

ANNEX 2

EVALUATION OF THE POPS ISSUE IN THE CZECH REPUBLIC

Assessment of chemicals pursuant to the Annex A, Part I (POPs pesticides): historical, current and planned production, use, import and export; Existing policy and regulatory framework

A2.1 Production

The two largest pesticide producers were Spolana Neratovice and Chemické závody Juraje Dimitrova (CHZJD) in the former Czechoslovakia. The history of the national production of the persistent organochlorinated pesticides started in 1950 when a research on the synthesis of the DDT was terminated at the Research Institute of Agrochemical technology in Bratislava. The conditions for the industrial production of the technical HCH at large were ready a year later; since 1959, (or 1956 according to other sources) only a pure lindane (>99 % of the γ -isomer HCH) was used in the agriculture, its use was limited only to the treatment of seeds (linen, winter rape). However, the technical HCH remained in use in the forestry. At the beginning of 1960s, the first cases of the DDT resistance were demonstrated (gold bug, *Leptinotarsa decemlineata*), later on other resistant insects appeared, i.e. (rape blossom beetle, *Meligethes aeneus*). Due to these findings the DDT production decreased and it was replaced by the lelevan (also chlorinated compound) at first, then by chlorophenynphose and carbamates. The unused stocks were gathered in individual collective farms (JZD) and in Agricultural storage and buying plants (ZZNZ) in 1950s and 1960s – not only DDT, but also other pesticides. Subsequently, it became necessary to control the removal of such unused and unusable OCPs stocks.

Production of hexachlorocyclohexanes by light catalysed addition to a benzene ring began in Spolana Neratovice in 1961. The product formed contained a mixture of spatial isomers α , β , γ , δ , ϵ -1,2,3,4,5,6-hexachlorocyclohexanes, hepta- and octachlorocyclohexanes and other substances. The most efficient insecticide of the mixture was the γ -isomer (lindane) that was formed by the reaction in approximately 13% of the total yield.

Hexachlorocyclohexane (hereafter HCH) was used as a raw material for the production of trichlorobenzene and other various pesticide preparations. It was also used for the development of preparations for the protection of forest growth against animal nibbling, of insecticide preparations, anthelmintic agents and also as an additive to certain paints.

HCB was used in the production of a combined fungicidal preparation for the dry seed treatment against the fungal diseases, called Agronal H. Agronal H contained 2% of the organically bound mercury and 10% hexachlorobenzene in a mixture with mineral filling agents. A part of the HCB was converted, with the help of caustic soda, into the sodium pentachlorophenolate and subsequently to the pentachlorophenol (hereafter PeCP).

Sodium pentachlorophenolate was sold dried as 7-11% water-diluted solution. However, PeCP was sold dried and as a xylene solution with a minimum 23% PeCP content. PeCP was also used as one of the active ingredients in the combined insecticidal and fungicidal preparation PENTALIDOL for the wood treatment of all types of wood, constructions, banisters, furniture, floors and roofing against wood-damaging pests, wood-damaging fungi and various types of moulds.

Tetrachlorobenzene (hereafter TeCBz) was converted to the sodium trichlorophenolate by using NaOH; this sodium trichlorophenolate was either transformed to the trichlorophenol by acidification, or to the sodium salt of 2,4,5-trichlorophenoxyacetic acid (hereafter just 2,4,5-T) in reaction with the chloroacetic acid. The reaction of the sodium salt of 2,4,5-T with the butanol produced the butylester of 2,4,5-T acid being the main active ingredient of arboricidal preparations ARBORICID E 50 and ARBORICID EC 50.

At the time, when the technology for the processing of ballast HCH isomers was being introduced, it was not known that side reactions of the above-mentioned syntheses produce trace amounts of substances hazardous for the human health, causing a liver necrosis and being manifested externally by the presence of chloro-acne – polychlorinated dibenzo-p-dioxins (PCDDs/Fs), and especially the most toxic congener 2,3,7,8,-tetrachlorodibenzo-p-dioxine.

Regarding the fact that for the trichlorobezene isolation a steam distillation was used and whose venting was located inside the operational space, a gradual contamination of the working environment and contamination of the whole building Ne42 (currently A1420) occurred. Moreover, the recycling of the mother liquors also contributed to the contamination, as it is the way of the TCDD gradual concentration, despite the fact that it was initially formed in trace amounts, and its release was facilitated by the steam distillation. However, when these facts were detected, the treatment of the ballast isomers in Spolana was terminated in 1968.

During the course of the 1970's, the technical practice begun to change from the commonly used trichlorethylene to the perchlorethylene, especially in sewage treatment plants, and in degreasing processes in metallurgy. This change was evoked partly by the economic, partly by the hygienic as well as toxicological reasons. Significant losses in the technological processes occurred due to the high volatility of the trichloroethylene. Moreover, its high volatility was also the cause of the air contamination in the working environment and thereby increasing the technological requirements on the maintenance of the clean working environment. Trichloroethylene is also characterised by the significantly higher acute toxicity than perchloroethylene, thus its higher toxicity combined with higher volatility generates a significantly higher risk of narcotic effects for workers and a higher occurrence of work-related diseases especially considering the hepatotoxicity.

The principal manufacturer – The Association for Chemical and Smelting Production, Ústí nad Labem – changed this commodity in the mid-1970. After the implementation of the otherwise very progressive computer-directed manufacturing process, there remained an oil-tar residue after the final distillation; it has been labelled as the “HEXA” mixture due to its undefined, semi qualitative chemical structure.

This residue (without a more detailed chemical analysis and toxicological evaluation) was temporarily filled into barrels and stored at an enclosed landfill of the company with the presumption of its liquidation by combustion as the main product in the planned company incinerator.

Therefore it was suggested to reisolate this component (HCB) of the waste product and reuse it. It was possible to gain highly pure HCB via relatively easy rafination by recrystalization and three ways of its use were proposed, i.e. export with its former agrochemical use into countries, where it is not yet banned, or as a component in the mixture for the screening smokes in the military or as an agent for the refining of aluminium and its compounds.

The largest HCB quantity was exported to the former-USSR, where HCB had been used as an herbicidal preparation for the defoliation prior to the machine (combine) harvest of cotton, especially in Uzbekistan for a longer time.

A2.2 Application

What concerns the rapidity of the application, it naturally depends on its mode. In the majority of the cases and for a majority of pesticides, the active substance dose ranged between 0,5 and 1,5 kg.ha⁻¹, but in some cases a dose applied could have been outside this interval. For example, the recommended dose of the Aerosol DDT were 6 l.ha⁻¹, corresponding to the 3,6 kg.ha⁻¹ of the active substance¹; the recommended dose² of the Cyclo Powder was 40 kg.ha⁻¹, corresponding to the 6,4 kg.ha⁻¹ of the active substance γ -HCH, and a recommended dose of the hexachlorobenzene (used for the soil disinfection)

¹ List of Registered Plant Protection Products. Federal Ministry of Agriculture and Nutrition of the Czechoslovak Socialist Republic, 1972

² Hrnčiar J.: Overview on Plant Protection Production CHZJD Bratislava. In: Agrochemia (CS), **12** (6), 1972, p. 180/181

was 50 kg, i.e. 12,5 kg.ha⁻¹ of the HCB; On the other hand, in the Endrin 20 case a recommended dose attained 0,5 l.ha⁻¹, and correspondingly only to the 0,1 kg.ha⁻¹ of the active substance, but eldrine is a very special case. Expert estimation stated that pesticide consumption per hectare of the agricultural land nowadays reaches 1 kg.ha⁻¹, however, it used to be about 4 kg.ha⁻¹, if not more, in 1960s. For example, the plant protection preparations consumption was 23 650 t in 1981; these preparations were used to protect 4 910 103 ha of the land, that means that the consumption was nearly 5 kg.ha⁻¹. However, we can assume that during the time of intensive use of the POPs pesticides, this application rate could have been much higher.

Data on application may be useful for the interpretation of the pesticide consumption, maybe to the larger extent that not-available data on production (table A2-1).

Table A2-1: Rate of application of the plant protection preparations

Active substance of the preparation	Application dose of the preparation per ha	Responses to the application of the active substance per ha or per other unit
aldrin	Very limited or no use, not necessary to evaluate	
DDT	Ranged from 1- 102 kg.ha ⁻¹ depending on the concentration of the preparation ³	0,8 - 3,6 kg.ha ⁻¹ (Dykol, Aerosol-DDT respectively)
dieldrin	Data do not exist	
endosulphan	Maximum 2,5 l.ha ⁻¹ in the majority of the cases < 1,5 l.ha ⁻¹	Maximum 1,1 kg.ha ⁻¹ majority of the cases < 0,55 kg.ha ⁻¹
endrin	0,5 l.ha ⁻¹	0,1 kg.ha ⁻¹
HCH technical	Ranged 10 - 102 kg.ha ⁻¹ in the agriculture, depending on the concentration of the preparation ⁴	2,5 - 9 kg.ha ⁻¹ (the highest values were used in the soil disinfection ; 3,5 - 5,6 kg.ha ⁻¹ was applied in the forestry and to the non-agricultural lands
heptachlor	Agronex hepta T 30 1,2 kg.100 kg ⁻¹ of seeds, for the seed treatment	400 g per 100 kg seeds
hexachlorobenzene	50 kg.ha ⁻¹ for the soil disinfection	12,5 kg.ha ⁻¹
metoxychlorine	Limited production, not evaluated	
quintozene	Used as Brassicol-Streumittel 300-400 g.m ⁻³ respectively. 30-40 g.m ⁻²	60-80 kg.ha ⁻¹ for the soil disinfection
toxaphene	20-30 kg.ha ⁻¹ , same as Melipax	2-3 kg.ha ⁻¹

³ As to Antrix see also Note 19; the corresponding rate of DDT would be about 100 g/m³

⁴ In forestry used only for protection of wood damaging insects; the application rate is expressed in l/m³; in most cases between and 5 and 10 l/m³ of concentration between 2 and 7 % of preparations; can concern only solutions (Forst-Nexen and both the Ipsotoxes); corresponds e.g. to 50 g/m³ HCH technical in case of Antrix applied at 10 L/m³ of 7 % solution as recommended