Comparison of the photoconversion of 1-chloronaphthalene and 2,3-dichlornaphthalene in water
Chunli Kang, Siqi Bao, Yuhan Wang, Kunkun Xiao, Ling Zhu, Fang Liu and Tao Tian

ABSTRACT
In this work, the photoconversion of 1-chloronaphthalene (CN-1) and 2,3-dichlornaphthalene (CN-10) under the simulated sunlight had been studied. The results showed that the photoconversion of CN-1 and CN-10 obeyed the first-order kinetics model. NO2/C0, NO3/C0, Fe3+ and Fe2+ extensively present in natural water can accelerate CN-1 photoconversion via generating ·OH, which may induce indirect photooxidation of CN-1. The photoproducts were treated by the derivatization method and analyzed by GC-MS after being irradiated for 6 h. Ten products were characterized for CN-1 and CN-10, and there were six common products. On this basis, the photoconversion pathways of CN-10 and CN-1 were proposed, and both of them have a similar conversion mechanism.

Key words | 1-chloronaphthalene, 2,3-dichlornaphthalene, hydroxyl radical, photoconversion, poly-chlorinated naphthalenes, singlet oxygen

INTRODUCTION
Polychlorinated naphthalenes (PCNs) are a group of compounds considered as potential persistent organic pollutants (POPs). They consist of naphthalene molecules with 1–8 chlorine substituents and thus can yield 75 possible congeners. PCNs are ubiquitous contaminants found in air, snow, rivers, sediments and biota, even in the polar environments (Liu et al. 2015; Ali et al. 2016; Lega et al. 2017). Historically, because of their special physiochemical properties such as high chemical stability, high insulativity and low inflammability, PCNs have been widely used in many applications, including the use as wood preservatives, electroplating masking compounds, lubricants, separators in batteries, additives to paints, flame retardants and for cable insulation in capacitors (Cetin 2016; Li et al. 2017; Odabasi et al. 2017). Although their production has been banned in most countries since the 1980s, PCNs also can be released into the environment via unintentional emissions from past applications and products (Yang et al. 2017). The emissions of PCNs in UNECE-Europe for the year 2000 were estimated to be 1.003 tonnes/year (Braune & Muir 2017). By industrial thermal processes or incineration processes of halogenated aromatic compounds, such as polychlorinated biphenyl (PCBs), polychlorinated dibenzodioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs), PCN are released to the environment (Nomura et al. 2013; Fernandes et al. 2017; Li et al. 2017). With the time going on, however, the contamination of the environment by PCNs and their dioxin-like toxicity toward humans has been recognized (Jin et al. 2016; Xue et al. 2016; Fernandes et al. 2017). Because they are resistant to environmental degradation (Järnberg et al. 1999) and easily bioaccumulate through the food web (Cui et al. 2018), they pose a risk of causing adverse effects on the humans and environment, and have been listed in Annexes A and C of the Stockholm Convention on POPs in May 2015 (Stockholm Convention), signifying that there will be an increase in activities aimed at monitoring and controlling unintentionally produced PCNs from industrial sources around the world.

Many chlorinated organic compounds are sufficiently toxic such that their presence, even in low concentrations, in water is unacceptable. Furthermore, most chlorinated organic compounds have long half-lives in natural environment (Sinha & Bose 2006). Because PCNs exhibit moderate absorption more than 300 nm region due to a π-π* transition, the photoconversion is an important way for the transformation of PCNs in water. However, the existing literature on the photoconversion of PCNs are all performed in organic solutions. Ruzo et al. (1975) deduced
that dechlorination and dimerization were the major reaction pathways of PCNs in methanol solution. Keum (2004) found that sequential dechlorination was the major photolysis mechanism of PCNs in hexane. Up to now, little information can be found on the photoconversion of PCNs in water.

As the components of PCNs, 1-chloronaphthalene (CN-1) and 2,3-dichloronaphthalene (CN-10) are mainly used for the production of dyes, wood preservatives, fungicides, special cleaning agents and organic synthesis intermediates. The aims of the work are: (1) to study the kinetic photoconversion process of CN-1 and CN-10 and the effect of ·OH and 1O2 during the photoconversion; (2) to study the effect of added NO2-, NO3-, Fe3+ and Fe2+; (3) to elucidate the intermediate products and pathways of the photoconversion.

MATERIALS AND METHODS

Materials

CN-1 (97% purity) and CN-10 (98% purity) were purchased from Sinopharm Chemical Reagent Co., Ltd and Ultra Scientific, respectively, without any further purification. CN-1 and CN-10 were dissolved in hot deionized water and ultrasonic solubilization to prepare experimental solutions. Methanol, isopropanol (IPA) and furylcarbinol (FFA) (HPLC grade; Tedia USA), benzoic acid (BA), sodium benzoate (BA-Na), sodium azide (NaN3), NaNO3, NaNO2, FeSO4 and Fe2(SO4)3 (analytically pure; Beijing Chemical Plant) were used directly without any treatment.

Irradiation experiments

The initial concentrations of CN-1 and CN-10 were 0.61 μmol·L−1 in this paper. Irradiation experiments were carried out in a self-made solar simulator apparatus equipped with a 400W high-pressure mercury lamp (Shanghai Philips Co., China). The temperature was measured and kept constant at 32 ± 1°C in all the experiments. The 10 mL samples subjected to irradiation were kept in a capped cylindrical glass tubes (15 mL) of 100 × 15 mm (length × diameter). Tubes were positioned set around the lamp at 10 cm to get the same quantity of photos by using a metallic shelf. The wavelength of the light through the glass is more than 280 nm, therefore, the irradiation the samples obtained can be almost considered as the sunlight. The light intensity measured with a digital photometer was 11 × 104 Lx. Dark control experiments were conducted in parallel for CN-1 and CN-10.

Analytical methods

The irradiation samples were analyzed using a high-performance liquid chromatography (Shimadzu) performed with a Shimadzu fluorescence detector (RF-20A), equipped with Shimadzu LC-20 AT pump. Injections were carried out using a Rheodyne valve with a sample loop volume of 20 μL fitted to a Shimadzu autosampler. An InertSustain C18 (150 mm × 3.9 mm, 5 μm), operated at 30 °C, was used as column. The mobile phase was methanol and purified water (88:12, v/v) with a flow rate of 1.0 mL·min−1 and the excitation and emission wavelengths were 280 nm and 335 nm, respectively, for CN-1. The mobile phase was methanol and purified water (90:10, v/v) with a flow rate of 1.0 mL·min−1 and the excitation and emission wavelengths were 275 nm and 334 nm, respectively, for CN-10.

A chemical probe method was used to determine the concentration of ·OH produced in the photoconversion process. The mixed solution containing 0.64 mmol/L BA and 5.76 mmol/L BA-Na was added into the initial reaction solution to capture ·OH in the system. The concentration of ·OH in the sample was indirectly determined by analyzing the concentration of p-hydroxybenzoic acid (p-HBA) in it (Kang et al. 2017). Since it was highly selective for singlet oxygen (1O2) and didn’t react with other active radicals such as ·OH, H2O2 and O2−, FFA was used as the probe for 1O2 (Haag et al. 1984; Appiani & McNeill 2015). The concentrations of FFA were measured using a HPLC system consisting of a: Shimadzu LC-20A UV-Vis detector; InertSustain C18 column; eluent of 10% CH3CN/90% purified water; flow rate of 0.6 mL·min−1; detection wavelength of 230 nm; and injection loop volume of 20 μL. Apparent-first order rate constants for loss of FFA (k′FFA) were determined from the slope of plots of ln([FFA]/[FFA]0) versus illumination time, where [FFA] and [FFA]0 are the molar concentrations of FFA at time t and t = 0, respectively. The 1O2 concentrations were estimated by monitoring the loss of FFA in illuminated samples containing PCNs as the source of 1O2: the measured rate constant for FFA loss, k′FFA, is proportional to the singlet oxygen steady-state concentration.

The photoproducts were treated by the derivatization method, which was reported previously (Liu et al. 2015). The organic phase was collected, and then analyzed by GC–MS after being concentrated to 1.5 mL under very gentle stream of nitrogen. Detailed description of
temperature program and other GC-MS parameters were reported previously (Kang et al. 2017).

RESULTS AND DISCUSSION

Comparison of the photoconversion of CN-1 and CN-10

The comparison of the light and dark reactions of CN-1 and CN-10 in water is presented in Figure 1. The comparison of the UV-Vis absorption spectra of CN-1 and CN-10 is shown in Figure S1 of the Supporting Information (SI) (available with the online version of this paper). In the dark controls, no loss of CN-1 and CN-10 were observed after 6 h in water, which indicated that CN-1 and CN-10 were stable in the absence of irradiation, and the loss of CN-1 and CN-10 were negligible during the whole illumination process under the experimental conditions. Under irradiations, CN-1 and CN-10 could be photoconverted. This was because CN-1 and CN-10 can absorb light of a wavelength greater than 300 nm. The photoconversion efficiency of CN-1 and CN-10 after 6 h of irradiation reached 64.51% and 31.20%, respectively. The kinetic data of CN-1 and CN-10 according to a first-order kinetic model are summarized in Table 1. As expected, the reaction rate constant of CN-1 was much higher than that of CN-10. This may be due to the fact that the chlorine atom is a strong electron-withdrawing group. With the number of chlorine atoms increasing, a triple-double-stabilizing structure can be formed (Figure S2, available online) (Ruzo et al. 1975; Kan et al. 2015), thus deteriorating the activity and reducing the photoconversion efficiency.

Effects of ·OH and 1O2

It has been shown that ·OH and 1O2 are the main factors affecting the photoconversion of pollutants in aqueous solution. Both of them have strong oxidative abilities. Especially, ·OH has a high oxidation activity (standard electrode potential of 2.80 eV), which ranks only second to fluorine, and can react with most organic compounds with a reaction rate constant up to 10^6–10^10 L·mol⁻¹·s⁻¹ (Elovitz & von Gunten 1999).

By investigating the concentration of ·OH and 1O2, it was found that both of ·OH and 1O2 were produced during the photoconversion of CN-1 (Figure 2). The production of ·OH may be that CN-1, as a kind of photosensitizer, generated its transient excited state under the simulated sunlight, which reacted with water to form ·OH (Equations (1) and (2)). 1O2 can be generated by the excitation of oxygen (Equation (3)), thus a small quantity of 1O2 was produced in pure water (Bower & Anastasio 2013). However, the reaction of O2 with the transient excited state of CN-1 seriously increased the production of 1O2 (Equation (4)).

\[
\begin{align*}
CN - 1 + \text{hv} &\rightarrow [CN - 1]^* \\
[CN - 1]^* &\rightarrow \cdot \text{OH} \\
O_2 + \text{hv} &\rightarrow ^1\text{O}_2 \\
[CN - 1]^* + O_2 &\rightarrow ^1\text{O}_2
\end{align*}
\]

To prove the effects of the active groups (1O2 and ·OH), 1O2 and ·OH were respectively quenched by adding NaN3 and IPA as scavengers during the photoconversion of CN-1, the results showed that the photoconversion efficiency of CN-1, which was 64.51% in water without the presence of...
the scavengers, was seriously inhibited after adding scavengers (Figure 3). Hence, such a conclusion can be drawn that $^1O_2$ and $\cdot$OH were produced in the photoconversion of CN-1 and showed positive effects on the photoconversion process.

**Effects of water constituents nitrate, nitrite, Fe(III) and Fe(II)**

The natural water contains numerous photo-active materials, which can absorb photons to produce active groups such as $\cdot$OH, and thus induce indirect photochemical degradation and photoconversion of organic pollutants (Velo-Gala et al. 2017). In order to investigate the effect of typical inorganic ions in natural water, NO$_2^-$, NO$_3^-$, Fe$^{3+}$ and Fe$^{2+}$ were tested. The photoconversion efficiency of CN-1 in the presence of photo-active materials was compared with the concentration of $\cdot$OH in the system. It can be seen from Figure 4 that the addition of four ions promoted the photoconversion of CN-1 (Figure 4(a)–4(d)), and with the concentration of four ions increasing, the concentration of $\cdot$OH in the system increased (Figure 4(a)–4(d)). It was proved that NO$_2^-$, NO$_3^-$, Fe$^{3+}$ and Fe$^{2+}$ can accelerate CN-1 photoconversion via generating $\cdot$OH, which may induce indirect photooxidation of CN-1.

NO$_2^-$ and NO$_3^-$ can absorb sunlight with wavelengths of more than 290 nm, and their characteristic absorption peak take place at 355 and 305 nm, respectively. NO$_2^-$ and NO$_3^-$ can generate $\cdot$OH during the photochemical reaction (Equations (5) – (7)), thus promote the photoconversion of organic matter (Jacobi et al. 2006).

$$\text{NO}_2^{-} \overset{h \nu}{\rightarrow} [\text{NO}_2]^* \rightarrow \text{NO}^+ + O^-$$  \hspace{1cm} (5)

$$O^- + H_2O \leftrightarrow \cdot \text{OH} + OH^-$$  \hspace{1cm} (6)

$$\text{NO}_3^- + H_2O + h \nu \rightarrow \text{NO}_2^+ + HO^- + \cdot \text{OH}$$  \hspace{1cm} (7)

Figure 4(a) and 4(b) show that along with the concentration of NO$_2^-$ and NO$_3^-$ increasing from 0.04 mmol/L to 0.4 mmol/L, the concentration of $\cdot$OH and the photoconversion efficiency of CN-1 had a significant promotion. With the concentration of NO$_2^-$ and NO$_3^-$ increasing to 4 mmol/L, the increase of photoconversion efficiency of CN-1 was not apparent, which can be explained by the reason that NO$_2^-$ and NO$_3^-$ absorbed a large amount of light, to some extent, and prohibited the absorption of light of CN-1 and

![Figure 2](image1.png)

**Figure 2 |** The production of $\cdot$OH (a) and $^1O_2$ (b) during the photoconversion of CN-1.

![Figure 3](image2.png)

**Figure 3 |** Effects of NaN$_3$ and IPA on the photoconversion of CN-1.
the photoconversion efficiency was accordingly inhibited. Furthermore, NO₂ in the original system or the NO₂ produced by the photolysis of NO₃ (Equation (8)) can react with the generated ·OH to consume ·OH (Equation...
(9). However, with the concentration of NO$_2$ and NO$_3$ increasing from 0.4 mmol/L to 4 mmol/L, the concentration of ·OH did not decrease significantly in the system (Figure 4(a) and (b)), indicating that the absorbance inhibition is the main reason.

\[ \text{NO}_3^- \xrightarrow{hv} \text{NO}_2^- + \text{O}(3P) \]  
(8)

\[ \text{NO}_2^- + \text{OH} \rightarrow \text{NO}_2 \cdot + \text{HO}^- \]  
(9)

Fe$^{3+}$ and Fe$^{2+}$ are one of the most abundant transition metal ions in natural environment, and play an important role in the water environment photochemical reaction and geochemical and biological process (Long et al. 2017). Fe$^{3+}$ can generate ·OH (Equation (10)) efficiently which has strong oxidizing capacity in photochemical reactions, thus promoting the transformation of organic pollutants.

\[ \text{Fe}^{3+} + \text{H}_2\text{O} \xrightarrow{hv} \text{Fe}^{2+} + \cdot \text{HO} + \text{H}^+ \]  
(10)

With the increasing of the concentration of Fe$^{3+}$ and Fe$^{2+}$, the concentration of ·OH in the system was accelerated (Figure 4(c) and 4(d)), promoting the photoconversion of CN-1 (Figure 4(c) and 4(d)). In the presence of Fe$^{2+}$, Fe$^{3+}$ reacted with oxygen or direct photolyzed to Fe$^{3+}$ ((Equations (11) and (12)), and then further produced ·OH (Equation (10)) (Catastini et al. 2002), leading to promoting the photoconversion of CN-1. Due to the cycle transformation process of Fe$^{3+}$ and Fe$^{2+}$, the reaction can occur in a row.

\[ \text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{O}_2 \]  
(11)

\[ \text{Fe}^{2+} \xrightarrow{hv} \text{Fe}^{3+} + \text{e}^-_{\text{aq}} \]  
(12)

The kinetic data of photoconversion of CN-1 and ·OH generation in the system are summarized in Table 2.

As shown in Table 2, in the presence of NO$_2$, the photoconversion efficiency of CN-1 was larger than NO$_3$, which was consistent with the ·OH generation efficiency. Therefore, the effect of NO$_2$ on the photoconversion of CN-1 was greater than NO$_3$, which is consistent with literature results (Boxe et al. 2005).

In the presence of Fe$^{2+}$ and Fe$^{3+}$, the order of the ·OH generation efficiency was Fe$^{3+} >$ Fe$^{2+}$, the same as the photoconversion efficiency of CN-1, which drew the conclusion that the promoting effect of Fe$^{2+}$ on the photoconversion of CN-1 was weaker than Fe$^{3+}$. It could be attributed to the ·OH generation efficiency which produced by Fe$^{3+}$ (Equation (10)). However, the promoting role can play after Fe$^{2+}$ was oxidized to Fe$^{3+}$ (Equations (11) and (12)).

**Effects of fulvic acid**

Natural water contains a large amount of humic acid, which as an important natural photosensitizer can absorb visible light to generate excited states and various reactive oxygen free radicals, thereby inducing indirect photodegradation and phototransformation of organic pollutants. In addition, humic acid has a light shielding effect, which inhibits photodegradation and photoconversion of organic pollutants (Rosario & Canonica 2018). In this section, fulvic acid (FA) was selected as the main component of humic acid. The effect of different concentrations of FA on the photoconversion of 1-chloronaphthalene is shown in Figure 5.

It can be seen from the figure that the addition of different concentrations of FA promoted the photoconversion of 1-chloronaphthalene. Specifically, when the concentration of FA increased from 0 to 8 mg·L$^{-1}$, the photoconversion rate of 1-chloronaphthalene increased, however, as the concentration of FA continues to increase to 10 mg·L$^{-1}$, the photoconversion rate was reduced. This is because when the concentration of FA was lower (0–8 mg·L$^{-1}$), its

**Table 2** | The first-order kinetic equations and parameters of photoconversion of CN-1 and ·OH generation in the presence of NO$_2$, NO$_3$, Fe$^{3+}$ and Fe$^{2+}$ (C = 0.04 mmol/L)

<table>
<thead>
<tr>
<th>Reaction system</th>
<th>First order kinetics equation</th>
<th>Reaction rate constant k/h$^{-1}$</th>
<th>Half-life t$_{1/2}$/h</th>
<th>Coefficient of determination R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoconversion of CN – 1</td>
<td>CN – 1 + NO$<em>2$ ln(C$</em>{CN}$/C$_0$) = $-0.3037t - 0.1337$</td>
<td>0.3037</td>
<td>2.2819</td>
<td>0.9456</td>
</tr>
<tr>
<td></td>
<td>CN – 1 + NO$<em>3$ ln(C$</em>{CN}$/C$_0$) = $-0.2582t + 0.0226$</td>
<td>0.2582</td>
<td>2.6840</td>
<td>0.9861</td>
</tr>
<tr>
<td></td>
<td>CN – 1 + Fe$^{3+}$ ln(C$_{CN}$/C$_0$) = $-0.4440t + 0.1261$</td>
<td>0.4440</td>
<td>1.5608</td>
<td>0.9615</td>
</tr>
<tr>
<td></td>
<td>CN – 1 + Fe$^{2+}$ ln(C$_{CN}$/C$_0$) = $-0.3599t - 0.0030$</td>
<td>0.3599</td>
<td>1.9472</td>
<td>0.9730</td>
</tr>
<tr>
<td>·OH generation</td>
<td>NO$<em>2$ (·OH) ln(C$</em>{CN}$/C$_0$) = $-0.0621t - 0.0201$</td>
<td>0.0621</td>
<td>11.1594</td>
<td>0.9879</td>
</tr>
<tr>
<td></td>
<td>NO$<em>3$ (·OH) ln(C$</em>{CN}$/C$_0$) = $-0.0562t + 0.0168$</td>
<td>0.0562</td>
<td>12.3310</td>
<td>0.9845</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$ (·OH) ln(C$_{CN}$/C$_0$) = $-0.0732t + 0.0156$</td>
<td>0.0732</td>
<td>9.4672</td>
<td>0.9870</td>
</tr>
<tr>
<td></td>
<td>Fe$^{2+}$ (·OH) ln(C$_{CN}$/C$_0$) = $-0.0646t - 0.0114$</td>
<td>0.0646</td>
<td>10.7276</td>
<td>0.9903</td>
</tr>
</tbody>
</table>
shielding effect was negligible and it only showed a promotion effect. When the concentration was higher (10 mg·L⁻¹), the shielding effect could not be neglected, but still higher than without adding FA.

Photoconversion mechanisms of CN-1 and CN-10

The photoproducts were treated by the derivatization method and analyzed by GC-MS after being irradiated for 6 h. Ten products were characterized for CN-1 and CN-10, and there were six common products. GC-MS spectra of the photoproducts of CN-1 and CN-10 are shown in Figures S3 and S4 (available online) and the scheme for the photoconversion of CN-1 and CN-10 in water are shown in Figures 6 and 7.

As can be seen from Figure 6, the photoconversion of CN-1 in water underwent four steps. Combining previous studies (Kang et al. 2017), it is known that the pathways a, b, c were similar to CN-2. In pathway d, 8-chloronaphthol (3) generated chloro quinone (10) through substitution reaction and oxidation reaction, then formed 1-chlorobenzene (7) through a series of reactions such as oxidation reaction and decarboxylic reaction. 1-Chlorobenzene (7) was substituted by hydroxyl to produce 1-chlorophenol (8) and 2-chlorophenol (9). By comparing the toxicity of the reactants with the intermediate products, it can be concluded that the photoconversion process of 1-chloronaphthalene is a process that is a toxic reduction process.

The photoconversion pathway of CN-10 was similar to that of CN-1.

CN-10 underwent dechlorination and Cl rearrangement to form CN-1, which would undergo phototransformation through pathways a, b, c, but the intermediate product were somewhat different. The product (3) in Figure 6 was not detected during the process of photoconversion of CN-1; its concentration in the water was negligible.

Figure 5 | Effect of FA on the photoconversion of CN-1 in water.

Figure 6 | Scheme for the photoconversion of CN-1 in water (the products in the square brackets are transition state intermediates deduced).
The difference might be only due to the errors of the detection method. In addition, CN-10 underwent dechlorination, substitution reactions and oxidation reactions to form ortho-phthalaldehyde (11). Ortho-phthalaldehyde underwent oxidation reaction and combined with \( \cdot \text{Cl} \) to form the dichloro products (12)–(14), \( \cdot \text{OH} \) substituted products (8) and (9) could not form during the process of the photoconversion of CN-10.

**CONCLUSIONS**

This study shows that CN-1 and CN-10 can undergo photoconversion under relevant experiments conditions. The photoconversion of CN-1 and CN-10 obeyed the first-order kinetics model, and the photoconversion efficiency of CN-1 was much higher than CN-10 due to electronic and steric factors. In addition, we verified that \( ^1\text{O}_2 \) and \( \cdot \text{OH} \) were produced in the photoconversion and showed positive effects on the photoconversion process. Typical inorganic ions in natural water, \( \text{NO}_2^- / \text{NO}_3^- \), \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) enhanced the concentration of \( \cdot \text{OH} \) in the system and improved the photoconversion efficiency of CN-1. The photoproducts were treated by the derivatization method and analyzed by GC-MS. The photoconversion pathway of CN-10 was similar to that of CN-1, and they had six common products.

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