Characterization of Natural Organic Matter as Precursors for Nitrosamines: Hydrophobicity, Molecular Weight and Fluorescence

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The DBP Iceberg

DHAAs

THMs, THAAs

~700 Known DBPs

50 MWDSC DBPs

ICR Compounds

Halogenated Compounds

Non-halogenated Compounds

NDMA

(Reckhow, 2003)

Stuart Krasner

Susan Richardson
Introduction

Emerging (Unregulated) DBPs:

- 9 identified nitrosamines
- In 1970s or even earlier, Nitrosamines were identified as cancerogen in the field of medicine
- Since 1989, NDMA was identified as the DBPs in the field of water and wastewater treatment
- 6 nitrosamines were listed in the USEPA Integrated Risk Information System database
Precursors for nitrosamines in water source:

- Certain chemicals: DMA and other chemicals containing DMA group for NDMA, such as poly-DADMAC (Mitch et al., 2002; Chio et al., 2002; Park et al., 2009)
- Dissolved organic nitrogen (DON) in wastewater discharge for NDMA (Mantas and Sedlak, 2008), SMP, amino acids
- Natural organic matter (NOM) (Gerecke and Sedlak, 2003; Chen et al., 2006; Zhao et al., 2008)
Introduction

- NOM fractions and nitrosamines formation
  - Hydrophilic and basic fraction of NOM are important precursor for NDMA (Chen and Valentine, 2007)
  - The role of NOM with different molecular weight in the natural water?
  - Other nitrosamines formation from NOM?
Introduction

- Nitrosamines were dominantly originated from N-contained materials, esp. DON.
- DON is more likely related with human activities such as EfOM, domestic and industrial wastewater discharge rather than natural process, such as NOM formation in swamp.
- Algae might also contribute to nitrosamine formation. It is also related with human nutrient discharge.
- Human always make problem to trouble themselves

- China has huge population, rapid economic development but not good environment protection.
- So, nitrosamines could be large problem
WHAT IS THE SITUATION OF DBPs IN CHINA?

Cl/Br-THMs, Cl/Br-HAAs: few over criteria
I-THM3s, I-HAAs: not conducted yet
N-DBPs: may be problem
Others: few investigation
Our Fellowship around China
Water companies and water quality inspections

MAP OF CHINA

Partner in Water Project
Collaboration in water project
THMs and HAAs: survey

Criteria in the drinking water quality standard (GB5749-2006)
- $\text{CHCl}_3$ 60 ug/L, $\text{CHBrCl}_2$ 60 ug/L, $\text{CHBr}_2\text{Cl}$ 100 ug/L, $\text{CHBr}_3$ 100 ug/L
- $\text{DCAA}$ 60 ug/L, $\text{TCAA}$ 100 ug/L
- $\text{ClO}_2^-$ 700 ug/L, $\text{BrO}_3^-$ 10 ug/L

Generally, THMs and HAAs are not great concern. Over-criteria of THMs and HAAs was seldom detected in finished water
- Beijing: about 5-30 μg/L of THAA5, about 5-30 μg/L of TTHM4
- Tianjin: about 10-50 μg/L of THAA5, about 10-50 μg/L of TTHM4
- Shanghai: about 5-20 μg/L of THAA5, about 30-50 μg/L of TTHM4
THMs and HAAs: survey

Possible answer

- Low forest acreage, limited humic substances (low color, low HPO) in source water
- Chlorine dosage, 1-4 mg/L, was not very high
- Chloramination is popular in metropolitan with huge networks
- Only large WTPs has been regularly monitored, lack of more info.
THM and HAA precursor: identification

- Hydrophobic matter (HPO), esp. HPOA contributes more to THM & HAA precursor
- Large ratio of HPO could be removed by enhanced coagulation, O₃-BAC
- Algae bloom also contributes to THM & HAA precursor during summer and autumn

| Table 2 – DBP contribution of different fractions of dissolved organic matter |
|--------------------------|--------|--------|--------|--------|--------|--------|
| Fraction                 | TOTAL  | HPOA   | HPOB   | HPON   | HPIA   | HPIB   | HPIN   |
| RATE (%)                 | 100    | 35.6   | 3.6    | 12.3   | 26.5   | 4.1    | 17.9   |
| THMFP (µg/mg C)          | 38.66  | 66.6   | 4.35   | 34.97  | 34.35  | 9.16   | 5.71   |
| THMs contribution (%)    | 100    | 61.4   | 0.4    | 11.1   | 23.5   | 1      | 2.6    |
| HAAFP (µg/mg C)          | 70.37  | 118.23 | 20.26  | 47.42  | 45.81  | 40.42  | 42.67  |
| HAA contribution (%)     | 100    | 60.1   | 1.0    | 8.3    | 17.3   | 2.4    | 10.9   |

Note: This experiment was conducted in November 2003. Basic raw water quality: TOC=3.78 mg/l, UV₂₅₄=8.1/m, SUVA=2.14 l/mg m.

(Chen, et al. STOTEN, 2008)
THM and HAA precursor: treatment

Table 5
Efficiency of organic matter removal of each unit process

<table>
<thead>
<tr>
<th>Process</th>
<th>COD$_{Mn}$</th>
<th>TOC</th>
<th>UV$_{254}$</th>
<th>AOC</th>
<th>BDOC*</th>
<th>TTHMFP</th>
<th>THAAFP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PreO$_3$</td>
<td>6±9%</td>
<td>2±5%</td>
<td>27±26%</td>
<td>10±3%</td>
<td>76±15%</td>
<td>36±16%</td>
<td>9±2%</td>
</tr>
<tr>
<td>KMnO$_4$</td>
<td>7±5%</td>
<td>6±11%</td>
<td>19±30%</td>
<td>17±20%</td>
<td>13±5%</td>
<td>-15±45%</td>
<td>-2±1%</td>
</tr>
<tr>
<td>C&amp;AF</td>
<td>25±10%</td>
<td>13±5%</td>
<td>20±13%</td>
<td>38±20%</td>
<td>26±26%</td>
<td>-9±37%</td>
<td>21±10%</td>
</tr>
<tr>
<td>FLTR</td>
<td>6±9%</td>
<td>2±4%</td>
<td>-6±8%</td>
<td>30±39%</td>
<td>48±47%</td>
<td>7±49%</td>
<td>19±25%</td>
</tr>
<tr>
<td>O$_3$</td>
<td>12±10%</td>
<td>20±12%</td>
<td>33±18%</td>
<td>-65±42%</td>
<td>-267±104%</td>
<td>-29±67%</td>
<td>-16±44%</td>
</tr>
<tr>
<td>BAC</td>
<td>27±22%</td>
<td>15±11%</td>
<td>32±40%</td>
<td>55±21%</td>
<td>54±25%</td>
<td>41±24%</td>
<td>55±17%</td>
</tr>
<tr>
<td>GAC</td>
<td>46±17%</td>
<td>30±12%</td>
<td>36±5%</td>
<td>66±8%</td>
<td>-64±109%</td>
<td>-22±43%</td>
<td>9±20%</td>
</tr>
<tr>
<td>SCD</td>
<td>14±9%</td>
<td>17±3%</td>
<td>20±7%</td>
<td>-37±3%</td>
<td>-65±19%</td>
<td>N.T.</td>
<td>N.T.</td>
</tr>
<tr>
<td>FCD</td>
<td>7±16%</td>
<td>20±5%</td>
<td>26±21%</td>
<td>-152±25%</td>
<td>-85±20%</td>
<td>N.T.</td>
<td>N.T.</td>
</tr>
</tbody>
</table>

# According to the results of three comprehensive assays in this investigation and regular monitoring for 2 years.
N.T.: not tested.
* High error range might be attributed to the fluctuation of raw water quality, organic accumulation in sand filter or activated carbon filter.

(Chen, et al. STOTEN, 2007)

- Enhanced coagulation, ozonation, activated carbon (GAC, BAC) are effective on TOC, THM and HAA precursor removal as well as bio-stability control.
- O$_3$-BAC are BAT for organic, esp. THM and HAA precursor removal
- Over 20 WTPs in China use O$_3$-BAC to remove organic matters, >10 mil. m$^3$/d.
NDMA survey: very preliminary

- City B: 1-3 ng/L (GAC, NH$_2$Cl, good water source)
- City T: 10-21 ng/L (conventional, NH$_2$Cl, bad water source)
- City W: 12-20 ng/L (conventional, Cl$_2$, bad water source)
- City G: 21-36 ng/L (conventional, NH$_2$Cl, bad water source)
- City D: 7-8 ng/L (conventional, Cl$_2$, bad water source)
High risk of stomach cancer in one town, mortality of 61.9/100k, was related with the drinking water contamination by industrial pollution. High concentration of 9 nitrosamines were detected in drinking water and surface water.
Introduction

Objective of this study

- Take water in Tianjin city as the target
- Characterization of NOM in raw water samples from the two water source: the Luan River and the Yellow River
- Investigation of the formation of NDMA as well as some other nitrosamines from NOM fractions: hydrophobicity, molecular weight
Materials and Methods

- Tianjin City and its water sources
  - The 4th biggest metropolitan in P.R. China
  - Two main water sources: the Luan River and the Yellow River

- Water samples collection
  - Water samples from the influent of WTP were collected on July 16, 2010 (Luan River) and December 22, 2010 (Yellow River), respectively.
TIANJIN
4th Largest Metropolitan in China
Population: 12 mil.

Water source:
Luan River during summer and autumn
Yellow River (via Great Canal) during winter and spring
Hai River, polluted, not suitable as water source

WTPs:
4 in downtown
Capacity: 2 mil. m³/d
Conventional process
Materials and Methods (resin fractionation)

Water sample (pH = 2) → XAD-8 → NAOH → Hydrophobic NOM

XAD-4 → NAOH → Transphilic NOM

Hydrophilic NOM

Schematic diagram of the XAD-8/XAD-4 isolation scheme (Aiken et al., 1992)
Materials and Methods (Molecular weight)

Millipore stirred ultrafiltration cells (Model: 8400) and ultrafiltration membranes (Millipore, MA, USA) with molecular size cut-offs of 3, 1kDa.
Nitrosamines formation potential test

Monochloramine solution prepared

Monochloramine (NH2Cl) solutions were freshly prepared by reacting equal volumes of ammonium chloride and sodium hypochlorite solutions in ice water bath at a size ration from 4mg/L to 1mg/L N. (Yang, et al 2008). The DPD-FAS method was employed to measure the concentration of monochloramine (APHA, AWWA, and WEF, 1992).

Reaction:

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 darkness, and the reaction was quenched by addition of excess sodium thiosulfate after 7 days.
SPE-UPLC/MS/MS for nitrosamines detection

Table 1 Multiple reactions monitoring transitions, MS/MS parameters, instrument detection limits for nine N-nitrosamines.

<table>
<thead>
<tr>
<th>N-nitrosamine</th>
<th>Precursor ion [M+H]+ (Qualify, Confirm)</th>
<th>Product ions [M+H]+</th>
<th>Cone voltage (v)</th>
<th>Collision energy (eV)</th>
<th>IDLs (μg/L) (RSD (%), n=3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDMA</td>
<td>75 (43, 58)</td>
<td>25</td>
<td>18</td>
<td>5</td>
<td>9.4 (43)</td>
</tr>
<tr>
<td>NMEA</td>
<td>89 (61, 43)</td>
<td>22</td>
<td>13</td>
<td>1</td>
<td>2.0 (43)</td>
</tr>
<tr>
<td>NPYR</td>
<td>101 (55, 83)</td>
<td>22</td>
<td>20</td>
<td>1</td>
<td>11 (43)</td>
</tr>
<tr>
<td>NDEA</td>
<td>103 (75, 47)</td>
<td>28</td>
<td>15</td>
<td>5</td>
<td>3.0 (43)</td>
</tr>
<tr>
<td>NPIP</td>
<td>115 (69, 41)</td>
<td>22</td>
<td>20</td>
<td>2</td>
<td>6.4 (43)</td>
</tr>
<tr>
<td>NMOR</td>
<td>117 (87, 45)</td>
<td>22</td>
<td>14</td>
<td>2</td>
<td>9.0 (43)</td>
</tr>
<tr>
<td>NDPA</td>
<td>131 (89, 43)</td>
<td>22</td>
<td>18</td>
<td>5</td>
<td>2.2 (43)</td>
</tr>
<tr>
<td>NDPA-d14</td>
<td>145 (96, 50)</td>
<td>22</td>
<td>15</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>NDBA</td>
<td>159 (103, 57)</td>
<td>22</td>
<td>15</td>
<td>1</td>
<td>6.2 (43)</td>
</tr>
<tr>
<td>NDPhA</td>
<td>199 (169, 66)</td>
<td>22</td>
<td>18</td>
<td>0.5</td>
<td>3.6 (43)</td>
</tr>
</tbody>
</table>

All precursor ions are [M+H]+; and the capillary voltage is 2.5 kv; the source temperature is 120; the desolvation temperature is 350; the desolvation gas flow is 700 L/hr. IDL = instrument detection limit, NA = not available.

Solvent A: acetonitrile
Solvent B: 0.05% formic acid
Total run time: 8 min.
The flow rate: 0.3mL/min.
The sample injection volume: 10μL
Three-dimensional excitation-emission matrix

Three-dimensional excitation-emission matrix (EEM) fluorescence spectra were measured using a spectrometry (F-7000 Fluorescence Spectrophotometer, Hitachi, Japan).
Apparent molecular weight distribution

- HPSEC
- Shimadzu (Japan) HPLC, 2 model LC-20AD pumps, a model SPD-M20A detector and a model CTO-10ASvp column
Other water parameters

- Dissolved organic carbon (DOC) analysis
- UV absorbance@254nm
- SUVA=UV254/DOC
- Ammonia, nitrate, and nitrite
- DON: DON = TDN - NO$_3^-$ - NO$_2^-$ - NH$_4^+$
Results and discussion (NOM characterization)

Table 1 Characteristics of raw water and NOM fractions prior to chloramination (Luan River, 07/16/2010)

<table>
<thead>
<tr>
<th>DOC (mg/L)</th>
<th>UV$_{254}$ (cm$^{-1}$)</th>
<th>SUVA (L/mg-m)</th>
<th>NH$_3$-N (mg/L)</th>
<th>NO$_3$-N (mg/L)</th>
<th>NO$_2$-N (mg/L)</th>
<th>DON (mg/L)</th>
<th>Br$^-$ (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.21</td>
<td>0.09</td>
<td>2.81</td>
<td>0.1</td>
<td>2.25</td>
<td>0.004</td>
<td>0.24</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>
Results and discussion (NOM characterization)

Table 2 Characteristics of raw water and NOM fractions prior to chloramination (Yellow River, 12/22/2010)

<table>
<thead>
<tr>
<th></th>
<th>DOC (mg/L)</th>
<th>UV$_{254}$ (cm$^{-1}$)</th>
<th>SUVA (L/mg-m)</th>
<th>NH$_3$-N (mg/L)</th>
<th>NO$_3$-N (mg/L)</th>
<th>NO$_2$-N (mg/L)</th>
<th>DON (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.66</td>
<td>0.069</td>
<td>2.59</td>
<td>0.1</td>
<td>4.64</td>
<td>0.038</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Results and discussion (NOM characterization)

Table 2 Excitation and emission wavelength boundaries and chemical descriptions used for FRI technique

<table>
<thead>
<tr>
<th>Region</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region 1</td>
<td>200-250</td>
<td>250-330</td>
<td>Aromatic proteins</td>
</tr>
<tr>
<td>Region 2</td>
<td>200-250</td>
<td>330-380</td>
<td>Aromatic proteins (BOD₃)</td>
</tr>
<tr>
<td>Region 3</td>
<td>200-250</td>
<td>380-550</td>
<td>Fulvic acid-like</td>
</tr>
<tr>
<td>Region 4</td>
<td>250-400</td>
<td>250-380</td>
<td>Soluble microbial products like</td>
</tr>
<tr>
<td>Region 5</td>
<td>250-400</td>
<td>380-550</td>
<td>Humic acid-like</td>
</tr>
</tbody>
</table>

Fig. 1 Fluorescence Excitation-Emission Matrix (EEM) of raw water and NOM fractions before chloramination
Results and discussion (Precursors of Nitrosamines)

Fig. 2 Nitrosamines formation potential of raw waters and NOM fractions, Luan River. (pH = 8, t = 25°C, \([\text{NH}_2\text{Cl}]_0\) = 20mg/L, reaction time = 7days. Error bars depict one standard error for three injection).
Results and discussion (Precursors of Nitrosamines)

Fig. 3 Nitrosamines formation potential of raw waters and NOM fractions, Yellow River. (pH = 8, t = 25, $[\text{NH}_2\text{Cl}]_0 = 20\text{mg/L}$, reaction time = 7 days. Error bars depict one standard error for three injection).
Results and discussion (Precursors of Nitrosamines)

Generally, the HPI fraction and the fraction with molecular weight below 1kDa, which were observed to produce more nitrosamines, had low DOC/DON ratios.

The formation of NDMA showed a negative correlation with DOC/DON ratio.

Fig. 3 Nitrosamines yields of raw waters and NOM fractions as a function of DOC/DON, Luan River, sampling date: 16/07/2010
Results and discussion (Precursors of Nitrosamines)

Similar result was observed from the Yellow River samples. The HPI fraction and the fraction with molecular weight below 1K had low DOC/DON ratio, while these fractions were found to produce high yields of N-nitrosamines.

Fig. 4 Nitrosamines yields of raw waters and NOM fractions as a function of DOC/DON, Yellow River, sampling date: 22/12/2010
Results and discussion (Precursors of Nitrosamines)

There were more low-molecular NOM in the HPI fraction than those in other fractions.

This result of the molecular weight distributions in the NOM fractions confirmed the conclusion that the NDMA precursors could be low-molecular organic matter.
Results and discussion
(Nitrosamines formation and SUVA$_{254}$)

Generally, HPI fraction and molecular weight below 1kDa fraction from the Luan River, which had fairly low SUVA$_{254}$, were found to produce high yields of these nitrogenous DBPs, as normalized in per unit DOC concentration (ng/mg-C).

Fig. 6 Nitrosamines yields of raw waters and NOM fractions as a function of SUVA$_{254}$, Luan River, sampling date: 16/07/2010
Results and discussion
(Nitrosamines formation and SUVA$_{254}$)

Similar result of relationship between nitrosamines formation and SUVA$_{254}$ were observed.

The N-nitrosamines formation in different water samples seemed to be inversely related to their SUVA$_{254}$ values.

However, it was hard to use SUVA$_{254}$ values as universal index to predict the formation of nitrosamines because of the complicated composition of NOM in different water sources.

Fig. 7 Nitrosamines yields of raw waters and NOM fractions as a function of SUVA$_{254}$, Yellow River, sampling date: 22/12/2010
Fig. 8 EEM spectrum change before and after chloramination of samples from Luan River
Results and discussion
(Nitrosamines formation and EEM change)

Fig. 9 EEM spectrum change before and after chloramination of samples from Yellow River
Results and discussion
(Nitrosamines formation and EEM change)

Fig. 10 The volume ($\Phi_{i,n}$) change of each region in the EEMs before and after chloramination, (A: raw water from Luan River, B: raw water from Yellow River)

Although EEM is useful to distinguish different types and changes of NOM before and after chloramination, it is very hard to establish the quantitative relationship between the change of EEM intensity and nitrosamines formation because of the non-monotonic change of fluorescence during the chloramination.
Conclusions and suggestions

◆ The hydrophilic and low molecular weight NOM were the major reservoirs of precursor for nitrosamines.

◆ The HPI fraction and the fraction with molecular weight below 1k Da, which were observed to produce more nitrosamines, had low DOC/DON ratios and low SUVA$_{254}$ values.

◆ It was hard to establish the quantitative relationship between the change of EEM intensity and nitrosamines.

◆ The two water sources for Tianjin city should be impacted by wastewater discharge because they contained abundant aromatic proteins (BOD$_5$) or soluble microbial products like material. The occurrence of nitrosamines should be detected in drinking water in Tianjin city to investigate the influence of the wastewater discharges on the formation of these DBPs.
Further work

NDMA formation from typical chemicals containing DMA group

Fig. 1 NDMA formation of different chemicals disinfection with monochloramine (CD—Chlordimeform; Pi—Pirimicarb; CT—chlortoluron; HMAC—2-Hydroxyethyltrimethylammonium chloride; BKC—Benzalkonium Chloride; HTAB—Hexadecyl trimethyl ammonium Bromide; PD—PolyDADMAC; L-Tyr; L-Lys; Tannins)
Further work
NDMA formation from typical chemicals containing DMA group

Fig. 2 NDMA molar yield of different chemicals disinfection with monochloramine
(CD—Chlordimeform; Pi—Pirimicarb; CT—chlortoluron; HMAC—2-Hydroxyethyltrimethylammonium chloride; BKC—Benzalkonium Chloride; HTAB—Hexadecyl trimethyl ammonium Bromide; PD—PolyDADMAC; L-Tyr; L-Lys; Tannins)
Further work
NDMA formation from typical chemicals containing DMA group

Fig. 3 The formation of NDMA and DMA of four chemicals as a function of time (hours)
Acknowledgments

The authors thank the National Natural Science Foundation of China for financial support (grant 51078208)

Any comments and questions?