bromate | B2 | Cancer |
| | Chlorite | D | Developmental and reproductive effects |

[a] A: Human carcinogen; B1: Probable human carcinogen (with some epidemiological evidence); B2: Probable human carcinogen (sufficient laboratory evidence); C: Possible human carcinogen; D: Non classifiable

[b] Inhalation exposure

Table 4. Standards/guidelines related to DBPs (mg/L) in various jurisdictions of the world

| Compound | Acronym | WHO (1993) | US EPA (2001a) | Health Canada (2001) | Aus-NZ (2000) | UK (2000) |
|---|---|---|---|---|---|---|
| Trichloromethane (chloroform) | TCM | 0.200 | 0.000* | | | |
| Bromodichloromethane | BDCM | 0.060 | 0.060* | | | |
| Dibromochloromethane | DBCM | 0.100 | 0.000* | | | |
| Tribromomethane (bromoform) | TBM | 0.100 | 0.000* | | | |
| Total trihalomethanes | TTHM | $\sum_{i=1}^{4}\frac{THM}{WHO}\leq 1$ | 0.080 | 0.100 | 0.250 | 0.100 |
| Chloroacetic acid | | | | | 0.150 | |
| Dichloroacetic acid | DCAA | 0.050 | | | 0.100 | |
| Trichloroacetic acid | TCAA | 0.100 | | | 0.100 | |
| Haloacetic acids | HAA5 | | 0.060 | ** | | |
| Dichloroacetonitrile | DCAN | 0.090 | | | | |
| Trichloroacetonitrile | TCAN | 0.001 | | | | |
| Dibromoacetonitrile | DBAN | 0.100 | | | | |
| Haloacetonitrile | HAN | | | ** | | |
| Chloral hydrate | CH | 0.010 | | ** | 0.020 | |
| Formaldehyde | | 0.900 | | | 0.500 | |
| Chlorite | | 0.200 | 1.000 | ** | | |
| Cyanogen chloride | | 0.070 | | ** | | |
| Bromate | | | 0.010 | 0.010*** | | |
| 2-chlorophenol | | | | | 0.300 | |
| 2,4-dichlorophenol | | | | | 0.200 | |
| 2,4,6-trichlorophenol | | | | | 0.020 | |

* Maximum contaminant level goals (MCLG)

** Under consideration

*** Interim maximum acceptable concentration (IMAC)

Table 5. A qualitative comparison of field and laboratory-scaled models

| Attributes | Laboratory-scaled models | Field-scaled models |
|---|---|---|
| Statistical significance | H | M |
| Applicability | H (General) | L (Site specific) |
| Inclusion of effects of distribution system (biofilm, pipe material, etc.) | N | H |
| Controllability over explanatory variables, e.g. reaction time | H | L |
| Predictability (actual human exposure) | M | H |
| Ease in model development | H | L |
| Cost and resources involved in model development | L | H |

H = high; M = medium; L =Low and N = No

Table 6a. A summary of THM, HAA and total organic halogenated (TOX) predictive models

| Author | Year | Data source | n | $r^2$ | Output | Units | Predictive models for chlorinated by-products |
|---|---|---|---|---|---|---|---|
| **1.** Minear and Morrow<br>**2.** Morrow and Minear* | 1983<br>1987 | Laboratory | 40 | > 0.90 | *TTHM* | µmol/L | $- 3.91 + (Br^-)^{0.15} + 0.23 (\log (Cl_2) + 0.24 (pH) + 10^{(0.009T)} + 0.26 (NVTOC)$ |
| **3.** Urano *et al.* | 1983 | Laboratory | NR | NR | *TTHM* | µg/L | $0.00082 (pH-2.8) (TOC) (D)^{0.25} (t)^{0.36}$ |
| **4.** Amy *et al.* *<br>**5.** Chowdhury *et al* * | 1987a,b<br>1991 | Laboratory | 995 | 0.90 | *TTHM* | µmol/L | $0.0031(UV \cdot TOC)^{0.440} (D)^{0.409} (t)^{0.265}(T)^{1.06} (pH-2.6)^{0.715} (Br+1)^{0.036}$ |
| **6.** Adin *et al.* | 1991 | Laboratory | NR | 0.90 | *TTHM* | ∝g/L | $(K_1)(K_2)(TOC)[(1/((K_1+K_3)(K_2+0.19)))$<br>$+(1/(K_1+K_3-K_2-0.19))x(((1/(k_1+K_3))exp^{-(k1+k3)(tc)})$<br>$-((1/(k_2+0.19))exp^{-(k2+0.19)(tc)}))]$ *where*<br>$K_1=4.38x10^{-8}(D) ; K_2=11.36x10^{-7}(D); K_3=7.14x10^{-13}(D)^2$ |
| **7.** Montgomery Watsor | 1993 | Laboratory | 864 | 0.88 | $CHCl_3$ | ∝g/L | $0.064(TOC)^{0.329}(UV)^{0.874}(Br^-+0.01)^{0.404}(pH)^{1.161}(D)^{0.561}(t)^{0.269}(T)^{1.018}$ |
| | | | 157 | 0.80 | *BDCM* | | $0.0098(Br^-)^{0.181}(pH)^{2.55}(D)^{0.497}(t)^{0.256}(T)^{0.519}$ (for $D/ Br^-<75$) |
| | | | 110 | 0.92 | *BDCM* | | $1.325(TOC)^{-0.725}(Br^-)^{0.794}(D)^{0.632}(t)^{0.204}(T)^{1.441}$ (for $D/ Br^->75$) |
| | | | 116 | 0.82 | *DBCM* | | $14.998(TOC)^{-1.665}(Br^-)^{1.241}(D)^{0.729}(t)^{0.261}(T)^{0.989}$ (for $D/ Br^-<50$) |
| | | | 99 | 0.83 | *DBCM* | | $0.028(UV)^{-1.175}(TOC)^{-1.078}(Br^-)^{1.573}(pH)^{1.956}(D)^{1.072}(t)^{0.2}(T)^{0.596}$<br>(for $D/ Br^->50$) |
| | | | 106 | 0.86 | $CHBr_3$ | | $6.533(TOC)^{-2.031}(Br^-)^{1.388}(pH)^{1.603}(D)^{1.057}(t)^{0.136}$ |
| | | | 81 | 0.82 | *MCAA* | ∝g/L | $1.634(TOC)^{0.753}(Br^-+0.01)^{-0.085}(pH)^{-1.124}(D)^{0.509}(t)^{0.300}$ |
| | | | 172 | 0.97 | *DCAA* | | $0.605(TOC)^{0.291}(UV)^{0.726}(Br^-+0.01)^{-0.568} (D)^{0.48}(t)^{0.239}(T)^{0.665}$ |
| | | | 172 | 0.98 | *TCAA* | | $87.182(TOC)^{0.355}(UV)^{0.901}(Br^-+0.01)^{0.679}(pH)^{1.732}(D)^{0.881}(t)^{0.264}$ |
| | | | 79 | 0.80 | *MBAA* | | $0.176(TOC)^{1.664}(UV)^{-0.624}(Br^-)^{0.795}(pH)^{-0.927}(t)^{0.145}(T)^{0.45}$ |
| | | | 81 | 0.95 | *DBAA* | | $84.945(TOC)^{-0.62}(UV)^{0.651}(Br^-)^{1.073}(D)^{-0.2}(t)^{0.12}(T)^{0.657}$ |
| **8.** Lou and Chiang | 1994 | Field | 16 | NR | *TTHM* | ∝g/L | $TTHM_O + 7.01(pH-2.3)^{0.11} (NVTOC)^{1.06} (t)^{0.764} (\beta)$ |
| **9.** Ibarluzea *et al.* | 1994 | Field | 12 | 0.82 | $CHCl_3$ | ∝g/L | $10.8 + 0.04 (Flu) + 1.16 (pH) + 0.12 (T) + 1.91 (C_O)$ |
| **10.** Rathbun | 1996a,<br>b, c | Laboratory | 669 | 0.98 | *TTHM*<br>*NPOX* | ∝g/L | $14.6 (pH-3.8)^{1.01} (D)^{0.206} (UV)^{0.849} (t)^{0.306}$<br>$42.0 (13.0-pH)^{1.07} (D)^{0.21} (Br^- + 1)^{-2.75} (UV)^{0.847} (t)^{0.142}$ |
| **11.** Chang *et al.* | 1996 | Laboratory | 120 | 0.94 | *TTHM* | ∝g/L | $12.7 (TOC)^{0.291} (t)^{0.271} (D)^{-0.072}$ |

Table 6a. A summary of THM, HAA and total organic halogenated (TOX) predictive models (Contd.)

| Author | Year | Data source | n | $r^2$ | Output | *Units* | Predictive models |
|---|---|---|---|---|---|---|---|
| **12.** Garcia-Villanova *e*<br>*al.* | 1997a<br>1997b | Field | 66 | 0.86 | *$CHCl_3$* | µg/L | $exp( 0.348 + 0.00059 (T)^3 – 0.000023 (T)^4 + 0.0237(pH)^2 + \alpha + \varepsilon)$<br>$exp (0.81 Y – 0.16 (NF)+ 0.00047 (T)^3 – 0.00002 (T)^4 + 0.0034 (pH)^2 + \varepsilon)$ |
| **13.** Huixian *et al.*$^{**}$ | 1997 | Laboratory | NR | 0.94<br>0.92 | *POX*<br>*NPOX* | ∝g/L | $7.20\, t^{0.08}\, TOC^{0.49}\, D^{0.41}\, (pH + 8.6)\, e^{(-468.5\, T)}$<br>$28.7\, t^{0.02}\, TOC^{0.53}\, D^{0.44}\, (20.9 - pH)\, e^{(-632.4T)}$ |
| **14.** Clark, R. M.$^{***}$<br>**15.** Clark and Sivaganesan$^{***}$ | 1998<br>1998 | Laboratory | 42 | *A* = 0.71<br>*K* = 0.78<br>*M* = 0.42 | *TTHM* | ∝g/L | $A\left(C_1 - \left(\frac{C_1(1-K)}{1-Ke^{-ut}}\right)\right)$ *where,*<br>$u = M(1\text{-}K)$; *and*<br>$A = 4.44\, C_1^{-0.44}\, TOC^{0.63}\, pH^{-0.29}\, T^{0.14}$<br>$K = 1.38\, C_1^{-0.48}\, TOC^{0.18}\, pH^{-0.96}\, T^{0.28}$<br>$M = e^{(-2.46 – 0.19\, TOC – 0.14\, pH – 0.07\, T + 0.01\, T \cdot pH)}$ |
| **16.** Golfinopoulos *et al* | 1998 | Field | 88 | 0.98 | *TTHM* | ∝g/L | $13.5\, Ln\, (Ch\text{-}a) – 14.5\, (pH) + 230(Br^-) – 140\, (Br^-)^2 – 25.3\, (S) + 110.6\, (Sp) – 6.6\, (T \cdot Sp) + 1.48\, (T \cdot D)$ |
| **17.** Amy *et al.*$^{*}$ | 1998 | Laboratory | NR | NR | *TTHM* | ∝g/L | $0.00412(DOC)^{1.10}\, (D)^{0.152}\, (Br)^{0.068}\, (T)^{0.61} (pH)^{1.60}\, (t)^{0.260}$ |
| **18.** Nokes *et al*. | 1999 | Field | | | *THMs* | ∝g/L | *Function of various reaction coefficients of intermediate products* |
| **19.** Rodriguez *et al.* | 2000 | Field | 174 | 0.34 | *TTHM* | ∝g/L | $1.392(DOC)^{1.092}\, (pH)^{0.531}\, (T)^{0.255}$ |
| | | Laboratory | 1800 | 0.90 | *TTHM* | ∝g/L | $0.044(DOC)^{1.030}\, (t)^{0.262}\, (pH)^{1.149}\, (D)^{0.277}\, (T)^{0.968}$ |
| **20.** Milot *et al.* | 2000 | Field | | | *TTHM* | | $p = \frac{e^{a(treatment)+b(region)+c(season)+d(source)+e}}{1+e^{a(treatment)+b(region)+c(season)+d(source)+e}}$<br>where p denotes the probability of exceedence from established (regulatory) *TTHM* levels; *a, b, c, d, e* denote the logistic regression coefficients. |
| **21.** Clark *et al.*$^{*}$ | 2001 | Laboratory | 17-2 | M = 0.70<br>K = 0.95 | *13 DBPs including THMs and HAAs* | ∝mol/L | $A_i\left(C_1 - \left(\frac{C_1(1-K)}{1-Ke^{-ut}}\right)\right)$ *where,*<br>$u = M(1\text{-}K)$ *and*<br>$M = 52.46\, e^{(-0.325\, Br-)} \cdot e^{(0.0145\, (Cl_1 \cdot pH))} \cdot Cl_1^{(-2.32)} \cdot e^{8.46\, (P)} \cdot e^{-2.31\, (pH)}$<br>$K = 6.62\, (pH)^{-0.13} \cdot (Br^- + 1)^{0.10} \cdot (Cl_1)^{-0.75}$<br>$Ai = -G + e^{ai} \cdot (pH)^{bi} \cdot (Cl_1)^{ci} \cdot (P + G)^{di} \cdot e^{(ei \cdot Br- + fi\, \cdot\, (Br-)2+gi\, \cdot\, (Br-)3}$<br>$\forall\ i = 1, 2, \ldots, 13 \qquad P = \frac{m \cdot Br^-}{m \cdot Br^- + m \cdot Cl_1}$<br>*where* $(m \cdot Br^-)$ *= moles of* $Br^-$ *ion and* $(m \cdot Cl_1)$ *= moles of initial chlorine* |

Table 6a. A summary of THM, HAA and total organic halogenated (TOX) predictive models (Contd.)

| Author | Year | Data source | n | $r^2$ | Output | *Units* | Predictive models |
|---|---|---|---|---|---|---|---|
| **22.** Golfinopoulos and Arhonditsis | 2002 | Field | 126 | 0.52 | *TTHM* | µg/L | $-0.26\ (Ch\text{-}a) + 1.57\ (pH) + 28.74\ [Br] - 66.72\ [Br]^2 - 43.63\ (S) + 1.13\ (Sp) + 2.62\ (T{\cdot}S) - 0.72\ (T{\cdot}D)$ |
| | | | 126 | 0.51 | *$CHCl_3$* | µg/L | $-0.32\ (Ch\text{-}a) + 0.68\ (pH) + 2.51\ (D) + 1.93\ (Sp) - 22.1\ (S) + 1.38\ (T{\cdot}S) - 0.12\ (T{\cdot}D)$ |
| | | | 126 | 0.62 | *BDCM* | µg/L | $-0.37\ (Ch\text{-}a) + 0.32\ (pH) + 16.16\ [Br] - 29.82\ [Br]^2 + 1.88\ (D) + 5.17\ (S) - 0.37\ (T{\cdot}S) - 0.12\ (T{\cdot}D)$ |
| **23.** Villanueva *et al*. | 2003 | Field | 18 | 0.57 – 0.97 | *HAAs* | ∝g/L | *Linear regression in function of various THM species* |
| **24.** Serodes *et al.* | 2003 | Laboratory | 51-53 | 0.56-0.92 | *TTHM*<br>*HAAs* | ∝g/L | *Single linear and non-linear regression models for water of each utility (in function of water temperature, TOC, chlorine dose and contact time)* |
| **25.** Gang *et al*. | 2003 | Laboratory | NR | NR | *TTHM* | | $\alpha_1 D\{1 - f\, e^{(-kr\cdot t)} - (1-f)\, e^{(-ks\cdot t)}\}$ |

**More than one model presented; ** Temperature (T) is in degrees K; *** Time in minutes*

***Nomenclature:*** *TTHM = total trihalomethanes; $TTHM_O$ = initial TTHM concentration; $CHCl_3$ = chloroform; BDCM = Bromodichloromethane; DBCM = Dibromochloromethane; $CHBr_3$= bromoform; MCAA=monochloroacetic acid; DCAA=dichloroaceic acid; TCAA=trichloroacetic acid; MBAA=monobromoacetic acid; DBAA= dibromoacetc acid; UV=UV absorbance at 254 nm ($cm^{-1}$); TOC = total organic carbon (mg/L); NVTOC = non-volatile organic carbon (mg/L); DOC =dissolved organic carbon (mg/L); POX = purgeable organic halide (∝g/L); NPOX = non-purgeable organic halide (∝g/L); T = water temperature (℃); Flu = fluorescence (%); D = chlorine dose (mg/L); f = fraction of the chlorine demand attributed to rapid reactions; $C_O$ = residual chlorine at the treatment plant after chlorination (mg/L); $Cl_1$ = initial chlorine concentration; $C_1$ = initial residual chlorine (mg/L); $\alpha$ = parameter depending on location at which chloroform is predicted; $\alpha 1$ = TTHM yield coefficuient; $\varepsilon$ = random error; $\beta$ = water dispersion parameter in the water distribution system; kr and ks = the first order rate constants for rapid and slow reactions, respectively; $Br^-$ = bromide ion (mg/L); t = reaction time (hrs); S = dummy variable (summer); Sp = dummy variable (spring); G = 1 for chlorinated compounds and G = 0.0001 otherwise; Ch–a = chlorophyll-a ($mg/m^3$); ai, bi, ci, di, ei, fi, gi = constants depending on type of DBP (see Clark et al., 2001); NF = dummy variable near or far; Y = Year of sampling expressed by binary numbers; NR = Not reported.*

Table 6b. A summary of predictive models for other DBPs

| Author | Year | Data source | n | $r^2$ | Output | Units | Predictive models |
|---|---|---|---|---|---|---|---|
| **1.** Ozekin, K.;<br>Ozekin, K. *et al* | 1994<br>1998 | Laboratory | NR | NR | *Bromate ($BrO_3^-$)* | µg/L | $1.55 \cdot 10^{-6} (DOC)^{-26} (pH)^{5.82} (O_3)^{5.82} (Br^-)^{0.73} (t)^{0.28}$<br>*for temperatures other than 20 C, the bromate concentration can be modified by following relationship*<br>$[BrO_3^-]_T = [BrO_3^-]_{20C} (1.035)^{T-20}$ |
| **2**. Siddiqui *et al.* | 1994 | Laboratory | 70 | 0.94 | *$CHBr_3$* | ∝g/L | $7.3 (DOC)^{1.33} (pH)^{-1.25} (O_3)^{0.771} (Br^-)^{1.56} (T)^{0.909}$ *(24 hrs predictions)* |
| | | | 30 | 0.78 | *$CHBr_3$* | | $2.68 (DOC)^{1.28} (pH)^{-1.31} (O_3)^{0.742} (Br^-)^{1.55} (T)^{0.956} (t)^{0.353}$ |
| | | | 70 | 0.95 | *TOBr* | | $5.1 (DOC)^{1.07} (pH)^{1.05} (O_3)^{0.766} (Br^-)^{1.53} (T)^{1.08}$ *(24 hrs predictions)* |
| | | | 54 | 0.88 | *Bromate* | | $1.5 \cdot 10^{-3} (DOC)^{-0.74} (pH)^{-2.26} (O_3)^{0.64} (Br^-)^{0.61} (\theta)^{2.03}$ |
| | | | 22 | 0.64 | *Bromate* | | $1.5 (DOC)^{-0.75} (pH)^{-2.25} (\pi + 1)^{1.31} (Br^-)^{0.60}$ |
| | | | 173 | 0.68 | *Bromate* | | $0.26 (DOC)^{086} (pH)^{3.27} (DO_3)^{0.22} (Br^-)^{0.67} (t + 1)^{0.25}$ *(for $0 < t < 1$ hr)* |
| **3.** Song *et al.* | 1996 | Field | 119-239 | 0.87-0.97 | *Bromate ($BrO_3^-$)* | ∝g/L | *13 different linear regression models (one per fraction and per water source) for bromate in function of bromide, DOC, nitrogen ammonia, ozone dose, inorganic carbon and reaction time.* |
| **4**. Korn *et al.* | 2002 | Laboratory | 112 | 0.95 | *Chlorite* | mg/L | $\exp(-0.346 - 0.07 \log(pH) - 0.025 \log(T) - 0.597 \log(C + 1) - 0.136 \log(t + 1) - 0.0038 \log(NPOC \cdot UV254) + 0.293 \log(T) \cdot \log(C + 1) + 0.393 \log(pH) \cdot \log(C + 1) + 0.67 \log(NPOC \cdot UV254) \cdot \log(C + 1) - 0.161 \log(NPOC \cdot UV254) \cdot \log(t + 1)$ |
| | | | 112 | 0.95 | *Chlorate* | mg/L | $\exp(-1.99 + 0.62 \log(pH) - 0.09 (T) + 0.698 \log(C + 1) - 0.104 \log(t + 1) + 0.046 \log(NPOC \cdot UV254) + 0.389 \log(T) \cdot \log(C + 1) + 0.346 \log(C + 1) \cdot \log(t + 1) + 0.486 \log(NPOC \cdot UV254) \cdot \log(C + 1) - 0.119 \log(NPOC \cdot UV254) \cdot \log(t + 1)$ |

***<u>Nomenclature:</u>*** *DOC =dissolved organic carbon (mg/L); $O_3$ = transferred ozone doses (mg/L); pH = ozonation pH value; $Br^-$ = bromide ion concentration (∝g/L); t = reaction time (mints); UV-254 = UV absorbance ($cm^{-1}$); C = chlorine dioxide concentration (mg/L); NPOC = non-purgeable organic carbon (mg/L); T = temperature (°C); $DO_3$ = dissolved ozone concentration (mg/L); TOBr = Total organic bromine (∝g/L); $\pi$ = peroxone ratio ($H_2O_2/O_3$); and $\theta$ = ozonation temperature (°C).*

Table 7a. A description of THM, HAA and total organic halogenated (TOX) predictive models (numbers refer to models presented in Table 6a)

| Model/study description | Main advantages | Main limitations |
|---|---|---|
| **1.** Untreated water from the Holsten River (Knoxville, Tennessee) was used in this study. A series of experiments was carried out under controlled conditions of pH, temperature, bromide-ion concentration and applied chlorine dosage. Concentrations of non-volatile total organic carbon (NVTOC) were also varied using commercially available humic acid. A constant reaction time of 96-hours was used for generating TTHM data in the model development. The model was calibrated using different iterative methods. A preliminary verification of the model was performed using data derived from a field-sampling program. | Good performance of model despite the number of observations. | Models do not contain reaction time as an explanatory variable. |
| **2.** With same data set, the authors used iterative modelling methods to calibrate the model, which included Gaussian, Dud, Maruardt, and Gradient methods. The models provided acceptable fits and more than 74% of the predicted values were within ± 15% of the measured values overall. | Present alternative modelling methodologies (most authors have used regression models). | These models do not contain reaction time as an explanatory variable. |
| **3.** Modelling carried out with a database from chlorination experiments with water samples collected from the Sagami River (Japan) which were combined with a solution of humic acid. They applied several sensitivity analysis techniques to study the effects of the three main experimental variables: chlorine dose, water temperature and pH. | Considered different organic matter content in water. | Model considered neither temperature nor bromide ion concentration as explanatory variables. |
| **4.** This work is the single most extensively cited reference in THM modelling. The authors developed a comprehensive database from laboratory chlorination experiments on raw waters with variable qualities selected from nine US rivers. Linear and non-linear regression models were developed to predict THM formation potential and kinetics. Boundary conditions of explanatory variables were defined. Different models were developed for short term ($t < 8$ hr) and long term reaction times ($t > 24$ hr). | Models based on a very robust database and on several waters with variable characteristics. | Water quality and chlorination doses do not represent characteristics of treated water and operations in real water utilities. |
| **5.** The authors used the database developed by Amy *el al*. (1987a) for building predictive models for specific THMs including chloroform, BDCM, DBCM and bromoform. | Models for the different THM species are available. | Models do not represent conditions of real water utilities. |
| **6.** Authors developed a mechanistic model for DBPs based on their formation kinetics. Humic acids were isolated from Lake Kinneret (Israel) in order to undertake chlorination at laboratory scale. Models were developed to predict TTHMs as a function of concentration of humic acids, chlorine dose and contact time. | Modelling approach allows at examining the kinetics of THM formation. | It is hard to judge about model capabilities since the number of data on which it is based is not known. |
| **7.** This work resulted in the development of models for the four THMs and five HAAs. This study is one of the first that considered chlorinated DBPs other than THMs. The project combined three laboratory scale databases developed in four different studies across the US, including the work by Amy *et al*. (1987a). Different models were developed according to the ratio between chlorine dose and bromide content in water. The explanatory variables for HAAs appeared to be comparable to those for THMs. Good predictive abilities of these models were observed. | The study use independent databases for model validation. | The water quality and the chlorination conditions do not represent situations encountered in real water utilities. |
| **8.** This work was based on a field scaled study in which samples from Taipei's (Taiwan) water utility were collected twice from 18 locations during a period of six months. Using this data, the authors developed a predictive regression model for TTHMs for the distribution system as a function of TTHMs in the finished drinking water (after treatment). | The model included the water dispersion in the distribution system as an explanatory variable for THM occurrence. | Models are based on very few data points. |
| **9.** Authors developed a multiple regression model for chloroform using monthly samples (during one year) from the water treatment plant and the finished water of the city of San Sebastian (Spain). In addition to the normal water quality and operational parameters, they used fluorescence as an indicator of NOM instead of more common indicators mentioned in the literature such as TOC and UV-254. | Very simple model with relatively good results. | It has very small database. The model does not contain reaction time as an explanatory variable. |

| | | |
|---|---|---|
| **10.** In this work, one of the most comprehensive laboratory scaled databases for developing models for THMs and NPOX were established. THM and NPOX formation potentials were determined from chlorination of water samples from the Mississippi, Ohio and Missouri Rivers. Regression coefficients for explanatory variables were comparable to those presented in previous literature. With the same data generated from the three US rivers above, models were also developed for predicting THM speciation and bromine incorporation factors with accurate results (Rathbun, 1996a-c). The author found that the predictive capacity of the model did not improve with both UV-254 and DOC incorporated in the regression analysis. A similar conclusion was obtained by Ossenbruggen *et al*. (1988) who used the ridge regression technique to eliminate one or more explanatory variables that are correlated. | Models based on a very robust database representing very variable water quality. | River waters do not represent raw waters used to be treated by utilities and chlorine doses are higher than those practiced in the drinking water industry. |
| **11.** In this work, three water samples were collected at the intake of the water utility in Taiwan. Chlorination experiments were undertaken with variable chlorine dosage at a constant temperature. For each sample, they developed a single regression model representing THM formation. A simple THM model was subsequently developed combining the information of three samples. | Simple model with very good predictive ability. | Model does not consider water temperature variations. |
| **12.** In this work, samples were collected at six different locations in the water distribution system of the city of Salamanca (Spain). At each location, 11 samples were taken to represent seasonal variations of chlorinated DBPs and other water quality parameters. These models used dummy variables to consider the location within the distribution system and the effect of time of sampling. The model contained 3rd and higher order polynomials of temperature which made it highly sensitive. | The predictive model incorporates spatial and temporal variations of chloroform. | The brominated THM species are not considered. |
| **13.** Models for the formation of POX and NPOX using chlorination of fulvic acid present in water. This study was planned to investigate TOX formation, because THM accounts for only 5-20% of the TOX compounds formed during chlorination. The sensitivity analysis results revealed that mainly chlorine dosage (35%), TOC (48%), and reaction time (12%) contributed to the variability of POX. Similar results were obtained for NPOX. | Model appeared with very accurate predictive abilities. | It is not possible to adequately judging the model capabilities since the number of data on which it is based is not known. |
| **14 and 15.** In this work, a second order kinetic model is developed to describe the formation of TTHMs. In the model, the rate of reactions is considered to be proportional to the first power of the concentration product of hypochlorous acid and the substances responsible for chlorine demand. The model is validated using two different laboratory-scaled databases generated in previous work by Clark *et al*. (1994) and AWWARF/EPA study (Vasconcelos *et al*., 1996). | The model allows characterizing THM formation as a function of chlorine demand. | It is not proved that the second order model would give better predictions than first-order kinetics. |
| **16.** Authors developed multiple regression models for TTHM using the data generated from samples collected at four locations at the treatment plant of Athens (Greece). Multivariate regression models were developed for TTHM in the finished drinking water leaving the plant. A particular feature of this model is that chlorophyll-*a* was introduced in the model as an indicator of NOM. | The model represents the seasonal variations of THMs and is very accurate. | Not common NOM surrogates are considered (TOC and UV absorbance). |
| **17.** TTHM models developed throughout this work were based on data generated from untreated US River waters. The model used the similar explanatory variables in their original work (Amy *et al*., 1987a), except that their latest model uses DOC instead of both TOC and UV as indicators of NOM. | Empirical based models were developed for haloacetic acids, chloral hydrate, and bromate. | Water quality does not represent characteristics of treated water. |
| **18.** In this work, authors developed a kinetic model for THMs which incorporate the ratio between bromide ion and chlorine. The kinetic model is calibrated using data from experimental chlorination of 17 surface and ground waters (with variable characteristics) in New Zealand | Models constitute a valuable tool to analyse the impact of bromide in the THM formation kinetics | Chlorination conditions were not comparable in each sample. |

| | | |
|---|---|---|
| **19.** In this work, authors combined different databases for the development of TTHM predictive models. They combined US laboratory scale data developed by Amy *et al*. (1987a), Rathbun (1996a) and Montgomery Watson/AWWA (1991) which they validated using a field-scaled THM database for small water utilities in the province of Quebec (Canada). Field-scaled models were also developed for typical values of DOC found in raw waters of southern Quebec. Sensitivity analyses and model validations were carried out using the field-scaled database. By combining US database, Milot *et al*. (2002) developed subsequently a THM model using artificial neural networks (ANN), a method commonly used in artificial intelligence (not listed in Table 6a) (Rumelhart, 1994). | A robust database is considered to develop simple and accurate models. | Many assumptions have to be made to applied models to field-scaled data. |
| **20.** This work examines a different modelling approach for THM occurrence using logistic regression. Instead of predicting THM concentrations, the probabilities of exceeding specified values of THM (thresholds of 40, 50, 60, 80 or 100 µg/L) were estimated. Modelling was carried out using THM data collected in several utilities of the province of Quebec (Canada). | Propose an alternative modelling approach which results can be used for THM assessment in epidemiological studies. | Models do not consider operational characteristics (chlorine dose, pH) at the utilities under study. |
| **21.** Authors combined kinetics of DBP formation with empirical-based modelling using regression analysis. They used a second order rate for DBP formation and chlorine decay kinetics to predict these concentrations in water distribution systems. The coefficients of second order reaction kinetics were determined using regression models. In fact, several papers on predicting chlorine residuals and the formation of halogenated by-products have been published by these authors (Clark, 1998; Clark and Sivaganesan, 1998; Clark *et al*., 2001; Clark and Sivaganesan, 2002). Clark and co-workers developed general formulation for 13 different DBPs including 4 THMs and 9 HAAs. The general model was developed at constant TOC and temperature. The $r^2$ values were more than 0.95 except for MCAA, which was less than 0.60. | The work of the authors proposes models which integrate mechanistic and empirical methods providing a high flexibility for model application | It was not proved that this approach gives better results than classical regression models. |
| **22.** In this work, three year data were generated through sampling of nine points of the Athens (Greece) water treatment plant. In addition to THMs, temperature, pH, dose and chlorophyll-a, bromide were measured. | Models represent seasonality for THM occurrence. | The performance of models is relatively low. |
| **23.** In this work, field-scaled data for THMs and HAAs were collected in water utilities of four different regions in Spain. Models were aimed at predicting occurrence of HAA species using the THM species at predictors through multivariate regression models | Data and models have potential applications for exposure assessment in epidemiological studies. | Models do not consider chlorine dose, temperature, NOM indicators, etc. |
| **24.** Data for development of THM and HAA regression models were generated through chlorination experiments of treated waters of three utilities of the Quebec city region (Canada). In bench-scale experiments, values for water temperature, chlorine dose and contact time reproduced the operational conditions of the utilities under study. | Data from the experimental chlorination allowed representing the real seasonal variations of environmental and watering quality characteristics. | Model performance varies according to the DBP specie to be modelled and to the utility. |
| **25.** Data for modelling were generated from chlorination of samples collected in the Mississipi river. Water samples were previously pre-treated using membrane ultrafiltration in order to investigate and model the formation of THMs according to various fractions of natural organic matter. | Model allowed examining the THM formation according to the molecular weights of NOM fractions. | Developed model is usable for research but not for operational purposes. |

Table 7b. A description of predictive models for other DBPs (numbers refer to models presented in Table 6b)

| Model description | Main advantage | Main outcome |
|---|---|---|
| **1.** Authors modelled the bromate production as a result of ozonation. More than 10 different sources of water were used. The model was developed at a constant temperature of 20°C To overcome this problem, a relationship was developed to estimate bromate formation at different temperatures of water (as shown on Table 6b). Later, Sohn *et al*. (2001) successfully used the results of this study for modelling and monitoring of bromate levels in water treatment systems. | Model is relatively simple to apply. | The number of data points on which the model was based is not known. |
| **2.** In this work, a series of predictive models for brominated by-products are proposed. Data for modelling were generated by ozonating different surface waters and ground waters in the US. The data were collected from 3 water treatment plants. | Model allowed to consider the effect of water temperature on bromate formation | Model performance for bromate formation is moderate. |
| **3.** Regression models for bromate formation were based on data generated through experimental ozonation of four different surface and ground waters in the U.S. For each water sample NOM was fractionated using ultrafiltration and reverse osmosis into three different fractions. Models were developed for each ozonated fraction. Models were validated with literature data. | Very good performance of models for both calibration and external validation databases. | Variation of water temperature was not considered in the experiments. Thus, models don't allow predicting seasonal variations of bromate. |
| **4.** Models were developed using data generated during bench-scale experiments using source water from seven drinking water treatment plants in Canada. A full factorial analysis ($2^4$) design was used to conduct the experiments in this study instead of using traditional one-factor-at-a-time approach. Models for chlorine dioxide by-products proposed in this work constitute the most complete available now days in the scientific literature. | Predictive capabilities of models are very high. | Model is applicable only to similar conditions than those used for their calibration. |

Table 8. Water quality and operational parameters

| Explanatory variables | Distribution | Mean | Standard deviation | Minimum | Maximum |
|---|---|---|---|---|---|
| Chlorine dose, *D* (mg/L) | Lognormal | 15 | 10 | 2 | 50 |
| pH | Normal | 7 | 1.5 | 4 | 10 |
| Contact time, *t* (hr) | Uniform | | | 24 | 72 |
| DOC (mg/L) | Lognormal | 5 | 2 | 1.5 | 7.2 |
| Temperature, *T* (C) | Uniform | | | 20 | 30 |

Table 9. Exposure assessment models for total THM (Joe *et al.*, 1990)

| Exposure route (µg/kg·day) | Models | Definitions of terminology |
|---|---|---|
| Ingestion | $I_g = E_i \cdot C_w \cdot A_w/W$ | $E_i$ = Absorptional efficiency of TTHM from gastro-intestinal tract = 1.0 |
| Inhalation<br>(shower only) | $I_h = E_r \cdot C_a \cdot R \cdot T/W$<br>where<br>$C_a = 10.45 \cdot (C_w) - 99.6$ | $C_w$ = TTHM concentration in water (∝g/L)<br>$A_w$ = Water amount ingested (L/day) = Normal ~ (2,0.5)<br>W = Body weight (kg) = Lognormal ~ (60,6)<br>T = Shower time = 10 min./day<br>R = Breathing rate = 0.014 $m^3$/min. |
| Dermal | $D_r = F \cdot I_h$ | $E_r$ = Absorptional efficiency via respiratory tract = 0.77<br>$C_a$ = TTHM concentration in shower (∝g/$m^3$)<br>F = Ratio of body burden from dermal exposure to that of inhalation exposure = 0.93 |