

## **Nomination Dossier for Hexachlorobenzene**

Submission by Mexico to the  
Sound Management of Chemicals (SMOC) Working Group  
for consideration as a candidate substance for development of a NARAP

**This nomination dossier is a working document and  
is not an official governmental or CEC document**

**Discussion Draft for Public Review and Comment  
6 June 1998**

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## Substance Nomination Dossier

### **Hexachlorobenzene**

#### **Identity, C.A.S. Number and Description<sup>1</sup>**

*C.A.S Registration Number:* 118-74-1

*Synonyms:* ENT-1719; Granox; No bunt; Perchlorobenzene; Voronit C; AI 3.01719; Amatin; Anticarie; Bunt-no-more; Caswell No. 477; Esaclorobenzene (Italian) Hexaclorobenceno (Spanish) Granox nm; HCB; HEXA CB; HEXACHLOROBENZOL (German) Julin's carbon chloride; No bunt 40; No bunt 80; Pentachlorophenyl chloride; Phenyl perchloryl; Saatbeizfungizid (German); Sanocide; Smut-go; Snieciotox.

*Molecular Formula:* C<sub>6</sub>-Cl<sub>6</sub>

*RTECS #:* NIOSH/DA2975000

*Shipping Name/Number – DOT/UN/NA/IMCO:*

IMO 6.1 – Hexachlorobenzene

UN 2729 – Hexachlorobenzene

*USEPA Hazardous Waste #:* U127 – A toxic waste when discarded as a commercial product or manufactured intermediate.

#### **Physiochemical Description<sup>2</sup>**

White needle-like solid at room temperature, derived from Benzene-alcohol.

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<sup>1</sup> Source: HSDB® Section 1.0

<sup>2</sup> Source: HSDB® Sections 3.0, 7.0

**Table 1 Physiochemical properties of Hexachlorobenzene**

<b>Hexachlorobenzene</b>	
Molecular Weight	284.80 g/mol
Boiling Point	323-326 °C
Melting Point	231 °C
Density/Specific Gravity	1.5691 at 23.6 °C
Octanol/Water Partition Coefficient	log K <sub>ow</sub> = 5.31
Water Solubility	0.035 ppm in water (practically insoluble)
Other Solubilities	Slightly soluble in cold alcohol, carbon tetrachloride; soluble in benzene, chloroform, ether, carbon disulfide
Vapor Pressure	1.09 x 10 <sup>-5</sup> mm Hg at 20 °C
Vapor Density (air = 1.0)	9.83
Henry's Law Constant	0.03-0.07 (unitless scale) equal to 131 Pa m <sup>3</sup> /mol
Half-life in Air (w/ OH)	2 years
Half-life in Soil	1530 days
Half-life in Water	8 hours
Hydrolysis	Resists
Photolysis	Resists
Oxidation	Resists
Biodegradation	Not significant
Soil Absorption	Strong
Volatization in Soil/Water	Rapid
Other aspects	Very stable, even in acids and bases; no universal method of final disposal
Organic carbon partitioning log K <sub>oc</sub>	4-5
<b>Persistence</b>	<b>High</b>
Bioaccumulation log P	6.80 (HSDB); 5.73 (USEPA WPMT)
Bioconcentration Factor (log BCF)	trout 3.7-4.3; sunfish 3.1-4.3; fathead minnow 4.2-4.5
<b>Bioaccumulation</b>	<b>High</b>

## *Uses*

In Mexico Hexachlorobenzene (HCB) is mainly used as a fungicide. Other countries have documented it as a raw material for synthetic rubber, a PVC plasticizer, and a rubber peptizing agent in the production of nitroso- and styrene-rubbers. It is a selective fungicide against Bunt pest of wheat. It is also used as a chemical intermediate in dyes, as well as in manufacturing process of pentachlorophenol in Europe and in the preservation of wood.

## **Sources**

### *Commercial Production*

HCB production in Mexico has been documented up to 1991. During the 1970's HCB was produced by three companies; from 1980 to 1984 two companies, and from then until 1991 only one company. The producer during that year was a government owned factory. Later on in 1993 it was sold to private owners.

Historically there have been 19 different companies that, at different time periods, have produced and distributed Hexachlorobenzene in Mexico. After a direct survey with these companies in 1998, it was found that all of them no longer produced or distributed HCB.

**HCB has not been produced commercially in Mexico since 1992.**

### *Imports*

Integrated data on HCB imports/exports balances in Mexico is shown in Table 2.

US production in 1977 was  $4.54 \times 10^8$  g (454 tonnes). No production in US in 1992. Imports to US 2.44 tonnes in 1977, 17.3 tonnes in 1982 (HSDB Section 2.0).

### *Natural Sources*

None/unknown.

### *Other Potential Sources*

- By-product or waste material in the production of tetrachloroethylene, trichloroethylene, carbon tetrachloride, chlorine, chlorinated solvents, dimethyl tetrachloroterephthalate, vinyl chloride, atrazine, propazine, simazine, pentachloronitrobenzene and mirex
- Also as a waste material from pyrotechnic production, sodium chlorate production, aluminum manufacturing
- Possibly used in synthetic rubber production
- Has been found in treated waste water from non-ferrous metal manufacturing plants
- Ingredient in several pesticides

- Might be emitted in gases from waste incineration facilities.

*An estimate of emissions from sources in Mexico has not been made to date.*

**Table 2 Integrated data on HCB imports/exports balances in Mexico**

**HCB in Mexico (Tons)**

YEAR	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981
PRODUCTION	3007	3820	3634	3890	1822	1268	1752	2051	1889	2102	1619	2889
IMPORTS	161	192	194	96	56	49	49	4	0	0	0	0
EXPORTS	0	0	0	0	0	0	0	0	0	0	0	0
CONSUMPTION (Ag.)	3168	4012	3828	3986	1878	1317	1801	2055	1889	2102	1619	2889
% CHANGE in Ag. use	98.5	26.6	-4.6	4.1	-52.89	-29.87	36.8	14.103	-8.1	11.3	-22.98	78.4
CAPACITY	n. d.	n. d.	n. d.	n. d.	2300	2300	2300	2300	2300	2300	2300	3000
SUBUTIL. CAP. %	n. d.	n. d.	n. d.	n. d.	20.8	44.9	23.8	10.8	17.9	8.6	29.6	3.7

YEAR	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	92-97	Total
PRODUCTION	1967	1431	1172	1424	1441	1366	1543	1717	948	420	0	<b>43172</b>
IMPORTS	0	0	0	0	7	2	0	0	0	0	0	<b>810</b>
EXPORTS	0	0	0	14	68	68	0	0	0	0	0	<b>150</b>
CONSUMPTION (Ag.)	1967	1431	1172	1410	1380	1300	1543	1717	948	420	0	<b>43832</b>
% CHANGE in Ag. use	-31.91	-27.25	-18.1	20.3	-2.1	-5.797	18.7	11.3	-44.79	-55.7	0	
CAPACITY	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	n. d.	
SUBUTIL. CAP. %	34.4	52.3	60.9	52.5	52	54.5	48.6	42.8	68.4	86	n. d.	

**Fate and Transport**

*Water*

HCB evaporates rapidly in water. Half life in the lab is 8 hours. Will adsorb to sediments. Will bioconcentrate in fish and aquatic organisms.

### ***Land***

Strong adsorption to solids (half life 1530 days). Little biodegradation. Slow transport to groundwater (depending on carbon content of soil). Some evaporation may occur depending on organic content of the soil.

### ***Atmosphere***

Exists mainly in the vapor phase; less is found in the adsorbed phase. Extremely slow degradation, estimated half life of 2 years. Rainfall and dry deposition may remove HCB from air to soil and water.

### ***Biodegradation***

No significant biodegradation. Loss from soil mainly through volatilization. May degrade with a dechlorination rate of 13.6  $\mu\text{mol/L-day}$  in fresh anaerobic digester sludge after a period of approximately 7 days.

### ***Bioconcentration***

High Bioconcentration Factors (BCF) have been documented in fish and invertebrates (3.1 to 4.5). It is transferred in water through food chains, such as algae, snails, plankton, water fleas, mosquitoes and fish. Its presence has been detected and documented in human adipose tissue of non-occupationally exposed individuals. Bioconcentration factors seem to be higher in humans than in rodents by several orders of magnitude.

### ***Persistence***

Data from Section 2.0 and the above subsections 5.1-5.5 indicate environmental persistence is **very high**.

**Documented Conditions for Mexico:** *None.*

## Presence in Environment, Biota and Humans

**Table 3. Range of concentrations identified & documented in Canada, the United States and worldwide**

\*\* Information on all environmental media not yet available for Mexico

<i>Environmental Media</i>	<i>Canada and the United States</i>	<i>World Wide</i>
<b>Drinking water</b>	0.06-0.2 ppt	
<b>Surface water</b>	8-30 ppm (Niagara); 0.02-0.1 ppt (Great Lakes); 0-0.04 ppt avg US industrialized river	
<b>Seawater</b>		
<b>Rainwater</b>	Great Lakes 1-4 ppt; North Pacific 0.03 ppt; Lakes Superior 2.8 ppt	0.002-0.01 ppb in 16% of Mediteranean samples
<b>Effluents:</b>		
• Industrial	2 of 26 effl. with 220 ppb max; 4 Canadian plants 1-2 ppt	
• Municipal	None identified	
<b>Soil concentrations</b> <b>Sediment concentrations</b>	37 of 50 US states found 0.7% positive samples 0.0-0.44 ppm; Mississippi 0-900 ppb; Great Lakes avg range 0.2-460 ppb; Gulf of Mexico 0.49 ppb; Portland 0.05-0.37 ppb	Rome data with 40 ppb Germany sediment 0-15 ppb;
<b>Atmospheric concentrations</b>	Great Lakes 0.008-0.024 ppt; SE US 0.001-0.016 ppt; North Atlantic 0.04 ppt; Near chlorine plants in US 0.006-2 ppb	Pacific Ocean New Zealand 0.055-0.061 ng/m <sup>3</sup>
<b>Food concentrations</b>	US total food surveys 1-8.3; concentrations 0.03 – 0.4 ug. Subgroup surveys 0.001 ppb to 0.01 ppm. Butter in US: Fresh 0.47; table 0.302; low cal 0.596 mg/kg Fish US: fresh water 0.001-0.34 ppm; marine 0.001-0.6 ppm; seafood 0.001-0.350 ppm	Egypt commercial samples 1.3 to 7.8 ug/kg
<b>Plant concentrations</b>		1-5 ng/g in fallen leaves in Italy

<b>Animal concentrations</b>	US samples 0-5.2 ppm;	Germany 0.03 – 0.31 ppm
<b>Milk concentrations</b>	US: 3.3% samples positive 0.001 ppm avg. Human Milk: in Canada, ranged from 0 – 5.13 ppm	Yugoslavia 1.31 ng/g West Germany 10 year decrease from 0.16 to 0.02 mg/kg Human Milk: in Norway, Finland, ranged from 0 – 5.13 ppm
<b>Other data:</b>		Worldwide, there seems to be a peak in concentrations in the late 1970's and then a decline into the 1980's

## Potential Human Exposure

Occupational Routes: Dermal, inhalation, ingestion

General Routes: Mainly through ingestion of food and milk

### *Occupational Exposure*

Occupational exposure studies indicated that workers were exposed to HCB when HCB concentrations in breathing air zones of chlorinated solvents and pesticides plants ranged from  $3 \times 10^{-4}$  to  $1.2 \times 10^{-1}$  mg / m<sup>3</sup>. In these surveys, blood content of exposed workers ranged from 14-233 ppb (pre 1983 US surveys). Some 4500 farmers applying pesticides or handling contaminated soil were also exposed to HCB (US estimate pre 1983).

*Occupational population potentially exposed not quantified in Mexico, but assumed to be low since HCB has been banned and not produced since 1992.*

### *Environmental Exposure*

Environmental exposure of the general population may occur amongst those living near a manufacturing or an incineration plant. Adipose tissue samples: US 0.05 ppm avg.; Canada 0.1-6.7 ppm; Japan 0.06-3.2 ppm. Human milk: Canada 0 – 5.13 ppm; Norway 2.1 ppb; Finland 0.7 – 6 ppb. Since it is banned in Mexico environmental exposure is assumed to be **low**.

Average body burden (US): 0.7 mg.

Average daily intake: through air 0.20-4 ng; through water 0.12 – 0.4 ng; food 0.03-0.3 µg.

*Proportion of the general population potentially exposed to environmental contacts is not quantified in any country.*

## Toxicity in Humans

**Table 4. Toxicity in Humans**

<i>Biological Function:</i> None
<i>Acute Exposure Effects:</i> Irritation of nose, throat and lungs. Contact can cause eye and skin irritation, and burn skin.
<i>Chronic Exposure Effects:</i> May damage liver, kidneys, immune system and thyroid. May damage CNS and cause irritability, difficulty walking and coordination problems, muscle weakness, tremor and feeling of pins and needles on skin. Repeated exposure can change skin pigment, cause thickening, scarring, fragile skin, and increased hair growth in face and forearms.
<i>Cancer Effects:</i> IARC Group 2B (2B probable human carcinogen , sufficient data in animals). ACGIH Group A3 – animal carcinogen. IRIS B2 – probable human carcinogen. Massive exposure in Turkey between 1954 –59 from seed grain treated with HCB as a fungicide: 37% increased incidence of enlarged thyroids, 4000 cases of porphyria.
<i>Genetic Effects:</i> In bacteria tests, specifically E. Coli, an increase in DNA adducts (lost fractions of nuclear cell DNA) has been shown at HCB concentrations of 6 mg /L. Mutations were identified in yeast at HCB concentrations of 100 ppm. Mutations in lung somatic cells of hamsters were also identified at HCB concentrations of 6 ml/L.
<i>Reproductive Effects:</i> May damage developing fetuses, crossing the placenta in humans and other species. Exposure in rats caused enlarged kidneys of offspring. In mice perinatal mortality and abnormal immune system development increased. No human teratogenicity studies have been reported. Lactational exposure of mice pups is a major route – higher exposure after suckling than transplacental. Effects on fertility are less known. Female monkeys fed up to 10 mg/kg/day for 13 weeks showed increased variability in menstrual cycle length and decreased luteal phase progesterone.
<i>Predisposing Conditions:</i> No data.

## ***Non Carcinogenic Effects***

### *Human Non Carcinogenic Studies*

In southeastern Turkey, approximately 5000 people ingested seed grain treated with HCB. In children <1 year of age pink sore disease was observed with a 95% mortality rate. In addition to porphyria cutanea tarda, the population experienced skin lesions, hypetrichosis and hyperpigmentation, neurotoxicity and liver damage. Follow up showed reduced growth and arthritic changes in children.

An Italian study showed that women who have had several miscarriages did not have higher blood levels of HCB than those who have never had a miscarriage. HCB has been identified in follicular fluid of women undergoing IV fertilization.

### *Animal Non Carcinogenic Studies*

A study was carried out on reproducing Sprague-Dawley rats. At high concentrations the rats experienced hepatic centrilobular basophilic chromogenesis. The mid exposure group showed increased pup mortality and chronic nephrosis. Recent studies on exposed rats have indicated adrenal cortex hyperplasia and changes in immunomodulation. In short term studies (15 weeks), Charles River rats displayed increased porphyrin levels, depletion of hepatocellular marker enzymes, increased liver-to-weight and kidney-to-body ratios, decreased survival, splenomegaly and ataxia. Changes occurred in the thymus and thyroid weight in hamsters, as well as in the RBC count in dogs, and the thyroid weight in pigs.

HCB has been shown to cross the placenta. Some studies have shown that teratologic effects in rodents' offspring depend on maternal toxicity. Other aspects are musculoskeletal system developmental abnormalities, reduced newborn survival, biochemical and metabolic abnormalities in newborns, spleen, bone marrow, lymphatic system, hydronephrosis, and immune developmental abnormalities, reduced weight gain, reduced live birth and viability index, craniofacial and urogenital abnormalities. Effects also occur on maternal ovaries and fallopian tubes.

Short term, single dose exposure in rats showed increased rib development. Relative toxicity is 2.5 higher in milk than in blood.

Exposed female monkeys showed increased variability in menstrual cycle length with a decrease in luteal phase progesterone; this was accompanied by ovarian epithelial damage. The effects were independent of other toxicities in the monkey, therefore being gonadotoxic.

Oral reference dose is estimated to be  $8 \times 10^{-4}$  mg/kg/day (USEPA).

## ***Carcinogenic Effects***

### *Human Carcinogenic Studies*

There is little human data to support carcinogenicity. In southeastern Turkey,

approximately 5000 people ingested seed grain treated with HCB. Children <2 years died; 4000 people developed porphyria; a follow up indicated 37% thyromegalia.

### *Animal Carcinogenic Studies*

Hepatic (hemangiohepatomas, hepatocellular carcinoma and bile duct) cancer, thyroid and kidney neoplasms have been observed in Sprague-Dawley rats, hamsters, and Swiss mice in chronic 2 year oral exposure studies. Lymphomas have been shown in mice, and thyroid tumors in hamsters. Females seem to be more susceptible. These relations are dose-dependent. Short term exposure did not have an effect.

HCB is also mutagenic in Saccharomyces, Salmonella and hamster somatic cell tests. There are documented DNA adducts in E. Coli.

### *Key Classifications etc.*<sup>3</sup>

- IARC Group: 2B (possible human carcinogen; inadequate evidence in humans, sufficient animal evidence).
- ACGIH Group: A2 suspected human carcinogen.
- USEPA (IRIS): B2 probable human carcinogen.
- NTP: suspected human carcinogen.
- California Cancer List: present.
- Cancer Potency Factor (USEPA):  $1.6 \text{ (mg/kg-day)}^{-1}$ .
- Endocrine Disruptor (Illinois proposed list): probable effects in animals.
- Massachusetts: extremely hazardous, carcinogen, teratogen.
- CERCLA/SARA Reportable Quantity: 10 pounds.
- Safe Drinking Water Act MCL: 0.001 mg/L.
- Safe Drinking Water Act MCLG: zero.
- Mexico Drinking Water: 0.00001 mg/L.
- ACGIH TLV-TWA 8 hour (1997):  $0.002 \text{ mg/m}^3$  for skin.
- ACGIH Skin: potential absorption
- CANADA Accelerated Reduction/Elimination of Toxics Plan: A1 (meets or exceeds toxicity, bioaccumulation and persistence criteria)

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<sup>3</sup> Source: List of Lists LOLI®

## **Ecotoxicity<sup>4</sup>**

Extensive evidence of various effects exists in rodents, dogs, fish and chicks (40 references in HSBBD Section 5.0), including immunotoxicity, reproductive toxicity. Ecotoxicity values (LC50, LD50) for 7 species designated.

RTECS:

Reproductive effects: rat, mouse, monkey, mammal (unspecified species).

Genetic effects: DNA adduct – bacteria – E-Coli; mutations in Yeast, hamster, mouse

Tumorigenic effects: rat, mouse, hamster.

## **Risk Management in Mexico**

The production of HCB in Mexico is prohibited.

### ***Occupational Limits***

Mexico's Total Allowable Concentration for HCB is not listed (since it is not produced); For related Chlorobenzene it is 75 ppm or 350 mg/m<sup>3</sup>.

### ***Environmental Limits***

Mexico Maximum Allowable Limits for Drinking Water (bottled , ice): 0.01 µg/L

Consideration in Toxic Waste Classification:

Chlorinated plants sludge (RP 16.2 / 3)

Chlorobenzene plants (RP 17.6)

Carbon Tetrachloride (RP 17.21)

HCB residues (RPNE 1.1 / 14)

Incompatibility lists (NOM 054)

Leachates Max. Allowable Concentration 0.13 mg/L.

## **Conclusions**

Considering its physiochemical, biological, ecotoxicological, and carcinogenic and non carcinogenic human effects HCB ranked in the second group of the national selection process. It also was on the top of the international and national lists of substances considered toxic and dangerous to humans and the environment.

Furthermore, animal data indicates that it is probably carcinogenic, teratogenic, affecting

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<sup>4</sup> Sources: HSBBD Section 5.0, RTECS

reproduction and development. The mutagenicity test has proven positive.

Data to support similar effects in humans is more scarce, although there are positive findings in tumor development, neurologic, immunologic hepatotoxic and skin effects. No data is available on this in Mexican studies.

It is persistent and will be transported both through environmental media and the food chain.

### ***Mexican Context***

Mexico has long detected the hazard of HCB. Although the production and import of HCB is no longer a problem, the remaining presence of the agent is yet to be determined. The potential reproductive hazards are important given the demographic situation of the country where the majority of the population is of reproductive age. The size of the exposed population and HCB concentrations are still unknown.

The effect of HCB on biota is relevant since the rich biodiversity of the country could be affected by its presence.

The simple prohibition of the use of this chemical has been demonstrated worldwide to reduce media concentrations. Further efforts to identify high risk groups and emission sources from by-product formation should prove to be effective in controlling its potential health effect both in occupationally and non-occupationally exposed populations.

### ***Knowledge Gaps***

**In Mexico, HCB waste product emissions from other production sources has not yet been estimated, nor has an estimate of the accumulated environmental concentrations per compartment been determined. Climatic, geographic and orographic conditions can make these parameters vary greatly.**

The economic impact on industries has yet to be estimated, specifically the detection and control of emissions of by-products.

Worldwide, epidemiological data is scarce. In Mexico the size of the population affected is not known.

Human carcinogenicity and reproductive effects have yet to be clearly documented. There are no studies of the effects on male reproduction, worldwide nor in Mexico.

There needs to be an integration of several exposure factors for specific human populations, including nutritional interactions which are required to understand the presence of susceptible individuals and populations. We believe developing infants could be included.

In spite of the knowledge gaps to be filled, we recommend the development of a National or North American Regional Risk Characterization, determining the exposure patterns and magnitudes of population exposure in order to establish reasonable management goals.

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**Note:**

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## **ANNEX A**

### **COMMERCIAL SUBSTANCE DATA FOR MEXICO (Spanish Text)**