# Photodegradation of Aroclor 1254 using diethylamine and simulated sunlight

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## Abstract

Photodegradation of Aroclor 1254 was studied using simulated sunlight and a photosensitizer – diethylamine. Diethylamine was added to aqueous Aroclor 1254 for promoting dechlorination of PCB using a xenon lamp. The degradation rate of Aroclor 1254 congeners was $4.74 \pm 1.51 \times 10^{-9}\,\text{mol}\,\text{l}^{-1}\,\text{h}^{-1}$. The half lives of 5 major congeners of Aroclor 1254 (66, 101, 110, 118, and 138) ranged from 30.31 to 52.11 h. Degradation of congener 101 was 5 time faster with simulated than with natural sunlight.

*Keywords:* PCB; Aroclor 1254; photodegradation; diethylamine

## 1. Introduction

Polychlorinated biphenyls (PCBs) have become ubiquitous pollutants because of their widespread use in industrial applications along with their extraordinary chemical and thermal stability [1]. Photodegradation is a process in which chemical bonds are broken under the influence of light. Many investigations have focussed on the use of high energy, low wavelength (254–290 nm) radiation for the dechlorination of PCBs [2–5]. However, Sworzyn and Ackerman [6] reported that the photodegradation of PCBs at a wavelength greater than 290 nm is possible on industrial scale.

Most PCB congeners do not strongly absorb at wavelengths above 300 nm, and sensitizers are used in the transfer of light energy to the PCB molecule in order to enhance dechlorination [3]. Sensitizers (amines, dyes, borohydrides, alkaline metals, aluminum and ferric chloride, etc.) have been added to enhance photodechlorination [7–9]. Diethylamine was most effective in enhancing the photodegradation of PCB congeners [10].
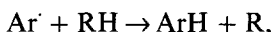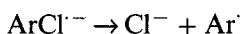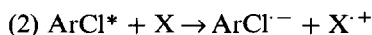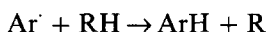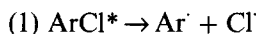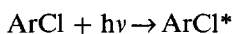
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The objectives of this study were (a) to determine the photodegradation rate of Aroclor 1254 (5 major congeners) with diethylamine as the sensitizer and (b) to compare the degradation rates of Aroclor 1254 (congener 101) using natural and simulated sunlight.

## 2. Theory

The initial photodegradation step usually involves fission of the parent molecule to form free radicals [11]. The chain dechlorination reaction has been explained as a process involving the transfer of an electron from electron donors to the PCBs [12]. Two possible dechlorination processes are described as [2]

$$ArCl + h\nu \rightarrow ArCl^*$$

$$(1) \quad ArCl^* \rightarrow Ar^{\cdot} + Cl^{\cdot}$$

$$Ar^{\cdot} + RH \rightarrow ArH + R$$

$$(2) \quad ArCl^* + X \rightarrow ArCl^{\cdot -} + X^{\cdot +}$$

$$ArCl^{\cdot -} \rightarrow Cl^- + Ar^{\cdot}$$

$$Ar^{\cdot} + RH \rightarrow ArH + R,$$

where ArCl is an aromatic chlorinated hydrocarbon, RH is aliphatic hydrocarbon and X is an electron donor.

## 3. Materials and methods

### 3.1. Preparation of Aroclor 1254, congener 101 and diethylamine

Aroclor 1254 in transformer oil (Sigma Chemical Company, St. Louis, MO), was diluted with acetone to 1000 ng/ml. Congener 101 (99% pure) (AccuStandard Inc., New Haven, CT) was dissolved in hexane to yield a stock solution (50 µg/ml), which was then diluted with acetone to 1000 ng/ml. Two ml of Aroclor 1254 or its congener 101 (1000 ng/ml each) were added to 18 ml distilled water in 25 ml glass vials (borosilicate) prior to exposure to light; the final concentration of Aroclor 1254 or congener 101 was 100 ng/ml. The amount of transformer oil (or hexane) in the final 20 ml solution was 0.02 ml compared to 1.98 ml of acetone. Acetone is known to sensitize the photoreaction of 3,4-DCB [13]. Acetone and PCBs were well mixed as a solution in water to ensure that the photodegradation will take place in the aqueous phase. Three replicates were prepared. Diethylamine (1.0 µg/ml), ten times higher than the concentration of Aroclor 1254 or congener 101, was used as a sensitizer to enhance the photodegradation.

## 3.2. Photoreaction

Aroclor 1254 or its congener 101, in glass vials, was placed on a merry-go-round rack 30 cm away from the lamp in the Ci35A Xenon Weather-Ometer (Atlas Electric Devices Co., Chicago, IL). The light energy of Xenon Weather-Ometer was simulated to that of natural sunlight for wavelengths between 250 and 800 nm. The temperature of the Weather-Ometer chamber was set at $27 \pm 2$ °C. The exposure times used were 0, 1, 2, 4, 8, and 24 h. In addition to exposure to simulated sunlight, congener 101 was exposed to natural sunlight outdoors on sunny days from 0900 to 1700 h (EST) for 0, 1, 2, 4, 8, and 24 h; the ambient temperatures varied from 25 to 32 °C.

## 3.3. Sample extraction and analyses

PCB congener 198 (2, 2', 3, 3', 4, 5, 5', 6-octachlorobiphenyl) (100 ng/ml) was added to hexane as an internal standard after irradiation prior to extraction, 2 ml of hexane was added to the samples for extraction, and the samples were shaken at 280 RPM for 45 min on an orbital shaker (VWR Scientific, Philadelphia, PA). A gas chromatograph (GC) equipped with an Electron Capture Detector (HP 5890) was used. The oven conditions were set at 100 °C initially for 2 min, increasing to 170 °C at 4 °C/min, then to 280 °C at 3 °C/min. Final holding time was 5 min at 280 °C. A DB 5, 30 m (i.d. 0.32 mm) column was used. Final congener concentrations were compensated for the internal standard loss $(< \pm 10\%)$ [14].

## 3.4. Determination of photodegradation rate

Five major congeners (66, 101, 110, 118, and 138) of Aroclor 1254 were chosen for the calculation of their degradation rates because they constitute 45.45% of all 53 Aroclor 1254 congeners by weight [15]. The concentrations of PCBs are given as means (ng/ml) $\pm$ standard deviation (mean $\pm$ SD). The first-order rate constant ($k$) was multiplied by the initial concentration of the sample to calculate the degradation rate (mol $l^{-1}$ $h^{-1}$). The degradation rate of individual congener was calculated, and then these values were averaged to calculate the degradation rate of Aroclor 1254. The half lives ($t_{1/2}$) of PCBs were calculated as ($t_{1/2} = 0.693/k$) [16]. Results were analyzed using analysis of variance (ANOVA) and least significant differences (LSD) to determine significant differences ($P < 0.05$) among six exposure times.

## 4. Results and discussion

### 4.1. Aroclor 1254

The recovery of control samples ranged from 85% to 107% [10]. The error factors include extraction, exposure, storage, and transportation losses and/or GC analyses errors. After 24 h exposure to simulated sunlight, the concentrations of

Table 1
Concentrations of 5 Aroclor 1254 congeners after exposure to simulated sunlight and diethylamine

| Hours | Mean ± SD (ng/ml) | | | | | |
|---|---|---|---|---|---|---|
| | 66 | 101 | 110 | 118 | 138 | Aroclor 1254 (Σ5 congeners) |
| 0 | 8.65 ± 0.38[a,*] | 8.22 ± 0.70[a,b] | 10.06 ± 0.58[a] | 5.94 ± 0.34[a] | 8.11 ± 0.20[a] | 40.98 ± 2.12 |
| 1 | 8.65 ± 0.41[a] | 9.09 ± 0.61[a] | 9.49 ± 0.50[a] | 5.35 ± 0.16[a] | 7.66 ± 0.18[a] | 40.25 ± 0.58 |
| 2 | 8.54 ± 0.08[a] | 8.69 ± 0.15[a] | 9.44 ± 0.06[a] | 5.44 ± 0.39[a] | 7.66 ± 0.36[a] | 39.78 ± 0.19 |
| 4 | 8.35 ± 0.54[a] | 7.29 ± 0.30[b] | 9.41 ± 0.98[a] | 4.96 ± 0.22[a] | 6.40 ± 0.06[b] | 36.41 ± 1.50 |
| 8 | 7.89 ± 0.42[a] | 7.18 ± 0.18[b] | 10.10 ± 1.24[a] | 5.19 ± 1.07[a] | 6.42 ± 0.34[b] | 36.81 ± 1.97 |
| 24 | 6.23 ± 0.54[b] | 5.97 ± 0.75[c] | 7.21 ± 0.65[b] | 3.42 ± 0.35[b] | 5.33 ± 0.47[c] | 28.17 ± 2.70 |

* Means with different letters are significantly different from each other at $P < 0.05$ (columnwise comparisons only).

Table 2
Percentage degradation of 5 Aroclor 1254 congeners after exposure to simulated sunlight and diethylamine

| Hours | 66 | 101 | 110 | 118 | 138 | Aroclor 1254 (Σ5 congeners) |
|---|---|---|---|---|---|---|
| 1 | 0.98 ± 4.74 | −20.30 ± 8.06* | 5.03 ± 4.99 | 3.28 ± 2.76 | 4.89 ± 2.16 | −0.91 ± 1.45 |
| 2 | 2.19 ± 0.93 | −14.98 ± 1.95 | 5.48 ± 0.64 | 1.70 ± 7.09 | 4.98 ± 4.41 | 0.28 ± 0.48 |
| 4 | 4.42 ± 6.14 | 3.52 ± 3.95 | 5.84 ± 9.82 | 10.43 ± 3.97 | 20.58 ± 0.71 | 8.72 ± 3.76 |
| 8 | 9.62 ± 4.75 | 5.00 ± 2.36 | −1.11 ± 12.40 | 6.19 ± 19.24 | 20.11 ± 5.91 | 7.73 ± 4.93 |
| 24 | 28.59 ± 6.19 | 21.03 ± 9.90 | 27.81 ± 6.53 | 38.25 ± 6.33 | 33.88 ± 5.84 | 29.39 ± 6.78 |

* A negative number means an increase in the concentration of the lower chlorinated congener from photodechlorination of higher chlorinated congener.

5 major congeners of Aroclor 1254 decreased from 40.98 ± 2.12 to 28.17 ± 2.70 ng/ml (Table 1). The percentage degradation of the Aroclor 1254 congeners ranged from 21% to 38% (Table 2). The degradation rate of the Aroclor 1254 congeners was $4.74 ± 1.51 × 10^{-9}$ mol $l^{-1}$ $h^{-1}$. The half lives of 5 congeners (66, 101, 110, 118, and 138) were 50.58, 52.11, 49.86, 30.31, and 39.6 h, respectively. The half life of Aroclor 1254 was 44.42 h.

The degradation of congeners 66, 101, 110, 118, and 138 was 28%, 21%, 28%, 38%, and 34%, respectively (Table 2). Lepine et al. [17] exposed Aroclor 1254 to sunlight in cyclohexane for 55 days from December to January and reported that photodegradation of Aroclor 1254 (congener 101, 110, 118 and 138) was −4%, 4%, 43%, and 19%, respectively. Zhang et al. [18] using titanium dioxide as catalyst, reported that 77% of Aroclor 1248 was destroyed in an aqueous solution after 4 h of exposure to natural sunlight; lower chlorinated congeners had greater rates of photocatalytic destruction possibly because of the greater solubility and desorption in aqueous systems. However, the intermediate and final products of PCB photodegradation were not identified. No biphenyl was found in our study and the research conducted by Carey et al. [19] and Sawai et al. [20]. During the

Table 3
Concentration and percentage degradation of congener 101 after exposure to natural and simulated sunlight

| Hours | Natural sunlight | | Simulated sunlight | |
|---|---|---|---|---|
| | Concentration Mean $\pm$ SD (ng/ml) | Percentage degradation | Concentration Mean $\pm$ SD (ng/ml) | Percentage degradation |
| 0 | $83.08 \pm 6.92^{a,*}$ | 0 | $95.54 \pm 1.23^{a,*}$ | 0 |
| 1 | $61.20 \pm 1.31^{b}$ | $38.80 \pm 1.31$ | $81.73 \pm 4.89^{a,b}$ | $18.27 \pm 4.89$ |
| 2 | $58.07 \pm 1.63^{b,c}$ | $41.93 \pm 1.63$ | $49.41 \pm 6.78^{b,c}$ | $50.60 \pm 6.78$ |
| 4 | $46.85 \pm 0.49^{c,d}$ | $53.15 \pm 0.49$ | $35.51 \pm 19.05^{c,d}$ | $64.50 \pm 19.05$ |
| 8 | $38.62 \pm 3.83^{d}$ | $61.38 \pm 3.83$ | $5.74 \pm 4.42^{d,e}$ | $94.26 \pm 4.42$ |
| 24 | $26.57 \pm 4.97^{e}$ | $73.43 \pm 4.97$ | $0.78 \pm 0.09^{e}$ | $99.23 \pm 0.09$ |

* Means with different letter are significantly different from each other at $P < 0.05$ (columnwise comparisons only).

photodegradation of Aroclor 1254, the concentrations of many higher chlorinated congeners decreased while the concentrations of lower chlorinated congeners increased due to photodechlorination (Table 2) [17].

*4.2. Congener 101*

Congener 101 showed 73.4% degradation (Table 3); the photodegradation rate was $1.25 \pm 0.22 \times 10^{-8} \, \text{mol} \, l^{-1} \, h^{-1}$ after 24 h exposure to natural sunlight. Using simulated sunlight, the photodegradation rate of congener 101 ranged from $5.99 \pm 1.33$ to $6.20 \pm 0.22 \times 10^{-8} \, \text{mol} \, l^{-1} \, h^{-1}$. It was about 5 times faster than the photodegradation rate with natural sunlight ($1.25 \times 10^{-8} \, \text{mol} \, l^{-1} \, h^{-1}$). After both 1 and 2 h exposure to simulated sunlight, the concentrations of congener 101 in Aroclor 1254 samples increased, possibly from the dechlorination of higher chlorinated congeners, explaining the reduction in its photodegradation rate (Table 2) compared to the photodegradation rate of congener 101 alone (Table 3). The half life of congener 101 was 16.90 h after exposure to natural sunlight compared to the half life of 3.48 h using simulated sunlight. The xenon lamp supplied constant and stable light as opposed to natural sunlight with changing radiation, wind, clouds, and temperature. The half life of metolachlor in water was $8.2 \pm 0.9$ and $54 \pm 6$ days in summer and winter, respectively [21]. In the study by Griller et al. [7], the dechlorination of Aroclor 1242 was complete, in the presence of hydrosiloxane, at ambient temperatures in about 10 to 24 h. The Aroclor 1254 congeners remaining after sunlight irradiation ranged from 58% to 181% after 1 week due to the lack of short wavelength radiation in sunlight [22].

## 5. Conclusions

The degradation of Aroclor 1254 congeners ranged from 21% to 38% after 24 h exposure to simulated sunlight. The half lives of the 5 congeners ranged from 30.31

to 52.11 h. The photodegradation rate of congener 101 was about 5 times faster with simulated than natural sunlight. Simulated sunlight can be a good energy source for the photodegradation of Aroclor 1254.

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