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Photodegradation of Rotenone in Soils under Environmental Conditions

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An environmental fate study was performed to analyze the effects of soil components on the photochemical behavior of rotenone. Photodegradation experiments were carried out on three types of soil collected in southern Italy, Valenzano (VAL), Turi (TUR), and Conversano (CON), from April to June 2006. Soil thin-layer plates (1 mm thick) were spiked with 1.5 mg/kg of rotenone and exposed under natural conditions of sunlight and temperature. The plates were removed from the sunlight at predetermined intervals of continuous irradiation. Other soil samples, control and sterilized, were kept in the dark to evaluate possible effects of chemical and microbiological degradation during the irradiation experiment. The time for 50% loss of the initially applied rotenone varied from 5 to 7 h, following the order TUR < CON < VAL. In environmental studies, changes in temperature and/or moisture affected the degradation rate and caused deviations from first-order kinetics. The photolysis reaction fit the two compartment or the multiple compartment model pathways better. A fast initial decrease during the first 5 h of rotenone irradiation was followed by a much slower decline, which clearly indicates the rather complex chemical process of rotenone photodegradation on soil surfaces. Also, the degradation was shown to be directly related to the soil concentration of clay and organic matter. Rotenolone (12aβ-hydroxyrotenone) was detected by HPLC/DAD/MS analysis as the only photodegradation byproduct of rotenone in soil thin layers. Results provide additional insights on the rates and the mechanisms of rotenone degradation, aiming to describe more clearly the degradation performance of chemical residues in the environment.

KEYWORDS: Rotenone; environmental fate; half-life; soil photolysis; LC/MS

INTRODUCTION

In arid and semiarid regions, such as the Mediterranean area, sunlight photolysis together with volatilization can play an important role in the behavior of pesticides in the environment. The photochemical degradation of organic compounds adsorbed in porous media (e.g., pesticide on soil) can be very important for their fate (*1*), especially shortly after their application when they still reside in the topsoil. The quantification of the photolysis on the soil surface is of higher complexity than it is in solution. In experiments carried out on soil layers, the observed overall degradation is not only determined by photolysis itself but also as a function of the layer thickness and, in many cases, of transport processes (*2*, *3*). In soils, photolysis will occur within a shallow depth, depending on soil characteristics and the mechanisms of photodegradation. Light absorption and photolysis of organic contaminants are influenced by sorption reactions that are related to the soil organic matter content and to singlet oxygen ($^1O_2$) formation (*1*). Both direct and indirect processes could be occurring depending on the depth. Hebert and Miller (1990) (*4*) concluded that the vertical depth of direct photolysis on the soil surface will be restricted to a region of approximately 0.2−0.3 mm. Mean indirect photolysis depths were reported to be greater than 0.7 mm for outdoor experiments. Although the investigation of the route and rate of degradation in soil (aerobic degradation) is always requested by the registration authorities, in specific cases, the photochemical pesticide transformation on the soil surface is also required as supplementary study in order to produce additional information on its relevant processes (*5*).

Rotenone is a broad-spectrum, nonsystemic botanical insecticide used to control aphids, trips, and suckers, with some acaricidal properties and as a specific procedure of water body management for fish eradication (*6*). Because of its natural origin, the use of rotenone as an insecticide has been allowed in the last two decades in organic crop production. Rotenone is used in European organic agriculture nowadays, with a strong restriction regarding its environmental hazards. The use of

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Table 1. Physicochemical Properties of Selected Soils[a]

parameters	VAL	TUR	CON
$pH_{1:2.5}$ (H_2O)	8.6	7.7	7.9
$pH_{1:2.5}$ (KCl)	7.7	6.8	7.3
$EC_{1:2}$ (dS/m)	0.13	0.24	0.22
clay (g/kg)	244	363	274
silt (g/kg)	335	524	653
sand (g/kg)	421	113	73
texture USDA	loam	silt clay loam	silt clay loam
−33 kPa water content (g water/100 g dry soil)	19	29	25
CEC cmol(+)/kg	10.6	21.1	16.1
OC (g/kg)	7.1	28.9	13.8
N total (g/kg)	0.7	3.1	1.4
C/*N*	9.5	9.6	10.1
color	pale brown	brown	reddish brown

[a] Key: VAL, Valenzano; TUR, Turi; CON, Conversano; EC, electrical conductivity, CEC, cation exchange capacity.

Table 2. Rotenone Recoveries on Soils Spiked with Different Concentrations ($n = 3$)

soil type	concentration (mg/kg)	recovery (%)	RSD[a] (%)	LOD[a] (mg/kg)	LOQ[a] (mg/kg)
VAL	0.015	98	3		
	0.15	98	3	0.01	0.015
	1.5	100	2		
	0.015	96	4		
TUR	0.15	97	2	0.01	0.015
	1.5	99	1		
	0.015	96	0		
CON	0.15	97	6	0.01	0.015
	1.5	95	5		

[a] Key: RSD, relative standard deviation; LOD, limit of detection (*S*/*N* > 3); LOQ, limit of quantification (*S*/*N* > 10).

rotenone is partially restricted in Austria, Italy, Spain, Switzerland, and the United Kingdom, but not in Denmark, Netherlands, Portugal, and Slovenia. In the United Kingdom, few private standard-setting organizations allow its use after preliminary permission, while others never permit its use (*7*). Because of lacking of scientific data related to the soil behavior of rotenone, an aerobic soil half-life of 12 days and a soil photolysis of 2.9 h were estimated based on the aerobic aquatic and foliar half-lives reported in literature (*8*). The photochemical behavior of rotenone in the liquid phase has been investigated by Draper (2002) (*9*) using a polychromatic light from fluorescent lamps in the laboratory to study kinetic parameters and quantum yields. Rotenone undergoes photochemical *O*-demethylation, epimerization, epoxidation, hydroxylation, and dehydration (*10*), and many different compounds have been already shown to undergo conversion and degradation by a variety of photochemical reactions (*11*). Data available on the fate of rotenone in the environment do not include the determination of the photolysis pathway on a soil surface. In other to fill this lack of information, the photochemical degradation of rotenone on three Italian soils together with the possible formation of chemical photoproducts was investigated.

MATERIALS AND METHODS

Chemicals and Materials. Acetonitrile and acetone (HPLC grade) and ethyl acetate (analytical grade) were purchased from BAKER (Mallinckrodt Baker, Holland). Ultrapure water was obtained from a Millipore (Billerica, MA) Milli-Q system. Rotenone [vapor pressure <1 mPa at 20 °C, water solubility 0.2 mg/L, log $K_{ow} = 4.16$ (*12*), purity = 95−98%] was purchased from Sigma Aldrich (Steinheim, Germany). A stock standard solution of rotenone (1000 mg/kg) was prepared in acetone. Working standard solutions were prepared daily by dilution with the mobile phase (acetonitrile/water; 50:50, v/v).

HPLC/DAD Determination. An Agilent Technologies (Waldbronn, Germany) 1100 model liquid chromatograph equipped with a diode array detector (DAD) UV6000LP (Thermo Quest, San Josè, CA) was used. A Waters XTerra (4.6 × 250 mm × 5 μm) column was employed. The HPLC was PC-controlled, and data were analyzed using Agilent Chem Station (1999/2000) software. Isocratic elution was performed with acetonitrile/water (65:35, v/v) for 20 min. The injection volume was 100 μL, and the flow was 1 mL/min. Rotenone was detected at the wavelength of 295 nm. An external calibration was provided, and the standard calibration curve was constructed by plotting concentration against peak area. Good linearities were achieved for all active ingredients between 0.01 and 5 mg/L, with a correlation coefficient of 0.9999.

LC/MS Analysis. A HPLC system (Shimadzu, Milan, Italy) equipped with an SPD11 Avp DAD detector, an SIL 11 AD vp auto injector, and a LC 10 AD binary pump coupled on line with an MS2010 mass spectrometer (Shimadzu, Milan, Italy) was used. UV and MS data were acquired and processed using Shimadzu "LCMS solution" software. The isocratic elution was performed with acetonitrile and water containing 0.1% trifluoroacetic acid (60:40, v/v) for 20 min. The column used was a Waters XTerra MS RP18 (250 × 2.1 mm, 5 μm particle size) (Milford, MA). The injection volume was 20 μL, and the flow rate was 0.4 mL/min. The ESI−MS interface was operated in the positive ion mode: ESI source probe 250 °C, CDL 250 °C, block at 200 °C, flow gas (N_2) at 4.5 mL/min, probe voltage at 3 kV, scan 200−500 amu, and single ion monitoring mode at 393 and 395 *m*/*z*.

Soil Sampling. Three soils were sampled in three different locations [Turi (TUR), Conversano (CON), and Valenzano (VAL)] of the Puglia region (South Italy) from the top 20 cm. Geographical coordinates for VAL (*x*, 657618.8; *y*, 4546479.7), TUR (*x*, 672410.6; *y*, 4531557.9), and CON (*x*, 682078.5; *y*, 4537530.2) were determined by UTM (Universal Transverse Mercator European Datum 1950). Plant macroresidual materials, macrofaunal remains, and stones were accurately removed, and soil larger aggregates were manually and gently fragmented into smaller ones prior to the subsequent fractionation procedure. Soils were air-dried and sieved (<2 mm) and stored for a 1 month at room temperature in the dark prior to further analysis.

Soil Analysis. Soil physical and chemical properties are shown in **Table 1**. Soil analyses were carried out following internationally recommended procedures and official methods (*13*). In brief, soil was air-dried, crushed, mixed thoroughly, and passed through a 2 mm sieve. The pH was measured by a glass electrode in distilled water and in a 1 M KCl suspension (pH_{H2O} and pH_{KCl}) at a 1:2.5 soil to liquid-phase ratio. Electrical conductivity (EC) was determined by a conductimeter on a soil filtrate at a 1:2 soil to water ratio. The texture and particle size distribution were determined by the pipet method after dispersion of the sample in sodium hexametaphosphate and sodium carbonate solution. Organic carbon (OC) was measured by the Walkley−Black method. Total nitrogen (N_t) was determined by the Kjeldahl method. Cation exchange capacity (CEC) was determined by a barium chloride and triethanolamine solution. The colors of the soils were measured using the Munsell soil color chart (Munsell Color Company, 1975). The soil water content was determined on three replicates of approximately 20 g of soil by using a pressure plate extractor system. Samples were left in cells under a pressure of −33 kPa until there was no further change in weight. The moisture content was then determined by the difference in weight from oven-dried sample.

Recovery Assay and Extraction Method. The rotenone was never applied in the field where the soils were collected. An amount of 5 g of soil samples was spiked with rotenone standard solutions to reach concentrations of 0.015, 0.15, and 1.5 mg/kg. Three replicates of each sample were left in the dark until solvent evaporation, and then the extraction protocol was used to evaluate recovery yields and accuracy for each type of soil. Untreated samples from all soils without fortification with rotenone were analyzed at the same time.

Soils from exposed plates were placed in Pyrex glass tubes, and aliquots of 10 mL of ethyl acetate were added. Samples were end-over-end mixed for 30 min. Then, the organic solvent phase was

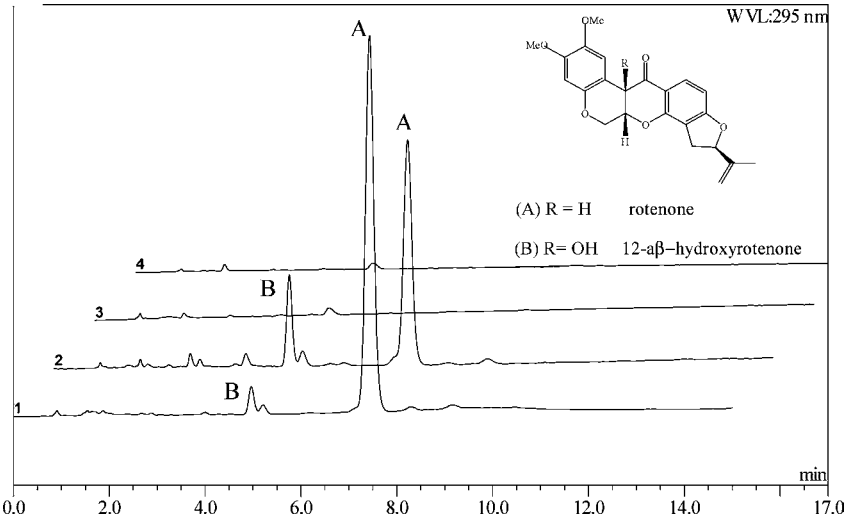

Figure 1. Chromatograms of soil (TUR) spiked with rotenone at the beginning (1) and at the end (2) of the experiment and of untreated soil extracts at the beginning (3) and the end (4) of photodegradation experiment. A: rotenone; B: 12aβ-hydroxyrotenone (ROT−OH).

separated by centrifugation at 6500 rpm for 10 min, and 1 mL of the organic extract was transferred to a 2 mL vial under a gentle nitrogen stream until complete evaporation of the solvent. Residues were redissolved with 500 μL of the mobile phase and injected into the HPLC/DAD for chromatographic analysis

Soil Thin-Layer Preparation. Soil saturated pastes were obtained by adding approximately 125 mL of water dropwise to 170 g of soil while gently stirring. Soil pastes were spread on glass plates (28 cm^2) to obtain 1 mm-thick soil layers and successively air-dried in darkness at room temperature for 1 day to reach a soil moisture of about 75% of the field moisture capacity at 0.33 bar. Each soil thin layer was then spiked with 100 μL of 50 mg/L of rotenone in an acetone solution by uniformly distributing small droplets over the whole soil surface with a 0.1 mL microsyringe (Hamilton Technology). The amount of rotenone (1.5 mg/kg) applied to the plates was calculated according to the maximum recommended use rate and related the surface area. Then, plates were left for 30 min in the dark before starting the irradiation experiment in order to evaporate the organic solvent.

Irradiation Experiments. Soil thin-layer plates were exposed to the direct sunlight at 39° 14′ latitude north and 3° 20′ longitude west from the Rome Monte Mario meridian and removed from the sunlight at predetermined intervals from the initial time (50, 100, 200, 300, 400, and 600 min). Samples were irradiated in April and May between 10:00 a.m. and 5:00 p.m. During this trial, the average solar radiation, recorded with an AD-2 automatic weather station SILIMET (Modena, Italy), was 352 w/m^2, with an average sunshine of 15 h from sunrise to sunset and temperature of 22 °C. The experiments were run several times during April and May, and all soil samples were exposed simultaneously to sunlight. The experiments were carried out in three replicates; control and sterilized soils were left in the dark to evaluate possible effects of chemical and microbiological degradation during the irradiation experiment.

Curve Fitting and Statistics. The actual degradation rate was calculated for each sampling time using the ModelMaker software, version 4.0; the graphical compartmental and system dynamic modeling software package provides the best fit line for the experimental data (*14*). Two kinetic models were used to fit the degradation data of rotenone (*15*), (1) a simple first-order equation (exponential kinetic model) and (2) a first-order multicompartment model (Gustafson and Holden or biphasic kinetic model) (*16*). Model parameters were optimized according to recommendations given by FOCUS (*15*) and using the least-squares method. A fitting error level of 15% is considered to be acceptable. All data were analyzed using the general linear models procedure (SAS Institute, Inc., 2001). Mean separation among lines was accomplished using the Duncan multiple range test at $P < 0.05$.

Table 3. Single First-Order (SFO) and First-Order Multicompartment (FOMC) DT_{50} and DT_{90} Values for Rotenone in Soils and Percentage Error Levels (χ^2)[a]

	SFO				FOMC		
soil type	DT_{50}[a]	DT_{90}[a]	χ^2 (%)	K[b]	DT_{50}[a]	DT_{90}[a]	χ^2 (%)
VAL	7	23	14	0.12	3.8	5111	2.9
TUR	5	17	4	0.18	5	39	4
CON	6	19	9.6	0.16	4	257	1.8

[a] All data are expressed in hours. The smaller the error, the better the fit; errors below 15% are considered acceptable, provided the visual fit is adequate (*15*). [b] K = factor of disappearance (10^{-2} mg/kg/min).

RESULTS AND DISCUSSION

Extraction Protocol. The recovery of rotenone from three types of soil is summarized in **Table 2**. Mean recoveries ranged from 95 to 100%, with coefficients of variation between 1 and 6%. According to Their and Zimmer (1987) (*17*), the limit of detection (LOD) and quantification (LOQ) were determined. LODs and LOQs were 0.01 and 0.015 mg/kg, respectively, for all type of soils. The applied chromatographic parameters produced a measured separation between rotenone ($t_r = 7.3$ min) and its metabolite rotenolone (12aβ-hydroxyrotenone) ($t_r = 5.3$ min) in all soil samples (**Figure 1**).

Photodegradation Experiment. DT_{50} (disappearance time 50), DT_{90} (disappearance time 90), the time within which the percentage of the test substance was reduced by 50 and 90%, and χ^2 error values are given in **Table 3**. Degradation was analyzed using the first-order (SFO) model and the first-order multicompartment (FOMC). Comparison was made on the basis of visual assessment (**Figure 2**) and χ^2 tests (**Table 3**). DT_{50}'s varied from 5 to 7 h following the order TUR < CON < VAL for the SFO model, while for FOMC, they varied from 4 to 5 h following the VAL < CON < TUR. The observed differences were, however, significant at the $P < 0.05$ level of significance according to statistical analysis. The results obtained were almost two times higher than the estimated ones (*8*). Nonetheless, the first-order fits are acceptable according to draft guidance (*15*). Degradation cannot always be described by SFO kinetics. A fast degradation in pesticide concentration (**Figure 2**) is often followed by a slower decline. SFO kinetics provides a poor fit

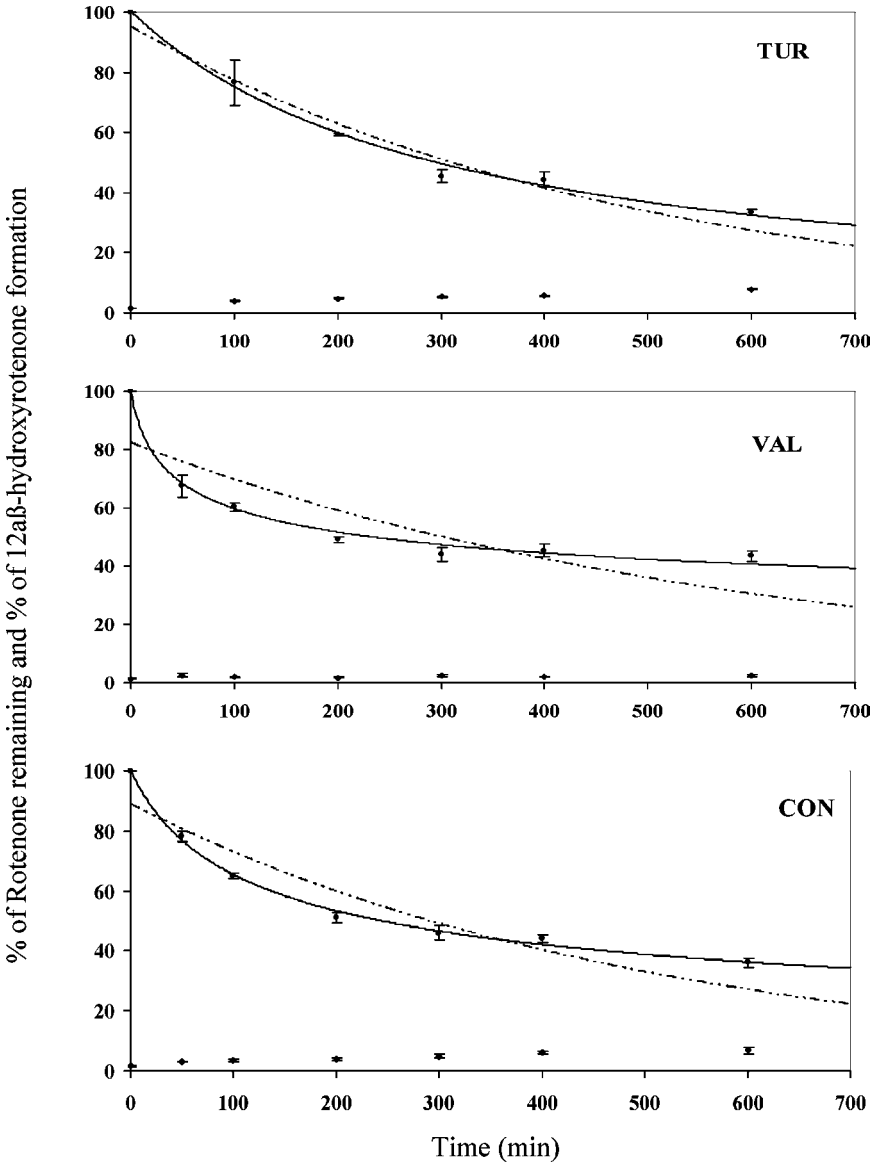

Figure 2. Experimental data (◆) of rotenone degradation and (●) ROT–OH formation on irradiated soils (vertical bars represent the standard deviation of three replicates). First-order fits (–•• –•• –••) (SFO) and first-order multicompartment (—) (FOMC).

to the data, as shown by all experiments (**Figure 2**). The calculated curve does not match the observed pattern. In environmental studies, changes in temperature and/or moisture affected the degradation rate and caused deviations from first-order kinetics. The biphasic FOMC model fit the data more closely than that of SFO in this experimental condition. The smaller χ^2 values and the better fitting of the data process description were achieved in the FOMC model. The available fraction often decreased with time due to slow sorption and diffusion processes (*18*). Scrano et al. (2004) (*19*) speculated that the photolysis reaction for oxyfluorfen arises with a double-step pathway. DT_{90} values were high up to 17 h, as the percent remaining did not drop below 30% (**Table 4**); they were calculated but not interpreted because 90% of rotenone degradation was not achieved during the experimental period. A photosensitization effect was also observed for the rotenone half-life in water ($t_{1/2}$ = 500 min) (*9*). The aim of the study was to obtain the half-life of rotenone on soil surfaces where DT_{90} generally is not considered to be so important regarding the pesticide photolysis, especially under environmentally uncontrolled systems such as this.

Table 4. Rotenone Residues (% ± SD) at the End of the Experimental Time in Different Treatments

	treatments		
soil type	sun	dark	sterilized
VAL	44.1 ± 1.2 c	98.3 ± 1.2 a	98.8 ± 0.6 a
TUR	33.6 ± 0.9 e	93.3 ± 1.0 b	96.5 ± 0.7 a
CON	36.6 ± 1.2 d	95.7 ± 1.3 b	97.6 ± 0.7 a

Photoproducts Identification. Retention time and ESI/LC/MS fragmentation patterns were the criteria used for compound identification, using the commercially available rotenone and a standard of 12aβ-hydroxyrotenone kindly provided by Professor J. E. Casida from the University of California at Berkeley. Rotenone gave the *m*/*z* 395 $[M + H]^+$ and 436 $[M + H + CH_3CN]^+$ adducts, while 12aβ-hydroxyrotenone (ROT−OH) gave the *m*/*z* 393 $[M + H - H_20]^+$ adduct. For all soil extracts, rotenone and its main product of photodegradation were identified and confirmed by LC/MS analysis monitoring in the single-ion mode, the ions 395 and 393 *m*/*z* corresponding to the most abundant adducts for rotenone and ROT−OH. The

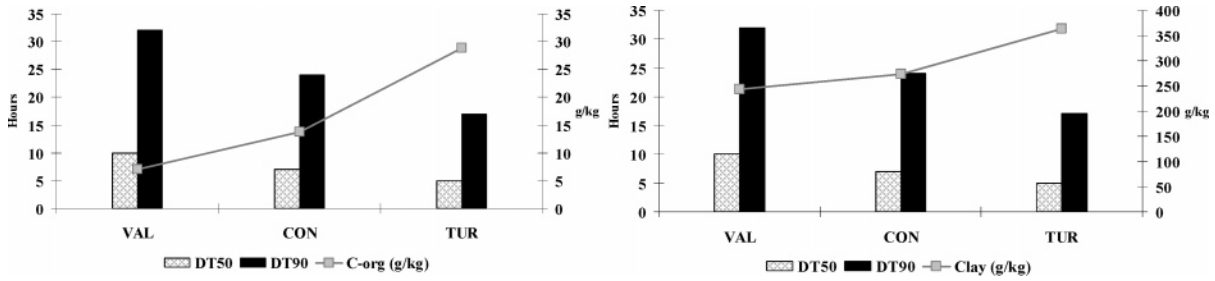

Figure 3. Relationships between organic carbon and clay contents in soils and calculated DT_{50} and DT_{90} values.

LC/MS retention time for rotenone and ROT−OH were 17.93 and 10.99 min respectively.

Degradation of rotenone and formation under different soils are also shown in **Figure 2**. The decline in rotenone residues extracted with organic solvent followed the serves VAL < CON < TUR. Since each data point in the degradation experiments was based on three replicates, the smoothness of the curves indicates the high reproducibility of the whole experimental procedure (**Figure 2**). The site of oxidation is the 12aβ position of rotenone; hydroxylation of this site induces formation of the biologically active ROT−OH in environmental condition. Initial percentages of extracted ROT−OH metabolites calculated on peak areas occurring at 295 nm were 1.5 ± 0.1 for TUR, 1.6 ± 0.2 for CON, and 1.3 ± 0.1 for VAL soils, reaching 7.8 ± 0.3, 6.7 ± 1.3, and 2.2 ± 0.4, respectively, at the end of the experimental time (**Figure 2**). The 12aβ-hydroxyrotenone formation was proportional to the rotenone photodegradation rate and slightly increased with time. The initial ROT−OH concentration is possibly ascribed to a small percentages of rotenone standard impurities.

Effect of Soil Compositions. The degradation rates increase as soil organic matter and clay content increase. **Figure 3** shows the positive direct relationship between their contents and photolysis half-lives. Konstantinou et al. (2001) (*20*) have shown the possible involvement of photosensitization based on faster photodegradation of herbicides in soil with higher organic matter content. Our work focuses on air-dried soils (considering that soil humidity during the experimental time was not controlled) because this is how pesticides are usually applied. In air-dry soils, pesticides and organic compounds do not sorb onto soil organic matter as they do in wet soils and often primarily onto mineral surfaces (*21*). It is typically the fraction adsorbed onto mineral surfaces that can be expected to absorb light and undergo direct photochemical reaction (*22*).

Furthermore, not more than 10% of rotenone was lost in any of the dark control and sterilized soil experiments (**Table 4**). The significant differences between irradiated and covered (dark control and sterilized) soil thin layers show that rotenone disappearance is due to photochemical reactions on soil particle surfaces within the experimental time range (**Table 4**). It was not a result of microbiological degradation, as recoveries were more than 90% and no transformation product in the dark and sterilized control were detected. Rotenone's low vapor pressure and Henry's law constant suggest that volatilization from the soil surface will not be an important environmental fate. Further, it was reported that, at 50 °C, rotenone was not effected by evaporation and thermodegradation (*11*).

Conclusions. Results indicate that the photochemical behavior of rotenone is significantly effected by the soil sample characteristics. Rotenone degradation phenomena are clearly described by the biphasic equation, which clearly fits measured data of the molecule remaining in the soils. The three soils show significantly different net losses due to the sunlight exposure, the photolysis rate ranging from 0.12 to 0.18 min^{-1}. However, the contribution of the photochemical processes to the global consumption rate is higher in soils richer in organic matter than that in sandy soil. The photodegradation of rotenone on soil surfaces principally produces an oxidized metabolite, rotenolone (12aβ-hydroxyrotenone). The photolysis reaction proceeds better fit two compartment or multiple compartment model pathways. A fast initial decrease during the first 5 h of rotenone irradiation is followed by a much slower decline (lasting more than 10 h), which clearly indicates the rather complex chemical process of rotenone photodegradation on soil surfaces. In the initial decrease, the degradation in soils of rotenone is mainly effected by direct sunlight irradiation and proceeds at a high rate; then, following rotenone adsorption on soil particle surfaces, it appears to reduced and be effected by several other physical−chemical mechanisms.

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