

Fig. 1 – Coagulant properties determined by the ferron method (A and C) and membrane filtration fractionation (B). Coagulants in Panels A and B were used for the first set of experiments while those in Panel C were used in the second set of experiments. The standard deviations for the determination of Ala contents (%) were <0.1%.

3.2. First set of experiments

3.2.1. Dissolved residual aluminum and DOC removal in jar tests

We determined dissolved residual aluminum concentration as a function of coagulation pH for PACI-71s, PACI-51s, AlCl₃, and alum (Fig. 2). PACI-71s showed the lowest dissolved residual aluminum concentration at both neutral and weakly alkaline pH, followed by PACI-51s. Yan et al. (2008a) shows that at neutral pH the dissolved residual aluminum concentrations are the same for PACIs with different basicities (0–67%), as are the minimum dissolved residual aluminum concentrations attained by adjusting the pH. In contrast, in

our study we found that the dissolved residual aluminum concentration decreased with increasing basicity to 71% at both neutral and alkaline pH. In their other data (Yan et al., 2007), 83%- and 73%-basicity PACIs shows lower residual aluminum concentration than 53%-basicity PACI even though the coagulation pH values were slightly higher alkaline pH. Therefore, basicity >70% was suggested as a key for reducing residual aluminum concentration.

PACI-71s removed DOC slightly more efficiently than did the other coagulants in both of the tested raw water samples (Fig. 2). Large floc particles were formed with PACI-71s, whereas the floc particles formed with AlCl₃ and alum were small at the same dosage (as determined by visual inspection).

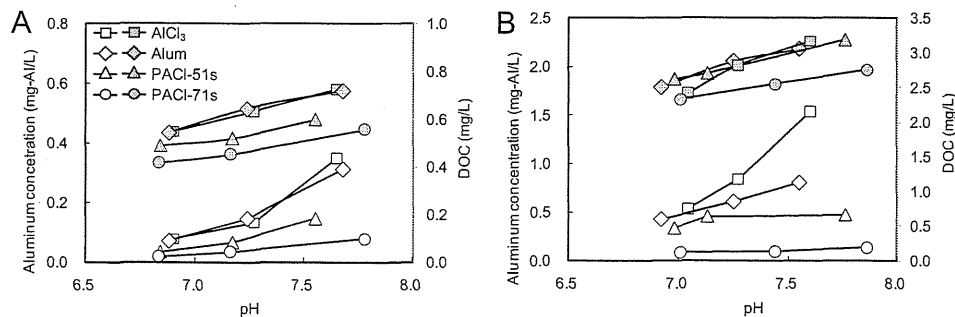


Fig. 2 – Plots of dissolved residual aluminum concentration (open symbols) and DOC (solid symbols) vs. pH for Toyohira River water A with a coagulant dosage of 1.06 mg-Al/L (A) and Chibaberi River water A with a coagulant dosage of 2.12 mg-Al/L (B).

Some investigators have assumed that Al_{13} species (Alb is an index of Al_{13}) are the most effective species for coagulation because they efficiently destabilize particles by means of charge neutralization (Parthasarathya and Buffle, 1985; Gao et al., 2005). On the basis of these previous results, we expected PACI-71s to be the least effective PACI coagulant because it contained the smallest amount of Alb. However, PACI-71s showed the best natural organic matter (NOM) removal. ^{27}Al NMR spectroscopy indicates that commercial PACI products contain less Al_{13} than laboratory-prepared PACIs (Lin et al., 2008). However, the coagulation efficiency of commercial PACIs is no worse than that of laboratory-prepared PACIs (Lin et al., 2008). Recently, Al_{30} polymer, which has been detected among the Alc species and which is formed in processes carried out at high concentrations and temperatures, has attracted attention as an effective coagulant (Chen et al., 2006, 2007, 2009). Because the conditions required for formation of Al_{30} polymer are met by the conditions under which commercial PACI coagulants are prepared, it is possible that some of the species in PACI-71s were structurally similar to Al_{30} polymer. Further study will be required for elucidating the high NOM removals.

3.2.2. MW distribution of dissolved residual aluminum, as determined by micro and ultrafiltration fractionation

The data in Fig. 3A–B, for Toyohira River water, indicate that the fraction with a MW range of 0–0.5 kDa was small for all coagulants, which means that most of the dissolved residual aluminum was not in monomeric form. At pH 7.0 for all the coagulants, some of the dissolved residual aluminum was

contained in the fraction with a MW range of 0.5–3 kDa. For alum and $AlCl_3$, dissolved residual aluminum was also present in the fraction at 100 kDa–0.45 μm , but aluminum of that MW range was observed at much smaller concentrations for the PACIs. Therefore, the lack of colloidal aluminum at 100 kDa–0.45 μm contributed to the overall low concentrations of dissolved residual aluminum observed for the samples after the PACI coagulation. PACI-71s showed a lower dissolved residual aluminum concentration in the fraction at 0.5–3 kDa than did PACI-51s; this further reduced the overall dissolved residual aluminum concentration for PACI-71s relative to that for PACI-51s. These same trends were also observed at pH 7.5.

For Chibaberi River water, which contained a higher NOM concentration than Toyohira water, most of the dissolved residual aluminum was observed in the fraction at 100 kDa–0.45 μm (Fig. 3C–D). The dissolved residual aluminum in this fraction may have been in the form of a soluble aluminum–NOM complex, which exists when the coagulant dosage is insufficient to precipitate all the NOM (Jekel and Henzmann, 1989). The aluminum concentration in this fraction was very low when PACI-71s was used, suggesting that PACI-71s has a smaller tendency to form the soluble aluminum–NOM complex but benefits to form insoluble precipitate Al–NOM. The observed highly efficient removal of NOM by PACI-71s (see Fig. 2) also supports this suggestion. Yan et al. (2007, 2008a) suggested that Ala might form a soluble complex with some types of NOM. If such a soluble complex had a size in the range 100 kDa–0.45 μm , the fact that the aluminum concentration was lowest for PACI-71s could be explained by the fact that PACI-71s had the lowest Ala percentage.

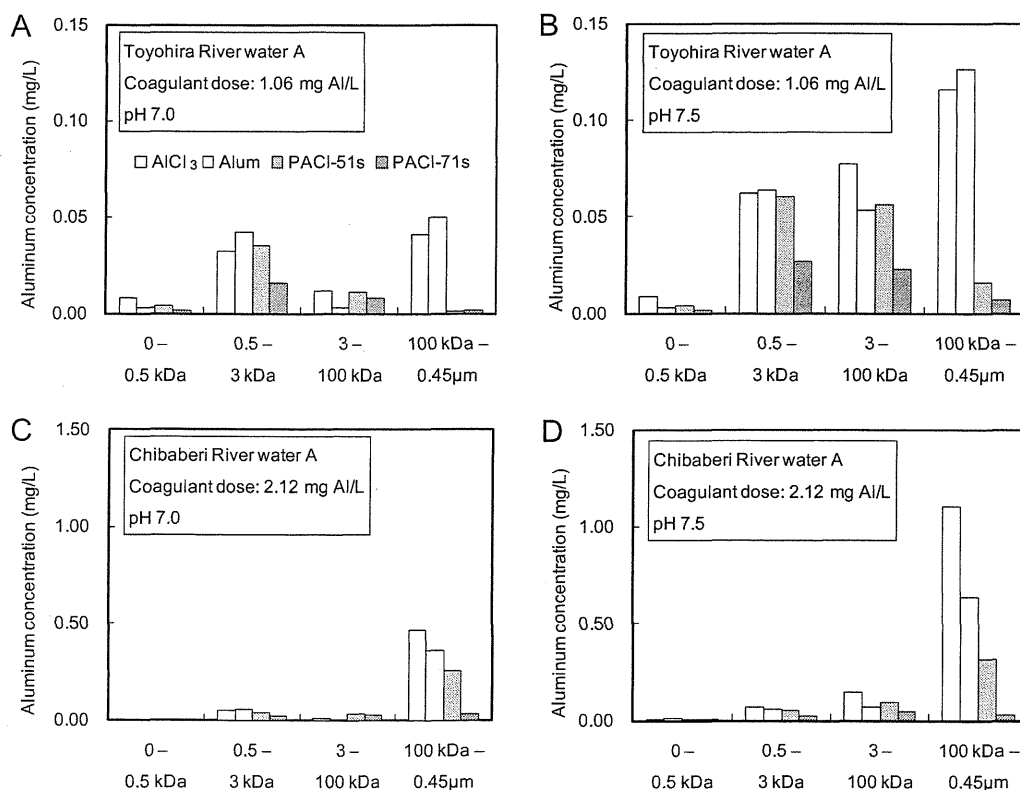


Fig. 3 – MW distribution of dissolved residual aluminum after jar tests, as determined by micro and ultrafiltration fractionation.

3.2.3. Effect of coagulant dosage on dissolved residual aluminum concentration

For PACI-51s, the dissolved residual aluminum concentration at pH 7.5 increased with increasing dosage and exceeded 0.2 mg/L at a dosage of 2.12 mg-Al/L (Fig. 1S-B, Supplementary Information). For PACI-71s, no such trend was observed. In all the experiments, PACI-71s removed more DOC than PACI-51s, in agreement with the results described earlier. For PACI-51s treating the other water at pH 7.5, the dissolved residual aluminum concentration approached 0.3 mg/L at the dosage 2.12 mg-Al/L (Fig. 1S-D, Supplementary Information), and almost no turbidity removal was observed (the turbidity of the treated water was 2.0 NTU, whereas that of the raw water was 2.4 NTU; Fig. 2S-D, Supplementary Information). At the same dosage and pH, PACI-71s lowered the dissolved residual aluminum concentration to <0.1 mg/L and lowered the turbidity to 0.4 NTU.

3.2.4. Effect of water temperature on dissolved residual aluminum concentration

The influence of water temperature on dissolved residual aluminum concentration was studied with PACI-51s, -61s, and -71s: PACI-61s was selected for these experiments because it has been widely used in commercial water treatment under low-temperature conditions. At high (28 °C) and low (4 °C) temperatures, as well as the standard temperature of 20 °C, PACI-71s reduced the residual aluminum concentration to its

lowest levels compared to those obtained for PACI-51s and PACI-61s (Fig. 3S, Supplementary Information). As predicted from the aluminum solubility diagram (Pernitsky and Edzwald, 2003; Geochemist's Workbench, ver. 6, RockWare, Inc., Golden, CO, USA), the higher the water temperature, the higher the residual aluminum concentrations. At pH 7.0, residual aluminum concentrations were almost unchanged between 4 and 20 °C but increased a little at 28 °C. At pH 7.5, the residual aluminum concentrations increased with increasing temperature.

3.3. Second set of experiments

To further investigate the low residual aluminum concentrations observed after PACI-71s coagulation, we conducted jar tests with a variety of PACIs, including a very-high-basicity PACI (90%), sulfated and non-sulfated PACIs, and PACIs composed mainly of Alb or Alc (Fig. 1C).

3.3.1. Effect of sulfate in PACIs on dissolved residual aluminum concentration

As shown Fig. 4A–C, the presence of sulfate ion in PACIs did not affect the residual aluminum concentration for pH > 6.5. For pH < 6.5, however, sulfate ions contributed to reducing the residual aluminum concentration. Low residual aluminum concentration, as well as good turbidity removal (Fig. 4S, Supplementary Information), was observed for pH > 7.0 for the non-sulfated PACIs, but the pH range for the minimum

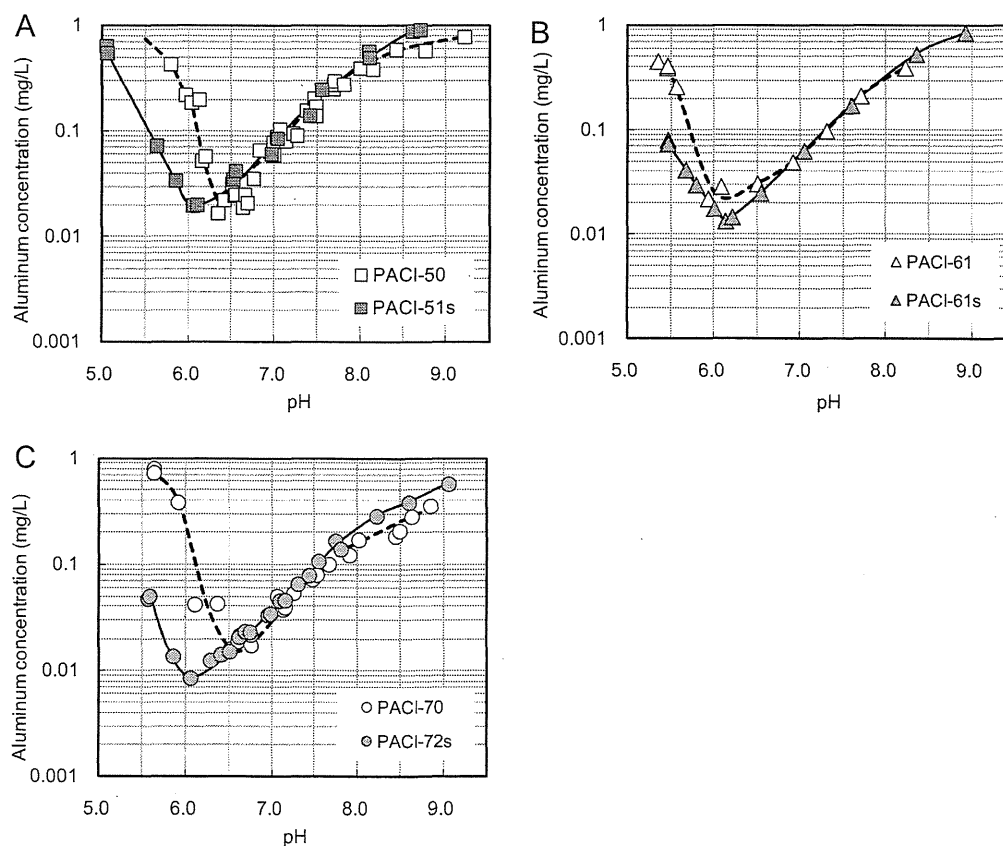


Fig. 4 – Comparison of residual aluminum concentrations between sulfated and non-sulfated PACIs (Toyohira River water C, coagulant dosage: 1.89 mg-Al/L).

residual aluminum concentration was shifted to the slightly acidic pH range around 6–6.5 by the presence of sulfate in the PACls. Because sulfate suppresses charge reversal and accelerates the kinetics of aluminum hydroxide precipitation (Amirtharaja and O'Melia, 1990), sulfate is often added to PACls, in particular to effectively treat raw water of low turbidity and low NOM concentrations. In these experiments, we observed that larger floc particles were formed by sulfated PACls than by non-sulfated PACls. The observed lower residual aluminum concentration at acidic pH for sulfated PACls compared to non-sulfated PACls could be due to charge neutralization effect: the suppression of positively charged polynuclear and microcrystalline hydrolysis products through adsorption and complexation of sulfate (Wang et al., 2002). It should be noted, however, that our results do not agree with those of Pernitsky and Edzwald (2003), who reported that the presence of sulfate did not affect aluminum solubility. They used pure water for comparing aluminum solubility, whereas we used natural waters. Therefore, ionic strength or the presence of other ions in our natural water samples may have affected the residual aluminum concentrations.

3.3.2. Effects of basicity and polymeric/colloidal species on dissolved residual aluminum concentration

The effect of the aluminum species (Alb/Alc) on residual aluminum concentration was investigated by comparing the results of PACl-72b and -72c, for which the basicity values are

the same but for which the dominant aluminum species are polymeric (Alb) and colloidal (Alc), respectively. Residual aluminum concentrations were almost the same between PACl-72b and -72c at the tested pH range of 5.5–8.5 (Fig. 5A); this data suggests that the residual aluminum concentration was determined by the Ala percentage.

The effect of aluminum species on residual aluminum concentration was further investigated by using a series of PACl coagulants, including the very-high-basicity PACls (PACl-90bx and -90y). As shown in Fig. 5B, aluminum concentrations at pH > 6.5 were the lowest with PACl-90y followed by PACl-90bx and PACl-70. Aluminum concentrations were not largely different between PACl-61 and PACl-50. At coagulation pH of 7.5–8.5, where problematic levels of residual aluminum are generally seen, a residual aluminum concentration <0.02 mg/L was attained with PACl-90y. Good turbidity removal after settling was observed at a coagulation pH of 7.0–8.5 (Fig. 5S, Supplementary Information). Among the PACls, aluminum concentrations decreased with increasing PACl basicity. For sulfated PACls, a similar trend was observed (Fig. 5C). The reason why AlCl₃ exhibited a lower aluminum concentration than PACl-50 was not clear, but the results suggest that a basicity ≥70% was required to reduce residual aluminum concentration. PACl-90bx and PACl-90y, in particular, exhibited extremely low residual aluminum: their minimum residual aluminum concentrations were <0.007 mg/L, which was far below the aluminum solubility

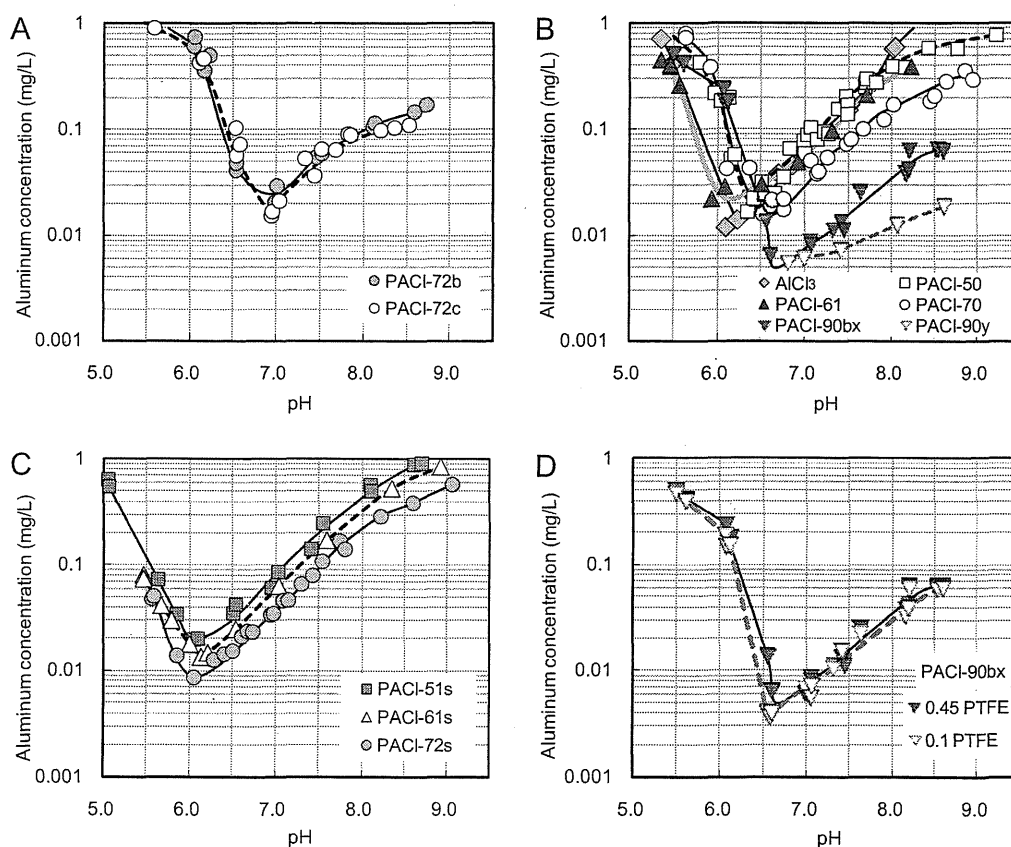


Fig. 5 – Effect of Alb/Alc (Panel A), basicity (Panels B and C), and membrane pore size on residual aluminum concentrations (Panel D) for Toyohira River water C (coagulant dosage: 1.89 mg-Al/L).

reported by Pernitsky and Edzwald (0.03 mg/L; 2003). While concentrations <0.007 mg/L were attained after 0.45- μ m membrane filter filtration, residual aluminum concentrations decreased even further, to <0.004 mg/L, when sample water was filtered by a 0.1- μ m membrane filter (Fig. 5D).

3.3.3. Effect of monomeric species on dissolved residual aluminum concentration

The concentration of residual aluminum observed after PACl-90y coagulation was clearly lower than that after the coagulation by PACl-90bx of the same basicity (Fig. 5B); this discrepancy would be due to the lower Ala percentage in PACl-90y compared with that in PACl-90bx because Alb/Alc ratio did not affect residual aluminum concentration. Therefore, we hypothesized that low Ala percentage, rather than high basicity, was a better indicator for minimizing residual aluminum concentration, although PACl basicity roughly determines the Ala percentage in PACl. The effect of Ala percentage on dissolved residual aluminum was verified by using water samples with high and low NOM concentrations and additional very-high-basicity PACls. Because of the necessity of discussing small differences of Ala percentages, the analytical accuracy of very low Ala percentage was evaluated in multiple measurements for the very-high-basicity PACls. Ala percentages of PACl-90x, 90by, 85x, and 85y were 0.22 ± 0.10 , 1.18 ± 0.02 , 0.43 ± 0.10 , and 1.00 ± 0.07 (avg. \pm sd.), respectively; the standard deviations were all <0.1 . Fig. 6 shows plots of dissolved residual aluminum concentration against Ala percentage. Among the three PACls with a basicity of 85% (circles in the

figure), dissolved residual aluminum concentrations increased with increasing Ala percentage in the order of PACl-85x (Ala: 0.5%) $<$ PACl-85y (1.0%) $<$ PACl-85z (1.7%) (Fig. 6A). A similar trend was also seen for the three PACls with a basicity of 90%. One with a lower Ala percentage showed lower residual aluminum concentrations. Comparison of Figures A–B and C–D demonstrates superiority of Ala percentage over basicity as an index determining residual aluminum concentration, in particular for concentrations <0.1 mg/L. Residual aluminum concentrations <0.015 mg/L were attained by the PACls (Ala $\leq 0.5\%$, basicity $\geq 85\%$) even at a weakly alkaline pH of 8.0. The PACls exhibited residual aluminum concentrations <0.02 mg/L at a pH range of 6.5–8.5 (some data are shown Fig. 7). At the optimum pH at which residual aluminum concentration was minimized, residual aluminum concentrations were <0.007 mg/L. Residual aluminum concentrations after the coagulation by high-basicity PACls was studied previously (Yan et al., 2007; Yang et al., 2011). However, such low residual aluminum concentrations were not attained. Our study suggests that their non-attainment would be due to the high Ala percentage ($>5\%$) even though the basicity was as high as 83%. In those studies, the observed residual aluminum concentration achieved with a PACl with 15.6% Ala was around 0.07–0.09 mg/L at pH 7.8 (Yang et al., 2011), and 0.1 mg/L with a PACl with 5.5% Ala at pH 8 (Yan et al., 2007). These data are roughly in line with our observation shown in Fig. 6. Notably, in our study the residual aluminum concentration drastically decreased to <0.015 mg/L at pH 8.0 when the Ala percentage of the PACl decreased to $<0.5\%$.

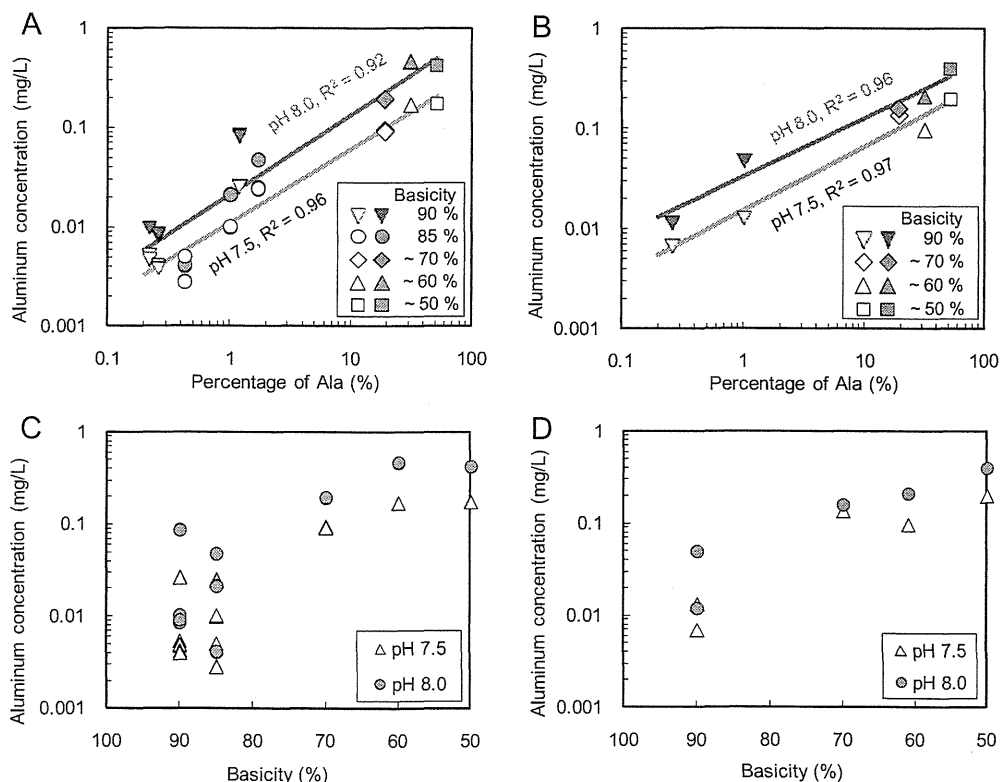


Fig. 6 – Effect of Ala percentage in PACls and their basicity on residual aluminum concentrations: (Panels A and C) Wani River water, coagulant dosage: 2.86 mg-Al/L; (Panels B and D) Toyohira River water, coagulant dosage: 1.89 mg-Al/L.

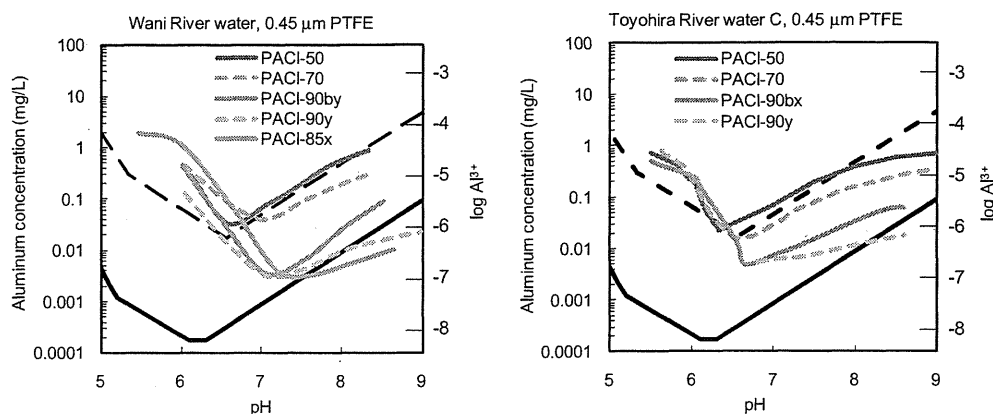


Fig. 7 – (solid black lines) Solubility diagram for aluminum at 20 °C calculated by Geochemist's Workbench, ver. 6 (RockWare, Inc., Golden, CO, USA), (dashed black lines) theoretical solubility for Al species in equilibrium with Al(OH)₃(am) at 20 °C calculated by Pernitsky and Edzwald (2003), and experimentally observed residual aluminum concentrations of PACI-50, PACI-70, PACI-85x, PACI-90bx/90by, and PACI-90y (blue, red, pink, green, and light green lines, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In Fig. 7, experimentally observed residual aluminum concentrations were compared with the solubility of amorphous aluminum hydroxide and gibbsite (Al(OH)₃). For pH < 6.5, residual aluminum concentrations exceeded the solubility limit of amorphous Al(OH)₃. The residual aluminum concentrations for PACI-70 were below the solubility limit of amorphous Al(OH)₃ at pH > 7, but they exceeded the solubility limit of gibbsite. The residual aluminum concentrations of PACI-85x, PACI-90by, and PACI-90y were much lower than the amorphous aluminum solubility and closely approached the solubility limit of gibbsite. In particular, residual aluminum concentrations of PACI-85x and PACI-90y at pH > 7.5 were close to or lower than the aluminum solubility. These PACIs are highly prehydrolyzed aluminum salts that are obtained by neutralizing the acidic polymer with base. In particular, the pH value of PACI-90y is 5.5, and the solubility diagrams (dashed and solid black lines) suggest the dissolved aluminum concentration at pH 5.5 is in agreement with the Ala content in PACI-90y (Fig. 1). Therefore, the low concentration of dissolved aluminum contained in this PACI would lead to a very low residual aluminum concentration after its dosing.

4. Conclusions

1. The amount of Ala in PACI mainly determined the dissolved residual aluminum concentration after coagulation, whereas polymeric (Al_b)/colloidal (Al_c) ratio in PACI did not affect dissolved residual aluminum concentration at a given basicity.
2. PACIs with Ala ≤ 0.5% and basicity ≥ 85% yielded residual aluminum concentrations < 0.007 mg/L at the optimum pH. Even at a wide pH range of 6.5–8.5 the concentration was always < 0.02 mg/L. Residual aluminum concentrations at pH > 7.5 were close to or lower than the gibbsite solubility limit. The very low monomeric aluminum content inherent

to these high-basicity PACIs appears to have contributed to the very low residual aluminum concentration.

3. When coagulation was performed at pH > 6.5, dissolved residual aluminum concentration was reduced by using high-basicity PACIs. For coagulation at pH < 6.5, the dissolved residual aluminum concentration was reduced by using sulfated PACIs instead of non-sulfated PACIs.
4. Dissolved residual aluminum was present in the fractions with MW ranges of 500 Da–3 kDa and 100 kDa–0.45 μm at pH 7.0, and aluminum was also present in the fraction with a MW range of 3–100 kDa at pH 7.5. The lower dissolved residual aluminum concentrations observed after treatment with PACI, compared with treatment with alum and AlCl₃, were due to the lower aluminum concentrations in the fractions at 100 kDa–0.45 μm. High-basicity PACIs produced higher reductions in aluminum concentrations in the MW fractions at 500 Da–3 kDa, 3–100 kDa, and 100 kDa–0.45 μm.
5. The dissolved residual aluminum in the fraction with an MW range of 100 kDa–0.45 μm would have been dissolved aluminum–NOM complex formed from Ala (monomeric aluminum). The low dissolved residual aluminum concentrations observed after coagulation by high-basicity PACIs may have been related partly to their low content of Ala, which tends to form dissolved aluminum–NOM complex.
6. Although increasing the dosage of normal-basicity PACIs led to an increased dissolved residual aluminum concentration at pH 7.5, increasing the dosage of high-basicity PACIs did not.
7. At higher raw water temperatures, the residual aluminum concentrations increased, yet the ability of high-basicity PACIs to lower the residual aluminum concentration was maintained.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2013.01.037>.

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Profiles of dissolved organic matter and haloacetic acid formation potential in drinking water treatment by a comprehensive fractionation technique

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ABSTRACT

A comprehensive fractionation technique was applied to a set of water samples obtained along a real drinking water treatment plant with ozonation and granular activated carbon (GAC) treatment to obtain detailed profiles of dissolved organic matter (DOM) and to evaluate the haloacetic acid (HAA) formation potentials of these DOM fractions. The results indicated that ozonation and GAC treatment showed limited ability to remove hydrophilic fractions (23%), while removal of hydrophobic fractions was 72%. The contribution of hydrophilic fractions to HAA formation increased from 30 to 61% along the treatment train because of better removal for hydrophobic fractions both in concentration and reactivity. Similar trends were also found for trihalomethanes.

Key words | disinfection byproducts, dissolved organic matter, fractionation, haloacetic acids

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INTRODUCTION

The precursors of disinfection byproducts (DBPs) – toxic compounds produced by the reaction between disinfectants and organic or inorganic constituents in source water – were believed to be mainly hydrophobic compounds (i.e., humic and fulvic acids). However, recent studies have suggested that the hydrophilic fraction is a major contributor to the formation of trihalomethanes (THMs, CHX_3 , where X = Cl, Br, or I) (Imai *et al.* 2003). THM formation potential per unit of dissolved organic carbon (DOC) from the hydrophilic fraction was shown to be comparable to that of aquatic humic substances (hydrophobic fraction), and the hydrophilic fraction could be a dominant precursor of THMs for low humic waters. Nagai *et al.* (2005) also found that the hydrophilic fraction of lake dissolved organic matter (DOM) was a major precursor of THMs. These and other studies clearly highlighted the importance of hydrophilic fractions for DBP formation, and have changed our view of DBP precursors.

This may also be true for other DBPs. Indeed, it has been reported that hydrophilic fraction could be a major precursor of haloacetic acids (HAAs, $\text{CH}_{3-n}\text{X}_n\text{COOH}$, where

X = Cl, Br, or I), another important class of DBPs (Liang & Singer 2003; Lu *et al.* 2009). In addition, the contribution of the hydrophilic fraction is significant for the formation of dichloroacetonitrile and *N*-nitrosodimethylamine (NDMA) (Lee *et al.* 2007). These findings suggest that hydrophilic fractions are important as precursors of various DBPs.

Most of the studies mentioned above focused on characterization of DOM and on evaluation of the DBP formation potentials of raw waters. However, the composition of DOM changes along the treatment system and the major precursors of DBPs could depend on the type of drinking water treatment. Thus, it is desirable to characterize DOM after treatment to identify the major fractions contributing to DBP formation in actual drinking water. Kim & Yu (2005) compared DOC profiles and DBP formation potentials between conventional rapid sand filtration and membrane treatment systems (ultrafiltration and nanofiltration). While this was a major advance in the field of DBP chemistry, their evaluation did not include ozonation, a key treatment step in advanced drinking water treatment

plants. In addition, DOM was divided into only two fractions (hydrophilic and hydrophobic).

The combination of ozonation and granular activated carbon (GAC) is a common and effective approach to control DBPs. However, to our knowledge, there have been no detailed reports regarding the DOM profile (e.g., the percentage of hydrophilic fraction) along the treatment train with ozonation and GAC treatment, or how the most important fractions for DBP formation shift with each unit operation. While both THMs (0.06, 0.03, 0.1, 0.09, and 0.1 mg/L for chloroform, bromodichloromethane, dibromochloromethane, bromoform, and total THMs, respectively) and HAAs (0.02, 0.04, and 0.2 mg/L for chloroacetic acid, dichloroacetic acid, and trichloroacetic acid, respectively) are regulated as chlorination byproducts in Japan, much less information is available for HAAs. In the present study, we applied a comprehensive fractionation technique of DOM to a set of water samples obtained along a real drinking water treatment plant with ozonation and GAC treatment, and evaluated the HAA formation potentials of these DOM fractions to identify the major precursors at each treatment step. THM formation potentials were also measured for comparison.

MATERIALS AND METHODS

Water samples

Water samples were collected at an actual drinking water plant in the Osaka area, Japan, on 17 December 2007. The pH, bromide ion concentration, DOC, and specific UV absorbance (SUVA) at 258 nm of the source water were 7.3, 32 µg/L, 2.5 mg/L, and 2.7 L/(m·mg), respectively. This plant employs ozonation (ozone dose: 0.3–0.5 mg/L on the day of sampling) and GAC treatment (contact time: 24 min) after coagulation with polyaluminum chloride (PAC), sedimentation, and rapid sand filtration. Four samples were collected in this study: inlet, after sand filtration, ozonation, and GAC.

Fractionation

The samples were fractionated into six fractions by a method similar to that described previously by Leenheer (2004). In

our experiment, no colloidal fraction was isolated. The method consisted of a series of adsorption onto DAX-8 resin (Supelco), XAD-4 resin (Supelco), and ion-exchange resins (Marathon MSA-1 and MSC-1; Dowex) under several different pH conditions (Figure 1). As a small but non-negligible level of bromide ions was found in hydrochloric acid and sodium chloride used in this study, sulfuric acid and sodium sulfate were used for desorption and pH adjustment. The fractions obtained by this procedure were hydrophobic acid (HoA), hydrophobic neutral (HoN), transphilic acid and neutral (Trs), base (Bas), hydrophilic acid (HiA), and hydrophilic neutral (HiN). These fractions were used for evaluation of HAA formation potentials without further purification (i.e., desalting).

Chlorination

Chlorination of each DOM fraction was performed at pH 7.0. Other conditions were as follows: chlorine dose, 3 mg/L; DOC, 2 mg/L, bromide ion, 0.17 mg/L (adjusted

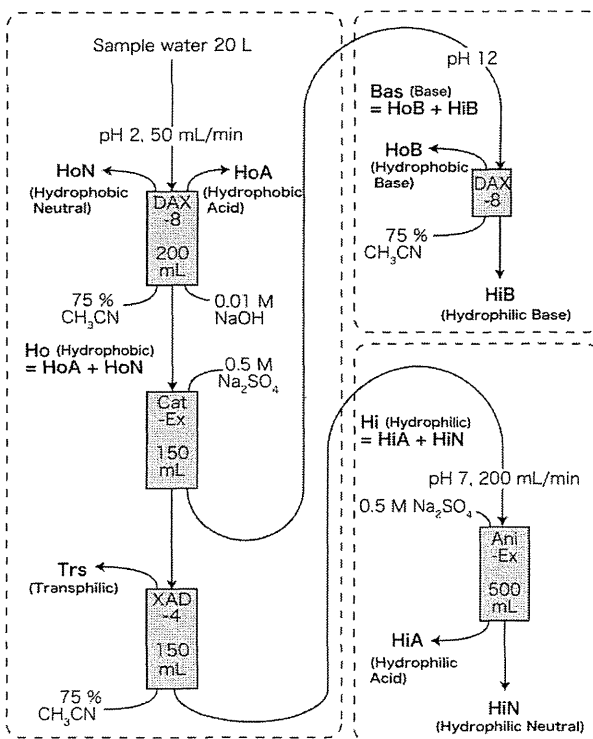


Figure 1 | Schematic of DOM fractionation.

to the highest concentration among the six fractions); incubation time, 24 h for most samples (see caption of Figure 2 for more details). The presence of free chlorine after 24 h was confirmed by the DPD method (APHA *et al.* 2005).

Analytical methods

The concentrations of nine HAAs (those with Cl and/or Br) were determined by GC/MS (QP2010-Plus; Shimadzu) analysis with a DB-5 ms capillary column (30 m × 0.25 mm i.d., 0.32 μm film thickness; J&W Scientific) after derivatization to the corresponding methyl esters (USEPA 2003). The limits of quantification were 1 μg/L for tribromoacetic acid (TBA) and 0.25 μg/L for the other eight HAAs. For this analysis, 1,2,3-trichloropropane was used as an internal standard. For comparison, THMs (with Cl and/or Br) were also measured by GC/MS analysis using

the same column as in HAA analysis following liquid-liquid extraction with pentane (APHA *et al.* 2005). The quantification limits of THMs were 0.5 μg/L, and 1,2-dibromopropane was used as an internal standard for this analysis. DOC concentration was measured with a TOC analyzer (TOC-5000A; Shimadzu) in non-purgeable organic carbon (NPOC) mode. The detection limit for this analysis and the standard deviation for 200 μg C/L were 30 μg C/L and 4%, respectively. All analyses were performed in duplicate.

RESULTS AND DISCUSSION

DOC profile

Figure 2 shows the DOM profile along the treatment plant. The detailed DOM contents at each treatment step are also summarized in Table 1. To our knowledge, this is one of the most detailed DOM profiles along with a treatment train with ozone and GAC treatment obtained by a comprehensive fractionation technique. The hydrophilic fraction (i.e., HiA + HiN) was the dominant DOM fraction throughout the treatment process at this drinking water treatment plant, with percentages of 41 and 57% for the inlet water and after ozonation, respectively. The removal percentage of the hydrophilic fraction (Hi) was only 23%, while hydrophobic (HoA + HoN) and basic compounds (Bas) were decreased by 72 and 67%, respectively. The base fraction consisted mostly of hydrophilic compounds (i.e., the HoB fraction was negligibly small). These observations clearly indicated that the behaviors of different

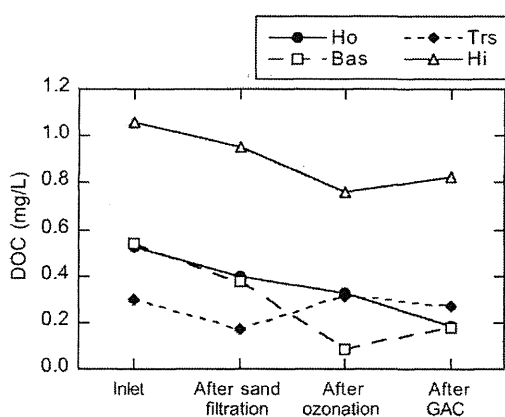


Figure 2 | Summary of DOM profile along the drinking water treatment with ozonation and GAC (Ho: the sum of HoA and HoN; Hi: the sum of HiA and HiN).

Table 1 | Detailed DOM profile along the drinking water treatment plant (Unit: mg C/L)

	Inlet	After rapid sand filtration	After ozonation	After GAC
HoA	0.48	0.37	0.22	0.18
HoN	0.17	0.03	0.11	0.00
Bas	0.54	0.38	0.08	0.18
Trs	0.30	0.17	0.32	0.27
HiA	0.61	0.35	0.38	0.35
HiN	0.45	0.61	0.38	0.47
Total	2.55	1.90	1.49	1.43

DOM fractions are different at various stages during drinking water treatment. It should be noted that the hydrophilic fraction remained dominant even following ozonation and GAC treatment. Thus, the combination of ozone and GAC may not be relevant in terms of DOC removal for source waters with high levels of hydrophilic compounds.

With regard to the various treatment steps, rapid sand filtration (coagulation and sedimentation) was effective for removal of five fractions other than HiN. The levels of removal for HoA, HoN, Bas, Trs, and HiA were 23, 82, 30, 43, and 43%, respectively. Ozonation increased the DOC levels of HoN, Trs, and HiA, while it decreased those of HoA, Bas, and HiN. The increase in Trs was attributed to the formation of low molecular weight compounds from hydrophobic fractions. The HiA fraction increased by 9% probably due to the formation of more hydrophilic functional groups during oxidation reactions with molecular ozone and hydroxyl radicals. Higher HoN after ozonation has also been reported previously (Swietlik *et al.* 2004); based on the results of size-exclusion chromatography, they suggested that the increase in HoN was mainly due to the formation of small hydrophobic compounds. After GAC treatment, only the Bas and HiN fractions increased presumably because of the release of organic compounds from the extracellular membranes of bacteria in GAC. HoN was removed completely in this treatment step.

Although GAC was used to serve as biological activated carbon at this plant, no removal of hydrophilic compounds was observed with this treatment.

HAA formation characteristics from different DOM fractions

Figure 3 shows a summary of HAA formation per unit DOC from different DOM fractions. No mono-HAA (i.e., chloroacetic acid and bromoacetic acid) was detected in this series of experiments. HAA formation per unit DOC decreased for HoA, HoN, and Trs along the treatment train; HoA and Trs showed 58 and 51% removal, respectively, and HoN was removed completely after GAC. In contrast, that of HiA remained constant throughout the treatment process. The levels of HAA formation per unit DOC from HiN increased along the treatment train by 89%. This change may have been due to the release of organic compounds from GAC, as mentioned above. Alternatively, the residual DOM may have had higher HAA formation potential. In addition, the ratio of dihaloacetic acids to trihaloacetic acids was higher in the Bas fraction. These observations indicated the dominance of aliphatic compounds in this fraction (Echigo *et al.* 2007). As the Bas fraction consists mostly of hydrophilic compounds, this observation was consistent with the pattern of HAA formation from DOM surrogates reported previously (Bond *et al.* 2009).

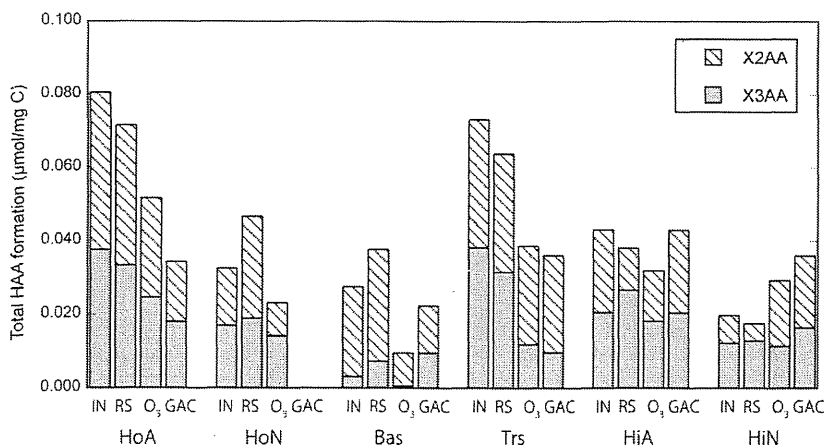


Figure 3 | HAA formation potentials from different DOM fractions (Total concentrations of nine HAAs are presented here. Chlorination conditions: chlorine dose, 3 mg/L; DOC, 2 mg/L (1.5 mg/L for the Bas sample after GAC because of lack of DOM amount recovered), bromide ion, 0.17 mg/L; incubation time 24 h; pH, 7.0. IN: inlet; RS: after rapid sand filtration; O₃, after ozonation; GAC: after GAC treatment).

The differences in HAA formation among the DOM fractions after GAC were smaller than those after other treatment steps and the raw water, thus indicating very similar precursor structures among the different fractions.

Figure 4 shows a comparison of the subclasses of HAAs (in $\mu\text{mol}/\text{mg C}$) along the treatment train. While the levels of chlorinated HAAs (HAAs with only Cl) per DOC decreased, those of brominated (HAAs with only Br) increased. This observation suggested a shift in the contents of HAAs from chlorinated to brominated species. As the bromide/chlorine/carbon matrix was adjusted at approximately the same level in this study, this result was attributed to the changes in reactivity of DOM. It is likely that brominated HAAs were preferentially produced for the DOM after ozonation or GAC because bromination by HOBr (an intermediate species from the reaction of bromide and chlorine ions) occurs more rapidly than chlorination (e.g., Acero *et al.* 2005). As brominated compounds are known

to more toxic than their chlorinated counterparts in general (Echigo *et al.* 2004) and among the HAAs (Plewa *et al.* 2002) regulations and monitoring focusing only on chlorinated HAAs may not be sufficient to guarantee the safety of finished water.

Figure 5 shows the relative contributions of DOM fractions to HAA formation potential at each treatment step. The total formation potential decreased by 55% along the treatment train, while the relative contribution of the hydrophilic fractions increased from 30 to 61%. Thus, the major contributor to HAA formation was different for the inlet sample and the sample after ozonation and GAC treatment. There are two major reasons for these results: (1) better removal of the hydrophobic fractions and (2) decreased yields of HAAs for hydrophobic fractions, but remaining constant for hydrophilic fractions.

These findings are important because most previous studies to identify the fraction important for DBP formation

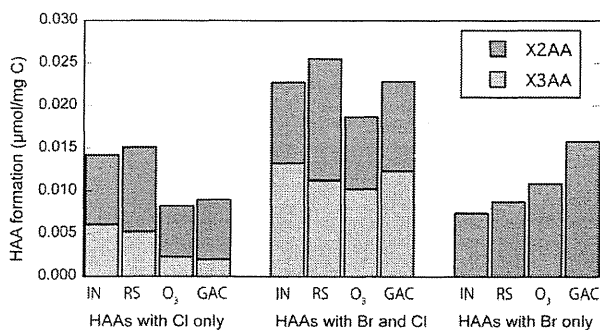


Figure 4 | Types of HAAs produced at each treatment step (See caption of Figure 3 for conditions).

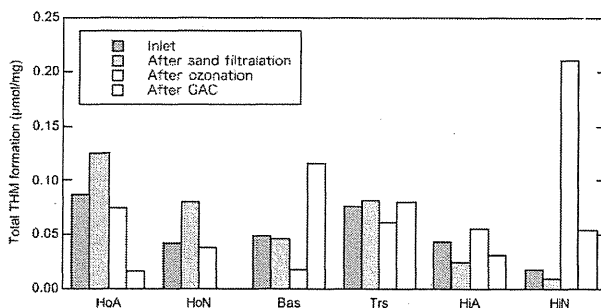


Figure 6 | THM formation potentials from different DOM fractions (Total concentrations of four THMs are presented here. See caption of Figure 2 for chlorination conditions).

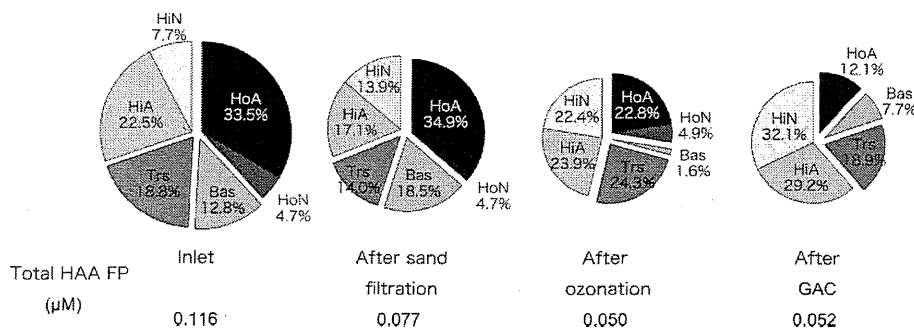


Figure 5 | Relative contributions of DOM fractions to HAA formation potential at each treatment stage (Relative contributions were calculated with the DOC percentages and HAA formation potentials. That is, HAA formation potentials were weighted by DOC percentages).

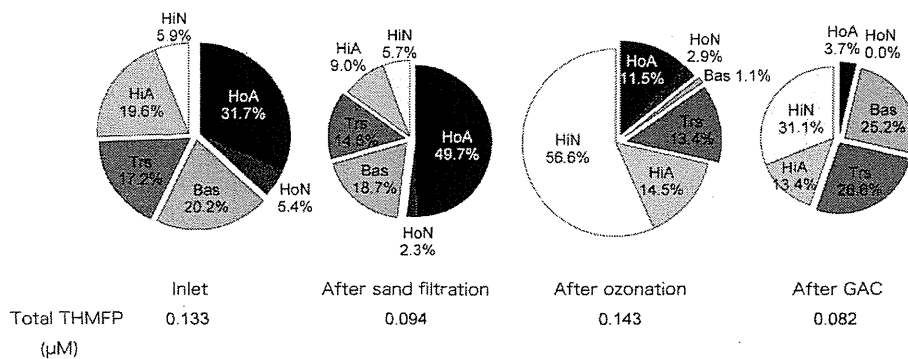


Figure 7 | Relative contributions of DOM fractions to THM formation potential at each treatment step (Relative contribution was calculated from the DOC percentages and THM formation potentials. That is, THM formation potentials were weighted by DOC percentages).

were conducted with source waters. Our results clearly indicated that the DOM content after treatment is completely different from that of the source water in terms of DBP formation, especially after ozone + GAC treatment (note: there was no HoN fraction after GAC) and that it is more appropriate to characterize DOM in the treatment train to identify the DOM fraction responsible for DBP formation.

Figure 6 shows the THM formation potentials per unit DOC at each treatment step for DOM fractions. THM formation potentials of hydrophilic fractions decreased along the treatment process, but those of other fractions did not change or even increased. Similar to HAAs, these observations indicated the importance of hydrophilic fractions after treatment as the precursors of THMs. Figure 7 shows this more clearly. The contribution of hydrophilic fractions was very small (3.7%), and this trend was similar to that of HAA formation potentials.

CONCLUSIONS

A comprehensive fractionation technique was applied to water samples obtained along a real drinking water treatment process with ozonation and GAC treatment to evaluate HAA formation potentials of these DOM fractions. The results indicated only limited removal of hydrophilic fractions by ozonation and GAC treatment (23%), while that of hydrophobic fractions was 72%. The contribution of hydrophilic fractions to HAA formation increased from 30 to 61% along the treatment train due to better removal and lower reactivity after treatment. Similar trends were

found for THMs. These observations suggested that the combination of ozonation and GAC treatment may not be relevant in terms of DOC removal and control of DBPs for source waters with high levels of hydrophilic compounds.

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東京の地下水中の塩素酸イオンおよび 過塩素酸イオンの実態調査

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東京の地下水を対象に塩素酸イオン、過塩素酸イオンの実態調査を行った。試料は2007、2009年に採取した。塩素酸イオンは49試料中24試料が、過塩素酸イオンは52試料中28試料が定量下限値以上の濃度で、その割合は被圧地下水より不圧地下水や湧水で高かった。試料の25%程度は塩素酸イオンまたは過塩素酸イオンが比較的高い濃度で存在し、塩素酸イオンでは1試料で水道水質基準値を超えていた(2000 µg/L)。東京の地下水は、国内の他の地下水(市販のナチュラルウォーターや専用水道の原水)に比べ、これらイオン濃度が高い試料は多かったが、定量下限値以上の濃度の試料の割合は最も低かった。これらイオン濃度が比較的高かった地下水では、その多くが水道水や下水の影響を受けている可能性が考えられた。

Key Words : chlorate, perchlorate, groundwater, Tokyo

1. はじめに

塩素酸イオンは、水溶性のイオンで、水中では安定で、移動性が高い物質である。塩素酸塩として、除草剤、酸化剤、二酸化塩素の原料、火薬、マッチ、花火等に使用されている¹⁾他、消毒剤である次亜塩素酸ナトリウム溶液中に不純物として含まれている²⁾。除草剤としての塩素酸塩の使用量は農薬の中でもとりわけ多く(2009 農薬年度での農薬原体としての国内生産量: 1080 t)³⁾、開墾地、公園、駐車場、道路、宅地等で使用されている⁴⁾。毒性としては、赤血球細胞への酸化ダメージが知られており¹⁾、水道水質基準項目に指定されている(基準値: 600 µg/L)⁵⁾。

過塩素酸イオンは、塩素酸イオンと同様、水溶性で水中では安定な物質である。過塩素酸塩や過塩素酸として製造、使用され、用途としては、ロケットやミサイルの推進剤、火薬、マッチ、花火、エアバッグ等が知られている⁶⁾。塩素酸イオン同様に、次亜塩素酸ナトリウム溶液中にも不純物として含まれている⁸⁾。過塩素酸イオンは、甲状腺におけるヨウ素の取り込みを抑制する作

用があることが知られ¹⁰⁾、米国環境保護庁では、暫定健康勧告値(Health advisory level, HAL)として15 µg/Lを公表している¹¹⁾。カリフォルニア州、マサチューセッツ州では、それぞれ州の基準値として6、2 µg/Lを定めている^{12,13)}。日本では、水道の要検討項目に指定されている(目標値: 25 µg/L)⁵⁾。

1990年代以降、米国では、環境水や水道水中の過塩素酸イオンの調査が広く実施されてきた^{8,9,14)}。近年では、米国以外の国々でも調査が進められ、その存在が報告されている⁹⁾。国内では、利根川流域上流にある発生源の影響で、同流域中に広く分布していることが知られている^{15,16)}。また、過塩素酸イオンは、花火の使用によって湖沼中の濃度が一時的に増加したことも報告されている¹⁷⁾。過塩素酸イオンは、自然起源でも存在し、大気からの降下物中の調査も行われている⁹⁾。

地下水中の過塩素酸イオンについても、飲用井戸や汚染地域の周辺、都市部や地方部を含む全米調査(ただし、塩素消毒の影響を受けていない地下水)等、様々な調査が行われている^{9,18,19)}。ところで、国内の都市部では、地下水は水道の原水としての割合は低いが²⁰⁾、専用水道

として利用されている場合がある。また、災害時における生活用水の確保の観点から、防災井戸（災害時協力井戸等）の設置等、その有効活用が進められている²¹⁾。東京では、災害時には多数の帰宅困難者も想定され、断水が発生した場合、地下水は生活用水として期待されている²²⁾。このとき、平常時の水質情報をもとに、利用者の適切な判断において、飲料用としても活用される状況もありうると考えられる²²⁾。

都市部での水収支の調査によると、都市部は不浸透面が多く、地下水涵養に対する雨水浸透量が小さいため、東京や大阪では、水道からの漏水の寄与が無視できないことが報告されている²³⁾。東京都 23 区の場合、2004 年において、雨水浸透による地下水涵養量が 123 mm/年、水道からの漏水による涵養量が 91 mm/年と推定されている²³⁾。また、東京都 23 区の場合、下水管からの漏れ等を通じた下水による涵養量が 19~38 mm/年と医薬品のカルバマゼピンを下水マーカーに使うことで推定されている²⁴⁾。

過塩素酸イオンは、2009年4月に水道の要検討項目に指定され²⁵⁾、2011年4月に目標値（25 µg/L）が定められたが⁹⁾、それ以前には、利根川中流域の水道水中からは 25 µg/L と同等以上の濃度での存在が報告されている¹⁵⁾²⁶⁾。しかし、同流域の地下水中の過塩素酸イオン濃度は、地下水を原水としている上流域の浄水場については報告されているが¹⁶⁾、それ以外についての報告はほとんど行われていない。塩素酸イオンの場合、水道水質基準項目であるため、国内では原水、浄水中の測定は数多く行われており²⁰⁾、また、過塩素酸イオンと同様に環境水中の調査も行われている²⁰⁾。一方、外国では水道水や地下水等を対象に調査した事例はあるものの¹⁸⁾²⁷⁾²⁸⁾、過塩素酸イオンに比較して調査は限定的である。

本研究では、東京の地下水を対象に、塩素酸イオン、過塩素酸イオンの実態調査を行った。このとき、過去に行われた国内の他の地下水、河川水、水道水中の塩素酸イオン濃度、過塩素酸イオン濃度と比較するとともに、同じ地下水を対象に行われた医薬品類等の他の項目の調査結果を参考に、塩素酸イオン、過塩素酸イオンの起源について推測を行った。

2. 調査方法

(1) 試料の採取

2007年10~12月および2009年10月、東京都23区中19区を対象に、それぞれ50および2地点の地下水を採取した。52地点の内訳は不圧地下水31地点、被圧地下水18地点、湧水3地点であった（図-1）。図中、各調

査地点の記号は、同一地下水中の他の項目の結果と比較できるように、統一してある²⁴⁾²⁹⁾³⁰⁾。試料は、採取後、速やかにガラス繊維ろ紙（GF/F, Whatman）によりろ過した後に、冷暗所に保管した。試料の測定は2010年2月に行った。水試料中の過塩素酸イオンの安定性について検討した研究では、ろ過後、冷暗保存状態の場合、2地下水中の過塩素酸イオンはいずれも調査期間中（330, 370日）変化しなかったことが報告されている³¹⁾。塩素酸イオンの場合、水試料中の安定性についての報告はないが、本調査のように、長期保存した地下水中の塩素酸イオン濃度を測定し、報告が行われている¹⁸⁾。

地下水を採取した井戸は、防災井戸等の公共井や私有井で²⁴⁾³⁰⁾、その用途は、井戸によって異なり、生活雑用水用、浴場用、飲料用、災害用等多岐にわたっている。所有者等からの聞き取り情報、およびポンプ形式・仕様、帯水層の状況等による井戸の深さは、不圧地下水では10~30m、被圧地下水では20~500mであった²⁴⁾。

(2) 測定方法

標準液や溶離液の作成は、水道水を Gradient A10 (Millipore) により精製した超純水を用いて行った。試料中の塩素酸イオン濃度、過塩素酸イオン濃度の測定は、イオンクロマトグラフータンデム質量分析法（IC-MS/MS法）により行った¹⁵⁾²⁶⁾。過塩素酸イオン濃度の測定では、¹⁸O_r 過塩素酸イオン（Cambridge Isotope Laboratories）を内部標準物質として用いた。電気伝導度が高かった場合等、一部の試料については、OnGuard II Ba/Ag/H カートリッジ（Dionex）を用いて、ハロゲン化物イオンと硫酸イオンの除去を行った後に測定を行った。

ICはICS-2000（Dionex）を、ガードカラムはIonPac AG20（2×50 mm, Dionex）を、分離カラムはIonPac AS20（2×250 mm, Dionex）を、サプレッサーはASRS ULTRA II（2 mm, Dionex）を使用した。溶離液は水酸化カリウムを用い、グラディエント条件は、水酸化カリウム濃度で10 mM（0 min）→80 mM（22 min）とした。溶離液流量は、0.25 mL/minとした。ポストカラムにより、アセトニトリル/水（9:1 v/v）溶液を流量0.2 mL/minで加えた。試料注入量は100 µLとした。

MS/MSはAPI 3200QTrap（Applied Biosystems）を使用した。イオン化法は、エレクトロスプレーイオン化法（エガティブイオンモード）とした。Multiple Reaction Monitoring（MRM）は、塩素酸イオンについては83/67を、過塩素酸イオンについては99/83（定量用）と101/85（確認用）を、¹⁸O_r過塩素酸イオンについては107/89を選択した。定量下限値は、塩素酸イオンでは0.05 µg/L、過塩素酸イオンでは0.01 µg/Lであった。

(3) 過去の調査結果の再解析

過去において、著者らが実施した塩素酸イオン、過塩素酸イオン濃度の調査結果^{15),16),29),32)}を再解析し、本調査の結果と比較した。再解析した調査結果は、地下水(市販の国内のナチュラルウォーター、専用水道の原水)、表流水(利根川中流域の河川水および他流域の表流水)、浄水(利根川流域)についての結果である。

市販の国内のナチュラルウォーターの調査結果は、2007年9~10月に購入した49試料のうち、外国製の3試料と、聞き取り調査で塩素添加の影響を受けていることがわかった国内製の3試料を除いた結果である(n=43)³²⁾。専用水道の原水の調査結果は、2006年10月に採取した20施設の結果である(n=20)²⁶⁾。利根川中流域の河川水の調査結果は、2006年3~4月に採取した荒川(武蔵水路合流地点より下流)の4試料と江戸川の1試料、および2006年4月に採取した3浄水場、2006年9月に採取した4浄水場、2007年1月に採取した2浄水場の原水の結果である(n=14)(2浄水場は3回、1浄水場は2回調査)^{15),16),26)}。利根川流域以外の表流水の調査結果は、2006年3~4月に採取した4浄水場、2007年1月に採取した20浄水場の原水の結果である(n=24)(1浄水場は2回調査。同調査では淀川下流域の浄水場も含まれていたが上流の下水処理場の影響を受けているため除いた)²⁶⁾。利根川中流域の浄水は、2006年2~5月に採取した10給水栓水、および2006年4月に採取した4浄水場、2006年9月に採取した4浄水場、2007年1月に採取した2浄水場の浄水場出口水である(n=20)(2浄水場は3回、1浄水場は2回調査)^{15),16),26)}。これら過去の調査での塩素酸イオン、過塩素酸イオン濃度の

測定方法は前項で述べた方法と同様である。定量下限値は、塩素酸イオンでは0.05 μg/L(一部の浄水場の結果は0.1 μg/L)、過塩素酸イオンでは0.05 μg/Lであった。

3. 結果および考察

(1) 東京の地下水中の塩素酸イオンと過塩素酸イオン

図-1に採取地点の分布と塩素酸イオン、過塩素酸イオン濃度の結果を示す。表-1に、調査結果のまとめを示す。塩素酸イオンの場合、49試料中24試料が定量下限値以上の濃度で、その範囲は<0.05~2000 μg/L、中央値は<0.05 μg/Lであった。濃度分布を見ると、<1, 1~10, 10 μg/L以上であった試料は、それぞれ31, 9, 9試料であった。水道水質基準と比較すると、3試料がその10%値以上で、そのうち1試料が基準値よりも高い値であった。過塩素酸イオンの場合、52試料中28試料が定量下限値以上の濃度で、その範囲は<0.01~4.2 μg/L、中央値は0.03 μg/Lであった。濃度分布を見ると、<0.1, 0.1~1, 1 μg/L以上であった試料は、それぞれ28, 11, 13試料であった。

目標値と比較すると、5試料がその10%値以上であった。しかし、水道水中からは過塩素酸イオンは目標値と同等以上の濃度での存在が報告されていたが^{15),26)}、地下水の場合はそのような試料は認められなかった。なお、塩素酸イオンの試料数が少ないが、これは、一部の試料は少量であったため過塩素酸イオン濃度のみを測定したことによる。

これらの結果から、本研究で対象とした東京の地下水

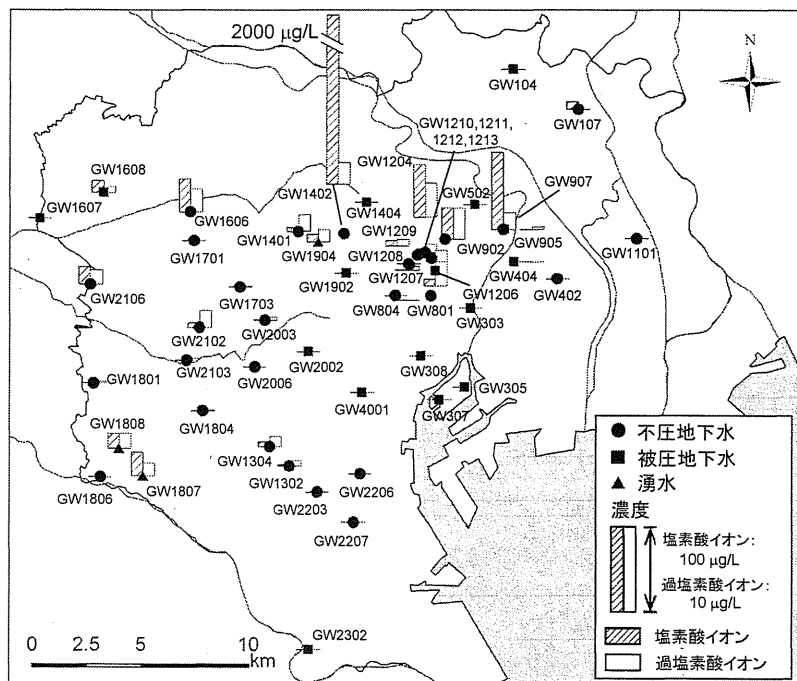


図-1 調査対象地点と塩素酸イオン濃度および過塩素酸イオン濃度の調査結果

表-1 東京の地下水中の塩素酸イオン濃度および過塩素酸イオン濃度

試料	塩素酸イオン		
	定量下限値以上の割合*	濃度 (μg/L)	中央値 (μg/L)
不圧地下水	17/30	<0.05~2000	0.71
被圧地下水	4/16	<0.05~14	<0.05
湧水	3/3	9.3~28	17
合計**	24/49	<0.05~2000	<0.05

試料	過塩素酸イオン		
	定量下限値以上の割合*	濃度 (μg/L)	中央値 (μg/L)
不圧地下水	20/31	<0.01~4.1	0.24
被圧地下水	5/18	<0.01~4.2	<0.01
湧水	3/3	1.4~1.8	1.5
合計**	28/52	<0.01~4.2	0.03

*定量下限値以上の試料数/測定試料数, **試料数が異なるのは一部の試料で過塩素酸イオン濃度のみを測定したため

の場合、その75%程度は、塩素酸イオン、過塩素酸イオンが定量下限値未満の濃度、あるいは存在していてもその濃度は低いが、残り25%程度は塩素酸イオンあるいは過塩素酸イオンが比較的高い濃度で存在していることが示された。また、様々な用途の地下水が調査対象ではあったが、水道水質基準や目標値と比較した場合、10%程度の試料はそれらの10%値以上であり、塩素酸イオンについては、基準値を超える地下水もあることがわかった。

地下水を不圧地下水、被圧地下水、湧水に分類した場合、塩素酸イオンは、それぞれ30試料中17試料、16試料中4試料、3試料中3試料で定量下限値以上の濃度であった。過塩素酸イオンは、それぞれ31試料中20試料、18試料中5試料、3試料中3試料で定量下限値以上の濃度であった。全ての分類の地下水からも塩素酸イオン、過塩素酸イオンは定量下限値以上の濃度の試料があったが、不圧地下水、湧水からの割合が高い傾向にあった。本研究の調査結果を、国内の過去の調査での地下水(市販のナチュラルウォーター、専用水道の原水)中の塩素酸イオン濃度、過塩素酸イオン濃度の結果と比較する(図-2)^{26,32)}。市販のナチュラルウォーターの場合、塩素酸イオン、過塩素酸イオンは43試料中それぞれ28, 24試料が定量下限値以上の濃度で、その範囲は<0.05~7.1, <0.05~0.57 μg/Lであった³²⁾。専用水道の原水中の塩素酸イオン、過塩素酸イオンは20試料中それぞれ17, 15試料が定量下限値以上の濃度で、その範囲は<0.05~12, <0.05~1.2 μg/Lであった²⁶⁾。したがって、これら過去の調査の地下水において、塩素酸イオン濃度、過塩素酸イオン濃度が、それぞれ10, 1 μg/L以上と比較的濃度が高かった試料は、専用水道の1試料のみであり、本研究の調査対象の地下水と比べると低い濃度範囲であった。また、利根川流域以外の表流水では(n=24)、塩素

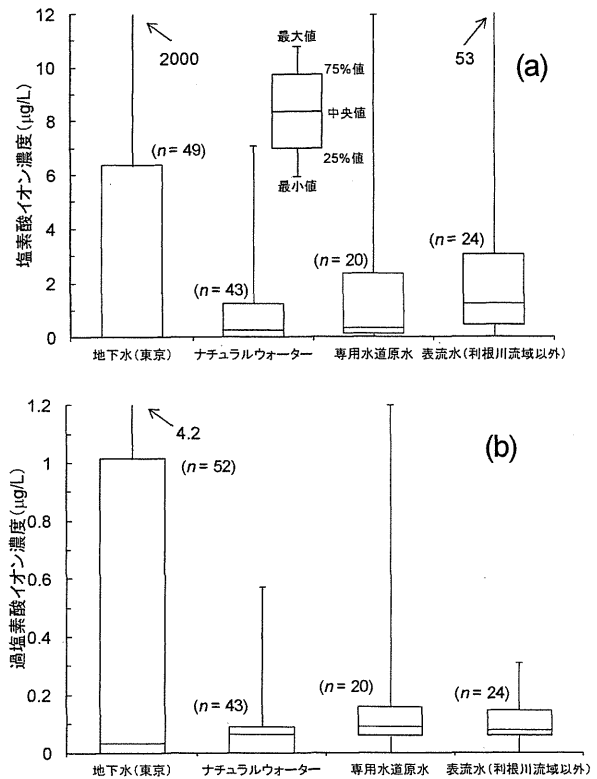


図-2 東京の地下水、市販のナチュラルウォーター、専用水道の原水、利根川流域以外の表流水中の (a) 塩素酸イオン濃度および (b) 過塩素酸イオン濃度 (定量下限値未満は0と表記)^{26,32)}

酸イオン濃度が 10 μg/L 以上であった試料は 1 試料で、過塩素酸イオン濃度が 1 μg/L 以上であった試料はなかった(図-2)²⁶⁾。すなわち、本研究の対象試料は、利根川流域以外の表流水と比較しても、比較的高い濃度の試料の割合は高かった。

一方、東京の地下水、市販のナチュラルウォーター、専用水道の原水において、定量下限値以上の濃度であった試料の割合は、塩素酸イオンでは、それぞれ49%、65%、85%、過塩素酸イオンでは、それぞれ48%、55%、75%であり、両イオンとも東京の地下水が最も低い値であった(過塩素酸イオンでは、定量下限値を過去の調査での値に合わせて評価)。また、中央値については、本調査と過去の調査の地下水との間で大きな違いは認められなかった(図-2)。

図-3に、塩素酸イオン濃度が10 μg/L未満、過塩素酸イオン濃度が1 μg/L未満であった試料について、塩素酸イオン濃度と過塩素酸イオン濃度の関係を示す。東京の地下水、市販のナチュラルウォーター、専用水道の原水、利根川流域以外の表流水のいずれも両イオンに関連性は認められなかった。しかし、東京の地下水、市販のナチュラルウォーター、専用水道の原水については、塩素酸

イオン濃度より過塩素酸イオン濃度の方が高い場合が認められた(図中の $y=x$ の上側). これら過塩素酸イオン濃度の方が高い試料の場合, 塩素酸イオン濃度, 過塩素酸イオン濃度はそれぞれ $<0.05\sim 0.16$, $0.03\sim 0.17$ $\mu\text{g/L}$ であり, 両イオン(特に塩素酸イオン)濃度は低い範囲であった.

利根川流域以外の表流水の場合, 両イオンともに定量下限値未満の場合があったものの, 塩素酸イオンの方が常に濃度が高かった. 北極圏の雪中の塩素酸イオン濃度と過塩素酸イオン濃度の調査の場合, 各地点での両イオンの平均濃度の比は $1.0\sim 15.6$ の範囲であった³³⁾. また, 南西テキサスのビッグ・ベンド国立公園, 東プエルトリコのエルヴェルデの湿性沈着物中の塩素酸イオンと過塩素酸イオンの濃度比はそれぞれ 0.12 ± 0.02 , 2.00 ± 0.40 であった¹⁹⁾. したがって, 自然起源の場合, 地域によって塩素酸イオン濃度の方が高い場合と低い場合があると考えられるが, 図-3の結果も考慮すると, 国内では, 塩素酸イオン濃度の方が高い場合が多いと推測された. とここで, 塩素酸イオンと過塩素酸イオンの生物分解は溶存酸素濃度が低い状態に進むこと³⁴⁾, 塩素酸イオンの方が速やかであることが報告されている³⁵⁾. このとき, 過塩素酸イオンや塩素酸イオンは, 過塩素酸イオン→塩素酸イオン→亜塩素酸イオン→塩化物イオン(および酸素)へと還元されていく³⁴⁾³⁵⁾. また, 電子供与体である有機物がある環境で, より進むことが報告されている³⁴⁾. 本研究の調査対象試料のうち溶存酸素濃度が 1.0 mg/L 未満であった試料は 18 試料で, これら試料中の溶存有機

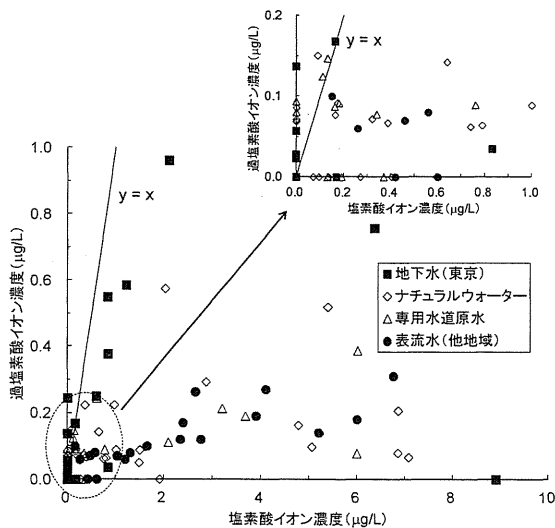


図-3 東京の地下水, 市販のナチュラルウォーター, 専用水道の原水, 利根川流域以外の表流水中の塩素酸イオン濃度と過塩素酸イオン濃度の関係(定量下限値未満は 0 と表記)²⁶⁾³²⁾

物濃度は, $1.3\sim 13$ mg/C/L と地下水としては高い範囲にあった²⁴⁾. この 18 試料中, 両イオンとも定量下限値未満であったのは 12 試料, それ以上の濃度であった場合でも, 塩素酸イオン濃度が 10 $\mu\text{g/L}$ 以上, 過塩素酸イオン濃度が 1 $\mu\text{g/L}$ 以上であった試料はなかった. また, 過塩素酸イオン濃度の方が塩素酸イオン濃度より高かった試料も 3 試料あった. 加えて, 両イオンとも定量下限値未満であった 12 試料中 6 試料からは医薬品類が存在していた²⁴⁾. 下水の影響を受けて医薬品類が存在したとすれば, これら 6 試料は, 利根川流域の河川水や次亜塩素酸ナトリウム溶液の影響で, 塩素酸イオン, 過塩素酸イオンの存在が考えられる試料である¹⁶⁾²⁶⁾. これらの結果から, 本研究で対象とした東京の地下水の場合, 少なくとも, 溶存酸素濃度が低い試料については, 塩素酸イオン, 過塩素酸イオンの生物分解が進んでいることが示唆された. ただし, 溶存酸素濃度が 1.0 mg/L 以上の試料でも, 両イオン濃度が定量下限値未満であった場合もあり, また, 硝酸イオン濃度も塩素酸イオン, 過塩素酸イオンの生物分解の速度に関連しているという報告³⁴⁾³⁶⁾もあるため, これらの点については検討が必要であると考えられた.

これらの結果から判断すると, 東京の地下水, 市販のナチュラルウォーター, 専用水道の原水において, 塩素酸イオン濃度より過塩素酸イオン濃度の方が高い場合があった原因は, 両イオンの生物分解とその速度の違いが関与していると推測された. 特に, 東京の地下水については, 全体的に溶存有機物濃度が比較的高く, また 35%程度は溶存酸素濃度が低い状態にあり²⁴⁾, 生物分解が進みやすい環境であった試料が比較的多かったと考えられた.

(2) 塩素酸イオン, 過塩素酸イオンの起源の推測

過去の調査において, 人為的な汚染がないと考えられる地点での結果から, 何らかの人為的な原因が推測される濃度のオーダーは, 経験的にはあるが, 塩素酸イオンで 10 $\mu\text{g/L}$ 以上, 過塩素酸イオンが 1 $\mu\text{g/L}$ 以上と見積もられた²⁴⁾. 本研究で調査した地下水の場合, 該当する試料は, 塩素酸イオンのみでは 1 試料, 過塩素酸イオンのみでは 5 試料, 両方では 8 試料で合計 14 試料であった. また, 塩素酸イオンの水道水質基準値, あるいは過塩素酸イオンの水道での目標値の 10%以上であったのは, 6 試料であった. 14 試料の中で, 被圧地下水は 2 試料(GW1206, 1208), 残り是不圧地下水(GW902, 907, 1204, 1304, 1401, 1402, 1606, 2102, 2106), 湧水(GW1807, 1808, 1904)であった. また, これら 14 試料中の溶存酸素濃度は全て 1.0 mg/L 以上であった. 本節では, これら比較的濃度が高かった試料を対象に, その

起源について推測する。

図4に、塩素酸イオン濃度、過塩素酸イオン濃度が比較的高かった東京の14地下水、利根川中流域の河川水、東京の浄水中の塩素酸イオン濃度、過塩素酸イオン濃度を示す^{19,26)}。

河川水と浄水の結果を比較すると、塩素酸イオン濃度は浄水中の方が高かったが、過塩素酸イオン濃度は、浄水中ではばらつきはあるものの同程度であった。この理由は、塩素酸イオンの場合、多くの浄水場で、その主な起源である次亜塩素酸ナトリウム溶液（あるいは生成次亜）を消毒剤として用いていたためと考えられた²⁶⁾。ただし、一部の浄水場では、消毒剤として液化塩素を用いており、この場合、浄水中の塩素酸イオン濃度は増加しなかったことが報告されている²⁶⁾。また、過塩素酸イオン濃度が、河川水中よりも低い場合があった。過塩素酸イオンは浄水処理では除去困難な物質であることから¹⁹⁾、この理由は、利根川上流域の発生源の影響を受けていない水を原水としている浄水場の影響によるものと考えられた。

荒川、その派川の隅田川、あるいは江戸川沿いに幾つか調査地点があるが、GW907以外は、塩素酸イオン、過塩素酸イオンともに濃度は低かった。したがって、利根川上流域の発生源近くの下流の川沿いの地下水の場合と異なり^{19,26)}、明らかな汚染は認められなかった。GW907の場合、塩素酸イオン濃度(92 µg/L)は、河川水中の濃度よりも高かった。また、塩素酸イオン濃度と過塩素酸イオン濃度比をとると、その値(46)は、河川水の場合よりも1桁程度大きい値であった(図5)。このことから、GW907での塩素酸イオン、過塩素酸イオンへの河川水の浸透による影響は小さいと考えられた。なお、図5における東京の地下水の結果は、塩素酸イオン濃度が非常に高かったGW1402を除いている。

14地下水のうち不圧地下水は9試料であったが、塩素酸イオン濃度(2000 µg/L)が水道水中の濃度よりも高かったGW1402以外は、両イオンの濃度は浄水と同程度あるいはそれより低い濃度(4.9~92 µg/L)であった。

塩素酸イオンと過塩素酸イオンの濃度比(2.5~46)も浄水と同程度であった。このうち、GW902, 907, 1401, 1606, 2102, 2106の6試料からは、ジエチルトルアミド、クロタミトン、エテンザミド、カルバマゼピンの4種の医薬品類のうち、1種類以上の存在が確認された²⁴⁾。東京の不圧地下水中の医薬品類は、下水による影響を受けていると推測されている^{24,37)}。したがって、GW1402を除くこれら8試料中の塩素酸イオン、過塩素酸イオンは、水道水や下水の影響を受けていると推測された。また、湧水3試料についても、塩素酸イオン濃度、塩素酸イオンと過塩素酸イオンの濃度比、医薬品類や大

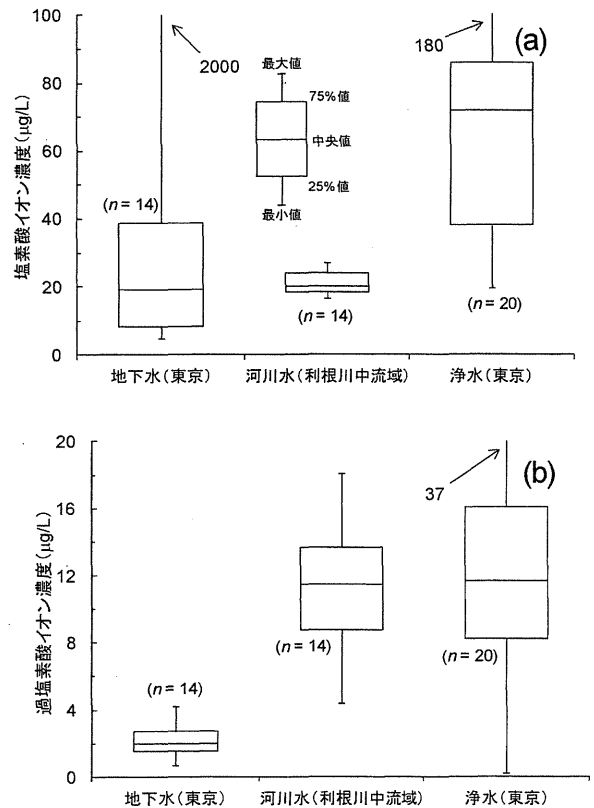


図4 東京の地下水、利根川中流域の河川水、東京の浄水中の (a) 塩素酸イオン濃度および (b) 過塩素酸イオン濃度 (東京の地下水については、塩素酸イオンまたは過塩素酸イオン濃度が比較的高かった14試料を対象)^{19,26)}

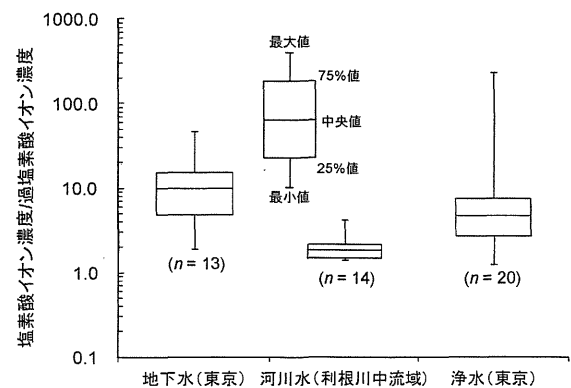


図5 東京の地下水、利根川中流域の河川水、東京の浄水中の塩素酸イオン濃度と過塩素酸イオン濃度の比 (東京の地下水については、塩素酸イオンまたは過塩素酸イオン濃度が比較的高かった14試料のうちGW1402以外の13試料を対象)^{19,26)}

腸菌の存在状況から判断すると²⁴⁾、同様に、下水による影響を受けていると推測された。

GW1402は、墓地に隣接した民家の生活用井戸水で、