Effects of inorganic anions on the photolysis of triclosan under UV irradiation
Lei Chen, Zhipeng Wang, Cheng Qian and Yuchen He

ABSTRACT
Triclosan is a widely used antimicrobial agent and may pose health risks to many aquatic organisms. Photodegradation is an important transformation pathway for triclosan, but studies on the effects of inorganic anions on photodegradation of triclosan are limited. In the present study, the single and combined effects of NO₃⁻/CO₃²⁻, Cl⁻/CO₃²⁻ and HCO₃⁻/CO₃²⁻ on the photolysis of triclosan in aqueous solutions under UV irradiation was evaluated. The results showed that photodegradation of triclosan was inhibited by NO₃⁻ and promoted by HCO₃⁻, while no significant effect was observed with Cl⁻/CO₃²⁻. When Cl⁻/CO₃²⁻ was added to NO₃⁻/CO₃²⁻, no effect was observed, but the addition of Cl⁻ hindered the promotion effect of HCO₃⁻. The coexistence of NO₃⁻, Cl⁻ and HCO₃⁻ inhibited the photolysis of triclosan. These results showed the complex effects of inorganic anions in the photolysis of triclosan and provide useful information for an accurate ecological risk assessment of triclosan in natural waters. It will also help to develop appropriate treatment ways of triclosan.

Key words | direct photodegradation, inorganic anions, triclosan

INTRODUCTION
Triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol, TCS) is an antimicrobial agent that has been widely used in personal care products, such as soap, toothpaste, shampoo, disinfectant, and skin cream. Triclosan from the daily use of these personal care products often ends up in municipal wastewater treatment plants. However, removal efficiencies of triclosan in conventional wastewater treatment plants were only in the range of 57–99% (Bedoux et al. 2012), and remaining triclosan eventually transfers to surface waters. Because of its widespread usage, triclosan is one of the most commonly detected contaminants in surface waters, with a concentration as high as 2.3 μg/L (Dhillon et al. 2015). The frequent detection of triclosan has generated great public health concerns because of its potential toxicity to wildlife and human beings. Previous studies have shown acute toxicity, genotoxic effects and even estrogen effects of triclosan to many organisms including crustaceans, zebra mussels, zebrafish, microalgae, insects and rats (Bedoux et al. 2012; Hwang et al. 2014; Dhillon et al. 2015).

Photolysis is one of the most important transformation pathways of triclosan in surface waters. Direct photolysis has been identified as a predominant photochemical process of triclosan in surface waters, and dioxin products are formed via an intramolecular photochemical substitution reaction (Wong-Wah-Chung et al. 2007). Nevertheless, recent studies showed that indirect photolysis of triclosan sensitized by dissolved organic matter in natural waters under sunlight irradiation was also important for photolysis of triclosan and humic acid at low concentrations enhanced photodegradation of triclosan and yielded less dioxin products (Chen et al. 2016a). Additionally, other commonly available inorganic anions in natural waters, such as nitrate (NO₃⁻), bicarbonate (HCO₃⁻) and chloride ions (Cl⁻) could promote or inhibit the photodegradation of many organic compounds (Ding et al. 2015; Ge et al. 2016; Peng et al. 2016; Xu et al. 2016). However, no studies have been reported on the effects of these inorganic anions on the photodegradation of triclosan. Therefore, there is a critical need to evaluate the effects of inorganic anions on photolysis of triclosan.

The objective of this study was to evaluate the effects of NO₃⁻, Cl⁻ and HCO₃⁻ on the photolysis of triclosan in aqueous solutions under ultraviolet (UV) irradiation. As the inorganic anions often coexist in natural waters, their combined effects on the photolysis of organic compounds were also investigated in this study.

doi: 10.2166/wst.2018.421
MATERIALS AND METHODS

Triclosan (powder, ≥97%) was purchased from Sigma-Aldrich (St Louis, MO, USA). Methanol, acetonitrile and 2-propanol were in high performance liquid chromatography grade. Sodium nitrate (NaNO₃), sodium chloride (NaCl) and sodium bicarbonate (NaHCO₃) were analytical-grade reagents purchased from Bailingwei Company (Shanghai, China). Ultrapure water (electrical resistivity >18.2 MΩ·cm) was collected from a Millipore purification system (Millipore S.A.S, Molsheim, France). Other chemicals and solvents were at least in analytical-reagent grade.

The stock solution of triclosan with a concentration of 1,000 mg/L was prepared in acetonitrile. Triclosan (1 mg/L), inorganic anions and ultrapure water were added into 30 mL quartz glass tubes with screw caps. As various concentrations were used in the literature, a relatively low concentration which represented the level in natural waters and a relative high concentration which represented the level in wastewater were selected for each anions (10 and 50 mg/L for NO₃⁻, 10 and 50 mg/L for HCO₃⁻, and 50 and 100 mg/L for Cl⁻) (Santiago et al. 2014; Ding et al. 2015; Ge et al. 2016; Peng et al. 2016; Wang et al. 2016; Xu et al. 2016). Initial pH of each solution was adjusted to 7.0 by adding perchloric acid or sodium hydroxide. The reaction tubes were then put into a photochemical reactor (YM-GHX-V, Yuming Instrument Company, Shanghai, China) with a cooled Hg lamp (350 W) in the center. The reaction solutions were magnetically stirred and a constant temperature of 25°C was maintained throughout the experiment. Control experiments with tubes covered with aluminum foil were also conducted in the reactor. Concentrations of triclosan were analyzed by Hitachi L-2000 HPLC (Japan) equipped with ODS-C18 column (4.5 mm × 250 mm, 5 μm) and DAD. The mobile phase consisted of 70% acetonitrile and 30% ultrapure water (v/v) at a constant flow rate of 1 mL/min. The detection wavelength of diode-array detector (DAD) was 280 nm.

All statistical analyses were conducted with Statistical Package for the Social Sciences (SPSS) 16.0. One-way analysis of variance (ANOVA) was applied to detect significant differences and the statistical significance was accepted at p < 0.05.

RESULTS AND DISCUSSION

No obvious degradation of triclosan was observed for each dark control, suggesting that volatilization, direct hydrolysis or biodegradation of triclosan was negligible without UV irradiation throughout the experiment. The influence of nitrate on the photodegradation of triclosan is shown in Figure 1, where C₀ was the initial concentration of triclosan and Cₜ was concentration at time t (Cₜ). The photolysis kinetics of triclosan in solutions with and without the addition of NaNO₃ all fitted well with the pseudo-first-order rate expression (r² values ranged from 0.98 to 0.99). The rate constants (k₀bs) and half-lives (t₁/₂) are shown in Table 1. Nitrate is ubiquitously present in natural water, with the concentration ranging from 10⁻⁵ to 10⁻³ mol/L (Ding et al. 2015).

![Image](https://iwaponline.com/wst/article-pdf/78/7/1476/505272/wst078071476.pdf)

**Figure 1** Effect of nitrate on the photolysis of triclosan in aqueous solution under UV irradiation.

**Table 1** Photolysis rate constants (k₀bs) and half-lives (t₁/₂) of triclosan (TCS) in different solutions under UV irradiation

<table>
<thead>
<tr>
<th>Solutions</th>
<th>k₀bs (min⁻¹)</th>
<th>t₁/₂ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCS</td>
<td>0.2601</td>
<td>2.665</td>
</tr>
<tr>
<td>TCS + 10 mg/L NaNO₃</td>
<td>0.2298</td>
<td>3.016</td>
</tr>
<tr>
<td>TCS + 50 mg/L NaNO₃</td>
<td>0.1612</td>
<td>4.300</td>
</tr>
<tr>
<td>TCS + 50 mg/L NaCl</td>
<td>0.2632</td>
<td>2.634</td>
</tr>
<tr>
<td>TCS + 100 mg/L NaCl</td>
<td>0.2695</td>
<td>2.572</td>
</tr>
<tr>
<td>TCS + 10 mg/L NaHCO₃</td>
<td>0.3407</td>
<td>2.034</td>
</tr>
<tr>
<td>TCS + 50 mg/L NaHCO₃</td>
<td>0.5132</td>
<td>1.351</td>
</tr>
<tr>
<td>TCS + 10 mg/L NaNO₃ + 50 mg/L NaCl</td>
<td>0.2265</td>
<td>3.060</td>
</tr>
<tr>
<td>TCS + 10 mg/L NaHCO₃ + 50 mg/L NaCl</td>
<td>0.3179</td>
<td>2.180</td>
</tr>
<tr>
<td>TCS + 10 mg/L NaNO₃ + 10 mg/L NaHCO₃</td>
<td>0.2752</td>
<td>2.519</td>
</tr>
<tr>
<td>TCS + 10 mg/L NaNO₃ + 50 mg/L NaCl + 10 mg/L NaHCO₃</td>
<td>0.2494</td>
<td>2.779</td>
</tr>
</tbody>
</table>
that nitrate usually enhanced the photodegradation of most organic compounds because of reactive oxygen species (ROS), such as \( ^\cdot \text{OH} \), \( ^{1}\text{O}_2 \), and reactive nitrogen species (RNS) produced from the excitation of nitrate under UV irradiation (Niu et al. 2015; Chen et al. 2015; Xu et al. 2016). However, the results in this study showed the addition of \( \text{NaNO}_3 \) inhibited the photodegradation of triclosan. Higher concentration of \( \text{NaNO}_3 \) reduced the photolysis rate constant of triclosan. The inhibition effects of nitrate on the photolysis of organic compounds were also observed in other studies (Ding et al. 2015; Dugandžić et al. 2017). Nitrate has a strong absorbance of UV light within the range of 200–240 nm (Ding et al. 2015). Besides, nitrate could scavenge the reactive oxygen species and the excited state of organic compound (Chen et al. 2015; Ding et al. 2015). The competitive absorbance for UV light and the scavenging of reactive substances both lead to the inhibition to the photolysis of organic compounds and the inhibition effect was stronger when the concentration of nitrate was higher (Peng et al. 2015).

Similar to other photoreactive species such as humic substances and Fe(III), \( \text{NO}_3^-/\text{C}_0 \) could show both inhibition or promotion effects and one of the effects may dominate depending on pollutant properties, light sources, and aqueous pH values (Vione et al. 2015; Ge et al. 2016). The promotion effects by producing reactive oxygen species were usually more apparent for organic compounds whose direct photolysis rate is relatively slow (Chen et al. 2012; Xu et al. 2016). In this study, triclosan could undergo direct photolysis under UV irradiation at a relatively high rate and the competitive absorbance for UV light of \( \text{NO}_3^- \) seemed to be stronger than its promotion effects.

No significant inhibition or promotion to the photodegradation of triclosan by chloride ions was observed in this study, as shown in Figure 2 and Table 1. The photolysis kinetics of triclosan in solutions added with chloride ions also fitted well with pseudo-first-order rate reactions and \( r^2 \) ranged from 0.996 to 0.998. The results suggested that chloride ions showed no effect on the photolysis of triclosan in this study. The production of \( ^\cdot \text{OH} \) radicals from chloride under UV irradiation was proved by Nowell & Hoigné (1992) and its promotion effect on the photolysis of organic compounds have been reported previously (Jin et al. 2011; Wang et al. 2016). Conversely, chloride ions have also been reported to inhibit photolysis of organic compounds because of their competitive absorbance for light or their hole scavenging properties (Wang et al. 2013; Ge et al. 2016). When the concentrations of organic compounds increased, chloride ions strongly inhibited photolysis of organic compounds (Dugandžić et al. 2017). In this study, both inhibition and promotion effects of chloride ions could coexist and be canceled out as the two effects were similar. The addition of \( \text{NaHCO}_3 \) significantly promoted the photodegradation of triclosan, as shown in Figure 3 and Table 1. The photolysis kinetics of triclosan in solutions added with \( \text{NaHCO}_3 \) fitted well with pseudo-first-order rate reactions and \( r^2 \) ranged from 0.995 to 0.996. The inhibition of bicarbonate ion was often observed during the indirect photolysis of organic compounds involving \( ^\cdot \text{OH} \) and the inhibition effect was due to the scavenging of \( ^\cdot \text{OH} \) by bicarbonate (Wang et al. 2015). The direct photolysis of triclosan under UV irradiation in this study did not involve...
any \( \cdot OH \), thus \( HCO_3^- \) did not show any inhibition effect on the photolysis of triclosan. Although \( HCO_3^- \) could not absorb UV light like \( NO_3^- \) to form reactive substances, \( HCO_3^- \) could react with the active radicals of triclosan from the direct photolysis of triclosan and generate carbonate radicals (\( CO_3^- \)), which is an oxidant (Peng et al. 2016; Xu et al. 2016), which may be the one of the reasons for the observed promotion of photodegradation of triclosan in this study.

The photolysis kinetics of triclosan in solutions with coexisted \( NO_3^- \), \( Cl^- \) and \( HCO_3^- \) fitted well with a pseudo-first-order rate reaction and \( r^2 \) values ranged from 0.96 to 0.99 and \( k_{obs} \) and \( t_{1/2} \) are shown in Table 1. The photolysis rate constant of triclosan in solution with coexistence of \( NO_3^- \) and \( Cl^- \) was similar to that in presence of \( NO_3^- \) alone, indicating that there was no observable interaction between nitrate and chloride ions. However, when \( HCO_3^- \) and \( Cl^- \) coexisted, the photolysis rate constant of triclosan decreased compared with that in the presence of \( HCO_3^- \) alone, which was possibly attributed to scavenged \( CO_3^- \) by \( Cl^- \) and hindered promotion effect of \( HCO_3^- \). The photolysis rates of triclosan in solutions added with both \( NO_3^- \) and \( HCO_3^- \) were higher than that in solutions added with \( NO_3^- \) alone but slower than that in solutions added with \( HCO_3^- \) alone, which was possibly explained by the antagonistic effects of these \( NO_3^- \) and \( HCO_3^- \) on the photolysis of triclosan. When all inorganic anions coexisted, the photolysis rate of triclosan was slower than that in the solution without any addition of inorganic anions, suggesting that the combined effects of the three inorganic anions was inhibition to the photolysis of triclosan.

Photolysis has been found to be one of the most important transformation pathways for triclosan in natural waters and water treatment. Triclosan can absorb sunlight or UV light and easily undergo direct photo-transformation (Sanchez-Prado et al. 2006; Dhillon et al. 2015). The direct photodegradation pathways of triclosan has been studied extensively and the main degradation products were monochlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol dichlorhydroxydiphenyl ether and polychlorodibenzo-p-dioxins (Aranami & Readman 2007; Chen et al. 2016a). With a similar chemical structure to some emerging contaminants such as polychlorinated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and diethylstilbestrol, triclosan and its degradation products are likely to absorb to the sediment and even accumulate in wildlife and human bodies due to their hydrophobic character (Palenske et al. 2010; Dann & Hontela 2011; Higgins et al. 2011). Among these products, polychlorodibenzo-p-dioxins with a formation yield of nearly 4% are mainly concerned because of their high acute and genetic toxicity (Kliegman et al. 2013). Chlorophenols has been proven to show lower acute toxicity and chronic toxicity to fish, daphnid and green algae than triclosan (Gao et al. 2014). In our previous study, increased acute toxicity and genetic toxicity of triclosan solutions were observed after 24 h of simulated sunlight irradiation (Chen et al. 2016b).

Therefore, the results of this study showed that the inhibition effect of coexistence of three inorganic anions might reduce the photo-induced ecological risk of triclosan in natural waters. In addition to the effects on the fate and ecological risk of triclosan in natural waters, the results in this study also suggest that the coexistence of nitrate, bicarbonate and chloride ions could help reduce the risk of triclosan during the UV disinfection process of water and wastewater treatment. Furthermore, it is suggested that direct photolysis might not be an appropriate way to treat triclosan in wastewater, especially when nitrate, bicarbonate and chloride ions are present.

**CONCLUSIONS**

\( NO_3^- \), \( HCO_3^- \), and \( Cl^- \) are ubiquitously present in natural waters and wastewaters. The present study showed that \( NO_3^- \) could inhibit the photodegradation of triclosan, while \( HCO_3^- \) would promote the photolysis of triclosan significantly. When \( HCO_3^- \) and \( Cl^- \) coexisted, \( Cl^- \) hindered the promotion effect of \( HCO_3^- \). The coexistence of three inorganic anions inhibited the photolysis of triclosan. The influence of these inorganic anions should be considered when elucidating the fate and ecological risk of triclosan in natural waters and engineering water and wastewater treatment. The findings of this study will help us to better understand the photolysis process and ecological risk of triclosan in natural waters as well as to develop appropriate treatment processes for effective triclosan removal.

**ACKNOWLEDGEMENTS**

This work was supported by the National Natural Science Foundation of China (No. 41301545) and the Priority Academic Program Development of Jiangsu Higher Education Institutions Fund. The authors also want to thank Prof. Zhi Zhou from Purdue University for the language checking of this paper.
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