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 $HCO_3^- \gg NO_3^- > Br^- > SO_4^{2-}$.

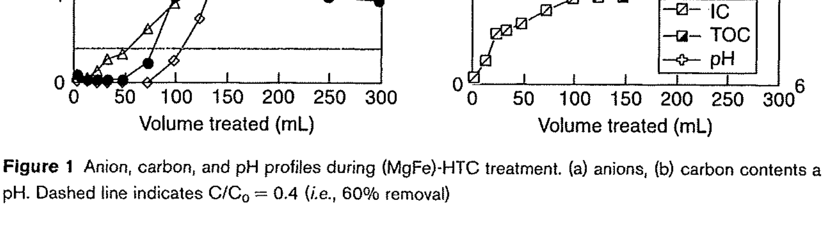

Figure 1 Anion, carbon, and pH profiles during (MgFe)-HTC treatment. (a) anions, (b) carbon contents and pH. Dashed line indicates $C/C_0 = 0.4$ (*i.e.*, 60% removal)

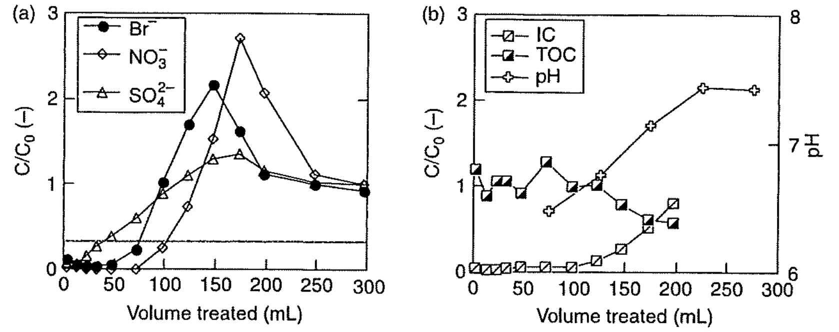

Figure 2 Anion, carbon, and pH profiles during (MgAlFe)-HTC treatment. (a) anions, (b) carbon contents and pH

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

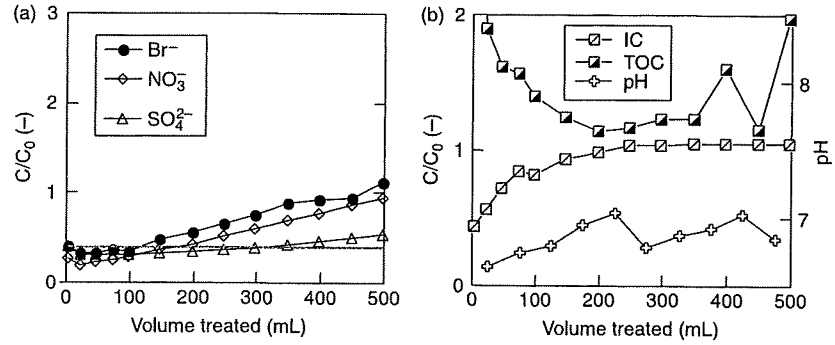

Figure 3 Anion, carbon, and pH profiles during Diaion SA10A. (a) anions, (b) organic and inorganic carbons and pH

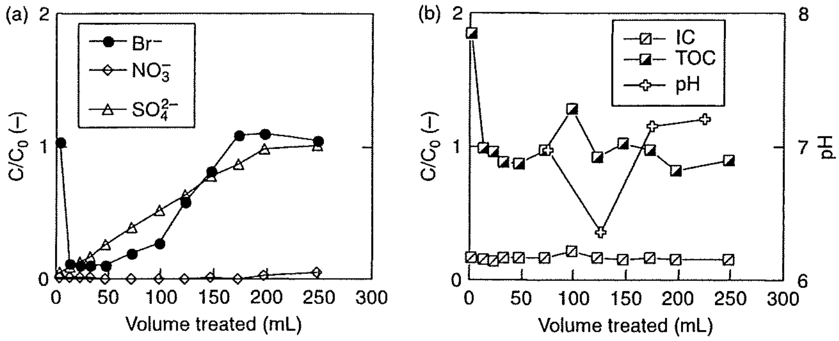

Figure 4 Anion, carbon, and pH profiles during (MgAlFe)-HTC after decarbonation. (a) anions, (b) organic and inorganic carbons and pH

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 secondary 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.

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

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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).

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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 km^2. 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.

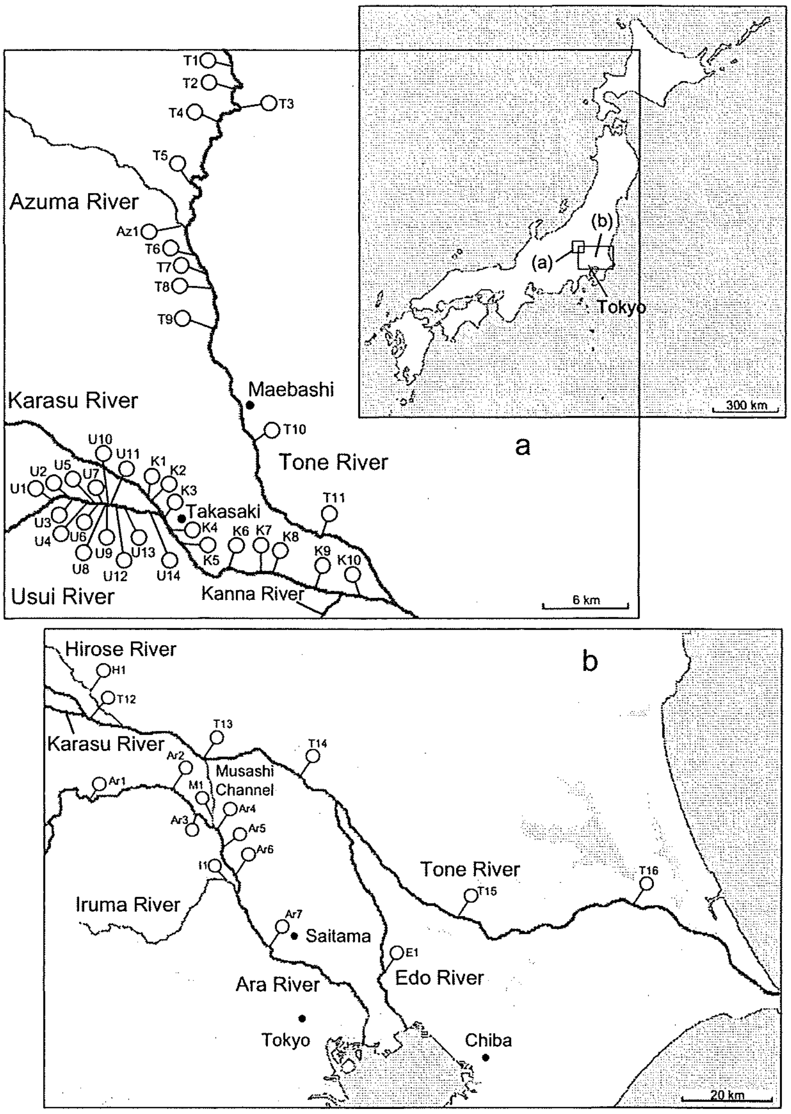

Fig. 1 – Sampling points (a) in the upper Tone River Basin and (b) in the middle and lower Tone River Basin.

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

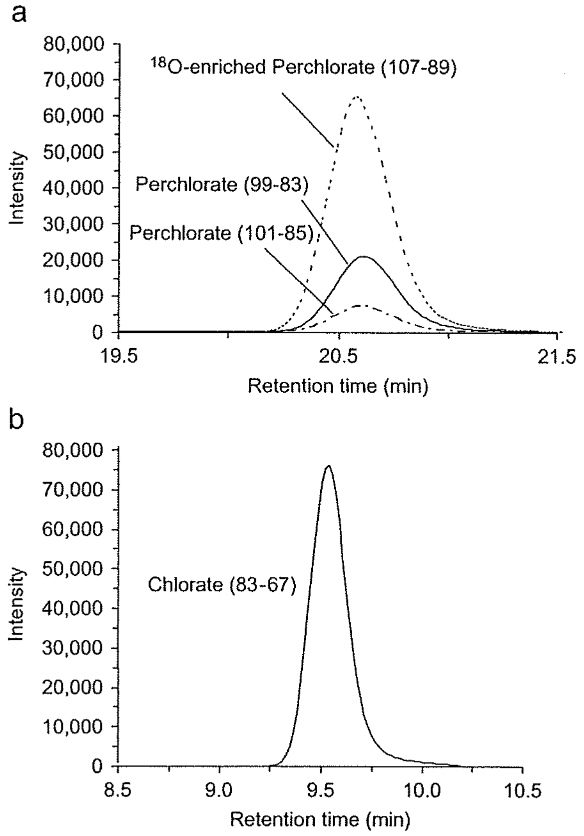

Fig. 2 – Chromatograms of (a) perchlorate and ^{18}O-enriched perchlorate and (b) chlorate in the sample.

flowed into its main river, the Tone River. Just before the confluence, the perchlorate concentration in the Karasu River was 34 μg/L at K10.

From these results, it was found that there were two areas in the upper Tone River Basin, where perchlorate concentrations were extremely high. However, except for these areas, perchlorate concentrations in the tributaries, waterways and effluents flowing into the Usui and Karasu Rivers were 0.15–27 and 0.13–5.4 μg/L, respectively. That is, perchlorate concentrations were more than 1 μg/L in some cases, which indicated that there were several sources of perchlorate although the amounts of discharge might not be large.

Table 2 shows perchlorate and chlorate concentrations in the discharging areas of perchlorate of the upper Tone River and Usui River (i.e., the two areas described above). The possible sources of perchlorate seemed to be industrial effluents. One was an effluent from perchlorate and chlorate production industry. However, the other was not. Since the latter was an effluent from an industry employing electrolysis processes for a purpose other than perchlorate production, it was considered that perchlorate might be produced as an unintended reaction by-product in electrolysis and perchlorate was contained in the effluent as a result.

In the case of the upper Tone River, perchlorate concentrations in an effluent and a tributary (or waterway) directly downstream of the outlet of the effluent were 1100 and 44–1500 μg/L, respectively. In the case of the Usui River, perchlorate concentrations in an effluent and a tributary (or waterway) directly downstream from the outlet of the effluent were 15,000 and 1100–3900 μg/L, respectively. Fig. 4 shows the relationships between perchlorate and chlorate

Table 1 – Perchlorate concentrations in upper Tone River Basin

Sampling point	Sampling date	Perchlorate concentration (μg/L)	Sampling point	Sampling date	Perchlorate concentration (μg/L)
Tone River			U7	18/05/2006	16
T1	10/04/2006	0.09	U8	18/05/2006	10
T2	10/04/2006	0.08	U9	23/05/2006	8.6
T3	10/04/2006	0.56	U10	18/05/2006	13
T4	10/04/2006	0.46	U11	18/05/2006	12
T5	10/04/2006	0.42	U12	18/05/2006	2100
T6	10/04/2006	0.74	U13	15/05/2006	2300
T7	21/04/2006	180	U14	10/05/2006	720
T8	10/04/2006	340		15/05/2006	1100
T9	10/04/2006	70	*Karasu River*		
T10	10/04/2006	13	K1	28/04/2006	0.36
T11	10/04/2006	12	K2	10/05/2006	0.46
Azuma River			K3	10/05/2006	110
Az1	10/04/2006	0.27	K4	10/05/2006	150
Usui River			K5	21/04/2006	92
U1	28/04/2006	0.23		10/05/2006	180
U2	10/05/2006	8.8	K6	21/04/2006	89
U3	15/05/2006	3.6	K7	21/04/2006	52
U4	15/05/2006	7.2	K8	21/04/2006	5.0
U5	10/05/2006	21	K9	10/04/2006	100
	15/05/2006	8.6		21/04/2006	31
U6	18/05/2006	10	K10	21/04/2006	34

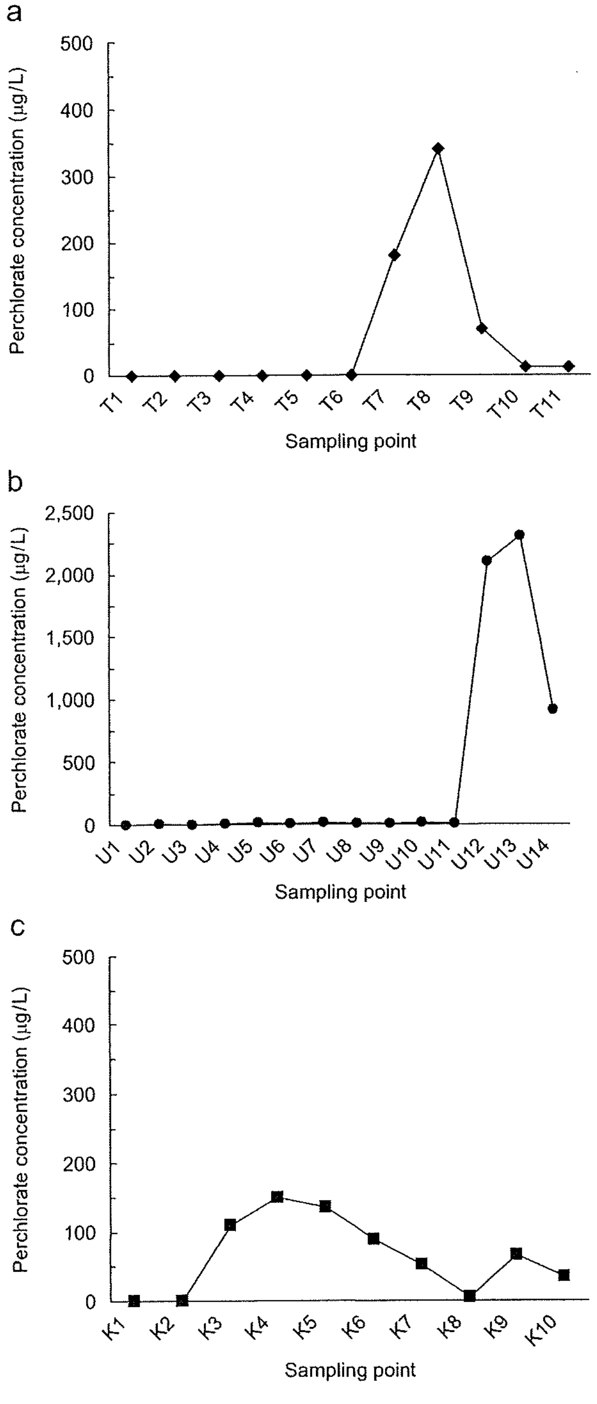

Fig. 3 – Profiles of perchlorate concentration (a) in the upper Tone River, (b) in the Usui River and (c) in the Karasu River. Perchlorate concentrations at U5, U14, K5 and K9 are average values of two samples taken on different sampling days.

concentrations in these two areas. The data of the effluents, the tributaries (or waterways) and the main rivers (i.e., the upper Tone River and Usui River) in the areas are plotted in Fig. 4. In the upper Tone River, the higher the perchlorate concentrations were, the higher the chlorate concentrations were. It was then inferred that the large amounts of perchlorate and chlorate were discharged into the upper Tone River. The maximum concentration of chlorate was 9000 µg/L, which was found in the tributary (or waterway). On the other hand, chlorate concentrations in the perchlorate discharge area of the Usui River were not very high and the maximum concentration was 46 µg/L in an effluent. However, chlorate concentration in the effluent was highest in the area; therefore, it was considered that chlorate was also discharged into the Usui River, although the amount of discharge was much smaller than that in the upper Tone River. In Japan, chlorate is set to be a complementary item for the drinking water quality standards (DWQSs) and its target value is 600 µg/L (Water Supply Division, Health Service Bureau, Ministry of Health, Labour and Welfare, Japan, 2003). Since chlorate has been proposed as a candidate contaminant to be included in the DWQSs, it is important to determine chlorate concentration, as well as perchlorate concentration, particularly in the upper Tone River.

3.2. *Perchlorate in middle and lower Tone River Basin*

Table 3 shows perchlorate concentrations in the middle and lower Tone River, Edo River, Iruma River, Ara River and the Musashi Channel. Perchlorate concentrations might be affected by daily variation because sampling dates were different among the samples.

After the confluence of the Karasu River, perchlorate concentration in the Tone River was 12 µg/L. Perchlorate concentrations were not much decreased in the middle and lower Tone River and were 3.4–18 µg/L. Also, perchlorate concentration in the Edo River, a branch of the Tone River, was similar to those in the middle and lower Tone River. In the case of the Ara River, perchlorate concentrations in the upstream area (Ar1–Ar3) were 0.54–0.73 µg/L. However, they increased after receiving water from the Tone River via the Musashi Channel. That is, perchlorate concentrations in the Ara River downstream of interflow point were 11–18 µg/L at Ar4–Ar7. Perchlorate concentration in the Iruma River, a tributary of the Ara River, was 1.2 µg/L. This suggested that a discharge source of perchlorate might exist along the Iruma River, but the amount of discharge was much smaller than those in the upper Tone River Basin. These results showed that, because of the discharge of perchlorate in the upstream area, perchlorate concentrations in the river waters in the middle and lower Tone River Basin were generally 10–20 µg/L.

3.3. *Effect of a firework display on perchlorate concentration in river water*

In Japan, firework displays are performed in many places, particularly in summer. Perchlorate salts are contained in fireworks, which are suspected to be another possible source of perchlorate in water (ITRC Perchlorate Team, 2005; The Department of Defense Environmental Data Quality Workgroup, 2006; Massachusetts Department of Environmental Protection, 2005). Table 4 shows the effect of a firework display on perchlorate concentration in the waters of the

Table 2 – Perchlorate and chlorate concentrations in effluents and tributaries (or waterways) in the discharging areas of perchlorate of the upper Tone River and Usui River

Sampling point	n^a	Sampling date	Perchlorate concentration (μg/L)	Chlorate concentration (μg/L)
Upper Tone River				
Effluent	1	22/04/2006	1100	7000
Tributary (or waterway) directly downstream of the outlet of the effluent	2	21/04/2006	44–980	19–840
	1	22/04/2006	1500	9000
Usui River				
Effluent	1	03/06/2006	15,000	46
Tributary (or waterway) directly downstream of the outlet of the effluent	1	18/05/2006	3500	9.7
	8	23/05/2006	1100–2600	12–16
	3	27/05/2006	2900–3200	15–16
	2	03/06/2006	3200–3900	17–19

[a] Number of samples analyzed.

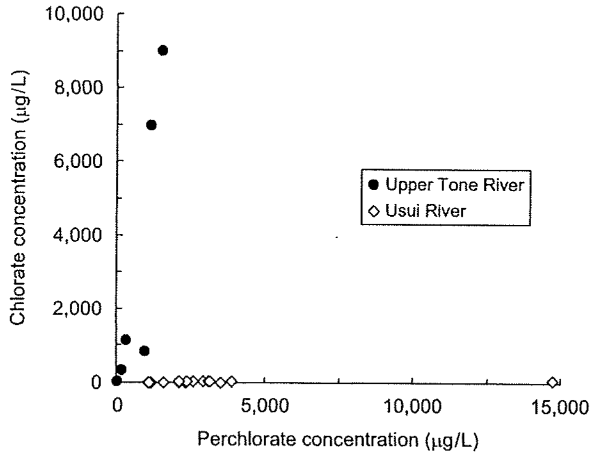

Fig. 4 – Relationships between perchlorate and chlorate concentrations in the discharging areas of perchlorate of the upper Tone River and Usui River.

Hirose River. The display was performed on a barge in the Hirose River, and a sampling point (H1) was located about 2 km downstream of the displaying area. Perchlorate was found at a high concentration (79 μg/L) just after a firework display. This was thought to be caused by the firework display because perchlorate concentration at the same point was low (0.39 μg/L) after 5 days from the display. From these results, it was found that a firework display, if performed in the river nearby, may cause a short-term increase in perchlorate concentration in river water.

3.4. *Perchlorate in tap water*

Fig. 5 shows perchlorate concentrations in tap water. The tap water samples were collected and classified into three groups. That is, the source waters for drinking water supply were taken from (a) the rivers in the upper Tone River Basin, (b) the rivers in the middle and lower Tone River Basin and (c) other basins. In the upper Tone River Basin, the points of water intake were more upstream of locations, where perchlorate was found in high concentrations in this study. At some water treatment plants, there were multiple water sources for a drinking water supply and some of them were river waters in the Tone River Basin. Also, at some service areas, treated waters of several treatment plants were blended and some of the treatment plants used river waters in the Tone River Basin as a water source. In such cases, the samples collected were classified into (a) or (b).

The number of the samples in group (c) was three. Two samples were collected from water taps in another basin in a metropolitan area, and one sample was collected from a water tap in a place outside of a metropolitan area. Perchlorate concentrations of the three samples were 0.16–0.87 μg/L. The number of samples in group (a) was 13. Ten, two and one samples were collected from water taps relatively near the places of the upper Tone, Usui and Karasu Rivers, respectively. Perchlorate concentrations of seven samples in group (a) were 0.06–0.55 μg/L. Perchlorate concentrations in the remaining six samples were 12–29 μg/L. At some service area in the upper Tone River Basin, treated waters using surface waters in the Tone River Basin for drinking water supply and those using ground water for drinking water supply were blended. In addition, some wells were located relatively near rivers in the Tone River Basin. Since all samples with high concentration of perchlorate were collected from water taps relatively near the places of the upper Tone River and perchlorate concentrations in the river waters in the Tone River Basin corresponding to group (a) were low, it was presumed that the waters in the wells located relatively near the upper Tone River might be contaminated by perchlorate. In case of group (b), the number of samples was 14. Nine, four and one samples were collected from water taps in Tokyo, Saitama and Chiba prefectures, respectively. Water sources for drinking water supply of most samples collected were the Ara and Edo Rivers. Perchlorate concentrations in the samples of group (b) were 0.19–37 μg/L. Except

Table 3 – Perchlorate concentrations in middle and lower Tone River Basin

Sampling point	Sampling date	Perchlorate concentration (μg/L)	Sampling point	Sampling date	Perchlorate concentration (μg/L)
Tone River			*Ara River*		
T12	01/04/2006	12	Ar1	31/03/2006	0.73
T13	01/04/2006	18	Ar2	31/03/2006	0.80
T14	29/03/2006	17	Ar3	19/04/2006	0.54
T15	16/04/2006	3.4	Ar4	31/03/2006	12
	18/04/2006	5.7	Ar5	19/04/2006	18
T16	12/04/2006	11	Ar6	19/04/2006	11
Edo River			Ar7	03/05/2006	13
E1	16/04/2006	14	*Musashi Channel*		
Iruma River			M1	19/04/2006	25
I1	19/04/2006	1.2			

Table 4 – Effect of a firework display on perchlorate concentration in river water[a]

Sampling point	Sampling date	Perchlorate concentration (μg/L)	Remark
Hirose River			
H1	26/08/2006	79	Just after fireworks display
	31/08/2006	0.39	Five days after fireworks display

[a] Fireworks display was performed on a barge in the Hirose River; H1 is about 2 km downstream of the display area.

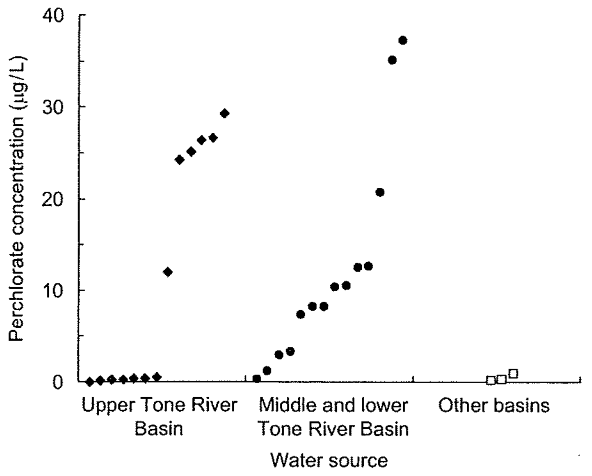

Fig. 5 – Ranges of perchlorate concentrations in tap waters drawn from different river basins.

for one sample, perchlorate concentrations were more than 1 μg/L, and those in seven samples were more than 10 μg/L. These results indicate that tap waters in the Tone River Basin were widely contaminated with perchlorate.

4. Discussions

The data of perchlorate concentrations in waters and soils in the US, which were detected at federal facilities such as Department of Defense (DoD), privately owned sites, sampling sites of Unregulated Contaminant Monitoring (UCM) program and sampling sites of Texas Technical University's study, were summarized by US EPA (2004). Maximum concentrations of perchlorate in the data were 811 μg/L in drinking water, 3,700,000 μg/L in ground water and 120,000 μg/L in surface water. There were also several sites at which concentrations of more than 1000 or 10,000 μg/L of perchlorate were found in ground and surface waters. In this study, perchlorate concentrations in the effluents discharging to the tributary (or waterway) of the upper Tone and Usui Rivers were 1100 and 15,000 μg/L, respectively. Comparing this study and the results in the US, it was thought that perchlorate concentrations in this study were comparable to high concentrations of perchlorate in the US, particularly in the Usui River. In relation to the type of facilities or industries of the sources of perchlorate, although the site with the maximum concentrations in both ground and surface waters in the summary of US EPA (2004) was a privately owned site of manufacturing perchlorate compounds in Henderson, Nevada (NV), other sites with extremely high concentrations of perchlorate were mainly the facilities using perchlorate-containing products or their manufacturers. In this study, the sources of perchlorate seemed to be the effluents from the perchlorate production industry and an industry employing electrolysis processes for a purpose other than its production. Thus, it was shown that one case of the sources of perchlorate in this study was similar to the case in Henderson, NV, and particularly the latter case, effluent of unintended production of perchlorate, has not yet been reported previously.

Next, the load of perchlorate in the upper Tone River Basin was roughly estimated using data obtained. Although the flow rates of the two effluents in the discharging areas of perchlorate of the upper Tone River and Usui River were not obtained in this study, the flow rates in the Tone, Karasu and Kanna Rivers at some points were obtained (Ministry of

Agriculture, Forestry and Fisheries, Japan). The flow rates of the upper Tone River and Karasu River on the sampling days were the difference between the flow rate of the Tone River at point near T12 and the sum of flow rates at a point near K7 and of the upper Kanna River, and that at a point near K7, respectively. In case on 10 April 2006, the sampling day of T10, T11 and K9 (Table 1), the flow rates of the Tone River at point near T12, the Karasu River at point near K7 and the upper Kanna River were 126, 9 and 4 m^3/s, respectively, and that of the upper Tone River calculated was 113 m^3/s. Perchlorate concentrations in the upper Tone River and Karasu River used were at T10 and T11, and at K9 and K10, respectively. As a result, the estimated loads of perchlorate discharged into the upper Tone River and Karasu River were 120–130 and 40–78 kg/day, respectively, although the temporal fluctuation of perchlorate concentration and river flow rate were not taken into consideration in calculation. Considering the results shown in Table 1, it was presumed that almost all perchlorate loads on each river was attributable to the two effluents discharged into the upper Tone River and Usui River, respectively. The estimated loads of perchlorate from the upper Tone River Basin were 110–170 kg/day, calculated from the flow rate at a point near T12 and perchlorate concentrations at T12 and T13. These values were not very different from the values obtained as the sum of the loads at the points of the upper Tone River and Karasu River.

Other than the source of perchlorate, there were several points at which perchlorate contamination in the Tone River Basin was similar to that in Henderson, NV. Firstly, as described above, since perchlorate was discharged in the upper Tone River Basin, surface waters in the Tone River Basin were entirely contaminated by perchlorate. In the case of Henderson, NV, perchlorate was discharged to the Las Vegas Wash and carried to downstream areas such as the Lake Mead and the lower Colorado River (US EPA Region 9, 2006). Secondly, surface waters in the Tone River Basin were used as source waters for drinking water supply in the basin. The number of water treatment plants whose source waters were surface waters in the Tone River Basin and their perchlorate concentrations were relatively high in this study, around 30. The estimated total population supplied by these treatment plants was around 20 million. In the case of Henderson, NV, the water in the lower Colorado River was used as source waters for drinking water supply and the population supplied was similar to that in the Tone River Basin. Also, both the surface waters in the Tone River Basin and the water in the lower Colorado River were used for irrigation; thus, it was thought that many more people might ingest foods produced in both these areas. However, it is of note that the rivers in the Tone River Basin flowed into the metropolitan area in Japan.

After perchlorate contamination became apparent, actions to reduce perchlorate discharge and remediate the area contaminated by perchlorate were conducted in Henderson, NV. It is difficult to remove perchlorate by conventional water treatment processes because perchlorate is highly soluble and stable in water. So, it is most preferable to remove perchlorate at its sources. By US EPA Region 9 (2006), it was reported that perchlorate concentrations in surface waters such as the Las Vegas Wash, the Lake Mead and the lower Colorado River declined by 85%, 70% and 60% since the treatment of perchlorate begun in 1999. Perchlorate in ground water in the area has also been removed. With the reference of the strategies in Henderson, NV, it is desired that perchlorate control strategies be conducted rapidly in the Tone River Basin.

Lastly, we discuss the perchlorate concentration in drinking water in the Tone River Basin. It is important to consider the amount of iodine uptake in daily life for the evaluation of perchlorate effect since perchlorate is known to inhibit iodine uptake by the thyroid gland (Greer et al., 2002; National Research Council, 2005). In Dietary Reference Intakes for Japanese, 2005 (Ministry of Health, Labour and Welfare, Japan, 2005), the recommended iodine uptake for a Japanese adult is 150 μg/day. Iodine is found in high concentrations in marine foods, particularly in seaweed (Katsura and Nakamichi, 1960; Muramatsu and Omomo, 1988); in general, Japanese people eat much more marine foods compared with people in other regions. The iodine uptake of Japanese people who regularly eat marine foods in their daily diet is estimated to be 500–3000 μg/day (Ministry of Health, Labour and Welfare, Japan, 2005). Thus, it is considered that Japanese people take sufficient iodine if they regularly eat marine foods.

Although the number of tap water samples and the periods of sampling were limited, perchlorate concentrations in several tap water samples were higher than 24.5 μg/L, the DWEL for perchlorate specified by the US EPA (2005a). NAS adopted 10 as an uncertainty factor in establishing the RfD for perchlorate (0.7 μg/kg/day) (National Research Council, 2005). Japanese people generally take more iodine in daily life than the recommended value, as described above. Thus, it is thought that Japanese people may not be affected physiologically shortly after drinking tap water with a perchlorate concentration of higher than 24.5 μg/L. On the other hand, perchlorate concentrations in rivers are unintentionally increased by explosives (e.g., fireworks) over a short period, and those in drinking water may also increase as a result. Also, perchlorate may be ingested via foods and beverages. Furthermore, in a recent study on perchlorate and iodine levels in urine of men and women $\geqslant 12$ years of age in the US and on their serum thyroid hormone levels, it was reported that the serum thyroid levels of women, particularly those with low iodine levels, might be affected by perchlorate exposure (Blount et al., 2006). Of course, there is a possibility that some may not ingest sufficient amount of iodine in daily life in Japan. Considering all the various factors together, it is therefore desired to reduce perchlorate concentration in drinking water in the Tone River Basin. Currently, the data of perchlorate concentration in drinking water in the Tone River Basin are limited; thus, it is necessary to collect such data more in details.

5. Conclusions

Perchlorate was found at high concentrations in the upper Tone River and Usui River. The maximum concentrations in the upper Tone River and Usui River were 340 and 2300 μg/L, respectively.

The possible sources of perchlorate in these two rivers were attributable to industrial effluents. In 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 were 44–1500 μg/L. In the Usui River, perchlorate concentration in an effluent was 15,000 μg/L and its concentrations in a tributary (or waterway) directly downstream of the outlet of the effluent were 1100–3900 μg/L.

Both perchlorate and chlorate were found at high concentrations in the discharging area of perchlorate of the upper Tone River, and the maximum concentration of chlorate was 9000 μg/L. On the other hand, chlorate concentrations were not remarkably high in the discharging area of perchlorate of the Usui River.

Because of the discharge of perchlorate in the upper Tone River Basin, perchlorate concentrations in the river waters in the middle and lower Tone River Basin were generally 10–20 μg/L.

Perchlorate concentrations in tap water whose source waters were coming from sources other than the Tone River Basin were 0.16–0.87 μg/L. Those in tap water with source waters from the upper Tone River Basin were 0.06–0.55 μg/L for seven samples and 12–29 μg/L for the remaining six samples.

Perchlorate concentrations in tap water drawn from the middle and lower Tone River Basin were 0.19–37 μg/L. Except for one sample, perchlorate concentrations were more than 1 μg/L, and they were more than 10 μg/L for half the samples. Tap waters in the Tone River Basin were widely contaminated with perchlorate.

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〈論　文—Original Paper〉

利根川流域の浄水場における過塩素酸イオンの実態調査

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Occurrence of Perchlorate in Water Purification Plants in Tone River Basin

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Abstract

The occurrence of perchlorate in water purification plants in the Tone River Basin was investigated. The sampling of raw, processed and treated water at the plants was conducted between September and October 2006. Perchlorate concentrations in raw surface water taken from the upper, middle and lower Tone River Basin were 0.09-0.82, 0.15-15 and 0.15-2.7 $\mu g \cdot l^{-1}$, respectively. Perchlorate concentrations in the upper Tone River Basin were low because the intake points were upstream of the discharge points of perchlorate. Perchlorate concentrations in the lower Tone River Basin were lower than those in the middle Tone River Basin. However, many of the perchlorate concentrations in the lower Tone River Basin were higher than those of the upstream of the discharge points of perchlorate; thus, it was found that perchlorate contamination of the surface water of the Tone River Basin was widespread. Perchlorate concentrations in raw ground water were < 0.05-40 $\mu g \cdot l^{-1}$, and were high at some water purification plants. The shorter the distance between a well and the Tone River, the higher the pechlorate concentration in the well. Perchlorate concentrations in treated surface water of the upper, middle and lower Tone River Basin were 0.12-0.86, 0.22-14 and 0.23-1.8 $\mu g \cdot l^{-1}$, respectively. Perchlorate concentrations in treated ground water were 0.08-24 $\mu g \cdot l^{-1}$. It was shown, in this study, that perchlorate concentrations in treated water were lower than 24.5 $\mu g \cdot l^{-1}$, the Drinking Water Equivalent Level (DWEL) of perchlorate defined by the United States Environmental Protection Agency (USEPA). From the comparison of perchlorate concentrations in raw and treated water at the same water purification plants, it was confirmed that perchlorate was not removed by either conventional or ozone/biological activated carbon (BAC) processes.

Key words: perchlorate, chlorate, water purification plant, Tone River Basin

1. はじめに

過塩素酸イオンは，水溶性の陰イオンで，水中では移動性が高く，非常に安定した物質である1-3)。通常，過塩素酸イオンは，過塩素酸塩(過塩素酸ナトリウム，過塩素酸アンモニウム，過塩素酸カリウム等)あるいは過塩素酸の形態で生産・使用されている1-3)。例えば，2004年の過塩素酸ナトリウムの推定国内生産量は1,600 tである4)。過塩素酸塩の場合，主な使用用途としてロケットやミサイルの推進剤が知られ1-3)，それ以外にも，火薬，花火，安全マッチ，エアバッグ等，様々な製品に使用されている1-3)。一方，過塩素酸イオンは天然起源でも存在している。チリのアタカマ砂漠にある硝酸ナトリウム堆積物には過塩素酸塩が含まれている1)。また，最近，過塩素酸イオンは大気中の光化学反応によっても生成することが報告された5)。

過塩素酸イオンは，甲状腺におけるよう素の取り込みを抑制する物質である1,3,6)。2005年2月，米国科学アカデミー(National Academy of Sciences，NAS)は，過塩素酸イオンの参照用量(Reference Dose，RfD)として0.7 $\mu g \cdot kg^{-1} \cdot day^{-1}$を勧告した6)。同月，米国環境保護庁(United State Environmental Protection Agency，USEPA)はNASの過塩素酸イオンのRfDを採用し，飲料水等価濃度(Drinking Water Equivalent Level，DWEL)として24.5 $\mu g \cdot l^{-1}$を公表した7)。DWELとは，70 kgの人が1日2 l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である。しかし，現段階では，基準となる最大許容濃度(Maximum Contaminant Level)は設定されていない。また，世界保健機関も飲料水水質ガイドラインを示していない。一方，米国の幾つかの州では，1~18 $\mu g \cdot l^{-1}$

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の範囲で過塩素酸イオンの勧告レベルを設定している[1,8-11]。飲料水基準に指定されている場合(マサチューセッツ州：2 μg·l^{-1})[9]，あるいは検討されている場合(カリフォルニア州：6 μg·l^{-1}，ニュージャージー州：5 μg·l^{-1})[10,11]もある。

1997年，カリフォルニア州保健局が，イオンクロマトグラフ(Ion Chromatograph，IC)を用いた，以前の方法より高感度の過塩素酸イオン分析方法を開発し，同州の地下水や河川水から過塩素酸イオンを検出して以来[12]，米国各地の環境水および水道水中から，過塩素酸イオンの存在が報告されている[3,13,14]。また，過塩素酸イオンは，米国のレタス[15]や牛乳[15,16]からも検出されている。これまで過塩素酸イオン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，世界各国の食品・飲料中の過塩素酸イオン濃度を調査した研究の中で，日本の食品・飲料中からも過塩素酸イオンが検出された[17]。また，日本のミルクから過塩素酸イオンが平均濃度9.39±2.71 μg·l^{-1} (試料数：54，±：標準偏差，濃度範囲：5.47〜16.40 μg·l^{-1})で検出され，この濃度は2004年の米国食品医薬品局の調査による米国のミルク中の平均濃度5.74±1.98 μg·l^{-1} (試料数：104，±：標準偏差，濃度範囲：1.5〜11.3 μg·l^{-1} (3試料からは過塩素酸イオンは検出されていないが平均濃度の計算には定量下限の半分値を採用したため，最小濃度は定量下限の半分の濃度を表示))より高い値であったと報告された[18]。一方，水中の場合，著者らが，全国12浄水場の原水・浄水中の過塩素酸イオン濃度を測定したところ，原水で4試料，浄水で5試料から10 μg·l^{-1}を超えて過塩素酸イオンが検出された[19]。また，利根川流域を対象に過塩素酸イオンの実態調査を行い，同流域に過塩素酸イオンの発生源が存在すること，同流域の河川水，水道水中に過塩素酸イオンが存在していることを報告した[20]。しかし，同流域の浄水場の実態について，その詳細は明らかとはなっていない。

そこで，本研究では，利根川流域の浄水場を対象に，過塩素酸イオンの実態調査を行った。そして，利根川流域での濃度分布および浄水処理工程における挙動についても検討した。このとき，塩素酸イオンについても測定した。

2．実験方法

2.1　水試料の採取および前処理

Fig. 1に利根川流域の地図を示す。浄水場の水試料(原水，工程水，処理水)は，2006年9〜10月，利根川流域の42浄水場から採取した。対象浄水場は，利根川流域の河川水または地下水を原水としている浄水場とし，各浄水場はPi (i=1〜42)浄水場とした。水試料数は原水が83，工程水が39，浄水が50で，合計172であった。採水地点が取水口〜着水井の水試料を原水とした。対象浄水場は便宜上，上流域，中流域，下流域に分類した(**Fig. 1**)。各区分における浄水場数および水試料数を**Table 1**に示す。一部の浄水場では原水が複数あること(同一原水で取水口〜着水井の水試料を複数採取した場合も原水が複数あるとした)，複数の浄水場で取水口が同じであるためこれら浄水場で原水を1試料だけ採取した場合があること，同一浄水場においても系列別(例えば通常処理系と高度処理系)に水試料を採取した場合があること，工程水は一部の浄水場のみから採取したこと等により，浄水場数と各水試料の数は一致していない。採取した水試料は，冷蔵輸送した後，冷蔵庫に保存した。全ての水試料について，ジエチル-*p*-フェニレンジアミン(関東化学製)により残留塩素の存在を確認し，存在していた場合には塩化アンモニウム(Aldrich製)により遊離塩素を結合塩素へと変換させた。結合塩素へと変換させた理由は，後述するように，過塩素酸イオンおよび塩素酸イオン濃度の測定はIC/タンデム質量分析計(Tandem Mass Spectrometer，MS/MS)を用いて行ったが，ICのオートサンプラーには冷却装置が装備されていないため，試料をオートサンプラーに準備してから測定するまでの間に，遊離塩素の分解による過塩素酸イオン，塩素酸イオンの生成を防ぐためである[3,21]。ただし，塩化アンモニウムを添加したのは，試料採取後，2〜3週間程度経った後であり，冷蔵保存中における遊離塩素の分解については考慮していない。ただし，本研究での対象イオンは，水中で非常に安定であるため，保存した期間内での分解はないと考えられる。水試料は，孔径0.2 μmの親水性polytetrafluoroethylene (PTFE)フィルター(Advantec Toyo製)でろ過した後に過塩素酸イオンの測定を行った。本研究でのICの分離条件の場合，塩素酸イオンは，塩化物イオン，硫酸イオンの共存によりMS/MSでのイオン化が阻害された[22]。しかし，試料を5倍以上希釈した場合には，これら共存イオンによるイオン化阻害の影響を受けなかったため，塩素酸イオン濃度の測定は試料を5倍以上希釈した後に行った[22]。ただし，一部の試料は，5倍希釈した後の塩素酸イオン濃度が定量下限値未満となったため，そのような試料については，前処理としてOnGuard II Ba/Ag/Hカートリッジ(Dionex製)を用いて水試料中のハロゲン化物イオンおよび硫酸イオンの除去を行った。

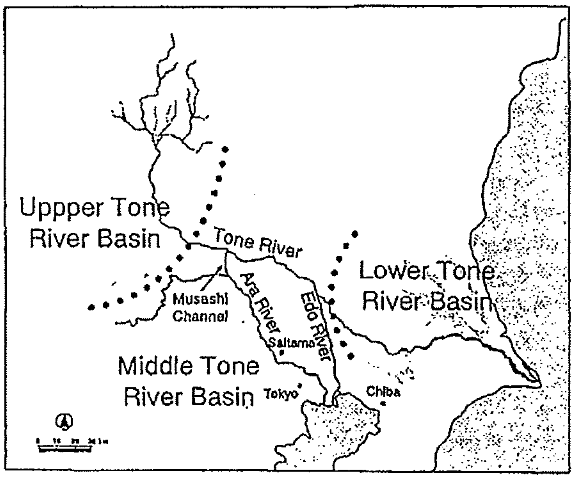

Fig. 1　Map of the Tone River Basin.

Table 1　Numbers of water purification plants and samples in the upper, middle and lower Tone River Basin.

Division of the Tone River Basin	Number of water purification plants	Number of samples analyzed		
		Raw water	Process water	Treated water
Upper basin	11	6[a], 39[b]	-	6[a], 5[b]
Middle basin	16	19[a]	32[a]	22[a]
Lower basin	15	19[a]	7[a]	17[a]

Samples whose raw waters were a) surface water and b) ground water.

2.1.2 分析方法

標準液や溶離液の作成等，本研究で使用した水は，全てMillipore製のGradient A10により精製した超純水である。過塩素酸イオン，塩素酸イオン濃度の測定には，IC/MS/MSを用いた。過塩素酸イオン濃度の測定では，内部標準物質として$^{18}O_4$-過塩素酸ナトリウム(Cambridge Isotope Laboratories製)を使用した。内部標準物質は，水試料をろ過した後に添加した。ICはDionex製のICS-2000を使用した。ガードカラムはIonPac AG20 (2 x 50 mm，Dionex製)を，分離カラムはIonPac AS20 (2 x 250 mm，Dionex製)を，サプレッサーはASRS ULTRA II (2 mm，Dionex製)を使用した。溶離液は水酸化カリウム(potassium hydroxide，KOH)を用いた(流量：0.25 $ml \cdot min^{-1}$)。グラディエント条件は，10 mM KOH (0 min) → 80 mM KOH (22 min)とした。ポストカラムで，アセトニトリル/水(9：1 v/v)溶液を流量0.2 $ml \cdot min^{-1}$で加えた。試料注入量は100 μlとした。MS/MSはApplied Biosystems製のAPI 3200QTrapを使用した(イオン源：ターボイオンスプレー)。Multiple Reaction Monitoring (MRM)モードで測定し，MRMは，過塩素酸イオンについては99/83 (定量用)および101/85 (確認用)を，$^{18}O_4$-過塩素酸イオンについては107/89を，塩素酸イオンについては83/67を選択した。定量下限値は，両物質ともに0.05 $\mu g \cdot l^{-1}$であった。

3. 結果および考察

3.1 原水中の過塩素酸イオン濃度

Fig. 2に，原水中の過塩素酸イオン濃度の測定結果を示す。表流水の場合，原水中の過塩素酸イオン濃度は，上流域，中流域および下流域でそれぞれ0.09～0.82，0.15～15および0.15～2.7 $\mu g \cdot l^{-1}$であった。

本研究での分類では，上流域において，利根川沿いとその支川沿いのそれぞれに事業場排水由来の過塩素酸イオンの発生源が存在する20)が，上流域では過塩素酸イオン濃度が低かった。これは，取水地点が過塩素酸イオンの発生源よりもより上流であったためと考えられた。一方，発生源より下流に位置する中流域，下流域では，多くの試料について上流域の試料より濃度が高かったことから，発生源の影響を受けて原水中に過塩素酸イオンが広く存在していることが示された。ただし，中・下流域でも，上流域の発生源の影響を受けていない利根川の支川を原水としている場合，過塩素イオン濃度は他の原水に比べて低かった。また，中流域と下流域を比較すると，中流域において濃度が高い傾向にあった。これは，過塩素酸イオンは水中では移動性が高く，安定であることから，後述するように他の表流水による希釈の結果と考えられた。

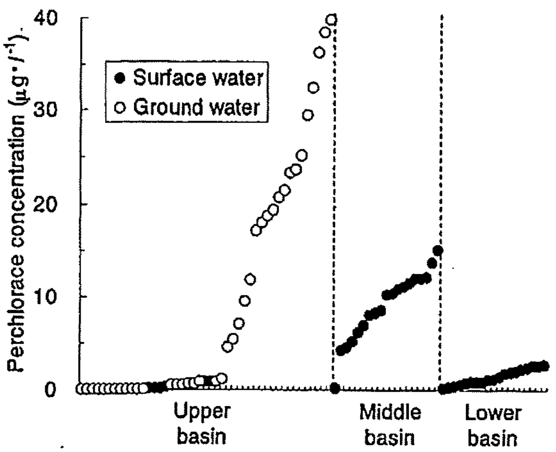

Fig. 2 Perchlorate concentrations in raw water (expressed in ascending order in each category).

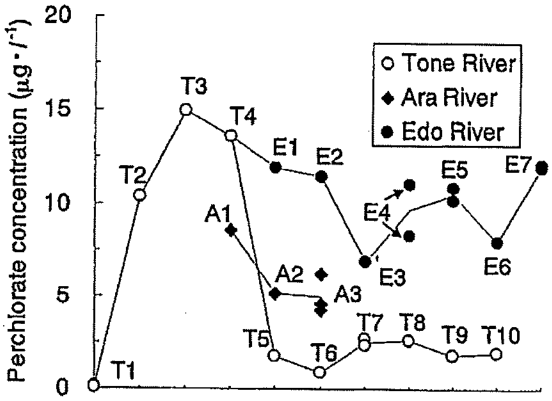

Fig. 3 Profiles of perchlorate concentrations in raw waters taken from the Tone, Ara and Edo Rivers.

上流から下流への過塩素酸イオン濃度の変化についてより詳細に検討するため，Fig. 2の結果の中から，原水が利根川，荒川，江戸川である浄水場の原水について取り上げた。Fig. 3に，これら原水中の過塩素酸イオン濃度の結果を示す。利根川，荒川，江戸川で，取水地点の位置により上流から下流に向けて，それぞれT1～T10，A1～A3，E1～E7とした。図中，上流域に該当するのはT1，中流域に該当するのはT2～T4，A1～A3およびE1～E7，下流域に該当するのはT5～T10であった。江戸川は利根川の派川であるため両河川はT4→E1を線で結んだが，荒川は利根川の派川ではなく武蔵水路を通じて利根川の水が合流しているという関係であるため両河川は線で結ばず表示した。T4の採水日は10月18日で，それ以外は9月19～28日の間であった。また，取水地点の右岸と左岸は区別していない。同一浄水場で原水が取水口と着水井等複数ある場合等を含めて，全ての結果をプロットした。

原水が利根川の下流(江戸川と分岐した後のT5～T10)，江戸川，荒川である浄水場の原水中の過塩素酸イオン濃度は，それぞれ0.90～2.7，6.9～12，4.2～8.5 $\mu g \cdot l^{-1}$であった。すなわち過塩素酸イオン濃度は，江戸川，荒川，利根川の下流の順に高かった。この結果について，上流域の2つの過塩素酸イオン発生源はいずれも事業場排水であるため，その河川への流入量は日によらず大きくは変わらない(同程度のオーダー)と考えられることから，各地点の採水日における河川の日平均流量を用いて，上述した希釈の点から考察した23,24)。なお，以下の考察は，利根川上流域の過塩素酸イオン発生源の影響を受けていない河川水には過塩素酸イオンは含まれていないと仮定している。この点は網羅的に検討してはいないが，本調査での渡良瀬川の支川や鬼怒川，以前の調査での利根川の水と合流する前の荒川の場合，過塩素酸イオン濃度は利根川および分岐した河川よりも非常に低かったことから，この仮定を用いた。

利根川の場合，過塩素酸イオン濃度は，発生源より上流のT1では低く，発生源より下流であるT2で上昇し，江戸川と分流後のT5以降で大きく低下した。利根川は，中流域において渡良瀬川と合流し，そのすぐ下流で江戸川と分流し，その後，鬼怒川等複数の支川と合流する。利根川が渡

良瀬川と合流するのは左岸側で，江戸川と分流するのは右岸側である。そこで，渡良瀬川の水は江戸川にはほとんど流入せず，分流後の利根川に流入していると仮定すると，希釈により23)，合流前の過塩素酸イオン濃度(T2～T4の過塩素酸イオン濃度を計算に使用)は，T5～T10では3～5 μg·l^{-1}と計算された。この濃度範囲は実際より若干高いが，大きくは外れてはいないため，利根川下流での過塩素酸イオン濃度の低下は希釈によるものと解釈できた。

一方，T4とT5の間で利根川から分流した江戸川の場合，過塩素酸イオン濃度は，ばらつきはあるものの分流前の利根川の濃度に比べて大きくは低下しなかった。支川との合流による江戸川流量の増加は23)，利根川に比べて大きくはなかった。上述したように，江戸川は，渡良瀬川の利根川への合流による希釈の影響をほとんど受けなかったとすると，**Fig.** 3の結果は，河川流量が大きくは変化しなかったためと考えられた。

また，武蔵水路を通じて利根川の水が合流している荒川の場合，過塩素酸イオン濃度は分岐前の利根川における濃度より低かった。これは，利根川の下流の場合と同様に希釈による結果と考えられた。希釈によって23,24)，合流前の過塩素酸イオン濃度(T2～T4の過塩素酸イオン濃度を計算に使用)は，A1～A3では2～12 μg·l^{-1}と計算され，この濃度範囲は，実測値に概ね近い範囲にあった。

次に地下水について見ると，原水中の過塩素酸イオン濃度は< 0.05～40 μg·l^{-1}であった。いずれの浄水場も複数の井戸から取水した地下水を原水としているが，過塩素酸イオン濃度が高かった地下水は，限られた数の浄水場のものであった。**Fig.** 4に，過塩素酸イオン濃度が高い値を示した浄水場を対象に，井戸と利根川との距離と過塩素酸イオン濃度との関係を示す。過塩素酸イオン濃度が高かった浄水場のみを対象とした理由は，これら浄水場は他の浄水場に比べて隣接しており，利根川との関連性について検討するには適していると考えられたためである。各プロットは，井戸の深さで分類した。

地下水中の過塩素酸イオン濃度は，井戸と利根川との距離が近い場合において，より高い傾向にあったことから，両者の間に関連性が認められた。一方，井戸の深さが100 m以上の場合でも6つの水試料で過塩素酸イオン濃度が15 μg·l^{-1}を超えていたこと，井戸の深さが120 mにおいて過塩素酸イオン濃度が40 μg·l^{-1}であったことから，井戸の深さと過塩素酸イオン濃度の関連性は認められないことがわかった。これらの結果から，本調査における地下水中の過塩素酸イオンは，利根川を経由した発生源由来であると考えられた。ただし，地下水が井戸の最深地点以外からも取水されている可能性もあるため，過塩素酸イオンが地中のどの程度の深さまで存在しているかについては，明らかにはできなかった。

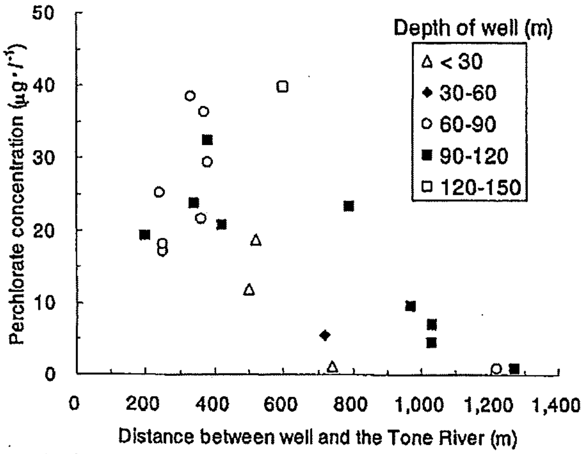

Fig. 4　Relationship between distances, between wells and the Tone River, and perchlorate concentrations in the wells.

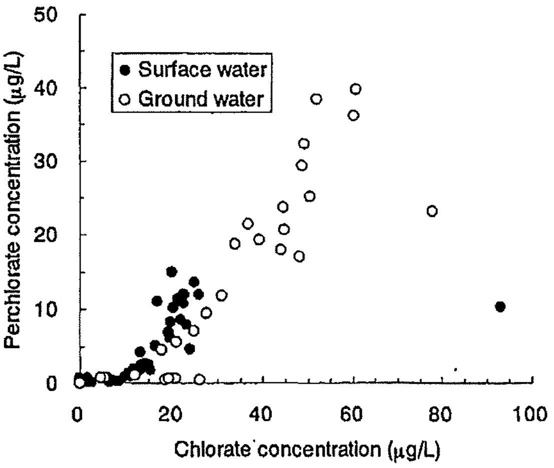

Fig. 5　Relationship between chlorate and perchlorate concentrations in raw water.

過塩素酸イオンの発生源のうちの一つは，塩素酸イオンの発生源でもある20)ことから，原水中の塩素酸イオン濃度について過塩素酸イオン濃度と関連付けて検討した(**Fig.** 5)。次亜塩素酸ナトリウム溶液(次亜)中には塩素酸イオンが含まれているため，その影響を防ぐため，残留塩素が検出された原水は除外した。**Fig.** 5より，原水中の過塩素酸イオン濃度と塩素酸イオン濃度の間に関連性が認められ，過塩素酸イオン濃度が高い試料は塩素酸イオン濃度も高い傾向にあることが示された。また，本調査では，概して，塩素酸イオン濃度は過塩素酸イオン濃度より2倍程度高かった。図中，2つのプロット(特に原水が表流水である試料)は，他のプロットに比べて過塩素酸イオン濃度に対する塩素酸イオン濃度が高かった。この理由は，本研究では明確にはできなかったが，いずれの場合も採水地点から判断すると，他の地点同様に発生源の影響によるものと考えられた。ところで，塩素酸イオンは，水道では水質管理目標設定項目に指定されており(目標値600 μg·l^{-1})25)，水質基準項目への格上げが検討されている26)。本調査では，原水中の塩素酸イオン濃度は4試料について目標値の10%を超え，最高93 μg·l^{-1}であった。後述するように，浄水中の塩素酸イオン濃度は次亜による影響が知られているが，利根川流域の浄水場については，原水中の塩素酸イオンの影響も無視はできない場合があると考えられた。

3.2　浄水中の過塩素酸イオン濃度

Fig. 6に，浄水中の過塩素酸イオン濃度の測定結果を示す。表流水の場合，過塩素酸イオン濃度は，上流域，中流域および下流域で，それぞれ0.12～0.86，0.22～14および0.23～1.8 μg·l^{-1}であった。上流域では低く，中流域と下流域を比べると中流域の方が高いという傾向は，原水の場合と同様であった。一方，地下水の場合，過塩素酸イオン濃度は0.08～24 μg·l^{-1}であった。浄水場によっては，全ての

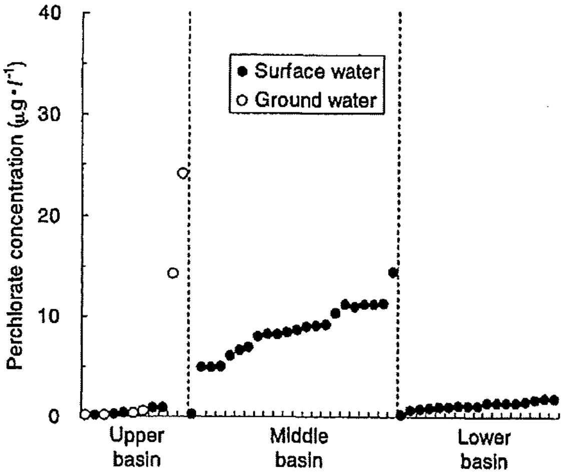

Fig. 6 Perchlorate concentrations in treated water (expressed in ascending order in each category).

井戸の地下水で< 0.05 μg·l^{-1}であった場合もあったが，浄水からは低いながらも過塩素酸イオンは全ての浄水から検出された。次亜中には過塩素酸イオンが含まれていることが知られており[3]，この結果は，次亜の影響と推測された。

また，過塩素酸イオン濃度が高い地下水とそれ程は高くない地下水とが混合・使用されているため，原水中の過塩素酸イオン濃度はUSEPAが示すDWEL(24.5 μg·l^{-1})を超えている場合があったが，浄水中ではDWELより低い値であった。著者らの以前の調査では[20]，利根川流域の複数の給水栓水中の過塩素酸イオン濃度はDWELを超え，最高濃度は37 μg·l^{-1}であった。水試料の収集時期は，以前の調査では2～6月，今回の調査では9～10月であり，今回の試料の方がより水量の多い時期に収集したためと考えられた。このため，今後，水量の少ない時期においても同様の調査を行い，利根川流域の浄水場における過塩素酸イオン濃度分布の季節変動について把握する必要があると考えられた。

ところで，よう素は，海産物(特に海藻類)に多く含まれ[27,28]，海産物を含む日本人の食事からのよう素の摂取量は，1人1日当たり0.5～3.0 mgと推定されている[29]。この値は成人の1人1日当たりのよう素の推奨摂取量(150 μg)の数倍以上である[29]。日本人の場合，日常の食事で海産物を摂取していれば，水道水中の過塩素酸イオン濃度がDWELを超えたからと言って，直ちに何らかの影響が現れるとまでは言えないと考えられた。

一方，浄水中の塩素酸イオン濃度は1.8～430 μg·l^{-1}であり，次亜の影響で濃度が上昇していることが確認された。ただし，この結果には塩素を使用している浄水場の結果も含まれている(塩素の使用によって塩素酸イオン濃度が上昇するかについては不明)。このとき，7試料が200 μg·l^{-1}を，2試料が300 μg·l^{-1}を，1試料が400 μg·l^{-1}を超えていたが，目標値600 μg·l^{-1}を超えるものはなかった。

3.3 浄水処理工程における過塩素酸イオンの挙動

Fig. 7に，原水と浄水が1対1に対応する浄水場の原水，浄水中の過塩素酸イオン濃度を示す。本研究で該当する1対1に対応する浄水場とは，①原水の種類が1つで，原水，浄水を採取した場合(原水の種類は1つであるが，取水口と着水井等異なる地点から複数の原水を採取した場合は，平均値を採用)，②異なる種類の原水が複数あるが，これらが混合した後の原水と浄水を採取した場合，③異なる種類の原水が複数あり，各原水の処理系列は別ではあるが，各処理系列で原水，浄水を採取した場合，④異なる処理方式(通常処理と高度処理)があり，各処理方式での浄水を採取した場合(同じ処理方式の浄水を複数採取した場合は平均値を採用)である。③，④では，Fig. 7において，PiA，PiB (i=1～42)と表示した。また，④では，各処理方式の原水の種類は，同じ場合と異なる場合があり，異なる場合は各原水を採取した。原水，浄水中の過塩素酸イオン濃度を比較

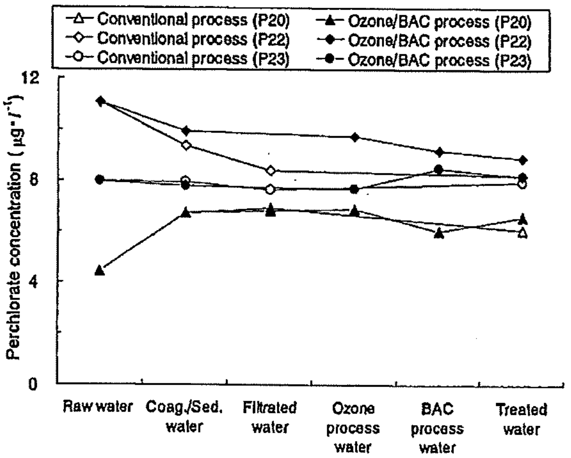

Fig. 8 Profiles of perchlorate concentrations in conventional and ozone/biological activated carbon processes.

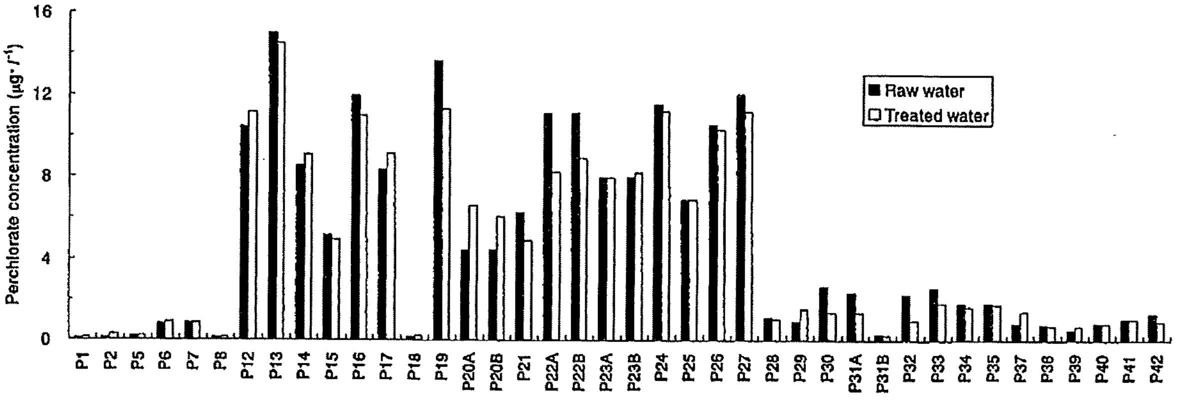

Fig. 7 Comparison of perchlorate concentrations in raw and treated waters (when samples were collected from different treatment systems at Plant Pi (i=1-42), each treatment system at Plant Pi was expressed as Plants PiA and PiB).

すると，P19，P22A，P22B，P32浄水場のように原水の方が若干高い場合，P17，P20A，P20B，P37浄水場のように浄水の方が若干高い場合があるが，ほとんどの浄水場では同程度であった。Fig. 8に，P20浄水場，P22浄水場およびP23浄水場について，通常処理工程，高度処理(オゾン/生物活性炭(Biological Activated Carbon，BAC)処理)工程での過塩素酸イオンの挙動を示す。通常処理では，工程順に原水，沈澱水，ろ過水，浄水の結果を，オゾン/BAC処理では，同様に，原水，沈澱水，ろ過水，オゾン処理水，BAC処理水，浄水の結果を示している。原水を取水口と着水井等の複数地点で採取した場合，沈澱処理水やろ過処理水を複数の池から採取した場合は平均値を採用した。また，オゾン/BAC処理において中間塩素処理を行っている浄水場では，中間塩素処理前後のろ過処理水を採取した場合があるが，このときは中間塩素処理前のろ過処理水の値を採用した。なお，中間塩素処理前後の過塩素酸イオン濃度はほぼ同じであった。P20およびP22浄水場では，原水と沈澱処理水との間で過塩素酸イオン濃度にばらつきがあったものの，3浄水場ともに，通常処理系，オゾン/BAC処理系のいずれにおいても，処理工程で過塩素酸イオン濃度はほとんど変化しなかった。オゾン/BAC処理では，BAC処理後の沈澱処理水やろ過処理水を採取した場合もあるが，これらの処理水でも，過塩素酸イオン濃度に変化は認められなかった(Fig. 8では省略)。以上の結果から，過塩素酸イオンは水溶性で安定であるため，通常処理やオゾン/BAC処理では除去困難であることが確認された。また，次亜注入による過塩素酸イオン濃度への影響も小さいことが確認された。実用化されている，浄水処理を目的とした過塩素酸イオンの除去法としては，イオン交換や嫌気性の生物処理が知られているが[30]，これらの処理を実際に導入することは費用の面から考えると困難である。また，この報告書では，粒状活性炭(Granular Activated Carbon，GAC)についても採り上げているが，通常のGACによる過塩素酸イオンの除去性は低く，GACに四級アミンを結合させイオン交換機能を持たせた場合には除去性が高くなると述べている[30]。これらのことから，現状では浄水処理での過塩素酸イオンの除去は困難であると考えられた。

4．まとめ

1) 原水中の過塩素酸イオン濃度は，表流水の場合，上流域，中流域および下流域でそれぞれ0.09〜0.82，0.15〜15および0.15〜2.7 μg·l^{-1}であった。中流域より下流域において過塩素酸イオン濃度が低い傾向にあったが，過塩素酸イオンは利根川流域の原水中に広く存在していることが示された。また，本調査では，利根川が分岐した後の河川水を原水としている浄水場の原水中の過塩素酸イオン濃度は，江戸川，荒川，利根川の順に高かった。

2) 地下水の場合，原水中の過塩素酸イオン濃度は< 0.05〜40 μg·l^{-1}で，限られた数の浄水場において濃度が高かった。過塩素酸イオン濃度が高かった浄水場の過塩素酸イオン濃度は，井戸と利根川との距離が近い場合に，より高い傾向にあった。一方，井戸の深さが100 m以上でも，6つの試料で過塩素酸イオン濃度が15 μg·l^{-1}を超えており，井戸の深さと過塩素酸イオン濃度との関連性は認められなかった。

3) 浄水中の過塩素酸イオン濃度は，表流水の場合，上流域，中流域および下流域でそれぞれ0.12〜0.86，0.22〜14および0.23〜1.8 μg·l^{-1}であった。地下水の場合，0.08〜24 μg·l^{-1}であった。本調査において，全ての浄水中の濃度はUSEPAが示すDWEL (24.5 μg·l^{-1})より低かった。

4) 過塩素酸イオンは，通常処理および高度処理(オゾン/BAC処理)のいずれにおいても除去困難な物質であることが確認された。

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