Characterization of Natural Organic Matter as Precursor for N-nitrosamines: Hydrophobicity, Molecular Weight and Fluorescence

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Abstract

Natural organic matter (NOM) in source water originated from Luan River and Yellow River, North China was isolated and fractionated with XAD resins and ultra-filtration membranes. The raw water samples and fractions were disinfected with sufficient monochloramine to determine their N-nitrosamines formation potentials. Fluorescence Excitation-Emission Matrix (EEM), molecular weight (MW), dissolved organic carbon (DOC), Specific Ultra-Violet Absorbance at 254nm (SUVA\textsubscript{254}), Ammonia, nitrate, nitrite, and dissolved organic nitrogen (DON) were also measured for the raw water and each fraction. The results showed that the hydrophilic fraction accounted for majority of NOM in these two raw water samples. The NOM fraction below 3k Da in the raw water samples from the Luan River and the Yellow River accounted for about 68% and 78% of the total DOC, respectively. The hydrophilic fraction showed much higher N-nitrosamines formation potentials than the corresponding hydrophobic in both samples. Meanwhile, the NOM fraction with MW below 1k Da had higher contribution to N-nitrosamines precursor than that with higher MW. It was observed that the much higher N-nitrosamines formation potential was related with the fractions with much lower DOC/DON ratio and much lower SUVA\textsubscript{254} values. The EEM results were used to monitor changes of NOM composition before and after chloramination. However, it was very hard to establish the quantitative relationship between the change of EEM intensity and N-nitrosamines formation. In addition, The EEM results showed the notable existence of soluble microbial products like materials and aromatic proteins (BOD\textsubscript{5}), which indicated that the river water might have been contaminated by wastewater discharge. The professionals in the water treatment plants should care about the high risk of N-nitrosamines formation brought by wastewater discharge upstream.

Keywords: Natural organic matter, N-nitrosamines, Hydrophobicity, Molecular Weight, Fluorescence Excitation-Emission Matrix

1. Introduction

The disinfection of drinking water by chlorine was the most successful public health measures because of the dramatic elimination of waterborne diseases. Unfortunately, more than unintended 500 disinfection by-products (DBPs) have been detected because of the reaction between the disinfectants and precursors in the natural water (Richardson, 2003). N-nitrosamines especially N-nitrosodimethylamine (NDMA) have been attracted more and more attentions due to their strong cytotoxicity and genotoxicity in recent years (Charrois et al., 2004; Asami et al., 2009). The U.S. Environmental Protection Agency (USEPA) indicated for 6 N-nitrosamines that drinking water concentrations in the low ng/L level were associated with a $10^{-6}$ lifetime cancer risk, and the USEPA has added NDMA,
N-nitrosomethylamine (NMEA), N-nitrosodiethylamine (NDEA), N-nitrosopyrrolidine (NPyR), N-nitrosodi-n-butylamine (NDBA), N-nitrosodi-n-propylamine (NDPA) into the Unregulated Contamination Monitoring Rule 2 (USEPA, 2005). Ontario has established a maximum allowable concentration of 9 ng/L for NDMA, while California has given a regulated level of 10ng/L for NDMA, NDEA, and NDPA (Zhao, 2006).

Previous works have shown that dimethylamine (DMA) contained in the water would lead to a high concentration of NDMA treated by chloramine (Mitch et al., 2002; Chio et al., 2002). Other organic nitrogen-containing precursors such as dimethyldithiocarbamate, diuron, and cationic polyelectrolytes also produced significant concentrations of NDMA by the release of DMA (Weissmahr et al., 2000; Chen et al., 2009; Park et al., 2009). Besides the certain chemicals discharged into the water, some researchers have shown that proteins or other polymeric forms containing nitrogen in the natural organic matter should account for a significant fraction of the precursors of NDMA (Gerecke et al., 2003; Mitch et al., 2004; ). A kinetic model was developed by Chen and Valentine to predict the formation of NDMA from the reaction of unfractionated NOM with monochloramine (Chen et al., 2006). This model could be used to predict the NDMA formation by the amount of NOM oxidized over an extended range of experimental conditions.

It is critical to figure out the key precursors existed in the natural water source for controlling the formation of these hazardous DBPs. Due to its heterogeneity and complex structure, previous works focused on NOM as precursors of the regulated DBPs such as trihalomethanes (THMs) always used XAD resins and ultra-filtration membrane to isolated the NOM into similar groups of compounds based on hydrophobicity and molecular weight (Leenheer, 1981; Zhao et al., 2006; Hua et al., 2007; Zhao et al., 2009). In general, the hydrophobic fraction has been proved to produce more THMs, haloacetic acids (HAAas) and total organic halogen (TOX) than that of the hydrophilic fraction in the natural water (Liang et al., 2003; Croue et al., 2000). However, Chen et al. (2007) suggested that hydrophilic fractions and basic fractions tended to have a larger NDMA formation potential than those of hydrophobic and acid fractions.

Although NOM has been found to be an important precursor for NDMA, there were few reports about the NDMA formation from NOM fractions based on Hydrophobicity and molecular weight. In addition, most of the previous studies mainly focused on NDMA, there was little information about the relationship between NOM and other N-nitrosamines. Therefore, The main objective of this research was to investigate the key components existed in natural water source as precursors of NDMA as well as some other N-nitrosamines. The identification of precursors was conducted by the analysis of hydrophobicity, molecular weight and fluorescence.

2. Materials and Methods

2.1 Water samples collection

Raw waters were collected from the water intake of Lingzhuang water treatment plant (WTP), which supplied water to Tianjin City. Two rivers were used as the water sources for this WTP. The Luan River was used from May to October while the Yellow River was used from November to next April. To investigate the N-nitrosamines formation from NOM in these two water sources, water samples from the Luan River were collected on July 16, 2010.
while water samples from the Yellow River were collected on December 22, 2010. All the samples were first passed through 0.45μm filters (Millipore, MA, USA) to remove any particulate matters.

2.2 Isolation procedures

The isolated technique using XAD-8 and XAD-4 resins (Rohm and Haas, Philadelphia, PA) in tandem developed by Aiken (Aiken et al., 1992) was used to isolate NOM into three fractions. The filtrated water samples were acidified to pH value below 2 and passed through the XAD-8 resin. The hydrophobic fraction (HPO) containing the humic substances (mainly composed of fulvic acids, humic acids, and hydrophobic neutrals) was retained on the resin and eluted with 0.1N NaOH. The effluent from XAD-8 resin contained hydrophilic acids, bases and neutrals and was passed through XAD-4 resin subsequently. Hydrophilic acids called the transphilic fraction (TPI) were then adsorbed onto XAD-4 resin and were also eluted with 0.1N NaOH. The hydrophilic bases and neutrals remained in the water after passing through the XAD-4 resin and were called the hydrophilic fraction (HPI). The pH of all the fractions was adjusted to 8 using sulphuric acid and sodium hydroxide.

Another set of water samples were fractionated with a set of Millipore stirred ultrafiltration cells (Model: 8400) and ultrafiltration membranes (Millipore, MA, USA) with molecular size cut-offs of 3, 1kDa. All the membranes were cleaned with Milli-Q water in advance to make the DOC residual was less than 0.2mg/L.

2.2 N-nitrosamines formation potential test

The disinfection of raw waters and each NOM fraction were conducted in batch reactors (2-L capacity amber bottle) with performed monochloramine freshly prepared by reacting equal volumes of ammonium chloride and sodium hypochlorite solutions in ice water at a weight ration from 4mg/L Cl₂ to 1mg/L N. (Yang et al 2008). This process was similar to the THMs formation potential test (Chu et al., 2002) and was also used in other studies for determination of the NDMA formation potential in water (Mitch et al., 2003; Chen et al., 2007). Briefly, an excessive dosage of monochloramine (20mg/L, Cl₂) was added into the reactor at pH = 8. The reactors were kept at 25°C in the dark, and the reaction was quenched by addition of excess sodium thiosulfate after 7 days.

2.3 Analytical procedures.

Nine N-nitrosamines were analyzed using a modified version of SPE-LC/MS/MS procedure detailed by Zhao et al (Zhao et al., 2006). The multiple reactions monitoring transition mode was selected as the quantitative detection in positive-ion mode for each nitrosamine. Analyst software MassLynx was used for equipment control and data analysis. A C8 BEH column (2.1×100mm, 1.7μm) (Waters, MA, USA) was employed for separation. The mobile phase was composed of solvent A (acetonitrile) and solvent B (0.05% formic acid in purity water). The solvent gradient consisted of 5% to 10% of solvent A for 1 min, increasing solvent A from 10% to 90% over 5 min, and coming back to 5%, and re-equilibration was carried out before the next injection. The total run time was 8 min. The flow rate was 0.3mL/min, and the sample injection volume was 10μL.

Three-dimensional excitation-emission matrix (EEM) fluorescence spectra were measured
using a spectrometry (F-7000 Fluorescence Spectrophotometer, Hitachi, Japan). In this study, the EEM spectra were collected with corresponding scanning emission spectra from 250 nm to 550 nm at 5 nm increments by varying the excitation wavelength from 200 nm to 400 nm at 5 nm sampling intervals. The PMT voltage was maintained at 600 V and the scanning speed was set at 1200 nm/min for this study.

A Shimadzu (Japan) HPLC system consisting of 2 model LC-20AD pumps, a model SPD-M20A detector and a model CTO-10ASvp column oven was used to obtain the molecular size distribution of water samples. Column temperature was 35°C and chromatographic separation was carried out on a PL Aquagel-OH 30 SEC column (300mm × 7.5mm i.d., 8μm, Agilent Technologies, USA). The mobile phase consisted of 70/30 (V/V) 10mmol/L NH₄HCO₃/methanol. The column was calibrated with molecular mass standards of poly styrenesulfonic acid sodium salt standards (PSS, Fluka Analytical, Sigma-Aldrich, Germany) from 210 to 32000 Da.

3. Results and Discussion
3.1 Characteristics of raw water and NOM fractions

The characteristics of water samples from the Luan River and the Yellow River and their NOM fractions were presented in Table 1.

<table>
<thead>
<tr>
<th>Table 1 Characteristics of raw water and NOM fractions prior to chloramination</th>
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<tr>
<td>Date</td>
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The DOC concentrations of HPO, TPI, and HPI fractions from the Luan River water sample were 0.81, 0.82, and 1.20 mg/L, respectively. The hydrophobic/hydrophilic ratio of 30%/70% indicated that low concentrations of humic and fulvic acid existed in this water
sample. NOM with molecular weight below 1k Da and 3k Da accounted for about 37% and 69% of the total DOC, respectively, which suggested that most of NOM in this water sample was mainly low-molecular-weight NOM. The low hydrophobic/hydrophilic value was also observed in raw water from the Yellow River, suggesting that the HPI fraction was the main DOC component in this river. In addition, the NOM fraction with molecular weight below 1k Da accounted for about 46% of the total DOC, showing that there were more low-molecular-weight NOM in the Yellow River than that in the Luan River.

The lower SUVA$_{254}$ value was observed in the raw water sample from the Yellow River than that from the Luan River. The SUVA$_{254}$ value was always attributed to the hydrophobic/hydrophilic ratio in the water. The water with low SUVA$_{254}$ value always contained more hydrophilic and transphilic carbon while the water with high SUVA$_{254}$ value always contained more hydrophobic carbon (Hua and Rechhow, 2007). Panyapinyopol et al. (2005) reported that SUVA$_{254}$ was related closely to aromatic organic substances, e.g., humic acid, in raw water. Both HPI fraction and molecular weight below 1k Da fraction may contain less humic acid since they had lower SUVA$_{254}$ values.

Parameters related to nitrogen including ammonia, nitrate, nitrite, and DON were measured and quantified for the two raw water samples and each fraction. The results indicated that the HPI fraction contained more nitrogen than those of other fractions. Meanwhile, the fraction with molecular weight lower than 1k Da contained more nitrogen than that with larger molecular weight.
Fig. 1 Fluorescence Excitation-Emission Matrix (EEM) of raw water and NOM fractions before chloramination

Fig. 1 showed the EEM spectrums of raw water samples from the Luan River and the Yellow River and their NOM fractions. The $x$-axis was the emission wavelength ranging from 250 to 550 nm, while the $y$-axis was the excitation wavelength ranging from 200 to 400 nm. The contour lines were the distribution of fluorescence intensity of each excitation-emission wavelength pair. The inner contour lines suggested higher fluorescence intensity than the outer ones. Generally, the specific peaks in an EEM presented the occurrence of specific fluorophores produced by some specific natural organic matter.

It was difficult to interpret EEM spectrums due to the interference and overlapping of different fluorophores. So far, various methods including traditional peak picking technique, fluorescence index (FI) technique, principal component analysis (PCA), parallel factor analysis (PARAFAC), fluorescence regional integration (FRI) technique have been developed to analyze EEM spectrums (Coble, 1996; Mcknight et al., 2001; Persson and Wedborg, 2001; Chen et al., 2003; Stedmon et al., 2003; Baghoth et al., 2011). The FRI technique developed by Chen et al (Chen et al., 2003) was employed to quantitatively analyze the EEM spectrums in this study because it was able to quantify the entire spectrum by taking spectral shoulders and other features into consideration (Rosario-Ortiz et al., 2007). Briefly, the EEM spectrums were divided into five regions, which represented specific component of NOM as shown in Table 2.

<table>
<thead>
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<th>Region</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
<th>Description</th>
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<tr>
<td>Region I</td>
<td>200-250</td>
<td>250-330</td>
<td>Aromatic proteins I</td>
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<tr>
<td>Region II</td>
<td>200-250</td>
<td>330-380</td>
<td>Aromatic proteins II (BOD$_5$)</td>
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<td>Region III</td>
<td>200-250</td>
<td>380-550</td>
<td>Fulvic acid-like</td>
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<td>Region IV</td>
<td>250-400</td>
<td>250-380</td>
<td>Soluble microbial products like</td>
</tr>
<tr>
<td>Region V</td>
<td>250-400</td>
<td>380-550</td>
<td>Humic acid-like</td>
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For raw water from the Luan River, a major peak was located around excitation-emission
pair (240 nm, 375 nm) which was related to simple aromatic proteins (BOD$_5$) in the water (Chen et al., 2003). Both NOM below 1k Da and HPI fraction isolated from the water of Luan River showed similar EEM spectrums to their original water indicating that they contained similar NOM components to the original water. EEM spectrums of the water from the Yellow River captured two major peaks. One was located around excitation-emission pair (280 nm, 320 nm) which was related to soluble microbial products like material (Chen et al., 2003). The other peak was located around excitation-emission pair (230 nm, 350 nm) which was related to simple aromatic proteins (BOD$_5$) in the water. Both HPI fraction and NOM with MW below 1k Da isolated from the Yellow River water samples also captured similar major peaks indicating that these two fractions accounted for most of DOC in the original water.

It was reasonable to conclude that there were abundant aromatic proteins (BOD$_5$) or soluble microbial products like material contained in these two original waters from their EEM spectrums. The characteristics of NOM in these two waters were very different from those of NOM contained in four main tributaries of Lake Mead reported by Rosario-Ortiz et al., which presented a higher concentration of humic acid-like (Rosario-Ortiz, 2007). Previous work conducted by Chen et al. has shown that the EEM of extracellular biological organic matter (EBOM) were dominated by fluorescence in Regions II and IV regions associated with soluble microbial products and other aromatic proteins (Chen et al., 2003). The occurrence of large amount of soluble microbial by-products or aromatic proteins (BOD$_5$) in the water samples here indicated that the two rivers may be polluted by wastewater discharge and caused abundant microbial derived organic matters (Holbrook et al., 2005).

The study conducted by Gerecke and Sedlak (2003) has suggested that unacceptable concentrations of NDMA would be produced when the WTP used wastewater effluent impacted rivers. Therefore, the precursor in the source water would be notable since the Luan River and the Yellow River was contaminated by the wastewater discharge. The WTP in this paper might suffer a high risk of formation of N-nitrosamines, especially when using chloramines as residual disinfectant in the distribution systems.

### 3.2 Characterization of N-nitrosamines precursors during chloramination

The N-nitrosamines formation in raw water samples and NOM fractions from the Luan River and the Yellow River were summarized in Fig. 2. All DBP concentrations (ng/L) were normalized per unit DOC concentration (mg/L).

Four specific N-nitrosamines including NDMA, NMOR, NPYR, and NPIP were detected in the Luan River water samples on July 16, 2010. The HPI fraction exhibited higher densities of NDMA precursor sites than the corresponding TPI and HPO fractions. This result was different from the reports on trihalomethanes (THMs) precursor which had been mainly attributed to the hydrophobic NOM in natural water (Hua and Reckhow, 2007). Similar to that of NDMA, the precursor of NPIP in water tended to be more hydrophilic, the HPI fraction produced 6.1ng/mg-C NPIP while the HPO fraction produced 4.7ng/mg-C NPIP.

Although both NDMA and NPIP were originated more from HPI fraction, an obvious difference could be found among the relative yields of these fractions. The yield of NDMA increased by about 40% from HPO to HPI fraction while the corresponding increasing of the yield of NPIP was about 23%, indicating that the NDMA precursor was more hydrophilic.
than NPIP precursor in this water. For NMOR, the HPI fraction produced the much higher concentration than those of HPO and TPI fractions indicating that the precursor of this DBP tended to be much more hydrophilic. HPI and TPI fractions seemed to be equally important precursors for NPYR since no difference of formations of NPRY were found in this two fractions.

The NOM fraction below 1k Da was found to have the highest formation potentials for all four DBPs in the samples collected from the Luan River. The lowest formation of NDMA was observed in molecular weight > 3k Da fraction while the lowest formations of NMOR, NPYR, and NPIP occurred in molecular weight 1-3k Da. Overall, for N-nitrosamines, the lower-molecular-weight fractions seemed to be more important than the higher-molecular-weight fractions in these water samples. The result obtained here was similar to the previous report in which Mantas and Sedlak found that the fraction of DON below 1k Da contained most of the precursors of NDMA (Mantas and Sedlak, 2008).

Compared to the samples from the Luan River, similar results of N-nitrosamines formation in the water from the Yellow River were observed. The HPI fraction and the NOM fraction below 1k Da produce higher concentrations of N-nitrosamines than those in other fractions. However, new specific N-nitrosamine, NMEA was found while NMOR was missing in these water samples, indicating that the certain organic component contained in the water would have important influence on the formation of N-nitrosamines.

So far, there has been no enough information to ensure the role of NOM fractions with different molecular weight on the formation of N-nitrosamines. Although the NOM fraction with low molecular weight was observed to have the high formation potential of NDMA as well as other N-nitrosamines in this study, the conclusion could not be fit for other water source since the NOM reactivity of different molecular fractions varied a lot among water samples from different locations due to their different chemical composition and production mechanism (Hua and Reckhow, 2007).

Another finding in this study was that the water samples from the Yellow River tended to produce more N-nitrosamines than those from the Luan River. Previous study conducted by Chen and Westerhoff (2010) has shown that the formation of DBPs was related to the specific precursor contained in source water. In addition, nitrogenous species (ammonia, nitrite, nitrate, and DON) may be the indicators of N-nitrosamines formation since the chemicals were nitrogen-contained DBPs. A single model

\[ DBPFP = a \times DOC^b \times UVF_{254} \times (Br + 1)^c \times (N^+ + 1)^d \]

\((N^+\) represents \(\text{NH}_3\)-N, \(\text{NO}_3\)-N, \(\text{NO}_2\)-N and DON) was developed by Chen and Westerhoff (2010) to predict the formation of NDMA in wastewater and potable water. The higher concentration of N-nitrosamines formed in the water from the Yellow River may be due to their higher concentrations of nitrogenous species including ammonia, nitrite, nitrate, and DON (Table 1).
Fig. 2 N-nitrosamines formation potential of raw waters and NOM fractions (pH = 8, t = 25°C, [NH₂Cl]₀ = 20mg/L, reaction time = 7 days. Error bars depict one standard error for three injections)

Fig. 3 presented the formations of N-nitrosamines as a function of DOC/DON ratios. Although the mechanism of formation of NDMA from natural organic matter was not clear (Chen et al., 2007), it was logical to conclude the NOM fraction containing some nitrogen-enriched functional groups could play an important role in the formation of these nitrogenous DBPs.

The HPI fraction and the fraction with molecular weight below 1k Da in both Luan River and Yellow River water samples had lower DOC/DON ratios, while these fractions were found to produce higher yields of N-nitrosamines. The finding in this experiment was consistent with previous reports, in which higher nitrogen contents in the hydrophilic and basic fractions were detected (Croué et al., 1999; Westerhoff et al., 2002). In addition, the hypothesis that the DON concentration promoted the production of NDMA has been confirmed previously by Lee et al. (2007). Mantas et al. (2008) also reported that NOM with molecular weight below 1k Da accounted for 67±24% of the total dissolved organic nitrogen (DON) in wastewater treatment plant effluent, which provided the proof that the dissolved NDMA precursors could be low-molecular-weight compounds.
Fig. 3 DBPs yields of raw waters and NOM fractions as a function of DOC/DON with monochloramine treatment (pH=8, t=25℃, [monochloramine]₀=20mg/L[Cl₂], reaction time = 7 days.)
In this study, the apparent average molecular weight distributions of raw water and NOM fractions were determined by high performance size exclusion chromatography as shown in Fig. 4. NOM below 1k Da and NOM 1–3k Da accounted for about 56% and 38% of the total DOC, respectively in the HPI fraction. This result of the molecular weight distributions in the NOM fractions confirmed the conclusion that the NDMA precursors could be low-molecular organic matter.

![Fig. 4 Molecular weight distribution in raw water and each fraction from the Yellow River](image)

**3.3 Relationship between N-nitrosamines formation and SUVA\textsubscript{254}**

SUVA value at 254nm has been widely used as an indicator of NOM reactivity with disinfectants, which was always attributed to the aromatic groups in the NOM (Westerhoff et al., 2004). Previous study conducted by Lee et al. (2007) found that the formations of chloroform correlated well with SUVA\textsubscript{254} values in different raw water sources.

However, this relationship did not exist between the nitrosamines and SUVA\textsubscript{254}. Fig. 5 presented the N-nitrosamines formation potentials and the individual SUVA\textsubscript{254} values of raw water and each NOM fraction. Generally, The HPI fraction and molecular weight below 1kDa fraction from the Luan River and the Yellow River, which had fairly low SUVA\textsubscript{254}, were found to produce high yields of these nitrogenous DBPs, as normalized in per unit DOC concentration (ng/mg-C).

Chen and Valentine (2007) suggested that SUVA\textsubscript{254} value of NOM was not a universal index for the NDMA formation. These observations suggested that the relationship between N-nitrosamines formations and individual SUVA\textsubscript{254} values of different waters may varied from source to source depending on the composition of the dissolved organic matter in the water sources. Although the SUVA\textsubscript{254} value represented the aromaticity of NOM, it was not well related to the specific precursor content of N-nitrosamines which may be more related to other specific functional groups. So the SUVA\textsubscript{254} value might not be very useful to evaluate the N-nitrosamines formation potential of different water sources.
Fig. 5 DBPs yields of raw water and NOM fractions as a function of SUVA \textsubscript{254} values with monochloramine treatment (pH=8, t=25°C, [monochloramine] \textsubscript{0}=20mg/L[Cl\textsubscript{2}], reaction time = 7days)
3.4 Relationship of EEM Characteristics to N-nitrosamines Formation

Fig. 6 showed the fluorescence excitation-emission matrix of raw water samples and NOM fractions from the Luan River and the Yellow River after chloramination.

For the raw water from the Luan River, an obvious change of the EEM after chloramination was that the major peak located around excitation-emission pair (240 nm, 375 nm) shift to the excitation-emission pair (255 nm, 400 nm), compared with the spectrum in Fig. 1. The shift suggested that the simple aromatic proteins (BOD$_5$) were consumed by monochloramine treatment.

Fig. 6 Fluorescence Excitation-Emission Matrix (EEM) of raw water and each NOM fraction after chloramination
Here we calculated the volume ($\Phi_{i,n}$) of each region in the EEMs before and after chloramination according to Chen’s method to represent the cumulative fluorescence response of each NOM region (Chen et al. 2003), as shown in Fig. 7. The cumulative fluorescence intensity in region II decreased significantly, suggesting that the aromatic proteins (BOD$_5$) may provide much more reaction sites with monochloramine than other organic matter in the raw water. Previous study always proposed the humic acid-like matter (Region V) would provide the more reaction sites with monochloramine (Chen and Valentine, 2007). The low concentration of the humic acid-like matter in the raw water from the Luan River weakened its contribution to the reaction sites with monochloramine. The major fluorescence peaks in the fraction with MW below 1kDa and HPI fraction from the Luan River also showed a similar shift when compared to that in the raw water, which confirmed that the these two fractions accounted for most DOC of this raw water.

![Fig. 7 The volume ($\Phi_{i,n}$) change of each region in the EEMs of raw water from Luan River](image)

For water samples from the Yellow River, the two major peaks located around (280 nm, 320 nm) and (230 nm, 350 nm) were instead by (250 nm, 415 nm) both in the raw water and <1k fraction, which suggested that the fulvic acid like matters has become to the main NOM residual in the waters due to the decomposition of the soluble microbial products like material and the simple aromatic proteins (BOD$_5$).

A great advantage of EEM was that it could distinguish different types and sources of natural organic matter in water (Coble et al., 1990). In this study, the EEM were used to monitor changes of NOM composition before and after chloramination. However, it was very hard to establish the quantitative relationship between the change of EEM intensity and N-nitrosamines formation.

### 3.5 Proposal for water treatment plant

The characterization of N-nitrosamines precursors in this study indicated that the hydrophilic and low molecular weight NOM were the major reservoir of precursors for the N-nitrosamines. Unfortunately, these N-nitrosamines precursors could hardly be effectively
removed by the conventional treatment process. Therefore, it is necessary to investigate the removal efficiency of Ozone/GAC or other advanced treatment processes on nitrosamine precursor.

Previous work suggested that the formation of unacceptable concentrations of NDMA would occur when the water source was contaminated by wastewater discharges or industrial pollution (Gerecke and Sedlak, 2003). The results of Fluorescence Excitation-Emission Matrix suggested that the two water sources might have been impacted by the wastewater discharge. The occurrence of N-nitrosamines should be detected in these water treatment plants to investigate the influence of the wastewater effluent discharges. In addition, enhanced treatment techniques should be used to improve the quality of the treated water in this watershed.

Acknowledgments
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