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

Shuang Xue, Yang Wen, Xiujuan Hui, Lina Zhang, Zhaohong Zhang, Jie Wang, Ying Zhang*

School of Environmental Science, Liaoning University, Shenyang 110036, China. E-mail: shuangxue_777@163.com

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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.

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

* *Corresponding author*. E-mail: ldxslw666@126.com (Xiujuan Hui).

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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.

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

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