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).
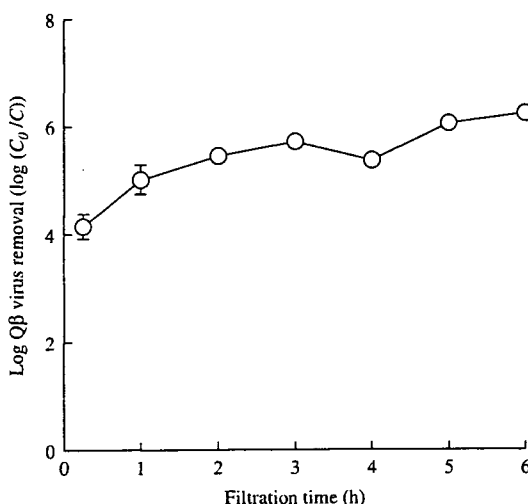

Figure 2 Change in the rate of removal of infectious Qβ virus with filtration time in the hybrid system. Values are means and standard deviations of four experiments

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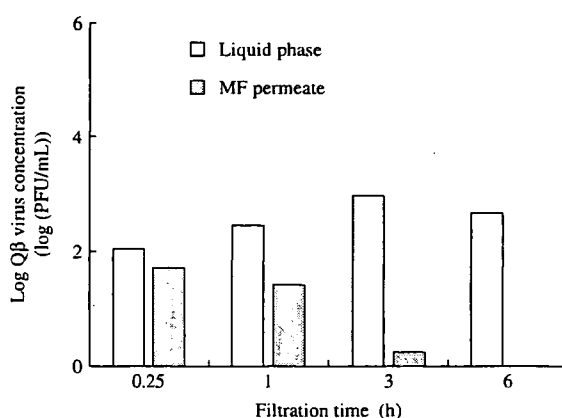
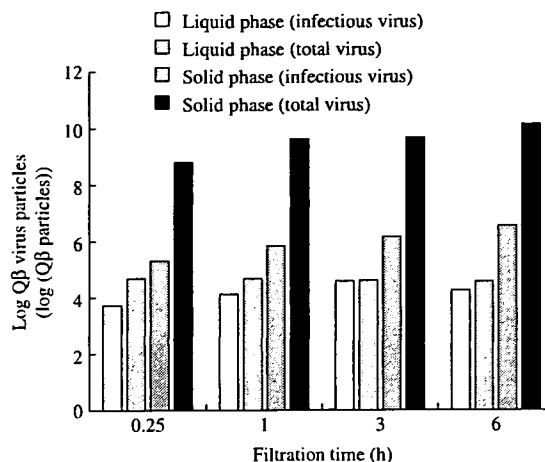Figure 3 Infectious Qβ virus concentrations in the liquid phase in the MF compartment, and in the MF permeate

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
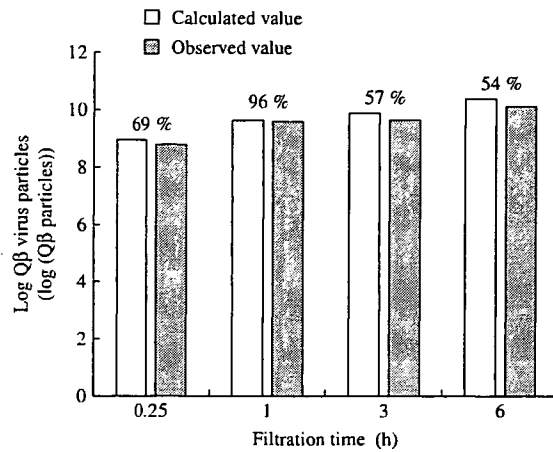
N. Shirasaki et al.

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.
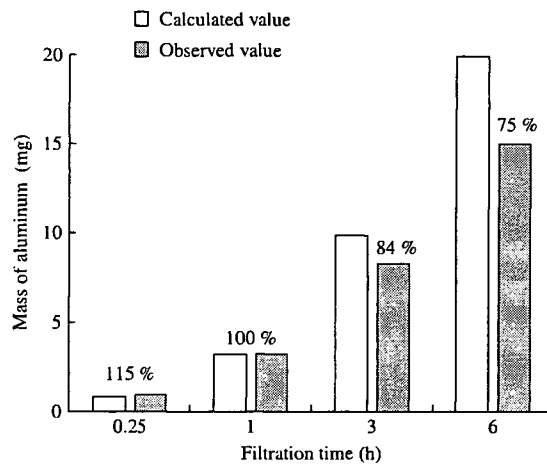

Figure 6 Mass balance of aluminium in the MF compartment. Values over the columns represent recovery rates (observed value divided by calculated value)

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.

References

Adams, M.H. (1959). *Bacteriophages*, Interscience, New York, NY, USA. pp. 450–454.

Fiksdal, L. and Leiknes, T.O. (2006). The effect of coagulation with MF/UF membrane filtration for the removal of virus in drinking water. *J. Membr. Sci.*, 279(1–2), 364–371.

Jacangelo, J.G., Adham, S.S. and Laîné, J.M. (1995). Mechanism of *Cryptosporidium, Giardia*, and MS2 virus removal by MF and UF. *J. Am. Water Works Assoc.*, 87(9), 107–121.

Matsui, Y., Matsushita, T., Inoue, T., Yamamoto, M., Hayashi, Y., Yonekawa, H. and Tsutsumi, Y. (2003a). Virus removal by ceramic membrane microfiltration with coagulation pretreatment. *Water Sci. Technol.: Water Supply*, 3(5–6), 93–99.

Matsui, Y., Matsushita, T., Sakuma, S., Gojo, T., Mamiya, T., Suzuoki, H. and Inoue, T. (2003b). Virus inactivation in aluminum and polyaluminum coagulant. *Environ. Sci. Technol.*, 37(22), 5175–5180.

Matsushita, T., Matsui, Y., Shirasaki, N. and Kato, Y. (2005). Effect of membrane pore size, coagulation time, and coagulant dose on virus removal by a coagulation-ceramic microfiltration hybrid system. *Desalination*, 178(1–3), 21–26.

Matsushita, T., Matsui, Y. and Shirasaki, N. (2006). Analyzing mass balance of viruses in a coagulation-ceramic microfiltration hybrid system by a combination of the polymerase chain reaction (PCR) method and the plaque forming units (PFU) method. *Water Sci. Technol.*, 53(7), 199–207.

Oh, H.K., Takizawa, S., Ohgaki, S., Katayama, H., Oguma, K. and Yu, M.J. (2007). Removal of organics and viruses using hybrid ceramic MF system without draining PAC. *Desalination*, 202, 191–198.

Otaki, M., Yano, K. and Ohgaki, S. (1998). Virus removal in a membrane separation process. *Water Sci. Technol.*, 37(10), 107–116.

Urase, T., Yamamoto, K. and Ohgaki, S. (1996). Effect of structure of membranes and module configuration on virus retention. *J. Membr. Sci.*, 115, 21–29.

Zhu, B., Clifford, D.A. and Chellam, S. (2005a). Virus removal by iron coagulation-microfiltration. *Water Res.*, 39, 5153–5161.

Zhu, B., Clifford, D.A. and Chellam, S. (2005b). Comparison of electrocoagulation and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes. *Water Res.*, 39, 3098–3108.

Exposure Assessment of Trihalomethanes in Households
for Estimating Allocation to Drinking Water

Dawei QUAN*, Teruo MUTO*, Yasuo YANAGIBASHI*, Sadahiko ITOH*, Shinya ECHIGO*,
Yumiko OHKOUCHI* and Hideto JINNO**

* Department of Urban Management, Graduate School of Engineering, Kyoto University,
Nishikyo-ku, Kyoto 615-8540, Japan
** National Institute of Health Sciences, Kamiyoga 1-18-1, Setagaya-ku, Tokyo 158-8501, Japan

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

	IDI (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:

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

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:

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

where D_{in} represents THMs dose from inhalation exposure to indoor air including shower and cooking $(\mu g/day)$; 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 m³ /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
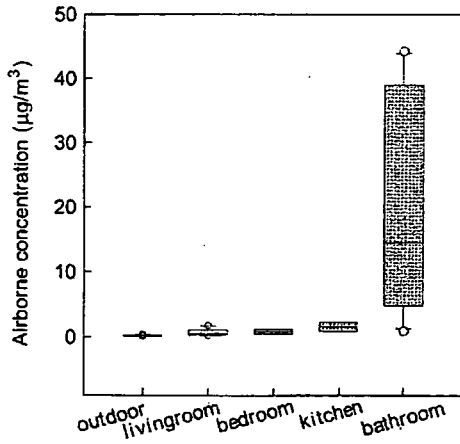
Fig. 4 Airborne concentration of TCM
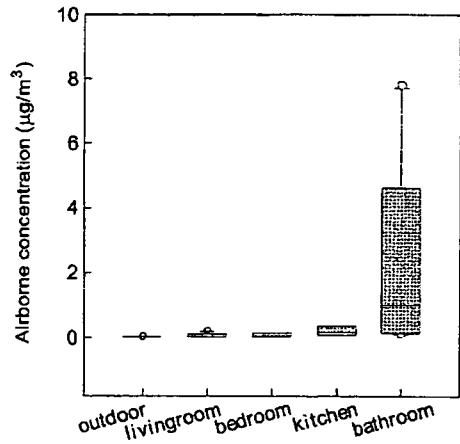Median airborne concentration in bathrrom was 14 55 μg/m³.

Fig. 7 Airborne concentration of TBM
Median airborne concentration in bathroom was 1 μg/m³
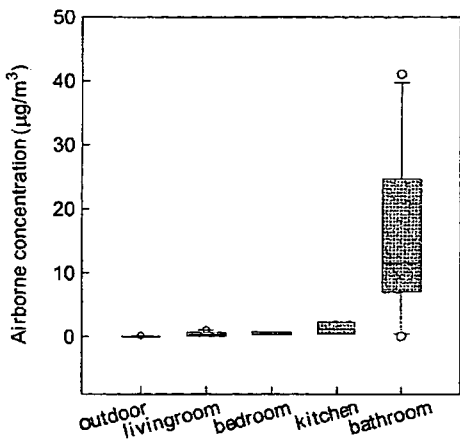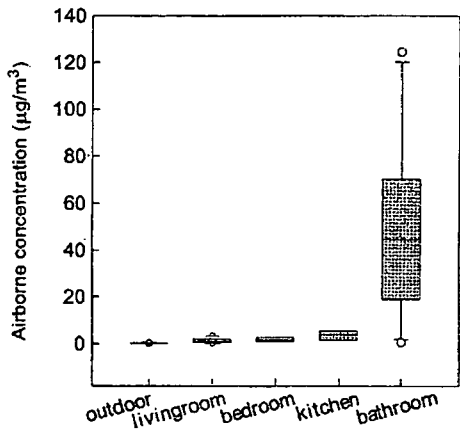

Fig. 5 Airborne concentration of BDCM
Median airborne concentration in bathroom was 11.55 μg/m³

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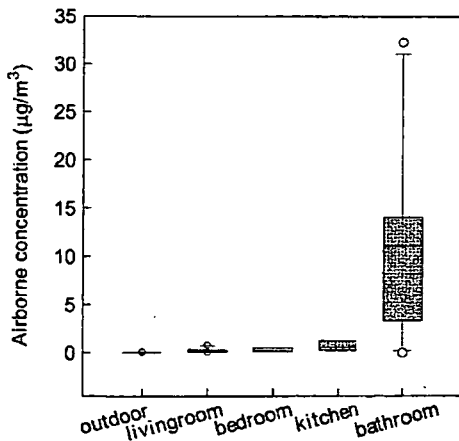Median airborne concentration in bathroom was 44.76 μg/m³

Fig. 6 Airborne concentration of DBCM
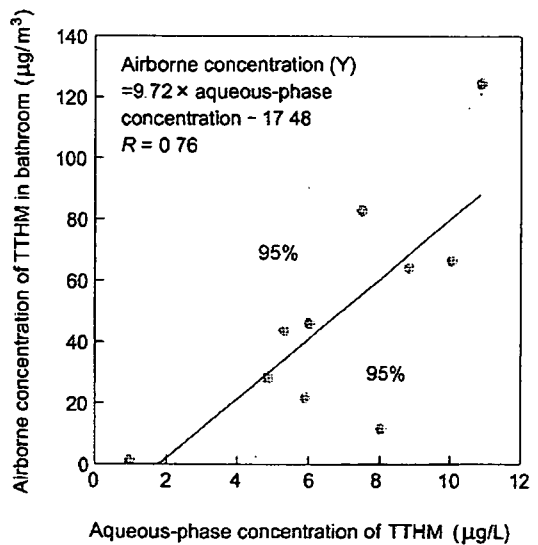Median airborne concentration in bathroom was 11.1 μg/m³

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

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 >
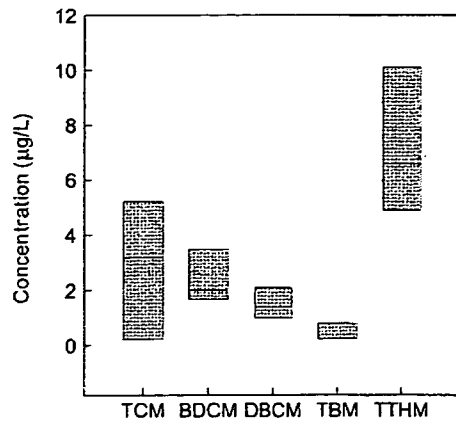

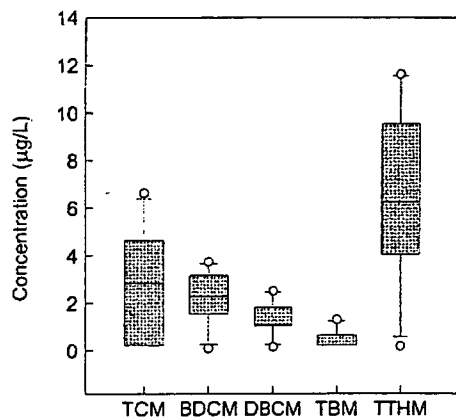Fig. 1 Tap water concentration
Median TTHM concentration was 6 5 μg/L

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

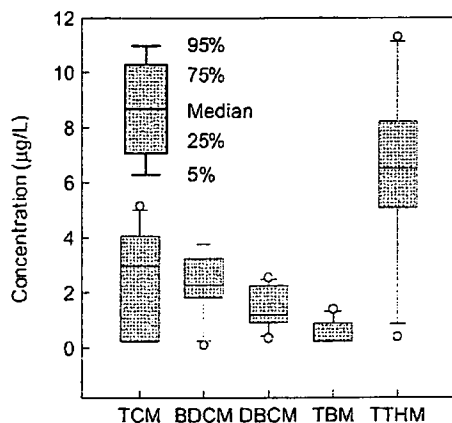Fig. 3 Shower water concentration
Median TTHM concentration was 6 25 μg/L

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 μg/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)

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

concentration in indoor air.

Exposure Analysis

The THMs exposure estimates from water inges-
tion, 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 ex-
posure of TTHM during bathing activity alone in the pre-
sent 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 af-
fected by other exposure scenarios The median value of
total THMs ingestion allocation was 32.5 %, which is al-
most 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 consid-
erable seasonal variation in both aqueous-phase and air-
borne concentrations (Jo et al., 2005). Also, in the
present study, no dietary intake exposure was included in
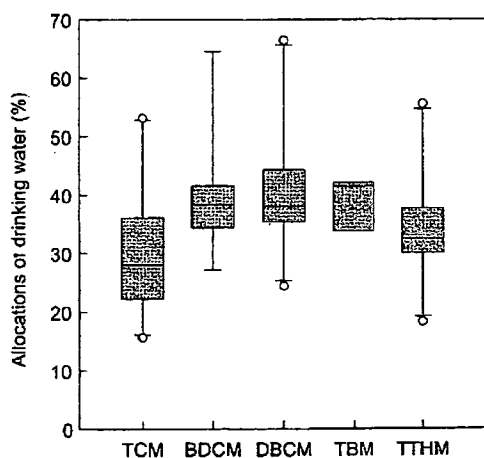the evaluation Therefore, more consideration should be

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

paid carefully in concluding the allocation to drinking
water.

CONCLUSIONS

The present study estimated multi-route THMs ex-
posure 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 concen-
tration, supporting that tap water THMs levels are asso-
ciated 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.

REFERENCES

Andelman, J, B., "Inhalation exposure in the home to
volatile organic contaminants of drinking water",
Sci. Total Environ, 47, 443-60 (1985).

Chang, E, Chao, S., Chiang, P., Lee, J., "Effects of
chlorination on THMs formation in raw water",
Environ Toxicol Chem, 56, 211-25 (1996)

Clark, R., M., Goodrich, J., A, "Drininger RA Drinking
water and cancer mortality", *Sci Total Environ*, 53,
153-72 (1992)

Weisel, C., P., Chen, W., J., "Exposure to chlorination
by-products from hot water uses", *Risk Anal*, 14,
101-106 (1994)

Jo, W., K., Weisel, C, P., Lioy, P, J., "Routes of chloro-
form exposure and body burden from showering
with chlorinated tap water", *Risk Anal*, 10 (a),
575-80 (1990).

Jo, W., K, Weisel, C., P., Lioy, P, J., "Chloroform ex-
posure and the health risk associated with multiple
uses of chlorinated tap water", *Risk Anal*, 10, 581-5
(1990).

Jo, W, K, Kwon, K, D, Dong, J, I, Chung, Y,
"Multi-route trihalomethane exposure in households
using municipal tap water treated with chlorine or
ozone—chlorine", *Sci Total Environ*, 339, 143-52
(2005).

Lin, T, F., Hoang, S., W, "Inhalation exposure to THMs
from drinking water in south Taiwan", *Sci Total
Environ*, 246, 41-9 (2000).

Morris, R., D, Audet, A., M., Angelillo, I., F., Chalmers,
I., C., Musteller, F., "Chlorination, Chlorination
by-products, and cancer: a metaanalysis", *Am J
Public Health*, 82, 955-63 (1992)

Nuckols, J., R., Ashley, D., L, Lyu, C., Gorden, S, M.,
Hinckley, A., F., and Singer, P., "Influence of tap
water quality and household water use activities on
indoor air and internal dose levels of
trihalomethane", *Environ. Health Perspect*, 113,
863-870 (2005).

Singer, P, C, Reckhow, D., A, In: Letterman RD,
(ed), Water quality and treatment, a handbook for

community water supplies, 5ᵗʰ edn. McGraw-Hill, New York, USA, 12.1-12 51 (1999).

Social Research, NHK, Japan, 56-60 (2000)

The Revision of Drinking Water Quality Standard, (in Japanese), Ministry of Health, Labour and Welfare, Japan, (2003).

Exposure Factors Handbook, U.S. EPA/ National Center for Environmental Assessment Office of Research and Development, Washington, DC, USA (1997).

Risk assessment guideline for superfund volume 1: Human health evaluation manual (Part E, Supplemental guidance for dermal risk assessment), U.S. EPA, Washington, DC, USA (2004)

Method 501, Federal Register Part III, U.S EPA, Washington, DC, USA (1979)

Von, Gunten, U., V., Driedger, A., Gallard, H., Salhi, E., "By-products formation during drinking water disinfection: a tool to assess disinfection efficiency", *Water Res,* **35,** 2095-9 (2001).

Wallace, L., A., "Human exposure and body burden for chloroform and other trihalomethanes", *Crit Rev. Environ. Sci. Technol.,* **27,** 113-94 (1997).

Trihalomethanes in drinking-water, background document for development of WHO Guidelines for drinking-water quality, Geneva, (2005).

Bromide removal by hydrotalcite-like compounds in a continuous system

S. Echigo*, S. Itoh* and M. Kuwahara**

*Department of Urban Management, Graduate School of Engineering, Kyoto University, C-1 Nishikyo, Kyoto 615-8540, Japan (E-mail: echigo@urban.env.kyoto-u.ac.jp; itoh@urban.env.kyoto-u.ac.jp)
**Osaka Gas Co., Ltd., Osaka, Japan (E-mail: kuwahara@urban.env.kyoto-u.ac.jp)

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

(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™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).

Results and discussion

Bromide removal by (MgFe)-HTC

Figure 1(a) shows the anion concentration (C/C_0) profiles during the (MgFe)-HTC treatment. The dashed line in the figure indicates $C/C_0 = 0.4$. Throughout this study, the breakthrough point was operationally defined as the treated volume at $C/C_0 = 0.4$. The result clearly shows that bromide removal by HTCs is possible even with higher concentration of competing anions (i.e., nitrate, sulfate, and bicarbonate ions). Especially, in the initial 50 mL, bromide concentration was reduced below 10 μg/L.

Bromide concentration increased and reached 60% bromide removal at approximately 78 mL. The volume treated before bromide breakthrough calculated was 777 mL/g. Also, the bromide uptake before breakthrough was estimated to be 1.4 mg/g. The bromide concentration of the effluent further increased, and a chromatographic peak of bromide ion was observed around 100–200 mL. The concentrations of sulfate, bromide, and nitrate ions similarly increased in this order, and eventually chromatographic peaks of these anions were observed. On the other hand, no breakthrough was observed for inorganic carbon during the treatment (Figure 1(b)). These results indicated that the selectivity sequence of the (MgFe)-HTC was $HCO_3^- \gg NO_3^- > Br^- > SO_4^{2-}$ in this system. This is consistent with the selectivity of common HTCs reported by other researchers (Bish, 1980; Miyata, 1983) at a higher anion concentration. Therefore, it is deduced that while the interference by sulfate ion is weak, carbonate/bicarbonate ion impacts strongly on the performance of bromide removal by HTCs.

Bromide removal by (MgAlFe)-HTC

The anion concentration (C/C_0) profiles during the (MgAlFe)-HTC were shown in Figure 2(a). The (MgAlFe)-HTC treatment showed similar anion removal profiles to those by the (MgFe)-HTC treatment. Until approximately 50 mL, the effluent bromide concentration was reduced to below 10 μg/L indicating fast anion exchange reaction. The volume treated before bromide breakthrough was 776 mL/g, which was almost identical to that of (MgFe)-HTC. Also, the bromide uptake before the breakthrough was the same as (MgFe)-HTC (1.4 mg/g).

Anion breakthrough for the (MgAlFe)-HTC treatment was also observed in the following order: sulfate, bromide, and nitrate ions. This is presumably due to the effect of higher selectivity to bicarbonate ion. From this result, the order of preference of (MgAlFe)-HTC was determined to be $HCO_3^- \gg NO_3^- > Br^- > SO_4^{2-}$.
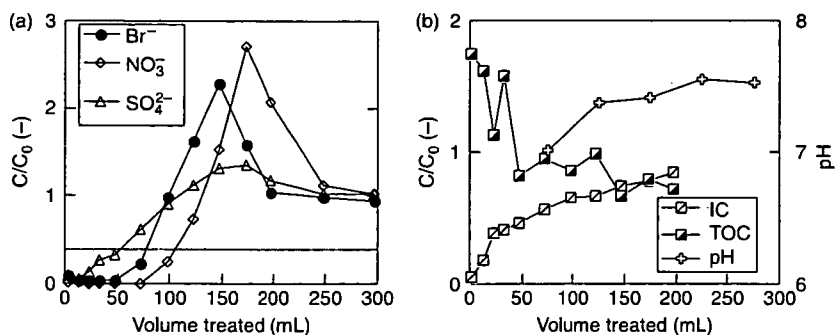

Figure 1 Anion, carbon, and pH profiles during (MgFe)-HTC treatment. (a) anions, (b) carbon contents and pH. Dashed line indicates $C/C_0 = 0.4$ (i.e., 60% removal)
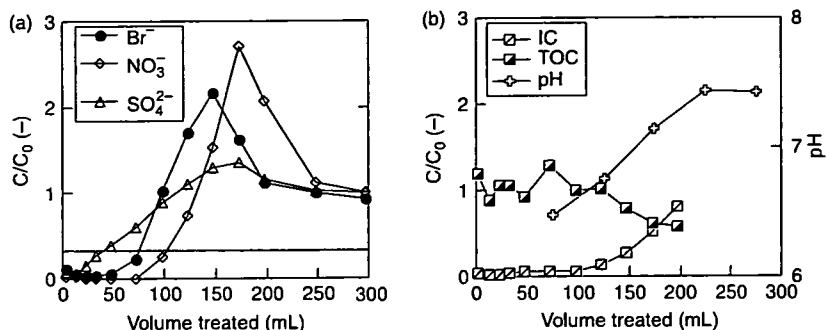
Figure 2 Anion, carbon, and pH profiles during (MgAlFe)-HTC treatment. (a) anions, (b) carbon contents and pH

In addition, TOC removal was not observed for both the HTCs. This result indicates that the TOC component in the feed water consisted of mainly large organic molecules and was rejected by the ion-sieve effect of HTCs (Tezuka et al., 2004).

Bromide removal by DIAION SA 10A

Anion concentration profiles by ion exchange treatment by Diaion SA10 A were quite different from those by the HTCs (Figure 3(a)). During the HTC treatment, the bromide concentration decreased to below 10 μg/L, but always above 70 μg/L during the treatment by Diaion SA10 A. Also, the volume treated before breakthrough was larger (1151 mL/g) than HTCs while the bromide uptake was similar (1.5 mg/g) indicating sufficient ion exchange capacity but slower ion exchange reaction.

The selectivity sequence was determined to be $SO_4^{2-} > NO_3^- > Br^- > HCO_3^-$ (Figures 3(a) and (b)). This order was consistent with the selectivity of common organic resins, and was totally different from that of HTCs in that bicarbonate ion was the least preferred and sulfate ion was the most preferred anion. From this result, it can be said that Diaion SA10A is better for high alkalinity water. On the other hand, for a water matrix with high sulfate ion, HTCs are better for bromide removal not only because both (MgFe)- and (MgAlFe)-HTCs preferred bromide ion to sulfate ion but also because of the faster ion exchange ratio during the early stage than Diaion SA10A.

Effect of alkalinity removal on the bromide removal profiles by HTCs

Figure 4(a) shows anion concentration profiles during the (MgAlFe)-HTC treatment after decarbonation (nitrogen bubbling and pH adjustment by sodium hydroxide and hydrochloric
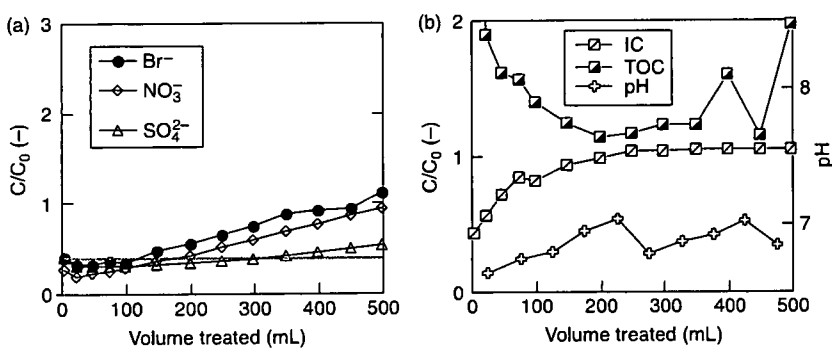

Figure 3 Anion, carbon, and pH profiles during Diaion SA10A. (a) anions, (b) organic and inorganic carbons and pH
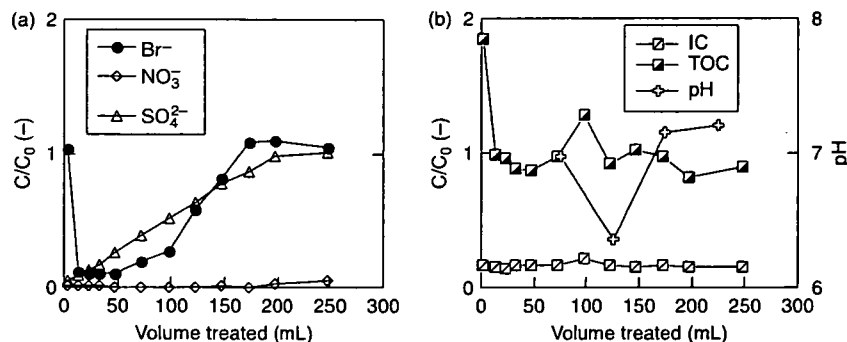
Figure 4 Anion, carbon, and pH profiles during (MgAlFe)-HTC after decarbonation. (a) anions, (b) organic and inorganic carbons and pH

Table 1 Summary of the performance of ion exchangers on bromide removal by a column reactor (influent SO_4^{2-} = 19 mg/L, NO_3^- = 5.5 mg/L)

Ion exchanger	MgFe-HTC	MgAlFe-HTC	MgAlFe-HTC*	DIAION SA10A
Influent Br^- (μg/L)	202	202	220	204
Influent IC (mgC/L)	9.1	9.3	2.8	9.2
Br^- breakthrough (mL/g)†	777	776	1071	1151
Bromide uptake (mg/g)‡	1.4	1.4	1.8	1.5
Ion selectivity	$HCO_3^- > NO_3^-$ $> Br^- > SO_4^{2-}$	$HCO_3^- > NO_3^-$ $> Br^- > SO_4^{2-}$	$HCO_3^- > NO_3^-$ $> Br^- > SO_4^{2-}$	$SO_4^{2-} > NO_3^-$ $> Br^- > HCO_3^-$

*With decarbonation before ion exchange
†Volume treated before reaching $C/C_0 = 0.4$
‡Bromide removed before breakthrough

acid). These results in the lower alkalinity condition were totally different from those with decarbonation. The chromatographic peaks observed in bromide, nitrate and sulfate ions were virtually disappeared during the treatment volume tested, and the treatment volume before bromide breakthrough increased to 1080 mL/g, and the bromide uptake before breakthrough increased to 1.8 mg/g. From these results, it can be said that alkalinity is the key factor to determine the "life" of HTCs, and to lower the chromatographic peaks.

Comparison of ion exchangers

The results of the column tests in the real water matrix were summarized in Table 1. All the ion exchangers tested showed 60% bromide removal at early treatment stage. The performance of HTCs was comparable to that of Diaion SA10A in terms of the treatment volume and the bromide uptake before breakthrough, though Diaion SA10A was slightly better.

To the best of our knowledge, this series of experiments demonstrated that HTCs are applicable to bromide removal in a real water matrix for drinking water treatment purpose. In addition to similar bromide capability to a commercially available resin, HTC treatment is a promising technology since there is no concern about secondary contamination (e.g., elution of precursors of NDMA (Najm and Trusseel, 2001)). Also, in the HTC treatment, ion exchange reactions were found to be faster. This can be an advantage of HTC over anion exchange resins when designing an actual treatment system.

Conclusions

Bromide ion removal in a real water matrix by HTCs was attempted in a column reactor. The performance of HTCs was found to be comparable to a commercially available

ion-exchange resin for relatively low alkalinity water without the concern about second-ary contamination. Also, it was deduced that HTCs are better than ion exchange resins for high sulfate water because of the unique ion selectivity of HTCs.

References

Amy, G.L. and Siddiqui, M.S. (1999). *Strategies to Control Bromate and Bromide*, American Water Works Association Research Foundation Final Project Report, Denver, USA.

Bish, D.L. (1980). Anion-exchange in takovite: applications to other hydroxide minerals. *Bull. Mineral.*, **103**, 170–175.

Clifford, D.A. and Weber, W.J. (1983). The determinants of divalent/monovalent selectivity in anion exchangers. *React. Polym.*, **1**, 77–89.

Echigo, S., Itoh, S., Natsui, T., Araki, T. and Ando, R. (2004). Contribution of brominated organic disinfection by-products to the mutagenicity of drinking water. *Water Sci. Technol.*, **50**(5), 321–328.

Johnson, C.J. and Singer, P.C. (2004). Impact of a magnetic ion exchange resin on ozone demand and bromate formation during drinking water treatment. *Water Res.*, **38**, 3738–3750.

Kimbrough, D.E. and Suffet, I.H. (2002). Electrochemical removal of bromide and reduction of THM formation potential in drinking water. *Water Res.*, **36**, 4902–4906.

Miyata, S. (1975). The synthesis of hydrotalcite-like compounds and their physico-chemical properties -I: the systems $Mg^{2+}-Al^{3+}-NO^{3-}$ $Mg^{2+}-Al^{3+}-Cl^-$, $Mg^{2+}-Al^{3+}-ClO_4^-$, $Ni^{2+}-Al^{3+}-Cl^-$ and $Zn^{2+}-Al^{3+}-Cl$. *Clays Clay Miner.*, **23**, 369–375.

Miyata, S. (1983). Anion-exchange properties of hydrotalcite-like compounds. *Clays Clay Miner.*, **31**, 305–311.

Najm, I. and Trussell, R.R. (2001). NDMA formation in water and wastewater. *J. Am. Water Assoc.*, **93**(2), 92–99.

Plewa, M.J., Kargalioglu, Y., Vankerk, D., Minear, R.A. and Wagner, E.D. (2002). Mammalian cell cytotoxicity and genotoxicity analysis of drinking water disinfection by-products. *Environ. Mol. Mutagen.*, **40**, 134–142.

Reichle, W.T. (1986). Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite). *Solid State Ionics*, **22**, 135–141.

Sanchez-Polo, M., Rivera-Utrilla, J. and von Gunten, U. (2006). Bromide and iodide removal from waters under dynamic conditions by Ag-doped aerogels. *J. Colloid Interface Sci.*, **306**, 183–186.

Tezuka, S., Chitraka, R., Sonoda, A., Ooi, K. and Tomida, T. (2004). Studies on selective adsorbents for oxo-anions nitrate ion-exchange properties of layered double hydroxides with different metal atoms. *Green Chem.*, **6**, 104–109.

ELSEVIER
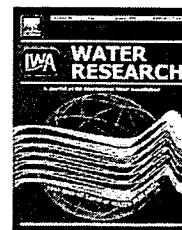
Occurrence of perchlorate in drinking water sources of metropolitan area in Japan

Koji Kosaka*, Mari Asami, Yukiko Matsuoka, Masahiro Kamoshita, Shoichi Kunikane

Department of Water Supply Engineering, National Institute of Public Health, 2-3-6 Minami, Wako, Saitama 361-0198, Japan

ARTICLE INFO

ABSTRACT

The occurrence of perchlorate in the Tone River Basin was investigated using an ion chromatograph (IC) coupled with a tandem mass spectrometer (MS/MS). Perchlorate was found at high concentrations in the upper Tone River and its tributary, Usui River, and the maximum concentrations were 340 and 2300 μg/L, respectively. The possible sources of perchlorate in two areas were attributable to industrial effluents. In case of the upper Tone River, perchlorate concentration in an effluent was 1100 μg/L and its concentrations in a tributary (or waterway) directly downstream of the outlet of the effluent ranged from 44 to 1500 μg/L. In case of the Usui River, perchlorate concentration in another effluent was 15,000 μg/L and its concentrations downstream of the outlet of the effluent were 1100–3900 μg/L. Due to the discharge of perchlorate in the upper Tone River Basin, perchlorate concentrations in the river waters of the middle and lower Tone River Basin were generally 10–20 μg/L. Perchlorate concentrations in 30 tap water samples were investigated. Water sources of three tap water samples were other than the Tone River Basin and their perchlorate concentrations were 0.16–0.87 μg/L. On the other hand, water sources of the remaining 27 samples were the upper, middle and lower Tone River Basin and their perchlorate concentrations were 0.06–37 μg/L. Perchlorate concentrations were more than 1 μg/L in 19 tap water samples and more than 10 μg/L in 13 samples. It was shown that tap waters in the Tone River Basin were widely contaminated with perchlorate. To our knowledge, this study was the first to report on perchlorate contamination of environmental and drinking waters in Japan.

1. Introduction

Perchlorate is highly soluble, mobile and stable in water (Interstate Technology & Regulatory Council (ITRC) Perchlorate Team, 2005; The Department of Defense Environmental Data Quality Workgroup, 2006; Massachusetts Department of Environmental Protection, 2005). Perchlorate compounds are manufactured in the form of their salts (e.g., ammonium perchlorate (NH_4ClO_4), sodium perchlorate ($NaClO_4$) and potassium perchlorate ($KClO_4$)) or perchloric acid ($HClO_4$). The estimated production of $NaClO_4$ was 1600 ton in 2004 in Japan (The

Chemical Daily, 2006). Perchlorate compounds are mainly used in missile/rocket propellants, and also in various industrial products (e.g., fireworks, matches, air bag inflators and flares) (ITRC Perchlorate Team, 2005; The Department of Defense Environmental Data Quality Workgroup, 2006; Massachusetts Department of Environmental Protection, 2005). The Atacama Desert nitrate deposit in Chile used as fertilizer is also known to be a natural source of perchlorate (Interstate Technology & Regulatory Council (ITRC) Perchlorate Team, 2005). More recently, it has also been reported that perchlorate is naturally formed in atmospheric processes (Dasgupta et al., 2005).

Perchlorate is known to interfere with iodine uptake by the thyroid gland (Greer et al., 2002; National Research Council, 2005). In 2005, the United States Environmental Protection Agency (US EPA) established an official reference dose (RfD) of 0.7 μg/kg/day of perchlorate and specified its drinking water equivalent level (DWEL) to be 24.5 μg/L (US EPA, 2005a), on the basis of the report by the National Academy of Sciences (NAS) (National Research Council, 2005). The Massachusetts Department of Environmental Protection (2006) has promulgated a 2 μg/L drinking water standard for perchlorate in Massachusetts. The California Department of Health Services (CDHS) (2006) has proposed 6 μg/L as the maximum contaminant level (MCL) for perchlorate in drinking water in California. Several states have advisory levels of perchlorate in the range of 1–18 μg/L (US EPA, 2005b). Neither a federal MCL for perchlorate nor a World Health Organization (WHO) drinking-water-quality guideline for perchlorate has been established.

In 1997, CDHS developed an analytical method for perchlorate involving ion chromatography, and detected perchlorate in drinking water wells in California and in the lower Colorado River (California Department of Health Services; Hogue, 2003). Since then, perchlorate has been found in environmental and drinking waters in many states in the US (Massachusetts Department of Environmental Protection, 2005; US EPA; Gullick et al., 2001; Brandhuber and Clark, 2005; Environmental Working Group, 2005; Rajagopalan et al., 2006). Perchlorate has also been detected in lettuce and milk (US Food and Drug Administration (FDA), 2004; Kirk et al., 2003, 2005; Krinitsky et al., 2004). So far, most reports of the occurrence of perchlorate have been in the US. However, two studies on perchlorate concentrations in Japanese samples were recently reported. One study was perchlorate in foods and beverages in many countries (El Aribi et al., 2006). In Japanese samples, perchlorate contents were 0.721 μg/kg in a food product, 0.756–14.85 μg/L in wine, 0.243–7.57 μg/L in beer, not detected in canned barley tea, 0.103 μg/L in sake (rice wine) and 0.296 μg/L in plum wine. The other study was perchlorate in Japanese milk (Dyke et al., 2007). In the study, it was shown that the mean concentration of perchlorate in Japanese milk of 9.39 μg/L (standard deviation (σ): 2.71 μg/L, number of samples analyzed (n): 54) was higher than that in the US milk of 5.74 μg/L (σ: 1.98 μg/L, n: 104) reported by US FDA (2004). These reports suggest that perchlorate may exist in environmental and drinking waters in Japan and perchlorate concentrations in the waters in Japan may be comparable to those in the US. However, there are no data on perchlorate concentrations in waters in Japan; therefore, an immediate study on the occurrence of perchlorate in water in Japan is required.

In this study, we investigated the occurrence of perchlorate in the Tone River Basin in Japan using an ion chromatograph (IC) coupled with a tandem mass spectrometer (MS/MS). Chlorate, another oxychloride anion, was also examined. Perchlorate concentrations in tap water were also investigated for the Tone River Basin and other basins. To our knowledge, this is the first report on perchlorate contamination of environmental and drinking waters in Japan.

2. Methods

2.1. Sampling

Fig. 1 shows sampling points in this study. In this study, the upper Tone River Basin was defined as the area of the Tone River upstream of the confluence of the Karasu River, and the middle and lower Tone River Basin were downstream of that point. Environmental water samples in the Tone River Basin were collected mostly in March–June 2006. Only samples at H1 were collected in August 2006. The Tone River is the second longest river in Japan, and its length is 322 km. The Tone River Basin is the largest basin in Japan, and it covers 16,840 km². The river waters in the Tone River Basin are the drinking water sources of the metropolitan area in Japan. Tap water samples were collected in February–June 2006, both in the areas of the Tone River Basin and in other basins in Japan.

Residual chlorine in the tap water was quenched by sodium ascorbate (Wako Chemical). All samples were stored at 4 °C, and filtered with a 0.2 μm hydrophilic polytetrafluoroethylene (PTFE) disposable filter (Advantec Toyo) before analysis.

2.2. Analysis

Calibration standards of perchlorate and chlorate were prepared by diluting 1000 mg/L certified standard solutions of perchlorate (GFS Chemicals) and chlorate (Kanto Chemical) into ultrapure water purified with a Gradient A10 water purification system (Millipore). The ^{18}O-enriched NaClO$_4$ (Cambridge Isotope Laboratories) was used as an internal standard for perchlorate. The separation was performed using an IC (ICS-2000, Dionex) with an eluent generator (EG50, Dionex) and an autosampler (AS50, Dionex). A guard column, IonPac AG20 column (2 × 50 mm, Dionex), a separation column, IonPac AS20 (2 × 250 mm, Dionex), and a suppressor, ASRS Ultra II (2 mm, Dionex), were employed. The eluent was potassium hydroxide (KOH) at a flow rate of 0.25 mL/min. The gradient was as follows: 10 mM KOH at 0 min, linear increase to 80 mM KOH in 22 min. The injection volume of the autosampler was 100 μL. As a postcolumn solvent, a mixture of acetonitrile (high-performance liquid chromatography grade, Wako Chemical) and ultrapure water (90/10 v/v) was supplied to the eluent, using a HP1100 binary pump (Hewlett-Packard), at a flow rate of 0.2 mL/min and mixed in a static mixing tee. The detection was performed using a MS/MS (API 3200QTrap, Applied Biosystems) operated in the turbo-ion-spray ionization mode. Multiple reaction monitoring (MRM) transitions were m/z 99–83 (quantification) and m/z 101–85 (confirmation) for perchlorate, m/z 107–89 for ^{18}O-enriched perchlorate and m/z 85–66 for chlorate. The minimum reporting limits (MRLs) for perchlorate and chlorate were set to be 0.05 and 0.1 μg/L, respectively. Each MRL was the minimum concentration for each calibration curve. For each compound, limit of quantification calculated as $10\sigma'/a$ was lower than MRL (σ': standard deviation of response at 0.05 μg/L (number of repetitions is five); a: slope of the calibration curve). The maximum concentration of the calibration curve for each compound was 10 μg/L; therefore, the samples were diluted before analysis if necessary.
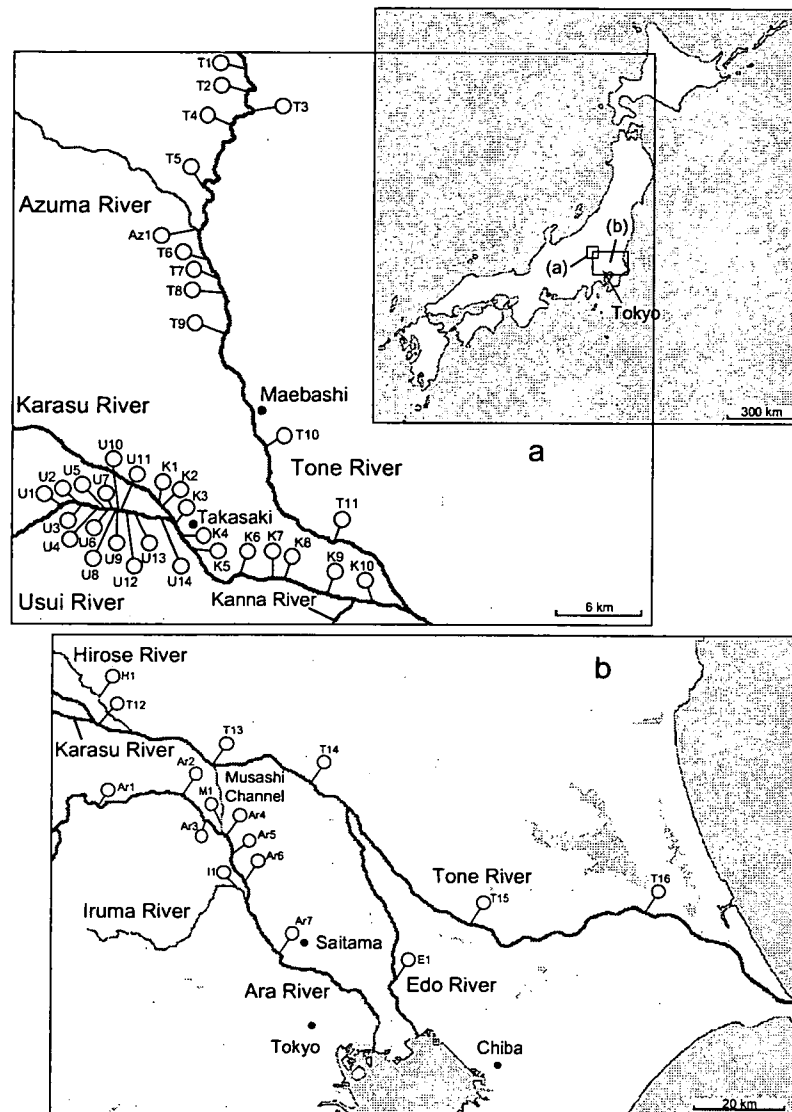
Fig. 1 – Sampling points (a) in the upper Tone River Basin and (b) in the middle and lower Tone River Basin.

Chromatograms of perchlorate, ^{18}O-enriched perchlorate and chlorate in the sample are shown in Figs. 2(a) and (b), respectively.

3. Results

3.1. Perchlorate in upper Tone River Basin

Perchlorate concentrations in the upper Tone River, Azuma River, Usui River and Karasu River are listed in Table 1 with the sampling date for each sample. Profiles of perchlorate concentration from the upstream to the downstream of the upper Tone River, Usui River and Karasu River are also shown in Figs. 3(a), (b) and (c), respectively. Perchlorate concentrations in the uppermost area of the Tone River in this study (T1–T6) were 0.08–0.56 µg/L, and that in the Azuma River, a

tributary of the Tone River, was 0.27 µg/L at A1. Perchlorate concentrations in the Tone River were increased at T7 and T8 and were 180–340 µg/L. Downstream of T8, perchlorate concentration decreased and was 12 µg/L at T11.

In the case of the Usui River, perchlorate concentration at the uppermost point in this study (U1) was 0.23 µg/L and it increased to 8.8 µg/L at U2 after receiving flow from its tributaries. Perchlorate concentrations at U3–U11 were not markedly changed, but considerably increased at U12 and U13. The highest concentration was 2300 µg/L at U13. Downstream of U13, perchlorate concentrations in the Usui River were not greatly decreased, and the river flowed into its main river, the Karasu River. In the Karasu River, perchlorate concentrations at K1 and K2 were 0.36 and 0.46 µg/L, respectively, and increased after the confluence of the Usui River. The maximum concentration of perchlorate in the Karasu River was 180 µg/L at K5. After that, the Karasu River