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Persistent Organic Pollutants Review Committee

Second meeting

Geneva, 6–10 November 2006

Item 6 (d) of the provisional agenda*

**Consideration of chemicals newly proposed for inclusion
in Annexes A, B or C of the Convention:**

Alpha-hexachlorocyclohexane

Summary of alpha-hexachlorocyclohexane proposal

Note by the Secretariat

1. The annex to the present note provides a summary prepared by the Secretariat of the proposal submitted by Mexico for listing alpha-hexachlorocyclohexane in Annexes A, B or C of the Stockholm Convention on Persistent Organic Pollutants pursuant to paragraph 1 of Article 8 of the Convention. It has not been formally edited. The complete proposal is contained in document UNEP/POPS/POPRC.2/INF/7.

Possible action by the Committee

2. The Committee may wish:

(a) To consider the information provided in the present note and in document UNEP/POPS/POPRC.2/INF/7;

(b) To decide whether it is satisfied that the proposal fulfils the requirements of Article 8 and Annex D of the Convention;

(c) To develop and agree on, if it decides that the proposal fulfils the requirements referred to in subparagraph (b) above, a workplan for preparing a draft risk profile pursuant to paragraph 6 of Article 8.

* UNEP/POPS/POPRC.2/1.

Annex

Proposal for listing alpha-hexachlorocyclohexane in Annexes A, B or C of the Stockholm Convention on Persistent Organic Pollutants

Introduction

1. The 1998 Aarhus Protocol on Persistent Organic Pollutants (POPs) addresses technical hexachlorocyclohexane (HCH, a mixture of isomers) as a substance for restriction on use under Annex II. The Aarhus Protocol is one of the protocols under the United Nations Economic Commission for Europe (UNECE) convention on Long Range Transboundary Air Pollution (LRTAP). The objective of the UNECE regional Protocol is to control, reduce or eliminate discharges, emissions and losses of persistent organic pollutants.
2. The Rotterdam Convention on the Prior Informed Consent also includes technical HCH, indicating that several countries have banned or severely restricted import and use of this mixture of isomers. The objective of this convention is to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm.
3. Mexico proposed on June 29, 2005 that gamma-hexachlorocyclohexane (Lindane) be added to Annex A of the Stockholm Convention. The proposal presented data on the gamma isomer but mentioned as well that "other isomers of hexachlorocyclohexane should also be considered in this proposal".
4. The POPs Review Committee (POPRC) evaluated Annex D information for Lindane at its first meeting, held in Geneva in November 2005, and decided that "the screening criteria have been fulfilled for Lindane". The Committee agreed that alpha and beta isomers could be included in the discussions, although any decision to propose inclusion of the chemical in the Convention would apply only to Lindane, the gamma isomer. As a consequence, Mexico is now proposing that alpha-HCH (and beta-HCH in another proposal) be added to Annexes A, B and/or C of the Convention to ensure that the global impacts of all three environmentally significant HCH isomers (alpha, beta and gamma) are addressed.
5. This dossier focuses solely on the information required under paragraphs 1 and 2 of Annex D of the Stockholm Convention and is mainly based on:
 - (a) CEC, 2000: North American Commission on Environmental Cooperation: North American Regional Action Plan (NARAP) on Lindane and other HCH isomers, <http://www.cec.org>;
 - (b) USEPA, 2006: Assessment of Lindane and Other Hexachlorocyclohexane Isomers, U.S. Environmental Protection Agency, <http://www.epa.gov/fedrgstr/EPA-PEST/2006/February/Day-08/p1103.htm>;
 - (c) ATSDR, 2005: Toxicological Profile for Hexachlorocyclohexanes, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, August, 2005, <http://www.atsdr.cdc.gov/toxprofiles/tp43.html>.
6. These reviews and other references (as provided in document UNEP/POPS/POPRC.2/INF/7) serve as a source of further information referred to in paragraph 3 of Annex D of the Stockholm Convention on this candidate POP chemical.

1 Identification of the chemical

1.1 Names and registry numbers

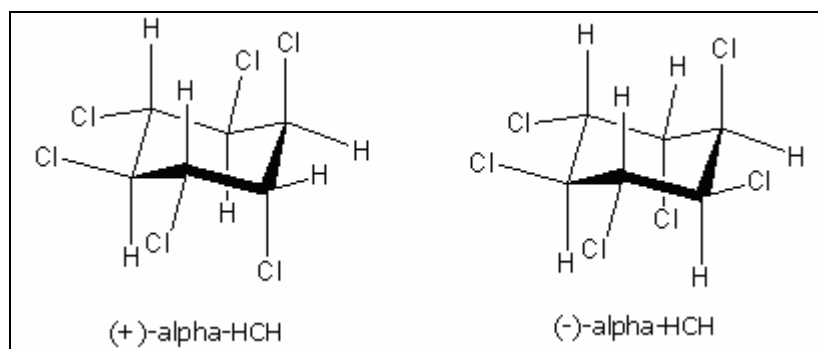
Chemical name:	alpha-hexachlorocyclohexane (alpha-HCH)
Synonym:	1-alpha, 2-alpha, 3-beta, 4-alpha, 5-beta, 6-beta-hexachlorocyclohexane
CAS ¹ number:	319-84-6

1 Chemical Abstracts Service.

1.2 Chemical Structure

7. Alpha-HCH is a brownish to white crystalline solid (ATSDR, 2005). Alpha-HCH is the only chiral isomer of the eight isomers of 1,2,3,4,5,6-HCH. The configurations of its enantiomers are shown in Figure 1.

Fig.1. Structure of the alpha-HCH enantiomers



Modified from Buser et al, 1995

Chemical formula: $C_6H_6Cl_6$

Molecular weight: 290.83

1.3 Chemical production

8. HCH isomers are produced as a result of the photochemical chlorination of benzene during the manufacture of technical HCH, which has been widely used as a commercial pesticide. Technical HCH is a mixture of five HCH isomers: alpha-HCH (53-70%), beta-HCH (3-14%), gamma-HCH (11-18%), delta-HCH (6-10%) and epsilon-HCH (3-5%).

9. As the gamma-HCH isomer, also known as Lindane, is the isomer with the highest pesticidal activity, technical-HCH is subject to subsequent treatment (fractional crystallization and concentration) to produce 99% Lindane. This process is extremely inefficient with only a 10-15% yield, producing 6-10 tons of other isomers for each ton of Lindane (IHPA, 2006). Alpha-HCH is the major by-product of the reaction (60-70%), followed by beta-HCH (7-10%) (WHO, 1991).

2 Persistence

10. The most common HCH isomers found in the environment are alpha-, beta- and gamma-HCH. Alpha-HCH is the predominant isomer in ambient air and in ocean water (Walker, 1999).

11. Alpha-HCH is stable to light, high temperatures, hot water and acid but it can be dechlorinated at high pH. At pH 8 and 5°C, the estimated hydrolytic half-life of alpha-HCH is 26 years (Willet, 1998). The hydrolysis rates were found to be slower at lower temperatures with an estimated half-life for alpha-HCH of 63 years at pH 8 and 0°C (USEPA, 2006). Other studies estimated half-lives in eastern Arctic Ocean water of 6 years for (+) enantiomer and 23 years for (-) enantiomer of alpha-HCH. The half-lives of (+) and (-) enantiomers of alpha-HCH in a small Arctic lake were also estimated to be 0.6 and 1.4 years respectively (ATSDR, 2005).

12. Direct photolysis in the atmosphere is not expected to be an important environmental fate process for HCH. However, some authors have reported a photodegradation half-life of 91 hours for thin films of alpha-HCH. It has also been found that alpha-HCH is degraded in the atmosphere by reacting with photochemically produced hydroxyl radicals. Using an average hydroxyl radical concentration of 5×10^5 molecule/cm³, the calculated half-life is about 115 days. In locations where the atmospheric hydroxyl radical concentration is very low, the average half-life of alpha-HCH has been estimated to be about 3 to 4 years (ATSDR, 2005).

13. Alpha-HCH also tends to associate with soils and sediments because of its low polarity. Biodegradation in soils of alpha-HCH has also been studied showing half-lives of 54.4 days for cropped plots and 56.1 days for uncropped plots (ATSDR, 2005). Another laboratory study reported half-lives of 125 and 48 days under aerobic and anaerobic conditions, respectively. A field experiment carried out in 1988 using soil treated with technical HCH revealed that although the concentration of alpha-HCH was the highest of the HCH isomers, the alpha-isomer disappeared more rapidly (WHO, 1991).

3 Bioaccumulation

14. The log octanol-water partition coefficient (log K_{ow}) for alpha-HCH is 3.8, indicating that it has the potential to bioaccumulate. A wide range of bioaccumulation factors (BAF) for alpha-HCH has been reported in several studies.

15. Bioconcentration factors of 1 500 – 2 700 on a dry-weight basis, and 12 000 on a lipid basis, have been reported for microorganisms. Studies in invertebrates show bioconcentration factors ranging from 60 – 2 750 on a dry weight basis and up to 8 000 on a lipid basis. Other studies report bioconcentration factors in fish from 313 to 1 216 (WHO, 1991). A bioconcentration factor (BCF) of 1 100 was found using zebra-fish under steady-state conditions by Butte et al. (1991). Oliver et al. (1995) have reported bioconcentration factors ranging from 1 600 to 2 400 in a variety of aquatic organisms.

4 Potential for long range environmental transport

16. Many studies have reported alpha and gamma HCH throughout North America, the Arctic, Southern Asia, the Western Pacific, and Antarctica. HCH isomers are the most abundant and persistent organochlorine insecticide contaminants in the Arctic, and their presence in the Arctic and in the Antarctic, where they have not been used or produced, is evidence of their long-range transport.

17. There are observations that suggest that alpha-HCH and other HCH isomers are subject to “global distillation”, in which warm climates at lower latitudes favor evaporation into the atmosphere enabling the chemicals to be carried to higher latitudes. At high latitudes, cold temperatures favor deposition. This latitudinal gradient was found to be more striking for alpha-HCH in seawater (Walker, 1999).

18. Other explanations have been suggested for the abundance of alpha-HCH in the environment, i.e., the conversion of gamma-HCH into alpha-HCH through isomerization. Laboratory research indicates that photo- and bio-isomerization of gamma-HCH can occur, but field studies have not found evidence that these processes are the main sources of accumulated alpha-HCH in the environment (Walker, 1999).

19. Because air-water partitioning for alpha-HCH favors the water phase, especially for cold water, alpha-HCH could be moved northwards by air, accumulated in the water and slowly build into a large reservoir in the Arctic Ocean (Li et al, 2002). It has been found that alpha-HCH has a longer atmospheric lifetime by approximately 25% than gamma-HCH (Willet, 1998).

5 Adverse effects

20. No specific studies are available on the effects of alpha-HCH on humans. Oral LD₅₀ values in rats have been found to range from 500 to 4 674 mg/kg bodyweight (WHO, 1991).

21. Liver and kidney damage as well as a significant decrease in body weight gain have been reported in animals fed alpha-HCH. Neurological effects have not been seen in animals treated with alpha-HCH. Genotoxicity data indicate that alpha-HCH has some genotoxic potential but the evidence for this is not conclusive (USEPA, 2006). Alpha-HCH has recently been shown to disrupt endocrine processes (Li et al, 2002).

22. Alpha-HCH appears to be carcinogenic in mice and rats following subchronic and/or chronic exposure (USEPA, 2006). The International Agency for Research on Cancer (IARC) has classified alpha HCH as a possible human carcinogen (ATSDR, 2005).

6 Statement of the reasons for concern

23. The proposal of Mexico contains the following Statement of Concern:

“Alpha-HCH is the most frequent isomer found in environmental compartments. Due to its physicochemical properties it has the potential to be transported long distances and it is persistent in the environment. Its proven carcinogenic potential should be of special concern.

Even though most countries have banned or restricted the use of technical HCH as a pesticide, replacing it in most cases by the use of Lindane (99% gamma-HCH), the production process to obtain a ton of pure gamma-HCH yields 6 – 10 metric tonnes of the other isomers that must be disposed of or otherwise managed. Up to 70% of these waste isomers is alpha-HCH. As Lindane is the only isomer in the mixture that has insecticidal properties, there is very limited to no commercial value for the other isomers obtained. Because of this waste isomer problem, the production of HCH/Lindane has been a worldwide problem for years.

Other HCH isomers, like alpha-HCH, can be as toxic and persistent a contaminant as Lindane, or even more so. The continued use of Lindane in the world is causing this important pollution source. Global action is therefore needed to halt the pollution caused worldwide by Lindane production.”
