Isolation of dissolved organic matter in effluents from sewage treatment plant and evaluation of the influences on its DBPs formation

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A B S T R A C T

Dissolved organic matter (DOM) in reclaimed water from a conventional sewage treatment plant was isolated using resin adsorption chromatography technique into six classes: hydrophobic bases (HoB), hydrophobic acids (HoA), hydrophobic neutrals (HoN), hydrophilic bases (HiB), hydrophilic acids (HiA) and hydrophilic neutrals (HiN). It was found that organic acids dominated in reclaimed water and the ratios of UV\textsubscript{254} (absorbance at 254 nm) to dissolved organic carbon (DOC) (SUVA\textsubscript{254}) ratio exhibited a common relationship: HoA > reclaimed water > HiA. The influences of chemical structures and experimental conditions on the formation of disinfection by-products (DBPs) were investigated, respectively. SUVA\textsubscript{254} was found to exhibit a positive and statistically significant correlation with DBPs formation potential. The specific trihalomethanes (THMs) and haloacetic acids (HAAs) formation potential decreased as the same sequence: acids, neutrals and bases. The formation of DBPs depended more on a combination of aromatic moieties and aliphatic structures such as hydroxy acids. Furthermore, THMs formed more easily at alkaline conditions; however, hydrophobic organics formed HAAs more easily at acidic conditions, whereas hydrophilic organics achieved relatively high HAAs at both acidic and strong alkaline conditions. Moreover, the observed rate constant for HAAs formation was larger than the rate constant for THMs formation. Addition of ammonia nitrogen (NH\textsubscript{4}-N) changed chlorine to chloramines with lower oxidation potential, and correspondingly influenced the formation of DBPs especially at the chlorination breakpoint.

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1. Introduction

Recalcitrant dissolved organic matter (DOM) has been observed to accumulate in lake water in China, even though an extensive effort has been made to cut down organic pollutant loadings generated in their catchment areas [1,2]. Imai et al. [3] suggested that DOM sources resulting from human activities – anthropogenic DOM sources – may play a substantial role in the observed DOM increase in lake water. Furthermore, effluents from sewage treatment plants have been utilized as recycled water for irrigation and recharge water to lake or groundwater. Generally, disinfectants such as chlorine are employed to assure the safety of reclaimed water before its use. Thus, a serious risk arises when lake water is used for drinking water sources, because recalcitrant DOM can be a major precursor of carcinogenic disinfection by-products (DBPs) during chlorination, such as trihalomethanes (THMs) and haloacetic acids (HAAs) [4–6]. Therefore, in order to assure the safety of drinking water, studies on the chlorine reactivity of DOM in effluents from sewage treatment plants are in need.

Previous research has studied the influences of temperature, pH, reaction time, chlorine concentration, as well as the concentration of total DOM on the formation of DBPs [7,8]. However, Shon et al. [9] and Wert et al. [10] demonstrated that DOM in effluents from sewage treatment plants is composed of kinds of organics, including recalcitrant natural organic matter (NOM) from drinking water, synthetic organic chemicals added during anthropogenic use and soluble microbial products. Thus, it is difficult to explore the mechanism of DOM reactions with chlorine during chlorination due to the complex composition of total DOM.

To understand the role of DOM in chlorination, it is often necessary to isolate DOM. Resin adsorption chromatography (RAC) is commonly used for isolating DOM from natural waters and has long been employed with a broad success. Furthermore, Leenheer et al. [11] used resins to fractionate DOM of tertiary-treated municipal wastewater into hydrophobic acids, hydrophobic neutrals, hydrophilic acids, colloidal hydrophobic neutrals and dissolved hydrophilic neutrals. Imai et al. [3] modified the DOM fractionation method developed by Leenheer [12] and isolated DOM in
effluents from sewage and human-wastes treatment plants into six classes: aquatic humic substances, hydrophobic neutrals and bases; hydrophilic acids, neutrals and bases.

Presently, influences of DOM fractions on the formation of DBPs have been little reported. Particularly, effect of chemical structures and performed conditions such as pH and reaction time on the formation of DBPs is poorly investigated. Even though Wang et al. [13] demonstrated that ammonia nitrogen (NH₄-N) at higher or lower concentrations could increase or decrease the genotoxicity of DOM fractions, effect of chlorine to NH₄-N ratios on the formation of DBPs has not been reported. Moreover, the effect of chemical characteristics of DOM on DBPs formation is little investigated, which are thought to influence the chlorine consumption and the formation of DBPs largely [6,11].

In this study, we isolated DOM into different fractions and investigated the influences of pH, reaction time and chlorine to NH₄-N ratios on the formation of DBPs. DOM fractions were also characterized to explore the mechanism of DOM reactions with chlorine.

2. Materials and methods

Water samples from G sewage treatment plant (G-STP) were fractionated according to the method described by Imai et al. [3]. According to this technique, the DOM was divided into six fractions: hydrophobic acids (HoA), hydrophobic bases (HoB), hydrophobic neutrals (HoN), hydrophilic acids (HiA), hydrophilic bases (HiB) and hydrophilic neutrals (HiN).

2.1. Description of G-STP

G-STP serves as the biggest and most important one among 15 sewage treatment plants proposed in Beijing municipal master plan. It is a major environmental protection project with a capacity of 1 million m³/day, which occupies about 40% of the total sewage discharge in Beijing. Much of the secondary treatment effluent after coagulation and sand filtration was used as reclaimed water without chlorination.

2.2. Sample collection and preservation

Water samples for this study were collected at sand filtration site in glass bottles and filtered immediately through a pre-rinsed 0.45 μm cellulose filter. The rinsed water samples were then stored in the dark at 4 °C until analysis.

2.3. Chemicals and materials

Solutions were prepared with ultra-pure water. Ammonia chloride (NH₄Cl) stock solution was 1 g/L. A free chlorine (HOCl) stock solution (about 5 g/L) was prepared from 7% sodium hypochlorite (NaClO) and its concentration was measured prior to use according to the DPD colorimetric method (EPA method 330.5). Sodium phosphate buffer solution (50 mM) was used to maintain solutions at pH 7.

Hexane and methyl tert-butyl ether were used to extract DBPs. We obtained resins from Fisher and J.T. Baker, respectively. Four THM standards, i.e. chloroform (CHCl₃), bromodichloromethane (CHClBr₂), dibromochloromethane (CHBr₂Cl) and bromoform (CHBr₃), and two HAAs standards, i.e. dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), were purchased from Aldrich.

2.4. Selection of resins

1 L filtered water samples were passed through a series of resins including nonionic resin (Amberlite XAD-8, 20–60 mesh), strong cation-exchange resin (Dowex Marathon MSC hydrogen form, 20–50 mesh) and strong anion-exchange resin (Duolite A-7 free base) [11]. The column-captivity factor, k′, for separating hydrophobic acids through the XAD-8 resin column was 20–25. In this study, the cleaning method of XAD-8 has been modified from Thurman and Malcolm [14] and Kim and Yu [15]. After the XAD-8 resin was soxhlet-extracted sequentially for 24 h with acetone, hexane and methanol, the resin was packed in the glass column and rinsed with Milli-Q water till the DOC of the effluent was below 1 mg/L. Lastly, the resin column was rinsed with 0.1 M NaOH, 0.1 M HCl and Milli-Q water to remove remaining impurities. Dowex MSC resin was soxhlet extracted with methanol for 24 h before packed in the glass column, then rinsed with 1 M NaOH and converted into hydrogen form with 2 M HCl, with distilled water following until the conductivity of the effluent was below 10 μΩ⁻¹. The Duolite A-7 resin was soxhlet extracted with acetone for 24 h, packed in the glass column and then rinsed with 1 M HCl until the DOC of the effluent was below 1 mg/L. Then, the column was rinsed with 1 M NaOH and Milli-Q water till the conductivity of the effluent was below 10 μΩ⁻¹.

2.5. Fractionation and collection of DOM samples

The fractionation of DOM was performed following the procedure described by Imai et al. [3]. This fractionation procedure is illustrated in Fig. 1.

11.0.45 μm filtered reclaimed water was firstly pumped through a glass column containing 30 mL XAD-8 Amberlite resin. After step 2 and step 4 (Fig. 1), DOM2 and DOM3 were collected consisting of hydrophobic bases (HoB) and hydrophobic acids (HoA),

![Fig. 1. Fractionation procedure. DOM2: hydrophobic bases (HoB); DOM3: hydrophobic acids (HoA); DOM4: hydrophilic organics; DOM5: hydrophilic acids (HiA) and hydrophilic neutrals (HiN); DOM6: hydrophilic neutrals (HiN).](image-url)
respectively. Then, the two fractions were diluted to 1 L with Milli-Q water. DOM6 containing hydrophilic neutrals (HiN) were first collected after 50 mL effluent from A-7 column was discarded. Subsequently, DOM5 and DOM4 were collected. DOM5 was a mixture of hydrophilic acids (HiA) and HiN. DOM4 referred to hydrophilic organics consisting of DOM5 and DOM6.

After elution or recovery, the pH of DOM fractions was immediately adjusted to the source water value. Dissolved organic carbon (DOC) and ultraviolet absorbance were measured for each fraction.

2.6. Disinfection by-products formation potential (DBPFP)

A 3-day chlorination DBPs test was carried out according to Standard Method 5710B with modifies. Sodium hypochlorite stock solution was above 5 g/L and a final residual chlorine of 3–5 mg/L remained in the sample after 3 days of incubation at 20 °C. All DOM fractions were adjusted to the pH of source water which was 7–8, so in this study the samples were easily buffered with a phosphate solution prior to incubation to remain pH 7 at 20 °C for 3 days. At the end of the incubation period, samples were dechlorinated using sodium sulfite (Na2SO3) as the dechlorinating agent as recommended by EPA method 552.2.

2.7. Analytical methods

THM and HAA analyses were conducted using an Agilent 6890N Gas Chromatograph (USA) that was equipped with two fused silica capillary columns (0.25 mm, 30 m), a linearized electron capture detector (ECD) and a Leap Technologies (Carrboro, NC CTC A200S) autosampler. Four species of THM, i.e. chloroform (CHCl3), bromodichloromethane (CHClBr2) and dibromochloromethane (CHClBr2) and bromoform (CHBr3), were analyzed in accordance with EPA method 551.1. Two species of HAA, i.e. dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), were analyzed in accordance with EPA method 552.3. All extracts were analyzed within 24 h of the completion of the liquid–liquid extraction (LLE) procedure.

Dissolved organic carbon was measured with a TOC analyzer (Multi N/C 3000) in accordance with Standard Method 5310D. UV254 (absorbance of UV at 254 nm) to DOC ratio was reported to represent the aromatic character of organic matters as they imparted the ability to absorb light in the UV range [16].

DOM powder obtained through freeze-drying the fractions was analyzed for the structural and chemical characteristics of DOM. KBr was mixed with the DOM powder about the ratio of 100 to 1 and the Fourier transform infrared (FTIR) spectra of the mixture were obtained by scanning it with IR spectrometer (Thermo Nicolet 5700, USA).

3. Results and discussion

3.1. Distribution and SUVA254 of DOM fractions

DOC was used as an indicator for the organic fractions in the water samples. Details of average organic mass balance and some characteristics of the reclaimed water are illustrated in Fig. 2.

It was found that the average distribution proportions of the hydrophobic and hydrophilic organics from September to November were 51 and 49%, respectively (Fig. 2a). The organic acids, HoA and HiA, dominated in reclaimed water, collectively accounting for more than 52% of their DOM as DOC. Thus, DOM in the effluent from G-SP is primarily acidic. The organic neutrals, especially HiN, constituted a less important fraction than organic acids. The HoB fraction was about 5% of DOM and it was low enough to be ignored. It was observed that the distribution of the weight fraction of organic species in each sample did not appear to be dramatically different. For all samples, the sequence of these six organic fractions can be summarized in the order from largest to smallest as: HoA > HiA > HiN > HoN > HiB, HoB.

Similarly, a common general relationship with respect to SUVA254 was as follows: DOM3 > total DOM > DOM4 (Fig. 2b), i.e. HoA > reclaimed water > HiA. The results indicated that HoA exhibited the highest aromaticity (caused by the presence of unsaturated bonds, i.e. chromophores and aromatic moieties).

3.2. Total THMs and HAAs (TTHM and THAA) formation potential of reclaimed water and its fractions

When reclaimed water DOM1 and its fractions were chlorinated and incubated for 3 days, average THMs and HAAs concentrations were determined (Fig. 3a). In order to consider the reactivity with chlorine on a per carbon basis of different hydrophobic and hydrophilic organics, all the DBPs data were normalized relative to the DOM concentrations according to the mass balance to obtain the specific yields (Fig. 3b). Organic acids, HoA and HiA, were observed to exhibit the highest specific DBPs formation potential. In particular, HiA possessed the highest specific TTHM formation potential and HoA showed the highest specific THAA formation potential. Generally, the specific TTHM and THAA formation potential decreased as the same sequence: acids, neutrals and bases.

SUVA254 of DOM1 and its fractions exhibited a positive and statistically significant correlation with specific TTHM formation
Fig. 3. DBPs formation potential of reclaimed water and its fractions. (a) TTHM and THAA formation potential; (b) specific TTHM and THAA formation potential. DOM fractions are as follows: HoB, hydrophobic bases; HoA, hydrophobic acids; HoN, hydrophobic neutrals; HiB, hydrophilic bases; HiA, hydrophilic acids; HiN, hydrophilic neutrals.

potential ($R^2 = 0.71$), whereas the linear correlation between SUVA$_{254}$ and specific THAA formation potential was less distinctive ($R^2 = 0.54$) (not shown). The different coefficient of DBPs formation potential indicated that the formation mechanism of THMs was different from that of HAAs. On the other hand, the less significant correlation suggested that the formation of DBPs was influenced by more factors in addition to the aromaticity of organics.

Therefore, the FTIR analysis was used to inform about the distribution of functional groups and provide a basis for comparison of compositional differences between fractions that can be suspected to be DBPs precursors. The FTIR spectra of DOM fractions are shown in Fig. 4.

Interpretation of the absorption bands of DOM has been described in the literature [11,15,17]. The chromatogram of each hydrophilic fraction was similar to that of DOM1 showing three peaks: 1630 cm$^{-1}$ exhibiting aromatic skeletal ($\eta_{\text{C-C}}$) or aldehydic and ketonic groups ($\eta_{\text{C=O}}$); the peak at 1384 cm$^{-1}$ suggesting aliphatic structures and 1153 cm$^{-1}$ referring to carbohydrates ($\eta_{\text{C-C}}$) or O-alkyl group ($\eta_{\text{C-O}}$), such as hydroxy acids. In particular, DOM5 showed a relatively high aliphatic peak. DOM2 and DOM3 were similar at 1637 cm$^{-1}$ corresponding to $\nu_{\text{C=O}}$ or $\nu_{\text{C=O}}$, whereas DOM5 also exhibited a relatively low peak at 1384 cm$^{-1}$ suggesting the presence of aliphatic organics.

The FTIR chromatograms of DOM3 and DOM4 exhibited distinctive difference: DOM3 contained more aromatic moieties and aldehydic or ketonic groups whereas the presence of $\nu_{\text{C-O}}$ was not observed, but DOM4 contained $\nu_{\text{C-O}}$ groups and aliphatic organics in addition to aromatic moieties. On the other hand, DOM3 and DOM4 exhibited the highest HAAs formation potential and THMs formation potential, respectively. Thus, it can be concluded that the formation of HAAs depended more on aromatic moieties and aldehydic or ketonic groups, whereas O-alkyl groups ($\eta_{\text{C-O}}$) such as hydroxyl acids contributed to the formation of THMs. It is suggested that the formation of DBPs depended on a combination of aromaticity and aliphatic groups.

3.3. Influences of performed conditions on the formation of DBPs

3.3.1. Effect of pH

DOM1 and its fractions were chlorinated at a chlorine dosage of 10 times DOC at different pH from 2 to 11 and exhibited different trend of the formation of THMs and HAAs (Fig. 5). Although reactions of chlorine may cause pH unstable during chlorination and lead to fluctuations of the formation of DBPs, THMs formation increased with the increasing of pH (Fig. 5a and b). The formation of HAAs varied significantly with pH from 2 to 11 and the maximum yields of DOM fractions generally occurred at pH 2. The exception was DOM1 and DOM2 with the greatest HAAs yields achieved at pH 4. Like DOM1, hydrophilic organics (i.e. DOM4, DOM5 and DOM6) were observed to exhibit increasing tendency beyond pH 10, much different from DOM3 and DOM2.

pH affects dissociation of sodium hypochlorite to form free chlorine as below [18]:

$$\text{NaClO} + \text{HCl} \leftrightarrow \text{NaOH} + \text{Cl}_2 \quad (pK_a = 7.5)$$

$\text{OCl}^-$ anion has much lower oxidative capacity than $\text{HClO}$. Therefore, increase in pH leads to the lowering of oxidation potential. Furthermore, at higher pH, the degree of protonization of some functional groups changes and the chlorination mechanism shifts from substitution to oxidation [7]. The difference of the increasing trend of THMs and HAAs may lie in the complex reactions including the formation of THMs by the hydrolysis of intermediate products, the decomposition of HAAs by oxidation and the gradual decrease of substitution reaction. At higher pH, the intermediate formers of THMs were more easily hydroylized and the hydrolysis played a most important role in leading to the increase of THMs formation. On the other hand, the decomposition at higher pH might be a dominant reaction attributable to the decrease of HAAs.
However, with respect to HAAs, the hydrophobic organics exhibited different trend from hydrophilic fractions with the latter displaying increasing tendency above pH 10. The difference might correspond to the different chemical structures of hydrophobic and hydrophilic organics. As shown in Fig. 4, hydrophilic organics contained more O-alky groups (\(\cdot\)C-O) such as hydroxyl acids. Thus, it can be concluded that \(\cdot\)C-O groups may result in high formation of HAAs even under strong alkaline conditions and such great contribution to HAAs formation even predominated over the large decomposition of HAAs. In particular, HiN, which contained relative high content of \(\cdot\)C-O groups, exhibited increasing trend beyond pH 6. Due to the high DOC percentage of hydrophilic organics in the effluent of sewage treatment plant, the HAAs formation of DOM1 showed an increasing shift at pH 10.

### 3.3.2. Effect of reaction time

Fig. 6 presents the results of DBPs formation after chlorination of DOM fractions at pH 7 under different reaction time, i.e. 24, 48 and 72 h. As shown in Fig. 6a, the yields of THMs increased with increasing time but the increase rate became lower after 2 days. Compared with THMs, the formation of HAAs exhibited different trend. Hydrophobic fractions, DOM2 and DOM3, showed higher yields of HAAs with longer reaction time. However, DOM4, DOM5 and DOM6 achieved the greatest DCAA and TCAA yields after a certain time but remained constant as the reaction time increased.

The above results again confirmed that the formation mechanisms of THMs and HAAs were different. In the formation of HAAs, hydrophobic organics had higher specific HAAs formation potential, but hydrophilic organics exhibited a higher HAAs formation rate. As shown in Fig. 4, hydrophobic organics contained more aromatic skel (\(\cdot\)C=C) or aldehydic and ketonic groups (\(\cdot\)C-O). Thus, in the chlorination process, it was necessary for the oxidant to take longer time to destroy such high aromaticity. However, the
formulation of THMs was a function of time for both hydrophobic and hydrophilic organics.

3.3.3. Effect of chlorine (as mg/L Cl2) to ammonia nitrogen (as mg/L NH4-N) ratios (Cl2/N)

Fig. 7a and b illustrates the DBPs formation of DOM fractions after 3 days of chlorination at different Cl2/N ratios. In all cases, the lowest yields of DBPs were achieved at Cl2/N 2. As Cl2/N increased, the formation of DBPs exhibited increasing tendency, but at higher Cl2/N above 5, the concentrations of DBPs increased gradually. For most fractions, decreases occurred at Cl2/N 9 or 10, but the exception one was DOM4, which showed no decrease of HAAs formation; however, the HAAs increasing rate of DOM4 was also found to become lower at Cl2/N 10.

As shown in Fig. 7c, the chlorination breakpoint occurred at Cl2/N 5. The exception was DOM5 with the lowest chlorine residual at Cl2/N 7. When reclaimed water containing ammonia is disinfected with aqueous chlorine, the ammonia reacts rapidly to form inorganic monochloramine [19]. Before the breakpoint, monochloramine dominated in the equilibrium system of chlorine and chloramines. However, chloramines are much weaker oxidants than HOCl. Furthermore, monochloramine is thought to hydrolyze to form HOCl before reacting with DOM as the following equation [8]:

\[ \text{NH}_2\text{Cl} + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{NH}_3 \]

As a result, the existence of equilibrium led to lower DBPs formation than the cases without ammonia. With the increasing of Cl2/N ratios after the breakpoint, NH4-N may only act as a reducing agent to decrease the concentration of chlorine, and the formation of DBPs increased consistently with the increasing of chlorine residuals (either chlorine or chloramines). At Cl2/N 9 or 10, decreases of DBPs formation occurred. It can be concluded that ammonia nitrogen at this point was completely transformed into other species such as nitrogen gas or nitrate unable to react with DOM [20]. And at this point, chlorine was consumed to the greatest extent, thus leading to the decrease of DBPs formation.

4. Conclusions

Organic acids were the dominant part of DOM in reclaimed water from G-STP, collectively accounting for more than 52%. In the chlorination process, chemical structures of DOM fractions and performed conditions seriously influenced the formation of DBPs. Hydrophobic acids and hydrophilic acids exhibited the highest specific HAAs and THMs formation potential, respectively. Thus, the formation of DBPs depended on a combination of aromatic moieties and aliphatic structures. In particular, the formation of HAAs corresponded largely to aromatic moieties and aldehydic or ketonic groups, whereas THMs formation was attributed to O-alkyl group (\(\text{C}–\text{O}\)) such as hydroxy acids.

THMs formed more easily at alkaline conditions and increased with increasing time. However, hydrophobic organics formed HAAs more easily at acidic conditions and exhibited a positive function of time, but hydrophilic organics achieved high HAAs at both acidic and strong alkaline conditions. This difference demonstrated that the \(\text{C}–\text{O}\) groups in hydrophilic organics were responsible for the great formation of HAAs under strong alkaline conditions.

Addition of NH4-N can decrease the formation of DBPs but chlorine to NH4-N ratios resulted in difference in DBPs formation. Generally, DBPs formed more at higher Cl2/N ratios; however, at a certain low Cl2/N ratio, NH4-N was transformed into substances such as nitrogen gas or nitrate, thus leading to the decrease of DBPs.

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