

# Factors Affecting Disappearance of BHC Isomers From Rice Field Soil

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BHC (1,2,3,4,5,6-hexachlorocyclohexane) was widely used in Japan during the 1950's and 1960's for rice plant pest control. In view of the contamination of cow's milk with this chemical, which was proved to be mainly derived from residues in rice straw, use of this insecticide in rice fields was banned in 1970. The BHC levels in milk, however, did not show rapid decrease and this chemical was found even in untreated rice plants, which suggested that BHC remaining in soils had been absorbed by the plants.

Gamma-BHC has been shown to be readily degraded in submerged soils. However, because of the use of technical BHC in dust and granular formulations in Japan,  $\beta$ -BHC was found at relatively high levels in soils, rice straw, and cow's milk, though  $\gamma$ -BHC levels were very low.

Considerable differences have been shown among BHC isomers in physical properties such as vapor pressure and solubility in water. Their chemical properties are also different. MacRae et al.<sup>1)</sup> reported that persistence of the  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  isomers of BHC in submerged tropical soil was between 70 and 90 days.

Based on the reported little difference among the isomers in persistence in the soil, Tatsukawa et al.<sup>2)</sup> explained high residue levels of  $\beta$ -BHC as a result of volatilization of other isomers and concentration of the  $\beta$  isomer before deposition on the soil. Their interpretation might be applied to the case of dust treatments, but would not be applica-

ble to the case of granular treatments.

In attempts to obtain information on persistence of BHC isomers in rice field soil and on effective measures to reduce residue levels of these isomers, studies were conducted in the author's laboratory on factors affecting disappearance of BHC isomers from flooded soil and on differences in these factors among the isomers. This paper is a brief description of the results obtained<sup>3,4,5)</sup>.

Experiments were carried out mostly in a greenhouse around 25°C on various factors which BHC isomers were supposed to be affected following granular application into soil surface water. Raw clay loam soil from a rice field was used. It was of alluvial origin and had a total carbon content of 1.93%. BHC solutions were prepared by 100-fold dilution of acetone solutions with water, though  $\beta$ -BHC was in suspension in some cases.

## Release from granules

Comparisons were made at intervals of concentrations of BHC isomers after BHC granules containing the  $\gamma$  isomer by 6% were dropped into water. The  $\delta$  and  $\gamma$  isomers showed the highest concentrations, while the  $\beta$  isomer was practically undetectable in water. The ratio of the amount in solution to the total amount in granules was largest for the  $\delta$  isomer, followed by the  $\gamma$  isomer, but was very low for the  $\alpha$  isomer due to its predominance in the formulation.

### Disappearance from water surface

Disappearance from water surface was investigated as one of the possible ways through which BHC isomers released from granules were lost. Fig. 1 shows the result obtained

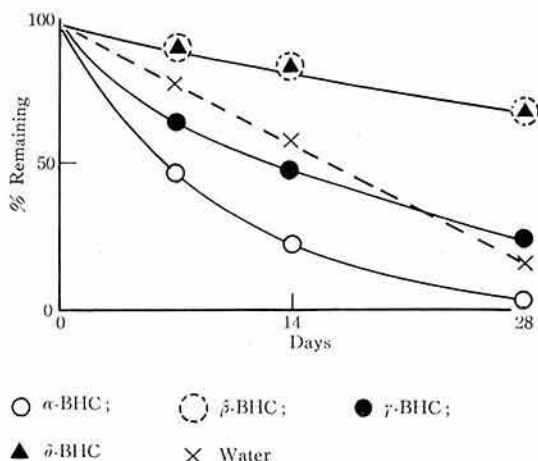


Fig. 1. Disappearance of BHC isomers from water surface

with a solution containing the four isomers each at 0.05 ppm. Alpha-BHC disappeared most rapidly, followed by  $\gamma$ -BHC, while  $\delta$ - and  $\beta$ -BHC were lost very slowly and were concentrated as water evaporated. The slow disappearance of the  $\delta$  isomer, despite its high vapor pressure, should be ascribed to its relatively high solubility.

### Translocation from standing water to soil

Water containing the four BHC isomers at 1.0 ppm was introduced onto flooded, leveled soil, and the surface water and the soil layer were analyzed at intervals for the isomers. In the presence of sodium azide, amounts of the four isomers in water decreased, while those in the soil layer increased during the first two weeks, the changes being mainly attributable to the adsorption of the isomers by the soil.

In the absence of the azide, the  $\alpha$ ,  $\beta$ , and

$\gamma$  isomers gave similar curves, but the amount of the  $\gamma$  isomer in the soil layer decreased considerably during the second week probably due to degradation in the soil (Fig. 2).

### Partition between soil and water

Comparisons were made of the partition of BHC isomers between soil and water with two soils. One was the clay loam soil of alluvial origin, and the other a silt loam soil from volcanic ash with a high total carbon content. Aqueous solutions (or suspensions) of each isomer were shaken with air-dried soil for two hours at 25°C.

The amounts of the isomers partitioned on unit weight of the soil were then calculated from the differences between the initial and final concentrations and plotted logarithmically against the final concentrations in water.

Linear relations were obtained with one exception as shown in Fig. 3, satisfying the Freundlich's adsorption isotherm,  $A=kC^n$ , and proving that BHC isomers partitioned on the soil were adsorbed by the soil. With the alluvial soil,  $\beta$ -BHC did not give a linear relation within the concentration range, which was ascribed to the relatively low adsorptivity of the soil and the low solubility of the isomer in water.

### Movement in soil

In relation to adsorption by soil, BHC isomers were tested for movability in a soil column. Water containing 62.5  $\mu\text{g}$  each of the four isomers was placed on a soil column of 8.5 cm long and 3.6 cm in diameter. After being percolated with a dilute sodium azide solution, the column was divided horizontally into four equal portions and analyzed.

The  $\beta$  and  $\delta$  isomers were found remaining in the top layer. On the other hand, the  $\alpha$  and  $\gamma$  isomers were distributed in the upper two layers, suggesting that the two isomers were carried downward by the percolated water.

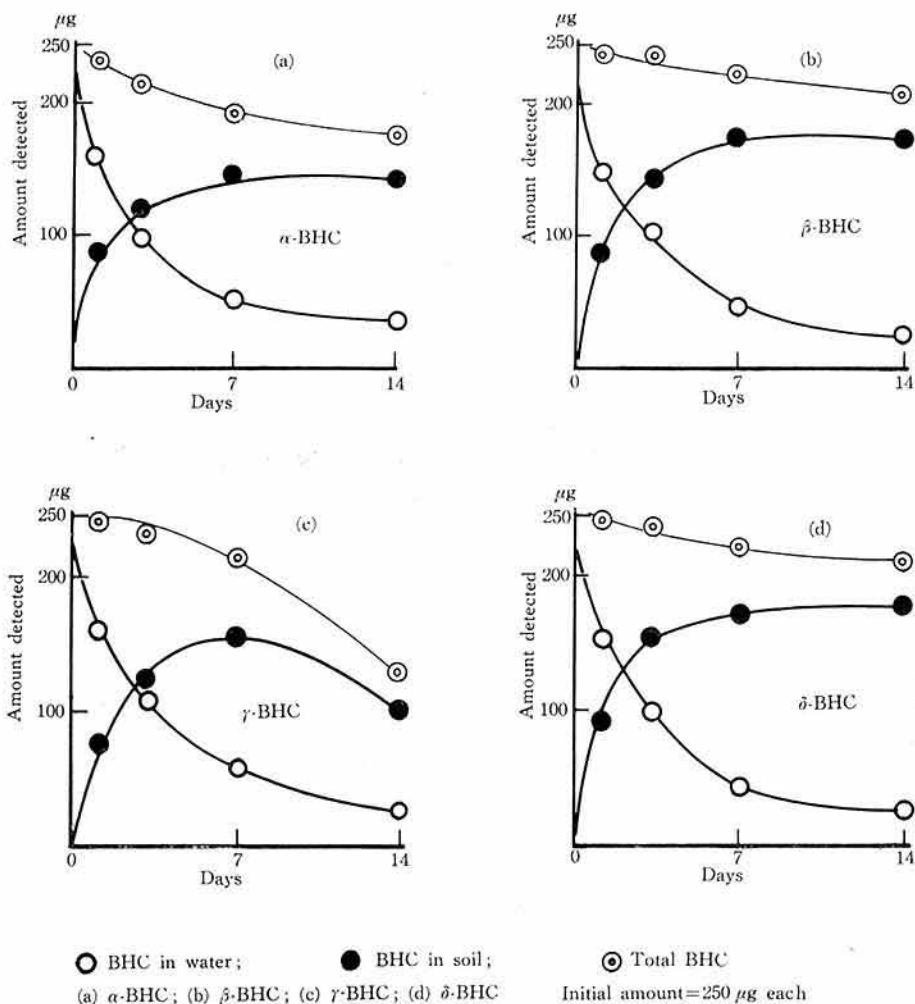


Fig. 2. Translocation of BHC isomers from standing water to soil

During the plant-growth season, daily water percolation of 2-3 cm is observed in many Japanese rice fields. The  $\alpha$  and  $\gamma$  isomers may be carried downward by the percolation water and distributed widely in the soil where these isomers are exposed to microbial attack.

#### Degradation in soil

Mixtures of soil and water were treated with the four isomers and incubated with or without sodium azide. As shown in Fig. 4,  $\gamma$ -BHC disappeared most rapidly, followed by

$\alpha$ -BHC, whereas  $\beta$ - and  $\delta$ -BHC slowly disappeared under nonsterilized conditions. In the presence of the azide, all of the four isomers disappeared very slowly with little difference among the isomers in the disappearance rate.

Rapid rates of disappearance of these isomers under nonsterilized conditions as compared with those in azide-treated soil suggested that a microorganism or microorganisms play an important role in the disappearance of BHC isomers in flooded soil.

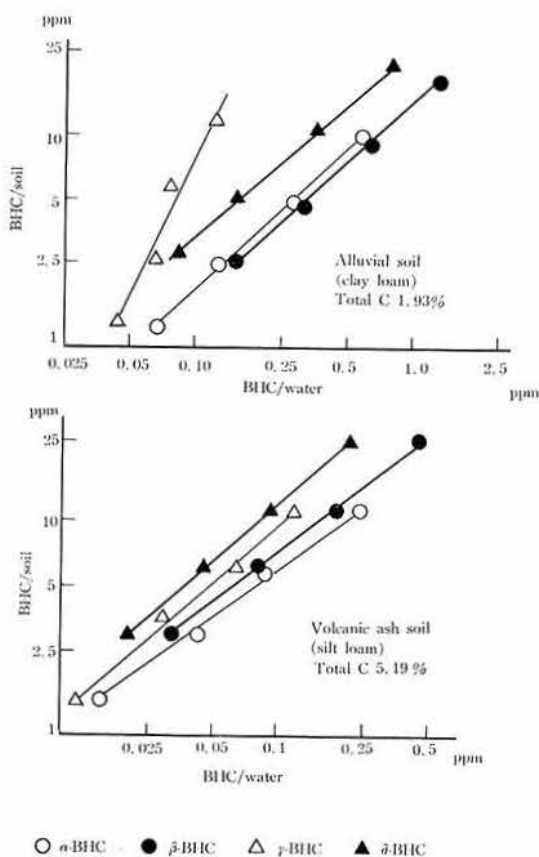


Fig. 3. Partition of BHC isomers between soil and water

### Degradation products

As a degradation product of  $\gamma$ -BHC, Yule

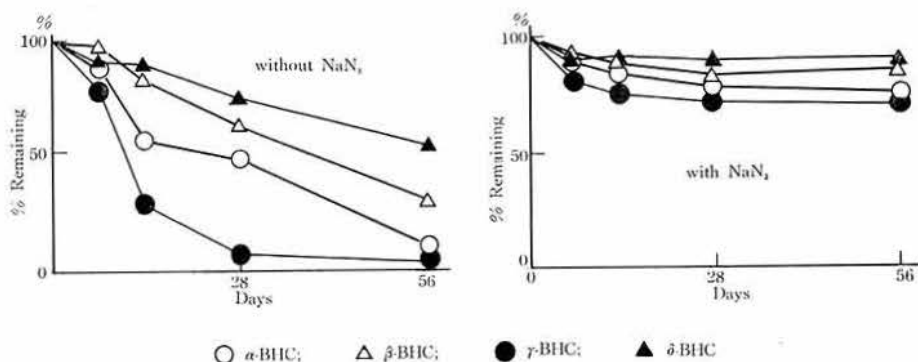


Fig. 4. Degradation of BHC isomers in flooded soil

et al. observed the formation of  $\gamma$ -PCCH ( $\gamma$ -2,3,4,5,6-pentachloro-1-cyclohexene) in percolated and standing moist soil treated with lindane. However, it remained unknown whether or not  $\gamma$ -BHC is degraded through the same substance under submerged conditions.

The author and his coworker succeeded in obtaining a degradation product different from  $\gamma$ -PCCH in flooded soil treated with the isomer<sup>3</sup>). Based on its gas chromatogram, melting point, and mass and infrared spectra, the products was identified as  $\gamma$ -BTC ( $\gamma$ -3,4,5,6-tetrachloro-1-cyclohexene).

Gamma-BTC was detected only in small amounts even at its maximum level, which may be explained by the fact that this compound is much more unstable than the parent insecticide in flooded soil.

The formation of  $\gamma$ -BTC was also observed in potted soils four weeks after the surface water was treated with lindane while rice plants were growing on them under common agricultural practice.

Degradation of  $\gamma$ -BHC through  $\gamma$ -BTC may, therefore, have occurred actually and commonly in rice field soils, and contributed to the reduction of  $\gamma$ -BHC levels.

Recently, a similar product has been detected in flooded soil treated with  $\alpha$ -BHC and tentatively identified as  $\delta$ -BTC based on its retention times in gas chromatography<sup>4</sup>).

## Conclusion

In summary,  $\gamma$ -BHC has favorable properties from the standpoint of decontaminating rice field soils, such as rapid release and diffusion from granules, volatility from water surface, relatively low affinity to soil, movability in soil, and high degradability in flooded soil. Beta-BHC, on the contrary, has unfavorable properties with these respects, resulting in prolonged persistence on or near the soil surface.

These studies were only concerned with persistence of BHC applied as granules in flooded soils. The results obtained do not necessarily mean that  $\gamma$ -BHC can be used without adverse effects. Various other factors such as possibility of contaminating air and water, toxicity to natural enemy, availability of more degradable insecticides should be taken into consideration in practical use of this substance even as the pure isomer. To discuss them is, however, beyond the purpose of this paper.

Recently,  $\gamma$ -BHC has been found to be very toxic to spiders, predators of planthoppers.

Since planthoppers are serious rice plant pests in Japan,  $\gamma$ -BHC would not be used in Japanese rice fields again even in the purified form.

## References

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