Test Material:	Propanil
MRID	47165603
Title:	Burgener, A. 2000. Aqueous photolysis of ^{14}C-propanil under laboratory conditions, determination of the quantum yield and calculation of environmental lifetime.
EPA PC Code:	028201
OCSPP Guideline:	835.2240

For Cambridge Environmental

Primary Reviewer: Dana Worcester **Signature:** Dana Worcester

Date: 1/19/12

Secondary Reviewer: Kathleen Ferguson **Signature:** Kathleen P. Ferguson

Date: 1/19/12

QC/QA Manager: Joan Gaidos **Signature:**

Date: 1/19/12

IIA 7.6 Photolysis of propanil in pond water

The photolysis of propanil was studied in unsterilized unbuffered pond water that was continuously irradiated at 25°C for up to 30 days.

Report:	Burgener, A. 2000. Aqueous photolysis of ^{14}C-propanil under laboratory conditions, determination of the quantum yield and calculation of environmental lifetime. Unpublished study performed by RCC Ltd., Itingen, Switzerland; sponsored by Rohm and Haas Company, Spring House, Pennsylvania; and submitted by Propanil Task Force II. Rohm and Haas Technical Report No. 34-00-88. RCC Study No. 769072. Experiment initiated, May 29, 2000 and completed August 7, 2000 (p. 9). Final report issued October 12, 2000.
Document No.:	MRID 47165603
Guideline:	Conducted under: Directives 95/36/EEC and 94/37/EEC; SETAC Guidelines 1995; OECD Guidance Document (97)21; OPPTS 835.2210; JMAFF OECD Guideline 16. Reviewed under: OCSPP 835.2240
Statements:	The study was conducted in accordance with OECD and Swiss GLP standards (pp. 3, 5-6). Signed and dated Data Confidentiality, GLP, and Quality Assurance, statements were provided (pp. 3, 5-6, 8). A statement of authenticity is included in the Quality Assurance Statement (p. 8).
Classification:	This study is classified as supplemental. A buffered sterilized aqueous solution was not studied. The pond water used in the study was not sterilized prior to use.
PC Code:	028201
Reviewer:	He Zhong, Biologist — Signature: Date: 2/27/2012

Executive Summary

In an aqueous photolysis study, the phototransformation of [phenyl-U-^{14}C]-propanil was studied at 25 ± 1°C in unsterilized nonbuffered pond water (pH 7.6-8.4) from Switzerland that was continuously irradiated using a Xenon arc lamp for 15 days or incubated in the dark for 15 days. Duplicate irradiated and single dark controls samples were collected and analyzed using LSC, TLC and HPLC.

Propanil dissipated with a SFO linear half-life of 24.2 days in the irradiated solutions, based on the continuous irradiation used in the study, and 203.9 days in the dark controls. The degradation may be microbially mediated due to use of unsterilized pond water. The **phototransformation half-life** of propanil is 27.5 days, based on the continuous irradiation used in the study, or 55 days based on a 12-hour light/12-hour dark cycle. Since 24 hours of artificial irradiation were reported to be equivalent to 2.21 days of spring sunlight in Japan (35°N), the **environmental phototransformation half-life** of propanil is 61 days.

The overall mass balance for the irradiated samples ranged from 96.6% to 100.8% of applied radioactivity. No major phototransformation products were isolated. Fourteen minor transformation fractions were isolated with one identified (3,4-dichloroaniline). CO_2 totaled 8.0-9.8% at 15 days posttreatment.

The overall mass balance for the dark samples ranged from 99.4% to 100.2% of applied radioactivity. No major transformation compounds were isolated and no minor transformation products were identified. Volatiles were not collected.

The study author determined a quantum yield where Φ = 0.000229 molecules degraded per photon.

Table 1. Results Synopsis: Phototransformation of Propanil in Pond Water

Compound Name	Observed DT_{50} [days]	Observed DT_{90} [days]	Calculated Half-life[1] [days]	Adjusted Half-life[2] [days]	Phototransformation Products	
					Major	Minor
					% of Applied, Day of maximum conc.	
Irradiated:						
Propanil	>15	>15	24.2	61	None	3,4-Dichloroaniline (M11)

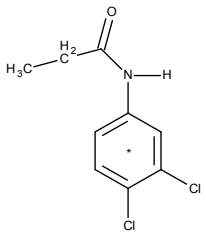
1 Simple First Order (SFO; Excel 2003), 24.2 days based on the continuous irradiation used in the study or 48.2 days based on a 12-hour light/12-hour dark cycle.
2 Based on (Ln 2) ÷ [(Ln 2/dark control half-life) - (Ln 2/irradiated half-life)] and assuming that 24 hours of artificial light exposure is equivalent to 2.21 solar days in spring at 35°N (Tokyo, Japan).

I. Materials And Methods

A. Materials:

1. Test materials

[Phenyl –U-^{14}C]propanil (p. 21, Appendix 4, p. 101)



Specific activity: 11.46 mCi/g, 0.424 MBq/mg
Radiochemical purity: 95.7%
Chemical purity: Not reported.
Lot 346.0120
Solubility in water: 152 mg/L at 25°C. (p. 20)
UV absorption: Between 290 and 500 nm, peak absorption at *ca.* 290 nm, decreasing rapidly to 310 nm and tailing to extinction at *ca.* 380 nm (Figure 3, p. 52).

2. Reference compounds:

Propanil Batch No. STRL-99-AG-005, purity 99.61% (p. 20)
3,4-Dichloroaniline Lot No. RH-74895, purity 99.32% (p. 22)

2. Natural Pond Water: The pond water used in the study was obtained from pond Ormalinger Teich near Weierhof, Switzerland on May 10, 2000 (p. 23). Properties of the water are described in **Table 2.** The water was not sterilized prior to use (p. 38).

Table 2. Physicochemical Properties Of Pond Water Used In Photolysis Study

Property	Reported value
pH (time 0)	7.6
pH (15 days)	Irradiated: 8.4; Dark: 7.6
Electrical Conductivity (µS/cm)	Not reported
Total Organic Carbon (mg/L)	2.6
Total Inorganic Carbon (mg/L)	Not reported
Total Suspended Solids (mg/L)	Not reported
Oxygen (mg/L)	11.9
Redox Potential	260
Alkalinity as HCO_3 (mg/L)	Not reported
Total Magnesium (mg/L)	Not reported
Total Calcium (mg/L)	Not reported
Total Iron (mg/L)	Not reported
Total Dissolved Iron (mg/L)	Not reported
Ferric Ion Concentration (mg/L)	Not reported
Ferrous Ion Concentration (mg/L)	Not reported

Data obtained from p. 23 and Table 5, p. 48 in the study report.

B. Study Design

1. Experimental Conditions

Table 3. Experimental Design

Parameter	Description
Nature of light source	Xenon arc lamp (Suntest CPS unit).
Emission wavelength spectrum	290 -800 nm p 51
Nominal light intensity	17.2 W/m^2 (1.486 MJ/m^2·day) in the 300-400 nm range.
Filters used	UV filtering (UV-edge 290 nm).
Relationship to natural sunlight	The irradiation spectrum of the artificial light was similar to sunlight. Twenty-four hours of simulated sunlight exposure was 2.21 days of spring (April-June) sunlight in Japan.

Parameter			Description
Method used to determine relations between light source and summer sunlight			The average intensity of the artificial light (17.2 W/m^2) was compared to the published average daily cumulative irradiation at 35°N latitude (Tokyo, Japan) in spring (April-June). Photons reaching the samples were estimated using a uranyl nitrate/oxalic acid actinometer.
Duration of the test			15 days
Solution volume			300 mL, which were subdivided into two 100 mL samples to be irradiated and one 100 mL sample to serve as the control.
Sterilization method			None
Test concentration			12.01 mg a.i./L
Control conditions			The dark control was maintained under conditions similar to those used with the irradiated samples.
Number of replicates		Irradiated	An aliquot from each of the two irradiated test solutions were collected at each sampling interval.
		Darkness	An aliquot from the single control test solutions were collected at each sampling interval.
Test apparatus		Irradiated	The irradiated test systems consisted of Pyrex glass vessels containing treated test solution (100 mL) that were closed with quartz lids, placed under the light source, and attached to a continuous (10 mL/minute) flow-through volatile trapping system. The vessels contained a septum through which samples were collected. The solutions were continually stirred with a magnetic stirrer. Water was circulated through a cooling block below the test vessels to maintain a constant temperature. The test apparatus is illustrated in Figure 1, p. 50.
		Darkness	Dark control samples were prepared in similar vessels, but were not attached to volatile traps.
Traps		Organics	Ethylene glycol
		CO_2	2N NaOH
Test material application	Solvent		Acetonitrile, <0.5% by volume
	Test solution volume used/treatment		1.25 mL/300 mL water.
	Application method		After addition to the water, the solution was ultrasonicated for 5 minutes.
	Evaporation of application solvent		No
Indication of test material adsorbing to walls of test apparatus			No
Experimental conditions	Temperature (°C)		25 ± 1°C
	Continuous irradiation		Yes.
	Continuous darkness:		Yes.
Sample storage before analysis			Not reported.

Data obtained from pp. 24-27, 33-34, 38; Figures 1-2, pp. 50-51 in the study report.

The quantum yield of propanil at 290-400 nm was determined using a uranyl nitrate/oxalic acid actinometer (p. 25, 31, 40). The units were irradiated for 20 minutes (p. 25).

2. Description of Analytical Procedures

Aliquots of the irradiated and dark control samples were analyzed directly by LSC, HPLC and TLC (p. 26). Normal-phase HPLC was conducted using a LiChrospher 100 C18 column eluted with (A) Millipore water and (B) acetonitrile (pp. 28-29). One-dimensional TLC was conducted on silica gel plates developed in either toluene:ethyl acetate (1:1, v:v) or chloroform:methanol (95:5, v:v; pp. 28-30).

Aliquots of the volatile trapping solutions were analyzed using LSC (p. 28).

Limits of Detection (LOD) and Quantitation (LOQ) were not reported. The study author uses both <0.1% of the applied and "n.d." in the data tables (Tables 3-4, pp. 46-47).

II. Results and Discussion

A. Data

Table 4. Photodegradation of Propanil in Pond Water, expressed as percentage of applied radioactivity.

	Percent Applied Radioactivity							
Sampling Interval (Days)	**0**	**0.7**	**1.8**	**3.0**	**4.8**	**6.8**	**10.0**	**15.0**
Component	**Irradiated**							
Propanil	**95.7, 95.7**	94.0, 92.0	88.9, 88.3	90.1, 86.8	64.3, 82.6	80.3, 76.6	72.1, 68.5	63.2, 61.3
3,4-Dichloroaniline (M11)	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	**0.7**, <0.1	<0.1, <0.1
M1	<0.1, <0.1	0.8, 0.8	2.0, 2.1	3.2, 3.6	1.6, 2.6	6.9, 6.9	2.3, **7.9**	2.3, 6.0
M2	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	2.2, 3.9	<0.1, <0.1	1.6, 3.2	2.6, **4.3**
M3	<0.1, <0.1	0.5, 0.2	0.4, 0.5	0.3, 1.1	1.5, 1.5	1.1, 2.8	1.8, 3.2	**5.5**, 2.6
M4	<0.1, <0.1	0.5, 0.5	0.3, 1.6	1.4, 0.5	2.3, 1.7	1.8, 2.3	**1.6**, 1.3	2.1, **5.3**
M5	<0.1, <0.1	0.3, 0.2	1.1, 0.2	<0.1, 1.4	0.7, 0.5	**1.5**, 1.0	<0.1, 0.4	1.0, <0.1
M6	<0.1, <0.1	<0.1, 0.2	<0.1, <0.1	<0.1, 0.3	<0.1, <0.1	0.7, 0.7	0.2, **1.5**	**1.5, 1.5**
M7	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	**6.1**, <0.1	2.7, 3.3
M8	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1
M9	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, 0.9	0.4, **1.0**
M10	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	0.5, <0.1	**1.0,** <0.1
M12	2.4, 2.4	2.3, 2.0	2.9, 2.2	0.7, 1.6	2.3, 0.5	1.4, 2.0	4.0, **4.9**	3.1, 4.5
M13	1.1, 1.1	0.7, 1.6	1.2, 2.1	2.4, 2.3	3.2, **3.5**	2.3, 2.3	1.5, 1.4	1.3, 1.4
M14	0.7, 0.7	0.6, 0.6	**1.4**, 0.7	0.5, 0.7	0.2, 0.7	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1
$^{14}CO_2$	--	0.1, 0.1	0.3, 0.5	0.8, 1.0	1.9, 1.5	2.4, 2.6	5.0, 4.7	**9.8**, 8.0
Other Volatiles	--	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1
Mass Balance	100.0, 100.0	99.9, 98.2	98.4, 98.2	99.3, 98.9	99.8, 98.8	98.5, 97.1	97.4, 97.9	96.6, 99.1
Sampling Interval (Days)	**0**	**--**	**2.0**	**--**	**--**	**6.8**	**10.0**	**15.0**
Component	**Control (Dark)**							
Propanil	95.7	--	95.1	--	--	94.7	94.1	90.4
M1	<0.1	--	<0.1	--	--	0.7	**1.3**	<0.1
M11	<0.1	--	ND	--	--	ND	2.4	**4.8**
M12	<0.1	--	**2.0**	--	--	1.4	1.9	1.5
M13	<0.1	--	1.7	--	--	2.1	0.5	**2.8**
M14	<0.1	--	**1.2**	--	--	0.5	<0.1	<0.1
$^{14}CO_2$	Volatiles were not collected.							
Other Volatiles	Volatiles were not collected.							
Mass Balance	100.0	--	100.0	--	--	99.4	100.2	99.5

Data obtained from Tables 1-4, pp. 44-47 of the study report. ND = not detected.

B. Mass Balance

The total recoveries and distribution of radioactivity from each soil are shown in **Table 4.** Recoveries ranged from 96.6% to 100.8% of the applied radioactivity for the irradiated samples and 99.4-100.2% for the dark controls (Tables 1-2, pp. 44-45).

C. Volatilization

Volatiles were collected in the irradiated samples and were a maximum 9.8% at 15 days posttreatment (Table 1, p. 44).

D. Transformation of Propanil

In the irradiated samples, propanil was 95.7% of the applied at time 0 and 61.3-63.2% at 15 days posttreatment (Table 3, p. 46). In the dark controls, propanil was 95.7% of the applied at time 0 and 90.4% at 15 days posttreatment (Table 4, p. 47).

Based on single first-order linear regression analysis and using all data points, propanil dissipated with a half-life of 24.2 days in the irradiated samples, based on the continuous irradiation used in the study, or 48.4 days of 12-hour light/12-hour dark (**Table 5)**. In the dark controls, propanil degraded with a half-life of 203.9 days. The **phototransformation half-life** of propanil is 27.5 days, based on the continuous irradiation used in the study, or 55 days based on a 12-hour light/12-hour dark cycle. Since 24 hours of artificial irradiation were equivalent to 2.21 days of spring sunlight in Japan (35°N), the **environmental phototransformation half-life** of propanil is 61 days.

Table 5. Phototransformation of Propanil in Pond Water

Compound Name	Observed DT_{50} [days]	Observed DT_{90} [days]	Half-life[1] [days]	Dark control adjusted Half-life[2] [days]	Environmental Half-life [days]
Irradiated: pond water, 25°C					
Propanil	>15	>15	24.2	27.5	61
Control (dark): pond water, 25°C					
Propanil	>16	>16	203.9	--	--

1 Simple First Order (SFO; Excel 2003), 24.2 days based on the continuous irradiation used in the study or 48.4 days based on a 12-hour light/12-hour dark cycle.
Based on (Ln 2) ÷ [(Ln 2/dark control half-life) - (Ln 2/irradiated half-life)].
3 Assuming that 1 day of artificial light exposure was equivalent to 2.21 solar days under summer sun at 35 °N latitude.

Using averaged data for each interval, the study author calculated a DT50 of 23.6 days under the continuous irradiation used in the study, and an environmental DT50 of 52.1 days (p. 40; Figures 4a-4b, pp. 53-54). Using GCSOLAR, the study author determined that this is comparable to a half-life of 47.6 days in summer at 40°N at the water surface (p. 41).

No major phototransformation products were isolated. One minor phototransformation product was identified; 3,4-dichloraniline (M11, Table 3, p. 46). Thirteen unidentified fractions were isolated. 3,4-dichloraniline was a maximum 0.7% of the applied and the unidentified fractions were ≤7.9%. CO_2 was a maximum 9.8% in the irradiated samples.

In the dark controls, no major or minor transformation compounds were identified (Table 4, p. 47). Five minor fractions were isolated.

The study author determined a quantum yield where $\Phi = 0.000229$ molecules degraded per photon (p. 40; Appendix 1, pp. 63-71).

A degradation pathway for propanil was not provided.

III. Study Deficiencies and Reviewer's Comments

1. The pond water was not sterilized or buffered (p. 38). Microbial analysis using agar plates incubated for 8 days determined "many" organisms were present at time 0 and 15 days in both the irradiated and dark control solutions (Table 6, p. 49).

2. Using GCSOLAR, the study author calculated half-lives for propanil at 30°, 40°, and 50°N, in each of the four seasons, at water depths of 0, 10, 20 and 30 cm (p. 41). In surface water during the summer, half-lives ranged from 46.3-50.7 days at 30-50°N.

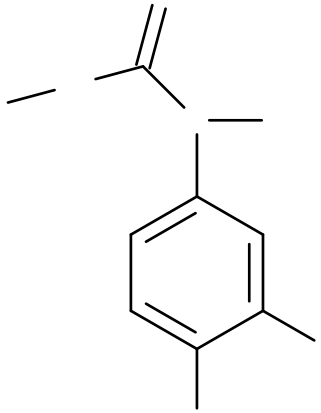
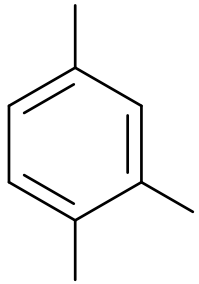
3. The pond water was collected from a rural area in north-western Switzerland that was mainly used for farming (p. 23).

4. Single samples of the dark controls were collected.

5. The study Guidelines were cited as being conducted under OPPTS 835.2210: Direct Photolysis in Water by Sunlight.

6. Study duration was in adequate according to the OPPTS 835.2240 guideline that "*at least one observation made after one-half of the test substance is degraded or after the equivalent of 30 days natural sunlight (12 hours of light per day), whichever comes first*."

DER ATTACHMENT 1a. Propanil and Its Environmental Transformation Product. [A]

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (days)	Final %AR (study length)
PARENT						
Propanil	**IUPAC:** 3',4'-Dichloropropioanilide **CAS:** N-(3,4-Dichlorophenyl)propanamide **CAS #:** 709-98-8 **Formula:** $C_9H_9C1_2NO$ **MW:** 218.1 g/mol **SMILES:** CCC(=O)Nc1ccc(c(c1)Cl)Cl		835.2240 Aqueous photolysis	47165603	95.7% (0 d)	**63.2** (15 d)
MAJOR (>10%) TRANSFORMATION PRODUCTS						
No major transformation products were identified.						
MINOR (<10%) TRANSFORMATION PRODUCTS						
3,4-DCA	3,4-Dichloroaniline **Formula:** $C_6H_5C1_2N$ **MW:** 162.02 g/mol **SMILES:** c1cc(c(cc1N)Cl)Cl		835.2240 Aqueous photolysis	47165603	0.7% (10 d)	<0.1% (15 d)
REFERENCE COMPOUNDS NOT IDENTIFIED						
All compounds used as reference compounds were identified.						

[A] AR means “applied radioactivity”. MW means “molecular weight”.

Attachment 2: Statistics Spreadsheets and Graphs