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MODELLING THE FORMATION OF BROMINATED TRIHALOMETHANES IN CHLORINATED DRINKING WATERS

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Abstract—The chlorination of water containing bromide and natural organic matter (NOM) leads to the formation of brominated trihalomethanes (THMs). The extent of brominated THM formation depends, *inter alia*, on the bromide:chlorine concentration ratio ([Br⁻]:[chlorine]). A reaction scheme is proposed from which a simple kinetic model is developed that mathematically relates the extent of bromination, and the relative abundances of the four THMs, to the [Br⁻]:[chlorine] ratio. In the scheme, the trihalogenated precursors to THMs are formed by three steps each of which substitutes either bromine or chlorine into an activated carbon site in the NOM. This leads to six pairs of competing bromination:chlorination reactions, whose rate constant ratios ($k_b:k_c$) have been estimated by using the model to fit THM data obtained from the chlorination of 17 waters from New Zealand. The individual $k_b:k_c$ ratios range from 4 to 15. From a plot of the ratio of total bromine to total chlorine present in the THMs as a function of the [Br⁻]:[chlorine] ratio, an apparent overall $k_b:k_c$ ratio of 9.1 is obtained.

Using USEPA cancer potency factors, the model is used to predict the relative cancer risk associated with THMs as a function of the $[Br^-]$:[chlorine] ratio. This risk increases steeply to a peak at a $[Br^-]$:[chlorine] ratio of approximately 0.15, then gradually decreases to the value associated with bromoform alone. The risk associated with THMs may vary considerably through changes in the $[Br^-]$:[chlorine] ratio as the result of natural variation in the $[Br^-]$, or through poor control of chlorine dosing. \bigcirc 1999 Elsevier Science Ltd. All rights reserved

Key words-bromination, disinfection by-products, drinking water, kinetics, trihalomethanes

INTRODUCTION

Reactions between chlorine (hypochlorous acid and hypochlorite ion) and natural organic matter (NOM) in water form a wide range of halogenated and non-halogenated compounds (de Leer *et al.*, 1985; Stevens *et al.*, 1989). The halogen-containing compounds appearing in the highest concentrations are small organic molecules, such as the trihalomethanes (THMs) and haloacetic acids (HAA) (Reckhow *et al.*, 1990). As might be expected, the prevalent halogen in these compounds is chlorine. However, where bromide is present in the raw water, even at trace levels, disinfection by-products (DBPs) with varying degrees of bromine substitution are also found (Cooper *et al.*, 1985).

Bromine substitution is a consequence of the rapid oxidation of bromide to bromine (hypobromous acid and hypobromite ion) by chlorine (Wong and Davidson, 1977). Once formed, bromine is capable of participating in reactions analogous to those of chlorine. The presence of both halogens

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leads to competition for substitution at suitable carbon atoms in the NOM, with the eventual production of DBPs containing chlorine, bromine, or a mixture of both. The relative rates at which chlorine and bromine react with NOM determine the extent to which each halogen appears in the DBPs (Morris, 1978). The composition of the NOM, particularly the degree of aromaticity and the nature and position of the functionalities within the aromatic structures, also have an influence on the relative amounts of chlorine and bromine incorporated into the organic matter (Rook, 1980; Boyce and Hornig, 1983; Heller-Grossman et al., 1993). Hypobromous acid (HOBr) has been noted to be a more powerful halogenating agent than hypochlorous acid (HOCl) (Morris, 1978), and this results in reactions incorporating bromine into NOM being faster than those incorporating chlorine (Symons et al., 1993).

This paper examines the incorporation of bromine into THMs from a kinetic standpoint. It does so using data collected as part of a programme, funded by the New Zealand Ministry of Health, the prime purpose of which is to identify chemical contaminants of health significance within the country's

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drinking-water supplies. As part of this programme, water samples are collected prior to chlorination for subsequent distribution system simulation experiments. Data from these experiments are the basis of the work reported here.

The chlorination conditions in the simulation experiments, though non-uniform, are defined, and the presence of measurable concentrations of bromide in some of the raw waters has provided the opportunity to address the following questions:

- 1. Can the extent of bromine incorporation, and the relative abundances of the four THMs, be mathematically related to the bromide:chlorine dose ratio?
- 2. Can measures of the relative rates of bromination and chlorination be extracted from the data?

The simple kinetic model described here was developed to seek answers to these questions. The paper discusses: how the model allows estimates of the relative rate constants for bromination and chlorination to be obtained from the data; the ability of the model to calculate the relative abundances of the four THMs as a function of the bromide:chlorine ratio; the model's limitations; and the use of the model to estimate how the bromide:chlorine ratio influences the cancer risk associated with THMs.

EXPERIMENTAL PROCEDURES AND METHODS

Chlorination procedure

Waters from New Zealand drinking-water supplies were sampled prior to their chlorination point, and stored in the dark at 4°C before chlorination in the laboratory. Chlorination conditions [pH, temperature, contact time and target free available chlorine (FAC) residual] were set to approximate distribution system conditions. The chlorine dose required to yield the target FAC was determined for each water by a chlorine demand measurement.

Chlorine demand measurements. Two sub-samples of each water were chlorinated, one at the chlorine dose estimated by the water supplier, and the second at twice this level. Sample chlorination was achieved by the addition of an appropriate volume of 10,000 mg/l (as Cl₂) chlorine solution. During the reaction, the samples were kept dark in a water bath thermostated at 13, 18 or $23^{\circ}C$ ($\pm 0.2^{\circ}C$), whichever was above, and closest to, the highest annual distribution system water temperature. After the required contact time the FAC residual was measured, and from the two sub-sample values an estimate was made of the chlorine dose required to obtain the target residual.

THM formation. The pH of a 500 ml sample of each water was adjusted using a small volume of concentrated phosphate buffer (based on tables contained in CRC, 1982). The sample was then chlorinated using the dose estimated from the chlorine demand measurement, the pH checked, and if necessary, adjusted by the drop-wise addition of 0.1 M HCl or 0.1 M NaOH. Sub-samples for THM formation were then rapidly poured into 100-ml amber glass bottles and the bottles firmly sealed with teflon-lined lids. In the same way, a 120 ml sub-sample was prepared to provide a measure of the chlorine residual when the reaction was quenched. The bottles were then

placed in a thermostated bath, and covered to exclude light. After the required contact time, the chlorine in the bottle designated for THM formation was quenched with 0.1 ml of 100 g/l sodium sulphite, and the pH lowered with 0.1 ml of conc HCl. The samples were stored in the dark at 4°C until analysis.

Analytical reagents and methods

All solutions used in this work were prepared with Millipore MilliQ (18 M Ω) deionized water. All reagents were analytical grade with the exception of the commercial lithium hypochlorite used to prepare the chlorinating solution, and the DPD indicator (BDH) used in the FAC titrations. Ultra-violet absorbance, bromide and total organic carbon (TOC) measurements were made on the samples before chlorination.

pH measurement. pH measurements were made using a radiometer PHM64 research pH meter with a GK 2401C electrode, calibrated with BDH "Colourkey" pH 4 and 7 buffer solutions.

Absorbance at 254 nm (A_{254}). A_{254} measurements were made in 1 cm path length quartz cells in a Perkin-Elmer Lambda 3B UV–VIS spectrophotometer. Measurements were made directly on the sample without pH adjustment.

TOC. A Dohrmann DC-180 TOC analyser with uv/persulphate digestion and using a 1 or 2 ml injection loop (depending on the organic content of the water) was used for the TOC measurements.

Bromide. Bromide concentrations were measured using suppressed ion chromatography (Dionex 4000i) fitted with an AS-14 column and an eluent composition of 3.5 mM Na₂CO₃/1.0 mM NaHCO₃. Injection loop volume was 50 μ l.

FAC. The FAC was determined by the DPD ferrous sulphate titration method, 4500-Cl F, APHA et al. (1992).

THM. THM measurements were made following USEPA Method 551. A Hewlett Packard HP5890 gas chromatograph with HP5970 mass selective detector was used for analysis. The column used was a DB5MS (30 m × 0.25 mm id & $1.0 \,\mu$ m). Operating software was G1701 AAMS Chemstation.



Fig. 1. Reaction scheme used as the basis for the development of the kinetic model.

Data processing

Model calculations were carried out using Microsoft[®] EXCEL version 7.0. A least-squares method was used to fit the data in Fig. 2, but the optimization of the model's parameters for Fig. 4 was achieved by judgement of the goodness of fit by eye; mathematically derived fits were poorer because of the model's limitations under some conditions, as discussed below.

THE MODEL

Concepts and mathematical development

The fundamental premise of this model is that the relative concentrations of the four THM species are *kinetically controlled*, i.e. that the relative rates of the competing halogenation reactions control the distribution of the reaction products. In practice, this means that sufficient bromide and chlorine must be present in the water to ensure that neither halogen is totally consumed during the reaction. For waters chlorinated to provide a free chlorine residual, as is the case here, this requirement is met for chlorine at least.

The conceptual basis for the model is shown schematically in Fig. 1. The starting points are activated carbon atoms, C^* , in the NOM. These are carbon atoms that undergo halogen substitution to form the carbon of the THM molecules. The model makes no assumptions as to how activated carbon atoms are formed; this is immaterial to its development.

The scheme allows two possible reaction outcomes from C^* : either chlorination to incorporate one chlorine atom, or bromination to incorporate one bromine atom. The mono-halogenated reaction intermediates may then each undergo either chlorination or bromination, and so this process continues until the trihalo-intermediates, from which the THMs are eventually formed, are produced. The reaction scheme therefore develops with a "tier" of intermediates after each halogenation step. The trihalogenated carbon atom of the final intermediate has been postulated to be part of a trihaloacetyl group, and base hydrolysis to be the final step leading to the THM (Peters *et al.*, 1980; Boyce and Hornig, 1983; Reckhow and Singer, 1985). The rate of this final step will not influence the ratio of bromine:chlorine incorporation because it is subsequent to the halogenation steps. However, unless THM formation in a water is complete when the measurements are made, differences in the rates of hydrolysis of the different intermediates (Aizawa *et al.*, 1989), and hence rates at which different THMs are formed, may affect the apparent bromine:chlorine incorporation ratio.

The concentrations of the four trihalo-intermediates are determined by the relative rates of chlorination and bromination at each intermediate. Twelve rate equations arise from the reaction steps of Fig. 1. It is assumed that the rate of any step, A, in the reaction scheme is given by:

Rate of
$$A = k_A$$
[HOX][Intermediate], (1)

where [HOX] is the concentration of the reacting hypohalous acid, [Intermediate] is the concentration of the intermediate (or C^{*}) with which it reacts, and k_A is the rate constant for that process. All concentrations are molar.

To make the derivation of expressions for the four trihalo-intermediates tractable, two simplifying approximations are required. First, changes in the concentrations of bromine and chlorine during the period in which the trihalo-intermediates are formed are relatively small, hence the rates of reaction of the intermediates are pseudo-first order with respect to the intermediates. Second, the rates of change of the mono- and dihalogenated intermediate concentrations during the reaction are very small. This allows the steady-state approximation to be made and simplified expressions for these two types of intermediate to be derived.

On the basis of these approximations the following expressions for the concentrations of the trihalo-intermediates are obtained:

$$[CCl_{3}] = \frac{k_{1}k_{3}k_{7}[HOC1]^{3}[C^{*}]_{0}}{(k_{1}[HOC1] + k_{2}[HOBr])(k_{3}[HOC1] + k_{4}[HOBr])(k_{7}[HOC1] + k_{8}[HOBr])}$$
(2)
$$[CCl_{2}Br] = \left(\frac{(k_{1}k_{3}k_{8}[HOC1]^{2}[HOBr])/((k_{3}[HOC1] + k_{4}[HOBr])(k_{7}[HOC1] + k_{8}[HOBr])) + k_{9}[HOC1]/\alpha}{(k_{1}[HOC1] + k_{2}[HOBr])}\right)$$
(3)
$$[CClBr_{2}] = \left(\frac{(k_{10}[HOBr]/\alpha) + (k_{2}k_{6}k_{11}[HOC1][HOBr]^{2})/((k_{5}[HOC1] + k_{6}[HOBr])(k_{11}[HOC1] + k_{12}[HOBr]))}{(k_{1}[HOC1] + k_{2}[HOBr])}\right)$$
×
$$[C^{*}]_{0}$$

(4)

$$[CBr_3] = \frac{k_2 k_6 k_{12} [HOBr]^3 [C^*]_0}{(k_1 [HOC1] + k_2 [HOBr])(k_5 [HOC1] + k_6 [HOBr])(k_{11} [HOC1] + k_{12} [HOBr])}$$

where $[C^*]_0$ is the initial C^* concentration and

$$\alpha = \left(\frac{k_1k_4}{(k_3[\text{HOC1}] + k_4[\text{HOBr}])} + \frac{k_2k_5}{(k_5[\text{HOC1}] + k_6[\text{HOBr}])}\right) \left(\frac{[\text{HOC1}][\text{HOBr}]}{(k_9[\text{HOC1}] + k_{10}[\text{HOBr}])}\right).$$



Fig. 2. The dependence of the molar ratio of bromine to chlorine incorporation into trihalomethanes on the [Br⁻]:[chlorine] ratio.



Fig. 3. The dependence of the molar ratio of bromine to total halogen incorporation into trihalomethanes on the [Br⁻]:[chlorine] ratio.

(5)

The *relative* concentrations of the four THMs are the same as those of the four trihalo-intermediates given by equations (2–5), provided: THM formation is complete when the measurements are made; and the percentage of each trihalo-intermediate that is converted to its corresponding THM (rather than other products) is the same for each intermediate.

Halogenating agents

Halogens in drinking waters exist in two forms,

the hypohalous acid and its dissociated form, the hypohalite ion. In equations (1-5) the hypohalous acids have been denoted as the species reacting with the NOM, because they are considered to be better halogenating agents than the corresponding hypohalite ions (Morris, 1978). However, better matches between calculated and experimental data are obtained when the total halogen concentrations (hypohalous acid plus hypohalite ion) are substituted for the hypohalous acid concentrations. For this reason, when equations (6 and 7) are derived,



Fig. 4. The influence of the [Br⁻]:[chlorine] ratio on the percentage of the total molar concentration of trihalomethanes constituted by each of the four trihalomethanes. (a) CHCl₃; (b) CHCl₂Br; (c) CHClBr₂; (d) CHBr₃. Circles are experimental data; lines are calculated.

chlorine and bromine (the total halogen concentrations) are identified as the halogenating agents rather than the hypohalous acids alone.

Estimates of the chlorine and bromine concentrations are required for the plots in Figs 2–5, but neither halogen concentration was monitored during the course of the reactions. Initial and final chlorine concentrations are known, but neither is a suitable approximation for the concentration of the chlorinating species; some intermediate conzcentration is likely to be a better estimate. Consequently, for this work, the chlorine concentration is approximated by the "average chlorine concentration", defined as:

(Initial chlorine dose + Final FAC residual)/2

This is abbreviated to [chlorine].

The concentration of bromine during the halogenation reaction is assumed to be approximately equal to the initial bromide concentration (in molar terms), [Br⁻], because the possible re-oxidation of bromide to bromine assists in maintaining the bromine concentration.



Fig. 4 (continued)



Fig. 5. Dependence of the cancer risk associated with trihalomethanes on the [Br⁻]:[chlorine] ratio relative to that due to chloroform alone.

RESULTS AND DISCUSSION

Raw waters and their characteristics

The data sets used here were obtained from 17 waters, all of which originated in the North Island of New Zealand. The data sets were selected according to two criteria: the minimum bromide concentration in the water was to be no less than 0.05 mg/l (the method detection limit); and the minimum total THM concentration was required to be 1×10^{-4} M to ensure an acceptable percentage uncertainty in the concentrations. Of the 17 waters, six were groundwaters, 10 were surface waters and one was a mix of ground and surface waters. Four characteristics of the 17 waters are given in Table 1.

An indication of the humic and fulvic acid content of the NOM in these waters, and hence the

degree of aromaticity of the organic matter, is provided by the A_{254} :TOC ratio. Reckhow et al. (1990), using organic matter from aquatic sources, reported ratios of 0.03-0.04 and 0.05-0.07 (AU 1/ mg-C) for fulvic and humic acid fractions respectively. Some of the waters (5, 9, 13, 17) in Table 1 show ratios considerably less than 0.03. These are all groundwaters, with the exception of water 5, and all have low, or relatively low, TOC concentrations. All other waters possess A_{254} :TOC ratios that fall within the 0.025-0.044 (AU l/mg-C) range. Using the A_{254} :TOC ratios reported by Reckhow's group as a guide, the humic substances in these waters appear to be predominantly fulvic, rather than humic, acids, and are probably of low to moderate aromaticity.

Table 1. Characteristics of the waters studied. Abbreviations: TOC-total organic carbon; A_{254} -absorbance at 254 nm (path-length = 1 cm); AU-absorbance units

Supply number	Source type	TOC (mg-C/l)	A_{254} (AU)	Br ⁻ (mg/l)	A_{254}/TOC (AU/mg-C/l)
1	surface	3.5	0.15	0.08	0.043
2	surface	3.4	0.15	0.05	0.044
3	surface	1.0	0.03	0.05	0.030
4	surface	1.2	0.03	0.05	0.025
5	surface	0.6	0.01	0.18	0.017
6	surface	3.4	0.12	0.08	0.035
7	surface	4.2	0.16	0.09	0.038
8	surface	2.5	0.11	0.09	0.044
9	ground	1.1	0.02	0.80	0.018
10	ground	0.8	0.03	0.09	0.038
11	ground	1.6	0.06	0.06	0.038
12	surface/ground	1.1	0.04	0.06	0.036
13	ground	0.6	0.01	0.70	0.017
14	ground	1.6	0.06	0.09	0.038
15	surface	1.0	0.03	0.05	0.030
16	surface	2.2	0.09	0.11	0.041
17	ground	1.3	0.02	0.20	0.015

Table 2. Chlorination conditions used for each water. Abbreviation: FAC-free available chlorine

Supply number	Temp (°C)	pH	Contact time (hr)	Cl ₂ dose (mg/l as Cl ₂)	FAC residual (mg/l as Cl ₂)
1	23	7.5	24	5.0	0.4
2†	23	7.2	40	5.0	0.0
3	23	7.6	48	3.0	0.3
4	23	7.3	36	3.0	0.1
5	18	7.1	24	1.0	0.3
6	13	7.0	48	5.0	0.3
7	18	7.8	10	4.5	0.6
8	18	6.9	48	5.0	1.0
9	13	8.1	24	2.5	0.8
10	13	7.9	168	1.2	0.6
11	13	8.4	6	1.0	0.3
12	18	7.6	6	1.2	0.3
13	18	7.8	24	5.0	2.2
14	18	7.4	24	2.8	0.5
15	23	7.8	36	2.0	0.1
16	23	7.2	48	3.5	0.4
17	13	7.7	36	1.0	0.2

[†]The FAC residual for this water dropped to zero before the end of the contact period.

THM formation

Listed in Table 2 are the five parameters defining the chlorination conditions for each water. The range of chlorination conditions is wide, and reflects the conditions water suppliers stated would allow simulation of their distribution system. The concentrations of the four THMs produced in each water are contained in Table 3.

The effect of the $[Br^-]$: [chlorine] ratio on the incorporation of bromine into THMs

The molar ratio of Br-TTHM (total concentration of bromine in THMs) to Cl-TTHM (total concentration of chlorine in THMs) is plotted as a function of the [Br⁻]:[chlorine] molar ratio in Fig. 2. While the differing experimental conditions have contributed to scatter in the data, a straight line, having a slope of approximately 9.1, can be fit well to the plot ($r^2 = 0.96$). Equation (6), which describes this relationship, can be derived from equations (2–5). These equations allow for the possibility that all bromination and chlorination rate constants are

different. However, the simplest hypothesis that can account for the linear relationship of Fig. 2 is that all bromination rate constants are the same (i.e. $k_2 = k_4 = k_6 \dots = k_b$), and that the same is true of the chlorination rate constants (i.e. $k_1 = k_3 = k_5 \dots = k_c$). Introducing this assumption and the approximations for the halogenating agents noted earlier, yields:

$$\frac{\text{Br}-\text{TTHM}}{\text{Cl}-\text{TTHM}} = \frac{k_{\text{b}}[\text{Br}^{-}]}{k_{\text{c}}[\text{chlorine}]}.$$
 (6)

Thus the slope of Fig. 2 provides an estimate of the $k_b:k_c$ ratio. The value of 9.1 for this ratio is consistent with bromination of NOM being a faster process than chlorination (Symons *et al.*, 1993). Note that the $k_b:k_c$ ratio value is dependent on the assumptions made in estimating the concentrations of bromine and chlorine reacting with the NOM.

An expression for the relationship between the Br-TTHM:X-TTHM (the total molar concentration of both halogens present in THMs) ratio and the [Br⁻]:[chlorine] ratio can also be obtained:

Supply number	CHCl ₃ (µg/l)	CHCl ₂ Br (µg/l)	CHClBr ₂ (µg/l)	CHBr ₃ (µg/l)
1	104	24	4.1	< 0.3
2	156	17	< 0.3	< 0.3
3	52	24	6.3	< 0.3
4	36	20	5.4	< 0.3
5	0.7	3.1	10	9.8
6	71	22	4.0	< 0.3
7	72	26	5.3	< 0.3
8	154	6	< 0.3	< 0.3
9	0.8	3.1	11	20
10	10	13	15	4.8
11	6.3	5.8	3.0	< 0.3
12	8.9	9	4.6	0.3
13	1.5	3.3	7.8	7.6
14	11	12	9.1	1.1
15	17	13	6.8	< 0.3
16	42	26	10	0.4
17	1	4	16	24

Table 3. Trihalomethane formation following chlorination of each water

$$\frac{\text{Br}-\text{TTHM}}{\text{X}-\text{TTHM}} = \frac{k_{\text{b}}[\text{Br}^-]/k_{\text{c}}[\text{chlorine}]}{(1+k_{\text{b}}[\text{Br}^-]/k_{\text{c}}[\text{chlorine}])}.$$
 (7)

Multiplying the Br–TTHM:X–TTHM ratio by a factor of three yields the *bromine incorporation factor* proposed by Gould *et al.* (1983) and since used by other groups (Symons *et al.*, 1993; Sketchell *et al.*, 1995). Equation (7) therefore provides a mathematical basis for the form of the relationship between the bromine incorporation factor and the [Br[–]]:[chlorine] ratio. The Br–TTHM:X–TTHM ratio is plotted as a function of the [Br[–]]:[chlorine] ratio in Fig. 3, in which the line is the calculated Br–TTHM:X–TTHM ratio obtained by substituting the $k_b:k_c$ ratio from the slope of Fig. 1 into equation (7).

The form of the plot in Fig. 3 is as expected from equation (7). However, where as the calculated line passes through the origin, extrapolation of the experimental data would result in a positive intercept with the horizontal axis. A similar effect, not expected from equation (6), is evident in Fig. 2; the collection of points at low [Br-]:[chlorine] ratios in this figure also pulls the regression fit to a positive intercept with the horizontal axis. In both figures the amount of bromine incorporated into THMs at low [Br-]:[chlorine] ratios is less than that calculated by the model. This behaviour probably arises from a significant, or total, depletion of the bromide during THM formation. This will progressively reduce the rate of bromination during the reaction, and should bromide be fully consumed, incorporation will be limited by its concentration rather than its ability to compete kinetically with chlorine, as assumed in the model.

This explanation for the discrepancy between observation and the model calculations is supported by the data in Tables 1 and 2. Waters with a low [Br⁻]:[chlorine] ratio are seen to have a high [TOC]:[Br-] ratio, and therefore their bromide content may not exceed their $[C^*]$. If it is assumed that the total concentration of THMs produced in a water is an indication of the minimum [C*] available for reaction with bromine, then for the bromide to be in excess, its concentration must exceed the THM concentration by at least a factor of three. Carrying out this calculation shows that the [Br⁻] meets this criterion in only four waters with a [Br]:[chlorine] ratio less than 0.1. The criterion is met by all four waters with [Br-]:[chlorine] ratios greater than 0.1.

The effect of the $[Br^-]$: [chlorine] ratio on the formation of the individual THMs

The relative concentrations of the four THMs, expressed as molar percentages of the total THM concentration, are plotted as a function of the [Br⁻]:[chlorine] ratio in Fig. 4. The characteristics of these plots are similar to those found by others (Minear and Bird, 1980; Oliver, 1980; Aizawa *et al.*,

1989). The chloroform concentration (Fig. 4(a)) shows a constant, and initially steep, decline with increasing [Br⁻]:[chlorine] ratio as bromination reactions begin to compete effectively with the chlorination reactions. The effectiveness of this competition increases as first bromodichloro-methane [Fig. 4(b)], then dibromochloromethane [Fig. 4(c)], reaches a maximum concentration before gradually decaying as the formation of the next THM in the series increases in probability. The bromoform concentration gradually increases [Fig. 4(d)], until, at very high [Br⁻]:[chlorine] ratios, (not present with these data) bromoform is virtually the only THM in the water.

The agreement of the experimental data with the model calculations (shown as lines) in Fig. 4 is remarkably good considering the wide range of chlorination conditions used in the experiments and the use of many different source waters. This said, the deviations of the experimental data from the calculated values in Figs 2 and 3 are also evident in Fig. 4. Below a [Br⁻]:[chlorine] ratio of 0.1, all chloroform concentrations lie above the calculated values. The concentrations of all the brominated THMs, on the other hand, tend to fall below the model line at low [Br⁻]:[chlorine] ratios. Again, this is consistent with halogen incorporation into THMs kinetically controlled not being at these [Br⁻]:[chlorine] ratios.

The fits to the plots in Fig. 4 were calculated using equations (2–5). The $k_b:k_c$ ratios that yielded the best fits are given in Table 4; absolute values for k_b and k_c do not affect the fit. Although the data in Table 4 show that the $k_{\rm b}:k_{\rm c}$ ratio is not the same for all reaction pairs in Fig. 1, as assumed in the derivation of equations (6 and 7), this combination of rate constant values still results in a linear plot of Br-TTHM:Cl-TTHM vs [Br-]:[chlorine] when the model is used to calculate Br-TTHM:Cl-TTHM values from input [Br-]:[chlorine] ratios. Furthermore, the slope of the plot is 9.5, which is in good agreement with the experimental value of 9.1. The $k_{\rm b}:k_{\rm c}$ ratio determined from the slope of Fig. 2 is therefore best regarded as an "overall" ratio resulting from the combined effects of the various reaction steps. The rate at which the halogenation of activated carbon sites in NOM occurs will depend upon the structural features of the NOM (Boyce and Hornig, 1983; Heller-Grossman et al.,

Table 4. Values obtained for $k_{b}:k_{c}$ ratios from the optimization of the fits to the data plotted in Fig. 4

$k_{\rm b}:k_{\rm c}$ ratio	Best fit valu	
k_2/k_1	8	
k_4/k_3	6	
k_{6}/k_{5}	9	
k_{8}/k_{7}	4	
k10/k9	10	
k_{12}/k_{11}	15	

1993). The A_{254} :TOC ratios for the waters in this study show that most NOM is of low to moderate aromaticity. NOM in other waters may possess quite different characteristics, and consequently may show different $k_{\rm b}:k_{\rm c}$ ratios from those determined here.

While the ratios of Table 2 are not the same for all reaction pairs in Fig. 1, there is a pattern to the variation in the ratios. For a given "tier" of intermediates (see Fig. 1), the $k_{\rm b}:k_{\rm c}$ ratio increases with the extent of bromine substitution. This cannot be explained by steric effects controlling the rate of reaction, because $k_{\rm b}:k_{\rm c}$ increases despite the increasing bulk of the halogens surrounding the central carbon atom. However, differences in the charge induced on the carbon atom as a result of changes in the bromine:chlorine substitution ratio may favour further bromine attack over chlorine attack, so that polarization effects dictate the kinetics of halogen incorporation.

The rate of hydrolysis of the trihalo-intermediates to form the corresponding THMs is reported to increase with increasing bromine content of the intermediate (Luong *et al.*, 1982; Aizawa *et al.*, 1989). The model takes no account of the step from the trihalo-intermediate to the THM, hence if the reaction is incomplete when it is quenched for measurement of the THMs, differences in the rate of the hydrolysis step may result in higher values for k_{10} : k_{9} and k_{12} : k_{11} being required to fit the data.

Figure 1 shows that there is a hierarchy of reaction steps: the first halogenation step influences the concentrations of all intermediates, while the influence of each of the final halogenation steps is much more localized. This has consequences for the sensitivity of the fit to the individual $k_{\rm b}:k_{\rm c}$ values, and for the "overall" $k_{\rm b}:k_{\rm c}$ ratio calculated from the individual ratios. The calculated fits to the four plots in Fig. 3 are most sensitive to the $k_2:k_1$ ratio, and least sensitive to the $k_{\rm b}:k_{\rm c}$ ratios of the reaction pairs leading to the trihalo-intermediates. The uncertainties in the k value ratios therefore increase in the order $k_2:k_1 < k_4:k_3$, $k_6:k_5 < k_8:k_7$, $k_{10}:k_9$, k_{12} : k_{11} . In a similar way, the calculated "overall" $k_{\rm b}$: $k_{\rm c}$ ratio is influenced more strongly by the early reaction steps than the final reaction steps. Hence, a calculated "overall" $k_{\rm b}:k_{\rm c}$ ratio may be close to the value of the $k_2:k_1$ ratio despite the $k_{10}:k_9$ and k_{12} : k_{11} values being much greater.

This work has been concerned primarily with establishing an understanding of how the [Br⁻]:[chlorine] ratio influences bromine incorporation, and the data set is not ideal for establishing the effects of pH. A pH effect would be expected if the hypohalous acids are the only significant halogenating agents, because of the pH-dependent dissociation of hypohalous acids, and further work would be of value in clarifying the influence of pH to assist in refinement of the model. Ichihashi *et al.* (1999), although working with different experimental conditions, have found the THM distribution to be pH-independent.

Evaluation of the risk associated with THMs

The present understanding of the toxicology of the four THMs indicates that the brominated THMs represent more of a risk to public health than chloroform. The USEPA (1994) has calculated cancer potency factors for chloroform, bromodichloromethane and bromoform of 6.1×10^{-3} , 6.2×10^{-2} and 7.9×10^{-3} (mg/kg/day)⁻¹, respectively. It considers evidence of the carcinogenicity of dibromochloromethane to be limited, and consequently has not calculated a potency factor for it. For the purposes of calculating cancer risk associated with THMs, Black *et al.* (1996) have assumed the potency factor for dibromochloromethane to be the same as that for bromodichloromethane.

Using the USEPA potency factors, and making the same assumption as Black *et al.* regarding the potency factor for dibromochloromethane, the model developed here can be used to determine how the relative cancer risk associated with THMs changes with $[Br^-]$:[chlorine] ratio. The theoretical relative risk associated with each individual THM, and the summed risk, are plotted in Fig. 5. The calculations assume a fixed $[C^*]$. The form of these plots is independent of the TOC concentration provided $[Br^-]$ and [chlorine] exceed $[C^*]$. This ensures that halogen incorporation is kinetically controlled.

Figure 5 shows that the total risk due to THMs in a water increases very rapidly as the [Br⁻]:[chlorine] ratio increases to approximately 0.15, after which the risk slowly decreases to the value associated with bromoform alone at high [Br⁻]:[chlorine] ratios. The form of the plot is primarily controlled by the rise and fall in the concentrations of the two mixed-halogen THMs and their greater cancer potency factors.

Chlorinated waters with low, variable concentrations of bromide may therefore undergo significant changes in the risk associated with THMs. Such situations may arise in bores near the coast that are subject to varying degrees of sea-water intrusion depending on the tide. Poor control of the chlorination of any water containing bromide may also create changes in the [Br⁻]:[chlorine] ratio resulting in marked changes in risk associated with THMs. In both cases, any changes in absolute THM concentrations will also lead to changes in the risk arising from THMs.

SUMMARY AND CONCLUSIONS

The chlorination of water containing bromide and natural organic matter leads to the formation of trihalomethanes (THMs) containing bromine. One of the factors that affects the extent of this incorporation is the $[Br^-]$:[chlorine] ratio. A reaction scheme, in which each step incorporating a halogen into the organic matter is considered separately, has been used to develop a simple kinetic model to mathematically describe the extent of bromine incorporation into THMs. For each reaction step, the rate constant ratio for the competing bromination and chlorination reactions has been estimated by using the model to fit THM data obtained from the chlorination of 17 waters whose organic matter was predominantly fulvic rather than humic in character. While the parameters obtained from these waters fit the experimental data well, they may not be appropriate for waters with organic matter of a different nature.

The model:

- interprets the slope of the linear relationship between the Br-TTHM:Cl-TTHM ratio and the [Br⁻]:[chlorine] ratio in terms of an "overall" bromination:chlorination rate constant ratio, which, on the basis of the data used in this study, has an approximate value of 9;
- provides a mathematical expression for the form of the Br-TTHM:X-TTHM ratio vs [Br⁻]:[chlorine] ratio plot;
- provides expressions for the relative concentrations of the four THMs;
- calculates relative THM concentrations produced in the waters as a function of the [Br⁻]:[chlorine] ratio which match the observed data well, despite the range of chlorination conditions used;
- calculates too little bromine incorporation into THMs where the bromide present is not in excess of reactive sites in the natural organic matter;
- allows the relative cancer risk, with respect to chloroform, associated with THMs to be calculated as a function of the [Br⁻]:[chlorine] ratio, and shows that situations in which this ratio is variable (e.g. seawater-intrusion, poor chlorination control) may lead to marked changes in the risk associated with THMs.

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