

Seasonal variations of chemical and physical characteristics of dissolved organic matter and trihalomethane precursors in a reservoir: a case study

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Abstract

Dissolved organic matter (DOM) and its potential to form disinfection by-products (DBPs) during water treatment are of great public health concern. Understanding the seasonal changes in DOM composition and their reactivity in DBP formation could lead to a better treatment of drinking water and a more consistent water quality. DOM from the East-Lake, a reservoir in the south-China, was fractionated and characterized by XAD resin adsorption (RA) and ultrafiltration (UF) techniques during different seasons within a year. The properties of chemical fractions (isolated by RA) appeared more stable than those of physical fractions (separated by UF) throughout the sampling period. The relative contribution of each chemical fraction to the total dissolved organic carbon (DOC), UV₂₅₄ absorbance and trihalomethane formation potential (THMFP) remained relatively constant across the sampling period. However, the physical (molecular weight) fractions of the DOM exhibited large seasonal changes in UV₂₅₄ and THMFP. Compared to the parameter of DOC, the THMFP and specific THMFP (STHMFP) of either chemical or physical fractions were more variable. In terms of DOC concentration, the hydrophobic acids (HoA) and hydrophilic matter (HiM) dominated in the DOM in most of the seasons; while the components with molecular weight of 10–30 kDa and less than 1 kDa were the predominant physical fractions.

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1. Introduction

The nature and properties of aquatic dissolved organic matter (DOM) are of growing research interest because it can cause aesthetic concerns such as color, taste, and odor; lead to the binding and transport of organic and inorganic contaminants; provide sources and sinks for carbon. Moreover, DOM has the potential to form various disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) during water disinfection [1]. The presence of THMs in potable water was first revealed by Rook in 1974 [2] and shown widespread by subsequent studies [3,4]. THMs are identified as potential carcinogens, and strict control of their formation is required by recent legislations around the world [5].

Both the chemical and physical properties of DOM are of great significance in the water treatment processes. Understanding chemical and physical characteristics of DOM is key to better treatment of drinking water [1]. In addition, knowledge on the seasonal changes in DOM composition and its reactivity in DBP formation during water disinfection should lead to a more consistent water quality [5]. Various chemical and physical fractionation techniques, such as resin adsorption (RA) and ultrafiltration (UF), were adopted successfully for characterization of DOM during the past decades [6–11]. However, little attention has been paid to the seasonal changes in the DOM compositions and their characteristics in the past. Panyapinyop and Marhaba et al. (2005) [12] suggested that future work should be conducted to investigate the effect of seasonal variation on the quality of organic matters and their trihalomethane formation potential (THMFP).

The purpose of this paper is to study the seasonal changes in the characteristics of the DOM from a reservoir in southern

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China. Much effort was made to elucidate the compositional changes of the DOM during one year monitoring, and the relationships between DOM compositions and THM formation potential were illustrated. The DOM fractions separated by RA and UF were examined and characterized in terms of dissolved organic carbon (DOC), UV_{254} absorbance and THMFP.

2. Materials and methods

2.1. Source water and sampling

All raw water samples were collected from the intake of the East-Lake water treatment plant (WTP) within a time span of three seasons in 2005: the spring (March to May), the summer (July to August) and the autumn (September to October). The East-Lake, a reservoir in Shenzhen city, supplies raw water for the East-Lake WTP. The source of East-Lake reservoir is the East River, which lies in the area close to Shenzhen city. The Shenzhen city is located in Southeast ($22^{\circ}N$, $114^{\circ}E$) of China and adjacent to the city of Hong Kong. Part of the drinking water produced in Shenzhen is distributed to the city of Hong Kong, which is one of the most important financial centers in Asia. The East-Lake reservoir and its source-East river are protected systematically and carefully nowadays by the local government so that no significant anthropogenic pollution is expected.

Samples were collected in precleaned 500 ml glass bottles every 2 h and five times each day. All samples collected in one day were blended into a larger glass bottle and stored immediately in an ice cooler. The samples were first filtered through $0.45\ \mu m$ membrane within 24 h after collection and always stored in a dark room at $4\ ^{\circ}C$ before and after fractionation experiments. The fractionation operations were performed at ambient temperature.

2.2. Fractionation of DOM by resin adsorption (RA)

The method of resin adsorption used in this study was modified from that reported by other authors [6–8]. Because of the high stability and other prominent properties [13], XAD-8 and XAD-4 resins (Amberlite, Sigma-Aldrich Co., USA) rather than ionic resins were selected. The resins were cleaned and conditioned as described by Leenheer [6]. The water-to-resin volume (wet volume) ratio was set at 35:1 for avoiding breakthrough, and other parameters, such as capacity factor (k') and void volume ratio (V_0), were 50 and 26.5%, respectively. The flow rate of sample loading onto the resins was lower than $30\ \text{bed-volumes h}^{-1}$, which could ensure adequate adsorption.

A schematic diagram of the DOM fractionation procedure is shown in Fig. 1a. The steps were as following: (1) the filtered sample was first passed through XAD-8 resin without any pH adjustment to isolate the hydrophobic bases (HoB) and hydrophobic neutral (HoN). (2) HoB was obtained by back-washing the XAD-8 resin immediately with 10 bed-volumes of $0.1\ \text{mol l}^{-1}\ H_3PO_4$ (all reagents used in this study were of guaranteed grade) at $15\ \text{bed-volumes h}^{-1}$. The hydrophobic neutral

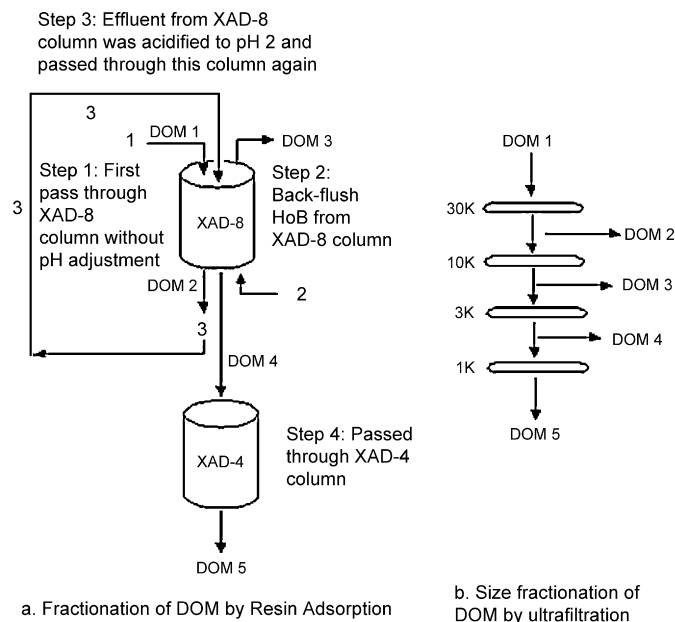


Fig. 1. Schematic diagrams of the procedures for DOM fractionation.

(HoN) could not be desorbed by H_3PO_4 and retained in the resin. H_3PO_4 was selected because of its minimum impact on the dissolved organic carbon (DOC) measurement compared to HCl or HNO_3 . (3) The first effluent of XAD-8 column was adjusted to pH 2 by $85\% H_3PO_4$ and added onto this XAD-8 resin column again. The hydrophobic acid (HoA) was adsorbed. (4) Then, the second effluent from XAD-8 column was passed through XAD-4 resin. The fraction adsorbed by this resin could be described as weakly hydrophobic acid (WHoA) [14], which is also commonly defined as transphilic acid (THPA) [1,15]. (5) Organics contained in the XAD-4 effluent (not retained by both XAD-8 and XAD-4 resins) were named hydrophilic matter (HiM).

To avoid the problem of losses upon concentration or isolation, the quantitative method as reported by Martin-Mousset et al. [8] and Imai et al. [9] was adopted. The parameters (DOC, UV_{254} and THMFP) of each fraction were determined successively by the concentration difference between the influent and the effluent from each resin column except the determination of HoB fraction. The HoB fraction was calculated based on the mass balance. Each fraction was calculated based on the following functions and the meaning of DOM1 to DOM5 is given in Fig. 1a.

$$\text{HoB} = (\text{DOM3}-\text{B1}) \times (\text{backeluentvolume})/(\text{samplevolume})$$

where B1 is the blank of effluent,

$$\text{HoN} = \text{DOM1}-\text{DOM2}-\text{HoB},$$

$$\text{HoA} = \text{DOM2}-\text{DOM4},$$

$$\text{WHoA} = \text{DOM4}-\text{DOM5},$$

$$\text{HiM} = \text{DOM5}$$

After the resins were cleaned carefully and just before loading samples, ultra-pure water and acidic solution of pH 2 (prepared by ultra-pure water) were passed through the resin columns respectively, and their DOC was measured immediately to make sure the blanks of columns were sufficiently low and negligible. (The blank of column refers to the difference between the concentration of influent pure water or pH 2 acidic solution and that of effluent.) Therefore, the blanks of columns could not be included in the calculation formulas of HoN, HoA, WHOA and HiM. In addition, fractionation experiments were all with duplicate samples.

2.3. Molecular size fractionation of DOM by ultrafiltration (UF)

Ultrafiltration was performed by using a stirred UF cell (Millipore, 8200) with YM disc membranes (Amicon, USA), and the nominal molecular weight (MW) cut-offs of the membranes are 1, 3, 10 and 30 kDa. In each step, the volumes of feed sample and retentate were determined based on a constant concentration factor (CF) of 6:1 [16]. The concentration factor (CF) or concentration ratio is defined as the ratio of the initial sample volume to the retentate volume. The DOC mass balance of our UF system was controlled in the range of $(100 \pm 5)\%$. The cleaning procedures were modified from [17,18], and a brief description is as follows: Membranes were first soaked several times (no less than three times during 24 h) in a beaker of ultra-pure water, skin side down, to remove glycerin, which was added by the manufacturer to the membrane to prevent drying in shipment. Each time when the pure water in the beaker changed, the membrane should be flushed thoroughly. After having been soaked, the membrane was installed into the UF cell and rinsed two times using 0.01 mol l^{-1} NaOH and HCl alternatively. The stirrer kept agitating more than 10 min for each rinse. Prior to filtering sample, the apparatus was rinsed with ultra-pure water again, and 100 ml of water was passed through the membrane to remove any contingent organic impurity from pores.

To minimize concentration polarization effects, we used a series of filtration steps (multi-stage) as suggested by Buffle et al. [19] and Gang et al. [20]. Following the multi-stage filtration method, high-molecular-weight molecules could be removed first. The filtrate from the former step was the feed sample of the next step (Fig. 1b). In order to evaluate the DOC mass balance, the retentate was also collected for DOC measurement. The concentration of each fraction was calculated based on the difference between the concentration of feed sample and corresponding filtrate in each UF step. If the feed sample volume was larger than the capacity of UF cell, feed sample was added separately. At the time when half cell volume of sample passed through the membrane, the cell pressure was released and then the remnant sample was added until the predetermined amount of filtrate was collected. The initial sample volume of 442 ml was needed in the first filtration step and 150 ml of filtrate would be obtained in the last step according to the CF of 6:1. Pressure was supplied with nitrogen gas (99.99%) from 20 kPa to 35 kPa and the actual pressure employed for a given membrane was based on the flow

rate recommended by the manufacturer. The DOC mass balance or recovery was checked as $(\%) = (C_p V_p + C_r V_r) / (C_0 V_0)$, where V_0 , V_p and V_r are the sample volumes of feed, filtrate and retentate respectively, and C_0 , C_p and C_r are the DOC concentrations of feed, filtrate and retentate sample, respectively [18].

2.4. Chemical analysis

All samples including raw water (filtered through $0.45 \mu\text{m}$ membrane), elutes and effluents from resin columns and filtrates through UF membranes were analyzed for DOC, UV_{254} and THMs formation potential (THMFP). DOC was measured with a Phoenix 8000 TOC Analyzer (Tekmar Dohrmann, USA) using the UV/persulphate oxidation method. The instrument error was controlled within 3% with runs of 2.0 mg l^{-1} standards after every ten samples. UV_{254} was measured using a DR/4000U spectro-photometer (HACH, USA) with a 1 cm quartz cell. Specific ultraviolet absorbance (SUVA_{254}) is defined as the UV absorbance at 254 nm measured in inverse meters (m^{-1}) divided by the DOC concentration measured in milligrams per liter (mg l^{-1}).

THMFP was measured according to the standard methods (1995) for the examination of drinking water (5710B and 6232B) [21]. The neutralized samples were buffered by a phosphate solution prior to the incubation at $25^\circ\text{C} \pm 2^\circ\text{C}$ in amber bottles with Teflon-lined caps. At the end of 7 days reaction period, samples with a remaining free chlorine residual of $3\text{--}5 \text{ mg l}^{-1}$ as Cl_2 were analyzed for THMs by a gas chromatography instrument (PerkinElmer Autosystem XL, USA) with an electron capture detector (ECD) and a capillary column (OV-17, $\text{O}0.32 \text{ mm} \times 30 \text{ m} \times 0.25 \mu\text{m}$). Pesticide grade n-hexane was used as extraction solvent and the oven temperature program was 70°C holding 2 min, ramp $20^\circ\text{C min}^{-1}$ to 100°C , then $10^\circ\text{C min}^{-1}$ to 120°C for 2 min. The injection volume was $1 \mu\text{l}$ and split injection ratio was set at 30:1 for appropriate signal range and sensitivity. THMs were quantified by external standard procedure. The minimum detectable limitations (MDL) of CHCl_3 , CHCl_2Br , CHClBr_2 , CHBr_3 were $0.0049 \mu\text{g l}^{-1}$, $0.0024 \mu\text{g l}^{-1}$, $0.0032 \mu\text{g l}^{-1}$, $0.0088 \mu\text{g l}^{-1}$ respectively, when the minimum ratio of signal to noise was set as three. The reproducibility of instrument measurement was controlled in 5% by at least triplicate measurements. The specific THMFP (STHMFP) was calculated as THMFP divided by the DOC concentration. The STHMFP of HoB and HoN were presented in a whole parameter as HoB&N to avoid the effects of strong acid (pH 1) or probable high ionic strength of eluate on the chlorination of HoB. The THMFP of HoB&N could be obtained directly from the difference between the original sample and the first effluent from XAD-8 column.

THM concentration was reported as a single value as micrograms CHCl_3 per liter ($\mu\text{g CHCl}_3 \text{ l}^{-1}$) and calculated as $\text{THM} = A + 0.728 B + 0.574 C + 0.472 D$, where $A = \mu\text{g CHCl}_3 \text{ l}^{-1}$, $B = \mu\text{g CHBrCl}_2 \text{ l}^{-1}$, $C = \mu\text{g CHBr}_2\text{Cl} \text{ l}^{-1}$, $D = \mu\text{g CHBr}_3 \text{ l}^{-1}$.

3. Results and discussion

3.1. Seasonal variations of fractional characteristics

3.1.1. Changes of chemical fractions

The variations of chemical fraction distribution of the DOM from the East-Lake water during the sampling period from March 20 to October 28 in the year 2005 are shown in Fig. 2. It is clear that the total DOC and UV₂₅₄ absorbance of the DOM varied notably from the highest of 2.0 mg l⁻¹ and 0.055 cm⁻¹ to the lowest 1.1 mg l⁻¹ and 0.02 cm⁻¹, respectively. However, the relative contributions of DOC and UV₂₅₄ from most chemical fractions, (except the HiM fraction in March and the HoN on March 25 and April 20) remained relatively constant during the sampling period (Fig. 2a and b).

As shown in Fig. 2a, an obvious characteristic of the chemical fraction distribution was that the HoA and the HiM were the dominant fractions as DOC masses across the sampling period and HoA was richer than HiM. The two fractions accounted

for more than 30% and 20% of total DOC respectively, with exceptions in March with little lower HoA (about 28%) and in September with lower HiM (about 13%). The results are similar to the findings reported by Imai [9] that HoA and hydrophilic acids (HiA) are dominant constituents of riverine DOM, which is of allochthonous origin. Chiang et al. [10] also found that the hydrophobic constituents were more commonly observed than hydrophilic constituents in a surface and two reservoir waters. The fact that the chemical fraction distribution of the DOM from East-Lake water is similar to that of riverine DOM can be attributed to its source water supplied by East River. The DOC percentages of WHoA and HoB in the East-Lake DOM accounted for around 15% and 4%, respectively, which also appeared rather stable in the sampling period except the sample on March 20 with WHoA lower than 10%.

Similar to the distribution of DOC, the UV₂₅₄ absorbance distribution, as shown in Fig. 2b, also remained constant across the sampling period (the samples in March and April were not measured for UV₂₅₄ and THMFP). The fractions contributing to the most UV₂₅₄ absorbance were HoA and HoN, which accounted for more than 35% and 20%, respectively. The percentages of UV₂₅₄, HiM, WHoA and HoB also remained in relatively stable levels over the sampling period.

Compared to the DOC and UV₂₅₄ distributions, the percentage of THMFP of most chemical fractions (except that of HiM) varied markedly with seasonal changes (Fig. 2c). There were consistent findings on the variability of THMFP of chemical fractions [22]. Moreover, it can be seen that the HoA fraction was the primary THM precursor, which contributed more than 25%.

According to the above results, it could be concluded that the DOM samples collected from the East-Lake water in one season could have a good representability for other seasons in terms of the DOC or UV₂₅₄ relative contributions from chemical fractions; However, the THMFP contribution from each chemical fraction should be evaluated specifically in different seasons.

3.1.2. Changes of physical fractions

As shown in Fig. 3, the physical (MW) distribution of the DOM from East-Lake water had greater variability than that of chemical fractions. In terms of DOC content, the fractions with MW of greater than 1 kDa and 10–30 kDa were dominant in the DOM during most of the sampling period (Fig. 3a). However, either the UV₂₅₄ or the THMFP contribution from each physical fraction (except the less than 1 kDa fraction with relatively constant percentage of THMFP of around 30%) varied greatly throughout the sampling period (Fig. 2b and c). Therefore, the primary MW fractions as the source of THM precursors, changed with the season. This indicates that the distribution of physical fractions in the DOM from East-Lake water might be more sensitive to the change of seasons than that of chemical fractions. And the chemical properties could play more critical roles in optimizing water treatment processes for reduction of DOM and THMs precursors, which is similar to the opinion of Kitis et al [23].

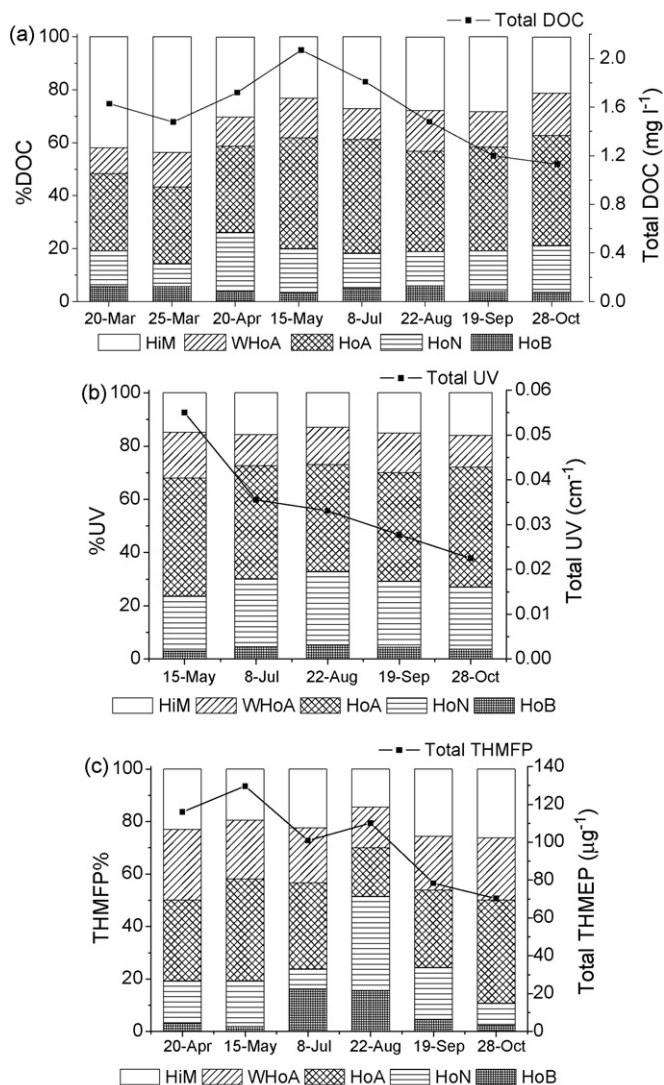


Fig. 2. The DOC (a), UV₂₅₄ (b), THMFP (c) contributions of chemical fractions in the DOM from the East-Lake reservoir.

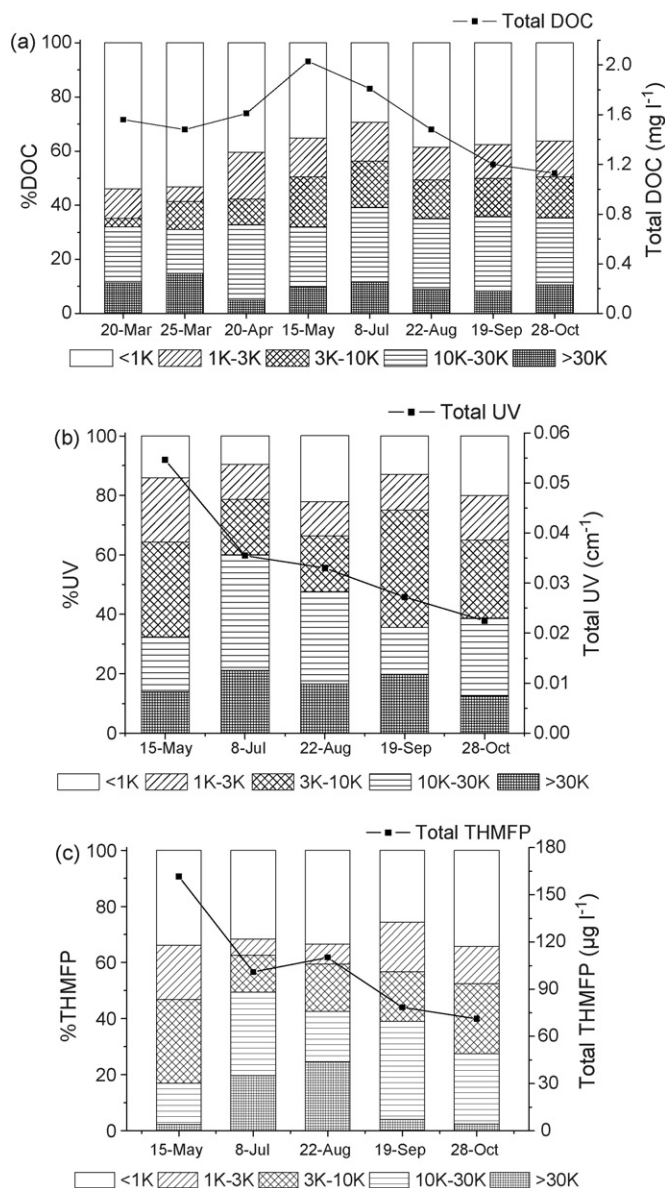


Fig. 3. The DOC (a), UV₂₅₄ (b), THMFP (c) contributions of physical (molecular weight) fractions in the DOM from the East-Lake reservoir.

3.2. Seasonal variations of SUVA₂₅₄ and STHMFP

3.2.1. Variations of SUVA₂₅₄

3.2.1.1. SUVA₂₅₄ of chemical fractions. To avoid the possible influence of strong acidic solution (0.1 mol l⁻¹ H₃PO₄ which was used for back-eluting the HoB fraction), the SUVA₂₅₄ and STHMFP of HoB and HoN were measured as a collective parameter (HoB&N). The SUVA₂₅₄ and STHMFP of HoB&N were calculated as the total UV₂₅₄ absorbance or THMFP divided by the total DOC of HoB and HoN fractions.

As shown in Fig. 4, most of the chemical fractions of the DOM, such as HoB&N, HoA, HiM (except WhoA), exhibited some extent of stability with respect to the SUVA₂₅₄ throughout the sampling period. The average SUVA₂₅₄, which defined as total UV₂₅₄ absorbance divided by total DOC of the DOM, appeared more constant than separated fractions.

The reason that the WhoA fraction varied considerably could be explained by its origin, since this fraction is mainly produced by autochthonous processes, such as phytoplankton, bacteria, and microbial degradation [24].

The HoB&N fraction had the highest SUVA₂₅₄ values, accounting for around 3.5, which was similar to the reported result based on a drinking water (a river) in Thailand [12]. The other fractions with lower UV₂₅₄ absorbabilities were HoA and HiM. The SUVA₂₅₄ values of HoA and HiM were around 2.5 and 1.5, respectively. Furthermore, if HoB&N were considered to be the fraction with the highest hydrophobicity (these fractions were retained on the XAD-8 resin firstly without pH adjustment), it could be concluded that the more hydrophobic the chemical fraction, the higher SUVA₂₅₄ it has (Fig. 4). Croue [15] has also found a similar trend for other natural waters.

3.2.1.2. SUVA₂₅₄ of physical fractions. The UV₂₅₄ absorbability of most physical fractions (except the fraction of less than 1 kDa) was more variable than that of chemical fractions across the sampling period (Fig. 5). This phenomenon together with those mentioned above related to the physical fractions demonstrate that the physical properties (mainly the MW) of DOM should be measured timely when evaluating certain water treatment processes during different seasons, such as coagulation and activated carbon adsorption, in which the molecular weights of DOM play important roles [5]. There existed a basic tendency that the fraction with larger molecular size has relatively higher level of SUVA₂₅₄, such as the SUVA₂₅₄ value of less than 30 kDa fraction significantly higher than that of the greater than 1 kDa fraction (Fig. 5b). The other fractions cannot be distinguished clearly in terms of SUVA₂₅₄ probably because of the relatively lesser differences among their MW. Similar findings have also been revealed by Imai [22] showing that a significant linear relationship was displayed between molecular weight and UV:DOC ratio when all data for fractions and whole DOM were plotted although it was not the same for separated fractions such as HoA.

3.2.2. Changes of STHMFP

3.2.2.1. STHMFP of chemical fractions. The STHMFP of each chemical fraction, except WhoA, appeared more variable than the SUVA₂₅₄ during the sampling period (Fig. 5). Moreover, the STHMFP of the chemical fractions did not correlate positively with the hydrophobicities of these fractions, which is different from the correlation of SUVA₂₅₄ with hydrophobicity. The STHMFP of HoA and HiM were close to each other, accounting for around 50 µg mg-C⁻¹, during most of the period although the SUVA₂₅₄ of HoA was considerably higher than that of HiM. The fraction with the highest yields of THMFP, was WhoA (around 85 µg mg-C⁻¹), which was adsorbed by XAD-4 resin, but its SUVA₂₅₄ was not always the highest during different seasons (Fig. 4d). Consistent results had been reported by Imai et al. [22] that it was the HiA (the main part of the fraction is the same as that of WhoA) not the HoA that control the characteristics of DOM as THM precursors in a eutrophic Lake, and the SUVA₂₅₄ of HiA was also lower than that of HoA. Considering the difference between the well protected East-Lake water and the eutrophic water studied by Imai et al. [22], an interesting

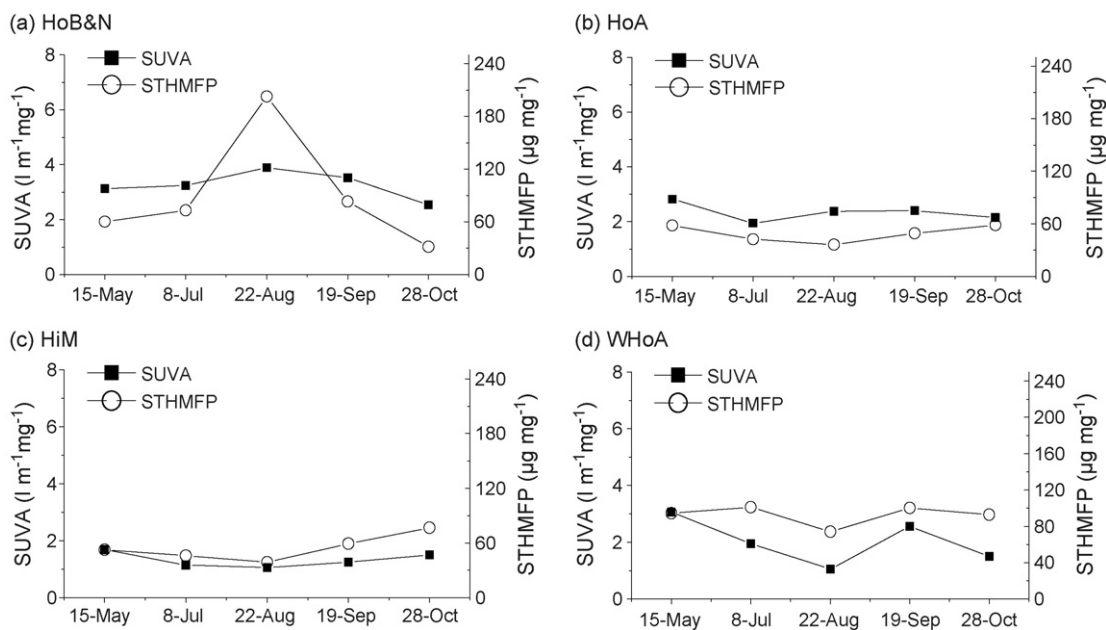


Fig. 4. Variations of the SUVA₂₅₄ and STHMFP of chemical fractions in the DOM from the East-Lake reservoir during different seasons.

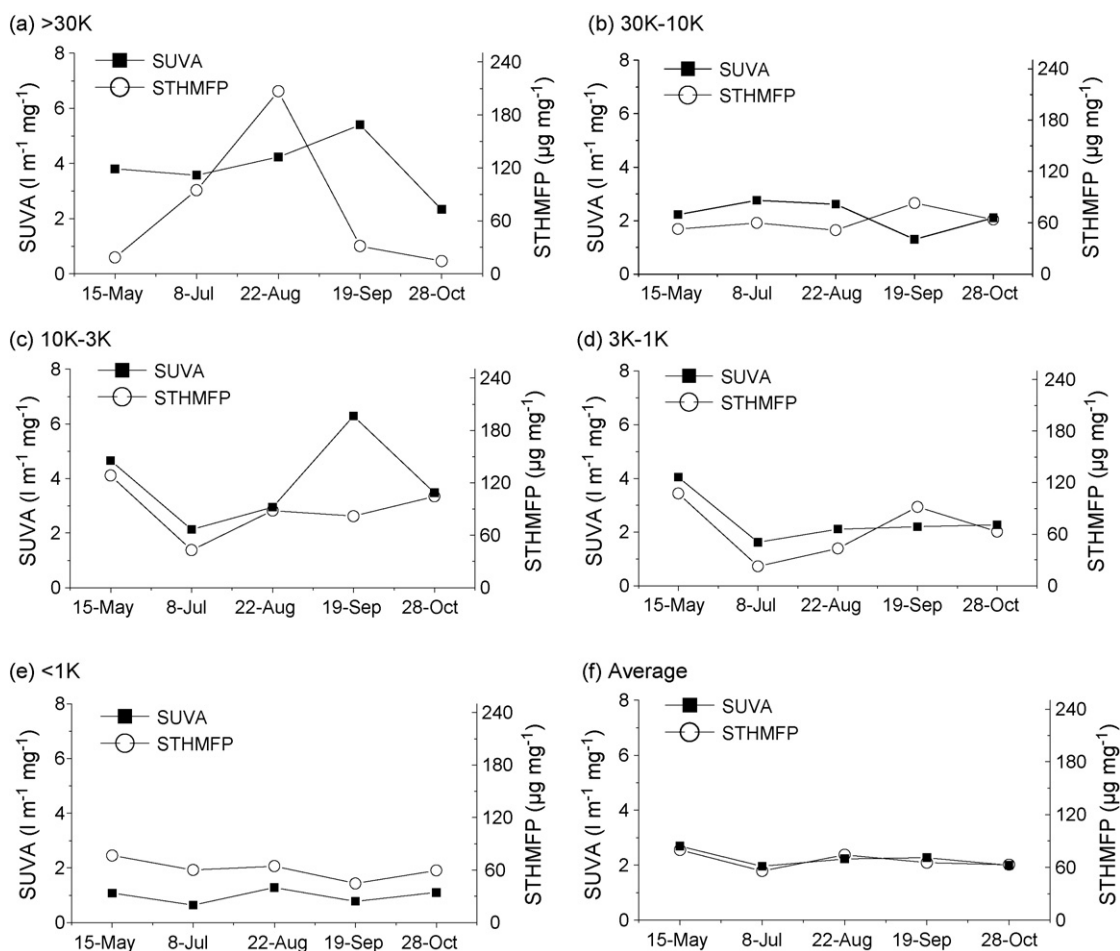


Fig. 5. Variations of the SUVA₂₅₄ and STHMFP of physical fractions in the DOM from the East-Lake reservoir during different seasons.

question may be raised concerning why similar characteristics existed with the HiA and WWhoA fractions from the two different waters. The reason may lie in the similar origins of the HiA and WWhoA, which are mainly derived from the autochthonous processes as mentioned above.

3.2.2.2. STHMFP of physical fractions. Comparing with the characteristics of chemical fractions, the contribution of per milligram carbon of each physical fraction to the THMs formation varied more remarkably than that of chemical fraction (Fig. 5). But the 10–30 kDa and lesser than 1 kDa fractions appeared relatively more stable than others, and the STHMFP of both fractions were around $60 \mu\text{g mg}^{-1}\text{C}^{-1}$ (Fig. 5b and e). Especially, the 3–10 kDa fraction with STHMFP of more than $80 \mu\text{g mg}^{-1}\text{C}^{-1}$ showed higher yield of THMs than other physical fractions in most period (Fig. 5c). It can be deduced that there is no significant correlation between the MW and STHMFP for the physical fractions, which is similar to the results observed by Kitis et al. [23] for Tomhannoc reservoir water that no positive correlation between the MW and DBP formation was observed.

In addition, the THMs yield of 3–10 kDa fraction was similar to that of WWhoA in the chemical fractions. Moreover, the relative contributions from the fractions of 3–10 kDa and WWhoA to the total DOC were all around 15% across most of the sampling period. It indicates that the MW of most WWhoA could probably be in the range of 3–10 kDa.

3.2.3. Relationships between SUVA_{254} and STHMFP

As shown in Fig. 4 and 5, the seasonal changes of STHMFP for most of chemical and physical fractions (except the lesser than 1 kDa fraction (Fig. 5e) as well as the total DOM (Fig. 5f)) were not completely consistent with those of SUVA_{254} during the sampling period. The STHMFP of some fractions, such as HiM, WWhoA and 1–3 kDa fractions, showed slight positive relations with their corresponding SUVA_{254} values during some time spans of the sampling period (Fig. 4c, d and 5d). Generally, there were no strong and unique correlations between SUVA_{254} and THMs yields (STHMFP) for either chemical or physical fractions, which is also shown clearly in Fig. 6. Weishaar et al. [25] also found that there was no significant correlation between SUVA_{254} and STHMFP, and SUVA_{254} was a weak universal indicator of reactivity for the formation of THMs based on the data of 34 samples from major river systems throughout the United States. But a contrary result has also been reported [24] that SUVA_{254} correlated well with STHMFP. Therefore, the correlation between SUVA_{254} and STHMFP is weak for either whole mixture of DOM or its fractions. The correlation might be dependent on the origins of DOM.

SPSS (13.0) software was used for clustering of both chemical and physical fractions and the cluster results based on the parameters of SUVA_{254} and STHMFP can be seen in Fig. 6. The points of either chemical or physical fractions tended to be discrete as a whole. Only one group points of each kind of fractions appeared more convergent than others such as the cluster 1 for chemical fractions and cluster 2 for physical fractions (Fig. 6a and b). The hierarchical cluster method was adopted

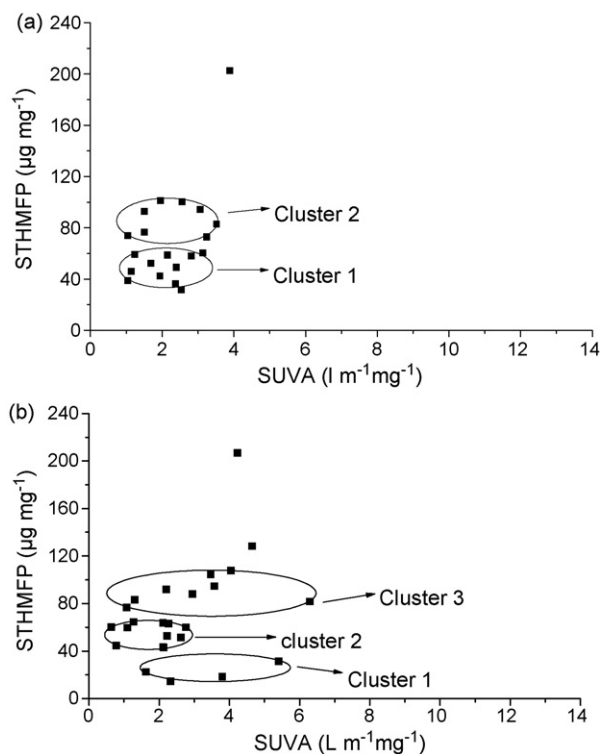


Fig. 6. Relationships between SUVA_{254} and STHMFP for chemical (a) and physical (a) fractions of the DOM from the East-Lake reservoir.

as follows: cases cluster, between-groups linkage and squared euclidean distance.

4. Conclusions

Seasonal variations in the composition and characteristics of the DOM from a reservoir in southern China were investigated within a year. The properties of chemical fractions in the DOM were more stable than those of physical fractions. The relative contribution of each chemical fraction to the total DOC, UV_{254} and THMFP remained relatively constant across most of the sampling period. However, the contributions of physical fractions to UV_{254} and THMFP were much variable. Compared with the DOC, the THMFP and STHMFP contribution of either chemical or physical fractions were more subject to change. In other words, the predominant fractions as the source of THMs precursors and the fractions with the highest yields of THMs could change with season.

The HoA and the HiM were the dominant fractions as DOC content during most of the sampling period and HoA was richer than HiM. With respect to the SUVA_{254} , there existed a trend that the more hydrophobic the chemical fraction, the higher the SUVA_{254} value. A similar correlation between MW and SUVA_{254} for the greater than 30 kDa and lesser than 1 kDa fractions was observed that the fraction with larger molecular size had relatively higher level of SUVA_{254} , but such correlation was weak for the fractions with MW in the range of 1–30 kDa. There were no strong and unique correlations between SUVA_{254} and STHMFP for either chemical or physical fractions, indicating that SUVA_{254} might not be a good indicator for STHMFP.

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Glossary

CF: concentration factors
DBPs: disinfection by-products
DOC: dissolved organic carbon
DOM: dissolved organic matter
FP: formation potential
HiA: hydrophilic acid
HiM: hydrophilic matter
HoA: hydrophobic acid
HoB: hydrophobic base
HoN: hydrophobic neutral
HoB&N: total of HoB and HoN
kDa: kilo-Dalton
MDL: minimum detectable limitations
MW: molecular weight
NMR: nuclear magnetic resonance
RA: resin adsorption
STHMFP: specific THMFP
SUVA₂₅₄: Specific UV₂₅₄ absorbance
THMs: trihalomethanes
THMFP: THMs formation potential
TPHA: transphilic acid
UF: ultrafiltration
UV₂₅₄: ultraviolet absorbance at 254 nm
WHOa: weakly hydrophobic acid
WTP: water treatment plant