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Reassessment and update of emission factors for unintentional dioxin-like polychlorinated biphenyls

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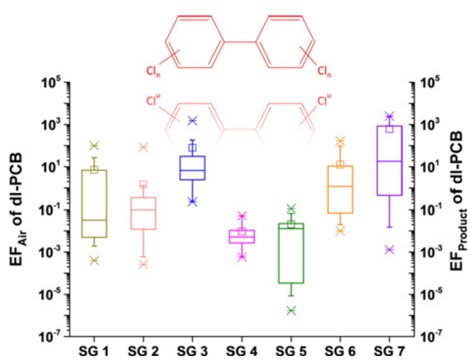
HIGHLIGHTS

- 286 published emission factors (EFs) of unintentional dl-PCB were collected from measured data.
- They were grouped and assigned to the source categories and/or classes used in the UNEP Toolkit.
- The already existing EFs of dl-PCB in the Toolkit were improved and amended.
- A correlation between the EFs (to air) of dl-PCB and that of PCDD/PCDF was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

One of the major goals of the Stockholm Convention on Persistent Organic Pollutants is to continuously reduce the releases of unintentional persistent organic pollutants (POPs) such as polychlorinated dibenzo-*para*-dioxins and dibenzofurans (PCDD/PCDF) or polychlorinated biphenyls (PCB) from anthropogenic sources. Until now, most efforts have focused on the releases of PCDD/PCDF and to a lesser extent on unintentionally generated PCB, and therefore, release inventories reported as toxic equivalents (TEQ) do not include the twelve dioxin-like PCB (dl-PCB). In order to facilitate the development of national release inventories for the total TEQ – consisting of PCDD, PCDF and PCB - this study collected and summarized published emission factors (EFs) of unintentional dl-PCB or calculated them from measured data for the sources listed in the UNEP Toolkit. In total, 286 EFs for dl-PCB were found (or could be calculated) whereby 233 described release to air, 23 EFs addressed to residue, 25 EFs to product; and only 5 EFs addressed releases to land. Taking into account performance criteria such as the facility type and scale or abatement technologies, the EFs were grouped and assigned to the source categories and/or classes used in the UNEP Toolkit. With these newly added data and EFs of dl-PCB, the already existing EFs in the Toolkit can be improved and amended. In addition, a statistically significant correlation between the EF_{Air} of dl-PCB proposed in this study and EF_{Air} of PCDD/PCDF recommended in the Toolkit was observed.

1. Introduction

Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/PCDF), and polychlorinated biphenyls (PCB) are listed in the

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Annex C of the Stockholm Convention as unintentionally generated persistent organic pollutants (POPs). Parties are required to develop action plans to identify, characterize and address releases of these POPs including development and maintenance of release inventories on national or sub-regional level. To support Parties in meeting these obligations, the UNEP "Toolkit for Identification and Quantification of Dioxins/Furans and Other Unintentional POPs" (UNEP, 2013) provides the methodology to develop release inventories by recommending default emission factors (EFs) to five release vectors (air, water, land, product or residue) for ten major source groups (SGs). The objective of the Toolkit is to ensure that source inventories and release estimates are complete with respect to coverage of the sources, harmonized by using the same methodology and comparable between countries and over time. Complete and transparent methods are particularly useful in countries where measured data are limited.

Until now, most research has focused on the releases of PCDD/PCDF. The congener profiles, EFs and the formation mechanism of PCDD/PCDF have been investigated from numerous thermal and combustion processes, and chemical production processes where chlorine is present, *e.g.*, waste incineration (Chi et al., 2005; Kocan et al., 1990; McKay, 2002; Ni et al., 2009; Yan et al., 2006), production of metals in thermal processes (Berho et al., 1999; Kim et al., 2003a, 2003b), combustion of solid and liquid fuels (Fernández-Martınez et al., 2004; Gullett and Ryan, 2002; Nussbaumer, 2003), and chlorinated chemical production or use (Horstmann et al., 1993; Ni et al., 2005). Based on high quality measured data and expert estimates, EFs of PCDD/PCDF are well established and updated in the Toolkit (UNEP, 2005, 2013). Since the entry into force of the Stockholm Convention, many Parties have been committed to develop and continuously update the national/regional PCDD/PCDF release inventories using the methodology of the Toolkit. The latest assessment had inventories from 86 countries/regions compiled and assessed (Fiedler, 2015). A subsequent publication by Wang et al. (2016) extrapolated these data to the global level and found that worldwide approximately 100 kg TEQ of PCDD/PCDF are formed and released annually. Our previous study overviewed the concentrations of other unintentional POPs in samples such as stack emissions, solid residues/ashes or products from potential sources in China (Liu et al., 2017). However, no systematic attempt has been made to estimate the amounts of the total toxic equivalent (TEQ_{total}), including dioxin-like PCB, formed and released due to the lack of EFs for dl-PCB. The available EFs of dl-PCB are limited compared with PCDD/PCDF and most data among them mainly addressing emissions to air. In addition, the reported EFs range widely, from few nanogram per tonne to gram per tonne, which leads to a large uncertainty. This state of knowledge is reflected in the most recent revision of the UNEP Toolkit published in 2013 (UNEP, 2013), where the full methodology is developed and successfully applied for PCDD/PCDF; while only few EF data for unintentional PCB – and other unintentional POPs such as hexachlorobenzene and pentachlorobenzene – is provided in the Annexes. This study provides an update and amendment of the EFs of unintentional dl-PCB to be included in the Toolkit 2013.

Some researchers have investigated the relationship between the concentration of PCDD/PCDF and other chlorinated organic compounds, or correlation between the congeners or groups of chemicals for different combustion or metal smelting processes (Blumenstock et al., 2001; Choi et al., 2008; Kato and Urano, 2001; Kaune et al., 1994, 1998; Kenichi et al., 2002; Kim et al., 2004; Oh et al., 2007; Pandelova et al., 2006, 2009). Since the guidelines developed in support of the Stockholm Convention such as the UNEP Toolkit or the "Guidelines on best available techniques and preliminary guidance on best environmental practices" (UNEP, 2007), stipulate that the same sources that generate PCDD/PCDF also generate other unintentional POPs and the same techniques or technologies that reduce PCDD/PCDF also reduce the emissions of other unintentional POPs, we assessed the correlation of EFs for PCDD/PCDF and dl-PCB. It shall be noted that the Toolkit and the BAT/BEP guidelines identify and quantify the unintentional POPs that are released at the source, no matter if the unintentional POPs are already present in the feed material or are newly formed in the process. Also, the Toolkit does not address the transfers between environmental compartments.

The aim of this study is to review the literature for EFs for unintentional PCB and group them accordingly. Particularly: i) to summarize available published information and identify information gaps regarding the information and releases of unintentional PCB; ii) to reassess the data in the scientific literature and the UNEP Toolkit, and then propose EFs for the different source categories and classes within the ten SGs of the Toolkit; and iii) elucidate the correlation of EFs of dl-PCB and PCDD/PCDF.

2. Methods and data

2.1. Data collection

This study covers research from a variety of sources, including i) the UNEP Dioxin Toolkit, version 2013; ii) scientific literature listed in the Toolkit; and iii) other publications or governmental reports containing EFs or source related quantitative information on releases of unintentional PCB. Information on releases of dl-PCB was obtained from peer-reviewed literature through Web of Science (http://apps.webofknowledge.com), Google® Scholar (www.scholar.google.com), Organohalogen Compounds database (www.dioxin20xx.org), and China Knowledge Resource Integrated Database (www.cnki.net), *etc.*

All accessible literature was consulted and assessed not only for published EFs but also for information as to operation of the sources, technologies, abatement equipment in order to classify the data into the classes in the Toolkit. For the purpose of this study, the formation process, mechanism and congener profiles of the unintentional dl-PCB were not included in the scope of this paper. We collected and summarized the published EFs of unintentional dl-PCB from the above-mentioned sources, and matched them with SGs of the Toolkit. The EFs were stored in MsExcel®.

Following the Stockholm Convention reporting and the UNEP Toolkit approach, all emission TEQs are used as the normative tool to summarize data of dioxin-like compounds with no specific TEF scheme ($I\text{-}TEQ_{1998}$ or $WHO_{2005}\text{-}TEQ$) applied. The differences between the TEF schemes for most technical matrices are minor and do not influence the order of magnitude estimation. The TEF scheme is specified only when reference is made to a specific study to maintain the accuracy but not used in the EF assignment. Emission factors reported in the publications and expressed in units other than in the Toolkit, *i.e.*, ng TEQ/t, μg TEQ/kWh, ng TEQ/L, were converted into the units used in the Toolkit. For sources related with combustion of solid fuels (SG 3), the units were converted from μg TEQ/t to μg TEQ/TJ using the calorific value of 25 MJ/kg and 15 MJ/kg for coal and biomass, respectively. For sources related with combustion of liquid fuels (SG 5), the units were converted from μg TEQ/L of diesel to μg TEQ/t using the conversion factor: 1 L of diesel equals to 0.85 kg; and from μg TEQ/kWh to μg TEQ/t using the calorific value of 40 MJ/kg for heavy oil.

2.2. Categorization and reassessment of EFs

All collected data on emissions of unintentional dl-PCB were reassessed and compared separately in accordance with different source categories. The source categories and classes (representing differences in production technology) as established in the Toolkit were used in this assessment. For the purpose of further analyzing and obtaining appropriate EF values, firstly, all reported data for each source category was placed in one of the several classes to assess the data range under technology differences or regional diversity based on the basic information mentioned above, or otherwise estimated based on expert judgment. Secondly, results with similar characteristics were aggregated into one EF based on the data within a same class. In general,