The migration and transformation of dissolved organic matter during the freezing processes of water

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ABSTRACT

This study investigated the partitioning behavior of dissolved organic matter (DOM) in liquid and ice phases, as well as the changes in the optical properties and chlorine reactivity of DOM during the freezing processes of water. DOM was rejected from the ice phase and accumulated in the remaining liquid phase during water freezing. Moreover, the decrease in freezing temperature, as well as the increase in dissolved organic carbon (DOC) concentration of feed water, caused an increase in DOM captured in the ice phase. The ultraviolet-absorbing compounds, trihalomethane precursors, as well as fulvic acid- and humic acid-like fluorescent materials, were more liable to be to be rejected from the ice phase and were more easily retained in the unfrozen liquid phase during water freezing, as compared with organics (on average) that comprise DOC. In addition, it was also found a higher accumulation of these organics in the unfrozen liquid phase during water freezing at higher temperature. The freeze/thaw processes altered the quantity, optical properties, and chlorine reactivity of DOM. The decrease in ultraviolet light at 254 nm as well as the production of aromatic protein- and soluble microbial byproduct-like fluorescent materials in DOM due to freeze/thaw were consistently observed. On the other hand, the changes in DOC, trihalomethane formation potential, and fulvic acid- and humic acid-like fluorescence caused by freeze/thaw varied significantly between samples.

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Introduction

Dissolved organic matter (DOM) consists of a continuum of macroscopic particles, biotic and abiotic colloids, dissolved macromolecules, and specific compounds (Barber et al., 2001). DOM causes esthetic concerns such as color, taste, and odor, and enables the microorganisms to grow in the treatment unit or distribution system (Leenheer and Croué, 2003; Kim and Yu, 2005). It is well known that DOM could potentially be converted to potentially harmful disinfection by-products during the disinfection process with chlorine, which is a common treatment technique in municipal water supply facilities (Kanokkantapong et al., 2006). DOM also plays a significant biochemical and geochemical role in aquatic ecosystems (Ma et al., 2001). The nature and properties of DOM in water are topics of significant environmental interest (Leenheer and Croué, 2003).

The phenomenon that water freeze in cold areas is universal. The winter is long and very cold in the north of China, where large bodies of water, such as lakes, reservoirs and rivers, are ice-covered for 3–5 months each year. The ice covering waters is commonly more than 1 meter thick in Liaoning, Jilin, Heilongjiang, Inner Mongolia, Xinjiang and other places. Some contaminants in water will be inevitably captured in ice during the freezing in winter thus affecting their distribution, transport and fate in aquatic ecosystems (Li et al., 2008). Considerable works had been done in the past to investigate the characteristics and behavior of DOM in various and distinct bodies of water (Retamal et al., 2007; Hong et al., 2008; Wei et al., 2008; Chen et al., 2009; Rantakari et al., 2010; Zhang

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et al., 2011). The distribution and transport of contaminants in a low-temperature water environment had also received attention. Li et al. (2008) examined the nitrobenzene ratio in water–ice system under different conditions. Shiller (2010) determined the seasonal variability of dissolved rare earth elements in a seasonally snow-covered, alpine/subalpine watershed, Loch Vale, Colorado, USA. However, studies about the migration of DOM in water–ice system are rare. Moreover, the transformation of DOM during the freezing processes of water still remains unclear.

The objectives of this study were threefold: (1) to investigate the partitioning behavior of DOM in liquid and ice phases during the freezing processes of water; (2) to identify the changes in the optical properties and chlorine reactivity of DOM during the freezing processes of water, and (3) to examine the effect of freeze/thaw on the quantity, optical properties, and chlorine reactivity of DOM in water.

1. Materials and methods

1.1. Sample collection and preservation

The feed water samples used in freezing experiments in this study were collected from the South Canal (SC) and the North Canal (NC) on 17 and 18 March 2012, respectively. The SC and NC are the two main canals in Shenyang, Liaoning Province. Water samples were carefully collected and transferred to the laboratory in an ice cooler. They were stored at 4°C in the refrigerator as soon as they were carried back to the laboratory to minimize changes in the constituents. The characteristics of the SC and NC water samples were summarized in Table 1.

1.2. Freezing experiments

To study the effect of freezing temperature on the migration and changes in the optical properties and chlorine reactivity of DOM during the freezing processes of water, a series of freezing experiments were carried out with both SC and NC water samples at −15, −20 and −24°C. In a set of freezing experiments, six 1.8-L feed waters from the same water sample were placed in cylindrical containers with an inner diameter of 10 cm and a height of 30 cm, and frozen in a freezer at the same temperature for different times. The freezing time was evaluated by preliminary experiments. Polystyrene insulations were applied at the bottom and outer surface of the container so that heat transfer during freezing mainly occurred unidirectional (axially from top to bottom). This unidirectional downward freezing manner was employed because of its similarity with the natural freezing occurring in waters during winter. After freezing, the containers were taken out from the freezer, and the unfrozen liquid phase and the ice phase were separated with each other. Then, the ice was melted at room temperature.

In order to evaluate the influence of DOM concentration on the partitioning behavior of DOM in liquid and ice phases during the freezing processes of water, a second similar series of freezing experiments were performed on the 2- and 4-fold dilutions of both the original SC and NC water samples at −24°C. For dilutions, which contain lower conductivity than the original water samples, sodium chloride was added to produce a conductivity value equal to that of the original water samples, prior to freezing experiments.

All freezing experiments were performed in triplicate. The volume, DOC, absorbance of ultraviolet light at 254 nm (UV-254) and trihalomethane formation potential (THMFP) of all unfrozen liquid and melted ice samples in this study were measured. The fluorescence spectra of the unfrozen liquid and melted ice samples obtained from the freezing experiments on both SC and NC water samples at −15 and −24°C were also measured.

1.3. Analysis

Dissolved organic carbon (DOC) was analyzed using a TOC-5000 Total Organic Carbon Analyzer (Shimadzu, Kyoto, Japan) with an auto-sampler. UV-254 was measured with a Cary50 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.

THMFP measurements were performed according to Standard Method 5710B. All samples were adjusted to a pH of 7 ± 0.2, buffered with a phosphate solution, and chlorinated with an adequate excess amount of concentrated sodium hypochlorite, to assure a residue concentration of free chlorine of about 3–5 mg/L at the end of the reaction period (requiring 7 days at 25 ± 2°C). At the end of this reaction period, the residual chlorine was immediately quenched with Na_2SO_3, and trihalomethanes (THMs) were extracted with methyl-tert butyl ether from the chlorinated samples using a modified EPA method 551.1 and analyzed by gas chromatography with an electron capture detector (GC/ECD, CP-3800, 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. The samples were diluted to 0.5 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 450 nm (5-nm intervals). Scan speed was set at 1000 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.

2. Results and discussion

2.1. Water freezing processes

As expected, the frozen water volume increased with freezing time during all freezing experiments (Fig. 1). Here, the frozen water volume was the volume of the liquid phase corresponding

Table 1 – Characteristics of South Canal (SC) and North Canal (NC) water samples.		
Parameters	SC	NC
pH	7.1	7.4
TOC (mg/L)	5.8	9.2
DOC (mg/L)	4.6	6.7
UV-254 (m^{-1})	6.8	10.9
Conductivity (μS/cm)	367.2	443.4
Turbidity (NTU)	4.9	5.3

to the ice formed during freezing experiments, which was measured after the ice completely melted into water at room temperature. The actual operational period of the crystallization process of both SC and NC water samples at −15, −20 and −24°C were about 168, 116 and 96 hr, respectively. The results indicated that the water freezing process was influenced significantly by temperature, which agreed with the 1-dimensional heat transfer theory of ice growth, where the ice growth rate has a linear relationship with the square root of absolute value of temperature (Li et al., 2008). On the other hand, the freezing processes of SC and NC at the same temperature were very similar (Fig. 1). The similarity was also found in freezing processes of 2- and 4-fold dilutions of both SC and NC at the same temperature of −24°C. These observations suggested that the concentration of DOM, within the ranges tested in this study, seemed to have no effect on the water freezing processes.

2.2. Partition of DOM in liquid and ice phases

The DOC concentration in all unfrozen liquid and ice samples was plotted as a function of freezing ratio in Fig. 2. The freezing ratio is determined as the ratio of volume of the frozen water to the original feed water. The freezing ratio corresponding to unfrozen liquid samples was about 0, 0.35, 0.50, 0.64, 0.77 and 0.89, respectively. Similarly, the freezing ratio corresponding to ice samples was about 0.35, 0.50, 0.64, 0.77, 0.89 and 1.0, respectively. As shown in Fig. 2a and c, DOC concentration in unfrozen liquid phase increased gradually with freezing ratio, from 4.6 up to 23.3 (at −15°C), 20.4 (at −20°C), and 18.3 mg/L (at −24°C) for SC, and from 6.6 up to 23.8 (at −15°C), 23.0 (at −20°C), and 22.7 mg/L (at −24°C) for NC. On the other hand, DOC remained consistently low (less than 0.9 mg/L) in ice phase up to freezing ratio of 0.5, after which it increased significantly until a value of freezing ratio 1.0, when DOM was all included in the ice phase (Fig. 2b and d). The results agreed with a long known fact that when water freezes up, the ice contains less impurity than the water from which it is formed. This is because when ice is crystallized, the crystal is built up by pure water leaving the foreign bodies in the remaining liquid phase (Zaritzky, 2006; Shafique et al., 2012; Petzold et al., 2013).

To further investigate the migration of DOM during water freezing, the partition coefficient of DOM between the liquid and the ice phases as a function of freezing ratio was also examined and is shown in Fig. 3. The partition coefficient of DOM is defined as the ratio of the DOC concentration of the unfrozen liquid sample to the ice sample after freezing experiments. The patterns of partition coefficient with increasing freezing ratio were similar for all freezing experiments; the partition coefficient increased initially and then decreased, with the peaks occurring at freezing ratios of 0.64 or 0.77. The trend of partition coefficient with freezing ratio was attributed to both trend of DOC concentration of unfrozen liquid and ice samples. As described above, DOC concentration of unfrozen liquid samples increased monotonically while that of ice samples initially remained relatively low but subsequently increased significantly. As a result, the partition coefficient increased initially and then decreased during water freezing.

It was worth noting that, for the same feed water, the DOC of each unfrozen liquid sample obtained in freezing experiments at −20°C was commonly higher than that with very similar freezing ratio at −24°C and at the same time was lower than that with very similar freezing ratio at −15°C (Fig. 2a and c). This trend was also found for ice samples obtained in freezing experiments conducted on SC and NC at different temperatures (Fig. 2b and d). The results suggested that temperature was an important parameter controlling the partitioning behavior of DOM in liquid and ice phases during freezing processes of water; the lower the temperature, the more DOM was retained in the ice. This was also corroborated by the corresponding partition coefficient results, where, for both SC and NC, the higher partition coefficient was consistently observed at higher temperature (Fig. 3). According to Matsuda et al. (1988), the lower the freezing temperature, the faster the freezing front moves. Therefore, more DOM is accumulated near the solid/liquid interface at lower temperature than that at higher temperature. The increased viscosity of water with increase in concentration as well as with decrease in temperature and the phenomenon called concentration polarization at ice/liquid interface causes a reduction in diffusion rate of DOM away from the interface (Bhatnagar et al., 2005; Hernández et al., 2010; Sánchez et al.,
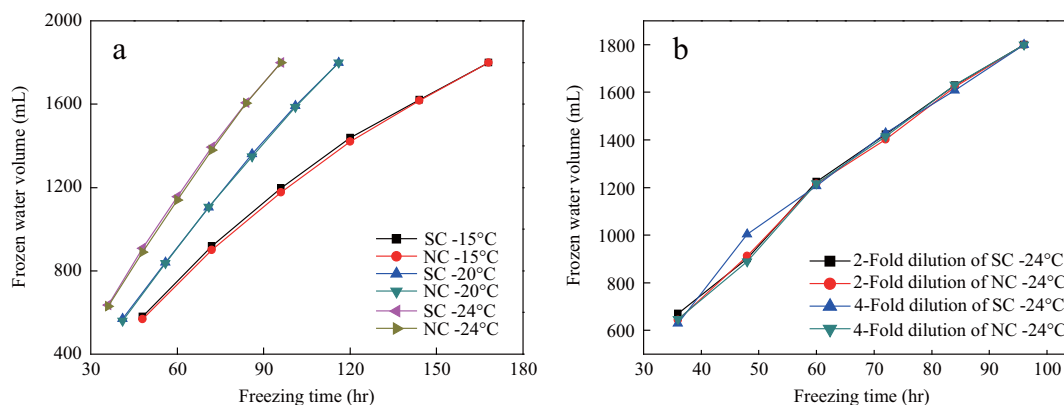

Fig. 1 – Frozen water volume as a function of freezing time for South Canal (SC) and North Canal (NC) at different temperatures, and 2- and 4-fold dilutions of South Canal (SC) and North Canal (NC) at −24°C.
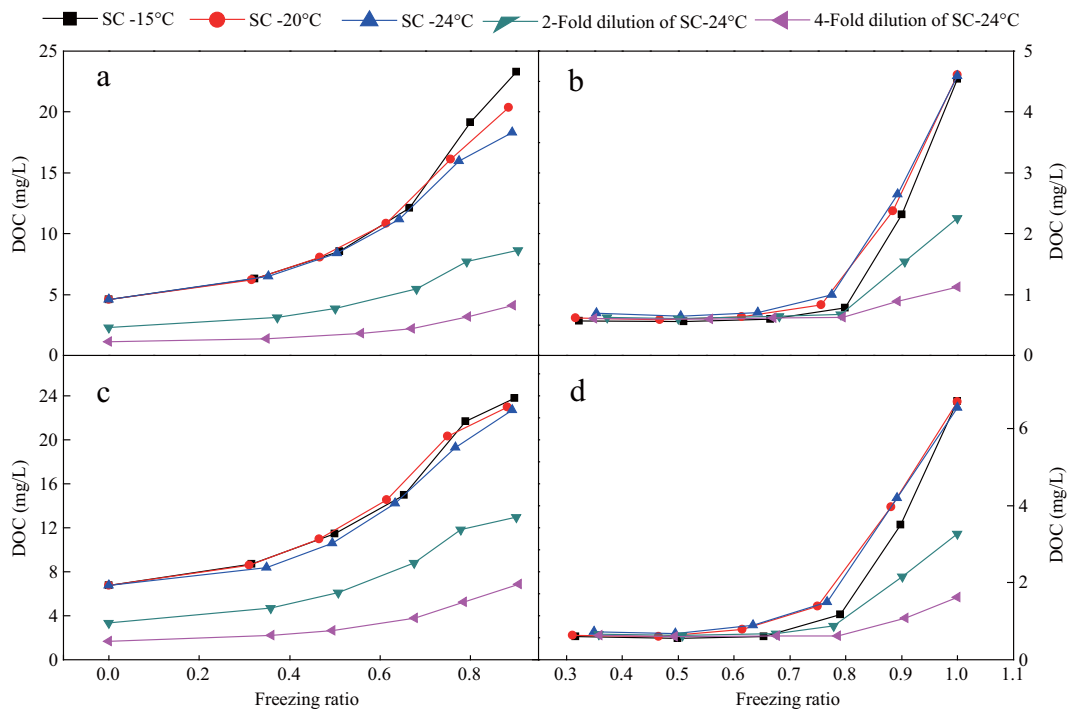
Fig. 2 – dissolved organic carbon (DOC) as a function of freezing ratio for (a) unfrozen liquid and (b) ice samples obtained from the freezing experiments on South Canal (SC) at different temperatures and 2- and 4-fold dilutions of South Canal (SC) at −24°C, (c) unfrozen liquid and (d) ice samples obtained from the freezing experiments on North Canal (NC) at different temperatures and 2- and 4-fold dilutions of North Canal (NC) at −24°C.

2010; Belén et al., 2012). Thus DOM is more easily incorporated in the ice being formed at lower temperature. Moreover, the lower the freezing temperature, the more area water needs to release latent heat; at lower temperature, ice crystals grow dendritically, producing sub-branches on the main branches (Kulaev and Vagabov, 1983; Daigger and Bailey, 2000). DOM is easily trapped at the gap between the end of branches at various levels, which also contributes to the more DOC captured in ice at lower temperature.

Although the concentration of DOM within the ranges tested in this study seemed to have no effect on water

freezing processes, it significantly affected the partitioning of DOM in liquid and ice phases during freezing processes of water. As shown in Figs. 2 and 3, for both SC and NC, the increased feed water concentration caused an increase in DOC of both unfrozen liquid and ice samples, as well as in partition coefficient. Similar results are found in the studies on the behavior of suspended materials, as well as soluble inorganic and organic compounds in freeze concentration; the higher the impurity concentration in feed water, the more impurities were incorporated in the ice formed during freezing (Shafique et al., 2012). It is believed that due to the
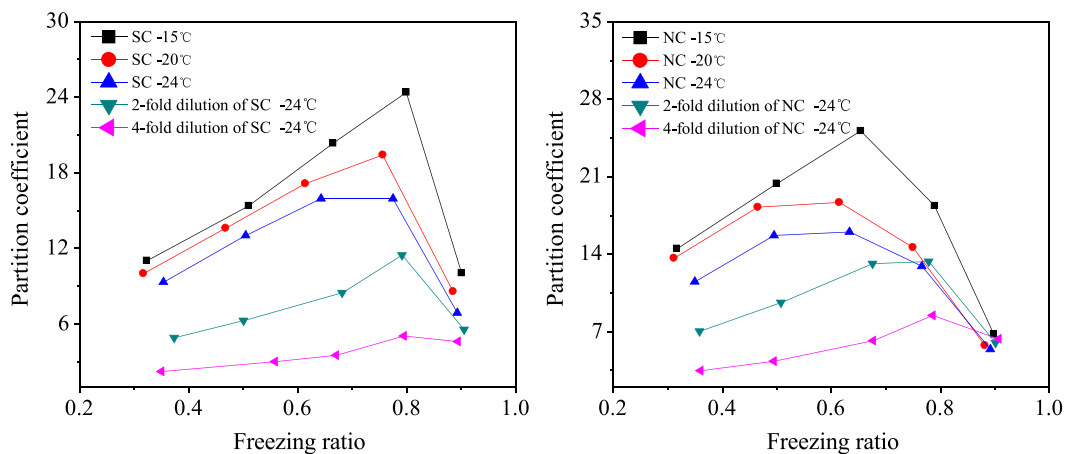

Fig. 3 – Partition coefficient of dissolved organic matter (DOM) between the liquid and the ice phases as a function of freezing ratio for South Canal (SC) and North Canal (NC) at different temperatures and 2- and 4-fold dilutions at −24°C.

increases in both viscosity of water and quantity of potential crystal nucleus in water with increasing impurity concentration, the impurities accumulated at the ice/liquid interface have a greater difficulty in moving towards the water and are more easily retained in the ice formed (Hernández et al., 2010; Belén et al., 2012).

It was found that DOC of ice sample with freezing time of 48 hr (at −15°C) was slightly higher than that of ice sample with freezing time of 72 hr. The same patter was also found at −20 and −24°C. During the initial process of unidirectional downward freezing, the water surface is suddenly subjected to cold thus reducing the solubility of impurities in the surface layer of water. Some impurities are rapidly deposited in the surface layer of water. They increase the possibility of formation of ice nucleus with a critical size, and promote heterogeneous nucleation of water. Hence, the purity of the surface ice declines. This might explain the slight higher DOC values for AI samples. The residual liquid was insulated from the freezing system due to the formation of surface ice thus hindering heat transfer. Therefore, the ice was crystallized slowly and stably in equilibrium and, besides, the crystal nucleus growth rate was greater than the nucleation rate, resulting in the formation the ice layer with high purity.

2.3. Changes in UV absorbance and chlorine reactivity of DOM

UV-254 is routinely measured as an indicator of aromatic content in water samples (Edzwald et al., 1985; Quanrud et al., 2003). THMFP is often the term employed to indicate the amount of THMs that could be produced during the chlorination process, and could indirectly represents the amount of THM precursors in water samples. The UV-absorbing compounds and THM precursors expressed by UV-254 and THMFP, respectively, are two subclasses of DOM. As shown in Fig. 4, for both SC and NC, the trend of UV-254 and THMFP in unfrozen liquid and ice samples with freezing ratio was very similar to that of DOC representing the bulk DOM; the values for unfrozen liquid samples increased monotonically, while those for ice samples initially remained relatively low but subsequently increased significantly. The partition coefficient of both UV-absorbing compounds and THM precursors also followed closely the pattern of that of the bulk DOM during water freezing (Fig. 5). In addition, the increase in concentration captured in ice, as well as the decrease in partition coefficient, with decreasing temperature, was observed for both UV-absorbing compounds and THM precursors during water freezing.

In order to further investigate the migration of UV-absorbing compounds and THM precursors during the freezing processes of water, the SUVA and specific THMFP for unfrozen liquid and ice samples as a function of freezing ratio, which were obtained from freezing experiments conducted on SC and NC at −15 and −24°C, were observed and shown in Fig. 4. Specific THMFP could be estimated as the ratio between THMFP and DOC of the same water sample, which represents the chlorine reactivity of DOC. As for SC and NC feed water, both SUVA and specific THMFP in unfrozen liquid phase increased gradually with freezing ratio during freezing experiments at two temperatures. Moreover, it was found that the values of SUVA and specific THMFP in unfrozen liquid samples obtained from freezing experiments at −15°C, were higher than those at −24°C. The results suggested that

when ice is crystallized, the DOM with higher aromaticity and that with higher chlorine reactivity were preferentially rejected from the ice phase and accumulated in the remaining liquid phase, as compared with organics (on average) that comprise DOC; moreover, the preferential rejection of DOM with higher aromaticity or with higher chlorine reactivity by the ice being formed was stronger during water freezing at higher temperature.

2.4. Changes in fluorescence properties of DOM

Fluorescence EEM provides an overall view of fluorescent properties of DOM in a selected spectral range and it has been employed to identify fluorescent compounds in DOM (Hur et al., 2007). The EEM spectra generated for DOM in unfrozen liquid and ice samples obtained from freezing experiments conducted on SC and NC at −15 and −24°C, are shown in Fig. 6, and the fluorescence EEM results are summarized in Table 2. Previous investigations have suggested that four fluorescence peaks related to fulvic acid-like, humic acid-like, soluble microbial byproduct-like (SMP-like) and aromatic protein-like fluorescent compounds can be distinguished at different locations (Chen et al., 2003; Drewes et al., 2006). In general, fulvic acid-like fluorescence is present at excitation/emission (Ex/Em) = 230–265 nm/390–445 nm, humic acid-like fluorescence at Ex/Em = 290–335 nm/390–435 nm, SMP-like fluorescence at Ex/Em = 275–285 nm/320–350 nm, and aromatic protein-like fluorescence at Ex/Em = 225–240 nm/335–350 nm (Chen et al., 2003; Drewes et al., 2006). Traditionally, fulvic acid- and humic acid-like peaks have been associated with humic-like substances, and aromatic protein- and SMP-like peaks have usually been recognized as belonging to protein-like fluorescence (Sierra et al., 2005).

As shown in Fig. 6a, both SC and NC were dominated by fulvic acid- and humic acid-like fluorescence, with NC having slightly higher fluorescence intensity than SC. For SC and NC, the EEM spectra shapes of DOM in unfrozen liquid samples were all similar to those of the original feed water, i.e., the sample with freezing time 0 hr. However, the intensity of fulvic acid- and humic acid-like fluorescence peaks of unfrozen liquid samples increased monotonously during the freezing processes of both SC and NC water samples at −15 and −24°C. As all EEM spectra were obtained for water samples with a DOC concentration of 0.5 mg/L, an increase in fluorescence intensity was an indication of increased relative content of fluorescent materials in DOM, and vice versa. The monotonously increased fluorescence intensity in unfrozen liquid samples implied that fulvic acid- and humic acid-like fluorescent materials were more liable to be to be rejected from the ice phase and were more easily retained in the unfrozen liquid phase during water freezing, as compared with the bulk DOM represented by DOC. In addition, it was found a higher accumulation of fluorescent materials in the unfrozen liquid phase during water freezing at higher temperature, as indicated by higher intensity values for each unfrozen liquid sample at −15°C than those for the corresponding sample at −24°C (Table 2).

It was apparent that the EEM features of DOM in ice samples obtained from freezing experiments on SC and NC at −15 and −24°C were very different from those in sample with
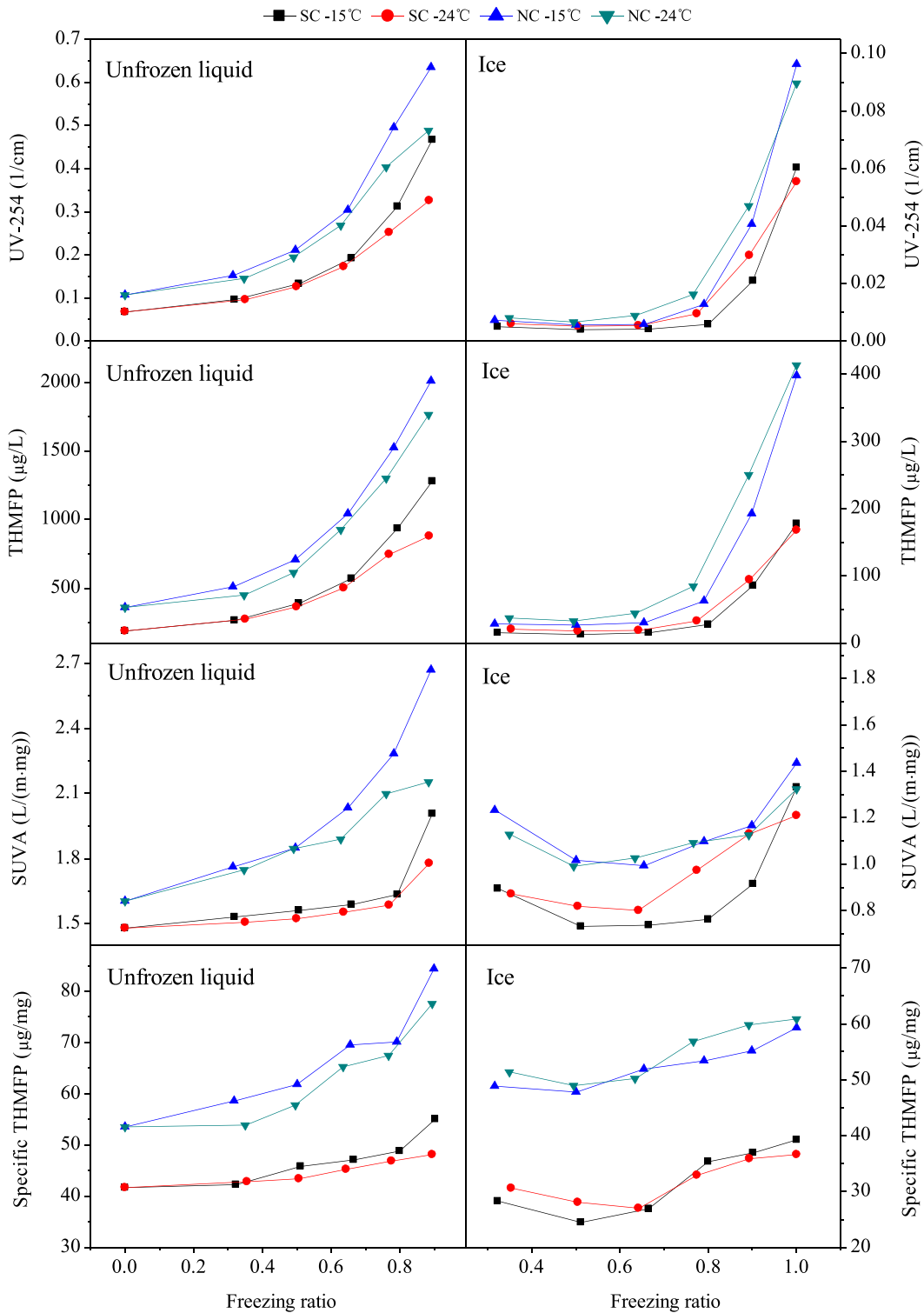
Fig. 4 – Absorbance of ultraviolet light at 254 nm (UV-254), trihalomethane formation potential (THMFP), specific ultraviolet light absorbance (SUVA) and specific trihalomethane formation potential (THMFP) as a function of freezing ratio for unfrozen liquid and ice samples which obtained from the freezing experiments on South Canal (SC) and North Canal (NC) at −15 and −24°C.
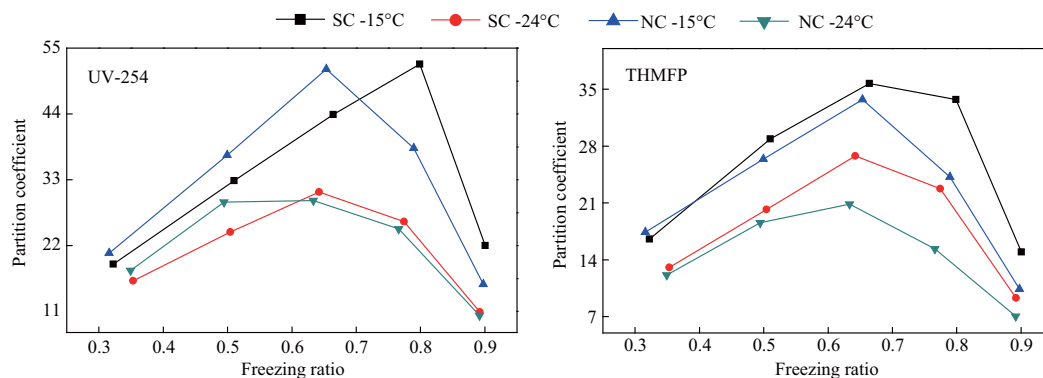
Fig. 5 – Partition coefficient of absorbance of ultraviolet light at 254 nm (UV-254) and trihalomethane formation potential (THMFP) between the liquid and the ice phases as a function of freezing ratio for South Canal (SC) and North Canal (NC) at −15 and −24°C.

freezing time of 0 hr and unfrozen water samples (Fig. 6), which indicated that freeze/thaw had a significant effect on the fluorescence properties of DOM. As shown in Fig. 6b, almost all the spectra of ice samples were characterized by strong aromatic protein-like fluorescence peaks which were not present in those of the two OL samples as well as of all unfrozen liquid samples in this study, suggesting that the production of aromatic protein-like fluorescent materials resulted from freeze/thaw. In addition, it was noteworthy that the intensity of aromatic protein-like peak in ice samples

of SC and NC formed at −15 and −24°C decreased monotonously with increasing freezing ratio. The results implied that those DOM which could be transformed into aromatic protein-like fluorescent materials due to freeze/thaw were more readily captured in ice as compared with organics (on average) that comprised DOC during water freezing.

The freeze/thaw processes also caused the formation of SMP-like fluorescent materials, as indicated by the appearance of a clear SMP-like fluorescence peak in all ice samples of NC, as well as by the higher intensity of SMP-like peak in all
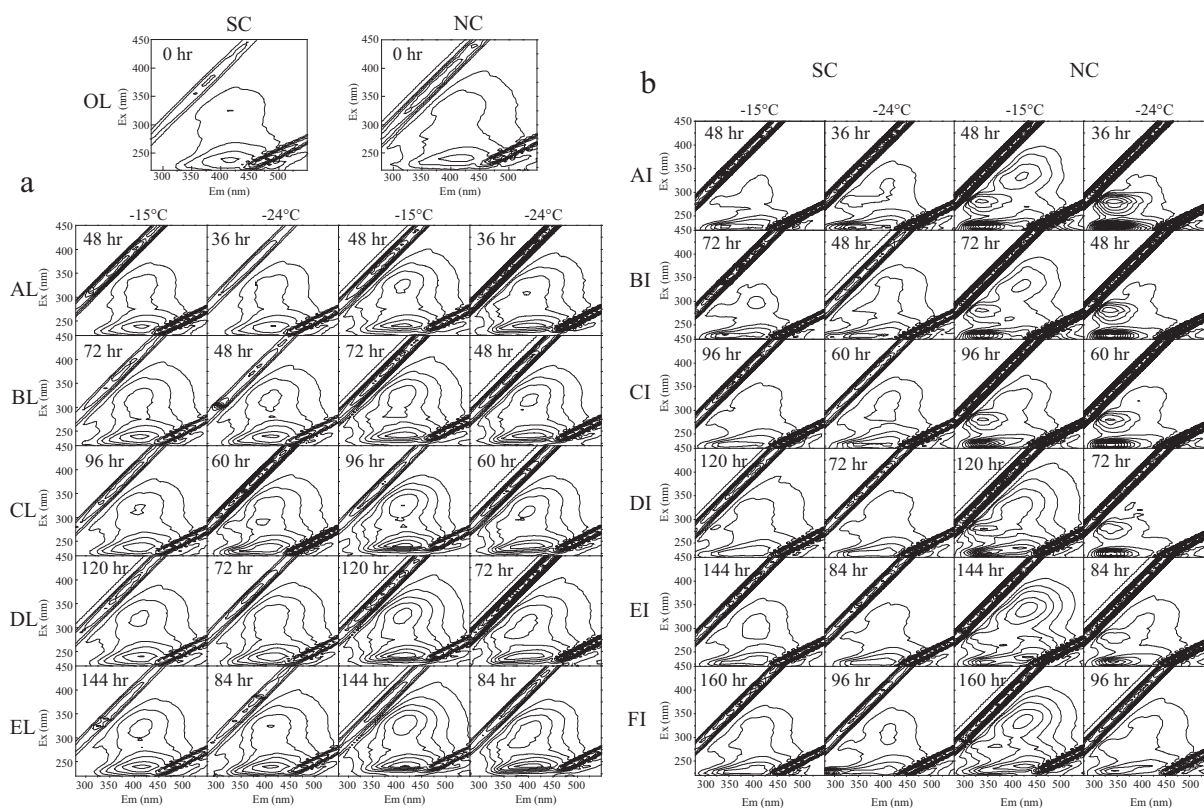

Fig. 6 – Fluorescence excitation-emission matrices (EEMs) for unfrozen liquid (a) and ice (b) samples obtained from the freezing experiments on South Canal (SC) and North Canal (NC) at −15 and −24°C.

Table 2 – Fluorescence data of dissolved organic matter (DOM) in unfrozen liquid and ice samples obtained from the freezing experiments on South Canal (SC) and North Canal (NC) at –15 and –24°C.

Freezing time (hr)	Fulvic acid-like peak		Humic acid-like peak		Aromatic protein-like peak		SMP-like peak		Fulvic acid-like peak		Humic acid-like peak		Aromatic protein-like peak		SMP-like peak	
	Ex/Em (nm)	Intensity (a.u.)	Ex/Em (nm)	Intensity (a.u.)	Ex/Em (nm)	Intensity (a.u.)	Ex/Em (nm)	Intensity (a.u.)	Ex/Em (nm)	Intensity (a.u.)	Ex/Em (nm)	Intensity (a.u.)	Ex/Em (nm)	Intensity (a.u.)	Ex/Em (nm)	Intensity (a.u.)
SC									NC							
0	235/415	40.6	310/415	19.3	–	–	–	–	240/413	45.3	325/415	27.5	–	–	–	–
–15°C unfrozen liquid sample																
48	240/408	52.1	320/413	23.5	–	–	–	–	240/413	63.7	320/409	41.8	–	–	–	–
72	240/408	54.0	315/406	24.1	–	–	–	–	240/410	68.7	320/411	47.1	–	–	–	–
96	240/407	59.5	310/406	30.8	–	–	–	–	240/414	74.7	330/415	47.4	–	–	–	–
120	240/419	60.5	320/410	31.8	–	–	–	–	240/414	77.8	320/411	53.5	–	–	–	–
144	240/414	65.0	320/411	32.3	–	–	–	–	240/415	81.6	325/415	56.6	–	–	–	–
–15°C ice sample																
48	230/397	42.1	295/405	16.7	230/342	52.8	280/343	15.1	–	–	330/421	41.6	230/338	126.1	280/339	53.51
72	230/402	42.8	295/410	23.5	230/343	51.0	280/324	17.9	–	–	330/423	32.7	230/338	101.4	280/340	42.8
96	230/390	43.0	315/408	18.0	230/348	49.7	280/323	15.8	–	–	320/403	29.6	230/339	92.8	280/341	52.8
120	230/412	45.9	310/401	26.8	230/346	48.1	280/322	20.7	240/431	72.3	325/416	48.2	230/347	85.0	280/342	61.8
144	230/407	46.1	305/411	24.9	230/349	42.8	285/331	14.8	240/432	72.2	335/428	55.7	230/345	65.4	280/349	39.5
168	230/402	46.8	310/404	19.5	230/347	42.1	280/341	12.7	240/426	76.7	330/421	53.6	230/344	58.7	280/347	40.0
–24°C unfrozen liquid sample																
36	235/412	48.5	315/412	22.7	–	–	–	–	240/396	57.5	310/398	30.5	–	–	–	–
48	240/414	52.9	310/408	23.3	–	–	–	–	240/408	66.3	315/402	41.6	–	–	–	–
60	240/407	57.6	285/395	30.4	–	–	–	–	240/401	68.5	310/401	42.6	–	–	–	–
72	240/418	59.1	325/416	30.7	–	–	–	–	240/402	69.0	310/399	42.7	–	–	–	–
84	240/411	62.8	325/415	31.3	–	–	–	–	240/406	76.8	310/399	46.9	–	–	–	–
–24°C ice sample																
36	230/407	50.5	310/412	21.7	230/337	68.0	280/343	25.5	–	–	–	–	230/337	163.0	280/342	79.5
48	230/404	50.9	330/416	22.9	230/349	55.5	280/347	20.6	–	–	–	–	230/335	127.7	280/337	56.6
60	230/404	50.7	320/413	23.5	230/349	52.0	280/347	19.3	–	–	–	–	225/335	116.6	280/338	51.8
72	230/400	45.0	325/417	15.3	230/347	48.5	280/344	19.0	–	–	–	–	230/337	87.3	280/332	37.4
84	230/371	46.6	325/415	17.2	230/343	43.7	285/332	12.5	–	–	–	–	230/341	73.6	275/345	32.8
96	230/419	45.6	305/411	20.1	230/345	42.9	280/330	11.1	240/391	40.6	325/408	24.6	230/345	51.2	280/349	28.6

ice samples of SC than the corresponding OL sample, although this peak was more like a shoulder in the majority of ice samples of SC. The intensity of SMP-like peak in ice samples of both SC and NC formed at −24°C behaved in a similar manner to that of aromatic protein-like peak, showing decreased values with the increase in freezing ratio during water freezing. On the other hand, the intensity of SMP-like peak in ice samples of SC and NC formed at −15°C fluctuated between 12.7 and 20.7, and between 39.5 and 61.8, respectively (Table 2). Thus the results suggested the inconsistency in the migration behavior of those DOM which could be transformed into SMP-like fluorescent materials due to freeze/thaw during the freezing processes of water at different temperatures.

Despite the enrichment of humic acid-like fluorescent materials in DOM remained in unfrozen liquid phase, the SC samples with freezing time 36, 48, and 60 hr at −24°C exhibited higher intensity of humic acid-like peak than the sample with freezing time 0 hr, reflecting newly produced humic acid-like fluorescent materials as a consequence of freeze/thaw. The partition of humic acid-like fluorescent materials in liquid and ice phases was similar to that of organics (on average) that comprised DOC during the freezing processes of SC at −24°C with freezing ratio increasing from 0.64 to 0.89, as demonstrated by the intensity of humic acid-like in samples with freezing time 72 and 84 hr that was very close to that in sample with freezing time of 60 hr. However, the intensity of humic acid-like peak in samples with freezing time 72 and 84 hr was significantly lower that in sample with freezing time of 60 hr, suggesting that some humic acid-like fluorescent materials captured in ice might be broken down into non-fluorescent structures as a result of freeze/thaw. Similarly, both production and reduction of humic acid-like fluorescent materials were also observed in ice samples of SC formed at −15°C. On the other hand, the ice samples of NC formed at −24 and −15°C exhibited opposite changes in humic acid-like fluorescence caused by freeze/thaw; the humic acid-like peak disappeared in all ice samples formed at −24°C while the intensity of this peak in all ice samples formed at −15°C was higher than that in the sample with freezing time 0 hr.

Based on the intensity of fulvic acid-like peak in ice samples of SC, it was obvious that the freeze/thaw processes caused the production of fulvic acid-like fluorescent materials. In addition, it was found that those DOM which could be transformed into fulvic acid-like fluorescent materials due to freeze/thaw were captured in ice during the initial freezing processes of SC at −24°C whereas they were trapped in ice during the final freezing processes of SC at −15°C. As described above, the fulvic acid-like peak was present as the strongest fluorescence peak in the sample with freezing time of 0 hr as well as in all unfrozen liquid samples of NC. However, it was not visible in ice samples of NC with freezing time of 36–84 hr at −24°C. Although this peak was observed in the sample with freezing time 96 hr, its intensity was lower than that in the sample with freezing time 0 hr. The results suggested that during the freezing processes of NC at −24°C, the freezing front strongly rejected fulvic acid-like fluorescent materials, and engulfed them at the end of freezing processes; moreover, some fulvic acid-like fluorescent materials in NC were broken down into non-fluorescent structures due to freeze/thaw. The

fulvic acid-like peak was not visible in ice samples of NC with freezing time 48–96 hr at −15°C while it was clear and strong in the other three ice samples, implying that fulvic acid-like fluorescent materials were produced due to freeze/thaw, and moreover, the original fulvic acid-like fluorescent materials present in NC were strongly rejected from the ice phase and until the final freezing processes were captured in ice.

2.5. Effect of freeze/thaw on the quantity, optical properties, and chlorine reactivity of DOM

To examine the effect of freeze/thaw on the quantity, optical properties, and chlorine reactivity of DOM, the values of DOC, UV-254, SUVA, THMFP, specific THMFP and fluorescence intensity for both liquid sample with freezing time 0 hr and ice sample with freezing time of 168 hr in each freezing experiment were compared, which represented parameters of the same water sample before and after freezing and subsequent thawing, respectively. As shown in Table 3, the changes of −4.34% to 0.68% in DOC due to freeze/thaw indicates that the freeze/thaw processes could alter DOM concentration; however, the DOC changes due to freeze/thaw were not correlated with freezing temperature as well as DOM concentration. On the other hand, the freeze/thaw processes caused decreases in UV-254 of both SC and NC, and moreover, the decrease in UV-254 due to freeze/thaw was greater at lower freezing temperature. SC showed decreased THMFP, whereas NC exhibited increased THMFP after freezing at both −15 and −24°C and subsequent thawing at room temperature. In addition, it was also found that the changes in THMFP of both SC and NC were more apparent at lower freezing temperature. The changes in UV-254 and THMFP of feed water caused by the freeze/thaw processes were significantly greater than the corresponding changes in DOC, resulting in changes in SUVA and specific THMFP similar to those in UV-254 and THMFP, respectively. The SUVA results were consistent with a previous study of Fellman et al. (2008), who reported a decrease in SUVA when surface water were frozen. Spencer et al. (2007) also examined the effect of freeze/thaw on a wide range of freshwater DOM samples from the United Kingdom, and observed that 80% of the samples exhibited a decrease in SUVA after freeze/thaw. SC and NC revealed a different fluorescence response to freeze/thaw, including varying amounts of increase or decrease in intensity of different fluorescence peaks, at different freezing temperatures. Both SC and NC exhibited increases of more than 50% in intensity of aromatic protein- and SMP-like peaks after freezing at both −15 and −24°C and subsequent thawing at room temperature, indicating that the proportion of the two types of fluorescent materials in DOM had increased significantly. The increase in intensity of SMP-like peak in both SC and NC was greater at higher freezing temperature. As with aromatic protein-like peak this was not consistent. The freeze/thaw processes caused an increase in intensity of both fulvic acid- and humic acid-like peaks in SC, and the magnitude of increase was similar at freezing temperatures of −15 and −24°C. On the other hand, freezing temperature seemed to have a significant effect on changes of fulvic acid- and humic acid-like fluorescence in NC caused by freeze/thaw; decreases in intensity of both fulvic acid- and humic

Table 3 – Changes in quantity, optical properties and chlorine reactivity of dissolved organic matter (DOM) caused by freeze/thaw.

Sample	Freezing temperature	Changes (%)								
		DOC	UV-254	SUVA	THMFP	Specific THMFP	Fulvic acid-like fluorescence intensity	Humic acid-like fluorescence intensity	Aromatic protein-like fluorescence intensity[a]	SMP-like fluorescence intensity[b]
SC	−15°C	−0.87	−10.78	−10.00	−6.76	−5.94	15.27	1.04	81.47	89.55
SC	−20°C	0.68	–	–	–	–	–	–	–	–
SC	−24°C	0.22	−18.10	−18.28	−11.84	−12.03	12.32	4.15	84.91	65.67
2-Fold dilution of SC	−24°C	−1.28	–	–	–	–	–	–	–	–
4-Fold dilution of SC	−24°C	−2.27	–	–	–	–	–	–	–	–
NC	−15°C	−0.70	−11.26	−10.65	9.85	10.61	69.32	94.91	95.67	110.53
NC	−20°C	−0.99	–	–	–	–	–	–	–	–
NC	−24°C	−3.21	−17.22	−17.63	14.21	13.65	−10.38	−10.55	70.67	50.53
2-Fold dilution of NC	−24°C	−3.00	–	–	–	–	–	–	–	–
4-Fold dilution of NC	−24°C	−4.34	–	–	–	–	–	–	–	–

[a] Calculated with the highest intensity in the region of aromatic protein-like fluorescence.
[b] Calculated with the highest intensity in the region of SMP-like fluorescence.

acid-like peaks were observed after freezing at −24°C and subsequent thawing at room temperature while increases in intensity of the two peaks were found after freezing at −15°C and subsequent thawing at room temperature. For both SC and NC, the changes in intensity of SMP-like peak caused by freeze/thaw were significantly greater than those of fulvic acid- and humic acid-like peaks. The similar results were also reported by Spencer et al. (2007), who believed that the SMP-like fraction of fluorescent DOM was less stable in response to the freeze/thaw processes in comparison to the humic- and fulvic-like fractions.

3. Conclusions

The goal of this study was to investigate the migration and transformation of DOM during the freezing processes of water. The following conclusions are drawn on the basis of the experimental results: (1) DOM was rejected from the ice phase and accumulated in the remaining liquid phase, during the freezing processes of water. The decrease in freezing temperature, as well as the increase in DOC concentration of feed water, caused an increase in DOM captured in the ice formed during water freezing. (2) The UV-absorbing compounds, THM precursors, as well as fulvic acid- and humic acid-like fluorescent materials, were more liable to be rejected from the ice phase and were more easily retained in the unfrozen liquid phase during water freezing, as compared with organics (on average) that comprise DOC. In addition, it was also found a higher accumulation of these organics in the unfrozen liquid phase during water freezing at higher temperature. (3) The freeze/thaw processes altered the quantity, optical properties, and chlorine reactivity of DOM. The decrease in UV-254 as well as the production of aromatic protein- and SMP-like fluorescent materials in DOM

due to freeze/thaw were consistently observed in this study. On the other hand, the changes in DOC, THMFP, fulvic acid- and humic acid-like fluorescence caused by freeze/thaw varied significantly between samples.

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