

Photochemical oxidation of short-chain polychlorinated *n*-alkane mixtures using H₂O₂/UV and the photo-Fenton reaction

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ABSTRACT. The photochemical oxidation of a series of short-chain polychlorinated *n*-alkane (PCA) mixtures was investigated using H₂O₂/UV and modified photo-Fenton conditions (Fe³⁺/H₂O₂/UV) in both Milli-Q and lake water. All PCA mixtures, including chlorinated (Cl₅ to Cl₈) decanes, undecanes, dodecanes and tridecanes degraded in 0.02 M H₂O₂/UV at pH 2.8 in pure water, with 80 ± 4% disappearance after 3 h of irradiation using a 300 nm light source. Degradation was somewhat enhanced under similar conditions but in natural water. The modified photo-Fenton system was more effective in degrading PCAs, with 72% and 80% disappearance of chlorinated decanes in 45 min of irradiation in pure and natural water, respectively. Carbon chain-length had minimal effect on degradation rates; however, increased degree of chlorination (from Cl₅ to Cl₈) resulted in slower initial degradation rates and less complete conversion after 3 h of irradiation. Three hours of irradiation in natural water/H₂O₂/UV resulted in 95% degradation of parent PCAs accompanied by 93% release of chloride ion. Quantitative dechlorination, which may be indicative of complete mineralization, suggests that this is an effective water remediation technique for PCAs.

1. INTRODUCTION

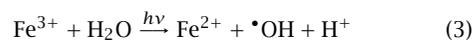
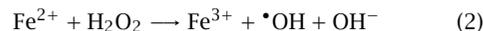
Homogeneous photodegradation is a well-known advanced oxidation process (AOP) for the treatment of water contaminated with persistent organic chemicals. In this process a primary oxidant, usually ozone (O₃), hydrogen peroxide (H₂O₂) or Fenton's reagent (Fe/H₂O₂), absorbs UV radiation generating hydroxyl radicals (•OH) which are capable of oxidizing many organic pollutants [1-3].

In the H₂O₂/UV system, hydroxyl radicals are produced by the photodissociation of hydrogen peroxide using UV irradiation with wavelengths below 360 nm [4]. The reaction is highly efficient in the gas phase with reported quantum yields (ϕ) of 0.98 ± 0.05 [5] and somewhat less efficient in aqueous solutions (quantum yields typically around 0.5) due to •OH scavenging by H₂O₂ [6].



The H₂O₂/UV system has been utilized for the oxidative degradation of a variety of organic pollutants [7] including hydrocarbon derivatives [8], halogenated phenols [9], pesticides and herbicides [10], and nitrotoluenes, nitrobenzenes and nitrophenols [11]. Fenton-type systems (Fe/H₂O₂), irradiated with UV or UV/visible light to enhance its oxidizing power [12, 13], provide another strategy for homogeneous generation of •OH radicals. These systems are termed photo-Fenton (Fe²⁺/H₂O₂/UV) or modified photo-Fenton

(Fe³⁺/H₂O₂/UV) depending on the initial oxidation state of iron [14, 15]. The generation of •OH radicals is enhanced in photo-Fenton systems since, in addition to the generation of •OH radicals on oxidation of Fe²⁺ to Fe³⁺ by H₂O₂, the Fe³⁺ produced absorbs light producing additional •OH and regenerating Fe²⁺:



In the modified photo-Fenton reaction [16], Fe²⁺ is photogenerated from Fe³⁺ *in situ* to avoid locally high concentrations of reagents. The Fe²⁺ formed reacts with H₂O₂ to produce •OH radicals as in (2). Both photo-Fenton and modified photo-Fenton reactions play important roles in the degradation of a wide variety of organic pollutants [17, 18].

Commercial chloroparaffins, used industrially as flame-retardant additives in high-pressure lubricants, plastics, sealants and adhesives, are complex mixtures of polychloro-*n*-alkanes (PCAs) with carbon chain-lengths ranging from C₁₀ to C₃₀. The physical properties of the short-chain PCAs (containing C₁₀-C₁₃ isomers) are comparable to those of many persistent organochlorines suggesting that their environmental transport may also be similar. The widespread environmental occurrence of short-chain PCAs in both surface water and biota [19] supports the notion that these compounds are relatively persistent environmental contaminants [20].

In previous studies we demonstrated that 1,10-dichlorodecane (D₂C₁₀) was rapidly photodegraded in

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the heterogeneous TiO₂ photocatalyst system [21], and that 1,2,9,10-tetrachlorodecane (T₄C₁₀) degraded with near stoichiometric release of chloride ion (Cl⁻) in the homogeneous H₂O₂/UV system [22]. The objectives of the present study were to extend our knowledge of the photodegradation of simple PCA isomers to more complex mixtures of short-chain (C₁₀-C₁₃) PCAs. More specifically, the suitability of H₂O₂/UV and modified photo-Fenton conditions for the photodegradation of short-chain PCA mixtures was investigated and the effects of natural water on their photodegradation rates in these systems was assessed.

2. EXPERIMENTAL

2.1. Chemicals and reagents. Polychlorinated decane (C₁₀), undecane (C₁₁), dodecane (C₁₂), and tridecane (C₁₃) mixtures, synthesized by free-radical chlorination of the respective *n*-alkanes [23], were provided by G. Tomy, Department of Fisheries and Oceans, Winnipeg (Canada). Each PCA mixture consisted of a complex mix of isomers and congener groups with chlorine numbers ranging from Cl₅ to Cl₈ as summarized in Table 1. Hydrogen peroxide solutions were prepared by diluting 30% (w/w) H₂O₂ with Milli-Q and natural water. Perchloric acid (HClO₄) was used for pH adjustment, sodium perchlorate (0.1 M) as ionic strength adjuster and *t*-butyl alcohol as radical scavenger. Ferric perchlorate, Fe(ClO₄)₃·9H₂O, purchased from Aldrich, was used in preparation of the Fenton-like reagent. Organic solvents, including hexane and dichloromethane, were HPLC grade.

Natural water with a pH of 6.8 and containing 420 mM dissolved inorganic carbon (DIC) and 430 mM dissolved organic carbon (DOC) was obtained from Lake 375 of the Experimental Lakes Area in northwestern Ontario (Canada). Suspended particles were removed by filtration through 1.2 μm Whatman GF/C glass-fiber filters to eliminate the potential for sorption during the experiments [24].

2.2. Preparation of solutions. Stock solutions of PCAs (44.0, 112.6, 100.0, and 204.3 μg/μL for chlorinated decanes, undecanes, dodecanes, and tridecanes, respectively) were prepared by carefully weighing individual amounts of each PCA mixture, dissolving each in 1.0 mL acetone and storing at 4 °C. Aqueous solutions of PCAs were prepared by carefully measuring out the appropriate aliquot of the stock solution (5.7 to 1.2 μL) into a 1.0 L volumetric flask, evaporating the acetone with a gentle stream of N₂ and dissolving in water. All PCA solutions used in photolytic experiments were prepared with a concentration of 250 μg/L to avoid exceeding the solubility limit [25].

In the modified Fenton reaction, acidic stock solutions of ferric perchlorate (1 mM) were prepared daily in perchloric acid (HClO₄) to prevent both precipita-

tion and the formation of polymeric Fe(III) species [26]. Perchlorate salts were used to avoid metal ion complexation (FeX⁽³⁻ⁿ⁾⁺ and FeX₂⁽³⁻²ⁿ⁾⁺), light absorption and chemical and photochemical reactions involving the counter ion [12]. Sodium perchlorate (100 mM) was added to all solutions to maintain constant ionic strength.

2.3. Photolysis procedures. The homogeneous photodegradation of PCA mixtures was investigated in aqueous solutions containing 0.02 M H₂O₂ and in solutions containing 1 × 10⁻³ M Fe(III) and 0.02 M H₂O₂ (modified Fenton conditions). Solutions (40 mL) were irradiated using a carousel Rayonet Photochemical Reactor fitted with 16 UV lamps emitting a band spectrum centered at 300 nm. Solutions, contained in borosilicate glass tubes, were exposed to 290-370 nm emissions with an intensity of 3.6 × 10⁻⁵ Ein/L · min as established by ferrioxalate actinometry. In experiments with H₂O₂, reactions were initiated by adding H₂O₂ and 0.1 M NaClO₄ with stirring (to keep the solution homogeneous and well-aerated), prior to placement in the photoreactor. For experiments with modified photo-Fenton conditions, the appropriate aliquot of the PCA mixture and the iron solution were added in quick succession to 0.02 M H₂O₂. The pH was adjusted with HClO₄ and/or NaOH and the samples were placed into the photoreactor. Samples were removed from the photoreactor after various irradiation times (0, 30, 60, 90, 120, 150, and 180 min) and extracted with 60 mL of 85 : 15 hexane/dichloromethane (extraction efficiency 70.5 ± 2.5%). Extracts were concentrated by rotary evaporation, transferred to a graduated centrifuge tube and evaporated to a volume of 300 μL with a stream of nitrogen. In selected experiments samples removed from the photoreactor were analyzed for chloride ion and total organic carbon (TOC) without solvent extraction.

PCA solutions were also irradiated in pure and natural water without added oxidants to determine the extent of direct and indirect photolysis. The significance of thermal or dark Fenton reactions was determined by wrapping sample tubes with aluminum foil prior to irradiation.

2.4. Analysis of PCAs. PCA mixtures were analyzed with a HP 5890 series II Gas Chromatograph interfaced with a HP 5880 Mass Spectrometer with a transfer line temperature of 280 °C. Samples were chromatographed on a 30 m × 0.25 mm × 0.25 μm PTE-5 capillary column (Supelco) after splitless injection of 1 to 2 μL at 200 °C by a 7673 HP autosampler. The column was temperature programmed as follows: 50 °C (2 min), 7 °C/min to 180 °C (5 min), 7 °C/min to 250 °C (15 min). Column head pressure was maintained at 14 psi, with an overall helium flow rate of 55 mL/min. The mass spectrometer was operated in negative chemical

Table 1. Classification of synthesized PCA mixtures summarizing the congener groups in each mixture and the abbreviated designation of each mixture.

Mixture	Precursor	Congener groups present
$\Sigma C_{10}Cl_{5-8}$	<i>n</i> -decane	$C_{10}Cl_5$, $C_{10}Cl_6$, $C_{10}Cl_7$, $C_{10}Cl_8$
$\Sigma C_{11}Cl_{5-8}$	<i>n</i> -undecane	$C_{11}Cl_5$, $C_{11}Cl_6$, $C_{11}Cl_7$, $C_{11}Cl_8$
$\Sigma C_{12}Cl_{5-8}$	<i>n</i> -dodecane	$C_{12}Cl_5$, $C_{12}Cl_6$, $C_{12}Cl_7$, $C_{12}Cl_8$
$\Sigma C_{13}Cl_{5-8}$	<i>n</i> -tridecane	$C_{13}Cl_5$, $C_{13}Cl_6$, $C_{13}Cl_7$, $C_{13}Cl_8$
$(\Sigma C_{10-13}Cl_{5-8})^a$	-	all congener groups above

^aComposite mixture prepared by mixing equal amounts of the four synthesized mixtures.

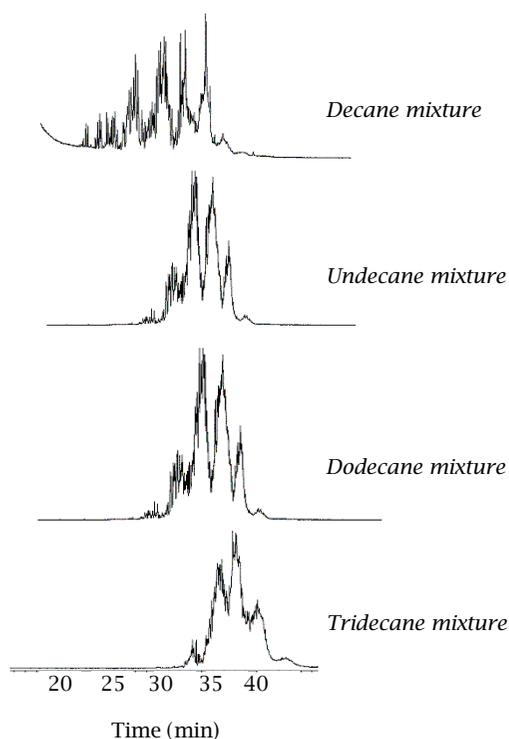


Figure 1. Total ion chromatograms of the chlorinated decane ($\Sigma C_{10}Cl_{5-8}$), undecane ($\Sigma C_{11}Cl_{5-8}$), dodecane ($\Sigma C_{12}Cl_{5-8}$) and tridecane ($\Sigma C_{13}Cl_{5-8}$) mixtures.

ionization (NCI) mode scanning at 0.9 sec per decade over the m/z range 15 to 550, with 1×10^{-4} torr methane as moderating gas. The ion source temperature was 150 °C and electron beam current 230 μA .

The concentration of a particular mixture was obtained by integration of its total ion chromatogram (TIC), illustrated in Figure 1 for the four PCA mixtures ($\Sigma C_{10}Cl_{5-8}$, $\Sigma C_{11}Cl_{5-8}$, $\Sigma C_{12}Cl_{5-8}$, and $\Sigma C_{13}Cl_{5-8}$). Due to the large number of isomers in each mixture resolution of individual components is not possible even with HRGC [27, 28]. Chromatograms of these complex mixtures are hence characterized by a wide range of elution times, covering 23.5 min for the composite mixture ($\Sigma C_{10-13}Cl_{5-8}$). The concentrations of each congener

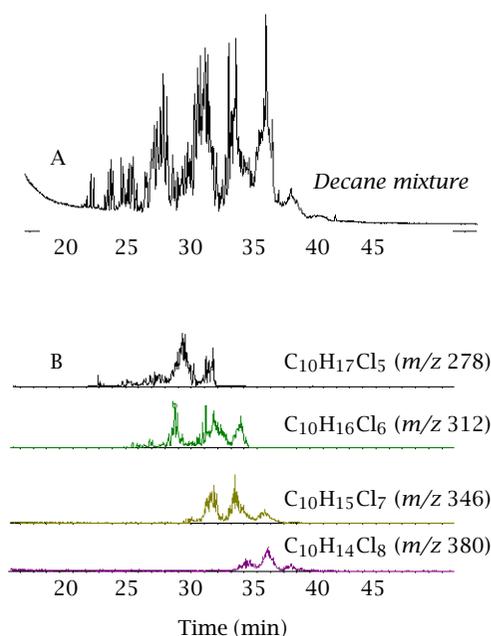


Figure 2. Total ion chromatogram of the chlorinated decane mixture (A) and extracted ion chromatograms of the $C_{10}Cl_5$, $C_{10}Cl_6$, $C_{10}Cl_7$, and $C_{10}Cl_8$ congener groups (B).

group (ΣCl_5 to ΣCl_8) in a given PCA mixture were determined by integration of extracted ion chromatograms which were obtained from the two most abundant ions in the $[M-HCl]^-$ cluster of each congener group (Table 2). Extracted ion chromatograms of the Cl_5 to Cl_8 congener groups in the chlorinated decane mixture are illustrated in Figure 2.

2.5. Determination of chloride ion (Cl^-). Chloride ion was measured with a Shimadzu LC-10AD Liquid Chromatograph utilizing a Phenomenex Star-ion A300 anion-exchange column and an Alltech 550 conductivity detector. The substituted styrene-divinylbenzene polymeric stationary phase contained a quaternary amine ligand to separate anions such as SO_4^{2-} and Cl^- . The instrument was calibrated daily using 70 μL of NaCl (VWR chloride certified reference standard) ranging from 0 to 5 mg/L.

Table 2. The m/z values of the two most prominent ions in the $[M-HCl]^-$ cluster for each congener group used to obtain extracted ion chromatograms.

Mixture	Cl ₅ group	Cl ₆ group	Cl ₇ group	Cl ₈ group
$\Sigma C_{10}Cl_{5-8}$	276/278	310/312	344/346	378/380
$\Sigma C_{11}Cl_{5-8}$	290/292	324/326	358/360	392/394
$\Sigma C_{12}Cl_{5-8}$	304/306	338/340	372/374	406/408
$\Sigma C_{13}Cl_{5-8}$	318/320	352/354	386/388	420/422

2.6. Determination of total organic carbon (TOC).

A TOC Analyzer (O.I. Corporation, Model 700) equipped with an autosampler with a 1.0 mL sample loop was used for total organic carbon analysis. Samples were acidified with phosphoric acid and sparged with carbon-free nitrogen to remove inorganic carbon. The sample was heated to 100 °C and treated with potassium persulfate to oxidize dissolved organic carbon (DOC) to CO₂ during a 6 min digestion period. The CO₂ produced was sparged from the sample with carbon-free nitrogen and trapped on a Molecular Sieve column at ambient temperature. After complete digestion the column was heated to 200 °C releasing CO₂ which was quantified by infrared (IR) detection.

3. RESULTS AND DISCUSSION

3.1. H₂O₂/UV process

Milli-Q water. Each of the short-chain PCA mixtures (decanes, undecanes, dodecanes, and tridecanes) was effectively photodegraded in Milli-Q water in the presence of 0.02 M H₂O₂ at pH 2.8, with 80 ± 4% disappearance in 3 h of irradiation. Carbon chain-length had minimal effect on degradation rates as illustrated in Figure 3. The rate of photodegradation of the chlorinated decane mixture decreased dramatically in the presence

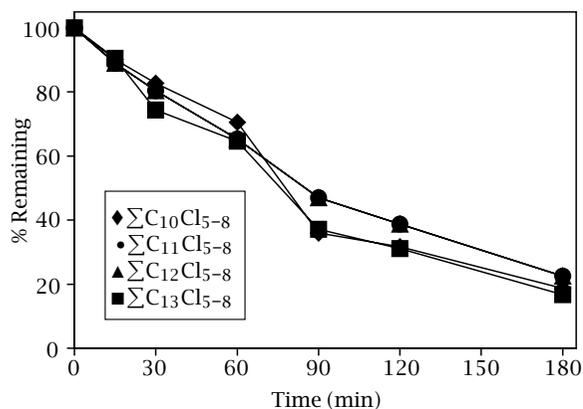


Figure 3. Homogeneous photodegradation of individual PCA mixtures ($\Sigma C_{10}Cl_{5-8}$ to $\Sigma C_{13}Cl_{5-8}$) in 0.02 M H₂O₂ (Milli-Q water) at pH 2.8 (0.1 M NaClO₄) using 300 nm UV light.

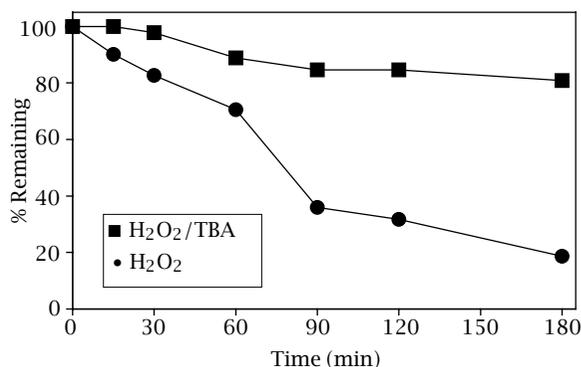


Figure 4. Degradation of the chlorinated decane mixture ($\Sigma C_{10}Cl_{5-8}$) in 0.02 M H₂O₂ (Milli-Q water) at pH 2.8 (0.1 M NaClO₄) using 300 nm UV light in the presence and absence of 0.10 M *tert*-butyl alcohol (TBA).

of 0.1 M *tert*-butyl alcohol (TBA) as shown in Figure 4. The inhibition, attributed to the scavenging of •OH radicals by TBA, [29, 30] supports free-radical



photooxidation of PCAs in the H₂O₂/UV process.

Chlorine number appeared to affect the photodegradation rate, however, the trend was not clearly delineated for individual mixtures as is illustrated for the decane mixture in Figure 5. For the $\Sigma C_{10}Cl_{5-8}$ mixture the Cl₅ congener group degraded faster than the Cl₆, Cl₇, and Cl₈ groups, with the latter appearing to degrade at similar rates. For example, after 90 min of irradiation the percent transformation decreased from 70% for the Cl₅ group to 59-64% for the Cl_{6,7,8} groups. Overall, the data for each of the PCA mixtures indicated that initial degradation rates of the Cl₅ congener group were consistently greater than for the Cl₈ group and that the extent of conversion decreased with increasing chlorine content after 2 to 3 h of irradiation. The slower initial rates may be due to decreased rate constants for reaction of •OH with higher chlorinated alkanes [29]. The less complete conversion for higher chlorinated alkanes may be attributed to scavenging of •OH radicals by chloride ion and/or the competition between the parent PCA and degradation products for •OH radicals. The release of chloride ion (see section 3.5) would have a greater •OH scavenging effect for higher

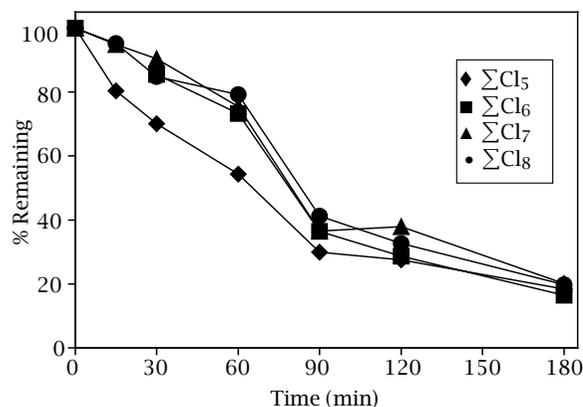


Figure 5. Homogeneous photodegradation of the chlorinated congener groups in the chlorinated decane ($\Sigma C_{10}Cl_{5-8}$) mixture in 0.02 M H_2O_2 (Milli-Q water) at pH 2.8 (0.1 M $NaClO_4$) using 300 nm UV light.

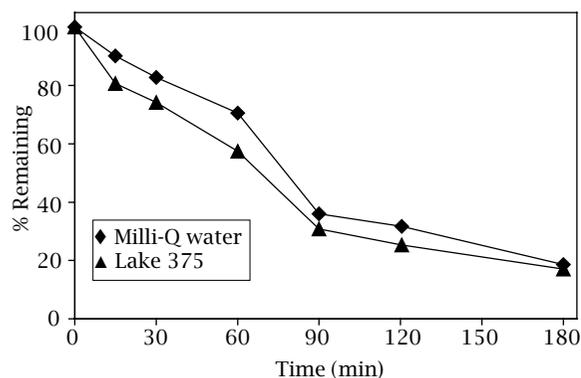
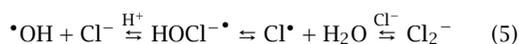


Figure 6. Degradation of the chlorinated decane ($\Sigma C_{10}Cl_{5-8}$) mixture in Milli-Q and Lake 375 water in the presence of 0.02 M H_2O_2 at pH 2.8 (0.1 M $NaClO_4$) using 300 nm UV light.

chlorinated PCA isomers, similar to the effects observed by Pignatello et al. [12] for the degradation of chlorophenoxy herbicides by hydrogen peroxide.



Lake water. PCA mixtures were also effectively photooxidized in Lake 375 water (pH 6.8) with 0.02 M H_2O_2 . As was the case in Milli-Q water, no clear trends in degradation rates were observed with respect to carbon chain-length, whereas degradation rates decreased with increasing chlorine number. The rate of degradation of PCA mixtures was slightly enhanced in Lake 375 water (83 to 94% disappearance in 3 h) compared to Milli-Q water (77 to 83% disappearance in 3 h). This may be due to the contributions of unknown photocatalysts or photosensitizers in the natural water. Figure 6 illustrates the difference in photodegradation rate of the chlorinated decane mixture in Lake 375 water relative

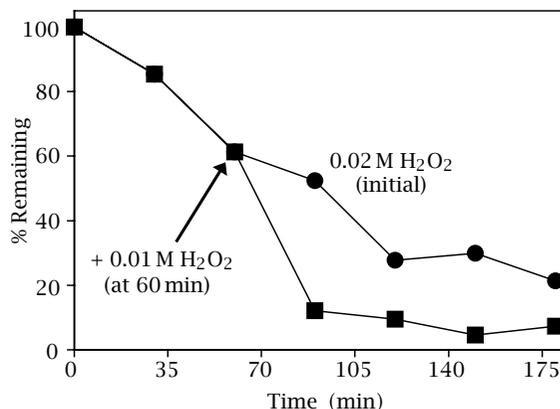


Figure 7. Effect of the addition of 0.01 M H_2O_2 during photodegradation of the composite PCA mixture ($\Sigma C_{10-13}Cl_{5-8}$) in 0.02 M H_2O_2 (Milli-Q water).

to Milli-Q water, with both at pH 2.8. Overall, aqueous solutions of 0.02 M H_2O_2 as a photooxidant are effective in degrading all of the PCA mixtures (decane, undecane, dodecane, and tridecane) in both natural and pure water.

3.2. The effect of H_2O_2 depletion. The rates of photodegradation of PCA mixtures by H_2O_2 tend to decrease after 90 min of irradiation (see Figures 3 to 6). The decreased rates of reaction may be due to depletion of H_2O_2 , and hence reduced generation of $\cdot OH$ radicals, during the irradiation period. We previously demonstrated that decreasing the concentration of H_2O_2 from 0.01 to 0.001 M significantly decreased the rate of degradation of 1,2,9,10-tetrachlorodecane [22]. The effect of H_2O_2 depletion was demonstrated in an experiment in which the composite PCA mixture was photodegraded using an initial H_2O_2 concentration of 0.02 M. The photodegradation rate decreased noticeably after approximately 60 min of irradiation. However, boosting the H_2O_2 concentration by an additional 0.01 M at 60 min produced an increase in the degradation rate (Figure 7). This result demonstrated that the degradation of PCA mixtures could be optimized by periodic addition of H_2O_2 during the reaction period.

3.3. Photo-Fenton conditions. PCA mixtures photodegraded rapidly under modified photo-Fenton conditions (0.001 M $Fe^{+3}/0.02$ M H_2O_2) in Milli-Q water at pH 2.8 as illustrated in Figure 8. As in the H_2O_2/UV system, there was no correlation between reactivity and carbon chain-length, with $81 \pm 3\%$ transformation for each of the PCA mixtures (C_{10} , C_{11} , C_{12} , and C_{13}) in 90 min of irradiation. Reactivity showed a weak correlation with chlorine number, with the Cl_5 and Cl_6 congener groups consistently degrading more rapidly than the Cl_7 and Cl_8 congener groups. The effects of chain-length and chlorine number were similar in Lake 375

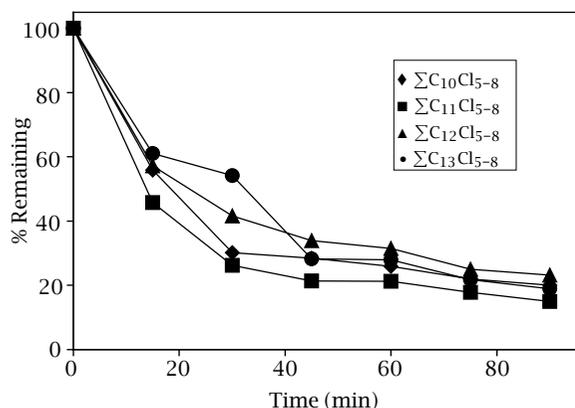


Figure 8. Degradation of individual PCA mixtures ($\Sigma C_{10}Cl_{5-8}$ to $\Sigma C_{13}Cl_{5-8}$) in Milli-Q water under modified photo-Fenton (0.02 M H_2O_2 /0.001 M Fe^{3+}) conditions at pH 2.8 (0.1 M $NaClO_4$) using 300 nm UV light.

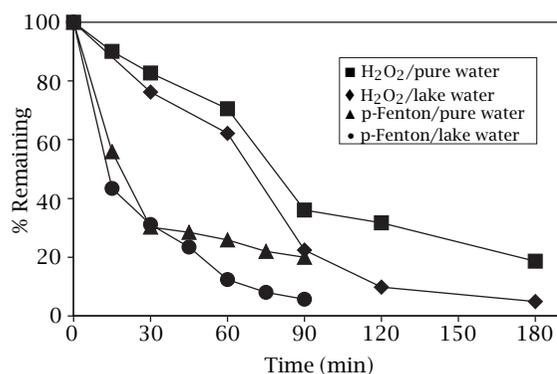


Figure 9. Comparison of the degradation rates of the composite PCA mixture ($\Sigma C_{10-13}Cl_{5-8}$) in Milli-Q and Lake 375 water under modified photo-Fenton (0.02 M H_2O_2 /0.001 M Fe^{3+} /UV) and 0.02 M H_2O_2 /UV conditions using 300 nm UV light. Milli-Q water is at pH 2.8, Lake 375 water at pH 6.8 and both contain 0.1 M $NaClO_4$.

water adjusted to pH 2.8; however, all PCA mixtures degraded more rapidly in lake water, with $93 \pm 2\%$ transformation in a 90 min irradiation period. The increased rates of degradation in lake water are again attributed to the contributions of photocatalysts and/or photosensitizers in the natural water. Thermal degradation of PCA mixtures was slow under modified-Fenton or dark conditions, in agreement with observations for 1,2,9,10-tetrachlorodecane [22].

3.4. Comparison between H_2O_2 /UV and modified photo-Fenton. Although PCAs are degraded in the H_2O_2 /UV system, the rate of degradation is significantly enhanced under modified photo-Fenton ($Fe^{3+}/H_2O_2/UV$) conditions in both Milli-Q and natural water due to the enhanced production of $\cdot OH$ radicals. For example, in 30 min of irradiation 17.3

and 23.7% transformation was observed for the composite PCA mixture in Milli-Q and Lake 375 water, respectively, in H_2O_2 /UV. Under photo-Fenton conditions the extent of transformation increased to 68.8 and 69.9% over the same 30 min irradiation period (Figure 9). The results are consistent with previous reports for the degradation of chlorinated aromatic compounds by the photo-Fenton reaction. Gallard et al. [31] observed increased oxidation rates of 1,2,4-trichlorobenzene (1×10^{-6} M) in the presence of modified photo-Fenton conditions at $pH \leq 3$. Pignatello et al. have shown that the degradation of chlorophenoxy herbicides [12], polychlorinated dibenzo-*p*-dioxins and dibenzofurans [32] and PCBs [33] were more efficient in the presence of $Fe^{3+}/H_2O_2/UV$ compared to Fe^{3+}/H_2O_2 and H_2O_2/UV . Furthermore, the complete oxidation of the pesticides metolachlor and methyl parathion was reported [34] under modified photo-Fenton conditions. Recently, Ghaly, et al. [35] studied the photodegradation of *p*-chlorophenol at pH 3 with 0.01 M H_2O_2 and 0.4 mM Fe^{3+} using a 700-W high-pressure Hg lamp. Their results indicated that the $Fe^{3+}/H_2O_2/UV$ system enhanced the rate of degradation of *p*-chlorophenol by a factor of 9 over the UV/ H_2O_2 process. The multiple production of $\cdot OH$ radicals via photolysis of H_2O_2 (eq. 1), photolysis of $Fe(III)$ (eq. 3) and regeneration of $Fe(II)$ (eq. 2) is advantageous for the homogeneous photodegradation of chlorinated aliphatic as well as chlorinated aromatic pollutants.

3.5. Mineralization of PCAs with H_2O_2 /UV. Details about the extent of degradation may be obtained by determining total organic carbon (TOC) and chloride ion during the course of the reaction. We monitored these parameters for the photooxidation of a composite mixture of short-chain PCAs in Lake 375 water at pH 6.8 in the H_2O_2 /UV system. Chromatograms of the composite PCA mixture ($\Sigma C_{10-13}Cl_{5-8}$), determined by selected-ion-monitoring, revealed that the lower mass fraction (the lower chlorinated isomers) degraded more rapidly than the higher mass fraction (the higher chlorinated components) and that the levels of the parent PCA components approach detection limits in 3 h of irradiation (Figure 10). It is of interest that total organic carbon, consisting predominantly of natural DOC, degraded at rates similar to the rate of degradation of the parent PCA (Figure 11). After 2 h of irradiation 78% of the parent PCAs degraded while TOC decreased by 80%. Continued irradiation to 3 h resulted in a further decrease of parent PCAs to 95%. However, the degradation of TOC appeared to slow with 85% disappearance after 3 h. The high levels of DOC, even after 3 h of irradiation, precluded detection of persistent PCA photo-products. The release of chloride ion which accompanied the photooxidation of PCAs (Figure 12) amounted to an estimated 93% dechlorination over the 3 h irradiation period. The near quantitative release of Cl^-

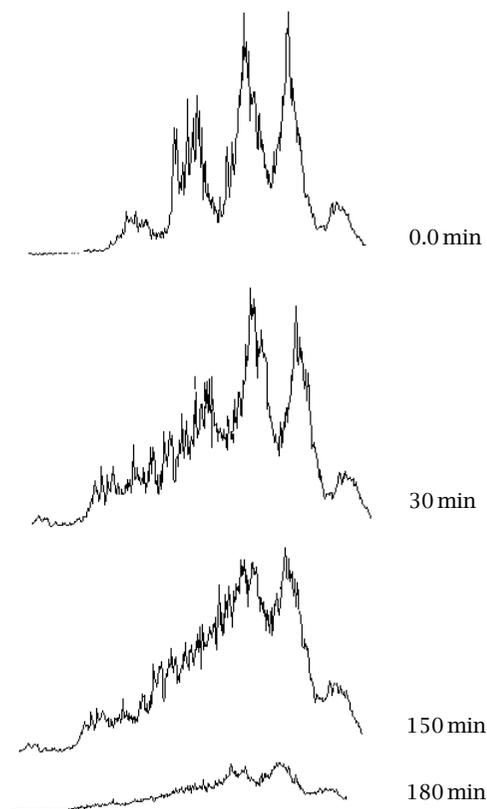


Figure 10. Photodegradation of the composite PCA mixture ($\Sigma C_{10-13}Cl_{5-8}$) in Lake 375 water (pH 6.8) with 0.02 M H_2O_2 using 300 nm UV light.

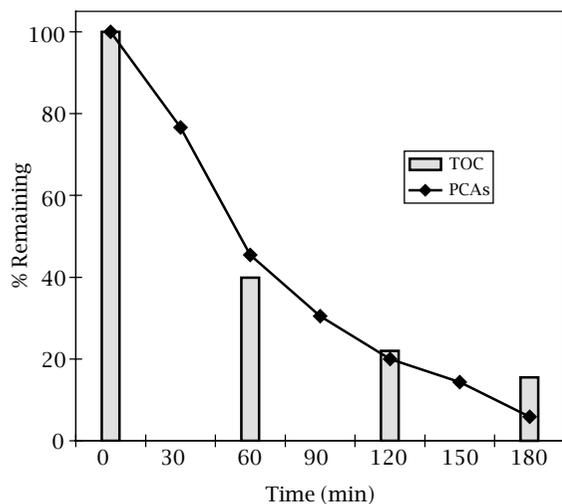


Figure 11. Degradation of total organic carbon and a composite mixture of PCAs ($\Sigma C_{10-13}Cl_{5-8}$) in Lake 375 water (pH 6.8) with 0.02 M H_2O_2 using 300 nm UV light.

indicates the absence of significant chlorinated organic photoproducts.

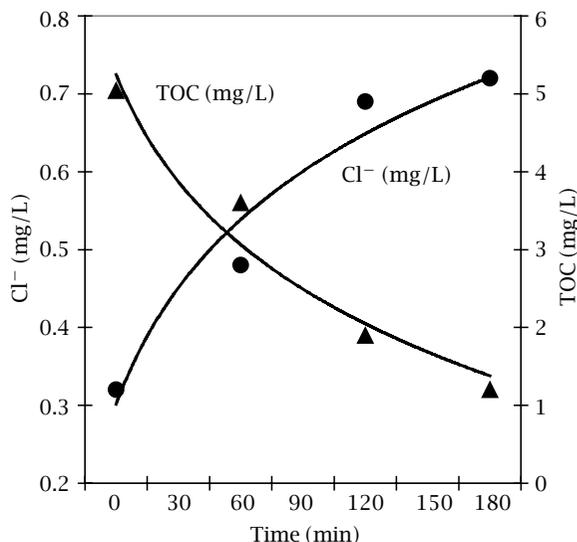


Figure 12. Release of chloride ion and degradation of total organic carbon during the photodegradation of the composite PCA mixture ($\Sigma C_{10-13}Cl_{5-8}$) in Lake 375 water (pH 6.8) in the presence of 0.02 M H_2O_2 using 300 nm UV light.

These results agree with an earlier study in which we reported the near stoichiometric release of Cl^- for 1,2,9,10-tetrachlorodecane (T_4C_{10}) after 80 min of irradiation in 0.01 M H_2O_2 at pH 2.8 [22]. However, Cl^- release was slower than degradation of the parent T_4C_{10} indicative of a pathway involving formation of chlorinated organic intermediates that degrade more slowly than the parent tetrachlorodecane.

Studies are continuing to determine the optimal Fe^{3+}/H_2O_2 ratios for photodegradation and the extent of mineralization of PCA mixtures in the modified photo-Fenton system.

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