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

Alpha hexachlorocyclohexane proposal**

Note by the Secretariat

The annex to the present note contains a proposal by Mexico for listing alpha hexachlorocyclohexane in Annexes A, B or C of the Stockholm Convention pursuant to paragraph 1 of Article 8 of the Convention. The annex is being circulated as submitted and has not been formally edited by the Secretariat.

* UNEP/POPS/POPRC.2/1.
** Stockholm Convention, Article 8, paragraph 1.

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Annex: Alpha hexachlorocyclohexane proposal

1. INTRODUCTION

1.1 Background

The 1998 Aarhus Protocol on Persistent Organic Pollutants (POPs) addresses technical hexachlorocyclohexane (HCH, 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)[1]. The objective of the Protocol is to control, reduce or eliminate discharges, emissions and losses of persistent organic pollutants.

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.[2]

The objective of the Stockholm convention is to protect human health and the environment by eliminating or restricting the production, use and release of 12 POP chemicals (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex and toxaphene, hexachlorobenzene, polychlorinated biphenyls, dioxins and furans). Under Article 8 of the Convention, a Party may submit a proposal to the Secretariat for listing a chemical In Annexes A, B or C by presenting the information requested under Annex D. Mexico, a party to the Convention since February 2003, proposed in June 29, 2005 that gamma-hexachlorocyclohexane (lindane) be added to Annex A. The proposal presented data on the gamma isomer but mentioned as well that “other isomers of hexachlorocyclohexane should also be considered in this proposal”.

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” concluding that “Lindane meets the screening criteria specified in Annex D.” 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. Mexico prepared the risk profile for lindane that is currently posted for public review at the Stockholm Convention website[3].

At the second meeting of the conference of the Parties of the Stockholm Convention on Persistent Organic Pollutants held in Geneva from May 1rst to May 5th, 2006, discussions where held between Mexican and European delegates. As a result of those discussions, Mexico proposes that alpha and beta HCH be added to its previous lindane proposal, to emphasize the necessity of approaching the three environmentally significant HCH isomers (alpha, beta and gamma) and their global impact.

[1] www.unece.org/env/lrtap/pops_h1.htm
[2] www.pic.int
[3] http://www.pops.int/documents/meetings/poprc/tech_comments/default.htm

1.2 Proposal of adding Alpha-HCH to the Stockholm Convention

The present document contains the information detailed in Annex D required to support Mexico's proposal to include alpha-HCH in the Stockholm Convention.

The importance to consider the alpha-HCH isomer has been identified in other settings: the North American Commission on Environmental Cooperation North American Regional Action Plan (NARAP) on lindane and other HCH isomers, stresses the importance of considering other HCH isomers[4] in any action plan for lindane; as a result of the United States Environmental Protection Agency continuing review of lindane process, "risks resulting from human and environmental exposures to other HCH isomers of environmental significance" are now being considered in the document "Assessment of Lindane and Other Hexachlorocyclohexane Isomers" released in February, 2006 for public consultation[5].

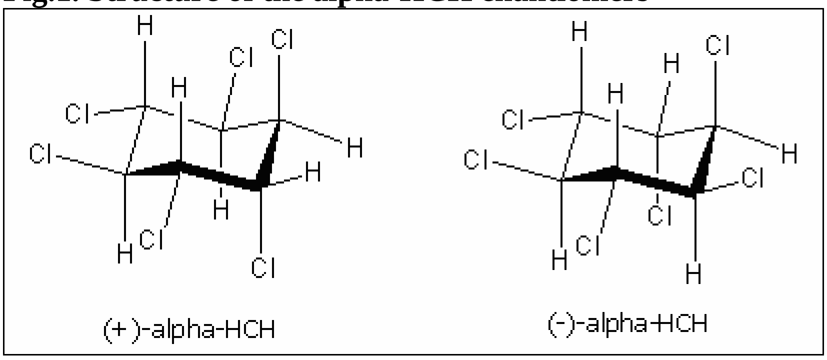
2. INFORMATION REQUIREMENTS AND SCREENING CRITERIA IN ANNEX D

2.1 Chemical identity

Chemical name: alpha-hexachlorocyclohexane (alpha-HCH)
Synonym: 1-alpha, 2-alpha, 3-beta, 4-alpha, 5-beta, 6-beta-hexachlorocyclohexane
Chemical formula: $C_6H_6Cl_6$
Molecular weight: 290.83
CAS number: 319-84-6

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

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[4] www.cec.org
[5] http://www.epa.gov/fedrgstr/EPA-PEST/2006/February/Day-08/p1103.htm

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%).

As the gamma-HCH isomer, also known as lindane, is the only isomer with 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 produced (IHPA, 2006). Alpha-HCH is the major by-product of the reaction (60-70%) (WHO, 1991). Table 1 shows the physicochemical properties of alpha-HCH

Table 1. Physicochemical Properties for alpha-HCH. Water solubility (Cs), vapor pressure (VP), octanol-water partition coefficient (K_{ow}), soil sorption coefficient (K_{oc}), Henry's Law Constant (H_c).

	Alpha-HCH
Melting Point (°C)	159-160
Boiling Point (°C)	288
Density (g cm^{-3} @ 20 °C)	1.87
C_s (mg L^{-1} @ 28 °C)	69.5
VP (mm Hg @ 25 °C)	4.5×10^{-5}
H_c (atm m^3 mol^{-1})	6.86×10^{-6}
log K_{ow}	3.8
log K_{oc}	3.57

Source: ATSDR, 2005

2.2 Persistence

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

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 minor temperatures showing 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).

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 $5x10^5$ molecule/cm^3, 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).

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).

2.3 Bioaccumulation

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

Bioconcentration factors of 1 500 – 2 700 on a dry-weight basis, and 12 000 on a lipid basis have revealed alpha-HCH bioconcentration in 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). Another study has reported bioconcentration factors ranging from 1 600 to 2 400 in aquatic organisms (Oliver et al, 1995).

2.4 Potential for long range environmental transport

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 nor produced, is evidence of their long-range transport.

There are observations that suggest that alpha and other HCH isomers are subject to “global distillation”, in which warm climates at lower latitudes favor evaporation into the atmosphere where the chemicals can 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).

Other explanations have been suggested for the abundance of alpha-HCH in the environment. The first one is related with 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).

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).

2.5 Adverse effects

No specific studies related to alpha-HCH adverse effects on humans are available. Oral LD_{50} values in rats have been found to range from 500 to 4 674 mg/kg body weight (WHO, 1991).

Liver and kidney damage as well as a significant decrease in body weight gain has been reported in animals fed with 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).

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).

3. STATEMENT OF THE REASONS FOR CONCERN AND NEED FOR GLOBAL ACTION

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 proved 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. Lindane being the only isomer in the mixture that has insecticidal properties, there is very limited to none 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, persistent and contaminant as lindane, or even more so. The continued use of lindane in the world is causing this important polluting source. Global action is therefore needed to halt the pollution caused worldwide by lindane production.

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