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on Persistent Organic  
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**Persistent Organic Pollutants Review Committee**

**Sixth meeting**

Geneva, 11–15 October 2010

Item 4 (c) of the provisional agenda\*

**Technical work: additional consideration of new persistent organic pollutants**

**Additional consideration of new persistent organic pollutants:  
pentachlorobenzene**

**Note by the Secretariat**

1. By its decision SC-4/16, the Conference of the Parties of the Stockholm Convention decided to list pentachlorobenzene in Annexes A and C to the Convention without any specific exemptions. The Committee has developed a risk profile, an addendum to that risk profile and a risk management evaluation for pentachlorobenzene as set out in documents UNEP/POPS/POPRC.3/20/Add.7, UNEP/POPS/POPRC.4/15/Add.5 and UNEP/POPS/POPRC.4/15/Add.2, respectively.
2. During the intersessional period between the Committee's fifth and the sixth meetings, new information related to unintentional sources of pentachlorobenzene was received. That information has been provided in the annex to the present note, which has been reproduced as received, without formal editing. The Committee may wish to take note of the information and consider any further action.

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\* UNEP/POPS/POPRC.6/1/Rev.1.

## Annex

### Additional consideration of new persistent organic pollutants: pentachlorobenzene

#### 1. Pentachlorobenzene release from degradation of quintozone/PCNB

3. The risk profile on pentachlorobenzene (PeCB) mentions the possible use of PeCB as an intermediate for quintozone (pentachloronitrobenzene<sup>1</sup> (PCNB) production and notes the possibility that PeCB may be present in pentachloronitrobenzene as a contaminant (UNEP/POPS/POPRC.3/20/Add.7). The risk profile also notes that PeCB sources could include quintozone (PCNB) degradation.
4. The peer reviewed literature indicates that quintozone/PCNB degrades in soil with a yield of approximately 3% unintentionally produced PeCB together with higher yields of other related compounds (Beck & Hansen 1974; Kamal et al. 1983, Bailey et al. 2009).
5. In 2009 the estimated total use of quintozone/PCNB by Australia alone was 3,800-9,100 tonnes (Holt et al 2010). Assuming 3% degradation of the quintozone/PCNB to PeCB, the estimated unintentional production and release of PeCB just in Australia alone, would be 114,000 – 273,000 kg y<sup>-1</sup>, largely to soil.
6. The most recent US data for agricultural use<sup>2</sup> is from 1999 when 1,803 tonnes of quintozone/PCNB (US EPA 2006) were used. It can therefore be estimated that US PeCB unintentional production and releases from the degradation of this quintozone/PCNB (@3% yield) would be approximately 54,000 kg - again largely to soil.
7. The unintentional production and releases from quintozone/PCNB application from just the US and Australia are therefore likely to significantly exceed 168,000 kg/annum. This can be compared with the 2007 estimates by ICCA/WCC for the **total** annual global PeCB emissions of 85,000 kg. The ICCA/WCC estimate was adopted in the risk profile on pentachlorobenzene (UNEP/POPS/POPRC.3/20/Add.7). For completeness it is also noted that the unintentional production and releases from quintozone/PCNB are likely to be much greater than the global PeCB inventory estimated by Bailey et al (2009) of 95,000 kg<sup>3,4</sup>.
8. The use of quintozone/PCNB has been banned or restricted in some countries, including Russia and the EU. Nonetheless the global usage and associated unintentional production and releases of PeCB are likely to be much larger than the above estimates from Australia and the US. It is therefore likely that the degradation of quintozone/PCNB and the associated unintentional formation and release of PeCB is a significant source of global PeCB emissions that was previously underestimated.

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1 It is more accurate to use the chemical name pentachloronitrobenzene or the abbreviation PCNB rather than the trade name quintozone as the use of trade names can lead to subsequent confusion, underestimation of inventory and usage levels and the omission of relevant data. Pentachloronitrobenzene was also marketed as PCNB, Quintozene, Terraclor, Turfcide, Avicol, Botrilex, Earthcide, Folosan, Kobu, Kobutol, Pentagen, Tilcarex, Tri-PCNB (Milne 1995). Since previous POPRC reports use “quintozone” instead of pentachloronitrobenzene we have used “*quintozone/PCNB*” in this document in order to provide a consistent link with previous reports documents whilst also making a clearer reference to the correct chemical name.

2 It should be noted that the experience in Australia indicates the main use of quintozone/PCNB is in non-agricultural uses such as golf courses and horticulture in private gardens.

3 Bailey estimated total global PeCB emissions of 121,000 kg y<sup>-1</sup> and the annual contribution from the degradation of quintozone was estimated 26,000 kg. This was based on an estimate of 880.6 t global quintozone use in agriculture (with the same 3% yield) (Bailey et al 2009). This may be an example of where the use of the trade name has masked the total usage of quintozone/PCNB. Crucially Bailey omitted to consider the (majority) non-agricultural usage. The combined global estimated releases from other sources of PeCB was 95,000 kg (Bailey et al 2009).

4 The Emission Factor for unintentional POPs production from biomass used for PeCB in the Bailey review was derived from an incinerator combusting waste-wood (Hogenboorn et al 2009, Bailey et al 2009, Zimmermann et al. 2001). Therefore this emission factor can be regarded as orders of magnitude too high for virgin biomass fires. The inappropriateness of this emission factor was also mentioned in a recent report of the National Institute of Public Health and the Environment of The Netherlands (RIVM) reviewing emission factors for PeCB sources from literature (Hogendoorn et al 2009). It is therefore likely that Bailey over-estimated emissions from combustion and seriously under-estimated the contribution from the degradation of quintozone/PCNB.

9. Recently quitozene/PCNB has also been restricted in Australia due to the discovery of high levels of PCDD/DF in different quitozene/PCNB formulations (Holt et al 2009). In the study of Holt et al.(2009) all pesticide formulations analysed (mainly Pesticides currently in use in Australia) contained measurable levels of unintentionally produced PCDD/DF. Unintentionally produced HCB or PeCB were not analysed. Considering the finding of Holt et al (2009) on unintentionally PCDD/DF in Australian pesticides it seems advisable to also screen current used pesticides in other countries and other chlorinated organics for unintentionally produced POPs including PeCB.

## 2. PeCB release and stockpile from production of chlorinated solvents

10. The risk management evaluation for PeCB notes the relevance of PeCB as impurity in chlorinated solvents as a contributor to diffuse emissions (UNEP/POPS/POPRC.4/15/Add.2). The risk profilenotes that the highest reported chlorobenzene concentrations in Canadian sediment have been observed near industrial sites (UNEP/POPS/POPRC.3/20/Add.7).

11. Waste from certain solvent productions (tetrachloromethane, tetrachloroethene, trichloroethene (Environmental Canada 1993), and possibly other chlorinated solvents) have generated thousands of tonnes of unintentionally produced POPs waste with HCB as a prime contaminant<sup>1</sup> (“HCB waste”) (Jacoff 1986, Jones 2005, Weber et al 2008). It has recently been discovered that single factories have deposited or stored wastes at level of around 10000 tonnes of HCB waste and that environmental contamination from these wastes contain significant levels of PeCB (UNEP/OCHA Environment Unit 2010, Ministry of Environment Czechoslovakia, 1991, Heinisch et al 2006a,b).

12. An example is Kalush City, Ukraine, where the chemical landfill from an organochlorine manufacturer producing chlorinated solvents including tetrachloromethane and tetrachloroethene are estimated to contain approximately 11,000 tonnes of HCB waste (UNEP/OCHA Environment Unit 2010, Weber et al 2008). A recent investigation of the site found PeCB levels averaging approximately one order of magnitude lower than the levels of HCB but in some samples PeCB was reported at the same order of magnitude as HCB (UNEP/OCHA Environment Unit Annex III 2010).

13. The total quantity of PeCB deposited with the 11,000 tonnes of “HCB waste” could therefore be roughly estimated to 1,100,000 kg. This estimate of the quantity of PeCB in waste from a single factory producing chlorinated solvents would thus be an order of magnitude higher than the estimated **total** global annual total emission of PeCB from all other sources combined (85,000 kg) suggested in the risk profile on pentachlorobenzene (UNEP/POPS/POPRC.3/20/Add.7) in reliance on the information from the International Council of Chemical Associations/World Chlorine Council (ICCA/WCC 2007).

14. At another factory (in the Czech Republic) 80,000 drums of HCB waste was deposited in a landfill adjacent to the river Elbe (Ministry of Czech Republic 1991). Subsequent leaching of the waste into the river resulted in high concentrations of HCB accumulating in Elbe sediments downstream of the production and landfill area (Heinisch et al 2006a, Heinisch et al 2006b). The concentration of PeCB in river sediment downstream of the site was reported at levels of approximately 15% to those of HCB (Heinisch et al 2006a).

15. A third well-documented case is maybe the world’s largest stockpile of HCB (Jones 2005). More than 10,000 tonnes of “concentrated HCB waste” arising mainly from the manufacture of chlorinated solvents, but with about 1,000 tonnes from the production of ethylene dichloride (EDC), is currently stored and awaiting treatment at Botany in Australia (Report to the Australian Minister of Planning, Independent Review Panel 2006, Weber et al 2008). Approval was given on 18<sup>th</sup> August 2010 for export of the waste to Denmark for disposal by high temperature incineration. According to a science dossier published by Eurochlor PeCB contamination of around 1.8% can be expected in technical HCB (Jones 2005). This level of contamination would be equivalent to more than 180,000 kg PeCB in the stored waste but it can reasonably be expected that the PeCB contamination level in this waste is likely to be even higher. The Basel Convention export application did not include details of the content 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 of this waste to Denmark for disposal.

16. These cases indicate high concentrations of PeCB tend to be present as co-contaminants in stockpiles of HCB wastes and that these deposited wastes need further global assessment for their current contribution to global PeCB and HCB releases. The examples also highlight the importance of

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<sup>1</sup> The concentration of HCB in distillation bottoms in the 1980s was estimated to be 25%, 15% and 5%, respectively, for perchloroethylene, carbon tetrachloride and trichloroethylene (Jacoff *et al*, 1986)

establishing a strict BAT/BEP regime with appropriate BAT/BEP destruction capacity for the production, use and disposal of chlorinated solvents. Without effective guidance and control there remains a high risk of release of large quantities of unintentionally produced POPs HCB, PeCB and possibly other UPOPs from chlorinated solvent production.

17. The high levels of HCB wastes and associated PeCB content arising from solvent production also brings into question the previous estimates of PeCB in solvent. This was estimated to be just 1.3 kg for global tetrachloroethene production in 2000 (Bailey et al 2009) but this estimate was based on data from only one industrial country (Canada). Furthermore other solvents were not considered or assessed. It is therefore recommended that an updated estimate should be made based on measurements of PeCB. Until this has been conducted, the current estimates of PeCB and other unintentionally produced POPs in solvents should be treated as having a low confidence level.

### 3. References

- Beck, J., Hansen, K.E., 1974. The degradation of quintozone, pentachlorobenzene, hexachlorobenzene and pentachloroaniline in soil. *Pestic. Sci.* 5, 41–48.
- Bailey RE, van Wijk D, Thomas PC (2009) Sources and prevalence of pentachlorobenzene in the environment. *Chemosphere* 75, 555-564.
- Environment Canada, 1993. Priority Substances List Assessment Report. Pentachlorobenzene.
- Heinisch E, Kettrup A, Bergheim W, Martens D, Wenzel S (2006a) Persistent chlorinated hydrocarbons, source-oriented monitoring in aquatic media. 4. The chlorobenzenes. *Fresenius Environ Bull* 15(3):148–169
- Heinisch E, Kettrup A, Bergheim W, Martens D, Wenzel S (2006b) Persistent chlorinated hydrocarbons, source-oriented monitoring in aquatic media. 5. The Polychlorinated Biphenyls (PCBs). *Fresenius Environ Bull* 15(11):1344–1362
- Holt E, Weber R, Stevenson G, Gaus C (2010) Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans (PCDD/Fs) Impurities in Pesticides: A Neglected Source of Contemporary Relevance, *Environ. Sci. Technol* 44, 5409–5415 (2010).
- Hogendoorn E.A., Bruinen de Bruin Y., Janssen M.P.M. (2009) Inventory emission factors for pentachlorobenzene. National Institute of Public Health and the Environment, Bilthoven/The Netherlands, RIVM Letter report 601773002, October 2009
- ICCA/WCC, International Council of Chemical Associations/World Chlorine Council (2007). ICCA-WCC Submission for PeCB & All Risk Profiles for the POPs Review Committee of the Stockholm Convention including annexes.
- Independent Review Panel (2006) Orica HCB Waste Stockpile Safe Interim Storage and Destruction. Report to the Australian Minister of Planning, November 2006
- Jacoff, F.S., Scarberry, R., Rosa, D. (1986) Source assessment of hexachlorobenzene from the organic chemical manufacturing industry. In: Morris, C.R.; Cabral, J.R.P. Hexachlorobenzene: Proceedings of an International Symposium. Lyon, IARC Sci. Publ. 77: 31-37.
- Jones K (2005) Hexachlorobenzene - Sources, environmental fate and risk characterisation. Science Dossier for Euro Chlor, January 2005.
- Kamal M, Scheunert I, Korte F (1983) Mass Balance of <sup>14</sup>C-Pentachloronitrobenzene and Metabolites in a Closed, Aerated Soil-plant or Soil-system *Bull. Environ. Contam. Toxicol.* 31,559-565 (1983)
- Milne, G., CRC Handbook of Pesticides. 1995
- Ministry of the Environment Czechoslovakia (1991) Feasibility study, hazardous waste remediation at the Chabarovice site. Vol 1 CH2M Hill, International Ltd.
- UNEP/POPS/POPRC.3/20/Add.7 (2007) Report of the Persistent Organic Pollutants Review Committee on the work of its third meeting: Risk profile on pentachlorobenzene.
- UNEP/POPS/POPRC.4/15/Add.2 (2008) Report of the Persistent Organic Pollutants Review Committee on the work of its fourth meeting: Risk management evaluation for pentachlorobenzene
- UNEP/OCHA Environment Unit (2010). Technical Scoping Mission Kalush Area, Ukraine. A Joint United Nations – European Commission Environmental Emergency Response Mission. March 2010.

UNEP/OCHA Environment Unit, Annex VIII (2010). Technical Scoping Mission Kalush Area, Ukraine. A Joint United Nations – European Commission Environmental Emergency Response Mission. March 2010.

USEPA (2006) Documentation for the Final 1999 Nonpoint Area Source National Emission Inventory for Hazardous Air Pollutants (Version 3).

Weber R, Gaus C, Tysklind M, Johnston P, Forter M, Hollert H, Heinisch E, Holoubek I, Lloyd-Smith M, Masunaga S, Moccarelli P, Santillo D, Seike N, Symons R, Torres J, Verta M, Varbelow G, Vijgen J, Watson A, Costner P, Wölz J, Wycisk P, Zennegg M (2008) Dioxin- and POP-contaminated sites—contemporary and future relevance and challenges. *Environ Sci Pollut Res* 15:363–293

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

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