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

Beta hexachlorocyclohexane proposal**

Note by the Secretariat

The annex to the present note contains a proposal by Mexico for listing beta 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: Beta 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 in 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 Beta-HCH to the Stockholm Convention

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

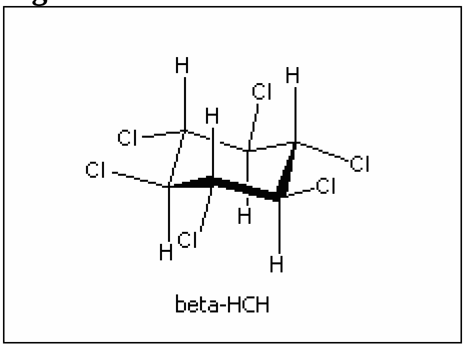
The importance to consider the beta-HCH isomer has been identified in other settings: the North American Commission on Environmental Cooperation North American Regional Action Plan (NARAP) on lindane and other HCH isomers, stresses the importance of considering other HCH isomers[4] in any action plan 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: Beta-hexachlorocyclohexane (beta-HCH)
Synonym: 1-alpha, 2-beta, 3-alpha, 4-beta, 5-alpha, 6-beta-hexachlorocyclohexane
Chemical formula: $C_6H_6Cl_6$
Molecular weight: 290.83
CAS number: 319-85-7

Fig.1. Structure of beta-HCH



Modified from Buser et al, 1995

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%).

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

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). Table 1 shows the physicochemical properties of beta-HCH

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

	Beta-HCH
Melting Point (°C)	314-315
Boiling Point (°C)	60
Density (g cm^{-3} @ 19 °C)	1.89
C_s (ppm)	5
VP (mmHg @ 20 °C)	$3.6 x 10^{-7}$
H_c (atm m^3 mol^{-1})	$4.5 x 10^{-5}$
Log K_{ow}	3.78
Log K_{oc}	3.57

ATSDR, 2005

2.2 Persistence

HCH isomers are resistant to abiotic processes like photolysis and hydrolysis (except at high pH), and degrade very slowly by microbial actions (USEPA,2006).

Beta-HCH is the most persistent isomer, with half-lives of 184 and 100 days on cropped and uncropped plots. It comprised 80-100% of the total HCH residues found in soil and vegetation on a land surrounding an industrial landfill in Germany 10 years after the final HCH input (ATSDR, 2005). Other laboratory studies have calculated half-lives values of 91 and 122 days for aerobic and anaerobic soil, showing persistence is dependent on environmental factors such as the action of soil microorganisms and evaporation as well as oxygen and organic matter content (WHO, 1991).

Beta-HCH has a much lower vapor pressure and a much higher melting point than the alpha-HCH. These properties are dictated by the great physical and metabolic stability conferred by the isomer structure (Willet, 1998).

Although photolysis is not expected to be an important environmental fate process for HCH, it may be degraded in the atmosphere by reacting with photochemically produced hydroxyl radicals. A photodegradation half-life for a thin film of beta-HCH equal to 152 hours has been reported (ATSDR, 2005).

2.3 Bioaccumulation

Beta-HCH is the predominant isomer in soils and animal tissues because its all equatorial configuration favors storage in biological media and affords it greater resistance to hydrolysis and enzymatic degradation (Walker, 1999).

The octanol-water partition coefficient (K_{ow} = 3.78) for beta-HCH indicates that it has the potential to bioaccumulate. A bioconcentration factor (BCF) equal to 1 460 was found for beta-HCH using zebra-fish under steady-state conditions compared to BCFs equal to 1 100 for alpha-HCH and 850 for gamma-HCH (ATSDR, 2005). BCFs from 250 – 1 500 on a dry weight basis or 500 000 times on a lipid basis within 3-10 days have also been reported (WHO, 1991).

Several studies suggest that the relative proportions of HCH isomers vary dramatically across species in the Arctic marine food web. A study carried out in 2000 indicated that upper trophic level mammals may be able to efficiently eliminate lindane and to a smaller extent alpha-HCH, but not beta-HCH, suggesting beta-HCH tends to bio-accumulate mainly in upper trophic levels (fishes, birds and mammals) at higher concentrations (USEPA, 2006).

2.4 Potential for long range environmental transport

Air concentrations of beta-HCH in the Alert and Tagish station in the Arctic have been measured regularly. The results indicate the concentration of beta-HCH in the Arctic atmosphere is very low in comparison with the more volatile alpha- and gamma-HCH. However, the concentration of beta-HCH in the Arctic surface water can be as high as 240 pg/L approaching the concentration of gamma-HCH in the same media (Li et al, 2003).

Li et al (2002) reported that in contrast to alpha-HCH, beta-HCH appears to be less subject to direct atmospheric loading into the high Arctic as most of beta-HCH stays in the source region after application. This can be explained by differences in their Henry’s law constant and air/water partition coefficient that make enhanced affinity for particles, greater resistance to degradation and reduced volatility.

According to Li et al (2002), rain scavenging is much more efficient for beta- than for alpha-HCH, besides frequency of precipitation is considerably higher in the North Pacific compared to the Arctic. This idea suggests that beta-HCH enters the Arctic probably by mechanisms involving wet deposition or partitioning into the North Pacific surface water and subsequently entering the Arctic in ocean currents passing through the Bering Strait (Li et al, 2003).

Bering and Chukchi Seas are the most vulnerable locations for beta-HCH loadings primarily originated from Asia via the Pacific. (Li et al, 2002).

2.5 Adverse effects

Beta-HCH has moderate toxicity for algae, invertebrates and fish. The acute LD_{50} values for these organisms are of the order of 1 mg/litre (WHO, 1991).

Studies of short-, intermediate- and long-term exposure to beta-HCH in diet have reported liver and renal effects in animals. A significantly decreased body weight gain has been seen in rats treated orally with 250 mg/kg beta-HCH. Neurological effects have also been reported in rats exposed to beta-HCH. Oral exposure of rats and mice to beta-HCH has resulted in degeneration of male reproductive organs and sperm abnormalities. The limited genotoxicity data indicate that beta-HCH has some genotoxic potential but the evidence is not conclusive (USEPA, 2006).

Beta-HCH may be the most toxicologically significant HCH isomer due to the recent reports of its estrogenic effects in mammalian cells, laboratory mammals and fish (Willet, 1998).

There are limited studies to estimate cancer risk from exposure to beta-HCH. However, EPA's Integrated Risk Information System (IRIS) currently lists beta-HCH as a possible human carcinogen based on the incidence of hepatic nodules and hepatocellular carcinomas observed in male mice administer beta-HCH at a single dose level in the diet (USEPA, 2006).

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

Beta-HCH is the most persistent isomer of hexachlorocyclohexane. Due to its physicochemical properties it has the potential to bioaccumulate. Its listing as possible human carcinogenic should also 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. 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 beta-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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