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Emerging investigator series: sunlight photolysis of 2,4-D herbicides in systems simulating leaf surfaces†

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Pesticides are commonly applied on foliage, forming dry deposits on the leaf cuticular wax. However, their photochemical transformation in this lipophilic environment is much less understood compared with that in surface water. In this work, sunlight photolysis of six chlorinated phenoxyacetic acid herbicides (*i.e.*, 2,4-D and structural analogues) was evaluated in four organic solvents, on quartz, and on paraffin wax. In solvents of low polarity (*i.e.*, *n*-heptane and 2-propanol), direct photolysis of 2,4-D herbicides was enhanced due to the relatively high quantum yields in these solvents. Photolysis on paraffin wax was slower than photolysis on quartz by a factor of 3–9, but was comparable with that in solvents of low polarity. With environmentally relevant irradiation and surface loading, the half-lives of 2,4-D herbicides on paraffin wax were 27–159 h, which are within the same range reported for biodegradation, the dominant dissipation pathway in the current 2,4-D fate model. Product analyses showed that photoreductive dechlorination is the dominant pathway in organic solvents, accounting for 68–100% of parent compound decay. On quartz and paraffin wax surfaces, however, photoreductive dechlorination products accounted for <60% of parent compound decay. Combining kinetic modeling and product analyses, it was shown that neither could the two additional putative pathways (photosubstitution of chlorine by hydroxyl group and cleavage of the ether bond) fully account for the total phototransformation on surfaces. These results suggest that rapid photolysis on surfaces can be attributed to unique pathways that are absent in the organic solvent phase.

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Environmental significance

Pesticides are often applied on foliage, but their photolysis in this environment is much less understood compared with that in water. This study systematically investigated the photolysis of 2,4-D herbicides in systems simulating the reaction environment of leaf surface, including non-polar organic solvents and quartz and wax surfaces. We determined photolysis rate constants and quantum yields, and analyzed photoproducts. Our results showed that direct photolysis of 2,4-D herbicides on paraffin wax can be as fast as their biodegradation in water, the dominant degradation pathway considered in the current fate model. Additionally, the major reaction pathway in organic solvents and on surfaces (*i.e.*, photoreductive dechlorination) is distinct from that previously reported in water.

1 Introduction

Photochemical transformation is a major pathway for pesticide degradation.¹ In a recent review, more than half of the 160 pesticides evaluated undergo direct photolysis under sunlight, with half-lives as short as 2 h.² For pesticides that do not absorb sunlight, indirect photolysis (*i.e.*, photolysis sensitized by natural organic matter, nitrate, or iron species) can be an important dissipation pathway.^{3–5}

Pesticides that are applied directly on foliage form dry deposits on the cuticular wax of leaves.⁶ Nevertheless, their photochemical transformation on leaves is much less understood compared with that in surface water. Lipophilic environments, such as cuticular wax,⁷ have been shown to promote direct photolysis by extending the life-times of excited state molecules.⁸ Spruce needle wax was shown to serve as a hydrogen donor in the photoreductive dechlorination of some persistent organic pollutants (*e.g.*, benzophenone and DDT).⁹ Additionally, when present as dry deposits, pesticide molecules may exhibit light absorption properties different from those in the solvent phase,¹ and may favor reaction pathways that minimize conformation change between reaction intermediates and parent compounds.¹⁰

Previous studies^{11–15} of the photochemical transformation of pesticides on leaves used two types of model systems. In the first type, organic solvents were used to represent specific

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components of the cuticular wax. For example, cyclohexane and cyclohexene were used as surrogates of the saturated and unsaturated hydrocarbons, respectively, of cuticular wax.^{11,12} The direct photolysis of fungicide folpet and insecticide parathion was 10–100 times faster in cyclohexene than in cyclohexane, suggesting that their photolysis proceeds more efficiently in olefinic media.^{11,12} When DDT, methoxychlor, and anilazine were irradiated in methyl oleate, a surrogate of the octadecenoic acids in cuticle wax, photoinduced addition of pesticides to methyl oleate was observed, suggesting that the solvent molecules directly participated in pesticide phototransformation.^{13,14} In methanol and 2-propanol representing the primary and secondary alcohol groups, respectively, common in cuticular wax, cyclohexanedione oxime herbicides clethodim and sethoxydim photodegraded 3–5 times faster than in water.¹⁵ The potential influence of solvent polarity on pesticide photolysis, however, was not considered in these studies.^{11–15}

The second type of model system employs surfaces with different physicochemical characteristics, such as glass,^{16–19} silica gel,^{20,21} or a thin layer of wax extracted from leaves.^{20,22–26} Differences between direct photolysis rates on surfaces compared to those in solutions vary among pesticides. Fungicide hexachlorobenzene persisted on glass surface after 5 months of irradiation by artificial sunlight, but achieved 70% decay in methanol after 15 days under sunlight.²⁷ In contrast, fungicide guazatine-triacetate degraded 67% after 84 h when present as a thin film on glass surface, but no degradation was observed in water or methanol.¹⁸ More recently, Richard and co-workers²⁶ developed a procedure to create simulated leaf surfaces by extracting wax from plants and reconstituting it on dishes. On the extracted maize and carnauba gray wax, photolysis rates of triketone herbicides were 10–900 times faster than those in water.^{26,28}

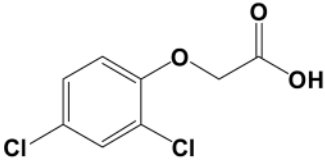
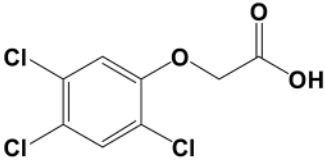
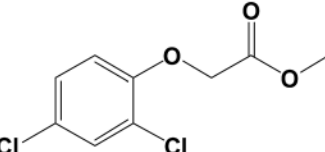
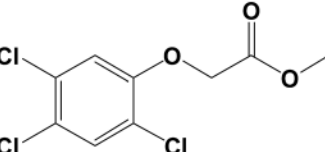
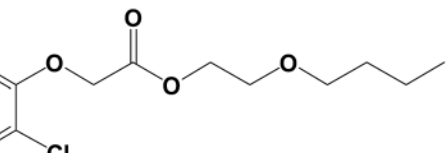
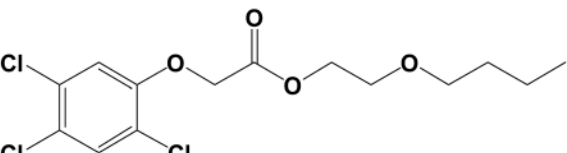
Although differences in the photochemical behavior of pesticides in water and on surfaces have been documented,

mechanistic interpretations have been scarce due to insufficient experimental controls in many of the studies employing surfaces. For example, surfactants are a common adjuvant in commercial pesticide formulations; however, some previous studies employed pure pesticides,^{15,29} which could form aggregates capable of interfering with light absorption. Surfactants have only recently been considered as an important adjuvant in photolysis experiments.³⁰ Additionally, most of the reported irradiation intensity was based on the output of the light sources,^{19,20,23–25} which cannot account for the variation in light attenuation attributable to differences in reactor geometry between solvent and surface experiments.

The goal of this work is to investigate the direct photolysis of 2,4-dichlorophenoxyacetic acid (2,4-D) and five related herbicides (Table 1) under conditions relevant to leaf surfaces. 2,4-D is an herbicide (frequently formulated as an ester) that is widely applied post-emergence to control broadleaf weeds. Developed in the 1940s, 2,4-D remains the 7th most used agricultural pesticide and the most used pesticide in non-agricultural sectors.³¹ In surface water, sunlight photolysis of 2,4-D and related herbicides is slow. For example, the photolysis half-life of 2,4-D in water is 13 d,³² while its biodegradation half-life is 30 to 40 h.³³ On leaf surfaces, however, photolysis may play a more significant role due to the lower microbial activity and the potential enhancement of photolysis by leaf surfaces.

In this work, direct photolysis of six chlorinated phenoxyacetic acid herbicides was examined in organic solvents and on surfaces under simulated sunlight. First, photolysis rate constants, molar extinction coefficients, and quantum yields were determined in four organic solvents with different polarity and hydrogen-donating ability. Subsequently, photolysis experiments were conducted on quartz and paraffin wax surfaces, and the reaction rate constants were compared with those obtained from solvent experiments. For selected

Table 1 Chemical structure of the six chlorinated phenoxyacetic acid herbicides investigated in this study

	
2,4-Dichlorophenoxyacetic acid (2,4-D) 	2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) 
2,4-D methyl ester (2,4-DME) 	2,4,5-T methyl ester (2,4,5-TME) 
2,4-D butoxyethyl ester (2,4-DBEE)	2,4,5-T butoxyethyl ester (2,4,5-TBEE)

herbicides, photodegradation products in organic solvents and on surfaces were analyzed. Lastly, the photolysis mechanisms relevant to leaf surfaces were discussed.

2 Materials and methods

2.1 Materials

Detail information on the chemicals used in this study is shown in Text S1.†

2.2 Photolysis experiments

A total of six structurally related phenoxyacetic acid herbicides were used (Table 1). Among them, 2,4-D and 2,4-DBEE are widely used in commercial formulations, while 2,4-DME and 2,4,5-T and its esters are banned in the United States due to their high volatility and/or high toxicity,³⁴ but are still used in other parts of the world.³⁵ For photolysis experiments in the solvent phase, pesticide stock solutions were prepared from pure compounds or used as purchased. The solvent of the stock solutions was selected based on pesticide solubility limits. Accordingly, some reaction solutions contained more than one solvent (Table S1†), but the co-solvent was less than 1.5 vol% in all reaction solutions except for 2,4-D and 2,4,5-T. The initial concentrations of 2,4-D and 2,4,5-T in the reaction solutions were 20 μM and those of 2,4-DME, 2,4,5-TME, 2,4-DBEE, and 2,4,5-TBEE were 5 μM . Aqueous reaction solutions were buffered with phosphate (pH 7.0, 5 mM).

For surface experiments, quartz dishes (diameter: 55 mm, depth: 15 mm, capacity: 20 mL) were used to provide quartz surfaces. To prepare paraffin wax surfaces, glass Petri dishes were dipped in melted paraffin wax (110 °C for 20 minutes), and then placed horizontally and cooled at room temperature to form a flat surface. The wax surfaces were inspected visually. No solvent pooling was observed during sample loading (see below). The wax coated dishes have the same dimensions as the quartz dishes. To apply pesticides on the surfaces, a mixture of the surfactant Tween® 20 and the target pesticide, dissolved in methanol or acetonitrile (3 mL), was added to the dishes. Because paraffin wax surface is more hydrophobic than quartz, a higher concentration of Tween® 20 was used on wax (10 : 1 molar ratio to the pesticide) than on quartz (1 : 1 molar ratio). The dishes were stored in the dark for 3–12 h to allow solvent to evaporate. Experimental verification (*e.g.*, *via* microscopy) of surface dryness following the solvent evaporation time was not performed. The recoveries of pesticides from the two surfaces were in the range of 87.8–99.8% (Table S2†), suggesting there was no substantial loss during sample loading or analysis (described below in Section 2.3). The pesticide surface loading used in the experiments (3×10^{-9} mol cm^{-2}) was similar in magnitude as the 2,4-D application rate in the field (265 g per hectare, equivalent to 1.2×10^{-8} mol cm^{-2}).³⁶ During preparation of surface samples, a sodium lamp ($\lambda = 589$ nm) was used for laboratory illumination to minimize photolysis loss.

Photolysis experiments were conducted in a Q-SUN Xe-1 test chamber equipped with a Xenon arc lamp to produce the full sunlight spectrum. A daylight-Q filter (X-7460) was used to

remove irradiation below 290 nm to simulate direct sunlight at the Earth's surface. The lamp was set to a light intensity of 0.68 W m^{-2} at 340 nm, and the total irradiation intensity was determined using chemical actinometry (see Section 2.4 below). A circulating water bath was used to maintain sample temperature at 26 ± 3 °C. For liquid samples, each reaction solution (10 mL) was placed in a quartz test tube capped with a silicone stopper. The test tubes were placed in the water tank at a 45° angle. At selected time points, 0.5 mL of reaction solution was removed from each test tube for analysis. For surface samples, dishes loaded with pesticides were covered by quartz disks and placed in the sunlight test chamber (half submerged in the circulating water bath). Dishes were removed at selected time points for analysis. All experiments were conducted in duplicates and included dark control samples.

2.3 Sample analysis

For solvent experiments, the 2,4-D and 2,4,5-T samples were analyzed using high performance liquid chromatography with a diode array detector (HPLC-DAD, Agilent 1260 Infinity), and 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. For surface experiments, the residual pesticides were dissolved by methanol and analyzed by HPLC-DAD. The details of the analytical methods are shown in Text S2.†

Photoproducts for the trichlorinated phenoxyacetic acid herbicides were evaluated. HPLC-DAD was first used to quantify the dechlorination products of 2,4,5-T, 2,4,5-TME, and 2,4,5-TBEE (*i.e.*, 2,4-D, 2,4-DME, 2,4-DBEE, and their isomers), as well as 2,4,5-trichlorophenol, the potential product from the cleavage of the ether bond. Because the isomers of 2,4-D and 2,4-DBEE were not commercially available, the total concentrations of isomers were estimated using the HPLC calibration curve for 2,4-D and 2,4-DBEE, respectively. Further discussion on this methodology is provided in Section 3.3. The methanol and 2-propanol solvent samples and the methanol extracted surface samples were directly analyzed. For the *n*-heptane samples of 2,4,5-TBEE, 1 mL of sample was blown down by nitrogen gas to dryness in an amber vial, and reconstituted in 1 mL methanol and immediately analyzed by HPLC-DAD. The recovery of 2,4-DBEE using this method was $102.8\% \pm 1.3\%$. Methyl esters were too volatile to be recovered using solvent blowdown; therefore, the *n*-heptane samples of 2,4,5-TME photolysis were not analyzed for photoproducts. The HPLC method for product analysis is described in Text S2.†

GC-MS (full scan) was used to explore other products for 2,4,5-TME photolysis in the solvents. Authentic 2,4-DME standard was used to verify one of the product peaks from 2,4,5-TME photolysis in solvents. The GC-MS method for product analysis is described in Text S2.†

The 2,4,5-T and 2,4,5-TBEE surface samples were also analyzed using ultra-performance liquid chromatography interfaced with high-resolution, quadrupole/time-of-flight mass spectrometer using an electrospray ionization source (operated in negative ionization mode) (UPLC-ESI(–)-qTOF). Methanol was

used to extract the photoproducts from the surfaces and blown down to dryness under nitrogen gas. The samples were reconstituted in acetonitrile for UPLC-ESI(-)qTOF analysis. Product identification was based on accurate mass measurement. The details of the UPLC-ESI(-)qTOF method are shown in Text S2.†

2.4 Determination of quantum yield

Eqn (1) describes the kinetics of a photolysis reaction.³⁷

$$-\frac{dC}{dt} = \sum \Phi_{\lambda} \left[\frac{E_p^0(\lambda)}{d} \right] \left[1 - 10^{-(\alpha_{\lambda} + \varepsilon_{\lambda} C)d} \right] \left[\frac{\varepsilon_{\lambda} C}{\alpha_{\lambda} + \varepsilon_{\lambda} C} \right] \quad (1)$$

where C is the pesticide concentration (mol L^{-1}) at time t (s); Φ_{λ} is the quantum yield of pesticide decay (dimensionless) at wavelength λ ; $E_p^0(\lambda)$ is the incident light intensity ($\text{Einstein cm}^{-2} \text{s}^{-1}$) at wavelength λ ; d is the sample pathlength (cm); α_{λ} is the absorption coefficient of the reaction matrix (cm^{-1}); ε_{λ} is the molar extinction coefficient of the pesticide ($\text{L mol}^{-1} \text{cm}^{-1}$).

Eqn (1) can be simplified to pseudo first-order kinetics (eqn (2)) if the following two constraints are met: (1) light absorption by the reaction matrix is not significant (*i.e.*, $\varepsilon_{\lambda} C \gg \alpha_{\lambda}$), and (2) total light absorption by pesticide and reaction matrix together is small, $F_{s\lambda} < 0.1$, where $F_{s\lambda}$ is the fraction of light absorbed by the system as determined from the absorption spectrum (eqn (3)).³⁷

$$-\frac{dC}{dt} = 2.303 \sum \Phi_{\lambda} E_p^0(\lambda) \varepsilon_{\lambda} C = -kC \quad (2)$$

$$F_{s\lambda} = 1 - 10^{-(\alpha_{\lambda} + \varepsilon_{\lambda} C)d} \quad (3)$$

In our experiments (sunlight spectrum), both criteria are satisfied: the solvents have negligible absorbance and the reaction solutions exhibited low optical density. For example, the maximum $F_{s\lambda}$ for 2,4-D in phosphate-buffered water is 0.09 at the absorption maximum 290 nm. Quantum yield Φ_{λ} was assumed to be wavelength independent within the sunlight spectrum.³⁷ Accordingly, quantum yield can be calculated as eqn (4).

$$\Phi = \frac{k}{2.303 \sum E_p^0(\lambda) \varepsilon_{\lambda}} \quad (4)$$

where k is the pseudo first-order rate constant of pesticide photolysis reaction (s^{-1}).

The molar extinction coefficients ε_{λ} for pesticides in solvents were calculated using the Beer-Lambert law based on the absorption spectra (200–800 nm) measured by an Agilent Cary 60 UV-Vis spectrophotometer. The background absorption of the respective solvent was subtracted. The molar extinction coefficients of pesticides on quartz were also estimated: a quartz dish loaded with a pesticide compound ($6.17 \times 10^{-8} \text{ mol cm}^{-2}$; Tween® 20 to pesticide molar ratio 5 : 1) was placed in the spectrophotometer, and the light transmission was compared with that measured through a disk loaded with surfactant alone. The difference was used to approximate the absorbance of pesticides in the solid form. Further details on the measurement of absorbance on quartz surface are provided in Text S4.† The molar extinction coefficients of pesticides on wax cannot be determined using this method due to the negligible

light transmission through wax. Additionally, because light scattering by pesticides and reflection by the quartz surface is not accounted for, this measurement yields the upper bound of molar extinction coefficients for pesticides on quartz. The molar extinction of a pesticide in solid form is calculated by eqn (5).

$$\varepsilon_{\lambda} = \frac{A}{q} \times 10^{-3} (\text{L cm}^{-2}) \quad (5)$$

where A is the absorbance (dimensionless) measured by UV-Vis spectrophotometry, and q is the surface concentration (mol cm^{-2}).

Chemical actinometry was used to determine the quantum yields of pesticides in different reaction environments. 2-Nitrobenzaldehyde (2-NB) was used as the actinometer, and its decay was monitored. The photolysis of 2-NB occurs intramolecularly with a reported quantum yield of 0.41.^{38,39} Studies have shown that the quantum yield of 2-NB is independent of temperature, solvent, and the state of the molecule (*e.g.*, dissolved or solid).^{38–42} 2-NB can be used either at a high concentration (*e.g.*, 0.1 M), where it absorbs all incident light and exhibits pseudo zero-order photolysis kinetics or at a low concentration (*e.g.*, 10 μM), where it exhibits pseudo first-order photolysis kinetics.^{38,42} For the solvent phase experiments, a low concentration (10 μM) of 2-NB aqueous solution was used, for which eqn (2) applies for its pseudo first-order kinetic decay. Thus, the quantum yield for each pesticide can be calculated using eqn (6). For the solvent experiments, the simulated sunlight intensity was 320 W m^{-2} as determined by the actinometer 2-NB.

$$\Phi_{\text{pesticide}} = \Phi_{2\text{-NB}} \times \frac{k_{\text{pesticide}}}{k_{2\text{-NB}}} \times \frac{\sum E_p^0(\lambda)_{2\text{-NB}} \varepsilon_{\lambda, 2\text{-NB}}}{\sum E_p^0(\lambda)_{\text{pesticide}} \varepsilon_{\lambda, \text{pesticide}}} \quad (6)$$

To quantify light intensity on surfaces, 2-NB was applied on dish surface in the same fashion and at the same loading as the pesticides ($3 \times 10^{-9} \text{ mol cm}^{-2}$). The molar ratios of Tween® 20 to 2-NB was 1 : 1 and 10 : 1 for experiments on quartz and paraffin wax, respectively. Photolysis of 2-NB was performed under the same irradiation condition as pesticide surface samples. After irradiation, 3 mL and 5 mL of deionized water, respectively, were added to the dishes with quartz or paraffin wax surfaces to dissolve residual 2-NB, and samples were taken after 5 min for analysis. The recovery of 2-NB on surfaces was between 92.8% and 95.7% (Table S2†). 2-NB was analyzed with HPLC-DAD. 2-NB eluted at 1.52 min with 60% Milli-Q water and 40% acetonitrile (flow rate 1 mL min^{-1}) and was detected at 230 nm. The molar extinction coefficient of the actinometer 2-NB on quartz surface was measured in the same way as that for the pesticides.

3 Results and discussion

3.1 Photolysis of chlorinated phenoxyacetic acid herbicides in solvents

Direct photolysis of the six chlorinated phenoxyacetic acid herbicides was first investigated in solvents spanning a range of polarities: water, acetonitrile, methanol, 2-propanol, and *n*-heptane. Due to solubility constraints, 2,4-D and 2,4,5-T were

not evaluated in *n*-heptane. Preliminary experiments showed that the ester compounds hydrolyzed rapidly in water: less than 10% of the initial 2,4-DME and 2,4,5-TME mass remained in water after 6 h in the dark, which is consistent with previous reports of facile hydrolysis of these esters.⁴³ Therefore, the photolysis of the four ester compounds was not evaluated in water. Additionally, we observed that significant transesterification occurred between butoxyethyl esters and methanol in the dark; less than 30% of the initial 2,4,5-TBEE mass remained in methanol after 48 h in the dark (Text S3†). Thus, photolysis experiments of butoxyethyl esters were not performed in methanol.

Upon irradiation, all six compounds decayed following apparent first-order kinetics (Fig. S1A–F†). No degradation was observed in dark control samples (data not shown). The apparent first-order photolysis rate constants in different solvents are shown in Fig. 1 (left panel) and Table S3.† Among the organic solvents tested, 2-propanol featured the fastest 2,4-D and 2,4,5-T photolysis. Methanol and acetonitrile yielded similar rate constants, 6–11 times lower than 2-propanol. For the four ester derivatives (2,4-DME, 2,4,5-TME, 2,4-DBEE, and 2,4,5-TBEE), a similar trend was observed: photolysis was fastest in *n*-heptane, followed by 2-propanol, methanol, and acetonitrile. The photolysis rate constants for 2,4-DME, 2,4,5-TME, 2,4-DBEE, and 2,4,5-TBEE in *n*-heptane were 2–4 times higher than the corresponding rate constants in 2-propanol. Photolysis of

methyl esters in 2-propanol was 6–9 times faster than that in methanol and at least 35 times faster than that in acetonitrile. In the same solvent, the rate constants across different phenoxyacetic acid herbicides were within the same order of magnitude.

Given that the polarity of the solvents followed the order *n*-heptane < 2-propanol < methanol $\approx$ acetonitrile, the results suggested that faster photolysis occurred in solvents of lower polarity. The correlation between photolysis rate constants and solvent polarity (measured by the dielectric constant) is shown in Fig. S3.† The influence of organic solvent polarity on the direct photolysis of chlorinated phenoxyacetic acid herbicides is consistent with that observed for the persistent organic pollutant octachlorodibenzo-*p*-dioxin and azoxystrobin fungicide, which photodegraded faster in organic solvents of lower polarity.^{8,44,45} However, the opposite trend was reported for polycyclic aromatic hydrocarbons and the vitamin riboflavin, both of which photodegraded faster in solvents of higher polarity (*e.g.* water, acetonitrile, and methanol) than in solvents of lower polarity (*e.g.* ethyl acetate, cyclohexane, and hexane).^{46–48} It is worth noting that the trend observed for organic solvents does not extend to water, the most polar solvent tested in this study. For example, 2,4,5-T photolysis in water (pH 7.0) was three times faster than that in methanol and acetonitrile, although still 3 times slower than in 2-propanol. This may be attributed to the different reaction pathways dominating in water compared to those occurring in organic solvents (see further discussion in Section 3.5).

To differentiate whether solvents influenced photolysis by altering light absorption of herbicides or by altering their reaction pathways, the molar extinction coefficients in different solvents were determined (Fig. 2 and S2†). As solvent polarity increases in the order of *n*-heptane < 2-propanol < methanol $\approx$ acetonitrile, the absorption spectra of all chlorinated phenoxyacetic acid herbicides exhibited a slight blue shift, but the shift

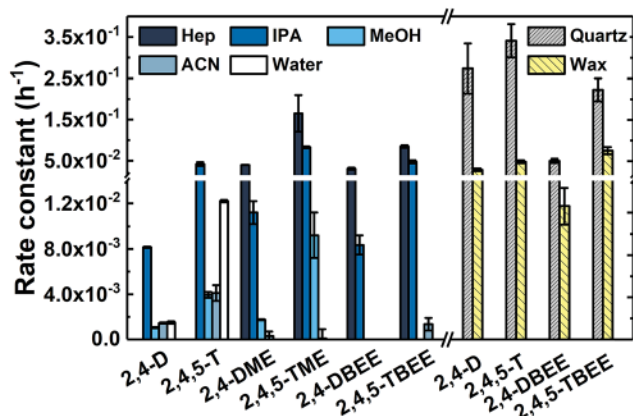


Fig. 1 Apparent first-order photolysis rate constants for 2,4-D, 2,4,5-T, and their methyl and butoxyethyl esters in different solvents (open and blue shaded bars), and on quartz and paraffin wax surfaces (hatched bars). Error bars represent the standard deviation of duplicate experiments. Hep = *n*-heptane, IPA = 2-propanol, MeOH = methanol, ACN = acetonitrile, quartz = quartz surface, Wax = paraffin wax surface. The values of the apparent first-order photolysis rate constants are listed in Table S3.† 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: $20 \mu\text{M}$ for 2,4-D and 2,4,5-T, and $5 \mu\text{M}$ for esters; 5 mM phosphate buffer (pH 7.0) for experiments in water; 26°C . Initial surface pesticide concentration: $3 \times 10^{-9} \text{ mol cm}^{-2}$ on quartz or paraffin wax surface; surfactant (Tween® 20) concentration: $3 \times 10^{-9} \text{ mol cm}^{-2}$ on quartz surface, and $3 \times 10^{-8} \text{ mol cm}^{-2}$ on paraffin wax surface. 2,4-D and 2,4,5-T were not evaluated in *n*-heptane; esters were not evaluated in water; 2,4-DBEE and 2,4,5-TBEE were not evaluated in methanol.

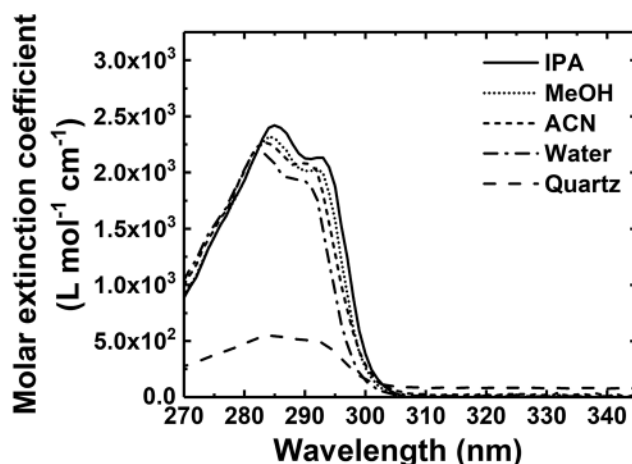


Fig. 2 Molar extinction coefficients of 2,4-D in solvents and on quartz surface. IPA = 2-propanol, MeOH = methanol, ACN = acetonitrile, quartz = quartz surface. Absorbance was measured using a $20 \mu\text{M}$ aqueous sample (5 mM phosphate buffer, pH 7.0), a $5 \mu\text{M}$ organic solvent samples, and a $6.17 \times 10^{-8} \text{ mol cm}^{-2}$ quartz surface sample, respectively.

was less than 1 nm at the absorption peaks near 290 nm. Considering the absorption spectra of the chlorinated phenoxyacetic acid herbicides and the sunlight spectrum, the amount of light absorbed can be calculated by $\int E_p^0(\lambda) \epsilon_\lambda d\lambda$, integrated across wavelength 290–315 nm (Table S4†). The variation of light absorption by pesticides in different solvents was within 41%, substantially smaller than the variation of their photolysis rate constants.

The quantum yields for the six chlorinated phenoxyacetic acid herbicides were calculated using eqn (6) and are shown in Fig. 3 and Table S3.† The relative magnitude of quantum yields in different organic solvents was similar to that of the apparent first-order rate constants (*n*-heptane > 2-propanol > methanol $\approx$ acetonitrile), as would be expected from the small difference in light absorption in different solvents. The quantum yields of 2,4-DME and 2,4-DBEE in *n*-heptane were 2.4×10^{-2} and 1.7×10^{-2} , respectively, which is lower than those previously reported in *n*-hexane and *n*-hexadecane (0.13–0.17).⁴³ The reason for this discrepancy is unknown.

3.2 Photolysis of chlorinated phenoxyacetic acid herbicides on quartz and paraffin wax surfaces

The direct photolysis of 2,4-D, 2,4,5-T, 2,4-DBEE, and 2,4,5-TBEE was examined on quartz and paraffin wax surfaces. The two methyl esters were not evaluated due to their high volatility. Similar to that in the bulk solvent phase, photolysis on surfaces also followed apparent first-order kinetics (Fig. S1G and S1H†). No degradation was observed in dark control samples (data not shown).

The apparent first-order rate constants for pesticide photolysis on surfaces are shown in Fig. 1 (right panel) and Table S3.† For all four compounds, photolysis was 3–9 times faster on quartz than on paraffin wax. Lower surfactant loading was used on quartz surface due to its lower hydrophobicity than wax. Nevertheless, differences in surfactant loading are unlikely to

account for the faster photolysis on quartz based on two lines of evidence: first, Tween® 20 has negligible sunlight absorption (Fig. S4†); second, the photolysis rate constants were not significantly different between experiments in which the molar ratios of 2,4,5-TBEE to Tween® 20 was 1 : 1 ($0.22 \pm 0.0088 \text{ h}^{-1}$) compared to 1 : 10 ($0.22 \pm 0.0077 \text{ h}^{-1}$). Neither can the difference be attributed to higher effective light intensity on quartz, because the chemical actinometer 2-NB, which photodegrades *via* intramolecular rearrangement, decayed at similar rates on quartz and on wax surfaces (<12% difference, Fig. S11†). Previously, herbicide isoproturon and plant activator acibenzolar-S-methyl were also reported to photodegrade faster on glass than on paraffin wax and leaf-extracted cutin surface by a factor of 1–3 upon UV and sunlight irradiation.^{49,50}

When compared with photolysis in solvents, photolysis on quartz was much faster. The rate constants of 2,4-D and 2,4,5-T photolysis on quartz were 34 and 8 times higher, respectively, than the corresponding rate constants in 2-propanol, where their photolysis was the fastest among the solvents tested. 2,4-DBEE and 2,4,5-TBEE photolysis on quartz were 2 and 3 times faster than in *n*-heptane. In comparison, photolysis on paraffin wax proceeded at similar rates as that in solvents of low polarity (*i.e.*, *n*-heptane and 2-propanol). The difference in photolysis rates among the four compounds on the same surface was within a factor 7.

The observation that chlorinated phenoxyacetic acid herbicides photodegraded faster on quartz surface than in organic solvents (*i.e.*, 2-propanol, methanol and acetonitrile) and water is opposite to the trends observed for herbicides clethodim and sethoxydim¹⁵ and fungicide benzothiostrubin,²⁹ but is consistent with those for fungicide guazatine, and herbicides bentazon, clopyralid, sulcotrione, and mesotrione.^{6,18,26,28} In the first two studies,^{15,29} pesticide solutions were directly pipetted onto the glass surface without surfactant, while the other studies^{6,18,26,28} used surfactants to load pesticides or used commercial formula that contained surfactants. Therefore, the

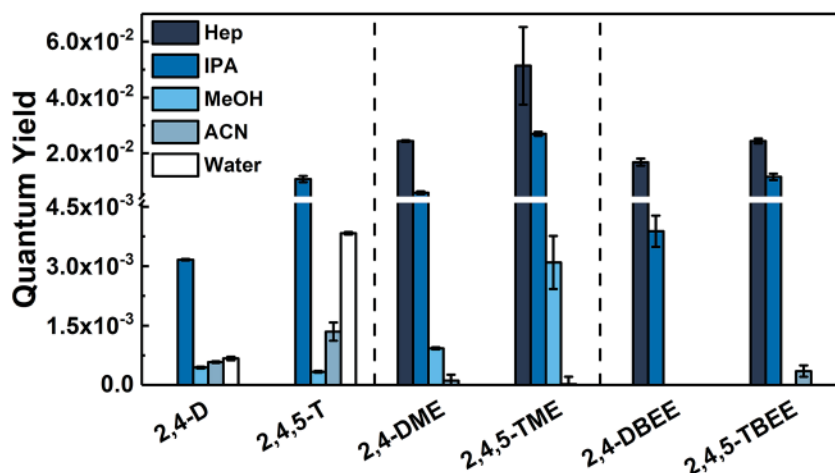


Fig. 3 Quantum yields for the direct photolysis of 2,4-D, 2,4,5-T, and their esters in different solvents. Error bars represent the standard deviation of duplicate experiments. Hep = *n*-heptane, IPA = 2-propanol, MeOH = methanol, ACN = acetonitrile. The values of the quantum yields are listed in Table S3.† 2,4-D and 2,4,5-T were not evaluated in *n*-heptane; esters were not evaluated in water; 2,4-DBEE and 2,4,5-TBEE were not evaluated in methanol.

slow photolysis on surface observed in the first two studies was likely attributable to the interference of light absorption by pesticide aggregates.

Out of the four organic solvents and two surface systems tested in this study, paraffin wax surface best simulates the reaction environment on leaves. Using the photolysis rate constants shown in Fig. 1 (320 W m^{-2} sunlight intensity) and accounting for the diurnal change in sunlight intensity for a midsummer day at 40° N latitude (sea level) under clear skies,^{3,51} the half-lives of 2,4-D, 2,4,5-T, 2,4-DBEE, and 2,4,5-TBEE were estimated to be 72, 42, 159, and 27 h, respectively. With the possible exception of 2,4-DBEE, these photolysis half-lives are on the same order of magnitude as the half-lives previously reported for biodegradation (30–40 h),³³ which is noteworthy given that biodegradation is currently considered as the major dissipation pathway for these herbicides.⁵²

As shown in Fig. 2 and S2,† the experimentally determined molar extinction coefficients of chlorinated phenoxyacetic acid herbicides on quartz surface, despite being the upper bound (Section 2.4), is significantly lower than those in the solvent phase. The quantum yields on quartz calculated using these molar extinction coefficients are therefore the lower bound of the true values, but they are still greater than those in the solvent phase. For example, the calculated quantum yields for 2,4-D and 2,4,5-T on quartz (0.12 and 0.070, respectively) are 38 and 6.4 times higher than those in 2-propanol, and the calculated quantum yields for 2,4-DBEE and 2,4,5-TBEE on quartz (0.074 and 0.028, respectively) are 4.3 and 1.2 times higher than those in *n*-heptane. Our results are among the very first attempts to quantify quantum yields for pesticide photolysis on surfaces. The only other such report⁵³ was on the quantum yield of imidacloprid, a neonicotinoid insecticide, on the top surface of a clean germanium ATR crystal (1.6×10^{-3} at 305 nm), and showed that it was 3–9 times smaller than that in water. Because the molar extinction coefficients on wax cannot be determined using the absorbance method (Section 2.4), the corresponding quantum yields were not calculated.

3.3 Photoproducts of chlorinated phenoxyacetic acid herbicides in organic solvents

Previous research suggested that 2,4-D and its esters undergo photolysis *via* three pathways in water: (I) photoreductive dechlorination, (II) photosubstitution of chlorine by a hydroxyl group, and (III) cleavage of the ether bond (Fig. 4 showing 2,4,5-T and its esters).^{43,54,55} Because photoreductive dechlorination was previously reported as a major pathway for the photolysis of 2,4-DME and 2,4-DBEE in non-polar solvents hexane and hexadecane,⁴³ the corresponding products were first targeted in the organic solvent samples of 2,4,5-TBEE and 2,4,5-TME.

For 2,4,5-TBEE, samples in *n*-heptane and 2-propanol were analyzed but not those in acetonitrile due to insignificant 2,4,5-TBEE decay (<10% after 72 h). Photoreductive dechlorination of 2,4,5-TBEE can form three isomeric butoxyethyl dichlorophenoxyacetates (DBEEs, *i.e.*, 2,4-DBEE, 2,5-DBEE, and 3,4-DBEE), but an authentic standard is only available for 2,4-DBEE. Because of the similar octanol–water partition coefficients of the three isomers,^{56–58} it was hypothesized that they would have very similar retention times in HPLC. We observed only one peak at the retention time corresponding to 2,4-DBEE, suggesting that either all three isomers co-eluted or 2,4-DBEE was the dominant product. Additionally, it was estimated that the three isomers would feature similar molar extinction coefficients at 230 nm (the DAD detection wavelength) with difference within 5%, which was the difference between the molar extinction coefficients for 2,4-DBEE and 2,4,5-TBEE in methanol at 230 nm (Table S5†). Accordingly, the total amount of DBEEs were estimated using the 2,4-DBEE calibration curve. Fig. 5A shows the evolution of DBEEs in *n*-heptane and 2-propanol from 2,4,5-TBEE photolysis. In the early phase of the experiments (*i.e.*, <40% 2,4,5-TBEE decay), DBEE formation accounted for all of the 2,4,5-TBEE decay. With more extensive 2,4,5-TBEE decay, the accumulation of DBEEs deviated from the 1 : 1 line, which may be attributed to their further photolysis. Indeed, a new HPLC peak, with a shorter retention time than the DBEE peak, appeared in the *n*-heptane sample when >83% of the initial 2,4,5-TBEE had decayed.

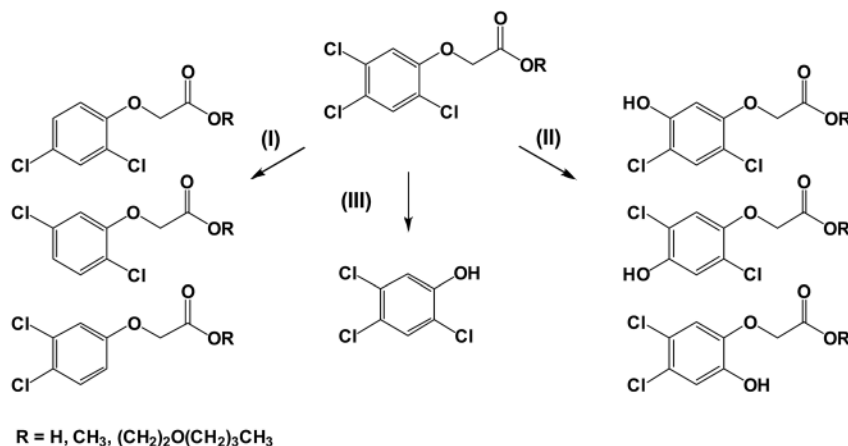


Fig. 4 Putative photolysis pathways of chlorinated phenoxyacetic acid herbicides: (I) photoreductive dechlorination, (II) photosubstitution of chlorine by a hydroxyl group, and (III) cleavage of the ether bond.

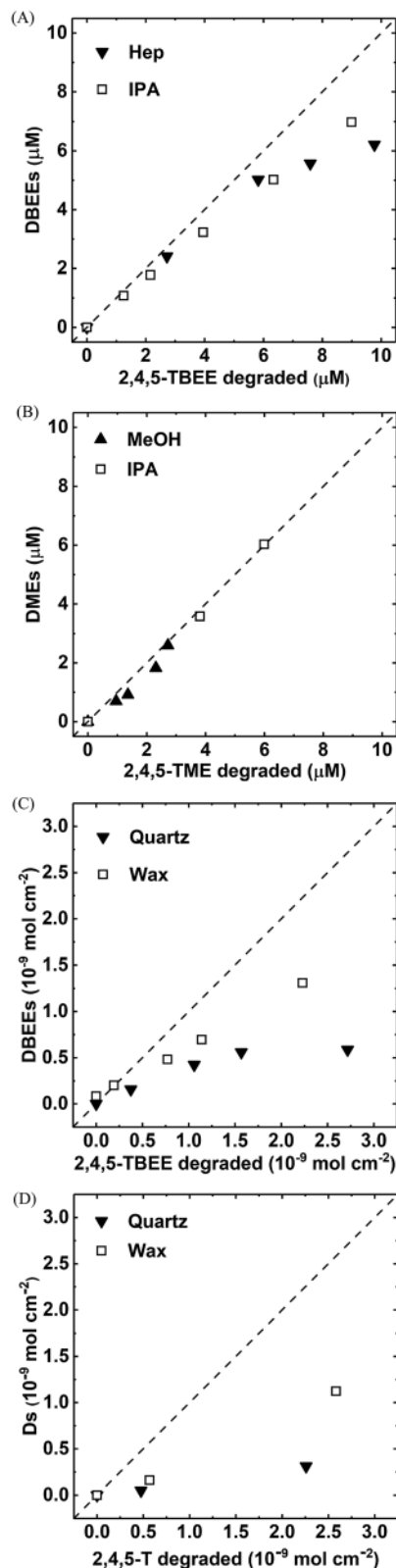


Fig. 5 Formation of reductive dechlorination products from the photolysis of (A) 2,4,5-TBEE and (B) 2,4,5-TME in organic solvents, and (C) 2,4,5-TBEE and (D) 2,4,5-T on surfaces. Hep = *n*-heptane, IPA = 2-propanol, MeOH = methanol, quartz = quartz surface, wax = paraffin wax surface. Conditions: the sunlight simulator intensity was set to 0.68 W m^{-2} at 340 nm; initial concentration of parent compound: $10 \mu\text{M}$ in organic solvents and $3 \times 10^{-9} \text{ mol cm}^{-2}$ on surfaces; 26°C .

Using a similar method, the methyl dichlorophenoxyacetates (DMEs, *i.e.*, 2,4-DME, 2,5-DME, and 3,4-DME) were quantified in the 2,4,5-TME samples in 2-propanol and methanol (Fig. 5B). In both solvents, the formation of DMEs accounted for 68–100% of 2,4,5-TME decay throughout the experiment. The *n*-heptane samples for 2,4,5-TME photolysis were not analyzed by HPLC due to the extensive loss (presumably due to volatilization) during solvent exchange for reverse-phase HPLC analysis. However, the formation of the three DMEs from 2,4,5-TME photolysis in *n*-heptane, as well as in 2-propanol and methanol, was confirmed by GC-MS using chemical ionization and the full scan mode of MS. The most distinct product peaks for the irradiated 2,4,5-TME samples are three consecutive peaks with retention times of less than 0.2 min apart (Fig. 6). These peaks show identical mass spectra featuring m/z 235, 237, and 239 with a ratio 9 : 6 : 1 (Fig. S7B–D†), which suggest the presence of two chlorine atoms in the molecule. The second peak was confirmed as 2,4-DME ($298.3 \pm 25.0^\circ\text{C}$)⁵⁷ using an authentic standard. Based on the boiling points of the three isomers,^{56,58} it was suspected that the first and third peaks were 2,5-DME ($296.1 \pm 25.0^\circ\text{C}$), and 3,4-DME ($302.9 \pm 27.0^\circ\text{C}$), respectively. The signal intensity for all three isomers increased as 2,4,5-TME degraded (Fig. S6†). For the 2-propanol and methanol samples (up to 24% 2,4,5-TME decayed), the GC-MS spectra did not show other product peaks (cutoff signal to noise ratio of 5). For the *n*-heptane sample in which 86% of 2,4,5-TME decayed, an additional product peak was detected with a retention time shorter than 2,4-DME and a mass spectrum consistent with the presence of one chlorine atom (m/z 201 and 203, ratio 3 : 1, Fig. S7E†). This suggests that the DMEs can further degrade to form monochlorinated products. This observation also suggests that the unidentified HPLC peak observed in the irradiated 2,4,5-TBEE *n*-heptane samples could be a butoxyethyl chlorophenoxyacetate. 2,4,5-TBEE samples cannot be analyzed by GC-MS because of the low thermal stability of butoxyethyl group, which can introduce GC artifacts.

The formation of 2,4,5-trichlorophenol, the product anticipated from the cleavage of the ether bond of 2,4,5-TBEE and 2,4,5-T (pathway III),^{43,54,59} was monitored using HPLC, but its concentration was below the detection limit in all samples, corresponding to a yield less than 1.0% from parent compound photolysis.

3.4 Photoproducts of chlorinated phenoxyacetic acid herbicides on surfaces

The 2,4,5-T and 2,4,5-TBEE surface samples were analyzed using HPLC and UPLC-ESI(–)qTOF. Fig. 5C and D show the evolution of DBEEs and dichlorophenoxyacetic acids from 2,4,5-TBEE and 2,4,5-T photolysis on surfaces, respectively, as determined by HPLC. Concentrations of the dechlorination products of 2,4,5-TBEE (sum of 2,4-DBEE, 2,5-DBEE, and 3,4-DBEE) were quantified by HPLC as described in Section 3.3. A

DBEEs = $\sum(2,4\text{-DBEE}, 2,5\text{-DBEE}, 3,4\text{-DBEE})$, DMEs = $\sum(2,4\text{-DME}, 2,5\text{-DME}, 3,4\text{-DME})$, and Ds = $\sum(2,4\text{-D}, 2,5\text{-D}, 3,4\text{-D})$. Dash lines correspond to 1:1 stoichiometric conversion from the parent compound to the product.

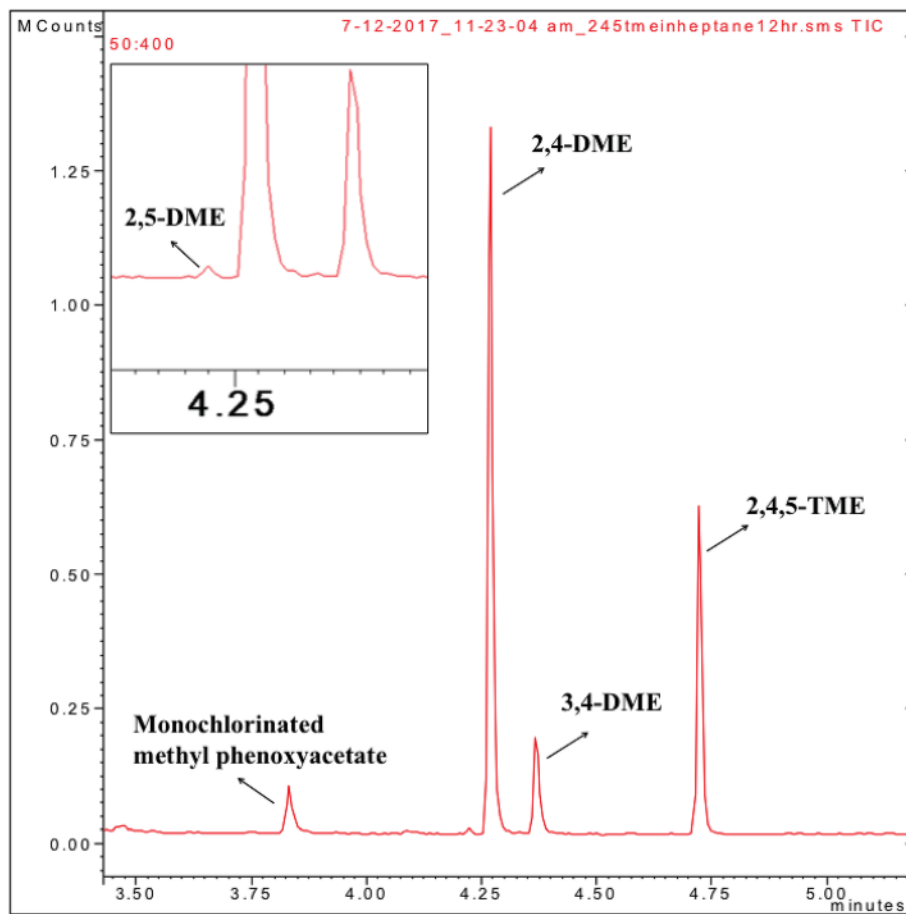


Fig. 6 Gas chromatogram for 2,4,5-TME and its degradation products after 12 h irradiation in *n*-heptane. GC-MS conditions: initial column temperature was set at 90 °C and held for 1 min, and then increased to 270 °C at a rate of 100 °C min⁻¹ and held for 10 min. MS full scan with chemical ionization using methanol. The mass range of the MS scan was 50–400 *m/z*.

similar method was also used to quantify the concentrations of dechlorination products of 2,4,5-T, for which the sum of 2,4-D, 2,5-D, and 3,4-D was estimated using the HPLC calibration curve of 2,4-D.

In contrast to that observed in organic solvents, the amount of photoreductive dechlorination products accounted for less than 60% of the parent compound decay on surfaces on a molar basis. On wax surface, DBEEs accounted for 51–60% of 2,4,5-TBEE decay, while dichlorophenoxyacetic acids accounted for 28–43% of 2,4,5-T decay; on quartz surface, the percentage was even lower (10–42%). Similar to that observed in solvents, the yield of 2,4,5-trichlorophenol from 2,4,5-T and 2,4,5-TBEE photolysis on surfaces was also less than 1.0%. A recent study on the photoproducts of 2,4-D ethyl ester on glass surface and leaf cutin surface proposed that 2,4-D ethyl ester can hydrolyze to form the corresponding acid (2,4-D),⁶⁰ but 2,4,5-T was not detected in the 2,4,5-TBEE surface samples, corresponding to a yield less than 1.5% from parent compound decay. These findings suggest that ester hydrolysis of 2,4,5-TBEE did not appreciably occur in the examined systems.

For each surface experiment, additional samples were collected for UPLC-ESI(–)-qTOF analysis at three time points: time zero (t_0), the time corresponding to ~25% parent

compound decay (t_m), and the time corresponding to approximately 90% parent compound decay or 48 h whichever is shorter (t_f). Table 2 summarizes the results regarding the three groups of putative photoproducts shown in Fig. 4 for the t_f samples. None of these putative products were detected in the t_0 or t_m samples with sufficient confidence. Dichlorophenoxyacetic acids were detected from 2,4,5-T photolysis on surfaces, while DBEEs were not detected from 2,4,5-TBEE photolysis. However, monochlorinated products were detected in both 2,4,5-T and 2,4,5-TBEE samples, suggesting further decay of the dichlorinated products. The putative products corresponding to photosubstitution of chlorine by a hydroxyl group (II) and the cleavage of the ether bond (III) were not detected. The absence of DBEE signals in the UPLC-ESI(–)-qTOF analysis for 2,4,5-TBEE is in contrast to their detection by HPLC (Fig. 5C). It may be attributed to the surfactant present in the extracts of surface samples, which can significantly suppress ionization during the UPLC-ESI(–)-qTOF analyses. Overall, the UPLC-ESI(–)-qTOF analysis of 2,4,5-T and 2,4,5-TBEE photoproducts confirmed the prevalence of the photoreductive dechlorination pathway (I), but did not identify new products that can close the mass balance for phenoxyacetic acid herbicide photolysis on surfaces. The analysis of 2,4-D and 2,4-DBEE photoproducts on

Table 2 Photoproducts of 2,4,5-T and 2,4,5-TBEE analyzed by UPLC-ESI(–)-qTOF.^a The three groups of putative photoproducts (I), (II), and (III) correspond to the structures in Fig. 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; $\Delta m/z$ = (measured m/z – calculated m/z)/calculated $m/z \times 10^6$; N.D. = not detected

Parent compound	Surface	t_f (h)	Parent decay	Putative products			
				(I) ^b			
				Dichlorinated	Monochlorinated	(II) ^c	(III) ^d
2,4,5-T	Quartz	6	87%	Detected ^e RT = 3.73 min m/z = 218.9620 $\Delta m/z$ = 1.8 ppm	Detected ^e RT = 1.62 min m/z = 185.0004 $\Delta m/z$ = –0.5 ppm	N.D.	N.D.
	Wax	48	90%	Detected ^e RT = 3.69 min m/z = 218.9624 $\Delta m/z$ = 3.7 ppm	Detected (weak signal) ^e RT = 1.62 min m/z = 185.0020 $\Delta m/z$ = 8.1 ppm	N.D.	N.D.
2,4,5-TBEE	Quartz	6	73%	N.D.	Detected ^e RT = 7.74 min m/z = 285.0834 $\Delta m/z$ = –21 ppm	N.D.	N.D.
	Wax	48	98%	N.D.	Detected ^e RT = 7.71 min m/z = 285.0899 $\Delta m/z$ = 1.8 ppm	N.D.	N.D.

^a Product identification was based on measurements of exact masses; authentic standards were not used. ^b Reductive dechlorination products: dichlorinated and monochlorinated phenoxyacetic acids or butoxyethyl phenoxyacetates, corresponding to pathway (I) in Fig. 4. ^c Products formed through photosubstitution of chlorine by a hydroxyl group, corresponding to pathway (II) in Fig. 4. ^d Ether bond cleavage product 2,4,5-trichlorophenol, corresponding to pathway (III) in Fig. 4. ^e It is unknown which isomer(s) is/are represented by this peak.

quartz and wax surfaces by UPLC-ESI(–)-qTOF also did not yield additional information (Table S6†).

3.5 Direct photolysis mechanism of chlorinated phenoxyacetic acid herbicides

We observed that reductive dechlorination is the dominant pathway for the direct photolysis of trichlorinated phenoxyacetic acid herbicides (2,4,5-TBEE and 2,4,5-TME) in methanol, 2-propanol, and *n*-heptane (Fig. 5A and B). Previously, the butyl, methyl, and butoxyethyl esters of 2,4-D were also shown to undergo photoreductive dechlorination in hexane and hexadecane.^{43,55} Our results suggest that photoreductive dechlorination can be important in the more polar solvents methanol and 2-propanol. Additionally, the results also suggest that the additional chlorine substitution on the aromatic ring does not significantly impact the reaction pathways of chlorinated phenoxyacetic acid herbicides. The similar photolysis behavior between the esters of 2,4,5-T and 2,4-D in organic solvents echoes the similarity in degradation pathways between 2,4,5-T and 2,4-D in water.^{43,54,59} Faster photolysis was observed in organic solvents of lower polarity, where the quantum yields were higher (Fig. 1 and 3). It was previously proposed that polar solvents are more likely to interact with and to quench polarizable excited states relative to less polar solvents; this rationale was used to explain the decrease in dioxin direct photolysis rates with increasing solvent polarity.⁸ This mechanism may also apply to our systems.

Previous studies have investigated photolysis of 2,4-D and 2,4,5-T in water and reported that the major pathways are

photosubstitution of chlorine by a hydroxyl group and cleavage of the ether bond (II and III in Fig. 4), rather than reductive dechlorination.^{54,59} This difference in pathways may account for the higher quantum yields of 2,4-D and 2,4,5-T in water than those in methanol and acetonitrile, despite that water is a more polar solvent. Nevertheless, the quantum yields of 2,4-D and 2,4,5-T in water is 3–9 times lower than those in 2-propanol.

In addition to polarity, H-donating ability also varies among acetonitrile, methanol, 2-propanol, and *n*-heptane. Because the photoreductive dechlorination process involves the generation of a radical *via* homolysis of the C–Cl bond in an excited molecule and subsequent abstraction of a hydrogen atom from solvent,⁹ the H-donating ability of solvent molecules may also influence photolysis. Table S7† compares the dissociation energy of the weakest C–H bond in the four solvent molecules.^{61–64} *n*-Heptane has the highest C–H bond dissociation energy, followed by methanol and acetonitrile, and then 2-propanol. Since the poorest H-donor (*n*-heptane) exhibited the fastest photolysis, it can be concluded that H-abstraction is not rate-limiting and that the H-donating ability of organic solvents does not appreciably influence photolysis rate.

On quartz and paraffin wax surfaces, the chlorinated phenoxyacetic acid herbicides degraded faster than or at comparable rates as in organic solvents of low polarity (Fig. 1). The fast photolysis on quartz was due to the high quantum yields rather than strong light absorption. In fact, the light absorption of phenoxyacetic acid herbicides on quartz is lower than that in organic solvents (Fig. 2 and S2†). Although the presence of surfactant in surface samples likely hindered product analysis

by UPLC-ESI(–)-qTOF, dechlorination was shown to be a prevalent pathway for 2,4-D, 2,4,5-T, and their butoxyethyl esters. However, the apparent yields of the dechlorination products (*i.e.*, dichlorophenoxyacetic acids and DBEEs from 2,4,5-T and 2,4,5-TBEE, respectively) on surfaces was much lower than those in organic solvents (Fig. 5). 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. Assuming the first reason to be valid, a preliminary kinetic model was developed for the accumulation of DBEEs from 2,4,5-TBEE photolysis on surfaces (detailed description provided in Text S5†). As shown in Fig. S8,† the time profile of DBEE concentrations predicted by the model does not agree with the experimental results. This suggests that the lower molar ratio of dechlorination products to parent compound decay on surfaces should be attributed to alternative reaction pathways in parallel with reductive dechlorination, and that these pathways are specific to surfaces. Further study is needed to identify these pathways.

4 Conclusion

The direct photolysis of six chlorinated phenoxyacetic acid herbicides (2,4-D, 2,4,5-T and their methyl and butoxyethyl esters) was investigated in organic solvents and on quartz and paraffin wax surfaces under simulated sunlight. Photolysis was enhanced in solvents of low polarity, and the enhancement was due to higher quantum yields rather than stronger light absorption in these solvents. Photolysis on paraffin wax, a surface closely resembling leaf cuticle,⁹ was slower than that on quartz, but was comparable to that in organic solvents of low polarity (*i.e.*, *n*-heptane and 2-propanol). Under the environmentally-relevant conditions employed in this study, most of the examined phenoxyacetic acid herbicides underwent photolysis at rates on par with rates of biodegradation, the major dissipation pathway currently considered for these herbicides.³² These results suggest that photolysis on leaf surfaces can appreciably influence the environmental fate of phenoxyacetic acid herbicides in the environment.

Product analysis shows that photoreductive dechlorination is the dominant pathway in organic solvents. While photoreductive dechlorination also plays an important role on quartz and paraffin wax surfaces, it cannot account for all of the photodegradation as quantified by loss of parent compounds. Photolysis on surface features unique pathways that requires further investigation.

Conflicts of interest

The authors have no conflict of interest to declare.

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