過塩素酸は実験ブランクの制御等の観点から、最小濃度を0.05 µg/L としたが、0.05 µg/L におけるピーク高さ及びピーク形状は良好で、S/N 比が 280（5 回の平均）であったことから、さらに低い濃度においても測定は十分可能であると考えられた。一方、ハロ酢酸については、感度は対象物質によって異なったが、検量線は、0.1〜10、0.2〜10 あるいは 0.5〜10 µg/L の濃度範囲で直線性が認められた。今回検討した 14 物質の感度は、従来の方法による感度と同等あるいはそれ以上である。したがって、IC/MS/MS 法は、水中に存在するハロ酢酸、ハロゲン化オキソ酸及び臭化物イオンの同時分析に対し有効な方法であることが示された。ただし、実試料の測定においては、物質により感度、濃度が大きく異なるため、検量線の直線範囲に入るように希釈して測定する必要がある。また、塩化物イオンや硫酸イオン等の共存物質の影響についても考慮する必要があると考えられる。

今回開発した分析方法を用いて、浄水場の原水・浄水中の過塩素酸の分析を行った。試料の採水は、2006 年 3〜4 月に行った。浄水の試料については、アスコルビン酸ナトリウム（和光純薬）により残留塩素を除去した。図 3 に、ある浄水場の原水中の過塩素酸のクロマトグラムを示す。実際の浄水場の原水中の試料の場合でも、過塩素酸は良好なピークを示した。

表 1 に、全国 12 浄水場の原水・浄水中の過塩素酸の測定結果を示す。測定は内部標準法によって行い、定量下限値は 0.05 µg/L とした。また、浄水場は、関東地方の浄水場とそれ以外の場所の浄水場に分類した。

関東地方の浄水場の原水及び浄水中の過塩素酸濃度は、それぞれ 0.19〜17 及び 0.16〜18 µg/L の範囲であった。このとき、原水の場合は 4 浄水場、浄水の場合は 5 浄水場について 10 µg/L を超えていた。一方、関東地方以外の浄水場の場合、原水及び浄水中の過塩素酸濃度は、それぞれ < 0.05〜0.35 及び 0.15〜0.36 µg/L の範囲で、全ての試料について 1 µg/L 未満であった。本調査は極めて限られたものではあるが、関東地方と関東地方以外で過塩素酸濃度に大きな差があったことから、関東地方において河川水中の過塩素酸濃度が高い地域があると推測された。

また、浄水場の原水と浄水の結果を比較すると、半分の浄水場では、原水より浄水中の方が若干高い値を示したが、概して原水と浄水中の過塩素酸濃度は同等であった。採水時間による変動の影響も考えられるが、過塩素酸は水溶性で、水中では移動性が高く、通常の浄水処理では除去困難であること、過塩素酸は消毒剤として使用している次亜塩素酸ナトリウム水溶液中にも微量ながら不純物として含まれることがあると報告されているが [4]、この影響はあってもわずかであることが推測された。

４．まとめ

本研究により得られた知見を、以下に記す。

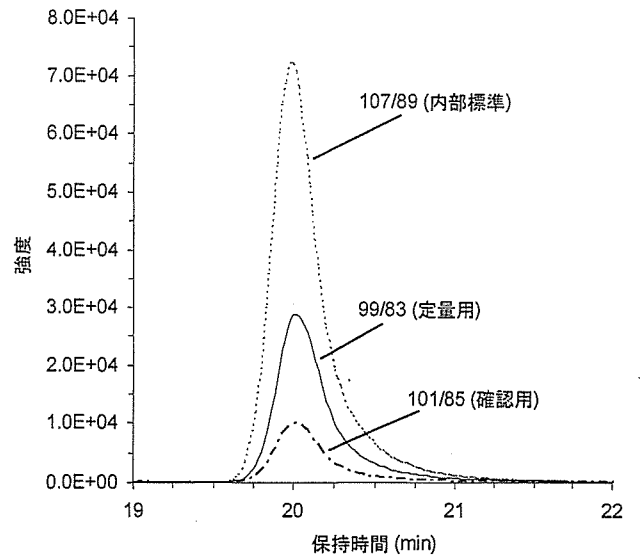1) IC/MS/MS 法は、水中のハロ酢酸、ハロゲン化オキソ酸及び臭化物イオン等のイオン性の物質の分析に対し、有効な方法であることが示された。特に、ハロゲン化オキソ酸は

図 3 浄水場の原水中の過塩素酸のクロマトグラム

表 1 浄水場の原水・浄水中の過塩素酸濃度 (µg/L)

浄水場	原水の種類	原水	浄水
関東地方			
A	水系 M	15	18
B	水系 M	13	16
C	水系 M	17	17
D	水系 N*	0.19	12
E	水系 M	13	16
F	水系 O	0.27	0.16
関東地方以外			
G	水系 P	0.35	0.33
H	水系 P	0.34	0.33
I	水系 Q	0.17	0.15
J	水系 P	0.25	0.35
K	水系 R	< 0.05	0.36
L	水系 S	0.18	0.24

*浄水は水系 M のものを混合

非常に高感度に検出されることがわかった。

2) 全国 12 浄水場の原水・浄水を対象に過塩素酸濃度を測定したところ、関東地方の浄水場の原水・浄水で 10 µg/L を超える濃度が検出され、一方、関東地方以外の浄水場の原水・浄水では、全ての試料で 1 µg/L 未満であった。

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3) 小松真紀子ら, *第 8 回日本水環境学会シンポジウム講演集*, 137 (2005).

4) Massachusetts Department of Environmental Protection, The Occurrence and Sources of Perchlorate in Massachusetts (Draft Report), (2005).

（8-22）水道用次亜塩素酸ナトリウム中の臭素酸に関する調査

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　浅見　真理（国立保健医療科学院）

1. はじめに

　水道水に含まれる臭素酸の由来の一つに次亜塩素酸ナトリウムが挙げられる。わが国の水道事業体で使用される消毒剤としては、次亜塩素酸ナトリウムが 8 割以上を占めている[1]。一方で、薬品中に高濃度の臭素酸が含まれる可能性や、長期間の貯蔵による次亜塩素酸濃度の減少、臭素酸の濃度上昇が指摘されている[2]。その品質の適正な管理が望まれるが、各事業体で使用されている薬品の品質に関する情報は限られている。

　そこで筆者らは、国内の水道事業体で使用されている次亜塩素酸ナトリウムを収集し、薬品中の臭素酸濃度と、高温保管時の濃度変化に関する調査を行ったのでここに報告する。

2. 調査方法

2.1 試料

　平成 17 年度国立保健医療科学院水道工学コースの受講生が所属する事業体等の協力を得て、関連する水道施設（配水施設等を含む）で使用されている次亜塩素酸ナトリウムを収集し、試料とした。試料の総数は 37 で、このうち 2 試料は表示有効次亜塩素酸濃度が 1%（生成次亜塩素酸ナトリウム）、1 試料は 8%で、その他は 12%以上であった。試料は暗所で冷蔵保存し測定を行った。また、製造業者名、製造日等に関する情報も同時に収集した。37 試料のうち 19 試料については、40℃に設定した暗所で 11 日間保存し、濃度変化に関する実験を行った。

2.2 測定方法

　臭素酸濃度は、試料を 1 万倍に希釈した後、イオンクロマトグラフーポストカラム法にて測定した。イオンクロマトグラフは日本ダイオネクス社製 DX-500 を、ポストカラムは同社製 PCM-510 を使用した。また有効次亜塩素酸濃度も測定した。試料を 10 万倍に希釈した後、DPD 試薬を加え吸光度を吸光光度計（日立製作所製 U-2800）にて測定した。

図1 臭素酸の検出状況

3. 結果と考察

3.1 検出状況

　臭素酸の検出状況を図1に示す。臭素酸濃度はおおむね 70mg/L 以下で、最大値は 235mg/L であった。図1には、対数正規分布による期待値も記載した。x^2 検定を適用した結果、臭素酸の検出状況は 3%有意水準で対数正規分布に適合した。大多数の水道事業体（施設）では、次亜塩素酸ナトリウム中の臭素酸が一定濃度以下に抑制されていたが、一部の施設では、高濃度の臭素酸を含む薬品を使用している可能性があることを意味する。また、有効次亜塩素酸の検出状況を図2に示す。濃度は 0.36g/L〜150g/L の範囲であった。
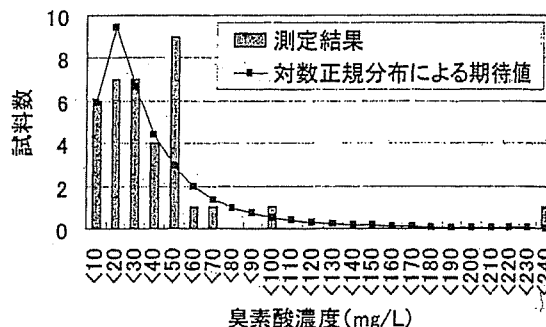
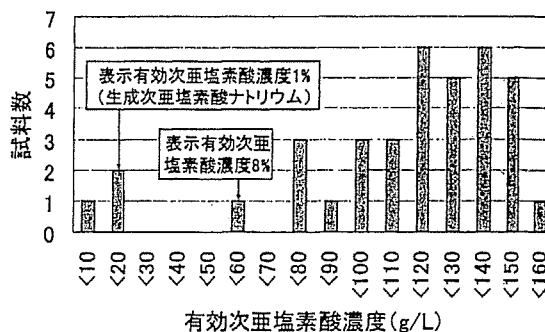　次に、納入数の多かった上位 2 業者の次亜塩素酸ナトリウム中に含まれる臭素酸濃度を比較したものが図

図2 有効次亜塩素酸の検出状況

3 である。製造業者間で薬品中の臭素酸濃度が異なることがわかる。また、貯蔵期間と臭素酸の平均濃度との関係を図4に示す。貯蔵期間の長い試料では、臭素酸濃度が高い傾向にあった。この理由として、「水道施設の技術的基準を定める省令」の施行前に製造されたと推測される試料では、製造時の品質が適正に管理されず、高濃度の臭素酸を含んでいた可能性があること、および薬品中の臭化物が時間の経過とともに酸化されたことの2点が考えられる。以上の結果は、薬品中の臭素酸の管理において、製造過程および水道施設での管理の両面が重要であることを意味する。

3.2 高温保管後の濃度変化

高温保管後の臭素酸および有効次亜塩素酸の濃度変化を図5、図6に示す。実験開始時の濃度に対する比率はそれぞれ 91〜163%（平均 108%）、41〜91%（平均74%）の範囲であった。次に、高温保管後の塩素注入率 1mg/L あたりの臭素酸付加量の変化を図7に示す。実験開始時の付加量に対する比率は106〜243%（平均152%）の範囲であった。長期間の貯蔵による薬品中の有効次亜塩素酸濃度の減少や臭素酸の濃度上昇にともない、臭素酸付加量が加速的に増加する可能性がある点に注意する必要がある。
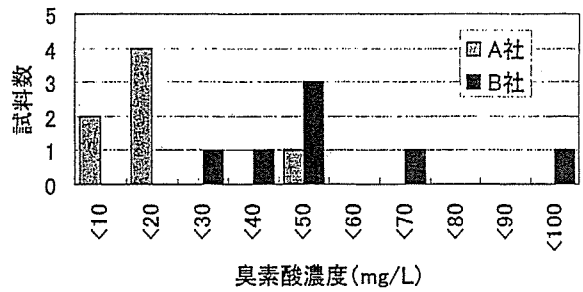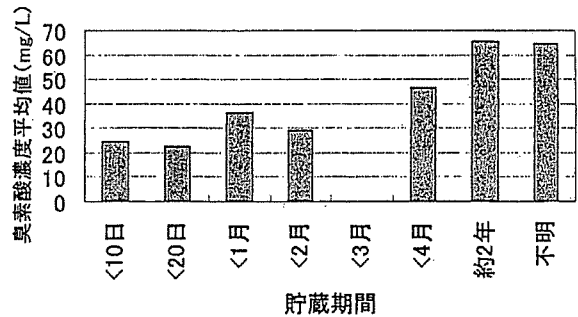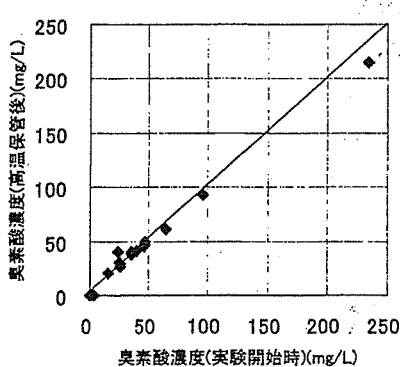

図3 製造業者別の臭素酸の検出状況

図4 貯蔵期間と臭素酸濃度の関係

図5 臭素酸濃度の変化
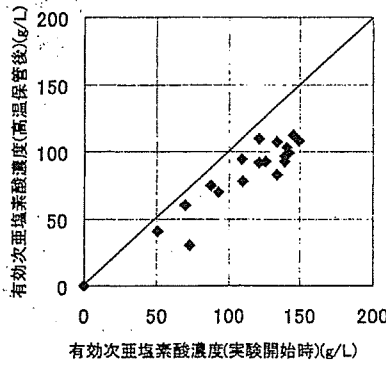
図6 有効次亜塩素酸濃度の変化
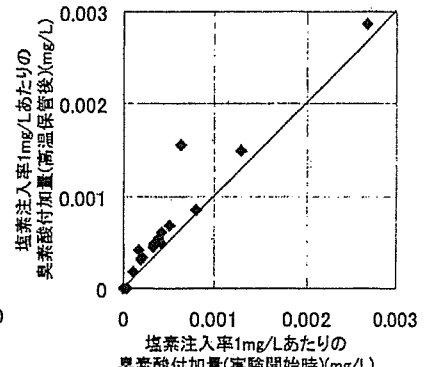
図7 塩素注入率1mg/L あたりの臭素酸付加量の変化

4. おわりに

本稿では、水道用次亜塩素酸ナトリウム中の臭素酸に関して、以下の3点を指摘した。

1) 大多数の水道施設では、薬品中の臭素酸が一定濃度以下に抑制されていたが、一部の施設では、高濃度の臭素酸を含む薬品を使用している可能性がある。2) 薬品中の臭素酸の管理において、製造過程および水道施設での管理の両面が重要である。3) 薬品中の有効次亜塩素酸濃度の減少や臭素酸の濃度上昇にともない、臭素酸付加量が加速的に増える可能性がある。

製造過程における品質管理を十分確認するとともに、配水施設等において貯蔵される次亜塩素酸ナトリウムについても十分な管理が必要となろう。

本調査は、平成17年度国立保健医療科学院水道工学コースの特別研究として実施したものであり、調査にご協力をいただいた事業体に謝意を表する。

参考文献：1) 厚生労働省健康局水道課、「水道統計」施設・業務編、2002. 2) 厚生労働省健康局水道課、 次亜塩素酸ナトリウム等水道用薬品の使用に当たっての留意事項について（平成16年6月16日事務連絡）、2004

Source Water Quality Management for Reducing Disinfection By-Products

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Abstract

To explore the possibility of reducing brominated disinfection by-products by controlling bromide level in source water, a basin-wide survey and origin analysis of bromide were conducted in the Lake Biwa-Yodo River Baisn, Japan. The survey showed that human activities greatly increase bromide level in source water in the downstream area. Also, it was suggested that industrial activity is considerably contributing to high bromide level. Thus, a regulation to reduce bromide discharge from industrial activity would be effective for better control of brominated DBPs.

1. Introduction

In a large river basin, water is repeatedly used for human activities before it reaches ocean. For example, in the Lake Biwa-Yodo River Basin in Japan, water used for agricultural purposes in upstream areas is discharged into Lake Biwa, the largest lake in Japan, and cities along the lake use the lake water as the source for drinking water. Then, the water used in the urban area returns to the river system after wastewater treatment. Cities in the downstream areas use this "used water" as drinking water source, and oftentimes the loop is repeated

several times. Hence, drinking water utilities in the downstream are required to remove contaminants released from the upstream cities. For this purpose, advanced drinking water treatment technology (e.g., ozonation and activated carbon treatment) has been introduced in many treatment plants in Japan.

While these treatment technologies are effective to control micropollutants, these technologies require large quantity of energy, and are not always the best solution for constructing a sustainable water supply system. That is, the effort to minimize the contaminants in source water is equally important.

Indeed, the Japanese government has been introducing legislation for preserving source water quality. However, the regulation is limited to several organic compounds and nutrients, and not much attention is paid to micropollutants and the precursors of micropollutants in source water. One major reason for this is the lack of information on their fate and source. Without this information, it would be impossible to evaluate the feasibility and effectiveness of regulating these compounds in source water. Among these compounds, this study addresses the origin of bromide ion, a precursor of disinfection by-products (DBPs) in the Lake Biwa-Yodo River Basin as a case study.

Bromide ion is a minor anion in fresh water, but is involved in various chemical reactions in drinking water treatment process [1-3]. While the toxicity of bromide ion itself is considered negligible, it is reactive to hypochlorous acid (HOCl) and ozone (O_3) to form hypobromous acid (HOBr) [4]. During ozonation, HOBr is further oxidized to bromate ion (BrO_3^-), a suspected carcinogen. Also, HOBr rapidly reacts with natural organic matter (NOM) in source water [5], and brominated organic compounds are produced. The source of bromide ion can be both natural (salt water intrusion and dissolution from geological formation) and anthropogenic [1, 3].

Recent toxicological studies have suggested the impotence of controlling brominated

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 µg/L), but bromide ion concentration was much higher in the downstream area of Yodo River (42-46 µg/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 µg/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.
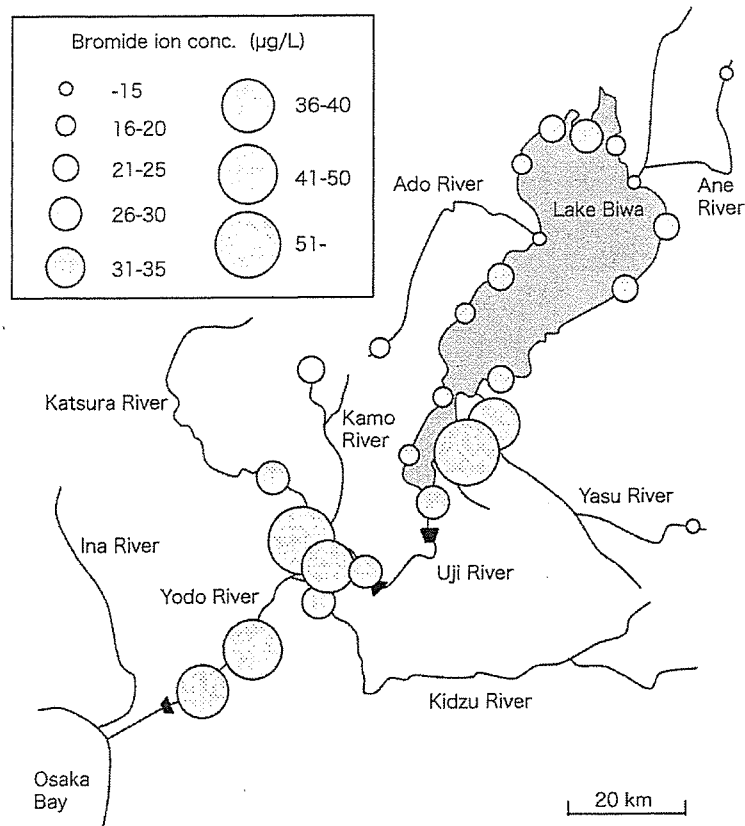
Figure 1. Bromide ion distribution in the Lake Biwa-Yodo River Basin.

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 70μg/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 μg/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.

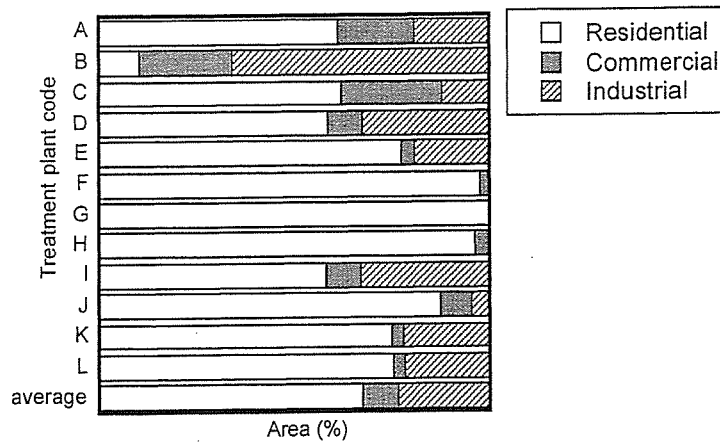| Plant code	Bromide ion conc. (μg/L)
A	94.0
B	113.6
C	110.0
D	111.0
E	152.0
F	41.8
G	66.3
H	51.5
I	356.5
J	436.2
K	64.8
L	58.9

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], indicting 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
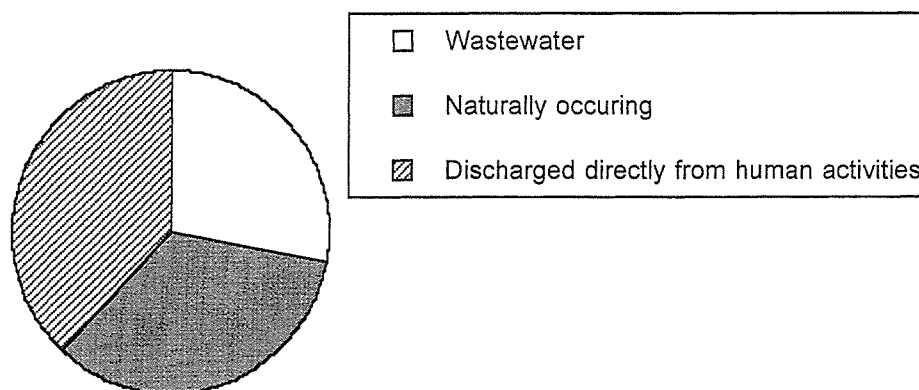
ion [16].

Figure 3. The origin of bromide ion in the lower Yodo River Basin (Hirakata City). Naturally occurring bromide was assumed to be 17 μg/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.
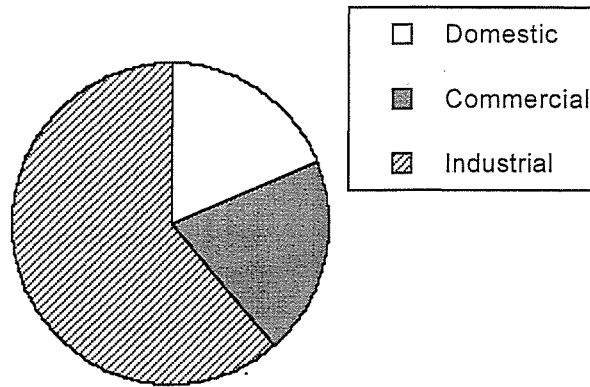
Figure 4. Origins of bromide ion in wastewater effluents. To estimate the loads from domestic and commercial wastewaters, the unit loads was assumed to be 11 mg/(day·person) and 7.9 g/(day·ha), respectively (also, see 3.2). The rest of bromide was assigned to industrial origins.

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 μg/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(μg/kg per day)	Allocation	Value(mg/L)
TCM	12.9	20%	0.06
BDCM	6.1	20%	0.03
DBCM	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:

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

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:

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

where D_{in} represents THMs dose from inhalation exposure to indoor air including shower and cooking (μg/day); C represents median indoor air concentration (μg/m³); 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 m³/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.
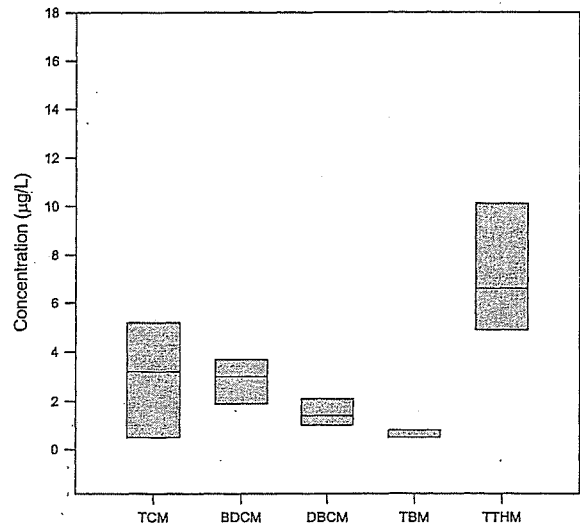

Fig. 2. Bath water concentration
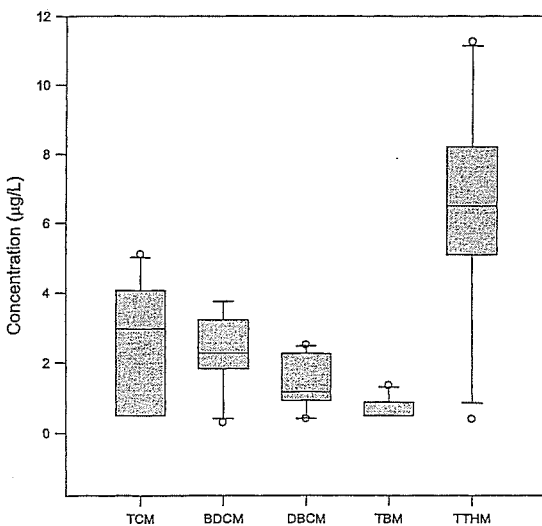Median total THMs concentration was 6.6μg/L

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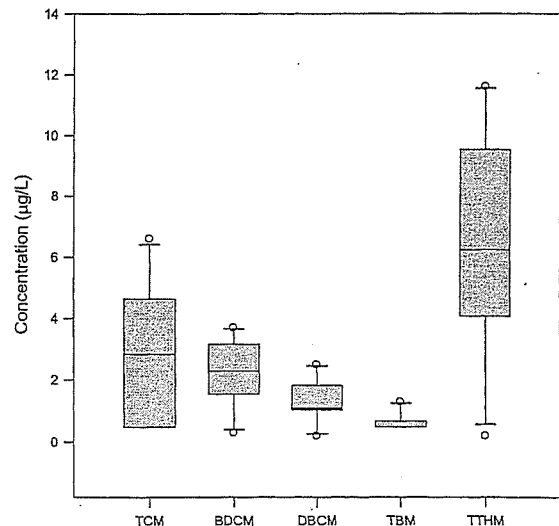Median total THMs concentration was 6.5 µg/L

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 $\mu g/m^3$ 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).
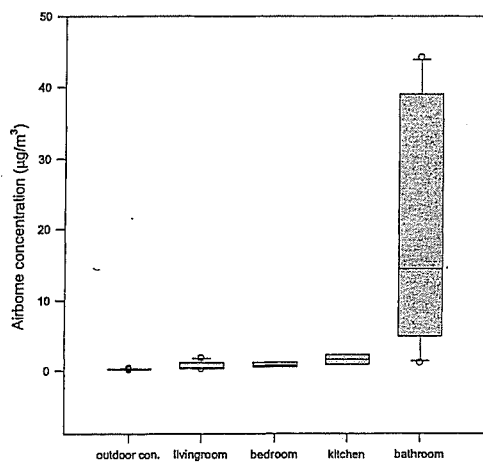

Fig.4. Airborne concentration of TCM
Median airborne concentration in bathroom was 14.54$\mu g/m^3$
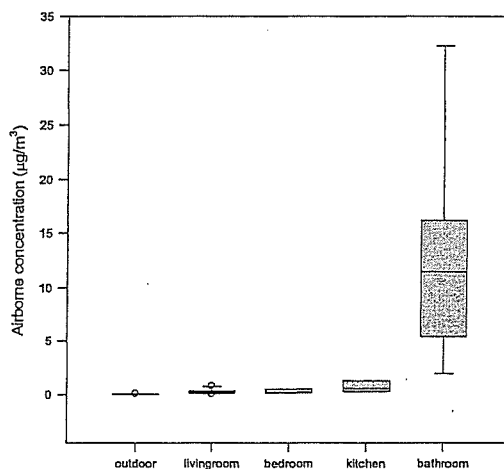

Fig. 6. Airborne BDCM concentration
Median airborne concentration in bathroom was 11.52$\mu g/m^3$
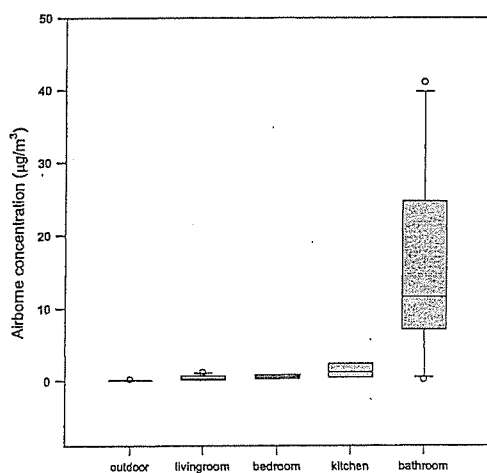

Fig. 5. Airborne concentration of DBCM
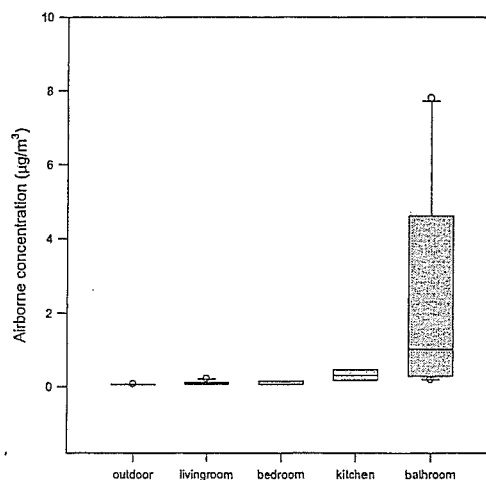Median airborne concentration in bathroom was 11.55$\mu g/m^3$

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

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).