Phototransformation of nitrobenzene in the Songhua River: Kinetics and photoproduct analysis

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Abstract
Nitrobenzene (NB) pollution of the Songhua River caused by an explosion at a petrochemical plant in Jilin City, Jilin Province, China, attracted public concern over the fate of NB in the river. As one of the efforts to predict the fate of residual NB in the river, the kinetics and mechanism of phototransformation of NB in natural water from four sections of the Songhua River were investigated. It was found that photodegradation of NB in water proceeded via pseudo-first-order reaction kinetics under simulated solar irradiation conditions, and the rate constant ($k$) in the ultrapure water system was 0.0168 h$^{-1}$, which was approximately half of those in the natural river water systems (0.323–0.402 h$^{-1}$). The relatively short half-life of NB in natural river water systems (17.2–21.5 h) indicates that photodegradation might have played an important role in the loss of NB flux in the river. Nitrate concentration and alkalinity were the two main factors affecting the photochemical fate of NB, suggesting that decomposition of NB mediated by $\cdot$OH was predominant in water solution with high nitrate concentrations. Three isomeric nitrophenols, $o$-, $m$-, and $p$-nitrophenols, as well as phenol were detected as the main organic products in natural water under natural and simulated solar irradiations.

Key words: nitrobenzene; phototransformation; mechanism; the Songhua River; nitrate; by-products

Introduction
Nitroaromatic compounds are among the most abundant of environmental pollutants because of their uses as military ordnance compounds and as precursors for monomer synthesis. Their occurrence in the environment is of great concern because of their toxicity, stability, and role as precursors in the formation of compounds of possibly greater toxicity (ATSDR, 1990). Of these compounds, nitrobenzene (NB) is listed as priority toxic pollutants by the USEPA (Larson et al., 2000). The NB pollution of the Songhua River caused by an explosion at a petrochemical plant in Jilin City, Jilin Province, China, on 13 November 2005 attracted public concern over the fate of NB in the river. It was necessary to determine the aquatic fate of NB in the Songhua River to assess its environmental impact and potential health threats. Among the different transformation processes (abiotic and biotic), photodegradation is an important one influencing the fate of organic pollutants (Zafiriou et al., 1984). The phototransformation of a pollutant in the hydrosphere may result from light absorption by the pollutant itself (direct photolysis) or may be photoinduced by the dissolved organic matters (DOMs) or nitrate ions present in water, as these chromophores are known to photoproduce reactive species (indirect photolysis) (Vialaton et al., 2001). Because NB absorbs sunlight strongly in the ultraviolet and blue spectral region, it is considered that direct photolysis might play an important role for the degradation of NB in aqueous systems.

In indirect photolysis, DOMs play an important role, which is ubiquitous in surface waters and known to sensitize the transformation of pollutants by generating reactive photooxidants comprised of both reactive oxygen species (ROS) (e.g., hydroxyl radicals ($\cdot$OH), peroxyl radicals ($\cdot$ROO), singlet oxygen ($1^2$O$_2$), etc.) and other non-ROS transients (Chin et al., 2004). Nitrate and nitrite are other photosensitizers in natural waters and nitrate-induced photooxidation may be a significant transformation mechanism for trace organic chemicals in shallow, clear water bodies because it is important precursor in the photoproduction of $\cdot$OH (Mack and Bolton, 1999; Zepp et al., 1987; Haag and Hoigne, 1985; Brezonik and Fulkerson-Brekken, 1998; Torrents et al., 1997). Among these reactive photochemically generated species in natural waters, $\cdot$OH plays an important role in the phototransformation of organic compounds due to the reaction between most organics and $\cdot$OH occurs with rate constants that are essentially diffusion controlled (Lam et al., 2003; Corin et al., 2000; Fisher et al., 2006). Major photochemical $\cdot$OH sources have been identified as nitrate, nitrite, and DOM, while DOM, (at a lesser extent) carbonate and bicarbonate play a major role.
as -OH sinks in freshwater (Vione et al., 2006).

Several studies have pointed out that NB could undergo aqueous photodegradation under natural conditions, and the determined half-lives of NB in natural water differ largely. For example, by direct photolysis, NB has a half-life of 2.5 to more than 6 d near the surface of water bodies in the vicinity of 40°N latitude (Zepp et al., 1987). Under natural sunlight in the presence of humic acids, a near-surface half-life of 133 d was estimated for NB at 40°N latitude (Simmons and Zepp, 1986). The half-life of NB in natural water was 100±15 h under natural sunlight at 46°N latitude in June, which decreased to only about 12 h under better weather conditions in July at the same place (Vialaton and Richard, 2002). Furthermore, from the typical concentration of hydroxyl radicals in surface waters (5.0×10−19–2.0×10−17 mol/L), the half-lives for NB were estimated to be between 125 days and 13 years at pH 7 (Howard et al., 1990). So the present knowledge was not sufficient to evaluated the photochemical fate of NB in the Songhua River.

As one of the efforts to predict the fate of residual NB in the river, this study examined the kinetic aspects of the photochemical degradation of NB. The goals of this research were: (1) to determine the photodecomposition kinetics and half-life of NB at different sections of the Songhua River, (2) to determine the effect of nitrate ion, DOM and bicarbonate/carbonate on reaction rate, and (3) to determine the photodecomposition products to provide information on the photochemical behavior of NB in aquatic environment.

1 Experimental procedures

1.1 Sample collection

Samples of river water were collected from the Songhua River at four sampling sites. Sample A was taken at the entrance of Shihaoxian Port (SHX, 43°53′27″N, 126°33′47″E) in Jilin City. Here, untreated wastewater containing high concentration of NB was discharged directly into the river on 13 November 2005. Sample B was taken at Sanjiangkou Port (SJK, 45°20′36″N, 124°43′51″E), sample C at Hulanhekouxia Port (HLHKX, 45°56′45″N, 126°48′13″E), and sample D at Jiamusi Port (JMS, 46°48′40″N, 130°13′54″E). All water samples were stored at 4°C and used without previous treatment, filtration or sterilization. A portion of water samples was analyzed to ensure that they were free of interfering compounds. Their physico-chemical characteristics are given in Table 1. All samples were analyzed for dissolved organic carbon (DOC), pH, inorganic anions, and alkalinity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sampling time (d-m-y)</th>
<th>pH</th>
<th>DOC (mg/L)</th>
<th>Alkalinity (mg/L CaCO₃)</th>
<th>Nitrate (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHX</td>
<td>24-12-2005</td>
<td>7.44</td>
<td>5.25</td>
<td>63.14</td>
<td>8.65</td>
</tr>
<tr>
<td>SJK</td>
<td>24-12-2005</td>
<td>7.25</td>
<td>7.56</td>
<td>139.98</td>
<td>10.87</td>
</tr>
<tr>
<td>HLHKX</td>
<td>10-01-2006</td>
<td>6.93</td>
<td>5.71</td>
<td>121.15</td>
<td>7.79</td>
</tr>
<tr>
<td>JMS</td>
<td>10-01-2006</td>
<td>7.42</td>
<td>6.01</td>
<td>122.10</td>
<td>7.44</td>
</tr>
<tr>
<td>Ultrapure water</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

SHX: Shihaoxian Port; SJK: Sanjiangkou Port; HLHKX: Hulanhekouxia Port; JMS: Jiamusi Port.

1.2 Chemicals

Nitrobenzene, phenol, 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol of analytical reagent grade were purchased from Beijing Chemical Reagent Company, China, and used as received. Ultrapure water (18 MΩ/cm) was supplied by a Purific-Mx II system (Organo Co., Japan). For HPLC analysis, acetonitrile (HPLC grade) supplied by Fisher Scientific (USA) was used. Other reagents were of reagent grade.

1.3 Photolysis kinetics of NB under simulated solar irradiation

Different natural water systems as well as ultrapure water were irradiated under simulated solar irradiation. Steady-state illumination of magnetically stirred degassed samples was performed in a cylindrical glass cell equipped with a water-cooling jacket that was placed 15 cm in front of a 350-W Xenon arc lamp (Shanghai Photoelectron Device Ltd., China). A special glass filter is placed on the reactor for restricting the transmission of wavelengths below 290 nm for simulating the solar irradiation. After a fixed time of illumination, the sample was filtered for analysis. The temperature was kept between 26 and 28°C. Previous experiments had been carried out to exclude the effect of vaporization or stripping of NB.

1.4 Photolysis in the presence of nitrate ions, DOM, and HCO₃⁻

To examine the effects of nitrate and DOM, 150 ml aqueous solutions of nitrobenzene (500 μg/L) in the presence of nitrate and humic acid (HA) (as DOM) were exposed to simulated solar irradiation. Concentrations of nitrate were 5, 10, and 15 mg/L. Concentrations of HA were 5 and 10 mg/L. The influence of HCO₃⁻ ion on the reaction rate was also examined by adding 2.5 and 5 mmol/L HCO₃⁻ into the SHX water. The above concentrations of nitrate ions, HA and HCO₃⁻ were chosen to resemble those found in natural waters.

1.5 Photolysis products of NB under simulated solar lamp and natural sunlight

A sufficiently high concentration (100 mg/L, i.e., 0.813 mmol/L) of NB in SHX water was used to allow the identification of minor phototransformation products. Water samples for the identification of NB photolysis byproducts were obtained by irradiation of 150 ml aqueous solutions for 12 h.
For confirming the photoproducts of low concentration NB (500 µg/L) in natural water under natural sunlight, outdoor experiments were performed with capped quartz reservoirs of 1,000 ml placed at the roof terrace of the laboratory building (40°N, 116°E). Solutions were filled into quartz reactors (10 cm internal diameter) that were closed by septa, attached on a rack inclined by about 15°. Water samples were filled into reaction reservoirs and spiked with nitrobenzene by adding an appropriate volume of stock solution. Photolysis was carried out over the period from 11:00 A.M. March 9, to 11:00 A.M. March 21, 2006. Four aqueous systems were prepared by using the samples from the four sites (SHX, SJK, HLHKX, and JMS).

1.6 Sample analysis

All solutions for the experiments were prepared immediately prior to irradiation, and were made in an appropriately sized volumetric flask and then immediately transferred to the reactor. Quantification by HPLC was performed as soon as possible following the completion of irradiation experiments. Samples were filtrated through 0.22-µm filters and stored at 4°C before analysis.

1.6.1 HPLC measurements

Samples were analyzed on a Waters Alliance 2695 separation module, equipped with a Waters 2996A photodiode array detector (Waters Co., USA) and a Waters X Terra® MS C18 reversed-phase column (250 mm × 4.6 mm i.d., 5 µm particle size, Waters Co., USA). For quantification of NB, the mobile phase was a mixture of water, acetonitrile and acetic acid (60% : 40% : 0.3%) isocratically delivered at a flow rate of 1.00 ml/min. The column was held at 25°C and quantification for NB was performed at 263.3 nm. For qualification and quantification of both NB and its transformation products, the run time were 21 min with an isocratic mixture (70:30, V/V) of water and acetonitrile at a flow rate of 1.00 ml/min. The wavelength of the UV absorbance detector was determined between 220 and 450 nm. Measurements of NB and phenolic products were made at the wavelength of maximum absorption of each component.

1.6.2 SPE-GC-MS measurement

For identifying the photoproducts of the outdoor experiments, the solutions (400 ml) were extracted by means of solid phase extraction (SPE) using Oasis HLB cartridges (6 ml, 120 mg; Waters, Milford, USA). SPE was performed with a vacuum manifold processing station (Agilent Technologies, USA). The organic extracts were analyzed by GC/MS using an Agilent 6890/6971 GC/MSD equipped with a 30 m × 0.25 mm i.d. DB-5 MS column (J&W Scientific, USA). The GC oven temperature was programmed from 40°C (3 min) to 300°C (1 min) at 10°C/min. The detector and injector temperatures were 300 and 100°C, respectively. Helium was used as the carrier gas with a flow rate of 1.0 ml/min. The splitless mode was used for injection. The MS was operated in electron ionization mode with a potential of 70 eV and the spectra were obtained in full scan mode.

1.6.3 Other measurements

The NO₃⁻ and NO₂⁻ anions were determined with a Metrohm Model 861 advanced compact IC (Metrohm, Herisau, Switzerland) equipped with a Metrosep A SUPP 4 analytical column (length 250 mm, diameter 4 mm). The UV-Vis spectra of the irradiation samples were recorded using a U-3010 UV-Vis spectrophotometer (Hitachi Co., Japan). Dissolved organic carbon (DOC) of the natural water was analyzed with a Phoenix 8000 TOC analyzer (Tekmar-Dohrmann Co., USA), and pH was measured using Orion 720APLUS Benchtop meter (Thermo Orion Co., USA).

2 Results and discussion

2.1 Kinetics experiments

Irradiation of NB-containing natural water as well as ultrapure water solution was performed under simulated solar lamp. Samples were collected over a period of approximately 8 h and the NB concentration was determined by HPLC. Fig.1 depicts the NB degradation curves. All experiments produced linear plots of ln(CNB/CNB0) vs. t, indicating that the photochemical degradation of NB is pseudo-first-order. The pseudo-first-order rate constant k was calculated from the first-order equation (Eq.(1)) (Dimoua et al., 2004):

\[
\ln\left(\frac{C_{NB}}{C_{NB0}}\right) = -kt
\]

(1)

where, CNB is the NB concentration at time t, CNB0 is the initial NB concentration. The half-life (t1/2) of NB can be determined by Eq.(2):

\[
t_{1/2} = \ln(2)/k
\]

(2)

The k and t1/2 values for the four natural water and one ultrapure water systems under simulated solar irradiation are summarized in Table 2. It is clear that different systems show quite different photolysis rates. The NB photolysis rate of ultrapure water was the slowest, with a pseudo-first-order degradation rate constant of 0.0168 h⁻¹, which was approximately half of those of river water systems.

![Fig. 1](https://example.com/figure1.png) Phototransformation of NB (500 µg/L) in ultrapure water and natural water under simulated solar irradiation.
Accordingly, the half-life of NB in the ultrapure water system was 41.3 h, approximately two times those of the river water systems. It is clear that NB in river water could be photolyzed very quickly, suggesting that photolysis should be an important process responsible for the loss of NB flux in the Songhua River. However, it is important to know the photolysis products for risk assessment of NB in the Songhua River.

At the same time, the four river water systems were also different from each other in photolysis rates, even though the differences were much smaller. The above results suggest that the NB photolysis was strongly affected by water compositions.

### 2.2 Influence of nitrite/nitrate ions

The effect of nitrate on NB photolysis rate was investigated, and the results are shown in Fig.2. It shows that the increase of nitrate concentration enhanced the NB photolysis markedly. It has been proved that nitrite/nitrate is a potential source of -OH in natural water, and nitrate is capable of producing -OH with quantum yields ranging from 9×10^{-3} to 17×10^{-3} when irradiated at wavelengths between 290 and 330 nm (Miller and Chin, 2002). The -OH generation mechanism of nitrate photolysis is that the irradiation of nitrate in its long-wavelength absorption band (maximum 302 nm) results in two primary photochemical processes (Zepp et al., 1987; Mack and Bolton, 1999):

\[
\begin{align*}
\text{NO}_3^- \xrightarrow{h\nu} & (\text{NO}_3^\cdot)^* \quad (3) \\
(\text{NO}_3^\cdot)^* & \rightarrow \text{NO}_2^- + \text{O}(^3\text{P}) \quad (4) \\
(\text{NO}_3^-) & \rightarrow \text{NO}_2^- + \text{O}^- \xrightarrow{\text{H}_2\text{O}} \text{NO}_2^- + \cdot\text{OH} + \text{OH}^- \quad (5)
\end{align*}
\]

From Table 1, it could be seen that there is a significant amount of NO$_3^-$ in the Songhua River and it might affect the photodegradation of NB in the natural river. For example, the concentration of nitrate in SHX was higher than that of HLHKX and JMS, which might be related with its photodegradation rate. However, the SJK system which has the highest nitrate concentration, did not show the highest photolysis rate. This might be related with its high alkalinity which will be discussed later.

### 2.3 Influence of DOM

The effect of DOM on NB photolysis was also investigated, and the result is shown in Fig.3. It is clear that changes of humic acid (HA) (as DOM) content from 0 to 10 mgC/L only affected NB photolysis rate slightly. This result is similar with the results of previous researches. Simmons and Zeep (1986) determined the degradation rate was 0.007 in the presence of humic substances, while 0.005 in distilled water. Vialaton and Richard (2002) also found humic acid only shortened the half-life of NB slightly.

### 2.4 Influence of alkalinity

Carbonate and bicarbonate are well-known radical scavengers, because hydroxyl radicals may react preferentially with CO$_3^{2-}$ and HCO$_3^-$, whose constants are $3.9 \times 10^8$ and $8.5 \times 10^6$ L/(mol-s), respectively (Buxton et al., 1988). Although secondary radicals, i.e., -CO$_2^-$ and -HCO$_3^-$, may also play a role in degrading organic pollutants, their oxidation potential values are lower than that of -OH. Since the inorganic carbon exists mainly in the form of bicarbonate under neutral pH conditions (Ma and Graham, 2000), HCO$_3^-$ was added into natural water for studying the effect of alkalinity. As shown in Fig.4, when HCO$_3^-$ was added into SHX water, the NB photodegradation rate was markedly slowed down. The effect of bicarbonate/carbonate on the oxidation rate may be significant, particularly when the concentration of the target organic is low (Wang et al., 2000). From Table 1, it could be seen that there is a significant amount of HCO$_3^-$/CO$_2^{2-}$ (alkalinity) in the Songhua River and it may compete with organic matter for -OH radicals. For example, the relatively low reaction constant of the SJK system in spite of its high nitrate content might be related with the high alkalinity in the system.
2.5 Photoproducts analysis
2.5.1 Products under simulated solar photolysis

A yellow color appeared during the irradiation of 100 mg/L NB solution in SHX water, and the UV-Vis spectra were recorded as a function of time as shown in Fig.5. It is apparent that the absorption in the region of 350–450 nm increased with increasing irradiation time, indicating that new compounds might be formed during the irradiation of NB. It is speculated that the new compounds might be nitrophenolic compounds formed from both disproportionation and recombination of nitrohydroxycyclohexadienyl radical (Ph(OH)NO$_2$) (Pozdnyakov et al. 2000a; Zhao et al., 2001; Pozdnyakov et al., 2000b).

Figure 6 compares the HPLC chromatogram of the solution after irradiation for 12 h with that before irradiation. It is clear that $o$-, $m$-, and $p$-nitrophenol (NP) as well as phenol were formed during simulated solar light irradiation. Changes of the concentrations of the three NPs with irradiation time are shown in Fig.7 together with that of phenol. It is clear that all of the four photoproducts increased with the irradiation time, with $o$-NP as the main photodegradation product. The result is in accordance with the results of previous researchers (Pozdnyakov et al. 2004; Loeb et al., 1949; Eberhardt and Yoshida, 1973; Fendler and Gasowski, 1968). Eberhardt and Yoshida (1973) have explained the observed isomer distribution using the SCF-MO theory. More $o$-NP was produced because the $\cdot$OH radical prefers to attack the HOMO and LUMO of NP. Fendler and Gasowski (1968) thought that the enhanced conjugation of the nitro group with benzene ring might be responsible for the selective activation of the ortho and para positions of NP.

Phenol could be generated from NB through two pathways. One is the cleavage of the C–N bond by H$_2$O under simulated solar light irradiation, resulting in generation of phenol and nitrite ion (photohydrolysis) (Chen et al., 2005;
Fig. 9  GC/MS analysis of natural solar irradiated SHX. (a) TIC for the NP isomers; (b), (c) TIC for phenol.

Table 3  GC-MS data of the identified intermediates corresponding to Fig. 9

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Retention time (min)</th>
<th>Molecular weight (m/z)</th>
<th>Ions (relative abundance (%))</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (product 1)</td>
<td>8.8</td>
<td>94</td>
<td>94 (100), 66 (30)</td>
<td>Phenol</td>
</tr>
<tr>
<td>2 (product 2)</td>
<td>11.5</td>
<td>139</td>
<td>139 (100), 81 (23), 65 (35)</td>
<td>o-Nitrophenol</td>
</tr>
<tr>
<td>3 (product 3)</td>
<td>16.4</td>
<td>139</td>
<td>139 (100), 93 (58), 65 (86)</td>
<td>m-Nitrophenol</td>
</tr>
<tr>
<td>4 (product 4)</td>
<td>17.2</td>
<td>139</td>
<td>139 (100), 109 (51), 9 (27), 65 (75)</td>
<td>p-Nitrophenol</td>
</tr>
</tbody>
</table>
Another pathway is the direct attack on the carbon connected with a nitro-group by -OH, leading to the formation of free phenyl radicals and nitrite ions. The phenyl radicals could be further transformed to phenol while nitrite could be rapidly oxidized to nitrate by other -OH (Loebl et al., 1950; Fendler and Gasowski, 1968). As shown in Fig. 8, both nitrate and nitrite were formed during simulated solar light irradiation of 100 mg/L NB-bearing pure water solution, suggesting that both of the above two pathways possibly exist simultaneously. However, the higher nitrate concentration suggests that the latter -OH radical attack pathway may have played a major role.

2.5.2 Contribution of photolysis to NB flux loss

The 500 µg/L NB-bearing SHX, SJK, HLHKX, and JMS water systems were under sunlight irradiation for 288 h, respectively, and GC/MS analysis of the irradiated solutions were performed. The analytical results of the irradiated SHX solution are shown in Fig. 9 as an example. It was found that all the four organic intermediates, the three NP isomers and phenol, existed in three river water systems (SHX, SJK, HLHKX) following natural solar irradiation. Only p-NP was not detected in the JMS system. The above results further demonstrated that photodegradation of NB might have happened in the Songhua River as did in the simulated solar irradiation systems.

According to the reports of Chinese State Environmental Protection Agency, it took approximately 22 d for the polluted strip to flow from the Harbin section to the Tongjiang section. The NB flux decreased from approximately 46 to 25 t at the same time, which means that 21 t of NB disappeared from river water during the 711 km journey. Since the Songhua River was in freeze-up period, it was speculated that biodegradation was not the process responsible for the loss of NB flux, but volatilization might be one of the main responsible processes (Li et al., 2008). Our study clearly demonstrates that photodegradation of NB was a relatively fast process, with a half-life of 17.2–21.5 h in river water systems under simulated solar light. Although the river water depth of 5–7 m and the coverage of ice over some part of the river possibly greatly reduced its contribution to the loss of NB flux, photodegradation of NB should have happened to some extent.

On the basis of above experimental data, a possible NB phototransformation pathway in natural water is depicted in Fig. 10. The sequence involved all intermediates detected, only showing the main oxidizing agent -OH for sake of simplicity.

3 Conclusions

Photodegradation of NB in natural water proceeded via pseudo-first-order reaction kinetics under simulated solar irradiation conditions, and the rate constants (k) were 0.323–0.402. The NB degradation rate in ultrapure water system was approximately the half of those in natural river water systems. The relatively short half-life of NB indicates that photodegradation might be one of the processes responsible for the loss of NB flux in the river. Three isomeric nitrophenols, o-, m-, and p-nitrophenols, as well as phenol were the main photodegradation products under both simulated and natural solar light irradiations.

Acknowledgements

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