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Original Article

Dieldrin Residue in the Soil and Cucumber from Agricultural Field in Tokyo

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Soil samples were obtained from 814 farms in Tokyo in 2002. Dieldrin residue was detected in 85 soil samples at concentrations ranging from 0.01 ppm to 2.6 ppm. The residual amount in 70% of dieldrin-positive samples was 0.1 ppm or less. Concentrations of dieldrin residue in cucumbers cultivated in Tokyo exceeded the tolerable level (0.02 ppm) and ranged from 0.02 ppm to 0.1 ppm in 12 of 330 samples. The horizontal distribution of dieldrin in fields was not uniform and the range varied from the quantitative limit (0.01 ppm) to 0.73 ppm. The vertical distribution of dieldrin was also inconsistent. With deeply plowed fields, the vertical distribution was from the surface to a depth of 70 cm, although dieldrin was detected at 30 cm in fields that had not been plowed. As the cucumber roots grew about 1 m in the horizontal and vertical directions, we need to analyze soil samples to a depth of 1 m to prevent dieldrin residue from contaminating cucumbers. © Pesticide Science Society of Japan

Keywords: dieldrin, residue, soil, cucumber.

INTRODUCTION

In Japan, aldrin, dieldrin and endrin were first registered in 1954, and used on farmland for 22 years until 1975 when the registration lapsed.[1] In 1967, for example, the quantity of these pesticides used in Japan was 360 t as the amount of active ingredient, and they were mainly used for cultivating vegetables. More than ten times the amount of these drins was used in Italy compared to Japan, and a hundred times more drins was used for corn cultivation in U.S.A. Considerable quantities of drins were used in other countries too.[2,3]

In the late 1960s, in Japan, concentrations of residue exceeding 0.02 ppm, the residue tolerable level for aldrin and dieldrin in cucumbers, became a problem.[2,4] In 1970, the Agricultural Chemicals Regulation Law was revised, and the monitoring of residues of agricultural chemicals was promoted. At that time, investigations into pesticide residue in crops and soil were conducted all over Japan.[4–10] Dieldrin, as well as aldrin, and endrin, persisted in cucumber.[8] In addition, these pesticides persisted in soil, with a half-life of one year or more.[11,12] Against this background, the registration for dieldrin, aldrin and endrin lapsed in 1975.[1]

Currently, about 30 years since the lapse of registration for drins, the same situation is being faced. Residue of dieldrin was found in Hokkaido vegetable products in 1998.[13] It was reported that cucumber, squash and root vegetables readily retain dieldrin. Food Station Law gives tolerance for dieldrin residue cucumber (0.02 ppm), Japanese radish (0.02 ppm) and potato (N.D.). In addition, in only cucumber, residue over the tolerance level (0.02 ppm) for pesticide residue was found in cucumbers produced in Tokyo in 2002.[14] Therefore, the focus of this paper is cucumbers.

The Agricultural Chemicals Regulation Law was again revised in 2003, and penal regulations for pesticide users were introduced. The precision of analysis has improved,[15] and it is possible to detect pesticide residues which were undetectable previously. The consumer and the public are very interested in pesticides and sensitive to these issues. Dieldrin is one of 12 chemical substances known as persistent organic pollutants (POPs).[3] Although dieldrin has not been used for 30 years, it remains in cucumbers at levels exceeding the tolerable limit for pesticides. This is a very serious problem in agriculture.

This study examined residual the concentration of dieldrin in the soil in Tokyo in 2002. In addition, the horizontal distribution and the vertical distribution of dieldrin on some farms were examined.

MATERIALS AND METHODS

1. *Chemicals and Reagents*

Aldrin, dieldrin and endrin were purchased from Kanto Ka-

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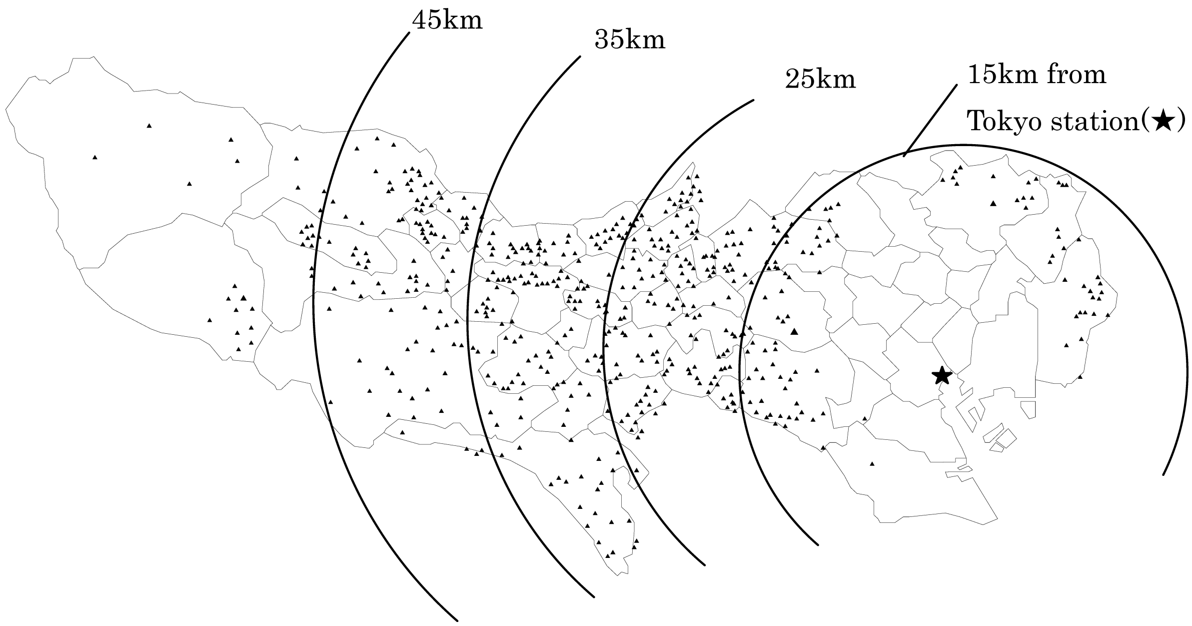

Fig. 1. Soil sampling points. Soil sample were obtained from areas indicated by solid triangles. A solid star shows Tokyo Station. A dashed line and numerical values show distance from Tokyo Station.

gaku Reagent Division, Tokyo, Japan. These chemicals were dissolved in *n*-hexane. Extrellut NT20 was purchased from Merck Co., Darmstadt, Germany. Mega Bond Elut NT20 FL (florisil 5 g/20 ml) was obtained from Varian Inc., U.S.A. Organic solvents were of pesticide residue-examinable grade and purchased from Wako Pure Chemicals Inc., Ltd., Osaka, Japan.

2. Soil and Cucumber Samples

Soil samples used to investigate actual conditions were obtained from 814 places shown in Fig. 1 from September to October 2002. The number of fields sampled was decided based in the area ratio of farmland in Tokyo. There is little farmland within a 15-km radius and beyond a 45-km radius of Tokyo Station. Most agricultural land in Tokyo lies 15 km, which is residential, to 45 km from Tokyo Station. The soil was collected from five sites chosen at random. The soil was collected from a depth of 0–15 cm using a core sampler 10 cm in diameter, and all gravel and plant pieces larger than 2 mm were removed.

Soil samples for investigating horizontal distribution were obtained from three fields containing dieldrin residue in Tokyo. Field A and Field B were both rectangular, 10 m×30 m and 10 m×36 m, respectively. Field C was a 20 m×20 m square. The three fields had no inclination. The soil was loamy. The number of soil samples in Field A, Field B, and Field C was 15, 18, and 25, respectively.

Soil samples for investigating vertical distribution were obtained from six fields containing dieldrin residue in Tokyo. Field D has not been plowed deeply over the past 30 years. On the other hand, Field E and Field F have been regularly plowed deeply. The soil was gathered every 10 cm from the surface of the earth after the soil was dug down to a depth of 1 m (Fields D, E, F) or 30 cm (Fields G, H, I).

A total of 330 cucumbers produced in Tokyo were obtained in September, 2002.

3. Determination of Dieldrin and Endrin Levels

Cucumber samples were homogenized with a home mixer without adding anything. The soil samples had a dry weight of 5 g, and the cucumber samples had a fresh weight of 20 g. A soil or cucumber sample and 100 ml of aceton was shaken for 30 min at room temperature. The soil samples were filtered with filter paper and cucumber samples were filtered with celite. The filtrate was concentrated to 20 ml at 40°C. It was applied onto Extrellut NT20. After 15 min, the adsorbate was eluted with 100 ml of *n*-hexane. The eluate was evaporated at 40°C. The residue was dissolved in 5 ml of *n*-hexane, and the solution was loaded onto Mega Bond Elut NT20 FL (florisil 5 g/20 ml). The column was eluted with 50 ml of diethylether/*n*-hexane (15/85, v/v), and the eluate was evaporated at 40°C. The residue was dissolved in 2 ml of *n*-hexane, and analyzed by gas chromatography with an electron capture detector (GC-ECD) and gas chromatography-mass spectrometry (GC-MS). The limit of detection in soil and cucumber was 0.01 ppm.

4. Gas Chromatography

A Hewlett Packard HP6890 series GC system and 5973 mass selective detector were used with a Hewlett Packard HP-1MS column (0.25 mm×30 m×0.25 mm i.d.) and helium (1 ml/min) as the carrier gas. The temperature for detection and in-

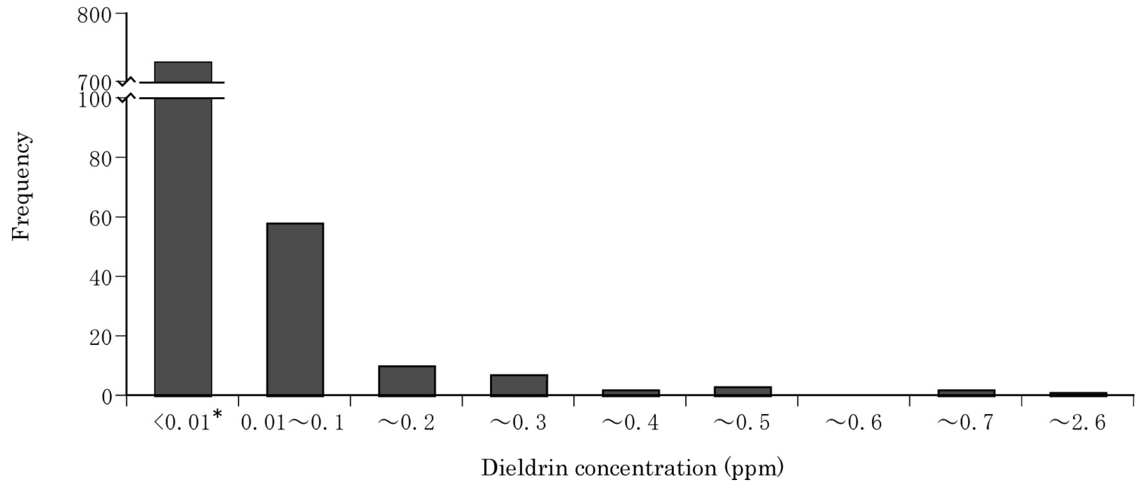

Fig. 2. Dieldrin soil residue in Tokyo. *, below the detection limit.

jection was 280°C and 300°C, respectively. The temperature of the column oven was maintained at 100°C during the first 2 min and raised to 300°C for 20 min. Conditions for mass spectrometry were as follows: ionizing energy; 70 eV, temperature of ion source; 230°C, and scan interval ; 1.7 sec.

A Shimazu GC-15A system with an electron capture detector was used with a J&W Scientific DB-17 column (0.32 mm×30 m×0.5 mm i.d.) and helium (3 ml/min) as the carrier gas. The temperature of detection and injection was 280°C and 300°C, respectively. The temperature for the column oven was maintained at 100°C during the first 2 min and raised to 300°C for 20 min.

RESULTS

1. Levels of Dieldrin Residue in Soil and Cucumbers in Tokyo

Aldrin was not detected in any soil samples, and endrin was detected in only three samples. On the other hand, dieldrin was detected in 85 of the 814 samples, 10.4%. In 70% of the samples in which dieldrin was detected, the concentration of residue was 0.1 ppm or less. The concentration was 0.5 ppm or less for 95% of these samples (Fig. 2). Among 330 cucumbers, dieldrin was detected at a concentration of 0.02–0.1 ppm in 12 samples, which is 3.6% of the total (data not shown).

2. Horizontal Distribution

The horizontal distribution of dieldrin was examined in three places where dieldrin remains on farms in Tokyo. In Field A, the dieldrin was not uniformly distributed, with the concentration varying from less than the limit of detection (0.01 ppm) to 0.73 ppm. In Field B, the concentration ranged from less than the limit of detection to 0.16 ppm, while in Field C, it ranged from 0.06 ppm to 0.26 ppm (Fig. 3). The area of each field was between 300 and 400 m^2, which is normal for the cultivation of a single crop in Tokyo. Even over a distance of only two or three meters within one small farm, dieldrin residue levels are very different.

3. Vertical Distribution

In Field D, dieldrin was distributed to a depth of 30 cm from the soil surface. On the other hand, the distribution of dieldrin was scattered in Fields E and F from the surface to a depth of 50–70 cm (Fig. 4). The vertical distribution in fields where there was dieldrin and endrin residue was investigated. The two pesticides had a very similar distribution (Fig. 5).

DISCUSSION

Aldrin changes into dieldrin and its half-life is about 1.5–5.2 years in soil. The half-life of dieldrin is longer, 2–15 years in soil. In addition, it will take 25 years for 90% disappearance of dieldrin.[3,7,11,16,17] For example, in Nagano in 1971, the concentration of aldrin and dieldrin in total was reported to be an average of 0.4 ppm in pesticide residue research in fields after aldrin had been used for ten years until 1971.[18] In Tokyo in 2002, the concentration of dieldrin residue was less than 0.1 ppm in almost all soil samples. When dieldrin used at a rate of 0.6 kg/ha, the half-life was an average of 2.6 years, at 2.2 kg/ha, the half-life averaged 4.1 years, and at 9.6 kg/ha the half-life was 12.5 years.[3,17] In brief, if the application rate of drins to soil increases 15 times, the half-life of drins becomes 5 times longer.[3] In addition, the chemical properties such as pH and cation exchange capacity of soil did not differ between high residual soil and low residual soil (data not shown). From these findings one can conclude that the current dieldrin residue levels in Tokyo are not a special phenomenon. The various levels of dieldrin residue are not caused by differences in degradation due to the chemical properties of soil, and it is thought that farmlands treated with a large quantity of drins in the 1960's currently have high residual levels.

In about 1970, it was suggested that deep cultivation had a restraining effect on drin residues in crops, and a diluting effect of the residual amount in soil.[19] Therefore, a lot of

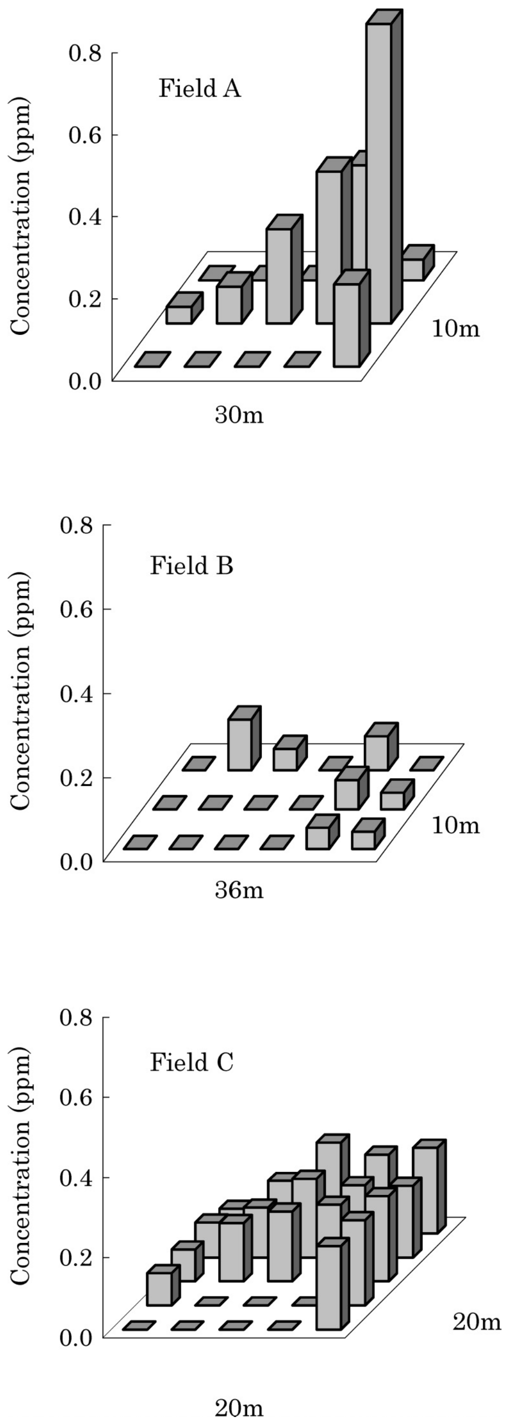

Fig. 3. The horizontal distribution of dieldrin residue in soil on farms. All farms were level areas.

fields were cultivated deeply. Deep cultivation is usually conducted even for reasons other than residue evasion. It is thought that the usage of a farm affects dieldrin distribution in the soil.

It was found that dieldrin readily remained in vegetables in the 1960s.[4,9,10,20–25] In this study, we obtained levels of drins residue in cucumbers. Dieldrin residue over the tolerance (0.02 ppm) was detected in 12 samples, which is 3.6% of 330 cucumbers produced in Tokyo. It was reported that dieldrin residue in cucumbers should not exceed the tolerance (0.02 ppm) if dieldrin residue in soil would be within the range of 0.06 ppm, because dieldrin uptake to cucumber was less than 30% of dieldrin residue in soil.[26,27] In this study, soil

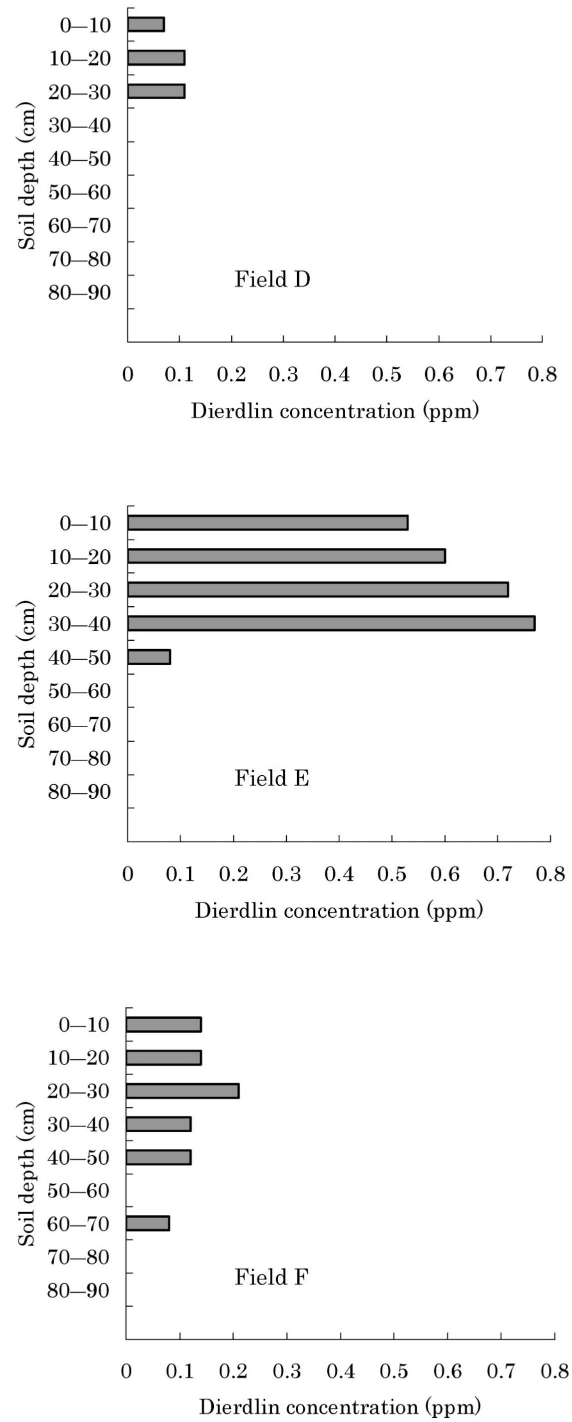

Fig. 4. The vertical distribution of dieldrin in soil at three farms in Tokyo. Field D has not been plowed deeply. Fields E and F have been regularly plowed deeply.

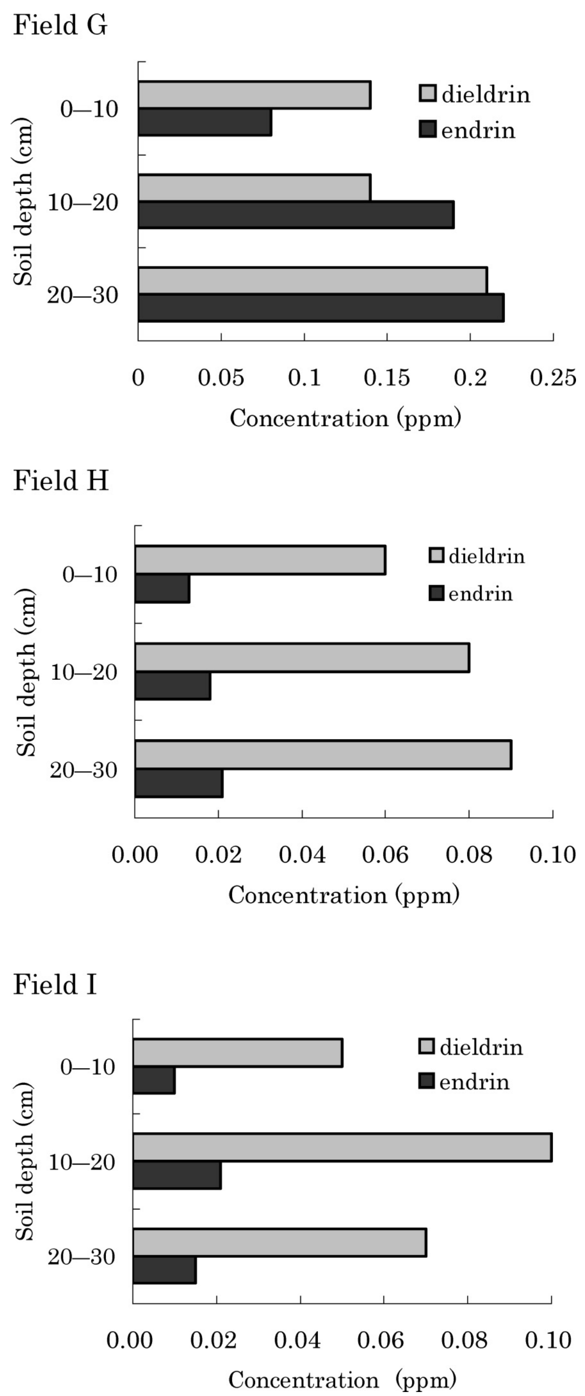

Fig. 5. The vertical distributions of dieldrin and endrin in soil at three farms in Tokyo.

and cucumbers were not gathered at the same time from the same field, so it is unclear from this study how cucumbers uptake dieldrin from soil.[28] A great deal of effort was made on provision against dieldrin residue in the first half of the 1970s. This was followed by (1) investigating the dieldrin residue into various crops, (2) residual dieldrin in crop persistency reduction by the application of active carbon and compost,[29] and (3) creating different residual conditions in the soil so as not to uptake to crops.[6,18,30] However, at present, which is a long time since dieldrin was applied to the soil, we must conclude that perhaps dieldrin is firmly absorbed by the soil, and dieldrin uptake to crops from soil differs from that in the 1970s.[31] Therefore, it is necessary to accumulate exact data on the uptake of dieldrin in crops in present dieldrin residual soil as countermeasures against avoidance of dieldrin residue in crops. It seems to be the most probable to evade dieldrin residue in cucumbers over the tolerance (0.02 ppm) by grasping the actual dieldrin residue in soil, if there is a relation of residue in cucmber and in soil. The roots of cucumber grow about 1 m in all directions (data not shown). Therefore, it is necessary to survey dieldrin residue in soil within a semicircle with a radius of 1 m around a plant base.

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