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Bromate, chlorate, chlorite and perchlorate in sodium hypochlorite solution used in water supply

Mari Asami, Koji Kosaka and Shoichi Kunikane

ABSTRACT

A survey was conducted to reveal the concentrations of bromate, chlorite, chlorate and perchlorate as impurities in sodium hypochlorite solutions and those of chlorate and perchlorate in raw and processed waters including a metropolitan area. High concentrations of bromate (max. 414 mg l^{-1}) and chlorate (max. $260,000 \text{ mg l}^{-1}$) were found in purchased sodium hypochlorite solutions for drinking water disinfection that had been stored for a long time, more than two years at a maximum. In the survey of chlorate and perchlorate in raw and processed waters in the Tone River Basin, the highest concentration of chlorate in raw water was $78 \mu\text{g l}^{-1}$ and that of perchlorate was $40 \mu\text{g l}^{-1}$. Chlorate and perchlorate concentrations in 32 purchased sodium hypochlorite solutions and six on-site-generated hypochlorite solutions were also analysed. In the purchased sodium hypochlorite solutions, perchlorate concentrations ranged from 0.170 to 33.0 mg l^{-1} . In hypochlorite solutions whose measured FAC (free available chlorine) concentration was lower than the manufacturer-specified FAC concentrations, the chlorate and perchlorate concentrations were higher than those in relatively fresh sodium hypochlorite solutions. In on-site-generated hypochlorite solutions, the maximum concentrations of chlorate and perchlorate were $1,700 \text{ mg l}^{-1}$ (140 mg g^{-1} of measured FAC) and 0.660 mg l^{-1} (0.053 mg g^{-1} of measured FAC), respectively.

Key words | bromate, chlorate, chlorite, perchlorate, sodium hypochlorite solution

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INTRODUCTION

Sodium hypochlorite solution is frequently used as a disinfectant and as an oxidizing agent in waterworks. Since the concentration of residual chlorine should be maintained at more than 0.1 mg l^{-1} in distribution systems, sodium hypochlorite solution is commonly used as a residual disinfectant in over 80% of treatment facilities in Japan. It is usually added at the final stage of the treatment process, and sometimes added at the first and/or the middle stage as an oxidizing agent. A 12% (or 6%) stock solution has been widely used in waterworks for the chlorination of water; more recently, on-site generation of hypochlorite has been introduced into 10% of treatment facilities (JWWA 2006).

The duration of storage of stock solutions is sometimes longer, over several months, for example, in small water treatment facilities. In addition, attention should be paid to impurities in hypochlorite solutions, especially in raw waters containing ammonia, which is a chlorine-consuming compound, since the injection ratios of hypochlorite solutions are relatively high in ammonia-contaminated raw water.

For example, in April 2004, bromate concentration in chlorinated drinking water in Hokkaido was found to be 0.168 mg l^{-1} , 16.8 times higher than the concentration limit stipulated by Japanese standards (*Hokkaido News* 2004). Later analysis showed bromate at a concentration of

668 mg l^{-1} in the sodium hypochlorite solution used in the water treatment process, illustrating the fact that sodium hypochlorite solution can be a major source of bromate in chlorinated drinking water.

Bromate, known as a carcinogenic ozonation by-product, was introduced in the Japanese drinking water quality standard in 2004 and has been regulated to be less than 0.01 mg l^{-1} . Chlorate and chlorite, known by-products of chlorine dioxide disinfection, have also been listed as chemicals to be monitored. The criterion has been set at 0.6 mg l^{-1} for both chlorate and chlorite based on their oxidative property for red blood cells in humans (MHLW 2003). In a national survey of monitored items (MHLW 2005), chlorate concentrations exceeded the criterion in 14 of the 598 monitored finished waters. The principal criterion for including a monitored compound in the list of drinking water standards is the detection of the compound in finished water at a concentration near or above one-tenth of its threshold standard. Accordingly, chlorate was introduced into the drinking water standards in April 2008. Perchlorate has only been recently addressed as a contaminant of concern in drinking water, though it is naturally occurring and was identified in Chilean salt caliche in the early 1900s (Dafert 1908). More recently it has been used as a chemical propellant in rocket fuels and an oxidizing agent in many products. Perchlorate is known to interfere with the iodine uptake of 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 $0.7 \text{ } \mu\text{g kg}^{-1} \text{ day}^{-1}$ of perchlorate and specified its drinking water equivalent level (DWEL) to be $24.5 \text{ } \mu\text{g l}^{-1}$ (US EPA 2005), based on a report by the National Academy of Sciences (NAS) (National Research Council 2005).

Chlorate and perchlorate have been detected in Japanese aquatic environments, especially in the Tone River Basin, which is one of the largest water sources for drinking water supply in the Tokyo metropolitan area (Asami *et al.* 2007; Kosaka *et al.* 2007). The maximum concentration of chlorate and perchlorate in river water affected by industrial effluents was measured at $9,000 \text{ } \mu\text{g l}^{-1}$ and $15,000 \text{ } \mu\text{g l}^{-1}$, respectively. One of the highest concentrations of perchlorate was attributable to unintentional production of perchlorate in an electrolysis process.

All oxyhalides listed here (i.e. bromate, chlorate, chlorite and perchlorate) are industrial chemicals and are also known to exist in chlorinated drinking waters as impurities from sodium hypochlorite solutions. The concentrations of bromate, chlorate, chlorite and perchlorate in hypochlorite solution have been shown to increase during storage (Gordon *et al.* 1995 for chlorate; Weinberg *et al.* 2003 for bromate). However, the quality of the hypochlorite solution used in water treatment plants and the parameters which may contribute to increased rates of production of undesirable oxyhalide species are not well known. In this study, we investigated the concentrations of bromate, chlorate, chlorite and perchlorate in raw, processed and finished waters and hypochlorite solutions collected from various water treatment plants.

MATERIALS AND METHODS

Bromate, chlorate and chlorite in stored sodium hypochlorite solutions

The primary study was conducted to detect bromate, chlorate and chlorite concentrations in hypochlorite solutions. Thirty-seven samples were collected from hypochlorite solutions used in water supply facilities from 11 prefectures including Kanto (east), Kansai (west), Hokkaido (north) and Okinawa (south) regions in Japan. The water supply facilities include 28 treatment plants and 9 distribution facilities. Out of 37 facilities, 14 stored the sodium hypochlorite solutions in an air-conditioned environment. Samples were collected and stored in cool and dark conditions and analysed within 2 days. Sodium hypochlorite solutions were diluted 10,000 times by pure water (MilliQ Gradient A10 water purification system, Millipore, Bedford, Massachusetts) and the concentration of free available chlorine (FAC) was analysed by the DPD method. Chlorate was analysed using ion chromatography (IC, DX-500, Dionex, Sunnyvale, California), electric conductivity with an Ion Pac AG19/AS19 (4 mm) column and KOH generator. Bromate and chlorite were analysed by the IC-post-column colouring method using the same eluent reacted with 1.2 mM l^{-1} NaNO_2 and 1.5 M KBr 1.0 M l^{-1} H_2SO_4 solution, according to the official Japanese notification method (MHLW 2004).

Chlorate and perchlorate in raw, processed and finished waters and hypochlorite solutions

An intensive survey of chlorate and perchlorate concentrations in source and finished waters was conducted in conjunction with the Ministry of Health, Labour and Welfare, Japan. Raw, processed and finished water and hypochlorite solutions were collected from water treatment plants, especially in the Tone River Basin, to quantify the effect of industrial effluents. The Tone River is the largest water source in the Tokyo Metropolitan area and has been previously found to be contaminated by chlorate and perchlorate (Kosaka *et al.* 2007). More than ten other large cities and water supply bodies previously reporting high concentration of disinfection by-products (DBPs) were selected (MHLW 2006). In addition, 32 purchased and six on-site-generated hypochlorite solutions were collected and analysed. Chlorate and perchlorate concentrations were analysed with IC-tandem mass spectrometry (MS/MS) (Dionex ICS-2000 and API 3200QTrap, Applied Biosystems) as described elsewhere in detail (Kosaka *et al.* 2007). ¹⁸O-enriched NaClO₄ (Cambridge Isotope Laboratories) was used as an internal standard for perchlorate. The minimum reporting limits (MRLs) for perchlorate and chlorate were set to be 0.05 and 0.05 mg l⁻¹, respectively, except the MRL for chlorate of the sample waters in several water treatment plants was 0.1 mg l⁻¹.

RESULTS AND DISCUSSION

Bromate, chlorate and chlorite in hypochlorite solutions

In the 37 sodium hypochlorite solutions collected, the concentration of measured free available chlorine (FAC) in the solution ranged from 0.04 to 15%, and the average concentrations of bromate in the solution were 96 mg l⁻¹ (maximum 414 mg l⁻¹). When the concentrations were converted into their finished water, bromate concentration was below 0.001 mg l⁻¹; chlorate and chlorite concentrations were below 0.20 and 0.003 mg l⁻¹, respectively, assuming the dose of the hypochlorite solution to be 1 mg l⁻¹. However, in some cases, chlorate concentration in the hypochlorite solution was extremely high when the measured FAC in the

solution was much lower than its manufacturer-specified FAC at the time of purchase. The concentration of FAC is a critical factor for controlling residual chlorine, chlorate and bromate, because, if the sodium hypochlorite solutions which contain lower FAC than manufacturer-specified are used for disinfection, bromate and chlorate concentration may increase subsequently because of the increased amount of hypochlorite solution used in order to accomplish residual chlorine concentration.

Bromate concentration varied as shown in Figure 1. One factor is that bromate concentration varied among manufacturers. Though the number of samples was limited in this study, the bromate concentrations in sodium hypochlorite solutions of one manufacturer ranged from 5.4 to 49.5 mg l⁻¹ (*n* = 7), while those of another manufacturer ranged from 24.5 to 96.5 mg l⁻¹ (*n* = 7).

The other factor seems to be the timing of the purchase of hypochlorite solutions. It was recently reported that the concentration of bromate is largely dependent upon the salts used to produce hypochlorite solutions and can be controlled by changing the salt to those salts whose concentration of bromide is lower or by refining the salts. It is also reported that the manufacturers have changed the salts to refined types in accordance with the revision of the standard (JWWA 2006). Therefore, the high bromate concentration in older samples may be attributable to the bromide present in salts that were used as a basic ingredient in the production process.

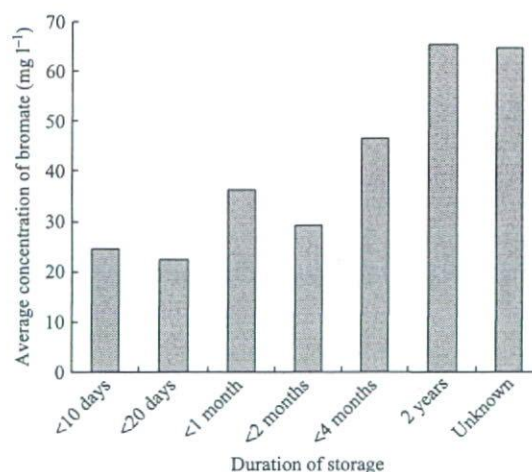


Figure 1 | Concentration of bromate in the hypochlorite solutions in relation to the duration of storage after purchase of each hypochlorite solution.

Weinberg *et al.* (2003) indicated the mechanism of bromate formation in hypochlorite solution as described in Equation (1) below. Since no residual bromide was found in any of the samples, and the reaction has been reported in the literature to occur very rapidly, the majority of bromide in sodium hypochlorite solution was expected to react to produce bromate.



Thus the authors consider that the high concentration of bromate might depend mainly on the bromide concentration in salts, while bromate concentration was higher in those sodium hypochlorite solutions that had been stored for more than two years or for an unknown period after the purchase of each hypochlorite solution.

Chlorite concentration was rather low in the hypochlorite samples, with an average of 145 mg l⁻¹ and a maximum of 397 mg l⁻¹. Chlorite concentrations in the treated water were below 0.003 mg l⁻¹ and 0.03 mg l⁻¹ assuming respective hypochlorite solution doses of 1 mg l⁻¹ and 10 mg l⁻¹. So chlorite concentrations were not expected to be very high in hypochlorite solutions and finished water.

The average concentration of chlorate in the hypochlorite solutions was 15,300 mg l⁻¹ (maximum 260,000 mg l⁻¹), and was largely different between samples and FAC levels. Chlorate concentrations in finished water were estimated to be 0.20 mg l⁻¹ and 2.0 mg l⁻¹ when the dose of the sodium hypochlorite solution was assumed to be 1 mg l⁻¹ and 10 mg l⁻¹, respectively. Thus, further study was conducted as described in the next section.

Chlorate and perchlorate in raw, processed and finished water

Chlorate and perchlorate concentrations in raw, processed and finished water in water treatment plants are shown in Table 1. Out of the 368 samples, chlorate was detected in 93.2% of the raw water samples and 100% of the processed and finished water samples. Perchlorate was detected in 98.8% of the raw water samples and 94.9% of the processed and finished water samples. The highest concentration of chlorate in raw water (78 µg l⁻¹) was found in groundwater apparently affected by the chlorate and perchlorate contamination in the Tone River. The concentrations of chlorate and perchlorate, and the ratio of their concentrations, were higher in the samples taken from the Tone River Basin. Perchlorate concentrations in raw, processed and finished waters at the same treatment plant were almost unchanged during the process. Chlorate concentrations were much higher in processed and finished waters, especially in the smaller facilities located in remote areas. The maximum concentration of chlorate in this study was 2.9 mg l⁻¹ (2,900 µg l⁻¹) due to chlorate in sodium hypochlorite solution used for disinfection.

Figures 2 and 3 show some examples of chlorate and perchlorate concentration through different stages of treatment in water treatment plants using different types of chlorine disinfectant. In Figure 2, the water treatment plant shown on the left-hand side used hypochlorite generated on-site while the plant on the right used manufactured sodium hypochlorite solutions. Chlorate concentrations increased during the treatment process. Both plants showed a large increase in chlorate concentrations. Figure 3 shows

Table 1 | Chlorate and perchlorate concentrations in raw, processed and finished water in water treatment plants

| | Chlorate (µg l ⁻¹) | | | Perchlorate (µg l ⁻¹) | | |
|--|--------------------------------|------|-------|-----------------------------------|------|-----|
| | Detection rate | Min* | Max | Detection rate | Min* | Max |
| Raw water of water treatment plants | | | | | | |
| Tone River Basin | 116/116 | 0.06 | 78 | 114/116 | 0.09 | 40 |
| Other than the Tone River Basin | 62/75 | 0.08 | 53 | 55/55 | 0.06 | 2.5 |
| Processed water and finished water from water treatment plants | | | | | | |
| Tone River Basin | 178/178 | 0.17 | 2,900 | 168/178 | 0.05 | 24 |

*The minimum is data detected above LO Q (limits of quantification).

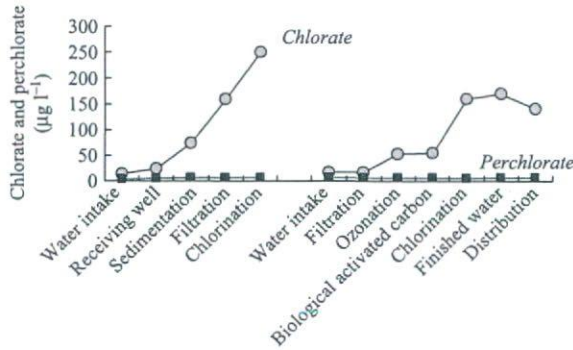


Figure 2 | Chlorate and perchlorate in water treatment plants using hypochlorite solutions (left-hand side, hypochlorite generated on-site; right-hand side, manufactured sodium hypochlorite solutions).

an example of two treatment plants where liquid chlorine was used in the disinfection processes. As such, concentrations of chlorate and perchlorate through the stages of treatment were not noticeably increased when liquid chlorine was used.

Chlorate and perchlorate in hypochlorite solutions

For the analysis of chlorate and perchlorate concentrations, hypochlorite solutions were collected mainly from the water treatment plants investigated in the previous section. Of these, 32 sodium hypochlorite solutions were purchased and 6 hypochlorite solutions were generated on site. Measured FAC concentrations in the purchased sodium hypochlorite solutions ranged from 8.0 to 16.4%, while the FAC in on-site-generated hypochlorite solutions ranged from 1.0 to 7.2%. Chlorate concentration in the purchased sodium

hypochlorite ranged from 1,200 mg l⁻¹ to 26,000 mg l⁻¹. The chlorate concentration varied and was above 10,000 mg l⁻¹ in 10 samples. Perchlorate concentrations in the purchased hypochlorite solutions ranged from 170 to 33,000 µg l⁻¹, as shown in Table 2.

FAC and concentration of chlorate and perchlorate

Figure 4 shows the relationship between the measured FAC concentration and the concentrations of chlorate and perchlorate per measured FAC in the hypochlorite solutions. The concentrations of chlorate and perchlorate in purchased hypochlorite solutions were higher in instances when the measured FAC was low. The maximum chlorate concentration was 26,000 mg l⁻¹ (320 mg g⁻¹ of measured FAC). The maximum concentration of perchlorate was 33,000 µg l⁻¹ (0.420 mg g⁻¹ of measured FAC) with the hypochlorite solution whose FAC was 8.0% while the manufacturer-specified FAC concentrations was ‘12.0% or above’. The manufacturer-specified FAC concentrations in the hypochlorite solutions were similar in range, from 12 to 13.2%, except for four samples for which information could not be obtained. However, the FAC concentrations ranged from 8.0 to 16.4% for purchased hypochlorite solutions. The chlorate and perchlorate concentrations were higher in hypochlorite solutions in which the FAC was lower than the manufacturer-specified FAC concentrations, while no difference was observed among nine different manufacturers. Thus, it was considered that the concentrations of chlorate and perchlorate increased with the decay of FAC in the hypochlorite solutions.

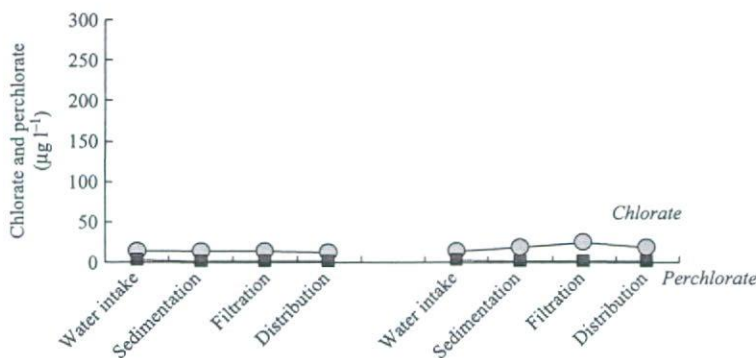


Figure 3 | Chlorate and perchlorate in water treatment plants using liquid chlorine.

Table 2 | Chlorate and perchlorate concentrations in hypochlorite solutions

| | Chlorate (mg l ⁻¹) | | | Perchlorate (μg l ⁻¹) | | |
|--|--------------------------------|-------|--------|-----------------------------------|------|--------|
| | Detection rate | Min* | Max | Detection rate | Min* | Max |
| Sodium hypochlorite (Purchased) | 32/32 | 1,200 | 26,000 | 32/32 | 170 | 33,000 |
| Sodium hypochlorite (On-site generation) | 6/6 | 160 | 1,700 | 6/6 | 13 | 660 |

*The minimum is data detected above LO Q (limits of quantification).

Figure 5 shows the relationship between chlorate and perchlorate concentration in purchased hypochlorite solution. Across the concentration range tested, the concentration of perchlorate was approximately three orders of magnitude lower than chlorate, though the ratio increased with the chlorate concentration, especially when the chlorate concentration was higher than 10,000 mg l⁻¹. Therefore, their relationship was expressed as an approximate equation of the second order.

Hypothesized mechanism of generation of chlorate and perchlorate in hypochlorite solutions

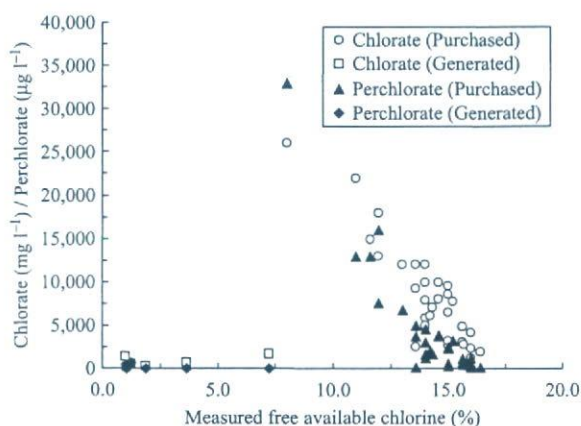
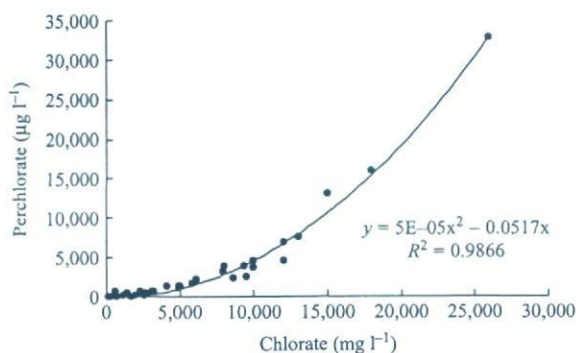
It is reported that, in hypochlorite solution, chlorate is generated from a disproportionation reaction of hypochlorous acid (HOCl) expressed by Equations (2) and (3), or a decomposition reaction of hypochlorite ion (ClO⁻) through chlorite ion (ClO₂⁻). It is of note that the reaction rate in Equation (2) is much faster than that in Equation (3)

(Gordon *et al.* 1995).



As shown in Figure 5, chlorate concentrations in the hypochlorite solutions were almost 1,000 times higher than perchlorate concentrations. The ratio of perchlorate to chlorate concentration was elevated under conditions where there was a corresponding increase in chlorate concentration from the decay of FAC in the hypochlorite solution. In addition, perchlorate was not found in stored chlorate standard solutions (data not shown). Considering these results, a hypothetical explanation for the presence of perchlorate in hypochlorite solution is from the reaction between chlorate and hypochlorite.

The manufacturer-specified FAC concentrations in the purchased sodium hypochlorite solutions normally ranged from 12 to 13.2%. Therefore, from the higher FAC samples (i.e. above 14%), chlorate and perchlorate concentrations in relatively fresh purchased hypochlorite solutions could be obtained. Chlorate concentrations in the solutions ranged from 1,200 to 12,000 mg l⁻¹ (average 5,900 mg l⁻¹)

**Figure 4** | Relationship between the measured FAC concentration and the concentrations of chlorate and perchlorate per measured FAC in the hypochlorite solution.**Figure 5** | Relationship between chlorate and perchlorate concentration in purchased hypochlorite solution.

and perchlorate concentrations ranged from 170 to $4,400 \mu\text{g l}^{-1}$ (average $1,800 \mu\text{g l}^{-1}$). The ratios of perchlorate to chlorate concentration ranged from 7.9×10^{-5} to 5.0×10^{-4} (average 2.7×10^{-4}), rather lower compared with the average of all solutions.

From these results, perchlorate concentrations in new hypochlorite solutions are normally low, but increase during storage. This might be controlled by controlling chlorate formation during storage.

Chlorate and perchlorate concentrations in the on-site-generated hypochlorite solutions

The on-site-generated hypochlorite solutions had concentrations of chlorate ranging from 160 to $1,700 \text{mg l}^{-1}$ and perchlorate from 0.013 to 0.660mg l^{-1} . Their concentrations per measured FAC are shown in Figure 4. Maximum ratios of chlorate and perchlorate were 140 and 0.053mg g^{-1} of measured FAC, respectively. The apparatus used to generate hypochlorite solutions was different in each of the companies, although the electrodes used in the apparatus were the same (titanium oxide). Thus, the reason for the difference of the chlorate and perchlorate concentrations between the on-site-generated hypochlorite solutions does not seem to be related to the material of the electrode. In addition, although the storage conditions of each on-site-generated hypochlorite solution were unknown, these conditions may have affected chlorate and perchlorate concentrations as in the case of the purchased hypochlorite solutions.

There were no reports of investigations on perchlorate generation in on-site-generated hypochlorite solutions. However, Tock *et al.* (2004) reported generation of perchlorate in water storage tanks that employed the electron voltage technique to prevent corrosion. In that study, perchlorate was generated in proportion to the contact time. It was thought that the same phenomenon might occur in on-site generation tanks.

Estimation of chlorate and perchlorate concentration due to hypochlorite solutions

Using the manufacturer-specified FAC, chlorate and perchlorate concentrations in hypochlorite solution, maximum

chlorate and perchlorate load concentrations in hypochlorite solution were calculated. Chlorine dosage was assumed to be 10mg l^{-1} . As in the case shown in Figure 5, the manufacturer-specified FAC concentration was taken as 12.5% for purchased and 1.0% for on-site-generated hypochlorite solutions when no data were available. For the purchased hypochlorite solutions, calculated load concentrations of chlorate ranged from 92 to $2,100 \mu\text{g l}^{-1}$; most of the measured values ranged from 100 to $1,000 \mu\text{g l}^{-1}$. The chlorate concentrations in four hypochlorite solutions exceeded $1,000 \mu\text{g l}^{-1}$. For on-site-generated hypochlorite solutions, the load concentrations of chlorate ranged from 160 to $1,400 \mu\text{g l}^{-1}$. It was shown that the load concentrations of chlorate in on-site-generated hypochlorite solutions were usually lower, but not necessarily lower than those in the purchased hypochlorite solutions.

For perchlorate, the calculated load concentrations in purchased hypochlorite solutions ranged from <0.05 to $2.8 \mu\text{g l}^{-1}$, with most values falling below $0.5 \mu\text{g l}^{-1}$. The load concentration of perchlorate in four hypochlorite solutions exceeded $1.0 \mu\text{g l}^{-1}$. The load concentrations in on-site-generated hypochlorite solutions ranged from <0.05 to $0.67 \mu\text{g l}^{-1}$. These values were much lower than those for purchased hypochlorite solutions.

Distribution channel of sodium hypochlorite solutions

Interviews were conducted with the manufacturers, distributors and users (waterworks) involved with the distribution channel of sodium hypochlorite solutions to identify the duration of time in each distribution process. One route is direct delivery of the products from manufacturer to large facilities by trucks. The other is indirect delivery of solutions distributed by trucks to packaging facilities followed by distribution in small packages to rather small facilities. The two main routes of distribution are shown in Figure 6. Normal distribution from manufacturer to the large treatment plants and distributors is accomplished 0–7 days after production. On the other hand, indirect delivery of small packages takes longer than direct distribution. It takes 0–7 days to deliver from manufacturer to distributors and more days to deliver to the smaller water treatment facilities, though the number of interviews was limited.

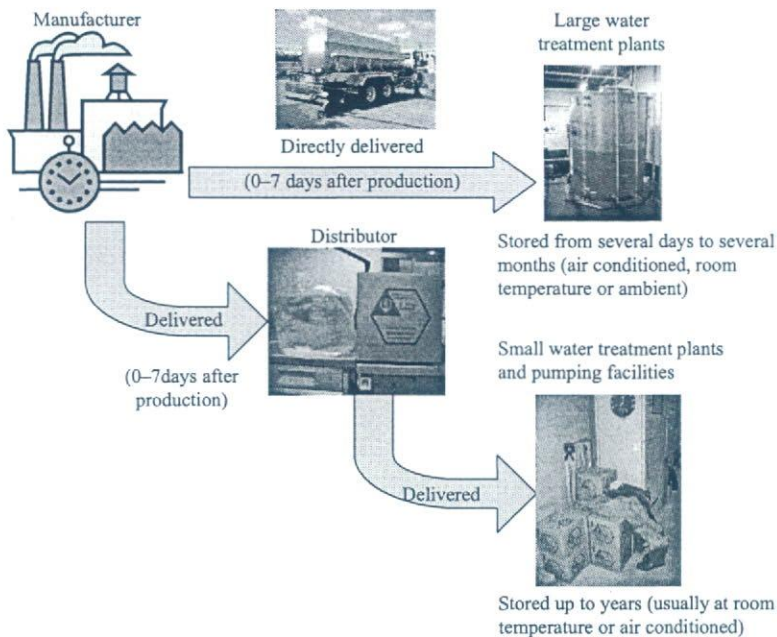


Figure 6 | Distribution channels for sodium hypochlorite.

In this study, initial concentrations of chlorate and perchlorate in hypochlorite solutions at the manufacturers were not studied; however, the concentrations of chlorate and perchlorate are not noticeably high in relatively fresh solutions. Control of the distribution process and storage is the key factor to control chlorate and perchlorate as far as this study is concerned. Since the temperature of storage and the impurities in the sodium hypochlorite solutions have been pointed out to affect the decay of hypochlorite (JWWA 2006), further study is needed to prove the factors affecting degradation of hypochlorite in sodium hypochlorite solutions. In addition, further research is required on the relationship between concentrations of chlorate and perchlorate and their generation conditions in on-site generation facilities for hypochlorite.

CONCLUSIONS

- Higher concentrations of bromate and chlorate were found in hypochlorite solutions stored for longer periods of time, more than two years at a maximum; their maximum concentrations were 414 and 260,000 mg l^{-1} , respectively.
- A survey was conducted to reveal the concentrations of chlorate and perchlorate in raw, processed and finished water and hypochlorite solutions. The highest concentration of chlorate in raw water was 78 $\mu\text{g l}^{-1}$ and that of perchlorate was 40 $\mu\text{g l}^{-1}$.
- In purchased hypochlorite solutions tested, perchlorate concentrations ranged from 0.170 to 33.0 mg l^{-1} .
- In hypochlorite solutions whose measured FAC concentration was lower than the manufacturer-specified FAC concentration, the chlorate and perchlorate concentrations were higher than those in the relatively fresh hypochlorite solutions. The ratio of perchlorate to chlorate concentration in the relatively fresh hypochlorite solutions was around 10^{-3} .
- In on-site-generated hypochlorite solutions, the maximum concentrations of chlorate and perchlorate were 1,700 mg l^{-1} (140 mg g^{-1} of measured FAC) and 0.660 mg l^{-1} (0.053 mg g^{-1} of measured FAC), respectively.
- Perchlorate in hypochlorite solutions was considered to be produced by degradation of hypochlorite and reaction with chlorate.

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A nationwide survey of NDMA in raw and drinking water in Japan

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ABSTRACT

A nationwide survey of *N*-nitrosodimethylamine (NDMA) in both raw and finished water samples from drinking water treatment plants (DWTPs) in Japan was conducted. NDMA was analyzed by solid-phase extraction (SPE) followed by ultra performance liquid chromatography (UPLC) coupled with tandem mass spectrometry (MS/MS). NDMA was detected in 15 of 31 raw water samples collected in the summer at concentrations up to 2.6 ng/L, and in 9 of 28 raw water samples collected in winter at concentrations up to 4.3 ng/L. The NDMA concentrations were higher in raw water samples collected from treatment plants with catchment areas that have high population densities. The NDMA concentrations were higher in river water samples collected from the east and west of Japan than in those collected from other areas. NDMA was detected in 10 of 31 finished samples collected in summer at reduced concentrations of up to 2.2 ng/L, while 5 of 28 finished samples collected in winter showed NDMA concentrations up to 10 ng/L. The highest NDMA levels were detected in finished water samples collected from the Yodo River basin DWTP, which uses ozonation. Furthermore, evaluation of the process water produced at six advanced water treatment plants was conducted. Influent from the Yodo River indicated that the NDMA concentration increased during ozonation to as high as 20 ng/L, and then decreased with subsequent biological activated carbon treatment. To our knowledge, this is the first nationwide evaluation of NDMA concentrations in water conducted in Japan to date.

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1. Introduction

N-Nitrosodimethylamine (NDMA) is a highly water-soluble nitrosamine that is a member of a family of extremely potent carcinogens known as *N*-nitrosoamines (Mitch et al., 2003). Some nitrosamines, including NDMA, have been classified as probable human carcinogens (B2) by the Integrated Risk Information System (IRIS) of the United States Environmental Protection Agency (US EPA, 2009a) and as 2A, probably carcinogenic, by the World Health Organization's International Agency for Research on Cancer (IARC, 2009). In the past, NDMA was used as an intermediate in the production of rocket fuel, an inhibitor of nitrification in soil, a plasticizer in the manufacture of rubber and polymers, a solvent in the fiber and plastic industry, an antioxidant, a softener of copolymers, and as an additive to lubricants (Najm and Trussell, 2001). Recently, NDMA was found to be a disinfection byproduct following chloramination or chlorination in the presence of ammonia (Mitch et al., 2003). NDMA precursors during chlorination and chloramination include nitrogenous organic compounds such as dimethylamine (DMA) and trimethylamine (TMA) (Lee et al., 2007). The US EPA has estimated that an NDMA concentration of 7 ng/L in drinking water is associated with an excess lifetime cancer risk of 10^{-5} (US EPA, 2009a), and NDMA is included among the 104 contaminants on Contaminant Candidate List 3 (CCL3) (US EPA, 2009b). Although the maximum contaminant level (MCL) for

NDMA in drinking water has not been established in the USA, other regulatory agencies have established NDMA guidelines. For example, the office of Environmental Health Hazard Assessment (OEHHA) in California has set a public health goal (PHG) of maintaining NDMA at concentrations ≤ 3 ng/L based on a cancer risk of 10^{-6} (California Department of Public Health, 2009). In addition, although no MCL for NDMA in drinking water has been established to date in Canada, the Ministry of the Environment (MOE) of Ontario has set the provisional maximum allowable concentration of NDMA at 9 ng/L (Ministry of the Environment of Ontario, 2009). Although estimates of the various sources of NDMA exposure indicated that water contributes less than 10% of the overall exposure in Canada and it is less than 1% of the overall human exposure to NDMA estimated in the USA, the relative source contribution (RSC) is usually not utilized in cancer risk calculations, and no official evaluation has been conducted to determine the contributions of each source in these risk assessments (California Department of Public Health, 2009).

NDMA was first detected in drinking water in Ontario, Canada in 1989 (Charrois et al., 2007). In the USA, NDMA was first discovered as a groundwater contaminant at a Northern California aerospace facility in 1998 (Najm and Trussell, 2001). Since then, the occurrence of NDMA in drinking water treatment plants (DWTPs) has been investigated throughout Canada and the USA. A survey of quarterly samples of raw, finished, and distribution system water collected from 21 North American DWTPs indicated the presence of NDMA in concentrations greater than the method detection limit (MDL) of 0.6–1.0 ng/L in only 1 of 81 raw water samples, and that the NDMA concentrations were

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<MDL–30 ng/L in 81 finished water samples and <MDL–24 ng/L in 95 distribution system water samples (Barrett et al., 2003). However, a survey of 20 municipal drinking water distribution systems in Alberta, Canada, revealed NDMA concentrations in some systems as high as 100 ng/L. In addition, an extensive survey of 179 DWTPs in Ontario, Canada, indicated that NDMA was present in concentrations as high as 66 ng/L in one distribution system water sample (Charrois et al., 2007).

Some of recent studies have evaluated the formation of NDMA during ozonation. For example, Andrzejewski et al. (2008) reported the formation of NDMA by DMA ozonation (initial DMA concentrations, 30–700 mg/L). In addition, Schmidt and Brauch (2008) reported that the plant growth regulator, daminozide, the fungicide, tolylfluanid, and their decomposition products were NDMA precursors during ozonation. However, there have been few evaluations of NDMA in Japan.

Here, a nationwide study of the occurrence of NDMA in DWTPs, including small facilities, was conducted using ultra performance liquid chromatography (UPLC) coupled with tandem mass spectrometry (MS/MS). NDMA concentrations were also investigated at each treatment process in all six DWTPs included in the study. In addition, the concentrations of nitrogen species (total nitrogen, organic nitrogen, and inorganic nitrogen) and organic substances were also determined. This information was then used to identify the relationships between the concentrations of NDMA and water quality parameters that could be potential indicators and/or precursors of the formation of NDMA.

2. Materials and methods

2.1. Sampling

This nationwide survey of raw water and finished water of DWTPs was conducted in September to October 2007 (summer) and December 2007 to January 2008 (winter). DWTPs were selected such that the major water sources in each of the six areas (Fig. 1) could be evaluated, and they also included three water facilities that employ hypochlorite treatment at a high injection ratio. Raw water and finished water samples were collected from DWTPs and transported immediately to our laboratory in glass containers under cool and dark conditions before analysis within 10 days. The process water samples were collected in September–October 2007 at each unit process in six large advanced water treatment plants selected based on their area. Sodium thiosulfate solution, a quenching agent, was added to process water and finished water samples containing hypochlorite.

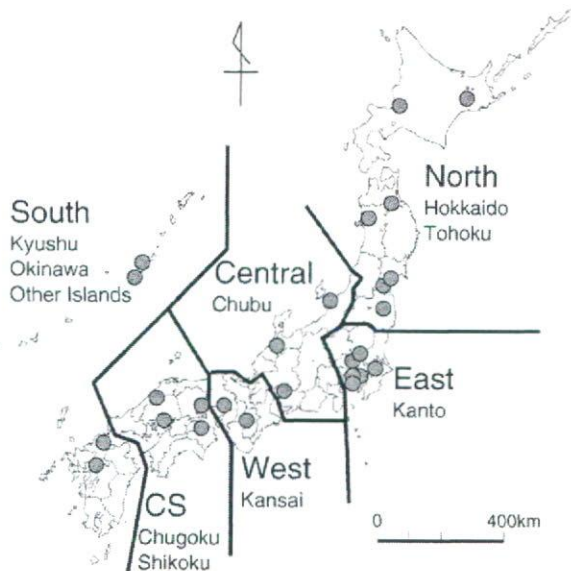


Fig. 1. Sampling areas evaluated in this study.

Table 1

NDMA analysis using UPLC/MS/MS.

| |
|---|
| UPLC/MS/MS: ACQUITY UPLC/TQD (Waters) |
| Column: BEH C18 (2.1 × 150 mm, Waters) |
| Eluent: A: 10 mM Ammonium bicarbonate, B: Acetonitrile |
| B: 5% (0–3.50 min) → 95% (3.85–6.35 min) → 5% (6.70–8.35 min) |
| Flow rate: 0.2 mL/min, injection volume: 30 µL, ionization: ESI positive |
| Capillary voltage: 2.2 kV, source temperature: 140 °C |
| Desolvation gas flow: 900 L/h, desolvation temperature: 400 °C, cone gas flow: 50 L/h |
| MRM:NDMA: 74.9>43.1 (quantitative), collision: 14 eV, |
| 74.9>57.9 (confirmative), collision: 12 eV, |
| NDMA-d ₆ : 81.0>46.0, collision: 14 eV |

2.2. Reagents

All reagents used in this study were of analytical grade. Ultrapure water prepared with a Gradient A10 water purification system was used (Millipore, Bedford, MA). Furthermore, a stock solution of NDMA (40 mg/L) was prepared by diluting 2000 mg/L certified nitrosamine mix standard solutions that included NDMA in methanol (Supelco, Bellefonte, PA). Working solutions (2.0–1000 µg/L) were prepared by diluting 40 mg/L NDMA methanol solution with dichloromethane (Wako Pure Chemical, Osaka, Japan). Each working solution contained 50 µg/L NDMA-d₆ (C/D/N Isotopes, Pointe-Claire, Canada) as an isotope-labeled surrogate standard.

2.3. Sample preparation

All of the water samples described below were stored in the dark at 4 °C prior to analysis, referring to previous researches (US EPA, 2009c, for example). Sodium bicarbonate (Wako Pure Chemical) was added at a final concentration of 2 g/L to adjust the samples to approximately pH 8. In addition, the samples were spiked with known concentrations of NDMA-d₆. The 500 mL of samples were then filtered through 0.7 µm GF/F filters (Whatman, Florham Park, NJ), after which they were passed through coupled Sep-Pak[®] Plus AC-2 cartridges (400 mg × 2; Waters, Milford, MA) at flow rates of 3–5 mL/min under vacuum. The Sep-Pak[®] Plus AC-2 cartridges had been preconditioned with 20 mL of a solution of dichloromethane (Wako Pure Chemical) and diethylether (Kanto Chemical, Tokyo, Japan) (50:50 v/v), followed in sequence by 20 mL of methanol (Wako Pure Chemical) and 20 mL of ultrapure water. After passing through the cartridges, the samples were dried under nitrogen gas and then eluted with 10 mL of a solution of dichloromethane and diethylether (50:50 v/v) at a flow rate ranging from 2 to 3 mL/min. The eluate was then purified by passing through a Sep-Pak[®] Vac Florisil[®] cartridge (1 g; Waters) preconditioned with 10 mL of hexane (Wako Pure Chemical) followed by 10 mL of a solution of dichloromethane and diethylether (50:50 v/v). The combination of these two solutions was used because it enabled better separation or recovery than either methanol or dichloromethane alone. The eluate was then concentrated to around 50 µL to minimize the amount of diethylether, after which it was diluted to 200 µL with dichloromethane. Multiple reaction monitoring (MRM) chromatograms of the samples indicated that a cleanup procedure was necessary to obtain the NDMA peak in raw and finished water samples, especially following chlorination.

Table 2

Recovery of NDMA from water samples.

| Category | Concentration (ng/L) | Absolute recovery (%) (RSD (%)) ^a | Relative recovery (%) ^b (RSD (%)) ^a |
|-----------------|----------------------|--|---|
| Ultrapure water | 2 | 55 (16) | 95 (17) |
| River water | 10 | 59 (1.1) | 102 (4.6) |
| Finished water | 10 | 64 (8.4) | 103 (3.4) |

^a Relative standard deviation.

^b Recovery adjusted relative to NDMA-d₆.

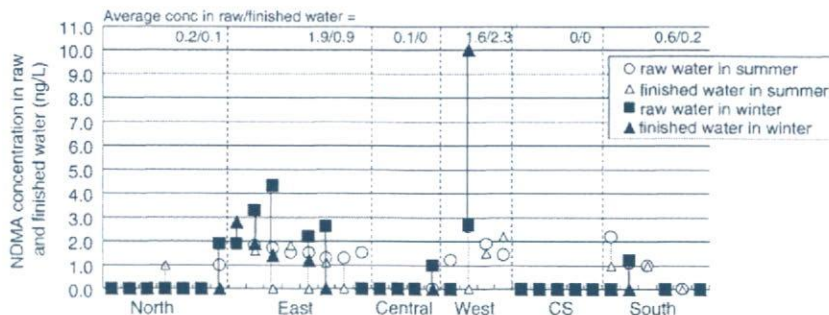


Fig. 2. NDMA in raw and finished water samples evaluated in this study. Average concentration was calculated by arithmetic mean applying zero for ND data.

2.4. Sample analysis

Separation was performed using an ACQUITY UPLC system (Waters) with a BEH C18 column (2.1 mm × 150 mm; Waters). The mobile phase was composed of 10 mM ammonium bicarbonate (Fluka, St. Louis, MO) aqueous solution (eluent A) and 100% acetonitrile (eluent B; Wako Pure Chemical). The ratio of eluent B was changed as follows: 5% for 3.5 min, which was then increased to 95% from 3.5 to 3.85 min, and then maintained at 95% for 2.5 min. The flow rate was 0.2 mL/min for all stages and the sample injection volume was 30 µL. Detection was performed using an ACQUITY TQD tandem mass spectrometer (Waters) operated in the electrospray ionization (ESI) positive-ion mode. The MRM transitions were *m/z* 74.9–43.1 (quantification) and *m/z* 74.9–57.9 (confirmation) for NDMA and *m/z* 81.0–46.0 for NDMA-d₆ (Table 1).

2.5. Method detection limit (MDL)

The average absolute recovery rates of NDMA in ultrapure water, river water, and drinking water samples were 55, 59, and 64%, respectively (number of replicates, *n* = 5, 3, 3, respectively) (Table 2). The relative recovery obtained using NDMA-d₆ ranged from 95 to 103%. The MDL for NDMA, which was calculated based on 3 × the standard deviation of five concentrated ultrapure water samples containing 2 ng/L NDMA, was 1.0 ng/L.

2.6. Basic parameters

The total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations were determined using a TOC analyzer (TOC-V CPH; Shimadzu, Kyoto, Japan). Nitrate and nitrite concentrations were

determined using an ion chromatograph (DX-500; Dionex, Sunnyvale, CA). Ammonia concentrations were determined spectrophotometrically as a derivative of phenol. Total organic nitrogen (TON) concentrations were determined by subtracting the nitrate, nitrite, and ammonia concentrations from the total nitrogen (TN) concentration, which were determined spectrophotometrically after oxidation by peroxodisulfate (Japan Water Works Association, 2001).

3. Results

3.1. National survey of NDMA in raw water

Fig. 2 shows the regional distribution of NDMA concentrations in raw water samples collected for this study. NDMA was detected in 15 of 31 raw water samples collected in summer, with concentrations ranging from not detected (ND) to 2.6 ng/L. In addition, NDMA was detected in 9 of 28 samples collected in winter, with concentrations ranging from ND to 4.3 ng/L. These concentrations of NDMA are rather low in comparison to previous studies conducted in Canada and the USA (Charrois et al., 2007). Specifically, the maximum concentrations of NDMA in the studies in Canadian and the USA were 8.0 ng/L and 9.4 ng/L, respectively. However, the detection ratio of NDMA was higher in the present study than in the Canadian study, in which NDMA was detected in only 3 of 11 raw water samples.

Samples from the east and west of Japan were found to have higher concentrations of NDMA than those from other areas (Fig. 2). NDMA is often discharged from sewage treatment systems (Krauss and Hollender, 2008), and can be present in discharge associated with industries, such as rubber manufacturing, leather tanning, pesticide manufacturing, food processing, foundries, and dye manufacturing. In the recent survey of discharge water from sewage treatment plants,

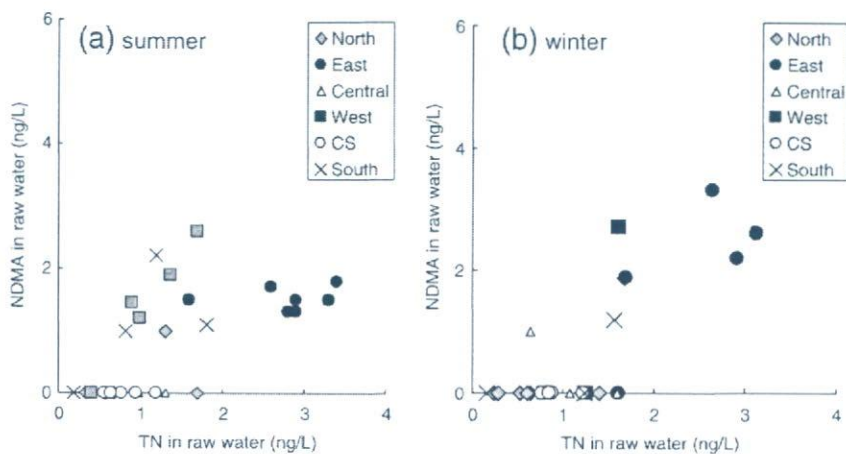


Fig. 3. TN and NDMA in raw water.

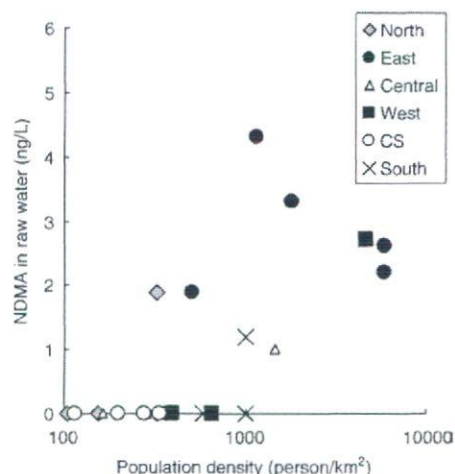


Fig. 4. Population density and NDMA concentration in raw water samples collected in winter.

NDMA was found during ozonation of water samples taken from sewage treatment plants located in the Yodo River Basin, the west area of Japan. The concentrations of NDMA before and after ozonation were 16–290 ng/L and 24–280 ng/L, respectively, and specific compounds related to the textile industry were identified in these discharges (Kosaka et al., submitted for publication). These contaminants may partially account for the NDMA in the west area.

The causes of contamination in the east and other areas are still unclear. However, NDMA levels were higher in waters containing nitrogen species. Although ammonia, nitrite, and nitrate all showed the same tendencies as NDMA concentrations, as shown in Fig. S1, TN seemed to be related to NDMA in raw water samples (Fig. 3). Although only limited data are available at present, this is probably because TN is an indicator of total nitrogen-related contamination, such as discharge from sewage treatment plants or other activities.

Fig. 4 shows the relationship between the population density of the each river basin and NDMA concentration in raw water samples. There is not a clear correlation between them because this study considered several large areas, where each area or processing plant may have source waters and treatment configurations with very different characteristics. However, NDMA was found in the water from areas in which the catchment population density was over 300 persons/km². Seasonal differences between summer and winter samples may exist due to flow rate, environmental fate, and/or NDMA burden. The ratio of NDMA to TN was slightly higher in the east in winter, but

was higher in the west in summer. In this study, the relationship between total organic carbon and NDMA was also examined but no obvious correlation was found (data not shown).

3.2. National survey of NDMA in finished water

Fig. 2 shows the regional distribution of NDMA in finished water samples. The concentration of NDMA in the finished water samples ranged from ND to 2.2 ng/L (10/31) in summer and from ND to 10 ng/L (5/28) in winter. The concentrations of NDMA in finished water samples were generally lower than those in raw water samples. In addition, the concentration of NDMA in the finished water samples was higher in the winter than in the summer.

Additional samples containing high concentrations of hypochlorite had NDMA concentrations that were equivalent to or less than the MDL. One DWTP included in this study utilized chloramination during the treatment process; however, no NDMA was detected in samples of finished drinking water collected from this plant.

In comparison to studies performed in Canada and the USA (Charrois et al., 2007), the concentrations of NDMA observed in the finished water samples in the present study were low (max. 65 ng/L in finished water in Canada and 30 ng/L in finished water in the USA). This may have been because chloramination is not generally used in Japanese facilities; to our knowledge, there is only one water treatment plant intentionally employs chloramination to reduce the formation of trihalomethane in Japan. In addition, the level of NDMA is decreased by biological activated carbon treatment (BAC), as described in the following section, even once it has been generated.

On comparison of NDMA concentrations between raw and finished water samples, the sample with the highest concentration of NDMA (10 ng/L) was collected from a DWTP at which the treatment process included ozonation. Fig. 5 shows the relationship between TN in raw water samples and NDMA in finished water samples. The results can be divided into two categories, i.e., east and other areas.

Fig. S2 shows the relationships between ammonia and nitrate in raw water and NDMA in finished water. NDMA tended to be detected more frequently in samples that contained high concentrations of each of ammonia, nitrite, and nitrate. It should be noted that the data from the finished water sample with the highest NDMA concentration from a DWTP in the Yodo River Basin, which employs ozonation, were obviously separated from the other data. Based on these results, the formation and degradation of NDMA in DWTPs appear to be dependent on the watershed in which these facilities are located, as the Yodo River is the largest water source in the western part of Japan with a population of tens of millions utilizing the river water as a

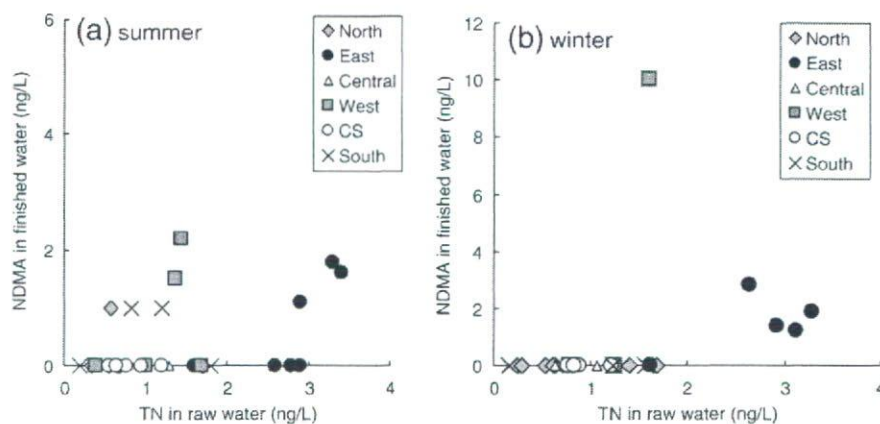


Fig. 5. TN in raw water and NDMA in finished water.

source and many water treatment facilities in this area employ ozonation.

3.3. Survey of NDMA in DWTPs

To clarify the behavior of NDMA during the purification process, NDMA concentrations were examined in each purification process in six major DWTPs (DWTP1–6) (Fig. 6). Each DWTP utilized various treatment processes, including coagulation, flocculation, sedimentation, and sand filtration. However, for convenience, these processes are simply classified here as before ozonation, after ozonation, after biological activated carbon treatment, and finished water. The NDMA concentrations of water samples following each process are shown in Fig. S3, and the concentrations before and after ozonation are summarized in Fig. 6.

The NDMA concentration increased to 7.0 ng/L following chlorination in DWTP2, which was higher than the level observed in raw water (1.5 ng/L). This increase was probably due to the use of a high dose of chlorine (4.5 mg/L) during the first stage of treatment at this facility. Although the ammonia:chlorine molar ratio of 6.8 exceeded the chlorine dose necessary for breakpoint chlorination, TOC was as high as 3.5 mg/L. Therefore, it was considered to consume chlorine so as to be combined chlorination condition at that time.

At DWTP3 and DWTP6, the NDMA concentration increased to as high as 15 ng/L following ozonation. Both of these treatment plants are located in the Yodo River Basin, and formation of NDMA likely occurred during the ozonation process.

The NDMA concentration decreased markedly (from 20 ng/L to 1.5 ng/L in DWTP3 and from 17 ng/L to 1.3 ng/L in DWTP6) following BAC treatment, regardless of the level formed by ozonation. Although it has been reported that NDMA shows poor absorption onto activated carbon due to its hydrophilic nature (Mitch et al., 2003; World Health Organization, 2008), removal of more than 90% of the NDMA following BAC treatment was observed in the present study. This finding indicates that the NDMA concentration decreased due to biological degradation during BAC treatment, similar to the findings of a previous study (Tateishi et al., 2008). However, the mechanism responsible for this decrease in NDMA concentration was not elucidated in this study. Following BAC treatment, the NDMA concentrations in the finished water samples ranged from <MDL (1.0) to 2.2 ng/L, which was below the concentration of 7 ng/L considered by the US EPA as the level in drinking water associated with an excess cancer risk of 10^{-5} (US EPA, 2009a), but was close to the public health goal of 3 ng/L proposed by California (California Department of Public Health, 2009).

As the behavior of NDMA varied among DWTPs, the relationships between NDMA concentration and other organic or inorganic water quality parameters were analyzed. The results revealed no clear relationships between the increase in NDMA concentration that occurred due to ozonation and the concentrations of organic compounds in the raw water samples (TOC, E260, and TON). In addition, no relationships were observed between the increases in

NDMA concentration and pH, nitrate, nitrite, or ammonia concentrations, or the ozone dose (Fig. S4 in Appendix A).

The water source for both DWTPs that showed marked increases in NDMA concentration following ozonation (DWTP3 and DWTP6) was the Yodo River, which is located in western Japan. These findings were in agreement with those of a previous study conducted to evaluate the concentrations of NDMA at DWTPs in the Yodo River Basin (Tateishi et al., 2008) and our previous study suggesting that these increases in NDMA concentration during ozonation at the two DWTPs with the Yodo River as the water source may be due to specific contaminants (Kosaka et al., submitted for publication).

4. Discussion

The present study was performed to determine the NDMA concentrations in water samples from various areas in Japan. Higher NDMA concentrations were found in water containing nitrogen species, which was consistent with the results reported previously (Mitch et al., 2003). The results of this study also indicated that NDMA formation occurs during ozonation in selected DWTPs, which was similar to the findings of other studies indicating that this phenomenon occurs in the presence of *N,N*-dimethylsulfamide (DMS), which is one of the decomposition products of tolylfluanid (Schmidt and Brauch, 2008). Coagulation polymers have also been indicated as precursors of NDMA (Mitch et al., 2003; Charrois and Hrudey, 2007). Although tolylfluanid is not approved for agricultural use and coagulation polymers are prohibited in Japan, the formation of NDMA from specific compounds was observed during ozonation in DWTPs, and further studies are required to determine the concentrations of chemicals that can lead to its formation.

Taken together, the findings of this study indicate that it is necessary to investigate the mechanism by which NDMA is formed during ozonation so that the specific compound(s) responsible for its formation in water in the western part of Japan can be identified. Accordingly, we are currently investigating the relationship between the load of NDMA precursors and its formation during ozonation in upstream sewage treatment plants (STPs) because the effluents from these STPs flow into river water that is subsequently used as the raw water supply for drinking water.

It is important to note that higher NDMA concentrations were detected in prefectures that had higher levels of human activity. Although this study provided only a rough estimate, the level of NDMA in raw water tended to increase in proportion to human activity in the area. Therefore, these activities should be regarded as area-specific and/or non-point sources of NDMA and NDMA precursors.

5. Summary

1. A national survey of *N*-nitrosodimethylamine (NDMA) levels in raw and finished water samples collected from drinking water treatment plants (DWTPs) was conducted using solid-phase extraction (SPE) followed by ultra performance liquid chromatography (UPLC) coupled with tandem mass spectrometry (MS/MS).
2. NDMA was detected in 15 of 31 raw water samples collected in winter at concentrations up to 2.6 ng/L. NDMA was also detected in 9 of 28 samples collected in summer, with a maximum concentration of 4.3 ng/L. NDMA was detected in 8 of 31 finished water samples collected in summer with a maximum concentration of 2.2 ng/L, while in winter, NDMA was detected in 5 of 28 samples with a maximum concentration of 2.8 ng/L, except in one sample with a high concentration of 10 ng/L.
3. The NDMA concentration was greater in raw water samples containing higher levels of nitrogen species. In addition, river water samples collected from the east and west of Japan showed

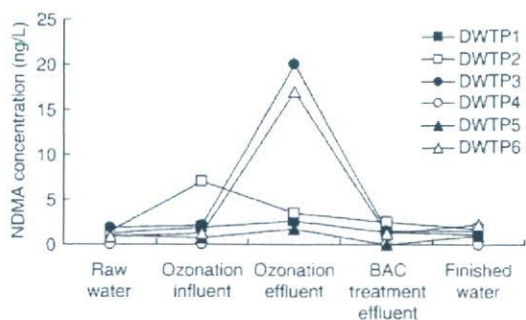


Fig. 6. NDMA concentrations at six treatment plants.

higher concentrations of NDMA than those collected from other areas.

- Process water was examined during each of the processes in six advanced water treatment plants. NDMA concentrations were shown to increase during ozonation when water from the Yodo River Basin was utilized as the source water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2009.02.014.

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水道水源および消毒剤中のハロゲン酸の存在状況と動向*

浅見 真理

1. はじめに

ハロゲン酸は、塩素、臭素、ヨウ素等を含む酸であり、塩素酸、臭素酸、ハロ酢酸などが含まれる。そのうち、ハロゲンと酸素が結合した酸であるオキシハロゲン酸の一つ、臭素酸は、オゾン処理の副生成物として、平成16年に水質基準が定められた¹⁾。塩素酸および亜塩素酸は、かねてより二酸化塩素処理の副生成物として知られ、亜塩素酸は水質管理目標設定項目に指定され、目標値 $600\mu\text{g}\cdot\text{l}^{-1}$ であったが²⁾、平成20年から、赤血球への酸化傷害性および検出状況から、塩素酸が基準(基準値 $600\mu\text{g}\cdot\text{l}^{-1}$)に加えられた³⁾。

また、トリハロメタンに続く代表的な消毒副生成物群の一つであるハロ酢酸は、塩素(Cl)あるいは臭素(Br)を1, 2, 3個含む種が9種存在し、このうち、トリクロロ酢酸(TCAA)、ジクロロ酢酸(DCAA)、モノクロロ酢酸(MCAA)の3種は水道水質基準項目に、残り6種は要検討項目に指定されている²⁾。MCAAの基準値は $20\mu\text{g}\cdot\text{l}^{-1}$ 、DCAAは $40\mu\text{g}\cdot\text{l}^{-1}$ 、TCAAは $200\mu\text{g}\cdot\text{l}^{-1}$ である。米国では、上記3種の水質基準項目のハロ酢酸にモノプロモ酢酸(MBAA)およびジプロモ酢酸(DBAA)を加えた5種の総濃度 $60\mu\text{g}\cdot\text{l}^{-1}$ が最大許容濃度として定められている⁴⁾。

これらのハロゲン酸は、①ハロゲン(塩化物、臭化物)の酸化により(意図的および非意図的に)生成される酸化物であり ②いずれも水中ではイオンで存在し、きわめて水溶性が高く ③(一部のハロ酢酸を除き)水系に残留し環境中ではあまり吸着・分解されず ④浄水場における除去や低減化が困難であり ⑤次亜塩素酸ナトリウム水溶液(次亜, 以下同様)の成分により影響を受ける場合があり ⑥毒性の観点から $\mu\text{g}\cdot\text{l}^{-1}$ レベルでの制御が課題である。また、⑦当初考えられていたより高濃度で存在することがあり ⑧副生成物としての生成量が把握しにくい等、従来の化学物質管理のスキームでは捉えきれない等の特性がある。

本稿では、消毒剤中の不純物、消毒副生成物や環境中に存在するハロゲン酸のうち、特に水道に関連する課題

となっている臭素酸、塩素酸、亜塩素酸、過塩素酸に関する最近の知見の一部を紹介したい。

2. 臭素酸、塩素酸、亜塩素酸、過塩素酸の基準と検出状況

2.1 臭素酸

臭素酸(水中では BrO_3^- として存在)は、発がん性があることから水道水質基準項目に指定され、基準値は $10\mu\text{g}\cdot\text{l}^{-1}$ である¹⁾。水中の臭化物イオンとオゾンが反応してできる副生成物であり⁵⁾、一度生成するとなかなか除去できない⁶⁾他、パーマネント剤の成分に含まれるため下水処理水、河川水等でも検出されることがある⁷⁾。現在でも、臭素酸の問題は既存施設の管理の大きな課題であり、オゾン注入率を下げる、pHを低く制御する、前塩素を入れてオゾン注入率を下げるなどの方策により、かなり低い濃度で制御が行われているが、オゾンを導入している水処理施設にとって避けては通れない課題となっている。

水道水質基準に関する基準項目調査⁸⁾(平成18年度には水道統計対象地点約5,819ヵ所)では、平成16年度には、基準値の16倍を超える事例を含む20件、平成17年度には3件、臭素酸の基準超過が見られた。平成18年度には、基準超過は見られなかったものの、この間に臭素酸濃度が高いと報告された施設ではオゾン処理は導入されておらず、臭素酸の濃度超過は次亜中の不純物に起因していた。筆者らは、次亜の実際の保管、使用状況や不純物に関する調査を行ってきたが、その中で保存期間が2年以上にわたる次亜もあり、それらの中の不純物濃度は高く、また有効塩素濃度が低いため実際の注入率が高くなる場合があり、そのような場合は臭素酸濃度や塩素酸濃度が高くなることを指摘した⁹⁾。

次亜中では、臭素酸生成は速く起こっており、製造から1~数日以内ではほぼ平衡に達する¹⁰⁾(図1、文献10より抜粋)。次亜中の臭素酸は、原料の電解過程¹¹⁾およびその後の製品中の次亜による酸化により生じるものであ



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* Occurrence and Direction of Halogenated Acids in Water Source and Disinfectants

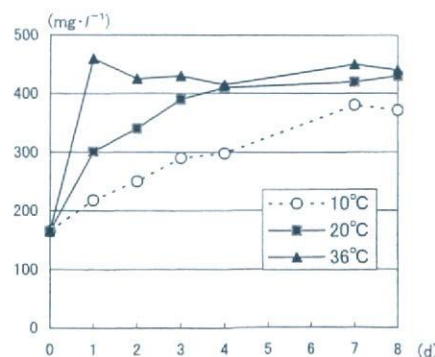


図1 保存濃度の違いによる次亜中の臭素酸濃度の変化¹⁰⁾(製造後間もなくから測定)

り、その低減化には、臭素の存在比の低い原料塩を使用することがあるが、臭素/塩素比は、食塩で0.06~0.2%、精製塩で0.004~0.01%、岩塩で0.003~0.02%であり、国内の塩やイオン交換膜を用いて製造した塩では、臭化物濃度が高いと報告されている¹²⁾。また、次亜製造プロセスにおいて原料の塩およびpH調整用苛性から析出する食塩を遠心分離等の技術で削減することや、食塩を電解して発生する臭素を含む塩素ガスを液体塩素で洗浄して臭素の含有量を低減する方法などにより、現在では、臭素酸濃度の低減化が図られている¹²⁾。(詳細については、本特集内の他の項で述べられているため割愛する。)

一方、原水中に臭化物イオンが含まれている場合に、次亜塩素酸と日光の影響があると、臭素酸が生成することがある。塩素消毒を受けた後の配水池で昼間日光が当たると臭素酸濃度が基準値近くなる事例¹³⁾や、海からの風送塩の影響を受けやすい場所などの屋外プールで、次亜を消毒に使用していた場合、臭素酸が水道水質基準値を大きく超えて(最高 $551\mu\text{g}\cdot\text{l}^{-1}$)検出される場合が報告されている¹⁴⁾。

昨年より、水道施設における原虫対策として紫外線照射の導入が認められるようになったが、臭化物イオンと残留塩素が存在する水に紫外線を照射した場合に臭素酸の生成が促進される可能性があるため、塩素注入の後段に紫外線処理設備を設置する場合は、処理対象水中の臭化物イオンに注意する必要があると注意喚起がなされている¹⁵⁾。

2.2 塩素酸・亜塩素酸

塩素酸および亜塩素酸は、塩として中間体や酸化剤等として使われる他、二酸化塩素処理の副生成物として知られていたが、平成16年度の水道水質基準の改正において、塩素酸(水中ではイオン、 ClO_3^- として存在)は、二酸化塩素処理を行った場合の副生成物として水質管理目標設定項目に挙げられた。亜塩素酸についてはほとんど検出されていないが、塩素酸については、下に示すように消毒に用いられる次亜中の不純物の影響などにより浄水、給水栓水における検出事例が多いため、内閣府食品安全委員会による毒性評価結果を受けて、水道水質基準が策定された¹⁾。

内閣府食品安全委員会が定めた塩素酸の耐容一日摂取量は、ラットを用いた90日間の飲水投与試験によるNOAEL $30\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ に不確実係数1,000を適用し、 $30\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ である¹⁶⁾。また、世界保健機関(WHO)飲料水水質ガイドラインにおいて、塩素酸の暫定ガイドライン値 $700\mu\text{g}\cdot\text{l}^{-1}$ は、飲料水の寄与率を80%とし、体重60kgのヒトが1日2l飲むという仮定から算定されている¹⁷⁾。なお、影響面では、酸化力による赤血球のダメージを重視している。現在のところ米国環境保護庁(USEPA)では最大許容濃度(MCL)、目標最大許容濃度(MCLG)等の規制は定めていないが、カリフォルニア州環境健康影響評価局(OEHHA)では、同様の毒性の観点から $200\mu\text{g}\cdot\text{l}^{-1}$ の目標値を推奨する意見も提出されている¹⁸⁾。

亜塩素酸については、ヒトにおいて、主要な毒性発現は赤血球細胞への酸化ダメージであるとされ、発がん性の証拠は認められないため、TDI法による評価値の算定が行われ、NOAEL: $2.9\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ に不確実係数:

100(種差と個体差それぞれに10)を適用して、TDIが $29\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ と求められた。この値は、ヒトにおけるNOAEL: $36\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ によって基づくものである。亜塩素酸は、二酸化塩素処理の場合は浄水処理に直接使用されることを考慮し、TDIに占める飲料水の寄与率を80%とし、体重50kgのヒトが1日2l飲むと仮定すると、評価値は、 $0.6\text{mg}\cdot\text{l}^{-1}$ と算定された⁴⁾。

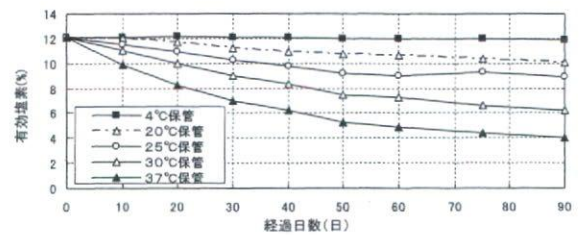
また、水道水質としての評価が変更されるかどうかはまだ確定していないが、国連食糧農業機関と世界保健機関合同食品添加物専門家会合(JECFA)では、食品添加物としての塩素酸について雄ラットの甲状腺の感受性を考慮し、ADIを $0\sim 10\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ (上と同様に仮定すると $200\mu\text{g}\cdot\text{l}^{-1}$ に相当)とする評価が出されており、今後の動向が注目される¹⁹⁾。

厚生労働省の水道統計18年度調査⁹⁾では、塩素酸は、測定値点数898件のうち、浄水で12地点が基準値を超過し、実に約半数の417地点が10%値を超過していた。

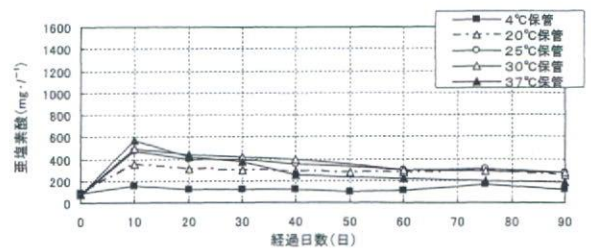
一方、亜塩素酸は、578件のうち、基準超過はなく、10%値超過が3地点であった。

水道水中の塩素酸・亜塩素酸は、消毒用の次亜中の分解物、塩素酸の生産等の工場排水、下水処理場等の排水などを起源とすることが明らかとなってきた。これらの検出状況について述べる。

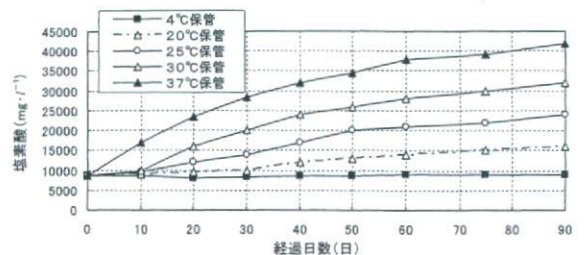
通常溶液で購入される次亜は、平成16年度の水道統計では消毒薬品別使用量の85%を占める主要な消毒薬品であり²⁰⁾、大規模浄水場から小規模浄水場まで幅広く用い



a) 次亜塩素酸ナトリウム中の次亜塩素酸濃度



b) 次亜塩素酸ナトリウム(a)中の亜塩素酸濃度



c) 次亜塩素酸ナトリウム(a)中の塩素酸濃度

図2 次亜塩素酸ナトリウムの保管温度別経日変化例¹²⁾

られている。次亜中の塩素酸については、次亜の不均化反応による分解により生成すると考えられ、次亜塩素酸の減少と共に、Gordonら²¹⁾や湖上と宮田²²⁾らが、貯蔵中の次亜中からの塩素酸の生成特性、品質管理等に関する理論的および実際的な検討を詳細に行っている。前述した筆者らの調査でも長期保存後の次亜中の塩素酸濃度は高い²³⁾。

次亜の分解と共に生成する亜塩素酸および塩素酸の濃度を図2に示す(文献¹²⁾より、抜粋して作成)。これらは温度依存性を持ち、保存温度が高ければ高いほど速く塩素酸が生成する。比較的高温時の次亜の分解時には一時的に亜塩素酸が生成するが、亜塩素酸は分解の中間物と考えられ、ほぼ同時に生成する塩素酸に比べて、極めて低濃度である。

塩素酸の生成は、温度と時間に大きく依存するため、次亜の分解抑制については、次亜塩素酸ナトリウムの保存期間の短縮化、貯留槽の冷却、不純物の低減化による分解の抑制、低濃度次亜による処理などの対策が挙げられる¹²⁾ほか、貯留槽の構造により、次亜が換気の制御²⁴⁾等についても効果が認められており、貯留槽の構造にも関心が払われる必要がある。

一方で、工場排水等に起因する環境中からも塩素酸は検出されており、利根川流域において河川水中に、塩素酸は $0.7\sim 9,000\mu\text{g}\cdot\text{l}^{-1}$ で検出された²⁵⁾。最高濃度は、後述する琵琶湖・淀川流域の環境水に比べて非常に高い濃度である。既報²¹⁾で述べたように、利根川上流域には塩素酸、過塩素酸の発生源と推測される複数の事業場が存在しており、その影響によるものと考えられた。このとき、利根川本川については、最高濃度は塩素酸で $1,100\mu\text{g}\cdot\text{l}^{-1}$ であった。また、今回の調査では、発生源の影響を受けた中・下流域の環境水(利根川、江戸川、荒川)中の塩素酸濃度は $20\sim 30\mu\text{g}\cdot\text{l}^{-1}$ 程度であった。一方、発生源の影響を受けていないと考えられる試料の場合、塩素酸濃度は、最上流域では $1\mu\text{g}\cdot\text{l}^{-1}$ 程度、それ以外では $数\mu\text{g}\cdot\text{l}^{-1}$ 程度であった²⁶⁾。

琵琶湖およびそれに流入する河川水(安曇川、野洲川、姉川)、宇治川、桂川、木津川および淀川の25試料について調査を行ったところ、塩素酸は、24試料から検出され、その濃度は $0.4\sim 26\mu\text{g}\cdot\text{l}^{-1}$ であった。2試料で $20\mu\text{g}\cdot\text{l}^{-1}$ を超えていたが、概して $数\mu\text{g}\cdot\text{l}^{-1}$ の濃度であり、また、下流域に行くにしたがって濃度が高くなる等の傾向は認められなかった²⁷⁾。下水処理水の6試料の場合、塩素酸濃度は $0.6\sim 180\mu\text{g}\cdot\text{l}^{-1}$ の範囲であったが、下水の流入元に工業製品として塩素酸を生成する業種は含まれていないことから、塩素酸濃度が高い試料については、塩素消毒に用いられる塩素剤の影響がある可能性が考えられた。これらの結果から、下水処理水は、負荷としては非常に大きいわけではないが、環境水中への塩素酸の排出源となる場合があることが示された²⁸⁾。

このような、表流水、地下水だけではなく、各種市販飲料においても塩素酸が検出されている。昨年、国内のボトル水106本に関する調査を行った際の塩素酸濃度を図3に示す²⁹⁾。水道事業者等が製造したボトル水(水道ボトル水)では、すべての試料から塩素酸が検出され、その濃度範囲は $25\sim 120\mu\text{g}\cdot\text{l}^{-1}$ であった。

水道ボトル水以外では、塩素酸濃度は、ほとんど試料

で $数\mu\text{g}\cdot\text{l}^{-1}$ 以下であったが、幾つかの一般的によく知られた飲料を含む試料で、水道ボトル水と同程度またはそれを上回る塩素酸濃度を示した。ミネラルウォーターでは、3試料が水道ボトル水と同等の塩素酸濃度を示した。これらの製造元に聞き取り調査を行った結果、2試料は原料に水道水を使用していること、残り1試料は塩素処理を行っていることがわかった。

お茶類では、12社中、A社の1試料で、水道水質基準値を超える高い濃度($700\mu\text{g}\cdot\text{l}^{-1}$)で塩素酸が検出された。また、炭酸飲料・清涼飲料については、8社中、A社の6試料すべてと、B社の3試料中2試料から、水道ボトル水中の濃度と同程度の濃度で塩素酸が検出された。A社について聞き取り調査を行ったところ、塩素酸濃度が $700\mu\text{g}\cdot\text{l}^{-1}$ であった工場では、井戸水と水道水を混合し、自社で水処理後使用していることがわかった。しかし、塩素酸濃度が基準値(測定当時は目標値)を超過していたことから、水処理工程または容器の洗浄等で、塩素化合物が使用されていることが推測された。このように塩素酸は、環境水やボトル水からも検出され、特にボトル水では塩素処理の履歴を示すことが分かった。

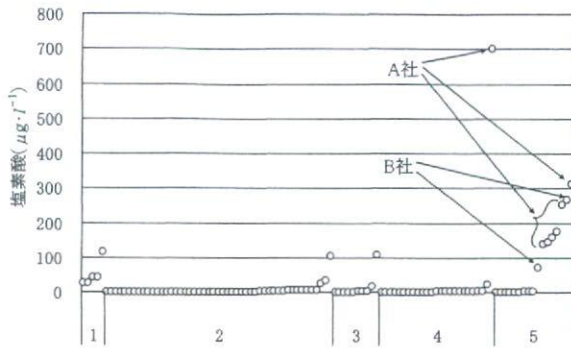
2.3 過塩素酸

過塩素酸も、水中ではイオン(ClO_4^-)で存在し、移動性が高く、非常に安定した物質である。通常、過塩素酸は、過塩素酸塩、過塩素酸の形態で生産・使用されている。過塩素酸塩の主な使用用途としては、ロケットやミサイルの推進剤が知られている³⁰⁾。それ以外にも、エアバッグ、火薬、花火、マッチ、信号炎管等、様々な製品に使用されている³¹⁾。また、塩素酸と同様に、大気中の光化学反応によって生成することが知られている^{32,33)}。

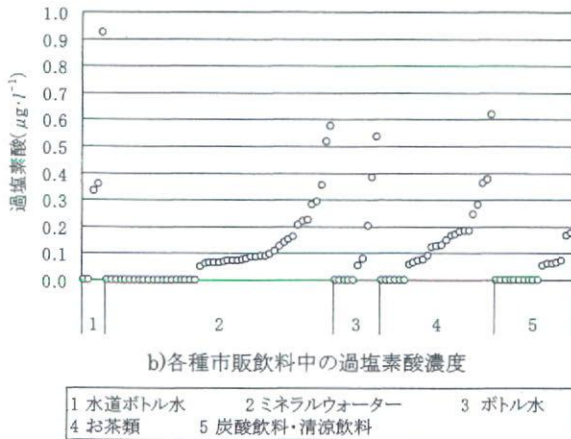
過塩素酸は、甲状腺におけるヨウ素の取り込みを抑制することが知られ、2005年2月、米国科学アカデミー(NAS)は、過塩素酸の参照用量(RfD)として、 $0.7\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ を勧告し、同月、USEPAは、NASの過塩素酸のRfDを採用し、飲料水等価濃度(DWEL)として $24.5\mu\text{g}\cdot\text{l}^{-1}$ を公表した(70kgの人が1日2lの飲料水を飲用し、飲料水の摂取寄与が100%であると仮定した値)³⁴⁾。現段階では、基準となる連邦のMCLは設定されていないが、カリフォルニア州は、飲料水中の過塩素酸の州基準として $6\mu\text{g}\cdot\text{l}^{-1}$ を定め、同州に移入される製品に過塩素酸が含まれる場合は、その旨の表示の添付を義務づけている。また、幾つかの州では、 $1\sim 18\mu\text{g}\cdot\text{l}^{-1}$ の範囲で、過塩素酸の勧告レベルを設定している。ただし、過塩素酸は、食品からも検出が見られるため³²⁾、これらのデータに飲料水の寄与率を考慮すると将来的な目標値は $数\mu\text{g}\cdot\text{l}^{-1}$ 以下になる可能性もある。

1990年代後半以降、米国各地の環境水および水道水中から、過塩素酸の存在が報告され^{32,33)}、また、米国のレタスや牛乳でも検出されている^{34,35)}。これまで過塩素酸の調査は米国内を対象としたものがほとんどであったが、最近、日本の飲料、食品からも過塩素酸が存在していることが報告された^{36,37)}。さらに、塩素酸と同様に、次亜中にも含まれており、分解が進んだ次亜で比較的高濃度の過塩素酸が検出されたが、通常の注入条件では、浄水に重大な影響が出ることは少ないと考えられた³⁸⁾。

筆者らは国内での利根川流域における過塩素酸の存在状況について調査を行い、利根川流域の広い範囲で、環



a)各種市販飲料中の塩素酸濃度



b)各種市販飲料中の過塩素酸濃度

図3 各種市販飲料中の塩素酸・過塩素酸濃度²⁹⁾

境水、水道原水および浄水、給水栓水中に過塩素酸が存在していることを報告した^{25, 26)}。過塩素酸は利根川流域圏の冬期の給水栓水において最高 $37\mu\text{g}\cdot\text{l}^{-1}$ 、夏期の浄水において最高 $24\mu\text{g}\cdot\text{l}^{-1}$ の濃度で存在しており、また、浄水工程での除去が困難な物質であった²²⁾。

利根川流域の環境水では、過塩素酸は、 $0.08\sim 1.500\mu\text{g}\cdot\text{l}^{-1}$ で検出された。これも上述したように、これまでの筆者らの調査により、利根川上流域の発生源と推測される複数の事業場の影響によるものと考えられた。このとき、利根川について見ると、最高濃度は過塩素酸で $340\mu\text{g}\cdot\text{l}^{-1}$ であった。また、今回の調査では、発生源の影響を受けた中・下流域の環境水(利根川、江戸川、荒川)中の過塩素酸濃度は $10\sim 20\mu\text{g}\cdot\text{l}^{-1}$ 程度であった。一方、発生源の影響を受けていないと考えられる試料の場合、過塩素酸濃度は、最上流域では $0.1\mu\text{g}\cdot\text{l}^{-1}$ 程度、それ以外では概ね $1\mu\text{g}\cdot\text{l}^{-1}$ 未満であった。これらの濃度が、同流域における自然由来の過塩素酸濃度と考えられた。

先に述べた各種市販飲料の調査²⁹⁾における過塩素酸濃度を図3に示す。すべての試料において、過塩素酸濃度は $1\mu\text{g}\cdot\text{l}^{-1}$ 未満と低い値であった。しかし、環境水中、水道水中から、過塩素酸は数 $\mu\text{g}\cdot\text{l}^{-1}$ 以上の濃度で検出されている場合があることから、流域、原水の種類によっては、より高い濃度で検出される可能性があると考えられた。なお、ミネラルウォーター中の過塩素酸濃度の地域による違いは特に認められなかった。

3. 工程水、浄水中の塩素酸、過塩素酸

これまで行った利根川流域の浄水工程中の塩素酸濃度

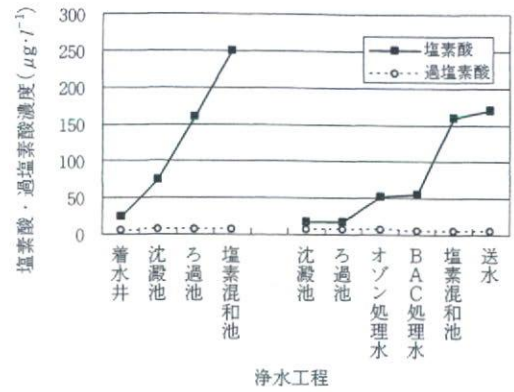


図4 次亜を用いた浄水場の浄水工程における塩素酸・過塩素酸濃度の例

に関する調査では、63試料すべてで塩素酸が検出され、濃度範囲は $1.8\sim 430\mu\text{g}\cdot\text{l}^{-1}$ であった。多くの試料で数十 $\mu\text{g}\cdot\text{l}^{-1}$ 未満であったが、幾つかの試料は $100\mu\text{g}\cdot\text{l}^{-1}$ を超えていた²⁴⁾。ほとんどの試料について、塩素酸濃度は原水に比較して上昇しており、次亜に由来するものと考えられた。今回の調査の範囲内で浄水と原水の対応がとれた試料について原水と浄水の差を計算したところ、購入次亜を用いていた23浄水場(系統ごとのべ数、以下同様)において、塩素酸濃度は最高 $430\mu\text{g}\cdot\text{l}^{-1}$ (中央値 $150\mu\text{g}\cdot\text{l}^{-1}$)に上昇していた。生成次亜を用いていた9浄水場については、同様に塩素酸の濃度上昇は $240\mu\text{g}\cdot\text{l}^{-1}$ (中央値 $63\mu\text{g}\cdot\text{l}^{-1}$)であった。液化塩素を用いている浄水場では、塩素酸 $36\mu\text{g}\cdot\text{l}^{-1}$ (中央値 $1.5\mu\text{g}\cdot\text{l}^{-1}$)であった。図4に、浄水工程における塩素酸、過塩素酸濃度の変化の様子の例を示す。これらの浄水の工程には、オゾン処理もあり、塩素酸濃度の上昇は次亜中の不純物だけではなく、オゾン処理の工程で次亜塩素酸イオン(ClO^-)が塩素酸に変化したためである可能性もある。

一方、過塩素酸も63試料すべてから検出され、濃度範囲は $0.08\sim 24\mu\text{g}\cdot\text{l}^{-1}$ であった²⁶⁾。その調査では、USEPAが示す過塩素酸のDWEL($24.5\mu\text{g}\cdot\text{l}^{-1}$)を超える浄水は認められなかった。なお、原水の最高濃度に比べて、浄水の最高濃度は低い値であったが、これは過塩素酸濃度最高値を示した原水は、地下水を複数取水している事業者の井戸水(地下水)の1つであり、浄水では他の水源からの原水により希釈されたためであった。また、原水よりも検出率が高くなったのは、塩素酸同様に次亜由来の場合があるためと考えられた。購入次亜を用いていた23浄水場において、過塩素酸の濃度上昇は $0.63\mu\text{g}\cdot\text{l}^{-1}$ (中央値 $0.03\mu\text{g}\cdot\text{l}^{-1}$)、生成次亜を用いていた7浄水場については、過塩素酸は $2.7\mu\text{g}\cdot\text{l}^{-1}$ (中央値 $0.06\mu\text{g}\cdot\text{l}^{-1}$)であった。液化塩素を用いている浄水場では、過塩素酸は $0.80\mu\text{g}\cdot\text{l}^{-1}$ (中央値 $0.15\mu\text{g}\cdot\text{l}^{-1}$)であった。今回の試料の場合過塩素酸の濃度変動は小さく、原水と浄水の対応がある程度明らかな試料について比較すると、過塩素酸はほとんど変化がないという傾向を示した。これらの結果から、過塩素酸は浄水処理工程で次亜の影響により若干増加することこそあれ、除去は困難であることが確認された。

利根川流域以外の全国調査等²⁷⁾における浄水場の全74浄水試料中、塩素酸はすべての試料から検出された。濃