Study of sorption, biodegradation and isomerization of HCH in sediment/water system

W.Z. Wu [1,], Y. Xu[1], K.-W. Schramm[2], A. Kettrup[2]

[1] State Key Laboratory of Freshwater Ecology and Biotechnology, Institute of Hydrobiology, Wuhan 430072, China

[2] GSF-Forschungszentrumn für Umwelt und Gesundheit, Institut für Ökologische Chemie, Ingolstädter Landstr. 1, D-85764 Obschleißheim, Germany

Introduction

Due to the low price, hexachlorocyclohexane (HCH) was produced in considerable amount and widely used as a board spectrum insecticide in many countries of the world. In China, the annual production of HCH once reached 200,000 tons, in spite of the ban of the use of HCH since 1983. In China, the farmers took the powder formulation of HCH, the mixture of α, β, γ and δ four isomers to spray it into the agriculture fields. Meanwhile, lakes were seriously polluted by HCH because the waste water from chemical plant was discharged directly into the lake. Through a long term movement and transfer, the most of them was finally deposited into sediment.

In order to understand the releasing behavior of HCH from field sediment and its long-term effect to aquatic environment, as well as verifying the obtained results from environment, the sorption, biodegradation and isomerization of α and γ-HCH isomers under aerobic and anaerobic conditions were reported in this paper.

Experimental Methods

The 20cm depth surface sediment was taken from East lake, Wuhan, China, water depth 1.5 meters, temperature 18.5^0C. Sediment was sieved with 1mm filter, then centrifuged 5mins with rotation rate of 4500rpm/min, the supernatant was discarded, the sediment was ready for test within a few days. Some physicochemical parameters of the lake sediment are given below: pH 7.42, particle size ≤ 0.1mm, total organic carbon 2.18%, no HCH by GC detection.

The purity of HCH standard was more than 99.99%. The concentration of stock solution was 400mg/ml in acetone. Glucose was analytical grade; the yeast extract was pure powder (Huamei Biotechnology Company, China).

In each group, 500g centrifuged fresh sediment mixing with 400ml distilled water was put in a 2liter glass flask. HCH was added at 4mg/l concentration under the stirring. The magnetic stirring speed was controlled at 200 rpm. The temperature was 20 ± 2^0C; pure nitrogen and

oxygen were connected inside the system at the flow rate of 20ml/min. The test period was 48 days. During the test, the oxidation-reduction potential (Eh) variations were observed by means of Pt electrodes monitoring.

Being predominant components in Chinese commercial product of HCH (α: 67%; β: 10%; γ: 15%; δ: 8%), pure α and γ-HCH were selected for the test. The experiment was divided into four groups: I, α-HCH under anaerobic condition; II, α-HCH under aerobic condition; III, γ-HCH under anaerobic condition; IV, γ-HCH under aerobic condition.

The organic nutrient was composed of glucose mixed with yeast powder in 50ml distilled water, then added to the sediment after system had been running for 30 days. There were two addition amounts for the parallel experiment from 30the day: (A) 2g glucose and 2g yeast powder, (B) 0.5g glucose and 0.5g yeast powder.

All samples for HCH analysis were according to the standard operation procedure (SOP) for the European Environmental Banking (ESB) in assessment of environmental chemicals [1].

Results and Discussion

1. Aerobic and anaerobic state control for the sediment/water system

After running 24 hours, strong odor occurred in group 1 and III with the Eh -215 to -335 mV (v.s. SCE), but not in the group II and IV with the Eh 225 to 325 mV (v.s. SCE). The Eh indicated the concentration of oxygen in the sediment/water system. As the Eh ranged from 200 to 300 mV, the concentration of oxygen was in the range of 0.1 mg/l to 10.3 mg/l; when the Eh was below 100mV, there was almost no oxygen found in the system [2, 3, 4]. Therefore, by means of the Eh variation, the group 1 and III were maintained in anaerobic condition, II and IV in aerobic condition, respectively.

2. Sorption equilibrium of HCH in the sediment/water system

After HCH was added to the system, there was continuous partitioning between sediment and water, and it was able to reach to the dynamic equilibrium state after a time. It is very important that the system reaches equilibrium state in the study of HCH sorption behavior. Figure 1 shows the HCH concentrations in sediment phase (Figure 1a) and water phase (Figure 1b) at the different time intervals.

The sorption behavior can be described by Freundlich empirical equation:

$$C_t = k_d * C_{eq}^{1/n} \quad \dots \dots \dots \dots \dots (1)$$

where:

C_t: HCH equilibrium concentration in sediment phase (ppm)

C_{eq}: HCH equilibrium concentration in water phase (ppm)

k_d: adsorption coefficient

n: empirical constant

Making logarithm to equation (1), then the following equation is obtained,

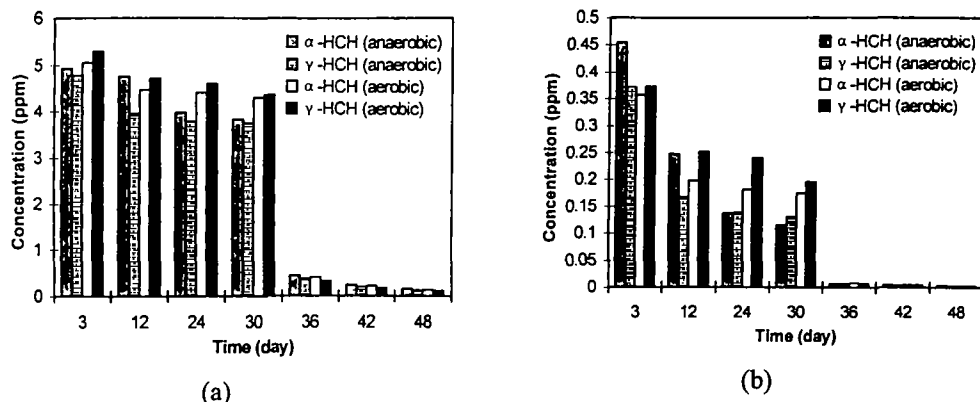$$\log C_t = \log k_d + 1/n * \log C_{eq} \quad \dots \dots \dots \dots (2)$$

(a)

(b)

Figure 1: (a) HCH concentration in sediment (ppm)   (b) HCH concentration in water (ppm)

Table 1:Adsorption coefficient (kd), 1/n, correlation coefficient (r) and Freundlich equation

	k_d	1/n	r	Freundlich equation
I	13.46	0.734	0.9801	$logC_t=1.1289+0.7336 * logC_{eq}$
II	14.85	0.776	0.9912	$logC_t=1.1718+0.775 * logC_{eq}$
III	15.13	0.790	0.9936	$logC_t=1.1797+0.7903 * logC_{eq}$
IV	13.98	0.799	0.9965	$logC_t=1.1455+0.7996 * logC_{eq}$

Based on the data from Figure 1 and equation (2), kd, 1/n and Freundlich equation are calculated, the results are listed in Table 1. The results indicated the partition equilibrium of HCH between sediment and water could be observed after 3 days. The adsorption coefficient kd showed HCH was able to be strongly adsorbed in the sediment. This means the sorption by the sediment plays a very important role when HCH is transferred into the water phase rich in the sediment.

As the organic nutrient was added on 30th day, the HCH concentration in the water phase was dramatically reduced, however the system still kept the equilibrium state. This could be explained: after the organic nutrient addition, the rapid increase of microorganism which dramatically degraded HCH in water phase speeded up transfer of HCH from sediment to water. Therefore, the equilibrium state can be maintained [5].

3. Degradation dynamics of HCH in sediment
The regularity of HCH degradation is assumed to be a second grade dynamics model [6]:

$$-\frac{d[t]}{dt} = k_2[Ct]^2 \quad ....(3)$$

$$\text{then}: \quad \frac{1}{Ct} = k_2t + m ....(4)$$

by equation (4), the half life can be calculated as following:

$$t_{1/2} = \frac{2/C_0 - m}{k_2} \dots\dots\dots(5)$$

where:

k_2: the coefficient of HCH degradation dynamics

m: constant

Ct: HCH concentration in sediment (ppm)

t: time (days)

The statistical results are listed in Table 2. Table 2 shows I, II, III, IV four groups have good correlation coefficient (r > 0.90). It demonstrates HCH degradation in sediment fits the second grade dynamic regularity. The degradation speed of HCH is related with initial concentration of sediment, the higher concentration the more rapid is the degradation, this phenomenon can be explained by the above model [7].

4. Effect of organic nutrient on HCH degradation

On 30th day, the mixtures of glucose and yeast were added to the system, the time course of HCH concentration in sediment is shown in Figure 2. Based on the obtained data (Figure 2) and equation (4) (5), the statistic analytical results are calculated and shown in Table 3. It indicates the degradation behavior of HCH in sediment still follows the regularity of second grade dynamics mode after the nutrient was added to the system. In summary, the following conclusions are obtained: the degradation of HCH mainly is a biotic process, and the organic nutrient can speed up the degradation of HCH both in aerobic and anaerobic conditions, but the regularity of degradation remains the same, the organic nutrient merely enhancing the biomass and activities of the microorganisms in the sediment.

Table 2: Several parameters and dynamics equation of HCH degradation in sediment under aerobic and anaerobic conditions

	C_0 (ppm)	k_2	m	r	$t_{1/2}$ (days)	equation
I	4.93	0.0024	0.1908	0.9761	89.58	1/Ct=0.0024t+0.1908
II	4.77	0.0021	0.2120	0.9254	86.08	1/Ct=0.0021t+0.2120
III	5.06	0.0012	0.2003	0.9011	162.4	1/Ct=0.0012t+0.2003
IV	5.29	0.0014	0.1890	0.9498	135.0	1/Ct=0.0014t+0.1890

From Table 2 and Table 3, the results demonstrate that the degradation of γ-HCH is more rapid than that of α-HCH both under aerobic and anaerobic condition. Whereas the degradation of α and γ-HCH under anaerobic condition is almost the same as that in aerobic condition, or even slower than that in aerobic condition. This phenomenon can also be found from other reports [8]. The reason that α-, γ-HCH were more easily degraded in aerobic condition than that in anaerobic condition was due to the high concentration of α-, γ-HCH inhibiting the population of methyl microorganisms. Biological mineralization plays an important role in the degradation of α-HCH. A. Bachman et al. [8] found the degradation of α-HCH in aerobic condition was twice more rapid than that in anaerobic condition, but the degradation of β-HCH was still very slow in this case.

The substance of HCH degradation by microorganisms is certain enzymes. The difference of degradation between α and γ-isomers was caused by different enzyme selections.
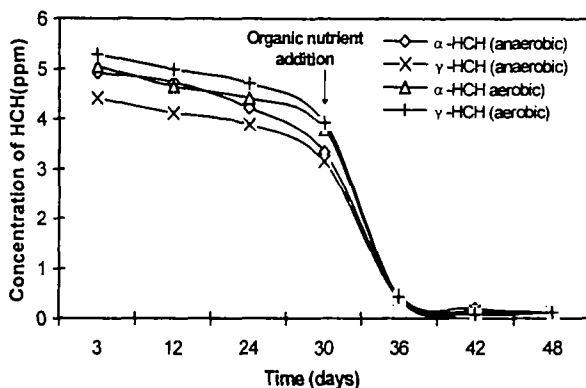

Figure 2: Time course of HCH concentrations in sediment/water system

Table 3: Several parameters of HCH degradation in second-grade dynamics mode in sediment/water system fortified with nutrients

	Test (A)				Test (B)			
	I	II	III	IV	I	II	III	IV
C_0	3.8213	3.7311	4.2840	4.3356	3.8982	4.4592	3.4036	3.2146
k_2	0.3169	0.4023	0.4426	0.4653	0.0329	0.0838	0.1671	0.1933
m	0.2586	0.2399	0.3879	0.2044	0.2542	0.1597	0.2090	0.3192
r^2	0.9994	0.9988	0.9405	0.9988	0.9992	0.9763	0.9803	0.9996
$t_{1/2}$	0.8356	0.7361	0.7256	0.5579	7.8663	3.4465	2.2658	1.5675
Equation	$1/C_t=$ 0.32t+0.26	$1/C_t=$ 0.40t+0.24	$1/C_t=$ 0.44t+0.39	$1/C_t=$ 0.47t+20	$1/C_t=$ 0.03t+0.25	$1/C_t=$ 0.03t+0.16	$1/C_t=$ 0.17t+0.21	$1/C_t=$ 0.19t+0.32

5. Isomerization of α-HCH

Figure 3 shows the isomerization of α-HCH at different time intervals. It indicates that there are three isomerization ways: $\alpha \rightarrow \beta$, $\alpha \rightarrow \gamma$ and $\alpha \rightarrow \delta$, because β-, γ- and δ-isomers were able to be detected on the 3rd day after the test was started. In addition, the concentrations of these isomers were increased with the time passed. In view of the quantitative data, it is argued that the isomerization of α-HCH to β-isomer is the main path among these three ways. The isomerization percentage (I %) is calculated by the following expression:

$$I\% = \frac{\text{Concentration of } \beta - \text{isomer}}{\text{total HCH concentration in different time intevals}} * 100\%$$
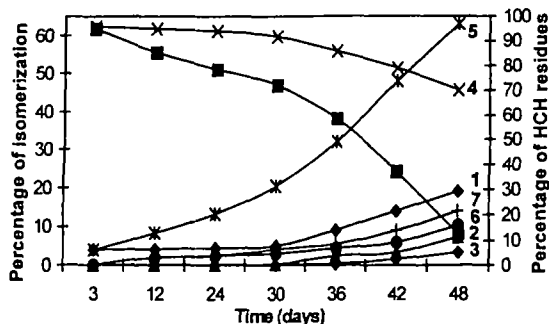
Figure 3: Isomerization of HCH in laboratory system
Anaerobic: 1. α → β, 2. α → γ, 3. α → δ, 4. α
Aerobic: 5. α → β, 6. α → γ, 7. α → δ, 8. α

It was found that the isomerization of α-HCH to β-isomer finally reached about 50% on the 48th day. In comparison of the results obtained under anaerobic and aerobic conditions, they showed the very close I % at the beginning (3-12 days) of the test, but finally the isomerization percentages of α-HCH under aerobic condition were higher than anaerobic. In the test, the effect of organic nutrient addition on the HCH degradation rate was observed (refer to Figure 2). After the addition of organic nutrient, the isomerization of α-HCH in the above three ways were greatly increased. In Figure 3 the effect of organic nutrient addition on the disappearance of HCH also was presented. It is clear that the disappearance of α- and γ-HCH is dramatically speeded up after organic nutrient addition. This is due to the fact that the amount of microorganism is greatly increased after the addition of nutrients. The speeding up of the isomerization of HCH proves that the reaction mainly belongs to biological process. It was found β-HCH was the most persistent in the field environment [9, 10], that is due to the isomerization of α-HCH in a big amount to β-HCH, besides its chemical stability.

References:
1. Oxynos K. et al., **Specimen Banking**, Springer Verlag Berlin (New York), P127 (1992).
2. Edwards K. et al., **Ann.Biol.** 46: 457-464 (1958).
3. Hargrave B., **Interactions Between Sediments and Fresh Water** (Amsterdam) 6-10 (1976).
4. Mclachlan J. et al., **Freshwater Biol.** 6: 59-67 (1976).
5. Hunb H. et al., **Environ. Sci. Technol** 24: 1349-1354 (1990).
6. Wang J.H. et al., **Environ. Chem.** 8: 20-27 (1989).
7. Yao J.R. et al., **Journal of Ecology** 6: 33-36 (1987).
8. Bachmann A. et al., **Appl. Environ. Microbiol.** 54, 548-554 (1988).
9. Jose W. et al., **Bull. Environ. Contam. Toxicol.** 45: 681-688 (1990).
10. Wu W.Z. et al., **Chemosphere** 34: 191-202 (1997).