

# The photoconversion of gamma-hexachlorocyclohexane under UV irradiation in water, snow and ice

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## ABSTRACT

The photochemistry of organic pollutants has received increasing attention in ice and snow. In this work, the photoconversion of gamma-hexachlorocyclohexane ( $\gamma$ -HCH) under UV irradiation was investigated in water, snow and ice. The photoconversion rate, products and mechanisms were inspected, and the effect of inorganic ions ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$  and  $\text{Fe}^{2+}$ ) was discussed. The results showed that  $\gamma$ -HCH could be photoconverted in water, snow and ice, with the photoconversion rate being fastest in snow, and slowest in ice. All photoconversion could be described by the first-order kinetics model. In water, snow and ice, the common photoproducts of  $\gamma$ -HCH were alpha-hexachlorocyclohexane ( $\alpha$ -HCH) and pentachlorocyclohexene.  $\alpha$ -HCH was generated by a change in the bonding of a chlorine atom in  $\gamma$ -HCH; pentachlorocyclohexene was generated by the removal of a molecule of chlorine hydride from a molecule of  $\gamma$ -HCH. Different concentrations of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  all inhibited the photoconversion of  $\gamma$ -HCH, and the inhibition effect decreased with increasing concentrations of  $\text{NO}_2^-$  and  $\text{NO}_3^-$ , but increased with the increasing concentrations of  $\text{HCO}_3^-$ . Different concentrations of  $\text{Fe}^{2+}$  promoted the photoconversion of  $\gamma$ -HCH in water and ice, but had little effect in snow.

**Key words** |  $\gamma$ -HCH, ice, photoconversion, snow, water

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## INTRODUCTION

Ice and snow are important components in the polar regions and high-altitude ecosystems. Organic pollutants in snow or ice may be biological in origin, deposited by aerosols or atmospheric gases, or formed chemically *in situ* (McNeill *et al.* 2012). The release of organic pollutants during the melting process of snow and ice also threatens the safety of the atmospheric and marine environments (Wania and Mackay 1993; Arctic Monitoring and Assessment Programme 1997). Recently, the environmental behaviors of organic pollutants in snow and ice have received increasing attention.

Gamma-hexachlorocyclohexane ( $\text{C}_6\text{H}_6\text{Cl}_6$ ,  $\gamma$ -HCH) is one of the priority pollutants, as it may stimulate the nervous and respiratory systems of human beings. Although using  $\gamma$ -HCH has been forbidden globally, the impact of  $\gamma$ -HCH on the environment and human beings may last for a long time owing to its environmental persistence. Researchers have found  $\gamma$ -HCH in the polar regions and

high-altitude mountains (Dickhut *et al.* 2004; Herbert *et al.* 2005).

$\gamma$ -HCH can be reduced by microorganisms and photochemistry; however, in snow and ice microbiological reactions are relatively weak, whereas photochemical reactions play an important role (Wania *et al.* 1998). Photochemistry is not strongly affected by temperature but it may be influenced by environmental factors, such as the medium and inorganic ions present. Previous research has shown that the reaction pathways of  $\gamma$ -HCH are mainly dechlorination, and the toxicity of the photoproducts is commonly lower than  $\gamma$ -HCH.

Until now, researchers have investigated the photochemistry of  $\gamma$ -HCH in water and soil (Fu *et al.* 2005; Yu *et al.* 2007), but the photochemistry of  $\gamma$ -HCH in ice and snow is little known. In this work, the photochemical reaction of  $\gamma$ -HCH in water, snow and ice was investigated; the photoconversion rate, products and mechanisms were

inspected, and the effect of inorganic ions ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$  and  $\text{Fe}^{2+}$ ) on the photoconversion of  $\gamma$ -HCH was discussed. Studying the photochemical behaviors of  $\gamma$ -HCH is essential for understanding the transformation and migration behaviors, and to assess the ecological risks, of  $\gamma$ -HCH.

## EXPERIMENTAL STRATEGY

### Sample preparation

A stock solution of  $\gamma$ -HCH (98.6% Dr. Ehrenstorfer) was prepared by dissolving solid  $\gamma$ -HCH in hot water, and then filtering the solution through a 0.22  $\mu\text{m}$  organic membrane before use. The solution of  $\gamma$ -HCH was diluted to 0.21  $\mu\text{mol/L}$ , and then 10  $\mu\text{L}$  was poured into a number of quartz tubes (15 mm  $\times$  150 mm), and the tubes were sealed.

The stock solutions of inorganic salts (sodium nitrite, sodium nitrate, sodium bicarbonate, ferric sulfate) were dissolved in distilled water separately; the mixed solution of  $\gamma$ -HCH and inorganic salt was prepared by dilution of the corresponding stock solutions.

Ice samples of  $\gamma$ -HCH were obtained by freezing the solution in the freezer (536-GA) ( $T = -15^\circ\text{C}$ ).

Snow samples were prepared by a spraying method (Matykiewiczová *et al.* 2007). After sieving through a 2  $\mu\text{m}$  standard sieve, the snow samples were made up.

### Irradiation procedures

The photoconversion reaction was conducted in a self-made low-temperature device. Four 20 W UV germicidal lamps (Hailian Co., China) were connected in parallel. The samples were irradiated below the lamps at a distance of 20 cm. The reaction temperature for the water samples was  $-5^\circ\text{C}$ , and  $-15^\circ\text{C}$  for the ice and snow samples. The light intensity was 400 lx. Two samples were taken at certain intervals.

### Analysis of $\gamma$ -HCH

Samples of  $\gamma$ -HCH were extracted by hexane (HPLC grade, Tedia), (ice and snow samples having been thawed at room temperature), and determined by gas chromatography-electron capture detector (GC-ECD) (GC-14C, Shimadzu). The chromatographic column was a Rtx-1 capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ); the carrier gas was high-purity nitrogen (99.999%), the flow rate of which was 1.6 mL/min; the inlet temperature was  $250^\circ\text{C}$  and the

detector temperature was  $300^\circ\text{C}$ . A 1  $\mu\text{L}$  sample was introduced using the splitless technique according to the following temperature program: the initial temperature was  $100^\circ\text{C}$ , rising at  $20^\circ\text{C}/\text{min}$  up to  $210^\circ\text{C}$ , and then rising at  $3^\circ\text{C}/\text{min}$  to  $220^\circ\text{C}$ .

### Analysis of photoproducts

After irradiation, the photoproducts of  $\gamma$ -HCH were also extracted by hexane. After concentration by nitrogen-blowing, the photoproducts were quantified by GC-mass spectrometry (GC-MS) (6890N-5975, Agilent). The chromatography column was a HP-1701 capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ); the carrier gas was high-purity helium; the inlet temperature was  $270^\circ\text{C}$  and the detector temperature was  $250^\circ\text{C}$ . The sample was introduced using the splitless technique; the temperature program was  $80^\circ\text{C}$  for 3 min, then rising at  $12^\circ\text{C}/\text{min}$  up to  $260^\circ\text{C}$ , which was maintained for 5 min. An electron bombing ion source was used and the electron energy was 70 eV, the emission current was 0.35 mA, the electron multiplier voltage was 1,000 V, the resolution rate was 2 M, and the mass spectra were collected in the scan range  $m/z$  20–400.

The pH value of  $\gamma$ -HCH solution was determined by PHS-3C pH meter (Leici, Shanghai).

Silver nitrate was directly used for qualitative determination of the chloride ions generated during the photoconversion of  $\gamma$ -HCH.

## RESULTS AND DISCUSSION

### Direct photolysis of $\gamma$ -HCH

Results of the direct photolysis of  $\gamma$ -HCH in water, ice and snow under dark and light conditions are shown in Figure 1.

It could be seen from Figure 1 that  $\gamma$ -HCH was unchanged under dark conditions in water, ice or snow, which indicated that  $\gamma$ -HCH cannot be degraded without irradiation and that the loss of  $\gamma$ -HCH during the preparation and thawing process for ice and snow samples was negligible. But under irradiation,  $\gamma$ -HCH could be photoconverted. This was because  $\gamma$ -HCH can absorb UV light and then photolyze.

The photoconversion of  $\gamma$ -HCH all obeyed the first-order kinetics model. The equations of  $\gamma$ -HCH in water, ice and snow were  $\ln(C_t/C_0) = -0.1271t + 0.2674$ ,  $\ln(C_t/C_0) = -0.0639t - 0.1079$ ,  $\ln(C_t/C_0) = -0.4367t - 0.1479$  respectively, and the apparent rate constants were 0.1271,

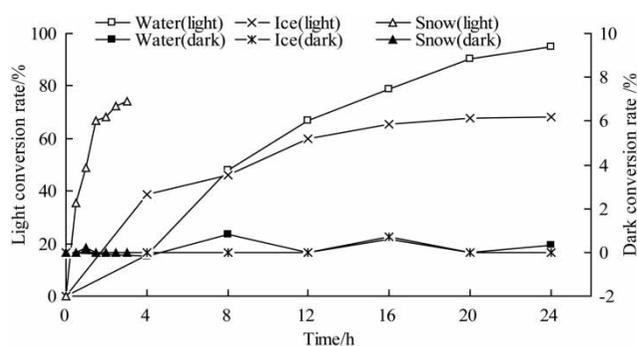


Figure 1 | The direct photolysis of  $\gamma$ -HCH in water, ice and snow.

0.0639, 0.4367/h<sup>-1</sup>. In previous literature, the photoconversion rate constant of  $\gamma$ -HCH in water was a little higher than ours (0.26 h<sup>-1</sup>) due to different experimental conditions (Nienow *et al.* 2008).

From Figure 1, we know that the photoconversion of  $\gamma$ -HCH in water is faster than in ice. This is because organic molecules are typically influenced by the surrounding 'cage' of solvent molecules, and the heterogeneous environments in ice cause a remarkable 'cage effect' (McNeill *et al.* 2012), so  $\gamma$ -HCH and its photoproducts are restricted in a 'cage', so the reaction is slower in ice.

In snow, the photoconversion rate of  $\gamma$ -HCH is faster than in water. This could be ascribed to the freeze-concentration effect, that is, the freezing of aqueous solutions of organic compounds results in the separation of ice crystals and solute molecules, which increases the solute concentrations in the quasi-liquid layer (QLL) covering the ice

crystal surface (Grannas *et al.* 2007), and previous research has shown that reaction in QLL is fast (Domine & Shepson 2002), so the reaction in snow is faster than in water.

The photoconversion rate of  $\gamma$ -HCH in snow is also faster than in ice. Previous research has shown that the 'cage effect' is incomplete in snow (McNeill *et al.* 2012), so the reaction in snow is not strongly restricted. In addition, the specific surface area of snow is large and there is more QLL in snow. Both reasons contribute to the fast photoconversion of  $\gamma$ -HCH in snow.

### Photoproducts and mechanisms of $\gamma$ -HCH

After the water and ice samples had been irradiated for 24 hours, and the snow samples for 3 hours, the photoproducts of  $\gamma$ -HCH were qualified. The common photoproducts of  $\gamma$ -HCH in water, ice and snow were alpha-hexachlorocyclohexane ( $\alpha$ -HCH) and pentachlorocyclohexene; there was also beta-hexachlorocyclohexane ( $\beta$ -HCH) in water, and tetrachlorocyclohexene in snow.

The GC-MS results showed that the retention time of  $\gamma$ -HCH was 15.13 min, and the retention times for the photoproducts  $\alpha$ -HCH,  $\beta$ -HCH, pentachlorocyclohexene, and tetrachlorocyclohexene were 14.41, 16.37, 11.64 and 12.34 min, respectively.

The toxicity of photoproducts  $\alpha$ -HCH (LD<sub>50</sub>, in rats, oral, 177 mg/kg) and pentachlorocyclohexene (LD<sub>50</sub>, in rats, oral, 2,930–4,180 mg/kg) was lower than that of  $\gamma$ -HCH (LD<sub>50</sub>, in rats, oral, 76 mg/kg) (Guillard *et al.* 1996),

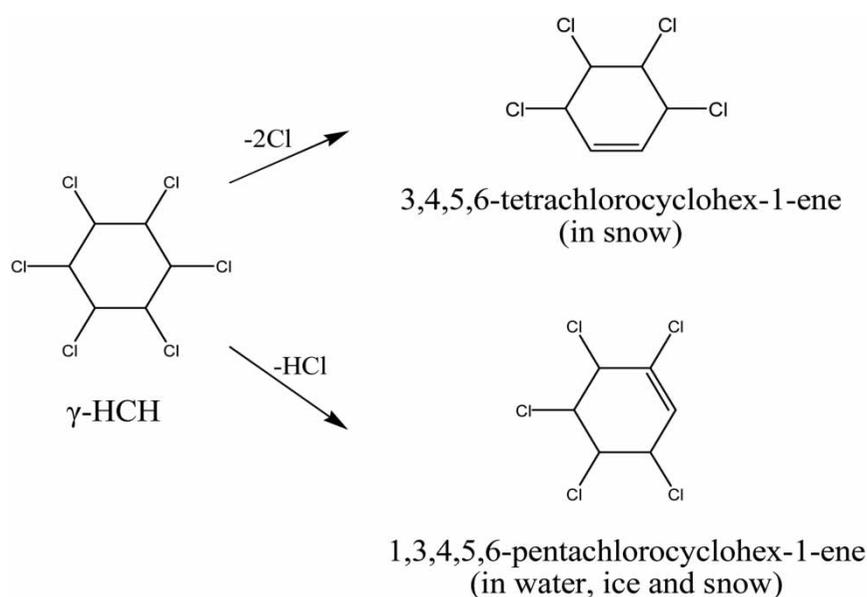


Figure 2 | Proposed mechanisms of the photoconversion of  $\gamma$ -HCH.

which indicates that the photoconversion of  $\gamma$ -HCH is a detoxification process and that the photochemical reaction is essential for assessing the environmental risk of  $\gamma$ -HCH.

The photo-isomerization schemes of  $\gamma$ -HCH were that the bonding of one or two chlorine atoms in  $\gamma$ -HCH (aaae) changed, resulting in the generation of isomers  $\alpha$ -HCH (aaeee) and  $\beta$ -HCH (eeee).

Results of the photoconversion mechanisms of  $\gamma$ -HCH are shown in Figure 2. Two adjacent chlorine atoms or a molecule of chlorine hydride was taken from  $\gamma$ -HCH molecules, forming tetrachlorocyclohexene and pentachlorocyclohexene.

During the experiment, the pH value of  $\gamma$ -HCH solution decreased from 6.34, 6.33, 6.34 to 5.57, 5.51 and 5.64 in water, ice and snow respectively, which confirmed that dehydrochlorination occurred during photoconversion.

Due to the low experimental concentrations of  $\gamma$ -HCH, titration analysis with silver nitrate was used to measure the chloride ions. White precipitate was generated in the photolysis solution of  $\gamma$ -HCH, which also indicated that chloride ions were generated.

## Effect of ions

Results of the effect of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  on the photoconversion of  $\gamma$ -HCH are shown in Figures 3 and 4.

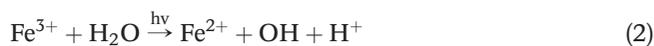
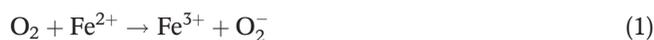
It can be seen from Figures 3(a) and 4(a) that different concentrations of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  all inhibited the photoconversion of  $\gamma$ -HCH in water, and the inhibition effect decreased with increasing concentrations of  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . We deduced that  $\text{NO}_2^-$  and  $\text{NO}_3^-$  could play two roles in the reaction. Firstly,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  could absorb light, and then inhibit the photoconversion; secondly, the photolysis of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  could generate active groups such as hydroxyl radicals and nitro radicals (Jacobi et al. 2004). Hydroxyl radicals that are generated in the presence of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  are strongly reactive and could react with organic pollutants. When  $\text{NO}_2^-$  and  $\text{NO}_3^-$  concentrations were low, the light-absorbing effect dominated and then inhibited the photoconversion of  $\gamma$ -HCH; when  $\text{NO}_2^-$  and  $\text{NO}_3^-$  concentrations were high, the role of generating reactive groups gradually increased, so the inhibition effect was weakened.

Similar to water, different concentrations of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  also inhibited the photoconversion of  $\gamma$ -HCH in ice, shown in Figures 3(b) and 4(b). This was because less active groups were generated in ice, thus the promotion effect was not obvious. The overall effect was inhibition produced by competitive absorption of photons.

In snow, both  $\text{NO}_2^-$  and  $\text{NO}_3^-$  inhibited the photoconversion of  $\gamma$ -HCH shown in Figures 3(c) and 4(c), as they did in water and ice. At the beginning, we also tried to inspect a series of concentrations of ions in snow, but the preparation of snow samples was difficult and time-consuming, and the results showed that the effect of these ions in snow conformed to that in water and ice, so we just used one concentration in snow.

The result of the effect of  $\text{HCO}_3^-$  on the photoconversion of  $\gamma$ -HCH is shown in Figure 5. It can be seen that  $\text{HCO}_3^-$  inhibited the photoconversion of  $\gamma$ -HCH in water, ice and snow, and the inhibition effect increased with the increasing concentration of  $\text{HCO}_3^-$  in water and ice. We presumed that  $\text{HCO}_3^-$  made the reaction system alkaline, and the photoconversion of  $\gamma$ -HCH was inhibited in alkaline conditions. In order to verify the hypothesis, we tested the photoconversion of  $\gamma$ -HCH in the presence of sodium hydrate, and the photoconversion of  $\gamma$ -HCH was also inhibited, which confirmed our inference.

The result of the effect of different concentrations of  $\text{Fe}^{2+}$  on the photoconversion of  $\gamma$ -HCH is shown in Figure 6. It can be seen that different concentrations of  $\text{Fe}^{2+}$  promoted the photoconversion of  $\gamma$ -HCH in water and ice, because  $\text{Fe}^{2+}$  can be oxidized to  $\text{Fe}^{3+}$  by oxygen, see Equation (1), and  $\text{Fe}^{3+}$  can generate hydroxyl radicals, see Equation (2), then the hydroxyl radicals can oxidize  $\gamma$ -HCH.



In ice, the promotion effect of  $\text{Fe}^{2+}$  on the photoconversion was weak, because the crystal structure of ice limited the free movement of hydroxyl radicals, so the photoconversion rate of  $\gamma$ -HCH in ice was low.

In snow,  $\text{Fe}^{2+}$  had little effect on the photoconversion of  $\gamma$ -HCH, which was different from that in water and ice. This was because there were many fewer hydroxyl radicals in snow.

## CONCLUSION

This work investigated the photoconversion of  $\gamma$ -HCH in water, snow and ice under UV irradiation; it was found that  $\gamma$ -HCH could be photoconverted in water, snow and

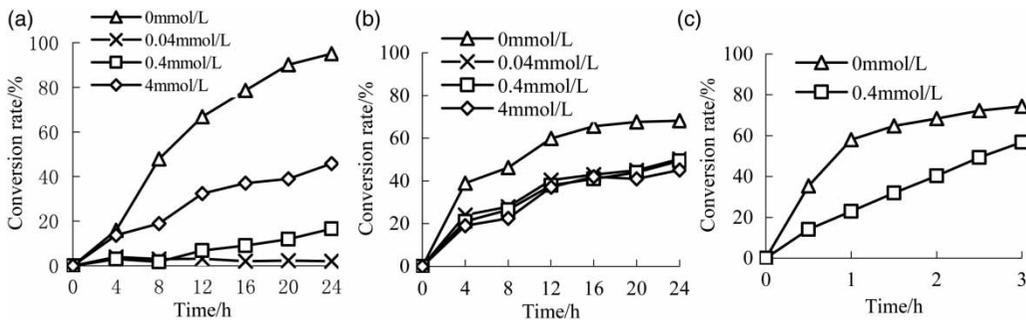


Figure 3 | Effect of  $\text{NO}_2^-$  on the photoconversion of  $\gamma$ -HCH in (a) water, (b) ice and (c) snow.

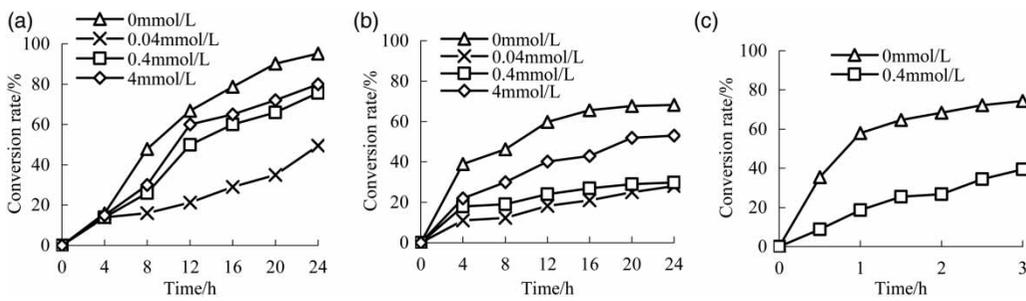


Figure 4 | Effect of  $\text{NO}_3^-$  on the photoconversion of  $\gamma$ -HCH in (a) water, (b) ice and (c) snow.

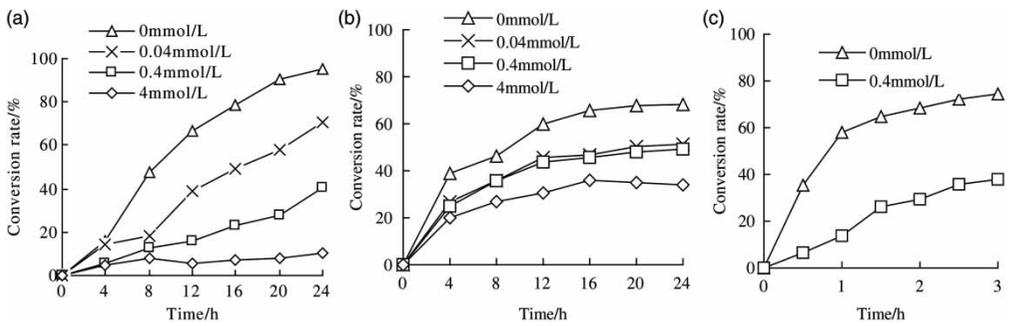


Figure 5 | Effect of  $\text{HCO}_3^-$  on the photoconversion of  $\gamma$ -HCH in (a) water, (b) ice and (c) snow.

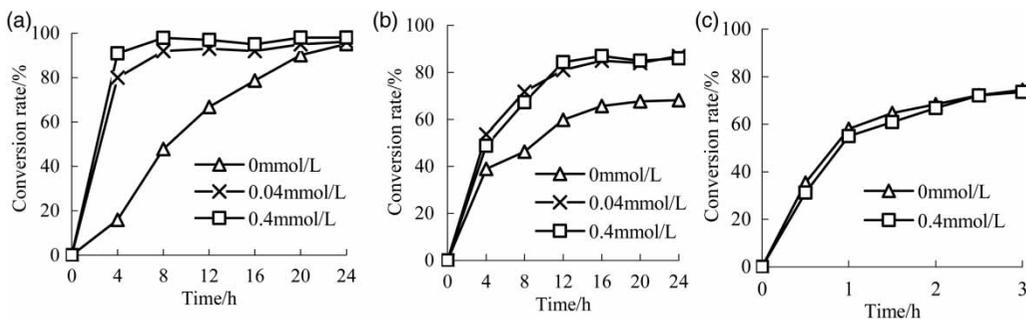


Figure 6 | Effect of  $\text{Fe}^{2+}$  on the photoconversion of  $\gamma$ -HCH in (a) water, (b) ice and (c) snow.

ice, and all the photoconversion could be described by the first-order kinetics model.

In water, snow and ice, the common photoproducts of  $\gamma$ -HCH were  $\alpha$ -HCH and pentachlorocyclohexene. The mechanisms were that the bonding of a chlorine atom was changed and a molecule of chlorine hydride was removed from each molecule of  $\gamma$ -HCH.

Adding different concentrations of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  all inhibited the photoconversion of  $\gamma$ -HCH in water, ice and snow, and the inhibition effect decreased with increasing concentrations of  $\text{NO}_2^-$  and  $\text{NO}_3^-$ , but increased with increasing concentrations of  $\text{HCO}_3^-$ . Different concentrations of  $\text{Fe}^{2+}$  promoted the photoconversion of  $\gamma$ -HCH in water and ice, but had little effect in snow.

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