



## Formation of dioxins during exposure of pesticide formulations to sunlight

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### ABSTRACT

Chlorinated pesticides can contain impurities of dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and their precursors, as a result of various manufacturing processes and conditions. As precursor formation of PCDD/Fs can also be mediated by ultraviolet light (UV), this study investigated whether PCDD/Fs are formed when currently used pesticides are exposed to natural sunlight. Formulations containing pentachloronitrobenzene (PCNB;  $n = 2$ ) and 2,4-dichlorophenoxyacetic acid (2,4-D;  $n = 1$ ) were exposed to sunlight in quartz tubes, and the concentration of 93 PCDD/F congeners were monitored over time. Considerable formation of PCDD/Fs was observed in both PCNB formulations (by up to 5600%, to a maximum concentration of  $57\,000\ \mu\text{g}\ \sum\text{PCDD/F}\ \text{kg}^{-1}$ ) as well as the 2,4-D formulation (by 3000%, to  $140\ \mu\text{g}\ \sum\text{PCDD/F}\ \text{kg}^{-1}$ ). TEQ also increased by up to 980%, to a maximum concentration of  $28\ \mu\text{g}\ \text{kg}^{-1}$  in PCNB, but did not change in the 2,4-D formulation. Assuming similar yields as observed in the present study as a worst case scenario the use of PCNB in Australia may result in the formation of  $155\ \text{g}\ \text{TEQ}\ \text{annum}^{-1}$ , contributed primarily by OCDD formation. This warrants detailed evaluations on the contemporary release of PCDD/Fs to the environment after the use of pesticides. Changes in congener profiles (including the ratio of PCDDs to PCDFs (DF ratio)) suggest that pesticide sources of PCDD/Fs after sunlight exposure may not be recognized based on matching source fingerprints established from manufacturing impurities. These changes also provide preliminary insights into the possible formation routes and types of precursors involved.

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### 1. Introduction

The presence of polychlorinated dibenzo-*p*-dioxin and furan (PCDD/F) impurities has been demonstrated repeatedly for chlorophenols. This includes wood treatment fungicides pentachlorophenol; PCP (Masunaga et al., 2001) and 2,3,4,6-tetrachlorophenol; 2,3,4,6-tetraCP (Persson et al., 2007), which are no longer used in many countries, and the banned phenoxy herbicide 2,4,5-trichlorophenoxyacetic acid; 2,4,5-T (Schechter et al., 1993). PCDD/Fs have also been detected in many currently used pesticides, including pentachloronitrobenzene (PCNB) and 2,4-dichlorophenoxyacetic acid (2,4-D) (Holt et al., 2010). The application of such pesticides, when used at high volumes, over long periods of time and/or if highly contaminated, has been associated with substantial release of PCDD/Fs, and local, regional or larger-scale contamination of soils (Stellman et al., 2003; Persson et al., 2007; Weber et al., 2008), sediments (Uchimiya et al., 2007; Sundqvist et al., 2010), biota and/or food (Huwe et al., 2004).

During pesticide production, the key pathway for PCDD/F impurity formation occurs via precursor chemicals (Esposito et al., 1980). PCDD/F precursors include numerous compounds that originate either from (a) starting materials used for pesticide production, (b) intermediates and by-products formed during production process and/or (c) the active ingredient itself (Esposito et al., 1980; Ree et al., 1988; Masunaga et al., 2001). These include for example, PCP, other chlorophenols (CPs) such as 2,4,6-triCP, and representatives of phenoxy herbicides (e.g. 2,4,5-T), chlorobenzenes (CBs), polychlorinated phenoxyphenols (PCPPs) and polychlorinated diphenylethers (PCDPes). PCDD/F formation in the presence of such precursors is generally favored under alkaline conditions, heat (150–600 °C), with even lower temperatures in the presence of catalysts (e.g. copper, iron, aluminum salts, Fe(III)–montmorillonite clay) or radicals, as well as during irradiation with ultraviolet light (UV) (Esposito et al., 1980; Ree et al., 1988; Weber and Hagenmaier, 1999; Gu et al., 2011). Thus, it is possible to minimize PCDD/F formation during pesticide production via the use of alternative materials and/or carefully controlled and stable production conditions (Esposito et al., 1980). However, precursors that have not reacted during pesticide production also remain in the product as impurity or as active ingredient itself.

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In addition, precursors may form during pesticide degradation. For example, CPs may form from phenoxy herbicides by cleavage of the acids (Barnekow et al., 2001), PCP is formed as a metabolic breakdown product of PCNB (Renner and Hopfer, 1983) and dichlorprop degrades to CPs during photolysis (Climent and Miranda, 1997).

The conditions favouring PCDD/F formation from precursors during pesticide manufacture are also present in the environment (e.g. high temperatures during fires, catalytic active surfaces like Fe containing clays, alkaline soils, and most ubiquitously, UV radiation). Thus, pesticide use may result in the (additional) formation of PCDD/Fs after the use of PCDD/F precursor containing/contaminated products. This has been repeatedly demonstrated for PCP, which readily forms higher chlorinated PCDDs (particularly OCDD) when exposed to UV as solid or in water (Piccinini et al., 1998; Skurlatov et al., 1998; Hong et al., 2000), soil (Liu et al., 2002) and treated wood (Lamparski et al., 1984). Aside from these studies, PCP has also been reported to form PCDDs on Fe(III)–Montmorillonite clay (Gu et al., 2008), during combustion (Vikelsøe and Johansen, 2000), pyrolysis (Liu et al., 2008) and microbial mediated conditions (Öberg and Rappe, 1992). Solar irradiation of the commonly used biocide triclosan also results in the formation of 2,8-di-, 2,3,7- and 1,2,8-tri- and 1,2,3,8-tetrachlorinated PCDDs, and was suggested to contribute a substantial proportion to environmental PCDD loads (Buth et al., 2010). In addition, substantial PCDD/F release can result from the combustion of a number of different pesticides (Chen et al., 2011), including dichlorprop, dimethachlor, and chlorothalonil (Vikelsøe and Johansen, 2000). While there is considerable evidence to conclude that PCDD/F formation can occur from pesticide derived precursors in the environment, the extent of these processes across currently used pesticides remains largely unknown. Although some PCDD/F precursors are generally known or expected to be present (or formed) during pesticide production, they are not or only poorly characterized and quantified. This may be partially due to their presence at trace levels, the diversity of possible impurity mixtures and the analytical difficulty to separate many of these from the active ingredients in formulations. However, if PCDD/F precursors are present in pesticide products or are formed during degradation of the pesticide, their exposure to UV would be expected to result in the formation of PCDD/Fs.

This study investigated whether PCDD/F formation may occur during photolysis of current use pesticide formulations. Three different formulations, containing the active ingredients 2,4-D or PCNB and known to contain PCDD/F impurities, were exposed to natural sunlight in sealed quartz tubes. PCDD/Fs were monitored over time of exposure on a congener specific basis, thus providing initial information regarding possible PCDD/F formation mechanisms and the possible type of precursors involved.

## 2. Methods

### 2.1. Sample details

Three pesticide formulations which were known to contain PCDD/Fs (Holt et al., 2010) (and thus suspected to contain PCDD/F precursors) were selected for sunlight experiments. These included one liquid formulation with the active ingredient 2,4-dichlorophenoxyacetic acid (2,4-D; as 2,4-D-2-ethylhexyl ester) and two formulations containing pentachloronitrobenzene (PCNB, also known as quitozene) as granulated solid (PCNB1) and fine powder (PCNB2)) (Figs. S1 and S2, Supplementary data (SD)). Information regarding the pesticide formulations used for this study (e.g. active ingredient, manufacture date, matrix, active ingredient concentration), are provided in Tables S1–S5, SD.

Approximately 30 g of PCNB formulations and 24 g (equivalent to 20 mL) of 2,4-D formulation were added to quartz (sunlight exposed (SUN)) and Pyrex (control (CTRL)) tubes. All tubes were sealed with glass stoppers and parafilm; and the CTRL tubes were wrapped in thick paper toweling (followed by aluminum foil for longer-term deployments) to completely prevent sunlight penetration. Tubes were then continuously rotated in sunlight and subsampled at various times of exposure ( $T_{\text{hours of sunlight}}$ ). Experiments were carried out in Brisbane, Australia (at subtropical latitude: 27°33'33.63"S; longitude: 153° 2'37.37"E). The fine powdered PCNB2 formulation tended to clump and coat the inside of the quartz tube, despite continuous rotation and manual agitation pre- and post-sampling, likely decreasing light exposure of the remaining formulation. During a first experiment (Experiment A), both PCNB formulations (PCNB1-A and PCNB2-A) were deployed from 6 am to 6 pm during austral summer 2009 (25 of February to 4 of March), equivalent to 84 h sunlight (Fig. S2, SD). A second deployment (Experiment B) of cleaned tubes, freshly loaded with PCNB formulations (PCNB1-B and PCNB2-B) occurred during Autumn/Winter 2010 (25th of March to 8th June 2010) from 6 am to 6 pm to lengthen the period of time that PCNB1 and PCNB2 were exposed to sunlight (to 196.6 and 150.5 h for PCNB1 and PCNB2, respectively). The 2,4-D formulation was exposed to sunlight for 1.6 h (96 min) within 11:30 am to 16:00 pm on 7 of March, 2008 (Fig. S2, SD). Sunlight intensity ( $\text{W m}^{-2}$ ) was monitored at a nearby Department of Environment and Resource Management (DERM) air monitoring station at Rocklea (distance of approximately 5.6 km) using a pyranometer (80SPC Pyranometer, Pacific Data Systems) with a spectral range of 300–2800 nm (DERM, 2010a). The average hourly sunlight intensity is reported online with measurements logged every 10 s (DERM, 2010a,b). Daily maximum sunlight intensity occurred at 12 pm and ranged from 745 to 1167 and 200 to 982  $\text{W m}^{-2}$ , for the PCNB formulation experiments A and B, respectively. Average hourly sunlight intensity during the deployment of 2,4-D ranged from 410 to 700  $\text{W m}^{-2}$  (DERM, 2010b).

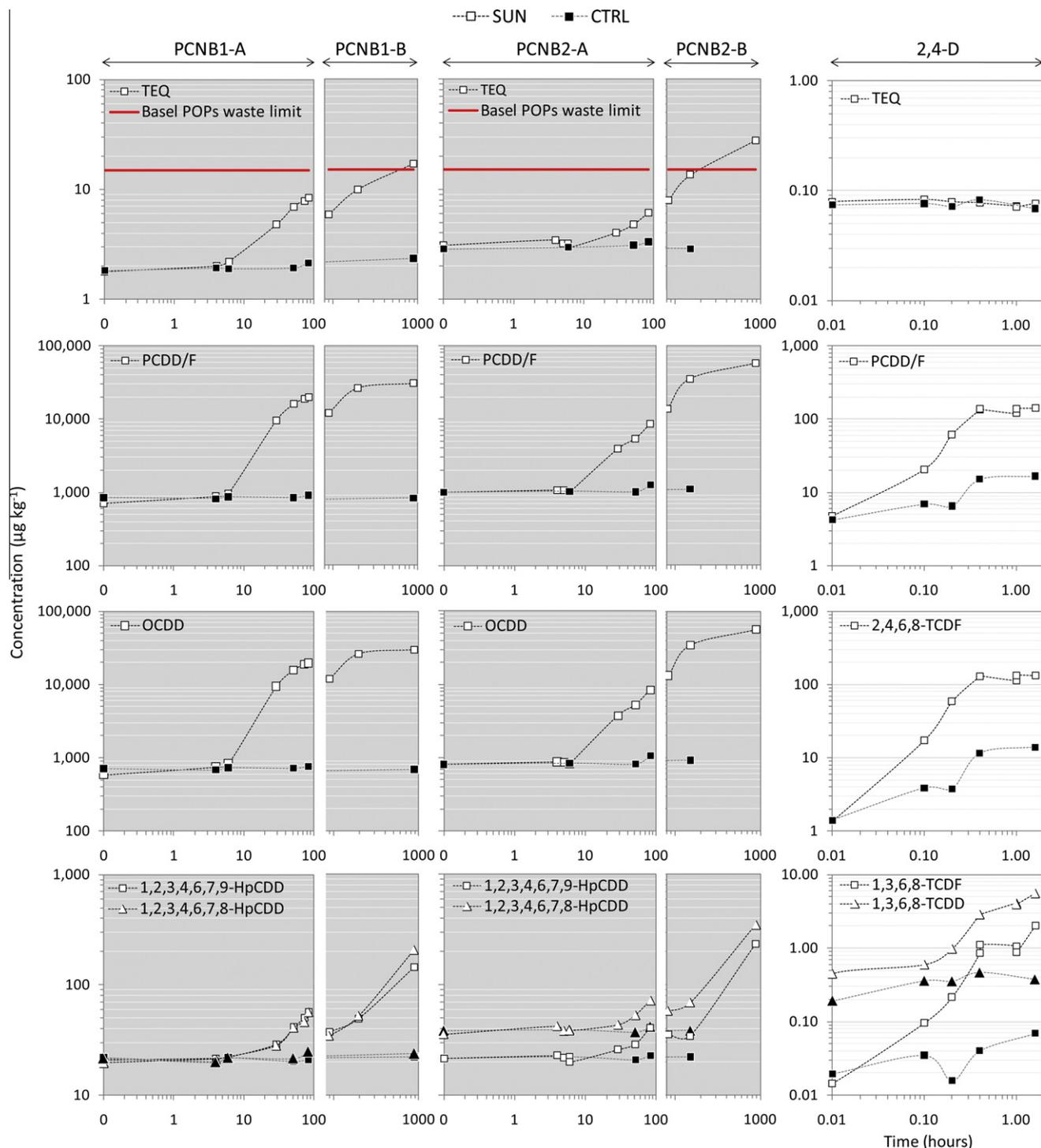
### 2.2. Analysis of PCDD/Fs

Sample extraction, cleanup, instrument analysis and identification/quantification of tetra- to octa-chlorinated PCDD/F congeners were carried out at an accredited laboratory (National Measurement Institute, Sydney) following US EPA method 1613 (isotope dilution method using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS)), and are detailed in (Holt et al., 2010). Non-2,3,7,8-substituted congeners (93 resolved peaks on a ZB-5 MS column) were identified based on their reported relative retention times (CIL, 2007; Fishman et al., 2007) and using fly ash analyzed under the same instrument conditions as the samples of the present study. A summary of the analytical procedures and detailed QA/QC process and measures for this study are included in the Supplementary data (Appendix S1).

## 3. Results and discussion

### 3.1. Formation of PCDD/Fs

Considerable formation of PCDD/Fs was observed during sunlight exposure of each of the three pesticide formulations (Fig. 1, Tables S1–S5, SD). Compared to unexposed ( $T_0$ ) samples, PCDD/F concentrations increased by approximately 2300% and 780% for PCNB1-A and PCNB2-A, respectively, during the initial 84-h exposure period of Experiment A. At maximum sunlight exposure duration of 833 h during Experiment B, PCDD/F concentrations in PCNB1-B and PCNB2-B had increased by approximately 3500%



**Fig. 1.** Concentrations of PCDD/Fs (sum of all congeners), selected congeners and TEQs in sunlight exposed and control pesticide formulations containing PCNB (Formulations 1 and 2; Experiments A and B) and 2,4-D. [Average concentrations are presented where replicate analysis was conducted; results for all samples are provided in Tables S1–S5 of the Supplementary data; <sup>†</sup> Basel Convention limit for defining ‘wastes consisting of, containing or contaminated with’ PCDD/Fs above the provisionally set low POP TEQ content of 15  $\mu\text{g TEQ kg}^{-1}$  (UNEP, 2011).]

and 6600%, respectively, compared to  $T_0$ , with final concentrations of up to 57 000  $\mu\text{g kg}^{-1}$ . Concurrently, TEQ levels in both PCNB formulations increased to a maximum of 17 and 28  $\mu\text{g TEQ kg}^{-1}$  (for PCNB1-B and PCNB2-B, respectively) with TEQ levels for both PCNB formulations after sunlight exposure finally exceeding levels above the low POPs limit (15  $\mu\text{g TEQ kg}^{-1}$ ) provisionally set by the Basel Convention (UNEP, 2011). Concentrations in dark control samples on the other hand remained relatively constant over the

experiment, and similar to the initial  $T_0$  or original PCNB formulations (Fig. 1, Tables S1–S5, SD). PCDD/F concentrations also increased in the 2,4-D formulation by 3000% during 96 min of sunlight exposure (from 4.5 to 140  $\mu\text{g kg}^{-1}$ ); however, there was no clear change in TEQ levels compared to respective  $T_0$  and dark controls (due to formation of non-2,3,7,8-PCDD/F (see below)). Photolytic formation of PCDD/Fs to the extent observed for these currently used pesticide formulations has to date only been

demonstrated for PCP, which is no longer used or strictly regulated in most countries. To our knowledge, PCNB has never been evaluated for its potential to form PCDD/Fs under sunlight. For 2,4-D, photolytic formation of PCDD/Fs was tested in 1971 (using purified 2,4-D dissolved in aqueous sodium hydroxide), but not observed in this previous study (Crosby and Wong, 1976). The authors suggested that the inability to detect di- to tetra-chlorinated dioxins (expected key formation products) may have been due to their higher instability under UV compared to higher chlorinated PCDDs (Crosby and Wong, 1976). Alternatively, predioxins to PCDD formation (see Fig. S7, SD) may not have been present in the purified 2,4-D used (see Section 3 on possible precursors and their proposed formation below).

### 3.1.1. Congener specific changes in pentachloronitrobenzene formulations

The observed increase in PCDD/F and TEQ concentrations during sunlight exposure of PCNB was primarily driven by formation of OCDD (Fig. 1). OCDD was also the dominant PCDD/F impurity in unexposed PCNB (i.e. manufacture impurity), but its predominant photolytic formation resulted in changes of the homologue and congener profiles between unexposed and exposed samples. Most prominently, the percent contribution of OCDD to  $\Sigma$ PCDD/F concentrations increased from 85% to 99% during sunlight exposure for both PCNB1 and PCNB2 (Fig. S3, SD). Similar to these results, OCDD has been reported as the main PCDD/F photo-product of PCP (Lamparski et al., 1980; Vollmuth et al., 1994; Piccinini et al., 1998; Skurlatov et al., 1998; Hong et al., 2000; Liu et al., 2002) and 3,4,5,6-tetrachloro-2-(2,3,4,5,6-pentachlorophenoxy)phenol (nonaC2PP) (Freeman and Srinivasa, 1983, 1986). For the present study, OCDD (and thus also PCDD/F) concentrations had not reached a plateau after 84 h of exposure to sunlight (Experiment A), and were still following a linear phase ( $R^2 = 0.99$ ) increase for PCNB2-A, but appeared to approximate a logarithmic function for PCNB1-A ( $R^2 = 0.97$ ) (Fig. 1). Results from Experiment B, for which sunlight exposure was prolonged showed further increases of  $\Sigma$ PCDD/F (again mainly OCDD) in both formulations but did not reach a plateau (Fig. 1). While maximum yields of OCDD may thus be higher than those observed during the experimental timeframes of the present study, these data demonstrate predominant formation of OCDD, and substantially increasing TEQ during sunlight exposure of PCNB formulations. A logarithmic increase of OCDD in the same order of magnitude has been described during 20-d exposure of PCP impregnated wood to artificial sunlight (Lamparski et al., 1980).

Apart from rapid formation of OCDD, a change in concentration of OCDF and other, hexa- to hepta-chlorinated PCDD and PCDF congeners was evident during exposure of both PCNB formulations to sunlight (Tables S2–S5, SD). However, their rate of formation was considerably slower compared to OCDD, and their mass contributed a relatively small proportion to PCDD/F or TEQ concentrations in both unexposed and exposed samples. Consistent with results from the present study, relatively minor and slow formation (compared to OCDD) of HxCDDs and HpCDDs (including, where identified, 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HpCDD; 1,2,3,4,6,7,9-HpCDD and 1,2,3,4,6,7,8-HpCDD) has previously been described from the photolysis of PCP in water (Piccinini et al., 1998) (Skurlatov et al., 1998) and photolysis of PCP impregnated into wood (Lamparski et al., 1980). However, formation of higher chlorinated PCDF congeners as observed in the present study during photolysis of pesticides or pesticide derived precursors has only been observed for rose bengal sensitized pesticide intermediate 2,4,5-trichlorophenol (2,4,5-triCP) (1,2,3,4,6,7,8-HpCDF and OCDF) (Skurlatov et al., 1998) and amongst the photo-products of the pesticide derived impurity nona2CPP in acetone (unidentified HpCDF) (Freeman and Srinivasa, 1983). The predominant

formation of OCDD and other congeners in PCNB, and their similarities to photolysis of PCP and nona2CPP, suggest that their formation occurs via similar precursor pathways, as discussed below.

### 3.1.2. 2,4-dichlorophenoxy phenol formulation (2,4-D)

The increase of  $\Sigma$ PCDD/F when 2,4-D was exposed to sunlight was largely influenced by formation of 2,4,6,8-TCDF (1.4–130  $\mu\text{g kg}^{-1}$ , or 9200% increase over the sunlight exposure period) which was also the dominant congener in the unexposed 2,4-D formulation (Figs. 1 and S4, SD). The contribution of 2,4,6,8-TCDF to  $\Sigma$ PCDD/F increased from 29% to 93% over the duration of sunlight exposure (Fig. S4, SD). Other congeners also increased considerably during 2,4-D sunlight exposure, including 1,3,6,8-TCDD (1100%); 1,2,3,6,8-PnCDD (300%); and 1,3,6,8-TCDF (14000%) (Table S1, SD); however, their contribution to total PCDD/F concentrations was relatively low (<4%). Some degradation of PCDD/F was also evident during sunlight exposure of 2,4-D with a ~95% and 90% decrease in concentration for 2,3,4,8-TCDF and 2,3,6,8-TCDF, respectively. While formation of PCDD/Fs has not previously been observed during photolysis of 2,4-D, it is interesting to note that the two primary photo-products observed in the present study (2,4,6,8-TCDF and 1,3,6,8-TCDD) are the main PCDD/F production impurities reported from 2,4-D and chloronitrofen manufacture (Yamagishi et al., 1981; Masunaga et al., 2001). 2,4,6,8-TCDF and 1,3,6,8-TCDD are also two major congeners reported to form biochemically from 2,4-diCP (Silk et al., 1997). These similarities in formation products, suggest that the PCDD/F formation processes involving the manufacture and/or thermal and metabolic transformation of 2,4-D, CNP and 2,4-diCP may provide more information on formation mechanisms during the sunlight exposure of the 2,4-D formulations of the present study (see below).

### 3.1.3. Possible precursors and PCDD/F formation routes

The formation of PCDDs and PCDFs from single aromatic molecules (phenols or benzenes) requires biaromatic intermediates (Esposito et al., 1980; Weber and Hagenmaier, 1999), which for the purposes of this study are referred to as predioxins or prefurans (Fig. S5, SD). Prefurans include compounds such as diphenylethers, *ortho*-hydroxy biphenyls and *diortho*-hydroxybiphenyls and are precursors to PCDFs only. The key predioxins are phenoxyphenols, which can form PCDDs via elimination of HCl and can theoretically form PCDFs, although this requires a mechanistically more demanding elimination of OH and H/Cl from the aromatic system (Fig. S5, SD). Previous studies where PCP was exposed to UV or sunlight proposed the formation of mainly OCDD via formation of nonaC2PP and cyclization to OCDD with (Freeman and Srinivasa, 1986) and without (Hong et al., 2000) sensitizer. These findings are also consistent with mechanistic considerations, as all that is required for cyclization of the phenoxyphenol, and OCDD formation, is the substitution of chlorine (Cl). The relatively slow formation of OCDD in the first 6 h followed by the increase in rate of formation suggests that the predioxins were only present at relatively low levels in the formulation at the beginning of the experiment and were mainly formed during the sunlight exposure. The increase in OCDD formation rates during the PCNB experiments indicates that PCP (a metabolite of PCNB (Renner and Hopper, 1983)) was formed initially during the sunlight exposure period, and that further predioxins and OCDD were formed via the known pathway shown in Fig. S6, SD.

The primary PCDD/F formation product from the sunlight exposure of 2,4-D was 2,4,6,8-TCDF, which indicates that prefurans were mainly responsible for formation (Fig. S7, SD). The 2,4,6,8-TCDF, was formed primarily within the first 30 min of sunlight exposure and when prolonging the experiment no further increase of 2,4,6,8-TCDF was observed (Fig. 1). This is a strong indication that the prefurans (most likely 2,2'-dihydroxy-3,3',5,5'-tetrachlorobiphenyl) were

already present in the formulation as an impurity from the production process and that the prefuran was largely converted within the first 30 min. The present results also suggest that the prefurans were not formed from 2,4-D, as it was present in high abundance (~12.5 g) and would be expected to give rise to a continuous increase of 2,4,6,8-TCDF over the entire exposure time of the study. In addition, the formation of prefurans – hydroxy biphenyls and dihydroxy biphenyls – requires the formation of a C–C bond between two aromatic compounds which is thought to require a bi-radical mechanism (Weber and Hagenmaier, 1999) (Fig. S7, SD). This may take place either at elevated temperatures of more than 350 °C or under conditions with high radical density, which are unlikely to occur during sunlight exposure but are present in the chlorination during the production process. Other congeners formed during sunlight exposure of 2,4-D, including 1,3,6,8-TCDD, and 1,3,6,8-TCDF (the observed second major PCDD/F formation products) are formed with continuously increasing levels over the time but at lower levels compared to 2,4,6,8-TCDF (Fig. 1). These two congeners can be formed via the predioxin 2,2'-dihydroxy-3,3',5,5'-tetrachlorobiphenyl (tetraCDOHB). The formation of this predioxin requires a mono-radical reaction of two 2,4-dichlorophenols (2,4-diCPs) or a 2,4-diCP and a 2,4,6-trichlorophenol (2,4,6-triCP) (Weber and Hagenmaier, 1999) (Fig. S7, SD). A preliminary screen using high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS) showed that 2,4,6-triCP was present in the 2,4-D formulation used for the experiment at levels of approximately 1–3%. The formation of 1,3,6,8-TCDD has also been described during the production of the pesticide intermediate 2,4-diCP via the condensation reaction involving 2,4-diCP and intermediate 4,6-dichloro-2-(2,4,6-trichlorophenoxy)phenol (pentaCPP) (Ree et al., 1988) (Fig. S7, SD). However, verification of these proposed precursors and more detailed assessments on the mechanisms of formation would ultimately require the establishment of trace analytical methods for identification and quantification of various predioxins and prefurans in pesticide formulations, to allow monitoring throughout sunlight exposure experiments.

The relatively minor increase of other PCDD/F congeners during the exposure of 2,4-D (and PCNB) formulations to sunlight in the present study may also be attributed to dechlorination of higher chlorinated congeners. It was not possible to determine the contribution of this process to the increase in concentration of individual congeners during the sunlight exposure of PCNB formulations. However, in sunlight exposed 2,4-D, a decrease in higher chlorinated 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,8-HxCDD along with a corresponding increase in 1,2,3,6,8-PnCDD and 1,2,3,7/1,2,3,8-TCDD, indicates that the latter congeners were most likely formed via dechlorination.

### 3.2. Environmental relevance

The present study demonstrates that substantial formation of PCDD/Fs can occur when currently used pesticide formulations (containing PCDD/F precursors) are exposed to sunlight. The formation yields and rates in the environment would, however, be dependent on a range of factors and prevailing environmental conditions. Generally, the concentration of reactants (i.e. precursors), their sorption to soil and light attenuation by soil particles affect photolytic reactions. Similarly, (precursor) chemical transport kinetics in soil, in particular their rate of diffusion from dark to irradiated zones within the soil, and their loss to the atmosphere via volatilization are key factors influencing the formation of photolysis products (Balmer et al., 2000). Information on the impact of such processes, conditions and factors on the precursor formation of PCDD/Fs in the environment are lacking, thus preventing quantification of their contribution to environmental contamination (USEPA, 2005). However, it has been demonstrated that elevated

(ppm–ppb) concentrations of PCDD/F precursors (including PCPP, PCP, CPs, HCB and PCDPes) can be present in soil and other environmental matrices (e.g. sediment/vegetation/biota) as a result of pesticide use (both agricultural and nonagricultural (e.g. wood treatment)) (Smelt and Leistra, 1974; Koistinen et al., 1997; Persson et al., 2007; Holt et al., 2008) and at pesticide manufacturing and waste disposal sites (Wu et al., 1997; Nascimento et al., 2004). It has also been shown that photolytic formation of PCDD/Fs occurs on a wide range of environmental matrices via precursors such as CPs, CBs, PCDPes and PCPPs including in soil (Liu et al., 2002), water (Hong et al., 2000) wastewater (Vollmuth et al., 1994) and impregnated wood (Lamparski et al., 1980). In addition, volatilization of precursors, while resulting in loss from soil, may nevertheless result in PCDD/F formation in the atmosphere, as proposed by Baker and Hites (2000) for the volatilization of PCP from soil and subsequent formation of PCDD/Fs in the condensed water phase. These studies provide further indications that photolytic formation of PCDD/Fs after application of current use pesticides is plausible. Assuming similar PCDD/F yields as observed in the present study as a worst-case scenario (greatest observed increase in concentration for 2,4-D or PCNB), the use of 2,4-D and PCNB in Australia would result in the formation of approximately 820 and 350000 g PCDD/Fs annum<sup>-1</sup> (155 g annum<sup>-1</sup> TEQ for PCNB), from a usage of 6000 and 6200 tons formulation annum<sup>-1</sup> (estimated average usage of active ingredient (Holt et al., 2010)), respectively. Considering estimated emissions from other sources in Australia (Bawden et al., 2004) and elsewhere (UNEP, 1999), release of PCDD/Fs to soil in this order of magnitude would represent among the most significant sources. This simple worst-case estimate serves to highlight a necessity to address the existing information gaps that prevent consideration of such sources in regional, national or global PCDD/F source inventories.

In addition to large increases in PCDD/F levels the results from the present study indicate that PCDD/F fingerprints identified for pesticide impurities can undergo considerable changes due to photolytic formation (and degradation) of individual congeners. This may give rise to fingerprints in the environment that no longer match the original pesticide source pattern (Figs. S3 and S4). In the present study, PCDD/F fingerprint changes for 2,4-D resulted in almost negligible contributions of most PCDD congeners and increased dominance of 2,4,6,8-TCDF. The congener fingerprint change for PCNB was drastic because of the dominant formation of OCDD and resulted in considerable increases in the ratio of PCDD to PCDFs (DF ratio), from approximately 7–8 to 220. Similar impacts on DF ratios may be expected during photolysis of PCP due to the predominant formation of OCDD. In this respect it is notable that pesticide manufacturing use and/or waste disposal has often been excluded as a source of contamination in soils and sediments with higher DF ratios compared to the known impurities (Ferrario et al., 2000; Gaus et al., 2001). The present study suggests that this ratio can alter markedly due to the formation of PCDD/Fs from specific pesticide derived precursors, as previously hypothesized for the relatively high OCDD contamination in Australian soils and sediments (Gaus et al., 2002). A better understanding on such fingerprint shifts from other pesticides or precursors, and in environmental matrices, would assist the apportioning of sources to existing environmental contamination in order to identify, prioritize and minimize their releases.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2012.03.058>.

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