



# **Guidance on preparing inventories of hexachlorobutadiene (HCBD)**

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**Secretariat of the Basel, Rotterdam and Stockholm  
Conventions**

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## Abbreviations and acronyms

ATSDR	Agency for Toxic Substances and Diseases Registry
BUA	Beratergremium für Umweltrelevante Altstoffe
CFC	Chlorofluorocarbon
CSM	Conceptual Site Model
DSI	Detailed site investigation
ECHA	European Chemical Agency
EQS	Environmental Quality Standard
ESIS	Existing Substance Information System of the European Commission
EU	European Union
GC-ECD	Gas chromatograph electron capture detector
HCB	Hexachlorobenzene
HCBD	Hexachlorobutadiene
HPVC	High Production Volume Chemical
IISD	International Institute for Sustainable Development
IACR	International Agency for Research on Cancer
IPCS	International Programme on Chemical Safety
LPVC	Low Production Volume Chemical
OCDD	Octachlorodibenzo- <i>p</i> -dioxin
OCDF	Octachlorodibenzofuran
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo- <i>p</i> -dioxins
PCDFs	Polychlorinated dibenzofurans
PCNs	Polychlorinated naphthalenes
PeCBz	Pentachlorobenzene
PERC	Perchloroethylene
POPRC	POPs Review Committee
POPs	Persistent Organic Pollutants
ppm	Parts per million
PSI	Preliminary site investigation
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
U.S. EPA	United States Environmental Protection Agency
UNIDO	United Nation Industrial Development Organisation
WWF	World Wide Fund for Nature

# 1. Introduction

## 1.1. Hexachlorobutadiene (HCBD) under the Stockholm Convention

In May 2015, by decision SC-7/12, the Conference of the Parties (COP) to the Stockholm Convention on Persistent Organic Pollutants (POPs) amended Annex A to list therein hexachlorobutadiene, hereinafter referred to as HCBD, without specific exemption.

On 15 December 2015, pursuant to paragraph 4 of Article 21 of the Convention, the amendment was communicated by the depositary to all Parties to the Convention. On 15 December 2016, one year after the date of communication by the depositary, the amendment listing HCBD in Annex A to the Stockholm Convention entered into force for most Parties<sup>1</sup>.

Also, at its seventh meeting, the Conference of the Parties adopted decision SC-7/11, by which it requested the Persistent Organic Pollutants Review Committee (POPRC) to further evaluate HCBD on the basis of newly available information in relation to its listing in Annex C and to make a recommendation to the Conference of the Parties on listing HCBD in Annex C for further consideration at its eighth meeting.

At its eleventh meeting, POPRC adopted decision POPRC-11/5 on unintentional releases of HCBD,<sup>2</sup> by which the Committee established an intersessional working group to undertake the activities requested in paragraphs 1 and 3 of decision SC-7/11 and requested the Secretariat to collect from Parties and observers any additional information that would assist the further evaluation by the Committee of the unintentional production of HCBD.

In accordance with the workplan set out in the annex to decision POPRC-11/5, the intersessional working group prepared a draft evaluation<sup>3</sup> of new information in relation to the listing of HCBD in Annex C to the Convention.

At its twelfth meeting, having evaluated new information on the unintentional production of HCBD in accordance with decision SC-7/11, the Committee adopted decision POPRC-12/5<sup>4</sup>, by which it concluded that there were unintentional releases of HCBD from the production of certain chlorinated hydrocarbons, the production of magnesium, incineration processes and the production of polyvinyl chloride, ethylene dichloride and vinyl chloride monomer; and noted nonetheless that there were some concerns regarding the cost-benefit implications of measures to address such unintentional releases.

Like all POPs, HCBD has toxic properties in particular for aquatic organisms and birds, resists degradation, and bioaccumulates in fatty tissues (ATSDR 1994; BUA 1991; IACR 1999; IPCS 1994; UNEP 2011). It is transported through air, water and migratory species, across international boundaries and deposited far from their place of release, where it accumulates in terrestrial and aquatic ecosystems (Environment Canada 2000; Hung 2012; UNEP 2011). Due to the scarcity of data it is difficult to identify a temporal trend for remote areas (UNEP 2012).

Parties to the Convention for which the amendment enters into force have to meet the obligations under the Convention leading to the elimination of HCBD from production and use. The use of unintentionally produced by-product HCBD is also prohibited.

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<sup>1</sup> Amendments shall not enter into force for those Parties that have submitted a **notification** pursuant to the provisions of paragraph 3(b) of Article 22 of the Stockholm Convention. Also, in accordance with paragraph 4 of Article 22, the amendment will not enter into force with respect to any Party that has made a **declaration** regarding the amendment to the Annexes in accordance with paragraph 4 of Article 25. Such Parties shall deposit their instruments of ratification regarding the amendment, in which case the amendment shall enter into force for the Party on the ninetieth (90) day after the date of deposit with the depositary.

<sup>2</sup> UNEP/POPS/POPRC.11/10, annex I.

<sup>3</sup> UNEP/POPS/POPRC.12/INF/12.

<sup>4</sup> UNEP/POPS/POPRC.12/11.

## 1.2. Purpose of the guidance

Under Article 7 of the Stockholm Convention, Parties are required to develop and endeavour to implement a plan for the implementation of their obligations under the Convention. National implementation plans (NIP) need to be updated with information on how Parties, for which the amendments have entered into force, will meet the obligations arising from amendments to Annexes A, B and/or C to the Convention to list new chemicals, in accordance with decision SC-1/12.

Under Article 15 of the Stockholm Convention, Parties are required to report to the Conferences of the Parties on the measures it has taken to implement the provisions of the Convention and on the effectiveness of such measures in meeting the objectives of the Convention.

To develop effective strategies for the elimination of HCBD and the environmentally sound management of products, stocks and wastes containing HCBD, Parties need to develop a sound understanding of their national situation concerning this chemical. Such information can be obtained through an inventory of HCBD that is generated, materials and wastes containing HCBD, and sites contaminated with HCBD. The establishment of inventories is thus one of the important phases in the development of NIPs (decision SC-2/7).

The objective of this guidance is to provide Parties with guidance on the establishment of inventories of HCBD, which was listed under the Convention in 2015. The inventory guidance should be used by official contact points or national focal points designated by Parties for the Convention and those involved in the process for NIP review and update, in particular the task teams responsible for establishing the inventory. The document and the inventory will also be of interest to other stakeholders concerned with elimination of HCBD.

Article 6, paragraph 1 (a), of the Stockholm Convention requires each Party to develop appropriate strategies for the identification of products and articles in use and wastes consisting of, containing or contaminated with POPs. The identification of HCBD wastes is the starting point for their effective environmentally sound management.

This document can be used in conjunction with documents developed under the Basel Convention which provide guidance on the development of identification strategies and inventories in relation to POPs wastes and in particular HCBD wastes:

- General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants (UNEP 2017a);
- Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with hexachlorobutadiene (UNEP 2017b);
- Methodological guide for the development of inventories of hazardous wastes and other wastes under the Basel Convention (UNEP 2015a).

### 1.3. Objectives of the inventory

The main objective of the inventory is to obtain information needed for the implementation of obligations of Parties under the Stockholm Convention. More specifically, the objectives are to:

- Establish the country baseline with respect to HCBD production/generation, use, stockpiles and disposal;
- Provide the basis for development of a strategy in the NIP (i.e. identify the economic sectors that should be prioritized and the type of actions required for those sectors);
- Report to the Conference of the Parties to the Stockholm Convention through national reporting on the progress made to eliminate HCBD;
- Identify areas where financial and/or technical support is needed when resources are limited, to fulfil the obligations under the Convention.

The information obtained about HCBD through the inventory includes the following:

- Past and current production of HCBD on the national level;
- Intentional uses of HCBD;
- Import/export of HCBD for use;
- HCBD in products, stocks and wastes;
- Import/export of HCBD containing wastes for environmentally sound disposal;
- Chemical and thermal processes in which HCBD is unintentionally generated as a by-product and associated releases<sup>5</sup>;
- Disposal practices for products and articles containing HCBD when they become wastes;
- Sites potentially contaminated by HCBD.

Information collected on the above will provide broader understanding of the sources of HCBD, the scope of its impact and the risks it poses to human health and the environment in a country. The information is important for Parties to implement the obligations under the Convention regarding HCBD and to identify areas where they need to develop effective strategies and action plans for managing HCBD in order to meet the obligations.

Information collected as part of the inventory will also provide a valuable basis for Parties to report to the Conference of Parties on measures taken to implement the provisions of the Convention and the effectiveness of such measures (reporting under Article 15).

The inventory process is usually iterative. In establishing the inventory of HCBD for the first time, Parties will also identify resources and technical capacity needed to further improve the accuracy of the inventory.

**PLEASE NOTE: The most relevant source of HCBD was (and is) the production of chlorinated solvents (tetrachloroethylene<sup>6</sup>, trichloroethylene, tetrachloromethane/carbon tetrachloride<sup>7</sup>) and hexachlorocyclo-pentadiene (intermediate of cyclodiene pesticides) and the related waste and landfills from (former) production. Therefore, in particular Parties which have or had production of these organochlorine substances and possibly production of other related organochlorines should establish detailed HCBD inventories. Parties that have neither current nor past production of relevant organochlorines in their countries are not expected to have major HCBD production, release, stockpiles**

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<sup>5</sup> Since HCBD as an unintentional by-product has been sold for commercial intentional uses in the past, as noted in UNEP/POPS/POPRC.9/13/Add.2, information on sources of HCBD by-product formation are important to be considered in the development of the inventory, although HCBD is not currently listed as an unintentionally produced POP in Annex C.

<sup>6</sup> Tetrachloroethylene is also known under the systematic name tetrachloroethene or known as perchloroethylene (PERC).

<sup>7</sup> Tetrachloromethane is the systematic IUPAC name while carbon tetrachloride is more commonly used in industry/literature.

or contaminated sites. As a consequence, such Parties can prepare inventories that are limited to possible imports of HCBD and imports of impacted organochlorines.

The inventory of HCBD (and HCB) in the production of organochlorines and elemental chlorine that was developed by the U.S. EPA for 1972 may serve as a useful case study (Mumma and Lawless 1975; Table 2-3).

## 1.4. Structure of the guidance

The guidance has seven chapters and one annex as follows:

**Chapter 1:** Outlines the purpose of the guidance and the major objectives for undertaking an inventory;

**Chapter 2:** Provides background information on HCBD that is essential to the inventorying process;

**Chapter 3:** Outlines the five main steps involved in conducting an inventory of HCBD and provides an overview of considerations that are important for planning the inventory and defining its scope;

**Chapter 4:** Provides guidance on inventorying HCBD in the production of certain organochlorine substances;

**Chapter 5:** Provides guidance on inventorying the use, potential stockpiles and wastes consisting of or contaminated with HCBD;

**Chapter 6:** Provides initial guidance on unintentional HCBD releases from major thermal processes, although HCBD is not yet listed in Annex C as an unintentional produced POP;

**Chapter 7:** Provides guidance on developing an inventory of sites potentially contaminated by HCBD;

**Annex:** Contains a questionnaire for compiling information on the current and former production of organochlorine substances during which HCBD is or was formed as a product or as a by-product.

The key design and content features of this guidance are:

**Step by step approach:** The guidance is designed to provide a clear step-by-step approach that can be followed and implemented by a wide variety of users. A five-step approach is provided for the overall inventory from the planning stage to preparation of the inventory report (see chapter 3). The tiered approach provides the opportunity to countries with different capacities to develop an inventory. Detailed and specific guidance on data collection for key sectors can be found in chapters 4 and 5.

**Questionnaires:** Questionnaire is provided to support the gathering of information from current and former production of organochlorines in which HCBD was formed as a product or as a by-product (Annex).

To allow flexibility, no specific reporting format is suggested in this inventory guidance.

## 2. Background information on HCBD

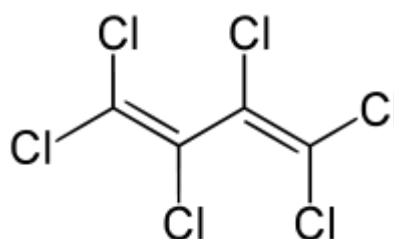
### 2.1. Description of characteristics of HCBD

HCBD is a halogenated aliphatic substance, mainly generated as a by-product in the manufacture of chlorinated solvents (tri- and tetrachloroethylene<sup>6</sup> and tetrachloromethane<sup>7</sup>) or hexachlorocyclopentadiene (intermediate of cyclodiene pesticide). Anthropogenic emission sources of HCBD are intentional production (see chapter 2.2), unintentional production (see chapter 2.3) and waste from historical application (see chapter 2.5) and related potentially contaminated sites (see chapter 2.6) (UNEP 2012). HCBD was used in a range of applications (see chapter 2.4). HCBD has an ozone depleting potential (ODP) higher than some ozone damaging substances which are banned under the Montreal Protocol (UNEP 2001). There are no known natural sources of HCBD (BUA 1991).

Basic information on HCBD including its chemical structure is compiled in Table 2-1. Information about chemical and physical properties of HCBD is listed in Table 2-2.

**Table 2-1:** Basic information and chemical structure of HCBD (UNEP 2013a; Lecloux 2004)

<b>Common name</b>	Hexachlorobutadiene
<b>IUPAC Name</b>	1,1,2,3,4,4-hexachlorobuta-1,3-diene
<b>Synonym</b>	HCBD; perchloro-1, 3-butadine; perchlorobutadiene; 1,3-hexachlorobutadiene; 1,3-butadiene, 1,1,2,3,4,4-hexachloro-; 1,3-butadiene, hexachloro-; hexachlorobuta-1,3-diene
<b>CAS registry number</b>	87-68-3
<b>Common trade names (IPCS 1994)</b>	C-46, Dolen-pur, GP40-66:120, UN2279
<b>Molecular formula</b>	C <sub>4</sub> Cl <sub>6</sub> , Cl <sub>2</sub> C=CClC=CCl <sub>2</sub>
<b>Molecular weight</b>	260.76 g/mol



**Figure 2-1:** Structure of hexachlorobutadiene (HCBD)

**Table 2-2:** Physical and chemical properties of HCBD (Horwath 1982; Mackay et al. 2006; UNEP 2013a)

Physical-chemical property category	Characteristics of HCBD
Melting Point (°C)	-21
Boiling Point (°C)	215
Density (g/cm <sup>3</sup> at 20°C)	1.68
Water solubility (mg/L at 25°C):	3.2 mg/L
Vapour pressure (Pa at 20°C and 100°C)	20 and 2926
Henry's law constant (Pa m <sup>3</sup> /mol)	1044 (experimental), 2604 (calculated)
Log K <sub>ow</sub>	4.78 - 4.9
Log K <sub>oa</sub> (at 10°C)	6.5
Log K <sub>oc</sub>	Reported range: 3.7 to 5.4
Physical state (at 25°C)	Liquid

## 2.2. Intentional production and trade of HCBD

HCBD can be directly produced by chlorination of butane and chlorinated butane derivatives (BUA 1991; Ullmann 1986). However no commercial production by such direct synthesis has been reported.

The primary source of HCBD production/formation was and possibly is during the manufacturing of chlorinated solvents such as tetrachloroethylene<sup>6</sup>, trichloroethylene and tetrachloromethane/carbon tetrachloride<sup>7</sup> (BUA 1991; Choudhary 1995; Lecloux 2004; U.S. EPA 2002; U.S. EPA 1980). For intentional production, HCBD is separated from the heavy fraction of the production of these solvents and was and possibly is marketed for various uses (see chapter 2.4) (UNEP 2013a).

HCBD was produced in high volumes between 1970 and 1980. Worldwide production of HCBD was estimated to be about 10,000 tonnes in 1982 (UNEP 2012). It has been more than a decade since the HCBD generated as a by-product of chlorinated solvent production was separated in the UNECE region and marketed (VROM 2002; UNEP 2012). Data about intentional production outside of the UNECE region were not available (Lecloux 2004; UNEP 2013a). Monitoring data from East Asia (Juang et al. 2010; Li et al. 2008; Zhang et al. 2014; Zhang et al. 2015) suggest that intentional production and/or unintentional generation and release have continued at least until recently (UNEP 2013a). Also some information suggests that intentional production and/or use of HCBD may still be relevant:

- The European Chemical Agency (ECHA) Classification and Labelling (C&L) inventory indicates that there are 65 notifiers for HCBD, which suggests some continuing interest in producing or importing HCBD. However, no application for registration has been submitted to ECHA since 2015 (Potrykus et al. 2015).
- The European Directive 88/347/EEC and Decision 92/446/EEC mentioned "industrial plants using HCBD for technical purposes" as a possible source for HCBD releases.

On the other hand, some information indicates that current or recent intentional production and/or use is not in quantities of significance for OECD countries:

- There are no data to indicate that a member state produced or imported HCBD in quantities greater than 1,000 tonnes in 1997. The classification of HCBD as High Production Volume (HPV) could not be confirmed in the OECD database<sup>8</sup>;

<sup>8</sup> Comment from the Netherlands for the POP Reviewing Committee, 2013.

- HCBD has not been reported by the EU Industry as an HPVC<sup>9</sup> or LPVC<sup>10</sup> within ESIS<sup>11</sup>;
- HCBD has not been reported as an HPVC<sup>12</sup> within the US HPV database<sup>13</sup>.

From a global perspective, it is apparent that chlorinated solvent production is shifting from western OECD countries to Asia. However, in 2014, the United States still accounted for approximately 41% of total world demand for tetrachloroethylene, followed by China at 32% and Western Europe at almost 10%. Chinese PCE consumption has surpassed Western European PCE demand since 2011, and Chinese PCE consumption is projected to experience the highest average annual growth rate among major consumers, at about 7.5%, during 2014–2019 (HIS Markit 2014).

The trading of HCBD is not regulated under the Rotterdam Convention. HCBD has not been included in the EU Regulation No 649/2012 of the European Parliament and of the Council of 4 July 2012 concerning the export and import of hazardous chemicals. Thus, no data on international trade of HCBD could be retrieved from the European database EDEXIM.<sup>14</sup>

Therefore inventories developed in the framework of Stockholm Convention implementation would assess and will show if HCBD is still being separated from the production of organochlorine solvents or related chemicals and marketed as product.

### 2.3. Unintentional generation of HCBD

At the date of preparation of this document, HCBD is not listed in Annex C as an unintentionally produced POP. However, information on sources of unintentional HCBD by-product formation is important to be considered in the development of the inventory, since as noted in UNEP/POPS/POPRC.9/13/Add.2, HCBD as an unintentional by-product has been sold for commercial intentional uses in the past.

HCBD is unintentionally generated during the production of certain organochlorines, particularly tetrachloroethylene<sup>6</sup> (Figure 2-2), trichloroethylene, and tetrachloromethane/carbon tetrachloride<sup>7</sup> (RIVM 2001, Lecloux 2004, UNEP 2012). HCBD and other unintentionally produced POPs are formed when smaller organochlorine chemicals undergo condensation reactions to form HCBD as well as chlorinated aromatic substances including unintentional POPs (Figure 2-2). In addition to HCBD, wastes from the production of organochlorine solvents also contain hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs) (Figure 2-2; Dow Chemicals 1990; Thornton 2001; UNEP 2013a, 2016; Weber et al. 2011a; Zhang et al. 2015), and lower concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDFs) (Zhang et al. 2015).

The production of tri-, tetrachloroethylene and tetrachloromethane is carried out by either low-pressure or high-pressure chlorolysis. The products of low-pressure chlorolysis contain 0.2 to 5 % HCBD in the raw material (BUA 1991; UNEP 2013a). In industrialized countries today, products of optimized low-pressure chlorolysis contain only 0.2 to 0.5 % HCBD (BUA 1991; UNEP 2013a).

The Toxics Release Inventory (TRI) of the United States includes relatively detailed data on HCBD production that may serve as a useful case study for countries with high production of chlorinated solvents. Already in 1982, where HCBD were still marketed as product in large volumes, the unintentional HCBD waste by-product chlorin solvents, was higher than the intentional production by 14,000 tonnes in 1982 in the US alone (IPCS 1994; UNEP 2012). In the US, 4515 to 4678 tonnes of annual HCBD generation were reported for the Toxics Release Inventory (TRI) from 2005 to 2007 (UNEP 2012) which represented an increase from the 3810 tonnes reported in the 1997 within TRI as total production-related waste in the

<sup>9</sup> High Production Volume Chemicals; Substances with a production or import volume in excess of 1000 tonnes/year.

<sup>10</sup> Low Production Volume Chemicals; Substances with a production or import volume between 10 and 1000 tonnes/year.

<sup>11</sup>ESIS = Existing Substance Information System of the European Commission:

<http://esis.jrc.ec.europa.eu/index.php?PGM=hpv>.

<sup>12</sup> Chemicals produced or imported into the United States in quantities of 1 million pounds or more per year.

<sup>13</sup> <http://www.epa.gov/hpvis/>

<sup>14</sup> Comment from the Netherlands, 2013.

U.S. (Rabovsky, 2000). The generation of the related HCBD (and HCB) volumes for the three major solvents and chlorine production is given as example for 1972 in the US (Table 2-3; Mumma and Lawless 1975). Also in the production of ethylene dichloride (EDC), HCBD is formed and present in relevant amounts in the waste. In a monitoring of Dow Chemical, the heavy ends of EDC included large quantities of highly persistent, bioaccumulative, and toxic substances: 12,000 mg/kg HCBD, 302 mg/kg PCBs, 3000 mg/kg hexachloroethane (HCE), and 30.6 % unidentified compounds (Dow Chemicals 1990; Thornton 2001). It is not reported whether from residues of EDC production the HCBD has been or was partly separated for commercial use.

Several reports mention the unintentional production of HCBD during the production of vinyl chloride, allyl chloride and epichlorohydrin (U.S. EPA 1980; Environment Canada 2000; VROM 2002). In a dossier for Eurochlor the presence of HCBD in these processes was considered unlikely from a chemical point of view (Lecloux, 2004). The relative low chlorinated substances detected in the only published study for allyl chloride and epichlorohydrin (Kusz et al. 1984) support this estimate.

HCBD is considered to be also formed during the production of other chlorinated solvents and possibly chloroprene (Botta et al. 1996; Mumma and Lawless 1975; Stringer and Jones 2001). However currently no quantitative information is available on the levels of HCBD formed during the production of other chlorinated solvents and other organochlorine substances.

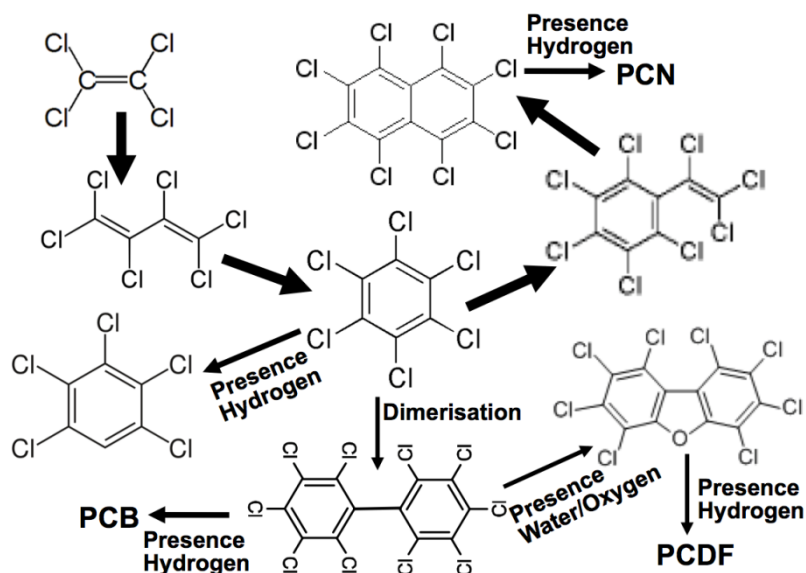
HCBD was unintentionally formed in the production of chlorine with graphite electrodes in tonnes scale while the formation using other technologies is considered low (Table 2-3; Mumma and Lawless 1975).

In addition to HCBD, wastes from these organochlorine productions might contain chlorobenzenes (PCBz)<sup>15</sup>, PCBs, PCNs and PCDD/PCDF as unintentional by-products (Thornton 2001; UNEP 2013a, 2016).

**Table 2-3:** Estimated total quantity of HCBD and HCB contained in U.S. industrial wastes, by-products, and products in 1972 (Mumma and Lawless 1975)

	HCBD in tonnes (in 000 lb)		HCB tonnes (in 000 lb)	
	High	Low	High	Low
Tetrachloroethylene <sup>6</sup>	3,902 (8,670)	1,953 (4,340)	1,575 (3,500)	787 (1,750)
Trichloroethylene	1,350 (3,000)	675 (1,500)	202.5 (450)	103.5 (230)
Tetrachloromethane/Carbon tetrachloride <sup>7</sup>	1,255.5 (2,790)	630 (1,400)	180 (400)	90 (200)
Chlorine production	32 (70)	18 (40)	175.5 (390)	72 (160)
Dacthal	0	0	45 / 100	36 (80)
Vinyl chloride	0	0	12.15 (27)	0
Atrazine, simazine	0	0	4,05 (9)	2.25 (5)
Pentachloronitrobenzene	0	0	2,7 / 6	1.35 (3)
Mirex	0	0	0.9 / 2	0.45 (1)
<b>Total</b>	<b>6,538.5 (14,530)</b>	<b>3,276 (7,280)</b>	<b>2,198 (4,884)</b>	<b>1,093 (2,429)</b>

<sup>15</sup> For some organochlorine substances the HCBD content were not known or below the detection limit while the levels of HCB resulted in a national estimate in tonnes scale (Table 2-3; Mumma and Lawless 1975).



**Figure 2-2:** Simplified mechanism of formation of unintentionally produced POPs in the production of tetrachloroethylene and tetrachloromethane (note: the presence of hydrogen is inherent e.g. in the production of trichloroethene) (UNEP 2015b; Weber et al. 2011a)

HCBD is also unintentionally formed in the production of magnesium (Lecroix 2004, Van der Honing 2007; Van der Gon et al. 2007). Deutscher and Cathro (2001) reported on organochlorine formation in Magnesium electro-winning cells with HCBD and HCB being one of the major components (Deutscher and Cathro 2001). The laboratory study indicated that depending on the current density applied during electrolysis up to approximately 3 g HCBD per tonne magnesium is formed. According to the German Federal Environment Agency 15 to 20 g HCBD is produced per tonne magnesium (UBA 2006). Another source of HCBD (and HCB) in magnesium and aluminium production was/is the use of hexachloroethane in manufacture of degassing pellets to remove hydrogen gas bubbles from molten aluminium in magnesium (U.S. National Toxicology Program 2011; Vogelgesang et al. 1986). This use, as well as similar uses in magnesium, is being phased out in the European Union. It was phased out as early as 1999 in the United States.

Hexachloroethane was and possibly is also used in smoke grenades, fog ammunition, smoke pots and artillery shells to produce hexachloroethane smoke (Eaton et al. 1994). Hexachloroethane smoke is produced by the combustion of hexachloroethane, zinc oxide and aluminium. This results in the formation and release of HCBD and HCB with HCB as a major pyrolysis product formed at higher concentration than HCBD (Eaton et al. 1994).

HCBD might also be unintentionally formed during incineration processes in particular when incinerating wastes with high chlorine content such as residues from organochlorine production (INERIS 2005; UNEP 2013a). In 2003, according to the Association of Plastic Producers (Syndicat des Producteurs de Matières Plastiques, SPMP) in France, HCBD was detected in the effluents of an incinerator eliminating chlorine residues (INERIS 2005). However it has also been demonstrated that organochlorine waste with high chlorine content can be destroyed in hazardous waste incinerators with minimum release of HCBD or below the detection limit in residues (Potrykus et al. 2015). There is no study showing that HCBD being formed and released from municipal waste incinerators.

Lenoir et al. (2001) observed the by-product formation of organochlorine substances including HCBD and PCDD/PCDF while using a special laboratory flow reactor to incinerate acetylene in the presence of copper chloride. The conditions during this laboratory test involving the availability of copper chloride for catalysing the formation of unintentional POPs is somewhat similar to those of secondary copper smelters with high availability of copper chloride to catalyse highly chlorinated unintentional POPs formation. Also the PCDD/F homologue pattern observed by Lenoir et al. (2001) is similar to the highly chlorinated

homologue pattern observed in copper smelters (Cagnetta et al. 2016; Wielgosinski et al. 2011). Therefore some HCBD is possibly formed in secondary copper smelters.

One source indicated that HCBD still can be present in rubber compounds in marginal amounts according to the national association on rubber and polymers in France (Syndicat National du Caoutchouc et des Polymères, SNCP) (INERIS 2005).

There are no natural sources of HCBD in the environment (BUA 1991, Environment Canada 2000) and therefore low background levels of HCBD are detected in air, water and soil (Table 2-4).

HCBD in wastes can be destroyed or recycled at the respective industries if appropriate technologies exist. However, total elimination of industrial HCBD emissions is difficult, as the production of a range of chlorinated hydrocarbons and other processes results in the generation of HCBD as an unintentional by-product (UNEP 2013a; chapter 4 and 6).

HCBD is released into the air from these processes and stockpiles and contaminated sites due to its high vapour pressure and into aqueous effluents due to its water solubility (3.2 mg/l; Table 2-2). Releases can be minimised to very low levels by technical abatement measures, but they are not eliminated with the current industrial practices (UNEP 2013a). Therefore HCBD enters into the environment at related sites of production and disposal (Table 2-4). Historical landfilling of heavy fractions from the production of organochlorine substances can also lead to secondary HCBD emissions or leachates to water and soil via sewage sludge (ASDTR 1994, Staples et al. 2003, Lecloux 2004, ESWI 2011).

Techniques, such as the use of closed loop systems and the substitution of chlorinated hydrocarbons by alternatives that do not lead to unintentional formation of HCBD and that prove to be technically and economically feasible and also advantageous from a life cycle management point of view, will be necessary to further minimise and ultimately eliminate HCBD releases (UNEP 2013a).

**Table 2-4:** HCBD levels in environmental matrices impacted and not impacted by industrial sources

Sample matrix	Level of HCBD contamination	References
Residues from organochlorine production	< 1 to 100,000 mg/kg	See Table 4.1 and 4.2
Tetrachloroethylene products (Germany)	< 5 µg/l or <100 µg/l	BUA 1991
Tetrachloromethane/Cabon tetrachloride products <sup>7</sup> (Germany)	< 5 µg/l	BUA 1991
Soil near an oxychlorination reactor for EDC	6,000,000 µg/kg*	Johnston et al. 1993
Soil at organochlorine production site	980,000 µg/kg	Li et al. (1976)
Soil after fumigation with HCBD	7,300 µg/kg (8 months after) 3,000 µg/kg (32 months after)	Vorobyeva (1980) in IPCS (1994)
Agricultural soils (China)	< 0.02 - 3.1 µg/kg	Tang et al. (2014)
Landfill leachate (Netherlands)	n.d. – 55 µg/l	Kotzias et al. (1975)
Ground water near landfill (Switzerland)	0.2 – 0.3 µg/l	Giger & Schaffner (1982)
Drinking water near landfill (Switzerland)	0.04 – 0.25 µg/l	Schmassmann (1981)
Community well near landfill (US)	n.d. – 2.53 µg/l	Clark et al. 1982
Drinking water Rhine	< 0.01	Zoeteman et al. 1980
Fresh water (Estonia)	0.003 µg/l (14 samples)	Estonia 2011
Marine water (Estonia)	0.0002 – 0.001 µg/l	Estonia 2011
Sediments at hotspot	430,000 µg/kg	ESWI 2011
Sediment at hotspot (St Claire river Canada)	310,000 µg/kg	Farara and Burt (1997).
Sediment Lippe river upsteam chlorine industry	10 µg/kg	BUA 1991
Sediment Lippe river downstream chlorine industry	200 µg/kg	
Sediment Lake Ontario	21 µg/kg (mean 38 samples)	Oliver and Niimi (1988)
Sediments Denmark (2007-2009)	0.005 – 0.8 (114 samples)	European Environmental Agency (EEA) (2012)
Sediments Germany (1990 - 2008)	<0.005 – 1 (152 samples)	
Sewage sludge (industrial waste water)	190 µg/kg	Potrykus et al. (2015)
Sewage sludge (municipal waste water)	10 µg/kg	Potrykus et al. (2015)

Sample matrix	Level of HCBd contamination	References
Sewage sludge China	median 0.30 µg/kg (<0.03 to 74.3 µg/kg)	Tang et al. (2014)
Air Southern Hemisphere (1982-85)	0.8 ng/m <sup>3</sup>	Class & Ballschmiter (1987)
Air Northern Hemisphere (background)	1.8 ng/m <sup>3</sup>	Class & Ballschmiter (1987)
American Cities (mean conc. 1980)	21-118 ng/m <sup>3</sup>	Singh et al. 1982

\*(and 19,000,000 µg/kg HCB)

## 2.4. Intentional uses of HCBd

HCBd was used in several technical and agricultural applications and as an intermediate in the chemical industry or as a product (Table 2-5).

Prior to 1975 the largest use of HCBd was for the recovery of “snift” (chlorine containing gas in chlorine plants). However, HCBd is no longer used for this process (ATSDR, 1994). HCBd was mainly used as a chemical intermediate in the manufacture of rubber compounds, and lesser quantities were used as solvent, fluid for heat transfer liquid, hydraulic fluid, gyroscopes, chemical intermediate in the production of chlorofluorocarbons and lubricants, and laboratory reagent (ATSDR, 1994).

HCBd was used as a seed-dressing fungicide or insecticide in vineyards, e.g. in the former Soviet Union, in Mediterranean European countries<sup>16</sup> and in Argentina (Lecloux, 2004, UNECE 2007, Potrykos et al. 2015). It is unclear whether HCBd is still used as a plant protection product anywhere.

In the EU, HCBd is no longer used as a plant protection product. It is unclear whether its use as a fumigant for treating grapes has also stopped outside the EU (UNEP 2012). Most of the (former) HCBd uses had short life span and several were dispersive uses with direct release to the environment (Table 2-5).

A method to synthesize graphite sheets by dechlorination of HCBd with sodium has been developed. Graphite flakes are used as electronically conducting fillers in the production of conducting polymer composites in various fields such as fuel cell electrodes, corrosion resistant materials, or batteries (Shi et al. 2004). However, there is no information on whether this method involving HCBd is commercially applied anywhere.

The European Chemicals Agency (ECHA) classification and labelling inventory indicates that there are 65 notifiers for HCBd<sup>17</sup>. HCBd is furthermore listed in the ECHA inventory of pre-registered substances with an envisaged registration deadline in 2010. Nevertheless, so far, no registration for HCBd has been submitted to ECHA. This suggests that there are no EU companies which produce or import HCBd in high volumes (i.e. > 1,000 t/year). The number of entries in the classification and labelling (C&L) inventory<sup>18</sup> and the fact that pre-registrations have been submitted to ECHA at least indicate that HCBd is of certain interest for EU companies, although pre-registrations could also have been submitted due to strategic reasons instead of real registration obligations (UNEP 2013a).

It has been indicated by several sources that HCBd has been used as a laboratory reagent (ATSDR 1994, Van de Plassche and Schwegler 2002, WWF 2005). According to Article 3(5), the use for laboratory-scale research or as a reference standard is excluded from the Stockholm Convention.

There were no notifications of uses reported for information gathering for POPRC Annex F survey (UNEP 2013a) indicating that current use might be low. However no detailed assessment might have been done in developing countries and countries with economies in transition for this survey.

<sup>16</sup> In France the fumigant use was extensive and discontinued in 2003 (ESWI 2011).

<sup>17</sup> <http://clp-inventory.echa.europa.eu/SummaryOfClassAndLabelling.aspx?SubstanceID=80395&HarmOnly=no?fc=true&lang=en>

<sup>18</sup> EU database containing classification and labelling (C&L) information on notified and registered substances received from manufacturers and importers (<http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database>).

Intentional uses of HCBd include some dispersive open applications that result in direct release of HCBd to the environment (Table 2-5).

**Table 2-5:** Summary of intentional uses\* of HCBd (ESWI 2011 with modifications)

Sector	Application
Agriculture (open applications)	<ul style="list-style-type: none"> <li>• Pesticide/phytosanitary purposes in the past:               <ul style="list-style-type: none"> <li>○ to combat soil pests including use as fumigant (ATSDR 1994; BUA 1991; Van der Honing 2007; Van de Plassche &amp; Schwegler 2002)</li> <li>○ as seed dressing, as fungicide (Van der Honing 2007)</li> <li>○ as pesticide (IARC 1999)</li> <li>○ as biocide (UBA 2006) as algicide (BUA 1991)</li> </ul> </li> </ul>
Industrial manufacture (open and semi-closed applications)	<ul style="list-style-type: none"> <li>• Chemical and intermediate in several industrial manufacturing processes:               <ul style="list-style-type: none"> <li>○ synthesis of rubber compounds (ATSDR 1994; Lecloux 2004; Van de Plassche and Schwegler 2002)</li> <li>○ production of lubricants (ATSDR 1994; Van de Plassche and Schwegler 2002)</li> <li>○ manufacture of chlorofluorocarbons (Lecloux 2004)</li> <li>○ manufacture of aluminum and graphite rods (UBA 2006))</li> <li>○ as solvent for rubber (Lecloux 2004), other polymers (Van der Honing 2007) and elastomeric plastics (UBA 2006)</li> </ul> </li> </ul>
Purification of gas streams (Semi-closed applications)	<ul style="list-style-type: none"> <li>• as purification agent for recovery of “snift”, a chlorine containing gas in chlorine plants, (Lecloux 2004; Van der Honing 2007)</li> <li>• as washing liquor for purifying gas streams by removing hydrocarbons (Van der Honing 2007)</li> <li>• as adsorption agent for gaseous contaminants (UBA 2006)</li> <li>• as well as solvent in chlorine gas production (IPCS 1993)</li> </ul>
Electrical and other technical equipment (closed/semi-closed application)	<ul style="list-style-type: none"> <li>• as heat-transfer liquid (Van de Plassche and Schwegler 2002, Van der Honing 2007, Lecloux 2004) particularly in transformers (BUA 1991, IARC 1999)</li> <li>• as hydraulic fluid and liquid in gyroscopes (UBA 2006, Van der Honing 2007; Lecloux 2004)</li> </ul>

\* In the 1990s, major uses of HCBd were stopped in most if not all industrial countries. However, some uses may still be present in other countries (in particular in/from countries with chlorinated solvent production).

## 2.5. HCBd in stockpiles and waste

The generation and presence/deposits of wastes and stockpiles depend on the management of the (former) uses of HCBd (chapter 2.4; chapter 2.5.1) and on the management of HCBd that was and is unintentionally generated (chapters 2.3 and 2.5.2). Actions aimed at identifying? waste streams of importance in terms of volume and concentration will be essential for eliminating, reducing and controlling the environmental load of HCBd from waste management activities and “Draft technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with hexachlorobutadiene” has been developed in the framework of the Basel Convention (UNEP 2017b). There exists neither the information on the total amount of waste sites worldwide nor on the related releases (Crump et al. 2004). This is expected to be improved when inventories are developed within the Stockholm Convention implementation.

### 2.5.1. HCBD in stockpiles and waste from former and contemporary disposal

HCBD-containing wastes are continuously unintentionally produced from the production of certain organochlorine solvents and with lesser relevance in some other processes (see chapter 2.3). Depending on the management of the HCBD-containing waste generated in these processes, the wastes have accumulated in landfills and generated stocks or were destroyed in high temperature incinerators.

In industrialized countries,<sup>19</sup> the residue containing HCBD generated from organochlorine solvents are commonly destroyed by high temperature incineration since the 1980s or 90s (Lecloux 2004; Markovec and Magee 1984; UNEP 2008). For instance, in 2007, virtually all HCBD was treated, mostly on site in the US (U.S. EPA 2010). Less than 0.1 % (ca. 4.5 tonnes) of the generated HCBD volume were disposed of or burned for energy recovery. At the same time, 740 tonnes HCBD-containing hazardous waste was reported in the US, more than half of which was used for reclamation or recovery (mostly energy). A further 41.5 % was destroyed or treated prior to disposal, and 5.3 % (39.4 tonnes) were disposed of in landfills (U.S. EPA 2010).

However before the 1980s, HCBD containing residues were reported to have been landfilled even in industrialized countries; e.g. 1,600 to 2,440 tonnes HCBD were disposed in landfills in the European Community in 1980 (BUA 1991). This has resulted in HCBD (and associated HCB) stocks in landfills with associated releases and contamination (Barnes et al. 2003; Environmental Agency Austria 2004; Environmental Canada 1999; U.S. Department of Health and Human Services 2011; U.S. EPA 2004; Weber et al. 2008, 2011a). Therefore for an inventory of HCBD, the current and former management of residues from organochlorine solvents productions should be assessed as well as the contemporary fate of the related stockpiles. The major stockpiles and waste stem from the manufacture of chlorinated solvents with high potential for HCBD formation (tri-, tetrachloroethylene, tetrachloromethane, hexachlorocyclopentadiene, and ethylene dichloride). These wastes also contain hexachlorobenzene (HCB) and other unintentional POPs and are often called "HCB waste" (Mumma and Lawless 1975; Rae 2012; Weber et al. 2011a; Zhang et al. 2015). Several cases document the generation of HCBD/HCB stocks from such solvent productions that can reach up to 10,000 tonnes scale for single productions (Lysychenko et al. 2015; Rae 2012; Weber et al 2008, 2011a). At the Orica dump in Australia, a large quantity of HCB contaminated with HCBD and other organochlorines is stored in drums (approx. 20,000 tonnes) (Rae 2012). Another example of HCBD stockpiles in waste dumps is the Devil's swamp area in Louisiana (US) where HCBD contaminated fish have been found (U.S. Department of Health and Human Services 2011; U.S. EPA 2004). Also at Weston Quarries (UK), the landfill released HCBD to neighbouring properties that had to be demolished for excessive indoor HCBD concentrations (Barnes et al. 2002; Crump et al. 2004; NICOLE 2004). These examples also document that HCBD can migrate from the wastes in disposal sites, creating nearby contaminated sites (see section 2.6) with possible related human exposure. These cases also demonstrate that the wastes/stocks in landfills can have current and future relevance (see also review Weber et al. 2008, 2011b).

In addition to waste from organochlorine solvent production, also wastes from the production elemental chlorine and other organochlorine substances may contain HCBD (Mumma and Lawless 1994; U.S. EPA 1980; Environment Canada 2000; VROM 2002; Stringer and Johnston 2001; Table 2-3). Wastes from these processes might have also generated HCBD and other unintentional POPs waste deposits to different degrees at production sites including landfills. The extent will depend on the contamination level of the waste and the respective historic waste management at production sites in particular the duration and share of disposal to landfills and the share of destruction.

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<sup>19</sup> The onset of destruction and cessation of landfilling depend on the level of technological development of individual facilities. Some facilities might have destroyed residues already in the 1970s. In developing countries with lack of destruction capacity the residues might still be disposed to landfills or dumpsites.

Also disposed residues from thermal processes like the production of magnesium and aluminium partly contain HCBD and might have built up HCBD waste at related landfills and dump sites.

### 2.5.2. HCBD in stocks and disposed waste from former use

The major use of HCBD in industrial countries took place in the 1970s to 1990s. Many of the (former) HCBD uses were open applications (see chapter 2.4) with relatively short lifespans in use hence no HCBD stock or wastes is expected still to be present from these uses. However, some of the HCBD applications have a long service-life and despite the uses being ceased in industrial countries<sup>20</sup>, HCBD may still be present in equipment and can enter into the waste management stage (e.g. hydraulic, heat transfer or transformer fluids) (UNEP 2017b).

For the developing countries and the countries with economies in transition where the use of HCBD might still be taking place today in particular in countries with high generation of HCBD from organochlorine solvents production, waste and stockpiles from uses might still be relevant. This depends on current and former uses and would be assessed within the HCBD inventory in these countries.

## 2.6. Sites potentially contaminated by HCBD

Listing of HCBD in Annex A, made HCBD subject to the measures under Article 6 of the Convention, and Parties will need to identify sites contaminated with HCBD and manage them in a manner protective of human health and the environment. Major HCBD contaminated sites are at production sites of trichloroethene, tetrachloroethylene, and tetrachloromethane where HCBD was intentionally or unintentionally produced (Botta et al. 1996; Environment Agency Austria 2004; Orica 2011; U.S. EPA 2004; Wright 2004). HCBD has been used for tracking groundwater pollution from production sites of organochlorine solvents (Botta et al. 1996).

Landfills and dump sites that have received HCBD-containing waste from the manufacture of chlorinated solvents and other sources (see chapter 2.5) are also potential HCBD contaminated sites with release of HCBD into the environment including ground/surface water, soil and air due to the water solubility (3.2 mg/l) and the relatively high vapour pressure (Table 2-2) (Clark et al. 1982; Environment Agency Austria 2004; Forter 2016; Orica 2011; Wright 2004). HCBD has been detected in ground water and surface water, as well as fish living in the water close to landfills (Clark et al. 1982; Lowis 2014; U.S. Department of Health and Human Services 2006; U.S. EPA 2004). One example of HCBD in waste dumps is the Devil's swamp area in Louisiana where fish in the Devil's swamp lake are contaminated (U.S. Department of Health and Human Services 2006). Fish have also been found to carry HCBD levels above EU Environmental Quality Standard (EQS) in some German rivers (Lowis 2014) with one river known to be impacted by a landfill of the organochlorine industry. HCBD accumulation in biota near sources is demonstrated by the detection of 36 µg HCBD / kg wet weight in caged mussels exposed near three industrial areas of the St. Clair River for three weeks (Environment Canada, 2000). In Australia, approximately 20,000 tonnes of drummed waste containing HCB contaminated with HCBD and other organochlorines was disposed at Orica dump in Australia (Rae, 2012). Subsequently, HCBD was detected in ground water and soil at the Orica site (Orica 2011; Wright 2004). In Switzerland and the U.S. drinking water close to landfills of chemical industries have been found to be contaminated with HCBD (Clark et al. 1982; Forter 2016) (Table 2.4). In the United Kingdom, houses built on quarry spoil next to the waste dump at the Weston Quarries had to be demolished for excessive indoor HCBD concentrations (Nicole 2004; Barnes et al. 2002; Crump et al. 2004). The examples of contaminated sites due to former waste disposal operations show that remediation costs and the cost for the protection of the environment and health can be significant (UNEP 2013a).

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<sup>20</sup> In a recent study for the German Environmental Agency (UBA) HCBD was not found relevant in current waste streams in Germany (Potrykus et al. 2015).

Both the total number of waste sites worldwide and the extent of releases from those sites are as yet unknown (Crump et al. 2004).

### 3. How to conduct an HCBd inventory

#### 3.1. Step by step approach for planning and conducting an HCBd inventory

This chapter outlines five broad steps for planning and carrying out a national HCBd inventory. The official contact point/national focal point of the Stockholm Convention or national project coordinator could be responsible for initiating the inventory process. The existing steering/coordinating committee on POPs that may have been formed for the original NIP development could be re-established for updating the NIP and involved in the planning of the inventory.

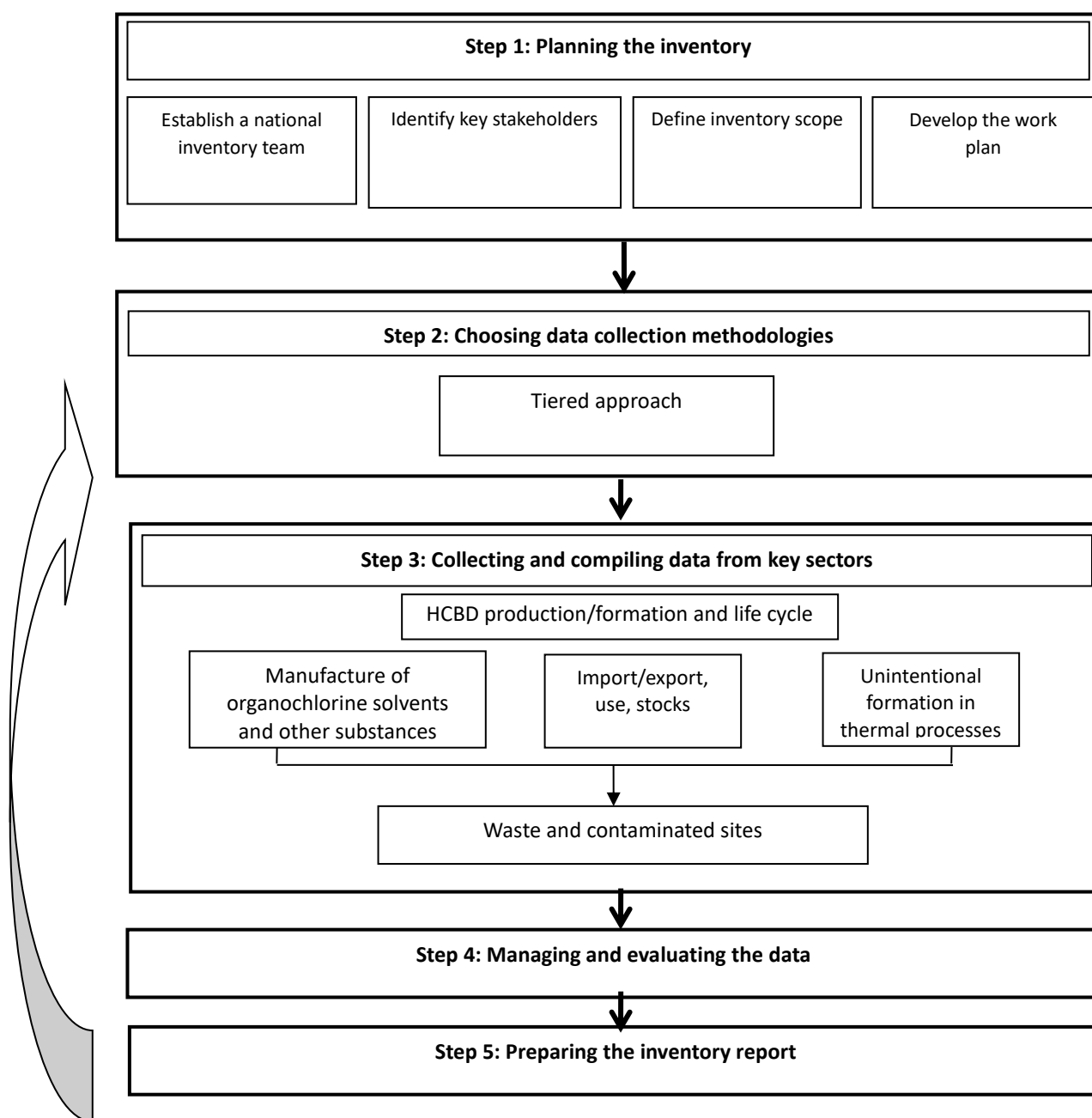


Figure 3-1: Overview of the national HCBd inventory development process.

The inventory process might not be conducted in an entirely linear fashion. The inventory team may need to repeat activities in earlier steps depending on how the inventory proceeds and which sectors are involved. For example, although the identification of stakeholders is shown in step 1 (Figure 3-1), there may also be a need to identify further stakeholders at different points during data collection (step 3). The arrow going from step 4 (Managing and evaluating the data) back to step 2 (Choosing data collection methodologies) in Figure 3-1 indicates that steps 2 to 4 can be repeated until the data quality and coverage reach a satisfactory level.

The inventory team will decide on the complexity of the methodology which is appropriate for their particular situations, taking into account their financial and technical capacities. For many countries, it could be evident at the beginning of the process that monitoring (within Tier III) may not be feasible (see chapter 3.2). Other countries could decide after evaluating the results of the initial inventory to undertake more in-depth data collection (move to a higher Tier) in the future, and include such activities within the action plan in their NIP.

## **3.2. Step 1: Planning the inventory**

The first step in developing a national inventory is to define the scope of the inventory and target the nationally relevant sectors for HCBD. To streamline the work, it is important to clearly define the responsibilities of the national inventory team in developing the inventory. Parties are advised to establish a multi-stakeholder national inventory team for the task. The development of a national inventory of HCBD requires cooperation with the relevant stakeholders involved during the HCBD life-cycle (see Table 3-1).

### **3.2.1. Establish a national inventory team**

The responsible focal point for the Stockholm Convention could establish and/or lead a multi-stakeholder national inventory team to acquire the necessary competencies and access to relevant inventory information. The team would comprise government ministries with a mandate for chemicals and waste management, industry, forestry, the national customs service, the private sector, non-governmental organizations (NGOs), and researchers from universities or research institutes working on old and new POPs, waste management and possibly material flows, among others (see Table 3-1). National POPs or waste management consultants and material flow experts knowledgeable in these issues could also be hired to facilitate the work of the team.

The national focal point and/or consultants would brief and educate the team on the Stockholm Convention's mandates, obligations and the new listed POP.

### **3.2.2. Identify key stakeholders**

The first meeting of the inventory team provides the opportunity to determine the available information in various stakeholder organizations and to brainstorm on how to best to proceed with the inventory.

The inventory development requires cooperation between relevant government authorities and official agencies, industries, importers, community-based organizations and NGOs, labour union, other private-sector organizations, the waste management and recycling sector, and owners of articles possibly containing HCBD. Representatives from the key sectors could be included in the inventory team, while others could simply be asked to provide data/information.

#### ***Making preliminary contact***

Making contact with stakeholders at the beginning of the inventory exercise can give them a better understanding of the background, scope and objectives of the inventory and provide them with an opportunity to communicate their views and questions. This initial feedback can help make the inventory more effective by targeting the relevant areas of national use.

General tools that can be used to identify and contact stakeholders include:

- Telephone interviews using phone books/registers;
- Postal communication using national registers;
- Email/Web-based information sourcing;
- Face-to-face interviews.

### *Consulting with a small number of relevant stakeholders*

During the inventory planning stage, it may be more efficient to contact and consult only a small number of relevant stakeholders such as large-scale manufacturers, national industrial associations and the customs service. Gap analyses conducted in the evaluation of the initial assessment or the preliminary inventory could result in the need to contact some of these stakeholders again to get more information or identify other stakeholders to be contacted to help fill in the information and data gaps.

### *Holding stakeholder group meetings*

There may be a large range of stakeholder groups involved depending on the areas of production generating HCBD, e.g. production of organochlorine solvents, and use of HCBD at the national level, e.g. in agricultural and industrial manufacture sectors, purification of gas streams and electrical equipment (see Table 3-1 and chapters 4 and 5).

**Table 3-1:** Sectors and stakeholders involved in the production, use or impact of HCBD

<b>Production</b>	<b>Stakeholders</b>
General stakeholders	<ul style="list-style-type: none"> <li>• Ministry of environment</li> <li>• Sector ministries: Ministry responsible for industries;</li> <li>• Ministry responsible for waste management;</li> <li>• NIP coordinator and steering committee;</li> <li>• Stockholm/Basel Convention focal points (and Basel stakeholders);</li> <li>• Custom authorities;</li> <li>• NGOs working on POPs/chemicals.</li> </ul>
Production organochlorine solvent and other relevant organochlorine substances	<ul style="list-style-type: none"> <li>• Authorities granting production permits;</li> <li>• Industry producing chlorinated solvents;</li> <li>• Chlorine industry;</li> <li>• Waste management facility owners;</li> <li>• Custom authorities.</li> </ul>
(Former) uses & stockpiles <ul style="list-style-type: none"> <li>• Transformers</li> <li>• Hydraulic/heat exchange fuel; lubricant oils</li> <li>• Agricultural sector</li> </ul>	<ul style="list-style-type: none"> <li>• Utility sector; other transformers owners;</li> <li>• Mining sector;</li> <li>• Industry producing and trading oils and lubricants;</li> <li>• Authorities granting related use/production permits;</li> <li>• Waste management facility owners;</li> <li>• Ministries responsible for agriculture and health;</li> <li>• Pesticide producers/importers;</li> <li>• Import/export of HCBD containing waste;</li> <li>• Custom authorities.</li> </ul>
Thermal facilities with unintentional production	<ul style="list-style-type: none"> <li>• Magnesium industry;</li> <li>• Aluminium industry; secondary copper industry;</li> </ul>

Production	Stakeholders
	<ul style="list-style-type: none"> <li>• Hazardous waste incinerator combusting waste with high chlorine content;</li> <li>• UPOPs task team leader.</li> </ul>
Contaminated sites	<ul style="list-style-type: none"> <li>• Relevant government organizations and impacted city authority;</li> <li>• Producers of chlorinated solvents and other relevant organochlorines;</li> <li>• Manufacturers using or having used HCBD;</li> <li>• Engineering offices specialized in contaminated sites;</li> <li>• University or research institute working on contaminated sites;</li> <li>• Community-based organizations (CBOs) and NGOs working on contaminated sites or related issues;</li> <li>• Labour union.</li> </ul>

### 3.2.3. Define the scope of the inventory

Defining the scope of the inventory involves identifying the relevant national sectors to be investigated. This can be achieved by consulting key stakeholders (see Table 3-1) and paying special attention to the use categories and life cycle stages discussed in chapter 2 and detailed in chapter 4 to 7. Since the major production generating HCBD (chapter 2.3) is manufacturing of organochlorine solvents and other relevant organochlorine substances, this is likely to be the main focus of the inventory.

Main information includes:

- Past and current production of organochlorine solvents at the national level;
- Past and current incineration processes where HCBD resulted as by-product;
- Intentional uses of resulted HCBD by-product;
- Presence of products and articles containing HCBD on the consumer market;
- Flows (import/export) into a country of products and articles containing HCBD;
- Disposal practices for products and articles containing HCBD when they become wastes;
- Any chemical stockpiles;
- Import/export of HCBD containing waste;
- Potential HCBD contaminated sites.

The following criteria are important in defining the scope of the inventory:

- Obligations for HCBD under the Stockholm Convention (see chapter 1);
- Objectives of a HCBD inventory (see chapter 1);
- Existing resources and capacity;
- National priorities.

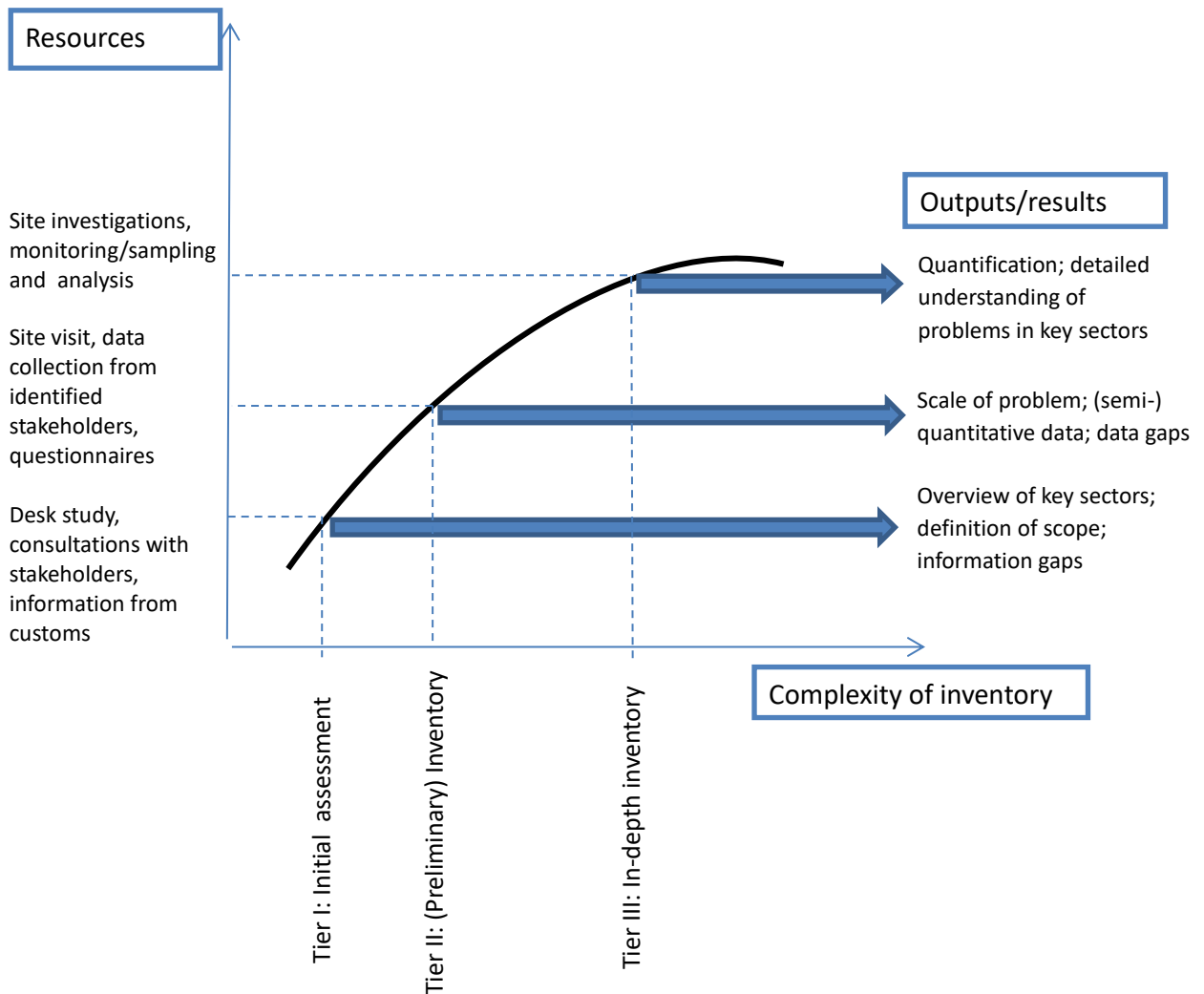
The degree and depth of the inventory can be defined by consulting the chapters 3.2 and 3.3 and the tiered approaches mentioned in chapters 4 to 6, and considering the resources needed.

## 3.3. Step 2: Choosing data collection methodologies

### 3.3.1. Tiered approach

The tiered approach to collecting data in an HCBD inventory is illustrated in Figure 3-2. The suggested methodologies for data collection in the three tiers are described in this chapter and mentioned in the chapter for the individual inventory sectors where appropriate. This approach provides flexibility to a wide range of Parties with varying priorities and capacities. Each tier represents a level of methodological

complexity. Moving from lower to higher tiers implies a Party is opting for approaches that are progressively more demanding in terms of complexity and data requirements, and therefore more resources may be needed.



**Figure 3-2:** The tiered approach to the inventory of HCBD

### *Tier I: Initial assessment*

Tier I methods usually rely on readily available information and statistics. Methods used for higher tiers involve more resource-intensive data collection activities and possibly country-specific measurements but should also yield more accurate results.

Parties should endeavour to use methods that provide robust level of certainty. This is especially true when, for example, the preliminary inventory concludes that HCBD could pose high human health and environmental risks, such as around contaminated sites. A more robust level of certainty is also required when more accurate data are needed to prioritize risk reduction measures and estimate their costs, while making efficient use of available resources and taking into account available technical capacity.

The initial assessment (Tier I) provides the inventory team with a general idea of where the problems may lie and, more importantly, which sectors require further investigation and information gaps. Tier I outputs are rather qualitative and require subsequent verification. The (preliminary) inventory (Tier II) focuses on the major sectors and generates (semi)quantitative data. The in-depth inventory (Tier III) uses in-depth assessment and possibly includes analytical measurement methods to obtain precise data on these sectors.

### *Tier II: (Preliminary) inventory*

The preliminary inventory generally focuses on specific sectors, as shown in Figure 3-2. It involves surveys and site visits to better estimate national data that were identified as missing in the Tier 1 preliminary assessment.

Possible applications (Table 2-4) and target locations can be identified, followed by site visits including:

- Current and former production sites of organochlorine solvents and other relevant substances;
- Current and former magnesium and aluminium production sites;
- Former production sites of HCBD containing products;
- Waste oil recyclers;
- Companies incinerating wastes with high chlorine content such as organochlorine productions.

### *Tier III: In depth inventory*

The in-depth inventory may be undertaken if the preliminary inventory concludes that HCBD could pose high human health and environmental risks in the country or near contaminated sites and if more accurate data are needed to prioritize risk reduction measures and estimate their costs. Data collection in this tier relies on the use of analytical methods that may include monitoring and possibly additional measurements with instrumental analysis (see Guidance on screening POPs in products (Secretariat of the Stockholm Convention 2017d)). It may also involve detailed inspections of sites mentioned in Tier II above and in the inventory chapters below.

## **3.3.2. Indicative, qualitative and quantitative methodologies**

A number of different methodologies can be used for gathering information about HCBD. The methodologies can be divided into three groups:

- **Indicative method:** provides initial information for further planning of the inventory depending on the availability of resources. This method is quick and does not require significant human and financial resources. Activities include desk study of existing information, workshops, and interviews. It is normally used in the initial assessment.
- **Qualitative method:** uses questionnaires to obtain more specific data. Data management is based on estimations from known levels of quantities of HCBD by-product generated. Workshops and interviews with stronger obligations (legal tools) may also be helpful in obtaining data from the industry. This method is normally used in the initial assessment and preliminary inventory.

- **Quantitative method:** provides accurate and specific numerical information, but needs to be carried out by experts or involve experts in the relevant fields of HCBD and the sectors of investigation. This is an advanced stage of the inventory that includes detailed interviews with industry and possibly site inspection. The quantitative methods might also use sampling and analysis for some areas where the extent of HCBD generation as by-product is not known. Such investigations might be extensive and labour intensive and if instrumental analysis (GC-ECD or GC-MS) is involved such an assessment would become costly. This method is normally used in the in-depth inventory.

Four approaches that can be used for data collection are discussed briefly in the next chapters.

#### *Desk study of existing information*

The desk study involves gathering information about existing past and current national data on former production of organochlorine solvents. This information might be obtained from this inventory guidance, related Basel Convention technical guidelines (UNEP 2017b), the customs service, national bureau of statistics, published literature in scientific journals, technical reports or notes from industry and industry associations, commissioned research reports, and Internet searches. The information should be collated, evaluated and verified if possible, and a gap analysis of the data could be undertaken as well. This approach is typically used in the Tier I assessment.

#### *National sensitizing/inventory workshop on Stockholm Convention and new listed POPs including HCBD*

A national workshop involves major stakeholders in the production of organochlorine solvents. The national importance of the inventory exercise would be emphasized to participants while demanding their cooperation and unhindered release of available data in their custody in the national interest. If confidential business information is involved, agreements should be reached with respective industries. Breakout sessions and group meetings can be organized during the workshop to ensure that all sectors generating HCBD as by-products are adequately covered as well as to get consensus on how best to collect and compile data.

#### *Questionnaires*

Questionnaires might be valuable instruments for primary data collection in inventory programs. Based on preliminary contact and consultation meetings with stakeholders, a questionnaire with explanatory notes can be developed and sent to the relevant stakeholders. Simple questionnaires could be developed covering questions to gather the information needed to compile data for a Tier II or Tier III assessment.

Questionnaires (see Annex) can be administered through various outreach mechanisms, including electronic distribution, postal distribution; supply chain distribution; distribution via trade unions, NGOs, local governments and community leaders. Questionnaires might also be used for one-on-one interviews or in the frame of a stakeholder workshop.

#### *Site inspection, sampling and analysis*

Samples can be gathered during in site inspections of relevant production sites, and waste disposal/storage facilities (landfills and dump sites).

The screening and analysis of articles and products containing HCBD is described in the *Draft Guidance on Sampling, Screening and Analysis of Persistent Organic Pollutants in Products and Articles* (Secretariat of the Stockholm Convention 2017c).

### **3.4. Step 3: Collecting and compiling data from key sectors**

The inventory team should investigate whether the following situations exist in the country:

- Past and current production of organochlorine solvents at the national level;
- Intentional uses of HCBD;

- Flows (import/export) into a country of products and articles containing HCBP;
- Past and current thermal processes where HCBP potentially resulted as by-product;
- Disposal practices for products and articles potentially/containing HCBP when they become wastes;
- HCBP stockpiles and wastes;
- Import/export of HCBP containing waste;
- Sites potentially contaminated by HCBP.

It is desirable to collect and compile the following numerical data in the inventory:

- Quantities of HCBP currently and formerly generated in the production of organochlorine solvents and suspected other organochlorine substances and chlorine using graphite electrodes;
- Current and/or former uses, stocks and wastes and accumulated wastes disposed in landfills;
- Quantities of HCBP formerly and currently generated as by-product from production.

Data collection approaches will vary from country to country based on the data gathered in steps 1 and 2; they may be by estimations, using statistical data, industry provided data or possibly measurements.

The focal sectors to be investigated in the national inventory fall under three key areas:

- HCBP formerly and currently generated from production of organochlorine solvents (chapter 4);
- Current and/or former use, stocks and wastes (chapter 5);
- HCBP formerly and currently unintentionally generated from thermal processes (chapter 6);
- Identification of HCBP potentially contaminated sites (chapter 7).

In addition, data collected for the first two key areas will form the basis for the preliminary inventory of the potentially contaminated sites.

### **3.5. Step 4: Managing and evaluating the data**

#### **3.5.1. Data management**

Since Parties have different designs and levels of legal framework, political organization and economic support for environmental management, different methodologies may be applied in the data gathering process as described in chapter 3.3. The management of collected data should be done as consistently and as transparently as possible. During the data processing, all the assumptions and conversion coefficients adopted as a result of expert judgement, where needed, should be recorded and mentioned when the results are presented.

Before the inventory development starts, all the data formats including questionnaire survey formats should be determined to maintain the consistency of the data collection as much as possible. If some data conversions and estimations are done by stakeholders, the inventory team should provide training on how to fill out the questionnaire. This will reduce the possibility of errors during the data management activities.

#### **3.5.2. Mechanism for evaluation of the inventory**

An evaluation of the process, strategy used and information collected can take place along with a decision on what further actions are needed to make the inventory more complete.

The evaluation includes identification of the following:

- Gaps and limitations;
- Need for validation of the information compiled in the inventory;
- Further actions needed to make the inventory more complete;

- Actions needed to meet the requirements of the Stockholm Convention.

Important elements in this evaluation step are to identify any gaps and limitations, and the measures needed to make the inventory more complete. Other ways to involve the stakeholders and other data collection strategies (see steps 2-4) could then be considered. A gap analysis in the evaluation of the initial assessment or preliminary inventory could result in the need to contact some of the stakeholders again to get more information or identify other stakeholders to be contacted to help fill the gaps.

For inventory sectors with limited information, stakeholder meetings may be a necessary measure. In some cases, government regulations may be required to ensure that stakeholders report their holdings, cooperate with the national authorities and engage in the national inventory. To draft a regulation and make it come into force may require a long time (a year at a minimum in some places).

Gaps and necessary actions to complete the inventory will also be valuable information for the NIP, especially for developing countries with a need of financial support. It is important for developing countries to identify whether and what technical and financial support is necessary to complete the inventory. Even if the inventory is very incomplete, the NIP is expected to provide information on gaps and the limitations of a Party's resources and capacities — information that is useful to identify technical and financial needs.

It is also important to identify whether the current situation meets the requirements of the Convention, including the actions needed to fulfil the obligations of the Convention.

The inventory might also require revision at a later stage when the action plan is updated. This can also be accomplished using the strategies described in this guidance.

### **3.6. Step 5: Preparing the inventory report**

The final step for the inventory team is to prepare the HCBP inventory report. This report will include the inventories of all sectors investigated by the Party (see chapters 4 and 5), as well as information on potential contaminated sites (see chapter 6).

Although its aim is to support the development of the NIP, the report can also be used for other purposes such as feeding into Article 15 reporting, developing post NIP projects, and developing effective strategies and action plans for managing HCBP to meet the obligations under the Convention.

The essential elements of the report are:

- Objectives and scope;
- Description of data methodologies used and how data were gathered, including all the assumptions and conversion coefficients adopted as a result of expert judgement;
- Final results of the inventory for each sector considered a priority for the Party (using a format to be provided in this guidance, as such or adapted from that format);
- Results of the gap analysis and limitations identified for completion of the inventory.

Further actions (e.g. stakeholder involvement, data collection strategies) to be taken to complete the inventory and recommendations.

## 4. Inventory of HCBD in the production of organochlorine substances and related potential use as product and generation of wastes containing HCBD

HCBD is listed in Annex A without exemption and therefore Parties to the Stockholm Convention shall prohibit and/or eliminate the production of HCBD. While production was stopped in industrialized countries more than 10 to 20 years ago, HCBD may still be produced and used in developing and transition economies.

As described in chapter 2.2, the main source of HCBD is the production of certain chlorinated solvents. Chlorinated solvents are produced in many countries in the world in large quantities (HIS Markit 2014). The volume generated in some of these productions is large and there is the possibility and risk that the HCBD generated in these processes can be separated and marketed for different uses. Therefore, processes in which HCBD is generated at a level between 0.5 to 5% or more so that HCBD might possibly be separated for commercial use are compiled in chapters 4.1 to 4.3. During the development of the inventory, these productions should be assessed for current and former production and management of HCBD. If current separation and use of HCBD are discovered for a production it should be stopped to comply with the Convention requirement. Also, in the assessment of an individual production, information on the technology used and production parameters such as temperature and pressure could be collected so that, in the NIP update, the production processes can be improved towards BAT/BEP<sup>21</sup>. HCBD can also be produced directly by specific synthesis routes (see chapter 2.2). However, a commercial production with direct synthesis has not been reported anywhere. The association of the chemical or organochlorine industry in the country could be approached to clarify this.

Furthermore, HCBD is unintentionally formed at lower levels in the production of a range of other organochlorine substances and in the production of elemental chlorine. It is assumed that the volume of unintentionally formed HCBD from the production and processes of these substances is too small to be separated for commercial use. These processes are compiled in chapter 4.4. It needs to be stressed that HCBD is not listed in Annex C and the Convention does not require the continuous minimization of HCBD in these and the other processes. However, a Party might find it useful to consider these processes in the inventory to assess the processes and the related current and past waste management. Therefore, although HCBD is not listed in Annex C, these Parties can also assess the processes listed in chapter 4.4.

### 4.1. Generation and production of HCBD in low-pressure chlorolysis of chlorinated solvents

The combined production of tetrachloroethylene and tetrachloromethane by conventional low-pressure chlorolysis (500-700°C; 1.7-5 bar) contain approximately 5 %<sup>22</sup> HCBD in the raw product (BUA 1991).

After process optimization in industrialized countries, the solvents produced via low-pressure chlorolysis contained 0.2 to 0.5 % HCBD (BUA 1991; Lecroix 2004). The HCBD-containing raw product is treated by distillation which results in a residue containing 7 to 10% HCBD (BUA 1991).

In BAT-technology facilities, HCBD is recycled in the process together with other high-boiling by-products or is destroyed by high temperature incineration.

In the past, the generated HCBD has been separated and commercially used for different applications (chapter 2.4) and might still be used possibly in developing and transition economies. This should be assessed for the individual productions sites (below chapter 4.1.1) as well as the respective waste management and disposal history (4.1.2).

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<sup>21</sup> Relevant BAT is specified e.g. in the BREF Document on production of Large Volume Organic Chemicals (EC BREF LVOC, 2003 (currently being updated) and Section VI.B Part III Chapter 4 of the UNEP BAT and BEP guidelines (UNEP, 2007).

<sup>22</sup> Depending on the production condition the raw product can also contain more than 5% HCBD (BUA 1991).

#### 4.1.1. Assessment and inventory of current production and use of HCB

For the assessment of current production and use of HCB, companies producing tetrachloromethane and tetrachloroethylene and possibly other stakeholders (Table 3.1) should be contacted and assessed for current and former production volumes and the current management of HCB containing residues. In particular, an assessment is necessary if HCB is still separated from the waste and is commercially marketed. Also information on the past uses of HCB from the respective production would be compiled to support the inventory of former uses in the county and related legacies (see also chapter 5).

A questionnaire has been developed for gathering information from current and former producers of chlorinated solvents and other productions possibly relevant for HCB generation (Annex).

#### 4.1.2. Assessment and inventory of waste, related stocks and management at production sites

The amount of current produced wastes and historically accumulated and disposed wastes and related stocks from tetrachloroethylene and tetrachloromethane/carbon tetrachloride<sup>7</sup> depend on the current and former management of the waste generated from production, the separation of HCB for use and the disposal practices. At technologically advanced facilities in industrialized countries the waste is destroyed mostly onsite in hazardous waste incinerators with recovery of chlorine/HCl (Lecloux 2004; UNEP 2017b). However, in the past these wastes were often disposed of to landfills with associated releases of HCB into the environment and contamination of biota and groundwater (see chapter 2.5 and 2.6).

Therefore information on the current and former management of production residues containing HCB should be compiled within the assessment of the individual production site. The assessment should include:

- Incineration of waste, technology used and appropriateness and related residues;
- Disposal of production waste and residues to landfills.

The assessment should cover the entire time of the respective production. In particular, HCB-containing waste might have been disposed in landfills or dumpsites during the early years or decades of production. The amount of disposed waste containing HCB might be known from the company or can be retrieved from documentation of production and waste management. For an estimate of the amount of disposed waste containing HCB, the amount of tetrachloroethylene formerly produced at a production site can be retrieved and the related waste volume be estimated considering the amount generated (table 4-1) (see chapter 4.6).

Also, information on other unintentional POPs (HCB, PCDD/PCDFs, PCBs and PCNs) should be collected or generated for these wastes and stocks from disposed wastes in a similar way. This assessment would contribute to the inventory of HCB, PCNs (UNEP 2017d) and other unintentional POPs (UNEP 2013b). The HCB volumes were normally somewhat higher than HCB (see table 2-3; Mumma and Lawless 1975). The amount of PCDD/PCDFs and PCBs might be estimated using data from the detailed analysis of solvent residues from Zhang et al. (2015).

Considering HCB contamination detected at production sites and at landfills from organochlorine solvent producers (see chapter 2.6), also information on contamination at and around the production sites and/or associated landfills and surface water would be gathered during the inventory development (see chapter 7 on contaminated sites).

## 4.2. Unintentional formation of HCB in the production of trichloroethylene

In the production of trichloroethylene via the chlorination of acetylene to tetrachloroethane and subsequent conversion, HCB is formed in concentrations of 0.4% of the raw product of tetrachloroethane (BUA 1991) (Table 4-1). Data are only available for a German production and it might possibly be higher in developing countries or economies in transition.

The amount of HCBd might be sufficient to justify separating HCBd from the raw product. Therefore for the assessment, companies producing trichloroethylene should be contacted and assessed for current and former production volumes and the current management of HCBd containing residues. In particular it should be assessed if HCBd is separated from the waste and is commercially marketed.

If HCBd is or has been separated, information on the past uses of HCBd from the respective production should be compiled to support the inventory of likely stocks and disposed waste from current or former uses of HCBd in the country (see also chapter 5).

Also, an assessment and inventory of wastes and their management and related stockpiles from current and former production and impacted landfills should be conducted (see chapter 4.6).

A questionnaire has been developed for gathering information from current and former producers of chlorinated solvents and other productions possibly relevant for HCBd generation (Annex).

### **4.3. Unintentional formation of HCBd in the production of hexachlorocyclopentadiene**

Hexachlorocyclopentadiene was mainly produced by a two-stage chlorination of pentane, isopentane or cyclopentane. The first stage is a photochemical chlorination at 80 to 90°C. The reaction mixture is subjected in the second step to chlorolysis over a catalyst at 300 to 430°C and then through a nickel tube at a temperature of 450 to 525°C (Mumma and Lawless 1975).

In the production of hexachlorocyclopentadiene, 1.1 % HCBd was formed as by-product in a production in the US (Velsicol Chemical Corporation) and 0.2% for a production in the Netherlands (BUA 1991). Therefore, considerable differences between factories exist. The amount of HCBd might be sufficient to justify separating HCBd from hexachlorocyclopentadiene raw product.

Another industrial process involves chlorination of cyclopentadiene with sodium hypochloride at 40°C with low HCBd formation potential (Mumma and Lawless 1975).

For the assessment, companies producing hexachlorocyclopentadiene would be contacted and assessed for the respective process technology used and data on HCBd content in waste and product (Tier II).

For the high temperature chlorolysis process, current and former production volumes and management of HCBd containing residues should be compiled. In particular, it should be determined if HCBd is/was separated from the waste and is/was commercially marketed. If HCBd is or has been separated, information on the past uses of HCBd from the respective production would be compiled to support the inventory of likely stocks, disposed waste and releases from uses in the county (see also chapter 5).

Also, an assessment and inventory of wastes and their management and related stocks from current and former production and impacted landfills should be done (see chapter 4.6).

A questionnaire has been developed for addressing current and former producers of chlorinated solvents and other productions possibly relevant for HCBd generation and use (Annex). This can be used for gathering relevant information.

**Table 4-1:** Processes with a high generation of HCBd (BUA 1991; UNEP 2013a) where HCBd recovery might take place

Process	HCBd concentration in the raw product
Conventional low-pressure chlorolysis for the manufacturing of perchloroethylene and carbon tetrachloride	5% (50,000 mg/kg)
Optimized low-pressure chlorolysis for the manufacturing of perchloroethylene and carbon tetrachloride	0.2 to 0.5% (2000 to 5000 mg/kg)
Manufacturing of tetrachloride and trichloroethylene from acetylene and chlorine and subsequent decomposition to carbon tetrachloride and trichloroethylene	0.4% (4000 mg/kg)
Manufacturing of hexachlorocyclopentadiene	0.2 to 1.11 % (2000 to 11,100 mg/kg)

#### 4.4. Assessment and inventory of HCBd in chlorinated solvents

Chlorinated solvents might be contaminated with HCBd (Environmental Canada 2004). The HCBd levels in tetrachloroethylene, trichloroethylene or tetrachloromethane/carbon tetrachloride will depend on the respective distillation process. In an assessment of tetrachloromethane and tetrachloroethylene the levels were below 5 and 100 µg/l for different producers (BUA 1991).

Companies might have data on the HCBd levels in their products. This information could be used for an assessment. For a Tier III inventory and confirmation of the company data, chlorinated solvents could be analysed to measure the HCBd contamination and releases from solvent be estimated.

#### 4.5. Inventory of HCBd in the production of other organochlorine substances and elemental chlorine not considered to be separated for commercial purposes

HCBd is unintentionally formed or reported to be possibly formed in other processes from the organochlorine and chlorine industry. The levels in the processes compiled in this chapter are likely small to moderate (Table 4-2) and therefore cannot be separated and recovered for HCBd production/use. These processes are compiled below and could be assessed if a Party decides to include unintentionally produced HCBd in their inventory even though HCBd is not listed in Annex C of the Convention. Wastes from these industries might contain HCBd at levels above the provisional low POPs content which would result in POPs wastes which should be included in the HCBd inventory. For a Tier II inventory data from the industries and from other sources would be gathered. For a Tier III inventory the products, production residues and releases from production would be measured.

##### 4.5.1. Ethylene dichloride and vinyl chloride monomer

HCBd is generated during the production of ethylene dichloride (EDC; dichloroethane) for vinyl chloride monomer (VCM) production (Dow Chemicals 1990; Thornton 2001). EDC is made in two ways: ethylene is chlorinated with chlorine gas, or ethylene is oxychlorinated with hydrogen chloride that has been formed as a waste in other synthesis processes. Most EDC producers use both methods in a linked cycle, since chlorination of ethylene generates hydrogen chloride as a by-product, which can then be used in oxychlorination. Both processes yield a complex mixture of reaction products, which are then distilled to yield three batches of materials: the distilled EDC product, the light ends (those substances more volatile than EDC), and the heavy ends (less volatile than EDC) (Thornton 2001). About two kilograms each of heavy and light ends are generated for each tonne of EDC produced. From the published information available, HCBd is present in 12,000 mg/kg in these wastes (Dow Chemicals 1990; Thornton 2001; Table 4-

2). This amount of HCBD might not be sufficient for recovery of HCBD within the distillation in the process. At modern, well-regulated facilities, such waste is destroyed by high temperature incineration.

#### **4.5.2. Tetrachloromethane/carbon tetrachloride (by high-pressure chlorolysis)**

In the high-pressure chlorolysis for the production of tetrachloromethane (600°C; 120 bar) and in the stepwise chlorination of methane (600°C; 120 bar) only very low levels of HCBD (< 1 mg HCBD/kg) content in the raw product have been reported for productions in Germany (BUA 1991; Table 4-2). This could therefore be considered as BAT technologies. However, productions in other countries in particular developing countries and economies in transition have not been assessed. Therefore in the inventory, assessments of individual production facilities could be performed, particularly where less advanced technologies may be in use and regulatory oversight less rigorous so that HCBD levels are higher than reported BAT operations. For a Tier II inventory HCBD (and other UPOPs) from respective industries and from other sources would be gathered. For a Tier III inventory, levels of HCBD and other UPOPs would be reported for residues and environmental releases.

#### **4.5.3. Allyl chloride and epichlorohydrin**

Several reports have mentioned the unintentional production of HCBD during the production of allyl chloride and epichlorohydrin (U.S. EPA 1980; Environment Canada 2000; VROM 2002). In a dossier for Eurochlor the presence of HCBD in these processes was considered unlikely from a chemical point of view (Lecloux, 2004). The relatively low-chlorinated substances detected in the only published study for allyl chloride and epichlorohydrin (Kusz et al. 1984) support this estimate. For a Tier II inventory HCBD (and other UPOPs) data from respective industries and from other sources would be gathered. For a Tier III inventory the production residues and possibly other releases would be measured for HCBD and other UPOPs content.

#### **4.5.4. Chloroprene**

Chloroprene is produced by chlorination and dechlorination steps, some of which might produce unintentional HCBD (Mummi and Lawless 1975). No monitoring data on HCBD are available in the scientific literature. For a Tier II inventory HCBD (and other UPOPs) data from respective companies and from other sources would be gathered. For a Tier III inventory the production residues and possibly other releases would be measured for HCBD and other UPOPs content.

#### **4.5.5. Production of elemental chlorine**

HCBD, PCDD/PCDFs, HCB, and PCNs are generated in the production of elemental chlorine using graphite electrodes (Mumma and Lawless 1975; UNEP 2013a). With the use of BAT technologies using metal electrodes and other BAT technologies, formation of UPOPs including HCBD is considered to have relatively low potential (Mumma and Lawless 1975) and other UPOPs (UNEP 2013a).

In an inventory study of HCBD and HCB generation from chlorine production in the US, it was estimated that 18 to 32 tonnes of HCBD and 72 to 175 tonnes of HCB were generated from graphite electrode use in 1972 (Mumma and Lawless (1975).

For a Tier II inventory HCBD (and other UPOPs) data from respective industries and from other sources would be gathered. For a Tier III inventory, measurements of HCBD and other UPOPs in production residues and possibly other releases would be assessed.

**Table 4-2:** Processes with proven or reported potential formation of HCBD where HCBD recovery is unlikely

Process	HCBD concentration (mg/kg)	Reference
Dichloroethane/Vinyl chloride monomer (EDC/VCM)	12,000 mg/kg (in the waste)*	Dow Chemicals (1990)
Tetrachloromethane (high-pressure chlorolysis or stepwise chlorination)	<1 mg/kg (raw product)	BUA 1991
Allyl chloride and epichlorohydrin	Suspected but no data	(U.S. EPA 1980; Environment Canada 2000; VROM 2002)
Chloroprene rubber	Suspected but no data	Mumma and Lawless 1975
Production of Chlorine (graphite electrodes)	<10000 mg/kg in the waste	Mumma and Lawless 1975

\* About two kilograms each of heavy and light end waste is produced for each tonne of EDC. About 0.6 kg heavy end waste (organochlorines) per tonne chlorine is produced when using graphite electrodes (Mumma and Lawless 1975).

#### 4.6. Assessment and inventory of stockpiles and waste disposed at production sites

The amount of historically accumulated and disposed wastes and related stocks from production of organochlorines listed in chapter 4.3 and 4.4 depend on the current and former management of the waste generated from production, the separation of HCBD for use and the disposal practices. At technologically advanced facilities in industrialized countries the waste is destroyed mostly onsite in hazardous waste incinerators with recovery of chlorine/HCl (Lecloux 2004; UNEP 2017b). However, in the past these wastes were often disposed of to landfills with associated releases of HCBD into the environment and contamination of biota and groundwater (see chapter 2.5 and 2.6).

Therefore information on the current and former management of production residues containing HCBD should be compiled within the assessment of the individual production sites of chemicals listed in chapter 4.3 and 4.4. The assessment should include:

- Incineration of waste, technology used and appropriateness and related residues and disposal;
- Disposal of production waste and residues to landfills.

The assessment should cover the entire time of the respective production. In particular, HCBD-containing waste might have been disposed in landfills or dumpsites during the early years or decades of production. The amount of disposed waste containing HCBD might be known from the company or can be retrieved from documentation of production and waste management. For an estimate of the amount of disposed waste containing HCBD, the amount of organochlorines formerly produced at a production site can be retrieved and the related waste volume be estimated considering the amount generated (table 4-1; table 4-2).

Also information on other unintentional POPs (HCB, PCDD/PCDFs, PCBs and PCNs) should be collected or generated for these wastes and stocks. This assessment would contribute to the inventory of HCB, PCNs (UNEP 2017c) and other unintentional POPs (UNEP 2013b).

It needs to be assured that the disposed waste in the landfills is not recovered as stockpile by landfill mining as has been documented for one landfill of the organochlorine industry for another chemical (Torres et al. 2013).

## 5. Use, stockpiles and wastes consisting of or containing HCBD

### 5.1. Import and export of HCBD for intentional use

HCBD is listed in Annex A without exemption. Therefore HCBD as a chemical (CAS 87-68-3) or products and articles containing HCBD should not be imported or exported for use but only for environmentally sound disposal (see chapter 5.4). However, import and export for production and use might still take place intentionally or unintentionally, and HCBD is still listed on large chemical trading platforms<sup>23</sup>. Therefore, imports and exports of HCBD should be assessed and recorded in the inventory including the volumes.

Currently HCBD is not listed in the Rotterdam Convention, so HCBD is not subject to the Prior Inform Consent (PIC) procedure and does not have a specific Harmonized System (HS) code. HCBD is traded under the HS code "Other unsaturated chlorinated derivatives of acyclic hydrocarbons" with other chemicals. Therefore, the currently HS code is not specific enough for assessing imports of HCBD. However, the HS code in combination with the CAS number or trade names (see Table 2-1) could be used for the search of HCBD at the custom level.

Information on exports should be gathered from the organochlorine industry within the assessment of production of HCBD (see chapters 4.1 to 4.3) and from exporting companies and trading platforms which are still offering HCBD<sup>Error! Bookmark not defined.</sup>. The information thus obtained should be included in the inventory report.

Care should be taken not to double count import, export and use of HCBD when documenting the life cycle.

### 5.2. Industrial use of HCBD

HCBD has formerly been used in a wide range of applications (see chapter 2.4; and Table 2-4). There is no specific information available on any existing current applications of HCBD (Environment Canada 2000, UNEP 2013a, Potrykus et al. 2015). While in industrial countries major uses were stopped already in the 1990s (UNEP 2013a), some uses might still be present in other countries in particular in/from countries that have chlorinated solvent production.

Within the inventory of HCBD production/generation in the country (chapter 5) information on former and current uses of HCBD from producers are gathered. The assessment of those used would have highest priority in the assessment of current uses.

Furthermore, the former uses of HCBD listed in Table 2-4 can be used for a more detailed assessment.

### 5.3. In use equipment and stockpiles

The most important HCBD uses for currently used equipment, stockpiles and waste streams in terms of potential releases or concentration are expected to be (UNEP 2017b):

- Transformer, heat exchange and hydraulic fluids;
- Obsolete HCBD insecticide stockpiles and fungicide waste.

#### 5.3.1. HCBD in transformer fluids and related stockpiles

HCBD has been used in transformer fluids (BUA 1991, IARC 1999). Due to the long service life of transformers, HCBD used in this application even from the 1970s or 1980s might still be present in operating transformers and out of use transformers (UNEP 2017b).

The amount of HCBD in transformer oils was considerably smaller than PCBs and the total amount used in this application is unknown. There has been no report of transformers containing HCBD in the framework

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<sup>23</sup> E.g. <http://www.molbase.com/en/87-68-3-moldata-153320.html>; <https://www.alibaba.com/category-chemical/cas-87-68-3/>

of the Stockholm Convention inventories or other studies until now. Therefore, the amount of transformers containing HCBD can be considered small.

Most of the assessments of transformer oils for PCBs have been conducted using test kits which measure the total amount of chlorine in the oil such as Clor-N-Oil or Dexsil test. Within those assessments, HCBD containing transformers are also tested positive through the same mechanism as PCBs and could be managed accordingly.

Capacitors and transformers potentially containing HCBD may be tested for organochlorine using the test kits for PCBs. The chlorine detected could stem from PCBs, HCBD or PCNs. HCBD-containing condensers/transformers could also be identified within the monitoring of capacitors or transformers for PCBs using GC-ECD (see Guidance for screening POPs in products; UNEP 2017d). HCBD is more volatile and has therefore a lower Kovats Retention Index (1229.98) compared to PCB mixtures used in transformers (Kovats Index >2000). Consequently, it has a shorter retention time in the gas chromatograph compared to PCBs and could therefore be measured together with PCBs without overlapping retention times.

If the amount of chlorine detected by chlorine-screening methods is considerably higher than the amount of PCBs detected by GC-MS, an analysis of HCBD (and PCNs) should be performed.

When using the density test for pre-screening of pure Askarel PCB transformers, HCBD-filled transformers would also be tested positive since the density of HCBD (1.66) is even higher than that of PCBs (1.2 to 1.5).

### **5.3.2. HCBD in heat exchanger and hydraulic fluid and related stockpiles**

HCBD has been used as heat-transfer liquid and hydraulic fluid (ATSDR 1994; Van de Plassche and Schwegler 2002, Van der Honing 2007, Lecloux 2004). Due to the long service life of heat exchangers and hydraulic machinery, HCBD used in these applications even from the 1970s or 1980s might still be present. The former use volumes for these applications are not known (UNEP 2012, 2013).

The presence of HCBD in heat-transfer liquids and hydraulic fluids would be assessed within the assessment of PCBs and PCNs in these uses.

### **5.3.3. Obsolete pesticides**

In the past, HCBD has been used for pesticidal/phytosanitary purposes, for example, to combat soil pests including use as fumigant (ATSDR 1994; BUA 1991; Van der Honing 2007; Van de Plassche & Schwegler 2002), as seed dressing, as fungicide (Van der Honing 2007), as pesticide (IARC 1999) and as biocide (UBA 2006).

While no current use of HCBD as pesticide has been reported, stockpiles containing or contaminated with HCBD might still exist (UNEP 2017b).

Therefore, HCBD should be included within the POPs pesticide stockpile assessment.

### **5.3.4. Stockpiles from other (former) uses**

Within the inventory of HCBD production/generation in a country, information on former uses of HCBD from producers is gathered (see chapter 4). The results from the assessment of former use would be utilized to decide if other former use should be addressed in the inventory.

Furthermore, the former uses of HCBD listed in Table 2-4 can be used for a more detailed assessment.

## **5.4. Import and export of HCBD waste for environmentally sound disposal**

Import and export of HCBD-containing wastes may take place for the purpose of environmentally sound disposal in accordance with the Basel Convention procedures for transboundary movement of hazardous wastes. A *“Draft technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with hexachlorobutadiene”* has been developed (UNEP 2017b). In this guideline, all waste/waste categories possibly contaminated with HCBD have been compiled (UNEP 2017b; Table 5-1).

Annex I lists some of the wastes which may consist of, contain or be contaminated with HCBd. Also list A of Annex VIII of the Basel Convention<sup>24</sup> includes a number of wastes or waste categories that have the potential to contain or be contaminated with HCBd, including (see Table 5-1; UNEP 2017b). Also list B of Annex IX of the Basel Convention<sup>25</sup> includes a number of wastes or waste categories that have the potential to contain or be contaminated with HCBd (Table 5-1).

A provisional low POP content value for HCBd define a waste as POPs waste and has been set to [1][100] mg/kg<sup>26</sup> (UNEP 2017b).

Notifications of import and export of wastes listed in the Basel Convention includes the categories in the respective import/export procedure. This information can be used for inventorying waste imports or exports that are potentially contaminated with HCBd. The notifications might include specific information on HCBd or other POPs content. For a Tier III inventory, selected imported/exported waste fractions with high risk of HCBd contamination such as category Y6, Y11, A3160 or A3170 could be analysed for HCBd content.

**Table 5-1:** Major Basel Convention waste categories which may consist of or contain HCBd (UNEP 2017b)

Basel Conv. Annex category	Category	Type of waste
Annex I	Y4	Wastes from the production, formulation and use of biocides and phytopharmaceuticals;
	Y6	Wastes from the production, formulation and use of organic solvents;
	Y9	Waste oils/water, hydrocarbons/water mixtures, emulsions;
	Y10	Waste substances and articles containing or contaminated with PCBs and/or polychlorinated terphenyls (PCTs) and/or polybrominated biphenyls (PBBs);
	Y11	Waste tarry residues arising from refining, distillation and any pyrolytic treatment
	Y18	Residues arising from industrial waste disposal operations;
	Y41	Halogenated organic solvents.
List A of Annex VIII	A3040	Waste thermal (heat transfer) fluids;
	A3160	Waste halogenated or unhalogenated non-aqueous distillation residues arising from organic solvent recovery operations;
	A3170	Wastes arising from the production of aliphatic halogenated hydrocarbons (such as chloromethane, dichloro-ethane, vinyl chloride, vinylidene chloride, allyl chloride and epichlorhydrin);
	A4030	Wastes from the production, formulation and use of biocides and phytopharmaceuticals, including waste pesticides and herbicides which are off-specification, outdated or unfit for their originally intended use;
	A4060	Waste oils/water, hydrocarbons/water mixtures, emulsions;
	A4100	Wastes from industrial pollution control devices for cleaning of industrial off-gases but excluding such wastes specified on list B;
	A4130	Waste packages and containers containing Annex I substances in concentrations sufficient to exhibit Annex III hazard characteristics;

<sup>24</sup> List A of Annex VIII of the Convention describes wastes that are “characterized as hazardous under article 1, paragraph 1 (a), of this Convention.” However, “[designation] of a waste on Annex VIII does not preclude, in a particular case, the use of Annex III [List of hazardous characteristics] to demonstrate that a waste is not hazardous” (Annex I, paragraph (b)) (UNEP 2016).

<sup>25</sup> List B of Annex IX lists wastes that will not be wastes covered by Article 1, paragraph 1 (a), unless they contain Annex I material to an extent causing them to exhibit an Annex III characteristic (UNEP 2017b).

<sup>26</sup> Currently these two low POPs limits are listed in the Basel guideline (UNEP 2017b).

Basel Conv. Annex category	Category	Type of waste
	A4140	Waste consisting of or containing of specification or outdated chemicals corresponding to Annex I categories and exhibiting Annex III hazard characteristics;
	A4160	Spent activated carbon not included on list.
List B of Annex IX	B1040	Scrap assemblies from electrical power generation not contaminated with lubricating oil, PCB or PCT to an extent to render them hazardous;
	B3040	Rubber wastes ((i) Waste and scrap of hard rubber (e.g., ebonite); (ii) Other rubber wastes (excluding such wastes specified elsewhere).

## 6. Unintentional production of HCBd in thermal processes

HCBd is unintentionally formed in thermal processes. While HCBd is not currently listed in Annex C of the Convention, Parties interested in the management and reduction of HCBd from thermal sources could assess the release of HCBd from thermal sources and related wastes and stockpiles.

At its twelfth meeting, POPRC concluded in its decision POPRC-12/5 that there were unintentional releases of HCBd from the production of certain chlorinated hydrocarbons, the production of magnesium, incineration processes and the production of polyvinyl chloride, ethylene dichloride and vinyl chloride monomer and noted nonetheless that there were some concerns regarding the cost-benefit implications of measures to address these releases.

### 6.1. Unintentional formation of HCBd in magnesium and aluminium production and refining

HCBd is unintentionally formed in the production of magnesium (Lecroix 2004, Van der Honing 2007; Van der Gon et al. 2007). Deutscher and Cathro (2001) reported on organochlorine formation in magnesium electrowinning cells with HCBd and HCB as major components (Deutscher and Cathro 2001). The laboratory study indicated that depending on the current density applied during electrolysis up to approximately 3 g HCBd per tonne magnesium is formed. According to the German Federal Environment Agency 15 to 20 g HCBd is produced per tonne magnesium (UBA 2006).

Another source of HCBd (and HCB) in the magnesium and aluminium production was and potentially is the use of hexachloroethane in the manufacture of degassing pellets to remove hydrogen gas bubbles from molten aluminium in aluminium foundries and magnesium production (U.S. National Toxicology Program 2011; Vogelgesang et al. 1986). This use is being phased out in the EU and was phased out in the US 1999.

### 6.2. Unintentional formation of HCBd in incineration processes

HCBd might also be unintentionally formed in incineration processes in particular when incinerating wastes with high chlorine content such as residues from organochlorine production (INERIS 2005; UNEP 2013a)<sup>27</sup>.

There is no study which has shown that HCBd is formed and released from municipal waste incinerators. While the formation potential of highly chlorinated POPs such as HCB and OCDD/OCDF in municipal waste incinerators is likely lower compared to the incineration of organochlorine waste, their occurrence indicates the potential for HCBd formation.

There are no HCBd data from incinerators and therefore no emission factors can currently be given. In a Tier III inventory HCBd (along with other UPOPs) could be measured in hazardous waste incinerators

<sup>27</sup> It has been demonstrated that organochlorine waste with high chlorine content can be destroyed by a BAT incinerator so that HCBd release is minimized or below the detection limit in residues (Potrykus et al. 2015).

treating high chlorine waste and in municipal waste incinerators. Such an assessment has rather low priority.

### **6.3. Unintentional formation of HCBd in secondary copper/metal smelters**

HCBd and PCDD/PCDF were formed in the laboratory when acetylene was incinerated in the presence of copper chloride (Lenoir et al. 2001). These laboratory conditions are similar to the setting in secondary copper smelters with high copper chloride content to catalyse high unintentional POPs formation. HCBd has not been measured in secondary copper smelters. Therefore, no emission factor can currently be given. In a Tier III inventory HCBd (along with other UPOPs) could be measured in copper and other metal smelters with high UPOPs formation potential.

## 7. Inventory of sites contaminated by HCBD

### 7.1. 7.1. Scope and background information

In accordance with the provisions of Article 6 (1) (e), Parties shall endeavour to develop appropriate strategies for identifying sites contaminated by chemicals listed in Annex A, B or C. Creating and maintaining an inventory and database of sites contaminated by POPs<sup>28</sup> is an important step for a regulatory agency in formulating a strategy for the management of contaminated sites.

This chapter aims at giving step-by-step guidance for identifying and establishing an inventory of sites contaminated by HCBD in a tiered approach.

The inventory team is recommended to consider the step-by-step approach of UNIDO's "*Persistent Organic Pollutants: Contaminated Site Investigation and Management Toolkit*" (UNIDO 2010), which addresses the identification of POP-contaminated sites (not specific to HCBD), assessing related risks and setting priorities.

The inventory should compile information collected during the site investigation from Module 2, preliminary site investigation, stage 1 and/or stage 2, of the UNIDO Toolkit. This information includes the site profile, past and present activities, spill releases, and site owners.

Contaminated sites may be created during the entire lifecycle of POPs, including their production, manufacturing of products containing POPs, use, recycling and their end-of-life.

To carry out the inventory of contaminated sites, the team is expected to use the information collected through activities described in chapters 4 to 6. This information is to be used, in particular, in assessing solid waste management by former and current producers of chlorinated solvents and other organochlorine chemicals (chapter 4), waste and stockpiles from uses (chapter 5), and processes where HCBD has possibly been unintentionally formed in thermal processes such as magnesium and aluminium production (see chapter 6).

A site is generally considered contaminated by POPs when the concentration of one or more contaminants exceeds the regulatory criteria or poses a risk to humans and/or the environment.

- Drinking water: WHO has established a limit for HCBD of 0.6 µg/litre considering current TDI (WHO 2004). Due to the genotoxic potential of HCBD (Brüschweiler et al. 2010), Switzerland set a drinking water limit of 0.075 µg/l (Swiss Federal Office of Public Health 2010). These limit values could be used for considering a groundwater contaminated in particular if the water is used for drinking water.
- Surface water: the European Water Directive classifies HCBD as a priority substance with 0.6 µg/l as Environmental Quality Standard (European Union 2013).
- Biota: For fish, the EU has set an Environmental Quality Standard for HCBD of 55 µg/kg wet weight (European Union 2013). This allows the contamination status of rivers or lakes to be defined.

### 7.2. 7.2. Step 1: Planning the inventory

Information from the identified relevant sectors (chapters 4 to 6) can be used to identify sites potentially contaminated by HCBD and, thereby, set priorities for securing such sites and possibly for their remediation.

The first step focuses on defining the scope of the inventory and developing a work plan (see chapter 3.1.).

An inventory of sites contaminated by HCBD should include an assessment of releases and related contamination along the life cycle (see Table 7-1), namely:

- Former production sites of HCBD;

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<sup>28</sup> It is recommended to integrate the POPs contaminated site database in a general database on contaminated sites.

- Former production sites of products where HCBd were unintentionally produced;
- Sites where HCBd or HCBd containing products were used (see Table 2-3);
- Sites where HCBd precursors (e.g. tetrachloroethylene, hexachloroethane) were used in thermal processes like aluminium and magnesium refining;
- End-of-life disposal sites of HCBd-containing wastes (e.g. chemical landfills).

Appropriate members of the inventory task team are selected to conduct the inventory of this sector. Specific stakeholders for the inventory of HCBd are listed in Table 3-1. The core inventory team can be extended as appropriate. The NIP coordinator or task team leader can decide which stakeholders to include in an inventory team and which stakeholders to contact for an interview or to receive a questionnaire.

### *Identification of stakeholders*

Identification of stakeholders could consider all those listed in Table 3-1, in addition to personnel from local government such as site inspectors, also landfill owners, and the general public.

Authorities and other stakeholders that might provide valuable information on identified sites contaminated with HCBd:

- Environmental protection agencies;
- Ministry for environment protection;
- Ministry for industries;
- Municipal authorities;
- State governments;
- Former or current producers of chlorinated solvents (tri-, tetrachloroethylene, tetrachloromethane, ethylene dichloride) other organochlorines and chlorine;
- Producers of magnesium
- User of HCBd precursors (hexachloroethane):
  - Refining of aluminium;
  - Military units responsible for fog ammunition and smoke grenades/pots containing hexachloroethane.
- Property development companies dealing with related brownfields.

Environmental contamination from industrial processes that release and dispose of HCBd can affect air, water/sediments and land as well as biota/animals and related food. Therefore, investigation is necessary to identify the relevant sectors involved, including manufacturing and waste disposal, including wastes being disposed; methods of waste disposal, treatment, and/or recycling; as well as related waste disposal locations and related releases.

Sites potentially contaminated by HCBd are listed in Table 7-1 below. The step-by-step approach in the *Contaminated Site Toolkit* (UNIDO 2010) can then be followed to systematically identify such sites, keep records, develop a registration system, and perform risk assessment and prioritization for the management of the sites contaminated by HCBd.

## **7.3. 7.3. Steps 2 and 3: Choosing data collection methodologies and collecting data**

### **7.3.1. Tier I: Initial assessment of potentially HCBd contaminated sites**

The expected output of the initial assessment includes:

- List of relevant stakeholders in the country;
- Compilation of information on sites (potentially) contaminated by HCBd;

- List of locations of sites potentially contaminated by HCBd;
- Compilation of gaps from Tier I assessment to be addressed by Tier II.

In the first step an overview information on sites potentially contaminated by HCBd would be compiled (internet and literature survey and phone interviews).

### *Contamination at current and former production sites of HCBd and related chlorinated solvents*

Major POPs-contaminated sites are at and near respective POPs production sites (Weber et al. 2008; Vijgen et al. 2011). HCBd was/is produced intentionally or unintentionally within the production of tri-, tetrachloroethylene, tetrachloromethane and dichloroethylene. Soil and gravel samples collected near a Swedish oxychlorination reactor for dichloroethylene contained a wide variety of persistent organochlorines in the high mg/kg (ppm) concentration range, with HCB and HCBd at the remarkable levels of 19,000 mg/kg and 6,000 mg/kg, respectively (Johnston et al. 1993). Also soil and ground water samples from an Australian organochlorine solvent producer were found to be contaminated with HCBd so that remediation was needed (Orica 2011; Wright 2004). Ground water can be heavily polluted with HCBd and other organochlorines at production sites of organochlorine solvents (Botta et al. 1996; Wycisk et al. 2013). Indeed HCBd was used for tracking sources of groundwater pollution from such production sites (Botta et al. 1996). The release to surface water from production sites and landfills can also result in contamination of sediments.

The largest volume of POPs at former or current organochlorine production sites are normally found at landfills that received production waste (Götz et al. 2012; Weber et al. 2008, 2011a,b; Vijgen et al. 2011; Wycisk et al. 2013). Historical landfilling of heavy fractions from the production of chlorinated solvents or other organochlorine substances can lead to secondary HCBd emissions in leachates or into air (ASDTR 1994, Staples, 2003, Lecloux, 2004, ESWI 2011). Due to its water solubility (3.2 mg/l; Table 2-2) HCBd can be released from landfills to ground water and surface water (Orica 2011; Wright 2004; U.S. Department of Health and Human Services 2011; U.S. EPA 2004), which can result in drinking water contamination (Clark et al. 1982; Forter 2016; table 2.4) or contamination of fish and shellfish (Lowis 2014; U.S. Department of Health and Human Services 2006). Also, sites where HCBd has been used for different purposes (Table 2-4) and associated landfills have been disposed after use can be contaminated with HCBd.

The release to surface water from production/use sites and landfills can also result in contamination of sediments. The highest concentrations reported in sediments were 430 mg/kg near a hotspot (ESWI 2011).

HCBd is also released to air from landfills containing HCBd with possible associated exposure of nearby populations. For example, houses had to be demolished for excessive indoor HCBd levels on the properties that were built close to the waste dump at Weston Quarries (UK) (Barnes et al. 2002; Crump et al. 2004; NICOLE 2004),

Therefore, for the production sites of organochlorine solvents and related waste disposal sites should be assessed for contamination of ground water and contamination of fishes and sediments in related potentially impacted surface water. Also contamination of drinking water wells including drinking water should be assessed. HCBd has a moderately high vapour pressure and is also released into air which creates the potential for contaminating surrounding housing, especially those located in the direction of a ground water plume. This would also be considered and assessed.

During the course of the production of chlorinated solvents, HCBd, HCB, PCNs, PCBs and PCDD/PCDFs are unintentionally formed. Therefore, these unintentionally produced POPs would also be included in the assessment of sites of chlorinated solvents production and related landfills and associated releases.

### *Sites where HCBd have been used*

Sites where HCBd have been used may be contaminated. In industrialized countries, HCBd was used in large quantities in the 1970s and 1980s. Since HCBd use largely stopped in industrial countries before 2000, the major issue relating to this chemical may be the contamination of land from former use. In

developing countries and countries with economies in transition, HCBd might still be in use and the related use could result in contaminated sites.

Due to the volatility of HCBd, sites where HCBd was used years or even decades ago, any remaining contamination is likely to be low. HCBd has been used in agriculture as fumigant, pesticide, seed dressing and as fungicide (ATSDR 1994; BUA 1991; Van der Honing 2007; Van de Plassche & Schwegler 2002). Sites where HCBd has been used were found contaminated. E.g. soils in Phylloxera-infected vineyards that were treated with 250 kg/ha HCBd were contaminated with HCBd at the level of 7.3 mg/kg after 8 months and 3 mg/kg after 32 months (Vorobyeva (1980) in IPCS (1994), indicating decrease/evaporation over a few years.

POPs contamination is found at and around factories where these substances have been used for the manufacture of goods. HCBd has been used as a purification agent for the recovery of “snift”, a chlorine containing gas in chlorine plants and as a solvent in chlorine production (Lecloux 2004; Van der Honing 2007). Also it has been used in the production of chlorofluorocarbons (CFCs) (Lecloux 2004). Therefore HCBd may have been dispersed as a contaminant at sites where chlorine and CFC were produced and in landfills that received wastes from these industries.

HCBd has also been used as a heat-transfer liquid (Van de Plassche and Schwegler 2002, Van der Honing 2007, Lecloux 2004) particularly in transformers (BUA 1991, IARC 1999). Therefore, factories that produced transformers (mainly in 1960s to 1980) may have used HCBd, some of which remained as a contaminant at production sites and related landfills. Since PCBs and PCNs were also used as transformer oils from 1930s to 1980s these POPs would be included in the assessment of transformer factories that were operating at that time (UNEP 2017).

HCBd has also been used in the synthesis of rubber compounds (ATSDR 1994; Lecloux 2004; Van de Plassche and Schwegler 2002) and as a solvent for rubber (Lecloux 2004). Since PCNs also have been used in the production of rubber these POPs groups are to be included in the assessment (UNEP 2017).

Furthermore, military areas may be contaminated with HCBd where fog ammunition like smoke pots or smoke grenades containing hexachloroethane have been used. Since PCN have also been used in these applications (Clausen et al. 2004; Hewitt et al. 2011; Generalstab Schweizer Armee 1945), PCN would also be assessed (UNEP 2017c). While the majority of use of such hexachloroethane- and PCN-containing fog ammunition might have taken place on restricted military areas, fog ammunition has been used to some extent outside military areas in the past (UNEP 2017c).

In addition, other sites where HCBd has been used in the country should be assessed for contamination.

#### *Sites where HCBd was formed in thermal processes and related disposal of wastes*

Potentially contaminated sites include areas where HCBd was unintentionally formed in high concentration in thermal processes (e. g. magnesium production; aluminium refining with hexachloroethane) and related landfills/dump sites where residues of HCBd containing waste have been disposed.

The unintentional formation of HCBd in municipal waste incinerators or secondary copper smelters is considered too low to result in contaminated sites. However, these areas can be contaminated with PCDD/PCDFs and other unintentional POPs (see chapter 10 of UNEP toolkit (UNEP 2013b).

**Table 7-1:** Potential HCBD-contaminated sites during the life cycle of HCBD

Life cycle stage; Sector	Activities	Locations (potential other POPs)
<b>HCBD production and production of chlorinated solvents</b>	(Former) production of HCBD	Production site (HCB)
	Disposal of waste from production	Landfills related to waste from production (HCB)
	Former water discharge sites from production	River sediment and flood plains related to releases from production site (HCB)
<b>Sites where HCBD has been used*</b>	Industrial use sites	Sites of chlorine and CFC production; Related landfills; Related impacted surface waters (sediment and flood plains) (HCB; UPOPs)
	Production of transformers and other electrical equipment	(PCB; PCN)
	Fumigant, pesticide, biocide, fungicide, seed dressing	Site of fumigant, pesticide application (e.g. vineyards and other use area)
	Other sites of production where HCBD has been used (e.g. lubricants, rubber, )	Production sites and related landfills
<b>Unintentional HCBD in thermal processes</b>	Production of magnesium; Refining/degassing of magnesium and aluminium using hexachloroethane	Disposal sites of residues from production of magnesium and from refining of magnesium/aluminium
	Use of smoke grenades using hexachloroethane smoke	Military areas where smoke grenades has been used (HCB; PCNs)
	Incineration of waste with high chlorine content	Sites where residues from these incineration processes are disposed
<b>End-of-life treatment</b>	Disposal of transformers and other equipment containing HCBD	Storage and treatment sites of transformers and other equipment (PCB; PCN)

\*While major uses were curtailed in industrialized countries in the 1990s, some uses might still be present in other countries (in particular in countries with chlorinated solvent production and associated HCBD separation).

### 7.3.2. Tier II: (Preliminary) Inventory of sites potentially contaminated by HCBD

The expected output of the initial assessment of HCBD-contaminated sites includes:

- Gathering information on types of individual sites within the country, in particular sites of former intentional and unintentional production and use;
- Detailed locations of potentially contaminated sites (GIS);
- Information by site visits of selected potentially contaminated sites;
- Information on the potentially HCBD-contaminated sites allowing prioritisation;
- Potentially impacted groundwater and drinking water;

- Information on possible human exposure
  - e.g. if HCBd is detected in meat, eggs, or in fish. An exposure assessment has been conducted for the Devil Swamp (U.S. Department of Health and Human Services 2006);
  - information on HCBd concentrations in air and potential exposure especially in housing in the areas surrounding HCBd-contaminated sites. An assessment has been conducted for e.g. the Weston Quarries site in the UK (Nicole 2004; Barnes et al. 2002; Crump et al. 2004);
  - information on drinking water contamination (Table 2.4). E.g. monitoring has been conducted in Switzerland resulting in the use of carbon filtration of water impacted by a chemical landfill (see Forter 2016); health impact from exposure to drinking water has been assessed for another site in the US (Clark et al. 1982).
- Compilation of gaps from Tier II assessment to be possibly addressed by Tier III.

Information would be collected by direct contacts, by questionnaire approach or by site visits from (selected) sites listed in Table 7-1.

Site investigation, comprising preliminary site investigation (PSI) and detailed site investigation (DSI), provides valuable information on a site, including:

- The nature and location of contaminants with respect to the soil and groundwater (table 2-4);
- Potential pathways for contaminant migration;
- The location of nearby sensitive receptors;
- Potential for direct human exposure to the contaminants;
- Potential of food and drinking water contamination.

Carrying out the PSI stages 1 and 2 for those locations of potential HCBd contamination listed in Table 7-1 is suggested for the purposes of the inventory with emphasis on sites of chlorinated solvent production and related disposal sites.

The objective of PSI stage 1 is to gather sufficient information to estimate the likelihood of HCBd and other POPs (in particular HCB, PCBs and PCNs) contamination that may be present at a site. Sampling relevant environmental media and investigations of subsurface conditions are not required at this stage (see Tier III).

A PSI stage 1 includes the following activities (see *Contaminated Site Toolkit* (UNIDO 2010)):

- **Historical review:** review of a site's historical use and records to determine current and past activities or uses and other POPs pollutants. This would include information such as:
  - How long has HCBd been produced or used at the site?
  - What other polluting processes or chemicals were and are present? Often HCB is associated with HCBd releases and often occurs at higher levels than HCBd (see e.g. Table 2.3). Also, PCBs and PCNs have been used in some similar application as HCBd (e.g. hydraulic oils, heat exchange oils, lubricants). Therefore, a transformer factory or factory producing equipment with heat exchange oils or hydraulic oils would be assessed for HCBd, PCB and PCN contamination.
  - Information on accidents and spills;
  - Practices and management relating to potential contamination at the site and at adjacent sites (including related landfills or thermal treatment of wastes);
  - Wastewater treatment;
  - Possible releases to surface water and related sediment and flood plain contamination.
- **Site visits:** one or more walk-through site visits to verify and complete the information gathered during the literature review for indicators or presence of contamination; in these

site visits, possible exposure of fish, livestock, and humans in the vicinity would also be noted.

- **Interviews:** interviews to verify and complete information by asking current or former owners, occupants, neighbours, managers, employees, and government officials who can, with reasonable attempts, be contacted about information on activities that may have caused contamination.

It should be noted, however, that while the information that is required in PSI stage 1 might be accessible in industrialized countries, it is not always available or accessible in developing countries and countries with economies in transition.

One outcome of Tier II assessment would also be a gap assessment of further information needed for selected sites and a prioritization of possible Tier III assessment of selected sites (in particular considering the source strength of sites and the risks to humans).

### **7.3.3. Tier III: In depth inventory of potentially HCBd contaminated sites**

Tier III would include PSI stage 2 assessments and measurements of HCBd contamination for the respective sites (and possibly other suspected POPs in particular HCB, PCB and PCN; see Table 7-1) (see also UNIDO 2010).

PSI stage 2 would be conducted only if stage 1 indicates that there is a likelihood of HCBd/POP contamination at the site or if there is insufficient information to conclude that there is no potential for HCBd/POP contamination. The objective of stage 2 is to confirm the presence or absence of the suspected contaminants identified in stage 1 and to obtain more information. To achieve this objective, site investigators would carry out the following activities:

- Development of a conceptual site model;
- Development of a sampling plan;
- Sampling of relevant environmental media laboratory or field instrumental analysis of sampled and selected environmental media for substances that may cause or threaten to cause contamination.

#### **Key elements of a conceptual site model include:**

- Site history and setting;
- Potential contaminants of concern – contaminant properties and behaviour;
- Potential areas of environmental concern (Source Zones);
- Geology and stratigraphy;
- Regional and local;
- Overburden – sedimentary, glaciology, depositional processes;
- Bedrock – fracture networks, representative elementary volume;
- Hydrogeology and surface waters;
- Aquifers and aquitards;
- Groundwater levels, drinking water levels and elevations;
- Hydraulic gradients and velocities;
- Boundaries;
- Plumes and pathways;
- Groundwater and vapour;
- Environmental transport and attenuation processes;
- Receptors (animals and humans) and risk.

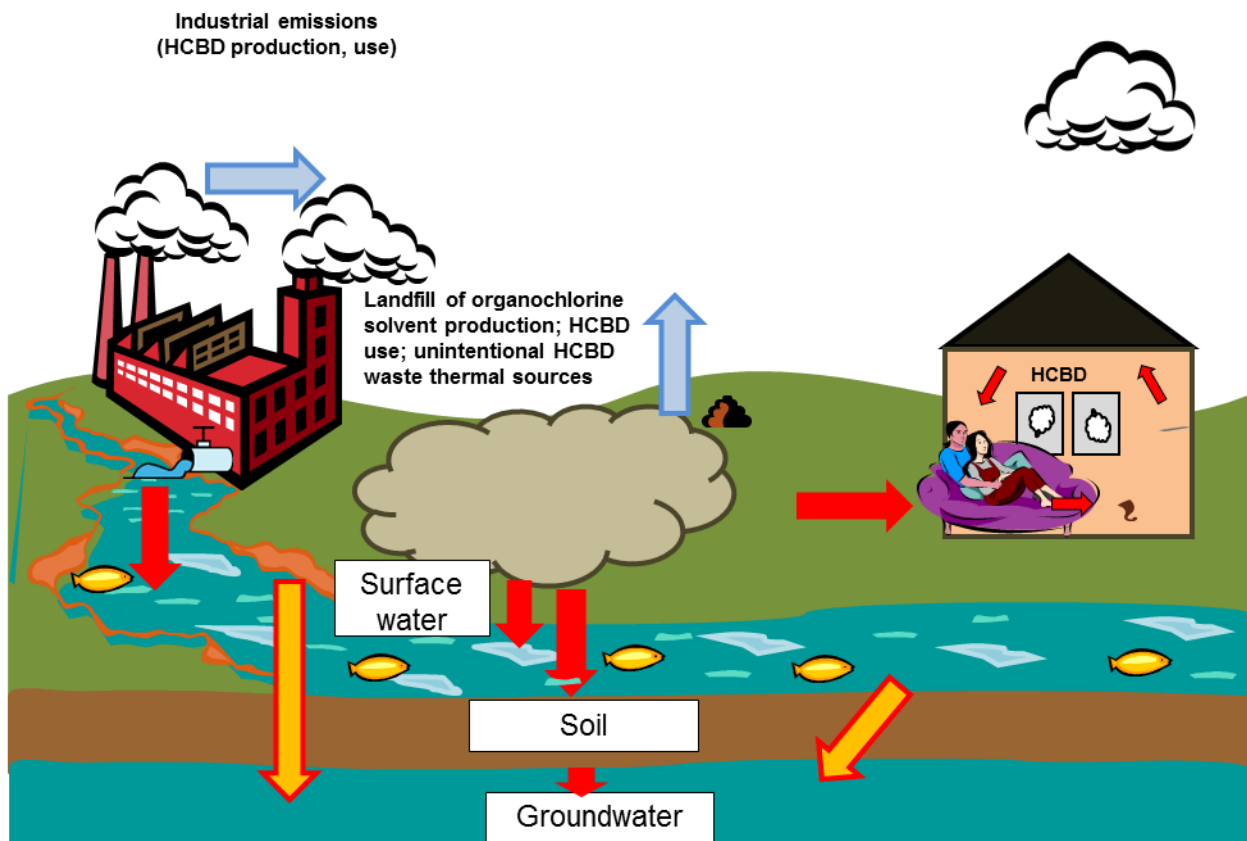
## 7.4. 7.4. Step 4: Managing and evaluating data

The information on the different potentially HCBD contaminated sites would be compiled and evaluated. The compilation would best be done according to the life cycle of HCBD (Table 7-1).

The contaminated sites data would best be included in a national contaminated site database. If such a database does not exist then the different POPs-contaminated sites might be compiled in one national database (HCBD, PCBs, PCDD/F, PCNs, PFOS, POP-Pesticides etc.) and be used as basis to develop an overall database of contaminated sites in the country.

Based on the data collected, a conceptual site model (CSM) can be developed to establish the relationship between the contaminants, exposure pathways and receptors (see Figure 7-1). The CSM, which would be developed at the very beginning of PSI stage 2, identifies the zones of the site with different contamination characteristics (i.e., whether contaminants in the soil are likely to be at the surface or at deeper levels, distributed over an entire area or in localized "hot spots" such as landfills).

Exposure pathways and receptors would be identified, where appropriate, for both current and future uses of the site. The CSM is based on a review of all available data gathered during stage 1, and would be continuously modified as more information becomes available during stage 2 and the detailed site investigation. See *Contaminated Site Toolkit* (UNIDO 2010).



**Figure 7-1:** Routes of HCBD/POP contamination and migration at sites of production and use and disposal

The accuracy of the information gathered and analysed during the investigation is vitally important because it forms the basis for the risk assessment phase, for making decisions on the need for, and type of, securing and remedial action and, eventually, for the design and implementation of necessary actions.

During a site investigation, every item of information collected should be recorded properly in words, along with photographs of the site and the surrounding area. Reporting is essential for each stage of the investigation as site-specific information is invaluable to decision makers in their efforts to protect the environment and human health.

It is suggested that contaminated site inventories would be established on the national level. Data collection and compilation, data management, and evaluation could refer to the *Contaminated Site Toolkit* (UNIDO 2010).

## 7.5. Step 5: Reporting

Reporting is essential for each stage of the investigation as site-specific information is invaluable to decision-makers in their efforts to protect human health and the environment and to understand the related risks.

Relevant findings would be included in the national contaminated sites database and in the NIP report. Also, further activities needed for assessing and possibly securing or remediation of contaminated sites would be included in the NIP.

Information which might be compiled for individual (relevant) contaminated sites would be included in the inventory report and in the national contaminate site database.

The PSI stage 1 report would identify potential contamination:

- Potential source of contamination;
- Potential contaminants of concern;
- Areas of potential environmental concern (potential lateral extent, vertical extent and media).

If for (selected) sites a PSI stage 2 assessment has been conducted, a report would identify contamination and potential contamination including:

- Source of contamination;
- Contaminants of concern (i.e. types of POPs);
- Areas of environmental concern (potential lateral extent, vertical extent, media);
- Recommendations for action.

For further information on reporting, refer to the *Contaminated Site Toolkit*.

The inventory of contaminated sites could include:

- Types and quantities of HCBd and HCBd-containing materials disposed;
- Other pollutants at the site;
- The names and addresses of entities responsible for disposal of HCBd and HCBd-containing materials; The names and addresses of entities responsible for disposal of other pollutants at the site;
- Details of the treatment of waste before disposal;
- Records of site contamination;
- Details of the clean-up process (if any) once a site has been registered as being contaminated;
- Information on the monitoring of contaminated sites;
- Records of on-going monitoring and research.

As mentioned above, a contaminated site management policy requires established “maximum permissible levels” and “levels of concern” (values that trigger action) in corresponding media such as e.g. soil, sediment or water. The existing permissible levels are partly established for HCBd at the national or international level (see above). For assessment of exposure risk and possible needed securing or remediation activities, such “maximum permissible levels” and “levels of concern” would be used and where not established further elaborated. For toxicological information on HCBd, the compiled information for WHO would be consulted (IPCS 1994).

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## Annex

# QUESTIONNAIRE for compiling information on the current and former production of chlorinated solvents and other substances where HCBd were formed as a product or by-product

### 1) Background information

In May 2015, the Conference of the Parties (COP) amended the Stockholm Convention on persistent organic pollutants (POPs) to add hexachlorobutadiene (HCBd) to Annex A of the Convention, without specific exemption (decision SC-7/12; United Nations 2015).

At its twelfth meeting, the POPs Review Committee recognized in its final decision that HCBd demonstrates the characteristics of a POP that by decision SC-7/12 the COP therefore listed the chemical in Annex A; concluded that there are unintentional releases of HCBd from the production of certain chlorinated hydrocarbons, the production of polyvinyl chloride, ethylene dichloride and vinyl chloride monomer; the production of magnesium, and incineration processes<sup>1</sup>.

### 2) Aim of the questionnaire

This questionnaire is aimed at gathering information on the current and former production of chlorinated hydrocarbons where HCBd was generated as a by-product as well as information on potential HCBd contaminated sites.

This information will be very valuable in order to assess the current situation and will constitute the basis for the country to propose further actions for HCBd elimination to be included in the updated National Implementation Plan of the country.

#### 1. Name and address of industry:

Name of industry/company or institution	Address

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<sup>1</sup> It was noted that there are some concerns regarding the cost-benefit implications of measures to address the unintentional releases of HCBd.

**2. Type of company or industry:**

Production of chlorinated hydrocarbons

Perchloroethylene

Trichloroethylene

Carbon tetrachloride

Current production Starting date.....

Historic production Starting date.....

Ending date.....

**3. Generation of HCBD in the production process**

Production of Chlorinated hydrocarbons	HCBD content (%)	Years of production (from and until)	Total volume of HCBD by-product (tonnes) (Total historic production/ Current production)
Perchloroethylene			.....t/.....t
Trichloroethylene			.....t/.....t
Carbon tetrachloride			.....t/.....t

#### 4. HCBd life-cycle after generation as by-product from chlorinated hydrocarbons production

Table Q1. HCBd life-cycle after generation as by-product from Perchloroethylene production

Production of Chlorinated hydrocarbons	Activity	Years (from and until)	Total volume of HCBd by-product (tonnes) (Total historic / Current)
Perchloroethylene	<input type="checkbox"/> Separation & cleaning of HCBd and sold for intentionally use in: <ul style="list-style-type: none"> <li><input type="checkbox"/> Agricultural sector<sup>2</sup></li> <li><input type="checkbox"/> Industrial manufacture<sup>3</sup></li> <li><input type="checkbox"/> Purification of gas streams<sup>4</sup></li> <li><input type="checkbox"/> Electrical equipment<sup>5</sup></li> </ul>		.....t/.....t
	<input type="checkbox"/> Re-distillation and reutilization in the production process (only in case of closed applications)		.....t/.....t
	<input type="checkbox"/> Landfilled/disposed in: <ul style="list-style-type: none"> <li><input type="checkbox"/> Hazardous waste disposal sites (If available, please provide below the exact disposal site) .....</li> <li><input type="checkbox"/> Own industrial facility waste disposal site (In case of landfilling on own industrial waste disposal site please describe below the ways in which HCBd containing waste is managed) ..... ..... .....</li> </ul>		.....t/.....t

<sup>2</sup> For phytosanitary purposes to combat soil pests including use as fumigant, as seed dressing, as fungicide, as pesticide and as biocide.

<sup>3</sup> As chemical intermediate in several industrial manufacturing processes: synthesis of rubber compounds, production of lubricants, manufacture of chlorofluorocarbons, manufacture of aluminum and graphite rods, as solvent for rubber, other polymers and elastomeric plastics.

<sup>4</sup> As purification agent for recovery of “snift”, a chlorine containing gas in chlorine plants, as washing liquor for purifying gas streams by removing hydrocarbons, as adsorption agent for gaseous contaminants, as well as solvent in chlorine gas production.

<sup>5</sup> As heat-transfer liquid particularly in transformers, as hydraulic fluid and liquid in gyroscopes, and as insulating liquid.

	<input type="checkbox"/> Destruction by incineration of HCBD (Please describe below how the heavy end is managed) ..... ..... .....		.....t/.....t
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**Table Q2. HCBD life-cycle after generation as by-product from Trichloroethylene production**

Production of Chlorinated hydrocarbons	Activity	Years (from and until)	Total volume of HCBD by-product (tonnes) (Total historic / Current)
Trichloroethylene	<input type="checkbox"/> Separation & cleaning of HCBD and sold for intentionally use in: <input type="checkbox"/> Agricultural sector <sup>1</sup> <input type="checkbox"/> Industrial manufacture <sup>2</sup> <input type="checkbox"/> Purification of gas streams <sup>3</sup> <input type="checkbox"/> Electrical equipment <sup>4</sup>		.....t/.....t
	<input type="checkbox"/> Re-distillation and reutilization in the production process (only in case of closed applications)		.....t/.....t
	<input type="checkbox"/> Landfilled/disposed in: <input type="checkbox"/> Hazardous waste disposal sites (If available, please provide below the exact disposal site) ..... <input type="checkbox"/> Own industrial facility waste disposal site (In case of landfilling on own industrial waste disposal site please describe below the ways in which HCBD containing waste is managed) ..... ..... .....		.....t/.....t

	<input type="checkbox"/> Destruction by incineration of HCBD (Please describe below how the heavy end is managed) ..... ..... .....		.....t/.....t

**Table Q3. HCBD life-cycle after generation as by-product from Carbon tetrachloride production**

<b>Production of Chlorinated hydrocarbons</b>	<b>Activity</b>	<b>Years (from and until)</b>	<b>Total volume of HCBD by-product (tonnes) (Total historic / Current)</b>
Carbon tetrachloride	<input type="checkbox"/> Separation & cleaning of HCBD and sold for intentional use in: <input type="checkbox"/> Agricultural sector <sup>1</sup> <input type="checkbox"/> Industrial manufacture <sup>2</sup> <input type="checkbox"/> Purification of gas streams <sup>3</sup> <input type="checkbox"/> Electrical equipment <sup>4</sup>		.....t/.....t
	<input type="checkbox"/> Re-distillation and reutilization in the production process (only in case of closed applications)		.....t/.....t
	<input type="checkbox"/> Landfilled/disposed in: <input type="checkbox"/> Hazardous waste disposal sites (If available, please provide below the exact disposal site) ..... <input type="checkbox"/> Own industrial facility waste disposal site (In case of landfilling on own industrial waste disposal site please describe below the ways in which HCBD containing waste is/was managed) ..... .....		.....t/.....t

	.....		
	<input type="checkbox"/> Destruction by incineration of HCBD (Please describe below how the heavy end is managed) ..... ..... .....		.....t/.....t

**5. Locations contaminated or possibly contaminated with HCBD**

Location/address	Type of contamination	Type of activity at the location	Have the site been investigated?	Levels of HCBD (if available)

**6. Further Remarks**

**7. Information on respondent**

Name	
Department	
Position	
Telephone	
Mobile Phone	
Email Address	
Signature	
Date	