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

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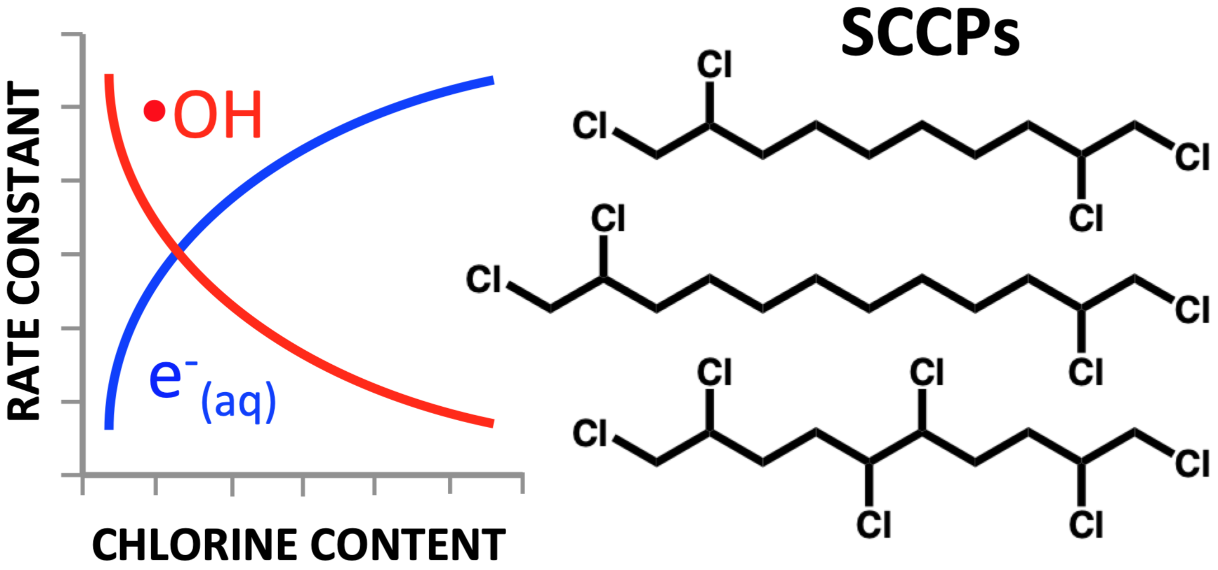

## Abstract

Short-chain chlorinated paraffins (SCCPs) are a complex mixture of polychlorinated alkanes ($C_{10}$-$C_{13}$, chlorine content 40-70%), and have been categorized as persistent organic pollutants. However, 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 $e^-_{(aq)}$ and ·OH to degrade SCCPs. 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. Trends in $e^-_{(aq)}$ and ·OH SCCP model compounds degradation rate constants of the investigated SCCPs were consistent with that of other chlorinated compounds, with higher chlorine content producing in higher rate constants for $e^-_{(aq)}$ and lower for ·OH. Above a chlorine:carbon ratio of approximately 0.6, the $e^-_{(aq)}$ second-order rate constants were higher than rate constants for ·OH reactions. Results of this study furthermore suggest that SCCPs are likely susceptible to photochemical degradation in sunlit surface waters, facilitated by dissolved organic matter that can produce $e^-_{(aq)}$ and ·OH when irradiated.

**Keywords**

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

**Highlights**

- **Photochemically-produced hydrated electrons and hydroxyl radicals can degrade SCCPs**
- **Hydrated electron rate constants increase with increasing chlorine content**
- **Hydroxyl radical rate constants decrease with increasing chlorine content**
- **SCCP photodegradation was also facilitated by dissolved organic matter**

## 1. 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% (U.S. Environmental Protection Agency, 2009). 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 (Bayen et al., 2006; U.S. Environmental Protection Agency, 2009). SCCPs are compounds of concern due to their toxicity, bioaccumulation potential (Houde et al., 2008), persistence, and long-range transport potential (Bayen et al., 2006; Fisk et al., 1999; Tomy et al., 1998; Zeng et al., 2013; 2017a; 2017b; 2012; 2011). 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 (Bayen et al., 2006; Bennie et al., 2000; Campbell and McConnell, 1980; Casà et al., 2019; Du et al., 2018; Feo et al., 2009; H. Li et al., 2017; Štejnarová et al., 2005; Tomy et al., 1997; UNEP, 2016), and they have since been added to Appendix A of the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2017).

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 (EPA, 1978; Mukherjee, 1990; UNEP, 2015), 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" (UNEP, 2016). While studies on biodegradation found the possibility of degradation in activated sewage sludge (Heath et al., 2004; Lu, 2012) and aerobic sediments (European Chemicals Bureau, 2008; Tomy et al., 1999; UNEP, 2015), 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 (Chen et al., 2016; El-Morsi et al., 2000; 2002; Friesen et al., 2004; Yan et al., 2021; Zhang et al., 2019). 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 (Friedman and Lombardo, 1975). However, indirect photodegradation pathways involving reactions with photochemically produced reactive intermediates (PPRI) are possible. Such intermediates, including hydroxyl radicals (·OH) and hydrated electrons ($e^{-}_{(aq)}$), can be formed in surface water following the absorption of light by constituents of natural water such as dissolved organic matter (DOM) or nitrate (Clark and Zika, 2000). Hydroxyl radicals have been implicated in the photochemical degradation of many organic pollutants (Atkinson, 1985; Haag and Hoigné, 1985; Haag and Yao, 1992; Vaughan and Blough, 1998). While it was hypothesized that ·OH are less important in the degradation of highly chlorinated alkanes (Milosavljevic et al., 2005), recent research suggests that the ·OH-mediated degradation might be relevant for the degradation of chlorinated paraffins in surface waters (Yan et al., 2021).

In addition to ·OH, $e^{-}_{(aq)}$ have been shown to be important in the degradation of chlorinated pollutants, including mirex (Burns et al., 1997; 1996), hexachlorobenzene (Grannas et al., 2012), chloromethanes (Calza and Pelizzetti, 2004), chloroethanes (Milosavljevic et al., 2005), and more recently per- and polyfluoroalkyl substances (PFAS) (Bentel, 2020; 2019). While $e^{-}_{(aq)}$ has been a known product of water radiolysis for more than 50 years (Herbert and Coons, 2017), it can also be produced in surface waters by the interaction of sunlight with constituents of DOM (Thomas-Smith and Blough, 2001). It appears that the lifetime of the $e^{-}_{(aq)}$ in the DOM phase is sufficient for its reaction with hydrophobic compounds sorbed into the DOM phase (Breugem et al., 1986). Due to the hydrophobic nature of SCCPs, with estimated octanol-water partition coefficients ($K_{ow}$) between $9\times10^{4}$ and $3\times10^{7}$ (Glüge et al., 2013), these compounds have the potential to be degraded by this mechanism. 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 (Bentel, 2020; 2019; Calza and Pelizzetti, 2004; Cui et al., 2020; Huang et al., 2007; Milosavljevic et al., 2005; Song et al., 2013; Yuan et al., 2015; Zona et al., 2008).

The aim of this study was therefore to determine the reactivity of SCCPs with $e^-_{(aq)}$ and ·OH, and to evaluate these pathways for the relevance of SCCP degradation in natural water, where degradation within the DOM phase has been hypothesized to provide a suitable environment for their degradation (Yan et al., 2021). We mainly focused on the reactivity of SCCP model compounds in DOM-free conditions, where $e^-_{(aq)}$ are produced using an artificial photosensitizer, N,N-dimethylaniline (DMA) (Thomas-Smith and Blough, 2001), and ·OH are produced by nitrate ($NO_3^-$) photolysis (Zepp et al., 1987b). Furthermore, we performed select experiments in the presence of DOM to evaluate the potential for DOM-mediated degradation of SCCPs.

## 2. Materials and methods

### *2.1 Chemicals*

Due to the lack of commercially available 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 by mass), 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 ($SO_2Cl_2$; obtained from Sigma-Aldrich) as a chlorine source and 2,2'-azobis(2-methylpropionitrile) (AIBN; Sigma-Aldrich) as a radical initiator (Fisk et al., 1999; Kharasch and Zavist, 1951; Nikiforov, 2010) (Figure A1 in Appendix A). Further details on the synthesis procedure are provided in Appendix A. Analytical standards (100 μg/mL) for TCD, HCD, and TCDod were obtained from Chiron (Trondheim, Norway) to identify and quantify the synthesized SCCPs.

In addition, the following chlorinated organic compounds (COCs) were included to increase the range of chlorine content and to facilitate comparison with literature data: 1,6-dichlorohexane (DCH), 1,10-dichlorodecane (DCD), chlorobenzene (CB), and lindane (γ-hexachlorocyclohexane) (Sigma-Aldrich). N,N-dimethylaniline (DMA) was used for hydrated electron ($e^-_{(aq)}$) generation (Thomas-Smith and Blough, 2001) and sodium nitrate for hydroxyl radical (·OH) generation (Sigma-Aldrich) (Zepp et al., 1987b). Both compounds were used at aqueous concentrations of 1 mM. Buffered solutions were prepared with mono- and dibasic potassium phosphate (Sigma-Aldrich). Suwannee River Natural Organic Matter (SR-NOM; International Humic Substances Society, 2R101N) was used as a source of DOM.

### *2.2 Preparing Solutions for Experiments*

Experiments were conducted in reagent grade water buffered to pH 7.0 with 1 mM phosphate buffer. All glassware was soaked overnight in 1% detergent (Extran 300; Sigma-Aldrich) followed by 10% hydrochloric acid to remove organic and trace metal contaminants. After rinsing with reagent grade water, the glassware was heated overnight at 450 °C to remove organic contaminants.

During a first set of experiments, chlorinated compounds with low water solubility were added directly in an acetonitrile (ACN) solution. ACN was selected because it was reported to be an inert co-solvent with minimal effect on the degradation mechanism (ASTM International, 2005; Zhang et al., 2019). 100 µL of chlorinated compound mixture in ACN was added per liter of solution to achieve desired final concentrations (approximately 10x below their water solubility), and the solution was stirred for 24 hours to ensure that the compounds were fully dissolved prior to beginning an experiment.

A passive dosing approach to add the COCs (Smith et al., 2010) was then used for the experiments with the SCCP model compounds, in order to avoid any possible complication by the presence of ACN in the reaction solutions. 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 subsequently soaking overnight in 1% detergent (Extran, SigmaAldrich), 10% HCl, and then three portions of methanol (MeOH). The discs were loaded with COCs by equilibrating in 20 mL MeOH solutions containing the COCs (see Table A1 for details) on a shaker table for 24 h. Due to the low partitioning of COCs from MeOH onto PDMS, the depletion of COCs in MeOH after equilibration of the discs was minimal (< 1%); therefore, the same MeOH solution was reused for each experiment. Loaded PDMS discs were gently rinsed with a small amount of reagent grade water to remove MeOH immediately before use. Two loaded discs were added per liter of buffered water (pH 7.0) and equilibrated overnight on a shaker table in glass media bottles. 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 (Goss, 2011). After an initial test, the COC concentrations in MeOH were adjusted as needed, achieving initial aqueous COC concentrations of ~15-120 nM (Table A1). For the experiment using DOM, PDMS chips were equilibrated directly in SR-NOM water, which was prepared in 1 mM phosphate buffer (pH 7.0) at 40 mg C $L^{-1}$ and filtered to 0.2 μm.

Experiments were performed with mixtures of COCs rather than single compounds, 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 $e^-_{(aq)}$ ($2.00\times10^{10}$ $M^{-1}$ $s^{-1}$) (Buxton et al., 1988) is equal to or greater than expected values for the COCs studied ($10^8$-$10^{10}$ $M^{-1}$ $s^{-1}$; Table A7) (Anbar and Hart, 1964; Burns et al., 1997; Buxton et al., 1988; Milosavljevic et al., 2005). 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 ($p = 0.36$) between the two solutions.

For experiments with lower oxygen concentrations, solutions were purged for 6 hours prior to passive dosing and irradiation using ultrapure nitrogen flowing through a gas dispersion tube (Ace Glass, porosity B, 70-100 μm). 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 $2.78\times10^{-4}$ M in air-saturated solution to $7.50\times10^{-5}$ M, or about 26 % saturation, after purging and transferring the solution to reaction vessels.

### *2.3 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 A2). 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 (The International Commission on Illumination (CIE). Table 4., 1989)). Absolute irradiance spectra of the solar simulator and natural sunlight measured with a FLAME spectroradiometer (Ocean Insight; Orlando, FL) are shown in Figure A2, and irradiance intensities at UVB (280-320 nm), UVA (320-400 nm), and PAR (400-700 nm) wavelengths are shown in Table A2.

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. Evaporative cooling of the water bath, controlled by an internal fan coupled with a submerged temperature sensor, kept the water and samples at 25 ± 1 °C. The fill level of the water bath was kept constant with a float switch-controlled pump and water reservoir. Teflon-coated magnetic stir bars were used to homogenize solutions during the irradiations. Initial irradiations in reagent grade water (Milli-Q) and DMA lasted 24 h, before determining that 6 h was sufficient to observe significant degradation. DMA concentrations dropped 12.5% over this period. Each experiment consisted of three to five irradiation durations (i.e., time points), each performed 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 (Kieber et al., 2007) were used to correct for variability in light intensity at the eight positions where flasks were placed within the irradiation chamber by quantifying light fluxes within the reaction vessels. The average light dose received by the sample calculated using the nitrate actinometer was 5.55 ± 0.31 $\mu E\ cm^{-2}\ h^{-1}$, with a 5.5% relative standard deviation between the positions. Calculating the actinic flux (outside the quartz flasks) using data collected with the FLAME spectroradiometer across the spectral bandwidth of this actinometer (307-333 nm) yielded values of 8.87, 7.27, and 6.56 $\mu E\ cm^{-2}\ h^{-1}$ 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 their 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$^{-2}$) (International Agency for Research on Cancer, 1992; Kiehl and Trenberth, 1997), 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.

### *2.4 Analytical Methods*

Following irradiation experiments, the full sample volumes were extracted three times with 15, 10, and 10 mL of dichloromethane (DCM) using o-terphenyl (oTP) as a recovery standard. The extraction method was modified for samples containing DOM to improve extraction efficiency by adding 5 mL of brine (saturated NaCl) along with 35 mL DCM to the solutions. This mixture was shaken for 24 h on a shaker table before the DCM was collected, followed by an additional 10 mL extraction in a separatory funnel. The extracts were combined and 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 (30 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 an internal standard (deuterated chlorobenzene, Sigma-Aldrich) to calculate relative responses. The recovery standard oTP was used to correct for losses during extraction.

### *2.5 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 ($[PPRI]_{ss}$), where its formation and scavenging rate remain constant over time. 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 $\mu E\ cm^{-2}\ h^{-1}$ or 15.4 $\mu E\ m^{-2}\ s^{-1}$). 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 slope of 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 (GraphPad, San Diego/CA) was used to evaluate statistical differences in rate constants using their calculated standard error.

## 3. Results and Discussion

### *3.1 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 A3). 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 (Friedman and Lombardo, 1975; Zhang et al., 2019).

### *3.2 Indirect SCCP Degradation in DMA system*

In irradiated aqueous solutions containing the $e^-_{(aq)}$-producing DMA (Köhler et al., 1985), degradation of all investigated COCs was observed (Figure 1). The SCCP first-order rate constants ranged from $2.5\times10^{-5}$ $s^{-1}$ (TCDod) to $3.9\times10^{-5}$ $s^{-1}$ (HCD). Dichlorinated compounds degraded more slowly than similar tetra- and hexachlorinated compounds (DCH/DCD vs. TCD/HCD; see Table A4 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 (γ-hexachlorocyclohexane; $k' = 7.8\times10^{-5}$ $s^{-1}$), which has previously been investigated for its $e^-_{(aq)}$ reactivity (Burns et al., 1997). Lindane was included in most experiments throughout this study to facilitate comparison with previous studies.

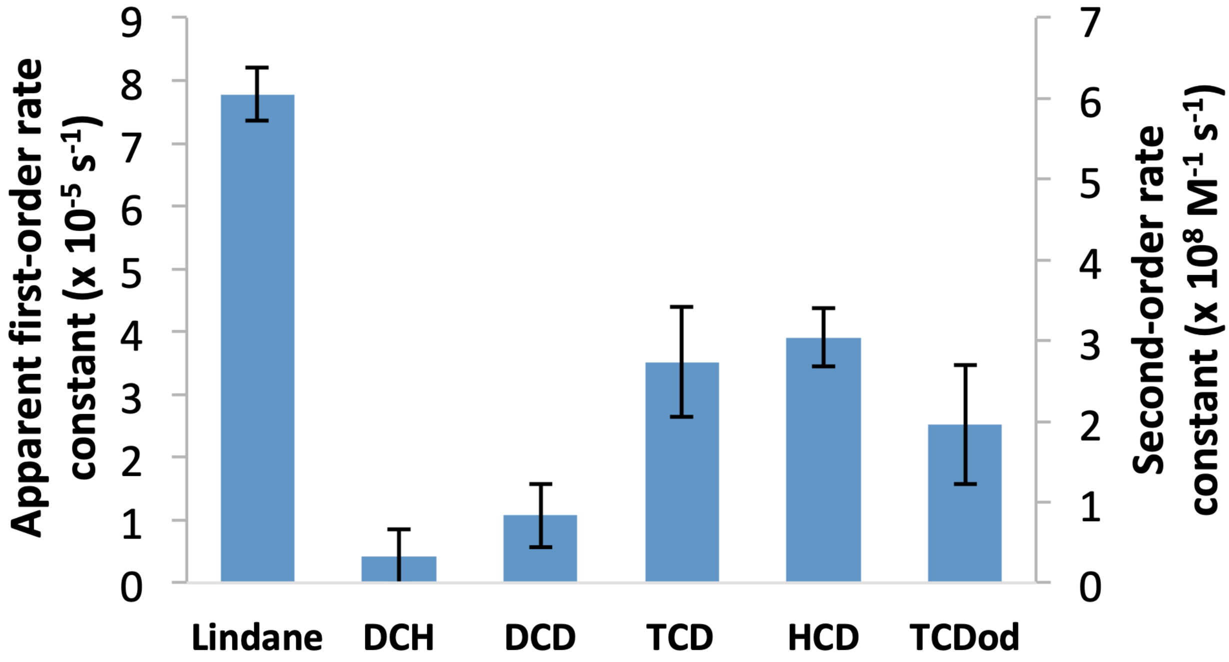

**Figure 1.** Apparent first and second-order rate constants for the photochemical degradation of chlorinated compounds lindane, 1,6-dichlorohexane (DCH), 1,10-dichlorodecane (DCD), 1,2,9,10-tetrachlorodecane (TCD), 1,2,5,6,9,10-hexachlorodecane (HCD), and 1,2,11,12-tetrachlorododecane (TCDod) in solutions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

### *3.3 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 ($H^+$) (Watkins, 1974), oxygen ($O_2$) (Buxton et al., 1988), and halogenated compounds such as 2-chloroethanol (ClEtOH) (Zepp et al., 1987a).

First, the effect of increased $H^+$ concentration was tested. At pH 3, the degradation rate constant of both TCD and lindane significantly decreased compared to a pH 7 solution (Figure 2, Table A5). 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 (Burns et al., 1997; Watkins, 1974). Our observations are consistent with that of Burns et al. (1997), who also observed a decrease in COC (mirex) degradation at low pH.

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 A5). While TCDod also degraded more quickly, the increase in rate constant was not significant ($p = 0.142$). The observed increase in k' with decreasing $O_2$ concentrations are consistent with $e^-_{(aq)}$ as the 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 ClEtOH, which has been reported to be an effective probe for $e^-_{(aq)}$ (Zepp et al., 1987a). The 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 A5). Again, TCDod followed the same trend, but the change was not significant ($p = 0.145$).

To further evaluate the role of $e^-_{(aq)}$ in the observed reactions, we calculated its steady-state concentration ($[e^-_{(aq)}]_{ss}$) using the previously published second-order rate constant for the reaction between lindane and $e^-_{(aq)}$ of $6.05\times10^8$ $M^{-1}$ $s^{-1}$ (Burns et al., 1997), along with our measured k' value for lindane. The resulting $[e^-_{(aq)}]_{ss}$ was $1.29\times10^{-13}$ M. Assuming that dissolved $O_2$ is the primary sink for $e^-_{(aq)}$ and thus controls its steady-state concentration, the production rate of $e^-_{(aq)}$ ($r_{e^-}^{prod}$) can be estimated from $r_{e^-}^{prod} = k_{e^-}[e^-_{(aq)}]_{ss}[O_2]$. With an $O_2$ concentration in our air-saturated solution of $2.78\times10^{-4}$ M and a rate constant for the reaction of $e^-_{(aq)}$ with $O_2$ of $2\times10^{10}$ $M^{-1}$ $s^{-1}$(Burns et al., 1997; Buxton et al., 1988), an $e^-_{(aq)}$ production rate of $7.15\times10^{-7}$ $M^{-1}$ $s^{-1}$ was determined. With an added ClEtOH concentration of 0.05 M and a reported rate constant for its reaction with $e^-_{(aq)}$ of $4.1\times10^{8}$ $M^{-1}$ $s^{-1}$(Anbar and Hart, 1965), 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. It is noteworthy to point out that despite our evidence supporting $O_2$ as the primary $e^-_{(aq)}$ scavenger, the $O_2$ concentration only dropped 21.5% during a 6-hour experiment (after remaining near 100% saturation for the first 2 hours) despite a predicted initial rate of disappearance of about 0.7 μM $s^{-1}$. This result suggests either a regeneration pathway for $O_2$ (e.g., through disproportionation of superoxide), the ability of $O_2$ to quench $e^-_{(aq)}$ precursors, or alternative $e^-_{(aq)}$ scavengers present in the solution.

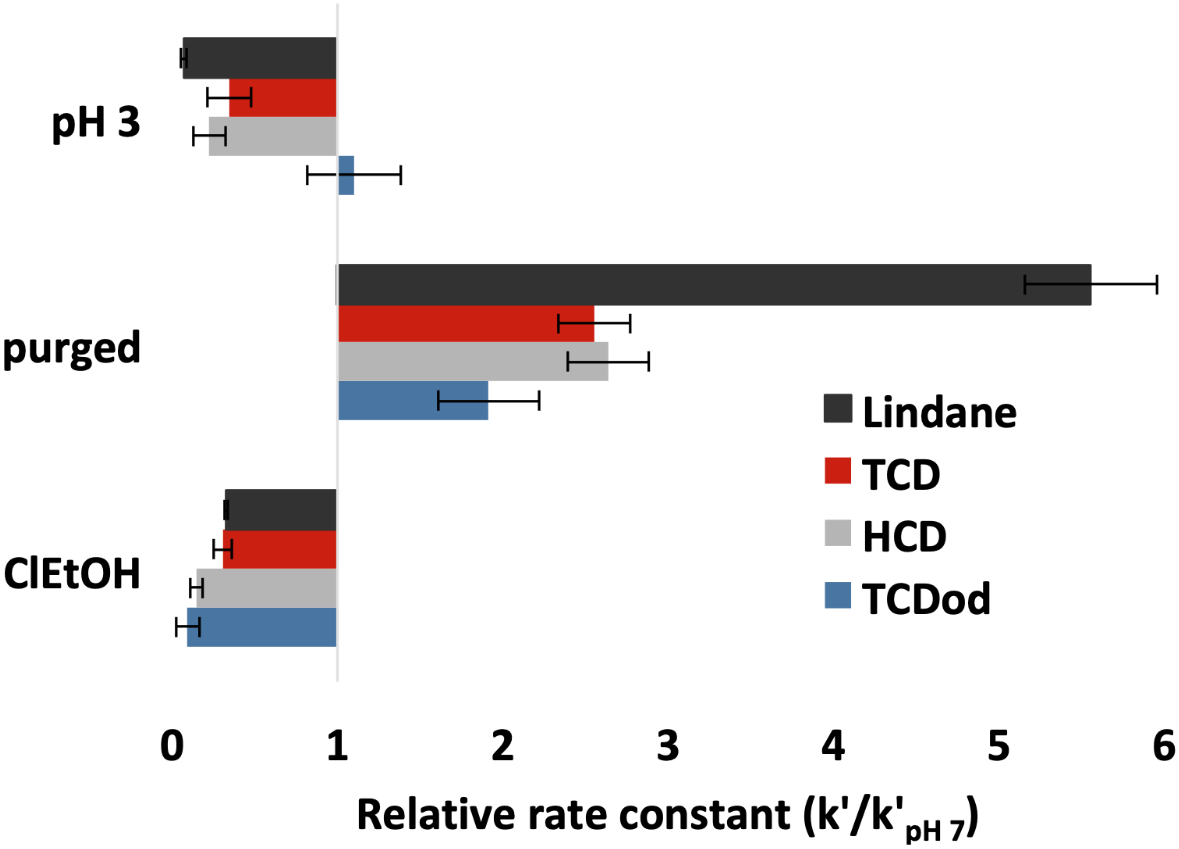

**Figure 2.** Effect of pH, deoxygenation, and addition of 2-chloroethanol on the apparent first-order rate constant for lindane, 1,2,9,10-tetrachlorodecane (TCD), 1,2,5,6,9,10-hexachlorodecane (HCD), and 1,2,11,12-tetrachlorododecane (TCDod) compounds relative to their rate constants in oxygenated,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

### *3.4 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 (Zepp et al., 1987b). 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 ($4.3\times10^9$ $M^{-1}$ $s^{-1}$) (Kochany and Bolton, 1992) was used to calculate a $[\cdot OH]_{ss}$ of $6.84\times10^{-15}$ M in our $NO_3^-$ containing system. Using this concentration, second-order rate constants for our investigated COCs were calculated. These rate constants were generally higher for ·OH than $e^-_{(aq)}$ for the investigated SCCPs (Table 1, statistics in Table A6), but the difference was only significant ($p < 0.05$) for DCD due to experimental variability. The faster reaction of lower substituted SCCPs with ·OH could indicate a H-abstraction pathway (Haag and Yao, 1992), which would be hindered by higher numbers of Cl atoms. While no specific congeners overlap with this study, Yan et al. (2021) reported similar rate constants for the reaction of SCCPs with ·OH (e.g., $2.0\times10^9$ $M^{-1}$ $s^{-1}$ for pentachlorododecane versus $2.3\times10^9$ $M^{-1}$ $s^{-1}$ for tetrachlorododecane in this study).

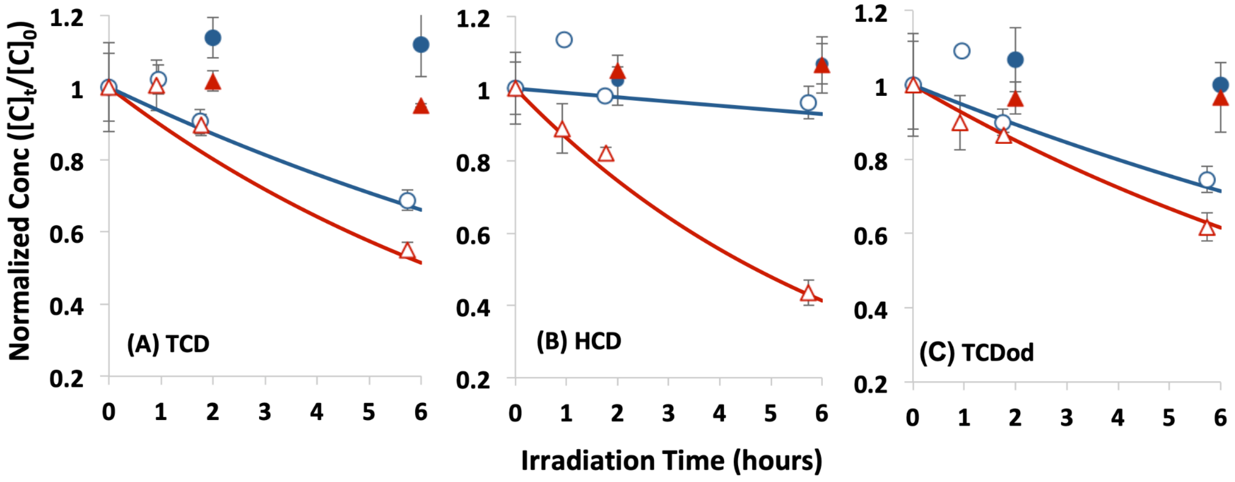

**Figure 3.** Fractional loss of 1,2,9,10-tetrachlorodecane (TCD), 1,2,5,6,9,10-hexachlorodecane (HCD), and 1,2,11,12-tetrachlorododecane (TCDod) during photodegradation experiments in solutions containing 1mM dimethylaniline (DMA; red triangles) or 1mM nitrate ($NO_3^-$; blue circles). Irradiated samples 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 (HCD), and 1,2,11,12-tetrachlorododecane (TCDod) in $NO_3^-$ and DMA solutions. Error represents 95% confidence intervals.

| | First-order ($\times 10^{-6}$ $s^{-1}$) | | Second-order ($\times 10^{8}$ $M^{-1}$ $s^{-1}$) | |
|---|---|---|---|---|
| | $NO_3^-$/·OH | DMA/ $e^-_{(aq)}$ | $NO_3^-$/·OH | DMA/ $e^-_{(aq)}$ |
| DCD | 40 ± 8 | 11 ± 5 | 59 ± 27 | 0.8 ± 0.4 |
| TCD | 19 ± 5 | 35 ± 9 | 28 ± 14 | 2.7 ± 0.7 |
| HCD | 3 ± 7 | 39 ± 5 | 5 ± 14 | 3.0 ± 0.4 |
| TCDod | 16 ± 8 | 25 ± 10 | 23± 14 | 2.0 ± 0.8 |

### *3.5 Review of Degradation of Other COCs by •OH and $e^-_{(aq)}$*

To put our obtained results for SCCPs in context with the degradation of other COCs, we reviewed reported ·OH and $e^-_{(aq)}$ mediated degradation of a large range of COCs. Many 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 ($Fe^{3+}/H_2O_2/UV$) (El-Morsi et al., 2002; Friesen et al., 2004). The hydroxyl radical 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 (Zhang et al., 2019). Surface bound ·OH in aqueous suspensions of $TiO_2$ have been used to degrade 1,10-dichlorodecane (El-Morsi et al., 2000), and other $UV/H_2O_2$ catalyzed processes have degraded SCCPs (Koh and Thiemann, 2001). Gaseous SCCP degradation by ·OH in the atmosphere has also been modeled (C. Li et al., 2014). Lindane has been degraded by photo- and electro-Fenton processes involving ·OH (Dominguez et al., 2018; Nitoi et al., 2013). Nitoi et al. (2013) 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 can also be degraded by ·OH, including chloroaromatics (Czaplicka, 2006) and chloroacetones (Williams et al., 2002). Haag and Yao (1992) 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 (Juang et al., 1998), with products identified including chlorophenol, chlorobenzoquinone, and dichlorobiphenyls (Kovacevic and Sabljic, 2013; Sedlak and Andren, 1991). The position of chlorine atoms on chlorophenols has also been shown to affect degradation rates (Krutzler et al., 1999; Moza et al., 1988). An addition of ·OH to an aromatic ring has also been observed with fluorinated benzenes (Köster and Asmus, 1973).

There are also a number of studies describing the degradation of chlorinated and fluorinated organic compounds by $e^-_{(aq)}$. Reductive dehalogenation involving $e^-_{(aq)}$ is a known pathway used to degrade halogenated organic compounds (X. Li et al., 2014). Anbar and Hart (1965) showed that neighboring electron-withdrawing groups enhanced dehalogenation. Compounds including chloromethanes (Calza and Pelizzetti, 2004), chloroacetones (Williams et al., 2002), and substituted aromatics such as chlorobenzene (Anbar and Hart, 1964; Yuan et al., 2015), chlorobenzoic acids (Zona et al., 2008), and fluorinated benzenes (Köster and Asmus, 1973) have all been shown to react with $e^-_{(aq)}$. PFAS, which are considered especially resistant to degradation, also react with $e^-_{(aq)}$ at varying rates depending on the length of fluoroalkyl chain and functional group present (Bentel, 2020; 2019; Huang et al., 2007; Park et al., 2009).

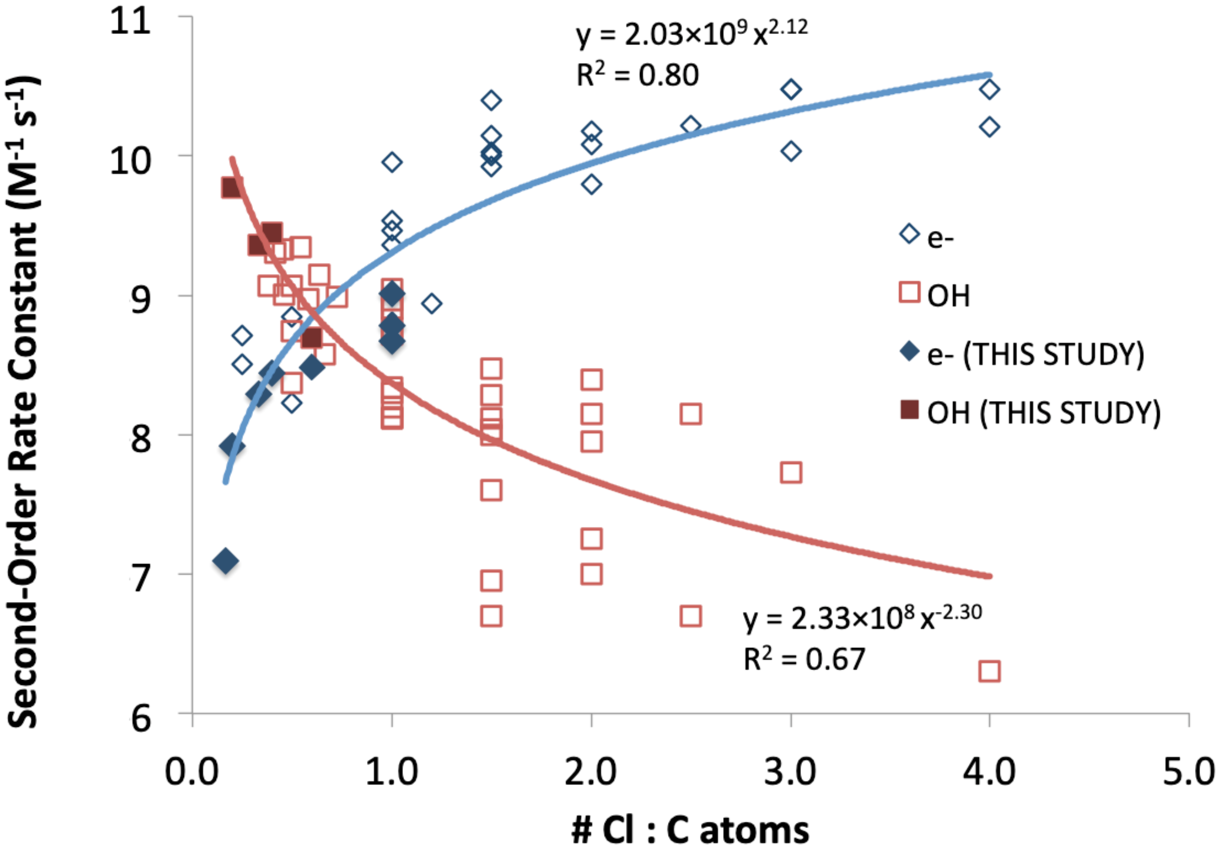

**Figure 4.** Compiled second-order rate constants for the reaction of chlorinated alkanes with hydrated electrons (blue diamonds) and hydroxyl radicals (red squares) vs. the chlorine content (number of chlorine atoms normalized to the number of carbon atoms per molecule). Data from this study are shown by solid symbols.

### *3.6 Trends in •OH and $e^-_{(aq)}$ Degradation Rates for SCCPs in Comparison to Other COCs*

To understand how our investigated SCCP degradation rates compared to other halogenated compounds, we compiled second-order rate constants from the literature for their reaction with ·OH and $e^-_{(aq)}$ (Figure 4, Table A7). Analysis of the data revealed a correlation between rate constants and degree of chlorination (# Cl atoms normalized to # C atoms). For similar compounds (e.g., chloroethanes), the relationship could be simplified to the number of chlorine atoms (Milosavljevic et al., 2005). An increasing Cl:C ratio 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 $1.7\times10^8$ to $1.6\times10^{10}$ $M^{-1}$ $s^{-1}$ with an increasing number of chlorine atoms, from monochloroethane (Cl:C 0.5) to pentachloroethane (Cl:C 2.5) (Milosavljevic et al., 2005). Values for mirex (Cl:C 1.2) and lindane (Cl:C 1.0) fell in between at $8.71\times10^8$ $M^{-1}$ $s^{-1}$ and $6.05\times10^8$ $M^{-1}$ $s^{-1}$, respectively (Burns et al., 1997). Note that geminal dihalides (with both halogens on the same carbon) were noted to be more easily reduced than isolated halides (Burns et al., 1997; Fingerling et al., 1996), 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:C resulted in decreasing rate constants. This trend supports a H-abstraction pathway for degradation by ·OH, where a higher Cl:C means a lower availability of H atoms. Additional Cl atoms could also sterically hinder the reaction. Milosavljevic et al. (2005) 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 $1.0\times10^7$ $M^{-1}$ $s^{-1}$ while 1,1,2,2-tetrachloroethane was $2.5\times10^8$ $M^{-1}$ $s^{-1}$, despite them both having a Cl:C ratio of 2.0. Also, 1,1,1-trichloroethane, which contains three primary C-H bonds, had a rate constant of $5.0\times10^6$ $M^{-1}$ $s^{-1}$, while 1,1,2-trichloroethane had a value of $3.0\times10^8$ $M^{-1}$ $s^{-1}$ (both Cl:C 1.5). Its two secondary and one tertiary C-H bonds are more reactive with ·OH. Other compounds with fully chlorinated carbons also fell below the ·OH trendline in Figure 4 (e.g., carbon tetrachloride Cl:C 4.0, $2.00\times10^{6}$ M$^{-1}$ s$^{-1}$) (Haag and Yao, 1992).

Trendlines for the two PPRI (·OH and $e^{-}_{(aq)}$) cross at ~0.6 Cl:C. Rate constants for both PPRI ranged from $1\times10^{6}$ to $1\times10^{10}$ M$^{-1}$ s$^{-1}$. Compounds in this study had Cl:C values on the lower end of data from the literature, but their rate constants appeared to follow similar trends as other compounds from the literature. Complex mixtures of SCCPs, which typically are 40-70% Cl by mass (Cl:C ~ 0.25-0.85) (U.S. Environmental Protection Agency, 2009), are expected to follow the same trends shown in Figure 4. This pattern is also supported by the results of Yan et al. (2021), who reported rate constants with ·OH of 0.94-$2.20\times10^{9}$ M$^{-1}$ s$^{-1}$, with higher values at lower degrees of chlorination. The trends for other classes of halogenated organic compounds were less robust (Figure A3). For example, chlorinated aromatics tended to degrade faster than similar non-aromatic compounds. For their reaction with $e^{-}_{(aq)}$, hexachlorobenzene (HCB, Cl:C 1) had a rate constant of $1.10\times10^{9}$ M$^{-1}$ s$^{-1}$ (Zacheis et al., 2000), while lindane (also Cl:C 1) was $6.05\times10^{8}$ M$^{-1}$ s$^{-1}$ (Burns et al., 1997). Similarly as for reaction with ·OH, lindane had a rate constant of $8.00\times10^{8}$ M$^{-1}$ s$^{-1}$ while various chlorobenzenes, which can react by addition of ·OH to double bonds rather than H-abstraction, had values of $4.00\times10^{9}$ M$^{-1}$ s$^{-1}$ (Haag and Yao, 1992).

### *3.7 Environmental Significance: DOM-mediated SCCP degradation*

The results of this study can be used to improve our understanding of the fate of SCCPs in surface waters. The presented experimental rate constants 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/partitioning). 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 (Mopper and Zhou, 1990; Zepp et al., 1987b). For reactions with $e^-_{(aq)}$, similar SCCP half-lives 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 (Breugem et al., 1986; Zepp et al., 1987a) have been reported.

In the environment, the degradation of hydrophobic SCCPs is likely a function of their reactivity as well as their partitioning into DOM, where microheterogeneous distributions of PPRI have been measured (Grandbois et al., 2008; Latch and McNeill, 2006; Yan et al., 2021). DOM is expected to facilitate SCCP photodegradation since the lifetimes of PPRI such as $e^-_{(aq)}$ and ·OH have been shown to be much longer in a DOM microenvironment with different characteristics (e.g., lower $O_2$) than the bulk aqueous solution (Grandbois et al., 2008; Hassett, 2006). 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 $1.1\times10^9$ $M^{-1}$ $s^{-1}$ (Zacheis et al., 2000) would have an estimated 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, a half-life of only 14 h was obtained by Grannas et al. (2012), 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 (Burns et al., 1997). Under the same conditions, the more hydrophobic pesticide mirex degraded with a half-life of about 10 h. These results indicate that $e^{-}_{(aq)}$ is quickly scavenged outside the DOM matrix, resulting in compounds in the bulk dissolved phase not having access to bound-phase reactivity.

Similar to $e^{-}_{(aq)}$, ·OH has also been suggested to have a higher concentration within DOM than in the bulk aqueous phase. While our data suggest that both $e^{-}_{(aq)}$ and ·OH are capable of degrading SCCPs, Yan et al. (2021) concluded that ·OH was more relevant than other PPRI including $e^{-}_{(aq)}$ in oxygenated DOM solutions, with ·OH concentrations two to three orders of magnitude higher within the DOM microenvironment versus the bulk aqueous phase.

Because SCCPs are hydrophobic compounds, with estimated $\log(K_{ow})$ values between 5.2 to 7.5 (Glüge et al., 2013), similar to that of HCB (5.7) (De Bruijn et al., 1989) and mirex (6.9) (U.S. EPA Environmental Protection Agency, 1995), they are expected to sorb to DOM in natural waters. We, therefore, expect DOM-sensitized photochemical degradation to be a relevant sink for SCCPs in surface waters. To test this hypothesis, We performed a preliminary experiment using 40 mg $C^{-1}$ SR-NOM and observed photodegradation of all three SCCPs. At this concentration, 50% of a SCCP with a log DOM partition coefficient ($K_{DOM}$) of 4.4 would be in the DOM "phase". First-order rate constants for TCD, HCD, and TCDod were $2.6 \pm 0.6 \times 10^{-6}$ $s^{-1}$, $0.7 \pm 0.5 \times 10^{-6}$ $s^{-1}$, and $4 \pm 1 \times 10^{-6}$ $s^{-1}$, respectively. The most hydrophobic SCCP tested, TCDod, degraded the fastest. This was expected since this compound likely also has the highest partitioning into the DOM phase, where the degradation reaction occurs. The slower degradation of HCD compared to TCD aligns better with our trend for ·OH rate constants, which decrease with increasing chlorine content, than for our $e^-_{(aq)}$ rate constants (with increase with increasing chlorine content). This result is in line with the results from Yan et al. (2021) and supports the hypothesis that the DOM phase is relevant for the photochemical degradation of SCCPs.

Our study also contributes to the available data of $e^-_{(aq)}$ mediated degradation of COCs. While the potential of $e^-_{(aq)}$ to degrade persistent organic pollutants (POPs) in aqueous environments has been investigated for more than three decades (Herbert and Coons, 2017), 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 (Anbar and Hart, 1965; Gu et al., 2017a; 2017b; Wach et al., 2004). In this context, $e^-_{(aq)}$ have received renewed attention with the report of $e^-_{(aq)}$ mediated degradation of the emerging PFAS (Bentel, 2020; 2019; Cui et al., 2020; Raul Tenorio, 2020; Van Hoomissen and Shubham Vyas, 2019). Our study implies that engineered systems that generate $e^-_{(aq)}$ for water treatment could be effective for degrading SCCPs, and demonstrates the versatility of $e^-_{(aq)}$ as a relevant PPRI for the degradation of persistent organic pollutants (POPs).

## Appendix A. Supplementary 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 ·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.

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