Photodegradation of Chloramben on a Soil Surface: A Laboratory-Controlled Study†

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Photodegradation of chloramben was conducted on a silt-loam soil under xenon irradiance using a laboratory soil photolysis apparatus. The study was conducted using three sets of soil conditions: active moist soil, sterilized moist soil, and dry (air-dry) soil, with temperature-controlled constantly at 25 ± 1 °C. Of all three soil conditions, application of chloramben on active moist soil, where moisture was maintained at approximately 75% field moisture capacity (FMC) at 0.33 bar, generated the most accelerated rate of degradation of the chemical. Further, chloramben degraded at a slower rate with a different degradation pattern when it was applied on air-dry soil surface as compared to when it was applied on an active soil at 75% FMC.

Keywords: *Pesticide; herbicide; photodegradation; soil; moisture; temperature; chloramben*

INTRODUCTION

The purpose of environmental fate studies is to determine the persistence of a pesticide in the environment as it comes in contact with soil, water, microorganisms, sunlight, and air (U.S. Environmental Protection Agency, 1982, 1993). Pesticide photodegradation on a soil surface encounters all of the above environmental factors (Miller et al., 1994, 1983). Besides direct photolysis, the soil moisture and the soil temperature greatly influence the chemical breakdown on the soil surface during solar irradiance. Photochemical transformation of a pesticide on the soil surface, an indirect photolysis process, involves active oxygen species, such as singlet oxygen, superoxide anion radical, and hydroepoxy and hydroxy radicals (Gohre et al., 1983; Katagi, 1990; Mervosh et al., 1995; Leifer, 1988; Mabury et al., 1994). The presence of water on a soil surface during a photolysis (1) generates the hydroepoxy and hydroxy radicals and (2) assists the diffusion of the singlet oxygen across the soil.

The primary competing processes of pesticide dissipation on the soil surface following solar irradiance are hydrolysis, biodegradation, and volatilization. The microbial activity in the soil greatly depends on the availability of organic nutrients, water being the primary transport medium for the nutrients to reach the active sites. Increased soil moisture and decreased organic content have been shown to increase the pesticide volatilization due to an increased partitioning of the pesticide in the solution phase. Further, the volatilization of a pesticide on a soil surface has been linked to soil properties such as moisture, texture, and organic content (Lembrich et al., 1994). Overall, the soil moisture (Shelton et al., 1991) is a vital factor in the mobility and degradation of a chemical in soil. The temperature affects the kinetics of biodegradation, hydrolysis, and volatilization processes. Therefore, any laboratory photodegradation on a soil surface should address an effective method of soil moisture and soil temperature control during irradiation. Hence, it is essential that a laboratory soil photolysis be conducted under controlled, simulated environmental conditions, in order to obtain meaningful data for the regulatory agency to evaluate the product application or to derive a useful extrapolation for a residue scientist to design an efficient field residue analysis protocol. Importantly, keeping the objective of an environmental fate study in mind, a laboratory soil photolysis should shed light on multiple dissipative processes (degradation via hydrolysis, aqueous photolysis, soil metabolism, and volatilization) of the pesticide during its exposure to natural sunlight on a soil surface. This paper reports a soil photodegradation study under laboratory-controlled parameters such as soil moisture, soil temperature, and aerobicity.

The herbicide 3-amino-2,5-dichlorobenzoic acid (Plimmer et al., 1969; Sheets, 1963) was selected for the soil photolysis study under laboratory-controlled conditions. A specialized soil photolysis apparatus was used to maintain the soil moisture and soil temperature during the irradiation. The apparatus was designed to address the deficiencies of the existing soil photolysis methods.

MATERIALS AND METHODS

Materials. Uniformly aromatic ring ^{14}C-labeled chloramben and nonradiolabeled chloramben were obtained from Rhône-Poulenc Ag. Co., Research Triangle Park, NC. The radiochemical purity of [^{14}C]chloramben was determined by a high-pressure liquid chromatograph (HPLC, Hewlett-Packard Series 1050 HPLC system, Varian 2550 UV detector, and Radiomatic FLO-ONE/βeta) and a liquid scintillation counter (LSC, Packard TriCarb, Model 1900TR) to be 90.5%. 3,5-Dihydroxybenzoic acid, 5-chlorosalicylic acid, 2,5−dichlorobenzoic acid, 3-hydroxybenzoic acid, and 2,5-dichloroaniline were purchased from Aldrich Chemical Co., Milwaukee, WI. All solvents used were of HPLC grade.

Soil. The soil was collected in Butler County, Pennsylvania, and was characterized by MidWest Laboratories, Inc., as silt-loam soil (pH 5.6, organic matter 2.0%). The field moisture capacity (FMC) was determined, and the soil moisture was adjusted to 75% FMC at 0.33 bar. The soil was then preincubated for 7 days (active soil) prior to chloramben application. The active soil was dried for 2 days at room temperature to obtain air-dry soil. To prepare a sterile soil, an aliquot of the air-dry soil was autoclaved at 121 °C and 16 psi for 2 h. Autoclaved soil was further treated with absolute alcohol, air-

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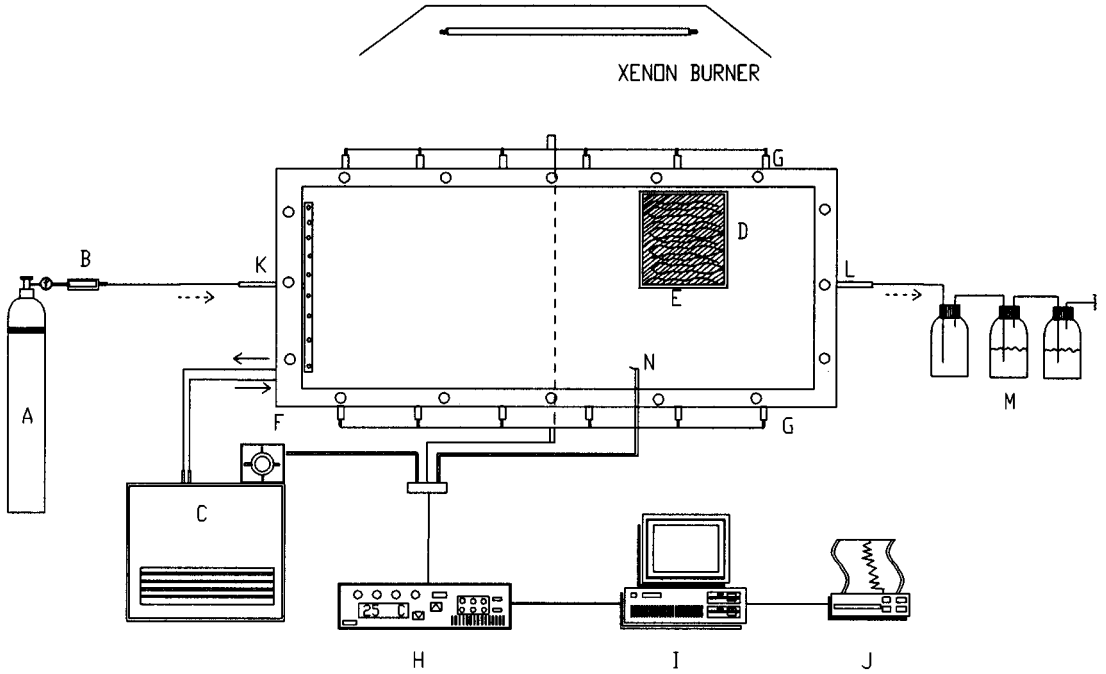

Figure 1. Schematic diagram of soil photolysis apparatus: (A) compressed air; (B) activated charcoal trap; (C) water cooler/circulator; (D) soil tray; (E) soil; (F) stainless steel chamber; (G) water spray nozzles; (H) controller box: (I) computer; (J) printer; (K) air inlet; (L) air outlet; (M) volatile trap; (N) moisture and temperature sensors.

dried, and finally dried in an oven at 110 °C for 4 h. Soil-bound residue was determined by combustion using a Biological Oxidizer (OX-500, R. J. Harvey Instrument Corp., Hillsdale, NJ).

Photolysis Apparatus. Specialized equipment was developed for the automatic control of soil moisture and soil temperature during photoirradiation. A schematic diagram of the apparatus is shown in Figure 1. The apparatus consisted of an open top stainless steel chamber with a water jacket to maintain the soil temperature. An airtight chamber designed to contain ^{14}C volatiles was attained by placing a quartz glass plate on the open top of the vessel. The test vessel contained access ports to maintain a flow of air. The test vessel housed stainless steel soil trays for irradiation. The test vessel was placed inside the Heraeus Suntest CPS photounit (DSET Laboratories, Inc., Phoenix, AZ). The test chamber utilized automated water spray nozzles to dispense a desired amount of water as determined by a moisture sensor. Both temperature and moisture sensors were placed in the soil during the experiment. The soil moisture level was continuously monitored, and the water spray cycle was activated when the soil moisture level fell below a preset value (75% FMC at 0.33 bar). The soil temperature was continuously monitored and controlled by a temperature controller. Soil temperature and moisture data were recorded by a computer and analyzed using a spreadsheet application software. The air outlet of the test chamber was connected to a volatile trap system containing 5% aqueous sodium hydroxide. A continuous air purge was maintained during incubation.

Procedure. The study was carried out using an active soil at 75% FMC at 0.33 bar, an autoclaved soil at 75% FMC at 0.33 bar, and an air-dry soil. In all cases the temperature of the soil was maintained constantly at 25 ± 1 °C. A control experiment corresponding to each soil type was conducted concurrently in the dark at 25 ± 1 °C. The dosing solution was prepared from nonradiolabeled and ^{14}C-labeled chloramben in acetonitrile (1.16 mg/mL) with a specific activity of 30 μCi/mg. An aliquot of soil (8 g, dry-weight equivalent) was treated with 30 μL of the dosing solution, and the soil was thoroughly mixed and then transferred to a soil tray. The treated soil was evenly spread on the trays to a thickness of approximately 2 mm and either exposed to a xenon irradiance continuously or incubated in the dark at 25 ± 1 °C. The test chamber was continuously purged with CO_2 scrubbed air at approximately 10 mL/min. At predetermined intervals (0, 24, 48, 72, and 144 h), the test chamber was purged with air at a higher flow rate (200 mL/min), the test chamber was opened, and the soil was sampled. The soil was extracted three times with a mixture of aqueous phosphoric acid (1 N)/diethyl ether (3:7). The organic and aqueous phases were pooled and then analyzed by LSC. The organic layer was concentrated and analyzed by HPLC. Finally, the soil was combusted and soil-bound ^{14}C-labeled residue determined. Volatile trap solutions were analyzed by LSC. The sample intervals for air-dry soil and autoclaved soil experiments were 0, 24, 72, and 144 h.

RESULTS AND DISCUSSION

Initial photolysis experiments in our laboratory resulted in rapid drying of soil, which prompted the development of the described apparatus. The major inconsistency in our initial experiments was a decreased rate of chemical degradation in irradiated systems when compared to the corresponding dark control experiments. Our experience suggests that both soil moisture ande soil temperature need to be controlled, simultaneously. It appears that both, the moisture and temperature control for the soil, have to be in a state of equilibrium, and any design to maintain soil moisture should spray water onto the soil surface to replenish the water/moisture lost due to vaporization. An alternate approach to suppress water vaporization during soil irradiation was to introduce water vapor into a sealed system at the expense of a flow-through system. Nevertheless, the expected loss of water from the soil during irradiation, an irreversible equilibrium, eventually depleted the water from the soil in the system. The described photolysis apparatus was developed to address this deficiency. It sprayed water on the soil surface at atmospheric pressure (a flow-through system) while maintaining the soil temperature at 25 ± 1 °C during irradiation. The apparatus was equipped with water spray nozzles and a moisture sensor to monitor the soil moisture level. The water spray frequency and soil temperature control were automated by a computer. A variety of chemicals have been tested for the chemical industry using the developed apparatus (PERL, Inc., 1993−1996). Each chemical exhibited a unique degra-

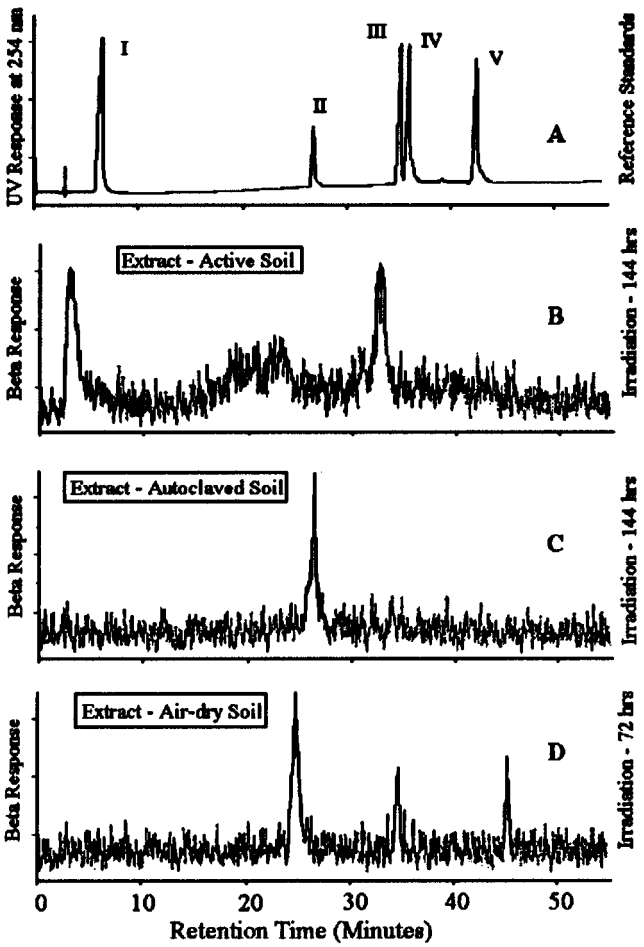

Figure 2. HPLC chromatogram of (A) chloramben and its potential degradates [(I) 3,5-dihydroxybenzoic acid, (II) chloramben, (III) 5-chlorosalicylic acid, (IV) 2,5-dichlorobenzoic acid, and (V) 2,5-dichloroaniline], (B) soil extract (irradiated active soil, (C) soil extract (irradiated autoclaved soil), and (D) soil extract (irradiated air-dried soil).

dation pattern and an accelerated rate of pesticide degradation and/or dissipation when this apparatus was used to monitor the photolysis of the chemical on soil. However, this paper describes the photolytic degradation rate/process of chloramben only, using the developed apparatus.

Soil was treated with chloramben at approximately 3 μg/g rate and was irradiated with a xenon or incubated in the darkness at 25 ± 1 °C. Duplicate soil trays were sampled at each sampling interval, and the remaining chloramben in soil was determined by analyzing the soil extract by HPLC. Chloramben photodegradates in soil extracts were different depending on the soil condition at the irradiation, as shown in Figure 2. The chloramben degradates in soil extract were tentatively characterized by comparing the retention times with those of reference standards. The active soil degraded chloramben to 3,5-dihydroxybenzoic acid and 5-chlorosalicylic acid, while dry soil generated 2,5-dichlorobenzoic acid and an unknown degradate. First-order regression analysis of the remaining chloramben on soil is shown in Figure 3. Chloramben photolyzed on an air-dry soil surface more slowly and with a different degradation pattern than it did on an active soil at 75% FMC. The half-life of chloramben under experimental conditions is shown in Table 1. The binding of chloramben on an autoclaved soil with moisture was greater than it was on an air-dry soil, due to the mobility of chloramben to

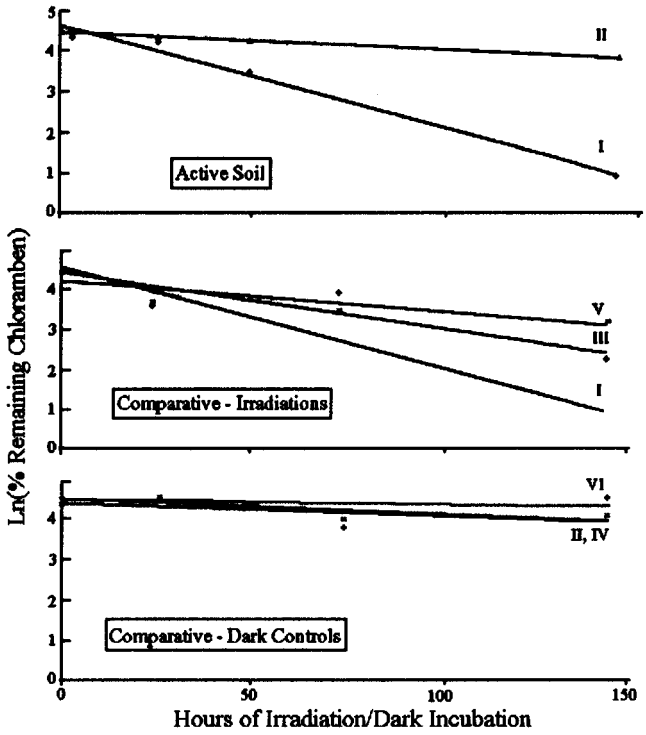

Figure 3. First-order decline curves: (I) irradiated active soil; (II) dark control active soil; (III) irradiated autoclaved soil; (IV) dark control autoclaved soil; (V) irradiated dry soil; (VI) dark control dry soil.

Table 1. Estimated Half-Life of Chloramben from First-Order Regression

soil type	irradiation h (R^2)	dark control h (R^2)
active	28.7 (0.98)	196.9 (0.97)
autoclaved	54.3 (0.91)	204.5 (0.64)
air-dry	108.8 (0.86)	497.6 (0.31)

chemically active sites in the presence of water (Fletcher and Kaufman, 1980).

No chloramben degradates were observed in moisture-maintained autoclaved-soil extracts (Figure 2C), which may suggest that the formation of the degradates in moisture-maintained active soil were due to microbial degradation (Figure 2B). However, dark-incubated active soil did not generate any of the degradates produced by irradiated active soil (Figure 2B). It appears that chloramben degradates produced by active soil were due to indirect photolysis by hydroxy radicals, the source of oxy radical being possibly the presence of water in soil; however, the lack of microbial activity in the moisture-maintained autoclaved soil apparently precluded its being the source of oxy radicals. The increased rate of chloramben degradation in irradiated and moisture-maintained active soil may also be explained by a photolytically activated biodegradation, which is under investigation.

In dark control experiments, the half-life values of chloramben on active and autoclaved soils were shorter than that of a dry soil. The decrease in chloramben levels may again be attributed to its higher mobility in soil with water. The presence of radiocarbon in dark control soil extracts was mainly due to the presence of chloramben in the soil, since it did not mineralize under dark incubation.

CONCLUSION

The qualitative and quantitative formation of chloramben degradates/metabolites was uniquely different when

moisture was maintained as compared to when moisture was not maintained, at constant temperature, in the course of soil photolysis. A laboratory soil photolysis system that can control the moisture and temperature of the soil is necessary to more closely simulate the chemical photodegradation rate and pattern in the environment.

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