

DBPs in drinking water (e.g., [6]). It has been demonstrated that bromoacetic acids are more mutagenic than chloroacetic acids [7]. In particular, mono bromoacetic acid is much more mutagenic than other haloacetic acids [6]. Also, it is known that the products of the reaction between hypobromous acid and humic acid are several times more mutagenic than the ones between hypochlorous acid and humic acid on TOX basis [8]. Nobukawa and Sanukida [9] showed that the mutagenicity of chlorinated water increased with increasing bromide ion concentration. These results indicated that brominated compounds formed during chlorination could be major contributors to the toxicity of drinking water.

Given the toxicological importance and the lack of information on the source and the fate of bromide ion in river basins in Japan, this study attempts (1) to find the distribution of bromide ion in the Lake Biwa-Yodo River Basin, and (2) to discuss the origins of bromide ion in the basin. Also, with this basic information on the origin of bromide ion, the feasibility and the effectiveness of regulating bromide ion in source water are briefly discussed.

2. Bromide distribution in the Lake Biwa-Yodo River Basin

2.1 Methods

Twenty-seven sampling points were selected to cover the entire basin (Figure 1). The samples were collected in the second week of November 2005. No major precipitation was observed during the preceding three days of sampling.

Each sample was passed through a 0.2 μm filter (Chloromatodisk, GL Science) before ion chromatographic analysis. The analytical conditions were: System, Shimadzu LC-VP; detection, UV absorbance at 210 nm; mobile phase, 12 mM sodium bicarbonate/0.6 mM sodium carbonate. The chemicals used for the analysis were of analytical grade or better. All

the aqueous solutions were prepared with the water treated by a Millipore Elix 10 system.

2.2 Bromide ion distribution

Figure 1 illustrates the bromide distribution in the Lake Biwa-Yodo River Basin. While this is a “snapshot” of bromide ion concentration, it has been confirmed that bromide ion concentration in this area is quite stable by a series of preliminary surveys (i.e., no daily, weekly, and seasonal variation). That is, one can assume this is a typical bromide distribution in this river basin. In the upstream areas of the rivers flowing into Lake Biwa, the bromide ion concentration was relatively low (10-16 $\mu\text{g/L}$), but bromide ion concentration was much higher in the downstream area of Yodo River (42-46 $\mu\text{g/L}$). This difference strongly suggests the discharge of bromide ion from human activities. It is of note that the bromide ion concentration in Katsura River dramatically increased to 63 $\mu\text{g/L}$ right after passing through Kyoto City (i.e., in the downstream of a major wastewater treatment plant).

The above results clearly show that bromide ion discharged from wastewater treatment plant has considerable impact on the bromide concentration in the downstream. For this reason, the bromide load from wastewater is discussed in detail in the next section.

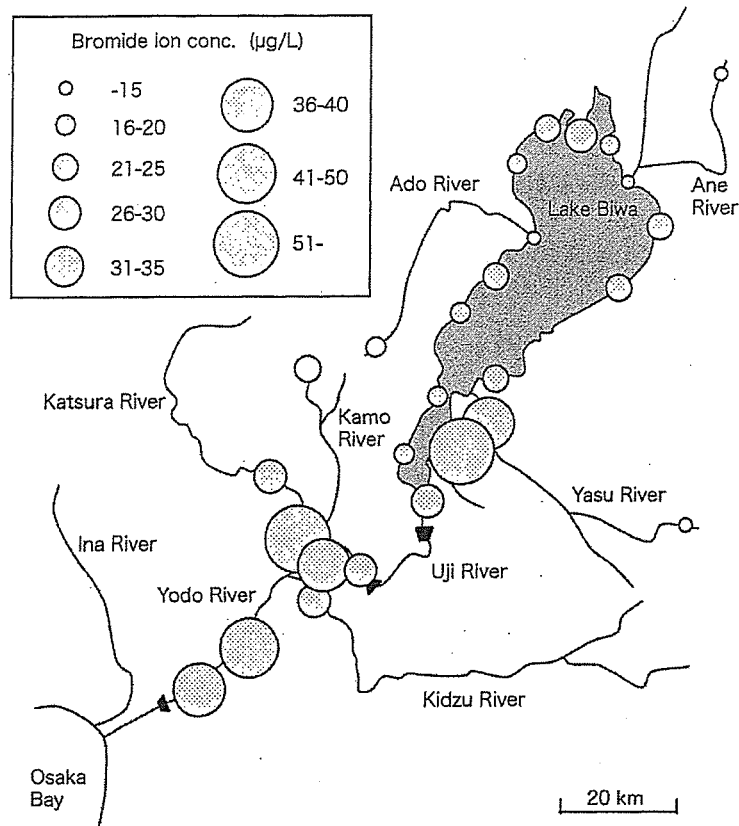


Figure 1. Bromide ion distribution in the Lake Biwa-Yodo River Basin.

3. Bromide discharge from wastewater treatment plants

3.1 Methods

Twelve major wastewater treatment plants were selected for the survey. These plants covers approximately 90% of the wastewater treated in the basin on flow rate basis [10]. The samples were collected around the second week of November 2005. See 2.1 for analytical conditions.

3.2 Bromide load from wastewater treatment plants

The bromide ion concentrations in effluent from wastewater treatment plants and

the bromide loads from these facilities are summarized in Table 1. Also, the land use of the area covered by each plant is shown in Figure 2 [11-14].

The bromide ion concentration of the effluents from the plants I and J was much higher (at least 3 to 4 times) than those from other plants. At this point, no specific reason is given for this observation, but the type of the industrial activity in the coverage area is likely to affect the bromide level. Also, the bromide ion concentration of the effluents A to E was above 70 μ g/L. These plants are in relatively large scale and cover commercial and industrial areas. To the contrary, the effluents from the plants F to H contained less bromide (40-60 μ g/L). These plants are small and cover residential areas. The effluents from K and L (medium-scale wastewater treatment plants) contained similar level of bromide ion.

Table 1. Bromide ion concentration in wastewater effluent.

Plant code	Bromide ion conc. (μ g/L)
A	94.0
B	113.6
C	110.0
D	111.0
E	152.0
F	41.8
G	66.3
H	51.5
I	356.5
J	436.2
K	64.8
L	58.9

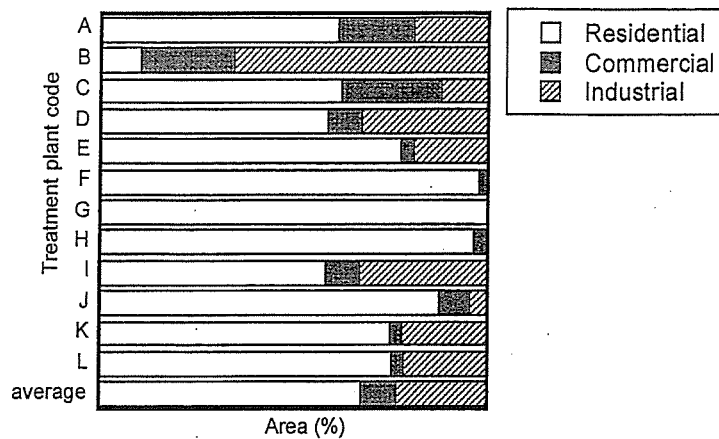


Figure 2. Land use of the treatment areas of 12 major wastewater treatment plants in the Basin.

Bromide load from each plant was also estimated (Table 2). For this purpose, average dry weather flow rates were used [10]. Bromide loads from J and I were also high because of very high bromide ion concentration, but the difference was not as much as in the concentration itself.

Table 2. Bromide load from wastewater effluents.

Plant code	Bromide load (mg/(day·person))
A	0.070
B	0.084
C	0.055
D	0.044
E	0.057
F	0.011
G	0.011
H	0.011
I	0.216
J	0.222
K	0.028
L	0.017

Among other large or medium-scale plants (A-E, K, L), B covering mostly commercial and industrial areas was the highest with respect to bromide load (80 mg/(day•person)). The order of bromide load was: B>A>E>C>D>K>L. Other than E, bromide load from commercial areas appeared relatively high. Also, bromide load from residential areas was 11 mg/(day•person) for the three plants (F-H). This value is in good agreement with the bromide load calculated from bromide concentration in human urine by Zhang et al.[15], indicating most bromide discharged from residential areas originates from foods. Furthermore, under the assumption that the unit bromide load from residential area is the same over the basin (11 mg/(day•person)), and that the bromide is directly discharged from industrial activity to the river system in the treatment area of C plant, the unit bromide load from commercial areas in the treatment area is found to be 7.9 g/(day•ha). In the analysis below, it is assumed that this value is applicable to other industrial areas in the basin.

4. The origins of bromide ion in the Lake Biwa-Yodo River Basin

The origins of bromide ion in the lower Yodo River Basin were estimated from the results in the previous two sections (Figure 3). The bromide ion in wastewater accounted for only 28% of the total bromide load. The bromide discharged to the river directly (i.e., without passing through public sewerage system) from human activities was 38%. Considering that approximately 80% of the population in the basin is covered by public sewerage service [10], the major fraction of the bromide directly discharged is likely from industrial and commercial activities. The detail of this fraction is unknown, but it might be possible to identify a specific industrial activity of high bromide load and to urge the reduction of bromide discharge. Also, bromide ion as an impurity in some antifreezing agents could be a major source of bromide

ion [16].

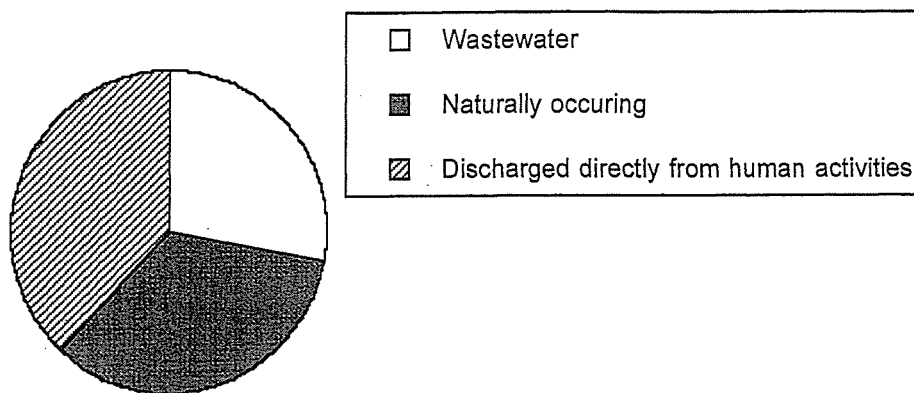


Figure 3. The origin of bromide ion in the lower Yodo River Basin (Hirakata City). Naturally occurring bromide was assumed to be 17 $\mu\text{g/L}$ (an average concentration in the upstream area), and average dry weather flow rates were used for this estimation [17].

Also, more than 60% of anthropogenic bromide ion in wastewater effluents was found to be from industrial activity. Thus, together with the discussion above, it was presumed that bromide discharge from industrial activity is a dominating factor for high bromide ion in the downstream. Hence, it would be more effective to regulate bromide from industrial activity than bromide in domestic wastewater.

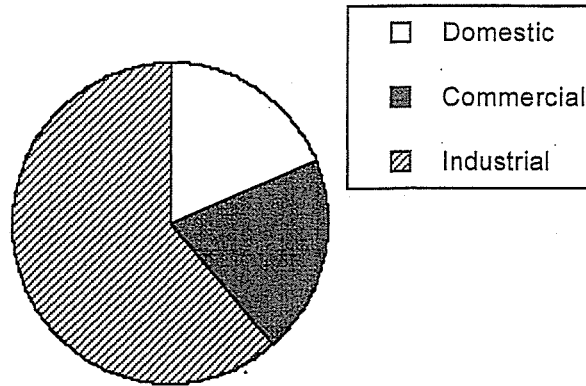


Figure 4. Origins of bromide ion in wastewater effluents. To estimate the loads from domestic and commercial wastewaters, the unit loads was assumed to be 11 mg/(day•person) and 7.9 g/(day•ha), respectively (also, see 3.2). The rest of bromide was assigned to industrial origins.

5. Conclusions

Clearly, human activities greatly increase bromide level in source water in the Lake Biwa-Yodo River Basin. Also, from the origin analysis of bromide, it was suggested that industrial activity is considerably contributing to high bromide level. Thus, regulation to reduce bromide discharge from industrial activity would be effective for better control of brominated DBPs.

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EXPOSURE ASSESSMENT OF TRIHALOMETHANES IN HOUSEHOLDS FOR ESTIMATING ALLOCATION TO DRINKING WATER

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Abstract

To obtain the present standard value for trihalomethanes (THMs) in Japan, a 20% allocation of ingesting drinking water among overall exposure was used as a reasonable default. However, this allocation may not be accurate because of the insufficiency of the data for multi-route THMs exposure in households. Accordingly, this study was designed to obtain those data by measuring the THMs concentration in tap water and indoor air in 10 households around the Kansai area. The air concentration of THMs in bathrooms was 20 to 40 times higher than other indoor environment, and the total inhalation exposure was found to be comparable to that of ingestion.

Key Words

THMs, exposure, ingestion, inhalation, indoor air, tap water, allocation

INTRODUCTION

Chlorine is the most commonly used chemical for disinfecting drinking water in Japan and many other countries. However, the use of chlorine to disinfect drinking water leads to the formation of halogenated hydrocarbon by-products, which are potentially harmful to human health (Singer and Reckhow, 1999; von Gunten *et al.*, 2001). Among those by-products, trihalomethanes (THMs) (chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (TBM)) have attracted extensive attention, as they have been found to exhibit potentially carcinogenic activity in humans (Clark *et al.*, 1992; Morris *et al.*, 1992).

In the present Drinking Water Quality Standard of Japan, it is considered appropriate to use the tolerable daily intake (TDI) approach for calculating the standard value for THMs as shown in Table 1. For example, the standard value for TCM derived from its TDI of 12.9 $\mu\text{g}/\text{kg}$ per day is 0.06 mg/L, based on an allocation of 20% of the total daily intake to drinking water and assuming a 50-kg adult with 2 L/day consumption of drinking water. This allocation means that over all the human exposure scenarios, which include oral ingestion as drinking water, inhalation, dermal intake and dietary, the contribution to drinking water as oral ingestion is 20%.

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Table 1 TDI and Drinking Water Quality Standard values of four types of THMs (Ministry of Health, Labour and Welfare, Japan, 2003)

	TDI($\mu\text{g}/\text{kg}$ per day)	Allocation	Value(mg/L)
TCM	12.9	20%	0.06
BDCM	6.1	20%	0.03
DBC	21	20%	0.1
TBM	17.9	20%	0.09

However, because the information on this point is insufficient, it stands as a default value temporarily, and has been used by many countries on setting up the water quality standard, including Japan. For decades, great efforts have been made to find a more accurate allocation value in western countries (Andelman, 1985; Jo *et al.*, 1990; Wallace, 1997). Studies suggest that besides the traditionally-thought exposure route of ingestion of tap water, other routes also result in an equal or greater exposure to THMs. These other routes include inhalation and dermal absorption resulting from bathing, toilet use, cooking and using dish-washer. However, since all these studies were conducted in Europe or the USA, and the exposure is a direct function of the local environment, (e.g., the style of daily water consumption or aqueous-phase concentration of THMs in tap water), the results of the previous studies may not be applicable to domestic environment in Japan. Also, daily bathing activity is a unique and traditional life culture in Japan. Therefore it is considered that this high-frequency activity may lead to considerable exposure to the contaminant in the tap water.

The objectives of the present study are: (1) to measure the THMs concentrations in common residences; and (2) to estimate the magnitude of total exposure to THMs based on the typical Japanese life-style.

EXPERIMENTAL METHOD

Survey Protocol

A series of experiments was conducted to measure the THMs concentrations in indoor air, outdoor air, and tap water. Ten residences were selected to represent each type of household, and permission was received from the residents to measure the THMs levels. The residences were dispersed geographically around the Kansai area, and each residence was occupied by a single family with one to six persons. The ventilation was not controlled.

It was considered that the residence occupants mostly take showers or baths in evening or morning. As such, one nighttime (nominally from 8 p.m. to 8 a.m.) indoor and outdoor air sample was collected from each residence to evaluate shower (bath) effect on indoor air THMs concentration. The indoor air sampling was conducted in the living room, bedroom, kitchen (during cooking time), and bathroom (during bathing time). Concurrently cold and hot tap water samples were collected.

Sampling

The water samples were collected in glass vials with Teflon-lined enclosures. Prior to sampling, 50 mg sodium ascorbate was placed in the vials to quench residual chlorine. Agitation of the water was avoided to minimize the production of bubbles in the vials.

Airborne THMs were collected in a tube containing Tenax-TA (Supelco) using a constant flow sampling pump (GL Science SP208-100Dual). The sampling pump was calibrated by a digital flow meter before the collection of each sample. The flow rates of 4 mL/min, 20 mL/min, and 30 mL/min

were set for outdoor, living room, bedroom, kitchen, and bathroom air sampling, respectively. The nominal flow rate was sufficiently high as regards the sensitivity of the analytical system, yet sufficiently low to remain below the breakthrough volumes of the target chemicals.

Analysis

Liquid samples: liquid samples were carried out according to USEPA Method 501 (USEPA, 1979) and liquid-liquid extraction gas chromatographic Method 6232 B (Standard Methods, 1995). According to these methods, samples were prepared by extracting 40 mL of water sample with 4 mL of Hexane by shaking for 3 min manually. Liquid samples were analyzed using a GC/ECD (SHIMADZU GC-14B) system. The GC parameters included an inlet temperature of 150 °C and a detection temperature of 200 °C. For each sample, the initial oven temperature was 30 °C, which was held constant for 0.5 min before being ramped at 5 °C/min to a final oven temperature of 70 °C. A Silicone GE SE-30 (2 m×2.6 mm) column was used for all analyses.

Gas samples: gas samples were analyzed using a thermal desorber with an autosampler and a purge trap system (SHIMADZU TDTS-2010). This system was also plumbed to the GC/MS (SHIMADZU GCMS-QP2010) system. Each tube was thermally desorbed at 280 °C for 10 min and the target compounds cryofocused at -15 °C and concentrated in a cold trap with helium gas flow. Once the desorption was complete, it was heated to 250 °C and the target compounds were desorbed again from the trap and injected into the GC/MS system. A RESTEK RTX-1 capillary column (60 m×0.32 mm×1 µm film thickness) was employed.

Estimation of THMs Exposure from Water Ingestion

The THM exposure from water ingestion was estimated as follows:

$$\text{Water Ingestion Exposure } (\mu\text{g/day}) = \text{Absorption} \times \text{Tap Water Concentration } (\mu\text{g/L}) \times \text{Intake (L/day)} \quad (1)$$

The key assumptions include a 100% THMs absorption efficiency by the gastrointestinal tract (maximum potential dose for an individual) and daily water intake of 2 L (Exposure Factors Handbook, EPA 1997), and the median values were applied in all the calculations.

Estimation of THMs Inhalation Exposure from Daily Indoor Activity

The dose from inhalation exposure to airborne THMs was calculated using the following equation:

$$D_{\text{in}} = C \times R \times T \quad (2)$$

where D_{in} represents THMs dose from inhalation exposure to indoor air including shower and cooking ($\mu\text{g/day}$); C represents median indoor air concentration ($\mu\text{g/m}^3$); R represents breathing rate; T represents time spent indoor (Exposure Factors Handbook, EPA 1997).

Using literature values, a time-spent model of typical Japanese life style (Social Research, NHK 2000) was constructed as shown in Table 2. Also, an average breathing rate of 15 m^3/day (Exposure Factors Handbook, EPA 1997) and 100% absorption were assumed. For bathing and cooking, the actual values were used in the estimation.

Estimation of THMs Dermal Exposure

In the present study, it is considered exclusively that in all the indoor activities the dermal exposure only happens while bathing. Also, the estimation was conducted following the equation of the Dermal Exposure Assessment Principles and Applications (EPA, 2004). The assumptions include a body surface area of 18,000 cm² and the contact body area was of 100% regardless both the activity of bath and shower.

Table 2 Time-spent model (Social Research, NHK 2000)

Indoor locations	Time-spent (min/day)
Living room	420
Bedroom	450
Kitchen	Actual values
Bathroom	Actual values

RESULTS AND DISCUSSION

THMs in Aqueous-Phase

The aqueous-phase concentration of the four THMs (TCM, DBCM, BDCM, and TBM) and TTHM associated with the use of municipal tap water in ten different residences are shown in Figs. 1 to 3.

The TCM was the major one among THMs, and the bromo-THMs were present in lower concentration than TCM. This is consistent with other studies (Chang *et al.*, 1996). However, no significant difference was found among total THM concentrations in three types of water samples.

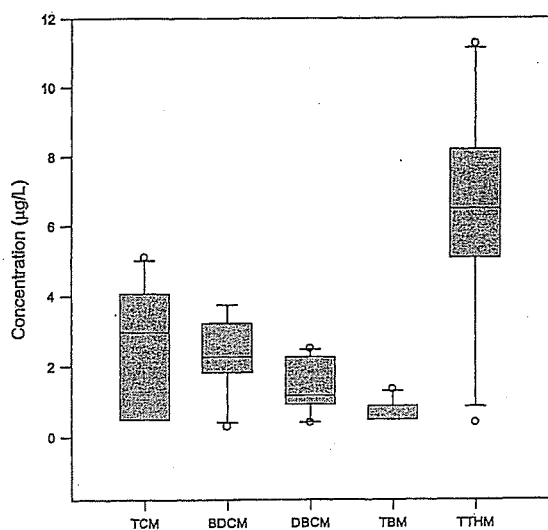


Fig. 1. Tap water concentration
Median total THMs concentration was 6.5 µg/L

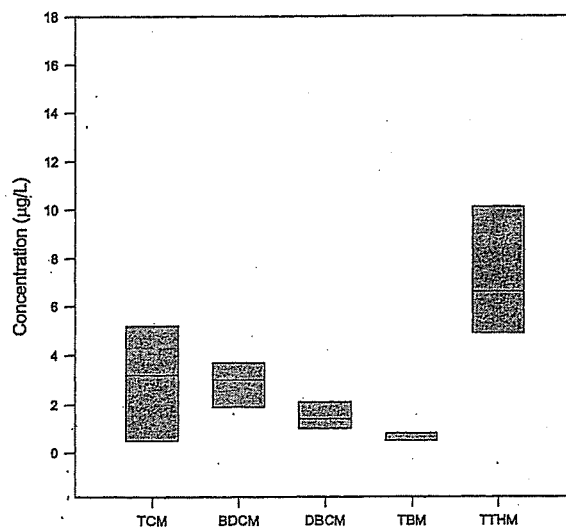


Fig. 2. Bath water concentration
Median total THMs concentration was 6.6 µg/L

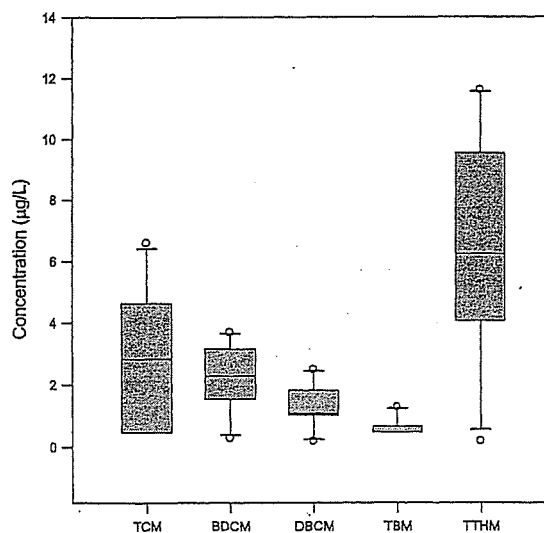


Fig. 3. Shower water concentration
Median total THMs concentration was 6.25 µg/L

THMs in Indoor Air

Figs. 4 to 8 show the indoor air concentrations of the four THMs in the same ten residences. Similar to the aqueous-phase concentrations, TCM was the most abundant THM in the indoor air, while almost no TBM was detected. Also, the order of TTHM concentration in the four types of indoor environment was: bathroom > kitchen > bedroom > living room. This could be attributed to the distance between the sampling spots and the location of faucet which has been considered as the main emission source of THMs. In the bathroom, a high TTHM concentration of $44.76 \mu\text{g}/\text{m}^3$ was detected, which is roughly 20 to 40 times higher than other indoor environment. Also, the relatively high TTHM concentration in kitchen is considered to be the result of cooking process which may involve transport of THMs from tap water into the air in kitchen. Actually, several researchers claimed that both water boiling and steam rice cooking may be the major sources of airborne THMs in kitchen. (Lin *et al.*, 1999).

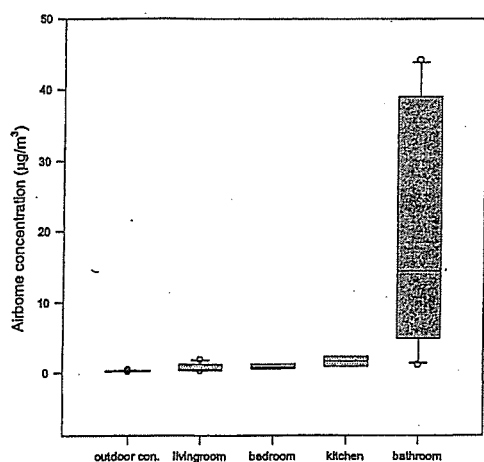


Fig. 4. Airborne concentration of TCM
Median airborne concentration in bathroom was $14.54 \mu\text{g}/\text{m}^3$

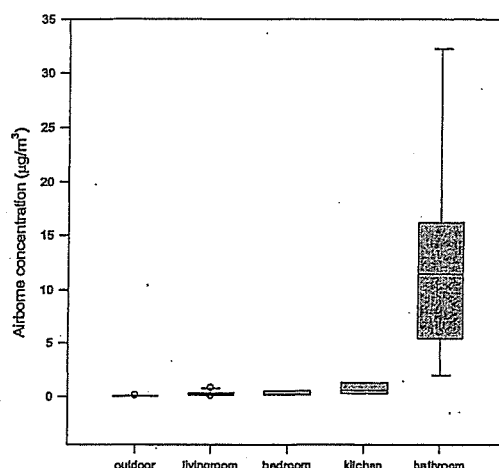


Fig. 6. Airborne BDCM concentration
Median airborne concentration in bathroom was $11.52 \mu\text{g}/\text{m}^3$

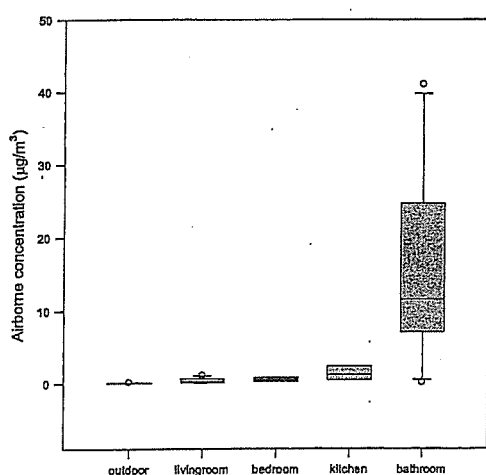


Fig. 5. Airborne concentration of DBCM
Median airborne concentration in bathroom was $11.55 \mu\text{g}/\text{m}^3$

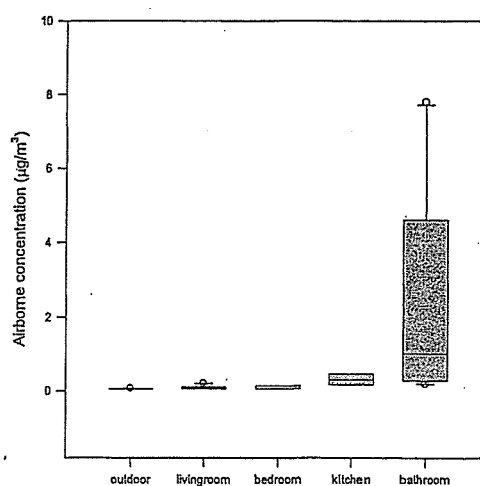


Fig. 7. Airborne TBM concentration
Median airborne concentration in bathroom was $1 \mu\text{g}/\text{m}^3$

Furthermore, the correlation test results showed strong positive correlations between aqueous-phase and airborne concentrations of TTHM in living room, bedroom and bathroom ($p = 0.022, 0.021, 0.004$, correlation coefficient = $0.741, 0.853, 0.803$, respectively).

Fig. 9 shows the linear regression test result between aqueous-phase and airborne concentrations of TTHM in bathroom. These findings confirm that of a previous study (Wallace, 1997), where aqueous-phase THMs concentration in tap water were found to be associated with airborne THMs concentration in indoor air.

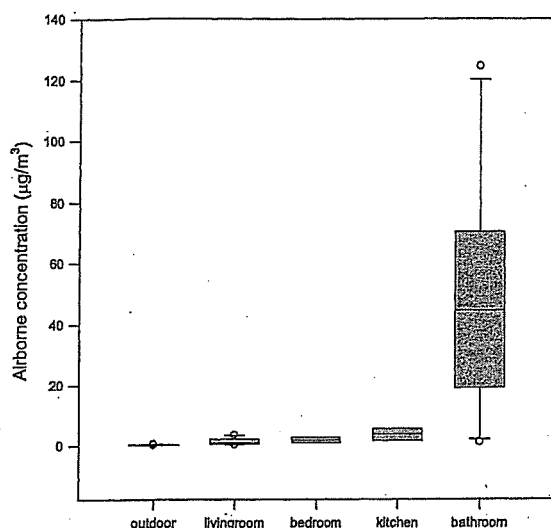


Fig. 8. Airborne TTHM concentration
Median airborne concentration in bathroom was 44.76µg/m³

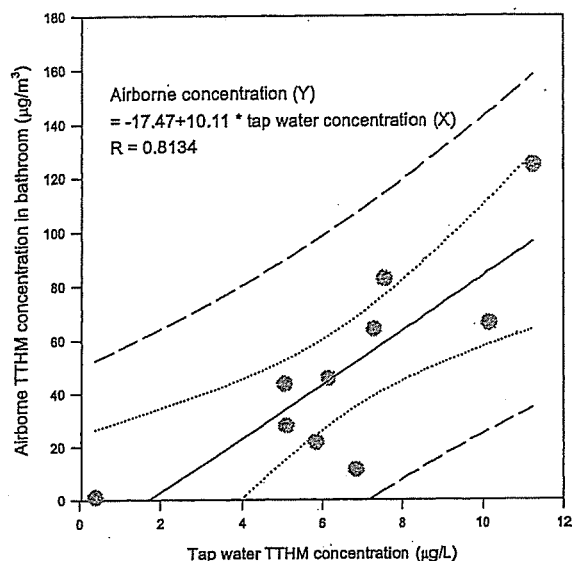


Fig. 9. Correlation between aqueous-phase and airborne concentrations of TTHM in bathroom

Exposure Analysis

The THMs exposure estimates from water ingestion, inhalation of indoor air, and dermal exposure while bathing are presented in Table 3.

The result is comparable to that in the previous studies (Jo *et al.*, 2005), and it was found that the TTHMs inhalation exposure from indoor air when not in the shower was estimated to contribute around or even less than 5% to the total exposure. Accordingly, the exposure of TTHM during bathing activity alone in the present study is derived of 21.41µg/day, which is also roughly 1.5 times higher than that of oral ingestion. In addition, the ingestion exposure is approximately 38% to the total exposure.

Table 3 Estimated THM exposure (µg/day) in residences using municipal tap water (medians values)

THMs	Ingestion	Inhalation ^a	Dermal	Total exposure
TCM	5.96	8.57	0.67	16.32
BDCM	4.54	7.13	0.34	12.50
DBCM	2.35	3.59	0.18	6.09
TBM	1	0.8	0.07	5.73
TTHM	13.03	22.54	1.17	34.16

a: It represents the inhalation exposure to indoor air including bathing.

Allocation to Drinking Water

As shown in Fig. 10, the allocation to oral ingestion among the total exposure ranges from 18.3% to

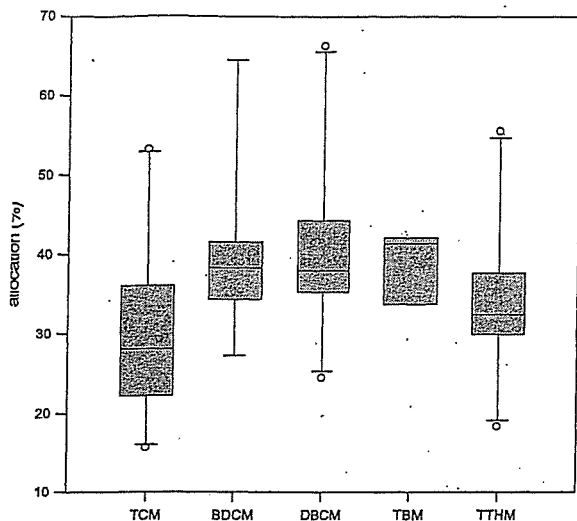


Fig. 10. Ingestion allocation to overall exposure
Median allocation of TTHM to overall exposure was 32.47%

55.4%. This indicates that the allocation to oral ingestion is affected by other exposure scenarios. The median value of total THMs ingestion allocation was 32.5%, which is almost 1.6 times higher than the currently applied value of 20% in setting up the drinking water quality standard. However previous studies showed that there is a considerable seasonal variation in both aqueous-phase and airborne concentrations (Jo *et al.*, 2005). Also, in the present study, no dietary intake exposure was included in the evaluation. Therefore, more consideration should be paid carefully in concluding the allocation to drinking water.

CONCLUSIONS

The present study estimated multi-route THMs exposure in common residences using municipal tap water. TCM was the main contaminant of the four THMs in water. The indoor airborne THMs concentration trend was also consistent with that of aqueous-phase concentration, supporting that tap water THMs levels are associated with indoor air levels of THMs. In the entire indoor environment measured, bathroom has the highest THMs concentration, followed by kitchen. The exposure analysis estimated that in common indoor life activities in Japan, inhalation exposure is 1.5 to 2.0 times larger than ingestion exposure as drinking water.

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Screening of Chemical Structures Related to Haloacetic Acid Formation in Drinking Water Chlorination Process

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Abstract Haloacetic acid (HAA) yields from 44 model organic compounds of dissolved organic matter (DOM) substructures were determined as screening process of the chemical structures responsible for HAA formation during drinking water chlorination. It was found that monohydroxybenzenes (phenols) tended to produce more HAA than dihydroxybenzenes. Also, a clear relationship was found between HAA and CHCl_3 formation for aliphatic compounds. Trihaloacetic acid concentrations were much higher than di- and mono-haloacetic acids for the chlorination of aromatic compounds tested while dihaloacetic acids were major products from aliphatic compounds. Moreover, in the presence of bromide ion (Br^-), the HAA yields increased by a factor of 1.5 on average than that in Br^- free condition for aromatic compounds while no significant effect was observed for aliphatic compounds.

Keywords bromide ion; chemical structures; disinfection by-products (DBPs); haloacetic acids; trihalomethanes.

Introduction

More than 200 compounds have been identified as disinfection by-products (DBPs) in actual tap water, and approximately 600 compounds are known as possible DBPs (Woo *et al.*, 2002). Among these compounds, haloacetic acids (HAAs) are one of the major groups of the DBPs, and their detection frequency and concentration in finished drinking water are next to trihalomethanes (THMs) (Zhang *et al.*, 2000). Also, all of nine HAAs containing chlorine and bromine atoms are known to be toxic and some of them are suspected carcinogens (Plewa *et al.*, 2002). Furthermore, brominated HAAs are more toxic than their chlorinated counterparts. Thus, it is important to understand the formation mechanism of HAAs in the presence of bromide ion to better control HAAs in drinking water treatment processes.

However, despite the toxicological importance of HAAs, the formation mechanism of HAAs is not fully understood. This is mainly because of the complexity of dissolved organic matter (DOM), the precursor of HAAs. DOM is a very complex mixture of organic compounds, and its structure is not clear, even today. To overcome this difficulty, the present study employs model compounds of DOM substructures. Similar approaches have been used for the studies on THM formation (*e.g.*, Rook, 1977; Ichihashi *et al.*, 1999), and successfully found the importance of *m*-dihydroxy structure for THM formation. However, no attempt has been made for HAA formation mechanism.

The main objective of this study is to investigate the relationship between simple substructures of DOM and HAA formation in chlorination, and to identify chemical

structures in DOM related to HAA formation. In addition, the effect of Br⁻ on the HAA formation from these model compounds was evaluated by chlorination in presence of Br⁻.

Experimental

Target compounds

Model compounds of DOM substructures (Table 1) used in this study were purchased from Wako Pure Chemical unless otherwise noted. Their purity was more than 95% except lactic acid (85-92%) and used without further purification. Many of the model compounds were with carboxylic acids because carboxy group is one of the most common functional groups in DOM (Thurman, 1985). Also, aromatic compounds with different number of phenolic hydroxy groups were selected, as the number of phenolic hydroxy groups is an important factor of the susceptibility of aromatic rings to electrophilic substitution reaction. For aliphatic compounds, most of the selected compounds were carbohydrates, carboxylic acids, and carbonyl compounds. They were chosen based on the abundance in DOM structures (Thurman, 1985; Leenheer, 2004) and the susceptibility to the haloform reaction (Larson and Weber, 1994).

Table 1. Model compounds of DOM substructures used in this study.

Aromatic compounds		Aliphatic compounds	
phenol	benzoic acid	crotonic acid	lactic acid
resorcinol	phthalic acid	maleic acid	acetylacetone
catechol	gallic acid	succinic acid	propionic acid
hydroquinone	5-hydroxyisophthalic acid	fumaric acid	1-propanol
salicylic Acid	2,3-dihydroxybenzoic acid	citric acid	ethylene glycol
<i>m</i> -hydroxybenzoic acid	2,4-dihydroxybenzoic acid	3-ketoglutaric acid*	D-glucose
<i>p</i> -hydroxybenzoic acid	2,5-dihydroxybenzoic acid	glyoxylic acid	sucrose
phloroglucinol	2,6-dihydroxybenzoic acid	formic acid	maltose
<i>o</i> -methoxy phenol	3,4-dihydroxybenzoic acid	pyruvic acid	lactose
<i>o</i> -cresol	3,5-dihydroxybenzoic acid	acetaldehyde	allyl alcohol
vanillic acid		acetic acid	glucosamine*
		acetone	

*purchased from Tokyo Kasei Kogyo

Chlorination

Chlorination was initiated by adding a stock NaOCl solution to a model compound solution. Before chlorination, the pH of the solution was adjusted to 7.0 with a phosphate buffer (final concentration was 13 mM). Other reaction conditions were as follows: model compound concentration, 3 mg-TOC/L; Cl₂ dose, 30 mg/L; pH, 7; reaction time, 24 hr. The chlorine dose in this experiment was higher than in actual drinking water disinfection practice for analytical reason, but the ratio of model compound-to-chlorine was roughly in the same range as actual treatment. When investigating the effect of Br⁻, Br⁻ solution was added to the mixture before adding NaOCl. The initial Br⁻ concentration was set to 4 mg/L.

HAA analysis

HAA concentrations were analyzed following USEPA method 552.3 (2003). Briefly, this method consists of liquid-liquid extraction, derivatization to methyl haloacetates with acidic