Original Article

Effects of UV/PS and UV/H\textsubscript{2}O\textsubscript{2} on Degradation of Natural Organic Matter and Formation Potential of Haloacetonitriles in Surface Water

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ABSTRACT
This study aimed to investigate how degradation of organic matters in surface water by ultraviolet-activated persulfate (UV/PS) contributed to mitigation of formation of haloacetonitriles (HANs) comparing with conventional UV-activated hydrogen peroxide (UV/H\textsubscript{2}O\textsubscript{2}). A surface water sample containing 10 mM of PS or H\textsubscript{2}O\textsubscript{2} was irradiated up to 3,000 mJ/cm\textsuperscript{2} of 254 nm UV lump. Consequently, 3,000 mJ/cm\textsuperscript{2} of UV/PS reduced formation potentials (FP) of dichloroacetonitrile (DCAN) and bromochloroacetnitrile (BCAN) from 3.8 to 0.2 µg/L and 2.8 to 0.6 µg/L, respectively. UV/H\textsubscript{2}O\textsubscript{2} also showed similar tendencies but reductions of DCAN and BCAN were less significant. However, both UV/PS and UV/H\textsubscript{2}O\textsubscript{2} were likely to increase FP of dibromoacetonitrile (DBAN). Additionally, correlation coefficient tests indicated that degradation of chromophore aromatic compounds and fulvic acid-like substances by both UV/PS and UV/H\textsubscript{2}O\textsubscript{2} showed significant correlations with reduction of DCAN-FP. Degradation of some fluorophore aromatic proteins by UV/PS correlated to reduction of BCAN-FP, while increase of other portions of fluorophore aromatic proteins by UV/H\textsubscript{2}O\textsubscript{2} correlated to increase of DBAN-FP. Precursors of DCAN were easily decomposed by both treatments, whereas precursors of brominated HANs (BCAN and DBAN) were not preferentially attacked by them. However, strong oxidation potential of UV/PS achieved decomposition of these organic moieties.

Keywords: advanced oxidation processes, chlorination, disinfection by-products, precursors of haloacetonitriles, excitation-emission matrix

INTRODUCTION

Disinfection by-products (DBPs) are unintentionally formed by reactions between specific types of organic matters which are called as precursors and disinfectants such as chlorine and monochloramine. Emergence of more than 600 species of DBPs and their characteristics have been reported, because unwilling effects on drinking water such as toxicity, carcinogenicity and odour are potentially occurred by DBPs [1,2]. Previous literature has demonstrated that nitrogenous DBPs are more toxic than carbonaceous ones [3]. For instance, haloacetonitriles (HANs) indicate approximately 100 to 1,000 times stronger cyto-toxicity than regulated haloacetic acids (HAAs) [3], though typical concentrations of HANs in finished water are much lower than the regulated trihalomethanes and HAAs [4–6]. However, despite of such high toxicity of HANs and concerning from many previous studies about health risks caused by HANs [3,7,8], HANs are not strictly regulated in many cases. For instance, Drinking Water Quality Standards in Japan currently does not clarify maximum levels of HANs in drinking water, although dichloroacetonitrile (DCAN) is provisionally included in Target Values for Complementary Items and bromochloroacetnitrile (BCAN), dibromoacetonitrile (DBAN) and

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trichloroacetonitrile (TCAN) are listed in Items for Further Study [9].

In a raw water source, dissolved organic nitrogen (DON) plays an important role on formation of HANs, and characteristics of natural organic matter (NOM) can influence formation potential (FP) of HANs [10,11]. NOM ubiquitously exists in all types of water bodies including surface waters and groundwaters, and structures of organic substances contained in NOM and their molecular weights vary depending on local environments such as climate, seasonal variations and temperature [12]. A lot of previous studies correlated HAN-FPs and fundamental characteristics of NOM such as molecular weight fraction, hydrophobicity and specific ultraviolet absorbance (SUVA) values [5,8,13]. Though these previous studies mainly investigated DCAN, brominated HANs should also be focused, because brominated HANs show stronger cyto-toxicity and slower recovery rate from DNA damage than chlorinated HANs [14]. However, no studies have shown relationships between brominated HANs and their potential precursors.

One effective method to mitigate formation of HANs is decomposing organic precursors prior to chlorination. Pre-treatments based on advanced oxidation processes have been getting interests as a useful technology to remove NOM efficiently [15]. Especially, ultraviolet-activated persulfate (UV/PS) showed favourable effect on degradation of organic matters with its higher mineralisation efficiency and stability than conventional UV/hydrogen peroxide (UV/H2O2) processes [16,17]. A mechanism of reduction of organic matters by UV/PS is generation of highly redox radicals: sulphate radicals (SO4·−) are generated by UV photolysis of an O-O bond in PS as shown in the equation (1), where a dissociation energy to break the bond (92 kJ/mol) is lower than breaking the O-O bond in PS as shown in the equation (1), where a dissociation energy to break the bond (92 kJ/mol) is lower than breaking the O-O bond in PS as shown in the equation (1), where a dissociation energy to break the bond (92 kJ/mol) is lower than breaking the O-O bond in PS as shown in the equation (1), where a dissociation energy to break the bond (92 kJ/mol) is lower than breaking the O-O bond in PS as shown in the equation (1), where a dissociation energy to break the bond (92 kJ/mol) is lower than breaking the O-O bond in PS as shown in the equation (1), where a dissociation energy to break the bond (92 kJ/mol) is lower than breaking

\[ \text{SO}_4^{2−} + hν \rightarrow 2\text{SO}_4^•− \]

However, only a few studies investigated how UV/PS influences HAN-FPs. Although a few studies focused on formation of DCAN from model solutions [21,22] or a raw water sample [23], a comprehensive evaluation about formation potential of HANs has yet to be studied. Moreover, according to the best knowledge of the authors, no studies have investigated how changes of NOM properties caused by UV/PS affect HAN-FPs.

In summary, objectives of the present study were: (i) to investigate HAN-FPs during 24 h of chlorination and NOM properties according to fluence during UV/PS, (ii) to compare effects of UV/PS on NOM properties and HAN-FPs with the conventional UV/H2O2 and (iii) to conduct correlation coefficient tests between each NOM property and each species of HAN-FPs to exhibit what changes of NOM properties caused by UV/PS or UV/H2O2 influenced HAN-FPs, possibly suggesting organic structures and moieties that precursors of each species of HANs contains. Measured NOM properties included dissolved organic carbon (DOC), UV absorbance at 254 nm (UV254) and excitation-emission matrix (EEM). Among four major types of HANs (DCAN, BCAN, DBAN and TCAN), monitored species of HANs were limited to three species of dihaloacetonitriles (DHNs), because TCAN is less stable to hydrolysis than DHANs [24].

**MATERIALS AND METHODS**

**Chemical reagents**

All chemical reagents were of analytical grade and used as received without further purification. Milli-Q water (Milli-Q Reference A+, Merck Millipore, Burlington, US) was used for preparation of aqueous solutions except where noted. Catalase from bovine liver was purchased from Sigma-Aldrich (St. Louis, US). Sodium hydroxide (NaOH) was obtained from Wako Pure Chemical Industry (Osaka, Japan). All of other reagents, H2O2, K2S2O8, disodium hydrogenphosphate (Na2HPO4), potassium dihydrogenphosphate (KH2PO4), sodium hypochlorite (NaOCl), sodium ascorbic acid, sulfuric acid (H2SO4), methyl tert-butyl ether (MTBE), HANs standard stock solution mixing six types of HANs (dichloro-, trichloro-, dibromo-, bromo-, bromochloro- and chloroacetonitrile) and chloral hydrate, 1,2-dibromo propane and sodium chloride (NaCl), were purchased from Kanto Chemical (Tokyo, Japan). Sodium sulphate cartridge (InertSep Slim-J Dry I) was purchased from GL Science (Tokyo, Japan). Stock solutions of H2O2 and K2S2O8 were freshly prepared prior to each experiment, and both concentrations of H2O2 and K2S2O8 in the stock solutions were 100 mmol/L. A stock solution of 250 mM of phosphate buffer was prepared by dissolving 15.438 g of Na2HPO4 and 19.223 g of KH2PO4 into 1 L of Milli-Q water. A stock NaOCl solution was prepared by diluting to 1/100 in a glass bottle with a screwcap surrounded...
by aluminium foil and kept in a refrigerator at 5°C, and the concentration of free chlorine was determined by a potable colorimeter (DR900, HACH, Loveland, US). An internal standard stock solution was prepared by mixing 0.100 g of 1,2-dibromopropane with MTBE, filling up until 10 mL to make the concentration of 1,2-dibromopropane 10 g/L. The stock solution was preserved inside a brown airtight double cap storage bottle and stored in a freezer at −20°C. The HANs standard stock solution contained 1 g/L of each species of HANs.

**Raw water sampling**

A raw surface water sample was taken from a water resource reservoir in Japan in March, 2022. The sampling spot is latitudinally located between 23.4° and 30.0° N, that is conventionally classified as a subtropical region [25]. The raw water sample was immediately filtered through a PTFE membrane (Merck Millipore) with 0.45 µm of the pore size after delivered to the laboratory. The sample was stored in a refrigerator at 5°C. Initial characteristics of NOM are summarised in Table 1. A relatively high SUVA value indicates that the sample was mainly consisted of hydrophobic and aromatic compounds [26]. Additionally, the ratio of bromide and chloride (Br−/Cl−) of the sample was 4.1 × 10−3 and higher than typical concentrations of other surface waters reported in previous surveys (2–3 × 10−3 as the average), because the collecting spot was close to sea and sea water naturally has high concentrations of bromide [27]. In contrast, almost no inorganic nitrogen was detected. Ammonium- and nitrite-nitrogen were lower than the lowest limit value.

**Experimental setups and procedures**

**UV/PS and UV/H₂O₂**

A collimated beam apparatus consisting of two 254 nm-wavelength UV lamps above three 500-mL glass beakers was employed for UV/PS and UV/H₂O₂ (Fig. S1, Supplementary Materials). PS or H₂O₂ was added to the glass beakers immediately before the UV treatments to make the end concentrations as 10 mmol/L. The concentrations of PS and H₂O₂ were determined based on results of preliminary experiments, which showed insignificant differences between effects of UV/PS and UV/H₂O₂ on degradations of DOC when 0.1 or 1 mM of PS or H₂O₂ were dosed (Fig. S2). Temperature of the water samples were kept at 20 ± 1°C throughout the experiments. DOC, UV254, EEM spectra and DHAN-FPs were measured at 0, 1,000, 2,000 and 3,000 ml/cm² of fluence. A raw water sample with neither PS nor H₂O₂ was also analysed as a control solution. The control solution was mixed with Milli-Q water, in which dosage was equivalent to PS or H₂O₂ in the samples to make the concentration of NOM as DOC equal to the other samples. Details about the experimental setups are described in Supplementary Materials. All the experiments were conducted in duplicate, and average values including the standard deviations will be shown as the results.

**Formation potential tests and DHANs detection**

After UV/PS, the sample solutions were neutralised by NaOH prior to FP tests, whereas UV/H₂O₂ caused only negligible acidification, and thus NaOH was not spiked. Then, 120 mL of the samples was extracted from the 500-mL beakers to Erlenmeyer flasks with magnetic bars and caps followed by replacing 0.96 mL of the extracts by the phosphate buffer to maintain pH at 7. The flasks were surrounded by aluminium foil. Ten microliters of catalase were spiked and stirred for 10 min only for the solutions after UV/H₂O₂ to quench residual H₂O₂ to prevent chlorination from being interfered by a reaction between H₂O₂ and NaOCl [28]. Increment of DHAN-FPs after UV/H₂O₂ by catalase was evaluated by subtracting from another independently prepared control solution including 10 µL of catalase. The NaOCl solution was added to make the concentration 5.0 mg/L as free chlorine, immediately followed by the commencement of chlorination in a dark room at 20 ± 1°C for 24 h. Excessive concentrations of sodium ascorbic acid were added to terminate the FP tests by quenching residual PS and/or free chlorine. Twenty microliters of (1 + 5) H₂SO₄ were added immediately before the MTBE extraction. Details about the FP tests are described in Supplementary Materials. MTBE extraction to prepare the samples for DHANs detection basically followed Water Examination Method [29]. DHANs were analysed with a gas chromatograph/mass spectrometry.
Fluorescence EEM was measured over an excitation wavelength range of 220–450 nm in 5-nm increment and emission wavelength range of 280–550 nm in 5-nm increment by a spectrofluorometer (FP-8200, Jasco, Tokyo, Japan). EEM spectra were firstly divided into 5 regions according to the ranges of excitation and emission wavelengths because each region correlates to a different group of organic matters: region I, aromatic protein I (ex: 220–250 nm; em: 280–380 nm); region II, aromatic protein II (ex: 220–250 nm; em: 330–380 nm); region III, fulvic acid-like (ex: 220–250 nm; em: 380–550 nm); region IV, soluble microbial product (SMP)-like (250 < ex < 450 nm; em: 280–380 nm); region V, humic acid-like (250 nm < ex < 450 nm; em: 380–550 nm). The EEM data were then quantitatively analysed based on fluorescence regional integration (FRI) using the equation (2), where \( \Phi_{i,a} \) is normalised volume beneath region \( i \), MF is a multiplication factor for region \( i \), which is equal to inverse of the regional areas, and \( I(\lambda_{ex}\lambda_{em}) \) is the fluorescence intensity at a specific pair of excitation and emission wavelengths [33]. The FRI calculations were pursued using the composite trapezoidal rule, which guarantees relatively high precision with the 5-nm wavelength increments [32]. Details about FRI calculations are written in elsewhere [32,33]. An EEM spectrum of a blank solution (Milli-Q water) was also measured, and the FRI calculations were performed after the EEM of each sample was subtracted from that of Milli-Q water [17,34].

\[
\Phi_{i,a} = MF\int_{\lambda_{ex}} I(\lambda_{ex}\lambda_{em}) d\lambda_{ex} d\lambda_{em} (i = I\cdots V)
\]

### RESULTS AND DISCUSSION

#### Effects of the UV/PS and UV/H\(_2\)O\(_2\) on NOM properties

Effects of UV/PS and UV/H\(_2\)O\(_2\) on NOM properties will be compared. Figure 1 showed reductions of DOC and UV\(_{254}\) by UV/PS and UV/H\(_2\)O\(_2\). Figure 1-a) indicates that UV/PS significantly decreased DOC by 20, 68 and 96% after 1,000, 2,000 and 3,000 mJ/cm\(^2\) of fluence, respectively. In contrast, almost no mineralisation of DOC was observed during UV/H\(_2\)O\(_2\). The results about reduction of DOC were in agreement with studies by He et al. and Ahn et al. that UV/PS indicates more effective TOC removal than UV/H\(_2\)O\(_2\) [17,35]. A study by Sarathy and Mohseni also shows a similar tendency to the present study that 2,000 mJ/cm\(^2\) of fluence with 15 mg/L of H\(_2\)O\(_2\) has almost no impact on reducing TOC in a raw water sample [36]. However, Fig. 1-b) reveals that UV/H\(_2\)O\(_2\) exhibited a pseudo-first order reaction between fluence and UV\(_{254}\) with 2.19 × 10\(^{-4}\) cm\(^2\)/mJ of reduction rate. UV/PS also decreased UV\(_{254}\) significantly: sharp degradation in the initial 1,000 mJ/cm\(^2\) of fluence with 9.69 × 10\(^{-4}\) cm\(^2\)/mJ of reduction rate followed by a relatively slower pseudo-first order reaction with 3.84 × 10\(^{-4}\) cm\(^2\)/mJ of the reduction rate in the latter 2,000 mJ/cm\(^2\) of fluence. A previous study mentioned that reduction of UV\(_{254}\) can be classified into two phases under a sulphate radical-based reaction [30]. The result about UV/PS in the present study also followed the similar tendency: the phase 1 corresponded to the reduction in the initial 1,000 mJ/cm\(^2\) of fluence, and the phase 2 corresponded to the latter 2,000 mJ/cm\(^2\) of fluence.

Reduction of UV\(_{254}\) means that degradation of chromophore aromatic compounds, and decrease of DOC reveals that complete mineralisation of organic matters. Therefore, efficient reduction of UV\(_{254}\) and no degradation of DOC during UV/H\(_2\)O\(_2\) possibly mean that aromatic compounds were effectively decomposed to non-chromophore and/or non-aromatic intermediates, but did not result in total mineralisation. Moreover, Zhang et al. illustrates a relationship between reductions of TOC and UV\(_{254}\) during a peroxymonosulfate (PMS)/Co (II) treatment, where only a small reduction of TOC is confirmed until UV\(_{254}\) is decreased by approximately 50%, and they conclude that the phase 1 is categorised when reduction of UV\(_{254}\) is not coincident with removal of DOC.
and the phase 2 is correlated to the reductions of both UV$_{254}$ and DOC [30]. The present study also illustrates relationships between reductions of DOC and UV$_{254}$ during UV/PS and UV/H$_2$O$_2$ in Fig. 2. After 3,000 mJ/cm$^2$ of UV/H$_2$O$_2$, the phase 1 had not finished, which was shown by 50% reduction of UV$_{254}$ but the negligible decrease of DOC. In contrast, UV/PS finished the phase 1 within the first 1,000 mJ/cm$^2$ of fluence. Thereafter, DOC was also started to be decomposed during the phase 2, and the decrease was linearly correlated to that of UV$_{254}$.

Results of quantitative evaluation of the EEM spectra based on FRI are illustrated in Fig. 3. Both UV/PS and UV/H$_2$O$_2$ showed effective reductions in the regions III, IV and V, and UV/PS yielded better declines than UV/H$_2$O$_2$ in these regions. Reduction percentages of the regions III, IV and V after 3,000 mJ/cm$^2$ of UV/PS were 41, 58 and 90%, respectively. Those of 3,000 mJ/cm$^2$ of UV/H$_2$O$_2$ were 21, 44 and 60%, respectively. High decreases about these regions during
UV/PS is also confirmed in the previous study using 1 mM of PS under UV irradiation of raw water [37]. UV/H₂O₂ also indicated similar results to a previous study using 32 mg/L of H₂O₂ with UV light on decolourisation of wastewater [38]. In contrast, both of UV/PS and UV/H₂O₂ increased the region I. UV/H₂O₂ gradually increased the region I by 19% after 3,000 mJ/cm² of fluence. UV/PS sharply increased the region I by 13% during the initial 1,000 mJ/cm² of fluence and finally turned to decrease during the last 1,000 mJ/cm² of fluence. Interestingly, reduction of the region II was only observed during UV/PS, while the degradation of region II was stagnated during UV/H₂O₂.

Reductions in the regions III, IV and V mean decrease of fulvic acid-like, SMP-like and humic acid-like matters, respectively. These substances naturally contain high molecular weight compounds [25,38], and large depletions of these regions were inferred from previous studies that UV/PS and UV/H₂O₂ preferentially attacked high molecular weight compounds [34,40,41]. Additionally, high molecular weight organic substances are generally rich in aromatic and conjugated double bond compounds which can be detected as UV₂₅₄ [42,43]. Figure S3 reveals a correlation between reductions of UV₂₅₄ and a summation of normalised EEM volume of the regions III, IV and V during UV/PS and UV/H₂O₂. Overall, reductions of UV₂₅₄ and the summation of EEM regions III, IV and V were highly correlated during both UV/PS and UV/H₂O₂. In short, Fig. 2 and Fig. S3 indicate that partial decomposition of fluorophore organic portions such as humic acid-like compounds were started with breakage of aromatic structures in the present study. This implication was in agreement with another research showing relations between degradations of humic acid and aromaticity [44].

Fluorophore organic matters corresponding to the region I are categorised as aromatic proteins and amino acids, naturally containing lower molecular weight substances than the regions III, IV or V [33]. Figure 4 illustrates relationships between increment of normalised EEM volume of the region I and reduction of the summation of the EEM volumes of the regions III, IV and V during UV/PS and UV/H₂O₂. The increment and the reduction were defined as equations (3) and (4), respectively. The increment of region I during UV/H₂O₂ was correlated to the reduction of the summation of regions III, IV and V, suggesting partial decomposition of the high molecular weight compounds resulted in a net increase of lower molecular weight ones [45,46]. In contrast, UV/PS decreased the regions III + IV + V more rapidly, and the region I was also eventually declined despite of the initial increment. The increment of the region I could be explained that UV/PS also increased lower molecular weight compounds via partial decomposition of higher molecular weight ones [34]. The final depletion of the region I could be explained
from another research that UV/PS could reduce both high and low molecular weight matters though higher molecular weight ones showed faster reduction rates [41]. Additionally, SO₄²⁻ favourably reacts with electron-donating groups such as amino group (NH₂) and aminoacyl group (-NH-CO-), that could be included in the fluorophore of region I, by single electron transfer [47].

\[
\text{Increment of } \Phi_{n,s} = \frac{\Phi_{n,s} - \Phi_{n,s,0}}{\Phi_{n,s,0}} \quad (3)
\]

\[
\text{Reduction of } \Phi_{\text{III+IV+V,n}} = \frac{\Phi_{\text{III+IV+V,n}} - \Phi_{\text{III+IV+V,n,0}}}{\Phi_{\text{III+IV+V,n,0}}} \quad (4)
\]

Consequently, Fig. 1-b) suggests that reduction of chromophore aromatic compounds can be classified as the phase 1 and the phase 2. Degradation during the phase 1 did not contribute to mineralisation of DOC (Fig. 2) and was associated with reduction of the EEM regions III, IV and V, implying partial decomposition of aromaticity in the corresponding fluorophore compounds (Fig. S3). Moreover, reductions of EEM regions III, IV or V was correlated to increments of EEM region I, suggesting partial degradation of the high molecular weight substances correlated to the net increase of lower molecular weight ones (Fig. 4). In contrast, degradation during the phase 2 was correlated to reduction of DOC (Fig. 2). UV/PS completed the phase 1 in the initial 1,000 mJ/cm² of fluence, and thus high mineralisation rate was confirmed in the end. On the other hand, 3,000 mJ/cm² of fluence was insufficient for UV/H₂O₂ to pursue the phase 1 totally, and thus no degradation of DOC and the increase of EEM region I were observed.

**Effects of UV/PS and UV/H₂O₂ on DHAN-FPs**

Effects of the UV/PS and UV/H₂O₂ on FP of each species of DHANs will be compared. Fluence dependences of each species of DHAN-FP are shown in Fig. 5. Both UV/PS and UV/H₂O₂ effectively declined DCAN-FP and BCAN-FP as fluence increased. UV/PS indicated more clear reductions than UV/H₂O₂ with 95% (from 3.8 to 0.2 µg/L) of reduction of DCAN-FP and 78% (from 2.8 to 0.6 µg/L) of decline of BCAN-FP with 3,000 mJ/cm² of fluence. Those of UV/H₂O₂ were 53% (from 3.8 to 1.8 µg/L) and 17% (from 2.8 to 2.3 µg/L), respectively. In contrast, DBAN-FP was increased regardless of the processes. UV/H₂O₂ showed a monotonic increase as fluence increased: from 0.44 µg/L as the initial FP to 0.57, 0.65 and 0.69 µg/L after 1,000, 2,000 and 3,000 mJ/cm² of fluence, respectively. UV/PS showed a more rapid increase during the initial 1,000 mJ/cm² of fluence from 0.44 to 0.99 µg/L, but DBAN-FP was dramatically dropped be-

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**Fig. 4** Correlations between reduction of summation of EEM regions III, IV and V and increment of EEM region I.
between 2,000 and 3,000 mJ/cm² of fluence from 0.95 to 0.21 µg/L. Overall, both UV/PS and UV/H₂O₂ indicated the most efficient reduction of DCAN-FP followed by BCAN-FP and DBAN-FP, suggesting that chlorinated HANs tended to be mitigated by UV/PS and UV/H₂O₂ easier than brominated ones.

Wang et al. showed BCAN-FP and DBAN-FP are increased depending on a concentration of PMS during a PMS/Cu (II) process [48]. The present study was in agreement with the increase of DBAN-FP, but BCAN-FP indicated an opposite result. This could be because of the differences in the concentration of the oxidants and activation processes. Wang et al. dosed PMS at a much lower concentration range (0.025 to 0.2 mM of PMS) than the present study (10 mM of PS). Moreover, little dissociation energy is required to break the O-O bond and generate sulphate radicals from PS in comparison with PMS, and PS contains higher oxidation potential than PMS [19].

The increment of DBAN during UV/PS could be related to high concentration of bromide in the sample. Bromide can be oxidised by SO₄⁻ to form reactive bromine species represented by hypobromous acid (HOBr) [49,50]. HOBr could take responsibility on forming Br-DBPs by subsequent reactions with NOM, potentially resulting in high DBAN-FP during UV/PS. However, exceeding SO₄⁻ can further oxidise generated Br-DBPs forming back to inorganic bromine [50,51], causing the sudden reduction of DBAN between 2,000 and 3,000 mJ/cm² of fluence.

**Correlation coefficient tests between NOM properties and DHANs-FP affected by UV/PS or UV/H₂O₂**

Correlations between effects of UV/PS or UV/H₂O₂ on changes of NOM properties and formation potential of DHANs were examined by the Pearson’s correlation coefficients test. The number of data was 4 for each correlation test, where actual measurement values were used for the analyses, and the results are listed in Table 2. Both UV/PS and UV/H₂O₂ yielded significant correlations between DCAN-FP and UV₂₅₄ or EEM region III. Significant correlations between DCAN-FP and EEM region IV during UV/PS and DCAN-FP and EEM region V during UV/H₂O₂ were also confirmed. The decrease of EEM region II during UV/PS indicated a strongly significant correlation to BCAN-FP, but no correlations between BCAN-FP and NOM properties during UV/H₂O₂ were detected. On the other hand, EEM region I during UV/H₂O₂ was significantly correlated to DBAN-FP, while UV/PS showed no clear correlations between DBAN-FP and NOM properties. UV/H₂O₂ also indicated strong negative correlations between DBAN-FP and UV₂₅₄, EEM regions III, IV and V. Furthermore, those showing significant correlations (p < 0.05) with each species of DHAN-FPs (e.g., UV₂₅₄ and DCAN, Φ₁₁₁, and BCAN, etc.) still indicated high correlation coefficients in the partial correlation coefficient test to remove influences of reduc-
tion of DOC on other factors (0.869 < r < 0.998). Therefore, fluctuations of DHAN-FPs were appropriately correlated to specific NOM properties rather than simply concluding that reduction of organic precursors decreased FPs. Calculation and the results of the partial correlation coefficient tests are written in Table S1, Supplementary Materials.

High correlations between DCAN-FP and UV$_{254}$ indicate that chromophore aromatic compounds contain precursors of DCAN and decomposition of these structures resulted in reduction of DCAN. Fluorophore organic compounds in EEM regions III, IV and V also showed strong correlations to DCAN-FP, and region III (fulvic acid-like) indicated the strongest correlations in both UV/PS and UV/H$_2$O$_2$. Therefore, fulvic acid-like substances combining aromatic bonds were major precursors to form DCAN, and efficient reductions of such compounds contributed to mitigation of DCAN. Because Zhang et al. and Zhou et al. indicated high DCAN-FP from high molecular weight compounds in NOM and in algal organic matters, respectively, the results in the present study showed similarity at some extent [6,8]. However, those studies also yielded formation of DCAN from low molecular weight compounds. More detailed understandings are required about reactions involving low molecular weight substances.

The significant correlation between BCAN-FP and EEM region II indicates that precursors of BCAN show fluorophore in region II, and the efficient reduction by UV/PS and stagnation during UV/H$_2$O$_2$ resulted in the difference of reduction of BCAN-FP. On the other hand, the correlation between EEM region I during UV/H$_2$O$_2$ and DBAN-FP revealed precursors of DBAN are included in the corresponding fluorophore organic matters. Moreover, thinking of negative correlations between the EEM regions III, IV and V, partial decomposition of high molecular weight compounds increased precursors in the EEM region I (also see Fig. 4).

EEM regions I and II are categorised as aromatic proteins and amino acids [33], potentially including precursors of HANs [11]. No significant reductions of these EEM regions during UV/H$_2$O$_2$ resulted in increase of DBAN-FP and only small reduction of BCAN-FP. In contrast, during UV/PS, sharp increase of EEM region I and bromination resulted from oxidation of bromide by SO$_4^-$ initially increased DBAN-FP [50]. However, as decomposition of fluorophore organic matters detected as EEM region I by single electron transfer by SO$_4^-$ progressed [47], DBAN-FP was dramatically decreased.

Consequently, the correlation coefficient tests revealed that chromophore aromatic compounds and fluorophore fulvic and humic acid-like substances mainly acted as precursors of DCAN, and aromatic proteins and amino acids took a role as precursors of BCAN and DBAN. Because brominated HANs have higher toxicity than chlorinated HANs [3,14],

### Table 2
Results of the correlation coefficient test (Pearson's correlation coefficient with a two-sided test taking 95% of the confidence interval, the number of data was 4 for each coefficient, upper figures: correlation coefficients, bottom figures: p-values, black boxes: p < 0.05).

<table>
<thead>
<tr>
<th></th>
<th>UV/PS</th>
<th>DCAN</th>
<th>BCAN</th>
<th>DBAN</th>
<th>UV/H$_2$O$_2$</th>
<th>DCAN</th>
<th>BCAN</th>
<th>DBAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>0.909</td>
<td>0.973</td>
<td>0.287</td>
<td>0.60</td>
<td>0.397</td>
<td>0.718</td>
<td>-0.222</td>
<td></td>
</tr>
<tr>
<td>UV$_{254}$</td>
<td>0.784</td>
<td>0.801</td>
<td>-0.192</td>
<td>0.989</td>
<td>0.985</td>
<td>0.784</td>
<td>0.852</td>
<td>-0.998</td>
</tr>
<tr>
<td>φ$_{III,a}$</td>
<td>-0.337</td>
<td>0.0942</td>
<td>0.935</td>
<td>-0.938</td>
<td>-0.724</td>
<td>0.989</td>
<td>0.062</td>
<td>0.281</td>
</tr>
<tr>
<td>φ$_{II,a}$</td>
<td>0.943</td>
<td>0.979</td>
<td>0.338</td>
<td>0.797</td>
<td>0.493</td>
<td>-0.895</td>
<td>0.20</td>
<td>0.51</td>
</tr>
<tr>
<td>φ$_{I,a}$</td>
<td>0.972</td>
<td>0.776</td>
<td>-0.203</td>
<td>0.984</td>
<td>0.832</td>
<td>-0.999</td>
<td>0.016</td>
<td>0.17</td>
</tr>
<tr>
<td>φ$_{IV,a}$</td>
<td>0.961</td>
<td>0.747</td>
<td>-0.250</td>
<td>0.911</td>
<td>0.671</td>
<td>-0.975</td>
<td>0.089</td>
<td>0.33</td>
</tr>
<tr>
<td>φ$_{V,a}$</td>
<td>0.934</td>
<td>0.686</td>
<td>-0.332</td>
<td>0.975</td>
<td>0.807</td>
<td>-1.00</td>
<td>0.025</td>
<td>0.19</td>
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</table>
efficient decomposition of aromatic proteins and amino acids will be important to mitigate health risks caused by HANs. UV/H2O2 showed weaker oxidation than UV/PS, resulting in no significant reduction of DBAN and BCAN. In contrast, UV/PS showed effective reductions of these precursors with 3,000 mJ/cm² of fluence, though amino acids are generally difficult to be removed by conventional water treatments due to their low molecular weights. Therefore, further researches to realise applications of UV/PS in drinking water treatment plants will contribute to removal of potential health risks from drinking water.

CONCLUSIONS

The present study investigated effects of UV/PS and UV/H2O2 on DHAN-FPs from NOM in a surface water sample during chlorination. The results demonstrated how UV/PS contributed mitigation of formation of DHANs by correlating DHANs-FP to NOM properties as well as comparison with the conventional UV/H2O2. Consequently, the following findings were obtained through the present study.

- Both UV/PS and UV/H2O2 decreased DCAN-FP and BCAN-FP as fluence increased, and UV/PS showed more effective reductions of them.
- Both UV/PS and UV/H2O2 increased DBAN-FP, but 3,000 mJ/cm² of UV/PS eventually decreased DBAN-FP.
- Degradations of chromophore aromatic compounds detected as UV254 and fulvic acid-like substances detected as EEM region III were significantly correlated to mitigation of DCAN-FP.
- The effective reduction of EEM region II during UV/PS was significantly correlated to the decrease of BCAN-FP, but UV/H2O2 did not yield efficient degradation of EEM region II, resulting in less clear reduction of BCAN-FP.
- Degradation of UV254 could be classified as the phase 1 and the phase 2. High molecular weight organic portions were preferentially attacked during phase 1, causing partial degradation and forming lower molecular weight ones. Thereafter, mineralisation of DOC was proceeded mainly during the phase 2.
- UV/PS completed the phase 1 within 1,000 mJ/cm² of fluence, while 3,000 mJ/cm² of UV/H2O2 was insufficient to complete the phase 1, resulting in stagnation of decrease of DOC.
- Partial degradation of high molecular weight organic matters detected as EEM regions III, IV or V resulted in net increase of lower molecular weight ones detected as EEM region I, and the increase of EEM region I during UV/H2O2 was significantly correlated to the increase of DBAN-FP.

ACKNOWLEDGEMENTS

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SUPPLEMENTARY MATERIALS

Supplementary Materials file for this article is available at the link below.

https://www.jstage.jst.go.jp/article/jwet/20/6/20_22-065_/supplement/_download/20_22-065_1.pdf

REFERENCES


