

# Utilization of Sunlight for the Destruction of Toxic Water Pollutants

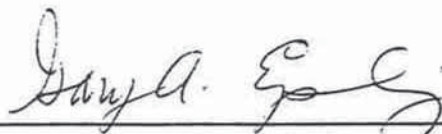
Gary A. Epling, Ph.D., Principal Investigator

Final Progress report submitted to the

## New Haven Foundation Quinnipiac River Fund

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## Utilization of Sunlight for the Destruction of Toxic Water Pollutants

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**Abstract.** The research team at the University of Connecticut, headed by Prof. Gary Epling, is working to develop an innovative approach for detoxification of chlorinated pollutants which are contaminating Connecticut's watersheds. The approach involves using a nontoxic dye as a catalyst, harnessing the energy of sunlight to achieve a chemical reaction leading to detoxification reaction. Humic acids, which are a component of natural waters, help the detoxification. The UConn investigators have studied water contaminated with PCB's, chlorodioxins, tetrachloroethylene, trichloroethylene, chloroform, methyl chloroform, and carbon tetrachloride. They have been able to achieve laboratory-scale detoxification of all these materials using this catalytic method.

One of the undesirable effects of the use and manufacturing of chemicals has been contamination of water supplies from runoff, spills, and improper disposal. In this way, many toxic and carcinogenic chemicals have become widely distributed through the watersheds of Connecticut. In particular, halogenated insecticides, PCB's, and chlorinated industrial solvents and degreasers (tetrachloroethylene, trichloroethylene, chloroform, methyl chloroform, and carbon tetrachloride) have been found to be significant problems in many parts of Connecticut due to their toxicity, their wide use, and their resistance to biological degradation. The Quinnipiac River watershed is of particular concern due to pollution from chlorinated solvents and degreasers.

Our research involves the development of a method for the alleviation of this problem by utilization of sunlight to chemically detoxify these pollutants. Our plan is to develop a catalytic method involving nontoxic dyes to direct the photochemical energy of sunlight into bond cleavage of the unreactive carbon-halogen bonds. If successful, our method would provide a method to reduce the levels of the pollutants to nontoxic levels. Our strategy has two particularly attractive features. First, it could provide an inexpensive means for detoxification of chemical wastes that would prevent environmental contamination in the future. Also, it would provide a safe method for treatment of a large body of water such as a polluted lake or pond.

During the year of support from the New Haven Foundation we have undertaken several directions of study that would develop our method sufficiently to achieve the goals we have described. While we have not yet achieved our long-term goals, we have successfully achieved several scientific breakthroughs which can lead to further advances. The advances we have achieved are outlined below.

We have shown that the energy contained in visible light (sunlight) can be harnessed, as described above, to destroy chlorinated aromatic compounds



(benzenes, PCB's, and chlorodioxins). In this photochemical process a nontoxic catalyst is used to absorb the energy from sunlight to make an electronically excited state. Upon interaction with a sacrificial reductant this dye becomes a radical anion, a species which reacts directly with the chlorinated material to cause dechlorination and regeneration of the dye. Thus, the energy of sunlight is utilized in a catalytic manner to detoxify the chlorinated pollutant.

We have further found that our catalytic process successfully detoxifies chlorinated organic solvents. We have examined tetrachloroethylene, trichloroethylene, chloroform, methyl chloroform, and carbon tetrachloride. All of these can be catalytically destroyed in the manner we originally suggested.

We have extensively examined the catalytic properties of nontoxic materials whose structural properties suggest they would be effective in causing the desired detoxification. We have identified several promising candidates. In particular, erythrosine (FD&C Red #3), phloxine (FD&C Red #28), methylene blue (a nontoxic dye used therapeutically as an antidote for cyanide poisoning), and the dinitration product of methylene blue are all effective as detoxification catalysts.

The last requirement for successful detoxification is for a "sacrificial reductant". We have found that this substance can be "humic acid", the main naturally-occurring organic component of water bodies. This material is present in natural waters because the water dissolves some of the organic components of soil. In essence, "dirty water" has a high concentration of humic acids, and its reaction is beneficial to the purification of that water. One of the reasons that humic acid appears to be so efficient as the sacrificial reductant may be its tendency to bind hydrophobic compounds (such as halogenated organic materials) so that the photochemical process can proceed with the reactants held in close proximity. Thus, our photochemical process may lead to the chemical destruction of the pollutant, with no other consequence than the reduction of the level of the humics in the water.

Through Foundation support we have obtained samples of pond water from two sources, artificially charged them with 200 ppm of trichloroethylene as a pollutant, and shown that the trichloroethylene is quickly destroyed by the action of sunlight when a small amount of catalytic dye is present. We have established that the chemical structure of the product is the dechlorinated material. We have also shown that in the absence of the dye minimal decomposition of the pollutant occurs. Finally, we have shown that if distilled water is used instead of pond water (so that no humic acids are present) no detoxification of the pollutant occurs. Consequently, the successful detoxification requires three elements: sunlight, dye, and humic acids (which are already present in natural water sources).

The success we achieved during this period prompted us to present some of our results at two major scientific meetings. The American Chemical Society National Meeting, Washington, D. C., Aug. 23-28, 1992 (Division of Environmental Chemistry), and the conference on Emerging Technologies for Hazardous Waste Management, Atlanta, GA, Sept. 21-23, 1992. In both of these conferences financial support from the New Haven Foundation was gratefully acknowledged; The last two pages of this report (Appendix A) provides an abstract of the "Emerging Technologies" presentation in which Foundation support was prominently cited.



# Appendix A

## "PREPRINT EXTENDED ABSTRACT"

Presented at the I&EC Special Symposium

American Chemical Society

Atlanta, GA,

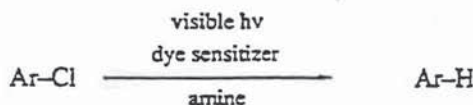
September 21-23, 1992

### DETOXIFICATION OF CHLORODIBENZODIOXINS USING SUNLIGHT AND DYES

Gary A. Epling\* and Qingxi Wang

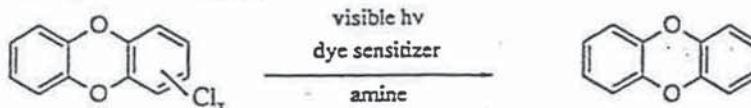
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We have previously reported<sup>1</sup> several visible dyes which were effective in detoxifying chlorobenzenes and PCB's by reductive dechlorination. The detoxification process relied upon a visible light-induced photoreduction, initiated by absorption of the light by the dye, and promoted by the presence of a mild "sacrificial reductant." Amines were shown to be effective as sacrificial reductants.



The role of the dye sensitizer was clearly catalytic—it was not consumed on sensitization of dechlorination of a 10-fold excess of aryl chloride. We have found methylene green, methylene violet, methylene blue, protoporphyrin IX, zinc protoporphyrin, acriflavin, rose bengal, and erythrosin to be successful in this catalytic process. We report two aspects of our continuing study of this reaction: (1) Extension of the study to demonstrate efficacy in photodechlorination of chlorodioxins, and (2) mechanistic studies to establish the nature of the photochemical pathway.

We have now examined several chlorinated dioxins, focusing on isomers of low toxicity as models for the more highly toxic isomers such as the 2,3,7,8-tetrachloro compound. Our experimental procedure closely patterned that of our previous study,<sup>1</sup> utilizing solutions of chlorodioxins at 200 ppm in acetonitrile-water, usually in the presence of 0.01 M triethylamine and about 3 millimolar concentrations of the dye sensitizer. Irradiation with sunlight or a 120-Watt GE Miser spotlight led to rapid dechlorination of the dioxin. Products were analyzed by GC/MS, and spectra of products were compared to those of authentic materials. An extremely clean photoreaction was observed, with the predominant reaction being the stepwise reductive dechlorination to yield unchlorinated dioxin as the ultimate product. A minor side reaction was dioxin ring opening to the phenol, a process which can be very important in "ordinary" direct photolyses.<sup>2</sup>



Following the reaction as a function of time allows the observation of the stepwise nature of the dechlorination process, with lesser-chlorinated dioxins observed as initially-formed photoproducts. The graph of product distribution versus time (Figure 1) for 2,7-dichlorodibenzodioxin and methylene green shows the rapid disappearance of the starting dichloro compound, with an initial rise, then decrease in monochlorodioxin concentration. The unsubstituted dioxin increases progressively until it is the only product observed. Figure 1 shows the reaction observed using the 120 Watt spotlight; rates observed with bright sunlight under optimal conditions were about the same. A control experiment examined the comparative rate of sunlight-promoted photoreaction of the dichlorodioxin *without the presence of a dye catalyst*. Under these conditions we found the reaction to proceed quite slowly, with only less than 0.5% reaction occurring with 90 minutes of sunlight exposure. Thus, the sunlight-promoted *direct* photolysis, which relies solely upon the UV component of sunlight to induce photoreaction, is more than 100-fold

# Appendix A

slower than our dye-promoted photoreaction. This rate enhancement is due to the more efficient harvesting of the energy of sunlight by the dye, as well as the higher inherent quantum efficiency of the dye-promoted reaction.

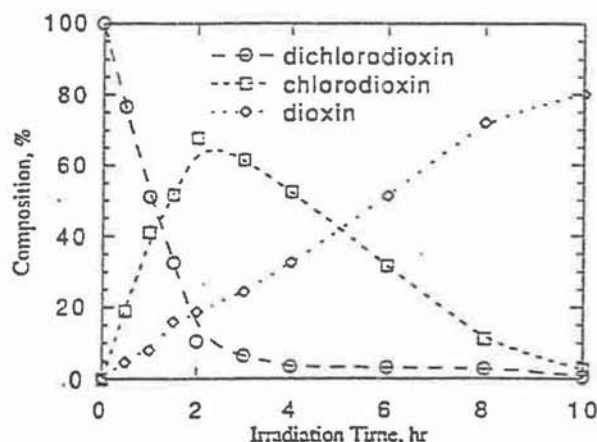


Figure 1. Dye-promoted Dechlorination of 2,7-dichlorodibenzodioxin using Visible Light

In a second aspect of our work we have been probing the mechanism of the dye-promoted photodechlorination. The most likely pathways of reaction seem to involve an exciplex photoreaction initiated by the absorption of the light by the dye. The two likely possibilities are the transfer of an electron from the electronically excited dye to the aryl chloride or, alternatively, the transfer of an electron from the sacrificial reductant (the amine in this case) to the excited dye. In the latter case the radical anion of the dye would be formed, which then transfers an electron directly to the aryle chloride. The radical anion of the aryl chloride would result in either case, and it would be expected to undergo loss of a chloride anion to give an aryl radical. This course of events is supported by mechanistic probes involving deuterium labels. In a solvent mixture containing  $D_2O$  the product dioxin does not incorporate any deuterium. This is consistent with an aryl radical as an intermediate, (which would abstract an ordinary hydrogen from the acetonitrile), but not consistent with an aryl anion, which would incorporate a deuterium by proton abstraction from the  $D_2O$ .

## Acknowledgment:

We are grateful to the New Haven Foundation for financial support of this research from the Quinnipiac River Fund.

## References Cited:

1. G. A. Epling, Q. Wang, and Q. Qiu, *Chemosphere* 22, 959 (1991).
2. D. Dulin, H. Drossman, and T. Mill, *Environ. Sci. Technol.* 20, 72 (1986).