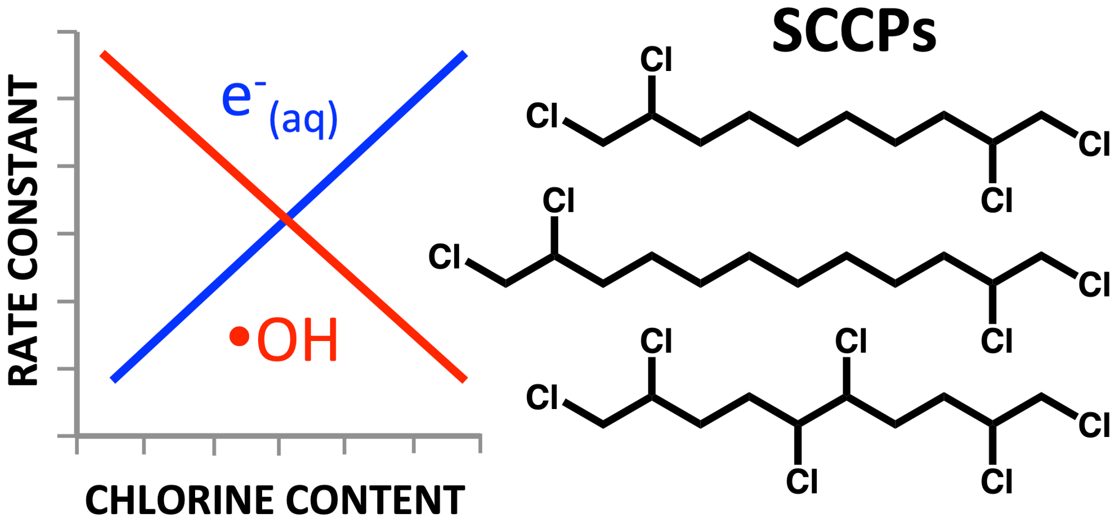
Photochemical degradation of short-chain chlorinated paraffins in aqueous solution by hydrated electrons and hydroxyl radicals

Brian P. DiMento,[1,2]* Cristina L. Tusei,[1,3] Christoph Aeppli[1,2]

1. Bigelow Laboratory for Ocean Sciences, East Boothbay, ME, USA
2. Colby College, Waterville, ME, USA
3. Humboldt State University, Arcata, CA, USA

ABSTRACT

Short-chain chlorinated paraffins (SCCPs) are a complex mixture of polychlorinated alkanes (C_{10}-C_{13}, chlorine content 40-70%). While these compounds are categorized as persistent organic pollutants, there are knowledge gaps about their environmental degradation, particularly the effectiveness and mechanism of photochemical degradation in surface waters. Photochemically-produced hydrated electrons ($e^-_{(aq)}$) have been shown to degrade highly chlorinated compounds in environmentally-relevant conditions more effectively than hydroxyl radicals (·OH), which can degrade a wide range of organic pollutants. This study aimed to evaluate the potential for $e^-_{(aq)}$ to degrade SCCPs, and compare this reaction to ·OH-mediated degradation. To this end, the degradation of SCCP model compounds was investigated under laboratory conditions that photochemically produced $e^-_{(aq)}$ or ·OH. Resulting SCCP degradation rate constants for $e^-_{(aq)}$ were on the same order of magnitude as well-known chlorinated pesticides. Experiments in the presence of ·OH yielded similar or higher second-order rate constants. By compiling literature data for a wide range of chlorinated compounds, it was found that higher chlorine content results in higher rate constants for $e^-_{(aq)}$ and lower for ·OH. Above a composition of approximately 60 % Cl, the $e^-_{(aq)}$ second-order rate constants were higher than rate constants for ·OH reactions. The results of this study imply that SCCPs are susceptible to photochemical degradation in the environment, facilitated by dissolved organic matter and other sources of reactive intermediates in sunlit surface waters.



KEYWORDS

Photodegradation, chlorinated paraffin, persistent organic pollutant, hydrated electron, hydroxyl radical

INTRODUCTION

Short-chain chlorinated paraffins (SCCPs) are a highly complex mixture of polychlorinated *n*-C_{10} through *n*-C_{13} alkanes with thousands of congeners and a chlorine content typically between 40 and 70%.[1] They are high-volume industrial chemicals that have been used since the 1930s as additives in high-pressure lubricants and cutting fluids for metalworking, as well as flame retardants and plasticizers in a variety of products such as paints, adhesives, and sealants.[1,2] SCCPs are compounds of concern due to their toxicity, bioaccumulation potential,[3] persistence, and long-range transport potential.[2,4-12] Due to the widespread usage and improper disposal of products containing SCCPs, they can now be found throughout the environment in surface waters, sediments, and biota.[2,13-21]

Understanding the fate of SCCPs in the aquatic environment is critical to estimating their bioaccumulation and environmental risk. Although SCCPs have undergone environmental risk assessment for more than 30 years,[22-24] the Persistent Organic Pollutants Review Committee (POPRC) of the Stockholm Convention concluded in 2016 that the current studies on photodegradation and biodegradation are of limited use for assessing the degradation of SCCPs in natural waters and that "there is insufficient information to conclude on the persistence of SCCPs in water."[21] While studies on biodegradation found the possibility of degradation in activated sewage sludge[25,26] and aerobic sediments,[22,27,28] SCCPs can still be detected in sediments after more than 50 years. Besides biodegradation, the other potentially relevant environmental sink for SCCPs is photodegradation; however, there are only a few studies focusing on this process.[29-33] These studies leave major knowledge gaps regarding photochemical degradation under environmentally relevant conditions. To constrain the fate of SCCPs in the environment, more research into their photochemistry is necessary.

Since SCCPs do not absorb light in the wavelengths relevant on the Earth's surface, direct photochemical degradation of SCCPs is not a viable pathway.[34] However, indirect photodegradation pathways involving reactions with photochemically produced reactive intermediates (PPRI) are possible. These intermediates, including hydroxyl radicals (·OH) and hydrated electrons ($e^{-}_{(aq)}$), are formed following the absorption of light by constituents of natural water such as dissolved organic matter (DOM) or nitrate.[35] ·OH have been implicated in the photochemical degradation of many organic pollutants.[36-39] However, they seem to be less important in the degradation of highly chlorinated alkanes,[40] suggesting that the ·OH-mediated degradation might not be relevant for all SCCPs.

On the other hand, $e^{-}_{(aq)}$ have been shown to be important in the degradation of chlorinated pollutants including mirex,[41,42] hexachlorobenzene,[43] chloromethanes,[44] chloroethanes,[40] and more recently per- and polyfluoroalkyl substances (PFAS).[45,46] While $e^{-}_{(aq)}$ has been a known product of water radiolysis for more than 50 years,[47] it can also be produced in surface waters by the interaction of sunlight with constituents of DOM.[48] It appears that the lifetime of the $e^{-}_{(aq)}$ in the DOM phase is sufficient for its reaction with hydrophobic compounds sorbed by DOM.[49] Due to the hydrophobic nature of SCCPs, with estimated octanol-water partition coefficients (K_{ow}) between 9×10^4 and 3×10^7, these compounds have the potential to be degraded by this mechanism.[50] However, the reactivity of $e^{-}_{(aq)}$ towards SCCPs has not yet been systematically investigated. In addition, the majority of previous research has focused on engineered systems for water treatment, not environmentally-relevant processes.[40,44,46,51-56]

The aim of this study was therefore to determine the reactivity of SCCPs with $e^{-}_{(aq)}$, and compare it to ·OH-mediated degradation. This knowledge will provide additional insights into their photochemical fate in surface waters. In the environment, the degradation of SCCPs is likely a function of their reactivity as well as their partitioning into DOM. Since the focus of this study was the reactivity of SCCPs, experiments were performed in DOM-free conditions, where $e^-_{(aq)}$ are produced using an artificial photosensitizer, N,N-dimethylaniline[48] (DMA), and ·OH are produced by nitrate (NO_3^-) photolysis.[57] Later studies will investigate SCCP sorption and degradation in the presence of DOM.

MATERIALS AND METHODS

Chemicals. Preliminary photodegradation experiments were conducted with the following chlorinated organic compounds (COCs) representing a range of K_{ow} values and degrees of chlorination: 1,6-dichlorohexane (DCH), 1,10-dichlorodecane (DCD), chlorobenzene (CB), and lindane (γ-hexachlorocyclohexane) (obtained from Sigma-Aldrich; St Louis, MO). N,N-dimethylaniline (DMA) was used for hydrated electron ($e^-_{(aq)}$) generation[48] and sodium nitrate for hydroxyl radical (·OH) generation[57] (Sigma-Aldrich). Both compounds were used at final aqueous concentrations of 1 mM. Buffered solutions were prepared with mono- and dibasic potassium phosphate (Sigma-Aldrich).

Due to the lack of commercially available, affordable single compounds or simple mixtures of SCCPs (in gram quantities), three model compounds were synthesized for use in photodegradation experiments. 1,2,9,10-tetrachlorodecane (TCD) (50.6 % Cl), 1,2,5,6,9,10-hexachlorodecane (HCD) (61.0 % Cl), and 1,2,11,12-tetrachlorododecane (TCDod) (46.0 % Cl) were chosen as representative SCCPs due to their varying degrees of chlorination and carbon chain length, as well as the commercial availability of their diene and triene precursors: 1,9-decadiene, 1,5,9-decatriene, and 1,11-dodecadiene (Combi-Blocks Inc.; San Diego, CA). Chlorination of the double bonds was achieved using sulfuryl chloride (SO_2Cl_2; Sigma-Aldrich) as a chlorine source and 2,2’-azobis(2-

methylpropionitrile) (AIBN; Sigma-Aldrich) as a radical initiator[4,58,59] (Figure S1 in Supporting Information). Further details on the synthesis procedure are provided in the Supporting Information (SI). Analytical standards (100 μg/mL) for TCD, HCD, and TCDod were obtained from Chiron (Trondheim, Norway) to identify and quantify the synthesized SCCPs.

Preparing Solutions for Experiments. Experiments were conducted in reagent grade water buffered to pH 7 with 1 mM phosphate buffer. To remove organic and trace metal contaminants, all glassware was soaked overnight in 1% detergent (Extran 300; Sigma-Aldrich) detergent followed by 10% hydrochloric acid. After rinsing with reagent grade water, the glassware was muffled overnight at 450 °C to remove organic contaminants.

During preliminary experiments with CB and lindane, chlorinated compounds were added directly in an acetonitrile (ACN) solution. ACN was selected because it is an inert co-solvent with minimal effect on the degradation mechanism.[29,60] 100 μL of chlorinated compound mixture in ACN was added per liter of solution to achieve final concentrations of 100 nM CB and lindane (approximately 10x below their water solubility). The solution was then stirred for 24 hours to ensure that the compounds were fully dissolved prior to beginning an experiment.

For experiments with low oxygen, purging was done using ultrapure nitrogen flowing through a gas dispersion tube (Ace Glass, porosity B, 70-100 um) for 6 hours. Oxygen concentrations were measured using a PreSens Microx 4 fiber optic oxygen meter with NTH-PSt7 microsensor (PreSens Precision Sensing GmbH; Regensburg, Germany). They dropped from 2.78×10^{-4} M in air-saturated solution to 7.50×10^{-5} M, or about 26 % saturation, after purging and transferring the solution to reaction vessels.

Due to the low solubility of SCCPs, a passive dosing approach was taken for adding these compounds to the reaction solution[61]. Discs (8 mm diameter) were cut out of a sheet of polydimethylsiloxane (PDMS; 0.8 mm thickness, 50 durometer; CS Hyde, Lake Villa, IL). They were cleaned prior to use by soaking overnight in 1% Extran, 10% HCl and then three portions of methanol (MeOH). To load the discs with COCs, they were equilibrated in 20 mL MeOH solutions containing the COCs (see Table S1 for details), placed on a shaker table for ~ 24 h. Loaded PDMS discs were gently rinsed with reagent grade water to remove MeOH. Two discs were added per liter of buffered water, which equilibrated overnight on a shaker table in glass media bottles. Due to the low partitioning of COCs from MeOH onto PDMS, the depletion of COCs in MeOH after equilibration discs was minimal (< 1%); therefore, the same MeOH solution was reused for each experiment. The concentration of chlorinated compounds needed in MeOH for desired final aqueous concentrations was estimated by predicting PDMS-MeOH and PDMS-water partition coefficients of COCs using the COSMO-RS based COSMOtherm software.[62] After an initial test, the COC concentrations in MeOH were adjusted as needed, achieving initial aqueous COC concentrations of ~15-120 nM (Table S1).

Experiments were performed with mixtures of COCs, as it was assumed that the presence of multiple COCs would not significantly decrease the steady-state concentration of $e^-_{(aq)}$ ($[e^-_{(aq)}]_{ss}$). The rationale for this assumption was that O_2 typically acts as the primary sink of $e^-_{(aq)}$ in aerated solution, and therefore controls $[e^-_{(aq)}]_{ss}$. The second-order rate constant for oxygen's reaction with $e^-_{(aq)}$ ($2.00\text{x}10^{10}$ M^{-1} s^{-1})[63] is equal to or greater than expected values for the COCs studied (10^8-10^{10} M^{-1} s^{-1}; Table S7).[40,41,63,64] Furthermore, the oxygen concentration in air-equilibrated aqueous solutions (278 μM) was much greater than the COC concentrations used in these experiments. As a result, the predicted decrease in $[e^{-}_{(aq)}]_{ss}$ resulting from the presence of numerous COCs was expected to be less than 1%. To confirm the validity of our assumptions, we measured the degradation rate constant of lindane independently and in a mixture of three COCs. The resulting degradation rate constants were not significantly different ($p = 0.3598$) between the two solutions.

Photodegradation Experiments. A solar simulator with a 1,800 W Xe arc lamp (Q-SUN Xe-1; Q-Lab Corp., Westlake, OH) was used for photodegradation experiments. A Daylight-Q filter (Q-Lab Corp.) was chosen to provide an accurate spectral match to direct sunlight at the Earth's surface (Figure S2). The irradiance was calibrated at 340 nm and 0.68 W m^{-2} using an irradiance sensor (Q-SUN Irradiance Smart Sensor; Q-Lab Corp.) to ensure that higher energy wavelengths were accurately represented. This intensity closely matches the solar maximum at the Earth's surface (global, noon sunlight, normal incidence during summer solstice[65]). Absolute irradiance spectra of the solar simulator and natural sunlight measured with a FLAME spectroradiometer (Ocean Insight; Orlando, FL) are shown in Figure S2, and irradiance intensities at UVB (280-320 nm), UVA (320-400 nm), and PAR (400-700 nm) wavelengths are shown in Table S2.

Reaction vessels consisted of custom quartz round bottom flasks (Quartz Scientific, Inc.; Fairport Harbor, OH) with a volume of about 330 mL (86 mm diameter) and Teflon lined screw caps. Flasks were filled to minimize headspace, and eight at a time sat partially submerged in a water bath inside the solar simulator. The solar simulator was modified so that the irradiation chamber sat horizontally to accommodate the water bath. An internal fan kept the water and samples at 25 °C. Teflon coated magnetic stir bars were used to homogenize solutions during the irradiations, which lasted up to 24 h. Each experiment consisted of three to five irradiation durations (i.e., time points), each repeated in duplicate or triplicate. Two time points were repeated with foil-wrapped samples for dark controls to account for potential non-photochemical loss of COCs. Generally, no loss was observed in the dark control samples.

Solar actinometry experiments[66] were used to quantify light fluxes within the reaction vessels and to correct for variability in light intensity at the eight positions where flasks were placed within the irradiation chamber. The average light dose received by the sample calculated using the nitrate actinometer was 5.55 ± 0.31 μE cm^{-2} h^{-1} (5.5 % relative standard deviation between positions). Calculating the actinic flux (outside the quartz flasks) using data collected with a spectroradiometer across the spectral bandwidth of the actinometer (307-333 nm) yielded values of 8.87, 7.27, and 6.56 μE cm^{-2} h^{-1} at the top, middle, and bottom height of the flask. This difference between actinometry and spectroradiometer-derived light fluxes highlights the importance of actinometry in accounting for the attenuation and scattering of light by the vessels and its surroundings.

Irradiance in the UV range is relevant for the investigated DMA and NO_3^--sensitized reactions. The total UV intensity of natural sunlight at sea level is about 5% of net surface shortwave (290 - 4000 nm) surface radiation (168 W m^{-2}),[67,68] or about 8.4 W m^{-2}. The total UV output by the solar simulator at the top of the reaction vessel was 69.1 W m^{-2}, which is about 8.2 times higher than global average sunlight (mean daily irradiance averaged spatially and temporally). Therefore, a 24 h irradiation corresponded to 8.2 days of average solar radiation on Earth reaching the flask.

Analytical Methods. Following irradiation experiments, samples were extracted three times with 15, 10, and 10 mL of dichloromethane (DCM) using o-terphenyl (oTP) as a recovery standard. The DCM was dried with sodium sulfate, and the volume was reduced to ~1 mL in a rotary evaporator followed by a nitrogen evaporator. COCs were analyzed by gas chromatography coupled to mass spectrometry (GC-MS) using a 7890B GC coupled to a 5977A MS (Agilent Technologies, Inc.; Santa Clara, CA) equipped with a DB-XLB column (60 m, 250 µm i.d., 0.25 µm film, Model 122-1262; Agilent Technologies). Samples were injected in splitless mode, using an injector temp of 300 °C and a transfer line temperature of 300 °C. The column temperature was 40 °C for 10 min, then ramped to 300 °C at a rate of 20 °C min^{-1}, and was held there for 15 min. Ultra-high purity He (99.999%) was used as carrier gas with a constant flow of 1.2 mL min^{-1}. The MS was operated in selected ion monitoring (SIM) mode using two dominant mass fragments for each compound. Quantification was performed using a 6-point calibration curve, using the internal standard (deuterated chlorobenzene, Sigma-Aldrich) to calculate relative responses. The recovery standard oTP was used to account for losses during extraction.

Data evaluation. Degradation of the COCs generally followed apparent (pseudo) first-order kinetics following the equation $d[C]/dt = -k'[C]$, where [C] is the concentration of the COC and k' is the apparent first-order rate constant. These kinetics rely on a steady-state concentration of a single PPRI ($[PPRI]_{ss}$). The apparent first-order rate constant is therefore defined as $k' = k_C[PPRI]_{ss}$, where k_C is the second-order rate constant for the reaction between the COC and the PPRI. Degradation in this study represents the loss of the parent COC – products with lower degrees of chlorination are potentially formed and further degraded during the experiments.

Apparent first-order rate constants were reported in s^{-1} units, but they can be converted to photon flux for comparison with other studies by dividing by the light dose (e.g., using the light dose from the nitrate actinometer, 5.55 μE cm^{-2} h^{-1} or 15.4 μE m^{-2} s^{-1}). In some experiments, first-order kinetics were not followed for the entire 6 or 24 h duration, possibly indicating that the PPRI concentration was changing due to factors such as a decreasing concentration of the PPRI source, an increasing sink, or increased light attenuation due to colored byproducts of the reaction. In these cases, rate constants were calculated from the linear portion of the ln(concentration) vs. time regression. When multiple experiments were conducted with the same compound, data were pooled to calculate degradation rate constants. The Prism software from GraphPad was used to evaluate statistical differences in rate constants.

RESULTS AND DISCUSSION

Evaluating Direct Photodegradation of SCCPs. Control experiments were conducted in pH 7 buffered Milli-Q water testing for the presence of direct photochemical degradation. No significant degradation was observed for irradiation times up to 24 h (Table S3). This is not surprising given the lack of light absorption in the range of the solar spectrum reaching the Earth's surface (> 290 nm) for SCCPs.[29,34]

Indirect SCCP Degradation in DMA system. In irradiated aqueous solutions containing the $e^-_{(aq)}$-producing DMA,[69] degradation of all investigated COCs was observed (Figure 1). The SCCP first-order rate constants ranged from $2.5\text{x}10^{-5}$ s^{-1} (TCDod) to $3.9\text{x}10^{-5}$ s^{-1} (HCD). Dichlorinated compounds degraded more slowly than similar tetra- and hexachlorinated compounds (DCH/DCD vs. TCD/HCD; see Table S4 for statistics). These SCCP degradation rate constants were lower, but in the same order of magnitude as that of well-characterized compounds such as lindane (ɣ-hexachlorocyclobenzene; k' = $7.8\text{x}10^{-5}$ s^{-1}), which has previously been investigated for its $e^-_{(aq)}$ reactivity.[43] We included this compound for all experiments throughout this study to facilitate comparison with previous studies.

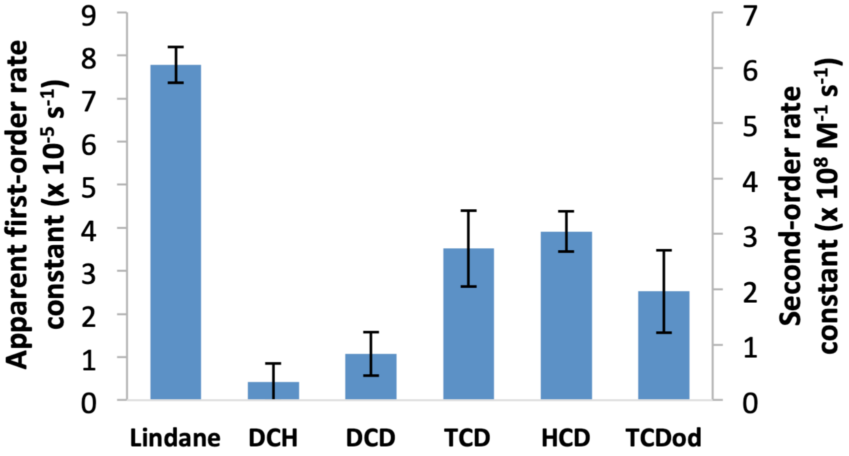


Figure 1. Apparent first and second-order rate constants for the photochemical degradation of chlorinated compounds lindane, 1,6-dichlorohexane (DCH), 1,10-dichlorodecane (DCD), 1,2,9,10-tetrachlorodecane, 1,2,5,6,9,10-hexachlorodecane (HCD), and 1,2,11,12-tetrachlorododecane (TCDod) in solutions of 1 mM dimethylaniline (DMA).

Confirming $e^-_{(aq)}$ as Reactive Species. To confirm that $e^-_{(aq)}$ is responsible for the observed degradation, amendments were made to the solution by changing the type and concentration of scavengers present (Figure 2). Known scavengers that affect $[e^-_{(aq)}]_{(ss)}$ and thus k' include hydrogen ions (H^+),[70] oxygen (O_2),[63] and halogenated compounds such as 2-chloroethanol (ClEtOH).[71]

First, we tested the effects of varying H^+ concentrations. At pH 3, the degradation rate constant of both TCD and lindane significantly decreased compared to a pH 7 solution (Figure 2, Table S5). This result supports the hypothesis that $e^-_{(aq)}$ is responsible for their degradation, as H^+ is known to react with it at a diffusion-controlled rate.[41,70] At a pH of 11, only TCDod showed a significant change (increase) in the apparent degradation rate constant compared to a pH 7 solution. Our observations are consistent with that of Burns et al.,[41] who also observed an increase in COC degradation at high pH, citing the potential for hydroxide ions to quench electron transfer reactions.[70]

Second, we varied the dissolved oxygen in the solution. With its rapid reaction with $e^-_{(aq)}$, O_2 is an important scavenger of $e^-_{(aq)}$ in aqueous solutions. In solutions purged with N_2, lindane, TCD, and HCD degraded significantly faster than in oxygen-saturated solution (Figure 2, Table S5). While TCDod also degraded more quickly, the increase in rate constant was not quite significant. The observed increase in k' with decreasing O_2 concentrations are consistent with $e^-_{(aq)}$ as reactive species, and rule out oxygen-based PPRI such as singlet oxygen and superoxide. Thereby, O_2 is either a scavenger of $e^-_{(aq)}$ or it quenches excited states that are $e^-_{(aq)}$ precursors.

Last, we added 2-chloroethanol (ClEtOH), which has been reported to be an effective probe for $e^-_{(aq)}$.[71] Addition of 0.05 M ClEtOH to a 1 mM DMA solution resulted in significantly slower degradation of lindane, TCD, and HCD (Figure 2, Table S5). Again, TCDod followed the same trend, but the change was not quite significant.

Assuming that dissolved O_2 is the primary sink for $e^-_{(aq)}$ and thus controls its steady-state concentration ($[e^-_{(aq)}]_{ss}$), the production rate of $e^-_{(aq)}$ ($r_{e^-}^{prod}$) can be estimated from $r_{e^-}^{prod} = k_{e^-}[e^-_{(aq)}]_{ss}[O_2]$. Using the previously published second-order rate constant for the reaction between lindane and $e^-_{(aq)}$ of 6.05×10^8 M^{-1} s^{-1},[41] a $[e^-_{(aq)}]_{ss}$ of 1.29×10^{-13} M was calculated. Given a O_2 concentration in our air-saturated solution of 2.78×10^{-4} M and a rate constant for the reaction of $e^-_{(aq)}$ with O_2 of 2×10^{10} M^{-1} s^{-1},[41,63] a $e^-_{(aq)}$ production rate of

7.15×10^{-7} M^{-1} s^{-1} was determined. With an added ClEtOH concentration of 0.05 M and a reported rate constant for its reaction with $e^-_{(aq)}$ of 4.1×10^{8} M^{-1} s^{-1},[72] a new $[e^-_{(aq)}]_{ss}$ was calculated using the previously determined production rate of $e^-_{(aq)}$. The predicted decrease in $[e^-_{(aq)}]_{ss}$ of 72 % was in close agreement with the observed 67 % decrease.

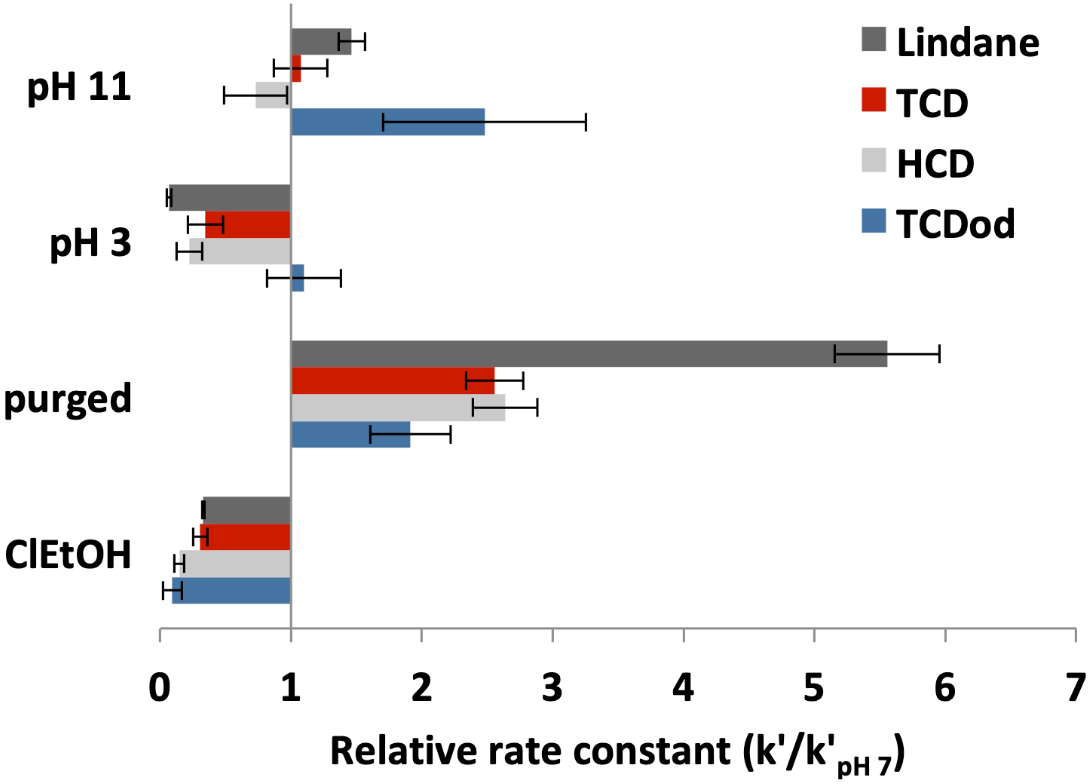


Figure 2. Effect of pH, deoxygenation, and addition of 2-chloroethanol on the apparent first-order rate constant for lindane, 1,2,9,10-tetrachlorodecane (TCD), 1,2,5,6,9,10-hexachlorodecane (HCD), and 1,2,11,12-tetrachlorododecane (TCDod) compounds relative to their rate constants in oxygenated, pH 7, 1 mM dimethylaniline (DMA) solution. Error bars represent the propagated 95% confidence intervals.

Comparison of $e^-_{(aq)}$ with •OH-Mediated SCCP Degradation. In addition to $e^-_{(aq)}$, ·OH can also degrade many COCs. To compare the reaction rate of our investigated compounds with $e^-_{(aq)}$ and ·OH, we performed experiments where ·OH is produced using NO_3^- as a photosensitizer.[57] Figure 3 shows the photochemical degradation of SCCPs in 1 mM DMA (source of $e^-_{(aq)}$) and 1 mM NO_3^- (source of ·OH) solutions. Loss of SCCPs was not observed in dark controls. While apparent first-order rate constants were higher for degradation in DMA solution, second-order rate constants for the reaction between SCCPs and PPRIs are dependent on the actual concentration of PPRIs in solution. As mentioned above, $[e^-_{(aq)}]_{ss}$ was calculated using the published second-order rate constant for the reaction of lindane with $e^-_{(aq)}$. Similarly, the second-order rate constant for the reaction of CB and ·OH (4.3×10^9 $M^{-1}\ s^{-1}$)[73] was used to calculate a $[\cdot OH]_{ss}$ of 6.84×10^{-15} M in our NO_3^- containing system. Using this concentration, second-order rate constants for our investigated COCs were calculated. Resulting second-order rate constants were generally higher for ·OH than $e^-_{(aq)}$ for the investigated SCCPs (Table 1, statistics in Table S6). The difference in rate constants was significant ($p < 0.05$) for TCD and TCDod, while there was no significant difference between rate constants for HCD. While DCD also reacted faster with ·OH, greater experimental variability led to an insignificant difference between the rate constants. The faster reaction of lower substituted SCCPs with ·OH could indicate a H-abstraction pathway[38], which would be hindered by additional Cl atoms.

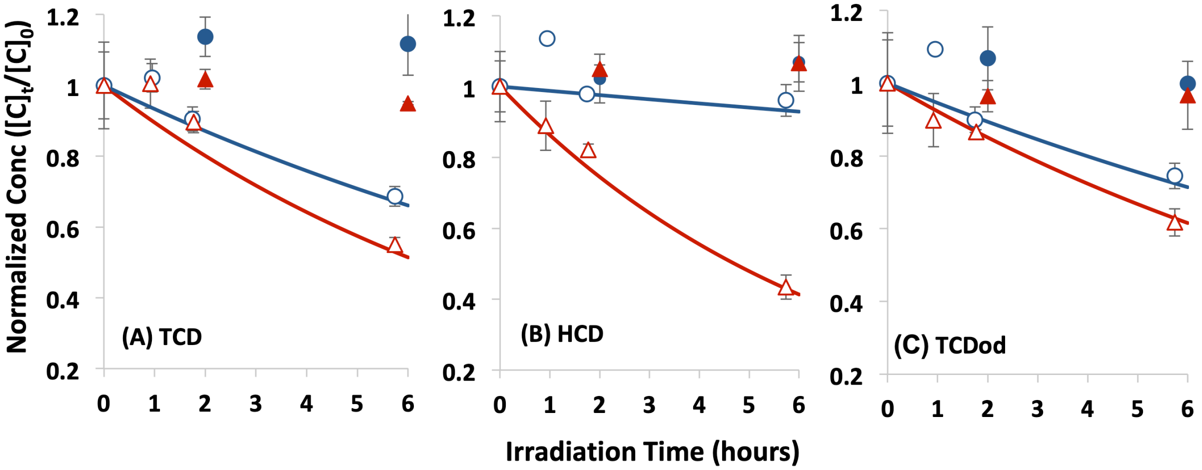


Figure 3. Fractional loss of 1,2,9,10-tetrachlorodecane (TCD), 1,2,5,6,9,10-hexachlorodecane, and 1,2,11,12-tetrachlorododecane (TCDod) during photodegradation experiments in solutions containing 1mM dimethylaniline (DMA) or 1mM nitrate (NO_3^-). Irradiated samples are indicated by open symbols, while dark controls are indicated by shaded symbols.

Table 1. Apparent first and second-order rate constants for the degradation of 1,10-dichlorodecane, 1,2,9,10-tetrachlorodecane (TCD), 1,2,5,6,9,10-hexachlorodecane, and 1,2,11,12-tetrachlorododecane (TCDod) in NO_3^- and DMA solutions. Error represents 95% confidence intervals.

	First-order (x10^{-6} s^{-1})		Second-order (x10^{8} M^{-1} s^{-1})	
	NO_3^-/•OH	DMA/ $e^-_{(aq)}$	NO_3^-/•OH	DMA/ $e^-_{(aq)}$
DCD	120 ± 107	10.7 ± 5.0	176 ± 172	0.83 ± 0.39
TCD	19.2 ± 5.38	35.2 ± 8.81	28.1 ± 13.9	2.74 ± 0.70

HCD	3.40 ± 6.55	39.1 ± 4.67	4.97 ± 14.4	3.04 ± 0.40
TCDod	15.6 ± 7.53	25.2 ± 9.56	22.8± 14.4	1.96 ± 0.75

•OH and $e^-_{(aq)}$ Degradation of COCs. Previous studies have shown ·OH to be capable of degrading a wide range of COCs. 1,2,9,10-tetrachlorodecane was degraded (dechlorinated) in the presence of ·OH during the photolysis of hydrogen peroxide (H_2O_2) and Fenton's reagent (Fe^{2+}/H_2O_2), as well as the modified Fenton reaction ($Fe^{3+}/H_2O_2/UV$).[30,32] ·OH was also shown to be important for the degradation of 1-chlorodecane (CD) by 254 nm UV radiation. H-abstraction pathways were determined to be an exothermic reaction, as opposed to endothermic Cl-abstraction, making Cl-abstraction an unlikely pathway for CD degradation.[29] Surface bound ·OH in aqueous suspensions of TiO_2 have been used to degrade 1,10-dichlorodecane,[31] and other UV/H_2O_2 catalyzed processes have degraded SCCPs.[74] Gaseous SCCP degradation by ·OH in the atmosphere has also been modeled.[75] Lindane has been degraded by photo- and electro-Fenton processes involving ·OH.[76,77] Nitoi et al.[77] found that dechlorination did not happen simultaneously with ·OH attack, but rather chlorinated intermediates were formed first. While these studies are generally aimed at engineered systems designed for remediation of contaminated water rather than understanding natural processes, they still indicate the possibility of a ·OH pathway occurring in the environment.

Besides chlorinated alkanes, other types of COCs (other than alkanes) can also be degraded by ·OH, including chloroaromatics[78] and chloroacetones.[79] Haag and Yao[38] found ·OH to be relatively nonselective with C-H bonds, but it was least reactive with aliphatic polyhalogenated compounds. On the other hand, it reacted at nearly diffusion-controlled rates with olefins and aromatics. Chlorobenzene (CB) can also be degraded with Fenton's reagent and UV/H_2O_2 systems,[80] with products identified including chlorophenol, chlorobenzoquinone, and dichlorobiphenyls.[81,82] The position of chlorine atoms on chlorophenols has also been shown to affect degradation rates.[83,84] Addition of ·OH to an aromatic ring has also been observed with fluorinated benzenes.[85]

There are also a number of studies describing degradation of COCs by $e^-_{(aq)}$. Reductive dehalogenation involving $e^-_{(aq)}$ is a known pathway used to degrade halogenated organic compounds.[86] Anbar and Hart[72] showed that neighboring electron-withdrawing groups enhanced dehalogenation. Compounds including chloromethanes,[44] chloroacetones,[79] and substituted aromatics such as chlorobenzene,[55,64] chlorobenzoic acids,[56] and fluorinated benzenes[85] have all been shown to react with $e^-_{(aq)}$. Per- and polyfluoroalkyl substances (PFAS), which are considered especially resistant to degradation, also react with $e^-_{(aq)}$ at varying rates depending on the length of fluoroalkyl chain and function group present.[45,46,53,87]

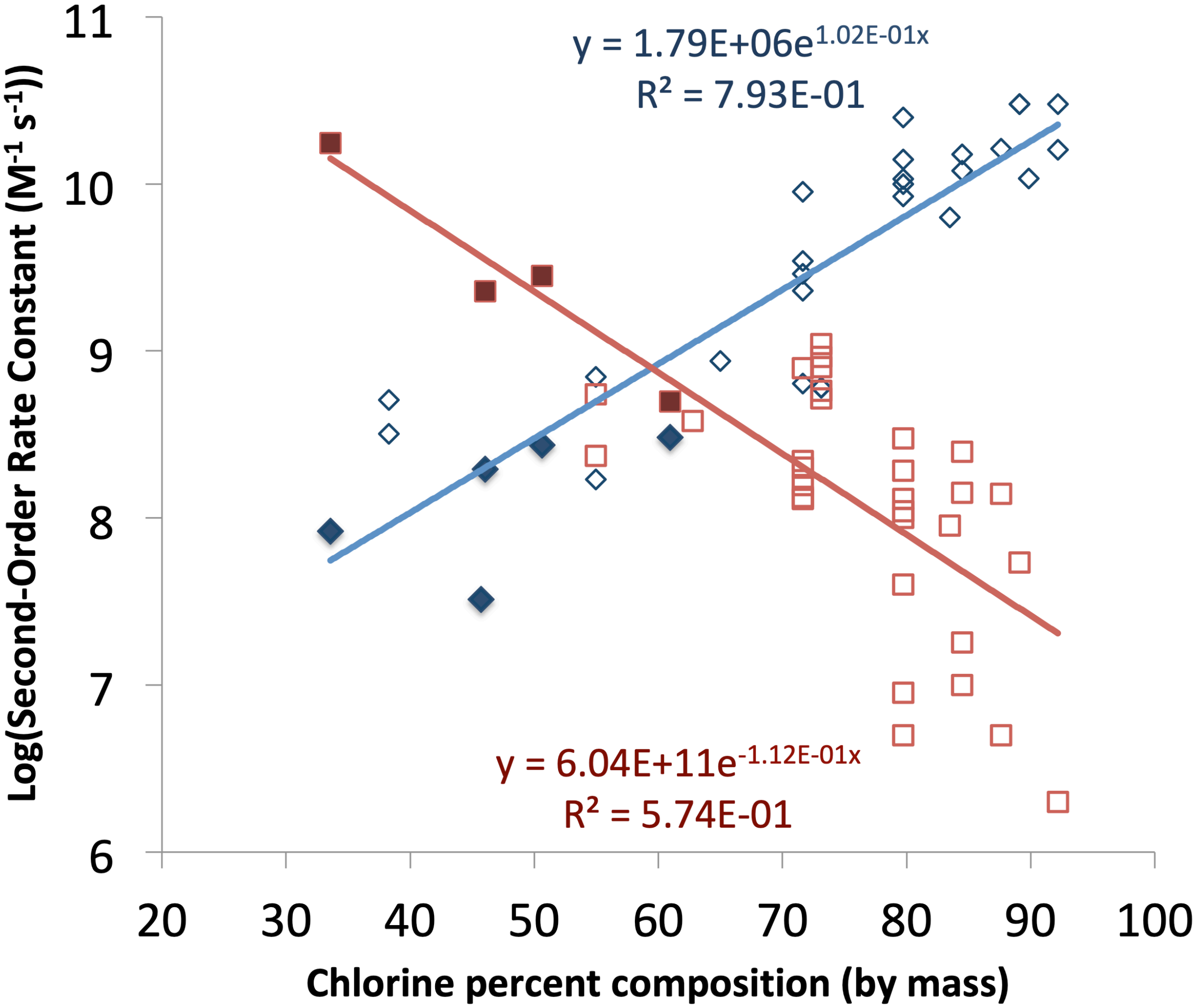


Figure 4. Compiled second-order rate constants for the reaction of chlorinated alkanes with hydrated electrons (blue diamonds) and hydroxyl radicals (red squares) vs. the chlorine percent composition of the compounds. Data from this study are shown by solid symbols.

Trends in •OH and $e^-_{(aq)}$ Degradation Rates for COCs. To understand how our investigated SCCP photodegradation rates compared to other halogenated compounds, we compiled second-order rate constants from the literature for the reaction of COCs with ·OH and $e^-_{(aq)}$ (Figure 4, Table S7). Analysis of the data revealed a strong correlation between rate constants and degree of chlorination (% Cl by mass). For similar compounds (e.g., chloroethanes), the relationship could be simplified to the number of chlorine atoms.[40] Increasing percent composition represents a greater relative amount of Cl atoms available to capture $e^{-}_{(aq)}$, resulting in higher rates of dechlorination. For example, $e^{-}_{(aq)}$ rate constants increased from 1.7×10^{8} to 1.6×10^{10} M^{-1} s^{-1} with increasing number of chlorine atoms from monochloroethane (55.0% Cl) to pentachloroethane (87.6% Cl).[40] Values for mirex (65.0% Cl) and lindane (73.1% Cl) fell in between at 8.71×10^{8} M^{-1} s^{-1} and $6.05x10^{8}$ M^{-1} s^{-1}, respectively.[41] Note that geminal dihalides (with both halogens on the same carbon) were noted to be more easily reduced than isolated halides,[41,88] potentially explaining some of the deviations from the trend in Figure 4.

The trend for ·OH rate constants was opposite to that of $e^{-}_{(aq)}$. Instead, increasing % Cl resulted in decreasing rate constants. This trend supports a H-abstraction pathway for degradation by ·OH, where a higher % Cl means a lower availability of H atoms. Additional Cl atoms could also sterically hinder the reaction. Milosavljevic et al.[40] observed that rate constants for ·OH with chloroethanes dropped by 1-2 orders of magnitude when no H atoms were present on a carbon atom. The type of C-H bond had a significant effect on the H-abstraction reaction rate. For example, 1,1,1,2-tetrachloroethane had a rate constant of $1.0x10^{7}$ M^{-1} s^{-1} while 1,1,2,2-tetrachloroethane $2.5x10^{8}$ M^{-1} s^{-1}, despite them both having 84.5 % Cl. Also, 1,1,1-trichloroethane, which contains three primary C-H bonds, had a rate constant of 5.0×10^{6} M^{-1} s^{-1}, while 1,1,2-trichloroethane had a value of 3.0×10^{8} M^{-1} s^{-1} (both 79.7% Cl). Its two secondary and one tertiary C-H bond are more reactive with ·OH. Other compounds with fully chlorinated carbons also fell below the ·OH trendline in Figure 4 (e.g., carbon tetrachloride 92.2 % Cl, $2.00x10^{6}$ M^{-1} s^{-1}).[38]

Trendlines for the two PPRI (·OH and $e^-_{(aq)}$) cross at 60.5% Cl. Rate constants for both PPRI were on the order of $1x10^6$ to $1x10^{10}$ M^{-1} s^{-1}. Compounds in this study had % Cl values on the lower end of data from the literature, but their rate constants still fell on the same trendlines as other compounds from the literature. Therefore, the complex mixture of SCCPs, which typically are 40-70% Cl by mass,[1] are expected to follow the same trends as indicated in Figure 4. The trends for other classes of halogenated organic compounds were less robust (Figure S3). For example, chlorinated aromatics tended to degrade faster than similar non-aromatic compounds. For their reaction with $e^-_{(aq)}$, hexachlorobenzene (HCB, 74.7% Cl) had a rate constant of $1.10x10^9$ M^{-1} s^{-1},[89] while lindane (73.1% Cl) was $6.05x10^8$ M^{-1} s^{-1}.[41] Similarly for reaction with ·OH, lindane had a rate constant of $8.00x10^8$ M^{-1} s^{-1} while various chlorobenzenes, which can react by addition of ·OH to double bonds rather than H-abstraction, had values of $4.00x10^9$ M^{-1} s^{-1}.[38]

Environmental Significance. The results of this study can be used to improve our understanding of the fate of SCCPs in surface waters. The presented experimental results are consistent with $e^-_{(aq)}$ as well as ·OH being capable of degrading SCCPs. The relative importance of these PPRI will depend on their concentrations as well as the SCCP properties (degree of chlorination, hydrophobicity). Based on our determined second-order rate constants, the investigated SCCPs would have half-lives of minutes in engineered systems (with typical •OH concentrations of 10^{-12} M). However, half lives of days to years would be expected in natural surface waters, where typical ·OH concentrations range from 10^{-15} to 10^{-18} M.[57,90] Therefore, the ·OH-mediated SCCP degradation is likely less relevant for the environmental fate of SCCPs in surface water.

For $e^-_{(aq)}$, similar SCCP half-lives as for ·OH would be expected if the reaction occurred in the bulk water phase, in which $e^-_{(aq)}$ concentrations between 10^{-13} M to 10^{-17} M[49,71] have been reported. However, since the lifetime of $e^-_{(aq)}$ has been estimated to be much longer in a DOM microenvironment with different characteristics (e.g., lower O_2) than the bulk aqueous solution,[91,92] DOM is expected to facilitate SCCP photodegradation in the environment. Such DOM-sensitized photolysis is known to be an important pathway for the degradation of organic contaminants with a high affinity for DOM. For example, HCB with its second-order rate constant with $e^-_{(aq)}$ of 1.1×10^9 M^{-1} s^{-1} [89] would have an estimated a half-life of approximately two months to two years in natural waters with a bulk $[e^-_{(aq)}]$ of 10^{-16} to 10^{-17} M. However, in the presence of 6 mg C L^{-1} DOM, half-lives of only 14 h were obtained by Grannas et al.,[43] suggesting a 100 to 1,000 times higher $[e^-_{(aq)}]$ in the DOM phase. Furthermore, lindane has a similar second-order rate constant to HCB, but a DOM-water partition coefficient about five times lower. No significant lindane degradation was observed over a 24 h irradiation in the presence of DOM, presumably due to its predicted negligible affinity for the DOM phase.[41] Under the same conditions, the more hydrophobic pesticide mirex degraded with half-lives around 10 h.[41] These results indicate that $e^-_{(aq)}$ likely does not escape the DOM matrix, resulting in compounds in the dissolved phase not having access to bound-phase reactivity.

SCCPs are hydrophobic compounds, with estimated $\log(K_{ow})$ values between 5.2 to 7.5,[50] similar to that of HCB (5.7)[93] and mirex (6.9),[94] and second-order rate constants with $e^-_{(aq)}$ within an order of magnitude of HCB and mirex (Table S7). We therefore expect DOM-sensitized photochemical degradation of SCCPs to be a relevant sink for SCCPs in surface waters. More research in DOM-containing systems will be necessary to confirm this hypothesis.

This study also contributes to the research on the versatility of $e^-_{(aq)}$ as a relevant PPRI for the degradation of pollutants. While the potential of $e^-_{(aq)}$ to degrade persistent organic pollutants in aqueous environments has been investigated for more than three decades[47], there are still relatively few published studies about this process available. Besides its relevance in natural water, $e^-_{(aq)}$ are also relevant in engineered systems, where high concentrations of $e^-_{(aq)}$ are produced using photosensitizers (generally paired with strong UV-C irradiation) or by radiolysis.[72,95-97] In this context, $e^-_{(aq)}$ have received renewed attention with the report of $e^-_{(aq)}$ mediated degradation of the emerging per- and polyfluoroalkyl substances (PFAS). [45,46,52,98,99] The results of this study also imply that $e^-_{(aq)}$-generating engineered systems for water treatment would likely be effective for degrading SCCPs, and provides further support to the notion that $e^-_{(aq)}$ is a versatile PPRI for degrading persistent organic pollutants.

ASSOCIATED CONTENT

Supporting Information

Supporting details describing the SCCP synthesis; Supporting figures showing the postulated chlorination mechanisms, spectrum of the solar simulator (Xe arc lamp), and plots of literature degradation rate constants for the $e^-_{(aq)}$ and $\cdot OH$ mediated degradation of halogenated compounds; Supporting tables with details for the passive dosing approach, the measured irradiance during the experiments, results from the statistical tests for the determined degradation rate constants described, and a compilation of literature degradation rate constants for the $e^{-}_{(aq)}$ and ·OH mediated degradation of halogenated compounds.

AUTHOR INFORMATION

Corresponding Author

*E-mail: bdimento@bigelow.org

ORCID

Brian DiMento: 0000-0002-7316-5856

Christoph Aeppli: 0000-0002-3758-0163

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