Multiple Organochlorine Pesticide Residues in Japan

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Environmental contamination by organochlorine pesticides has been studied by many reseachers(1-3). In Japan, contamination of vegetables, milk and dairy products by the pesticides was reported(4,5) and has become a serious public problem.

The Japanese agricultural system has been intensive and diversified, and many kinds and great amounts of pesticides were due to circumstances peculiar to Japan amply employed, so that the pesticide residues are to be found in great quantity in the soil. The pesticide residues in soil are absorbed by vegetables, evaporated into the air or pour into river water and thereby enter into many food sources. Therefore, contamination of soil by these pesticide residues is one of the environmental hazards in Japan.

We analysed organochlorine pesticide residues in the agricultural soil of the Kyushu district (the southwestern region of Japan), which is one of the most pesticide-consumed regions in Japan, and we will discuss these multiple pesticide residues in soil in this article.

Experimental

1) Sampling

All soil samples were collected from fields in 15 cm deep and stored at -30°C until pretreatment. Soil texures were from sandy to loam soil.

2) Pretreatment

Soil samples were air-dried, pulverized with a mortar and screened with a 20 mesh-sieve. The screened samples were put into a ball mill jar, rotated without balls for 5 hrs and well-mixed.

3) Analysis

Duplicate analyses were carried out for all samples.

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One hundred grams of dry soil was mixed with a 0.70 volume of water in high speed mixer and deactivated for 30 min.. After this treatment, 200 ml of acetonitrile was added and blended at a high speed for 5 min.. An extract was filtered, and the filtrate was poured into 1 liter separatory funnel, was shaken with 100 ml of n-hexane for 5 min. and partitioned with 600 ml distilled water by shaking for 1 min.. Then the n-hexane layer was washed twice with 100 ml distilled water. The n-hexane layer was dried by passing through a 5 cm column on anhydrous sodium sulfate, and the column was rinsed twice with approximately 5 ml of n-hexane, and washings were mixed into the layer. The dried n-hexane solution was applied to a Shimazu GC-5AIEE gas chromatograph equipped a tritium foil electron capture detector. Gas chromatographic determination was carried out by combining three different columns: 2% diethylene glycol succinate-0.5% phosphoric acid on Chromosorb W HP (80/100 mesh) for DDT and related compounds, 5% Apiezon L grease on Gas-chrom Q (80/100 mesh) for BHC isomers and cyclodiene pesticides, and 3% silicone OV-17 on Gas-chrom Q (80/100 mesh) for BHC isomers and endrin.

Results and Discussion

TABLE 1
Multiple organochlorine pesticide residues in soil of the Kyushu District, Japan (ppm on dry matter bases)

Sample No. / Pesticides	45	46	51	66	70	85
α-BHC	0.057	0.182	0.012	0.040	0.014	0.028
β-BHC	0.711	1.792	0.195	0.503	0.288	0.302
γ-BHC	0.097	0.101	0.004	0.025	0.016	0.030
δ-BHC	0.054	0.152	Tr[a]	0.065	0.014	0.031
Aldrin	0.097	0.153	Tr[a]	0.015	0.016	0.034
Dieldrin	0.624	0.541	0.194	0.677	0.035	0.314
Endrin	0.117	0.329	0.082	0.099	0.057	0.629
p,p'-DDE	2.048	0.079	0.192	0.047	0.084	1.044
p,p'-TDE	0.822	0.260	0.484	0.307	0.128	1.544
p,p'-DDT	3.526	0.646	3.450	1.061	0.233	6.661
o,p'-DDT	0.822	Tr[a]	0.375	Tr[a]	Tr[a]	1.745

Tr: <0.001

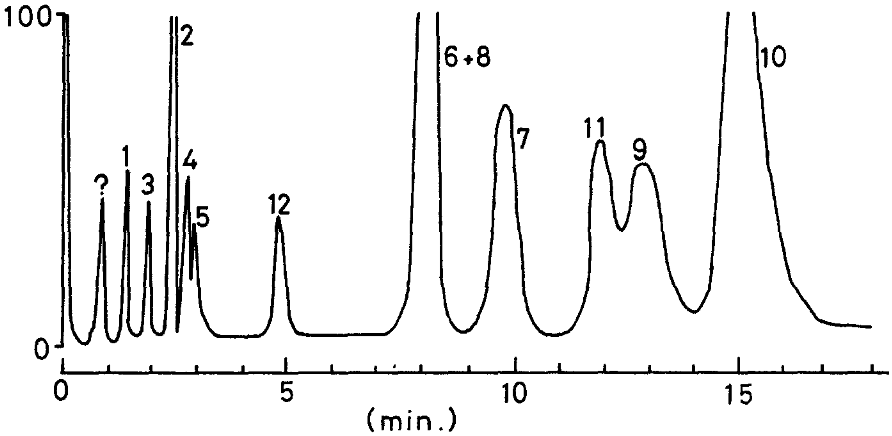

FIG. 1
Typical chromatogram of multiple organochlorine pesticide residues(1). 1. α-BHC, 2. β-BHC, 3. γ-BHC, 4. δ-BHC, 5. Aldrin, 6. Dieldrin, 7. Endrin, 8. p,p'-DDE 9. p,p'-TDE, 10. p,p'-DDT, 11. o,p'-DDT 12. Heptachlor epoxide(internal standard).
column: 3% silicone OV-17, detector temp.: 190°C, column temp.: 190°C, inlet temp.: 210°C, prepurified nitrogen carrier gas: 45 ml/min.

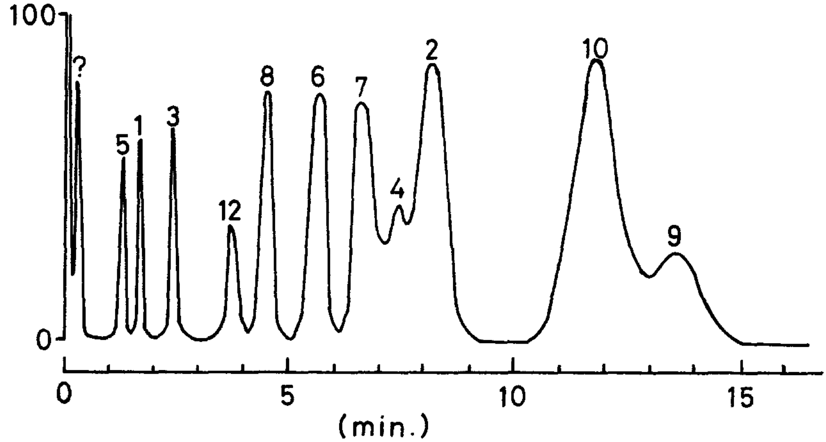

FIG. 2
Typical chromatogram of multiple organochlorine pesticide residues(2).
column: 2% diethylene glycol succinate - 0.5% phosphoric acid, detector temp.: 190°C, Column Temp.: 190°C, inlet temp.: 210°C, prepurified nitrogen carrier gas: 100 ml/min.

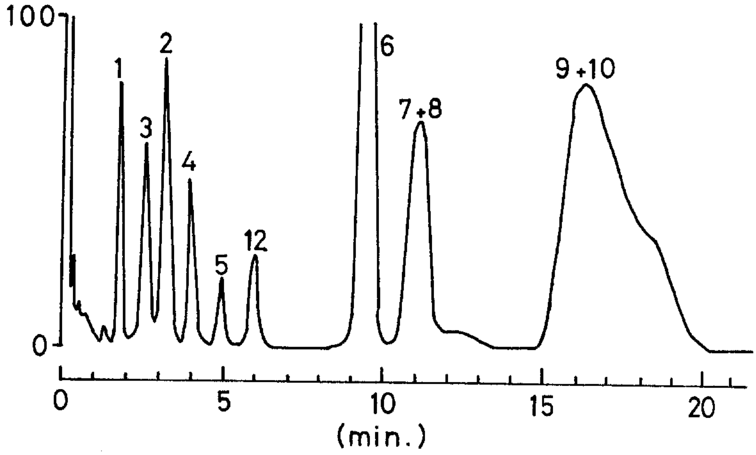

FIG. 3
Typical chromatogram of multiple organochlorine pesticide residues(3).
column: 5% Apiezon L grease, detector temp.: 210°C, column temp.: 210°C, inlet temp.: 220°C, prepurified nitrigen carrier gas: 100 ml/min.

TABLE 2.

organochlorine pesticide residues in the soil of the Kyushu district, Japan (ppm on dry matter bases)

Pesticides	No. of Sample	Range	Mean
α-BHC	99	7.605 - 0.002	0.226
β-BHC	99	2.806 - 0.021	0.563
γ-BHC	99	1.785 - 0.003	0.106
δ-BHC	99	1.530 - 0.001	0.099
Aldrin	31	1.012 - 0.002	0.070
Dieldrin	52	1.726 - 0.002	0.290
Endrin	29	0.629 - 0.016	0.183
p,p'-DDE	70	2.058 - 0.008	0.173
p,p'-TDE	47	1.544 - 0.018	0.324
p,p'-DDT	60	9.801 - 0.015	1.147
o,p'-DDT	20	1.745 - 0.007	0.416

The typical multiple organochlorine pesticide residues in soil are shown in table 1 and Fig. 1-3, and the residue range and mean value of each pesticide in soil samples are in table 2.

α-, β-, γ-and δ-BHC were detected in all 99 soil samples. The result indicated that the technical grade BHC used in Japan was a mixture of insecticidal active γ-BHC (Lindane) and α-, β-and δ-isomers, and that it was one of the most consumed pesticides in Japan. It was reported by Melnikov(6) that this grade BHC was composed of α-BHC 53-70%, β-BHC 3-14%, γ-BHC 11-18%, δ-BHC 6-10% and others, and Uyeta(4) reported α-BHC 74%, β-BHC 7%, γ-BHC 16% and δ-BHC 3%. On the other hand, by our studies, on an average, α-BHC 22.7%, β-BHC 56.7%, γ- BHC 10.6% and δ-BHC 10.1% were detected from BHC residues in soil. Also the studies of Stewart and Chrisholm(7) reported that the BHC residues in soil were composed of α-BHC 36.0%, β-BHC 36.0%, γ-BHC 16.0% and δ-BHC 12.0%. Judging from this data, a significant difference in the composition was found between the technical grade BHC and BHC residue in soil. A high percentage of β-BHC in BHC residue might suggest that β-BHC is stable in soil and important factor in the BHC contaminated environment.

Considerable residual amounts of aldrin, dieldrin and endrin were detected in the soil (table 1 and 2). These cyclodiene pesticides were highly toxic and tolerably transferred into vegetables. For example, translocation rates of aldrin and dieldrin into carrots, radishes and beets from soil were 25.4%, 11.4% and 7.7%, respectively(8). And translocation

TABLE 3.

Pesticide Residue Tolerance in Japan[a] (ppm)

	BHC[b]	DDT[c]	Endrin	Dieldrin[d]
Cabbage	0.2	0.2	ND[e]	0.02
Cucumber	0.2	0.2	ND[e]	0.02
Radish	0.2	0.2	ND[e]	0.02
Potato	0.2	0.2	ND[e]	ND[e]
Spinach	0.2	0.2	ND[e]	ND[e]
Lettuce	0.2	0.2	ND[e]	0.02

a: this table was a part of pesticide residue tolerance.
b: α + β + γ + δ-BHC.
c: DDT + DDE + TDE.
d: Dieldrin + Aldrin.
e: must not be detected.

rates of endrin into cucumbers and cabbages from soil were 21.8% and 14.5%, respectively(9). Considering the pesticide residual levels in soil and these translocation rates, there might be a possibility that these amounts found in vegetables exceed the pesticide residual tolerance in Japan (table 3).

High residual levels of DDT and its related compounds were detected in soil. p,p'-DDE which is a metabolite of p,p'-DDT was frequently detected in soil, and this compound was found to play an important role in eggshell-thinning of wild birds(10 and 11). Biological magnification of DDT and related compounds — soil → earthworms → little birds → big birds (birds of prey) — has been indicated. comparing with the residual values reported previously in the USA and Canada(12 and 13), similar levels were detected related compounds was one of the environmental hazards present in Japan.

These organochlorine pesticides in soil mentioned above are reported to be stable in soil(14), and are still present in the environment of Japan.

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