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研究課題名（英文） Removal of precursors of nitrogenous disinfection by-products in drinking water sources by advanced treatment processes

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研究成果の概要（和文）：本研究は、日本とタイの水道原水中に含まれるN-DBPsの前駆物質の性状と、各種高度浄水処理技術による前駆物質除去効果を明らかにした。ポリスチレン系の陰イオン交換樹脂は、ポリアクリル系のイオン交換樹脂に比べて臭化物イオンの吸着能力が高く、そのため、臭化物系のTHMsの生成能をより高い割合で低減した。分子量3,000Da以上の有機物が多く含まれる原水の場合、DBP生成を低減するためには、フェリハイドライトが適した吸着剤であると言える。原水中の臭化物イオン濃度が高い場合は、ポリスチレン系のイオン交換樹脂は臭化物イオンと溶存有機化合物(DOC)を同時に除去することて、DBP生成を抑制することができる。

研究成果の概要（英文）：This research elucidated the precursors of N-DBPs in various drinking water sources of Japan and Thailand, and the effectiveness of different advanced water treatment processes to remove the DBP precursors. Polystyrene anion exchange resin had the greatest ability to remove bromide and subsequently decreased formation potentials of brominated THMs in comparison to polyacrylic resins. Ferrate (Fe(VI)) oxidation could oxidize aromatic DOM into smaller MW DOM that could be removed by subsequent coagulation using polyaluminium chloride. When the large MW (> 3000 Da) aromatic DOM is dominant in the water, ferrihydrite may be a suitable adsorbent to mitigate the DBP formation. When the source water contained high bromide concentration, adding anion exchange adsorption using polystyrene resin could offer simultaneous removal of both bromide and DOM.

研究分野：drinking water treatment engineering

キーワード：nitrogenous DBPs　anion exchange resin　brominated DBPs　dissolved organic amtter　ferrihydrite　microfiltration　membrane fouling　water treatment

１．研究開始当初の背景

(1) 窒素系消毒副生成物 (nitrogenous disinfection by-products, N-DBPs): an increase in the release of N-DBP precursors in drinking water sources e.g. from sewage treatment effluent, algal bloom raises concern in N-DBPs in drinking water due to its potential adverse health impact to humans. Haloacetonitriles (HANs, i.e. ジクロロアセトニトリル, DCAN) is listed in the Targets for Water Quality Management (水質管理目標設定項目と目標値). However, there is no detailed report in Japan on the N-DBP formation potentials (N-DBPFPs).

(2) Removal of N-DBPs: the most effective means of controlling N-DBPs is to remove precursors before chlorination or chloramination. However, nitrogen enriched dissolved organic matter (nitrogen-enriched DOM) that has small molecular sizes and poses hydrophilic characters is not readily removed by conventional drinking water treatment processes. Our previous works have reported that ion exchange resins (IERs) and ferrihydrite can remove hydrophilic charged DOM in surface waters and adsorption can be integrated with membrane filtration to ensure simultaneous adsorbent separation. Polystyrene IER has a high affinity to bromide ion and hence it could potentially eliminate formation of both brominated and chlorinated DBPs.

２．研究の目的

(1) To elucidate the N-DBPFPs in natural waters of Japan and Thailand during chlorination and chloramination.

(2) To examine the effectiveness of advanced water treatment processes including ferrihydrite adsorption or powdered activated carbon (PAC) adsorption in combination with microfiltration, IER in removing the N-DBP precursors and oxidation using ferrate (VI).

３．研究の方法

(1) Sampling site and water collection: Water samples were collected as grab sampling from: two reservoirs in Chichijima Island, namely CH1 and CH2, in October 2014 and June 2015; one reservoirs in Hahajima (HA) in October 2014 and June 2015; from Aragawa river (AR) in October 2014; from upstream and downstream of Chao Phrya river (Thailand), i.e. UC, DC1 and DC2, respectively, in November 2015 and March 2016. The samples were then pre-filtered through 0.45 µm hydrophilic PTFE membrane filters (Millipore, JHWP09025). The filtered samples were hereafter referred to as raw waters and kept refrigerated at 4 ºC until use.

(2) Anion exchange resin (AER) adsorption experiments: IRA400 (polystyrene AER) and purolite (polyacrylic AER) were used to compare ability of the DOM removal. The experiments were performed by adding 4.8 g of the AERs into a 1000-mL flask containing 600 mL raw water, corresponding to an AER dosage of 8 g/L. Adsorption experiments were conducted at 25°C by horizontally shaking at 200 rpm for 30 min.

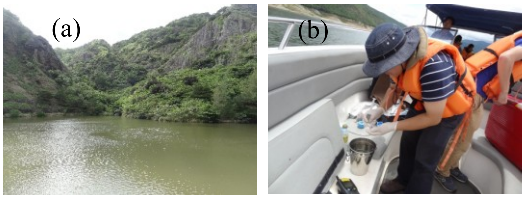

図 1 Sampling points (a) Chichijima island (CH1); (b) Bhumipol Dam, Thailand (UC).

(3) Ferrihydrite (Fh) and PAC: The 2-line Fh was synthesized according to the method of our previous publication. The Fh had a volumetric mean diameter of 0.15 µm based on the dynamic light scattering analysis (Nanotrac$^{\text{TM}}$ 150, Nikkiso). The Fh concentration was measured by inductively coupled plasma mass spectrometry (ICP-MS) after digestion with nitric acid. The wood-based PAC (Shirasagi S-10, Japan EnviroChemicals, Ltd.) had a mean particle size of 151.2 µm as reported by the manufacturer.

(4) Hybrid adsorption–microfiltration (MF) processes: hybrid membrane filtration processes were performed in a stirred cell with a capacity of 50 mL. PVDF membrane with a nominal pore size of 0.1 µm and effective surface area of 13.4 cm^2 was used. At the beginning of the experiment, Fh or PAC was dosed (1 g/L as Fe or PAC) into the filtration cell, and then the filtration was operated at a constant trans-membrane pressure (TMP) of 50 ± 1 kPa and a stirring rate of 600 rpm until a permeate volume of 900 mL (ca. 672 L/m^2) was obtained.

(5) Ferrate oxidation: 実験に用いるFerrate(VI)として、純鉄を陽極・陰極とし、電解質としてNaOH 12M＋KOH 4M溶液, 500 mL を用いて溶存態の FeO_4^{2-}を得た。

(6) Chlorination and chloramination: chlorination was performed by adding NaOCl into buffered samples (pH 7.0 ± 0.2). The chlorinated samples were incubated at 20±1˚C, in the dark, for 10 min, 30 min, 60 min, 6 h, 24 h, 3 days and 7 days. Chloramination was performed on samples buffered to pH 7.0 using pre-formed NH_2Cl and incubated for 96 h at 20±1˚C.

(7) DBP analysis: trihalomethanes (THMs) were measured by headspace technique with a gas chromatography-electron capture detector (GC-ECD) (GC-2010 plus; Shimadzu Corp.,

Japan), according to the Japanese Standard Methods for the Examination of Water (2011). Analysis of HANs and haloketones (HKs) was performed using the GC-ECD, following USEPA method 551.1. The GC column was an Rtx®-1 fused silica capillary column (30 m × 0.32 mm I.D. with 1 µm film thickness, Restek Corp., PA, USA). The GC temperature program comprised an initial temperature of 35 ºC for 5 min, ramping to 50 ºC at 2 ºC/min and holding for 10 min, ramping to 225 ºC at 10 ºC/min and holding for 15 min, ramping to 260 ºC at 10 ºC/min and holding for 15 min. *p*-bromofluorobenzene was added as an internal standard.

４．研究成果

(1) Characteristics of DOM water samples: Table 1 shows that CH2 waters was weakly alkaline (up to pH 8.9) while it was nearly neutral for others. A high pH condition of CH2 waters might be caused by algal bloom. Raw waters from Ogasawara islands had higher DOC, UV_{254} absorbance and bromide than raw waters from Aragawa and Chao Phraya rivers. The $SUVA_{254}$ values (= UV_{254}×100/DOC) of raw waters from Ogasawara islands were higher than 3.0 L/m-mg, indicating mainly hydrophobic fractions and predominant DOM structures rich in unsaturated carbon bonds.

表 1 Water quality parameters of raw waters used in this research.

Samples	pH	DOC (mg/L)	UV_{254} (cm^{-1})	Br^- (mg/L)
CH1	7.4	5.63	0.255	0.26
CH1*	7.3	5.14	0.181	0.23
CH2	8.2	6.60	0.287	0.20
CH2*	8.9	5.66	0.196	0.24
HA	7.9	5.48	0.223	0.17
AR	7.4	1.02	0.026	0.04
UC	8.5	3.21	0.065	< DL
DC1	7.4	5.83	0.171	0.06
DC2	7.3	2.13	0.053	0.05

* Samples collected in June 2015.

(2) DOM and bromide reduction by AERs: Efficiency of IRA400 was compared with Purolite for reductions of DOM and bromide. $SUVA_{254}$ values of treated waters by IRA400 were higher than those by Purolite since IRA400 had a higher DOC removal while UV_{254}-absorbing DOM reduction was nearly identical. As compared with Purolite, more bromide reduction was obtained by IRA400, probably due to the fact that polystyrene AER exhibits greater affinity in removing bromide than that of polyacrylic AER.

The effect of operating factors and AER structures on bromide removal was examined using simulated water as shown in Fig. 2A-2C. The amount of bromide adsorbed on the AERs decreased from 28.4–32.6 mg-Br/g-AER to 1.04–1.05 mg-Br/g-AERs as AER dosage increased from 0.25 to 8.0 g/L. This phenomenon may be associated with lower utilization of the adsorbent adsorptive capacity. Indeed, the adsorbent surface consists of sites with different binding energies. At low adsorbent amount, as all types of sites are entirely exposed, the adsorption on the surface becomes saturated. At a high adsorbent amount, as a larger fraction of lower energy sites were occupied, resulting in decrease in availability of higher energy sites, leading to a low adsorption capacity. In contrast, the amount of bromide adsorbed on AER increased as increasing the initial bromide concentration (Fig. 2D) due to the facts that higher bromide concentration exhibited the greater interaction between bromide concentration and AERs.

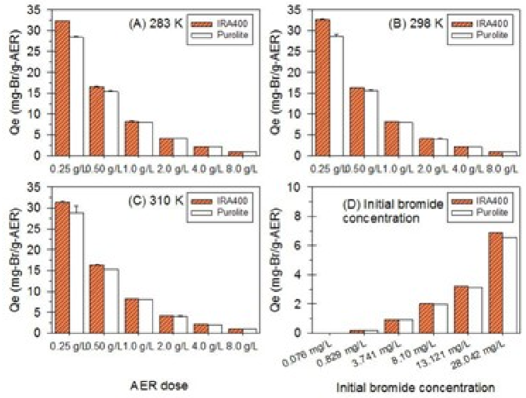

図 2 Effect of AER dosage and temperature (A, B and C) and initial bromide concentration (D) on bromide removal by AERs. Contact time: 24 h; initial bromide concentration: 8.38±0.04 mg/L.

(3) The formation potential (FP) of THMs: figure 3 present formation of each THM species as a function of contact time (10 min–7 days) during chlorinating CH1 and CH2 raw waters and AER-treated waters.

Chloroform (クロロホルム, TCM) was dominant THM species accounting for 58–71% of total THMs in chlorinated raw waters, followed by bromodichloromethane (ブロモジクロロメタン, BDCM) of 25–34% and dibromochloromethane (ジブロモクロロメタン, DBCM) of 3–8% for entire contact time (Fig. 3). Bromoform (ブロモホルム, TBM) was not detected in all samples although high bromide and DOC concentrations in the raw waters (Table 1). Low occurrence of brominated THMs was probably related to the DOM characteristics. Bromine appears to be more effectively incorporated into hydrophilic fraction, which was minor in these waters.

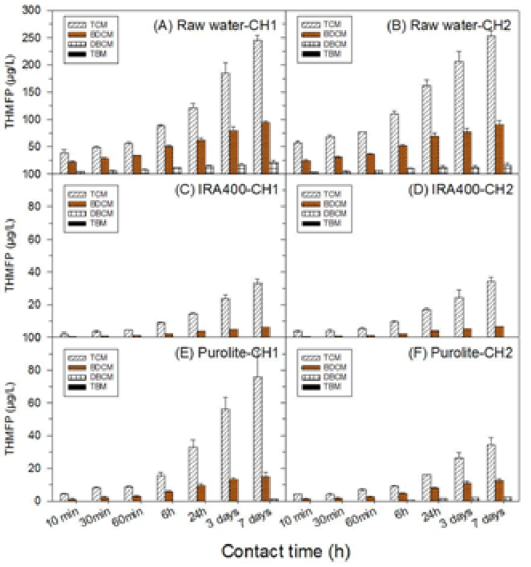

図 3 Effect of contact time on the formation potential of THM between raw waters and AER treated waters. Each error bar represents duplicate analysis.

(4) Hybrid ferrihydrite (Fh) adsorption–MF and PAC adsorption–MF processes:

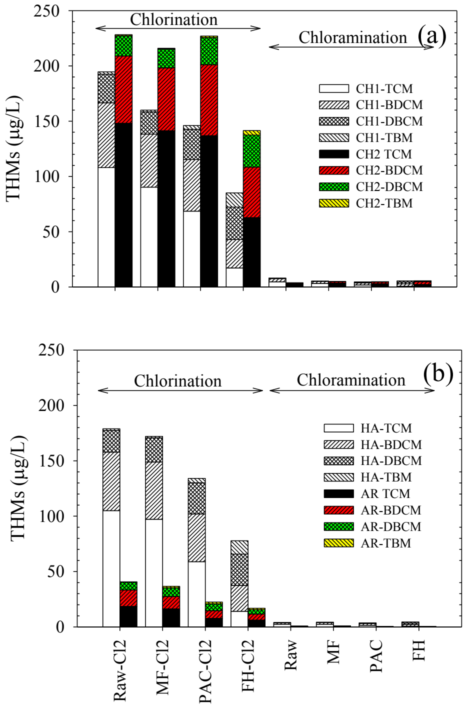

図 4 THMFPs before (Raw) and after treatment processes at the filtered volume of 336 L/m^2; Chlorination: 24 h; Chloramination: 4 days. (a) CH1, CH2 and (b) HA, AR waters.

TCM, the fully chlorinated DBP, was efficiently removed by the Fh+MF treatment in all waters tested (Fig. 4). In contrast, the removal of TCM precursor by the PAC+MF process was insignificant probably because PAC prefers to remove aromatic micromolecular DOM, which was not the main TCM precursor. TBM, the fully brominated DBP, increased after the Fh+MF process compared to MF alone. It was suggested that TBM formation prefers high bromide, high alkalinity and low DOC conditions.

Chloramination lowered the formation potentials of total THMs substantially as shown in Fig. 4. This suggests that THM precursors in the reservoir water and AR water were not reactive against monochloramine (dominant chloramines species) at the controlled condition in this experiments. Nonetheless, chloramination method applied in the full-scale drinking water treatment plant may be different from the lab experiment, and thus THMFPs in the real chloraminated waters could be potentially higher than the reported in this study.

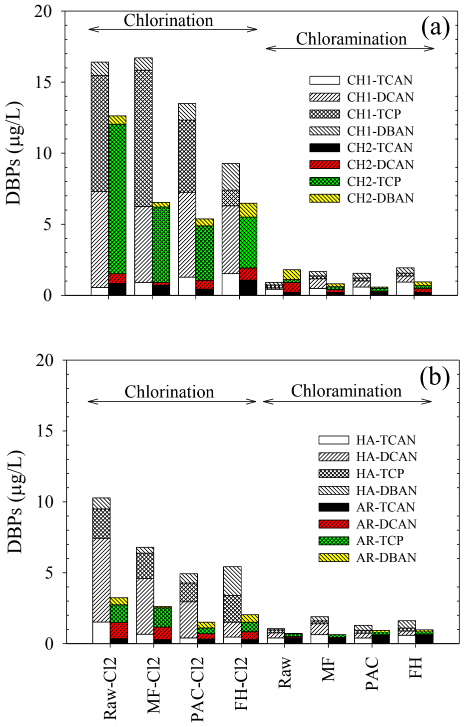

図 5 HANFPs and HKFPs before (Raw) and after treatment at the filtered volume of 336 L/m^2; Chlorination: 24 h; Chloramination: 4 days. (a) CH1, CH2 and (b) HA, AR waters.

In Fig. 5, DCAN is typical chlorinated DBPs occurring at highest concentrations, followed by trichloroacetonitrile (トリクロロアセトニトリル, TCAN) among HANs in the “no treatment” samples under the low Br/DOC condition. In all samples, DCAN concentration was below the provisional guideline for drinking water set at 10 µg/L published in April 2015 by Ministry of Health, Labour and Welfare (厚生労働省). Dibromoacetonitrile (ジブロモアセトニトリル, DBAN) formation might be increased by treatments with either Fh+MF or PAC+MF, relative to “no treatment” samples (Fig. 5). However, DBAN formation potential was below the provisional guideline value of 60 μg/L. Fh+MF could efficiently remove precursor of 1,1,1-trichloropropanone (TCP) despite an increase in Br/DOC ratio. This suggests that the formation of TCP is inversely related to Br/DOC.

Significantly lower HANFPs were observed as compared to THMFPs (dihaloacetonitrile, DXAN was ca. 4 % of total THMFP in raw waters). The total molar concentration of HANs are reported to be about 10 % of the total molar THMs concentration, though it ranged from 2 to 20 % in USA and Australia, depending on the water quality.

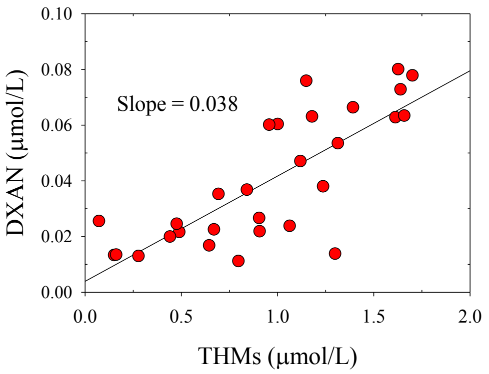

図 6 Linear correlation of THMFP and dihaloacetonitriles (DXAN = DCAN + DBAN) for the chlorinated water samples on the molar basis.

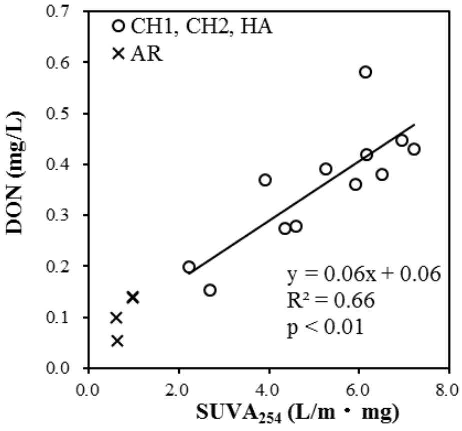

図 7 Linear correlation between dissolved organic nitrogen (DON) and $SUVA_{254}$ for the chlorinated reservoir and Aragawa river water samples.

Dissolved organic nitrogen (DON) in water mainly comprises amino sugars, peptides and porphyrins. For the chlorinated water samples, nitrogen source for HAN formation is solely derived from DON. As shown in Fig. 7, a significant positive correlation between DON and $SUVA_{254}$ was observed in CH1, CH2 and HA waters, suggesting that aromatic DON is dominant in reservoir waters. This result can explain the findings that FH+MF and PAC+MF could remove the HAN precursors due to high adsorption affinity to aromatic DON in the source waters.

(5) Ferrate oxidation: ferrate (Fe(VI)) has a high oxidation capacity and products of ferrate reduction in water are Fe(III) precipitate that adds benefit to the DOM removal. In this study, influent of water purification plant in Chichijima (nearly similar to CH1, CH2 source waters) was used to assess effectiveness of ferrate oxidation with high $SUVA_{254}$ water. Ferrate oxidation was evaluated as stand-alone process and combination with polyaluminium chloride (PACl) coagulation.

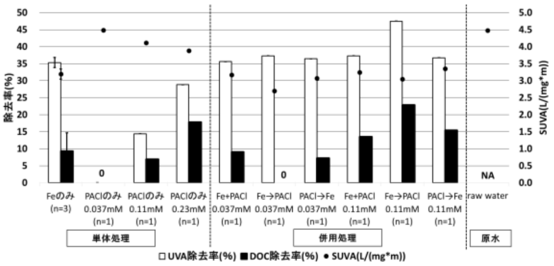

図 8　UVA_{254}、DOC、$SUVA_{254}$ 結果(エラーバーは SE). (Fe(VI) : 全て 0.042 mM, PACl : 表記のモル濃度).

In Fig. 8, for the stand-alone treatment processes, when compared with PACl (0.23 mM), Fe(VI) showed a greater reduction of UV_{254} and lowered $SUVA_{254}$ of raw water to greater extent than PACl, suggesting oxidation target toward aromatic DOM such as humic substances. For the combined processes of Fe(VI) and PACl (0.037 mM), the UV_{254} and DOC removals were nearly similar to Fe(VI) oxidation alone, and treatment sequence (order) of Fe(VI) and PACl did not have a significant impact on the overall DOC removal. Nonetheless, when increasing PACl dosage from 0.037 to 0.11 mM, Fe(VI) oxidation followed by coagulation showed the best performance in removing DOM. The result demonstrates a potential use of ferrate oxidation in combination with coagulation to enhance aromatic DOM removal.

(6) 研究成果の概要：本研究は、日本とタイの水道原水中に含まれる N-DBPs の前駆物質の性状と、各種高度浄水処理技術による前駆物質除去効果を明らかにした。日本国内では、小笠原父島と母島の水源貯水池および荒川の水を採水し、またタイでは、チャオプラヤ川の水を採水して実験に用いた。分子量1,000Da 以下の芳香族炭化水素は、トリハロメタン(THMs)とハロアセトニトリルの重要

な前駆物質であることが分かった。吸着－限外膜ろ過のハイブリッド処理では、吸着材として実験室で合成したフェリハイドライトと、水道用の粉末活性炭（PAC）を吸着剤として使用し、両者を比較した。フェリハイドライトは、THM およびジクロロアセトニトリル前駆物質のうち分子量が大きい芳香族系の有機物をよく吸着し、PAC は分子量が小さい前駆物質をよりよく吸着した。ポリスチレン系の陰イオン交換樹脂は、ポリアクリル系のイオン交換樹脂に比べて臭化物イオンの吸着能力が高く、そのため、臭化物系の THMs の生成能をより高い割合で低減した。フェレート(Fe(VI))による酸化処理は、芳香族系の有機物をより分子量が小さな有機物へと分解し、その分海生生物はポリ塩化アルミニウムにより除去できた。分子量 3,000Da 以上の有機物が多く含まれる原水の場合、DBP 生成を低減するためには、フェリハイドライトが適した吸着剤であると言える。原水中の臭化物イオン濃度が高い場合は、ポリスチレン系のイオン交換樹脂は臭化物イオンと溶存有機化合物(DOC)を同時に除去することて、DBP 生成を抑制することができる。

５．主な発表論文等

〔雑誌論文〕（計　１　件）

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〔その他〕

ホームページ等

https://jenyukloh.wordpress.com/2013/04/04/peer-reviewed-international-journals/

６．研究組織

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