AJChE 2007, Vol. 7, No. 1, 30-42

Photodegradation of Chlordane in Soil and Water Matrix Using Induced UV and Solar Light

Alexander C. Sioson, Jr.
Dr. Susan M. Gallardo
Mapua Institute of Technology
Intramuros-Manila, Philippines
Asian Regional Research Programme on Environmental Technology (ARRPET)
National Research Institute on Industrial and Hazardous Wastes
De La Salle University-Manila, PHILIPPINES
E-mail: arrpet@dlsu.edu.ph

The photodegradation of chlordane in soil and water matrix using induced ultraviolet (UV) radiation and solar light was evaluated in this study. A batch photolytic reactor equipped with a low-pressure mercury lamp (17 W) sterilight ultraviolet (UV) lamp with a supplied wavelength of 254nm was used in the photodegradation experiments. The pesticide's initial concentration in water was varied using three different concentrations (0.80, 2.60, and 8.0 mg/L) and soil samples were prepared at three different dosages (0.20, 2.0, and 4.0 mg/kg). At preferred time intervals, samples were withdrawn from the reactor. The pH and temperature of the samples were continuously monitored. Samples were extracted using solid-phase extraction (SPE) and the degradation of components was verified using a GC-ECD setup. Solar experiments were conducted during the months of April and May (14^0 33.971'N, 120^0 59.515'E); with a mean sunlight intensity of 85,187.5 lux.

Results of the photodegradation experiments using the batch photolytic reactor showed an average of 91.65% degradation of the chlordane pesticide dissolved in water after hours of exposure to UV light. High degradation efficiencies were achieved at higher chlordane initial concentrations. For solar photodegradation experiments, an average of 71.59% degradation was achieved. Photodegradation in soil showed an average of 62.54% degradation of the compound. As such, percentage degradation increases as the initial concentration of the pollutant increases. Further, solar photodegradation experiments in soil samples showed an approximate 56.35% degradation of the compound throughout the duration of the experiment.

Chloride-ion analysis using high-performance liquid chromatography (HPLC) equipment was conducted at chlordane aqueous solution. At higher chlordane concentrations, higher chloride ion concentrations in the solution were achieved. As such, more chloride ions detached themselves from the parent compound every two hours of sampling time and soon reached an almost steady state concentration at a maximum exposure time of eight hours.

Keywords: Chlordane, dechlorination, photolysis, solar photodegradation

INTRODUCTION

Chlordane (1,2,4,5,6,7,8,8a-octachlor-2,3,3a,4,7,7a-hexahydro-4,7-methanoindane) was discovered in 1945 as a mixture of over 140 different compounds. It is synthesized first by Diel-Alder fusion between cyclopentadiene and hexachlorocyclopentadiene, forming chlordene. Chlordane is then produced by addition of two Cl-atoms across the double bond of chlordene at high temperature and pressure. This results in the formation of two isomers of chlordane-α-trans and β-cis. Figure 1 shows the structure of the cis- and trans-chlordane. The β-isomer has significantly greater insecticidal activity (Kirk-Othmer 1995).

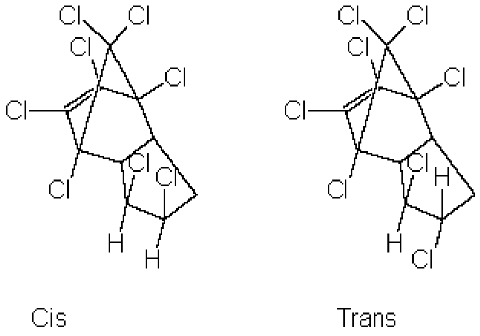

Figure 1. Structure of cis- and trans- chlordane

Chlordane is an environmentally persistent, all-purpose soil and household insecticide (ATSDR 1994b), preservative for wood and underground cables, and fire ant control in power transformers (ATSDR 1994a). Chlordane enters the environment through the direct application to crops, lawns, and to control termites. It is very persistent in soil, sorbing strongly to organic particles. Its half-life in soil is 20 years. Volatilization from soil may be the only major route of chlordane entering air. Because chlordane is insoluble in water and very rapidly binds to soil, potential for surface and groundwater contamination is very low. Table 1 shows the physical properties of the pesticide chlordane (ATSDR 1994a).

At the height of production, chlordane was the second most widely used organochlorine insecticide in the United States (U.S.), with the annual production at about 11 million kilograms per year. U.S. formulations previously available or available outside of the United States include dusts, emulsifiable concentrates, granules, oil solutions, and wettable powders (Meister 1992). Over 70,000 tons of chlordane has been manufactured since 1946 (Dearth and Hites 1990). Because of concern about the risk of

Table 1. Physical Properties of Chlordane

Description	**Amber, viscous liquid**
Warning properties	Nearly odorless; inadequate warning for acute or chronic exposure
Molecular weight	409.8 daltons
Boiling point (2 mm Hg)	347ºF (175ºC)
Melting point (cis isomer)	225-228ºF (107-109ºC)
Melting point (trans isomer)	217-221ºF (103-105ºC)
Vapor pressure	0.00001 (1 x 10-5) mm Hg at 77ºF (25ºC)
Specific gravity	1.59-1.63 at 77ºF (water = 1)
Water solubility	0.0001 g/L of water at 25ºC; Insoluble in water
Flammability	Noncombustible liquid (but the commercial product may be dissolved in various flammable solvents)

cancer, all use of chlordane was banned in April 1988 (ATSDR 1994a). In the Philippines, a baseline study conducted by Weston International at Clark Development Corporation (CDC) reveals that chlordane is present in large concentrations in soil. Chlordane was detected at 140 mg/kg, Risk-Based Concentration (RBC) residential criteria is 0.49 mg/kg (Weston International 1997). Field sampling at an identified contaminated site at Clark Field, Pampanga, disclosed that chlordane is present at 5200 μg/Kg in soil (ARRPET-DLSU 2004).

One of the most promising technologies currently established for pesticide degradation is through photolysis (Bryant Fulton, and Budd 1992; Murov, Carmichael, and Hug 1993;Albanis et al. 1998; Lin et al. 2000; Mabury and Wilson 2000). Reactant molecules are allowed to pass the excited states to promote reactions, where UV radiation served as the supplying energy that produces free radicals from one or more of the organic components of the solution by cleavage of a bond followed by a reaction with oxygen. Other reactions are possible until chain termination occurs. For reactions to occur, however, there must be a solution present that absorbs UV radiation at the supplied wavelength.

Photodegradation is one possible fate for a chlordane pesticide in the environment (Fishel 1997). With the aid of light, particularly sunlight (500-700 nm), photodegradation can destroy pesticides on the surface of the soil. In soil, photolysis will occur within a shallow surface zone, the depth of which depends on soil characteristics and the mechanism of photodegradation. Light absorption and photolysis of organic contaminants are influenced by sorption reactions that are related to the soil organic matter content and by singlet oxygen formation. Both direct and indirect processes can occur depending on the depth. Hebert and Miller (1990) reported that the vertical depth of direct photolysis on the soil surface would be restricted to a region of approximately 0.2 to 0.3 mm. For outdoor experiments, the mean indirect photolysis depths were reported to be greater than 0.7mm (Albanis et al. 1998). Like any other degradation processes, photodegradation reduces the amount of chemicals present and can reduce the level of pest control. Soil incorporation by mechanical methods during or after application or irrigation by water or rainfall following application can reduce pesticide exposure to sunlight.

Although there have been reported studies on the use of UV light in the degradation of organic pollutants, no information is available on whether chlordane undergoes photochemical reactions in soil and water under high intensity UV and solar light. This study, therefore, aims to present the possibility of using high-intensity UV light (254nm) and solar light for the degradation of trace amounts of chlordane in soil and water matrices.

MATERIALS AND METHODS

The technical chlordane (1,000 mg/L dissolved in hexane) was acquired from ATL, USA. Other chemicals used were of reagent grade and used as such without further purification. Dupont, Phils., provided the FEP thin plastic film (0.5 mil thickness). The UV lamp in the photoreactor is a low-pressure mercury lamp (Sterilight 17W) with a supplied wavelength of 254nm. Analysis of chlordane concentration in the sample was done using Shimadzu GC-14B equipped with an Electron Capture Detector (ECD). The gas chromatograph is installed with Restek chlorinated pesticides column.

Photoreactor

The photoreactor that was used consists of the UV lamp enclosed in an aluminum housing to prevent stray UV light from interfering in the degradation of the sample. Figure 2 shows a schematic diagram of the photoreactor. The samples are placed in the crystallization dish and exposed to UV light. The simulated samples were subjected to an eight-hour irradiation inside the photoreactor. Every two hours, one sample from each matris is taken placed in an amber bottle, and kept in the dark inside a refrigerator at 4^0C.

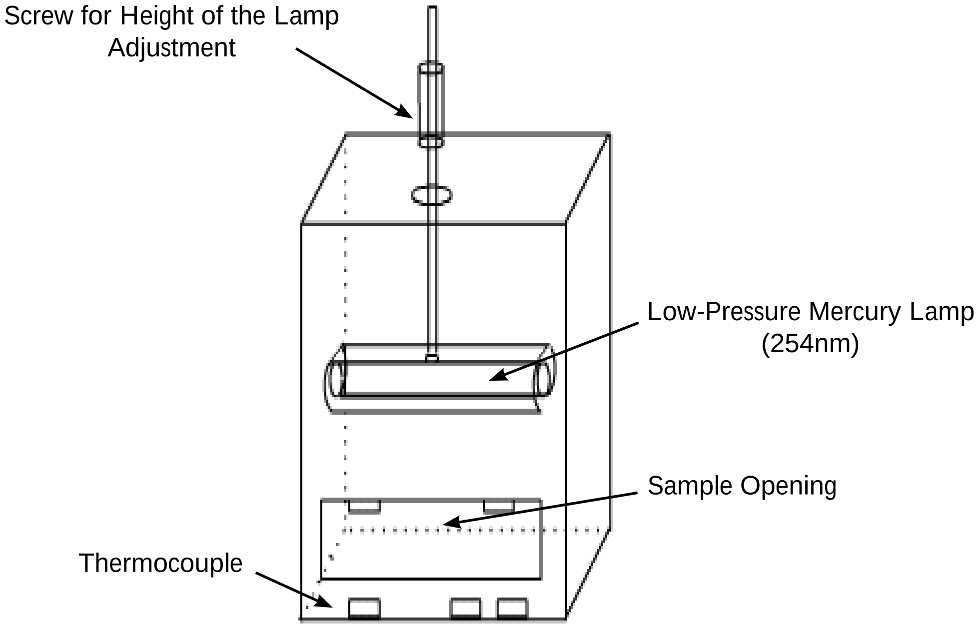

Figure 2. Schematic Diagram of the Batch Photolytic Reactor

EXPERIMENTAL PROCEDURES

Preparation of Stock Solution

Stock chlordane solution was prepared upon dilution of a specified amount of the standard solution with methanol to achieve desired concentrations. Three different initial concentrations were prepared, namely: 100, 80, and 60 mg/L. Aqueous solutions of chlordane were prepared for irradiation at varying initial concentrations. Photolytic experiments were carried out in crystallization dishes covered by a thin plastic film (0.12mm). Spiked solutions were stirred under the hood overnight to allow solvent evaporation.

The physicochemical characteristics of the soil selected for this study are presented in Table 2. Soil samples were prepared with fine soil particles passed through a 2-mm sieve. The soils were spiked with standard methanol solutions in order to achieve desired concentrations. The mixture is then thoroughly mixed by manual shaking. The bulk of the solvent is slowly evaporated at the fume hood overnight.

Table 2. Characteristics of the Control Soil

Soil Texture	pH	Soil Separate			OM*	OC**	$CaCO_3$	Conductivity
		Sand	Silt	Clay				
Sandy Loam	7.82	61.2	20.6	18.2	3.23	1.88	7.56	0.57

OM = Organic Matter; ** OC = Organic Carbon
Source: Bureau of Soils and Water Management, Quezon City

Chloride Ion analysis

At different initial concentrations, the dechlorination of chlordane spiked in distilled water was monitored using a high-performance liquid chromatography (HPLC) setup.

Solar Photodegradation Experiments

Crystallization dishes were exposed to direct sunlight at t = 0, in both simulated soil and water samples: 5g of the simulated soil and 10ml of the simulated water, respectively. An eight-hour mean sunshine duration from sunrise to sunset was observed, from 8 o'clock in the morning up to 4 o'clock in the afternoon. Every two hours, one sample from both matrices will be taken, placed in amber bottles, and kept in the dark inside a refrigerator for chlordane extraction prior to analysis. Solar light intensity was measured using a Lux meter (Control USA) at 15-min intervals, allowing the average light intensity over the duration of each experiment to be calculated. Solar photodegradation experiments were done on three sunshine days at the rooftop of the Science and Technology Research Center (STRC) Building, DLSU-Manila. Figure 3 shows the schematic diagram of the solar photodegradation set up.

RESULTS AND DISCUSSION

Photodegradation in Water

The results of the degradation of cis- and trans-chlordane at varying initial concentrations are shown in Figure 4. Since pollutants in the solutions were understood to play the dual roles of UV light photon absorber and OH• scavenger, the higher their initial concentration, the lower is the amount degraded.

This, however was not observed from the results showed in Figure 4. Percentage degradation was highest with 8.00 mg/L (96.82%-trans, 90.17%-cis) followed by the 2.60 mg/L (95.95%-trans, 92.81%-cis). Lastly, 0.80 mg/L (88.07-trans, 86.07-cis) got the lowest percentage degradation efficiency. A probable explanation for this would be the formation of reaction intermediates. Fast formation of reaction intermediates could have occurred when low initial concentrations were used that the reaction favored the degradation of these compounds rather than the prominent components of the pesticide.

Such results verify the study conducted by Tabak et.al (1981 a, b) on the photodegrability of the technical chlordane. They highlighted that cis- and trans-chlordane are two specific

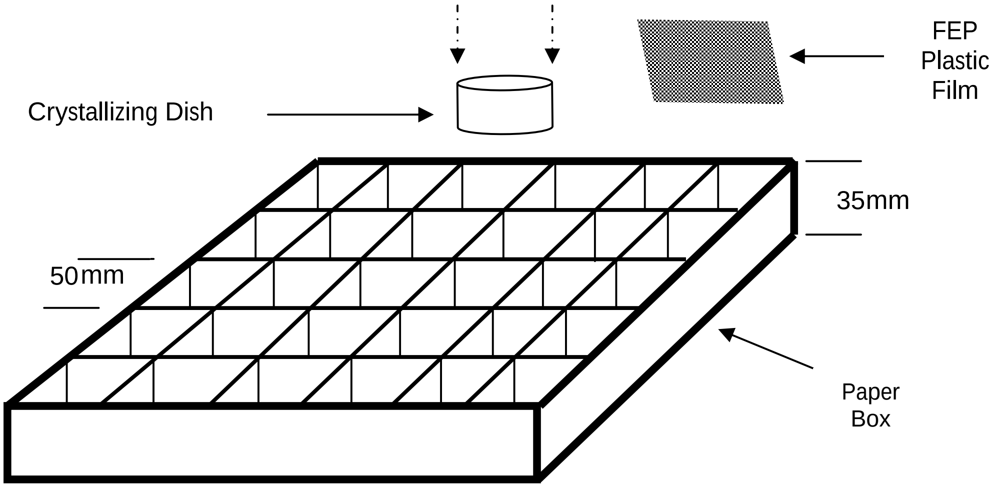

Figure 3. Schematic Diagram of the Solar Photodegradation Setup

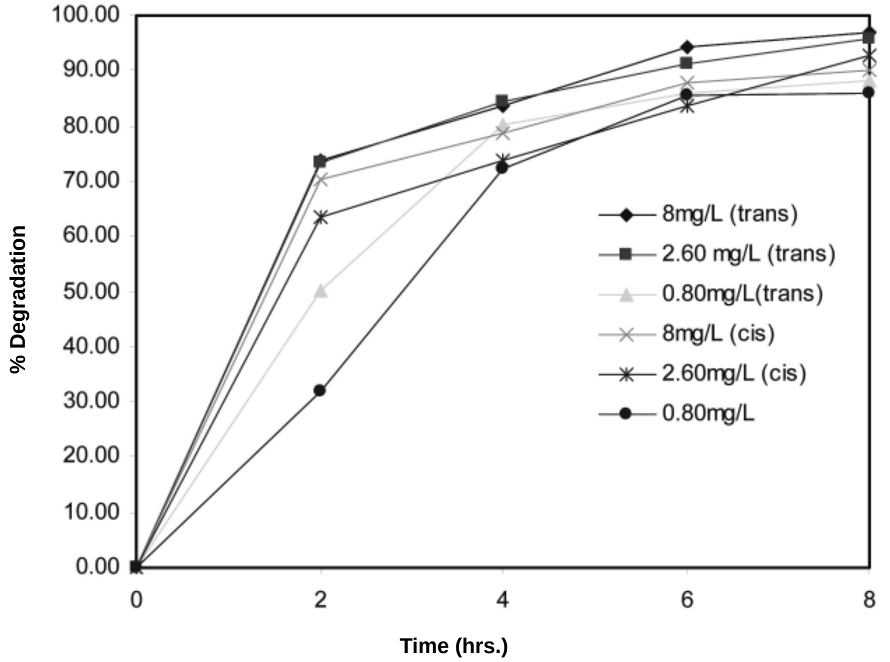

Figure 4. Percentage Degradation of cis- and trans-Chlordane over Time

isomers that may form photo-isomers with high-intensity UV that would eventually lead to photodegradation by prolonging the exposure of these compound to UV light. In all the initial chlordane concentrations used, a decrease in the pH of the solution was observed as shown in Figure 5. However, it may be noticed that there was a greater decrease in pH at higher concentration. Such behavior may be explained by the possible dechlorination occurring in the solution and that, at higher concentration, more Cl^- ions may detach themselves from the cis- and

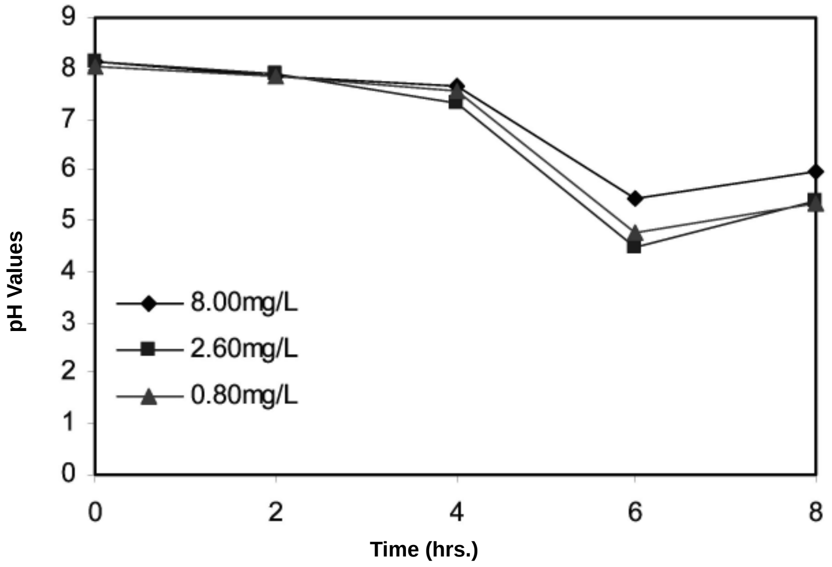

Figure 5. Change in pH over Time

trans- components. After 6 hours of irradiation, an increase in pH was observed which could be accounted for the possible formation of intermediates.

To verify the effectivity of the UV photodegradation process, an analysis of variance (ANOVA) was done. The mean of the degradation efficiencies from 0 hour to 8 hours of irradiation from ANOVA analysis shows that chlordane degradation percentages were not significantly homogenous. Further, ANOVA analysis signified that, beyond 6 hours of exposure to UV light, degradation efficiency would not necessarily improve. Such results could be highly significant in the economics of the technology.

Photodegradation in Soil

Results of the degradation of chlordane in soil are shown in Figure 6. In the three different concentrations employed, a decrease in pH was observed from time = 0 to time = 8 of exposure to UV light as shown in Figure 7. Photodegradation in soil showed that the trans-chlordane and cis-chlordane degraded. The highest degradation was achieved with 4.0mg/kg (67.01% cis, 74.19%-trans), followed by 2.0mg/kg (58.68%-cis, 68.29%-trans), and lastly 0.20mg/kg (48.22%-cis, 60.93%-trans).

The degradation efficiency increases with higher concentrations of the compound employed. The presence of organic matter and humic acids that acted as competitors in the degradation reaction could have brought about the lower degradation efficiency achieved. Humic acids are known to be photoreactive in nature that they tend to absorb photons during photolytic process.

This similar observation was reported by Albanis et al. (1998) in their study on the photodegradation of atrazine, propazine, propachlor, propanil, and molinate. Photodegradation experiments were conducted in different soil textures with varying organic matter and humic acid content.

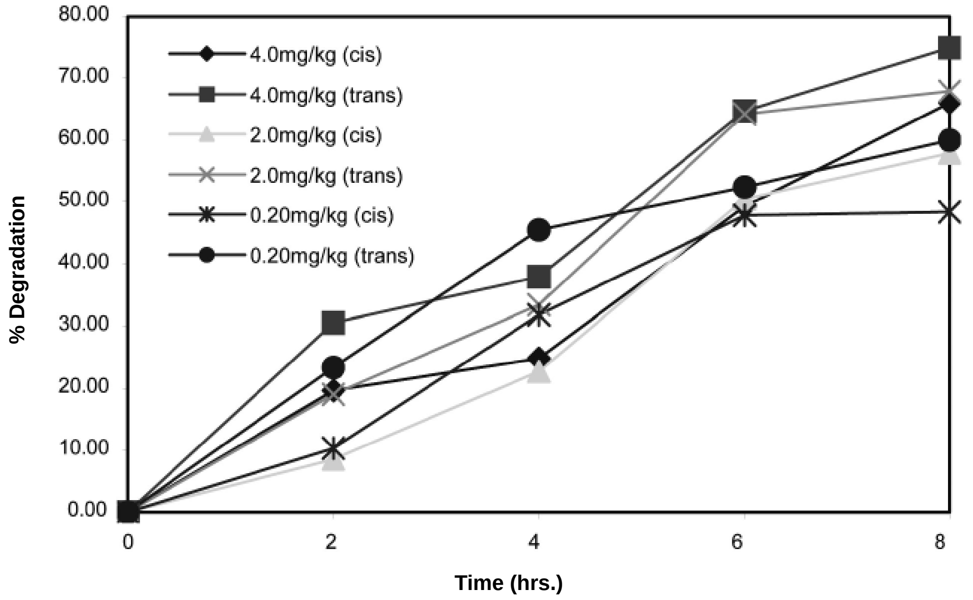

Figure 6. Degradation of cis & trans-chlordane over time

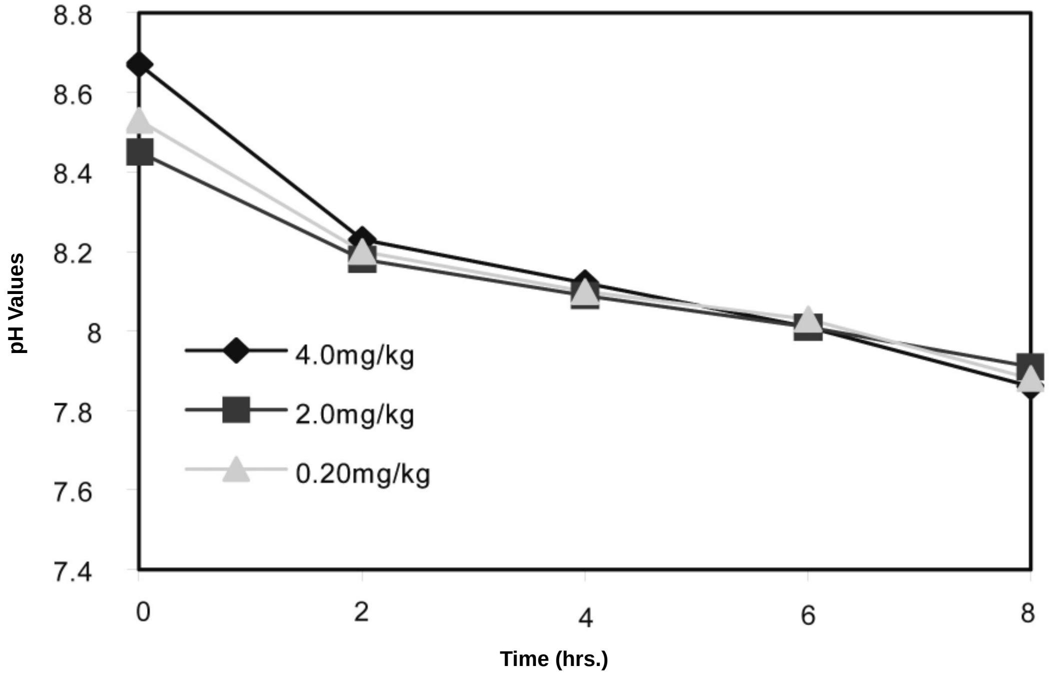

Figure 7. Change in pH over Time

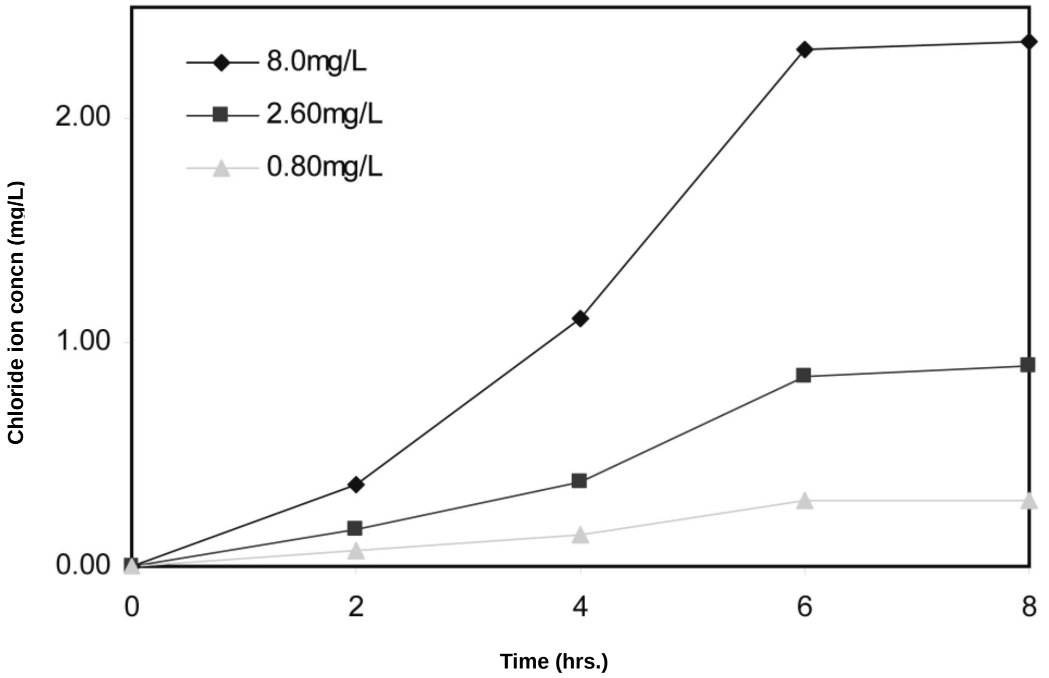

Figure 8. Change in Chloride Ion Concentration over Time

Chloride Ion Analysis

Chloride ion concentration was measured at two-hour intervals over a maximum exposure time of 8h at initial chlordane concentrations of 0.80, 2.60, and 8.00 mg/L using the high-performance liquid chromatography equipment. Experiments were performed with artificial irradiation using the photoreactor to assure stable conditions of light intensity in the reactor.

Plotting the chloride ion concentration against time for all the samples tested, Figure 8 shows the change in chloride ion concentration over time. As time proceeds, dechlorination progressed. The decrease in pH, as shown in Figure 5, during the first 2 to 6 hours of the reaction may be attributed to the presence of chloride ions in the solution as a result of dechlorination of chlordane. A continuous increase in the concentration of chloride ions were observed for up to 4 hours of exposure to UV light. From 4 to 6 hours of irradiation, a slight change to steady state was observed in the chloride ion concentration in all of the initial chlordane concentrations employed as depicted in the figure. However, a drastic decrease in pH was observed from 4 to 6 hours of irradiation. This behavior suggests the possibility that reaction intermediates could have formed within this reaction time. After irradiation for two hours, the chloride ions present in the solution reached an almost steady state concentration. The data presented here, however, are of significance in terms of determining the behavior of the chlordane solution at three different initial concentrations. The data also gave credence to some of the data previously presented, especially with the pH profile.

Solar Photodegradation Experiments

Figures 9 and 10 show the percentage degradation of trans-chlordane and cis-chlordane in water during the three-day solar photodegradation experiments. The chlordane concentration used in the solar photodegradation experiments was 8.00 mg/L. This concentration achieved the highest percentage degradation during the photodegradation experiments using the photoreactor. For the three-day photolysis, an average of 36.32%-trans and 13.07%-cis percentage degradation was calculated from 8:00 to 10:00 A.M. Between 10:00 A.M. and 12:00 P.M., an average of 39.31%-trans and 27.33%-cis percentage degradation was recorded. Further irradiation led to an average of 43.59%-trans and 32.75%-cis percentage chlordane degradation.

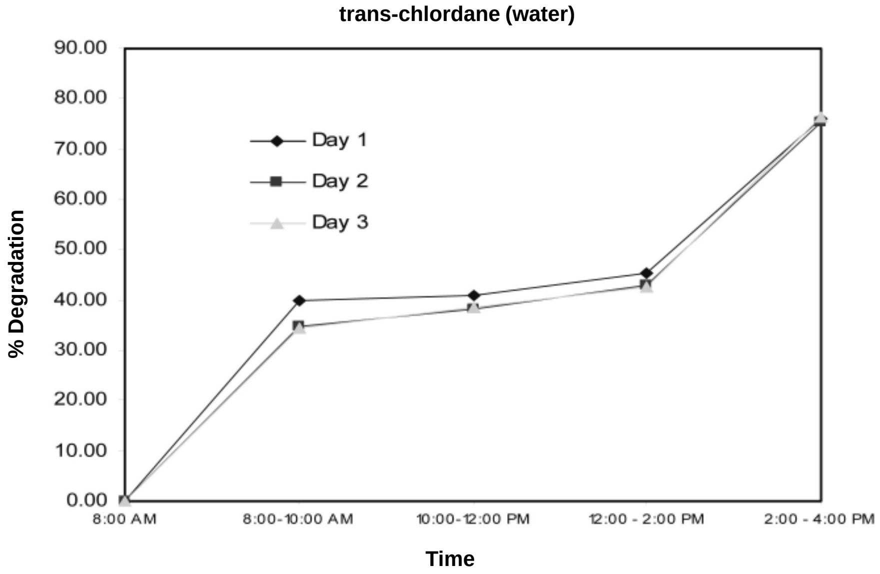

Figure 9. Percentage Degradation of trans-chlordane over time

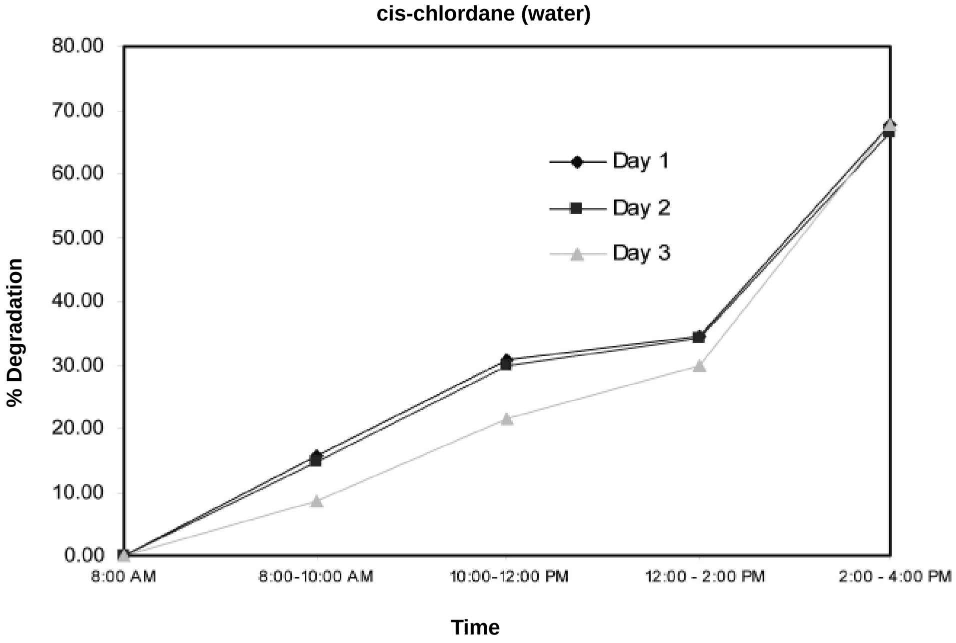

Figure 10. % Degradation of cis-Chlordane over Time

Finally, between 2:00 P.M. – 4:00 and the average chlordane degradation were 75.87%-trans and 67.31%-cis chlordane. In tropical countries like the Philippines, solar light could be effectively used for the photodegradation of pesticides in water. In case of large surface demanding photodegradation, sunlight would be the ultimate source.

Meanwhile, figures 11 and 12 show the percentage degradation of trans-chlordane and cis-chlordane in soil during the three-day solar photodegradation experiments. Further irradiation leads to an average of 50.95%-trans and 43.60%-cis percentage chlordane degradation. Finally, between 2:00 and 4:00 P.M. the average chlordane degradation were 59.84%-trans and 52.86%-cis chlordane. Lower percentage degradations were observed for the soil samples compared to those for the water samples. This could be attributed to the presence of organic matters that have acted as filters. Particulate matter, such as sediment particles, may scatter incident light, greatly reducing penetration of light beneath the surface.

CONCLUSION

The photodegradation of chlordane in soil and water has been investigated using a low pressure mercury lamp (Sterilight 17W) at a supplied wavelength of 254nm. At varying initial concentrations, the percentage degradation of chlordane using UV radiation increases with respect to time. An average of 91.65% degradation of the chlordane pesticide dissolved in water was achieved after 8 hours of exposure to UV light while photodegradation in soil showed an average of 62.54% degradation of the compound. The higher the initial concentration, the higher is the degradation for both soil and water. Higher degradation efficiency was achieved with the organic compound spiked in water than in soil.

Dechlorination experiments proved that the technology is indeed efficient in the destruction of chlorinated compounds present in the solution. At higher chlordane concentrations, more chloride ions detach themselves from the parent compound every two hours of sampling time and soon reached an almost steady state concentration at a maximum exposure time of 8 hours.

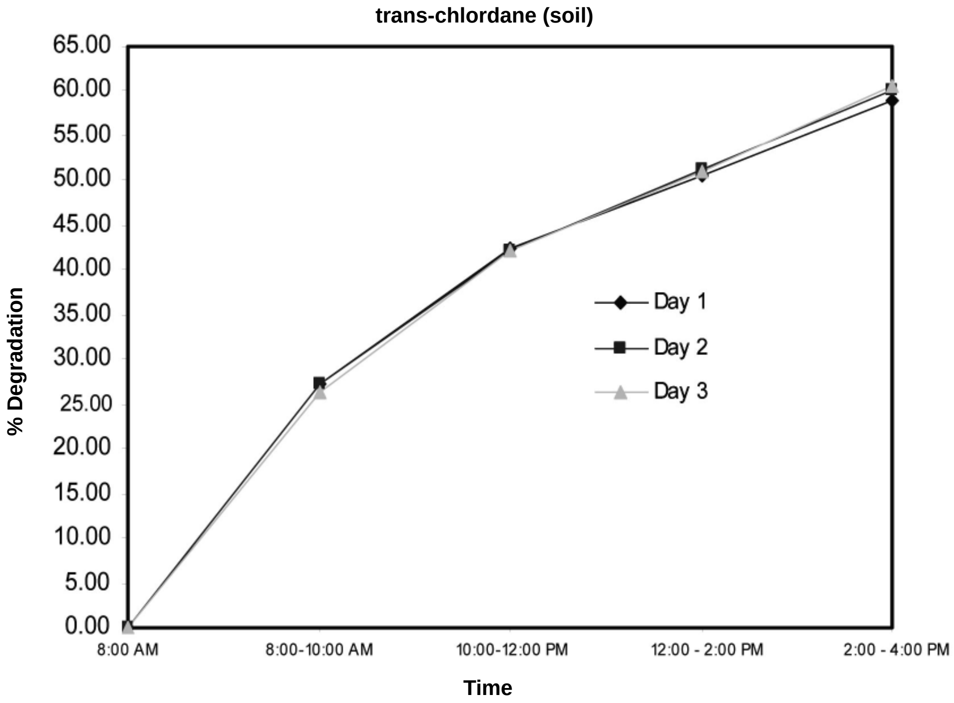

Figure 11. % Degradation of trans-Chlordane over Time

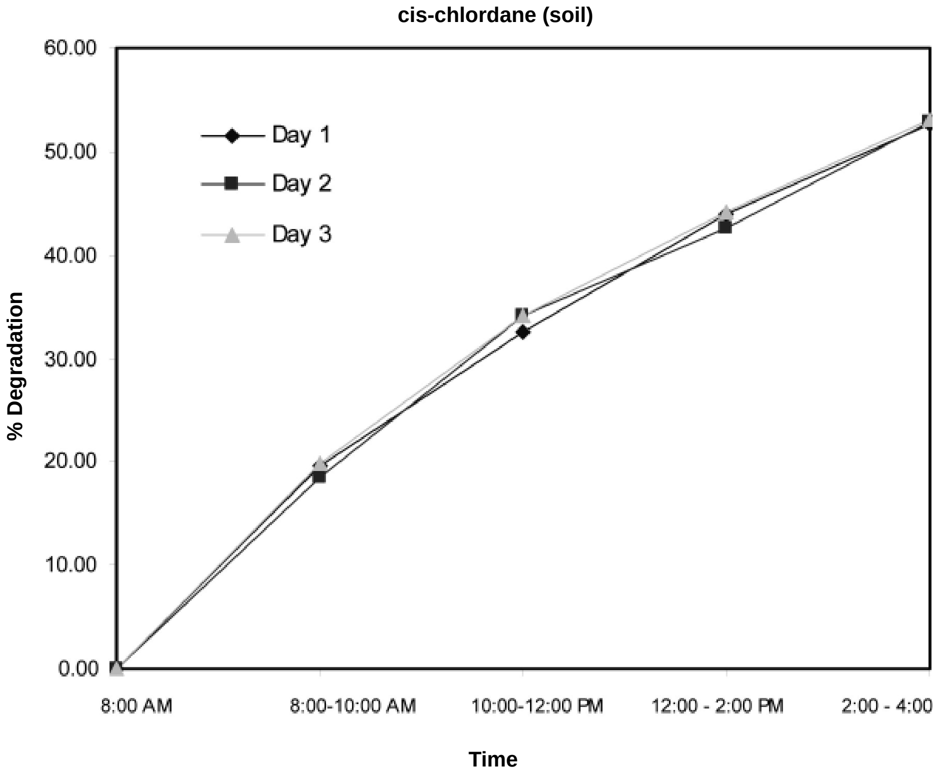

Figure 12. % Degradation of cis-Chlordane over Time

The influence of solar light on the degradation of chlordane was investigated at various time intervals. In the three photolysis days conducted, the maximum degradation was observed between 2:00 and 4:00 P.M. Solar photodegradation experiments showed an average of 71.59% degradation for aqueous samples while an approximate 56.35% degradation of the compound was achieved for soil samples. In tropical countries like the Philippines, intense sunlight is available almost throughout the year and solar light could be used for the photodegradation of pesticides in soil and water effectively through not comparable to the utilization of induced UV light.

A comparison on the effectiveness of using induced UV light and solar light on the degradation of chlordane in soil and water was conducted using t-test analysis on independent samples. Results of the statistical analysis show that UV photodegradation is more effective than solar photodegradation of chlordane in water. However, t-test analysis on the soil samples from UV and solar photodegradation experiments reveals that UV photodegradation is as effective as solar photodegradation. The nature of the samples, the presence of organic matters that have acted as filters, and the particulate matters such as sediment particles, that may scatter incident light were some of the factors attributed to such findings.

Based on the results presented in the study, further verification test could be done. It is recommended that identification of reaction intermediates and toxicity testing be conducted to find out if certain new species are more toxic than the original compound. Studies analyzing different pollutants have found that breakdown products in some cases are more toxic than the original pollutant.

A preliminary kinetic study is a possible venue for future studies to understand further the behavior of the reaction. Due to the nature of the samples used in this study, a complete and detailed kinetics was too intricate to be undertaken. Determination of a reaction mechanism, if desired, should be done on a specific chlordane component since each component of the technical compound will have its own reaction mechanism when subjected to photodegradation. By then, a proposed degradation pathway could be anticipated based on the result of the kinetic analysis of an individual chlordane component.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the generous financial support of the Swedish International Development Cooperation Agency (SIDA) through the Asian Regional Research Programme on Environmental Technology (ARRPET), the Department of Science and Technology–Philippine Council for Industry and Energy Research and Development (DOST–PCIERD), and the Commission on Higher Education (CHED). Special thanks go to the Department of Mathematics and Mechanics (MIT).

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