FINGERPRINTING PESTICIDES: EXPANDING DIOXIN SOURCE KNOWLEDGE

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Introduction

Source identification is an important step to reduce or eliminate polychlorinated dibenzo-*p*-dioxin and furan (PCDD/F) emissions to the environment. Pesticide sources are poorly represented in source tracing studies where often only the PCDD/F fingerprint of pentachlorophenol (PCP) is used to characterize pesticide use. Recent studies show that many other pesticides contain PCDD/Fs[1], the use of which may represent an important source of PCDD/Fs to the environment. New information also suggests that formation from pesticide derived precursors in the environment may significantly alter the original PCDD/F fingerprint in pesticide products[2] a consideration not previously made in source tracing studies. Detailed congener-specific data on the PCDD/F levels in nineteen different pesticide products are presented in this study.

Materials and methods

Sampling and chemical analysis

For the present study, HRGC-HRMS raw data files of samples previously analysed and reported for the seventeen 2,3,7,8-substuted PCDD/F congeners and homologues were integrated to determine concentrations for all congeners (73 after data treatment, see below). These samples included a total of 21 pesticide formulations (13 active ingredients)[1] .

Identification and quantification of congeners

Congener-specific PCDD/F concentrations were determined as previously reported[1,2,3]. Results for some congeners were combined to enable direct comparison between source (pesticides from the present study and those analysed previously[2]) and receptor (e.g. Australian soils[4]) profiles, the analysis of which were carried out on different columns (DB-5 or ZB-5MS). Congeners that were combined or coeluted are marked with an asterix (*) throughout the text (Table 1). Where congeners were combined, the lower bound concentrations were summed and where all combined congeners were <LOQ, maximum LOQs were used.

Table 1. Abbreviations for combined or co-elutioned congeners

PCDDs: 1,2,4,7-TCDD* (1,2,4,7/1,2,4,8/1,3,7,8/1,4,6,9/1,2,4,6/1,2,4,9-TCDD); 1,2,3,4-TCDD* (1,2,3,4/1,2,3,6/1,2,6,9-TCDD); 1,2,3,6,9-PnCDD* (1,2,3,6,9/1,2,4,6,7/1,2,4,8,9-PnCDD); 1,2,3,7,8,9-HxCDD* (1,2,3,4,6,7/1,2,3,7,8,9-HxCDD)	PCDFs: 1,2,6,8-TCDF* (1,2,6,8/1,4,6,7/1,4,7,8-TCDF); 1,2,7,8-TCDF* (1,2,7,8/1,3,4,9/1,2,6,7-TCDF) 2,3,6,7-TCDF* (2,3,6,7/3,4,6,7/1,2,6,9-TCDF); 1,3,6,7,8-PnCDF* (1,3,6,7,8/1,2,4,6,7/1,3,4,6,7/1,3,4,7,8/1,2,3,6,8/1,2,4,7,8/1,4,6,7,8/1,3,4,7,9-PnCDF); 1,2,3,4,6-PnCDF* (1,2,3,4,6/1,2,4,6,9/2,3,4,6,8/1,2,3,4,7-PnCDF); 2,3,4,7,8-PnCDF* (2,3,4,7,8/1,2,4,8,9/1,2,6,7,9/1,2,3,6,9/2,3,4,6,7-PnCDF); 1,2,3,4,7,8-HxCDF* (1,2,3,4,6,7/1,2,3,4,7,8-HxCDF); 1,2,3,7,8,9-HxCDF* (1,2,3,4,8,9/1,2,3,7,8,9-HxCDF)

Results and discussion:

PCDD/F congener profiles in current use pesticides

Levels of PCDD/Fs in pesticide formulations included in this study ranged from 0.0043 – 1,500 ng ∑PCDD/F g^{-1} as reported previously[1]. Notably, the congener profiles of several of these pesticides were characterised by relatively high (61 - 98%) contributions of octachlorodibenzo-*p*-dioxin (OCDD), particularly PCNB, imazamox, mecoprop and chlordane (Figure 1). Similarly high OCDD contributions have previously been known for pentachlorophenol (PCP)[5,6] and *p*-chloranil[7]. Other congeners in the OCDD dominated pesticides included in the present study, which may provide additional congeners (markers) contributed <10% to ΣPCDD/F concentrations. These congeners include traces of 1,2,3,4,6,7,9-heptachlorodibenzo-p-dioxin (HpCDD), 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-heptachlorodibenzofuran (HpCDF) and octachlorodibenzofuran (OCDF) for PCNB; 1,2,3,4,6,7,9-HpCDD and 1,2,3,4,6,7,8-HpCDD for imazamox and OCDF for mecoprop. The chlordane formulation, analysed for the present study, contained 1,2,3,4,6,7,9-HpCDD, 1,2,3,4,6,7,8-HpCDD, OCDF,

1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,6,8,9-HpCDF it also contained 1,3,6,9-tetrachlorodibenzofuran (TCDF). In the past many of the congeners (1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDF) detected in the OCDD dominated pesticides (PCNB, MCPA, chlordane and imazamox) from the present study were previously only observed in PCP formulations and hence are used to identify PCP usage as a source of PCDD/Fs[5]. The contributions of PCDD/Fs via these pesticides may thus be difficult to distinguish based on congener profiles in environmental matrices dominated by OCDD, in particular in aged deposition matrices influenced by various fate processes and source mixtures.

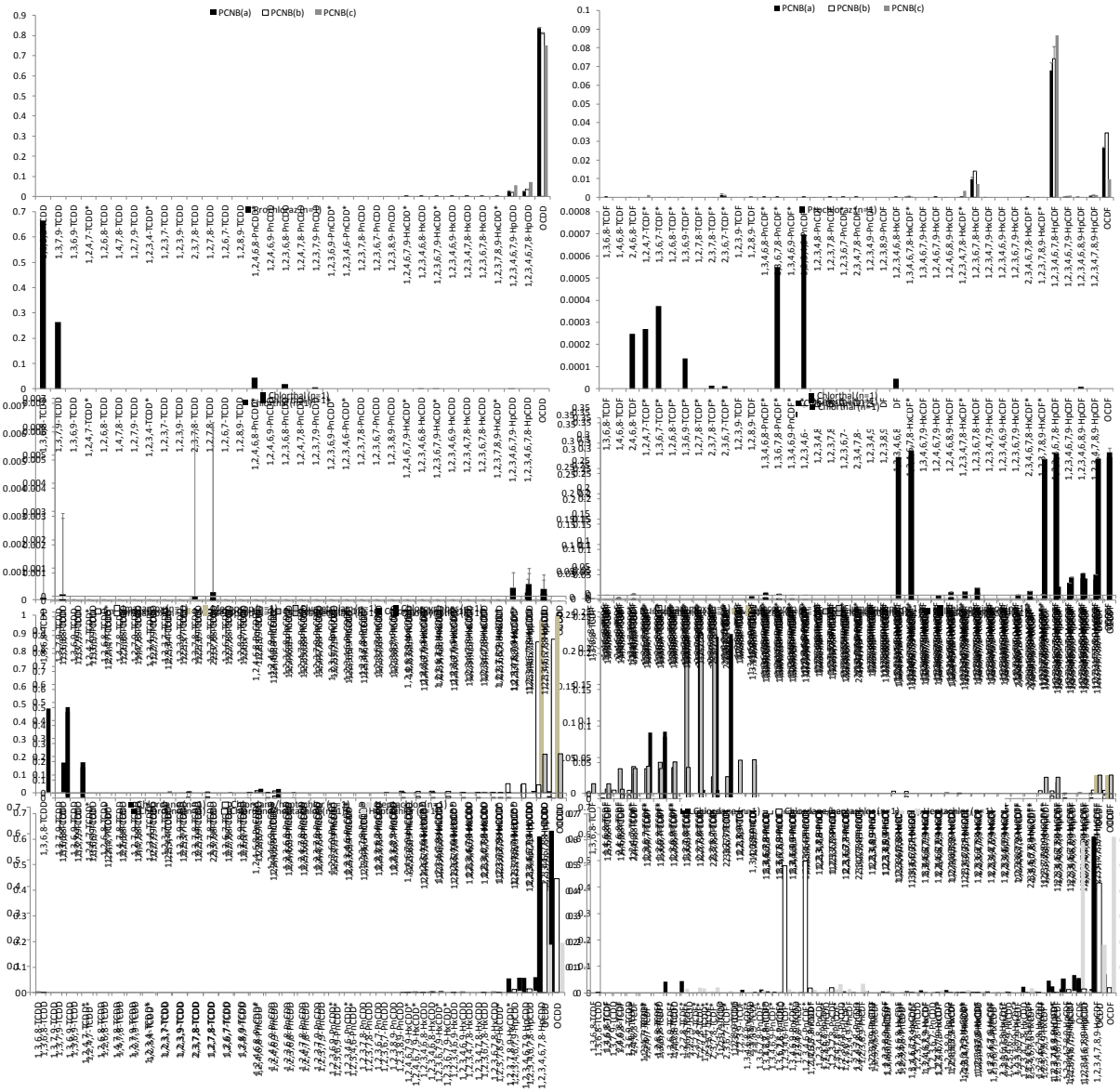

Figure 1. Congener profile (contribution to ∑PCDD/F) of PCNB; prochloraz; chlorthal [Average, minimum and maximum values of two replicates are presented for PCNB(a); PCNB(b) and chlorthal]; imazamox; mecoprop; flumetsulam; chlorpyriphos, and organochlorine pesticides - heptachlor and chlordane

PCDD/F congener profiles of the herbicides chlorpyriphos and flumetsulam and the fungicide prochloraz (Figure 1) were characterised by the lower chlorinated congeners 1,3,6,9-TCDD (47%), 1,3,7,9-TCDD (17%), 1,3,6,7-

TCDF* (9%) and 2,3,6,7-TCDF* (22%) in chlorpyriphos, TCDFs (including 1,2,7,8-TCDF* and 2,3,7,8-TCDF* with 22 and 23% contribution to the ∑PCDD/F, respectively) in flumetsulam, and 1,3,6,9- (67%) and 1,3,7,9-TCDD (26%) in prochloraz. In contrast, chlorthal and heptachlor formulations contained mainly higher chlorinated PCDD/Fs, including 1,3,4,6,7,8-hexacchlorodibenzofuran (HxCDF), 1,2,34,6,7,8-HpCDF and OCDF (with % contributions of 29, 28 and 28 to the ∑PCDD/F, respectively), for chlorthal, and 1,2,3,4,6-PnCDF* (50%) and OCDD (43%) in heptachlor/chlordane formulation.

Phenoxy herbicides 2,4-dichlorophenoxyacetic acid (2,4-D); 2,4-dichlorophenoxybutyric acid (2,4-DB) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T)/2,4-D were characterized by the presence of lower chlorinated PCDDs (in 2,4-DB) or lower chlorinated PCDFs (in 2,4-D and 2,4,5-T/2,4-D) (Figure 2). Fingerprints in these pesticides could be clearly distinguished, with relatively high contribution of 1,2,4,6,8-pentachlorodibenzo-p-dioxin (PnCDD)* (~50%) in 2,4-DB, 2,4,6,8-tetrachlorodibenzofuran (TCDF) (~25 - 30%) in 2,4-D, and 2,3,7,8-TCDF*(~50%) in 2,4-D/2,4,5-T, respectively. Other phenoxy herbicides analysed included two formulations containing 2-methyl-4-chlorophenoxy-acetic acid (MCPA) as an active ingredient (although dicamba was also present as a secondary active constituent); these were characterised by ~30% contribution of OCDD to the congener profile and both contained similar and distinctive contributions of 1,3,6,8-tetrachlorodibenzo-p-dioxin (TCDD), 2,4,6,8-TCDF, 1,3,4,6,8- pentachlorodibenzofuran (PnCDF) and OCDF (5 - 10% each).

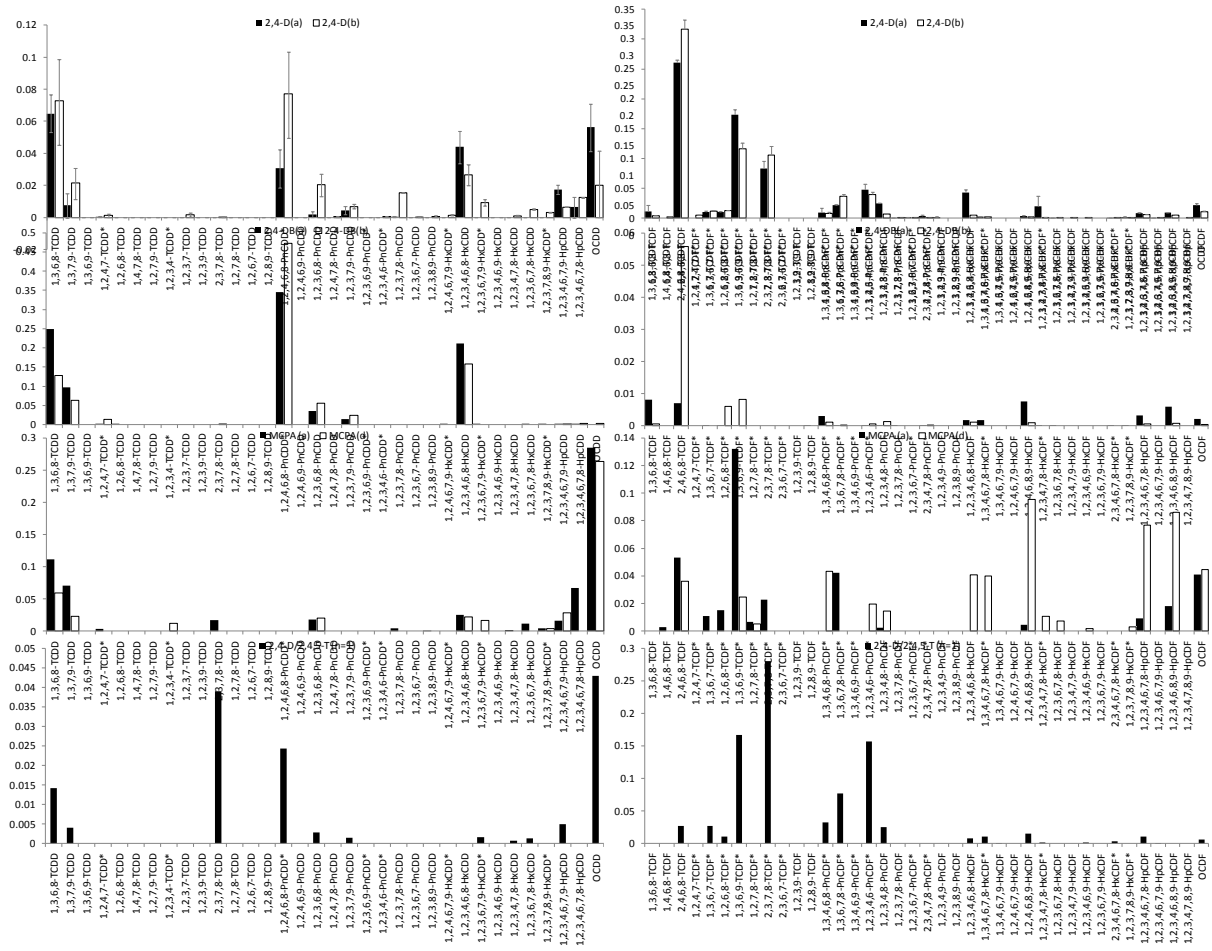

Figure2. Congener profiles (contribution to ∑PCDD/F) of phenoxy herbicide formulations: MCPA; 2,4-DB; 2,4-D & 2,4-D/2,4,5-T [Average, minimum and maximum values of two replicates are presented for 2,4-D(a) and 2,4-D(b)]

Among the congener profiles identified in the present study, only 2,4-D and MCPA have previously been reported, comprising formulations obtained in Japan[5]. While the PCDD/F congener profiles of these formulations are comparable, the contribution of some congeners show marked differences between 2,4-D sourced from Japan and Australia. Most notably, 2,4,6,8-TCDF and 1,3,6,9-TCDF contributed the highest proportions to the ΣPCDD/F concentrations in both 2,4-D formulations analysed for the present study, while 1,2,3,8-, 2,3,4,8- and 2,4,6,8-TCDF dominate (in descending order) the profile of 2,4-D from Japan[5]. Differences in congener profile were also evident for MCPA formulations analysed in the present study, where OCDD dominates amongst all congeners, as opposed to Japanese MCPA, which contains mainly 1,3,6,8-TCDD[5]. These examples indicate that source identification based on one or few source fingerprints, as typically necessitated by the sparse data available for pesticide impurities to date, is likely associated with some uncertainties as a result of changes in PCDD/F profiles /patterns (and concentrations) between pesticide production years, batches, manufacturers and/or countries.

Generally, pesticides of the same active ingredient are manufactured using similar production processes, and are thus likely to contain in similar PCDD/F impurity profiles but there is potential for variation in the PCDD/F fingerprints due to changes in pesticide production processes over time or differences between manufacturers, as well as fluctuations in process conditions[9,10] or during the variety of subsequent pesticide formulation processes[10]. In addition to pesticide production processes and conditions, relatively small congener-specific changes of PCDD/F profiles are expected to occur after their release to the environment, for example, diffuse atmospheric PCDD/F patterns from mixed sources are typically dominated by the most stable congener OCDD[11]. Furthermore, a recent study[2] has shown that PCDD/F congener profiles in pesticides may undergo considerable changes via PCDD/Fs formation from precursors when exposed to natural sunlight. For example, predominantly OCDD was formed in PCNB formulations, associated by an increase of its contribution to ΣPCDD/F concentration from 85 to 99%, as well as considerable increase in the ratio of PCDD to PCDFs (DF ratio) (from 8 to 220)[2]. Similarly, photolytic formation of particular PCDD/F congeners (2,4,6,8-TCDF, 1,3,6,8-TCDD; 1,2,3,6,8-PnCDD; and 1,3,6,8-TCDF) has been observed in sunlight exposed 2,4-D, resulting in marked changes to the PCDD/F congener profile (e.g. contribution of 2,4,6,8-TCDF increased from 29 to 93%)[2]. Over long time periods, such concurrently occurring processes may result in complex changes of fingerprints that may be important when relying on minor marker congeners for source identification, but are difficult to reconstruct retrospectively.

The results from the present study show that there are numerous other source fingerprints representative of PCDD/F contamination from pesticide use, apart from PCP, that may need to be considered in future source tracing, including consideration of a pesticide precursor formation pathway.

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