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Sunlight Photolysis of 2,4-D Herbicides in Systems Simulating Leaf Surfaces

Supporting Information

Lei Su¹, John D. Sivey², Ning Dai^{1*}

¹Department of Civil, Structural and Environmental Engineering University at Buffalo, The State University of New York Buffalo, NY 14260, United States

> ²Department of Chemistry Towson University Towson, Maryland 21252, United States

*Corresponding author: Post address: 231 Jarvis Hall, Buffalo, NY 14260 Phone: (716) 645-4015; Fax: (716) 645-3667 Email: <u>ningdai@buffalo.edu</u>

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Figure S1. Direct photolysis of (A) 2,4-D, (B) 2,4,5-T, (C) 2,4-DME, (D) 2,4,5-TME, (E) 2,4-DBEE, and (F) 2,4,5-TBEE in solvents. Direct photolysis of 2,4-D, 2,4,5-T, 2,4-DBEE, and 2,4,5-TBEE on (G) quartz and (H) paraffin wax surface. Direct photolysis of (I) 2-NB (chemical actinometer) on quartz and paraffin wax surfaces. Solid lines represent the fitting for apparent first-order kinetics. Hep = *n*-heptane, IPA = 2-propanol, MeOH = methanol, ACN = acetonitrile, Quartz = quartz surface, Wax = paraffin wax surface. Conditions: the sunlight simulator intensity was set to 0.68 W m⁻² at 340 nm, with total irradiation of 320 W m⁻² as determined by the actinometer 2-NB; initial concentration of pesticides: 20 μ M for 2,4-D and 2,4,5-T, and 5 μ M for esters; 5 mM phosphate buffer (pH 7.0) for experiments in water; 26 °C. Initial surface pesticide concentration: 3×10^{-9} mol cm⁻² on quartz surface, and 3×10^{-8} mol cm⁻² on paraffin wax surface.







2,4-D 2,4,5-T 2,4-DBEE 2,4,5-TBEE

40

0

 \diamond

30

20 Time (h)

10

-2.5

-3.0

-3.5

0

(F)





4

Figure S2. Molar extinction coefficients of (A) 2,4-D, (B) 2,4,5-T, (C) 2,4-DME, (D)2,4,5-TME, (E) 2,4-DBEE, and (F) 2,4,5-TBEE in solvents and on quartz surface. Hep = *n*-heptane, IPA = 2-propanol, MeOH = methanol, ACN = acetonitrile, Quartz = quartz surface. Sample concentration: 20 μ M in water with 5 mM phosphate buffer (pH 7.0), 5 μ M in organic solvents, and 6.17 $\times 10^{-8}$ mole cm⁻² on quartz surface.



Figure S3. Dependence of photolysis rate constants on solvent polarity. Photolysis experiment conditions are as described in the caption of Figure S1.



Figure S4. Molar extinction coefficients of 2,4-D and Tween[®] 20. Tween[®] 20 absorbance was measured using a methanolic solution of 10 g/L (8.1 mmol L^{-1}).



Figure S5. The difference in absorbance at 290 nm between dishes loaded with Tween[®] 20 + pesticide (open boxes) and those loaded with Tween[®] 20 alone (shaded boxes) from the 12 measurements for four chlorinated phenoxyacetic acid herbicides. The box spans the 25th to 75th percentiles, and the whiskers span the 5th to 95th percentiles. A *t*-test was performed to analyze the difference between two independent groups. The null hypothesis was the absorbance at 290 nm is not significantly different between dishes loaded with Tween[®] 20 + pesticide and those loaded with Tween[®] 20 alone. The *p*-values for 2,4-D, 2,4,5-T, 2,4-DBEE, and 2,4,5-TBEE were 2.7 × 10⁻⁵, 1.9×10^{-5} , 1.1×10^{-3} , 2.7×10^{-7} . With α equal to 0.05 (i.e., at the 95% confidence interval), the null hypothesis was rejected. The absorbance at 290 nm is significantly different between dishes loaded with Tween[®] 20 alone.



Figure S6. Formation of methyl dichlorophenoxyacetates from 2,4,5-TME photolysis in (A) *n*-heptane, (B) 2-propanol, and (C) methanol. Experimental conditions are as described in the caption of Figure S1, except that the initial concentration of 2,4,5-TME was $10 \,\mu$ M.



(A)





(C)



Figure S7. The mass spectra for (A) 2,4,5-TME and its degradation products (B) 2,4-DME, (C) suspected 2,5-DME, (D) suspected 3,4-DME, and (E) suspected methyl chlorophenoxyacetate. GC-MS conditions: Initial column temperature was set at 90°C and held for 1 min, and then increased to 270 °C at a rate of 100 °C min⁻¹ and held for 10 min. MS full scan with chemical ionization using methanol. The mass range of the MS scan was 50–400 m/z.



(A)



(C)



(B)





(E)



Figure S8. Comparison of experimental data and kinetic model prediction of DBEE time profile during 2,4,5-TBEE photolysis on quartz and paraffin wax surfaces. Detailed process and assumptions are shown in Text S5. Quartz = quartz surface, Wax = paraffin wax surface. Solid and dash lines show the concentration of DBEEs predicted by the kinetic model described in Text S5, and symbols show the concentrations of DBEEs obtained from experiments. DBEEs = \sum (2,4-DBEE, 2,5-DBEE, 3,4-DBEE).



Compound	Solvent for		Solvent of reaction solutions		
Compound	stock solutions	ACN	MeOH	IPA	Нер
2,4-D	Water	2% water	2% water	2% water	
2,4,5-T	Water	8% water	8% water	8% water	
2,4-DME	MeOH, hexane	0.1% MeOH		0.1% MeOH	1.2% hexane
2,4,5-TME	MeOH, hexane	0.1% MeOH		0.1% MeOH	1.4% hexane
2,4-DBEE	MeOH	0.5% MeOH		0.5% MeOH	
2,4,5-TBEE	ACN	_	_	0.5% ACN	—

Table S1. The volume percentage of co-solvents in reaction solutions introduced from the stock solutions. Hep = n-heptane, IPA = 2-propanol, MeOH = methanol, ACN = acetonitrile.

Compound	Recovery (%)			
Compound	Quartz	Wax		
2,4-D	93.0 ± 3.9	99.8 ± 2.1		
2,4,5-T	89.4 ± 0.4	98.1 ± 1.7		
2,4-DBEE	87.8 ± 5.0	97.7 ± 3.7		
2,4,5-TBEE	98.1 ± 7.5	96.0 ± 2.5		
2-NB	92.8 ± 4.5	95.7 ± 5.5		

Table S2. Recovery of pesticides and the chemical actinometer (2-NB) from tested surfaces. Quartz = quartz surface, Wax = paraffin wax surface.

Table S3. Apparent first-order rate constants (*k*) and quantum yields (Φ) for 2,4-D, 2,4,5-T, and their methyl and butoxyethyl esters in different solvents, and on quartz and paraffin wax surfaces. Hep = *n*-heptane, IPA = 2-propanol, MeOH = methanol, ACN = acetonitrile, Quartz = quartz surface, Wax = paraffin wax surface. Experimental conditions are as described in the caption of Figure S1.

Compound		Rate constant (k) (h ⁻¹)	Quantum yield (Φ)
2,4-D	IPA	$8.2\times 10^{-3}\pm 5.0\times 10^{-5}$	$3.2\times 10^{-3}\pm 1.9\times 10^{-5}$
	MeOH	$1.1\times 10^{-3}\pm 5.0\times 10^{-5}$	$4.4 \times 10^{-4} \pm 2.1 \times 10^{-5}$
	ACN	$1.5\times 10^{-3}\pm 5.0\times 10^{-5}$	$5.8 \times 10^{-4} \pm 2.0 \times 10^{-5}$
	DI	$1.5 \times 10^{-3} \pm 1.0 \times 10^{-4}$	$6.7 \times 10^{-4} \pm 4.5 \times 10^{-5}$
	Quartz	$2.7 \times 10^{-1} \pm 6.1 \times 10^{-2}$	$1.2 \times 10^{-1} \pm 2.6 \times 10^{-2}$
	Wax	$2.9\times 10^{-2}\pm 3.3\times 10^{-3}$	_
2,4,5-T	IPA	$4.2\times 10^{-2}\pm 4.4\times 10^{-3}$	$1.1 \times 10^{-2} \pm 1.1 \times 10^{-3}$
	MeOH	$4.0\times 10^{-3}\pm 2.5\times 10^{-4}$	$3.3 \times 10^{-4} \pm 2.1 \times 10^{-5}$
	ACN	$4.1\times 10^{-3}\pm 7.0\times 10^{-4}$	$1.3 \times 10^{-3} \pm 2.3 \times 10^{-4}$
	DI	$1.2 \times 10^{-2} \pm 1.0 \times 10^{-4}$	$3.8\times 10^{-3}\pm 3.1\times 10^{-5}$
	Quartz	$3.4 \times 10^{-1} \pm 4.0 \times 10^{-2}$	$7.0\times 10^{-2}\pm 8.4\times 10^{-3}$
	Wax	$4.8 \times 10^{-2} \pm 3.5 \times 10^{-3}$	—
2,4-DME	Нер	$4.0\times 10^{-2}\pm 5.0\times 10^{-4}$	$2.4 \times 10^{-2} \pm 3.1 \times 10^{-4}$
	IPA	$1.1 \times 10^{-2} \pm 1.0 \times 10^{-3}$	$5.9 \times 10^{-3} \pm 5.3 \times 10^{-4}$
	MeOH	$1.8\times 10^{-3}\pm 5.0\times 10^{-5}$	$9.3 \times 10^{-4} \pm 2.7 \times 10^{-5}$
	ACN	$3.1\times 10^{-4}\pm 4.0\times 10^{-4}$	$1.1 \times 10^{-4} \pm 1.5 \times 10^{-4}$
2,4,5-TME	Hep	$1.7\times 10^{-1}\pm 4.5\times 10^{-2}$	$5.1 \times 10^{-2} \pm 1.4 \times 10^{-2}$
	IPA	$8.3\times 10^{-2}\pm 2.3\times 10^{-3}$	$2.7 \times 10^{-2} \pm 7.5 \times 10^{-4}$
	MeOH	$9.2 \times 10^{-3} \pm 2.0 \times 10^{-3}$	$3.1 \times 10^{-3} \pm 6.7 \times 10^{-4}$
	ACN	$1.0\times 10^{-4}\pm 8.0\times 10^{-4}$	$2.3 \times 10^{-5} \pm 1.8 \times 10^{-4}$
2,4-DBEE	Hep	$3.1\times 10^{-2}\pm 2.4\times 10^{-3}$	$1.7 \times 10^{-2} \pm 1.3 \times 10^{-3}$
	IPA	$8.4 \times 10^{-3} \pm 8.5 \times 10^{-4}$	$3.9 \times 10^{-3} \pm 3.9 \times 10^{-4}$
	ACN	$< 5.0 \times 10^{-5} \pm 1.0 \times 10^{-3}$	$<2.0\times10^{-5}\pm4.0\times10^{-4}$
	Quartz	$5.1 \times 10^{-2} \pm 5.1 \times 10^{-3}$	$7.4\times 10^{-2}\pm 7.6\times 10^{-3}$
	Wax	$1.3 \times 10^{-2} \pm 1.7 \times 10^{-3}$	—

2,4,5-TBEE	Нер	$8.5 \times 10^{-2} \pm 3.1 \times 10^{-3}$	$2.4 \times 10^{-2} \pm 8.8 \times 10^{-4}$
	IPA	$4.7 \times 10^{-2} \pm 3.7 \times 10^{-3}$	$1.5 \times 10^{-2} \pm 1.1 \times 10^{-3}$
	ACN	$1.4 \times 10^{-3} \pm 5.5 \times 10^{-4}$	$3.5 \times 10^{-4} \pm 1.4 \times 10^{-4}$
	Quartz	$2.2 \times 10^{-1} \pm 2.8 \times 10^{-2}$	$2.8 \times 10^{-2} \pm 3.5 \times 10^{-3}$
	Wax	$7.5 \times 10^{-2} \pm 8.6 \times 10^{-3}$	

Solvent			$\int E_p^0(\lambda) \varepsilon_\lambda d$	λ (L cm ⁻³ s ⁻¹)		
Borvent	2,4-D	2,4,5-T	2,4-DME	2,4,5-TME	2,4-DBEE	2,4,5-TBEE
Нер			$5.9 imes10^{-8}$	$2.2 imes 10^{-7}$	$8.3 imes10^{-8}$	$2.3 imes 10^{-7}$
IPA	$1.2 imes 10^{-7}$	$3.0 imes 10^{-7}$	$7.3 imes10^{-8}$	$1.8 imes 10^{-7}$	$8.4 imes10^{-8}$	$2.2 imes 10^{-7}$
MeOH	$1.0 imes 10^{-7}$	$2.1 imes 10^{-7}$	$6.3 imes10^{-8}$	$1.8 imes 10^{-7}$		
ACN	$1.1 imes 10^{-7}$	$2.7 imes 10^{-7}$	$5.8 imes10^{-8}$	$1.9 imes 10^{-7}$	$6.5 imes10^{-8}$	$1.7 imes 10^{-7}$
DI	$8.1 imes 10^{-8}$	$2.0 imes 10^{-7}$				
Average	$1.0 imes 10^{-7}$	$2.5 imes 10^{-7}$	$6.3 imes10^{-8}$	$1.9 imes 10^{-7}$	$7.7 imes10^{-8}$	$2.1 imes 10^{-7}$
Variation	38%	41%	24%	21%	25%	29%

Table S4. The amount of light absorbed by pesticides in solvents across wavelength 290–315 nm. Hep = n-heptane, IPA = 2-propanol, MeOH = methanol, ACN = acetonitrile. Variation of light absorption by each herbicide in different solvents was calculated as the ratio between the largest difference and the average.

	2,4-DBEE	2,4,5-TBEE	Difference
Solvent	ϵ_{230nm}	ϵ_{230nm}	Difference
	(L'IIIOI CIII)	(L'mor em)	
IPA	8860	9086	2.5%
MeOH	9152	8779	4.2%
ACN	9077	8830	2.8%

Table S5. Molar extinction coefficients of 2,4-DBEE and 2,4,5-TBEE at 230 nm in different solvents. IPA = 2-propanol, MeOH = methanol, ACN = acetonitrile.

Table S6. Photoproducts of 2,4-D and 2,4-DBEE analyzed by UPLC-ESI(-)-qTOF. The three groups of putative photoproducts (I), (II), and (III) correspond to the structures in Figure 4. t_f = reaction time corresponding to approximately 90% parent compound decay or 48 h, whichever is shorter; RT = retention time; m/z = measured mass-to-charge ratio; Δ m/z = (measured m/z – calculated m/z) / calculated m/z × 10⁶; N.D. = not detected.

Parent	0 0			Putative products		
compound	Surface	$t_{f}(h)$	1) decay	$(\mathbf{I})^a$	$(II)^b$	$(III)^c$
2,4-D	Quartz	6	80%	Detected ^d RT = 1.61 min m/z = 184.9997 $\Delta m/z = -4.3$ ppm	N.D.	N.D.
	Wax	48	45%	Detected ^d RT = 1.61 min m/z = 185.0021 $\Delta m/z = 8.6$ ppm	N.D.	Detected RT = 8.62 min m/z = 160.9557 $\Delta m/z = -2.5$ ppm
2,4 - DBEE	Quartz	48	91%	N.D.	N.D.	N.D.
	Wax	48	38%	N.D.	N.D.	N.D.

^{*a*} Reductive dechlorination products: monochlorianted phenoxyacetic acids or butyoxyethyl phenoxyacetates, corresponding to pathway (I) in Figure 4.

^b Products formed through photosubstitution of chlorine by a hydroxyl group, corresponding to pathway (II) in Figure 4.

^c Ether bond cleavage product 2,4-dichlorophenol, corresponding to pathway (III) in Figure 4.

^d It is unknown which isomer(s) is/are represented by this peak.

Solvent	Dielectric constant ¹	C-H bond energy ¹⁻⁴ (kJ mol ⁻¹)
Нер	1.9	410
IPA	18.3	374-391
MeOH	32.6	389-403
ACN	36.6	389-402

Table S7. Dielectric constants and C-H bond dissociation energies of the selected solvents. Hep = n-heptane, IPA = 2-propanol, MeOH = methanol, ACN = acetonitrile.

Time (min)	vol% A	vol% B
0	75	25
6	75	25
6.5	40	60
10.5	40	60
11.0	75	25
12.0	75	25

Table S8. Gradient elution method for UPLC-ESI(-)-qTOF analysis. (A) LC-MS grade water (containing 0.1 vol% formic acid) and (B) LC-MS grade acetonitrile (containing 0.1 vol% formic acid).^{*a*}

^a Changes in solvent composition were linear between designated time steps.

Text S1. Chemicals

The following chemicals were obtained from Sigma-Aldrich: 2,4-dichlorophenoxyacetic acid (2,4-D, 99.9%), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T, 99.0%), 2,4-D methyl ester (2,4-DME, 200 µg/mL in hexane), 2,4,5-T methyl ester (2,4,5-TME, 200 µg/mL in hexane), 2,4-D butoxyethyl ester (2,4-DBEE, 97.2%), 2-nitrobenzaldehyde (2-NB, 98%), paraffin wax (mp \geq 65 °C) and Tween[®] 20. The following chemicals were obtained from Fisher Scientific: 2,4-D methyl ester (1000 µg/mL in methanol), 2,4,5-T methyl ester (1000 µg/mL in methanol), 2,4,5-T methyl ester (1000 µg/mL in methanol), 2,4,5-T trichlorophenol (1000 mg/mL in methanol), potassium phosphate monobasic (99.6%), acetonitrile (ACN, HPLC grade, 99.9%), methanol (MeOH, HPLC grade, 99.9%), and 2-propanol (IPA, HPLC grade, 99.9%). 2,4,5-T butoxyethyl ester (2,4,5-TBEE, \geq 98%) was purchased from Santa Cruz Biotechnology. *n*-Heptane (\geq 99.0%) was purchased from J.T.Baker. Potassium phosphate dibasic (98.0%) was purchased from VWR. All chemicals were used as received. Deionized water from a Milli-Q Integral Water Purification System was used.

Text S2. Sample Analysis

The 2,4-D and 2,4,5-T solvent and surface samples were analyzed using high performance liquid chromatography with a diode array detector (HPLC-DAD, Agilent 1260 Infinity). An Agilent Poroshell 120 EC-C18 column (4.6 mm \times 50 mm, 2.7 µm) was used and maintained at 30 °C during the analysis. Flow rate was set at 1 mL min⁻¹ and the detection wavelength was 230 nm. Sample injection volume was 15 µL. With an isocratic elution using 50% phosphate buffer (pH 2.5, 15 mM) and 50% acetonitrile, the retention times for 2,4-D and 2,4,5-T were 1.3 min and 1.7 min, respectively. The surface samples were extracted from quartz and paraffin wax surfaces using 2.5 mL and 5 mL of methanol, respectively, and analyzed within 30 min. The detection limits for 2,4-D and 2,4,5-T are 1 µM. This HPLC-DAD method was also used to quantify the dechlorination photoproducts of 2,4,5-T on the surfaces.

The methyl and butoxyethyl ester samples from solvent experiments were analyzed by gas chromatography-mass spectrometry (Agilent Model 7890B GC-240 MS) with chemical ionization using methanol. The carrier gas was helium with a flow rate of 1.2 mL min⁻¹. Samples (1 μ L) were injected in splitless mode. The inlet was held at 270°C during sample injection. For 2,4-DME and 2,4,5-TME, the initial column temperature was set at 90 °C and held for 1 min, and then increased to 270 °C at a rate of 100 °C min⁻¹ and held for 10 min. Selected reaction monitoring mode was used with isolation window set to 5 m/z. 2,4-DME (m/z 235) was eluted at 4.3 min and quantified using fragmentation ions m/z 175 and 177. 2,4,5-TME (m/z 269) was eluted at 4.7 min and quantified using fragmentation ions m/z 209 and 211. For 2,4-DBEE and 2,4,5-TBEE, the initial column temperature was set at 90 °C and held for 2 min, and then increased to 260 °C at a rate of 10 °C min⁻¹ and held for 2 min, and then increased to 260 °C at a rate of 10 °C min⁻¹ and held for 2 min, and then increased to 260 °C at a rate of 10 °C min⁻¹ and held for 2 min, and then increased to 260 °C at a rate of 10 °C min⁻¹ and held for 3 min. 2,4-DBEE (m/z 321) was eluted at 16.8 min and quantified using fragmentation ions m/z 247 and 249. 2,4,5-TBEE (m/z 355) was eluted at 18.0 min and quantified using

using fragmentation ions m/z 281 and 283. The detection limits of the ester compounds are 0.5 μ M. The same GC injection and oven program was used for the analysis of photoproducts of 2,4,5-TME in organic solvents, but the MS was changed to full scan mode (50–400 m/z).

The 2,4-DBEE and 2,4,5-TBEE surface samples were analyzed by HPLC-DAD. The sample injection volume was 10 μ L. With an isocratic elution using 40% phosphate buffer (pH 2.5, 15 mM) and 60% acetonitrile, the retention time for 2,4-DBEE and 2,4,5-TBEE was 4.1 min and 5.6 min, respectively. Column temperature was maintained at 30 °C during the analysis. Flow rate was set at 1 mL min⁻¹ and the detection wavelength was 230 nm. This HPLC-DAD method was also used to quantify the dechlorination photoproducts of 2,4,5-TME and 2,4,5-TBEE in organic solvents and those of 2,4,5-TBEE on surfaces.

In addition to the HPLC-DAD and GC-MS analyses mentioned above, the photoproducts of surface samples were also analyzed using liquid chromatography with high-resolution mass spectrometry. Separations were performed on an ultra-performance liquid chromatograph (UPLC, Waters Acquity H-Class) configured with an Acquity UPLC BEH C18 column (50-mm length, 2.1-mm inner diameter, 1.7- μ m particle size) maintained at 30 °C. The sample injection volume was 1.0 μ L. A gradient elution method was employed with a total flow rate of 0.6 mL min⁻¹ and a total run time of 12.0 min (Table S7). The high-resolution, quadrupole/time-of-flight mass spectrometer (Waters Xevo G2-S) was equipped with an electrospray ionization source (operated in negative ionization mode) and included the following parameters: capillary voltage = 3.8 kV; sampling cone = 40 V; source offset = 80 V; source T = 130 °C; desolvation T = 350 °C; cone gas (N₂) = 20 L h⁻¹; desolvation gas (N₂) = 650 L h⁻¹.

Text S3. Eliminating Interference from Transesterification Reactions

Methanol can react with 2,4-DBEE and 2,4,5-TBEE to form the corresponding methyl esters.⁵ For example, when injecting the standard methanolic solutions of 2,4-DBEE and 2,4,5-TBEE to GC-MS, 2,4-DME and 2,4,5-TME were detected, confirmed by their chromatographic retention time and mass spectra using authentic standards. No parent 2,4-DBEE or 2,4,5-TBEE peaks were detected. These instantaneous transesterification reactions may be attributed to the high temperature at the GC injection port (270 °C).

Although at a slower rate, transesterification also occurrs under room temperature. In the dark, only 30% of the initial 2,4,5-TBEE remained after 48 h, a time scale relevant to photolysis experiments. Therefore, the photolysis of butoxyethyl esters was not evaluated in methanol. The pseudo first-order transesterification decay of 2,4,5-TBEE has an estimated rate constant of 0.025 h^{-1} . In experimental operations where there was contact between methanol and butoxyethyl esters (e.g., the extraction of surface samples), the contact time was controlled to below 30 min, within which the extent of transesterification was expected to be less than 1.2%

Text S4. Measurement of Molar Extinction Coefficients on Quartz Surface

A quartz dish, either loaded with a pesticide + surfactant $(6.17 \times 10^{-8} \text{ mol cm}^{-2}; \text{Tween}^{\$}$ 20 to pesticide molar ratio 5:1) or loaded with Tween[®] 20 alone, was placed in the spectrophotometer. The absorbance of pesticides on the surface was calculated based on the difference in absorbance between the dishes loaded with pesticide + surfactant and those loaded with surfactant only. The absorbance of each dish (either loaded with pesticide + surfactant or with surfactant alone) was measured four times, with each measurement taken after the dish was rotated 90°. The same process was repeated for three dishes.

Figure S5 compares the difference in absorbance at 290 nm between dishes loaded with pesticide + surfactant and those loaded with surfactant alone from the 12 measurements. Despite the use of surfactant, some heterogeneity was observed. The mean values were used to calculate pesticide surface absorbance and molar extinction coefficient.

It is worth noting that this method has inherent limitation for determining pesticide absorbance on surfaces. For example, light scattering was not accounted for, which may add to the variability in the apparent surface absorbance readings.

Text S5. Kinetic Modeling for 2,4,5-TBEE Photolysis on Surfaces

On surfaces, the concentration of photoreductive dechlorination products only accounted for a fraction of the parent compound decay (Figures 5D and 5D). There are at least two possible reasons: (1) photoreductive dechlorination on surfaces is so facile that the photoproducts rapidly undergo further dechlorination; and/or (2) alternative reaction pathways are significant on surfaces. In order to identify the reason, a kinetic model was developed for 2,4,5-TBEE photolysis on surfaces, assuming the first reason to be valid. If the measured DBEE concentrations fit the kinetic model prediction, then the lower molar ratio between DBEEs formation and 2,4,5-TBEE decay observed on surfaces could be attributed to rapid, further dechlorination of DBEEs.

For the reaction of 2,4,5-TBEE photolysis on surfaces, 2,4,5-TBEE first degrades to DBEEs, which then further degrade to monochlorinated products (equation S1). Figure S1 shows that the photolysis of 2,4,5-TBEE and 2,4-DBEE follows first-order kinetics. Assuming the three DBEE isomers have similar photoreactivity, kinetic equations S2 and S3 can be obtained:

2,4,5-TBEE → DBEEs → monochlroinated products Eq. S1

$$\frac{d[TBEE]}{dt} = -k_{TBEE}[TBEE]$$
 Eq. S2

$$\frac{d[DBEE]}{dt} = k_{TBEE}[TBEE] - k_{DBEE}[DBEE]$$
Eq. S3

where [TBEE] and [DBEE] are the concentrations (mol L⁻¹) of 2,4,5-TBEE and DBEEs (i.e., 2,4-DBEE, 2,5-DBEE, and 3,4-DBEE) at time *t* (h), respectively; k_{TBEE} and k_{DBEE} are the experimentally determined pseudo first-order rate constants (h⁻¹) for 2,4,5-TBEE and DBEEs, respectively. Because the ortho chlorine was reported to be more reactive than the others,⁶⁻⁸ the

rate constant of 2,4-DBEE represents the upper bound of DBEE decay rate constants. The time profile of 2,4,5-TBEE and DBEEs concentrations can be obtained by solving equations S2 and S3.

$$[TBEE] = [TBEE]_0 e^{-k_{TBEE}t}$$
 Eq. S4

$$[DBEE] = \frac{k_{TBEE} [TBEE]_0}{k_{DBEE} - k_{TBEE}} (e^{-k_{TBEE}t} - e^{-k_{DBEE}t})$$
Eq. S5

The measured DBEE concentrations from surface experiments are compared with the prediction from the kinetic model (Figure S8). It is apparent that the model prediction does not agree with the experimental results. This suggests that pathways in parallel with photoreductive dechlorination contributed to the low molar ratio of dechlorination products to parent decay observed on surfaces.

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