FORMATION OF PCDF FROM PHOTODEGRADATION OF SOLUTIONS OF POLYCHLORINATED PHENOXYACETIC ACID HERBICIDES

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Introduction

First introduced in 1940s, phenoxy herbicides are inexpensive and selective in targeting broad leave weeds, and are harmless to commercial crops. Unfortunately, the most common industrial process for production of one of the herbicides, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), involves a side-reaction forming highly toxic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD). In spite of its attractive herbicidal properties, by late 1980s, difficulties in manufacturing 2,4,5-T without the 2,3,7,8-TCDD contamination resulted in the banning and phase-out of this herbicide. Since then, other phenoxy herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-methyl-4-chlorophenoxyacetic acid (MCPA), have replaced 2,4,5-T.

Photodegradation[1], biodegradation[2] and combustion, through accidental fires control the fate of phenoxy herbicides in the environment. In particular, photodegradation of these herbicides has been reported to induce the production of polychlorinated phenols (PCP)[3]. The polychlorinated phenoxy species that form PCP might also produce polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) in solutions of phenoxy herbicides. A large body of literature exists on condensation of chlorophenols into various congeners of PCDD/F, via side reactions in thermal oxidation processes, as reviewed by Altarawneh et al.[4] The absorbance of high energy from UV radiation could also initiate ring activation, dechlorination and radical condensation reactions in aqueous phase that could result in the formation of PCDD/F. However, until present, the UV-induced generation of PCDD/F from solutions of phenoxy herbicides via PCP has not been reported in the literature. Likewise, no measurements exist on the formation of PCDD/F from photodegradation of chlorophenols, except for pentachlorophenol[5,6].

This contribution reports new measurements of PCDD/F forming in solutions of phenoxy herbicides as a consequence of their photodegradation, indicating a new source of PCDD/F in the rural environment. We selected 2,4,5-T and 2,4-D, the former because of its high chlorine content and the latter due to its widespread use, and applied methanol as solvent to achieve higher initial concentration of the herbicides. The results demonstrate formation of several PCDF congeners, especially 2,3,7,8-TCDF, by UV irradiation of solutions of phenoxy herbicides.

Materials and methods

Methanol (99.9 %) was obtained from RCI Labscan Ltd, while Merck Pty Ltd supplied high purity hexane and dichloromethane, both of gas chromatography mass spectroscopy (GCMS) grade. Sigma-Aldrich provided the herbicides, 2,4,5-T (97 %) and 2,4-D (98 %), and chlorophenol standards originally made by Fluka (3-CP, 3,4-DCP) and Supelco (2-CP, 2,4-DCP). Alfa Aesar furnished 2,5-DCP and 4-CP and Univar supplied phenol. The pesticide methyl ester mix was acquired from Restek. Wellington laboratories supplied the EPA 1613 standards and the $^{13}C_6$ labelled solution of 2,4,6-trichlorophenol, applied as an internal standard to quantitate the VOC products.

A typical experiment involved placing a quartz tube with 60 mL of a methanolic solution containing 18 mg of herbicide, into a photochemical reactor (South New England Ultraviolet Company, USA), then continuously stirring and irradiating the solution for up to 120 min. The reactor operated at a wavelength of 300 nm, while the light intensity, measured using ferrioxalate actinometry method[7], amounted to 2.63×10^{-8} E s^{-1}. The identification and quantitation of intermediate products involved a single quadrupole Agilent GCMS (6890 series GC system coupled with a Agilent 5973 Network MS detector) equipped with a Rtx-200MS column (30 m × 0.25 mm i.d. × 15 μm). The analysis conditions were as follows: front inlet temperature 220 °C; helium as

carrier gas (1.4 mL min^{-1}); injection mode split 15:1; injection volume 1 μL; oven temperature 45 to 290 ^{o}C; total analysis time 41 min.

A Varian HPLC served to quantitate the unreacted herbicides from the irradiation reaction under the following conditions: UV detector 254 and 289 nm; Ultra-C18 HPLC column (Restek, 150 mm × 4.6 mm i.d. × 5 um); acetonitrile as mobile phase A (99.7%, Unichrom) and 0.2 % diluted formic acid as mobile phase B (99 %, Univar). Initial ratio of A:B corresponded to 30:70 (v/v) ramped to 70:30 (v/v) in 18 min at a flow rate of 1 mL min^{-1}, with the column held at 25 ^{o}C.

The MS/MS methodology of Chen et al.[8] was adopted for the analysis of PCDD/F, based on the subsequent pollutant concentration in a rotary evaporator (to a final solution volume of 1 mL), sample clean-up, and application of labelled standards of the US EPA Method 1613[9]. We modified the US EPA Method 1613 to include the determination of mono- to trichlorinated congeners of CDD/F. A volume of 1 μL of the final concentrated samples (20 μL) was injected into a high resolution gas chromatograph - ion trap mass spectrometer (HRGC-ITMS/MS) operated with a VF-5MS column (Varian, 60 m × 0.25 mm i.d. × 0.25 μm). In this analysis, helium flowed at 1 mL min^{-1} as the carrier gas. The instrument detection limits to PCDD/F corresponded to between 0.2 to 3.6 pg μL^{-1}. The supplied herbicides were analysed for their PCDD/F impurities using the same analytical method. Procedural blank runs confirmed the absence of PCDD/F contamination from the solvent, glassware and clean-up columns.

Results and discussion

Following exposure to UV radiation at 300 nm for 120 min, the 2,4,5-T herbicide experienced around 27.7% degradation, while 26.3% of 2,4-D degraded within the same time period. Figure 1 illustrates typical chromatograms for the photodegradation of 2,4,5-T and 2,4-D while Table 1 lists the detected species.
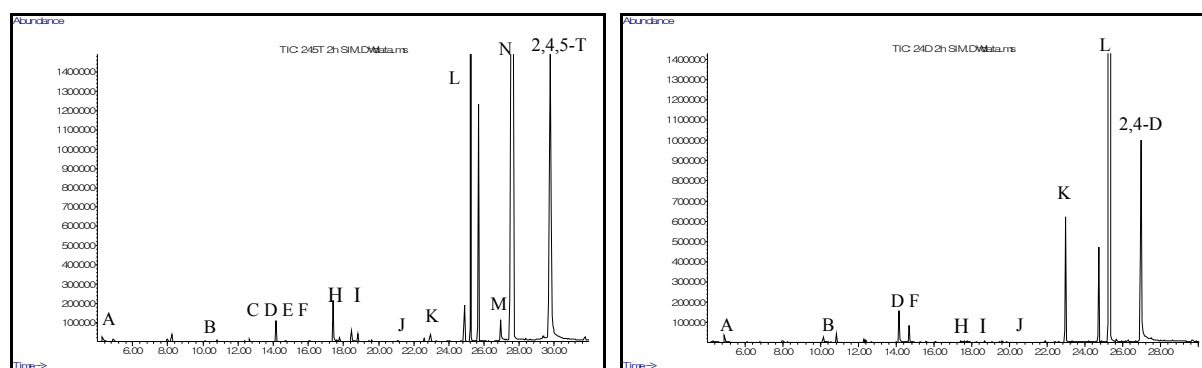

Fig. 1: *GCMS chromatograms of samples of 2,4,5-T and 2,4-D after 120 min of irradiation*

Table 1: *Photodegradation products of 2,4,5-T and 2,4-D*

No.	Compound	Retention time (min)	2,4,5-T	2,4-D
A	Hydroxyacetic acid, methyl ester	4.88	√	√
B	Phenol	10.15	√	√
C	2,5-dichlorophenol	14.14	√	
D	2,4-dichlorophenol	14.15	√	√
E	3-chlorophenol	14.45	√	
F	4-chlorophenol	14.69	√	√
G	2,4,5-trichlorophenol	17.43	√	
H	3,4-dichlorophenol	18.45	√	
I	Phenoxyacetic acid methyl ester	18.68	√	√
J	2,4,5-trichlorobenzaldehyde	20.68	√	
K	4-chlorophenoxyacetic acid methyl ester	22.60	√	√
L	2,4-D methyl ester	25.25	√	√

M	2,4-D	26.89	√	
N	2,4,5-T methyl ester	27.57	√	

Photodegradation of 2,4,5-T and 2,4-D in methanolic solution yielded several aromatic products including lower chlorinated phenoxyacetic acid herbicides, chlorinated phenols, phenol, chlorinated benzenes and chlorinated benzaldehyde, as well as methyl esters of acidic moieties present in molecules of 2,4,5-T and 2,4-D, such as hydroxyacetic methyl ester. UV irradiation of solutions of phenoxy induces homolytic cleavage of phenoxy molecules into chlorine and phenylhydroxyacetic acid radical (with the radical site located on the ring C2 atom), initiating the photodegradation process. The Cl radical further abstracts a hydrogen atom from the solvent forming the hydroxymethyl radical, CH_2OH[10]; $Cl + CH_3OH \rightarrow H^+ + Cl^- + CH_2OH$. The CH_2OH and CH_3O radicals interconvert in the presence of an acid catalyst[11]. Abstraction of a H atom from the methanol solvent by the phenylhydroxyacetic acid radical produces 2,4-D as the first product from 2,4,5-T. The reaction between a CH_3O radical and a phenoxy formed a phenoxyOCH_3 adduct that decomposes into phenoxy methyl ester and OH radical. Once the concentration of OH radicals builds up, they can produce displacement reaction of the side chain leading to the formation of polychlorinated phenols. Subsequent dechlorination (homolytic cleavage of C-Cl bond) produces congeners of less chlorinated phenols.

The analysis of the supplied phenoxy herbicides revealed traces of PCDF impurities, presumably from the manufacturing process. But, exposing the phenoxy herbicides to UV radiation at 300 nm significantly increased the amount of PCDF present in the system, as illustrated in Fig. 2.
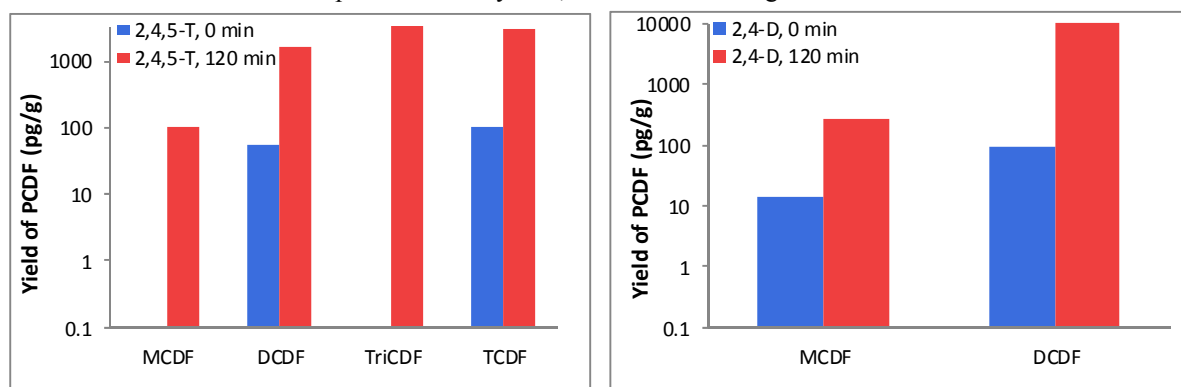

Fig. 2: PCDF impurities and photodegradation products (pg/g) of 2,4,5-T (left) and 2,4-D (right)

Under irradiation, 2,4,5-T and 2,4-D in solutions degrade to form mainly lower chlorinated PCDF congeners, with no PCDD detected in the reacting systems[12]. The extra chlorine atom present at position 5 in 2,4,5-T results in the formation of more PCDD/F congeners in comparison to 2,4-D (cf. right hand sides of Figs. 3 and 5). Only 2,4,5-T produced 2,3,7,8-TCDF, one of the most toxic PCDD/F congeners[9]. The formation of PCDF from phenoxy herbicides cannot occur directly through phototransformation of the herbicides themselves, but rather through a chain reaction involving polychlorinated phenols as PCDF precursors. Tetrachlorinated DF arising from photodegradation of 2,4,5-T is expected to occur via the condensation of two dichlorophenoxy radicals. The formation of lower chlorinated PCDF proceeds either via the same radical-radical reactions of less chlorinated phenoxy radicals or by dechlorination of higher chlorinated PCDF congeners.

This contribution has reported a new source of PCDD/F in rural environment, by demonstrating the existence of pathways for the formation of PCDF from the photolysis of solutions of phenoxyacetic acid herbicides.

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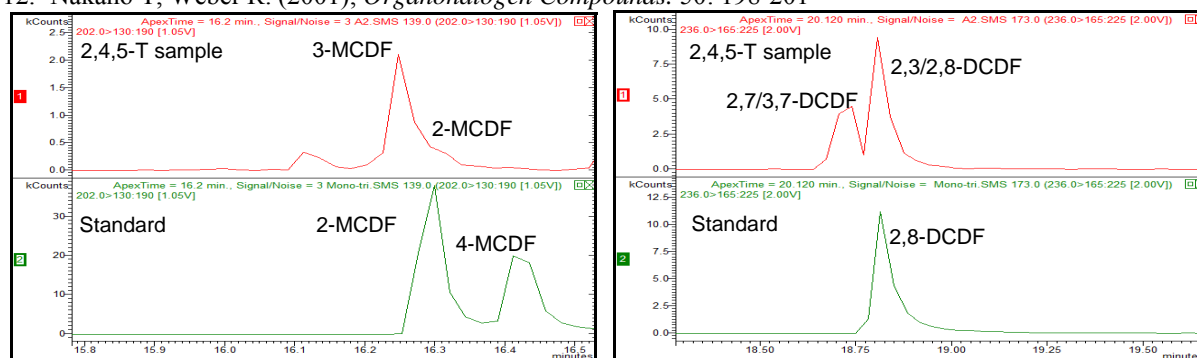
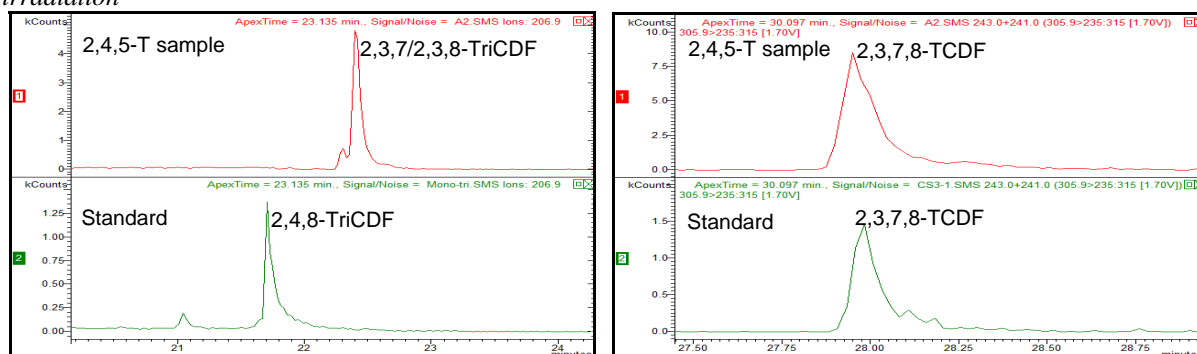**Fig. 3**: *GC-MS/MS chromatogram of the MCDF (left) and DCDF (right) in 2,4,5-T sample after 120 min irradiation*

Fig. 4: *GC-MS/MS chromatogram of the TriDF (left) and TCDF (right) in 2,4,5-T sample, after 120 min irradiation*
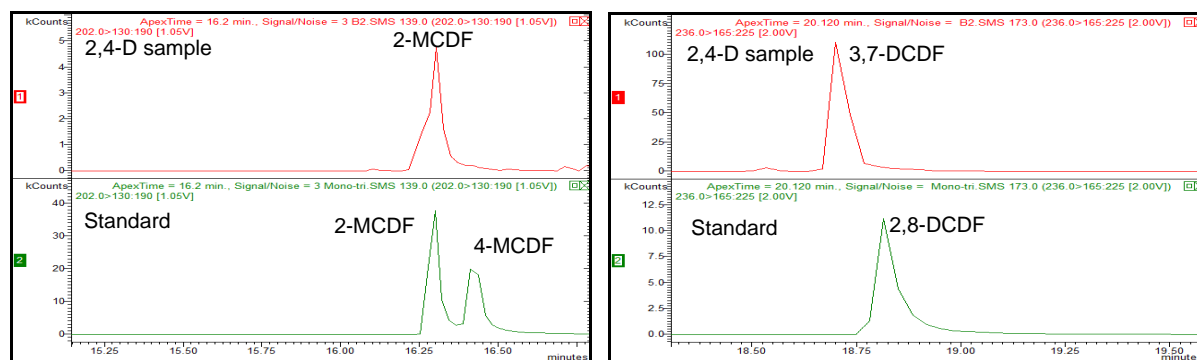
Fig. 5*: GC-MS/MS chromatogram of the MCDF (left) and DCDF (right) in 2,4-D sample, after 120 min irradiation*