# UNINTENTIONALLY PRODUCED HEXACHLOROBENZENE AND PENTACHLOROBENZENE POPs WASTE FROM SOLVENT PRODUCTIONS - THE NEED TO ESTABLISH EMISSION FACTORS AND INVENTORIES

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## Introduction

Four of the original 12 POPs listed in the Stockholm Convention are included in Annex C relating to unintentionally produced POPs ('UPOPs'). These are polychlorinated dibenzo-p-dioxins (PCDD) polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB)[A] and hexachlorobenzene (HCB)[A]. The UPOPs are commonly formed as by-products during the production of chlorinated organics; in processes where elemental chlorine is present; and in thermal processes in the presence of all forms of chlorine.

In 2009, nine new POPs[B] were added to the Convention including pentachlorobenzene (PeCB) which was added to the unintentionally produced POPs in Annex C. Very recently (10th May 2011) hexachlorobutadiene (HCBD), polychlorinated naphthalenes (PCN) and pentachlorophenol (PCP) have been proposed by the EU for listing as POPs in the Stockholm Convention. Their properties as POPs will now be assessed by the POPs Review Committee following which they may be listed by the Conference of the Parties.

For PCDD and PCDF, the Dioxin Toolkit containing emission factors for key sources has been developed, initially by UNEP Chemicals, with subsequent revision and continuous updating by an expert group. Many countries are now using this methodology to develop their PCDD/PCDF inventories as part of their National Implementation Plans for the Stockholm Convention. No similar comprehensive emission factors have yet been developed for PCB, HCB or PeCB. For many sources it is considered that PCDD/PCDF are an "indicator" UPOP and thus reflect emissions of the other UPOPs for the purpose of inventories and emissions reductions.. In some cases, however, other UPOPs are the prime pollutants and releases are not covered by a PCDD/PCDF inventory. Important examples include wastes from the production of certain solvents (including carbon tetrachloride, tetrachloroethene, trichlorobenzenes, trichloroethene, trichlorotoluenes, and vinyl chloride)[1] from which HCB is a prime contaminant ("HCB waste")[2-4]. HCB is also the prime UPOP in the production of certain dyes (e.g. chlorinated phthalocyanines)[5]. For solvent productions it is reported that individual factories have deposited or stored tens of thousands of tonnes of HCB waste. More recently it has been discovered that some of these wastes also contain high levels of PeCB, newly listed as a POP[6]. Furthermore it is known that HCBD is mainly produced as a by-product in the manufacture of chlorinated solvents such as tri- and tetrachloroethene (Figure 1) and tetrachloromethane. No detailed emission factors have yet been established for HCB, PeCB or HCBD from these production processes.

This paper includes a brief overview of the production of chlorinated solvents in cases where there is currently some information available on "HCB waste". The likely contamination of the wastes with other UPOPs including PeCB (Figure 1) is also discussed. The study highlights the importance of a more detailed assessment of wastes from chlorinated solvents and, most likely, other organochlorine productions and the need to establish appropriate emission factors in order to facilitate the preparation of useable inventories of current productions and existing stockpiles and thus support future assessment and clean-up of these sites.

## Materials and methods

Information from peer reviewed literature and from national and international agencies and other source reports have been assessed in relation to three organochlorine producers. Additional information has been collected and assessed from personal contacts with regulatory agencies and authorities as well as from non-governmental organizations (NGOs).

[A] PCBs and HCB were also produced intentionally and are also listed in Annex A for elimination.
[B] Alpha-HCH and beta-HCH are listed in Annex A of the Convention as intentionally produced POPs but are also waste isomers unintentionally formed in the production of Lindane (gamma-HCH)[17].

**Results and discussion**

Three cases of organochlorine solvent productions were assessed for their "HCB waste" inventory, information useful to determine emission factors for UPOPs, and for the current environmental and management situation.

***"HCB waste" deposit and remediation at Kalush Chemical & Metallurgical Industrial Complex in Ukraine***

In Kalush City, Ukraine, wastes from the production of chlorinated solvents at the former Kalush Chemical and Metallurgical Industrial Complex were buried. The solvents produced included carbon tetrachloride, tetrachloroethene and dichloroethene (ethylenedichloride EDC) for PVC manufacturing. Solvent production started in 1973 with an estimated production capacity of 30,000 metric tonnes per year. Approximately 540 tonnes of hazardous solid waste with HCB as a primary contaminant was produced annually suggesting an emission factor of 1.8% of production volumes for "HCB waste". The total inventory of "HCB waste" deposited was estimated to be approximately 11,000 tonnes[4, 7]. These wastes presented an imminent threat to the Sivka River, a tributary of the Dniester River Basin supplying the drinking water to 8 million people and in February 2010, the Ukrainian government declared part of the Kalush area, containing the "HCB wastes" together with 10 million $m^3$ of potassium salts to be an "*Environmental Emergency Zone*". A Joint United Nations – European Commission Environmental Emergency Response Mission visited Kalush in March 2010 to assess the situation and to make recommendations[6] Sampling of the "HCB waste" deposit also found PeCB at levels in some cases as high as, but overall averaging approximately an order of magnitude lower than, the concentrations of HCB [7]. The total quantity of PeCB waste dumped along with the 11,000 tonnes of "HCB waste" can therefore be estimated to be approximately 1,000 tonnes. This estimate of the quantity of PeCB in waste from a single chlorinated solvents production can be compared with the estimated **total** global annual emission of PeCB from all other sources combined (85 tonnes) suggested in the Risk Profile on pentachlorobenzene of the POPs Review Committee[8] an estimate based in turn upon information provided by the International Council of Chemical Associations/World Chlorine Council[9].

During the recent excavation activities (second half of 2010) at the HCB landfill it was found that the drums had corroded over time and a considerable amount of soil has been contaminated. Under the contract 8,500 tonnes were shipped to the UK for high temperature incineration. Still about 3,000 tonnes of concentrated "HCB waste" and 19,000 tonnes of contaminated soil remain at the site awaiting environmentally sound disposal.

***Stored "HCB waste" and export attempts from Orica Australia* PTY LTD *(former ICI) Botany/Australia***

The manufacture of chlorinated solvents by Orica between 1963 to 1991 produced more than 10,000 tonnes of concentrated "HCB waste"[4, 10] (www.oricabotanytransformation.com). Unfortunately the production volumes of the various organochlorines are not in the public domain and therefore at present emission factors can not be derived from this site. It is known, however, that about 1,000 tonnes of this waste arose from the production of ethylene dichloride (EDC) synthesised for use as an intermediate in the production of PVC.

The waste is currently stored at the Botany Industrial Park in Australia and is awaiting treatment[4, 10]. After unsuccessful efforts to establish a treatment plant in Australia, Orica attempted between 2006 and 2010, to export the waste to Europe for destruction in high temperature incinerators. The Basel Convention export application omitted details of unintentionally produced POPs (PCDD, PCDF, PCB or PeCB) contamination levels in the "HCB waste". This lack of information about the concentration and total content of POPs within the waste is notable given the scale of the stockpile and the planned shipments and in December 2010 the Danish Government reversed an earlier approval for the destruction of the waste at an incinerator in Denmark.

Due to deterioration of drums, in 2007 Orica commenced a (semi-)automated repackaging of the "HCB waste" into UN approved containers for possible shipment due to deterioration of the drums. This was completed by April 2011 and future repackaging will be undertaken when required. As at Kalush, the original drums deteriorated/corroded within about three decades and, without repackaging, containment could not be guaranteed. These experiences are likely to be relevant to wastes at other storage facilities and dumps where original containers can now be expected to be leaking[4, 10, 11].

***Deposited "HCB waste" near the River Elbe from Spolchemie, Chabaiovice/Czech Republic***

Spolchemie, an organochlorine manufacturer in the Czech Republic, dumped 80,000 drums of "HCB waste" along with approximately 4 million tonnes of other wastes, in a landfill adjacent to the River Elbe[12, 13]. Subsequent leaching of the waste into the Elbe resulted in high concentrations of HCB accumulating in sediments downstream of the production and landfill area.[13-15]. The concentration of PeCB in river sediment downstream of the site was reported at levels of approximately 15% of those of HCB[14]. These data indicate firstly that PeCB is present in significant concentrations in the "HCB wastes" and secondly that these deposits are releasing UPOPs into the wider environment as the original containment systems fail.

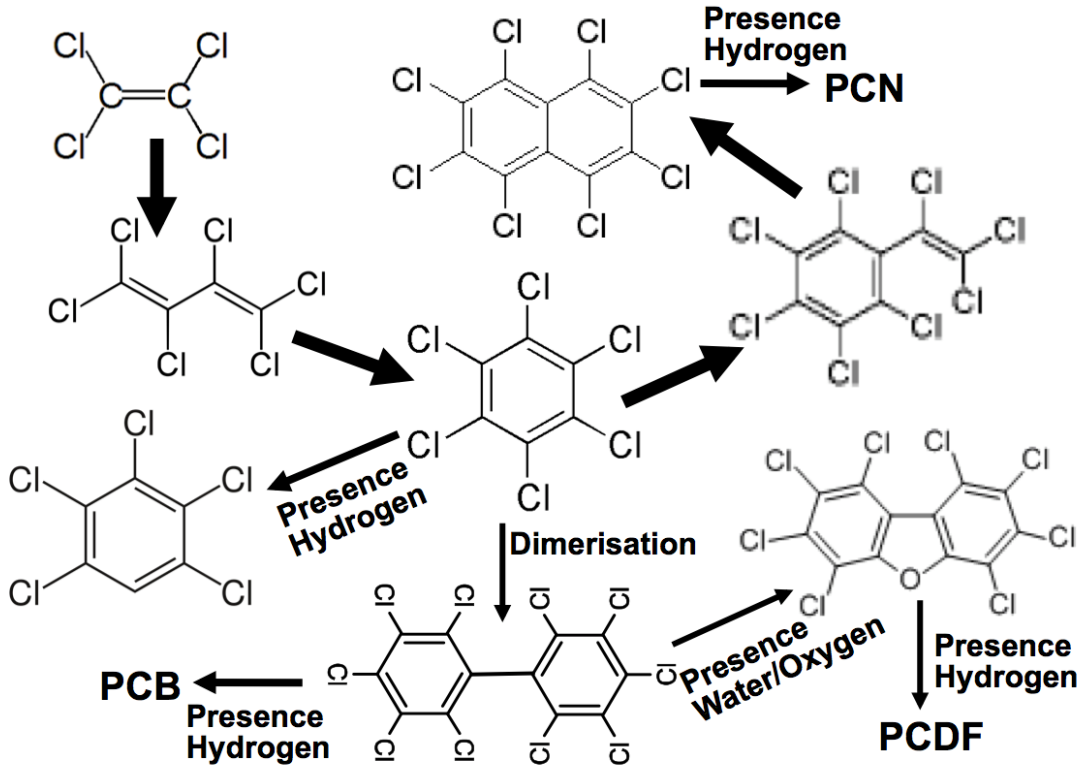


**Figure 1:** Simplified mechanism of formation of unintentionally produced POPs in the production of tetrachloroethene (note: the presence of hydrogen is inherent e.g. in the production of trichloroethene)

***Necessity for developing UPOPs emission factors for solvent productions***

These three case studies demonstrate that production of key chlorinated solvents in factories without adequate waste treatment generated thousands of tonnes of hazardous waste containing high levels of the UPOPs HCB and PeCB. These historic deposits are probably now the major stocks of HCB and PeCB[D]. Furthermore high levels of HCBD, now proposed as a POP, are also present in these wastes. As a consequence of the formation chemistry (Figure 1) it is also likely that chlorinated styrene (octachlorostyrene), chlorinated naphthalene and chlorinated biphenyls possibly along with PCDF/PCDD (depending on the oxygen and water content) can be expected in some or all deposits. However, measurements of these UPOPs in the solvent wastes are to our knowledge not available in the public domain.

The cases highlight the urgent need to develop UPOPs inventories for former and current solvent productions including historic production and the likely deposits of wastes. Specific emission factors for the different production scenarios need to be established. For a few chlorinated solvents and other organochlorines the

[D] Another important source of PeCB is the degradation of the pesticide pentachloronitrobenzene (quintozene) which form approximately 3% PeCB during degradation and is considered as the largest PeCB sources in addition to solvent production[5].

amounts of unintentionally HCB have been suggested in literature. There is however somewhat conflicting information on the HCB content in the "HCB wastes". In the 1980s Jacoff et al. reported that concentrations of HCB in distillation bottoms were estimated to be 25%, 15% and 5%, respectively, for tetrachloroethene, carbon tetrachloride and trichloroethene[2]. For the former production in Kalush up to 90% of HCB in the "HCB waste" is estimated. The PeCB content has not been measured in the samples of such wastes but has only been estimated from the contamination levels around the "HCB waste" deposits[6]. For reliable inventories, emission factors for HCB, PeCB, HCBD and other UPOPs should be based on measurements of the wastes from former and current solvent production.

The examples highlight the importance of establishing a strict BAT/BEP regime with appropriate destruction capacity for production waste together with a full life cycle assessment of solvents. While destruction capacity has been developed in most industrial countries since the 1970's developing/transition countries often still lack capacity. Without effective control and enforcement there remains a high health and environmental risk associated with the release of unintentionally produced POPs HCB, PeCB and possibly other UPOPs from organochlorine production. All organochlorine productions should be assessed for UPOP formation and release.

The large quantities of "HCB wastes" and associated PeCB content arising from solvent production also brings into question a previous estimates of PeCB releases which were suggested to be just 1.3 kg for global tetrachloroethene use in 2000[16]. This estimate was based on data from only one industrial country (Canada) and other solvents were not considered or assessed. Therefore an updated estimate of HCB, PeCB and other UPOPs in solvents should be made based on measurements including current solvent production/use in developed and transition/developing countries.

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