National Institute
for Public Health
and the Environment

Letter report 601773002

E.A. Hogendoorn | Y. Bruinen de Bruin | M.P.M. Janssen

Inventory emission factors for pentachlorobenzene

RIVM Letter report 601773002

Inventory emission factors for pentachlorobenzene

E.A. Hogendoorn, Y. Bruinen de Bruin, M.P.M. Janssen

Oktober 2009

Dit onderzoek is verricht in opdracht van VROM-DGM RB ten behoeve van het programma Invulling artikel 11 van het Stockholmverdrag, Beleidsondersteuning Milieu, project M/601773/07/JA

RIVM, Stoffen Expertise Centrum (SEC) P.O. Box 1, 3720 BA Bilthoven, telephone:+ 31 - 30 - 274 91 11; telefax: 31 - 30 - 274 29 71

Summary

In 1995, the Governing Council of the United Nations Environment Programme (UNEP) called for global action to be taken on persistent organic pollutants (POPs), which it defined as “chemical substances that persist in the environment, bio-accumulate through the food chain, and pose a risk of causing adverse effects to human health and the environment”. The global action resulted into the Stockholm Convention on Persistent Organic Pollutants, which is an international legally binding agreement on POPs.

At present, pentachlorobenzene (PeCB) is being considered for inclusion in the Convention. To support the decision-making process for inclusion, this document contains available information on sources and emissions of PeCB with a specific focus on emission factors. Emission factors indicate the amount of PeCB released per unit burned material and is one of the methods to estimate the emissions.

The literature review revealed that:
1. The risk profile of PeCB revealed that PeCB is largely unintentionally emitted by various combustion related processes, such as the combustion of industrial and municipal waste, coal, and uncontrolled back-yard barrel burning,
2. For controlled waste incineration an emission factor range of 0.1-273 µg/kg waste was estimated for PeCB., while 2.5 µg/kg was estimated for coal combustion. Emission factors between 4.5 and and 80 µg/kg were found for uncontrolled back-yard barrel burning,
3. PeCB emissions are correlated with other more emission data-rich combustion related compounds, such as dioxins and hexachlorobenzene (HCB). Based on these ratios, PeCB emissions can be derived for various combustion processes and sources, and
4. PeCB can be measured in a relatively easy and economical manner.

Table of contents

1. Introduction and scope of study

The European Community and its Member States being Parties to the Stockholm Convention have proposed to add pentachlorobenzene (PeCB) to the Convention's POP list. Listing of chemical substances to an Annex of the Convention is subject to decision making by the Conference of the Parties, based on recommendations by the Persistent Organic Pollutants Review Committee (POPRC). The POPRC concluded that the screening criteria set was met and decided to establish an ad-hoc working group to guide and review two required supporting documents. The first document concerned the risk profile of PeCB (UNEP draft, 2007) and concludes that global action is warranted. UNEP (draft, 2007) states that PeCB is likely, as a result of its long range environmental transport, to lead to significant adverse human health and/or environmental effects. The second document concerned a risk management evaluation (RME) (UNEP draft, 2008). This RME reconfirmed the previous statement of the draft Risk Profile document and, in addition, concluded that it is important to prevent the re-introduction of PeCB into commerce and its related use. Like hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs) and dioxins/furans, PeCB is also formed as an unintentional by-product of combustion and other thermal processes. Consequently, most measures to reduce unintentional emissions of dioxins will undoubtedly lead to significant reduction of PeCB emissions. At present, unintentional release of PeCB is by far the largest source of emission (UNEP draft., 2007). Therefore, in accordance with paragraph 9 of Article 8 of the Convention, the POPRC recommended the Stockholm Convention's Conference of the Parties, to list and specify existing related control measures of PeCB in Annexes A (without any specific exemptions) and C.
The recommendations made by the POPRC at its fourth meeting, state the following:
"As PeCB was formed as an unintentional by-product during combustion and thermal processes, listing it in Annex C would establish the goal of continuing minimization and, where feasible, ultimate elimination of PeCB emissions. Most measures taken to reduce PCDD/F (dioxin) releases, as described in the Stockholm Convention's best available techniques/best environmental practices (BAT/BEP) guidelines for incinerators and other thermal processes, would lead to a significant reduction of the release of PeCB.
Unintentional production of PeCB was also caused by diffuse sources, namely, impurities in products such as solvents, pesticides and wood preservative products; barrel burning; open fireplaces; accidental fires; and forest burning for agricultural purposes. For those sources abatement techniques were not feasible and release reduction measures could only be affected through the enactment of legislation or the provision of information and education by national and local authorities."

The listing on Annex C, which collates sources of unintentional release from anthropogenic sources, may be facilitated by mechanisms or tools to estimate PeCB emissions. There are usually four basic types of release estimation techniques: (i) monitoring or direct measurements, (ii) assessment of mass balance(s), (iii) estimation by using emission factors and (iv) engineering estimates. Detailed information can be obtained in guidance documents such as EPA (1999), and NPi (2009). Appendix 2 provides a short description of the four estimation techniques.
To support the decision-making process for inclusion, an inventory on available information on emission factors of PeCB to air was made. The emission factors express the amount of PeCB released per unit of burned material (e.g. µg/kg). When the amount of burned material is known, the amount of PeCB emitted can be estimated using the available PeCB emission factor for that combination of fuel and equipment.

2. Methods

As has been reported in the risk profile (UNEP, 2007), the emission of PeCB is related to many processes. Besides releases from previous production and use, secondary emission sources are the release of organochlorine pollutants to air during combustion processes involving carbonaceous materials in the presence of chlorine and - to a minor extend - releases from industrial/chemical processes. Hence, when organochlorine compounds like PCDD/Fs (dioxins) and PCBs are emitted, it is likely that PeCB will be released too.
A comprehensive list of processes believed to be likely sources of POPs was compiled (UNEP, 1999) and is presented in **Appendix 1** of this report. The overview reflects the possible emission sources of PeCB.
Information on PeCB releases is rather scarce. However, for dioxins and HCB, more information is available. Due to similar physical and chemical properties, such as inertness and hydrophobicity, and similar temperature dependence of PeCB in the formation processes, information on dioxin and/or HCB releases to air is expected to be useful for the estimation of PeCB emissions. Therefore, this inventory also includes information on the correlation/ratio between PeCB/dioxin and PeCB/HCB and on dioxin and HCB emissions.

3. Results

The current chapter describes the information found during the current literature review on emission factors and emission ratios of pentachlorobenzene, dioxins and hexachlorobenzene.

3.1 Available emission factors for pentachlorobenzene

An overview of information found in the literature is given in **Table 1**. Most information has been collected by an earlier inventory made by Bailey (2007) on the major sources of PeCB and with related emission factors and global annual loads. As can be seen from table 1, the latter inventory includes emission factors for PeCB for the most relevant processes being controlled incineration of solid waste, uncontrolled back-yard barrel incineration of solid waste, combustion of coal and combustion of biomass.
The emission factor of PeCB for coal combustion was estimated on the basis of the measured concentration of hexachlorobenzene in the flue gas from coal combustion in a lab experiment (Oberg and Bergstrom, 1985).
The emission by various waste incinerators reported in eight different studies were summarised by Bailey (2007). Bailey (2007) noted that the range of PeCB yields varied over a factor of 100, and estimated an average emission factor of 25 µg/kg. One study with a relatively high emission factor was not included in the averaging.

From 1999 to 2004, a comprehensive Dutch research program studied the occurrence of chlorinated organic micro contaminants (Hattum van et al, 2004). The study investigated whether and if so, to what extent known and un-known chlorinated compounds with PBT properties (accepted or potentially persistent, bioaccumulative and/or toxic compounds) are emitted from the Dutch chlorine chain. The study involved the screening of 16 industrial waste water effluents, the vent-gas of three industrial incinerators, and the flue gas of a Municipal Solid Waste Incinerator (MSWI). The latter served as a reference for known non-chlorine chain sources of dioxins (PCDD/Fs). Emission samples of the selected sources were analyzed up to about 250 organochlorine compounds, including PeCB. From all sources investigated, emission of PeCB was found in the flue gas of an industrial incinerator (2-7 µg/Nm^3). With a flue-gas volume of about 2300 Nm^3/h, the annual load of PeCB translates to about 0.04-0.14 kg/yr. At the other air sampling points, PeCB was not measured above the limit of detection level of 0.1 μg/Nm^3. Dioxin emissions, however, corresponded to 0.0002 and 0.0022 μg/Nm^3 for two industrial vent gases and was 0.00044 μg/ Nm^3 for the MSWI.

In Canada, PeCB emissions from waste incineration were estimated on the basis of fundamental thermodynamic and kinetic principles being the potency for formation of PeCB as a product of incomplete combustion. Annual emissions from hazardous waste incinerators (HWI) were estimated to be 1.8 kg PeCB/year. Knowing the average annual load of six HWIs – being 2420 kg PeCB/year – the average PeCB emission factor for a Canadian HWI translates to 14.4 μg/kg of burned hazardous waste (Chandler, 2004a).

To estimate an emission factor for PeCB and the annual load of PeCB for biomass burning, Bailey et al. (2007) used additional data from Zimmerman et al. (2001). This data, however, were generated under controlled incineration processes in a 1 MW combustion plant to study emission profiles of products of incomplete combustion with shredded waste wood contaminated with plastics and paints as feed material. Hence, these data might not be sufficiently representative for the estimation of the PeCB emission in case of the open burning of biomass, such as forest fires and agricultural burnings. In a USEPA study on emissions of air toxics from barrel burning of household waste (EPA, 2002), emission factors of 80 and 5.8 μg/kg burned material were obtained for PeCB and dioxins, respectively. In addition, emission factors for a number of other open sources of burning were given for dioxins. The data, however, showed significant variations within the various source categories. Bailey (2007) also reported a PeCB emission factor of a specific process being $3.1.10^5$ μg/kg hexachloroethane (HCE). HCE was used to remove dissolved hydrogen from molten aluminum in foundries.

The European Pollutant Release and Transfer Register (PRTR) regulation 166/2006/EC states that in case of PeCB releases, facilities have to report annual emission to air, water and soil above 1 kg. However, the first E-PRTR dataset will reach the COM only on the 30th of June 2009 and it will be available on-line in October 2009. “Only then it will be possible to have an overview of the emission factor used by Member States to report pentachlorobenzene releases” (Cristofaro, 2009). Some other countries already have a release inventory for PeCB, such as the Toxic Release Inventory (TRI) of the United States, but no emission factors could be retrieved from these sources.

***Table 1**. Overview of emission factors (EF) and the related global annual loads (GAL) of PeCB in various combustion processes.*

Type of process	Type of burner	Type fuel	EF PeCB µg/kg	GAL PeCB kg/y	Reference
PVC combustion, experimental	Muffle furnace at 600 ºC	PVC	4700	-	Kim et al., 2004
Controlled incineration (special purpose experiments)	Pure PVC in pilot plant burner	PVC	969	-	Ahling et al., 2001**
Controlled incineration (special purpose experiments)	Pure PVC in lab burner	PVC	300	-	Kim et al., 2004**
Controlled incineration	City incinerator	various	273	-	Tiernan et al., 1983**
Controlled incineration	City fluidized bed	various	175	-	Akimoto et al., 1997**
Controlled incineration	Lab fluidized bed	various	161	-	Fängmark et al., 1993 **
Controlled incineration	Lab fluidized bed	various	84	-	Fängmark et al., 1994**
Back yard burning	Open barrel	household waste	80	-	EPA, 2002
Back yard burning	Open barrel	household waste	76	27740	Bailey, 2007
Uncontrolled burning . (pit burners and conical burners)	Municipal Solid Waste Incin	Municipal Solid Waste	70	-	Chandler, 2004b*
PVC combustion, experimental	Muffle furnace at 900 °C	PVC	65	-	Kim et al., 2004
Back yard burning	Open barrel	household waste	53	-	EPA, 1998
Controlled incineration	Hazardous Waste Incinerator	various	14.4	1.8	Chandler, 2004a*
Controlled incineration	Hazardous waste incinerator	various	14	-	Oberg et al., 1985 **
High temperature incineration	Various	Wood & Plant material	11.8	43900	Bailey, 2007
Controlled incineration	24 city incinerators	various	7	-	Kato and Urano, 2001**
Controlled incineration	Lab fluidized bed	various	6.4	-	Wikstrom et al., 1999**
Uncontrolled back-yard barrel burning	Open barrel	Municipal Solid Waste	4.5	-	Chandler, 2004b*
Controlled incineration	City incinerator	various	2.9	-	Jay and Stieglitz et al., 1995**
Coal combustion	Coal burner	coal	2.5	6113	Bailey, 2007
Controlled incineration (special purpose experiments)	Wood burner	Biomass	0.6	-	Zimmerman et al., 2001**
Controlled burning	Municipal Solid Waste Incinerators	Municipal Solid Waste	0.1	-	Chandler, 2004b*

* The potential for formation of PeCB as product of incomplete combustion was evaluated using fundamental thermodynamic and kinetic principles.
**Cited in in Bailey, 2007.

3.2 PeCB/dioxin emission correlation

An overview of the discussed information from literature on PeCB/dioxin emission correlation is presented in **Table 2**.
Lavric et al. (2005) made a review on dioxin emissions from municipal and industrial waste incineration. This review considers information on the PeCB/dioxin emission correlation based on data from laboratory scale testing of waste combustion and on-line measurements at industrial/municipal waste incinerators. The review indicates that PeCB can serve as a good surrogate for the measurement of expensive dioxin emissions. Vice versa, such correlations can be used to estimate the PeCB emissions of industrial incineration processes.
PVC is considered to be one of the major precursors for organo chlorine compounds formed and emitted during combustion of waste. A high correlation (R^2 = 0.99) was found between the emission of PeCB and PCDD/Fs (Kim et al., 2004) during the combustion of PVC under experimental conditions at three different temperature levels. The emission of all chlorinated compounds studied, reached a peak at 600 °C, with low emission recorded at 300 °C and 900 °C. At 900 °C, the (lowest) emission factors for PeCB and PCDD/Fs were 65 µg/kg and 3 µg/kg, respectively. At 600 °C, the highest emission factors were 4700 µg/kg and 100 µg/kg, respectively.
Another study by Reinmann et al. (2006) measured by continuous monitoring of unintentionally formed POPs (in the frame of the Stockholm Convention) total PCDD/Fs and PeCB concentrations of 180.10^3 $\mu g/m^3$ and 750.10^3 $\mu g/m^3$ in the flue gas of an MWI.
The behavior of dioxins and chlorobenzenes were investigated in two MSWIs (Takaoka et al., 2003). This study showed that, after the passing of a wet scrubber, the PeCB/dioxin ratio was 0.5 for both incinerators.
The Dutch chlorine chain study (Hattum van et al., 2004) reported an average emission of PeCB of 4.5 $\mu g/Nm^3$ in the vent gas of an industrial incinerator that is used for the production of terphtaloyldichloride (TDC) form p-xylene and chlorine. At that sample point, the dioxin emission was 0.029 $\mu g/Nm^3$ rendering an emission ratio for PeCB/dioxins of about 155.
Regarding uncontrolled back-yard barrel burning, information on PeCB/dioxin emission was found in two studies (EPA 1998; Lemieux et al 2004). EPA (1998) found a PeCB/dioxin emission ratio of 1.2 while Lemieux et al. (2004) found a higher ratio, being 14.
Table 2 presents information on atmospheric emission ratios of PeCB/dioxin and PeCB/HCB. As can be seen, the ratios are variable. This variation can be explained because the ratios reflect highly variable combustion related processes and types of products. These PeCB/dioxin ratios can be used for the estimation of PeCB emissions in cases when solely dioxin emission data is known. Therefore, the current inventory also collects additional information on dioxin emissions as described in the next paragraph.
Because dioxins refer a broad class of compounds, that vary widely in toxicity, the concept of toxic equivalent (TEQ) has been developed to facilitate risk assessment and regulatory control. Hence, in literature, one can find dioxin concentration expressed as ng I-TEQ[1] or ng WHO-TEQ. The current work did not focus on eventual predictable correlations between ng PeCB and TEQ value. Therefore, I-TEQ and WHO-TEQ are not included in **Table 2**.
Blumenstock et al. (2001) studied possible suitable surrogates for the analysis of dioxins and found a good correlation (r=0.80) between the concentration of PeCB and I-TEQ (international toxic equivalent) PCDD/Fs in the flue gas and stack gas of a Hazardous Waste Incinerator (HWI). Wikström et al. (1998) suggested that this was due to a similar temperature dependence of PeCB and PCDF in the formation processes.

[1] An I-TEQ value is highly depending the experimental conditions during which measurements were taken to derive an I-TEQ. Examples of such experimental conditions are the composition of incinerated waste during the measurement period, burning temperature, etc. It is assumed that especially the waste composition within the Western cultures that is being burned by large incinerators will not differ substantially. Consequently, an I-TEQ value might serve for other comparable incineration processes. However, in case of smaller incineration processes with a more batch wise operation, it will become less likely that I-TEQ values derived from other burning processes are sufficiently representative for the use of these smaller burning processes.

A study on the influence of atmospheric organochlorine patterns originating from pollutants from various sources in Germany (Wenzel et al 2006) provided useful information on PeCB/HCB emission ratios at selected sampling sites. Based on air measurements taken at 2-5 km distances from the selected source (site), it appeared that for all investigated locations the emitted concentration of HCB was higher than PeCB. The PeCB/HCB ratio's for the different sites were 0.09 (hazardous waste dump containing organochlorine pesticides), 0.25 (coal fired furnace of steam locomotive), 0.20 (charcoal production plant), 0.09 (metal working/smelting plant), and 0.44 (road traffic and shipping). **Table 2** reveals that the variation in the PeCB/HCB ratio is quite limited.

***Table 2**. Information on atmospheric emission ratios (w/w) of PeCB/dioxin and PeCB/HCB.*

Type of process/burner	Type fuel	PeCB/dioxins ratio	PeCB/HCB ratio	Reference
Industrial production of terphtaloyldichloride (TDC) from p-xylene and chlorine; fluegas of incinerator	vent gasses	155	6	Hattum van et al., 2004
HWI	Hazardous waste	50	0.1	Kaune et al., 1998
Experimetnal PVC combustion. Muffle furnace at 600 ºC	PVC	47	1	Kim et al., 2004
See above at 900 ºC	PVC	22	1	Kim et al., 2004
Back yard burning in open barrel	household waste	14	2	Lemieux et al., 2004
MWI	household waste	4.2	5.6	Reinmann et al., 2006
MSWI-A	household waste	0.5	3.0	Takaoka et al., 2003
MSWI-B	household waste	0.4	3.1	Takaoka et al., 2003
Back yard burning in open barrel	household waste	1.2	-	EPA, 1998
MWI	shredded wood added with paint, plastic	-	4.1	Zimmerman et al., 2001
MSW and IW	household waste; industrial waste	-	2	Kato and Urano, 2001
Road traffic and shipping	Petrol and diesel	-	0.44	Wenzel et al., 2006
Coal fired furnace of steam locomotive	Coal	-	0.25	Wenzel et al., 2006
Industrial charcoal production	Coal	-	0.20	Wenzel et al., 2006
Hazardous waste dump	OC pesticides	-	0.09	Wenzel et al., 2006
Metal working/melting plant	-	-	0.09	Wenzel et al., 2006

Kato and Urano (2001) analyzed emissions of (toxic) organic chlorine compounds in the flue gas of six municipal waste incinerators (MWIs) and four different types of industrial waste incinerators (IWIs). Despite the variation of parameters, such as the composition of waste and flue gas treatment, an overall good correlation (r = 0.92) of the I-TEQ concentration values (ng-TEQ/m^3) with the PeCB concentrations (µg/m^3) was found with a concentration range of several orders of magnitude. The study expressed the correlation as [I-TEQ dioxins] = 2.1 $[PeCB]^{1.1}$. In the studies by Kato and Urano (2001) and Zimmerman et al. (2001) PeCB/dioxins ratio's were found of 550 and 1478, respectively.

A similar reasoning as for the PeCB/dioxin relationship is believed to be applicable for PeCB/HCB emissions. Therefore, **Table 2**, also includes information on PeCB/HCB emissions. These ratios will be further discussed in the next paragraph. The measurement of POPs in the flue gas of a MWI (Reinmann et al., 2006) provided information on the release of PeCB, HCB and dioxins with corresponding ratio's of 4.2 and 5.8 for PeCB/dioxins and PeCB/HCB, on a weight/weight basis, respectively.
As demonstrated by Hattum van et al. (2004), PeCB/dioxin ratios can be on average up to about 150 for specific industrial incineration processes. Comparing the PeCB/dioxin ratio one should consider that the high value of 155 is related to a specific industrial process. Excluding this value will lower this variation in the PeCB/dioxin ratio. Hence, on the basis of the data in **Table 2**, one can recommend a PeCB/dioxins ratio for back yard burning of household waste of about 10, for MWIs about 5 and for HWIs about 50. Recommended PeCB/HCB ratios for back yard burning of household waste is about 2, for MWIs about 5, for MSWIs about 3 and for coal fired furnaces about 0.2.

3.3 Available emission factors for dioxins

3.3.1 Overview/surveys of dioxin sources and emission factors

A compilation of default dioxin emission factors originating from a wide scope of source categories is available in a standardized toolkit prepared by the United Nation Environment Programme to facilitate countries in making first estimates of (potential) dioxin sources and releases (UNEP, 2005). Using the UNEP toolkit information (UNEP 2003), the Australian government published a comprehensive report on national sources of the dioxin emissions (Bawden, 2004). **Table 3** presents the Australian data of the annual load of dioxins of the most important sources and emission factors of the top 20 emitters (sub category sources). **Table 3** shows that uncontrolled biomass burning is far out the largest emission source of dioxins. Assuming a emission relation between dioxins and PeCB, this will probably also be the main emission source of PeCB.
An extensive and comprehensive study on the exposure of dioxins is in preparation including information on emission factors of many sources/processes in the US (EPA, 2003). However, the current version concerns a review draft and does not allow to quote or cite the useful information. Nevertheless, it is expected that this information becomes accessible in the nearby future.

3.3.2 Controlled combustions

Dioxin emissions from various types of waste incinerators is described previously (see paragraph PeCB/dioxine emission correlation). Based on measurements, dioxin levels in house hold waste processed MSWIs, typically range from 0.01-0.05 µg I-TEQ/kg (Hedman et al 2007; Abad et al., 2002). Involving the stack gas measurements (n=8), the average dioxin emission factor for a municipal waste treatment plant was estimated to be 0.002 µg I-TEQ/kg waste (Abad et al 2002). Literature was also reviewed on the emission factors of dioxins for wood waste incinerators and power boilers (Uloth et al., 2002). These high capacity combustors are used to burn uncontaminated wood waste, that was not transported or stored in salt water. Average emission factors were estimated to be 0.039 µg I-TEQ/ton burned wood and 0.005 µg I-TEQ/ton burned wood for the power boilers and wood incinerators, respectively. Uloth et al. (2002) also informed that for residential wood combustion the emission factor of dioxins range between 0.00077 – 0.0019 µg I-TEQ/kg of dry wood. Higher emissions were found by combustion of various types of wood pellets and firewood in residential stoves and boilers being 0.011 µg WHO-TEQ/kg combusted fuel (dry weight) (Hedman et al., 2006).

Table 3. *Overview of dioxin emissions to air of the major Australian sources (Bawden, 2004). Main source categories and split subcategories are presented.*

Source Category	Emission factor µg I-TEQ/kg	Annual load g I-TEQ/y
Main category		
Waste incineration	-	6.5
Power generation and heating	-	112
Metal production	-	35
Mineral products	-	1.9
Transportation	-	9.1
Uncontrolled combustion processes	-	330
Production of chemicals and consumer goods	-	0.43
Miscellaneous	-	0.31
Subcategory		
Aluminum production	0.035	5
Biomass burning (uncontrolled)	0.0004-0.001	240
Cement production	0.00008	0.5
Ceramics production	0.0001	1
Copper production	0.05	1
Crematoria	0.005	0.3
Diesel engines	0.0007	5
Domestic heating and cooking with fossil fuels*	0.04	0.4
Fossil fuel power plants	0.01	14
Heavy oil fired engines	0.004	3
Household heating and cooking with biomass*	0.253	20
Iron and steel production plants	0.003	20
Lead production	0.008	0.5
Medical waste incineration	0.005	6
Metal ore sintering	0.005	32
Other non-ferrous metal production	0.002	4
Pulp and paper production	0.0003	0.4
4-Stroke Engines	0.0002	0.3
Waste burning and accidental fires (uncontrolled)**	0.06-1	88
Zinc production	0.1	50

* Emission factor in µg TEQ/TJ

** Includes landfill fires (EF = 1000), accidental vehicle fires (EF = 94), building fires (EF = 400), domestic waste burning (EF = 300), and open burning of wood (EF = 60).

3.3.3 Uncontrolled combustions

Due to its large impact on air pollution, emissions to air of dioxins and other related toxic compounds from uncontrolled combustion have been studied extensively. For example, emissions from open burning, on a mass pollutant per mass fuel (emission factor) basis, are greater than those from well-controlled combustion sources. Some types of open burning, e.g. biomass burning, are large sources on a global scale compared to other sources classes (e.g. mobile and industrial sources) (Lemieux et al., 2004).

The uncontrolled burning of household waste in barrels has been identified as a major source of airborne emissions of dioxins. The emissions of dioxins from the barrel burning of household waste with nominal compositions were investigated (Lemieux et al., 2003) under experimental conditions. The average emissions were 0.0768. µg WHO-TEQ /kg waste combusted (range 0.009-0.308 µg TEQ/kg waste combusted). Emissions from the replicate baseline runs showed approximately one order of magnitude in variability.

Dioxin emissions from experimental combustion of two types of forest biomass (such as crown fires versus understory and duff fires) were sampled to obtain estimated emission factors for forest fires (Gullett and Touati, 2003). The average emission factors were 0.025 µg TEQ/kg burned (range: 14-47) and 0.015 µg I-TEQ/kg burned (range: 1-56), for the two types of forest biomass, respectively. The emissions were about 20 times higher than the concentration from the extracted biomass, suggesting that dioxins are predominantly formed de novo during the biomass combustion.
According to a report of the Australian national dioxins program (Meyer et al., 2004), emission factors for field burns ranged between 0.0001-0.0029 µg I-TEQ /kg. However, in laboratory tests the emission rates for grass fuels of straw, sorghum, and sugar cane were about 10 times higher.
Lemieux et al. (2000) reported emissions of dioxins that were examined in an experimental set-up for barrel burning of different types of household waste. Emissions of total PCDD/Fs ranged between 4.6 and 480 µg/kg waste burned indicating that backyard burning emits much more dioxins per mass of refuse burned basis than Municipals Waste Incinerators (MWI). For example, for the open barrel burning of household waste, the emission factor of dioxins was estimated to be more than 1000 times higher compared to a modern, clean-operating MWI (4.4 µg /kg vs. 0.0035 µg/kg of waste burned).
In another study, the total emissions of dioxins and PCBs from backyard burning of domestic waste were assessed (Hedman et al 2005). For the burning of waste that was little to moderately contaminated with (organo) chlorine, such as garden waste, straw, paper with and without the addition of refuse-derived fuel, an emission range of 0.004-0.0072 µg (WHO-TEQ)/kg was estimated.
It should be noted, however, that local burning conditions could significantly change these relative levels, and, hence, emissions of dioxins and other persistent organochlorine compounds like PeCB can vary greatly from source to source and can exhibit significant variations within the source categories considered (Lemieux et al., 2004).
Biomass combustion from prescribed burning and wild bushfires are potentially the most significant sources of dioxins emission to air. Similarly, other sources - like open fireplaces and biomass cooking - are also known emission sources. It should be noted, however, that natural sources such as wild bushfires are not included in the Convention while prescribed burning corresponds to a human activity.

3.4 Emission factors for hexachlorobenzene (HCB)

It is well known that beside PeCB also hexachlorobenzene (HCB) and other related organochlorine compounds, like PCBs and PCDD/Fs, may be formed as by–products due to chemical reactions in combustion processes. Therefore, besides dioxin data, emission data on HCB may also be useful to estimate PeCB emissions.
Based on US and Canadian emission data from the mid 1990s, a comprehensive overview of global atmospheric emissions of HCB was made that also included HCB emission factors for several processes (Bailey, 2001). The mean estimated global emission factors of HCB are shown in **Table 4**. The study indicated that in case of combustion processes, it was impossible to assign factors with much confidence, rendering a 100-fold range of the reported data.
By combining the PeCB/HCB ratio emissions from studies involving dioxin and related organochlorine surrogate compounds (**Table 2**) with global HCB atmospheric emissions (**Table 4**), global emissions of PeCB can be estimated for defined source categories.

Table 4. Mean estimated global atmospheric emissions of HCB (Bailey, 2001).

Source	Emission factor µg /kg	Annual load kg/y
Metals:		
Aluminum casting using hexachloro/ethane	2.2×10^6	7770
Secondary copper smelters	390	104
Combustion:		
Municipal	29	5626
Hazardous waste	19	95
Medical	29	86
Coal	0.08	350
Cement	0.17	43
Iron sintering	1.5	70
Sewage sludge	4.7	12
Biomass	0.06	496

4. Discussion and conclusions

This work reviewed available literature on emissions of PeCB from various combustion related sources. The main focus was to collect emission data and factors of PeCB. Few data generated by direct measurements is available. Most data available concerns various combustion processes.

The following conclusions can be made:

- At present, unintentional release from anthropogenic sources is by far the largest emission source of PeCB.
- For controlled waste incineration an emission factor range of 0.1-273 µg/kg waste was estimated for PeCB. Emission factors for PeCB of 2.5 µg/kg was estimated for coal combustion and in case of back yard barrel burning reported average emission factors for PeCB ranged between 4.5 and 80 µg/kg.
- PeCB emissions are correlated with other more emission data-rich combustion related compounds, such as dioxins and hexachlorobenzene (HCB). Based on these ratios, PeCB emissions can be derived for various combustion processes and sources. Proposed values for such an estimation are as follows: PeCB/dioxins ratio for back yard burning of household waste is about 10, for MWIs about 5 and for HWIs about 50. Recommended PeCB/HCB ratios for back yard burning of household waste is about 2, for MWIs about 5, for MSWIs about 3 and for coal fired furnaces about 0.2. Because of the range in emission data, a careful interpretation is recommended.
- There are still uncertainties in emissions factors for PeCB and the estimation of the world-wide emission. Further development of emission factors for other processes may facilitate a more thorough estimation of the world-wide emission of PeCB. Lack of emission data should not hamper PeCB to be listed. In context of articles 8.7 and 8.9 of the Stockholm Convention, the Conference of the Parties, shall decide whether to list the chemical, and specify its related control measures in a precautionary manner, including any scientific uncertainty.

Acknowledgements

This project has been supported by the Ministery of Spatial Planning, Housing and the Environment (VROM). We would like to thank Mr. Cees Luttikhuizen (VROM) for the support and input we received during this project. We also gratefully would like to thank Ms. Anke Joas (BiPRO GmbH, Beratungsgesellschaft für integrierte Problemlösungen), Mr. Christopher Marshall (Chemical Management Division, Environment Canada), Ms. D. Cristofaro (DG Environment, European Commission) and Ms. Heidiloze Fiedler (UNEP) for the data and information provided during this project. We also would like to thank Mr. Martijn Beekman and Mr. Joost Bakker (RIVM) for reviewing the current work.

References

Abad E., Adrados M.A., Caixach J., Rivera J. (2002), *Dioxin abatement strategies and mass balance at a municipal waste management plant*, Envro. Sci. Technol. 36, 92-99.

Bailey R.E. (2001), Global hexachlorobenzene emissions, Chemosphere 43, 167-182.

Bailey R.E. (2007), Pentachlorobenzene –Sources, environmental fate and risk characterization, Science dossier, Euro Chlor, 41 pages.

Bawden K. (2004), Technical report No. 3, *Inventory of dioxin emissions in Australia, 2004*, National Dioxins Program, Australian Government, Department of the Environment and the Heritage, http://www.environment.gov.au/settlements/publications/chemicals/dioxins/report-3/pubs/report-3.pdf.

Blumenstock M., Zimmermann R., K.-W. Schramm, Kettrup A. (2001), *Identification of surrogate compounds for the emission of PCDD/F (I-TEQ value) and evaluation of their on-line real-time detectability in flue gases of waste incineration plants by REMPI-TOFMS mass spectrometry*, Chemospher 42, 507-518.

Chandler A.J. (2004a) Assessment of the Potential for Emissions of Tetrachlorobenzenes and Pentachlorobenzenes from the Incineration of Hazardous Waste. Environment Canada, National Office of Pollution Prevention, 36 pages.

Chandler A.J. (2004b) Assessment of the Potential for Emissions of Tetrachlorobenzenes and Pentachlorobenzenes from the Incineration of Municipal Solid Waste. Environment Canada, National Office of Pollution Prevention, 37 pages.

Cristofaro D. (2009), e-mail communication from DG Env C4 Industrial Emissions & Protection of the ozone layer.

EPA (1999). *Estimating Releases and Waste Treatment Efficiencies for the Toxic* Chemical Release Inventory Forms. 1999.

EPA Research and Development (2002), *Emission of Organic Air Toxics from Open Burning*, EPA-600/R-02-076.

EPA/600/P-00/001Cb (2003), *Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo*-p-*Dioxin (TCDD) and Related Compounds National Academy Sciences (NAS) Review Draft*, http://www.epa.gov/ncea/pdfs/dioxin/nas-review/.

Gullett, B.K. and A. Touati (2003), *PCDD/F emissions from forest fire simulations*, Atmospheric Environment 37, 803-813.

Hattum B. van, Senhorst H., Tukker A., Lamoree M., Sanderson T., Koning A. de (2004), *Evaluation of current emission of chlorinated microcontaminants from the Dutch chlorine chain. Final Technical Report of the Chlorine Chain Follow-up Research Programme on Chlorinated Micro contaminants (OVOC)*, Institute for Environmental Studies IVM), Free University (VU), Amsterdam, 126 pages

Hedman B., Bruvall J., Nilsson C., Marklund S. (2007), *PCCD/F in source-sorted waste fractions and emissions from their co-combustion with reed canary-grass*, Waste Management 27, 1580-1592.

Hedman B., Näslund M., Marklund S (2006), *Emission of PCDD/F, and HCB from combustion of firewood and pellets in residuential stoves and boilers*, Environ. Sci. Technol. 40, 4969-4975.

Hedman B., Näslund M., Nilsson C., Marklund S. (2005), *Emissions of Polychlorinated Dibenzodioxins and Dibenzofurans and Polychlorinated Biphenyls from Uncontrolled Burning of Garden and Domestic Waste (Backyard Burning)*, Environ. Sci. Technol. 39, 8790 – 8796.

Kato M., Urano K. (2001), *Convenient substitute indices to toxic equivalent quantity for controlling and monitoring dioxins in stack gas from waste incineration facilities*, Waste Mangement 21, 55-62.

Kim K.-S., Hong K.-H, Ko Y.-H (2004), *Emission characteristics of PCDD/Fs, PCBs, chlorobenzenes, chlorophenols, and PAHs from polyvinylchoride combustion at various temperatures*, J. Air & Waste Mange. Assoc. 54, 555-562.

Lavric, E.D., A.A. Konnov, J. De Ruyck (2005) S*urrogate compounds for dioxins in incineration. A review*, Waste Management 25, 755-765

Lemieux P.M., Gullett B.K., Lutes C.C., Winterrowd C.K., Winters D.L. (2003), *Variables affecting emissions of PCDD/Fs from uncontrolled combustion of household waste in barrels*, J. Air & Waste Manage. Assoc. 53, 523-531.

Lemieux P.M., Lutes C.C., Abbott J.A., Aldous K.M. (2000), *Emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from the open burning of household waste in barrels*, Environ. Sci. Technol. 34, 377-384.

Lemieux P.M., Lutes C.C., Santoianni D.A. (2004), *Emissions of organic air toxics from open burning: a comprehensive review*, Progress in Energy and Combustion Science 30, 1-32.

Meyer C, Beer T., Müller J. (2004), Technical report No. 1, *Dioxins emissions from bushfires in Australia*, Australian Government Department of the Environment and Heritage, http://www.environment.gov.au/settlements/publications/chemicals/dioxins/report-1/index.html.

NPi (2009), National Pollutant Inventory Guide Version 5.0, Australian Government, Department of the Environment, Water, Heritage and the Arts.

Oberg T., Bergstrom J.G.T. (1985), *Hexachlorobenzene as an indicator of ioxin production from combustion*, Chemosphere 14, 1081-1086.

Pandelova M., Lenoir D., Kettrup A., Schramm K.-W. (2004), *Correlation between PCDD/F, PCB and PClBz in coal/waste combustion. Influence of various inhibitors*, ORGANOHALOGEN COMPOUNDS, 66, 966-970.

Pandelova M.P. (2004), *Emissions minimization of chlorinated micropullants in coal solid waste co-combustion by primary measures*, Thesis, Technischen Universität München, Germany.

Reinmann J., Kuch B., Weber R. (2006), *Continuous Monitoring of Unintentionally Formed POPs Listed Under the Stockholm Convention (PCDDs/PCDFs, PCBs, HCB) Using AMESA® Long Term Sampling System*, Organohalogen Compounds, 68, 852-855.

Takaoka M. Liao P., Takkeda N., Fujiwara T., Oshita K.(2003), *The behavior of PCDD/Fs, PCBs, chlorobenzenes and chlorophenols in wet scrubbing system of municipal solid waste incinerato*r, Chemosphere 53, 153-161.

Uloth V., Whitford T., Heek R. van (2002), *Dioxin and Furan emission factors for Wood Waste Incinerators*, Report of Pulp and Paper Research Institute of Canada, Vancouver, Canada, 32 pages.

UNEP (1999), *Dioxin and Furan Inventories, National and Regional Emissions of PCDD/PCDF*, UNEP Chemicals, Geneva, Switserland.

UNEP (1999b), *1st Scientific and Technical Evaluation Workshop on Persistent Manufactured Chemicals Produced for Non-Agricultural Applications, Persistent Toxic and Persistent Unintentional Byproducts of Industrial and Combustion Processes*, Geneva

UNEP (2003), *'Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases'*, UNEP Chemicals, Geneva, Switzerland.

UNEP (2005), *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*, Edition 2.1, UNEP Chemicals, Geneva, Switzerland., http://www.pops.int/documents/guidance/toolkit/ver2_1/Toolkit-2005_2-1_en.pdf.

UNEP (2007), *Draft pPentachlorobenzene risk profile*, Report of the Persistent Organic Pollutants Review Committee on the work of its third meeting, UNEP/POPS/POPRC.3/20/Add.7

UNEP (2008), *Draft risk management evaluation: Pentachlorobenzene*, draft report of the Persistent Organic Pollutants Review Committee of its fourth meeting, POPS/POPRC.4/7.

Wenzel K.-D., Hubert A., Weissflog L., Kühne, R., Popp P., Kindler A., Schüürmann G. (2006), *Influence of different emission sources on atmospheric organochlorine patterns in Germany*, Atmospheric Environment 40, 943-957.

Wikström E., Persson A, Marklund S. (1998), *Secondary formation of PDDDs, PCDFs, PCBs, PCBzs, PCPhs and PAHs during MSW combustion*, Organohalogen Compounds 36, 65-67.

Zimmermann R., Blumenstock M., Heger J.J., Schramm K.-WA. (2001), *Emission of Nonchlorinated and Chlorinated Aromatics in the Flue Gas of Incineration Plants during and after Transient Disturbances of Combustion Conditions: Delayed Emission Effects*, Environ. Sci. Technol. 35, 1019-1030.

Appendix 1. Industries and processes likely to emit organochlorine persistent pollutants (UNEP 1999)

Industry or Process or Product Use	Special Indicators
Manufacturing:	
Production of chlorinated organic chemicals	chloro-aromatics (phenols, benzene *etc.*), Cl-solvents, oxychlorinators
Cl_2-production using graphite electrodes	
Oil refining and catalyst regeneration	
Pulp and paper production	Cl_2-bleaching
Thermal Processes:	
Iron ore sintering for blast furnaces	flyash recirculation
Primary copper smelting	
Secondary scrap metal processing, incl. steel, aluminum, lead, zinc, copper and magnesium	cable burning, metal recovery from flyash
Coke production and carbo-chemical processes	use of lignite/brown coal
Cement kilns	use of halogenated hazardous waste as a fuel source
Asphalt mixing	
Mineral processing (lime, ceramic, glass, brick)	small scale, uncontrolled
Municipal waste incineration (technological)	old, APC-unequipped
Industrial waste combustion (technological)	old, APC-unequipped
Waste wood combustion (technological)	treated wood
Hazardous waste incineration (technological)	old, APC-unequipped
Sludge incineration (technological)	industrial sludge
Medical/clinical waste incineration	APC-unequipped, batch-type incinerator
Crematorium and animal carcass burning	APC-unequipped
Wood/biomass combustion (technological)	large quantities, salt content
Landfill gas/biogas combustion	APC-unequipped
Coal combustion (technological)	brown coal/lignite, old, small
Oil combustion (technological)	waste oil, heavy oil
Internal combustion engines (*i.e.* vehicles and stationary motors)	leaded gasoline, Diesel, old, low maintenance
Biomass burning (intentional, uncontrolled)	forest, bush, agricultural residues (*i.e.* straw)
Accidental fires (unintentional, uncontrolled)	industrial complexes, residential houses

Appendix 1 (continued)

Industry or Process or Product Use	**Special Indicators**
Thermal Processes (continued)	
Landfill fires (unintentional and intentional)	
Burning of waste, *i.e.* flaring of drilling mud, landfill gas, construction debris, domestic waste	uncontrolled (backyard) burning
Plastic container/barrel burning	halogenated plastic
Rubber/tire/cable/circuit board waste	
Product Application and Use:	
Pesticide/herbicide application	2,4,5-T, PCP
Preservatives for wood/leather/textiles	leaching, waste disposal
Textile/wool/leather dying and finishing	use of chloranil, alkaline extraction
Industrial bleaching processes	use of chlorine
Transformer and electrical equipment use	PCB-oil
Solvent use and application	de-greasing, dry-cleaning
Use of paint containing PCB or PCP	mostly from old stockpiles
Recycling Processes	
Metal (incl. vehicle) recycling	by-products, *i.e.* shredder, waste oil, refrigerant, electronic scrap
Paper recycling	de-inking sludge
Sewage and paper sludge and effluent application on land, *i.e.* fertilizer	agriculture, composting
Solvent recovery	residue sludge
Waste oil recovery	
Plastics recycling	extrusion
Metal flyash recycling	extraction
Waste Disposal (non-thermal) and Reservoirs:	
Landfills and leachate from these	sludge, fly ash, metal ash
Ocean dumping	solid/sludge/liquid waste
Transformer storage/stockpiles	PCB-oil
PCP-treated wood	telephone poles, railroad ties

Appendix 2. Short description of four commonly used release estimation techniques

1 The **direct measurement** method obtained from source testing and provides a snapshot of the releases during a test period. Contaminant concentrations are multiplied by the flow rate to obtain a release value per unit time. This loading is then multiplied by the total period of operation to determine the release over a specific time period. This method is one of the more accurate methods to estimate emissions.

2 A **mass balance** is based on the application of the law of conservation of mass to a process. Essentially, if there is no accumulation within the system, all the materials that go into the system must come out, either in the product, in or as by-products, waste streams or as releases. Mass balance can provide an accurate estimate of emissions where known quantities of substances are supplied to the process and the process fate of the substance is both known and quantifiable. The use of mass balance in estimating minor emissions is not recommended due to inherent errors, and, therefore, not very useful for the estimation of PeCB emissions, mostly formed as a by-product in various combustion processes.

3 An **emission factor** is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. These factors are usually expressed as the weight of pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant (e.g., kilograms of Particulate Matter (PM) emitted per megagram of coal burned). Such factors facilitate estimation of emissions from various sources of air pollution. In most cases, these factors are simply averages of all available data of acceptable quality, and are generally assumed to be representative of long-term averages for all facilities in the source category (i.e., a population average).

4 **Engineering calculations** utilize standard physical and chemical laws and constants to allow the estimation of particular emissions.

RIVM

National Institute
for Public Health
and the Environment

P.O. Box 1
3720 BA Bilthoven
The Netherlands
www.rivm.com