Toxicity profile of labile preservative bronopol in water: The role of more persistent and toxic transformation products

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The preservative bronopol is non-persistent and low toxic, but some transformation products can cause higher or prolonging adverse impacts.

A R T I C L E   I N F O

Article history:
Received 15 March 2010
Received in revised form 17 September 2010
Accepted 27 September 2010

Keywords:
Bronopol
Transformation products
Hydrolysis
Photolysis
Toxicity

A B S T R A C T

Transformation products usually differ in environmental behaviors and toxicological properties from the parent contaminants, and probably cause potential risks to the environment. Toxicity evolution of a labile preservative, bronopol, upon primary aquatic degradation processes was investigated. Bronopol rapidly hydrolyzed in natural waters, and primarily produced more stable 2-bromo-2-nitroethanol (BNE) and bromonitromethane (BNM). Light enhanced degradation of the targeted compounds with water site specific photoactivity. The bond order analysis theoretically revealed that the reversible retroaldol reactions were primary degradation routes for bronopol and BNE. Judging from toxicity assays and the relative pesticide toxicity index, these degradation products (i.e., BNE and BNM), more persistent and higher toxic than the parent, probably accumulated in natural waters and resulted in higher or prolonging adverse impacts. Therefore, these transformation products should be included into the assessment of ecological risks of non-persistent and low toxic chemicals such as the preservative bronopol.

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1. Introduction

The increasing ubiquitous contamination of industrial and agricultural chemicals is occurring in freshwater systems, and has been considered as one of the emerging key environmental problems (Gasser et al., 2007; Schwarzenbach et al., 2006; Sinclair et al., 2008). Once released into the environment, these pollutants inevitably degrade to new compounds (i.e., transformation products) by biological and chemical processes (Holtze et al., 2008; la Farré et al., 2008; Schulze et al., 2010). Some transformation products are found to be more toxic and/or more persistent than the parents, and thus pose higher risks to the environment (Belfroid et al., 1998; Celiz et al., 2009; Hainzl and Casida, 1996; Holtze et al., 2008). For example, in a risk assessment for 60 pesticides and 485 transformation products, 30% of these transformation products are more toxic than their parents, and 4.2% are more than an order of magnitude higher toxic (Sinclair and Boxall, 2003). Note also that some transformation products are detected more frequently and/or in higher concentrations than the parents (Belden et al., 2007; Gasser et al., 2007; la Farré et al., 2008; Sinclair et al., 2006).

Transformation products usually differ in environmental behaviors and toxicological effects from the parents, and probably are concurrent with the parents in the environment (Sinclair and Boxall, 2003; Gasser et al., 2007; la Farré et al., 2008). Formation of higher toxic and/or more persistent transformation products contributes greatly to an increased toxicity of the parents over degradation processes, represented by a degradation-dependent toxicity evolution of the parents (Cai et al., 2009; Kralj et al., 2007; Zhou et al., 2009). The potential risks caused by these transformation products are actually indirect effects of the parent which are the precursors of the products. Therefore, incorporation of transformation products into risk assessment of the parent pollutants will be helpful to distinguish the nature of risk evolution of the parent in the environment.

Presently, many chemicals which were once considered as non-persistent and low toxic pollutants (e.g., 2-bromo-2-nitropropan-1,3-diol (bronopol, shown in Fig. 1)), are widely used, and thus are released into the environment. Bronopol is used as a preservative in cosmetics, hygiene products, pharmaceuticals, and industrial products such as glue and paints. It can also be used as a biocide in industrial processes, e.g., textiles, paper mills, and cooling water systems (USEPA, 2005). Despite a high consumption of the preservative (Doi et al., 2010; Rastogi, 2000), bronopol is not detected in the environment (Dye et al., 2007; Remberger et al., 2006), due to its relatively poor stability in the environment. In industrial products...
and aequous solutions, bronopol rapidly degrades to various transformation products (Fig. 1), consisting of 2-bromo-2-nitro-1,3-propanediol (BNP), bromonitromethane (BNM), tri(hydroxymethyl) nitromethane (TNM), nitromethane (NM), 2-bromomethanol (2-BE), formaldehyde (FA), and other unidentified chemicals, but its antimicrobial activity is still acceptable (Bryce et al., 1978; Challis and Yousaf, 1991; Sanyal et al., 1996). A few degradation products, BNE was identified by GC/MS and FTIR. Bromonitromethane (BNM, purity 98%) was purchased from Sigma–Aldrich (USA). The analytical reagent formaldehyde (FA) was purchased from Shenyang Huihang Reagent Factory (Shenyang, China).

As no standard was available, 2-bromo-2-nitroethanol (BNP) was prepared in our laboratory according to the reported reaction pathway that bronopol can hydrolyze to equimolar BNE at alkaline solutions (Challis and Yousaf, 1991; Sanyal et al., 1996; Wang et al., 2002). In brief, bronopol solution was adjusted to pH 9–10 by sodium hydroxide. At certain intervals, the reaction solution was monitored by a high performance liquid chromatography (HPLC) to enable complete degrada-
tion of the preservative to BNE. Hydrochloric acid was added to the reaction solution (pH 4.0) to prevent further degradation of BNE to BN and other degradation products. BNE was identified by HPLC-ESI-MS. The obtained BNE solution was stored in a refrigerator (0–4°C) and remained intact for at least three months.

2.2. Hydrolysis experiments

Five water samples were collected from the Baiyangdian Lake valley to investigate water site–dependent degradation of these compounds. The lake is the largest natural freshwater body in North China Plain, with a surface area of ca. 360 km² (Chen et al., 2008). The water body receives not only direct discharge of wastewater of Baoding City via Fuhe River, but also agricultural runoff and domestic waste in the valley, and thus consists of heterogeneous waters. Water sample 1 (Liu’kou) was collected from upstream Fuhe River, indicating the water of input stream. Water sample 2 was collected from Nanliuzhuang located at the intersection of the lake and the river. Other three sample sites were away from the river and exhibited a high number of reactive sites in the molecule (Challis and Yousaf, 1991; Kajimura et al., 2008; Wang et al., 2002). A few degradation products, BNE was identified by GC/MS and FTIR. Bronopol was readily hydrolyzed and photolyzed in aqueous solutions because of its high reactivity and aromaticity.

Prior to the addition of bronopol, NaN₃ (0.2%) was added to natural waters and aqueous solutions, and the hydrolysis reactions were conducted in a water bath of 20°C. At certain intervals, the reaction solutions were sampled and 100 μL of 5% HCl was added to terminate the reaction. The mixed solutions were analyzed using an HPLC system. Bronopol and major transformation products were simultaneously determined in terms of the corresponding standard curves. The rate constants and half lives were calculated by fitting one-order kinetics equation.

2.3. Photolysis experiments

In the experiments, degradation of bronopol and major transformation products in the light (i.e., photodegradation) comprised of concurrent hydrolysis and photolysis. The hydrolysis was represented by degradation of the compounds in the dark, whereas the latter was calculated by subtracting the fraction of hydrolysis from the photodegradation of the chemicals. Solar-simulated (λ > 290 nm) photolysis of BNP and major degradation products were conducted under a water-refrigerated 500 W xenon lamp. The mean temperature in the reactor was 34 ± 3°C. Bronopol and major transformation products were added to natural waters and deionized waters, and the reaction solutions were kept in Pyrex tubes. The tubes wrapped by aluminum foil were retained in the reactor and acted as dark control, in which the photolysis reactions were conducted in a water bath of 20°C. At certain intervals ranging from 15 min to 72 h, 200 μL of the reaction solutions were sampled and acidified with 5% HCl and the target compounds were measured by the HPLC system. The kinetics data were analyzed according to the above procedures.

2.4. Algal toxicity assays

The algae Chlorella pyrenoidosa was obtained from the Institute of Hydrobiology of Chinese Academy of Sciences (Wuhan, China). The algae, commonly used for ecotoxicology tests, and the hydrolysis reactions were conducted in a water bath of 20°C. At certain intervals ranging from 15 min to 72 h, 200 μL of the reaction solutions were sampled and acidi

Table 1 Physicochemical characteristics of five natural waters.

<table>
<thead>
<tr>
<th>No. Sampling sites</th>
<th>pH (μS/cm)</th>
<th>Conductivity (mS/cm at 22°C)</th>
<th>Oxidation–reduction potential (mV)</th>
<th>Total P</th>
<th>TOC (mg/L)</th>
<th>PO4 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Liu’kou</td>
<td>7.68</td>
<td>1800.5</td>
<td>−45</td>
<td>35.30</td>
<td>0.97</td>
<td>12.27</td>
</tr>
<tr>
<td>2 Nanliuzhuang</td>
<td>7.53</td>
<td>1618.8</td>
<td>−37</td>
<td>30.67</td>
<td>1.65</td>
<td>10.04</td>
</tr>
<tr>
<td>3 Wangjiazhai</td>
<td>7.40</td>
<td>1460.9</td>
<td>−28</td>
<td>4.17</td>
<td>0.07</td>
<td>7.33</td>
</tr>
<tr>
<td>4 Zhangzhuang</td>
<td>7.37</td>
<td>1280.5</td>
<td>−27</td>
<td>2.11</td>
<td>0.04</td>
<td>18.91</td>
</tr>
<tr>
<td>5 Quantou</td>
<td>7.75</td>
<td>1133.3</td>
<td>−49</td>
<td>1.81</td>
<td>0.03</td>
<td>8.77</td>
</tr>
</tbody>
</table>

Fig. 1. Proposed degradation pathways for bronopol (BNP) in natural waters. Bond lines represent primary degradation processes of the preservative occurring in this study.
toxicity tests, was maintained in the algal growth medium HB IV at 24 ± 1 °C with a photoperiod of 16 h light (3000 lx) and 8 h dark. The algal growth-inhibition tests were carried out according to the updated OECD guideline 201 for freshwater algal and cyanobacterial growth inhibition tests (OECD, 2002). The algae from the exponentially growing precultures were inoculated into the test solution at a density of 4.0 × 10^5 cells/mL. The concentration of these chemicals in the solutions ranged from 10.0 to 80.0 μM/L for bronopol, 2.94 to 94.12 μM/L for BNE, 2.86 to 10.89 μM/L for BNM, and 80 to 3200 μM/L for 2-BE, respectively. All blanks were incubated in a culture chamber and repositioned daily to minimize possible spatial differences in illumination and temperature. According to the linear equation relating direct cell counts and optical density at 680 nm (OD680), the inhibition of algal growth relative to the control was determined by measuring OD680.

3.1. Hydrolysis of bronopol and major transformation products

According to the linear equation relating direct cell counts and optical density at 680 nm (OD680), the inhibition of algal growth relative to the control was determined by measuring OD680.

The hydrolysis of bronopol (BNP) and 2-bromo-2-nitroethanol (BNE) in natural waters was investigated. The experimental procedure for the determination of hydrolysis followed the updated OECD guideline 201 for freshwater algal toxicity tests, which was maintained in the algal growth medium HB IV at 24 ± 1 °C with a photoperiod of 16 h light (3000 lx) and 8 h dark. The algal growth-inhibition tests were carried out according to the updated OECD guideline 201 for freshwater algal and cyanobacterial growth inhibition tests (OECD, 2002). The algae from the exponentially growing precultures were inoculated into the test solution at a density of 4.0 × 10^5 cells/mL. The concentration of these chemicals in the solutions ranged from 10.0 to 80.0 μM/L for bronopol, 2.94 to 94.12 μM/L for BNE, 2.86 to 10.89 μM/L for BNM, and 80 to 3200 μM/L for 2-BE, respectively. All blanks were incubated in a culture chamber and repositioned daily to minimize possible spatial differences in illumination and temperature. According to the linear equation relating direct cell counts and optical density at 680 nm (OD680), the inhibition of algal growth relative to the control was determined by measuring OD680.

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with formaldehyde to produce the parent again (Challis and Yousaf, 1991). These results indicate that BNE is a major intermediate of bronopol in the environment as well as in the industrial products and industrial water systems.

The bond order analysis of bronopol and BNE (Fig. 3), theoretically, demonstrates that the retroaldol reaction is a primary degradation route for both compounds which involves BNE and BNM as the reactive intermediates, respectively. In molecules, bond strength decreases as bond order decreases. The oxygen atom and the hydrogen atom of the hydroxyl group in the molecules of bronopol and BNE gave the least bond orders (Fig. 3), suggesting the lowest stability of hydroxyl bond. The mobility of hydroxyl hydrogen atoms is also confirmed by weak acidity of bronopol that has pH 5.0–5.5 in aqueous solutions (Legin, 1996) and by the disappearance of the absorbance band at 244 nm of BNE containing an α-hydrogen atom which results in a facile transformation of BNE to the sodium salt of the nitronic acid with poor absorbance at the wavelength via a tautomeric change (Sanyal et al., 1996). Additionally, an increase in the pH leads to rapid decomposition of bronopol and BNE, which is

Fig. 2. Hydrolysis of bronopol (BNP) in natural waters. In the figure, square (□) represents BNP, cycle (○) represents 2-bromo-2-nitroethanol (BNE), and upward triangle (▲) represents bromonitromethane (BNM).

Fig. 3. Bond order analysis of bronopol (BNP) and 2-bromo-2-nitroethanol (BNE).

Fig. 4. Photolysis of bronopol (BNP) and two major transformation products in deionized water. In the figure, square (□) represents BNP, cycle (○) represents 2-bromo-2-nitroethanol (BNE), and upward triangle (▲) represents bromonitromethane (BNM).
consistent with the fact that an alkaline medium catalyzes the retroaldol reaction of all the primary and secondary nitroalcohols (Novikov et al., 1974).

### 3.2. Photolysis of bronopol and major transformation products

As shown in Fig. 4, bronopol and major transformation products, in deionized water, reduced at higher rates under continuous xenon irradiation than in the dark, indicating the occurrence of photolysis. Their photoactivity, represented by net reaction rates, increased in the order BNP ($K_T = 0.016$ h$^{-1}$ and $t_{1/2} = 5.975$ h) < BNM ($K_T = 0.032$ h$^{-1}$ and $t_{1/2} = 21.448$ h) < BNE ($K_T = 0.116$ h$^{-1}$ and $t_{1/2} = 5.975$ h). Once BNP was initially exposed to the light, BNE rapidly increased with reaction time and other transformation products (Fig. 1) such as TNM, BNM, 2-BE, NM and unidentified compounds also occurred at various intervals. However, only BNE and minor 2-BE were detected as end products. As BNE was the initial contaminant, BNP and BNM rapidly formed in the solution, while some unidentified compounds were also detected. In the case of BNM, it degraded at relatively slower rate to produce fewer transformation products, of which NM was a primary degradation product. An unidentified chemical which gave strong chromatographic response with retention time of 5.5 min was detected at 5 h but rapidly dissipated with the continuous light exposure.

In natural waters (Fig. 5), bronopol degraded via similar degradation pathways but at higher rates (Table 3), compared to the preservative in deionized water. Interestingly, BNE produced from the preservative was significantly less photoactive in natural waters than in deionized water, while the parent exhibited a reverse photoactivity. This product was 18.37 (Water sample 4) to 84.80 (Water sample 5) times more resistant to photolysis in natural waters than the parent, but their photoactivity was the exact opposite in deionized water. Additionally, their photoactivity in natural waters was not correlated to water characteristics ($P = 0.05$). As a result, light could differentially affect the degradation of bronopol in natural waters, showing water site-dependent photodegradation.

### 3.3. Toxicity assays of bronopol and major transformation products

Table 4 presents the EC$_{50}$ values for bronopol and its major transformation products to the algae. The determined EC$_{50}$ values may not most accurately reflect the toxicities of labile compounds since these compounds (including bronopol) probably readily degrade in algae suspension (Cai et al., 2009). The obtained values, however, highly illustrate the relative toxicities of the compounds, indicating that BNM is the most toxic, followed by BNE, BNP, and BE, respectively (Table 4). The absence of time-dependent toxicity for these compounds, represented by the EC$_{50}$ values with overlapping 95% confidence intervals (Table 4), is probably ascribed to the formation of nearly equal to or higher toxic degradation products (e.g., BNE and BNM).

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**Table 3**

Photolysis kinetics of bronopol (BNP) and 2-bromo-2-nitroethanol (BNE) in natural waters ($R > 0.989$, $P < 0.0001$).

<table>
<thead>
<tr>
<th>Water sample</th>
<th>Degradation</th>
<th>Hydrolysis</th>
<th>Photolysis</th>
<th>Degradation</th>
<th>Hydrolysis</th>
<th>Photolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_T$ (h$^{-1}$)</td>
<td>$K_T$ (h$^{-1}$)</td>
<td>$t_{1/2}$ (h)</td>
<td>$K_T$ (h$^{-1}$)</td>
<td>$K_T$ (h$^{-1}$)</td>
<td>$t_{1/2}$ (h)</td>
</tr>
<tr>
<td>1</td>
<td>19.513</td>
<td>17.952</td>
<td>1.561</td>
<td>0.444</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>22.393</td>
<td>20.729</td>
<td>1.664</td>
<td>0.416</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>20.506</td>
<td>17.768</td>
<td>2.738</td>
<td>0.253</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>21.323</td>
<td>19.321</td>
<td>2.002</td>
<td>0.346</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>19.684</td>
<td>15.444</td>
<td>4.240</td>
<td>0.163</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Represents degradation rates of BNE after reaching maximum concentrations, based on the suppose that degradation of the compound was ignored before reaching maximum concentrations.
The toxicity potential of these compounds to the algae (Table 4) was consistent with their toxicity potential to Vibrio fischeri that decreased in the order BNM (IC$_{50}$ = 24.74 mmol/L) > BNE (IC$_{50}$ = 24.96 mmol/L) > BNP (IC$_{50}$ = 95.95 mmol/L) > FA (IC$_{50}$ = 1.71 mmol/L) > BE (IC$_{50}$ > 40 mmol/L) (Wang et al., 2008). The antimicrobial activity of bronopol and major transformation products is mostly due to the presence of electron-deficient bromine atoms in the molecules rather than the liberation of formaldehyde (Legin, 1996; Wang et al., 2008). Oxidation properties of the bromine atoms lead to the cross-linking of sulfohydride groups of dehydrogenase enzymes on the surface of microbial cells by oxidation reactions, and the disulfide bridges produced block microbial metabolism (Bryce et al., 1978; Legin, 1996). These results further confirm the non-specific action of mechanism of bronopol and/or major degradation products, and suggest that adaptation to these compounds is theoretically impossible (Legin, 1996).

3.4. Toxicity profile of bronopol under degradation processes in natural water

The light increased toxicity of bronopol to both species during all exposure period, represented by a water site-dependent increase in relative PTI (Fig. 6). However, the light led to lower relative PTI compared to their corresponding dark controls. As it is mentioned above, bronopol can both hydrolyze and photolyze to two major degradation products BNE and BNM in the light, and these products easily decompose via photodegradation. However, only hydrolysis occurs in the dark controls, and both degradation products are resistant to further reduction and hence accumulated in the dark.

![Fig. 6. Relative PTI of bronopol (BNP) over its photodegradation in five natural waters.](image)

![Fig. 7. Relative PTI of bronopol (BNP) over its hydrolysis in five natural waters.](image)

As shown in Fig. 7, remarkable differences in the relative PTI of bronopol occurred upon its hydrolysis in five natural waters. Water sample 2 and 3 had high relative PTI all through the incubation period. The relative PTI of other three waters first increased, then reduced, and on day 40 recovered to a comparable level of initial values. These results indicated that the toxicity of bronopol to the algae remained for a relatively long term. In the case of Vibrio fischeri, the relative PTI of bronopol exhibited similar evolution in five natural waters.

In general, an increase in toxicity for various reaction systems occurred when products of higher toxicity were formed in adequate levels and/or could expose for appropriate period (Cai et al., 2009; Kralj et al., 2007; Zhou et al., 2009). Accordingly, such degradation products (e.g., BNE and BNM) which are more persistent and toxic than the parent, have greater potential to occur in the environment and be exposed to biota, and then cause prolonging adverse impacts to environment.

The PTI, in theory, is the sum of toxicity quotients for individual compound detected, based on the concentration addition of toxicity (Munn et al., 2006). However, the PTI in the present study was actually less than the intrinsic risks of the preservative, because formaldehyde and other transformation products (e.g., 2-BE, NM, TNM, nitrite, and other unidentified compounds) were ignored as well as the occurrence of synergistic interaction of bronopol and transformation products (Wang et al., 2008).

4. Conclusions

The preservative bronopol can rapidly degrade via hydrolysis and photolysis in natural waters, representing water-site dependent degradation rates and pathways. In natural waters, some reversible degradation pathways (e.g., retroaldol reaction) resulted in a complicated mixture of degradation products which were affected by pH, light, and water characteristics. Combining the simulated experiments and the bond order analysis, 2-bromo-2-nitroethanol (BNE) and bromonitromethane (BNM) identified as major transformation products via the retroaldol reactions, were found to be more persistent than the parent, and probably accumulated in the environment. Most of the degradation products of the preservative were found to be equal to higher toxic to aquatic biota. Accordingly, the occurrence of these transformation products...
can lead to comparable or higher risks for a considerable period despite a rapid and complete degradation of the parent.

Overall ecological risks of bronopol, actually, should consist of the direct impacts caused by bronopol itself and the indirect impacts caused by its transformation products. As a result, its ecological risk will greatly depend on its environmental processes, such as hydrolysis and photolysis, in which corresponding transformation products occur with intrinsic toxicity and environmental stability.

More transformation products are increasingly detected as emerging contaminants in natural waters, and are derived from both persistent toxic substances and labile pollutants. In general, they exhibit significantly different toxicity and/or persistence compared to the parent, which should be considered as indirect impacts of the parent. More attention therefore should be given to labile pollutants (e.g., bronopol) which are often considered as low risks and sometimes cause formation of more persistent and/or toxic degradation products.

Acknowledgements

This study was supported by the National Basic Research Program of China (No. 2006CB403302), the National Natural Science Foundation of China (No. 20707002), the Fok Ying Tung Education Foundation of China (No. 20090450103), and the Program for Changjiang Scholars and Innovative Research Team in University (No. IRT0813).

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