

## Photodegradation of Aroclor 1254 Using Simulated Sunlight and Various Sensitizers

Y. Lin,<sup>1</sup> G. Gupta,<sup>1</sup> J. Baker<sup>2</sup>

<sup>1</sup>Department of Natural Sciences, University of Maryland Eastern Shore,  
Princess Anne, Maryland 21853, USA

<sup>2</sup>Chesapeake Biological Laboratory, University of Maryland,  
Solomons, Maryland 20688, USA

Received: 9 May 1995/Accepted: 13 September 1995

Incineration is the most widely used method for the disposal of PCBs, but combustion often leads to the formation of more toxic oxygenated derivatives such as dioxins and polychlorinated benzofurans (Borman 1993). Sunlight can be a good energy source for the photodegradation of polychlorinated biphenyls (PCBs) in the presence of photosensitizers. Because most PCB congeners do not strongly absorb wavelength above 300 nm, sensitizers are used in the transfer of light energy to the PCB molecule (Hawari et al 1992). Many investigations have focussed on the use of high energy, low wavelength (254 - 300 nm) radiation for the destruction of PCBs (Bunce et al 1978; Hawari et al 1992; Lepine and Masse 1990; Lepine et al 1991; Ruzo et al 1973). In the presence of electron donors amines can greatly enhance the overall quantum yields of certain chlorinated aromatic compounds such as hexachlorobenzene (Freeman et al 1986). Titanium dioxide has been shown to effectively photocatalyze the reduction of chlorinated organics (Pruden and Ollis 1983; Borello et al 1989; Zhang et al 1993). Dyes can be used to absorb visible light and then transfer an electron to carry out a desired photodegradation reaction (Illman 1993). Sworzyn and Ackerman (1982) reported that the photodegradation of PCBs at a wavelength greater than 290 nm is possible on the industrial scale in terms of its cost and effectiveness.

The objective of this research was to study the effect of various sensitizers on the photodegradation of Aroclor 1254 using simulated sunlight.

### MATERIALS AND METHODS

Aroclor 1254, in transformer oil, was purchased from Sigma Chemical Company (St. Louis, Missouri). One mL of Aroclor 1254 (100 µg/mL) was diluted with acetone to 1.0 µg/mL. All glassware was cleaned by heating at 550 °C for 2 hr (Thermolyne Muffle Furnace 1400, Dubuque, Iowa). Teflon lined lids of glass vials were soaked in methanol for 20 min to solubilize any contaminants. All samples were stored in a refrigerator at 4 °C until extraction.

Correspondence to: G. Gupta

Various sensitizers (lithium hydroxide, potassium hydroxide, diethylamine, diethyl phenylene diamine, methylene blue, methyl orange, aluminum chloride, and titanium dioxide) (purity: 98 - 99.9%) were purchased from Fisher Scientific, Aldrich and Eastman Kodak Companies. Two mL of the Aroclor 1254 (1.0 µg/mL) was added to 18 mL sensitizer solution in glass vials prior to exposure to simulated sunlight. Sensitizer solution (1.0 µg/mL in distilled water), ten times higher than the concentration of Aroclor 1254, was used to enhance the photodegradation.

Samples in glass vials were placed on a merry-go-round rack of the Ci35A Xenon Weather-Ometer (Atlas Electric Devices Company, Chicago, Illinois). Light in the Xenon Weather-Ometer was provided by a single water cooled xenon arc lamp. The inner and outer filters of the xenon lamp are made up of borosilicate for irradiation with light energy simulating natural sunlight at wavelength of 250 to 800 nm. Two exposure times, 16 and 32 hr, were used resulting in 20 and 40 kJ/m<sup>2</sup> energy, respectively. The temperature in the Weather-Ometer chamber was 27±2 °C.

After exposure to simulated sunlight, 2 mL of hexane were added to the sample for extraction, and the sample was shaken at 280 RPM for 45 min on an Orbital Shaker (VWR Scientific, Philadelphia, Pennsylvania). This extraction procedure was repeated once. All extracts were stored in a refrigerator at 4 °C before analyses. Analyses were performed using a Gas Chromatograph (GC) equipped with Electron Capture Detector (Hewlett Packard 5890). The temperature program was 100 °C initially for 2 min then 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) split/splitless column was used. The carrier gas was hydrogen (H<sub>2</sub>) (Baker et al 1991). The recovery of control samples ranged from 85 to 107% (Lin 1995).

Analysis of Variance (ANOVA) and Least Significant Differences (LSD) (P<0.05) were computed from the results of the three replicates.

## RESULTS AND DISCUSSION

Samples with diethylamine and diethyl phenylene diamine showed the best result in the degradation (73 and 61%) of Aroclor 1254 after exposure to simulated sunlight for 32 hr (Fig. 1). Freeman et al (1986) found 83 and 17% of 1,2,3,4 tetrachlorobenzene dechlorinated to 1,2,4 trichlorobenzene and 1,2,3 trichlorobenzene after 30 min irradiation of UV light (254 nm) in the presence of triethylamine. Zhang et al (1993) used titanium dioxide to catalyze the photolytic process and reported 80% degradation of PCBs after 4 hr of radiation with natural sunlight. The color and/or cloudiness from sensitizers titanium dioxide, methylene blue and methyl orange (Fig. 1) in sample solutions may have inhibited the penetration of simulated sunlight in our study reducing the degradation of Aroclor 1254. Methylene blue and methyl orange were used as sensitizers by

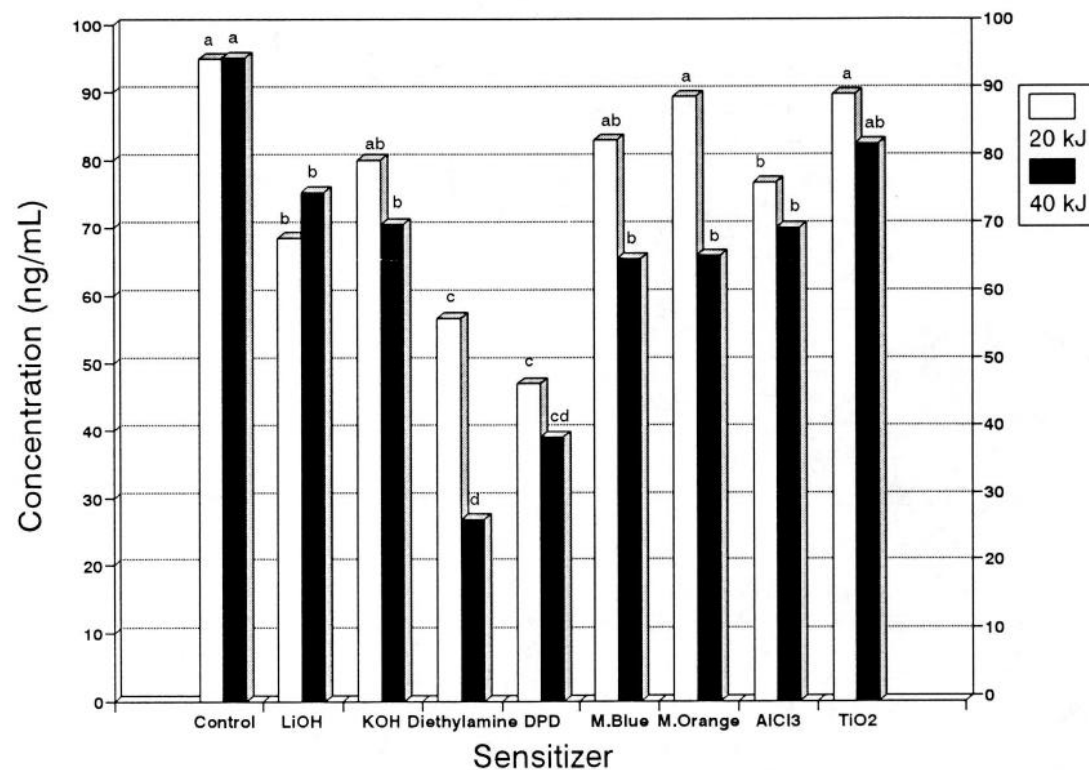


Figure 1. Concentration of Aroclor 1254 after exposure to simulated sunlight and various sensitizers (Bars with different letters are significantly different from each other at  $P < 0.05$ )

Stallard et al (1988), and the degradation of Aroclor 1254 was 79 and 22 % , respectively after 15 min irradiation with incandescent light compared to 35 and 34% degradation after 32 hr in our study with simulated sunlight.

Griller et al (1990) found that the degradation of Aroclor 1242 with lithium and potassium hydroxide was complete in 10 to 24 hr with no light energy. In our study, only 25 and 29% degradation of Aroclor 1254 with LiOH and KOH, respectively, were observed. Wilwerding and Hoch (1992) reported that at temperatures above 300 °C, PCBs were completely degraded in the presence of aluminum chloride in 2 hr. In our study, 30% of Aroclor 1254 was degraded without heating.

Based on these observations it can be concluded that simulated sunlight can be a good energy source for the photodegradation of Aroclor 1254 in the presence of diethylamine or diethyl phenylene diamine.

## REFERENCES

- Baker JE, Eisenreich SJ, Eadie BJ (1991) Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons, and polychlorobiphenyl congeners in Lake Superior. *Environ Sci Technol* 25:500-509
- Borello Minero C, Pramauro E (1989) Photocatalytic degradation of DDT mediated in aqueous semiconductor slurries by simulated sunlight. *Environ Toxicol Chem* 8:997-1002
- Borman S (1993) Novel ideal developed to destroy toxic chemicals. *Chem Eng News* 71(42):5
- Bunce NJ, Kumar Y, Ravanal L, Safe S (1978) Photochemistry of chlorinated biphenyls in isooctane solution. *J Chem Soc* :880-884
- Freeman PK, Srinivasa R, Campbell JA, Denizer ML (1986) The photochemistry of polyhaloarenes: (5) Fragmentation pathways in polychlorobenzene radical anions. *J Am Chem Soc* 08:5531-5536
- Griller D, Hawari JA, McPhee DJ (1990) Dehalogenation of halogenated aromatic compounds. US Patent:4,973,783
- Hawari J, Demeter A, Samson R (1992) Sensitized photolysis of polychlorobiphenyls in alkaline 2-propanol: dechlorination of Aroclor 1254 in soil samples by solar radiation. *Environ Sci Technol* 26:2022-2027
- Illman DL (1993) Green technology presents challenge to chemists. *Chem Eng News* 36:26-27
- Lepine FL, Masse R (1990) Degradation pathways of PCB upon gamma irradiation. *Environ Health Perspect* 89: 183-187
- Lepine FL, Milot SM, Vincent NM, Grave D (1991) Photochemistry of higher chlorinated PCBs in cyclohexane. *J Agri Food Chem* 39:2053-2056
- Lin Y (1995) Photodegradation of Aroclor 1254 with simulated sunlight using diethylamine. Ph.D. Dissertation, University of Maryland Eastern Shore.

- Pruden AL, Ollis DF (1983) Degradation of chloroform by photoassisted heterogeneous catalysis in dilute aqueous suspensions of titanium dioxide. *Environ Sci Technol* 17:628-631
- Ruzo LO, Zabik MJ, Schuetz RD (1973) Photochemistry of bioactive compounds photochemical processes of polychlorinated biphenyls. *J Am Chem Soc* 96:3809-3813
- Stallard ML, Sherrard JH, Ogliaruso MA (1988) Dye-sensitized photochemical reduction of PCBs. *J Environ Eng* 114: 1030-1051
- Sworzyn EM, Ackerman DG (1982) Interim guidelines for the disposal/destruction of PCBs and PCB items by non-thermal methods. EPA-600/2-82-069, Washington DC 1-24
- Wilwerding M, Hoch R (1992) Degradation of polychlorinated biphenyls. US Patent 05,152,844: 1-14
- Zhang JJ, Scrudato RJ, Pagano JJ, Roberts RN (1993) Photodecomposition of PCBs in aqueous systems using  $\text{TiO}_2$  as catalyst. *Chemosphere* 26:1213-1223