

CONTEMPORARY RELEVANCE OF DIOXIN AND DIOXIN LIKE COMPOUND CONTAMINATIONS IN RESIDUES FROM RECYCLING OF HCH WASTE

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Introduction

1, 2, 3, 4, 5, 6-Hexachlorocyclohexane (HCH)^A has been one of the most extensively used pesticides. The application of Lindane and technical HCH during the last 5 decades has resulted in environmental contamination with global dimension¹⁻⁴ and Lindane and HCH is presently evaluated by the Persistent Organic Pollutants Review Committee of the Stockholm Convention for inclusion in the POPs list⁵.

HCH is available in two formulations: technical HCH and Lindane^B. Generally, technical HCH contains the isomers in the following percentages: α : 55-80%, β : 5-14%, γ : 8-15%, δ : 2-16%, and ϵ : 3-5%. Of these isomers only the gamma isomer has specific insecticidal properties. In the late 1940s and 50s the Technical HCH mixture as a whole was sprayed in Europe (and other countries). However it was soon discovered that the application of the technical HCH resulted in inedible crops, vegetables and fruits due to the bad smell and taste of some of the HCH isomers. Therefore, some companies started already in the 1950s with the isolation of the active, and in the applied concentration tasteless, gamma isomer and sold it under the trade name Lindane. The other HCH isomers resulting from production remained as by-products and became finally hazardous waste, creating one of the globe's largest hazardous organic waste problem. The production of Lindane is inefficient as for each ton of Lindane 8 - 12 tons of other HCH isomers are produced⁶⁻⁸ and therefore between 1.6 to 4.8 million tons have ended mostly as hazardous waste, which were dumped uncontrolled at many sites around the world^{1, 9}. These sites and the fate of the waste as well as the consequences for humans and the environment have virtually been ignored but need to be addressed^{1, 9}.

Alternatively, some HCH waste isomers have been recycled by companies to trichlorobenzene and further products (Figure 2). One of these products in the recycling chain was 2,4,5-T, known to contain high PCDD concentrations and resulting in highly PCDD/PCDF contaminated residues from such production (Table 1).

In the present study, the distillation residue from HCH decomposition to trichlorobenzene (the key residue of HCH recycling) and the residue of 2,5-Dichlor-4-bromophenol production (an intermediate of the Bromophos¹¹ production and the brominated-chlorinated analogue of 2,4,5-TCP) (Figure 2) were analysed by high resolution GC/MS and bio assay and the contemporary relevance of these residues is discussed. A second aim of this study was to evaluate samples from industrial processes by means of DR CALUX bioassay and to demonstrate the capability of bioassays for TEQ evaluation of products and residues from the chemical industry.

Materials and Methods

Samples from the "HCH waste recycling chain" (Figure 2): The residue from the thermal decomposition (250 – 260°C) of HCH to trichlorobenzene and a residue from 2,5-Dichlor-4-bromophenol from the Bromophos production chain were taken in a chemical factory in Hamburg in the early 80th and stored under room temperature in closed glass flasks under exclusion of light.

Instrumental analysis: The instrumental analysis for both samples was done in duplicate. The residue from HCH decomposition was sent to MTM Research Centre Örebro (Sweden) and Eurofins|ERGO (Germany) for PCDD/PCDF and PCB analysis. The residue from 2,5-Dichlor-4-bromophenol production sample was sent to

^A The Hexachlorocyclohexane compound is called "HCH" by the WHO. Another common name of Hexachlorocyclohexane is "benzene hexachloride", or "BHC" by UN FAO and ISO, which is, however, incorrect according to the IUPAC rules.

^B The term "lindane" should be differentiated from γ -HCH in order to avoid some confusion. γ -HCH is one of several isomers of HCH, and is contained in both technical HCH and Lindane. Lindane is one of two grades of HCH, and contains almost pure γ -HCH.

Örebro University and EMPA (Switzerland). All three laboratories used high resolution GC/MS with a resolution of >10000.

Bioassay: The DR CALUX analysis of both samples was done by BioDetection Systems (The Netherlands).

2,3,7,8-TCDD calibration range: For the standard 2,3,7,8-TCDD calibration curve used for sigmoidal curve-fitting, the following stock solutions of 2,3,7,8-TCDD in DMSO were prepared: 0, 37.5, 125, 375, 1250, 3750, 1250, 3750 pM. Two new stock concentrations of 2,3,7,8-TCDD in DMSO were added: 75 and 250 pM. The final concentrations of 2,3,7,8-TCDD in exposure medium (0.8% DMSO) are respectively 0, 0.3, 1.0, 3.0, 10, 30, 100, 300 pM/well for the standard calibration range and 0.6 and 2 pM/well for the additional calibration concentrations.

DR CALUX[®] bioanalysis: The procedure for the DR CALUX[®] by BDS bioassay is described in detail previously¹². Briefly, the bioassay is performed using a rat hepatoma H4IIE cell line stably transfected with an AhR-controlled luciferase reporter gene construct. Cells were cultured in α -MEM culture medium supplemented with 10% (v/v) FCS under standard conditions (37°C, 5% CO₂, 100% humidity). Cells were exposed in triplicate on 96-well microtiterplates containing the standard 2,3,7,8-TCDD calibration range, the additional 2,3,7,8-TCDD calibration concentrations, a DMSO blank, an internal reference material and various samples extracts at multiple dilutions (e.g. sediment, foodstuffs, feeding stuffs). Following a 24 hour incubation period, cells were lysed, a luciferine containing solution was added and the luciferase activity was measured using a luminometer equipped with 2 dispensers

Both tested samples have been tested by DR CALUX[®] bioassay in several dilution series and two kinetics (24 hrs and 48 hrs). The samples have been soluble in the interesting concentration range in DMSO, Hexane and Toluene and have been analysed with (sulphuric acid/silica column) and without clean-up procedures.

Results and Discussion

HCH decomposition residue

The quantitative instrumental analysis revealed extremely high TEQ_{WHO} (PCDD, PCDF and PCB) values of 286 ppm and a total PCDD/PCDF concentration of 20000 ppm (2%) in the HCH decomposition residue. The bioanalysis with DR CALUX showed full EC₅₀ curves (see Figure 1) and the results were in good agreement with the instrumental results having slightly higher TEQ values with the 24 hour kinetic measurements: 440 ppm TEQ with the sulphuric acid/silica clean-up and an average of 450 ppm without clean-up (sample dissolved in DMSO 530 ppm, in Toluol 470 ppm, and in Hexane 350 ppm). The 48 hour kinetics EC₅₀ value had 256 ppm TEQ indicating some metabolism of AH-active compounds and resulted in a value in close agreement with the instrumental analysis.

This HCH residue is one of the highest PCDD/PCDF contaminated sample ever measured and only one study reported higher TEQ levels for residues from 2,4,5-T production with 2000 ppm (Table 1).

The present study shows ca. 3 times higher TEQ concentrations in HCH decomposer residue compared to an analogous sample from the same factory in a former study¹⁰ (86 ppm TEQ; 14000 ppm total PCDD/PCDF; table 1). However, the total PCDD/PCDF concentration measured in two other HCH decomposer residues^{13, 19} (46000 ppm, table 1) were even higher compared to our study. Therefore, the former 86 ppm TEQ reported by a contractor of the producer indicate measurement of a lower contaminated batch.

Residue from 2,5-Dichlor-4-bromophenol production

In the 2,5-Dichlor-4-bromophenol residue, PCDDs/PCDFs could be detected. Additionally, a complex mixture of brominated-chlorinated aromatic compounds including 2,3,7,8-PXDD was identified. The TEQ concentration from polychlorinated PCDD/PCDF only amounted to 3.25 ng/g (0.00325 ppm). The analysis of mixed brominated-chlorinated PXDD/PXDF was not finalized at the time of abstract submission. In a preliminary quantification the TEQ from mixed brominated-chlorinated PXDD/PXDF was estimated to approx. 1 ppm.

The results from bioanalysis with DR CALUX assay showed differences in the activity of the sample with and without the sulphuric acid/silica column clean-up: The 24 hour kinetic measurements without clean-up showed consistently values of ca. 19 ppm TEQ (sample dissolved in DMSO 19 ppm, in Toluene 17 ppm, and in Hexane 20 ppm). However, the analysis of the sample sample which had been subjected to sulphuric acid/silica column clean-up, the activity considerably decreased to a value below 1 ppm. Therefore, a large share of the active compounds was eliminated by the clean up.

Table 1: PCDD/PCDF concentrations in contaminated products and residues from chlorinated aromatics in comparison to residues from chloralkali electrolysis and fly ash from waste incineration.

Sample	Sum PCDD/PCDF (µg/kg)	TEQ (µg/kg)	Reference
Electrode sludge chloralkali electrolysis (Graphite electrodes)	Up to 62 300	Up to 3900 ^{d)}	Ref. 18
HCH (product and waste isomers)	20 and 4 Up to 87 600	0.32 and 0.005 Up to 252	Ref. 23 Ref. 24
HCH decomposer residue	14 000 000 46 000 000	86 300 ^{a)} 286 000 ^{a)} 450 000 ^{b)}	Ref. 10 Ref. 13, 19 This study This study
Residues 2,4,5-T production		Up to 60 000 ^{c)} Up to 2 000 000 ^{c)}	Ref. 13 Ref. 14
2,4,5-T (product)		Up to 7000 ^{c)} Up to 100 000 ^{c)}	Ref. 15 Ref. 14
Residue 2,5-Dichlor-4-bromphenol production		500 ^{a,b)} to 19 000 ^{b)}	This study
Residues from PCP production	9 015 000	9580 ^{d)}	Ref. 16
PCP (product)	Up to 6 000 000	Up to 1300 ^{a)}	Ref 17
PCP Na (product)		Up to 3400 ^{c)}	Ref. 16
Fly ash municipal waste incinerator	10 to 2000	0.2 - 20	

^{a)}WHO TEQ, ^{b)}TEQ DR CALUX[®] EC 50, ^{c)}I-TEQ NATO/CCMS ^{d)}TEQ (BGA)

Contemporary relevance of deposited residues and ongoing recycling practice

Bromophos was produced only in Hamburg for ca. 16 years (end of 60s to early 80s) with a daily capacity of 7 to 10 tons amounting to total 30000 to 50000 tons. However the produced and deposited amount of the 2,5-Dichlor-4-bromophenol residues is not known. Also the fraction of the PCDD/PCDF and PXDD/PXDF finally transferred to the Bromophos product and released via product applications into the environment (treated products, plants and soil) is unknown.

The recycling of waste HCH by thermal decomposition was applied in at least two factories in Germany, recycling together 70000 tons of HCH by thermal decomposition to trichlorobenzene¹. From these processes several 1000 tons of HCH decomposition residues and contaminated activated carbon used as catalyst for the decomposition reaction were sent to landfills in Hamburg and other locations in Germany¹⁹. The process was, however, also applied in other factories in Europe (e.g. France²³, Spain and Czech Republic) and other parts of the world. However, information is scarce and quantitative data are not available^{1,9}. Therefore, a quantification on historic total PCDD/PCDF release cannot be undertaken at the moment for the residues of HCH decomposition but could be estimated in the order of tons TEQ^c. These highly PCDD/PCDF contaminated residues (table 1) deposited in the landfills and dumps can be of contemporary interest since:

a) Experiences from the remediation of the former pesticide production site in Hamburg and related landfills revealed that PCDD/PCDF, the pesticides residues and other chlorinated aromatics and aliphatics can leach from the sites depending e.g. on the quality of the landfill, the geological conditions and on other wastes co-deposited with the PCDD/PCDF and pesticide residues. The high concentrations of (chlorinated) organics in leachates from these types of landfills support the leaching of PCDD/PCDF from the landfill and concentrations of 2,3,7,8-TCDD up to 75000 ng/kg were detected in oily leachates from one landfill²¹. Therefore the plant history where thermal HCH decomposition have been operated need to be investigated and the contaminated sites where the residues have been deposited need to be assessed.

b) When these or other chemical landfills/contaminated sites need remediation, the deposited highly PCDD/PCDF contaminated residues present as local hot spots can pose a high risk for the operating staff performing the remediation and personal further handling the residues²².

^c The estimated contemporary total PCDD/PCDF release from 55 countries amounted to ca. 20 kg TEQ/year²⁰.

Furthermore, in India - the country with the last operating HCH productions worldwide^{9, 25, 26} - the HCH waste is thermally decomposed to trichlorobenzene still today and the wastes dumped in the vicinity of the factories^{25, 26}. This practice call for immediate assessment of these sites when considering the extremely high PCDD/PCDF contamination in residues from a comparable process found in this study and former investigations^{10, 19} (table 1).

Last not least the question of the PCDD/PCDF contamination in the 1.6 to 4.8 million tons HCH waste isomers stored and dumped around the globe^{1, 9} need to be addressed when considering possible PCDD/PCDF concentration of up to 252 ppb²⁴ (table 1) and in particular to clarify the relevance of PCDD/PCDF contamination of this waste in view of the large variation found in different HCH waste isomer samples (table 1).

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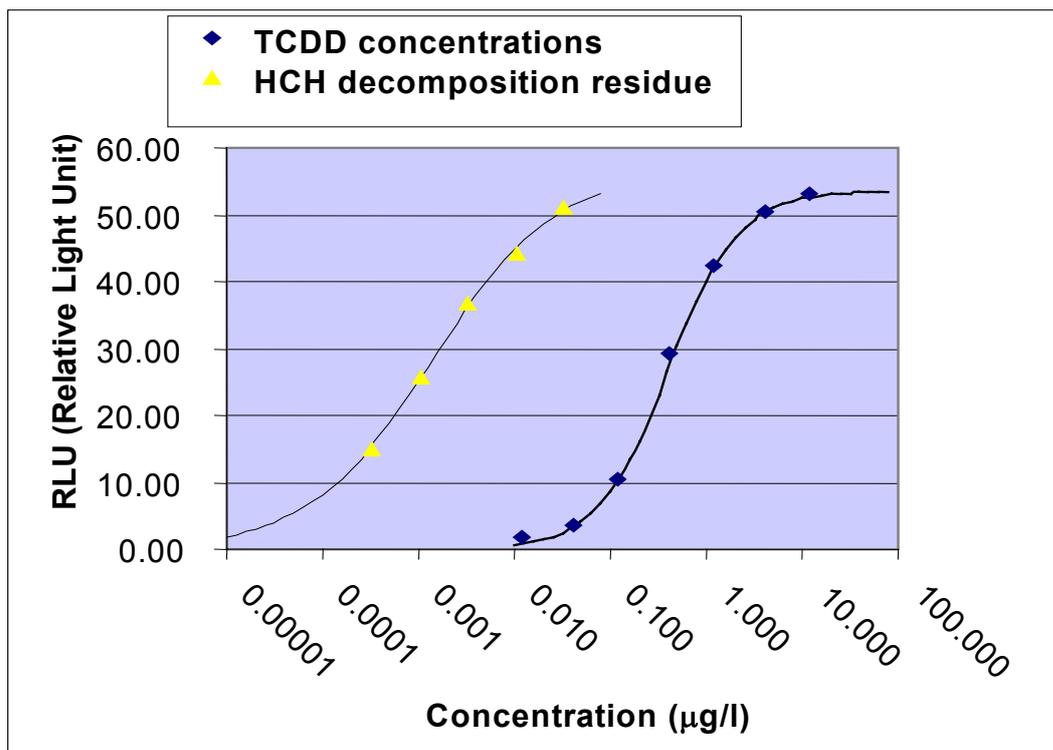


Figure 1: Calibration curve of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) in the DR CALUX[®] bioassay. Concentrations are in µg 2,3,7,8-TCDD TEQ per liter DMSO. Calibration curve of HCH decomposition residue 11798 in the DR CALUX[®] bioassay. Concentrations are in µg 2,3,7,8-TCDD TEQ per liter DMSO.

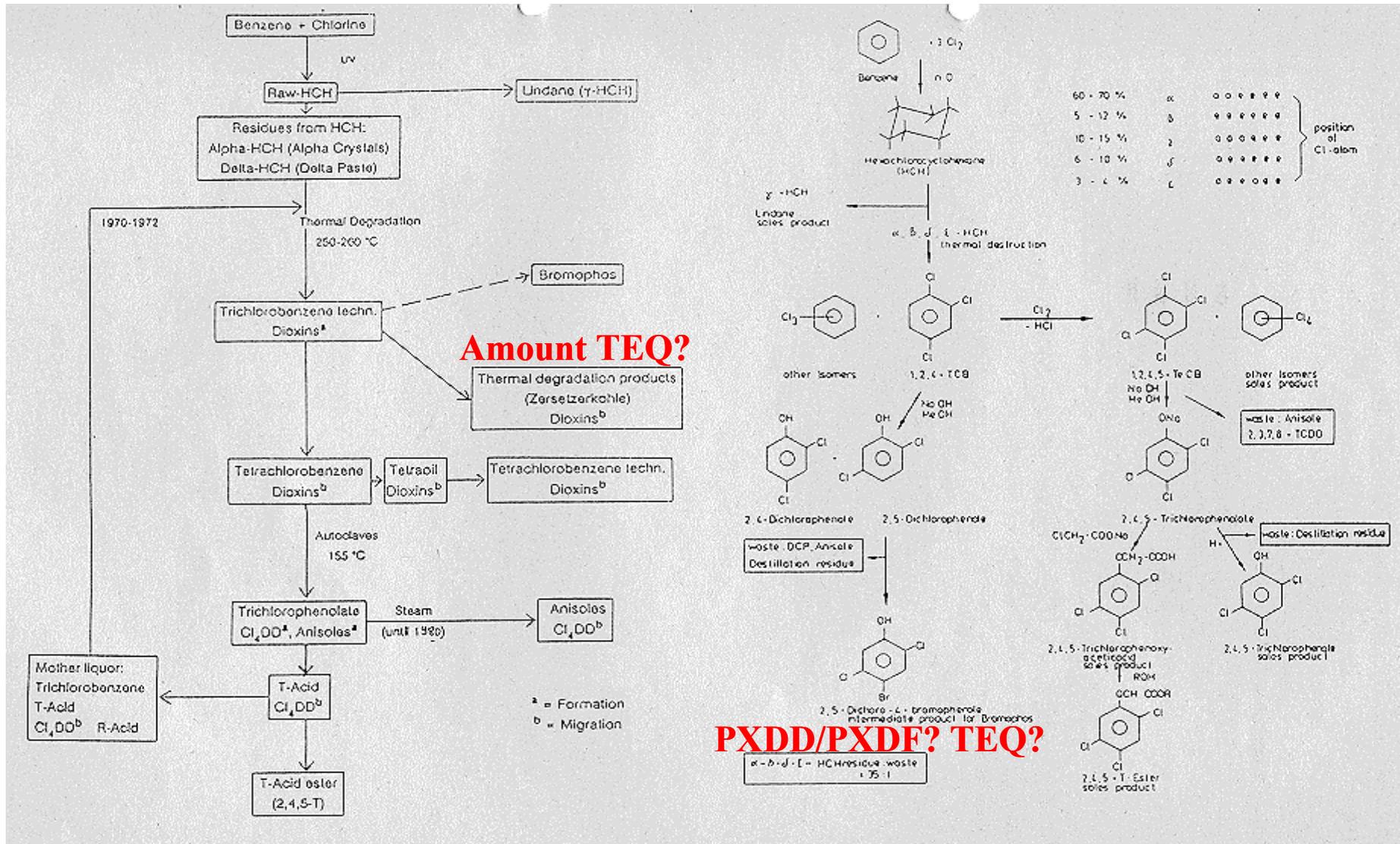


Figure 2: Production of HCH and recycling of HCH residues of a former HCH and pesticide producer in Hamburg^{10, 19} (Including formation and migration pathways of PCDD/PCDF in the production and recycling chain.) and questions addressed by the present study.