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EISEI KAGAKU
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**Chemical Changes of Organic Compounds in Chlorinated Water. XV.
The Concentrations and Compositions of Halogenated
Organics Formed during Chlorination of Water
from the Tama River**

SUKEO ONODERA, TOSHIAKI NISHIKAWA, KIYOSHI IGARASHI,
AKIHIKO NISHIMURA and SHIZUO SUZUKI

*Faculty of Pharmaceutical Sciences, Tokyo University
of Science, 12, Ichigaya Funagawara-machi,
Shinjuku-ku, Tokyo 162, Japan*

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Water samples collected from the Tama River were treated with chlorine under the conditions utilized for water renovation, in order to characterize and determine the halogenated organics formed in this reaction. Non-chlorinated water samples showed total trihalomethanes (THMs) and total organic halogen (TOX) levels ranging from 0.4 to 12.2 $\mu\text{g/l}$ (mean value, 4.1 $\mu\text{g/l}$) and from 7 to 51.5 $\mu\text{g/l}$ (mean value, 25.9 $\mu\text{g/l}$), respectively. It was found that the concentrations and compositions of organic halogen in chlorinated river water are strongly dependent on the sampling points and periods. The ranges of total THMs and TOX levels in chlorinated river water were from 2 to 158 $\mu\text{g/l}$ (mean value, 33.1 $\mu\text{g/l}$) and 12 to 400 $\mu\text{g/l}$ (mean value, 151 $\mu\text{g/l}$), respectively. Higher concentrations of both THMs and TOX and a high ratio of brominated THMs to total THMs were found on chlorination of water samples taken from the midstream of the Tama River, as compared with those observed from the upstream region. The concentrations of both THMs and TOX in chlorinated river water increased during spring and summer and decreased during fall and winter. In addition, the amounts of THMs and TOX in chlorine-treated river water were found to be dependent on the pH of the solutions and the time of contact with chlorine.

Keywords — brominated trihalomethane; chloroform; halogenated organics; Tama River; total organic halogen; water chlorination

Introduction

Three important rivers drain into Tokyo Bay, namely the Edo, Ara, and Tama Rivers, which have been used for agricultural and recreational purposes or as a source of potable water. Particularly in the Tama River, pollution from industrial, agricultural and domestic waste waters including heavy metals and organic contaminants has increased over the last 30 years due to the development of industries and the concentration of population in this area. The increase in pollution by organic matter in the Tama

River is critical, and the use of this river as a source of potable water has been sharply reduced since 1970. Although the major inorganic components, *i.e.*, heavy metals, total-N, total-P, and the chemical biological behavior in the Tama River have been well characterized,¹⁻⁸⁾ the specific organic components are still not well known.^{4,5,8)}

Chlorination is a practical water treatment process used to control harmful microorganisms in water, though this process is now a major source of organic halogens found in drinking water.^{9,10)} Among these organic

halogens, trihalomethanes (THMs) are easily quantified by gas chromatographic procedures.¹¹⁾ Unfortunately no simple and accurate method exists for identification and quantification of individual non-purgeable halogenated organic compounds that are formed as the result of chlorination. Although THMs are of concern, because of their effects on health¹²⁻¹⁴⁾ and their significant levels in water supplies, recent work has shown that even higher levels of total organic halogens (TOX) can be formed as the results of chlorination of natural water.¹⁵⁻²¹⁾ It has also been shown that the mutagenic character of chlorinated drinking water is more closely associated with the non-volatile high-molecular-weight fraction of chlorinated organic compounds.^{14,22)} It seems therefore reasonable to consider not only the formation of THMs but also of TOX when monitoring chlorination processes.

In order to provide further insight into the possible role of dissolved organic matter in the formation of chlorine-incorporated compounds and chlorine-induced mutagens, this laboratory has continued the study of the aqueous chlorination chemistry of organic compounds.⁸⁾ The data presented here show the seasonal and regional changes in the concentrations of THMs and TOX in the Tama River water before and after chlorination under those conditions utilized for water renovation. These findings provide background information that will undoubtedly be required in assessing the health implications and trends of organic compounds in this river.

Materials and Methods

Chemicals — A mixture of reference organohalides (CHCl_3 , 2 mg/l; CHBrCl_2 , 1 mg/l; CHBr_2Cl , 4 mg/l; CHBr_3 , 20 mg/l; CCl_2CHCl , 0.5 mg/l; CCl_2CCl_2 , 0.2 mg/l and CCl_3CCl_3 , 0.1 mg/l) in methanol was obtained from Kantoh Chemical Co. Standard solutions of these compounds were prepared by dissolving the above methanol solutions in boiled and then cooled water, with subse-

quent dilutions. An analytical grade of 2,4,6-trichlorophenol, used as a standard halogenated organic compound in determination of TOX in water samples, was obtained from Tokyo Chemical Industry Co. A hypochlorite solution was prepared by diluting sodium hypochlorite (NaOCl) solution (*ca.*, 10% available chlorine, Nakarai Chemical, Ltd.) with deionized and distilled water and was adjusted to the required pH by addition of 0.1 M $\text{Na}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ buffer solution. The hypochlorite concentration was determined by iodometric titration.

Sample Collection — Water samples were collected from the Tama River at eight sampling stations (Fig. 1), during Dec. 1985 to Sept. 1987 (Table I). Great care was taken to avoid contamination: all utensils and containers were scrupulously cleaned and rinsed with deionized and distilled water before use. A Heyroth water sampler was employed and all the 3-l samples were taken from the middle layer below the water surface, at the middle of the river. In the laboratory, all these samples were filtered through a membrane filter (0.45 μm ; Advantec Co.) to avoid biodegradation, and stored at 5 °C until TOX determination.

In addition, 10 ml of the water from each sampling station was collected in a 15 ml serum vial, which was immediately sealed with a PTEE-lined septum and aluminum cap. After shaking vigorously, the vial was placed upside down in an ice box and transported to the laboratory for determination of THMs.

Chlorination — All the filtered samples were adjusted to pH 7 with either 1 N HCl or 1 N NaOH, and chlorination was carried out in a 1-l glass reactor. Prior to use, the reactors were washed and rinsed with deionized and distilled water and heated at 200 °C for at least 2 h. Chlorine was added as NaOCl to give 10 mg/l of free chlorine for TOX formation. A non-chlorinated control was employed for each chlorinated sample. All chlorinated samples were stirred gently with a magnetic stirrer at 20 °C for the desired time. A 10-ml aliquot of a 3% Na_2SO_3 solution was then added to the sample in each

reactor to quench the TOX formation reaction, before adjusting the pH to 2 with concentrated HNO_3 . The same chlorination procedure was also performed for THMs formation reaction in the vial.

Organic Halogen Determination — The activated carbon/microcoulometric method was carried out with a Mitsubishi Chemical TOX-10 organic halogen analyzer to determine TOX in chlorinated samples and the non-chlorinated control. Samples with contents of organic halogen higher than approximately $500 \mu\text{g/l}$ were diluted several times with deionized and distilled water. The sample was then passed through two glass columns in series, each containing 40 mg of activated carbon (Mitsubishi Chemical Industry Co.), at a rate of 3 ml/min. The columns were washed with 8 ml of 0.08 M NaNO_3 solution to remove inorganic chloride remaining on the carbon. The carbon from each column was combusted separately at 850°C in an atmosphere of oxygen and the organic halogen was determined microcoulometrically, as organic chlorines. The detection limits were approximately $1 \mu\text{g/l}$ for this carbon adsorption method.

The head spaces from the chlorinated samples and non-chlorinated control were analyzed, using a Hitachi 263-30 gas chromatograph

equipped with a ^{63}Ni (10 mCi) electron capture detector (ECD-GC). A stainless steel column (2 m x 1.5 mm i.d.) packed with 10% silicon DC-200/Gas Chrom Q (80–100 mesh) was used for determination of the THMs and other volatile organic halogen levels in water samples. The temperature of the column oven was 85°C . The injector and detector temperatures were 260°C . The carrier gas (nitrogen) flow-rate was 25 ml/min. A Hitachi D-2000 Chromato-Integrator was used to determine the retention times and the areas of peaks on the chromatograms. THMs and other volatile organic halogens were identified by comparison of their retention times with those of authentic standard samples injected under the same GC conditions.

Results and Discussion

Background Levels of THMs and TOX in the Tama River

In the Tama River, two main dams, namely Den-enchofu and Hamura, have been constructed between stations 2 and 3 and stations 6 and 7, respectively (Fig. 1). This river is, therefore, divisible into 3 regions in terms of water quality^{6,7}: upstream [relatively clean, biochemical oxygen demand (BOD) *ca.* 1 mg/l], midstream (heavily polluted, BOD

Fig. 1. Locations of Sampling Sites in the Tama River
Names of the sites; see Table I.

ca. 7 mg/l) and downstream (moderately polluted with tidal effect, BOD ca. 3.5 mg/l). In the midstream, relatively polluted water is diluted with clean water from the Akikawa stream near station 6 and then polluted again heavily with industrial and domestic effluents through the Asaka, Nogawa and other small streams between stations 3 and 6. At the present time, it is known that over 80% of the BOD in this river is loaded by the effluents from domestic waste-water through these

small streams flowing into the river.^{6,7)}

In order to obtain background information about THMs and TOX in the Tama River before and after chlorination, water samples were collected eight times from eight sampling sites on this river during December 1985 to September 1987 (Fig. 1 and Tables I and II). Head space/gas chromatographic and activated carbon/microcoulometric analyses were carried out to determine the concentrations of total THMs and TOX in chlorinated

TABLE I. Distribution of Total Trihalomethanes (T-THMs) and Total Organic Halogen (TOX) in Water Samples Collected from the Tama River during December 1985 to September 1987

Name of the sampling station No.	Concentration ($\mu\text{g/l}$) in water sample ^{a)}			
	T-THMs		TOX	
	Range	Mean $\pm$ S.D.	Range	Mean $\pm$ S.D.
1 Daishi (3.8km) ^{b)}	1.1–8.3	4.4 $\pm$ 2.5	33.0–41.3	37.5 $\pm$ 3.8
2 Maruko (14km)	1.4–10.6	4.4 $\pm$ 3.2	13.6–37.5	28.6 $\pm$ 8.3
3 Tamasuido (25km)	1.1–11.6	4.4 $\pm$ 3.1	16.0–42.3	26.6 $\pm$ 9.0
4 Koremasa (34km)	0.4–10.2	5.5 $\pm$ 3.5	18.3–38.8	27.3 $\pm$ 9.5
5 Hino (43km)	1.2–12.2	5.0 $\pm$ 4.1	14.0–51.5	34.3 $\pm$ 11.0
6 Nagata (54km)	0.7–10.3	4.5 $\pm$ 3.5	11.7–33.7	20.9 $\pm$ 6.6
7 Mannen (64km)	0.4–7.1	2.4 $\pm$ 2.6	7.1–29.1	13.8 $\pm$ 6.4
8 Kawai (78km)	0.4–5.7	2.6 $\pm$ 2.3	11.5–25.0	18.1 $\pm$ 4.4

a) During the surveyed years, two water samples were collected from each station of the river at every sampling time (see Materials and Methods) and the concentrations of T-THMs and TOX in the water samples were determined by using ECD-GC and TOX analyzer.

b) Distance from the river mouth.

TABLE II. Distribution of Trihalomethanes (THMs-FP) and Total Organic Halogen Formation Potentials (TOX-FP) of Water Samples Collected from the Tama River, during December 1985 to September 1987

Name of the sampling station No.		Concentration ($\mu\text{g/l}$) in water sample ^{a)}				Ratio of
		THMs-FP		TOX-FP		TOX-FP:
		Range	Mean $\pm$ S.D.	Range	Mean $\pm$ S.D.	THMs-FP
1	Daishi (3.8km) ^{b)}	50–158	64 $\pm$ 43	89–192	140 $\pm$ 52	2.2
2	Maruko (14km)	8– 81	25 $\pm$ 23	73–168	159 $\pm$ 100	6.4
3	Tamasuido (25km)	11–122	39 $\pm$ 35	67–352	171 $\pm$ 89	4.3
4	Koremasa (34km)	15– 98	48 $\pm$ 31	79–357	181 $\pm$ 92	3.8
5	Hino (43km)	8– 89	47 $\pm$ 28	56–400	200 $\pm$ 109	4.3
6	Nagata (54km)	2– 72	29 $\pm$ 22	21–247	121 $\pm$ 67	4.2
7	Mannen (64km)	16– 28	22 $\pm$ 5	16–276	116 $\pm$ 72	5.3
8	Kawai (78km)	14– 30	22 $\pm$ 6	12–232	112 $\pm$ 59	5.1

a), b); Same as in Table I, but water samples were treated with hypochlorite (initial chlorine concentration, 10 mg/l) at 20°C for 24 h at neutral pH.

and non-chlorinated river waters. Table I shows the total THMs and TOX concentrations in these water samples before and after chlorination. In the present work, tetrachloromethane, trichloroethylene, tetrachloroethylene and 1,1,1-trichloroethane were also detected but their concentrations were very low (below $0.2 \mu\text{g/l}$).

Water samples collected from the Tama River showed total THMs levels ranging from 0.4 to $12.2 \mu\text{g/l}$ with a mean value of $4.1 \mu\text{g/l}$, depending on the sampling site and period (Table I). Although the data given in Table I showed some seasonal scatter, it seems that the concentrations of total THMs in the river water increase in the mid- and downstream regions and in summer (Fig. 2). On the other hand, the range of TOX levels in the water samples taken from this river was 7 to $51.5 \mu\text{g/l}$ with mean value of $25.9 \mu\text{g/l}$, depending on the sampling point and season (Table I). Comparatively high concentrations

of TOX were found for water samples collected in winter and early spring, whereas low values were observed for summer and fall samples (Fig. 2). In addition, an increase in the concentrations of total THMs and TOX in water samples from the mid- and downstream regions (Table I) indicates the increase of anthropic contamination entering the river.

Concentrations and Compositions of Organic Halogens Formed during Chlorination of the River Water

On the basis of background information about THMs and TOX levels in the Tama River, subsequent experiments were carried out to determine the concentrations and compositions of total THMs and TOX formed during chlorination of waters from this river. Table II shows the results of total THMs and TOX measurements for water samples after

Fig. 3. Distribution of Trihalomethanes (THMs) and the Ratios of Brominated THMs to Total THMs Formed during Chlorination

Fig. 4. Seasonal Changes in the Concentrations of Total Trihalomethanes (T-THMs) and Total Organic Halogen (TOX) in Chlorine-Treated River Water

Water samples were collected from the stations 3 (○ and ●), 5 (△ and ▲), and 7 (□ and ■) of this river and subsequently treated with chlorine (initial chlorine concentration; 10 mg/l) at 20 °C for 24 h under neutral pH.

treatment with chlorine (initial chlorine concentration, 10 mg/l) at 20 °C for 24 h under pH 7.0. To compare results more easily, the concentrations of total THMs formed during chlorination of waters from each sampling period and point are presented graphically in Fig. 3. Seasonal variations in the concentration in water from the Tama River at selected sampling points are also presented graphically in Fig. 4.

Water samples taken from the Tama River and subsequently treated with chlorine showed total THMs levels ranging from 2 to 158 µg/l with a mean value of 33 µg/l, depending on the sampling point and period (Table II). These values were found to be 6–10 times higher than those observed for the non-chlorinated control (Table I). These results also correspond to those reported from America,^{23–27} Western Europe,^{28–30} and other countries.^{31–33} The highest total THMs formation potential (Table II) was found in water taken from station 1 of the Tama River on July 1986, whereas the lowest value was observed for the sample taken from station 6 on April 1986.

The changes in compositions of the total THMs formed during chlorination of water

samples collected from the Tama River are noteworthy (Fig. 3). Usually, chlorinated drinking water contains a relatively high concentration of chloroform as compared to other THMs.^{23,24,31} In the present work, considerably higher concentrations of brominated THMs were found in the samples collected from stations 3–6 of the Tama River and subsequently treated with chlorine. Several workers have demonstrated that chlorination or ozonation of surface and ground water containing bromide ion produces high concentrations of brominated THMs.^{9,27,29,32,33} Higher ratios of brominated THMs to the total THMs were also found in water samples taken from Asaka and Hodokubo streams between 4–5 along the Tama River and subsequently treated with chlorine, as compared to those observed for Akikawa, Zanbōri, Ōkuri and Nogawa stream waters. However, the origin of the bromide ion in the water samples could not be clarified because of the limited sampling points and periods in this survey. Further investigation is needed to determine the reason for the higher ratios of the brominated THMs to the total THMs in the Tama River water.

The range of TOX levels in water samples taken from the Tama River and subsequently treated with chlorine was from 12–400 µg/l, depending on the sampling point and period (Table II). These values were found to be 3–6 times higher than those observed for the non-chlorinated control (Table I). A relatively high TOX formation potential was also found for the water samples taken from midstream of the Tama River, whereas a lower value was observed for the samples collected from upstream (Table II). It seems probable that the higher levels of THMs and TOX precursors in water samples taken from stations 3–6 of the Tama River originate from industrial and domestic waste waters.

The concentrations of total THMs and TOX formed during chlorination of the water

taken in summer were found to be 2–6 times higher than those observed in winter samples (Fig. 4). This may be due to the increase in water temperature and microbiological activities, which cause the biological conversion of organic matter present in water into organohalogen precursors,³⁴⁾ during spring and summer. Although a great deal of attention has recently been focused on the problem of THMs formation, THMs are only a minor component of TOX found in chlorinated drinking water.^{15–21)} Table II and Fig. 4 show that chlorination of water samples taken from the Tama River produced from 4 to 8 times as much TOX as the total THMs. Thus, it seems that production of TOX is more significant than that of THMs in chlorinated drinking water.

Effects of Experimental Conditions on the Production of Organic Halogens in Chlorine-Treated River Water

Further investigations were carried out to determine the influence of the experimental conditions on the production of halogenated organics during reactions of chlorine with organics present in water samples. The water samples taken from station 5 of the Tama River was employed, because this water is heavily polluted with organohalogen precursors (Table II) but will be re-used as a source of potable water.

Several investigators^{16,18)} have shown

that both THMs and TOX levels in chlorinated water increase with chlorine dose and the ratios of THMs to TOX increase with the times of contact with chlorine. Figure 5 shows the time courses of the production of both total THMs and TOX in a water sample treated with chlorine (initial Cl concentration, 10 mg/l) at 20 °C and at neutral pH. In contrast to the THMs production, a rapid increase in the amounts of TOX was observed initially. However, no secondary reactions similar to those observed for THMs production were found, even at longer reaction times in the chlorinated water, with the exception of summer water. This phenomenon can be interpreted in terms of the competition between the production of TOX and the destruction, giving THMs and highly oxidized products such as halogenated carboxylics. Thus, it seems that higher concentrations of total THMs in chlorinated drinking water would be found at a terminal water supplying system, as compared to those observed for effluent from the treatment plants. As can be seen in Table III, the effect of chlorine dose on the production of total THMs and TOX in chlorinated river waters was similar to those observed for the chlorine contact time.

The production of both THMs and TOX in chlorinated water is strongly influenced by the pH of the solution, as illustrated in Fig. 6. It was found that the THMs concentrations

TABLE III. Effect of Chlorine Dose on the Formation of Total Trihalomethanes (T-THMs) and Total Organic Halogen (TOX) during Chlorination of Water Samples Collected from Station 5 of the Tama River

Experimental conditions				Concentration of T-THMs				Concentration of TOX			
pH	Temp.	Time	Cl-dose	formed ($\mu\text{g/l}$) ^{a)}				formed ($\mu\text{g/l}$) ^{a)}			
	(°C)	(h)	(mg/l)	1986 Apr.	1986 Jul.	1986 Oct.	1987 Feb.	1986 Apr.	1986 Jul.	1986 Oct.	1987 Feb.
7.0	20	24	1	0.2	0.5	0.5	2.0	9	48	30	19
7.0	20	24	2	0.8	1.8	1.2	3.8	22	101	62	30
7.0	20	24	3	3.1	8.3	6.2	5.4	28	184	124	31
7.0	20	24	5	14.5	11.4	24.9	8.7	56	267	124	30
7.0	20	24	10	40.5	52.8	30.2	26.9	176	272	261	52

a) Average of three experiments.

decrease and the TOX level increases to an even greater extent as the pH is lowered, with the exception of summer water. Only the summer sample showed similar concentrations of TOX in water after treatment with chlorine at various pH values. This can probably be attributed to the rapid and complete production of TOX precursors by the biological conversion of organic matter during summer time.

Conclusion

As river water is often exposed to halogenated organic pesticides contained in agricultural waste-water, pesticides are often detectable, though at low levels in the river water (Table I and Fig. 2). Aqueous chlorine is used to disinfect sewage water and raw water destined for human consumption. Water samples taken from the Tama River have been shown to produce THMs and TOX when the samples are treated with chlorine under the conditions utilized for water renovation (Table II). Relatively higher concentrations of brominated THMs to total THMs were found in water samples taken from midstream and subsequently treated with chlorine (Fig. 3). It has been reported that brominated organics are more mutagenic than chlorinated compounds,³⁵⁾ so it is particularly significant that brominated organics were found in this work in chlorine-treated river-water.

The amounts of THMs and TOX formed during chlorination of river-water and the ratios of TOX to THMs were strongly dependent on the sampling points and periods (Table II and Fig. 4). Comparatively higher levels of total THMs and TOX formed were found in water samples taken from midstream, as compared to the values observed in upstream waters. In addition, the concentrations of THMs and TOX precursors in water samples taken from the Tama River increased during late spring and summer and decreased during fall and winter (Fig. 4), whereas high BOD levels in this river was observed for winter

Fig. 5. Time Courses in the Production of Total Organic Halogen (TOX, Top) and Total Trihalomethanes (T-THMs, Bottom) during Chlorination (Initial Chlorine Concentration; 10 mg/l, 20°C and pH 7) of Water Samples Taken from Station 5 of the Tama River

Fig. 6. Effect of pH on the Formation of Total Organic Halogen (TOX, Top) and Total Trihalomethanes (T-THMs, Bottom) during Chlorination (Initial Chlorine Concentration; 10 mg/l, 20°C and 24h) of Water Samples Collected from Station 5 of the Tama River

samples and low values in summer water (Fig. 2). Furthermore, the residual chlorination products, THMs and TOX, in chlorinated river water were found to be dependent on the dose (Table III), contact time with chlorine (Fig. 5), and the pH of the solution (Fig. 6).

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