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Effect of freezing–thawing on dissolved organic matter in water

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ABSTRACT

The aim of this study was to investigate the effect of freezing–thawing on the content, spectroscopic characteristics, and chlorine reactivity of dissolved organic matter (DOM) and its fractions in water. DOM was fractionated using XAD resins into five fractions: hydrophobic acid, hydrophobic neutral, transphilic acid, transphilic neutral, and hydrophilic fraction. The bulk DOM showed DOC variation rates ranging from −2.65 to 26.94%, and the five DOM fractions exhibited DOC variation rates ranging from −22.48 to 78.16%, after freeze–thaw treatments. DOC of water samples were significantly affected by freezing and thawing temperatures, times of freeze–thaw cycles, and freezing time. The aromaticity of DOM and its fractions decreased as a result of freezing–thawing. Both freezing and thawing temperatures had a significant impact on aromatic substances contained in DOM, while the times of freeze–thaw cycles and freezing time made a relative slight influence on them. The freeze–thaw treatments reduced the chlorine reactivity of DOM and its fractions. The freezing temperature and freezing time were significant factors influencing the reactivity of DOM. The freeze–thaw treatments led to an increase in the contents of four types of fluorescent materials contained in DOM. The effect of freezing–thawing was most significant on aromatic protein- and SMP-like fluorescent materials, secondary significant on humic acid-like fluorescent materials, and slightly on fulvic acid-like fluorescent materials.

Keywords: Freezing–thawing; Dissolved organic matter; Water; Fractionation; Chlorine reactivity

1. Introduction

Dissolved organic matter (DOM) is defined as the organic materials below 0.45 μm, and is a heterogeneous mixture composed of carbohydrates, proteins, lignins, organic acids, and humic substances such as fulvic and humic acids [1]. And, it is not only a major concern in drinking water treatment since it causes adverse esthetic qualities such as color, taste, and odor, but also has a significant effect on the biogeochemical processes, particle stability and transport, and metal complexation in the aquatic systems [2,3]. Furthermore, past research works have shown that the chlorination process of natural water containing DOM may cause the production of harmful disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids [4], which are concerned for human health security [5]. Therefore, the nature and

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properties of DOM in water are topics of significant environmental interest. Because of their complex polymeric properties, it is often necessary to isolate DOM for a better understanding of its role in water chemistry. The XAD resin method has been reported in many applications for fractionation of DOM and is generally considered as the state-of-art method at present for such fractionation [6].

In boreal and temperate regions, soils and waters are exposed to freezing–thawing mainly during late autumn and early spring, and also during mild winters [7]. Recently, with the onset of global warming, there has been an increasing concern of greenhouse gas release from permafrost, and therefore, interest in monitoring freezing and thawing dynamics is increasing [8]. The ice formed at the surface of waters at low temperature is no doubt a storage of pollutants. Consecutive freeze–thaw cycles in water, which resulted from special temperature variations during the snowmelt period, may inevitably affect the distribution, transport, characteristics, and fate of pollutants in water. Currently, studies on freezing–thawing are mainly conducted on the greenhouse gas emission, physical property of soil, soil micro-organisms, and soil carbon and nitrogen transformations [9–11]. Yet, the effect of freezing–thawing on the pollutants in water has so far received much less attention. Recently, Spencer et al. [12] studied freezing–thawing effects on the spectroscopic characteristics of bulk DOM in freshwater. However, the effect of freezing–thawing on the chlorine reactivity of DOM in water as well as on the concentration and properties of DOM fractions in water still remains unclear. The objectives of this study are, therefore, to investigate the effect of freezing–thawing on the content, spectroscopic characteristics, and chlorine reactivity of DOM and its fractions in water. The operation parameters of freeze–thaw treatment examined in this study included the freezing temperature, thawing temperature, times of freeze–thaw cycles, and freezing time. Besides serving as important DBPs precursors, it is well known that solubility and transport of organic contaminants as well as heavy metals in water are linked to DOM properties. Hence, a better understanding of the effect of freezing–thawing on DOM may improve our predictive capabilities of the behavior of DOM and environmental pollutants in water and, in turn, may facilitate the water treatment choices as well as water quality control during the period in which freeze–thaw cycles occur frequently. Moreover, freezing is commonly used as a storage method for water samples that cannot be analyzed quickly or for archiving water samples for later analysis. The thorough understanding of the implications of freezing water samples on the concentration and characteristics of DOM and its fractions is necessary to evaluate whether freezing is an appropriate preservation technique when analyzing DOM in water.

2. Materials and methods

2.1. Sample collection and preservation

Water samples for this study were collected from the Xinkaihe River (XR) and the Hunhe River (HR) on 25 November 2014, respectively. The XR and HR are the two main rivers in Shenyang, Liaoning Province, China. The characteristics of the XR and HR water samples are summarized in Table 1.

2.2. DOM fractionation

DOM in HR was fractionated into five classes: hydrophobic acid (HPO-A), hydrophobic neutral (HPO-N), transphilic acid (TPI-A), transphilic neutral (TPI-N), and hydrophilic fraction (HPI), using XAD-8/XAD-4 resin chromatography [13]. The isolation methods were described in detail by Xue et al. [14].

2.3. Freeze–thaw treatment of water samples

To study the effect of freezing–thawing on the content and characteristics of DOM, a series of freeze–thaw treatment were carried out with the XR and HR water samples as well as with five DOM fraction samples isolated from the HR. All water samples were filtered using 0.45-μm cellulose nitrate membrane filter on a vacuum system before freeze–thaw treatments. Each water sample was put in eight cylindrical bottles designated as O, A, B, C, D, E, F, and G, respectively. Each bottle contained 550 mL of sample. In the freeze–thaw treatment, the XR and HR water samples remained in their original DOC concentrations, while

Table 1
Water quality data for the XR and HR water samples

Parameters	XR	HR
pH	6.8	7.1
TOC (mg/L)	2.9	3.3
DOC (mg/L)	1.8	2.5
UV-254 (cm^{-1})	0.0651	0.0895
Conductivity (μs/cm)	697.8	789.5
NH_4-N (mg/L)	4.5	3.1
SS (mg/L)	7.4	11.1
VSS (mg/L)	5.2	7.9
Turbidity (NTU)	1.3	1.6

the five DOM fraction samples were diluted to 1 mg/L of DOC. The O samples were kept at 4℃ in a refrigerator (Haier, Qingdao, China) as control samples. The A, B, C, and D samples were frozen at −15, −20, −24, and −50℃ for 1 d in a refrigerator, respectively, and then thawed at 5℃ for 1 d in an environmental climate box. The E samples were frozen at −20℃ for 1 d, and then thawed at 15℃ for 1 d. The F samples were exposed to 10 repeated freeze–thaw cycles with each freeze–thaw cycle consisting of freezing at −20℃ for 1 d, and thawing at 5℃ for 1 d. The G samples were frozen at −20℃ for 30 d, and then thawed at 5℃ for 1 d.

Dissolved organic carbon (DOC), absorbance of ultraviolet light at 254 nm (UV-254), trihalomethane formation potential (THMFP), and fluorescence spectra of the O samples, as well as the A–G samples after freeze–thaw treatment, were measured.

2.4. Analysis

DOC was analyzed using a Shimadzu TOC-5000 total organic carbon analyzer (Shimadzu, Kyoto, Japan) with autosampler. UV-254 was measured with a Cary 50 ultraviolet-visible (UV–vis) spectrophotometer (Varian, Palo Alto, California, USA) at 254 nm using a quartz cell with a 1-cm path length. The instrument was zeroed using Milli-Q water as a blank. Specific ultraviolet light absorbance (SUVA) was calculated as (UV-254/DOC) × 100 [15].

THMFP measurements were performed according to Standard Method 5710B. The chlorine dosage for each water sample was determined such that a final residual chlorine of 3–5 mg/L remained in the sample after the 7 d of incubation at 25℃. All samples were adjusted to a pH of 7 ± 0.2 using H_2SO_4 and NaOH. The neutralized solution was then buffered with a phosphate solution prior to incubation in amber bottles at 25 ± 2℃ for 7 d. At the end of the incubation period, samples were dechlorinated using sodium sulfite (Na_2SO_3). THMs were extracted with methyl tert-butyl ether (MTBE) from the chlorinated samples using a modified EPA method 551.1 and analyzed by gas chromatography (CP-3,800) with an electron capture detector (GC/ECD, CP-3,800, Varian, Palo Alto, California, USA).

Fluorescence spectra were obtained with a Cary Eclipse spectrofluorometer (Varian, Palo Alto, California, USA). The spectrofluorometer used a xenon excitation source, and slits were set to 5 nm for both excitation and emission. Filtered water extracts were diluted to 1 mg/L of DOC with 0.01 mol/L KCl. The emission (Em) wavelength range was fixed from 290 to 550 nm (1 nm intervals), whereas the excitation (Ex) wavelength was increased from 220 to 400 nm (5 nm intervals). Scan speed was set at 1,000 nm/min, generating an excitation–emission matrix (EEM) in about 15 min. Blank sample (0.01 mol/L KCl) fluorescence was subtracted from all spectra. To eliminate the Rayleigh scattering interference in EEMs, the intensity values at points where the emission wavelength was the same as or twice the excitation wavelength, as well as those adjacent to them (±10 nm emission wavelength at the same excitation wavelength), were excised from the scan data and the excised values were replaced with zero [16]. In addition, this procedure was also applied to the data points in EEMs with an emission wavelength < the excitation wavelength or > twice the excitation wavelength. All the data points whose value had been replaced with zero were excluded when calculating projected excitation–emission area in quantitative analyses of EEM spectra by means of the fluorescence regional integration (FRI) technique proposed by Chen et al. [17].

The EEM spectra were divided into five regions which represented specific components of DOM. The five regions are as follows: Regions I (Ex: 220–250 nm–Em: 290–330 nm) and II (Ex: 220–250 nm–Em: 330–380 nm) recognized as belonging to aromatic protein-like fluorescence, Region III (Ex: 220–250 nm–Em: 380–550 nm) associated with fulvic acid-like fluorescence, Region IV (Ex: 250–400 nm–Em: 290–380 nm) related to soluble microbial byproduct-like (SMP-like) florescence, and Region V (Ex: 250–400 nm–Em: 380–550 nm) assigned to humic acid-like fluorescence [17]. Traditionally, fulvic acid- and humic acid-like fluorescence have been associated with humic-like substances, and aromatic protein-like and SMP-like fluorescence have usually been recognized as belonging to protein-like materials. Chen et al. [17] proposed that integration beneath EEMs within selected regions represents the cumulative fluorescence response of DOM with similar properties. Important parameters in FRI were: (a) normalized region-specific EEM volume ($\Phi_{i,n}$), obtained by normalizing the volume beneath region "i" of the EEM to the fractional projected excitation–emission area and (b) cumulative EEM volume ($\Phi_{T,n}$), equal to the sum of $\Phi_{I,n}$–$\Phi_{V,n}$.

3. Results and discussion

3.1. Effect of freezing–thawing on bulk DOM

3.1.1. DOC

As shown in Fig. 1(a) and (f), DOC values for the XR and HR samples before freeze–thaw treatment, i.e. the O samples, were 1.81 and 2.47 mg/L, respectively.

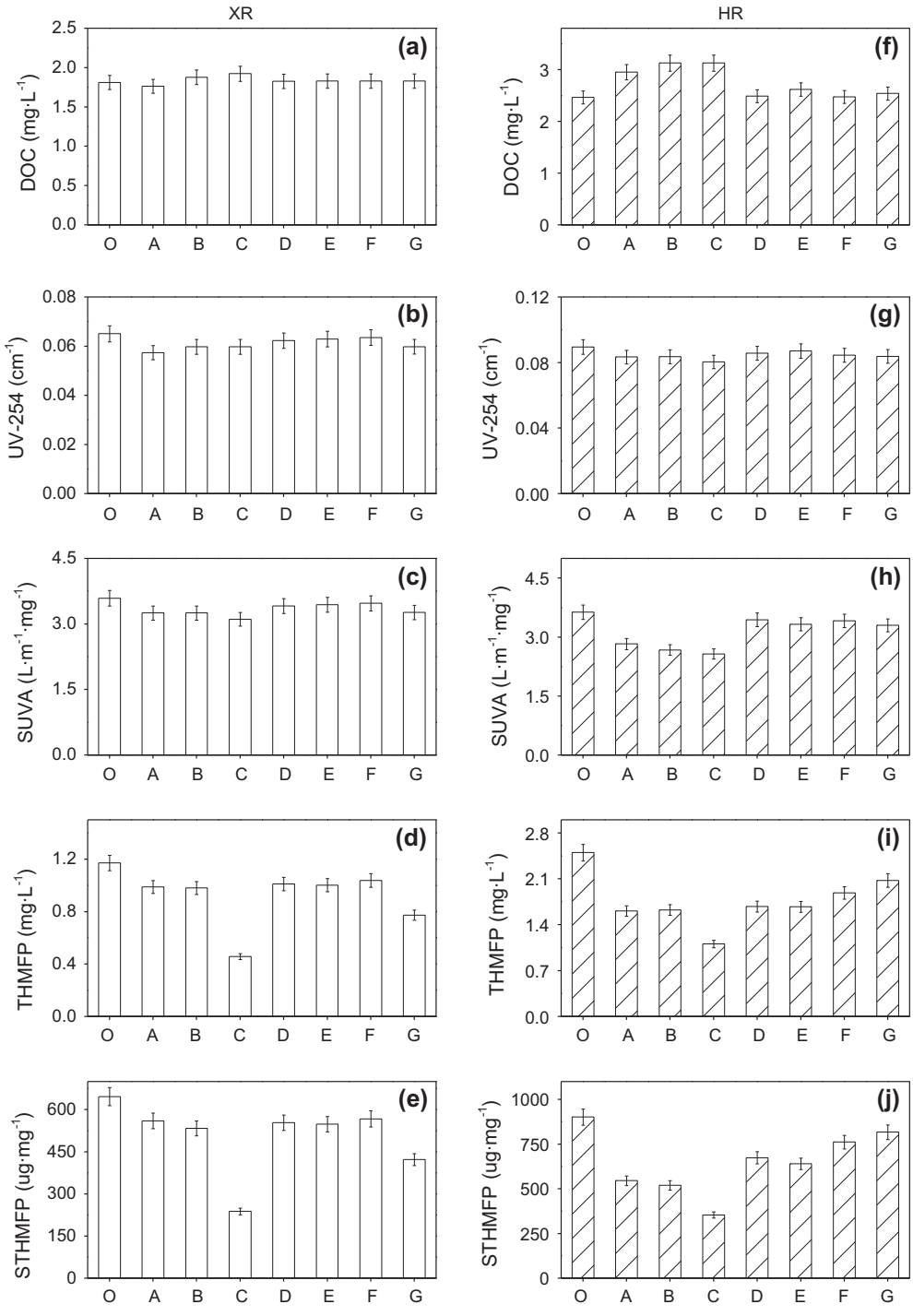

Fig. 1. DOC (a), UV-254 (b), SUVA (c), THMFP (d), and STHMFP (e) of XR, and DOC (f), UV-254 (g), SUVA (h), THMFP (i), and STHMFP (j) of HR before and after freeze–thaw treatments.

DOC values for the XR samples after different freeze–thaw treatments, i.e. A–G samples, were 1.76–1.92 mg/L, with insignificant changes of −2.65 to −6.13%. On the contrary, DOC values for the HR samples after different freeze–thaw treatments were 2.49–3.13 mg/L, with changes of −0.43–26.94% which were relatively significant. The highest DOC values of 1.92 and 3.13 mg/L for the XR and HR water samples, respectively, were both observed in the C samples with freezing temperature of −24℃. On the other

hand, DOC of the XR and HR samples after freeze–thaw treatment with freezing temperature of −50˚C (flash freezing), i.e. the D samples, were 1.83 and 2.49 mg/L, exhibiting insignificant changes of 0.72 and 1.01%, respectively. The results suggested that the impact of freeze–thaw treatment with freezing temperature of −24˚C on DOC was greater than the other freeze–thaw treatments examined in this study, while the impact of freeze–thaw treatment with flash freezing on DOC was slight. The changes in DOC resulted from freeze–thaw treatments were also observed by other researcher. Giesy and Briese [18] presented evidence from a single location suggesting that freezing water samples with high DOC concentrations can result in a loss of DOC through precipitation that cannot be re-solubilized with 0.5 mol/L NaOH. Spencer et al. [12] summarized the changes of DOC on 15 water samples and found that after freezing, DOC concentrations in one-third surface water samples increased and others decreased by as much as 10%. A number of studies had shown that the immediate freezing of filtered water samples is an effective technique for preserving dissolved C concentrations [19]. Results in study suggested that DOC of water samples should be measured immediately. However, water samples that could not be measured immediately should be preserved with flash freezing. The DOC values for the XR and HR B samples (with thawing temperature of 5˚C) were 1.88 and 3.13 mg/L, respectively, E samples (with thawing temperature of 15˚C), respectively, 1.83 and 2.62 mg/L; the DOC change rates of XR and HR B samples relative to O samples were 4.13 and 4.33 times the E samples, respectively, suggesting that the freeze–thaw treatment with a lower thawing temperature had a greater influence on the DOC of water samples. Compared to O samples, DOC of XR and HR B samples (with single freeze–thaw cycle) increased 3.64 and 26.90%, respectively; the changes were significant. On the other hand, DOC of XR and HR F samples (with 10 freeze–thaw cycles) increased 0.94 and 0.43%, respectively; the changes were insignificant. Based on the data, the increasing rates of B samples of XR and HR were 3.88 and 63.14 times F samples, respectively, suggesting DOC of water samples were significantly affected by single freeze–thaw cycle and relatively slightly affected by repeated freeze–thaw cycles. DOC of XR and HR B samples (with freezing time of 1 d) increased 3.64 and 26.89%, respectively, while of XR and HR G samples (with freezing time of 30 d) increased only 0.99 and 3.04%, respectively, suggesting that the freeze–thaw treatment with a shorter freezing time (1 d) caused a significant increase of DOC, while the freeze–thaw treatment with a longer freezing time (30 d) exerted a relatively slight effect on DOC.

3.1.2. UV-254 and SUVA

UV-254 is mainly caused by electron-rich sites, such as aromatic functional groups and double-bonded C groups, in the DOM molecule [20,21]. SUVA is obtained by dividing the UV-254 with its DOC, which can indicate the aromaticity of the DOM samples [22].

The UV-254 values of the XR and HR samples before and after freeze–thaw treatments are shown in Fig. 1(b) and (g), and SUVA as in Fig. 1(c) and (h). Before freeze–thaw treatment, the UV-254 values of the XR and HR samples were 0.0651 and 0.0895 cm^{-1}, respectively, while after different freeze–thaw treatments, the UV-254 value of the XR and HR A–G samples decreased with rates of 2.39–12.79% and 1.96–10.19%, respectively. The variation trend of UV-254 was contrary to that of DOC. The results suggested that, although freezing–thawing might generally increase the content of bulk DOM represented by DOC, the aromatic substances contained in DOM decreased, therefore, SUVA declined (Fig. 1(c) and (h)). Based on UV-254 changes of the XR and HR A–D samples relative to the corresponding O samples, it was found that XR A sample and HR C sample showed the highest decreasing rate, respectively; both XR and HR D samples exhibited the lowest decreasing rate. Besides, both XR and HR C samples had the lowest SUVA values of 0.0311 and 0.0257 L/(m mg), respectively. Thus, it was indicated that the freeze–thaw treatment with the freezing temperature of −24˚C resulted in a significant decrease in aromaticity of DOM, whereas the effect of freeze–thaw treatment with flash freezing on aromatic substances in DOM was slight. This further illustrated that flash freezing treatment might be used as a proper technology for preserving DOM samples. In addition, the UV-254 values of XR and HR B samples were 0.0598 and 0.0836 cm^{-1}, respectively, which decreased 8.16 and 6.67% in comparison with the corresponding O samples, respectively. The UV-254 values of XR and HR E samples decreased 6.29 and 2.76%, respectively, indicating that the freeze–thaw treatment with a lower thawing temperature had a greater impact on aromatic substances in DOM. The UV-254 values of XR and HR F samples were 1.06 and 1.01 times their B samples, respectively. Meanwhile, their G samples had almost equal UV-254 values with their B samples. The observations indicated that both the times of freeze–thaw cycles and the freezing time had slight impact on aromatic substances in DOM.

3.1.3. THMFP and STHMFP

THMFP is often the term employed to indicate the amount of THMs that could be produced during the chlorination process, and could indirectly represent the amount of trihalomethane (THM) precursors in water samples [23]. Because THMFP is dependent upon DOC concentration, the reactivity of DOC is also reported in terms of specific THMFP (STHMFP), that is, micrograms of THMFP formed per milligram of DOC precursor material in the water (μg/mg).

As shown in Fig. 1(d) and (i), after different freeze–thaw treatments, THMFP of the XR and HR samples showed decreases of different degrees ranging from 11.44 to 60.96% and from 15.77 to 55.70%, respectively. They were significantly greater than the degrees of DOC and UV-254 variations. These results indicated that the impact of freezing–thawing on THM precursors in DOM was more significant, and freezing–thawing caused decrease in the content of THM precursors in water. Freezing–thawing seemed to have a greater impact on STHMFP of DOM, as indicated in Fig. 1(e) and (j). It was observed by comparing STHMFP of XR A–D that, relative to O sample, C sample had the greatest degree of decrease, reaching 63.21%, while A and B samples ranked middle, and D sample had the slightest decrease of 14.37%. This indicated that STHMFP of DOM might be significantly decreased after freeze–thaw treatment with the freezing temperature of −24˚C, however, the freeze–thaw treatment with an extreme low freezing temperature of −50˚C made a relative slight influence on STHMFP. In terms of thawing temperature, STHMFP of B sample was 533.2 μg/mg and that of E was 548.2 μg/mg. The difference between them was less than 3%. Thus, it was shown that the thawing temperature made a slight impact on STHMFP. As for times of freeze–thaw cycles, STHMFP decreasing rates of B and F samples were 17.53 and 12.26%, respectively, suggesting that STHMFP of DOM decreased after single freeze–thaw cycle. Instead, the changes in STHMFP decreased after repeated freeze–thaw cycles. With respect to freezing time, STHMFP decreasing rate of G sample was 34.67%, which was 1.98 times the rate of B sample. These results indicated that freezing time was a significant factor that influenced the reactivity of DOM, although it made slight influence on the content of bulk DOM represented by DOC. Similar results were also obtained from the HR samples (Fig. 1(j)).

Based on SUVA and STHMFP results of XR and HR (Fig. 1(c), (e), (h), (j)), it could be stated that SUVA had the same variation trend with STHMFP, namely the SUVA and STHMFP of XR and HR were all decreased after different freeze–thaw treatments. SUVA was used to indicate the DOM character and its coagulation ability for the removal of THM precursors, and the high SUVA values of samples notably indicate large amounts of aromatic DOM [24]. The results in this study consistently revealed that aromatic substances in XR and HR were the main THM precursors [25,26].

3.1.4. Fluorescence spectra

The fluorescence spectra of XR and HR before and after freeze–thaw treatments are shown in Fig. 2. Since each sample was diluted to same DOC concentration when fluorescence spectra were obtained, all $\Phi_{i,n}$ and $\Phi_{T,n}$ values, shown in Fig. 3, were obtained by multiplying DOC by the corresponding DOC-normalized EEM volume calculated from Fig. 2, representing the amount of fluorescent materials. This study plused $\Phi_{I,n}$ and $\Phi_{II,n}$ to represent the cumulative aromatic protein-like fluorescence, with $\Phi_{I+II,n}$.

As shown in Fig. 3(e), the $\Phi_{T,n}$ increasing rates of XR A–G samples, relative to O sample, were 2.93, 0.06, 28.82, 22.46, 1.77, 28.07, and 6.14%, respectively, which were -1.11 (negative number referred to a decline of DOC of sample A), 0.04, 4.71, 31.31, 2.01, 29.92, and 6.18 times of the corresponding rates of DOC, respectively. The results indicated that the responses of fluorescent materials to freezing–thawing were different from that of bulk organics. $\Phi_{T,n}$ increasing rates of D and F samples were 22.46 and 28.07% after freeze–thaw treatments, respectively, whereas the corresponding DOC increasing rates were less than 1%, which suggested that, although the freeze–thaw treatments with 10 repeated freeze–thaw cycles or with an extreme low freezing temperature of −50˚C made a slight effect on DOC, both of them might lead to a formation of fluorescent materials in DOM. The similar phenomenon was also observed in the HR samples.

It was also observed in Fig. 3(a)–(d) that after different freeze–thaw treatments, except for $\Phi_{III,n}$ of XR B and E samples and $\Phi_{IV,n}$ of XR B sample showing slight decrease, all $\Phi_{i,n}$ values of both XR and HR increased. The results suggested that freezing–thawing led to an increase in contents of four types of fluorescent materials in DOM. In terms of freezing temperature, the contents of four types of fluorescent materials in both XR and HR reached the highest after the freeze–thaw treatment with freezing temperature of −24˚C; and, after the freeze–thaw treatment with freezing temperature of −50˚C, the contents of four types of fluorescent materials ranked second; while, after the freeze–thaw treatment with relatively high temperatures

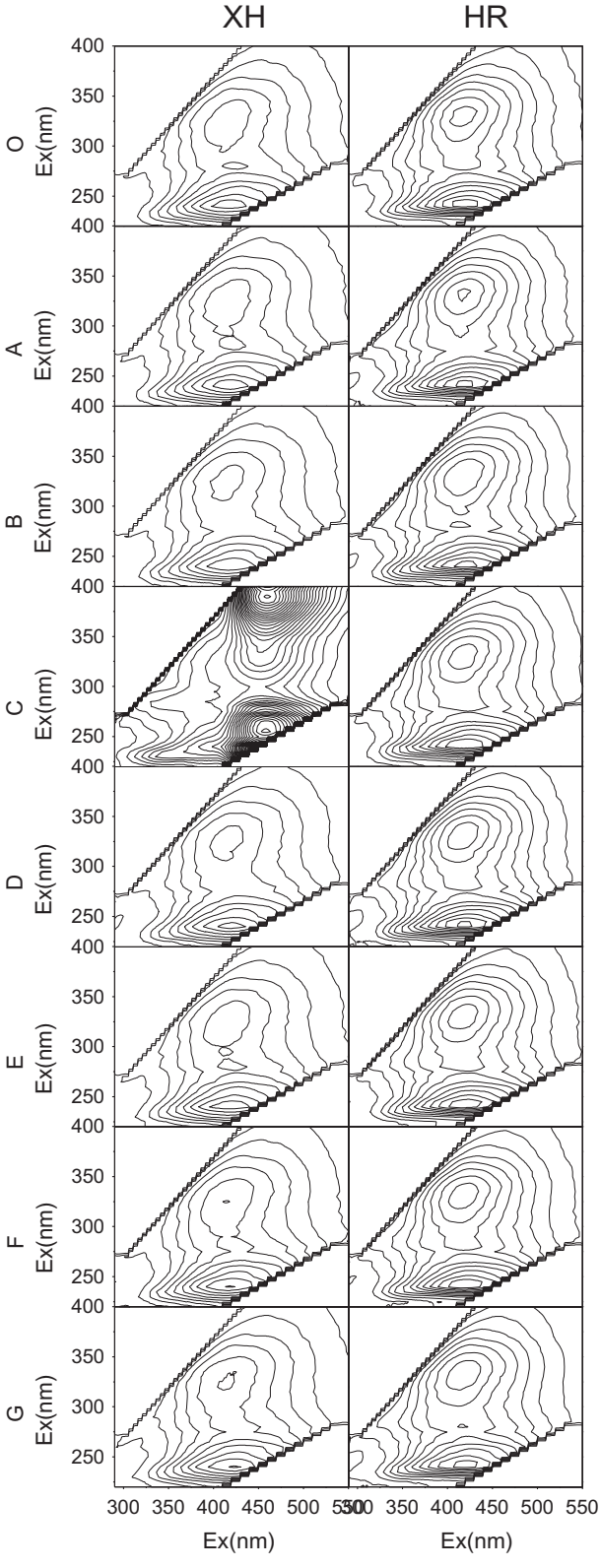

Fig. 2. Fluorescence spectra of XR and HR before and after freeze–thaw treatments.

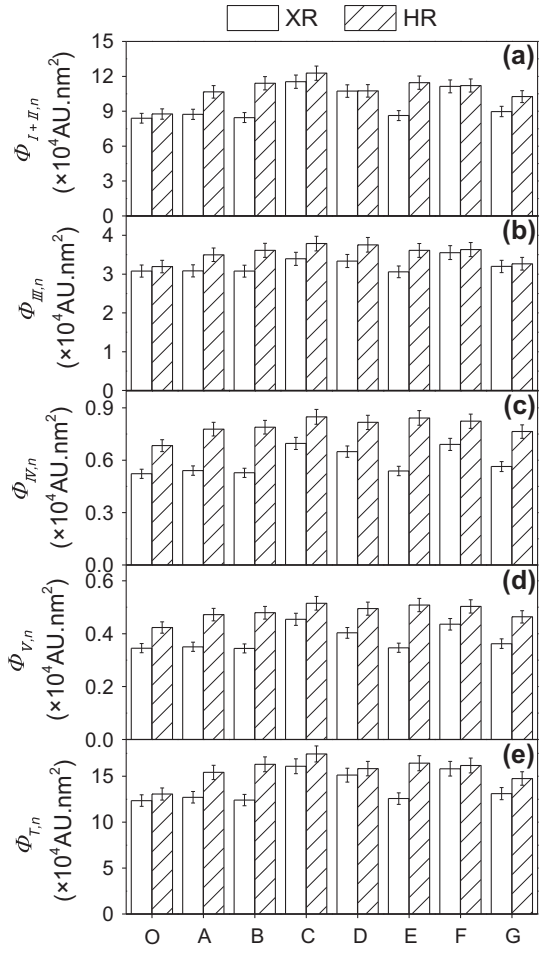

Fig. 3. $\Phi_{I+II,n}$ (a), $\Phi_{III,n}$ (b), $\Phi_{IV,n}$ (c), $\Phi_{V,n}$ (d), and $\Phi_{T,n}$ (e) values for XR and HR before and after freeze–thaw treatments.

(−15 and/or −20˚C), four types of fluorescent materials were slightly affected. With respect to thawing temperature, the content increasing rates of four types of fluorescent materials in XR and HR E samples were all higher than those of B samples, indicating that with higher thawing temperatures, the freeze–thaw treatment exerted a more significant effect on four types of fluorescent materials. Concerning about XR, the $\Phi_{I+II,n}$–$\Phi_{V,n}$ variation rates of F and G samples were higher than those of B sample, suggesting that times of freeze–thaw cycles and the freezing time significantly influenced the four types of fluorescent materials; moreover, with the more times of freeze–thaw cycles and longer freezing time, the changes in contents of four types of fluorescent materials in DOM resulted from freezing–thawing were more significant. However, such phenomena were not found in HR.

As shown in Fig. 3, in XR and HR, the proportions of four types of fluorescent materials in the total fluorescent materials could be ranked as follows: $\Phi_{I+II,n}$ (67.1 and 71.5% for XR and HR, respectively) > $\Phi_{III,n}$ (20.8 and 24.9% for XR and HR, respectively) > $\Phi_{IV,n}$ (4.1 and 5.2% for XR and HR, respectively) > $\Phi_{V,n}$ (2.7 and 3.6% for XR and HR, respectively). This indicated that aromatic protein-like fluorescent materials were the major fluorescent materials in both XR and HR.

It could be found from Table 2 that the effect of freezing–thawing on four types of fluorescent materials could be ranked as follows: aromatic protein-like fluorescent materials > SMP-like fluorescent materials > humic acid-like fluorescent materials > fulvic acid-like fluorescent materials. Taking the example of XR A sample, the content increasing rates of aromatic protein-, SMP-, humic acid-, and fulvic acid-like fluorescent materials were 3.95, 3.58, 1.46, and 0.18%, respectively. The results indicated that the effect of freezing–thawing was most significant on aromatic protein- and SMP-like fluorescent materials, secondary significant on humic acid-like fluorescent materials, and slightly on fulvic acid-like fluorescent materials. This is possibly related to the stability of the fluorophores that contribute to fulvic acid-like fluorescence and might indicate that protein-like fractions of fluorescent DOM was less stable in response to freezing–thawing in comparison to humic acid-like fractions [27].

3.2. Effect of freezing–thawing on DOM fractions

3.2.1. DOC

DOC of five DOM fractions isolated from HR before and after freeze–thaw treatments are shown in Fig. 4(a). Except the C samples of HPO-A and TPI-N, the A samples of HPO-N and TPI-A, and the B sample of HPI, DOC of five DOM fractions were all increased after freeze–thaw treatments. The DOC variation rates of HPO-A, HPO-N, TPI-A, TPI-N, and HPI were −22.48–61.91%, 4.20–7.03%, −27.37–23.03%, −5.71–78.16%, and −14.75–20.90%, respectively, as a result of freezing–thawing. The results indicated that the effect of freezing–thawing on DOC of HPO-A and TPI-N was significant, while on HPO-N was slight. With respect to freezing temperature, DOC of HPO-A and TPI-N reached the highest values of 1.62 mg/L and 1.78 mg/L, respectively, in their A samples; DOC of HPO-N and TPI-A reached the highest values of 1.06 and 1.20 mg/L, respectively, in their B samples; and DOC of HPI reached its highest value of 1.07 mg/L in C sample. All the five fraction samples had their low DOC values in D samples, which was also observed in bulk DOM, suggesting that the freeze–thaw treatment with an extremely low freezing temperature (−50˚C) made a slight influence on contents of five DOM fractions. The DOC variation rates of TPI-A and HPI-E sample relative to their B samples were −12.93 and 41.82%, respectively, while the

Table 2
Changes of four types of fluorescent materials in XR and HR after freeze–thaw treatments

Water samples	Changes (%)			
	Aromatic protein-like fluorescent materials	Fulvic acid-like fluorescent materials	SMP-like fluorescent materials	Humic acid-like fluorescent materials
XR				
A	3.95	0.18	3.58	1.46
B	0.63	−0.03	1.11	−0.33
C	37.28	10.26	33.23	31.59
D	27.73	8.42	24.30	16.70
E	2.65	−0.67	3.09	0.36
F	32.51	15.44	32.29	26.20
G	6.83	3.89	7.92	4.83
HR				
A	21.79	9.54	13.74	11.46
B	30.28	13.11	15.39	13.23
C	40.08	18.61	24.12	21.59
D	22.79	17.58	19.42	16.83
E	30.83	13.05	23.15	20.05
F	27.95	13.75	20.39	18.86
G	17.07	2.29	11.72	9.53

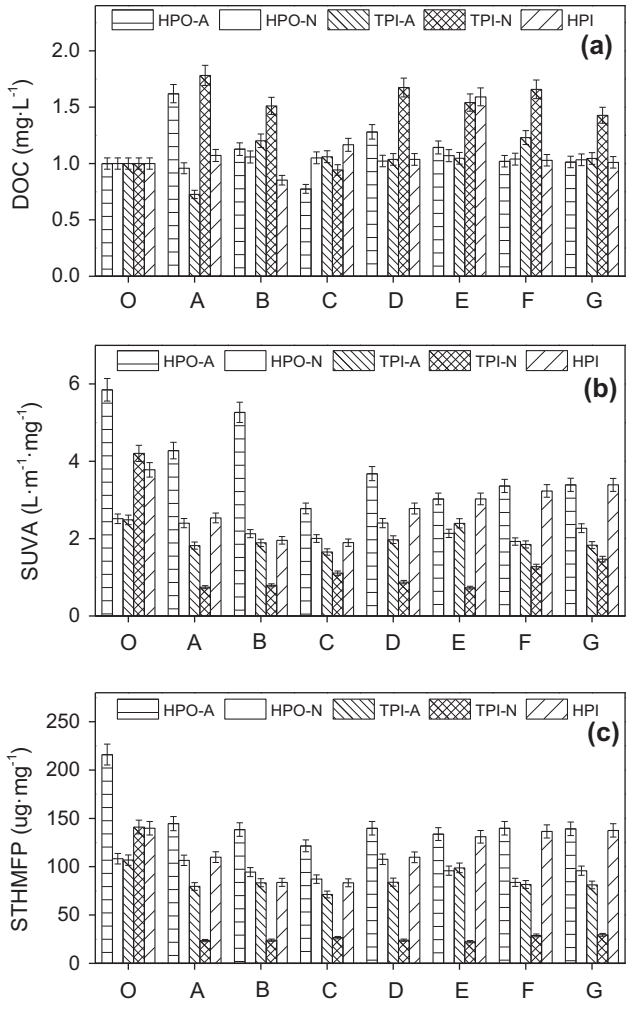

Fig. 4. DOC (a), SUVA (b), STHMFP, and (c) of DOM fractions in HR before and after freeze–thaw treatments.

corresponding DOC variation rates of the other three fractions were all lower than 2%, indicating that the thawing temperature made almost no impact on contents HPO-A, HPO-N, and TPI-N. After 10 repeated freeze–thaw cycles, DOC of TPI-A and TPI-N were relatively high, with the values of 1.23 and 1.66 mg/L, respectively, while the other three fractions had DOC variation rates lower than 3%. The results suggested that repeated freeze–thaw cycles led to a significant increase in contents of TPI-A and TPI-N, but made a slight influence on the other three fractions. After the freeze–thaw treatment with freezing time of 30 d, the DOC variation rate of TPI-N was relatively high, while the other four fractions almost had no changes in DOC. DOC of G samples of HPO-A, HPO-N, TPI-A, TPI-N, and HPI had variation rates of 10.1, 2.3, 1.3, 5.5, and 18.5%, respectively, relative to their B samples, which indicated that the freezing time made a significant impact on contents of HPO-A and HPI.

3.2.2. SUVA

As shown in Fig. 4(b), before freeze–thaw treatment, HPO-A had the highest SUVA value of 5.85 L/(m mg), TPI-N and HPI had SUVA values of 4.20 L/(m mg) and 3.78 L/(m mg), respectively, which ranked second, while HPO-N and TPI-A had their values of 2.51 and 2.49 L/(m mg), respectively, which were relatively low. The results indicated that, among these five DOM fractions, HPO-A was the highest in aromaticity, while HPO-N and TPI-A had the lowest. The SUVA values of HPO-A, HPO-N, TPI-A, TPI-N, and HPI all decreased after different freeze–thaw treatments, with decreasing rates of 9.99–52.49%, 4.45–23.39%, 3.67–33.39%, 65.07–82.60%, and 10.31–49.83%, respectively, indicating that freezing–thawing exerted the greatest impact on the aromatic substances contained in TPI-N, while the slightest effect on those in HPO-N and TPI-A.

3.2.3. Specific trihalomethane formation potential

STHMFP of DOM fractions before and after freeze–thaw treatments are shown in Fig. 4(c). STHMFP of five fractions before and after freeze–thaw treatment could be ranked as follows: HPO-A > TPI-N > HPI > HPO-N > TPI-A. Among five fractions before freeze–thaw treatment, STHMFP of HPO-A was significantly higher than the other four fractions, with a value of 215.9 ug/mg, indicating that HPO-A was the main THM precursors in DOM. Singer [28] also believed that, in natural waters, the reactivity of HPO-A toward chlorine and formation of THMs was stronger than the other fractions. Recently, Ma et al. [29] found that HPO-A contributed up to 68% of the overall THMFP. STHMFP of all five DOM fractions decreased after different freeze–thaw treatments. In terms of freezing temperature, except TPI-N, all the other four fractions had their most significant decreases of STHMFP in C samples; had a low decreasing rate of STHMFP in their D samples, which was also observed in bulk DOM. With respect to thawing temperature, the B samples of TPI-A and HPI had their decreasing rates of 22.00 and 40.10% relative to their O samples, respectively, which were 2.91 or 6.33 times those of their E samples, respectively. On the other hand, for the other three fractions, STHMFP values for B samples were very close to those for E samples. Therefore, it could be stated that the freeze–thaw treatment with a lower thawing temperature

reduced STHMFP of TPI-A and HPI; however, the thawing temperature exerted almost no effect on the other three fractions. In terms of times of freeze–thaw cycles, STHMFP of F samples of HPO-A, HPO-N, TPI-A, TPI-N, and HPI had decreasing rates of 10.1, 2.3, 1.3, 5.5, and 18.5 relative to that of O samples, respectively, which were 0.98, 1.76, 1.08, 0.96, and 0.06 times B samples. The results suggested that repeated freeze–thaw cycles, in comparison with single freeze–thaw cycle, reduced STHMFP of HPO-N, but increased that of HPI; however, the times of freeze–thaw cycles exerted a relatively slight influence on STHMFP of the other three fractions. As for freezing time, the STHMFP decreasing rates of G samples of HPO-A, HPO-N, TPI-A, TPI-N, and HPI were 0.99, 0.90, 1.10, 0.95, and 0.04 times the rates of their B samples, respectively, indicating that the freeze–thaw treatment with a relatively long freezing time, in comparison with a relatively short time, resulted in an increase in STHMFP of HPI; however, the freezing time exerted almost no effect on STHMFP of the other four fractions.

4. Conclusions

The goal of this study was to investigate the effect of freezing–thawing on the content, spectroscopic characteristics, and chlorine reactivity of DOM in water. The following conclusions were obtained from the study:

(1) DOC of water samples were significantly affected by freezing and thawing temperatures, times of freeze–thaw cycles, and freezing time.
(2) The aromaticity of DOM and its fractions decreased as a result of freezing–thawing. Both freezing and thawing temperatures had significant impact on aromatic substances contained in DOM.
(3) The freeze–thaw treatment reduced the chlorine reactivity of DOM and its fractions. The freezing temperature and freezing time were significant factors influencing the reactivity of DOM.
(4) The freeze–thaw treatments led to increases in contents of four types of fluorescent materials contained in DOM.

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