

Prediction of Total organic halogen (TOX), Trihalomethanes (THMs) Formation and Residual Chlorine Decay by Sequential First-Order Parallel Reaction Model

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A series of simple and practical kinetic equations were developed based on a sequential first-order parallel reaction model for the prediction of total organic halogen (TOX), trihalomethanes (THMs) formation and residual chlorine decay. In place of the determination of the actual reactive sites in the precursors, the concept of prospective reactive sites of precursors expressed in terms of TOX and THMs concentration was incorporated into the sequential first-order parallel reaction model. These prospective reactive sites of precursors were categorized into three groups according to the difference of TOX, THMs formation rate or chlorine decay rate, and their concentration were successfully expressed as a function of UV absorbance at 260 nm (E260) and chlorine dose. The concentration of TOX, THMs, and residual chlorine predicted by the proposed model were found to be in reasonable agreement with the observed data obtained by the use of different types of natural water samples. As TOX, THMs, and residual chlorine levels at any contact time can be easily predicted by this model using just only E260, chlorine dose, and temperature, this model may be used for the simple management of chlorination process.

1. Introduction

There has been a concern that chlorination of water, while providing protection against microbial and estrogenic chemical risks^{1,2}, could also pose chemically induced cancer risks for human³. Although numerous amount of reports concerning THMs formation have been presented since the discovery of haloforms formed as a result of chlorination of natural waters,³⁻²⁹ relatively little work of a practical nature has been done on the kinetics of TOX and THMs formation and chlorine consumption.¹⁰⁻¹⁷ The factors so far reported that might influence the rate or amount of THMs formation are; pH, temperature, contact time, chlorine concentration, precursor concentration, type of precursor, and inorganic concentration such as ammonia or bromide ion. Among these factors, reports concerning pH, temperature, contact time, chlorine concentration, bromide ion, and precursor concentration are found elsewhere.³⁻¹⁹ Some uncertainty, however, still exists about the effect of ammonia

concentration, reaction temperature, and the types of organic precursors on the rate and the yield of TOX or THMs. For example, if there are measurable levels of ammonia nitrogen as $\text{NH}_4\text{-N}$ in water, not all of the chlorine applied initially appears as free chlorine. Thus, in order to predict the concentration of THMs formed from the water containing ammonia as a result of chlorine dose, it is necessary to estimate the concentration of free chlorine consumable by ammonia so that actual free chlorine (effective chlorine = free chlorine dosed – free chlorine reacted with ammonia) could be found out. Stevens et al.⁴ reported based on the restricted experimental results that during chlorination of water where ammonia breakpoint is not achieved, very little THMs is produced. Rebhum et al.¹⁹ mentioned that in ammonia-containing but bromide-free water, monochloramine formation is the fastest reaction, therefore, in very low-bromide waters, very little THMs is obtained before the breakpoint. In this case, effective chlorine may be determined on the basis of simple stoichiometry of breakpoint where free chlorine is not available, by taking into account ambient levels of ammonia. However, the rate of conversion of free chlorine to chloramines depends on pH, temperature, and the chlorine to ammonia ratio. Thus, as Symons et al.⁷ pointed out that although the reaction to form chloramines

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occur in hundredths of a second at high temperatures and optimum pH, it may occur at much slower rates at lower temperatures and lower or higher pH values. Consequently, free chlorine could be present for several minutes and may result in the formation of THM. Arber et al.²⁰ also speculated that due to the competitive reaction between chlorine and ammonia vs. chlorine and organic precursors lead to some THMs formation. Experimental results obtained by De Laat et al. supports above mentioned speculations in that the formation of high THMs was observed although their experiments were conducted using single model precursors.²¹ In this case, it is required to find another appropriate initial chlorine/NH₃-N weight ratio for the determination of the effective chlorine so that reasonably accurate prediction of THM formation could be conducted. On the other hand, although it has been reported that temperature has a dramatic effect on the rate of THMs formation,³ it is still not clear whether temperature also has a significant effect on the equilibrium yield at any given time or not, because equilibrium is not achieved even after ten days at lower temperature due to the slow rate of reaction.²²

Another factor affecting THM formation is the types and concentration of THM precursors in the raw water. Symons et al.⁷ indicated that although precursor materials from various water sources may be of largely natural origin, the composition of that material is likely to be different depending on the type of source water involved and the origin of precursors in the watershed. Babcock and Singer⁹ showed that the fulvic acid yields less than half as much chloroform as the humic acid. Therefore, as there may be so much variation in the basic organic precursor among water supplies, no effective generalization may not be able to predict the amount of THM formation. On the other hand, although TOX is currently not regulated in drinking water, it should be monitored because it covers all the halogenated compounds. However, measurement of TOX also requires sophisticated equipments and relatively highly experienced analysts. Accordingly, the objectives of this research are;

- 1) To further elucidate factors affecting THM formation with an emphasis on the influence of ammonia and the difference of apparent molecular size or water source.
- 2) To develop a practical kinetic model for the simultaneous rapid and simple prediction of TOX, THM formation, and chlorine decay based on the analysis of above experimental results.

2. Scope of the study

During chlorination, the bromide is oxidized to bromate, which in turn, reacts more readily than chlorine with THM

precursors to form mainly brominated THM. However, no particular attention was paid to the effects of the concentration level upon the formation rate of THMs because the mechanisms of bromination and chlorination are similar²¹. Chlorination was carried out at pH7 because coagulation pH employed in most municipal water treatment plant is around 7.

3. Experimental methods

3.1. Water samples and miscellaneous analytical procedures

Different types of water samples were used in the experiments in order to be able to make general conclusion. These water samples can be crudely characterized as those of high, medium, and low quality in terms of dissolved organic carbon (DOC; total organic carbon(TOC) after 0.45 μ m pore size membrane filtration). The source of water supply for Sapporo city, Japan, - Toyohira River - is considered a high quality surface water as shown in Table 1. Secondary municipal wastewater effluents from Soseigawa domestic wastewater treatment plant in Sapporo, and natural organic colored water at Kitamura near Sapporo were used to represent a medium and a low quality surface water, respectively. All water samples were passed through prewashed 0.45 μ m membrane filters before chemical analysis such as pH, ammonia nitrogen (NH₄-N), DOC, and UV absorbance at 260 nm (E260) and at 220 nm (E220). UV absorbance was measured at a wave-length of 260 nm and at 220 nm in a 1 cm quartz cell using a UV-visible spectrophotometer (Model 200-10, Hitachi Ltd., Tokyo, Japan). DOC was measured using a total organic carbon analyzer (Model TOC-500, Shimadzu Co., Kyoto, Japan). After the measurements of both DOC and E260, E260-to-DOC ratios (E260/DOC) were taken to estimate whether or not the sample water contains biologically degradable organic compounds (if E260/DOC is lower than 60, it indicates the absence of biologically degradable organic matter).²³ E220-to-E260 ratios (E220/E260) were also taken to estimate the extent of pollution with the municipal secondary effluents (if E220/E260 is higher than around 2, it indicates the presence of relatively higher NO₂⁻ or NO₃⁻, the higher NO₂⁻ or NO₃⁻ levels in the source water could be attributed to the contamination with the municipal secondary effluents or the water draining from the agricultural land areas).²³

3.1. Fractionation of precursors

Water samples were concentrated by evaporation under reduced pressure at 40 to 45°C. All water samples were filtered through 0.45 µm membrane filters prior to concentration. Sephadex G-15 gel column (upper exclusion limit of molecular weight: 1,500 dalton) was used to fractionate concentrates into group of compounds.²³ Preswollen Sephadex G-15 gel was packed by gravity into two columns (2.5 cm inner diameter with a bed height of 10 cm and 2.5 cm inner diameter with a bed height of 70 cm). These columns were connected in series with the shorter column preceding the longer one. The shorter column was used as a precolumn to protect the longer column. Blue dextran 2000, with a molecular weight of 2×10^6 dalton was used to determine the void volume of the column. A 10 mL concentrate was placed on top of the column and then operated downflow with distilled water at a rate of 150 mL/hr. Fractions (10 mL) from the effluent of the column were collected in test tubes by a fraction collector. E260 and DOC were determined on each fraction. Calibration of the Sephadex G-15 with carbohydrates of known molecular weight indicate the following apparent molecular weights: >1,500 dalton for Group 1, between 1,500 dalton and 600 dalton for Group 2, and <600 dalton for Group 3.

3.3. Chlorination

Sodium hypochlorite solution was diluted just before use and added to 100 mL sample solution. After adjustment of pH to 7.0 with HCl or NaOH, the reaction bottle was capped with teflon rubber gas-tight septa to prevent the loss of total trihalomethanes (THMs, the arithmetic sum of the mass concentration of compounds CHCl_3 , CHBrCl_2 , CHBr_2Cl and CHBr_3) and allowed to react in the dark without head space at various reaction temperature. Chlorine stock solution was measured by iodometric method. Total residual chlorine and free residual chlorine were analyzed by the DPD colorimetric method with minor modification. TOX, THM and chlorine concentration were monitored over 360 hrs for each reaction bottle. If it was necessary to increase the ammonia content, reagent grade ammonium chloride was added to sample water prior to chlorination. If it was required to reduce the ammonia content, sample water such as secondary municipal wastewater effluents was passed through the column (2.5 cm inner diameter with a bed height of 60 cm) packed with zeolite beads (14–30 mesh) at a rate of 150 ml/hr.

3.4. THM analysis

THM analysis was carried out with a gas chromatograph (Model 073, Hitachi Ltd., Tokyo, Japan) incorporating an electron capture detector or with a Hewlett Packard Gas Chromatograph

Table 1. E260 and DOC of source water

Source water	E260(cm^{-1}) [†]	DOC(mg/L)
Toyohira river (sampled in April)	0.115	2.4
Toyohira river (sampled in January)	0.04	1.3
Hasamu river	0.085	2.4
Chitose river	0.054	1.8
Tobestu river	0.074	1.5
Kusiro river	0.110	2.6
Fukuoka river	0.018	0.8
Lake Kasumigaura	0.070	3.2
Hoshioki river	0.075	2.1
Ishikari peat water	1.00	24
Secondary municipal effluents	0.118	8.6
Rapid sand filtered water at Bangkhen water treatment plant)	0.039	1.3

[†] UV absorbance at 260 nm(cm^{-1})

HP 6890/Mass Spectrometer HP 5973 by headspace injection method. Chlorine was quenched before THM analysis by addition of sodium thiosulfate. A look at the individual THM species revealed that chloroform was the principal trihalomethane formed in this experiment (in case of secondary municipal effluents, brominated haloforms sometimes accounted for approximately 30% of the overall THMs yield). Therefore, the term THM are used in this article to indicate chloroform.

3.5. TOX analysis

TOX concentration ($\mu\text{g/L}$ as Cl) was measured by using a Mitsubishi-kasei Model 10, TOX analyzer (adsorption-pyrolysis-microcoulometric procedure). Solutions of trichlorophenol were analyzed to verify accuracy and precision.

Blanks consisted of dechlorinating reagents and nitric acid. Before measurement of TOX, the excess of chlorine was removed by adding appropriate amount of Na₂SO₃.

4. Results and discussions

4.1. Surrogate parameter for TOX and THMs precursors

Dissolved organic carbon(DOC) and ultraviolet absorbance have been reported to serve as useful surrogates of THMs precursor concentration²³. However, as indicated in Figs 1 and 2, the correlation between E260 and THMs (THMFP; THMs formed at pH 7 and 20°C after 24 h with 1.0 ± 0.2 mg/L residual chlorine) is much higher than the correlation between DOC and THM s.

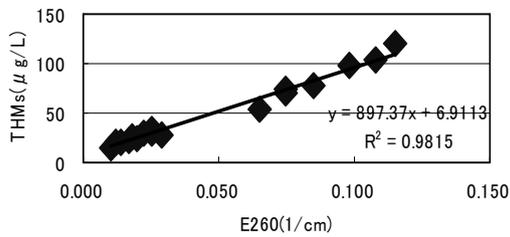


Fig. 1. Correlation between E260 and THMs

4.2. Individual THM species in total THM(TTHM)

In the absence of bromide ion, only chlorinated THMs are formed. As indicated in Fig.3, in the presence of bromide, free chlorine rapidly, oxidizes bromide to hypobromous acid(HOBr), which then, along with the residual free chlorine, reacts with natural organic material(NOM) to produce mixed chloro-bromo substitution.

4.3. Results of fractionation

One of the results of fractionation obtained for the sample(peat water) is presented in Fig 4. Following fractionation, the 10 mL elution samples were combined into groupings of various apparent molecular weight ranges and adjusted the DOC concentration and ionic strength using distilled water and NaCl, respectively. The Sephadex G-15 fractions collected and pooled were referred to as Group 1, Group 2, and Group 3; these labels correspond to the fraction number by order of elution as shown in Table 2.

4.4. Effect of ammonia on THM formation

In Figs 5,6 and 7, THMs formed from peat water with or without ammonia in the 24-hr reaction time are shown together

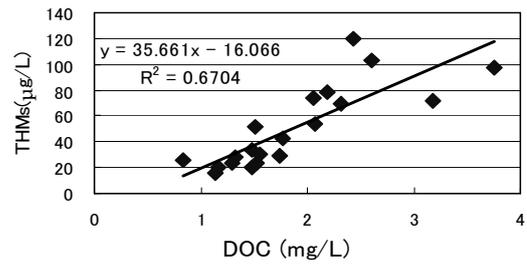


Fig.2. Correlation between THMs and DOC

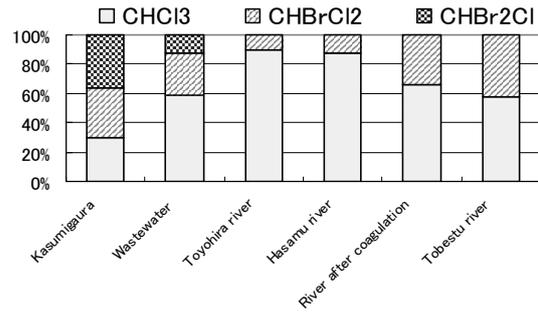


Fig.3. Individual THM species in total THM(TTHM)

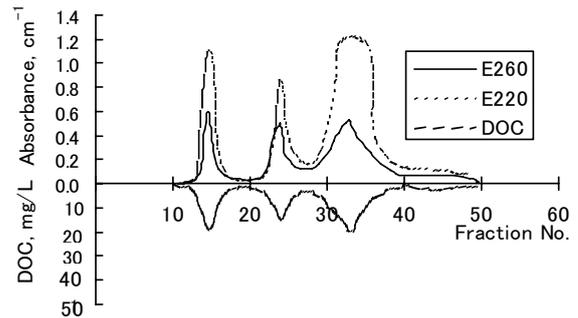


Fig.4. Elution pattern of peat water using Sephadex G-15 gel. Sample concentration factor before gel chromatography; × 20

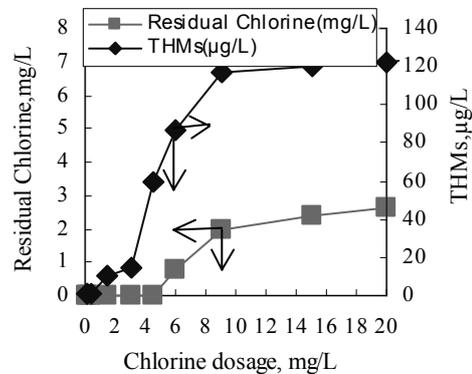


Fig.5. Chlorine dose vs. residual chlorine and THMs formation from peat water at pH 7 after 24 h. Initial NH₄⁺-N; 0 mg/L, Temperature; 20°C.

with residual chlorine. Very little THM was formed before the peak point (the hump of the breakpoint curve), however, relatively high THM yields was obtained at the breakpoint. These results indicate that before the peak point, the reaction between free chlorine and ammonia is much faster than the reaction between free chlorine and organic precursors, whereas, from peak point to breakpoint, the free chlorine-organic precursors reaction rate is as rapid as the destruction reaction rate of mono- and dichloramine. These results imply that the effective chlorine obtainable by subtracting the free chlorine used for the reaction with the ammonia is not effective for the estimation of free chlorine actually used.

Table 2. Water quality of peat water after gel chromatographically fractionated(with Sepadex G-15), pooled, and diluted with distilled water

Fraction Number	pH	Electrical Conductivity [$\mu S/cm$]	DOC [mg/L]	E260 [cm^{-1}]
Group 1 13~17	7.0	640	3	0.130
Group 2 22~25	7.0	640	3	0.090
Group 3 30~40	7.0	640	3	0.102
Diluted raw water	7.0	640	3	0.095

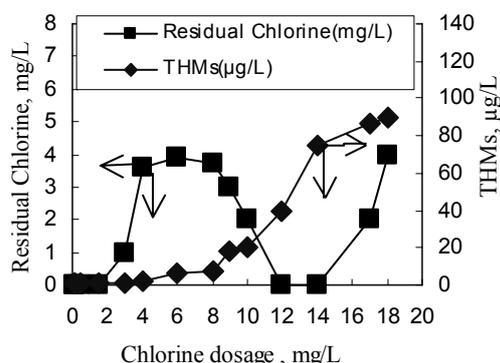


Fig.6. Chlorine dose vs. residual chlorine and THMs formation from peat water at pH 7 after 24 h. Initial $NH_4^+ - N$; 2mg/L, 20°C.

4.5. Rapidly consumable chlorine

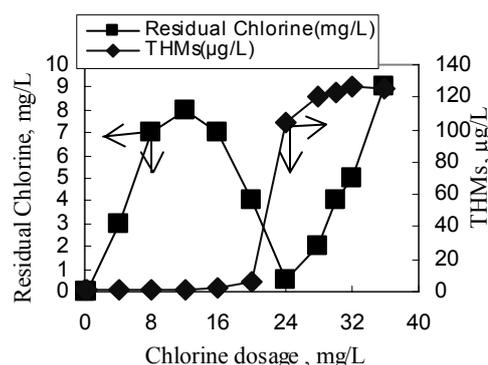


Fig.7. Chlorine dose vs. residual chlorine and THMs formation from peat water at pH 7 after 24 h. Initial $NH_4^+ - N$; 2mg/L, 20°C.

It was seen from the preliminary experiments that initially chlorine consumption was very high as compared to the chlorine consumption in the later stages. This rapidly consumable chlorine was defined as the amount of chlorine consumption within two minutes of chlorine application.²⁵ It was thought that other inorganic compounds such as ammonia-nitrogen, hydrogen sulfide etc. were more faster than that of the reactive sites of humics. The advantages of the measurement of rapidly consumable chlorine is that no other characteristics of water need to be analyzed, only measurement of rapidly consumable chlorine is enough to estimate effective chlorine dose. The difference between the initial chlorine dose and the rapidly consumed chlorine is the effective chlorine dose which is used for the reaction with the reactive sites of humics. This effective chlorine dose was used for all sort of prediction of theoretical residual free chlorine unless otherwise mentioned.

4.6. Effects of apparent molecular weight on THM formation

Fig. 8 illustrates the effect of apparent molecular weight on THM formation level and rate of THM formation. In this Fig. 8, apparent molecular weight has little impact on THM formation level and the rate of THM formation, contrary to the results of other researchers.²³⁻²⁵ It is not known at this time whether there are indeed difference in the rate and yield of THM formation from different apparent molecular weight fraction or whether the discrepancies result from how yields of THM were calculated. In this experiment, the yields of THM formation from each apparent molecular weight fraction were calculated as $\mu g/L$ THMs per unit E260, whereas yields of THM were calculated $\mu g/L$ THM per mg/L TOC by other researchers.²³⁻²⁷ Though not indicated here, no significant changes were observed for THM yield on a E260 basis at any reaction time for Group 2 of different origin. However, on a 1mg/LDOC basis, Group 2 of Kitamura peat

water(5mg/L) yielded the higher THM than two other water samples such as municipal secondary effluents(DOC; 5mg/L and 7mg/L). This result indicates that E260 insensitive DOC is not the precursors for THMs. Consequently, E260 is a more important parameter than DOC in modeling TOX and THM formation. Studies using raw and treated natural waters also have shown excellent correlations between THM formation potential(THMFP) and UV absorbance(254 nm).^{26,27}

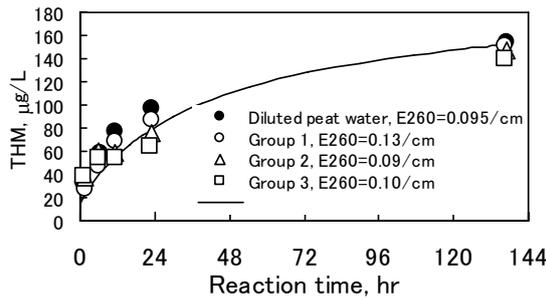
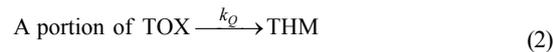


Fig.8. THMs formation from gel chromatographically fractionated groups; Effect of apparent molecular weight on THM formation for peat water. Chlorination conditions. Free chlorine; 9 mg/L, Temperature;20 °C

4.7. Kinetic model for TOX and THM formation

As mentioned above, no distinct difference in terms of the level and the rate of THM formation was found between the higher molecular fraction (Group 1) and the lower molecular fraction(Group 2). This result seems to imply that almost same types of reactive sites are contained in both the higher molecular fraction and the lower molecular fraction. However, because the precursor is actually a mixture of compounds with differing reactivity, it is practically impossible to identify and quantify such reactive sites. Hence, the following general scheme for the TOX and THM formations as a result of chlorination may be proposed using the concept of “prospective reactive sites of precursor” in place of actual “reactive sites of precursor”:



in which prospective reactive sites of precursor expressed in concentration of TOX or THM are the portion of reactive sites which reacted with chlorine dosed to produce TOX or THM, k_P is the TOX formation rate constant (h^{-1}), and k_Q is the THM formation rate constant (h^{-1}). If it is assumed that the reaction of TOX and THM formation is consecutive unimolecular-type

first-order reaction and the rate of TOX formation is equal to that of reactive sites consumption, the following integral form for TOX($\mu\text{g/L}$ as Cl) and THM($\mu\text{g/L}$ as chloroform) formation is obtained;

$$[\text{TOX}] = P \left(1 - e^{-k_P t} \right) \quad (3)$$

$$[\text{THM}] = Q \left[\frac{k_Q}{k_Q - k_P} \left(1 - e^{-k_P t} \right) + \frac{k_P}{k_P - k_Q} \left(1 - e^{-k_Q t} \right) \right] \quad (4)$$

in which P is the concentration of prospective reactive sites which could react with dosed chlorine to form TOX($\mu\text{g/L}$ as Cl) and Q is the concentration of prospective reactive sites which could react with dosed chlorine and could finally form THM ($\mu\text{g/L}$ as chloroform). If $k_P \gg k_Q$, equation (2) then becomes;

$$[\text{THM}] = Q \left(1 - e^{-k_Q t} \right) \quad (5)$$

Humic substances have been shown to be predominant THM precursors in natural waters.^{1,2} However, very little definitive information is available concerning the details of its chemical structure. Therefore it is very difficult to determine which reactive sites in the humic molecules could be responsible for the formation of TOX and THM.

Hence, not actual reactive sites but prospective reactive sites in the humic molecules were tentatively categorized into three groups with respect to the difference of reaction rate with chlorine:

- 1) Prospective reactive sites of a fast formation rate with respect to TOX or THM formation (P_1 for TOX and Q_1 for THM formation expressed in concentration)
- 2) Prospective reactive sites of a medial formation rate with respect to TOX or THM formation (P_2 for TOX and Q_2 for THM formation expressed in concentration)
- 3) Prospective reactive sites of a slow formation rate with respect to TOX or THM formation (P_3 for TOX and Q_3 for THM formation expressed in concentration P_3)

Therefore, it is evident as conceptually shown in Fig.96 that:

- 1) If a small amount of chlorine is applied to natural water containing such precursors, fast-reaction-rate active sites dominantly react with chlorine to form prospective reactive sites of a fast formation rate with respect to TOX or THM formation, i.e. P_1 for TOX and Q_1 for THM formation expressed in concentration. Therefore, although the total amount of organic halogen formed is the lowest, the formation occur most rapidly.
- 2) If a medial amount of chlorine is applied, not only fast-reaction-rate reactive sites but also medial-reaction-rate active

sites can react with chlorine in parallel to form prospective reactive sites of a medial formation rate with respect to TOX or THM formation i.e. P_2 for TOX and Q_2 for THM formation expressed in concentration. Consequently, although it takes much longer time for the formation of organic halogen to reach an equilibrium condition, the total amount of organic halogen formed is higher than that of obtained from only P_1 or Q_1 .

3) If a large amount of chlorine is applied, not only above mentioned reactive sites but slow-reaction-rate reactive sites also can participate for the reaction with chlorine to form prospective reactive sites of a slow formation rate with respect to TOX or THM formation i.e. P_3 for TOX and Q_3 for THM formation expressed in concentration. Although it takes the longest time to come to an equilibrium, the total amount of organic halogen is the highest. Based upon the above assumptions, the final rate expressions for the formation of TOX($\mu\text{g/L}$ as Cl) and THM($\mu\text{g/L}$ as chloroform) are then given by:

$$[\text{TOX}] = \sum_{i=1}^3 P_i (1 - e^{-k_{P_i}t}) \quad (6)$$

$$[\text{THM}] = \sum_{i=1}^3 Q_i \left[\frac{k_{Q_i}}{k_{Q_i} - k_{P_i}} (1 - e^{-k_{P_i}t}) + \frac{k_{P_i}}{k_{P_i} - k_{Q_i}} (1 - e^{-k_{Q_i}t}) \right] \quad (7)$$

If $k_{P_i} \gg k_{Q_i}$, equation (5) then becomes,

$$[\text{THM}] = \sum_{i=1}^3 Q_i (1 - e^{-k_{Q_i}t}) \quad (8)$$

in which P_i ($i=1-3$) is the concentration of prospective reactive sites which could react with chlorine dosed to form TOX ($\mu\text{g/L}$ as Cl) (P_1 for fast, P_2 for medial, and P_3 for slow rate TOX formation), Q_i is the concentration of prospective reactive sites which could react with chlorine dosed to form THM ($\mu\text{g/L}$) (Q_1 for the fast, Q_2 for the medial, and Q_3 for the slow rate THM formation). k_{P_i} [h^{-1}] is TOX formation rate coefficient from P_i and k_{Q_i} [h^{-1}] is THM formation rate coefficient from Q_i .

4. 8. Measurements of concentrations of prospective reactive sites

As previously mentioned, the concept of “prospective reaction sites which could react with chlorine dosed to produce TOX or THM” was presented because there is no practical method to identify and measure the concentration of reactive sites. It was assumed this “prospective reaction sites” could be experimentally determined as the yield of maximum TOX (TOXmax) or maximum THM (THMmax). This TOXmax or THMmax was defined as the terminal concentration of TOX or THM for a given

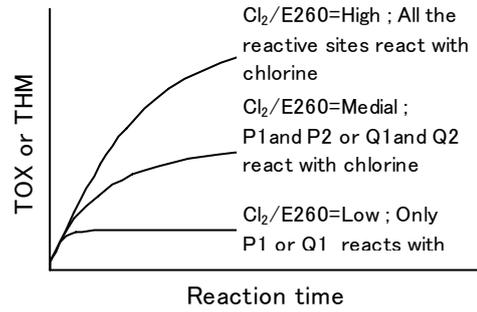


Fig.9. THMs formation model; Effect of $\text{Cl}_2/\text{E260}$ ratios on maximum yield or rate of TOX and THM formation(conceptual model)

quantity of E260 in a given free chlorine dose at any reaction temperature and pH 7. THM formation reaction usually does not terminate even after 10 days at lower reaction temperatures. It was assumed that THM or TOX formation reaction terminates in a short time by elevating the reaction temperature up to 80°C . Therefore, TOXmax and THMmax were determined as follows: Sample waters were dosed with the desired concentration levels of sodium hypochlorite, adjusted to pH 7.0 with hydrochloric acid or sodium hydroxide, tightly capped, and allowed the reaction to approach completion at 80°C . These TOXmax and THMmax vary with the amount of chlorine applied to water samples. In order to find the minimum required reaction time for a quick evaluation of TOXmax and THMmax, peat waters with or without dilution were tested according to the above mentioned methods. As it was found out that both TOXmax and THMmax are available in 20 minutes, a series of experiments were conducted to find the relationship between TOXmax or THMmax and applied chlorine using E260 as a parameter. Figs.10 and 11 show the relationship between TOXmax or THMmax and initial chlorine dosage for various E260 level. The relationships illustrated in Figs. 10 and 11 can be formulated as follows;

In case of $[\text{Cl}_2]/[\text{E260}] \geq 94$;

$$\text{TOXmax} = 822 [\text{Cl}_2]^{0.365} [\text{E260}]^{0.529} \quad (9)$$

In case of $[\text{Cl}_2]/[\text{E260}] < 94$

$$\text{TOXmax} = 67.1 [\text{Cl}_2]^{0.968} \quad (10)$$

In case of $[\text{Cl}_2]/[\text{E260}] \geq 74$;

$$\text{THMmax} = 819.7 [\text{Cl}_2]^{0.333} [\text{E260}]^{1.00} \quad (11)$$

In case of $[Cl_2]/[E260] < 74$

$$THM_{max} = 12.65 [Cl_2]^{0.246} \quad (12)$$

Fig. 11, or Eq. 11 indicates that at $Cl_2/E260$ ratios greater than (or equal to) seventy-four, effect of Cl_2 on THM formation is not so significant, while $Cl_2/E260$ ratios smaller than seventy-four, increase in Cl_2 significantly influence the increase of both TOX and THM. These results are consistent with those obtained by Babcock and Singer⁶ who studied chlorination of humic and fulvic acids. For those systems conducted by them in which chlorine was in excess relative to TOC (Cl_2/TOC ratios greater than five), two fold increase in TOC just resulted in just two and a half fold increase in THM after forty-eight hours, while those systems with Cl_2/TOC ratios less than one, two fold increase in chlorine resulted in four fold increase in THM formation. These results indicate that prediction of THM or TOX formation is

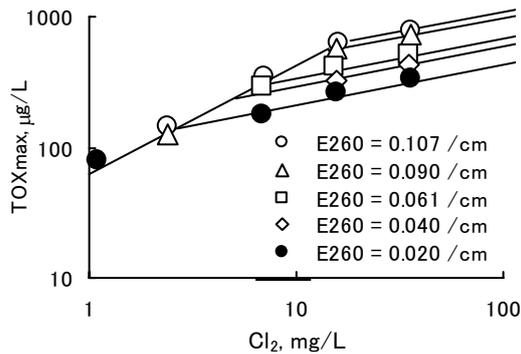


Fig.10. Effect of Cl_2 and E260 on maximum yield of TOX(TOXmax)
difficult to perform for the wide range of experimental condition

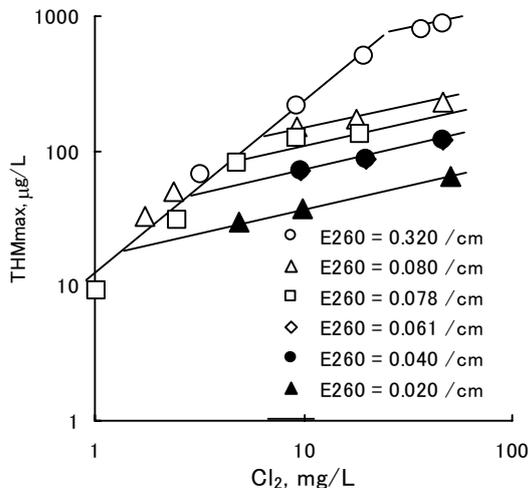


Fig.11. Effect of Cl_2 and E260 on maximum yield of THM(THMmax)

by use of a simple empirical power function .

4.9. Determination of k_{P1} , k_{Q1} , $P_i/[TOX_{max}]$ and $Q_i/[THM_{max}]$ ($i=1\sim 3$)

THM precursors such as humic substances, according to Christman et al.²⁹, consist of various types of core structures such as resorcinol and aliphatic carboxylic acids. The report of Norwood³⁰ suggested that reaction rates of THM yields for these structures representative of humic degradation products such as resorcinol substitution pattern are approximately 100-fold larger than that of the smallest reaction rate constant (such as cinnamic acid substitution pattern). Therefore, first-order rate constants for those three prospective reactive sites (k_{P1} and k_{Q1}) were tentatively defined as $k_{P1} = 10 k_{P2} = 100 k_{P3}$ and $k_{Q1} = 10 k_{Q2} = 100 k_{Q3}$.³⁰ Hence, if k_{P1} and k_{Q1} are determined, rest of the other coefficients will be defined automatically. On the other hand, according to the concept presented in Fig.12, P_i/TOX_{max} or Q_i/THM_{max} ($i = 1\sim 3$) must be a function of chlorine dosed-to-E260($Cl_2/E260$). Thus, a set of k_{P1} at 20°C and P_i/TOX ($i=1\sim 3$) as a function of $Cl_2/E260$, or a set of k_{Q1} at 20°C and Q_i/THM ($i = 1\sim 3$) as a function of $Cl_2/E260$ was determined by trial and error that best fits the experimental TOX or THM formation data at any reaction time obtained from the chlorination of peat water.³¹ The relationship between P_i/TOX and $Cl_2/E260$ thus obtained and shown in Fig 9, is equal to that between Q_i/THM and $Cl_2/E260$. This indicates that THM also is formed not from the specific reactive site but from the various types of reactive sites. The pattern of occurrence for the three reactive sites among THMmax and TOXmax, as a function of $Cl_2/E260$ given in Fig. 12, confirms the concepts shown previously in Fig 9. For example, the ratio of fast-reaction-rate prospective reactive sites (P_1 and Q_1) decreases with the increase of $Cl_2/E260$, whereas the ratio of slowest-reaction-rate prospective reactive sites (P_3 and Q_3) increases with increasing $Cl_2/E260$. These ratio of prospective reactive sites expressed in terms of THM or TOX seems to be

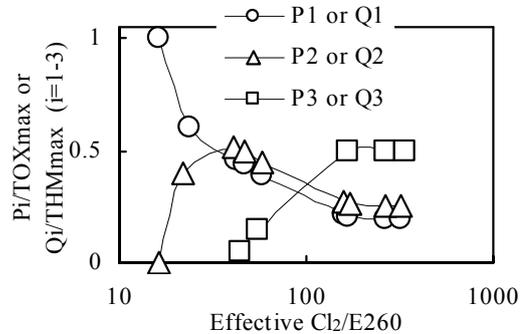


Fig.12. Effect of effective $Cl_2/E260$ on $P_i/TOX_{max}(i=1\sim 3)$ or Q_i/THM_{max} . Solid lines were eye fitted to experimental data.

universal for precursor of natural origin. The value of k_{p1} , thus obtained at 3°C and 20°C was 3.0[h⁻¹]. This result is closely consistent with what is reported in the literature.³² The calculated TOX formation using 3.0 as the value of k_{p1} together with the diagram given in Fig. 12 was compared with the observed TOX formation. Hydrolysis reaction rate coefficient k_{Q1} (THM formation rate coefficient) was plotted as a function of temperature as shown in Fig. 13 and given by the following equation.

$$\text{Log } k_{Q1} = 0.052T - 1.56 \quad (13)$$

In which T is the reaction temperature(°C). TOX formation rate constant is ten times higher than that for THM formation at 20°C, indicating the validity of previous assumption ($k_{p1} \gg k_{Q1}$).

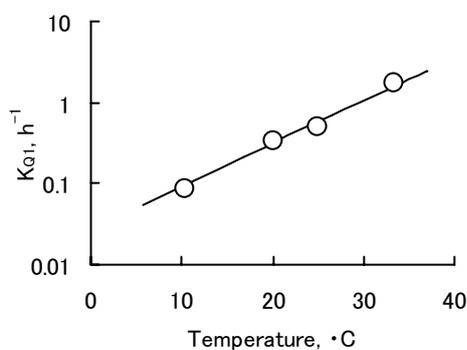


Fig.13. Effect of reaction temperature on THM formation rate coefficient k_{Q1} [h⁻¹]

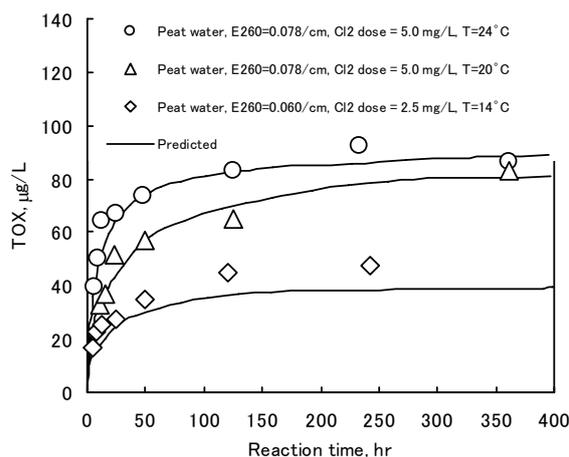


Fig.14. Comparison between predicted and observed TOX from various source water as a function of E260 and chlorine dose at 20°C

4. 10. Prediction of TOX and THM formation using the

kinetic model

The proposed kinetic model has been evaluated using batch chlorination results from various types of water sources with various levels of E260, Cl₂/E260, reaction temperature, and reaction time. The results shown in Figs 14 ~ 16, and other data not presented here, indicate that it is generally possible to predict TOX and THM formation using only E260, effective free

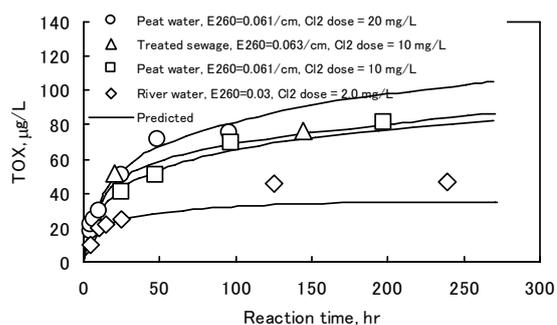


Fig.15. Comparison between predicted and observed THM from various source water as a function of E260 and chlorine dose at 20°C

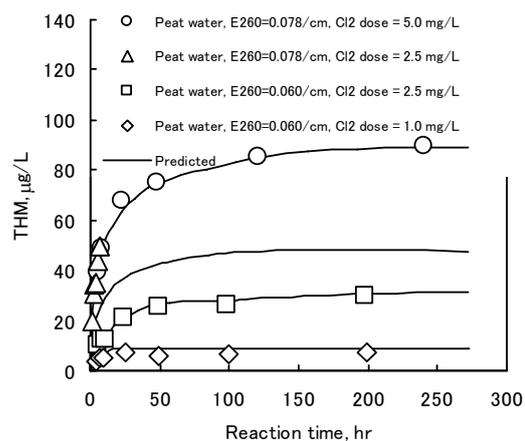


Fig.16. Comparison between predicted and observed THM from various source water as a function of E260 and chlorine dose at 20°C

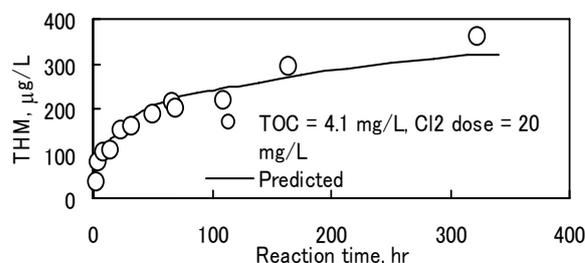


Fig.17. Comparison between predicted and observed THM from Black Lake fulvic acid solution at 20°C and pH=7.0 (adapted from Reckhow and Singer³⁴)

chlorine dose and reaction temperature with a reasonable accuracy. Comparison between experimental THM formation reported by Reckhow and Singer³⁴ and THM formation curve predicted based on the proposed kinetic model was also conducted as shown in Fig 17. The predicted THM based on this proposed kinetic model using experimental parameters reported agrees reasonably well with the measured THM by Reckhow and Singer.³⁴

4. 11. Chlorine decay

Disinfectant is used in water treatment mainly to reduce pathogens. There are several disinfectants such as chlorine, chlorine dioxide, ozone, and others. Among all of these, chlorine is the most common disinfecting chemical because of its effectiveness, relative ease of application and low cost. However, reactions of chlorine with organic compounds can produce undesirable by-products, such as THMs. The presence of THMs in drinking water gives rise to public health concern, because of a possible carcinogenic link. Hence it has long been required to reduce the THMs formation and yet to keep the necessary amount of residual free chlorine to ensure the disinfection capacity of distributed water. Accordingly, the study has been conducted to investigate the possibility of extending TOX and THM formation model for the prediction of chlorine decay in the bulk water so that simultaneous prediction of TOX and THM formation and chlorine decay could be performed.

4.12. Kinetic model for chlorine decay

Residual chlorine may be determined by the extent of decomposition, reaction by inorganic compounds such as ammonia, and reaction by organic compounds such as humics as follows.

$$[\text{Residual chlorine}] = [\text{Cl}_2 \text{ dose}] - [\text{Cl}_2]_1 - [\text{Cl}_2]_2 - [\text{Cl}_2]_3 \quad (14)$$

where $[\text{Cl}_2]_1$ = Chlorine consumption by decomposition, $[\text{Cl}_2]_2$ = Chlorine consumption by inorganic components such as ammonia, and $[\text{Cl}_2]_3$ = Chlorine consumption by organic components such as humics.

As initial study²³ indicated that the stability of free chlorine in pure water was very high, the effect of decomposition upon the free chlorine decay can be ignored for the approximate chlorine decay. On the other hand, the major factors which have been reported^{7,16} to influence chlorine decay by organic components such as humics includes chlorine dose, the types and concentration of organic components, contact time, temperature,

and pH. If it is assumed that the reaction of chlorine with organic components is unimolecular-type first-order reaction and the rate of chlorine decay is equal to that of reactive sites consumption, the following integral form for chlorine decay equation is obtained.

$$[\text{Residual chlorine}] = [\text{Cl}_2 \text{ dose}] - [\text{Cl}_2]_2 - C(1 - e^{-kt}) \quad (15)$$

in which C is the concentration of free chlorine (mg/L) used for the reaction with reactive sites. k is the decay rate coefficient (h^{-1}) of prospective reactive sites of a reaction rate with respect to the chlorine. The majority of organic components in natural water are fulvic acid and humic acid. Humics actual structure is still not well known and its precise structural formula has not yet been expressed. Accordingly, reactive sites of the humics with free chlorine may be tentatively categorized into three groups with respect to the reaction rate as follows:

1. Reactive sites of the fastest reaction rate with respect to substitution reaction.
2. Reactive sites of fast reaction rate with respect to substitution reaction.
3. Reactive sites of slow reaction rate with respect to substitution reaction.
4. Reactive sites of the fastest reaction rate with respect to oxidation reaction.
5. Reactive sites of fast reaction rate with respect to oxidation reaction.
6. Reactive sites of slow reaction rate with respect to oxidation reaction.

Therefore, it is evident that;

- 1) If a small amount of chlorine is applied to natural water containing such precursors, the fastest reaction rate reactive sites dominantly react with chlorine to reduce chlorine. Thus, although the total amount of chlorine consumed is the lowest, the chlorine decay reaction occurs most rapidly.
- 2) If a medial amount of chlorine is applied, not only the fastest reaction rate reactive sites but also fast reaction rate reactive sites can react with chlorine in parallel to reduce chlorine. Consequently, although it takes much longer time for the chlorine decay to reach an equilibrium condition, the total amount of chlorine consumed is higher than that of consumed by the fastest reaction rate reactive sites.
- 3) If a large amount of chlorine is applied, not only above mentioned reactive sites but slow-reaction-rate reactive sites also can participate for the reaction with chlorine to reduce chlorine concentration. Although it takes the longest time to come to an

equilibrium, the total amount of chlorine decay is the highest. At this stage, it is not clear which one between the reaction rate by oxidation and the reaction rate by substitution is faster. On the other hand, as previously mentioned, although humic substances have been shown to be predominant organic components in natural waters^{2,3}, however, very little definitive information is available concerning the details of its chemical structure. Therefore it is very difficult to determine which reactive sites in the humic molecules could be responsible for the chlorine decay. Hence, the concept of prospective reactive sites in the humic molecules in place of actual reactive sites were presented as follows:

- 1) Prospective reactive sites of the most rapid reaction rate with respect to the chlorine consumption (C_{O1} for the amount of chlorine consumption by “oxidation” expressed in chlorine concentration and C_{S1} for the amount of chlorine consumption by “addition” or “substitution” reaction expressed in expressed in chlorine concentration)
- 2) Prospective reactive sites of more rapid reaction rate with respect to the chlorine consumption (C_{O2} for the amount of chlorine consumption by “oxidation” expressed in chlorine concentration and C_{S2} for the amount of chlorine consumption by “addition” or “substitution” reaction expressed in chlorine concentration)
- 3) Prospective reactive sites of a slow formation rate with respect to the chlorine consumption (C_{O3} for the amount of chlorine decay by “oxidation” expressed in chlorine concentration and C_{S3} for the amount of chlorine decay by “addition” or “substitution” reaction expressed in chlorine concentration).

Accordingly, the sum of the all prospective reactive sites becomes the total maximum chlorine consumption as follows;

$$[\text{Chlorine}] = [\text{Cl}_2]_{\text{dose}} - [\text{Cl}_2]_t - \sum_{i=1}^3 C_{oi}(1 - e^{-k_{oi}t}) - \sum_{i=1}^3 C_{si}(1 - e^{-k_{si}t}) \quad (16)$$

$C_{O1} + C_{O2} + C_{O3}$ = maximum chlorine consumption by oxidation reaction(C_{Omax})

$C_{S1} + C_{S2} + C_{S3}$ = maximum chlorine consumption by substitution reaction(C_{Smax})

Based upon the above assumptions, the rate expression for the chlorine decay (mg/L) is then given by:

$$[\text{Residual chlorine}] = [\text{Cl}_2]_{\text{dose}} - [\text{Cl}_2]_t - \sum_{i=1}^3 C_i(1 - e^{-k_i t}) \quad (17)$$

$[\text{Cl}_2]_t$ is the rapidly consumable chlorine within a few minutes. k_{oi} is the decay rate coefficient(h^{-1}) of prospective reactive sites of a reaction rate with respect to the chlorine consumption by oxidation. Subscript i indicates the i th reactive site ($i=1,2, \text{ and } 3$ indicates the most rapid, more rapid, and slow reaction rate coefficient, respectively). k_{si} is the decay rate coefficient(h^{-1}) of prospective reactive sites of a reaction rate with respect to the chlorine consumption by substitution. C_{oi} is the amount of chlorine consumed for oxidation reaction with “ i ” active sites of humics($C_{O1}, C_{O2}, \text{ and } C_{O3}$ is the amount of chlorine consumed for oxidation reaction with “the fastest”, “fast”, and “slow” reaction rate, respectively). C_{si} is the amount of chlorine consumed for substitution reaction with “ i ” active sites of humics($C_{S1}, C_{S2}, \text{ and } C_{S3}$ is the amount of chlorine consumed for substitution reaction with “the fastest”, “fast”, and “slow” reaction rate, respectively). As preliminary chlorination experiments using peat water revealed that roughly 8% of the chlorine dosed was used for the formation of TOX after 60 hours, the effect of substitution reaction upon the free chlorine decay can be ignored for the approximate chlorine decay. Thus, the final rate expression for the approximate chlorine decay (mg/L) can be expressed as; in which C_i is the chlorine consumption due to the prospective reactive sites i (mg/L) and k_i is the chlorine consumption rate coefficient due to the prospective reactive sites i (mg/L). As TOX and THM growth curves are mirror images of the chlorine decay curves, it was assumed that almost all the equations and diagram used for the prediction of TOX and THM growth curves could be applied for the prediction of chlorine decay. Thus the relationship between the maximum chlorine consumption (terminal chlorine consumption at equilibrium) by all the reactive sites and $\text{Cl}_2/\text{E260}$ ratio and the relative reaction rate of three reactive sites could be estimated from Fig.12 and eq.(18), respectively.

$$k_1 = 10 \quad k_2 = 100 \quad k_3 \quad (18)$$

5. Experimental methods for chlorine decay

5.1. Measurements of concentrations of prospective reactive sites expressed in terms of maximum chlorine consumed(C_{max})

As previously mentioned, the concept of “prospective reaction sites which could react with chlorine dosed to reduce chlorine” was presented because there is no practical method to identify and measure the concentration of reactive sites. It was assumed this

“prospective reaction sites” could be experimentally determined as the maximum chlorine consumed (C max)by fast, medium and slow active sites of humics. This maximum chlorine consumed (C max) was defined as the terminal residual free chlorine concentration for a given quantity of E260 in a given free chlorine dose at any reaction temperature and pH 7. THM formation reaction usually does not terminate even after 10 days at higher concentration of humics and chlorine dose. It was assumed that free chlorine decay reaction terminates in a short time by elevating the reaction temperature up to 80°C. Cmax was determined as follows: Sample waters were dosed with the desired concentration levels of sodium hypochlorite, adjusted to pH 7.0 with hydrochloric acid or sodium hydroxide, tightly capped, and allowed the reaction to approach completion at 80°C. Cmax varies with the amount of chlorine applied to water samples. In order to find the minimum required reaction time for a quick evaluation of C max, sample waters with or without dilution were tested according to the above mentioned methods..

6. Results and discussion for chlorine decay

6.1. Concentrations of prospective reactive sites expressed in terms of maximum chlorine consumed(Cmax)

Experimental results of the determination of the maximum chlorine consumed (Cmax) is expressed as the function of E260 of the sample water and chlorine dose as shown in Fig.18.

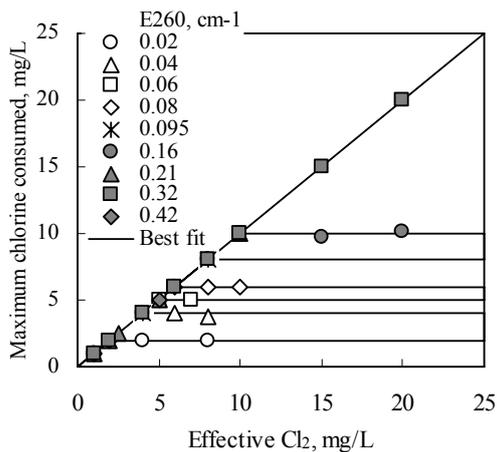


Fig.18. Estimated maximum chlorine consumed by effective chlorine and E260.

6.2. Estimated Ci/Maximum Chlorine Consumed

As mentioned previously, the chlorine decay curves are

mirror images of TOX and THM growth curves, the diagram for estimating $P_i/TOX_{max(i=1\sim3)}$ or Q_i/THM_{max} was modified as indicated in Fig. 19.

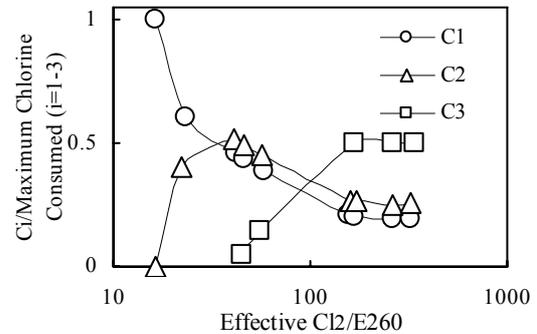


Fig.19. Estimated $C_i/Maximum Chlorine Consumed (i=1\sim3)$ by effective $Cl_2/E260$

6.3. Determination of k_1

For each effective chlorine dose and for the same temperature by trial and error procedure, k_1 was estimated by comparing experimental and theoretical residual free chlorine using peat water collected Hokkaido, Japan. From the different values of k_1 through regression analysis, a relationship between the chlorine decay reaction constant (k_1) and temperature was estimated. This relationship is shown below ;

$$k_1 = \exp (0.019633T - 0.36733) \tag{19}$$

In which T is the reaction temperature (°C).

6.4. Results of chlorine decay prediction

The proposed kinetic model has been evaluated using batch chlorination results from five types of water sources with various level of E260, reaction temperature, $Cl_2/E260$ and reaction time. Some of the comparisons between predicted and the observed are shown in Figs 20 and 21. Given the range of experimental conditions investigated, the consistency between the predicted chlorine decay curves and observed ones is quite remarkable . Though the chlorine decay curves may be mirror images of TOX and THM growth curves, it is still exactly not clear why the same model including the same diagram can be used for the prediction of chlorine decay, however, reaction rate coefficients used in this model can well account for the rapid TOX formation and chlorine

decay, and relatively slow THM formation as presented in Table. 3. Finally, the procedure for predicting TOX, THM formation and chlorine decay may be outlined as indicated in Fig.22.

Table 3. Reaction rate coefficients used in this model

		Reaction rate coefficient [h ⁻¹]
THMs formation		0.1
TOX formation		3
Chlorine decay	Substitution reaction	3
	Oxidation reaction	1

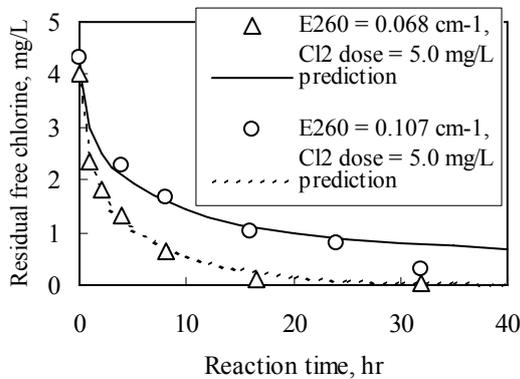


Fig.20. Typical chlorine decay curve. Conditions: chlorine dose, 5 mg/L; E260, 0.068 cm⁻¹; E260, 0.107 cm⁻¹, pH 7.0; 20 ° C.

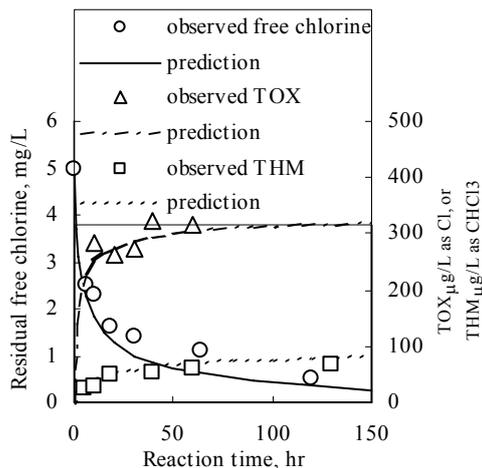


Fig. 21. Typical TOX and THM formation, and chlorine decay curve. Conditions: chlorine dose, 5 mg/L; E260, 0.068 cm⁻¹; pH 7.0; 20 ° C.

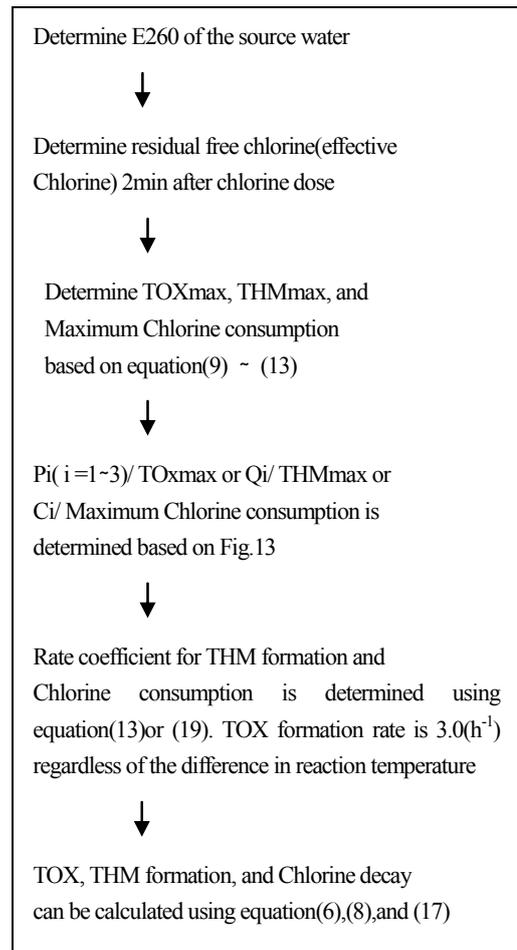


Fig. 22. Procedure for predicting TOX, THM, and Chlorine decay

It has been shown that the proposed kinetic model for the prediction of TOX and THM formation has enough utility as a general predictive model for wide range of experimental conditions. Both TOX and THM formation can be predicted from the proposed model, without any experimental inputs except for E260, free chlorine dose, and temperature. Thus the proposed model is expected to be a simple alternative for TOX and THM monitoring. As this kinetic model, however, aimed at predicting the TOX or THM formation from natural waters, it is necessary to find the another relationship between P_i/TOX_{max} (i =1~3) or P_i/THM_{max} and Cl₂/E260 for the prediction of TOX or THM formation from specific waters such as pulp waste waters. It should be noted that as this model was proposed based on the concept of "prospective reactivities of precursor", some modification is necessary for the prediction of TOX and THM formation in multi-stage chlorination. The proposed model also did not take into account the possible variation in bromide ions, however, the measured halogenated organic compounds formed

7. Conclusions and future work

from the water in the presence of bromide ion are well correlated with predicted values by the modified model³⁴ developed based on this proposed model. The possibility of using this model to predict the free chlorine decay in order to reduce TOX and THM yield levels while maintaining minimum necessary residual chlorine is currently being evaluated. This will enable the reasonable simple management of disinfection process together with this proposed kinetic model. The chlorine decay model developed based on TOX and THM formation model can be used for the simultaneous prediction of TOX or THM formation and chlorine decay so that adequate balance between minimizing the formation of TOX and THM while at the same time maintaining adequate free chlorine residuals. It was shown from experimental investigation that the model proposed for predicting residual free chlorine had enough utility for wide range of experimental conditions such as the initial chlorine dose, types of water sources with various level of organic components, and reaction temperature. However, as the chlorine decay in pipe network may be influenced by not only the initial conditions such as the initial chlorine dose, organic components, and temperature, but by the types of pipe wall, chlorine decay coefficient needs to be modified depending on the local conditions such as the types of pipe material for the accurate prediction of the chlorine decay in the pipe network.

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