

JES

JOURNAL OF
ENVIRONMENTAL
SCIENCES

ISSN 1001-0742
CN 11-2629/X

January 1, 2013 Volume 25 Number 1
www.jesc.ac.cn



Sponsored by
Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

CONTENTS

Editorial letter

- We are integrating with the world – Journal of Environmental Sciences Journey of twenty five years
 Qingcai Feng, Xiaoshan Tie 1

Aquatic environment

- Characterization of the airborne bacteria community at different distances from the rotating brushes in a wastewater treatment plant by 16S rRNA gene clone libraries
 Yunping Han, Lin Li, Junxin Liu 5
- Growth and nutrient accumulation of *Phragmites australis* in relation to water level variation and nutrient loadings in a shallow lake
 Ying Zhao, Xinghui Xia, Zhifeng Yang 16
- Cost-performance analysis of nutrient removal in a full-scale oxidation ditch process based on kinetic modeling
 Zheng Li, Rong Qi, Bo Wang, Zhe Zou, Guohong Wei, Min Yang 26
- Sulfur-containing amino acid methionine as the precursor of volatile organic sulfur compounds in algae-induced black bloom
 Xin Lu, Chengxin Fan, Wei He, Jiancai Deng, Hongbin Yin 33
- Nitrous oxide reductase gene (*nosZ*) and N₂O reduction along the littoral gradient of a eutrophic freshwater lake
 Chaoxu Wang, Guibing Zhu, Yu Wang, Shanyun Wang, Chengqing Yin 44
- Influence of oxygen flow rate and compost addition on reduction of organic matter in aerated waste layer containing mainly incineration residue
 Hiroshi Asakura, Kei Nakagawa, Kazuto Endo, Masato Yamada, Yusaku Ono, Yoshiro Ono 53
- Removal and transformation of organic matters in domestic wastewater during lab-scale chemically enhanced primary treatment and a trickling filter treatment
 Qingliang Zhao, Huiyuan Zhong, Kun Wang, Liangliang Wei, Jinli Liu, Yu Liu 59
- Occurrence and distribution of hexabromocyclododecane in sediments from seven major river drainage basins in China
 Honghua Li, Hongtao Shang, Pu Wang, Yawei Wang, Haidong Zhang, Qinghua Zhang, Guibin Jiang 69
- Influencing factors and degradation products of antipyrine chlorination in water with free chlorine
 Meiquan Cai, Liqiu Zhang, Fei Qi, Li Feng 77
- Characterization of dissolved organic matter as N-nitrosamine precursors based on hydrophobicity, molecular weight and fluorescence
 Chengkun Wang, Xiaojian Zhang, Jun Wang, Chao Chen 85
- Simultaneous removal of selected oxidized contaminants in groundwater using a continuously stirred hydrogen-based membrane biofilm reactor
 Siqing Xia, Jun Liang, Xiaoyin Xu, Shuang Shen 96
- Effect of dissolved organic matter on nitrate-nitrogen removal by anion exchange resin and kinetics studies
 Haiou Song, Zhijian Yao, Mengqiao Wang, Jinnan Wang, Zhaolian Zhu, Aimin Li 105
- Natural organic matter quantification in the waters of a semiarid freshwater wetland (Tablas de Daimiel, Spain)
 Montserrat Filella, Juan Carlos Rodríguez-Murillo, Francçis Quentel 114

Atmospheric environment

- Carbon dioxide capture using polyethylenimine-loaded mesoporous carbons
 Jitong Wang, Huichao Chen, Huanhuan Zhou, Xiaojun Liu, Wenming Qiao, Donghui Long, Licheng Ling 124
- Simultaneous monitoring of PCB profiles in the urban air of Dalian, China with active and passive samplings
 Qian Xu, Xiuhua Zhu, Bernhard Henkelmann, Karl-Werner Schramm, Jiping Chen, Yuwen Ni, Wei Wang, Gerd Pfister, Jun Mu, Songtao Qin, Yan Li 133

Terrestrial environment

- Profiling the ionome of rice and its use in discriminating geographical origins at the regional scale, China
 Gang Li, Luis Nunes, Yijie Wang, Paul N. Williams, Maozhong Zheng, Qiufang Zhang, Yongguan Zhu 144

Environmental biology

- Effects of solution conditions on the physicochemical properties of stratification components of extracellular polymeric substances in anaerobic digested sludge
 Dongqin Yuan, Yili Wang 155

Environmental health and toxicology

- In vitro* cytotoxicity of CdSe/ZnS quantum dots with different surface coatings to human keratinocytes HaCaT cells
Kavitha Pathakoti, Huey-Min Hwang, Hong Xu, Zoraida P. Aguilar, Andrew Wang 163
- Effect of heavy metals and phenol on bacterial decolourisation and COD reduction of sucrose-aspartic acid Maillard product
Sangeeta Yadav, Ram Chandra 172

Environmental catalysis and materials

- Mesoporous silicas synthesis and application for lignin peroxidase immobilization by covalent binding method
Zunfang Hu, Longqian Xu, Xianghua Wen 181
- Adsorption of naphthalene onto a high-surface-area carbon from waste ion exchange resin
Qianqian Shi, Aimin Li, Zhaolian Zhu, Bing Liu 188
- Adsorption of lead on multi-walled carbon nanotubes with different outer diameters and oxygen contents:
Kinetics, isotherms and thermodynamics
Fei Yu, Yanqing Wu, Jie Ma, Chi Zhang 195

Environmental analytical methods

- Application of comprehensive two-dimensional gas chromatography with mass spectrometric detection for the analysis of
selected drug residues in wastewater and surface water
Petr Lacina, Ludmila Mravcová, Milada Vávrová 204
- Determination of gaseous semi- and low-volatile organic halogen compounds by barrier-discharge atomic emission spectrometry
Yifei Sun, Nobuhisa Watanabe, Wei Wang, Tianle Zhu 213
- Electrochemical treatment of olive mill wastewater: Treatment extent and effluent phenolic compounds monitoring
using some uncommon analytical tools
Chokri Belaid, Moncef Khadraoui, Salma Mseddi, Monem Kallel, Boubaker Elleuch, Jean François Fauvarque 220

Municipal solid waste and green chemistry

- Evaluation of PCDD/Fs and metals emission from a circulating fluidized bed incinerator co-combusting sewage sludge with coal
Gang Zhang, Jing Hai, Jiang Cheng, Zhiqi Cai, Mingzhong Ren, Sukun Zhang, Jieru Zhang 231
- Serial parameter: CN 11-2629/X*1989*m*235*en*P*26*2013-1



Characterization of dissolved organic matter as N-nitrosamine precursors based on hydrophobicity, molecular weight and fluorescence

Chengkun Wang, Xiaojian Zhang, Jun Wang, Chao Chen*

School of Environment, Tsinghua University, Beijing 100084, China

Received 10 April 2012; revised 19 June 2012; accepted 22 June 2012

Abstract

It is very important to identify the dominant precursors for N-nitrosamine formation from bulk organic matter, to enhance the understanding of N-nitrosamine formation pathways in water treatment plants and allow the development of practical treatment technologies. In this study, dissolved organic matter (DOM) from two source waters was fractionated with XAD resins and ultra-filtration membranes. The N-nitrosamine formation potential (FP) (ng of N-nitrosamines formed per mg of dissolved organic carbon (DOC)) from raw water and each fraction were measured and correlated with the fluorescence excitation-emission matrix (EEM), molecular weight (MW) and other assays. The results showed that the hydrophilic fraction had N-nitrosamine FP 1.3 to 3.5 times higher than the hydrophobic fraction from both source waters. The DOM fraction with low MW was the dominant fraction in these two source waters and contributed more precursors for N-nitrosamine formation than the larger MW fraction. The EEM spectra indicated there were notable amounts of soluble microbial products (SMPs) and aromatic proteins in the two studied rivers, which probably originated from wastewater discharge. The SMPs tended to be more closely correlated with N-nitrosodimethylamine formation potential than the other DOM components. Higher N-nitrosamine FP were also related to fractions with lower DOC/DON ratios and lower SUVA₂₅₄ values.

Key words: N-nitrosamine; hydrophobicity; molecular weight; fluorescence excitation-emission matrix; soluble microbial products

DOI: 10.1016/S1001-0742(12)60029-1

Introduction

N-nitrosamines, especially N-nitrosodimethylamine (NDMA), have attracted considerable attention in recent years due to their high cytotoxicity and genotoxicity (Charrois et al., 2004; Zhao et al., 2006; Asami et al., 2009; Wang et al., 2010). The Province of Ontario in Canada has established an interim maximum acceptable concentration in drinking water of 9 ng/L for NDMA, while the State of California in USA has set the notification level for NDMA at 10 ng/L (Zhao et al., 2006). The US EPA (2006) has added six N-nitrosamines: NDMA, N-nitrosomethylethylamine, N-nitrosodiethylamine, N-nitrosopyrrolidine, N-nitrosodi-n-butylamine, and N-nitrosodi-n-propylamine to the Unregulated Contamination Monitoring Rule 2.

Previous studies indicated that dimethylamine (DMA) in water treated with monochloramine might lead to a high NDMA concentration via the unsymmetrical dimethylhydrazine intermediate formation pathway (Choi and Valentine, 2002; Mitch and Sedlak, 2002). Other organic

nitrogen-containing chemicals, such as dimethyldithiocarbamate, diuron, and quaternary amines, can also produce significant concentrations of NDMA due to the release of DMA (Weissmahr and Sedlak, 2000; Chen and Young, 2009; Park et al., 2009; Kemper et al., 2010).

In addition to the chemicals described above, previous works have also indicated that proteins or other polymeric forms containing nitrogen in dissolved organic matter (DOM) might account for a significant fraction of the NDMA precursors (Gerecke and Sedlak, 2003; Mitch and Sedlak, 2004). Chen and Valentine (2007) investigated the formation of NDMA from DOM from the Iowa River, and found that river water contains a dissolved organic carbon (DOC) of 3.4 mg/L with 112 ng/L NDMA. Mitch and Sedlak (2004) suggested that there were many more NDMA precursors contained in wastewater than in natural waters. A higher NDMA formation potential (FP) (ng of NDMA formed per mg of DOC) in wastewater treatment plant effluents than in rivers was also reported by Guo and Krasner (2009).

It is critical to identify the key precursors contained in natural water for controlling the formation of these

* Corresponding author. E-mail: chen_water@tsinghua.edu.cn

hazardous disinfection by-products (DBPs). Due to the heterogeneity and complex structure of DOM, previous works focusing on DOM as precursors to regulated DBPs such as trihalomethanes used XAD resins and ultra-filtration membranes to isolate the DOM into similar groups of compounds based on hydrophobicity and molecular weight (Leenheer, 1981; Hua and Reckhow, 2007). In general, the hydrophobic fraction of DOM produces more THMs, haloacetic acids (HAAs) and total organic halogens (TOX) than the hydrophilic fraction of DOM in natural water (Liang et al., 2003). However, Chen and Valentine (2007) reported the hydrophilic and basic fractions of DOM tended to have a larger NDMA FP than the hydrophobic and acidic fractions. This result indicates that the N-nitrosamine precursors in natural water might have different characteristics than the THM or HAA precursors.

The fluorescence excitation-emission matrix (EEM) has been widely used to characterize different functional groups and sources of DOM (Coble et al., 1990; Baker, 2001). It has also been used as a predictive tool for disinfection by-product formation potential due to its ability to identify the presence of humic and fulvic acids (Marhaba and Kochar, 2000). Various methods have been developed to analyze EEM spectra, including the traditional peak picking technique, the fluorescence index, principal component analysis, parallel factor analysis, and the fluorescence regional integration (FRI) technique (McKnight et al., 2001; Chen et al., 2003; Stedmon et al., 2003; Baghoth et al., 2011; Persson and Wedborg, 2001). All these methods have made EEM a more feasible tool for analyzing DOM in natural water.

Although DOM has been found to be an important precursor for NDMA, there are few reports relating NDMA formation to DOM fractions based on hydrophobicity, molecular weight and fluorescence. To better understand the characteristics of DOM as a N-nitrosamine precursor, the main objective of this study was to investigate the key components present in natural water that may be precursors to NDMA and other N-nitrosamines, based on hydrophobicity, molecular weight, fluorescence and other water quality parameters. The results may provide information for establishing strategies to reduce the formation of N-nitrosamines in water treatment plants.

1 Materials and methods

1.1 Water sample collection

Raw water samples were collected from the water intake at the one water treatment plant, which supplies water to Tianjin City, northern China. Two rivers are the main water sources for the water treatment plant. The Luan River is the water source from May to October while the Yellow River is used from November to April. Raw water samples were collected on July 16, 2010 (Luan River) and December 22, 2010 (Yellow River) to investigate the characteristics of

DOM from these two rivers. Both samples were initially passed through 0.45 μm filters (Millipore, MA, USA) to remove any particulate matter.

1.2 Fractionation procedures

The isolation technique using XAD-8 and XAD-4 resins (Rohm and Haas, USA) developed by Aiken et al. (1992) was used to separate the DOM into three fractions. The filtered water samples were first acidified to pH 2 and passed through the XAD-8 resin. The hydrophobic fraction (HPO), which contained the humic substances (mainly fulvic acids, humic acids, and neutral hydrophobic compounds) was retained on the resin and eluted with 0.1 mol/L NaOH. The effluent from the XAD-8 resin contained hydrophilic acids, bases and neutral compounds and was then passed through the XAD-4 resin. Hydrophilic acids, identified as the transphilic fraction (TPI), were adsorbed onto the XAD-4 resin and were also eluted with 0.1 mol/L NaOH. The hydrophilic bases and neutral compounds remained in the water after passing through the XAD-4 resin and were identified as the hydrophilic fraction (HPI). The pH of all fractions was adjusted to 8 using sulfuric acid and sodium hydroxide.

Another set of water samples were fractionated using a set of stirred Millipore ultra-filtration cells (Model: 8400) and ultra-filtration membranes (Millipore, MA, USA) with molecular size cut-offs at 3 and 1 kDa. All the membranes were rinsed with Milli-Q water to ensure a residual DOC concentration of less than 0.2 mg/L.

1.3 N-Nitrosamine formation potential test

The disinfection of the raw water samples and each DOM fraction were conducted in batch reactors (2-L amber bottles) with freshly prepared monochloramine. The monochloramine was prepared by reacting equal volumes of ammonium chloride and sodium hypochlorite solutions in ice water at a weight ratio of 4 mg/L Cl_2 to 1 mg/L N (Yang et al., 2008). This process was similar to the THM formation potential test (Chu et al., 2002) and has also been used in other studies for the determination of the NDMA formation potential in water (Chen and Valentine, 2007). Briefly, an excess of monochloramine (20 mg/L, Cl_2) was added to the reactor at pH 8. The reactors were maintained at 25°C in the dark, and the reaction was stopped by the addition of excess sodium thiosulfate after 7 days.

1.4 N-Nitrosamine analysis

Nine N-nitrosamines were analyzed using a modified version of the SPE-LC/MS/MS procedure described by Zhao et al. (2006). The multiple reactions monitoring transition mode was selected for the quantitative detection of each nitrosamine in positive-ion mode. MassLynx analysis software was used for the equipment control and data analysis. A C8-BEH column (2.1 mm \times 100 mm, 1.7 μm) (Waters, MA, USA) was used for the separation. The

mobile phase was composed of solvent A (acetonitrile) and solvent B (0.05% formic acid in Milli-Q water), with a solvent gradient comprising 5% to 10% of solvent A for 1 min; increasing the amount of solvent A from 10% to 90% over 5 min; and returning to 5% solvent A to allow for re-equilibration before the next injection. The total run time was 8 min; the flow rate was 0.3 mL/min; and the sample injection volume was 10 μ L.

1.5 Fluorescence excitation-emission matrix

The EEM spectra were measured using a spectrometer (F-7000 Fluorescence Spectrophotometer, Hitachi, Japan). The spectrometer used a xenon excitation source, with the excitation and emission slits set at 5 nm. The EEM spectra were collected from corresponding scanning emission spectra between 250 and 550 nm at 5 nm increments by varying the excitation wavelength from 200 to 400 nm at 5 nm sampling intervals. The EEM spectrum of the Milli-Q water was determined and subtracted from EEM spectra for each sample to remove most of the Raman scattering peaks. The photomultiplier tube voltage was maintained at 600 V and the scanning speed was set at 1200 nm/min for this study.

The EEM data were quantified using the fluorescence regional integration (FRI) technique (Chen et al., 2003). The EEM spectra were divided into five regions, which represent specific components of DOM (Table 1). The volume (Φ_i) was used to represent the cumulative fluorescence response of DOM with similar properties in each region was calculated as Eq. (1):

$$\Phi_i = \sum_{\text{ex}} \sum_{\text{em}} I(\lambda_{\text{ex}}\lambda_{\text{em}})\Delta\lambda_{\text{ex}}\Delta\lambda_{\text{em}} \quad (1)$$

where, $\Delta\lambda_{\text{ex}}$ is the excitation wavelength interval, $\Delta\lambda_{\text{em}}$ is the emission wavelength interval, and $I(\Delta\lambda_{\text{ex}}\Delta\lambda_{\text{em}})$ is the fluorescence intensity of each excitation-emission wavelength pair.

For secondary or tertiary responses at longer wavelengths, $\Phi_{i,n}$ was calculated as follows:

$$\Phi_{i,n} = \text{MF}_i\Phi_i \quad (2)$$

where, MF_i is the multiplication factor used to account for the secondary or tertiary responses at longer wavelengths.

Table 1 Excitation and emission wavelength boundaries and chemical descriptions used in the fluorescence regional integration technique (Chen et al., 2003)

Region	Excitation (nm)	Emission (nm)	Description
Region I	200–250	250–330	Aromatic proteins I
Region II	200–250	330–380	Aromatic proteins II
Region III	200–250	380–550	Fulvic-like acids
Region IV	250–400	250–380	Soluble microbial-like products
Region V	250–400	380–550	Humic-like acids

1.6 Apparent average molecular weight distributions

High performance size exclusion chromatography was used to determine the apparent average molecular weight distributions of DOM in the water samples. A Shimadzu (Japan) HPLC system consisting of two LC-20AD pumps, a SPD-M20A detector and a CTO-10ASvp column oven was used. The column temperature was 35°C and the chromatographic separation was carried out on a PL Aquagel-OH 30 SEC column (300 mm \times 7.5 mm i.d., 8 μ m, Agilent Technologies, USA). The mobile phase consisted of a 70/30 (V/V) mixture of 10 mmol/L NH_4HCO_3 /methanol. The mobile phase was prepared fresh each day, filtered through a 0.45 μ m micropore filter, degassed using an ultrasonic bath, and delivered at a flow rate of 1.0 mL/min. The column effluent was monitored at 254 nm. A 20 μ L aliquot of sample solution was injected onto the analytical column with an HPLC injector. The column was calibrated with molecular mass standards comprising polystyrene sulfonic acid sodium salt standards (PSS, Fluka Analytical, Sigma-Aldrich, Germany) from 210 to 32000 Da.

1.7 Analysis

The DOC content of the water samples was measured with a Shimadzu 5000A TOC analyzer. Particulates in the water were removed with a 0.45 μ m membrane filter prior to analysis.

Ammonium was analyzed using the 4500-NH₃ F. Phenate Method; nitrate was measured using the 4500-NO₃⁻ B. Ultraviolet Spectrophotometric Screening Method; and nitrite was measured using the 4500-NO₂⁻ B. Colorimetric Method (APHA, AWWA and WEF, 1995). The total dissolved nitrogen (TDN) was measured after all the organic material was converted to nitrate by potassium persulfate under alkaline conditions. The dissolved organic nitrogen (DON) content was determined by Eq. (3) (Westerhoff and Mash, 2002):

$$\text{DON} = \text{TDN} - [\text{NO}_2^-] - [\text{NO}_3^-] - [\text{NH}_4^+] \quad (3)$$

The SUVA_{254} (L/(mg·m)) is obtained from the Eq. (4)

$$\text{SUVA}_{254} = (\text{UV}_{254}/\text{DOC}) \times 100 \quad (4)$$

The UV_{254} was measured using a set of UV-Vis spectra (Model: T6, Puxi, Beijing).

2 Results and discussion

2.1 Characteristics of raw water and DOM fractions

2.1.1 Hydrophobicity and molecular weight distribution

The typical water quality parameters of raw water and each fraction from the Luan River and Yellow River are shown in Table 2. In the Luan River water, a hydrophobic/hydrophilic ratio of 30% to 70% was observed, which

Table 2 Typical water quality parameters in raw water and each fraction originating from the Luan River and Yellow River

Parameter	Luan River							Yellow River						
	Raw water	HPO	TPI	HPI	< 1 kDa	1–3 kDa	> 3 kDa	Raw water	HPO	TPI	HPI	< 1 kDa	1–3 kDa	> 3 kDa
DOC (mg/L)	3.20	0.81	0.82	1.20	1.16	1.04	1.00	2.66	0.73	0.56	1.02	1.23	0.86	0.57
UV ₂₅₄ (cm ⁻¹)	0.09	0.03	0.02	0.02	0.02			0.069	0.028	0.010	0.014	0.026		
SUVA ₂₅₄ (L/(mg·m))	2.81	3.70	2.44	1.67	1.72			2.59	3.84	1.79	1.37	2.11		
Ammonia (mg/L)	0.10	0.02	0.02	0.04	0.06			0.10	0.032	0.020	0.065	0.080		
NO ₃ ⁻ -N (mg/L)	2.25	0.86	0.45	1.67	1.98			4.64	1.40	0.90	3.20	3.82		
NO ₂ ⁻ -N (mg/L)	0.004	0	0	0	0.002			0.038	0.007	0.006	0.010	0.029		
DON (mg/L)	0.27	0.05	0.09	0.18	0.17			0.32	0.04	0.09	0.13	0.20		

HPO, TPI, HPI represent hydrophobic, transphilic, and hydrophilic fractions, respectively.

indicated that there might be low concentrations of humic and fulvic acid in this river. The DOM with molecular weights below 1 and 3 kDa accounted for about 37% and 69% of the total DOC, respectively. In the Yellow River water, a low hydrophobic/hydrophilic ratio was also observed. The DOM fractions with molecular weights below 1 and 3 kDa accounted for about 46% and 78% of the total DOC, respectively. In general, there seemed to be larger amounts of hydrophilic and low molecular weight DOM in both rivers. The composition of DOM in the source waters could be affected by water sources, physicochemical processes, and climatic conditions (Amy et al., 1990; Sachse et al., 2005). In comparison to natural water, wastewater effluent has a low hydrophobic concentration (Kimura et al., 2006). This suggests that source waters with a large wastewater contribution may have a low hydrophobic/hydrophilic ratio.

2.1.2 Typical water quality parameters

As shown in **Table 2**, lower SUVA₂₅₄ values were observed in the Yellow River water. It has been reported that water with lower SUVA₂₅₄ values typically contains more hydrophilic or transphilic carbon, while water with higher SUVA₂₅₄ values contains more hydrophobic carbon (Hua and Reckhow, 2007). Panyapinyopol et al. (2005) reported that SUVA₂₅₄ was related closely to the aromatic organic substances in raw water, e.g., humic acids. Both the HPI fraction and the molecular weight below 1 kDa fraction may contain less hydrophobic carbon or aromatic organic substances, as they had lower SUVA₂₅₄ values.

The water quality parameters related to nitrogen, including ammonia, nitrate, nitrite, and DON were measured in the raw water and each fraction. The results indicated that the HPI fraction contained more nitrogen than the other fractions, while, the fraction with molecular weight lower than 1 kDa contained more nitrogen than the larger molecular weight fraction.

2.1.3 Excitation emission matrix

Figure 1 shows the EEM spectra of raw water and each fraction originating from the Luan River. The X-axis is the emission wavelength, ranging from 250 to 550 nm, while the Y-axis is the excitation wavelength ranging from 200 to 400 nm. The contour lines are the distribution of fluorescence intensity of each excitation-emission wavelength

pair. The inner contour lines suggest higher fluorescence intensity than the outer ones. The specific peaks in an EEM spectrum relate to the occurrence of specific fluorophores produced by specific types of DOM.

The FRI technique developed by Chen et al. (2003) was used to analyze the EEM spectra. The volumes ($\Phi_{i,n}$), which represent the cumulative fluorescence response of each region in the EEM spectra, were calculated based on the FRI technique (**Fig. 2a**). In the raw water from the Luan River, it can be determined that the fluorescence intensities were in the order of: region II > region I > region IV > region III > region V, indicating there were notable amounts of aromatic proteins and soluble microbial products in this water. The weakest fluorescence intensity in region V indicates that there was little humic acid-like material in the water. The fractions below 3 kDa and below 1 kDa showed similar distributions of fluorescence intensities indicating they had similar DOM compositions. The HPI fraction seemed to have relatively higher soluble microbial products content, while the HPO fraction seemed to have a relatively higher fulvic acid-like content.

Figure 3 shows the EEM spectra for raw water and each fraction originating from the Yellow River. The raw water spectrum showed two major peaks, one located around excitation-emission pair (280, 320 nm), which was related to soluble microbial products (Chen et al., 2003), and the other located around excitation-emission pair (230 nm, 350 nm) which was related to aromatic proteins in the water. The volumes ($\Phi_{i,n}$) in each region of the EEM spectra were also calculated, as shown in **Fig. 2b**. In the raw water of the Yellow River, the fluorescence intensities were in the order of: region II > region IV > region I > region III > region V, which indicated that there were large amounts of soluble microbial products and aromatic proteins, but little humic acid-like material in this raw water. The HPI fraction, the fraction below 1 kDa, and the fraction below 3 kDa isolated from the raw water had similar orders in their fluorescence intensities to the raw water. The HPO fraction seemed to have a relatively higher content of fulvic acid-like material than the HPI and TPI fractions.

The FRI results from the EEM spectra indicated that abundant aromatic proteins and soluble microbial products were present in both the Luan River and the Yellow River.

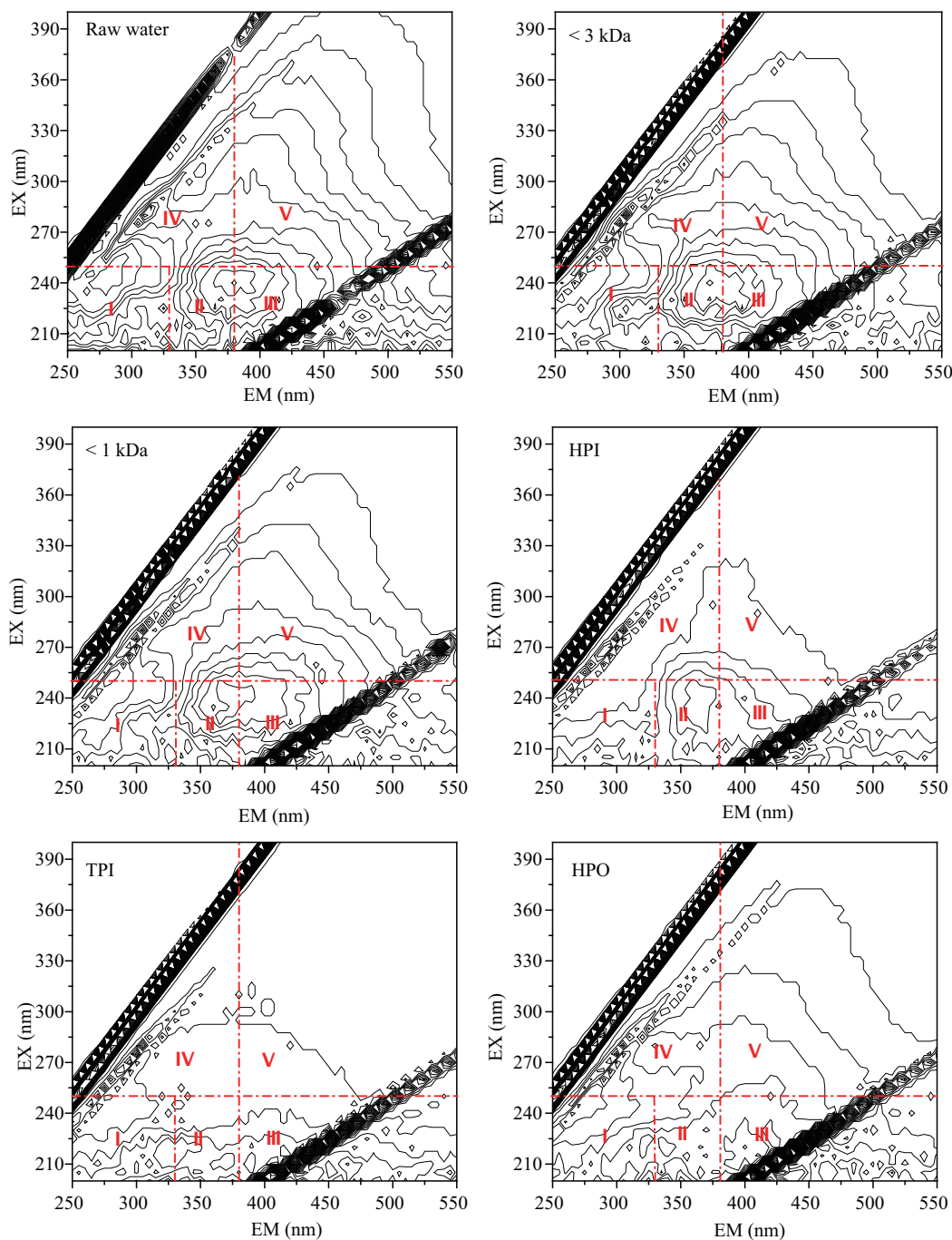


Fig. 1 EEM spectra of raw water and different fractions originating from the Luan River before chloramination. DOC concentrations of the raw water, < 3 kDa, < 1 kDa, HPI, TPI, and HPO fractions were 3.21, 2.20, 1.16, 1.20, 0.82, and 0.80 mg/L, respectively at pH = 8.

The characteristics of DOM in these two rivers were very different from the DOM contained in four main tributaries to Lake Mead reported by Rosario-Ortiz et al. (2007), where higher concentrations of humic acid-like material were present. Previous work conducted by Chen et al. (2003) has shown that the EEM spectra of extracellular biological organic matter (EBOM) dominates the fluorescence in regions II and IV, which are associated with soluble microbial products and other aromatic proteins. The occurrence of large amounts of soluble microbial

by-products and aromatic proteins in the DOM of the water samples here indicated that the two rivers might be polluted by wastewater discharge, leading to abundant microbial-derived organic matter (Holbrook et al., 2005). Gerecke and Sedlak (2003) suggested that unacceptable concentrations of NDMA could be produced when a water treatment plant used source water that was impacted by wastewater discharge. Therefore, the N-nitrosamine precursors contained in these two rivers should be evaluated to control the formation of N-nitrosamines in the studied

water treatment plant.

2.2 Characterization of N-nitrosamine precursors during chloramination

The N-nitrosamines FP from raw water and each fraction from the Luan River and the Yellow River are shown in Fig. 4. All N-nitrosamine FP were normalized per mg of DOC (ng of N-nitrosamines formed per mg of DOC). Four individual N-nitrosamines, NDMA, NMOR, NPYR, and N-nitrosopiperidine (NPIP), were detected in the samples from the Luan River. The presence of NMOR in the raw water sample prior to monochloramine treatment might result from wastewater discharges.

The HPI fraction had higher densities of NDMA precursor sites than the TPI and HPO fractions. This result is different from reports on trihalomethane precursors, which have been mainly associated with hydrophobic DOM in natural water (Hua and Reckhow, 2007). As for NDMA, the precursors of NPIP in the water also tended to be hydrophilic, with the HPI fraction producing 6.1 ng NPIP/mg-C while the HPO fraction produced 4.7 ng NPIP/mg-C. Although more NDMA and NPIP originated from the HPI fraction, a clear difference could be found among the relative FP of these fractions. The FP of NDMA increased by about 69% from the HPO to HPI fractions while the increased FP of NPIP was only about 30%, indicating that the NDMA precursors are more hydrophilic than the NPIP precursors in these water sources.

For NMOR, the HPI fraction produced a much higher concentration than the HPO and TPI fractions, indicating that the precursors for this DBP tend to be much more hydrophilic. The HPI and TPI fractions were equally important fractions for NPYR as there were no differences in the NPYR FP between these two fractions.

The DOM fraction below 1 kDa had the highest FP for all four DBPs in the samples collected from the Luan River. The lowest FP of NDMA was observed in the molecular weight > 3 kDa fraction while the lowest FP of NMOR, NPYR, and NPIP occurred in the 1–3 kDa

molecular weight fraction. Overall, the lower molecular weight fractions seemed to be more important than the higher molecular weight fractions for the formation of N-nitrosamines in the Luan River. This result was similar to a previous report in which Pehlivanoglu-Mantas and Sedlak (2008) found that the below 1 kDa fraction of DON contained the most NDMA precursors.

Similar results were also observed for N-nitrosamine formation in the Yellow River, with the HPI fraction and the below 1 kDa DOM fraction producing higher N-nitrosamine FP than the other fractions. However, the additional presence of N-nitrosomethylethylamine indicated that typical organic components or precursors for this DBP might also be present in the Yellow River. Zhao et al. (2008) investigated the N-nitrosamine precursors contained in seven source waters, and found that DOM and/or anthropogenic contaminants might contain different subunits, which would lead to the formation of various N-nitrosamines in the different source waters.

To date, there has not been enough information to define the role of DOM fractions with different molecular weights in the formation of N-nitrosamines. Although the low molecular weight DOM fraction had the highest NDMA and other N-nitrosamine FP in this study, this conclusion may not fit other water sources as the DOM reactivity in different molecular fractions can vary greatly between water samples from different locations, due to their different chemical composition and production mechanisms (Hua and Reckhow, 2007).

Another finding from this study was that water samples from the Yellow River tended to have higher normalized N-nitrosamine FP than water samples from the Luan River. A previous study conducted by Chen and Westerhoff (2010) suggested that the formation of DBPs was related to specific precursors contained in the source water. Nitrogenous species (ammonia, nitrite, nitrate, and DON) should be indicators of N-nitrosamine formation as N-nitrosamines are nitrogenous DBPs. The high concentrations of N-nitrosamines formed in water from the

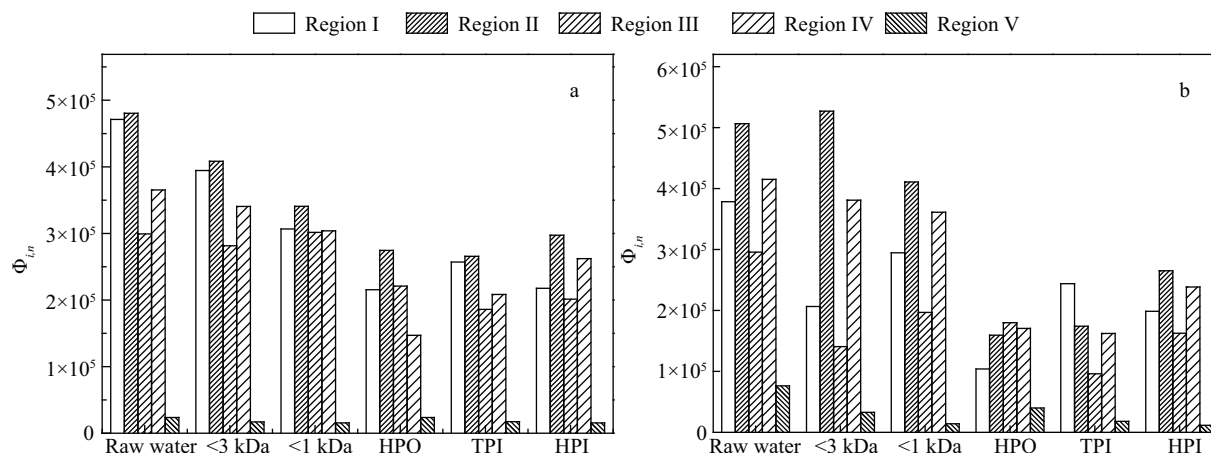


Fig. 2 FRI results for raw water and each fraction from the Luan River (a) and Yellow River (b). $\Phi_{i,n}$ is the cumulative fluorescence response of DOM in each region.

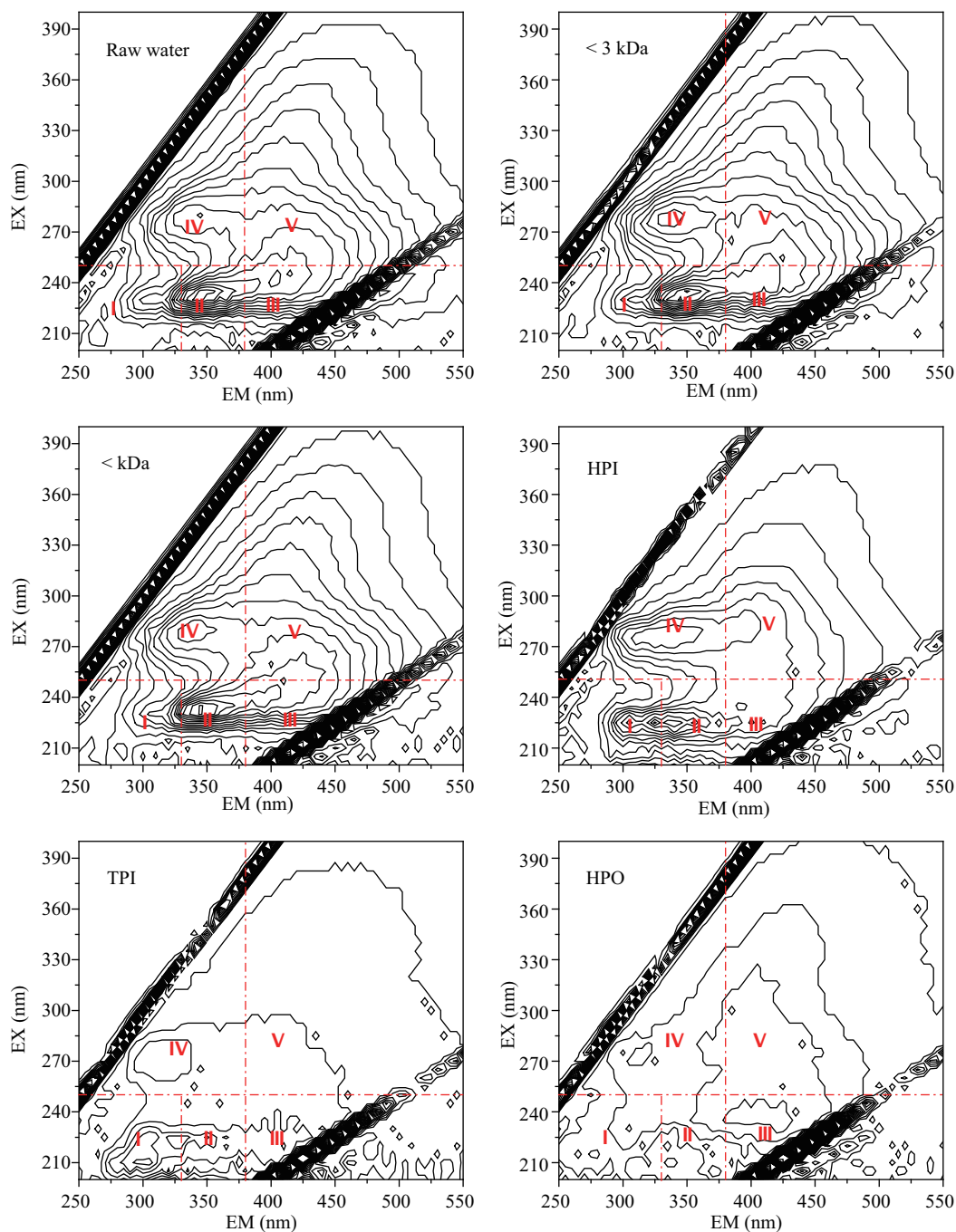


Fig. 3 EEM spectra of raw water and each fraction originating from the Yellow River before chloramination. DOC concentrations in the raw water, < 3 kDa, < 1 kDa, HPI, TPI, and HPO fractions are 2.66, 2.09, 1.23, 1.02, 0.56, and 0.73 mg/L, respectively at pH = 8.

Yellow River might be due to the higher concentrations of nitrogenous species including ammonia, nitrite, nitrate, and DON as shown in **Table 2**.

We found that NDMA had a higher FP than the other N-nitrosamines in both rivers. This result was similar to previous reports of N-nitrosamine occurrence in real water supplies, in which NDMA was always found to have a much higher concentration than the other N-nitrosamines (Charrois et al., 2004, 2007; Planas et al., 2008). The frequent detection and the higher concentrations of NDMA

suggest that NDMA may be a suitable surrogate for N-nitrosamine exposure assessment (Zhao et al., 2008).

In this study, the apparent average molecular weight distributions in raw water and the DOM fractions from the Yellow River were determined by high performance size exclusion chromatography as shown in **Fig. 5**. The DOM below 1 kDa and the DOM at 1–3 kDa accounted for about 56% and 38%, respectively, of the total DOC in the HPI fraction. This result confirms previous suggestions that the NDMA precursors may be low molecular weight dissolved

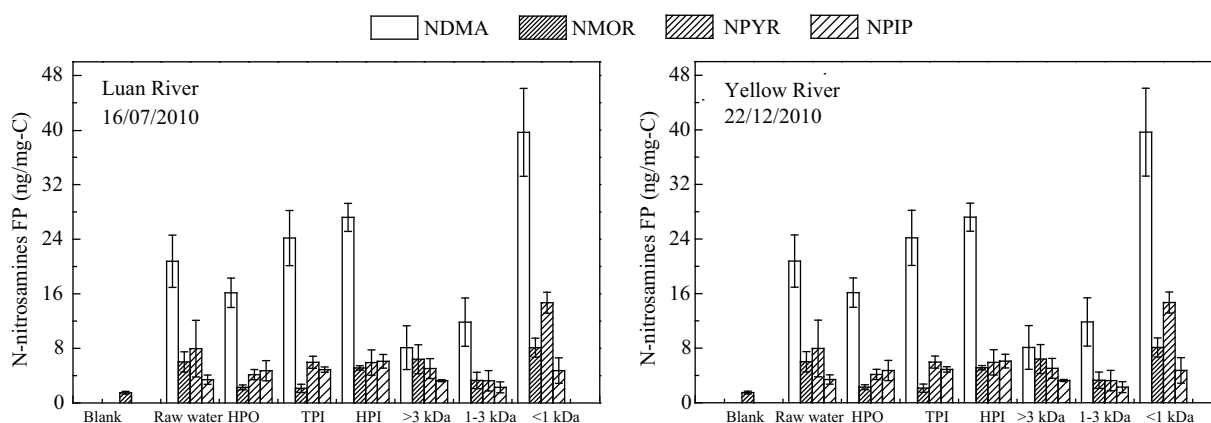


Fig. 4 N-nitrosamines formation potential (FP) from raw waters and each fraction during chloramination in the Luan River and the Yellow River. The blank was raw water without monochloramine. Reaction conditions were pH 8, 25°C, initial NH_2Cl concentration 20 mg/L Cl_2 , reaction time 7 days. Error bars indicate one standard deviation for three injections.

organic matter.

2.3 Correlation between dissolved organic matter properties and N-nitrosamine formation

2.3.1 Relationship between N-nitrosamine formation potential and DOC/DON

Figure 6 shows the N-nitrosamine FP as a function of the DOC/DON ratio. The HPI fraction and the fraction below 1 kDa from both river water samples, which produced higher FP of N-nitrosamines, were found to have lower DOC/DON ratios. This finding is consistent with previous reports, in which higher nitrogen contents were detected in the hydrophilic and basic fractions (Croue et al., 1999). The hypothesis that higher DON concentrations promoted the production of NDMA has also been confirmed previously by Lee et al. (2007). Mantas et al. (2008) also reported that DOM with molecular weights below 1k Da accounted for 67% \pm 24% of the total DON in wastewater treatment plant effluent, providing proof that the dissolved

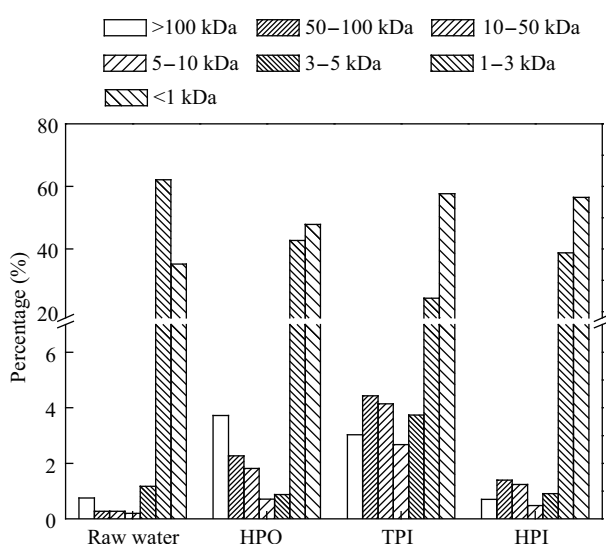


Fig. 5 Molecular weight distribution in raw water and each fraction from the Yellow River.

N-nitrosamine precursors are likely to be low molecular weight DOM.

2.3.2 Relationship between N-nitrosamine formation potential and SUVA_{254}

Figure 7 shows the N-nitrosamine FP and the individual SUVA_{254} values for raw water and each DOM fraction. Generally, the HPI fraction and the molecular weight below 1k Da fraction from the Luan River and the Yellow River, which had fairly low SUVA_{254} values, were found to produce high FP of these nitrogenous DBPs.

The SUVA value at 254 nm is widely used as an indicator of DOM reactivity with disinfectants, which is always attributed to the aromatic groups in the DOM (Westerhoff et al., 2004). A previous study conducted by Lee et al. (2007) found that the formation of chloroform was well correlated with SUVA_{254} values from different raw water sources. However, this relationship was not present between the N-nitrosamine FP and SUVA_{254} . This result indicated that the SUVA_{254} value of DOM may be not a universal index for NDMA FP. Although the SUVA_{254} value represents the aromaticity of the DOM, it is not closely related to the specific N-nitrosamine precursor content, which may be more closely related to other specific functional groups. Consequently, the SUVA_{254} value may not be particularly useful for evaluating the N-nitrosamine FP of different water sources.

2.3.3 Correlation between dissolved organic matter components and N-nitrosamine formation potential

Figure 8 shows the correlations between NDMA FP and the fluorescence intensities of specific DOM components in raw water and each DOM fraction from the Luan River and the Yellow River. We used NDMA because it had much higher FP than the other N-nitrosamines and it may serve as a surrogate for N-nitrosamine exposure assessments (Zhao et al., 2008). Region V, which represents humic acid-like materials, was not examined due to its very

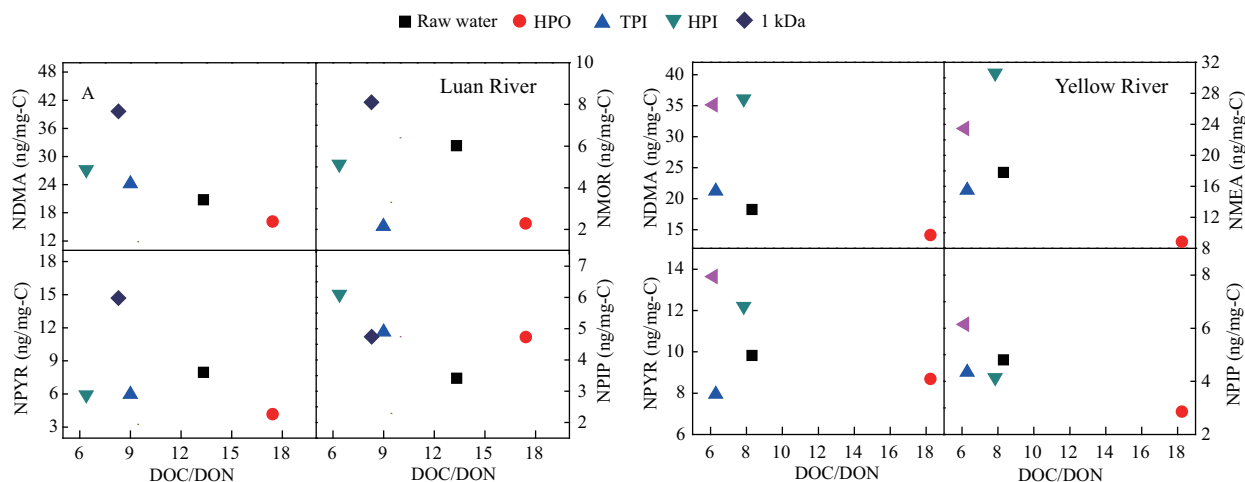


Fig. 6 N-nitrosamines FP from raw water and DOM fractions as a function of the DOC/DON ratio after monochloramine treatment in the Luan River and Yellow River. Reaction conditions were pH 8, 25 °C, initial NH_2Cl concentration 20 mg/L Cl_2 , reaction time 7 days.

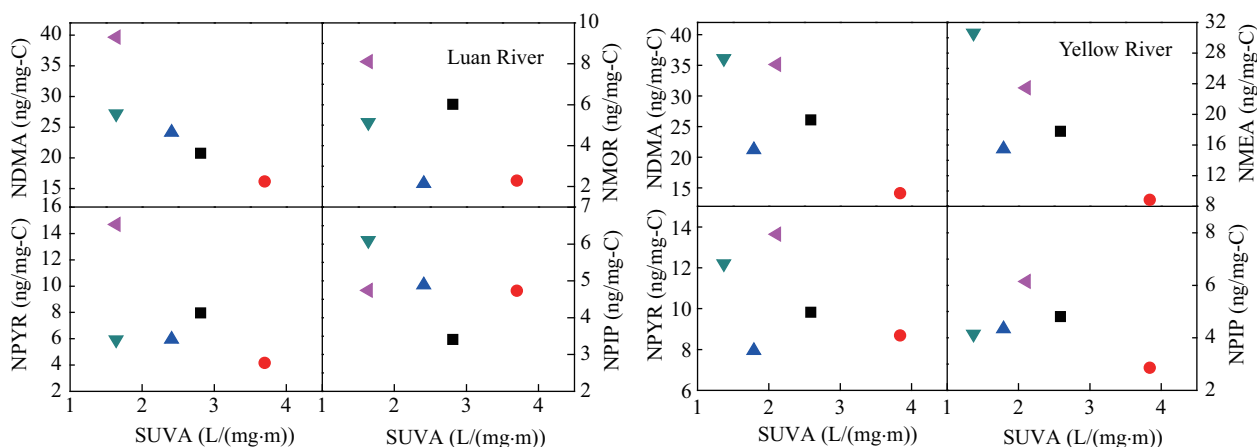


Fig. 7 N-nitrosamines FP from raw water and DOM fractions as a function of SUVA_{254} values after monochloramine treatment in the Luan River and Yellow River. Reaction conditions were pH 8, 25 °C, initial NH_2Cl concentration 20 mg/L Cl_2 , reaction time 7 days.

low content in these water samples.

Generally, only weak correlations were observed between the NDMA FP and the fluorescence intensities of specific DOM components. However, region IV, which represents soluble microbial products, tended to have a better correlation with NDMA formation than the other DOM components. Westerhoff and Mash (2002) reviewed the occurrence of soluble microbial products in natural waters, and concluded that soluble microbial by-products generally were comprised of nitrogen-enriched compounds, less hydrophobic fractions, more basic fractions, and low molecular size fractions. These characteristics of soluble microbial by-products indicate that they might be important precursors for NDMA formation.

3 Conclusions and suggestions

This study identified the dominant N-nitrosamine precursors in bulk organic matter. The main conclusions and suggestions are as follows: (1) The hydrophilic

and low molecular weight fractions tend to form more N-nitrosamines than the corresponding hydrophobic and high molecular weight fractions, which may be due to the higher content of nitrogen-enriched compounds in these two fractions. (2) The amount of soluble microbial products tends to be better correlated with NDMA formation than other DOM components. The higher relative content of nitrogen-enriched compounds in this fraction might make them important precursors for NDMA formation. (3) The EEM spectral results indicated that the two source waters might have been impacted by wastewater discharge. The presence of N-nitrosamines in water treatment plants in these two watersheds should be studied to evaluate the influence of the wastewater effluent. (4) Conventional water treatment processes are ineffective at removing the low molecular weight and hydrophilic fractions of DOM, which may be important precursors for N-nitrosamine formation. Therefore, enhanced treatment techniques such as ozone/granular activated carbon should be used to improve the quality of the treated water in this watershed.

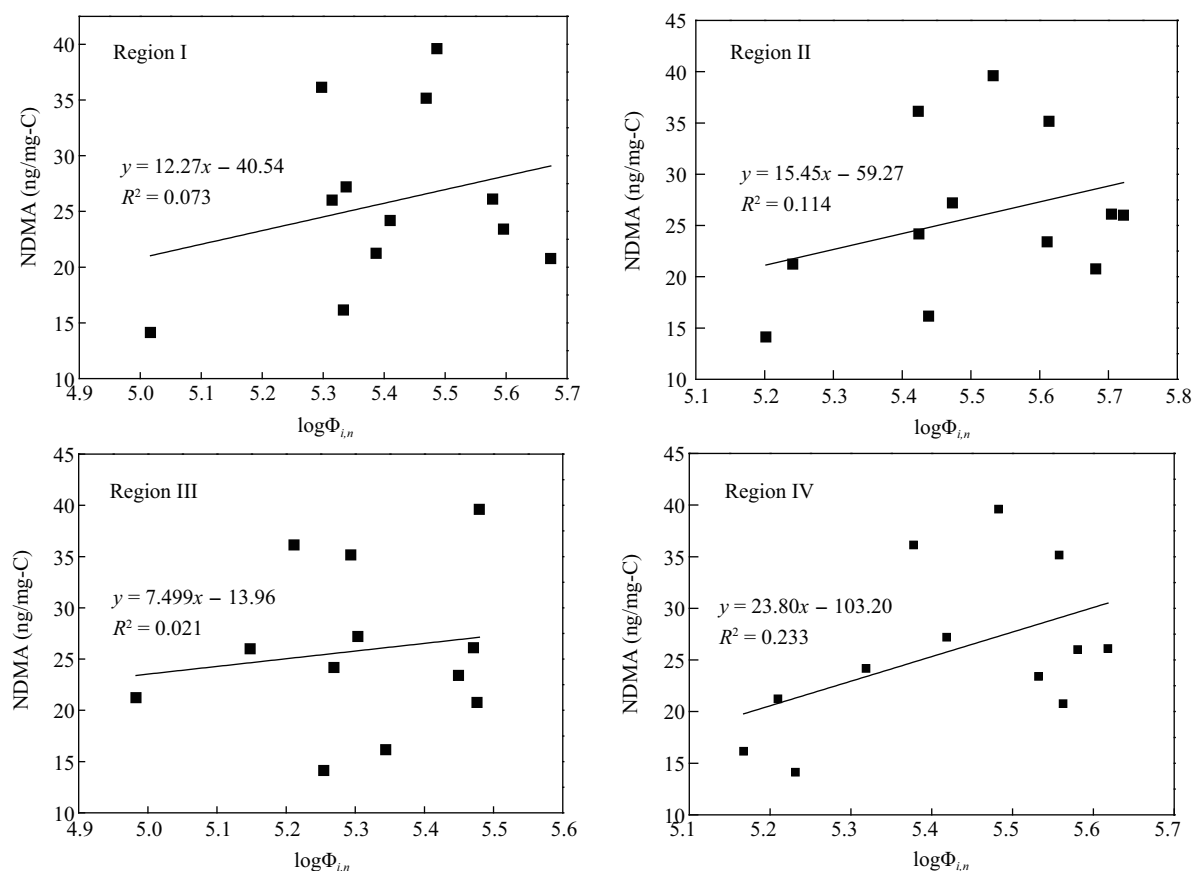


Fig. 8 Correlations between NDMA FP and fluorescence intensities of specific DOM components of raw water and each DOM fraction from the Luan River and the Yellow River.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51078208) and the Major Science and Technology Program for Water Pollution Control and Treatment (No. 2008ZX07420-005, 2008X07423-002).

References

- Aiken G R, McKnight D M, Thorn K A, Thurman E M, 1992. Isolation of hydrophilic organic acids from water using nonionic macroporous resins. *Organic Geochemistry*, 18(4): 567–573.
- Amy G L, Thompson J M, Tan L, Davis M K, Krasner S W, 1990. Evaluation of THM precursor contributions from agricultural drains. *Journal of American Water Works Association*, 82(1): 57–64.
- APHA (American Public Health Association), AWWA (American Water Works Association), WEF (Water Environment Federation), 1995. *Standard Methods for the Examination of Water and Wastewater* (19th ed.). Washington DC, USA.
- Asami M, Oya M, Kosaka K, 2009. A nationwide survey of NDMA in raw and drinking water in Japan. *Science of the Total Environment*, 407(11): 3540–3545.
- Baghtho S A, Sharma S K, Amy G L, 2011. Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation-emission matrices and PARAFAC. *Water Research*, 45(2): 797–809.
- Baker A, 2001. Fluorescence excitation-emission matrix characterization of some sewage-impacted rivers. *Environmental Science & Technology*, 35(5): 948–953.
- Charrois J W A, Arend M W, Froese K L, Hrudey S E, 2004. Detecting N-nitrosamines in drinking water at nanogram per liter levels using ammonia positive chemical ionization. *Environmental Science & Technology*, 38(18): 4835–4841.
- Charrois J W A, Boyd J M, Froese K L, Hrudey S E, 2007. Occurrence of N-nitrosamines in Alberta public drinking-water distribution systems. *Journal of Environmental Engineering and Science*, 6(1): 103–114.
- Chen B Y, Westerhoff P, 2010. Predicting disinfection by-product formation potential in water. *Water Research*, 44(13): 3755–3762.
- Chen W H, Young T M, 2009. Influence of nitrogen source on NDMA formation during chlorination of diuron. *Water Research*, 43(12): 3047–3056.
- Chen W, Westerhoff P, Leenheer J A, Booksh K, 2003. Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. *Environmental Science & Technology*, 37(24): 5701–5710.
- Chen Z, Valentine R L, 2007. Formation of N-nitrosodimethylamine (NDMA) from humic substances in natural water. *Environmental Science & Technology*, 41(17): 6059–6065.
- Choi J, Valentine R L, 2002. Formation of N-

- nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product. *Water Research*, 36(4): 817–824.
- Coble P G, Green S A, Blough N V, Gagosian R B, 1990. Characterization of dissolved organic matter in the Black Sea by fluorescence spectroscopy. *Nature*, 348(6300): 432–435.
- Croue J P, Korshin G V, Benjamin M, 1999. Characterization of Natural Organic Matter in Drinking Water. AWWA Research Foundation, Denver, CO.
- Gerecke A C, Sedlak D L, 2003. Precursors of N-nitrosodimethylamine in natural waters. *Environmental Science & Technology*, 37(7): 1331–1336.
- Guo Y C, Krasner S W, 2009. Occurrence of primidone, carbamazepine, caffeine, and precursors for N-nitrosodimethylamine in drinking water sources impacted by wastewater. *Journal of American Water Resources Association*, 45(1): 58–67.
- Holbrook R D, Breidenich J, DeRose P C, 2005. Impact of reclaimed water on select organic matter properties of a receiving stream-fluorescence and perylene sorption behavior. *Environmental Science & Technology*, 39(17): 6453–6460.
- Hua G H, Reckhow D A, 2007. Characterization of disinfection by product precursors based on hydrophobicity and molecular size. *Environmental Science & Technology*, 41(9): 3309–3315.
- Kemper M J, Walse S S, Mitch M A, 2010. Quaternary amines as nitrosamine precursors: a role for consumer products? *Environmental Science & Technology*, 44(4): 1224–1231.
- Kimura K, Yamamura H, Watanabe Y, 2006. Irreversible fouling in MF/UF membranes caused by natural organic matters (NOMs) isolated from different origins. *Separation Science and Technology*, 41(7): 1331–1344.
- Lee W, Westerhoff P, Crou J P, 2007. Dissolved organic nitrogen as a precursor for chloroform, dichloroacetonitrile, N-nitrosodimethylamine, and trichloronitromethane. *Environmental Science & Technology*, 41(15): 5485–5490.
- Leenheer J A, 1981. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environmental Science & Technology*, 15(5): 578–587.
- Liang L, Singer P C, 2003. Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. *Environmental Science & Technology*, 37(13): 2920–2928.
- Marhaba T F, Kochar I H, 2000. Rapid prediction of disinfection by-product formation potential by fluorescence. *Environmental Engineering and Policy*, 2(1): 29–36.
- McKnight D M, Boyer E W, Westerhoff P K, Doran P T, Kulbe T, Anderson D T, 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography*, 46(1): 38–48.
- Mitch W A, Sedlak D L, 2002. Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination. *Environmental Science & Technology*, 36(4): 588–595.
- Mitch W A, Sedlak D L, 2004. Characterization and fate of N-nitrosodimethylamine precursors in municipal wastewater treatment plants. *Environmental Science & Technology*, 38(5): 1445–1454.
- Panyapinyopon B, Marhab T F, Kanokkantapong V, Pavasant P, 2005. Characterization of precursors to trihalomethanes formation in Bangkok source water. *Journal of Hazardous Materials*, 120(1-3): 229–236.
- Park S H, Wei S T, Mizaikoff B, Taylor A E, Favero C, Huang C H, 2009. Degradation of amine-based water treatment polymers during chloramination as N-nitrosodimethylamine (NDMA) precursors. *Environmental Science & Technology*, 43(5): 1360–1366.
- Pehlivanoglu-Mantas E, Sedlak D L, 2008. Measurement of dissolved organic nitrogen forms in wastewater effluents: Concentrations, size distribution and NDMA formation potential. *Water Research*, 42(14): 3890–3898.
- Persson T, Wedborg M, 2001. Multivariate evaluation of the fluorescence of aquatic organic matter. *Analytica Chimica Acta*, 434(2): 179–192.
- Planas C, Palacios O, Ventura F, Rivera J, Caixach J, 2008. Analysis of nitrosamines in water by automated SPE and isotope dilution GC/HRMS Occurrence in the different steps of a drinking water treatment plant, and in chlorinated samples from a reservoir and a sewage treatment plant effluent. *Talanta*, 76(4): 906–913.
- Rosario-Ortiz F L, Snyder S A, Suffet I H, 2007. Characterization of dissolved organic matter in drinking water sources impacted by multiple tributaries. *Water Research*, 41(18): 4115–4128.
- Sachse A, Henrion R, Gelbrecht J, Steinberg C E W, 2005. Classification of dissolved organic carbon (DOC) in river systems: influence of catchment characteristics and autochthonous processes. *Organic Geochemistry*, 36(6): 923–935.
- Stedmon C A, Markager S, Bro R, 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Marine Chemistry*, 82(3-4): 239–254.
- Wang W F, Hu J Y, Yu J W, Yang M, 2010. Determination of N-nitrosodimethylamine in drinking water by UPLC-MS/MS. *Journal of Environmental Sciences*, 22(10): 1508–1512.
- Weissmahr K W, Sedlak D L, 2000. Effect of metal complexation on the degradation of dithiocarbamate fungicides. *Environmental Toxicology and Chemistry*, 19(4): 820–826.
- Westerhoff P, Chao P, Mash H, 2004. Reactivity of natural organic matter with aqueous chlorine and bromine. *Water Research*, 38(6): 1502–1513.
- Westerhoff P, Mash H, 2002. Dissolved organic nitrogen in drinking water supplies: A review. *Journal of Water Supply: Research and Technology-AQUA*, 51(8): 415–448.
- Yang X, Shang C, Lee W, Westerhoff P, Fan C, 2008. Correlations between organic matter properties and DBP formation during chloramination. *Water Research*, 2008, 42(8-9): 2329–2339.
- Zhao Y Y, Body J M, Woodbeck M, Andrews R C, Qin F, Hrudey S E et al., 2008. Formation of N-nitrosamines from eleven disinfection treatments of seven different surface waters. *Environmental Science & Technology*, 42(13): 4857–4862.
- Zhao Y Y, Body J, Hrudey S E, Li X F, 2006. Characterization of new nitrosamines in drinking water using liquid chromatography tandem mass spectrometry. *Environmental Science & Technology*, 40(24): 7636–7641.

JOURNAL OF ENVIRONMENTAL SCIENCES

(<http://www.jesc.ac.cn>)

Aims and scope

Journal of Environmental Sciences is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via <http://www.elsevier.com/locate/jes>.

For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: journal@mail.sciencep.com, or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

Submission declaration

Submission of an article implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Editorial

Authors should submit manuscript online at <http://www.jesc.ac.cn>. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: jesc@263.net, jesc@rcees.ac.cn. Instruction to authors is available at <http://www.jesc.ac.cn>.

Journal of Environmental Sciences (Established in 1989)

Vol. 25 No. 1 2013

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences		Elsevier Limited, The Netherlands
Edited by	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Distributed by	Domestic Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China
Editor-in-chief	Hongxiao Tang	Foreign	Elsevier Limited http://www.elsevier.com/locate/jes
CN 11-2629/X	Domestic postcode: 2-580	Printed by	Beijing Beilin Printing House, 100083, China
		Domestic price per issue	RMB ¥ 110.00

ISSN 1001-0742

