(4-41)ナノ沪過膜ファウリングと前処理(凝集沈澱・膜処理)及び原水濃度との関係についての研究

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1.　はじめに

ナノろ過(NF)膜の除去性能については、様々な知見が得られているが、ファウリングに関する調査研究は少ない。そこで本研究では、前処理水(凝集沈殿・MF/UF膜処理)を原水として、ファウリングの加速実験を行った。NF膜のファウリングと凝集剤及び原水濃度との関係について、膜透過流束(以下「フラックス」という)及び各成分の阻止率の経時変化、膜面付着物分析から検討を行った。

2.　実験方法

実験装置の概要を図1に示す。膜は東レ社製UTC-60(平膜)を使用し、事前に膜差圧 0.9MPa で 3 時間超純水を透過し、膜を圧密化させフラックスを安定化させた後実験を行った。

実験装置は、ろ過水量の減少分をタンクに原水を補給する半回分式とし、原水濃度の上昇をおさえた[1]。実験中は、ポンプ循環による水温上昇を避けるため、循環冷却装置を用いて水温を 25℃に保った。また、膜間のばらつきを抑えるため 3 個の平膜用セル(有効膜面積 32.2cm^2)を並列して使用し、測定値は平均値を用いた。ファウリングを促進させるため膜差圧は 0.75MPa (96時間連続運転)または0.9MPa(52時間連続運転)、膜面流速の最も遅い条件として、循環水量を装置の下限値に近い1セルあたり 0.3L/min とした。実験に使用した原水の水質を表1に示す。凝集剤の比較では、人工原水をAl系凝集剤とFe系凝集剤で凝集沈殿処理後、UF膜処理水を用いた。原水濃度の比較では、河川水をFe系凝集剤で凝集沈殿処理後、MF膜処理水とその処理水をNFろ過した際に生じる濃縮水を用いた。すべての実験原水は、pH が 7.0±0.2 になるように調整した。また、膜面付着物質を特定するため、実験終了後、使用したNF膜を硝酸溶液(pH2)に 24時間浸漬させ、1時間超音波振動をかけて得られた溶液の水質分析を行った。

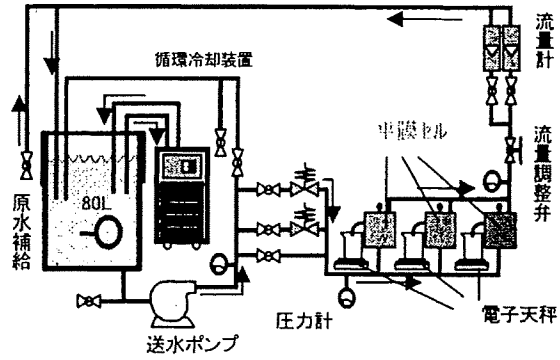

図1　実験装置

表1　使用原水の水質

項目		RUN1	RUN2	RUN3	RUN4
実験使用原水		人工原水		河川水	
		Al系凝集剤 + UFろ過	Fe系凝集剤 + UFろ過	Fe系凝集剤 + MFろ過	
pH	(−)	7.0	7.0	6.8	7.0
Ca	(mg/L)	38.0	38.3	21.9	137.8
Al	(mg/L)	0.17	<0.01	<0.01	<0.01
Fe	(mg/L)	<0.01	<0.01	<0.01	<0.01
E260	(−)	0.020	0.017	0.070	0.610

3.　実験結果および考察

3.1　凝集剤の違いが及ぼす影響

図2にRUN1、2のフラックス経時変化を示す。ここではろ過量から算出した平均透過流束を25℃で温度補正し、かつ実験条件の初期フラックスのバラツキを除いて評価するため、各フラックスを初期フラックス(実験開始1時間後のフラックス)で除した相対フラックスにより評価した。

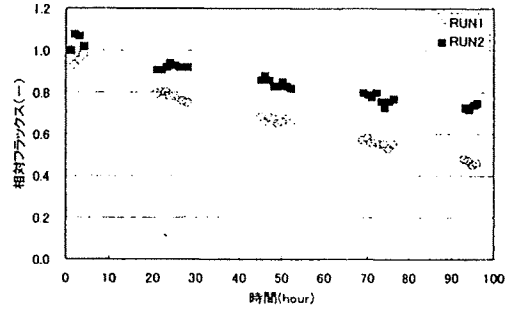

図2　フラックスの経時変化(凝集剤の違い)

両者ともフラックスの低下が認められるがAl系のほうが低下率は大きくなっている。表1より、各原水水質はAl濃度(RUN1:0.17mg/L、RUN2:0.01 mg/L 以下)以外ほぼ同程度であり、RUN1 のAlは凝集剤のAlが残留したものと考えられる。また膜面付着分析(図3)でも、RUN1 はAlの付着割合が最も大きい。一方、RUN2 ではFe濃度が低く、RUN1 と同程度であった。Fe系凝集剤を用いた場合、不溶化したFeがUF膜により除去されることから、凝集剤による残留Feは少なく、Al系のように凝集剤がフラックス低下の要因とならないと考えられる。

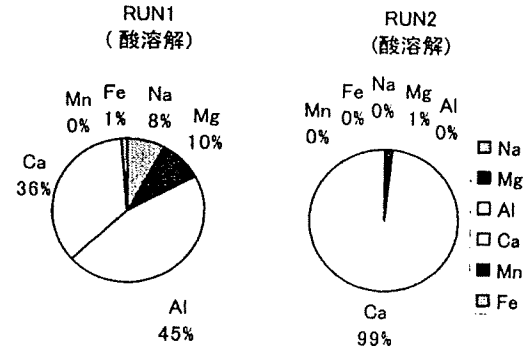

図3 膜面付着物質(凝集剤の違い)

3. 2 原水濃度の違いによる影響

図3に共存物質濃度が異なる河川水を原水とした場合のフラックスの経時変化を示す。フラックスは、RUN3が初期の 80%程度に低下したのに対し、RUN4 は初期の 30%程度まで大きく低下した。このことから共存物質濃度が高ければ、付着層の形成や目詰まり等のファウリングが促進されることが確認された。これは、共存物質の供給量が多いことから膜面濃度の上昇、濃度分極の進行が速くなることで膜面の水の移動抵抗が増加するためと推測している。

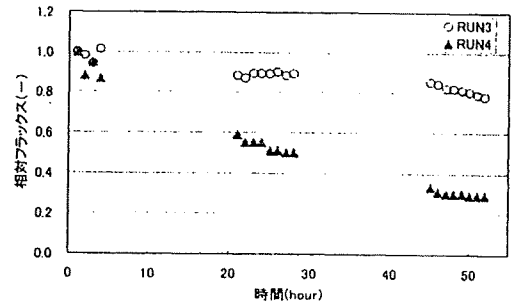

図4 フラックスの経時変化(原水濃度の違い)

使用した膜に付着している金属成分の割合を図5に示す。Caの濃度が低い RUN3 では、FeとCaで付着物質の約 75%を占めている。またCaの濃度が高い RUN4 では、Feの付着割合が低下しCaが 90%以上を占めている。さらに原水のCa濃度がRUN3 の2倍程度であるRUN2 でも、Caの付着割合が高くなることから、Caの存在がFeの膜面付着量に影響を及ぼすと推察される。膜面付着物質の構成割合から環境水中のCa、Fe、Al等の無機物質がファウリング形成の要因であり、共存物質の含有量やその割合により膜面付着物質の主要因子が異なると考えられる。

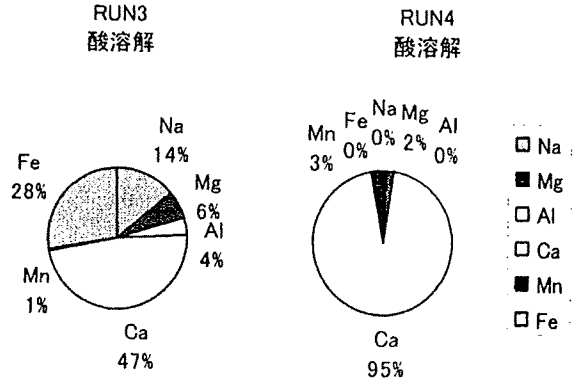

図5 膜面付着物質(原水濃度の違い)

4. まとめ

本研究から得られた結果を基にしてNFろ過における凝集剤および原水濃度とファウリングへの影響を検討した結果は次のとおりである。

・Al系凝集剤＋膜処理(MF/UF)の場合、 残留凝集剤成分がファウリング形成の要因となることが確認されたが、Fe系凝集剤＋膜処理(MF/UF)は、Al系と異なり残留凝集剤成分が少なくファウリング形成の要因となりにくい。よってNFの前処理としてFe系凝集剤＋膜処理(MF/UF)が有効である可能性が示された

・同一環境水であっても共存物質濃度が高い場合、フラックスが低下することが確認された。その要因として、原水濃度及び膜面付着物の割合からCaの影響が示唆された

・環境水中のCa濃度が低い場合、Feの膜面蓄積物に占める割合が増加したことから、無機物は共存物質濃度の違いにより膜面への付着状況が異なる可能性が考えられる

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(4-43)ナノ沪過膜による浄水処理についての研究(Ⅰ)

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1. はじめに

浄水処理においてナノろ過（NF）は、溶解性物質の除去に優れ、既存のオゾン・活性炭吸着処理技術の代替手法として注目される。海外では消毒副生成物対策や農薬除去などで既に実用化されているが、日本では十分な実績がなく未だ研究段階である。過去の研究例としては *e-Water* プロジェクト（環境影響低減化浄水技術開発研究）にて、循環型装置による多段型装置の水質予測、性能予測評価を検証した例がある[1)]。本研究は、*e-Water* の成果を踏まえ、東京都の水源である荒川を原水とし、前処理に鉄系凝集剤を使用した場合の性能等について知見を得ることを目的として実施した。

2. 研究の概要

2．1研究の目的

本研究は平成20年度までを予定しているが、本報告では以下の内容について中間報告をする。

1) 鉄系凝集剤を用いた前処理設備、NFろ過水の水質面での評価
2) 小型装置による水質予測（大型装置と小型装置の水質比較）

2．2実験フロー

実験の概要を表-1に、実験フローシートを図-1に示す。原水は東京都水道局朝霞浄水場の原水接合井から取水している。設備は前処理(凝集沈殿＋MFろ過)と、大型NF膜装置、２つの小型NF膜装置からなる。前処理は塩化第二鉄による凝集沈殿を行っている。大型NF膜装置は、実際のプラントを想定して、多段型装置(ベッセル配置 8-4-2-1 で、各ベッセルに5エレメント)となっている。また水質調査を詳細に行うため、各バンクの一部分(図-1 中の着色したエレメント)のろ過水を単独で採水できる構造となっている。一方小型装置は、直列2エレメントのみの構成で、濃縮水を供給水に循環することで、大型装置のエレメントの一部分（着色エレメント部分）の処理条件を再現し比較評価することが可能である。各装置の仕様を表-2にまとめた。

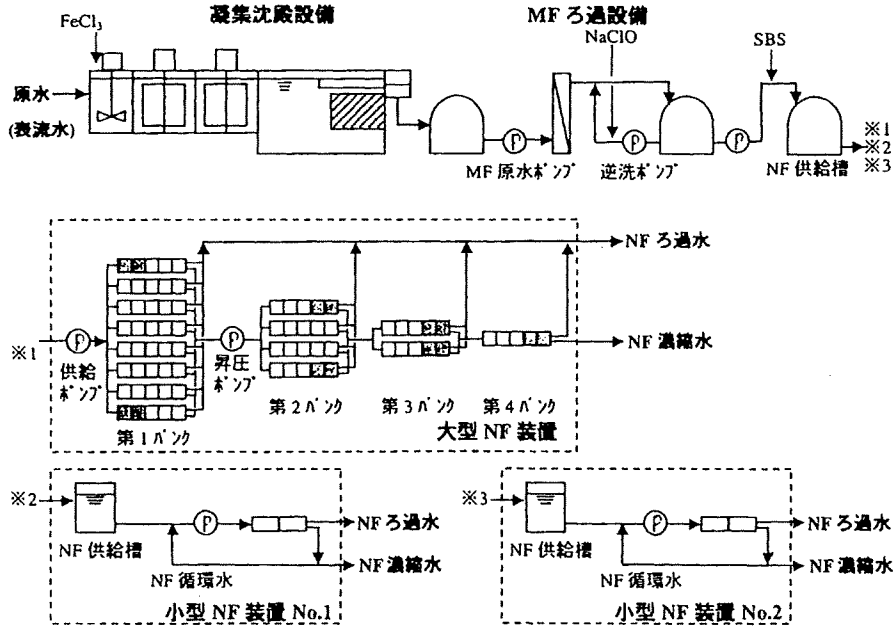

表-1　実験の概要

実験場所： 東京都水道局三園導水ポンプ場内
実験期間： H18年7月～H20年3月（本報告ではH18年12月迄）
原水： 朝霞浄水場原水接合井より取水
取水量： 600m³/d

図-1　実験フローシート

3. 実験結果

3. 1 原水及び処理水質

実験における原水及び各工程の水質を表-3 に示す。本原水は河川表流水のため、原水濁度は通常時 10 度程度、降雨直後には最大で約 300 度まで上昇した。MF ろ過水ではアルミニウム及び鉄はほとんど検出しなかった。一方原水中の溶解性マンガン濃度が高く、凝集沈澱、MF ろ過ではほとんど除去できなかった。NF ろ過水では水道水質基準値を満足した。

3. 2 小型装置による水質性能予測

小型装置による水質実測結果から、システム回収率と物質除去率の関係を求め、大型装置の水質性能予測を行った。

本手法による測定結果の一例を図-2 に示す。システム回収率と TOC 濃度の関係である。大型装置の実測値（△,○）は濃縮水、ろ過水いずれもシステム回収率が上昇するにつれ大きくなる。一方、小型装置による水質実測結果から回収率と除去率の関係を求め、水質予測値を計算すると、破線及び実線となり、ほぼ正確に大型装置の水質を予測することができた。

これより、より安価で簡便な小型装置による水質予測試験を実施することで、実設備に近い大型装置の水質を予測可能であることが示された。本手法は *e-Water* における実証実験[1]でも実績はあるが、今回異なる水源で妥当性が検証されたことにより、この手法の汎用性が示された。

4. まとめ

河川表流水を原水とした、NF ろ過システムの実証実験を実施し、以下の知見を得た。

1) 塩化第二鉄による凝集沈殿を前処理としたシステムにおいて、良好な NF ろ過水水質を得た。
2) 2 エレメントを用いた小型装置により、4 段 75 エレメントの大型装置の水質予測が可能であることを示した。

5. 今後の予定

今後は以下の方針により、ナノろ過膜の実用化を目指して研究を進めていく。

1) 高度処理水(ｵｿﾞﾝ+活性炭)との水質比較
2) 鉄系凝集剤を用いた前処理による、NF ろ過システムの確立
3) 実用化に向けた、最適設計を行う上でのシステム構成の検討

表-2 実験設備の仕様及び運転条件

凝集沈殿	型式	：傾斜管付凝集沈殿
	凝集剤	：塩化第二鉄 15mg/L(as$FeCl_3$)
	処理量	：600m^3/d
MF ろ過	膜型式	：加圧型 MF 膜
	膜種類	：外圧式中空糸(材質 PVDF)
	公称孔径	：0.05μm
	処理量	：530～580m^3/d
NF 設備	膜材質	：ﾎﾟﾘｱﾐﾄﾞ系複合膜
	塩排除率	：55%
	膜面積	：7m^2/エレメント
	システム構成	
	大型	5 ｴﾚﾒﾝﾄ/ﾍﾞｯｾﾙ
		多段型(8-4-2-1 ﾍﾞｯｾﾙ)
	小型	1 ｴﾚﾒﾝﾄ/ﾍﾞｯｾﾙ,2 ｴﾚﾒﾝﾄ直列

表-3 大型 NF ろ過装置の水質(平均値,n=10～14)

水質項目	原水	凝集沈澱水	MF ろ過水	NF ろ過水	NF 濃縮水
pH(-)	7.5	6.7	6.8	6.5	7.5
濁度(NTU)	11.5	1.0	<0.1	-	-
TOC(mg/L)	1.7	1.3	1.2	0.3	9.8
E260(1/cm)	-	-	0.02	<0.01	0.16
電気伝導率 (μS/cm)	229	234	237	132	1090
Al(mg/L)	0.24	0.02	<0.01	<0.01	<0.01
Fe(mg/L)	0.40	0.76	0.01	<0.01	0.02
Mn(mg/L)	0.057	0.052	0.052	0.022	0.387
Ca(mg/L)	-	-	22.7	12.0	140.3
Na(mg/L)	-	-	11.2	9.8	30.2
Si(mg/L)	-	-	13.9	13.2	23.4

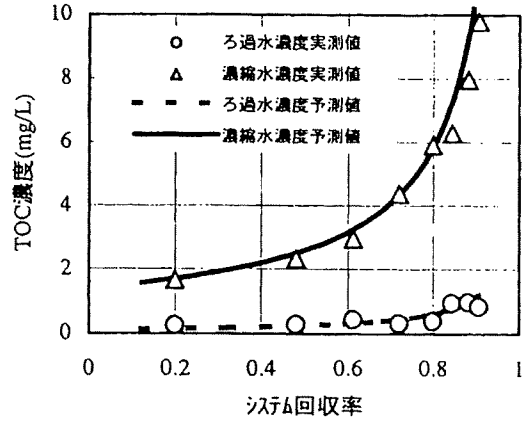

図-2 システム回収率と TOC 濃度の関係
運転条件：平均膜ろ過流束 0.6m/d

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Virus removal in a hybrid coagulation–microfiltration system–Investigating mechanisms of virus removal by a combination of PCR and PFU methods

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Abstract Virus removal performance and mechanisms were investigated in a hybrid coagulation–microfiltration (MF) system by using river water spiked with bacteriophage Qβ. Virus removal increased with filtration time: the rate of virus removal was 4 log at the beginning of filtration and gradually increased to 6 log over 5 h, probably because of the growth of a cake layer that accumulated on the membrane surface. Quantification of the virus particles in the MF compartment by a combination of a polymerase chain reaction (PCR) method and a plaque forming unit (PFU) method revealed that most of the virus (> 99.999%) in the MF compartment was entrapped in the aluminium floc and then located in the solid phase; most of the virus (> 99.9%) in the solid phase was inactivated. The rate of recovery of virus particles from the MF compartment decreased with filtration time: after 3 h of filtration approximately half of the virus particles in the MF compartment were not recovered by hydraulic backwashing, indicating that the virus might have been retained on the MF membrane as part of an irreversible foulant.
Keywords Coagulation; mass balance; microfiltration (MF); virus removal

Introduction

Microfiltration (MF) can remove turbidity, bacteria, algae, and protozoa from water and wastewater. However, the pore sizes of MF membranes are not small enough to remove particles with diameters less than tens of nanometers. Included among such small particles are pathogenic waterborne viruses, such as hepatitis A viruses, polioviruses and noroviruses, which are approximately 0.02 to 0.04 μm in diameter. Therefore, these viruses cannot be removed by MF membranes alone. To compensate for this disadvantage, a coagulation process has been sometimes used as a pretreatment for microfiltration. Hybrid coagulation–MF systems have actually already been applied to the treatment of drinking water in Japan, and some researchers have reported that these systems result in a high rate of virus removal (Matsui *et al.*, 2003a; Matsushita *et al.*, 2005; Zhu *et al.*, 2005a, b; Fiksdal *et al.*, 2006).

Although the hybrid system ensures high time-averaged virus removal, virus removal is not very high at the beginning of filtration (only approximately 1–2 log removal). The rate of virus removal increases with filtration time (Matsushita *et al.*, 2005). This means that the rate of virus removal will probably fall to a low level at every backwashing, by which the cake layer accumulated on the membrane surface is flushed.

To date, the mechanisms of virus removal in hybrid systems are not clearly understood. One reason is the difficulty in investigating the fate of viruses in the hybrid system, which is attributable to the poor recovery rate of viruses from the MF compartment (Matsushita *et al.*, 2006). Elucidating the main factors of virus removal

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would possibly help to improve the rate of virus removal, particularly at the beginning of filtration and in the period just after backwashing.

Accordingly, the objective of the present study was to investigate the mechanisms of virus removal in the hybrid system. For this purpose, the change in the quantity of viruses with filtration time in the MF compartment was determined by using a combination of a polymerase chain reaction method (PCR; for quantification of both infectious and inactivated viruses) and a plaque forming unit method (PFU; for quantification of infectious viruses).

Materials and methods

Source water, coagulant, and MF membranes

River water was sampled from the Toyohira River (Sapporo, Japan, water quality shown in Table 1) on 12 December 2006. Polyaluminium chloride (PACl; 10% Al_2O_3, basicity 62.5%; Sumitomo Chemical Co. Ltd., Tokyo, Japan) was used for coagulation pretreatment. The membrane used was a monolithic ceramic MF module (multichannel tubular, nominal pore size 0.1 μm, effective filtration area 0.048 m^2; NGK Insulators, Ltd., Nagoya, Japan), which was installed in a stainless-steel casing.

Virus used

Bacteriophage Qβ (NBRC 20012) obtained from the NITE Biological Resource Center (NBRC, Chiba, Japan) was used as a model virus. The genome of Qβ consists of a single-strand RNA molecule encapsulated in an icosahedral protein shell (capsid) approximately 0.023 μm in diameter, without an envelope. Qβ is widely used as a surrogate for pathogenic waterborne viruses (Urase *et al.*, 1996; Otaki *et al.*, 1998) because of its morphological similarities to hepatitis A viruses and polioviruses, which are important to remove during the treatment of drinking water. Qβ was propagated for 22 to 24 h at 37 °C in *Escherichia coli* (NBRC 13965) obtained from NBRC. The Qβ culture solution was centrifuged (2,000 × *g*, 10 min) and then filtered through a 0.45 μm pore size membrane filter (hydrophilic cellulose acetate, Dismic-25cs, Toyo Roshi Kaisha, Ltd., Tokyo, Japan). The filtrate was purified with a centrifugal filter device (molecular weight cutoff 100,000; Centriplus-100, Millipore Corp., Billerica, MA, USA) to prepare the virus stock solution. By this purification, the DOC increase as a result of spiking of the river water with the stock solution was reduced to less than 0.1 mg/L.

Experimental setup

The experimental setup is shown in Figure 1. The river water was spiked with virus in the raw water tank at $10^{5.9}$–$10^{6.2}$ PFU/mL. The river water was fed into the system at a constant flow rate (62.5 L/(m^2·h)) by a peristaltic pump. Hydrochloric acid was added before the first in-line static mixer (hydraulic retention time 2.4 s, Noritake Co., Ltd., Nagoya, Japan) to maintain the pH of the MF permeate at 6.8. PACl was injected after the first in-line static mixer and before the second in-line static mixer at a constant dose rate (1.08 mg-Al/L). After the PACl had been mixed in, the water was fed into the ceramic MF module in dead-end mode. Filtration was performed for 0.25, 1, 3, or 6 h

Table 1 River water quality

pH	7.5
DOC (mg/L)	1.10
OD260 (cm^{-1})	0.027
Turbidity (NTU)	1.13
Alkalinity (mg-$CaCO_3$/L)	17.6

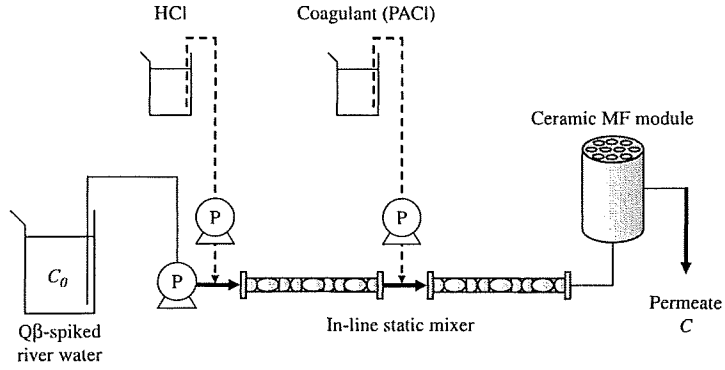

Figure 1 The experimental hybrid coagulation-MF system. C_0 and C are the virus concentrations (PFU/mL) in the raw water tank and the MF permeate, respectively, at each sampling time

without backwashing. Virus concentrations in the raw water tank and in the MF permeate were periodically measured every 1 h.

Quantification of virus in MF compartment

After the filtration experiments, the water (floc mixture) in the MF compartment was withdrawn by gravity. To quantify the virus concentration in the liquid phase of the floc mixture, the mixture was centrifuged (2,000 × g, 10 min) and then the virus concentration in the supernatant was measured by the PFU and PCR methods, as described below: the PFU method measured the concentration of infectious viruses, and the PCR method measured the concentration of total virus particles, regardless of their infectivity. Next, to quantify the virus concentrations in the suspended aluminium floc as well as in the liquid phase of the floc mixture, the floc was dissolved by raising the pH of the water to 9.5 with aqueous sodium hydroxide in 12% beef extract (Kyokuto Pharmaceutical Industrial Co., Ltd., Tokyo, Japan) solution and vortexing it intensely for 5 h. Beef extract was used in an effort to prevent the inactivation of virus during floc dissolution (Matsui *et al.*, 2003b). After that, the virus concentrations in the floc mixture were measured by PFU and PCR methods. In addition, to elute floc retained on the membrane surface after the floc mixture had been withdrawn by gravity, hydraulic backwashing (pressure, 0.5 MPa) with 200 mL of ultrapure water was conducted. The floc in the backwash eluent was dissolved by the method described above. The virus concentrations in the backwash eluent were measured by the PFU and PCR methods. Finally, the quantities of virus particles in the solid phase in the MF compartment were calculated from the virus concentrations in the floc mixture and the backwash eluent.

Virus assay

To measure the concentration of infectious viruses, the PFU method was used in accordance with the agar overlay method (Adams, 1959) by using the bacterial host *Escherichia coli*. Average plaque counts of triplicate plates prepared from one sample gave the virus concentration.

To measure the concentration of virus particles regardless of their infectivity, real-time PCR with a reverse transcription (RT) reaction was used. A 100 μL sample was heated at 90 °C for 10 min then cooled to 4 °C in a thermal cycler (Thermal Cycler Dice Model TP600, Takara Bio Inc., Otsu, Japan) to extract viral RNA by destroying the capsid. The RNA solution was added to a High-Capacity cDNA Reverse Transcription Kit with RNase Inhibitor (Applied Biosystems Japan Ltd., Tokyo, Japan) for the RT reaction, which was

Table 2 Oligonucleotide sequences of the primers and the probe used in PCR quantification of Qβ

Qβ + primer	5′-TCA AGC CGT GAT AGT CGT TCC TC-3′
Qβ − primer	5′-AAT CGT TGG CAA TGG AAA GTG C-3′
TaqMan probe	5′-CGA GCC GCG AAC ACA AGA ATT GA-3′

conducted at 25 °C for 10 min, 37 °C for 120 min, and 85 °C for 5 s, and then cooled to 4 °C in the thermal cycler. The cDNA solution was then amplified by a TaqMan Universal PCR Master Mix with UNG (Applied Biosystems Japan Ltd.), a 400 nM concentration of each primer (HQ-SEQ grade, Takara Bio Inc.), and a 250 nM concentration of TaqMan probe (Applied Biosystems Japan Ltd.). The oligonucleotide sequences of the primers and the probe are shown in Table 2. Amplification was conducted at 50 °C for 2 min, 95 °C 10 min, then 50 cycles of 95 °C for 15 s and 60 °C for 1 min in an ABI Prism 7000 Sequence Detection System (Applied Biosystems Japan Ltd.).

Quantification of aluminium

The aluminium concentration in the sample, which contained 1% (v/v) nitric acid (ultrapure, Kanto Chemical Co. Inc., Tokyo, Japan) was measured by Inductively Coupled Plasma Mass Spectrometry (HP4500, Yokogawa Analytical Systems Inc., Tokyo, Japan).

Results and discussion

Virus removal

The rate of removal of infectious Qβ virus [$\log(C_0/C)$] in the hybrid system changed with filtration time (Figure 2). It was 4 log at the beginning of filtration and gradually increased to 6 log over 5 h, possibly because of the growth of the cake layer. The time-averaged rate of virus removal was 5.4 log, indicating that most of the virus particles in the MF feed water were retained in the MF compartment. Our research group previously reported a similar time-course increase in virus removal in a hybrid system (Matsushita *et al.*, 2005).

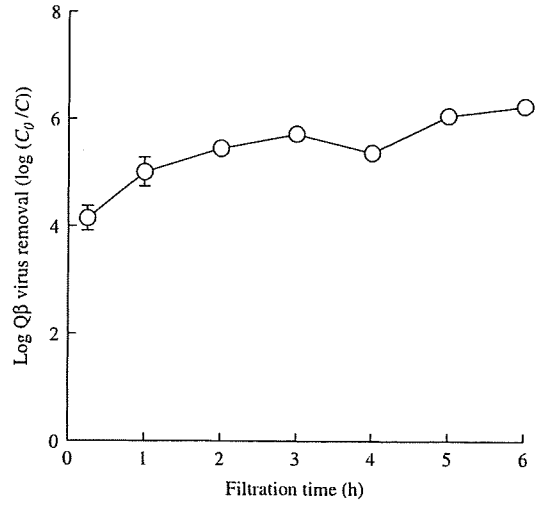

Figure 2 Change in the rate of removal of infectious Qβ virus with filtration time in the hybrid system. Values are means and standard deviations of four experiments

Effect of cake layer on virus removal

To investigate the effect of the cake layer on virus removal, infectious Qβ virus concentrations were directly measured in the liquid phase in the MF compartment and in the MF permeate with filtration time and then compared (Figure 3). The infectious virus concentration in the MF permeate was lower than that in the liquid phase after filtration for each of the test times. This suggests that the cake layer that accumulated on the membrane surface acted as a barrier to viruses.

In addition, the concentration of infectious virus particles in the liquid phase in the MF compartment increased with filtration time, indicating that the virus became concentrated in the MF compartment. In contrast, the infectious virus concentration in the MF permeate decreased with filtration time, and the difference between the virus concentration in the liquid phase and that in the MF permeate increased with filtration time. This could indicate that growth of the cake layer with filtration time contributed to the time-course increase in virus removal. Some researchers have reported that the presence of a cake layer enhances virus removal in membrane filtration. Jacangelo *et al.* (1995) reported that a cake layer that had accumulated on the membrane surface through the addition of kaolinite before the virus was fed into the system increased virus removal. Oh *et al.* (2007) reported that a powdered activated carbon (PAC) cake layer might contribute to virus removal in a hybrid PAC–MF system. Our research group previously conducted a virus-removal study with a hybrid coagulation–immersed ceramic MF system and reported that the floc retained on the membrane surface played an important role in virus removal (Matsui *et al.*, 2003a). In contrast, Matsushita *et al.* (2006) reported that the cake layer did not act as a barrier for the virus in the hybrid system. This result did not correspond with ours, even though the same hybrid system was used in both cases. The reason for the discrepancy between the results of this previous study and ours in terms of the effect of the cake layer on virus removal is not clear, and further investigation is needed.

Effects of entrapment and inactivation on virus removal

To investigate the mechanisms of virus removal in the hybrid system, we determined the change in quantity of Qβ virus particles in the MF compartment with filtration time by using a combination of the PCR and PFU methods after filtration for 0.25, 1, 3, or 6 h (Figure 4). Because the total virus concentration in the liquid phase in the MF

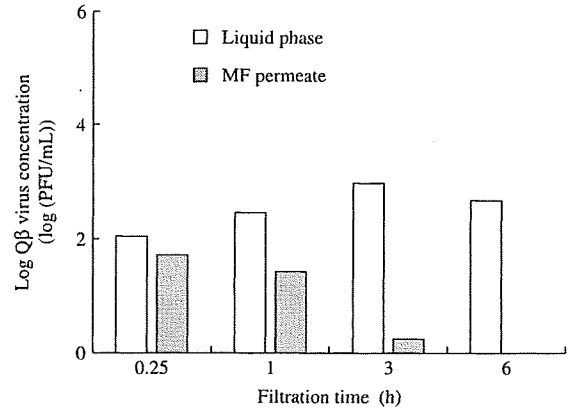

Figure 3 Infectious Qβ virus concentrations in the liquid phase in the MF compartment, and in the MF permeate

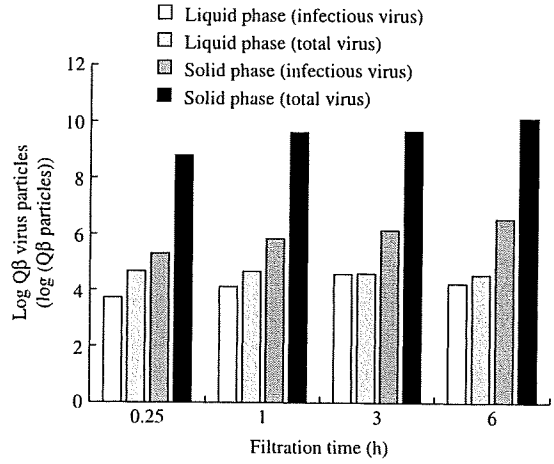

Figure 4 Quantity of Qβ virus particles in the MF compartment as measured by various methods

compartment was lower than the detection limit of the PCR method (10^3 Qβ particles/mL), the total count of virus particles in the liquid phase represent the maximum value as estimated in accordance with the detection limit of the PCR method. The each count of virus particles in the MF compartment increased with filtration time, indicating that virus became concentrated in the MF compartment. The total count of virus particles in the solid phase was at least 5 log greater than that of the virus particles in the liquid phase. This result suggests that most of the virus (>99.999%) in the MF compartment was entrapped in the aluminium floc and then located in the solid phase. In addition, the total count of virus particles in the solid phase was more than 3 log greater than that of infectious virus particles in the solid phase. This means that most of the virus (>99.9%) in the solid phase was inactivated, possibly owing to the virucidal activity of the aluminium coagulant. In a drinking water treatment plant employing a membrane system without coagulation pretreatment, when the raw water of the plant was polluted with a virus the infectious virus would be concentrated in the sludge produced by the plant. This would potentially increase the risk of sludge treatment. In contrast, in a plant employing a membrane system with coagulation pretreatment, most of the virus in the sludge would be inactivated, as demonstrated here. Therefore, the risk associated with the sludge-treatment process could be expected to be smaller with coagulation pretreatment.

Our research group has suggested that the virucidal activity of the aluminium coagulant (Matsui *et al.*, 2003b) enhances virus removal. However, the virus particle concentrations in the liquid phase in the MF compartment and in the MF permeate were lower than the detection limit of the PCR method, as described above. Therefore, it is not clear whether the virus in the liquid phase was inactivated by the virucidal activity of the aluminium coagulant and whether this virucidal activity contributed to the time-course increase in virus removal rate; further investigations are needed.

Mass balance of virus and aluminium

We calculated the mass balance of Qβ virus particles in the MF compartment with filtration time. (Figure 5). The observed values represent the total count of virus particles in the MF compartment (liquid phase + solid phase) as measured by the PCR method; subtracting the quantity of infectious virus particles in the MF permeate from that in the feed

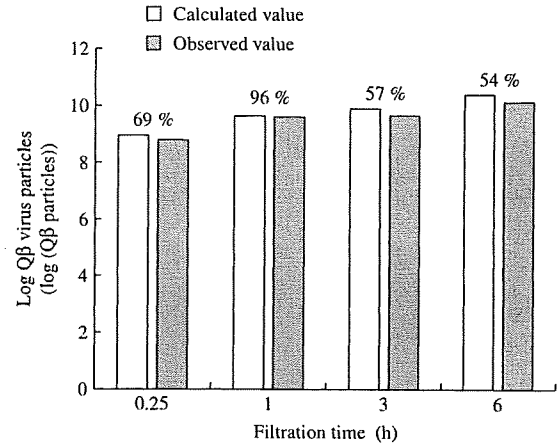

Figure 5 Mass balance of Qβ virus particles in the MF compartment. Values over the columns represent recovery rates (observed value divided by calculated value)

water gives the calculated value. The rate of recovery of virus particles from the MF compartment decreased with filtration time, and the number of virus particles in the MF compartment was approximately 50% of the calculated value after 3 h of filtration. This means that the mass balance of virus was not completely taken in the MF compartment. This low recovery ratio might be due to the entrapment of submicrometre floc, enmeshing virus particles onto the internal structure of the MF pores; the other 50% of the virus particles might accumulate as part of the irreversible fouling of the MF membrane. This hypothesis is supported by the mass balance of aluminium in the MF compartment (Figure 6). The trend in aluminium recovery was similar to that in virus recovery: the recovery rate tended to be higher early on in the filtration and lower late in the filtration. According to the results, accumulation of irreversible fouling containing virus particles might partly account for the time-course increase in virus removal rate in the hybrid system.

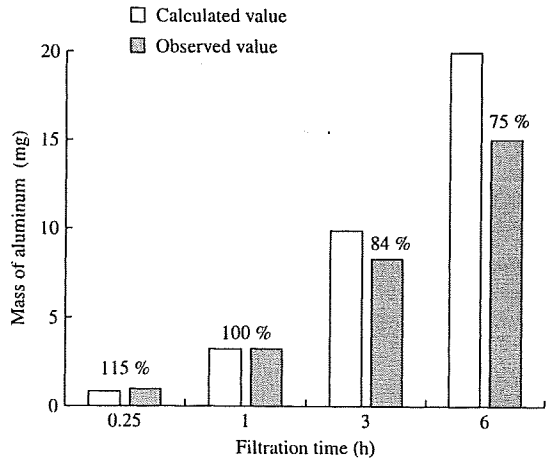

Figure 6 Mass balance of aluminium in the MF compartment. Values over the columns represent recovery rates (observed value divided by calculated value)

Conclusion

1. The time-course increase in virus removal rate in the hybrid coagulation–microfiltration system was due to two main factors: growth of a cake layer that accumulated on the membrane surface, and accumulation of virus on the internal structure of the membrane pores as part of irreversible fouling.
2. Most of the virus particles (>99.999%) were enmeshed in the solid phase (aluminium floc) in the MF compartment, where most of the virus (>99.9%) was inactivated, possibly by the virucidal activity of the aluminium coagulant.

Acknowledgements

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[Original Paper]

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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

Keywords: 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 %.

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.

Table 1 TDI and Drinking Water Quality Standard values of four types of THMs

	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

EXPERIMENTAL METHOD

Survey Protocol

A series of experiments was conducted to measure the THMs concentrations in indoor air, outdoor air, and tap water during 26 days in the winter of 2005

(November 20 ~ December 15). Ten residences were selected to represent each type of household, 5 residential flats and 6 bungalows, 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, N930-7012, USA) using a constant flow sampling pump (GL Science, SP208-100Dual, Japan). 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, Japan) system. The GC parameters included an inlet temperature of 150℃ and a detection temperature of 200℃. For each sample, the initial oven temperature was 30℃, which was held constant for 0.5 min before being ramped at 5℃/min to a final oven temperature of 70℃. A Silicone GE SE-30 (2 m×2.6 mm, SHIMADZU, Japan) 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, Japan). This system was also plumbed to a GC/MS (SHIMADZU GCMS-QP2010, Japan) system. Each tube was thermally desorbed at 280℃ for 10 min and the target compounds cryofocused at −15℃ and concentrated in a cold trap with helium gas flow. Once the desorption was complete, it was heated to 250℃ 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, RESTEK, USA) was employed.

Statistical Analyses

Statistical differences were tested using the nonparametric Mann-Whitney test. Linear regression analyses were conducted to examine the association between the aqueous-phase and airborne THMs. For the above statistical procedures, $p < 0.05$ was set as the criterion for the significant of a test.

Estimation of THMs Exposure from Water Ingestion

The THM exposure from water ingestion was estimated as follows:

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

The tap water concentration in the above equation is applied as the average result of the three types of water samples. 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)

Estimation of THMs Inhalation Exposure from Daily Indoor Activity

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

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

where D_{in} represents THMs dose from inhalation exposure to indoor air including shower and cooking (μg/day); C represents median indoor air concentration ($\mu g/m^3$); 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. The information of health effects in humans of THMs through multi-route exposure is rather limited at present time. According to the document from WHO, health risk from ingestion route appears to be higher than either inhalation route or dermal route (WHO, 2005), but in the mean time, several reports showed that inhalation exposure of THMs may lead to the highest health risk. (Nuckols *et al*, 2005) In view of above, the outside-body environment exposure has been focused in this research. Additionally, considering of the safe-side, 100 % absorption of THMs through ingestion route and inhalation route was applied. 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 cm^2 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). Although researchers have found that heating water will affect the aqueous-phase concentration of THMs (Weisel and Chen, 1993), no significant difference was found among total THM concentrations in three types of water samples in this survey ($p < 0.05$).

THMs in Indoor Air

Figures 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)

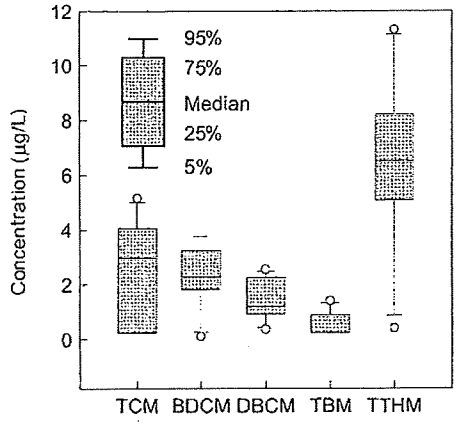

Fig. 1 Tap water concentration
Median TTHM concentration was 6.5 $\mu g/L$

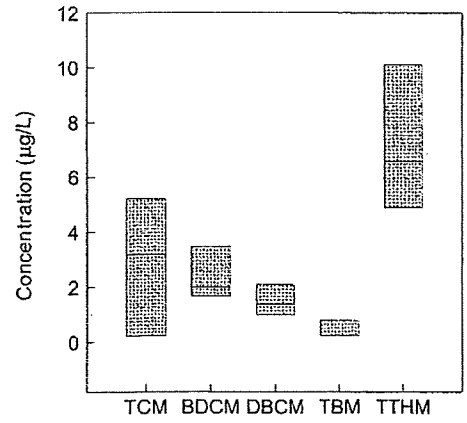

Fig. 2 Bath water concentration
Median TTHM concentration was 6.6 $\mu g/L$

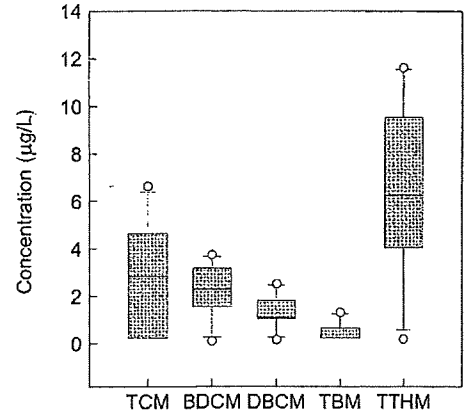

Fig. 3 Shower water concentration
Median TTHM concentration was 6.25 $\mu g/L$

Furthermore, the correlation test results showed 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).

Figure 9 shows the linear regression test (confidence 95 %) 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

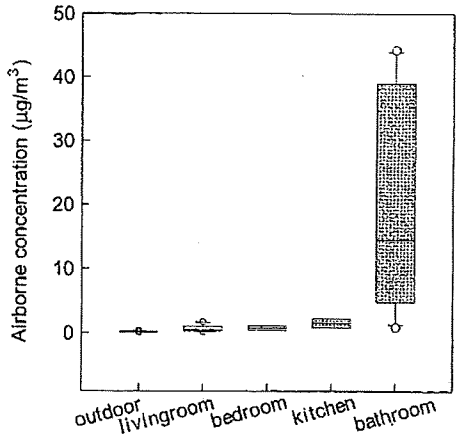

Fig. 4 Airborne concentration of ICM
Median airborne concentration in bathrrom was 14 55 $\mu g/m^3$.

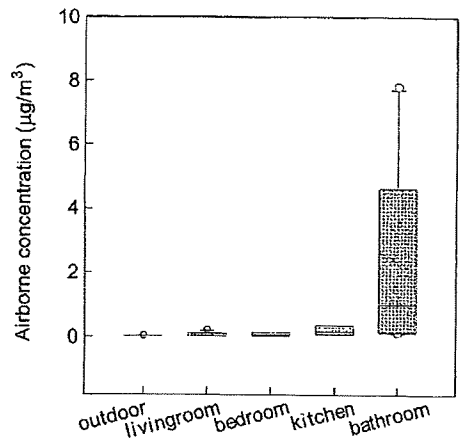

Fig. 7 Airborne concentration of IBM
Median airborne concentration in bathroom was 1 $\mu g/m^3$.

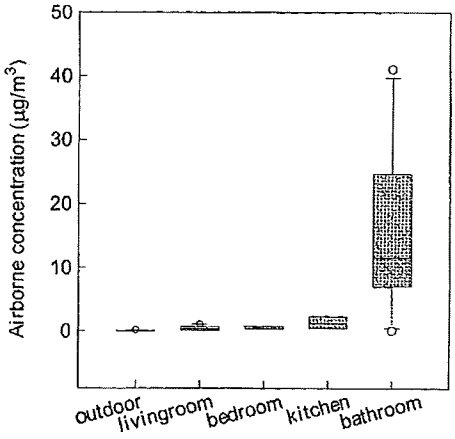

Fig. 5 Airborne concentration of BDCM
Median airborne concentration in bathroom was 11.55 $\mu g/m^3$

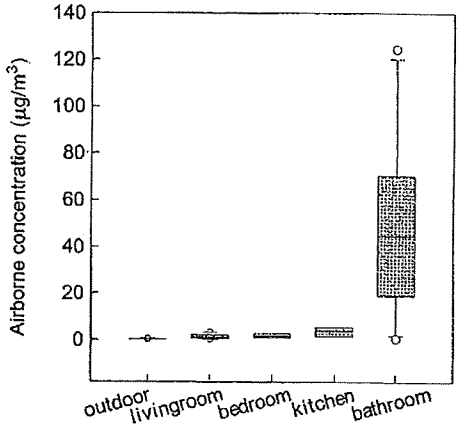

Fig. 8 Airborne concentration of TTHM
Median airborne concentration in bathroom was 44.76 $\mu g/m^3$

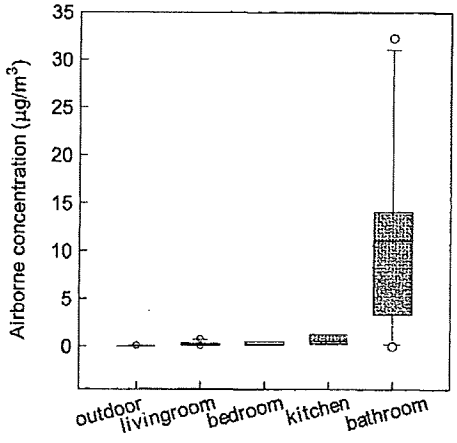

Fig. 6 Airborne concentration of DBCM
Median airborne concentration in bathroom was 11.1 $\mu g/m^3$

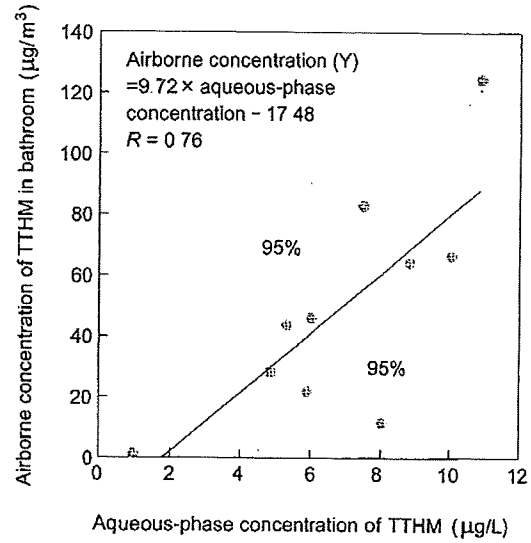

Fig. 9 Correlation between aqueous-phase and airborne concentration of TTHM in bathroom.

concentration in indoor air.

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 THMs 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 THM during bathing activity alone in the present study is derived of 21.41 μg/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	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

Allocation to Drinking Water

As shown in **Fig. 10**, the allocation to oral ingestion among the total exposure ranges from 18.3 % to 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 0.6 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.

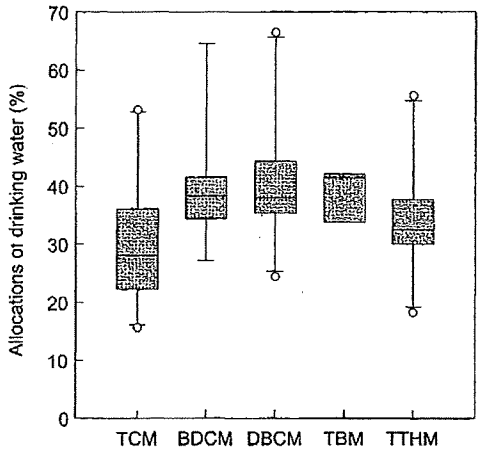

Fig. 10 Ingestion allocation to overall exposure
Median allocation of TTHM to overall exposure was 32.5 %

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 0.5 to 1.0 times larger than ingestion exposure as drinking water.

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Bromide removal by hydrotalcite-like compounds in a continuous system

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Abstract Bromide ion removal from a real water matrix by hydrortalcite-like compounds (HTCs) was attempted in a column reactor to control the formation of brominated disinfection by-products in drinking water treatment process. The performance of HTCs was found to be comparable to a commercially available ion exchange resin for relatively low alkalinity water. Also, it was deduced that HTCs are better than ion exchange resins for high sulfate water because of their unique ion selectivity. In addition, the ion exchange reactions by HTCs were faster than a commercially available resin. Thus, HTCs are expected to provide similar performance to organic resins without the concern about secondary contamination (*i.e.*, elution of organic compounds from resins).

Keywords bromide; disinfection by-products; hydrotalcite-like compounds; ion exchange

Introduction

Brominated disinfection by-products (DBPs) have been recognized as major contributors to the toxicity of chlorinated drinking water. Plewa *et al.* (2002) found that brominated acetic acids are more toxic than their chlorinated counterparts. Echigo *et al.* (2004) estimated that organic bromines produced during chlorination were five times more toxic than organic chlorines on TOX basis. Alternative disinfectants cannot be a perfect solution for this problem because other types of brominated DBPs are produced. For example, bromate ion (BrO_3^-) is produced during ozonation.

One way to control these brominated DBPs is bromide removal. In the past, several attempts have been made for bromide removal: membrane filtration (Amy and Siddiqui, 1999), adsorption by silver-doped aerogel (Sanchez-Polo *et al.*, 2006), electrochemical oxidation of bromide to bromine (Br_2) (Kimbrough and Suffet, 2002), and ion exchange (Johnson and Singer, 2004). While these approaches successfully reduced bromide ion concentration, each process has its drawback. Membrane filtration and silver-doped aerogel processes would not be cost-effective as relatively tight membrane (RO or NF) or expensive metal ion is required for these processes. Electrochemical oxidation is an excellent approach in terms of selectivity, but may produce different type of DBPs. Ion exchange treatment appears to be a promising technology for bromide control, but the use of organic ion exchangers may lead to the formation of other DBPs (*e.g.*, *N*-nitrosodimethyl amine (NDMA) (Najm and Trussell, 2001)). In addition, uptake of monovalent ions by organic ion exchangers is interfered by co-existing divalent ions (*i.e.*, sulfate ion) (Clifford and Weber, 1983).

Given the above situation, we propose bromide removal by inorganic ion exchangers. Among various types of inorganic exchangers, hydrotalcite-like compounds (HTCs) were selected because of their simple chemical composition and unique ion exchange properties. The HTCs used in this study consisted of only Al, Mg, Fe, O, H, and counter ion (Cl^-). HTCs are unique in their preference to monovalent ions over multivalent ions

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(Tezuka, *et al.*, 2004). However, at this point, virtually no information is available on the performance of HTCs for bromide removal in dilute solution. Therefore, the present study evaluates the performance of HTCs for bromide ion removal from a real water matrix in a continuous system.

Material and methods

Material

Chemicals. All the chemical reagents used in this study were of reagent grade or better (mostly analytical grade), and were purchased from Wako pure chemical unless otherwise noted. All the aqueous solutions were prepared with ultra pure water treated by a Millipore Elix20 system.

Test solutions. Water sampled from a real drinking water treatment plant was used as the test solution. This plant is one of the major drinking water treatment plants in Japan. The water was sampled from the sampling tap between rapid sand filtration and ozonation. The anion concentrations of this sample water were as follows: Cl^-, 19 mg/L; Br^-, 40 μg/L; NO_3^-, 5.5 mg/L; SO_4^{2-}, 19 mg/L. Also, the IC and TOC of the sample water were 9.2 and 1.5 mgC/L, respectively. Prior to column experiments, bromide concentration was adjusted to 200 μg/L to simulate a high bromide situation. Also, to evaluate the effect of bicarbonate, decarbonation (nitrogen bubbling and pH adjustment) was performed prior to ion exchange in one case.

Ion exchangers. Two types of HTCs were synthesized: (MgFe)-HTC and (MgAlFe)-HTC (note that elements in parentheses indicate the metal ions used). DIAION SA10A (Mitsubishi Chemical), a commercially available ion exchanger, was also used for comparison. HTCs were synthesized by the hydrothermal method (Miyata, 1975; Reichle, 1986) from metal cation solutions (Mg^{2+}:Fe^{3+} = 4:1 (mol/mol) for (MgFe)-HTC and Mg^{2+}: Al^{3+}: Fe^{3+} = 8:1:1 (mol/mol/mol) for (MgAlFe)-HTC). The HTCs were crystallized and aged in a 1 L Teflon-lined hydrothermal reactor (TEM-D 1000 M, Taiatsu Techno). The crystal structure of the HTCs was confirmed by XRD. Also, the metal compositions of (MgFe)-HTC and (MeAlFe)-HTC were found to be Mg:Fe = 0.787:0.213 (mol/mol) and Mg:Al:Fe = 0.789:0.103:0.108 (mol/mol/mol), respectively by ICP-AES.

Column test

The bench-scale single column system was constructed using a glass column (Vantage^{TM}L, Millipore). The diameter of the column was 11 mm and the length between the spacers in the column was set to 52 mm. In the gap, 0.1 g of a HTC or an ion exchange resin was placed. At the top of the gap, 0.2 μm grass fiber filter (ADVANTEC) was placed to prevent the leakage of ion exchangers. The influent was continuously pumped to the column at a flow rate of 0.5 mL/min to maintain the retention time approximately at 10 minutes. Effluent samples were collected at every 10 minutes with a fraction collector (CHF-100AA, Advantec).

Analytical methods

Bromide ion and other anion concentrations were determined by ion chromatography (LC-VP, Shimadzu) with a Shim-pack IC-A3 analytical column (Shimadzu) protected by a Shim-pack IC-GA3 guard column (Shimadzu). The mobile phase was 50 mM of boric acid/ 8 mM of *p*-hydroxybenzoic acid/ 3.2 mM bistris (TCI). The pH values of the effluent were monitored by a pH meter (Horiba). Also, TOC and IC were determined by a TOC analyzer (TOC-5000A, Shimadzu).