

ASSESSING PESTICIDES AS A SOURCE OF DIOXINS TO THE AUSTRALIAN ENVIRONMENT

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Abstract

Chlorinated pesticide production, use and disposal, has contributed significantly to polychlorinated dibenzo-*p*-dioxins and dibenzofuran (PCDD/F) contamination in the environment. Global pesticide application has been and continues to be extensive, including those which are known to contain or potentially contain PCDD/Fs. The aim of this study was to investigate the significance of pesticides as historical and current sources of PCDD/Fs to the Australian environment by determining their levels in a range of different formulations. PCDD/Fs were detected in all pesticide formulations analysed in this study at concentrations ranging from 0.0081 to 1,000 ng PCDD/F g⁻¹ formulation (0.037 to 2,100 ng PCDD/F g⁻¹ active ingredient), with the highest levels detected in current use pesticides containing pentachloronitrobenzene (PCNB). For most pesticides, data on volume of use are not available in Australia. However, using estimates based on market value and use volume trend data, label information and respective application area in Australia, pesticides have the potential to contribute significantly to the current PCDD/F emissions in Australia.

Introduction

It is well recognised that pesticide production, use and disposal have contributed significantly to polychlorinated dibenzo-*p*-dioxins and dibenzofuran (PCDD/F) emissions in the past. However, beyond the two pesticides notorious for PCDD/F contamination - 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) and pentachlorophenol (PCP) - there is a general lack of historical and current data on PCDD/F impurities. Accordingly, PCDD/F emissions from pesticide production and in particular pesticide use are difficult to quantify and generally not included into source inventories. This information gap leads to the inability to assess the significance of pesticides as (both primary and secondary) dioxin sources to the environment and whether these should be addressed. The USEPA lists >70 pesticides that have the potential to contain halogenated PCDD/Fs (1), many of which are still used globally (2) and some of which are applied in high volumes (3).

This study was carried out to screen a limited range of historical and current use pesticides from Australia in order to evaluate the potential for, and levels of PCDD/F impurities. Results were combined with pesticide use estimates and compared to the Australian emission inventory (4) to evaluate the significance of pesticides as a current source.

Materials and Methods

Twenty one pesticide formulations were selected for PCDD/F analysis. These included mainly agrochemical formulations (n=16) but also some household formulations (n=5). Samples included redundant pesticide formulations (banned, restricted or largely phased out) and pesticide formulations currently used in Australia. Active ingredients included a number of phenoxy herbicides (MCPA; 2,4-D; 2,4-DB; 2,4,5-T), fungicides (chlorothalonil; quintozone), insecticides (lindane; heptachlor; chlordane) and other herbicides (chlorthal; fluroxypyr; triclopyr/picloram). For pesticides in liquid form, PCDD/Fs were extracted by liquid/liquid partitioning into dimethyl sulphoxide (DMSO). DMSO was collected and diluted with 500mL MilliQ water. The samples were then re-extracted into *n*-hexane. Solid pesticide samples, PCDD/Fs were extracted by accelerated soxhlet extraction with toluene. Crude extracts for all samples underwent the same cleanup process. All extracts first underwent an acid pre-clean using pure concentrated sulphuric acid. Samples were then purified using *Powerprep*TM automated system (Fluid Management Systems, Waltman, MA, USA) (5). In brief, sample extracts

were applied to multilayered acid/neutral/basic silica, - basic alumina column in sequence and eluted with hexane, dichloromethane:hexane (2:98) and dichloromethane:hexane (50:50). The 50:50 dichloromethane:hexane solvent mix was transferred to a carbon column which was then eluted by ethyl acetate:toluene (50:50) in the forward direction and toluene in the reverse direction. The toluene fraction was collected for all samples and concentrated for high resolution gas chromatography/ high resolution mass spectrometry (HRGC/HRMS). HRGC/HRMS was conducted on a MAT95XL HRMS (ThermoFinnigan MAT GmbH, Bremen, Germany) and an Agilent GC (Palo Alto, USA) equipped with a CTC autosampler. The DB-5MS capillary column was operated under temperature programmed conditions of 100 - 200°C at 40°C min⁻¹ followed by 200 - 235°C at 3°C min⁻¹ and 235 - 310°C at 5°C min⁻¹. The injection port temperature was maintained at 290°C. GC carrier gas was helium maintained at a flow rate of 1.0 ml/min. Mass spectra were recorded with an electron impact ionisation source operated at 70eV. PCDD/Fs were quantified according to isotope dilution techniques using surrogate (internal) standard that included 15 ¹³C labelled PCDD/Fs.

PCDD/F emissions were estimated for PCNB (n=2) 2,4-D (n=1) and 2,4-DB (n=1) formulations. Emissions estimates were calculated using minimum and maximum PCDD/F levels detected in this study, combined with two different approaches to estimate their volumes of use in Australia:

1. Estimated pesticide use volumes in Australia based on market value (6) and survey data of non-agricultural pesticide use conducted by Parker (7) (volume of use: 20 - 1,000 tonnes per annum for PCNB and 100 - 1,000 tonnes per annum for 2,4-D and 2,4-DB).
2. Minimum and maximum label application rates for key agricultural crops (8) (and turf cultivation for PCNB) (9), cropping area according to the Australian Bureau of Statistics (10) and the Australian Government (9), a range of application frequencies derived from pesticide label information (8) and a range for % crop area treated with pesticide based on USEPA data (11-13) (volume of use: 130 - 29,000; 190 - 32,000 and 90 - 22,000 tonnes annum-1 total active ingredient for 2,4-D; 2,4-DB and PCNB, respectively).

Emission estimates were calculated using NATO-CCMS toxic equivalency factors for better comparison with UNEP toolkit emission estimates (14).

Results and Discussion

PCDD/Fs were detected in all pesticide formulations analysed in this study, including those where PCDD/F impurities have previously not been reported, at concentrations ranging from approximately 0.0081 to 1,000 ng PCDD/F g⁻¹ formulation (0.037 to 2,100 ng PCDD/F g⁻¹ active ingredient) (Figure 1). The highest levels were present in current use pesticides containing pentachloronitrobenzene (PCNB) and redundant types containing 2,4,5-T (on an active ingredient basis). The PCDD/F concentrations in these formulations are within the range of those observed in 2,4,5-T and Agent Orange (2,45-T/2,4-D; range <LOD to 5100 ng g⁻¹ (15, 16)). As observed in other studies (17, 18), concentrations of PCDD/Fs in the pesticides analysed for this study represent a wide range of contamination levels. Variation in PCDD/F impurity levels occurs not only for those pesticides with different active ingredients but also between some formulations with the same active ingredient (e.g. 2,4-D: 0.26 to 28 ng g⁻¹ this study; 0.004 to 273 for 2,4-D in other studies (17, 19, 20)). The variation in the levels of PCDD/F impurities in pesticides is most likely due to the conditions of their respective production processes. Despite this variability, the present results indicate that PCDD/F impurities in pesticide formulations can be high, especially in those that are currently used.

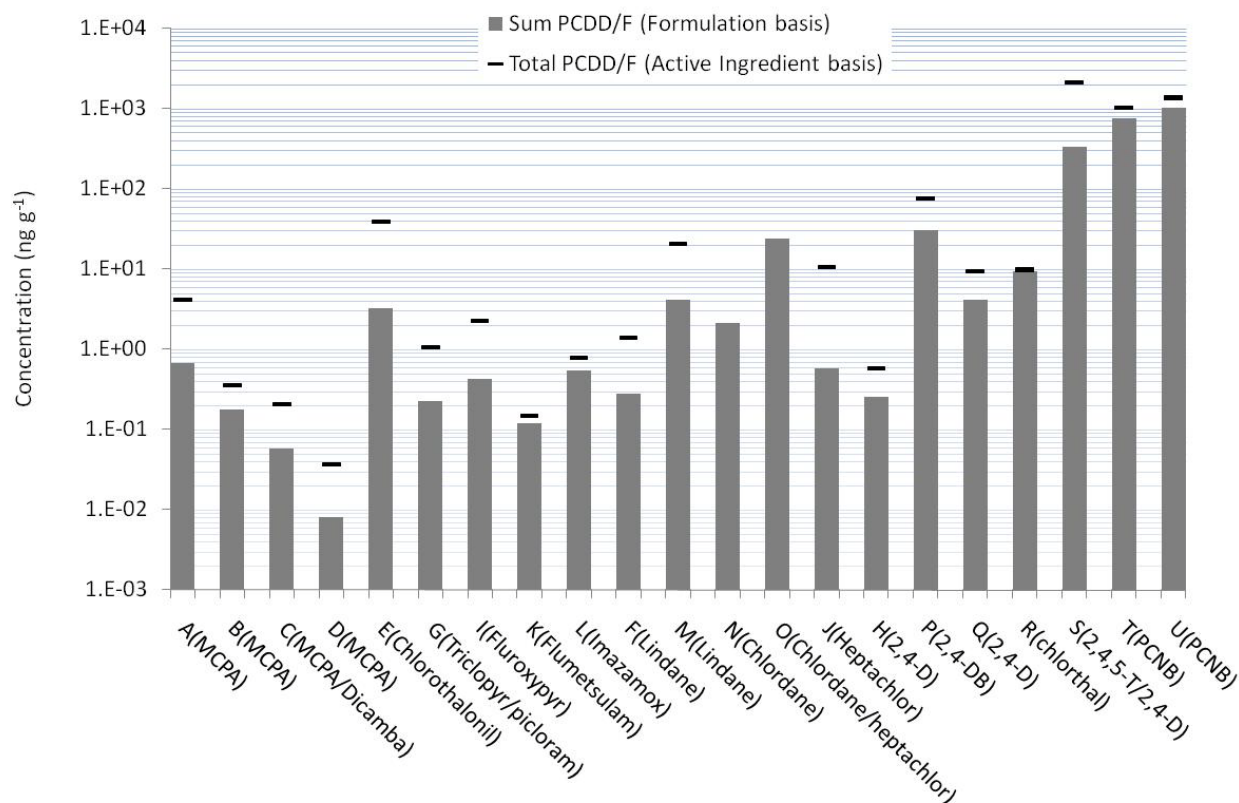


Figure 1. Summary of PCDD/F levels in pesticide formulations [percent active ingredient was not available for N_(Chlordane) and O_(Heptachlor/Chlordane), therefore the level of PCDD/Fs in these samples could not be normalised to active ingredient]

Estimating the emission of PCDD/Fs to the environment as a consequence of pesticide use in Australia is challenging, given that the current study represents the only data on impurity levels and only very limited information is available on pesticide volumes applied in Australia. Using information on pesticide volumes estimated with the first approach (see methods), the application of PCNB would emit 0.065 – 4.8 g I-TEQ annum⁻¹ (Figure 2). Estimated PCDD/F emissions from 2,4-D and 2,4-DB, the most commonly applied herbicides in Australia, are substantially lower (0.00093 – 0.0091 and 0.0013 – 0.013 g I-TEQ annum⁻¹, respectively), due to the lower PCDD/F impurity levels in the formulations analysed.

For comparison, PCNB, 2,4-D and 2,4-DB associated PCDD/F emissions were also calculated using label application rates and land area of respective crops (see methods). Based on this approach, PCDD/F emissions from PCNB, 2,4-D and 2,4-DB use were estimated to range from 0.26 – 105; 0.0012 – 0.26 and 0.0024 – 0.42 g I-TEQ annum⁻¹, respectively (Figure 2). These second estimates are considerably higher, although pesticide volume of use has been calculated only for major crops (n=7; 4 and 10 for 2,4-D; 2,4-DB and PCNB, respectively), using reported application rates and frequencies and respective crop land area (see methods). This highlights the extent of uncertainties associated with pesticide use data in Australia, which is a commonly acknowledged issue to be addressed (6).

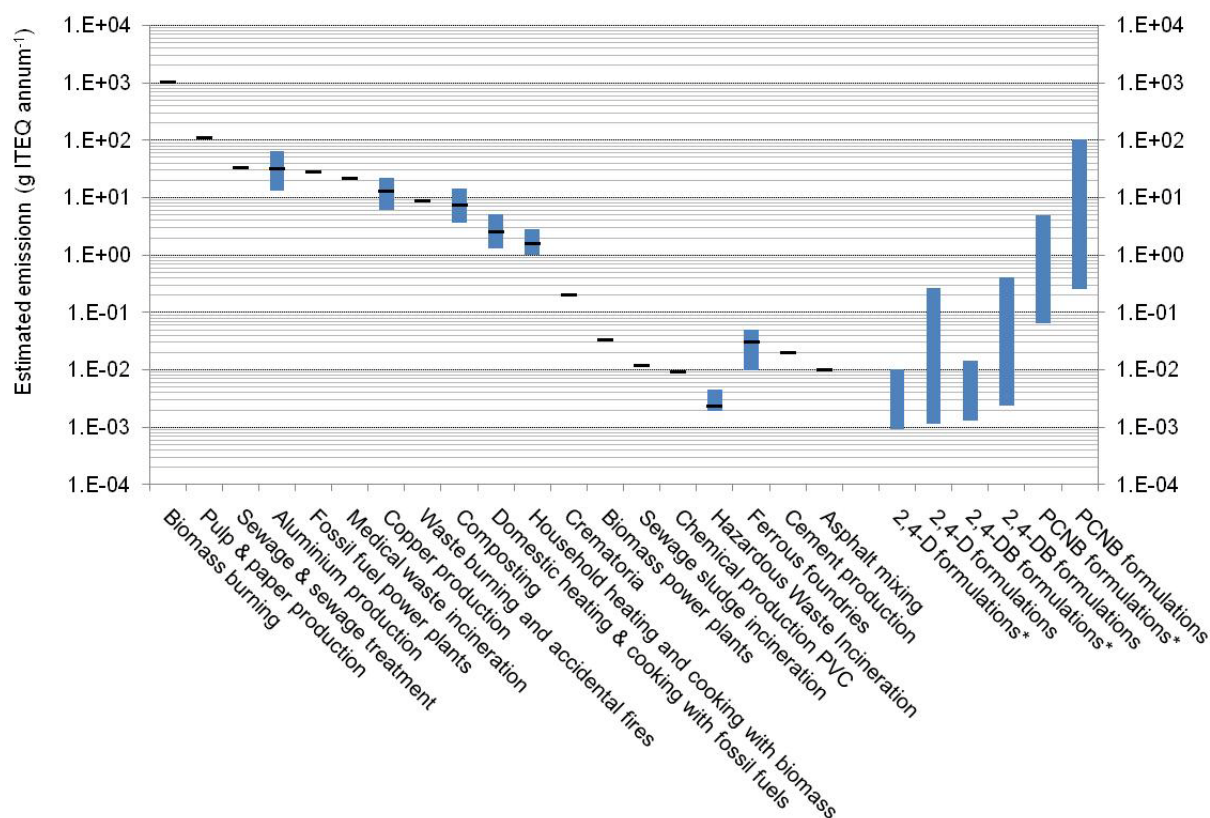


Figure 2. Estimated emissions from pesticide formulations (containing 2,4-D; 2,4-DB or PCNB) calculated using Approach 1 use volume data (*) (6) and emissions estimated using Approach 2 use volume data - compared to Australian dioxin inventory 2004 (4) top 19 PCDD/F emitters (low to high estimate or best estimate; includes total emissions to land).

Maximum estimated PCDD/F emission from PCNB formulations using label application rates (105 g I-TEQ annum⁻¹) are high compared to emissions to land from the most important sources identified in the Australian dioxin inventory (4) (Figure 2), suggesting the use of this pesticide alone may represent a key source to the environment. Similarly, the maximum estimated PCDD/F emissions from the application of 2,4-D and 2,4-DB (0.26 and 0.42 g I-TEQ annum⁻¹, respectively) are amongst the 19 priority sources to land (0.0019 – 1,020 g I-TEQ annum⁻¹ in Australia (4)) (Figure 2). Even the lower end estimates based on market value and use volume trend data (Approach 1) place PCNB use among the top PCDD/F emission sources to land in Australia (Figure 2). The present study also demonstrates that numerous other pesticides have the potential to contain PCDD/F impurities (Figure 1). Their combined emissions to the environment are difficult to estimate due to lack of accurate pesticide use-data and limited information on impurity concentration ranges, however, considering high volume use of many current-use pesticides, monitoring would be warranted to facilitate reduction of such ongoing dioxin emissions. In addition, this study indicates that past-use of pesticides may have contributed significantly to existing dioxin contamination in soils and sediments of Australia, providing secondary sources for uptake into the food chain. This should be taken into account when evaluating possible source origins in environmental matrices.

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