

# Occurrence and Control of Disinfection By-products in Drinking Water

**Mari ASAMI<sup>1</sup>**

Department of Water Supply Engineering  
National Institute of Public Health, Japan

**Sadahiko ITOH<sup>2</sup>**

Department of Urban Management,  
Graduate School of Engineering, Kyoto University

<sup>1,2</sup> Research Group on DBPs in Drinking Water MHLW Research Grants

## 1. Introduction

Disinfection by-products, DBPs are one of major group of chemicals in the water quality standard items. The results of DBP survey for the Standard Items of approximately 6000 sites in the fiscal year 2004 showed some incompliance of DBPs, especially on these three items;

- Bromate (exceeded 0.010 mg/l) 20 cases
- Total THM (0.10 mg/l) 1 case
- Bromodichloromethane 4 cases

In addition, the results of DBP survey for the Monitoring Items of 2031 water supply bodies in the fiscal year 2004, some DBPs exceeded their target values as described below. Among them, chlorate exhibits higher concentration close to and above its target value.

- Dichloroacetonitrile 2 cases
- Chloral hydrate 3 cases
- Chlorate (0.6 mg/l) 6 cases
- Residual Chlorine 101 cases  
(exceeded 1.0 mg/l for aesthetic reasons)

## 2. Bromate, Chlorate, and Perchlorate control in Hypochlorite Solution<sup>1)</sup>

Bromate exhibits highest portion of calculated risk of DBPs as a carcinogen. Bromate concentration has been decreased according to the control of ozonation condition. However, bromate has been detected at certain concentrations in hypochlorite solutions used in water treatment systems. Chlorate has found increased especially after duration of storage at higher temperature. Perchlorate is recently found to show the same trend. Fig.1 shows the existence of perchlorate in sodium hypochlorite solutions and on-site generation process.

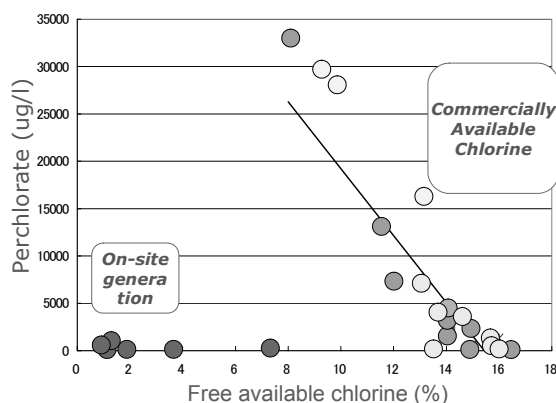


Fig.1 Perchlorate concentration in stored hypochlorite solution

<sup>1</sup> Department of Water Supply Engineering, National Institute of Public Health, 2-3-6 Minami, Wako, 351-0197 Japan Tel:+81-48-458-6304, Fax:+81-48-458-6305, asami@niph.go.jp

<sup>2</sup> Department of Urban Management, Graduate School of Engineering, Kyoto University C-1, Nishikyo, Kyoto 615-8540 Japan Tel/Fax: +81-75-383-3255

Since chlorate and chlorite exhibit oxidative damage to red blood cells and perchlorate is known to interfere with iodine uptake by the thyroid gland, control of these chemicals should be taken into consideration in managing hypochlorite solution.

### 3. Perchlorate Pollution in Water Source of the Tokyo Metropolitan Area

Perchlorate is used in rocket propellants and also in various oxidative materials. In 2005, the United States Environmental Protection Agency (USEPA) has established 0.7  $\mu\text{g}/\text{kg}/\text{day}$  of the reference dose (RfD) for perchlorate and announced 24.5  $\mu\text{g}/\text{L}$  of its drinking water equivalent level (DWEL). The river and tap waters in the Tone River Basin located in the east area in Japan were contaminated by perchlorate, mainly due to industrial discharges<sup>2)</sup>. Estimation of perchlorate load to upstream of the

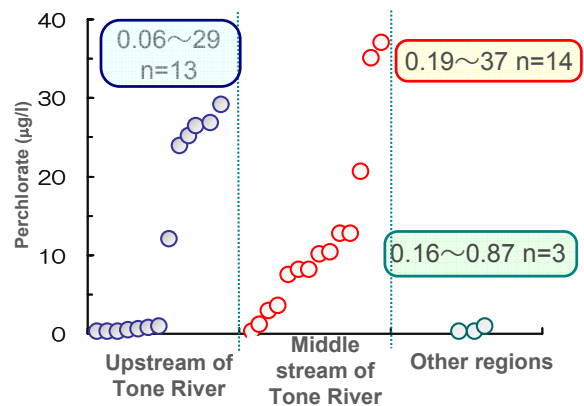


Fig.2 Perchlorate in drinking water<sup>2)</sup>

Estimation of perchlorate load to upstream of the Tone River was calculated from the perchlorate concentration and the river flow assuming constant discharge and river flow as follows;

- From the upstream of the Tone River: 95 to 100 kg/day
- From a river flow into the Tone River: 40 to 78 kg/day
- Estimated total load to the Tone River: 110 to 170 kg/day

Water of the Tone River is introduced to many water treatment plants and distributed to Tokyo metropolitan area. Estimated population affected by this water is over 20 million. In addition, this water is used for irrigation and food production. Although iodine uptake of normal Japanese diet is higher than in other countries, it is necessary to estimate total exposure of perchlorate.

### 4. Exposure Assessment of Volatile DBPs<sup>3)</sup>

Since exposure to DBPs is not limited to drinking water, respiratory exposure to DBPs is examined in several houses in Kyoto area. Personal air sampler with absorbent was employed to accumulate DBPs in bath room, kitchen, living room, and others, for the time spending in each room, in typical Japanese houses. The total exposure through respiratory route and dermal

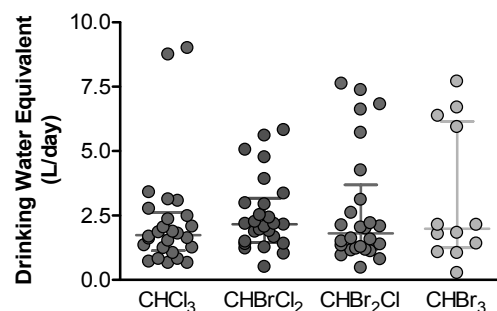


Fig.3 Exposure to THMs from respiratory and dermal route (adult)

route was calculated. In some cases, respiratory route exhibits maximum 8 times higher. Fig.3 shows the concentration calculated from equivalent to almost 2 times in average and maximum 9 times higher than in estimated exposure through drinking water.

## 5. Occurrence of NDMA

Nitrosodimethylamine, NDMA, one of nitro-DBPs was also found in water purification process. Other halogenated acetonitriles should be examined.

## 6. Bromide in water source

Bromide is one of precursors of brominated DBPs, such as bromate, brominated trihalomethanes and brominated haloacetic acids. Discharge of bromide into the Lake Biwa and the Yodo River was examined and contribution of artificial discharge is estimated. Source of bromide was calculated; 28% from sewerage (daily use and service industry), 34% from natural sources and rest 38% from direct discharge such as industrial and agricultural water. Since discharge from daily use is mainly from foods, bromide control in source water seems difficult.

## 7. Future direction

Human exposure to DBPs is not restricted through drinking water, but also via inhalation of indoor air, dermal exposure and cooked foods. Thus the total exposure should be considered when allocating theoretical exposure of DBPs from water. In addition, ionic and hydrophilic compounds are being found in water, such as carcinogenic bromate, toxic nitro compounds and hormone inhibiting perchlorate.

1) Asami M., Kosaka K., Kunikane S., Bromate, Chlorate, Chlorite and Perchlorate in Sodium Hypochlorite Solution Used for Water Supply, 2<sup>nd</sup> IWA-ASPIRE Conference and Exhibition 2007 (Submitted)

2) Kosaka K., Asami M., Matsuoka, Y., Kamoshita K., Kunikane S., Determination of perchlorate in the Tone River Basin using IC/MS/MS, *Journal of Environmental Instrumentation Control and Automation*, 2006.10, 11(2/3), 215~218.

3) Ken T., Muto T., Yanagibashi Y., Itoh S., Echigo S., Ohkouchi Y. and Jinno H.: Exposure assessment of trihalomethanes in households for estimating allocation to drinking water, Proceedings of The 15th Joint KKNN Symposium on Environmental Engineering, 21-24 June, Kyoto, Japan, 2006.6.

# Occurrence and Control of Disinfection By-products in Drinking Water

The U.S.-Japan Governmental Conference on Drinking Water Quality Management and Wastewater Control  
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Mari ASAMI  
National Institute of Public Health  
Sadahiko ITOH  
Kyoto University  
(Research Group on DBPs in Drinking Water  
MHLW Research Grants)

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- 6 Control of Halogen in Water Source

## Occurrence of DBPs

### Standard Items (App. 6000 sites, 2004 FY)

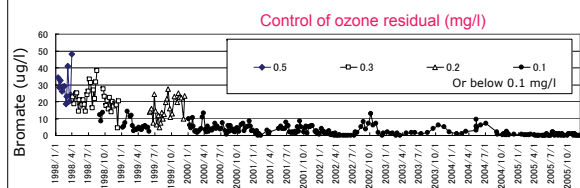
- Bromate (exceeded 0.010 mg/l) 20cases
- Total THM (0.10 mg/l) 1 case
- Bromodichloromethane 4 cases

### Monitoring Items

#### (2031 water supply bodies, 2004 FY)

- Dichloro acetonitrile 2 cases
- Chloral hydrate 3 cases
- Chlorate (0.6 mg/l) 6 cases
- Residual Chlorine 101 cases  
(exceeded 1.0 mg/l for aesthetic reasons)

## Control of Bromate in Chatan Water Treatment Plant, Okinawa (1998-2005)

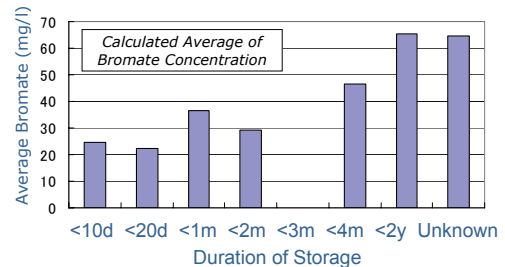


Bromate concentration has been decreased according to the control of ozonation condition.

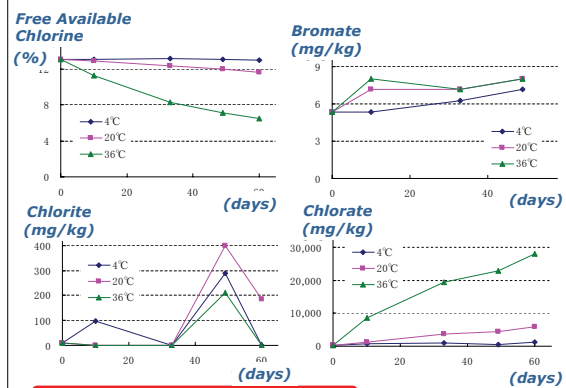
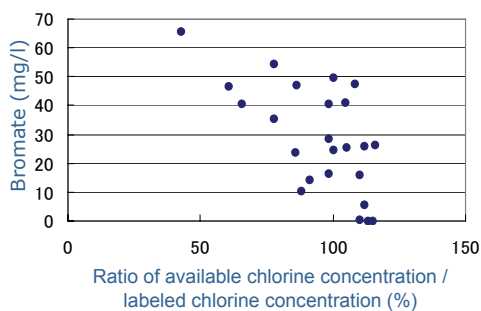
## Bromate Concentration in Sodium Hypochlorite Solution

- Bromate is a group B2 carcinogen in IARC
- Currently listed in the drinking water quality standard in Japan.
- In April 2004, bromate was detected at a concentration of **0.168 mg/l** in chlorinated drinking water in Hokkaido.
- 16.8 times higher than its standard value.
- Bromate in a sodium hypochlorite solution was detected at a concentration of **668 mg/l**.

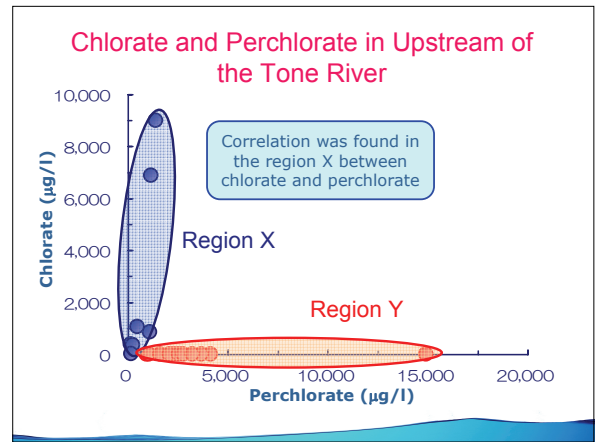
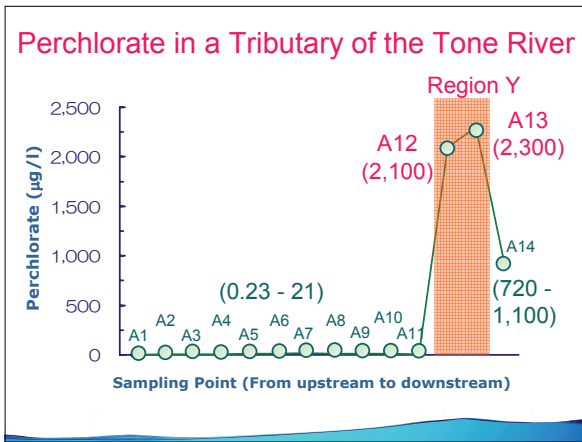
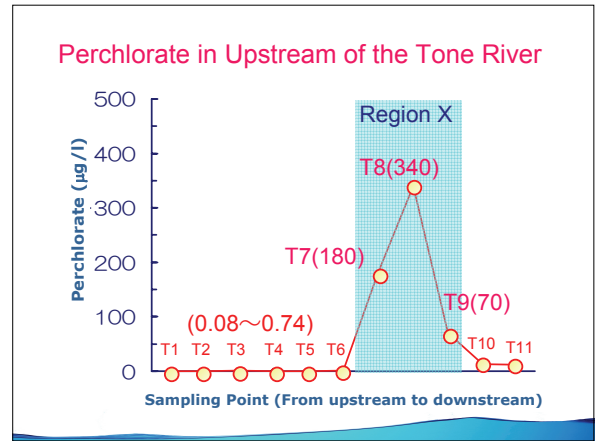
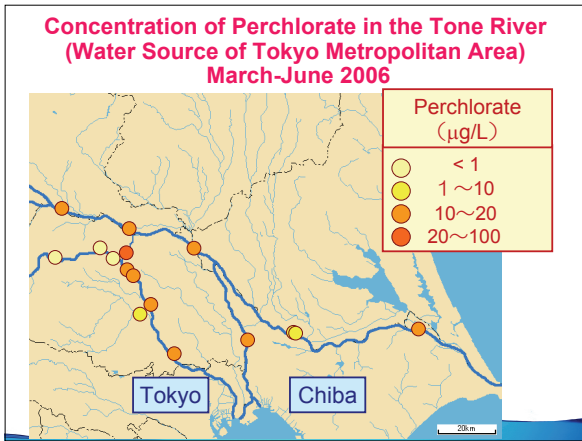
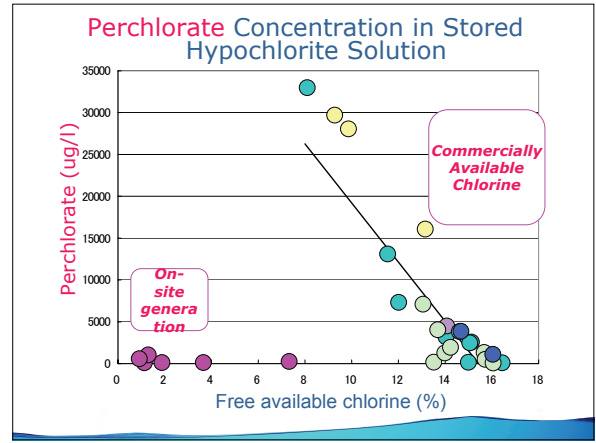
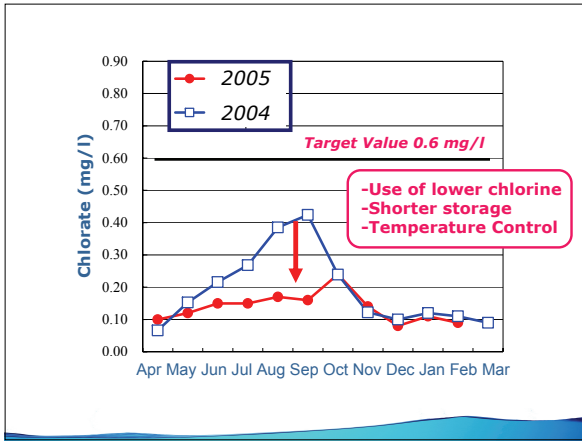
## Bromate Concentration in Sodium Hypochlorite Solution



## Bromate Concentration in Stored Hypochlorite Solution



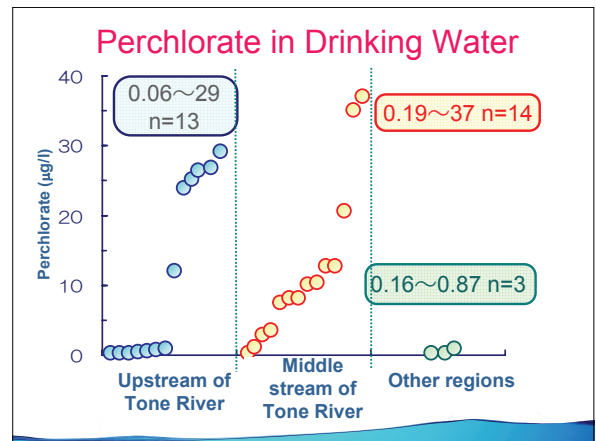
Temperature control is necessary



**Effect of Fireworks Exhibition to Perchlorate Concentration**

Time	Perchlorate (ug/l)
Just after the firework exhibition	79
5 days after the firework exhibition	0.39

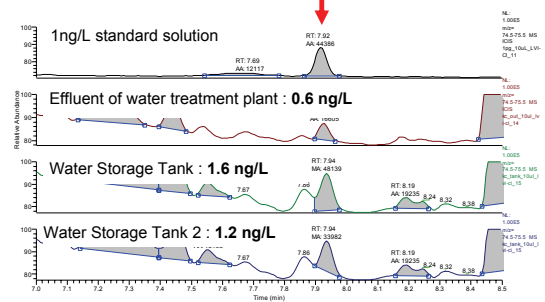
Sample water was taken from 2km downstream of the site of firework



## Load of Perchlorate and Population affected

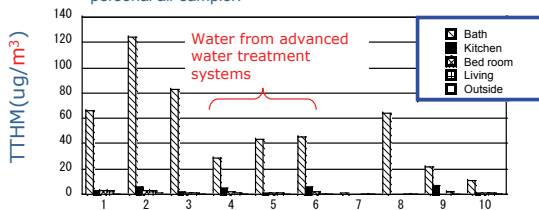
- **Estimation of perchlorate load to upstream of the Tone River**
  - Calculated from the perchlorate concentration and the river flow assuming constant discharge and river flow
  - From the Upstream of the Tone River : **95 to 100 kg/day**
  - From a river flow into the Tone River : **40 to 78 kg/day**
  - Estimated total load to the Tone River : **110~170 kg/day**
- **Estimated population**
  - Water of the Tone river is introduced to many water treatment plants and distributed to Tokyo metropolitan area
  - Estimated population affected by this water is over **20 million**.
  - In addition, this water is used for irrigation and food production.

## Occurrence of NDMA



## Exposure Assessment of Volatile DBPs

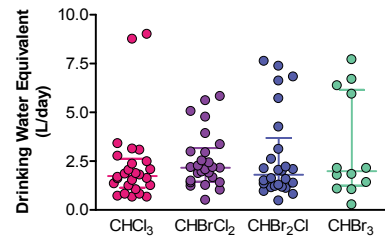
Exposure of DBPs in each house is analyzed using personal air sampler.



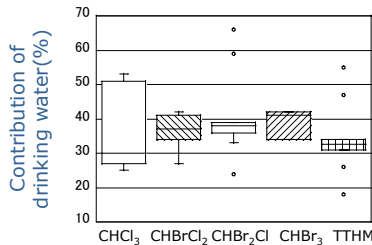
Exposure in bath room is much higher than other exposures.

## Exposure Assessment of Volatile DBPs

Exposure to THMs from respiratory and dermal route (adult)



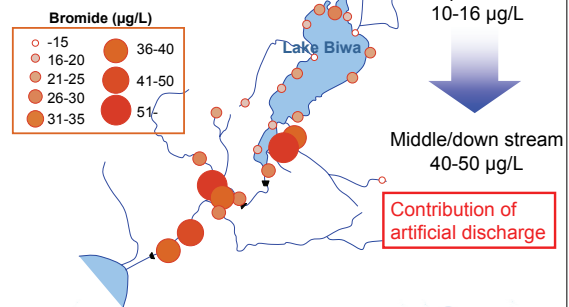
## Current Contribution of Drinking Water to Volatile DBPs Exposure



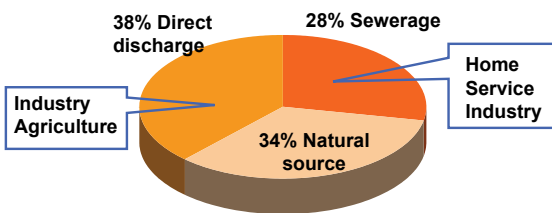
Other route of exposure such as food consumption should also be considered.

## Discharge of Bromide into the Lake Biwa and the Yodo River

Map of bromide concentration



## Estimated Source of Bromide



Discharge from daily use is mainly from foods

## CONCLUSION

- 1 Occurrence of Disinfection By-products  
Control of DBPs in hypochlorite solution is important.
- 2 Control of Bromate, Chlorate and Perchlorate  
Control of bromate is large concern in introduction of ozonation.  
Concentration of chlorate, bromate and perchlorate in hypochlorite solution which must be controlled in water source and water supply system.
- 3 Perchlorate in Water Source  
Perchlorate pollution of the metropolitan area is an emerging issue.
- 4 NDMA  
NDMA is detected in water treatment process.
- 5 Exposure Assessment of Volatile DBPs  
DBPs through air occupy large portion of personal exposure.

Exposure assessment and research on ionic and hydrophilic compounds are needed !!