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Emission factors of unintentional HCB and PeCBz and their correlation with PCDD/PCDF☆

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A B S T R A C T

Hexachlorobenzene (HCB) and pentachlorobenzene (PeCBz) have been listed as unintentional POPs in the annex of the Stockholm Convention and thus, attracted attention by government and researchers. Since the intentional production and use has ceased in most countries, the unintentional releases to the environment have increased. This study gathered 206 and 78 emission factors (EFs) of unintentional HCB and PeCBz from scientific publications and governmental reports, respectively. Most of the EFs referred to the release vector "air" (EF_{Air}) and to a less extent to "product" ($EF_{Product}$). EFs were proposed for different source categories/classes used in the Toolkit according to the technologies that released the HCB or PeCBz. Overall, lowest and highest EF_{Air} for HCB were found in the metallurgical industry range from 1 μg/t in well controlled plants (coke, iron and steel) up to 40,000 μg/t (secondary zinc). EFs for PeCBz were in similar order of magnitude. Due to lack of data, EFs to water, land or residue cannot be proposed. Using linear regression and statistical analysis such as Pearson correlation, we found strongest correlation of EF_{Air} between HCB and PeCBz ($R^2 = 0.79$, $P < 0.01$) and weaker, but still significant, correlations for EF_{Air} between PCDD/PCDFTEQ and HCB ($R^2 = 0.56$; $P < 0.01$) or PeCBz ($R^2 = 0.31$ $P < 0.01$) for various thermal processes.

1. Introduction

Hexachlorobenzene (HCB) and pentachlorobenzene (PeCBz) have been detected in environment and biota as a result of their persistent and long range environmental transport potential (Shen et al., 2005; Simonich and Hites, 1995; Weber and Goerke, 1996; Yun and Kannan, 2011). Both of them have been listed in the annexes of the Stockholm Convention on Persistent Organic Pollutants (POPs). Past uses of HCB or PeCBz were as chemical intermediates or as fungicides and flame retardants (EMEP/CORINAIR, 2005; Van de Plassche et al., 2002). Literature sources show that production and uses of HCB or PeCBz have ceased over the last decades (Rossberg et al., 2006; Van de Plassche et al., 2002), but it is important not to ignore their unintentionally releases as byproducts of incomplete combustion processes and/or impurity in several chemical processes using chlorine. Understanding the national/regional emissions of unintentional HCB and PeCBz has important implications for successfully developing strategies with concrete measures, timelines and goals to minimize or eliminate their releases.

Many efforts have been done to estimate the annual releases and main sources of HCB or PeCBz (Bailey, 2001; Bailey et al., 2009; Berdowski and Bloos, 1997; Government of Canada, 1993; Carpenter et al., 1986; Cohen et al., 1995; Environment Canada, 2005; U.S. EPA, 2007). Bailey (2001) estimated global HCB emissions in the mid-1990s as approximately 23000 kg/yr with a range of 12000 kg/yr −92000 kg/yr based on the information on HCB emissions in the U.S. and Canada. And the ICCA/WCC (2007) provided an estimation of the annual global emissions of PeCBz of 85000 kg/yr based on the U.S. Toxics Release Inventory (U.S. EPA, 2007). However, there is considerable uncertainty on the releases of HCB and PeCBz from various sources and available data are limited to the U.S. and Canada. The limited data available makes it difficult to provide a proper regional/global estimate on amounts and trends. In order to ensure that release estimates of various unintentional POPs are complete and comparable, the UNEP Toolkit (UNEP, 2013) provides a simpler and more promising methodology by recommending default emission factors (EFs) to five release vectors (air, water, land, product or residue) for specific processes.

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The Toolkit takes into account the type and efficiency of control equipment, and the differences in materials, fuels and wastes. This methodology has been fully developed and successfully applied for PCDD/PCDF and it is assumed to work for HCB and PeCBz as well.

Nevertheless, due to the limited availability of measured data on EFs of unintentional HCB and PeCBz, only few default EFs for unintentional HCB and no any EFs for PeCBz were provided in the latest version of the Toolkit published in 2013. Moreover, it is always very difficult to obtain EFs for all potential source categories and/or classes. Therefore, appropriate statistical models might be attractive alternatives to fill the gaps of the EFs of unintentional HCB and PeCBz. It is considered that HCB or PeCBz are formed and released by the same processes as PCDD/PCDF. Numerous research has tried to elaborate the relationships of PCDD/PCDF and some other chlorinated compounds (including HCB and PeCBz) from various thermal sources (Blumenstock et al., 2001; Kato and Urano, 2001; Kenichi et al., 2002; Kim et al., 2004; Lavric et al., 2005; Oh et al., 2007; Pandelova et al., 2006, 2009). However, comparisons were very difficult due to the inconsistent results. This may be because the concentrations and compositions of these unintentional POPs could be varied depending on some plant-specific conditions (*i.e.*, operating conditions, technologies, fuels, and even sampling methods). Therefore, general models described the emission correlations between PCDD/PCDF and unintentional HCB and PeCBz are needed to be developed.

This study summarized the information relevant to unintentional HCB and PeCBz releases and subsequently proposed EFs for the application at global level so that with these EFs, national inventories can be developed for HCB and PeCBz to complement PCDD/PCDF release inventories. Particularly: i) to compile EFs of unintentional HCB and PeCBz to each vector for source groups (SGs) 1–10 of the UNEP Toolkit; ii) to reassess the default EFs derived from publications listed in the Toolkit and update EFs on the basis of newly identified data, and then iii) test the EFs for correlations among the unintentional POPs, *i.e.*, EFs of unintentional HCB and PeCBz with the EFs of PCDD/PCDF.

2. Methods

The source categories and classes (representing differences in production technology) as established in the Toolkit were used in this assessment (Table S1). Published EFs of unintentional HCB and PeCBz to each release vector for numerous potential sources were gathered and summarized from recent scientific literature and government reports (Table S2). In order to allocate these EF data to appropriate source categories/classes and evaluate the need for changes of existing EFs in the Toolkit, corresponding basic information on improvement of operational approaches, technologies, air pollution control devices (APCDs), and other factors was also summarized in Table S2. Results with similar characteristics were aggregated into one EF based on the data within a same class. Averages instead of geometric means were applied in this estimation because the data numbers for most source categories were too small to generate geometric statistics. Consequently, a rounded average EF value was assigned for each source category and/or class based on these average values by expert judgment. Due to the very scarce data on releases to water, land and residue, we only proposed the EFs to air (EF_{Air}) and product ($EF_{Product}$) for both of HCB and PeCBz in this research.

3. Results and discussion

3.1. Emission factors of unintentional HCB

Emission factors of unintentional HCB along with the detailed information needed for the classification of the sources were gathered and summarized (Table S2). Totally, 27 relevant scientific publications or governmental reports were identified, and most of them were related with releases of HCB from waste incineration (SG 1), metal production (SG 2) and heat and power generation (SG3). From these 27 publications, 206 independent EF data were found for unintentional HCB. It should be noted that most information had the release vector “air” (149 EF_{Air}) and to a less extent the vector “product” (57 $EF_{Product}$); very few data was found for the release to water and residue; and no data was found for the release to land yet. Among them, however, some data were not included in the estimation since they were considered to be outdated or unreliable, or otherwise no any specific information for classification. For instance, Bailey (2001) reviewed several measurement data on HCB yield from municipal solid waste, hazardous waste and medical waste incinerators reported in 1983–1995, some of which without any APCDs, and applied EF_{Air} with a range of two orders of magnitude (shown as “global” in Table S2) which are highly aggregated and supposed to no longer represent the present global situation. Zhang et al. (2011) have reported the EF_{Air} of HCB (and PeCBz) for open burning of domestic wastes; whereas it is considered that the sampling method was not optimized to securely derive EF_{Air} for these two volatile unintentional POPs. Another example is for fossil fuel power plant. The Japanese studies (Iwata et al., 2008; Ota et al., 2005) reported HCB EF_{Air} of 122 μg/TJ –216 μg/TJ derived from 10 measurements achieved in different fossil fuel-fired facilities. However, the actual EFs may be higher than these since it is likely that the data was the average of tests using coal, heavy oil and natural gas.

Based on the corresponding information about the region of the data source, production technology (including facility design, operation level, abatement devices, *etc.*), collected EF data was assigned into different source categories/classes. Fig. 1 presented the results of data classification of EF_{Air} of unintentional HCB for SGs 1–5 and $EF_{Product}$ for SG 7. For SGs 6 and 8, it was not presented in the figure due to limited data. It can be seen that, there was only one or two EF data was reported for several source categories/classes at present stage, especially for some non-ferrous metal production. However, it should be pointed out that, many data was reported as the average value derived from a numbers of measurements. For instance, the unique HCB EF_{Air} of 0.6 μg/t was the average of measurements form eight typical coke plants in China (Liu et al., 2009); and the reported EFs for primary and secondary zinc production from the Japanese studies (Iwata et al., 2008; Ota et al., 2005; Yamamoto et al., 2011) was also the average of measurements form 10 and 15 plants, respectively (Table S2). This situation is similar for PeCBz as well. On the basis of these available data, EF value of HCB was proposed for each source category and/or class; certainly, most of them were related to release vector of “air”.

The frequency distribution of all EF_{Air} of unintentional HCB for SGs 1–7 proposed in this study shown in Fig. 2A illustrated that more than 80% of the EF_{Air} are less than 1000 μg/t, and the distribution tendency approximated a lognormal distribution (Fig. 2B). For comparison, the unit of EF_{Air} data for SG 3 was converted from μg/TJ to μg/t in Fig. 2. The higher EF_{Air} values of unintentional HCB were from medical waste incineration (10000 μg/t for 1c class 3), secondary zinc production (40000 μg/t and 10000 μg/t for 2 g classes 2 and 3, respectively), brass and bronze production (9400 μg/t for 2 h class 3), and high chlorine coal/waste/biomass co-fired stoves (equivalent to 12500 μg/t for 3e class 1).

It should not be ignored that HCB could also be unintentionally released into various components of environment, wastes and even products in the course of chlorine-bearing production processes. In particular, the release vector “product” is potentially the largest route of unintentional HCB releases from such processes. Generally,