Persistence of Some Insecticides in Subtropical Soil

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A long-term experiment was undertaken to investigate the persistence of selected insecticides following their repeated seasonal application to soil under subtropical conditions. Residues of DDT and dieldrin declined 20 and 25% in the fall and winter months, and there was no accumulation of residue with further application of these chemicals during spring and summer. Two organophosphates (fonofos and phorate) and one carbamate (carbofuran) degraded rapidly resulting in only 8, 0.4, and 32% recoveries, respectively, at the end of the fall and winter seasons. Their breakdown was further accelerated during the hot, rainy spring and summer months when their recoveries were lower. When grown in treated silt loam soil, sweet potatoes and white potatoes absorbed the residues of these chemicals and their metabolites at different levels.

Many pesticides are applied directly to the soil to control soil inhabiting pests or as systemics to control phytophagous insects. Others eventually reach the soil from treated plant parts. Soil acts as a reservoir for these chemicals until they move into the bodies of invertebrates and microorganisms, volatilize into the atmosphere, seep into the water, or are broken down. All pesticidal chemicals are absorbed to varying degrees and in some cases are translocated to the edible parts of plants growing in contaminated soils.

The amount of pesticidal residues that can be accumulated in soil depends on factors such as the chemical itself, soil type, moisture, soil pH, temperature, cultivation, mode of application, soil organisms (Lichtenstein, 1965), etc. Pesticide persistence, therefore, differs greatly under combinations of these factors. Even though high temperatures and moisture accelerate the breakdown of pesticides, abnormally high rates of applications may alter the soil ecosystem (National Academy of Science, 1974) even under humid tropical conditions.

Voluminous information is available in the literature concerning the persistence and interaction of pesticides in soils and elsewhere in the environment of temperate regions. However, there is little information available on the behavior of these chemicals under tropical or subtropical conditions. This probably is due to the limited use of agricultural chemicals in these regions. Publicity generated by the restrictions of certain pesticides, especially organochlorines, in developed countries has adversely affected the use of insecticides and some subtropical and tropical countries have banned or restricted the use of these chemicals without sufficient information on their impact on local environment.

Accelerated use of pesticides is necessary in subtropical and tropical Asia to protect the higher yields made possible through improved technology and intensive cultivation of crop land under continuous and multiple cropping systems. A long-term experiment was initiated in 1974 at the Asian Vegetable Research and Development Center (AVRDC), Shanhua (120° 17′E longitude and 23° 07′N latitude) to obtain information on the fate of selected insecticides in soil. The insecticides used in this study were two organochlorines (DDT and dieldrin), two organophosphates (fonofos and phorate), and one carbamate (carbofuran). This paper reports on the persistence of these selected chemicals applied during two seasons in cultivated soil and their absorption into crops.

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MATERIALS AND METHODS

Insecticides. *Formulated Insecticides.* DDT 25% EC (18.75% *p,p′*-DDT and 6.25% *o,p′*-DDT), dieldrin 50% WP, fonofos 10% G, phorate 10% G, and carbofuran 3% G, used for field application, were obtained locally. Gifts of analytical grade insecticides were obtained from EPA's Pesticides and Toxic Substances Effects Laboratory at Research Triangle Park, N.C. (*p,p′*-DDT, *p,p′*-DDE, *o,p′*-DDT, and dieldrin); Stauffer Chemical Co., Mountain View, Calif. (fonofos and fonofos-oxon), American Cyanamid Company, Princeton, N.J. (phorate and its metabolites), and FMC Corporation, Middleport, N.Y. (carbofuran and its metabolites).

Insecticide Application. A field was divided into 10 m × 10 m plots in two rows 10 m apart with a distance of 5 m between adjacent plots. The insecticide rates used were 5 kg of active ingredient (AI)/ha of DDT and dieldrin, and 10 kg of AI/ha of fonofos, phorate, and carbofuran each season (fall and spring). These dosages were slightly above the average amounts of insecticides applied by farmers during an entire season in Taiwan. Each treatment was duplicated. Insecticides were sprayed or broadcasted uniformly and rototilled immediately to a depth of 15 cm. Control plots received no chemicals. The first application was made on Dec 9, 1974. Each plot was subdivided into three subplots with a cultivated central strip of 4 m × 10 m and a fallow strip of 3 m × 10 m on either side. A second identical application was made on April 15, 1975.

Crop Growth and Harvesting. Sweet potato (Variety Tainan 14) and white potato (Variety Nohrin 1) were planted in the central strip immediately after the first insecticide treatment. Only sweet potato was planted in the spring 2 weeks after the second treatment. Plants received sprinkler irrigation and were fertilized once each season with ammonium sulfate and potassium chloride. At the end of the growing seasons, sweet potato roots and white potato tubers were harvested, washed under running tap water to remove adhering soil particles, and rinsed lightly with acetone. They were then finely chopped in a Hobart food chopper and stored in polyethylene bags in a freezer at −20 °C until analysis.

Soil Sampling. One day before the experiment was initiated, soil in each plot was sampled with a soil auger to a depth of 15 cm to determine the residues of pesticides already present in the soil. Immediately after the first

Table I. Thin-Layer Chromatographic Systems and Their Uses

Designation	Layer	Solvent system	Use
A	Silica gel G[a]	Pentane-propionic acid (99:1)	Separates *p,p*-DDT, *o,p'*-DDT, and *p,p*-DDE
B	Aluminum oxide[a] F-254	Hexane-acetic acid (9:1)	Separates TDE and DDA
C	Silica gel G + aluminum oxide (1:1)	Hexane-acetic acid (9:1)	Separates dieldrin and photodieldrin
D	Aluminum oxide F-254	Hexane-acetic acid (9:1)	Separates dieldrin and photodieldrin
E	Silica gel G	Hexane-acetone (9:1)	Separates fonofos and fonofos-oxon
F	Silica gel G	Hexane-acetone (9:1)	Separates phorate, phoratoxon, phorate sulfoxide, and phorate sulfone
G	Silica gel G	Hexane-acetone (7:3)	Separates carbofuran, 3-hydroxycarbofuran, and 3-ketocarbofuran

[a] Precoated plates obtained from Brinkman Instruments; layer thickness 0.25 mm.

insecticide treatment the entire plot was sampled to a depth of 15 cm at the intersections of a 1 m grid with an auger. All bores were combined and stored in polyethylene bags at −20 °C in the freezer. Six weeks after the initial treatment, the soil was sampled again to determine the degradation of the chemicals. At the end of the first growing season on April 14, 1975, immediately after the sweet potato harvest, soil samples were taken once more. After the second insecticide treatment, soil was sampled only once at the end of the growing season in September 1975.

Extraction Procedure. *Organochlorines.* Redistilled hexane–acetone (H:A), 1:1, solvent mixture was used to extract organochlorines from soil and plant material. Soil samples were thawed at room temperature, pulverized, and screened through 7-mesh sieve. Two-hundred and fifty grams of soil was weighed in a 1000-ml mason jar and 200 ml of H:A was added. The insecticides were quantitatively extracted from soil by homogenizing in an Omni-Mixer (Du Pont Sorvall) as described by Lichtenstein et al. (1964). Hexane phase was later subjected to Florisil cleanup (Lichtenstein et al., 1967) and adjusted to volume for analysis. Simultaneously a 50-g sieved soil sample was dried to constant weight at 70 °C for 4 h in an oven to determine the soil moisture content.

One-hundred grams of plant material was weighed in a 600-ml tall beaker and the insecticide residues were extracted quantitatively by blending in H:A for 2 min with Polytron Homogenizer (Brinkman Instruments, Inc.) using a PT 35 generator at moderate speed. The solvents were filtered through a Buchner funnel using gentle suction and the plant material was reextracted for an additional 2 min. The combined extract was partitioned and subjected to Florisil cleanup (Lichtenstein et al., 1967).

Organophosphates. A 1:1:1 mixture of methanol–acetone–benzene (M:A:B) was utilized for the extraction of organophosphates from soil as well as plant material. A 250-g thawed soil sample was weighed in a 1000-ml mason jar and covered with M:A:B, and the insecticide residues were quantitatively extracted 2 × 15 min using an Omni-Mixer (Lichtenstein et al., 1972). Phorate and its metabolites were partitioned in benzene; however, ethyl acetate instead of benzene was used for partitioning fonofos and its metabolites.

One hundred grams of plant material was weighed in a 600-ml tall beaker, covered with M:A:B, and extracted 2 × 2 min in a Polytron Homogenizer. The extract was concentrated in a flash evaporator at 35 °C until most of the solvent had been evaporated. The remaining extract was then adjusted to 100 ml with 1% aqueous Na_2SO_4 and shaken 3 times with 50 ml of benzene for phorate and its metabolites, or with ethyl acetate for fonofos and its metabolites. Benzene or ethyl acetate extracts were adjusted to volume before analysis.

Carbofuran. Soil and plant material were extracted and analyzed in identical fashion. Carbofuran was extracted and derivatized with 1-fluoro-2,4-dinitrobenzene (FDNB) (Turner and Caro, 1973). Repeated attempts to analyze 3-hydroxycarbofuran by forming a derivative first by ethoxy at the 3-OH position and later with FDNB failed because of poor recoveries (average 40%) from fortified plant and soil samples.

Analytical Procedure. (a) *Gas–Liquid Chromatography (GLC).* All insecticides and their major metabolites were analyzed by GLC. Two detection systems were employed to identify and quantify the residues. DDT, dieldrin, and carbofuran were analyzed by electron capture detector (ECD) and fonofos and phorate, by alkali flame ionization detector (AFID) sensitive to phosphorus.

DDT, Dieldrin, and Carbofuran. These chemicals were analyzed on a Varian Aerograph Model 2860 GLC equipped with 250 mCi of tritium ECD operated at −90 V. A 1.83 m stainless steel column (2 mm i.d.) containing either 3% SE 30 on 100–120 mesh Varaport 30 (Varian Aerograph) or 5% DC 11 on 60–80 Chromosorb W/AW DMCS was conditioned for 3 days at 250 °C before use. Carrier gas (N_2) flow through the column was adjusted at 55 ml/min. For the analysis of DDT and dieldrin, injector temperature was maintained at 200 °C, detector cell at 220 °C, and column oven at 190 °C. The peak heights were used for computing the results. For carbofuran analysis, the injector temperature was held at 220 °C, detector cell at 225 °C, and column oven at 210 °C. An authentic carbofuran–FDNB derivative was used to identify and quantify carbofuran, and the concentrations in samples were calculated after the necessary corrections for molecular weight difference.

Fonofos and Phorate. A Varian Aerograph Model 2860 GLC equipped with Rb_2SO_4 tip AFID operated at −300 V was utilized. Fonofos and phorate analyses were done on a 1-m Pyrex glass column (2 mm i.d.) packed with 10% DC 200 on 60–80 mesh Gas-Chrom Q conditioned at 225 °C for 3 days and loaded by several injections of phorate and its metabolites mixed in plant extract. Gas flow rates in ml/min were nitrogen 25, hydrogen 50, and air 240. The column oven temperature was maintained at 190 °C, that of the injector at 210 °C, and the detector at 220 °C. To analyze phorate and its metabolites, all samples were first partitioned into fractions A (phorate and phorate sulfone) and B (phoratoxon and phorate sulfoxide) by liquid

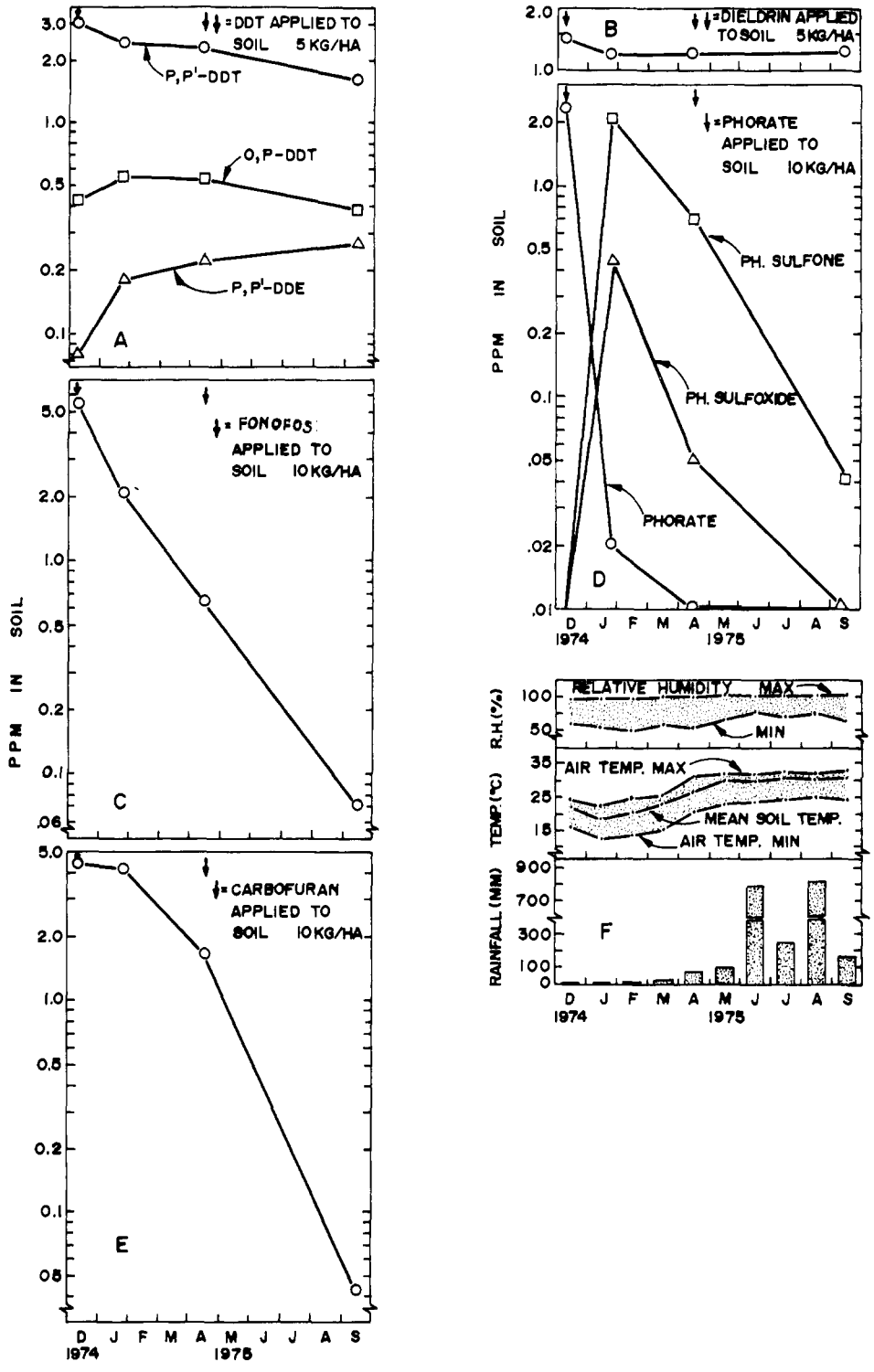

Figure 1. (A–E) Persistence of different insecticides applied during two seasons. (F) Temperature, relative humidity, and rainfall during experimental period.

chromatography (Bowman et al., 1969). The identity of the metabolites in each fraction was confirmed by thin-layer chromatography.

(b) *Thin-Layer Chromatography (TLC).* The insecticides and their metabolites present in the soil at the end of each growing season were confirmed by TLC. Following GLC analysis, except for carbofuran, the solvent extracts were concentrated and analyzed by TLC using standards and solvent systems described in Table I. For carbofuran, soil samples were extracted and chromatographed before making the FDNB derivative. Organochlorines were detected by the method described by Bishara et al. (1972). Organophosphates were detected by spraying the plates with palladium chloride (Blinn, 1963), and carbofuran was detected by the procedures described by Bruce (1972).

RESULTS AND DISCUSSION

Insecticide Persistence in Soil. *DDT and Dieldrin.* The patterns of persistence of these two organochlorines were similar (Figure 1, A and B). During the fall and winter, residues of DDT (para,para' + ortho,para' isomers) declined by only 20%. However, the decline was accelerated during spring and summer. Despite the addition of 5 kg/ha DDT at the beginning of the spring season, the

Table II. Soil Properties of the Land Used for the Experiment

Soil type	Take series silt loam
pH top soil	8.5
sub soil	8.7
Total carbon	0.54%
Total nitrogen	0.07%
C/N ratio	7.7
Sand	35.7%
Silt	40.0%
Clay	16.3%
CEC	7.4
MWHC	36.9
Apparent density	1.45
True density	2.64
Electric conductivity	0.11 mmho

soil residues were found to be lower than before the second application. This is possibly because of the relatively higher temperatures, humidity, and rainfall (Figure 1, E) during these seasons. Although DDT formulations contained 25% ortho,para′ isomer, the recovery of this isomer was consistently lower than 20% of the total DDT. This could be due to higher vapor pressure of this isomer compared to *p,p′*-DDT, thus increasing the possibility of loss by volatilization (Spencer and Cliath, 1972). The concentrations of *o,p′*-DDE were too small to provide data of any significance. As expected, with a decrease in the concentration of *p,p′*-DDT, there was a concurrent increase in the levels of *p,p′*-DDE. TLC (system A, Table I) confirmed the presence of *p,p′*-DDT (R_f 0.39), *o,p′*-DDT (R_f 0.46), and *p,p′*-DDE (R_f 0.53). In addition, traces of TDE (R_f 0.51) and DDA (R_f 0.13) were also detectable when samples were chromatographed using system B.

The decline in the concentrations of dieldrin was 25% in the fall and winter. Addition of 5 kg/ha of this chemical during the following spring did not lead to an accumulation of dieldrin residues in soil. The concentration of dieldrin at the end of summer was virtually identical with its concentration immediately before the treatment. The low recovery immediately after the first treatment is due to a sampling error with freshly rototilled soil. TLC analysis of soil samples by systems C and D confirmed the presence of dieldrin (R_f 0.56 and 0.55, respectively). We could not detect photodieldrin with either of the two TLC systems. However, a compound with R_f 0.50 (system C) and 0.40 (system D) was observed in treated soil samples.

The persistence of these two organochlorines in this subtropical area thus appears to be much shorter than the results obtained under temperate conditions. At this early stage of this experiment, there does not appear to be an additive effect as observed by Lichtenstein et al. (1971) in temperate regions, due to successive application of organochlorine insecticides every season. Based on our results for the fall and winter months, the time required for 50% *p,p′*-DDT to disappear was calculated to be 8 months and that for dieldrin 7.5 months. This period could be considerably shorter for the spring and summer months. Our data show that these organochlorines metabolize rapidly under subtropical conditions. Therefore, in extending the concept of general half-life standards to pesticidal degradation in soil, the exact soil and climatic conditions should be given as they are so variable.

Fonofos and Phorate. These organophosphates degraded very rapidly in soil (Figure 1, C and D). The breakdown of fonofos was relatively slower than that of phorate. Six weeks after the initial treatment, 36% of the applied insecticide was recovered while the recovery was only 8%, 12 weeks later (harvest). After the second application, the degradation was much faster and, by September, barely 0.7% of the total fonofos received by the

Table III. Insecticide Absorption by Sweet Potatoes and White Potatoes from Treated Soil

Season	Crop	Recovered from crops, ppm							
		DDT				Fonofos			
		p,p′-DDT	*p,p′*-DDE	*o,p′*-DDT	Dieldrin	Fonofos	Fonofos-oxon	Phorate sulfoxide	Carbofuran
Fall 1974	Sweet potato[a]	0.15 ± 0.05	0.02 ± 0.01	0.06 ± 0.03	0.07 ± 0.02	0.00	0.00	0.04 ± 0.01	0.02 ± 0.00
	White potato[b]	0.26 ± 0.11	0.03 ± 0.01	0.09 ± 0.07	0.33 ± 0.10	0.10 ± 0.05	0.01 ± 0.00	0.04 ± 0.01	0.01 ± 0.00
Spring 1975	Sweet potato[c]	0.06 ± 0.00	0.02 ± 0.01	0.03 ± 0.00	1.05 ± 0.16	ND[d]	ND	ND	0.04 ± 0.04

[a] Harvested on April 14, 1975. [b] Harvested on March 4, 1975. [c] Harvested on September 15, 1975. [d] ND, not detectable.

soil could be recovered. Fonofos-oxon was not detectable in any of the soil samples. By TLC (system E, Table I), we could detect only fonofos (R_f 0.66).

Only 4% of the initially applied phorate could be recovered 6 weeks after the initial application and the recovery was only 0.4%, 12 weeks later (harvest). As expected with a rapid decrease in phorate concentration, there was a concurrent increase in the concentrations of its metabolites, phorate sulfoxide and sulfone. For example, 6 weeks after the insecticide treatment, the concentration of phorate sulfoxide was 18% and that of phorate sulfone 74%, respectively, of the total measurable phorate derived metabolites that could be recovered. At harvest the proportions of these two metabolites were 6.7 and 92%, respectively, indicating the conversion of phorate sulfoxide to sulfone as outlined by Blinn (1963). Degradation of phorate in summer months was more rapid and measurable quantities of only phorate sulfoxide and sulfone could be recovered. Phorate was detectable but the concentration was too low to provide reliable data of any significance. Phoratoxon could not be detected. Only phorate sulfone (R_f 0.12) could be detected by TLC (system F, Table I).

Carbofuran. The overall persistence of this carbamate in soil was similar to that of fonofos and phorate (Figure 1, E). However, this chemical is more persistent than the organophosphates, especially during the dry and relatively cooler fall and winter months. During the hot, rainy season carbofuran residues degraded as rapidly as that of organophosphates, and only 0.6% of the residues present initially could be recovered as parent compound at the end of the season. This calculation assumes that, during the second treatment, the soil received 5 ppm (10 kg/ha) of this insecticide at the upper 15-cm soil layer. We could not quantitate 3-hydroxycarbofuran and 3-ketocarbofuran due to poor (average 40%) recoveries after derivatization with FDNB. We were able to detect these metabolites and carbofuran by TLC (system G, Table I) at the end of the first growing season only, and carbofuran alone at the end of the second growing season following the second application. The R_f values for these compounds were 0.18, 0.36, and 0.43 for 3-hydroxycarbofuran, 3-ketocarbofuran, and carbofuran, respectively.

The rapid degradation of organophosphates and carbamates is probably due to alkaline reaction of the soil (Table II). The high temperatures, humidity, and rainfall during the spring and summer months (Figure 1, F) in addition to soil alkalinity appear to accelerate the degradation of these chemicals during these months.

In addition to climate, various other factors could have been responsible for the faster degradation of these insecticides in the soil of this humid subtropical region. This initial work did not take into consideration the factors such as soil type, insecticide runoff, microbial degradation, photodecomposition, etc. Because of the potential usefulness of such information, research is underway to determine the contribution of these environmental components in determining the pesticides' persistence.

Insecticide Absorption by Crops. The insecticides were absorbed either as parent compounds or their metabolites by sweet potato and white potato grown in treated soil (Table III). Higher concentrations in soil generally resulted in higher uptake of these chemicals in the plants. White potatoes had higher concentrations of these chemicals than sweet potatoes. This was probably because of the relatively shorter growing period of this crop and its early harvest, while the concentrations of the insecticidal residues were still high in the soil. Dieldrin was detected at greater concentrations in the plant parts than the other insecticides and had a longer persistence in the soil. We failed to detect phorate or phoratoxon in the crops grown in the fall and winter, whereas fonofos and fonofos-oxon were absorbed in measurable quantities. Fonofos-oxon could have been formed within the white potato tubers from adsorbed fonofos. None of the organophosphates or their toxic metabolites were detected in the roots of sweet potatoes grown in the summer. Residues of carbofuran were present in both sweet potatoes and white potatoes grown during the fall and winter and in sweet potatoes grown during the spring and summer. Generally the amounts of residues present in the soil were reflected in the absorption of these chemicals by crops grown in the contaminated soil.

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