Persistence of BHC (1, 2, 3, 4, 5, 6-Hexachlorocyclohexane) and Dieldrin Residues in Field Soils

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Introduction

Occurrence and persistence of organochlorine pesticides in the environment were studied by many researchers. BREIDENBACH et al. (1967) reported the residue of chlorinated hydrocarbon pesticides in major river basins of U.S.A., and the residues of these pesticides in rain-water were also detected (WHEATLEY and HARDMAN 1965, ABBOTT et al. 1965, WEIBEL et al. 1966, TARRANT and TATTON 1968, BEVENUE et al. 1971). BHC residues of rivers and tap water in the Kitakyushu district were reported at a concentration of sub-parts per billion (SUZUKI et al. 1972 and 1974a), and these levels of BHC were significantly higher than previously reported. ABBOTT et al. (1965) found the DDT, lindane and dieldrin residues in the atmospheric environment of Great Britain at parts per trillion levels.

The pollution by organochlorine pesticides in soil was introduced by the direct incorporation of pesticides to control the soil inhabitating pest and the fallout from crop application of pesticides. Many reports on the organochlorine pesticide residues in field soil were published (HARRIS et al. 1966, SAHA et al. 1968, McLANE et al. 1971, MULLINS et al. 1971, KIIGEMAGI and TERRIERE 1972, KUHR et al. 1972, SUZUKI et al. 1973). Degradation of these pesticides in soil depended on pH, organic matter content, type, structure, clay content, mineral ion content and upland or flooded conditions. Four-step processes on pesticide break-down until pesticide became a terminal residue were suggested (EDWARDS 1966).

In this paper, the persistence of the terminal BHC and dieldrin residues in three different field soils in which these pesticides were applied prior to 1971, there being no history of these pesticide applications afterwards, and the degradation of BHC isomers in field soil applied with the BHC pesticide at 3kg/10a (3% lindane as an active ingredient),were investigated.

Experimental

Application of BHC pesticide at Sampling Station No.1: BHC powder (3% lindane as an active ingredient was applied at 3kg/10a to control cabbage pests in June 1972.

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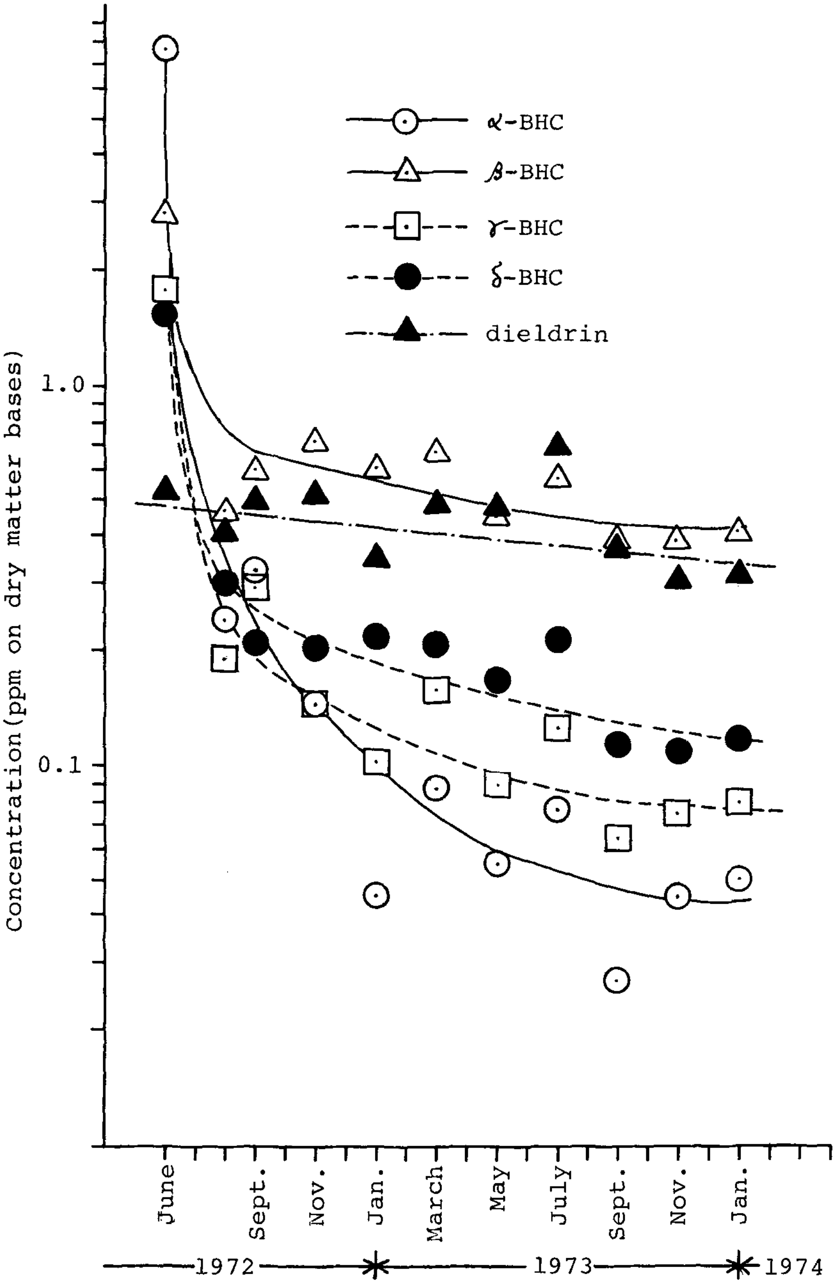

Fig.1. Loss of BHC and dieldrin residues from soil treated at 3kg/10a of BHC insecticide (3% lindane as an active ingradient). Sandy soil, organic matter content 2.1%. Sampling Station No.1.

Soil sampling and pretreatment: Soil sampling was done periodically 15cm in depth and 10cm i.d., and stored in a refrigerator at -30°C until air-dried. Soils were dried at room temperature, pulverized with a mortar and screened with a 20 mesh sieve. The screened soil was put into a ball mill jar, rotated without balls for 5 hr. and well-mixed. The soil texture of the Sampling Station No. 1 was sandy soil with organic matter content(OMC) 2.1% , Station No.2, loam soil with OMC 10.5%, Station No.3 and No.4, sandy loam soil with OMC 5.5 and 2.7%, respectively. At Sampling Stations No. 2,3 and 4, there was no application of a pesticide during the investigation, but there was a pest control history.

Extraction: All analyses were carried out in duplicate. One hundred gram of well-mixed soil was added with a 0.70 volume of pesticide-free distilled water in a high speed mixer and deactivated for 30 min. After this treatment, 200ml of acetonitrile was added and blended at a high speed for 5 min. An extract was filtered through a glass funnel, and the filtrate was poured into a 1L separatory funnel, was shaken with 100ml of n-hexane for 5 min., and partitioned with 600ml pesticide-free redistilled water and a small quantity of anhydrous sodium sulfate (approximately 4g) by shaking for 1 min. Then the n-hexane layer was washed twice with 100ml pesticide-free distilled water. The n-hexane layer was dried by passing through column of anhydrous sodium sulfate (2x5cm), and the column was rinsed twice with approximately 5ml of n-hexane, and rinsings were combined to the layer. The dried n-hexane was concentrated by a Kuderna-Danish evaporative concentrator, and subjected to a gas chromatograph after adjusting a suitable concentration.

Analysis: A shimadzu GC-5AIEE Gas Chromatograph, equipped with a dual electron capture detector and dual detection system, was used. The columns were 2mx3mm i.d. U-shaped glass columns packed with either a 3 % silicone OV-17 on Gas Chrom Q (80/100 mesh) or a 5∞ Apiezon L grease on Gas Chrom Q (80/100 mesh). Confirmation and determination of BHC and dieldrin were made by comparing relative retention times with two different columns and internal standard method. The temperatures of injector, column and detector with OV-17 column were 200°, 180°and 180° C, and with Zpiezon L grease 220°, 215° and 215°C, respectively. The carrier gas flow rate with OV-17 column was 45ml/min., and with Apiezon L grease column 100ml/min., respectively. The sample solution injected was 5μl.

Results

Sampling Station No.1: The decreasing of the BHC isomers was in the order of alpha->gamma->delta->beta-BHC, and alpha-BHC was most dissipated (Fig.1). The BHC pesticide employed to the pest control in Japan, contained alpha-, beta- and delta-BHC besides insecticidally active gamma-BHC (lindane) because of crude BHC used. A little decreasing of dieldrin residue applied prior

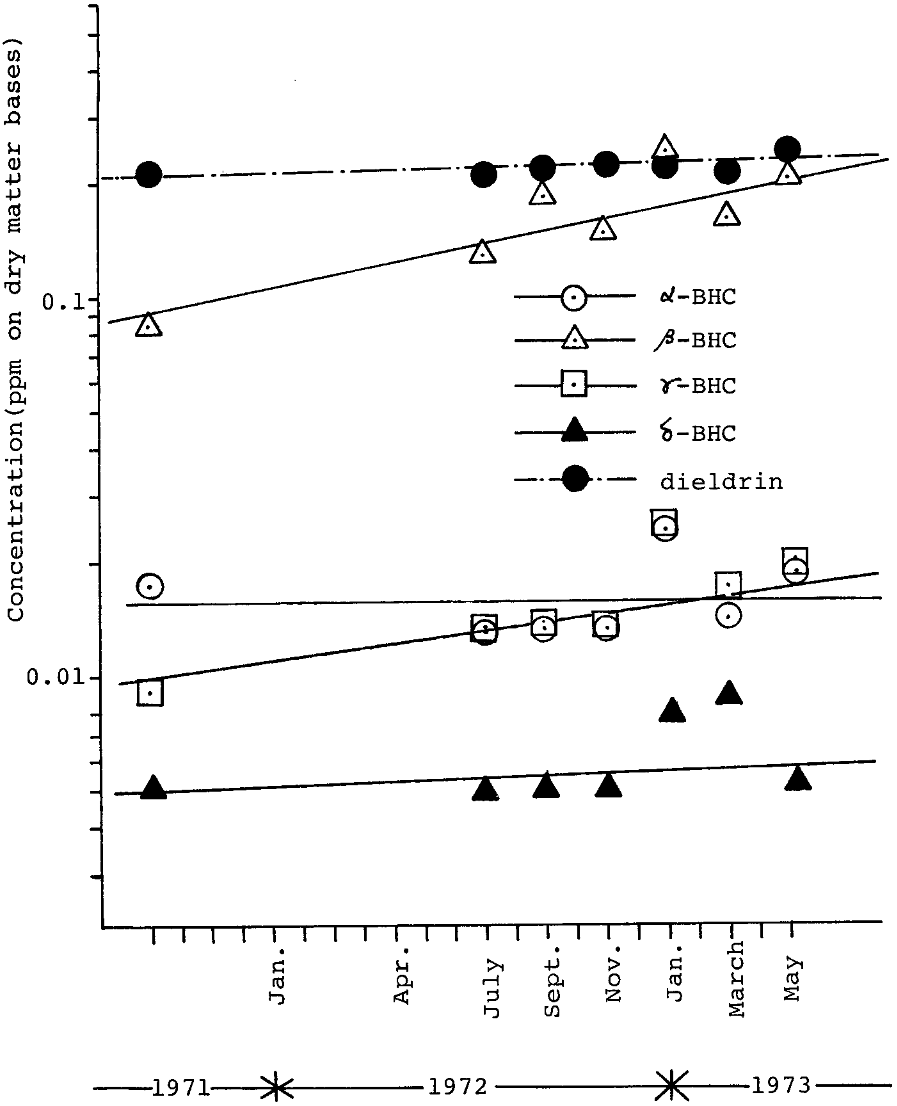

Fig. 2. Loss of BHC and dieldrin residues from soil taken at sampling station No.2. Loam soil, organic matter content 10.5%.

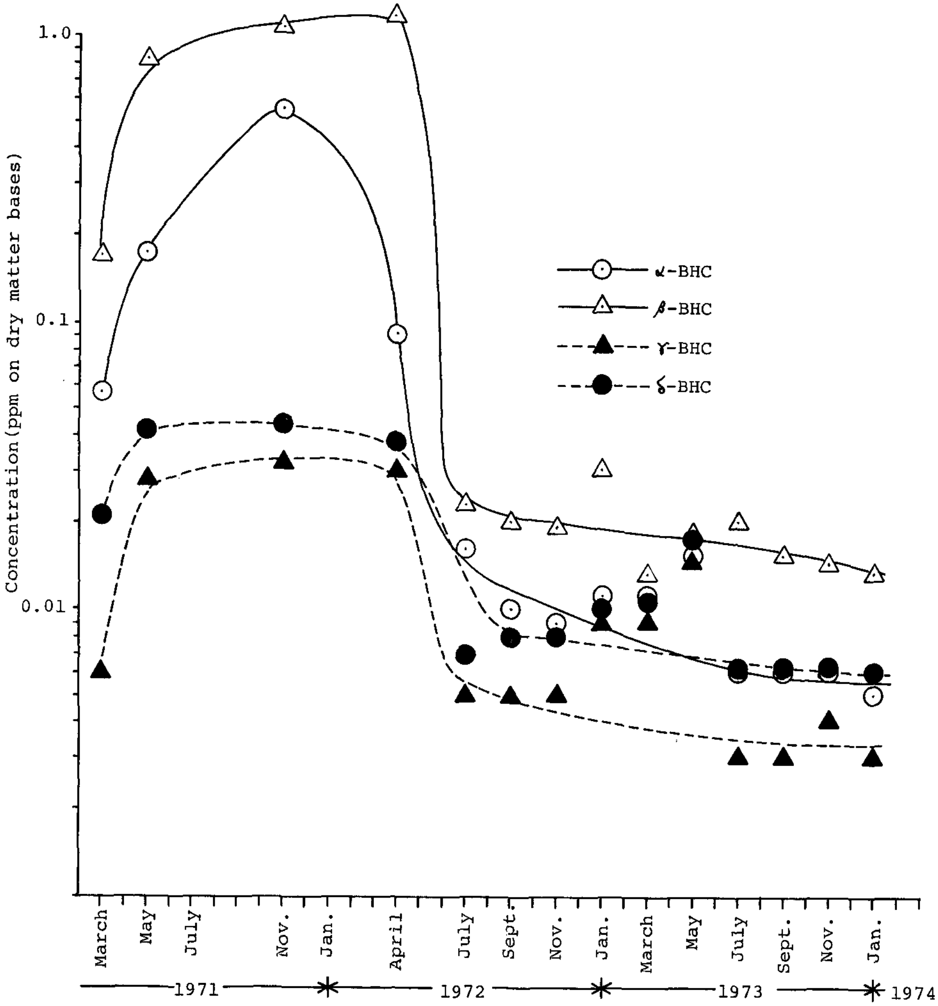

Fig. 3. Loss of BHC residues from soil taken at Sampling Station No.3. Sandy soil, organic matter content 5.5%.

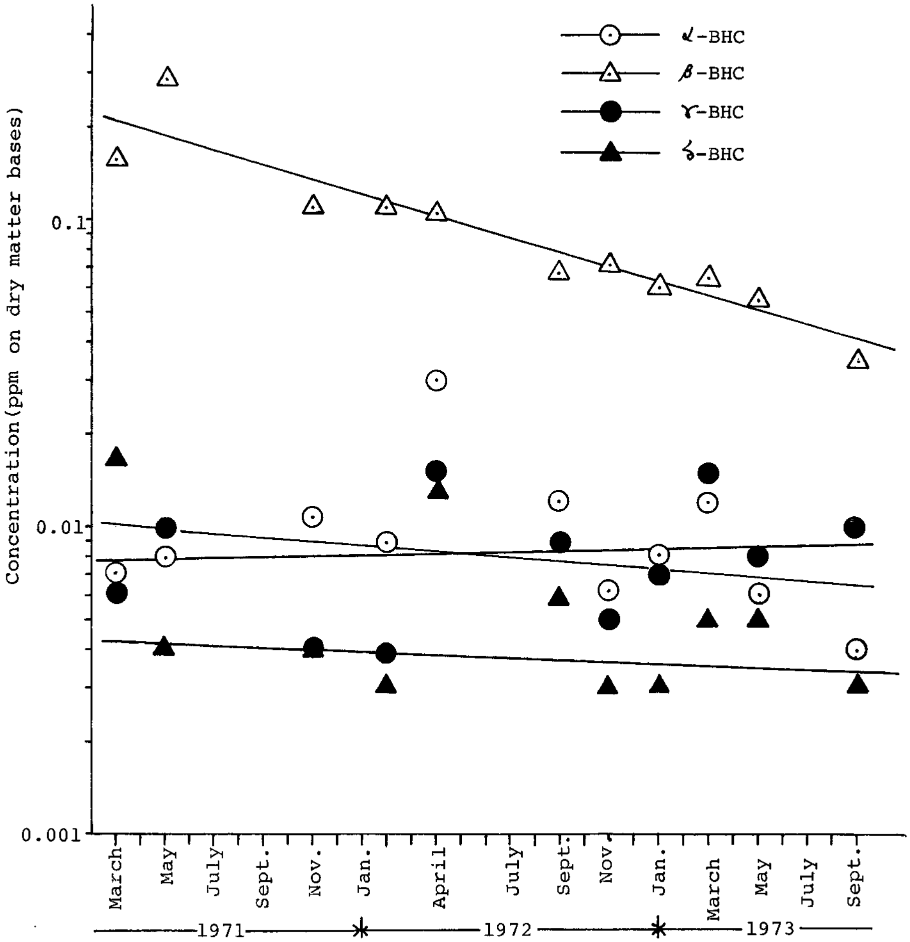

Fig. 4. Loss of BHC residues from soil taken at sampling station No. 4. Loam soil, organic matter content 2.7%.

to this experiment, was observed. A cabbage grown in this experimental field contained alpha-BHC 0.014, beta-BHC 0.160, gamma-BHC 0.043 and delta-BHC 0.007 ppm, respectively, upon 5 months after pesticide application. These BHC residue levels exceeded the pesticide tolerance of Japan (0.2 ppm as total BHC).

Sampling Station No. 2: No apparent decrease of pesticide residues was observed in this experimental period, because this field had not been cultivated (Fig. 2). On the contrary, slight increase of beta- and gamma-BHC was found.

Sampling Station No.3: This experimental field was used as a rice field. Significant BHC residue levels were detected in early 1971 because of treatment of BHC pesticide in the autumn of 1970 (Fig. 3). However, rapid decreasing of BHC was observed from spring to summer in 1971, because of flooded and biologically active conditions of the field, high temperatures and humidity at this time. Since then, a little decreasing was found.

Sampling Station No.4: No significant decrease of alpha-, gamma- and delta-BHC residue levels was shown (Fig.4). However, residue of beta-BHC was slightly decreased. That was because this experimental field was cultivated twice in one year.

Discussion

i) Persistence of BHC

The most persistent BHC isomer was beta-BHC followed by delta-BHC (Fig.1). Alpha-BHC and insecticidally active gamma-BHC (lindane) were relatively degraded. LICHTENSTEIN et al. (1971a) reported that 99.5% of applied lindane was lost after eleven years, and under flooded conditions, lindane was converted to gamma-pentachlorocyclohexene (YULE et al. 1967) and gamma-tetrachlorocyclohexene (TSUKANO and KOBAYASHI 1971). Transformation of lindane to alpha-BHC was demonstrated by incubating lindane with sediment taken from Pearl Harbour, Hawaii (BENEZET and MATSUMURA 1973).

The BHC isomers residing in soil were dissipated from environmental factors such as action of soil microorganisms, co-distillation and evaporation from soil. However the degradation of BHC in the soil was maximum when biological activity was high (MacREA et al. 1967). Under these conditions, water content in the soil was also an important factor on evaporation and co-distillation of BHC (SPENCER and CLIATH 1973). Edwards (1966) mentioned in his review that the organic matter content in soil influenced the persistence of organochlorine pesticides. However in this investigation, no correlation between organic matter content and persistence of BHC in soil was observed.

The ratio of each BHC isomers to total BHC reported by STEWART and CHRISHOLM (1971), was alpha-BHC 36%, beta-BHC 36%, gamma-BHC 16% and delta-BHC 12%, respectively, 15 years after soil application. However, data in this investigation one year after treatment showed alpha-BHC 7%, beta-BHC 59%, gamma-BHC 12% and delta-BHC 21%, respectively. Those differences depended upon an insecticide formulation, climate, soil texture and temperature. As shown in Fig.1, decreasing of beta-BHC was small compared with the other isomers, so that beta-BHC can be one of the most persistent environmental pollutants among BHC isomers

From data in Fig.2-4, it was suggested that BHC in soil at these low residue levels was resistant to microbial and physicochemical action. BHC at these low residue levels could not be utilized as a carbon source in microbial metabolism of soil organic matter. The absorption of lindane on aquifer sand was smaller than dieldrin (BOUCHER and LEE 1972). Also, the absorption of lindane on three different types of soils increased with an increase in concentration, following Freundlich's equation (CHOPRA and GOEL 1971). However these factors did not affect those low residue levels in this investigation. The comparatively low but stable residue of BHC isomers in surface soil remained in longer periods because organochlorine pesticides including BHC were immobilized in soil (HARRIS 1969). The influence of plowing which dissipated the BHC in the soil, was shown upon a comparison of the data found in Fig. 2 and 4, only in the case of beta-BHC, as demonstrated in another report (LICHTENSTEIN et al. 1971).

ii) Persistence of dieldrin

A little or no decrease of dieldrin residues in the field soil was observed in the experimental term. Run-off (CARO and TAYLER 1971), soil erosion, crop uptake (LICHTENSTEIN et al. 1965 and 1970, SAHA and McDONALD 1967, NASH and BEALL 1970), volatilization and co-distillation (WILLIS et al. 1972, IGUE et al. 1972, FARMER et al. 1973), and microbial action (MATSUMURA et al. 1968a and 1970, BIXBY et al. 1971) have been shown, as dissipation pathway of dieldrin from soil. Among these, the attack by soil microorganisms was major on the degrading of dieldrin in soil.

The dieldrin in soil was converted to more toxic compound such as photodieldrin (MATSUMURA et al. 1970) and to more hydrophilic metabolites such as aldrindiol (MATSUMURA and BOUSH 1968b) and dihydrochlordene dicarboxylic acid (KLEIN et al. 1973, KOHLI et al. 1973) which were leached out with water. Such metabolites were detected in the soil environment (SUZUKI et al. 1974b). The microbial co-metabolism of dieldrin with soil organic matter as a carbon source might occur as a high residue level. However, such metabolic conversion could not be observed, because the level found in this investigation was relatively low. So, the significant decreasing was not shown because of a slow degradation of dieldrin in the soil.

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