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Hexachlorocyclohexane (HCH) Residues in Ya-Er Lake Area, China

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HEXACHLOROCYCLOHEXANE (HCH) RESIDUES IN YA-ER LAKE AREA, CHINA

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Ya-Er lake region samples — soil, mud, rice, rice seed grain, sediment, snail and fish — were analysed for α -, β -, and γ -HCH, according to the standard operating procedure, as used for the necessities of the German Environmental Specimen Bank.¹

The results obtained indicate unexpectedly low concentrations of the HCH-isomers in soil and mud. According to the HCH concentrations in sediment, snail and fish the pollution of the Yanjia lake is significantly higher than the pollution of the Wusi and the Honglian lakes.

The bioconcentration factor of total HCH residues in rice seed grain is 0.3, which indicates that HCH residues in soil could probably be the main pollution source for crops after the banning of HCH use. Meanwhile, 1, 4-, and 1, 2- dichlorobenzenes, 1, 2, 4-trichlorobenzene, 1, 2, 3, 4-, and 1, 2, 3, 5-tetrachlorobenzenes were identified by GC-MS as the potential degradation products of HCH residues in field soil.

KEY WORDS: Ya-Er lake area, HCH residues, soil, mud, sediment, rice, rice seed grain, snail, fish.

INTRODUCTION

Hexachlorocyclohexane is a cheap broad spectrum insecticide, which is widely used in large quantities for agricultural purpose in many developing countries of the world. This extensive use of the persistent pesticide caused considerable contamination in China^{2,3} and has led to deterioration in environmental quality.

Although much research on the environmental behaviour of HCH has been done⁴⁻⁸, most of this research is focused on the γ -isomer, which is the known active constituent of the four common isomers.

It is also important to understand the dynamics of HCH residues and its potential conversion products in various environments, e.g. subtropical climatic conditions. Only very little attention has been focused on the environmental fate of HCH in wet agricultural lands⁹⁻¹². The objective of this study was to identify and quantify HCH

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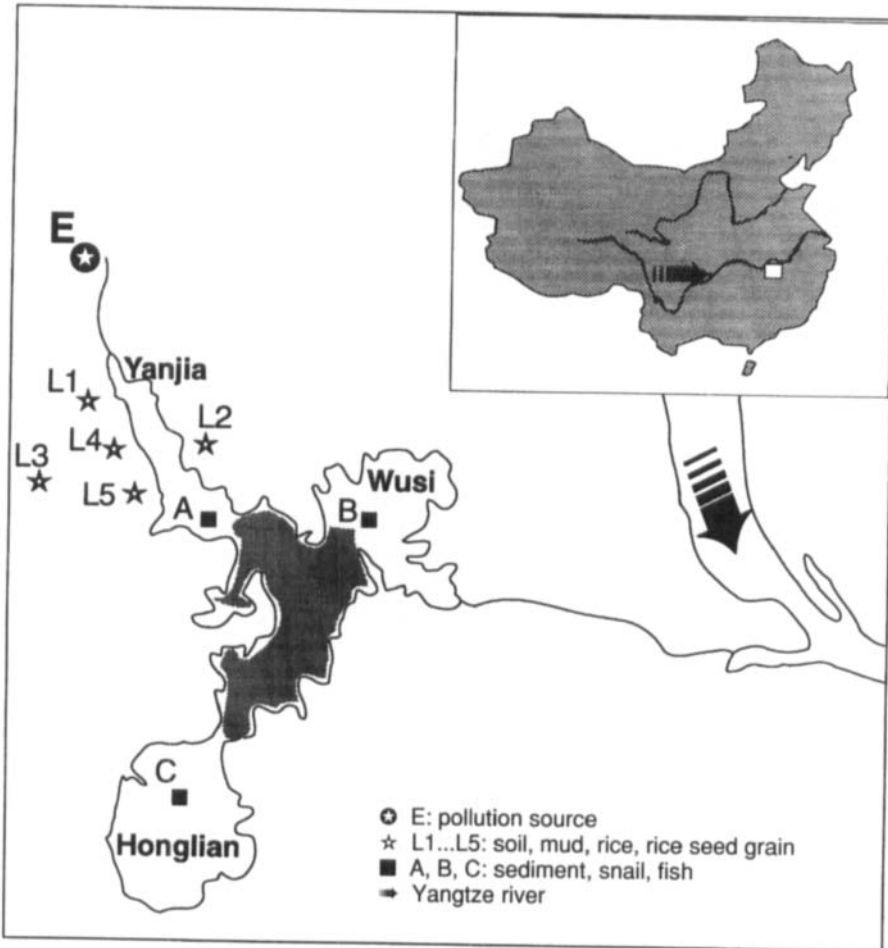


Figure 1 The Ya-Er lake with the outline map; sampling locations; dark area stands for the original lake which is dry land now

residues and their potential chlorinated conversion products in paddy areas, sediments, mud and biota.

Ya-Er lake is located in the western part of Hubei, China (Figure 1). It is a shallow, eutrophic lake in the middle and lower reaches of the Yangtze River. The water originally covered 6000 ha, but now only 2000 ha remain. Along the lake, there are 27,000 ha of farmland with a population of 300,000 people. From 1962 - 1978, the lake was seriously polluted by HCH-isomers and other pesticides because the wastewater from a large chemical plant was discharged into the lake directly.

The Ya-Er lake consists of 13 small lakes with the Yanjia lake the first sublake to be affected by the wastewater. After Yanjia lake, the wastewater then flows through a partially drained area to the Wusi lake and Honglian lake into the Yangtze River. The Yanjia lake was a natural lagoon, which has been divided into a series of five ponds for a 1978 study of oxidative self purification. The present study reports the results of a survey carried out in summer 1991 in the Yanjia lake area.

MATERIAL AND METHODS

Solvents, chemicals and glassware

All solvents used in the study were of analytical grade. Sodium sulphate and sea sand were activated in a furnace at 600°C for 6 hours before use. All the glassware used was cleaned and rinsed three times with acetone and three times with n-hexane prior to use.

Sampling

Samples were taken at mid summer, just after an extreme period of heavy rainfall in August 1991. All the sampling locations for the study are indicated in Figure 1 (five selected vegetable plots and five paddy fields). Soil and mud were collected at a depth of 10 - 20 cm from 10 locations. A Chinese Peterson style sampler consisting of two halves located together with screw bolts, was used to sample sediments from three sublakes of Ya-Er lake. For each sublake, the sediment sample is an aliquot of the mixture from three locations of that lake. Afterwards, the samples were transported to the laboratory for drying at room temperature.

Soil, mud and sediment samples

Each of these samples was prepared in the same manner: 30 g of dried sample were taken and divided into two equal portions. One of these portion was then saturated with double distilled water. The two portions were remixed with 60 g anhydrous sodium sulphate and 30 g sea sand, and were then ground in a mortar to a fine powder.

Rice seed grain samples

Rice seed grain (20 g) were placed in liquid nitrogen for freezing, then pulverized in an ultra centrifugal mill (Retsch, 42759 Haan 1, Germany), equipped with a sieve of diameter 2 mm, at 4000 r.p.m. The resultant powder was then mixed with 40 g of anhydrous sodium sulphate and 20 g of seasand to a homogenous mixture.

Extraction and concentration

A glass column (L: 50 cm; Ø: 1.5 cm) with teflon tap was packed with a 2 cm bed of seasand and then the prepared sample. A further 2 cm of seasand were added; 300 ml of n-hexane/acetone (2:1,v:v) mixture were added from the top of the column via a reservoir; the flow rate of the sample extraction was approximately 1.0 ml/min. Prior to evaporation of the sample extracts, pentachlorobenzene (PCBe) and decachlorobiphenyl (DCB) were added into each sample extract as internal standards.

The extracts were reduced to about 100 ml by rotary evaporation and then to 2 ml in a Kuderna-Danish apparatus; 10 ml ethylacetate were then added to the samples and were re-concentrated again to a volume of 2 ml. This process was repeated three times to ensure no n-hexane remained in the samples. The final extract was submitted to clean-up as indicated below.

Gel permeation chromatography (GPC)

Before starting the GPC step, all the samples underwent glass microfibre filtration (Whatman International Ltd., Maidstone, Great Britain) with the pore size of 0.2 μm , using an automated GPC system composed of a column (L: 100 cm; \O : 2 cm) packed with Biobeads SX8 and mobile phase of cyclohexane/ethylacetate (1:1; v:v). The samples were run under the specified programme discarding the first 55 ml and collecting the following 45 ml of elution. For plant samples, the conditions were the same, except benzene was used as the loading solvent and the mobile phase.

High performance liquid chromatography (HPLC)

After GPC clean-up, the collected solution was concentrated to 2 ml and transferred back to n-hexane by adding 10 ml n-hexane to a Kuderna-Danish apparatus, and reconcentrating three times to a final volume of 2 ml. At last, this extract was filtered before HPLC application as a further clean-up step. The HPLC-system included a stainless steel column (L: 24 cm; \O : 0.8 cm) packed with silicagel SI 60. The mobile phase was 0.1% isopropanol in n-hexane (v/v) and the elution flow rate was 4 ml/min.

Quantification by gas chromatography (GC)

After HPLC clean-up, the samples collected were concentrated again to 2 ml and analysed in Hewlett Packard 5890 A and Carlo Erba Mega Series gas chromatographs equipped with electron capture detector (ECD, 300°C) and autosampler. The samples were run via two fused silica capillary columns coated with bonded phase DB 1701 and DB 5, respectively (1:30 m; i.d.: 0.32 mm). The carrier gas was H_2 with a flow rate of 2 ml/min. The temperature programme was 60°C to 120°C with 30°C/min, 1 min isothermal, then further to 285°C with 7°C/min. Sample amount injected: 1 μl , splitless mode; injector temperature: 285°C.

Identification of chlorinated conversion products of HCH by GC-MS

Mud and soil sample extracts after GC analysis were concentrated 10 - 50 times under a gentle stream of pure nitrogen gas at room temperature for GC-MS analysis. A GC-MS with ion trap system (ITS 40, Finnigan MAT, 28088 Bremen, Germany) was used for the identification. The start temperature was 70°C with a heating rate of 6°C/min and the end temperature was 260°C. The carrier gas was helium at 12 p.s.i. The spectra were obtained under the electron impact (EI) mode.

RESULTS AND DISCUSSION

The analytical results, expressed in dry weight, are listed in Tables 1 and 2. Taking into consideration that from 1962 - 1978 the amount of HCH used in the farmland of the area was more than 20 kg/ha, the obtained concentrations of α -, β -, and γ -HCH are unexpectedly low. It should be especially noted that all observations in rice are lower than 1 ng/g, as well as in riceseed grain, except α -HCH (2.25 ng/g) in location L5 (Table 1).

Table 1 Analytical results of HCH isomers in materials from the Yanjia lake (ng/g dry wt)

Material	Sampling locations*	α -HCH	β -HCH	γ -HCH
Rice seed grain	L1	0,20	0,35	0,15
	L2	0,30	0,55	0,18
	L3	0,20	0,35	0,15
	L4	0,25	0,55	0,17
	L5	0,25	0,25	0,16
Rice	L1	0,50	0,80	0,20
	L2	0,50	0,65	0,10
	L3	0,50	0,80	0,25
	L4	0,45	0,90	0,10
	L5	0,40	0,55	0,10
Mud	L1	1,70	2,90	0,75
	L2	1,00	1,90	0,35
	L3	0,20	0,50	0,20
	L4	1,00	2,10	0,20
	L5	0,35	0,65	0,15
Soil	L1	1,10	1,50	0,40
	L2	1,00	4,20	0,55
	L3	0,40	0,70	0,20
	L4	0,75	2,30	0,35
	L5	1,00	2,10	0,50

* see Figure 1

Comparing the HCH concentrations in the considered materials, using the non-parametric test according to Kolmogorov-Smirnov (Figure 2), it can be seen that there is a continuous trend in accordance with the persistence of the HCH-isomers (γ -HCH < α -HCH < β -HCH).

Non-significant correlations ($p < 0.05$; Spearman) were found between the HCH-isomers in each matrix; this is interesting and means that HCH pollution reaches the sampling locations via several pathways and that several pollution sources exist. Furthermore, non-significant correlations between the concentrations of each HCH-isomer in the several materials are observed.

Using the rank places - non parametric - of the HCH concentrations in the several samples and sampling locations it is able to order the pollution as follows (Figures 1 and 3):

$$[\text{ricesed grain}] < [\text{rice}] \leq [\text{mud}] \leq [\text{soil}]$$

and

$$[\text{L3}] < [\text{L5}] \leq [\text{L4}] \leq [\text{L1}] \leq [\text{L2}]$$

The lowest pollution in the location L3 is probably caused by the distance to the Yanjia lake. L2 is the unique sampling location on the eastern site of the lake.

The analytical results of fish, snail and sediment samples from the lakes Yanjia (A), Wusi (B) and Honglian (C) are indicated in Table 2. The lipid contents of fish and snail tested (calculated in dry weight) were about 15% and 5%, respectively.

Supposing the main pollution source at point E and taking into consideration that the water from Yanjia lake runs off, mainly to the Wusi lake and then to the Yangtze river, the obtained results are according to the expectations.

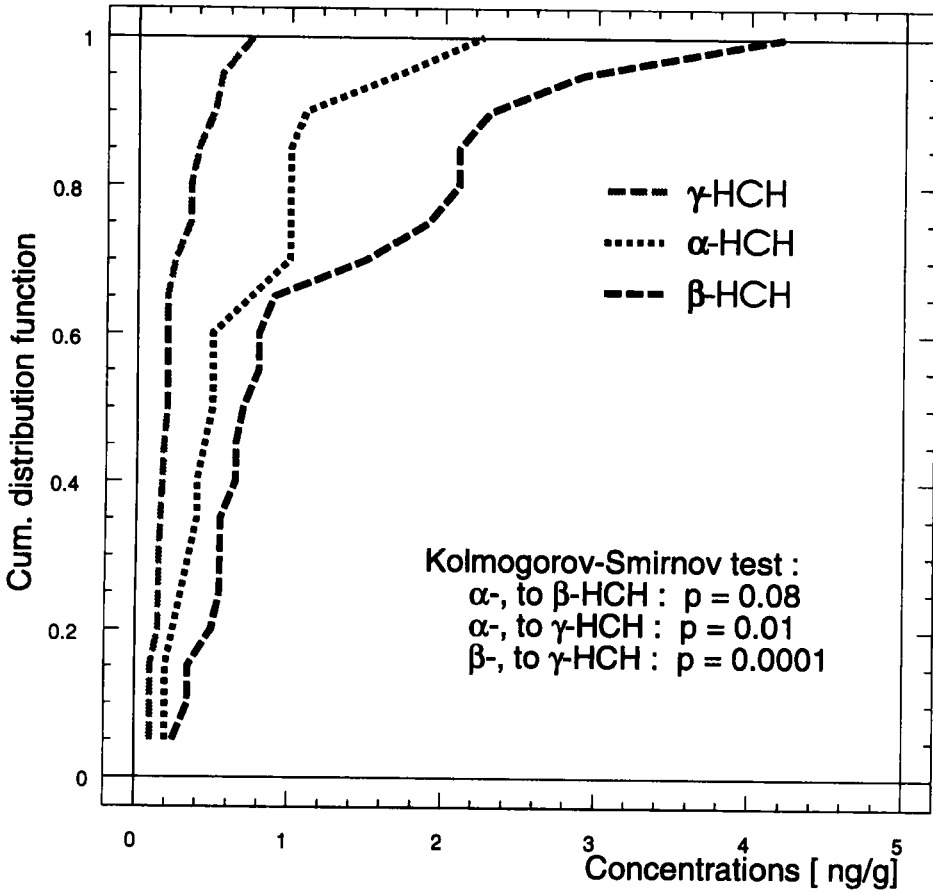


Figure 2 Comparison of the HCH-isomers in all samples from L1...L5.

Table 2 Analytical results of HCH isomers in materials from the Ya-Er lake area (ng/g dry wt)

Sampling locations*	Materials	α -HCH	β -HCH	γ -HCH
Yanjia lake (A)	Sediment	1,35	6,30	0,31
	Snail	4,50	18,00	0,60
	Fish	7,00	42,00	1,15
Wusi lake (B)	Sediment	0,65	1,50	0,20
	Snail	1,40	6,50	0,35
	Fish	2,90	17,00	0,55
Honglian lake (C)	Sediment	1,00	1,10	0,12
	Snail	0,90	3,10	0,30
	Fish	0,70	4,00	0,40

* see Figure 1

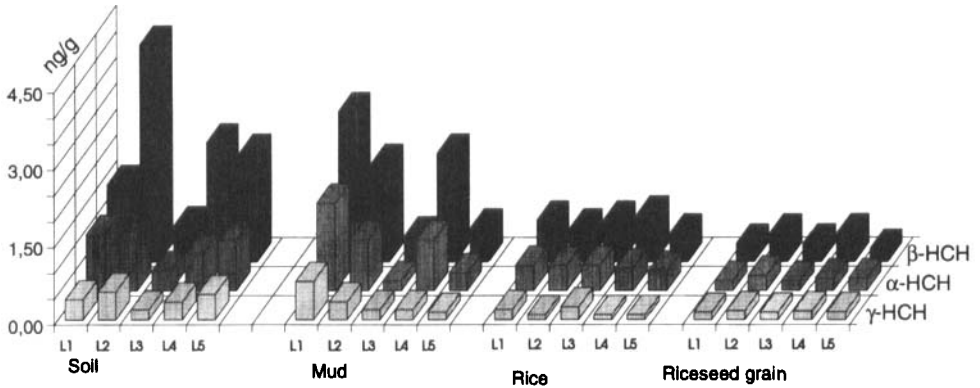


Figure 3 Comparison of the HCH-Pattern around Yanjia lake. L1... L5 : Sampling locations (see Figure 1)

The sum of the measured HCH pollution in the Yanjia lake is about 2.5 times higher than that in the Wusi lake and this is about three times higher than in Honglian lake (Figure 4).

The HCH concentrations in the sediments of the Yanjia lake are much higher than in mud and soil samples taken around the same lake. This may be caused by the sampling mode at a depth of 10 - 20 cm (plow depth about 20 cm) for mud and soil and also by the fact that the Yanjia lake is directly polluted, both, from the source E and from the surrounding area.

The common formulation of the HCH-insecticide for agricultural use in China was a mixture of a powder containing 6% γ -HCH isomer. The ratios of the none-active isomers to the active γ -constituent were as follows: α/γ 4.50, β/γ 0.67¹³. Macral *et al*¹⁴ found that these ratios were changed rapidly after HCH was applied into field soil. The observed ratios in this study are listed in Table 3.

To look for the transfer of HCH residues from contaminated soil into riceseed grain, which is the staple food for Asians, the riceseed grain samples harvested in June 1991,

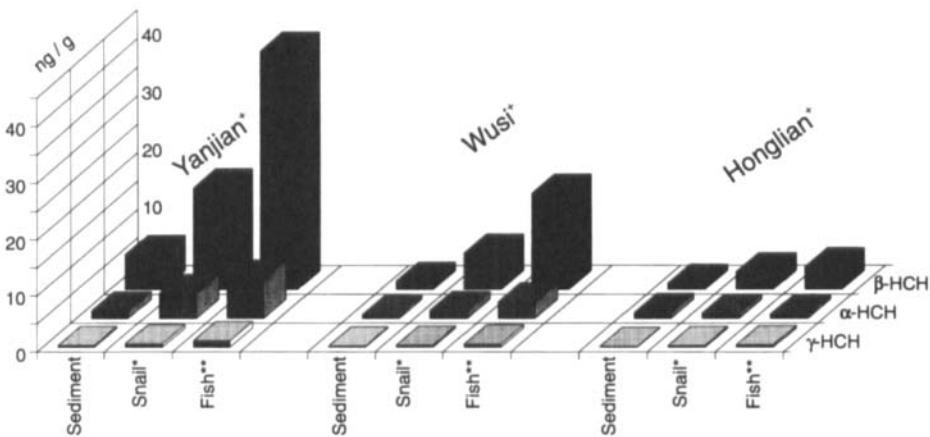


Figure 4 Comparison of the HCH-Pattern in Ya-Er lake.

* snail flesh ; *Bellamy aerugiosa* ** fish flesh ; *Hypophthamichthys molifrix* + sublakes (see Figure 1)

Table 3 Ratios of α -, and β -HCH to γ -HCH in soil and mud.

	α/γ	β/γ	
6% γ -HCH-formulation*	4.50	0.67	22.5 kg/ha in 1962 – 1978
soil of vegetable plot	2.13	5.05	residues of HCH under anaerobic conditions
mud of paddy field	3.06	5.45	residues of HCH under semianaerobic conditions
sediment of Yanjia lake	4.39	20.42	residues of HCH under anaerobic conditions

* Content of the original formulation

grown in selected paddy field soil, were collected at the same time as the soil samples. The bioconcentration factor of HCH residues was 0.3 in the edible portion of the crops. The HCH residues in soil could probably be the main pollution source for crops after the banning of HCH application as well as the use of the water from Yanjia lake for agricultural irrigation.

In the soil samples, the following chlorobenzenes were identified by GC-MS: 1, 2- and 1, 4-dichlorobenzenes (only qualitatively); 1, 2, 4- trichlorobenzene (1,5 ng/g); 1, 2, 3, 4- and 1, 2, 3, 5- tetrachlorobenzenes (0,5 ng/g and 0.3 ng/g respectively). We proposed the pathway steps of HCH residues in field soil of Ya-Er lake area as shown in Figure 5. The primary bioconversion product pentachlorocyclohexane (PCCH) which is expected not to be stable in the environment could not be identified. This is in a good agreement with Bachmann *et al*¹¹ for α -HCH in contaminated soil under anaerobic conditions.

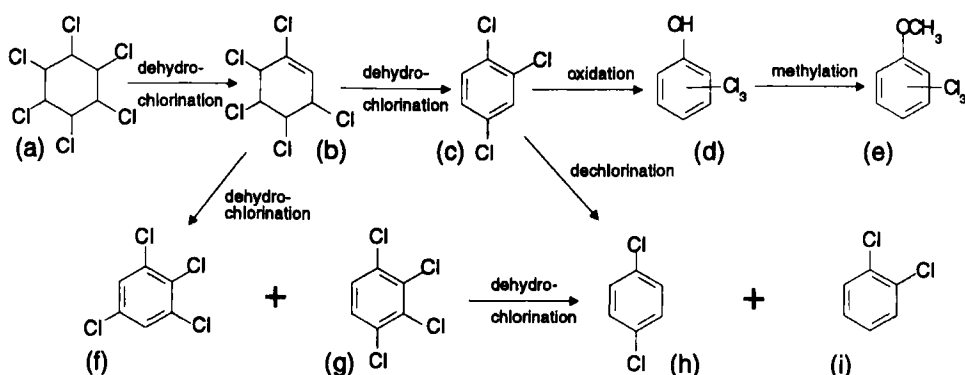


Figure 5 The pathway steps of HCH-residues in field soil. hexachlorocyclohexane (a); pentachlorocyclohexene (b); 1, 2, 4- trichlorobenzene (c); trichlorophenol (d); methoxy-trichlorobenzene (e); 1, 2, 3, 4- tetrachlorobenzene (f); 1, 2, 3, 5- tetrachlorobenzene (g); 1, 4- dichlorobenzene (h); 1, 2-dichlorobenzene (i)

CONCLUSIONS

The reported facts have to be regarded as screening results to define a strategy of sampling as well as analytical requirements (sample amount, sampling pattern). The unexpected low HCH concentrations found have to be confirmed by further investigations and it is necessary to extend the number of pesticides to be analysed.

Acknowledgements

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