Chlorination Byproducts Formation Potentials of Typical Nitrogenous Organic Compounds in Water

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Abstract: Twelve typical nitrogenous organic compounds including herbicides, pesticides, amino acids, industrial products etc in polluted raw water were selected to investigate formation of typical carbonaceous and nitrogenous DBPs during chlorination and chloromation. To indentify the formation mechanism of carbonaceous and nitrogenous disinfection byproducts from nitrogenous chemicals, chlorination and chloroamination of urea herbicides, triazine herbicides, amino acid, and other compounds were investigated. As a result, the potential precursors for different DBPs were defined as well. It has been identified that widely used urea herbicides could produce as many as 9 specific DBPs. The chlorotoluron shows highest reactivity and yields chloroform ( CF ), monochloroacetic acid ( MCAA ), dichloroacetic acid ( DCAA ), 1,1-dichloro-acetone ( 1,1-DCP ), 1,1,1-trichloro-acetone ( 1,1,1-TCP ), chloropicrin ( NTCM ), dichloro-acetonitrile ( DCAN ), dimethyltriamine ( NDMA ). The results indicated that aldicarb and dinoseb are important precursors of CF, DCAA, MCAA, NTCM as well. High concentrations of CF and DCAA were found during L-tryptophan chlorination. Furthermore, DBPs formation pathways and mechanisms were suggested during chlorination and chloroamination of chlorotoluron, ametryn, dinoseb L-tryptophan.

Key words: nitrogenous organic compounds; chlorination disinfection; chloramine disinfection; disinfection DBPs; NDMA
析

正戊烷为萃取剂

性消毒副产物混标

自

硫酸钠

盐酸

理化学性质详见表

三卤甲烷混标

$\text{品或优级纯}$

$\text{购自美国}$

$(\text{UPLC-MS-MS})$

1.

1.1

Dr. Ehrenstorfer $(\text{Sigma})$

Milli-Q $(\text{J. T. Baker})$.

$(\text{MTBE}), (\text{NDMA})$

$(\text{THMs, HAAs})$

$(\text{HAAs})$

(EPA502. 1, EPA552. 2, MTBE $\text{(HANs)}, \text{(HAKs)}$).

EPA551. 1 $\text{MTBE}$ $\text{GC-}$

$\text{ECD (})$

$\text{GC2010)}$

$\text{HP5} (30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ mm})$.

NDMA $\text{(UPLC-MS-MS)}$

$\text{Thermo Fisher}$

Scientific $\text{TSQ Quantum}$

1.2

\[ m(\text{Cl}_2)/m(\text{DOC}) = 10 \text{ (DOC } \text{C } \text{)} , \text{ 10 mmol/L} \]

$\text{pH} 7.0 \pm 0.1$

$\text{7 d}$

\[ (\text{25 } \pm 1){^\circ} \text{C} \]

\[ (\text{10 mmol/L}), \text{ pH } 7.0 \pm 0.1, \text{ 25}{^\circ} \text{C} \]

\[ (\text{LC-MS-MS}) \]

2

2.1

Dr. Ehrenstorfer $(\text{EPA502. 1})$

$(\text{NDMA})$

$(\text{EPA552. 2})$

MTBE $\text{(HANs)}, \text{(HAKs)}$.
Table 1  Physical and chemical characteristics of the twelve typical nitrogenous organic compounds

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>CAS</th>
<th>Molecular weight</th>
<th>log $K_{ow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>330-54-1</td>
<td>232</td>
<td>2.68</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>15545-48-9</td>
<td>212.68</td>
<td>2.41</td>
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<tr>
<td>3</td>
<td></td>
<td>34123-59-6</td>
<td>206.29</td>
<td>2.87</td>
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<tr>
<td>4</td>
<td></td>
<td>41394-05-2</td>
<td>201.21</td>
<td>0.83</td>
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<tr>
<td>5</td>
<td></td>
<td>834-12-8</td>
<td>227.33</td>
<td>2.98</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>7287-19-6</td>
<td>373.7</td>
<td>0.99</td>
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<td>7</td>
<td></td>
<td>61-82-5</td>
<td>84</td>
<td>-0.86</td>
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<tr>
<td>8</td>
<td></td>
<td>116-06-3</td>
<td>190.26</td>
<td>1.13</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>57966-95-7</td>
<td>198.18</td>
<td>4.24</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>88-85-7</td>
<td>240.21</td>
<td>3.56</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>73-24-5</td>
<td>135.13</td>
<td>-0.05</td>
</tr>
<tr>
<td>12</td>
<td>1-methyl-2</td>
<td>73-22-3</td>
<td>204.23</td>
<td>-1.06</td>
</tr>
</tbody>
</table>

- DCA (DCAA), TCA (TCAA), 1,1-DCA (1,1-DTCP), 1,1,1,1-TCA (1,1,1-TTCP), CF (MCAA), N,N-NTCM, DCAN, NDMA
从图可以看出，取代脲类除草剂同样也是产生三氯甲烷的重要来源。其中反应活性更高的绿麦隆和异丙隆经过量氯氧化可产生较高浓度的三氯甲烷。绿麦隆的生成量分别为185.5 μg/L和153 μg/L，略高于异丙隆的148 ng/L和32 ng/L。从卤乙酸（氯代丙酮产生量上分析，可以推断经氯化后脲类除草剂的苯环必然会发生开环和氯加成的反应，这与间二苯酚经氯氧化生成三氯甲烷和卤乙酸的生成机制相似。从图可以看出，经次氯酸氧化绿麦隆用羰基取代苯环上的氢原子，并进一步氧化断裂碳氮键，随后在次氯酸的继续作用下，苯环上的双键成为单键并被氯原子取代，并进一步产生断环反应从而生成三卤甲烷（卤乙酸、卤乙腈和卤化丙酮）。物质结构中的氨基经氯氧化后形成硝基，相邻6上的拼被所取代。生成二甲基亚硝胺（NDMA），其生成量分别达到138%。
期 徐倩等
水中典型含氮有机物氯化生成消毒副产物的潜能研究

图 PM
绿麦隆经氯化和氯胺化生成

- 5 I 2
与
= 5 I 2
的机制推断图

一 官 能 团
例 如
_ A F @ 9 :< ; G F A 8@
( [ G 8A 9 A ?A 8@
( [2 7 ; < ; S ; >G 8A ?@
等
"*
B
可以认为在氯胺左右条件下
_ U W N
将释放出二甲胺基团

$\text{O} = \text{N} - \text{N} \text{CH}_3$
(NDMA)

(1, 1-DCP)

(1, 1, 1-TCP)

(DF)

(DCNA)

$\text{Cl} \underset{\text{Cl}}{\text{C}} - \text{C} \text{CH}_3$

$\text{Cl} \underset{\text{Cl}}{\text{C}} - \text{C} \text{CH}_3$

$\text{Cl} \underset{\text{Cl}}{\text{C}} - \text{Cl}$

$\text{CH} - \text{C} \equiv \text{N} \rightleftharpoons \text{CH} - \text{C} \text{OH}$

3 C-DBPs N-DBPs

Fig. 3 Formation mechanisms of C-DBPs and N-DBPs during chlorination and chloramination of Chlorotoluron

2.2

20 50

2

4

DBPs 4

DBPs 4

C-DBPs

Fig. 4 C-DBPs formation potentials of triazine herbicides
2.3 C-DBPs vs N-DBPs

Fig. 5 Formation mechanism of C-DBPs during chlorination of Ametryn

Fig. 6 DBPs formation potential variations between other nitrogenous organic compounds

Fig. 7 Formation mechanism of HAAs during chlorination of L-Tryptophan


[18 ] Andrzejewski P, Kasprzyk-Hordern B, Nawrocki J. N-nitrosodimethylamine (NDMA) formation during ozonation of