Uptake of a PCB (Aroclor 1254) from Soil by Carrots under Field Conditions

by

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Polychlorinated biphenyls (PCB's) are worldwide environmental contaminants, resistant to degradation, subject to biological magnification, and have been reported in human, animal, and bird tissues and in milk. Their properties, production and uses, transport and transformation in the environment, environmental distribution, toxic impurities, biological effects, and analytical methodology have been reviewed (GUSTAFSON 1970, REYNOLDS 1971, FISHBEIN 1972, PEAKALL 1972, and SELIKOFF 1972). The toxicity, metabolic fate, and environmental chemistry of the PCB's are the subject of much current study. Evidence for the ubiquitous distribution of PCB's in water, soils, fish, birds, and mammals continues to accumulate. As the consequences of ingesting and accumulating PCB's by human beings, though known, are not fully understood, and as little is known of the behavior of PCB's in the terrestrial environment, a study to obtain data on the translocation of PCB's from the environment, specifically soil, into food crops was initiated. As carrots are outstanding in their ability to absorb or "scavenge" organochlorine pesticide residues from soil (LICHTENSTEIN 1959, SCHUPAN 1960, LICHTENSTEIN et al. 1965 a and b), the extent and selectivity of translocation of PCB's from soil into carrots were studied. Preliminary results for one carrot crop are reported here, and a detailed report will be made elsewhere when data for several more growing seasons are available.

Experimental

On December 20, 1971, four replicate 10×50 ft field plots separated from each other by untreated buffer strips were treated to a 6 in. depth with 100 ppm of the PCB Aroclor® 1254 (Monsanto Co.) and immediately rototilled. The plots were seeded with carrots on July 31, 1972 with Goldinhart® (Burpee Seed Co.), special strain of Red Cored Chantenay, a variety previously shown (HERMANSON et al. 1970) to be an intermediate scavenger of endrin from soil.

 \underline{Soil} . Each soil sample taken from each plot was a composite of 30 random core samples (6 x 1 in diam.). After each sample was passed through a 2 mm sieve and mixed, soil moisture was determined. Two subsamples of 20 g of oven-dry soil each were extracted without drying by mechanically shaking for 1 hr

with acetone-hexane (1:1) (SAHA $\underline{\text{et}}$ $\underline{\text{al}}$. 1969). A 5% aliquot of each soil extract was cleaned up by column chromatography on Florisil (REYNOLDS 1969).

Carrots. Carrots were selected at random from each plot on October 11 and November 20, 1972, scrubbed using warm water to remove adhering soil particles, then chopped with a food chopper. Each October sample consisted of 68 carrots averaging 21 g each and November samples had 28 carrots each averaging 62 g each. Duplicate 100-g samples of chopped carrots were extracted by blending with acetonitrile (MILLS et al. 1963). Each filtered acetonitrile extract was measured, flooded with water, and extracted twice with hexane. A 2% aliquot of each hexane extract was cleaned up by column chromatography on Florisil (REYNOLDS 1969).

Peeled carrots and carrot peel. Carrots from control plot A and treated plot D were sampled on December 18, 1972; each sample consisted of 20 carrots averaging 92 and 82 g, respectively. The cleaned carrots were peeled with a commercial household vegetable peeler; weight of peel was 14% of total carrot weight. Duplicate 100-g subsamples of peel and chopped peeled carrots were extracted with acetonitrile. The volume of the extract recovered was 91% of the theoretical 280 ml value for all samples. Florisil column cleanup was used on a 0.5% aliquot of the carrot peel and a 50% aliquot of the peeled carrot hexane extracts.

<u>Procedural recovery from carrot extracts</u>. Duplicate carrot root extracts were fortified with $1000~\mu g$ of Aroclor 1254 in 10 ml of hexane. After removing the hexane with a gentle stream of air, the extracts were partitioned with hexane, and an aliquot cleaned up. Recoveries for peaks 1, 4, 5, 8, and 10 (see Fig. 1) were 97, 100, 93, 100, and 97%, respectively. Aroclor 1254, once extracted from the substrate, can be quantitatively partitioned into hexane and recovered from the Florisil column.

<u>Gas chromatography</u>. Samples were analyzed using an electron-capture (tritium) detector. A $5\frac{1}{2}$ ft x 2 mm ID borosilicate column packed with a 1:1 mixture of 10% DC-200 and 15% QF-1, each coated on 60/80 mesh Gas Chrom Q, was used with nitrogen carrier gas flow rate 30 ml/min. Injector, column, and detector temperatures were 230, 185, and 205°C, respectively.

Quantitation was by peak height using standard curves and the average of duplicate injections. As PCB's are complex mixtures of compounds, each gas chromatographic peak (see Fig. 1) did not necessarily represent a single compound, and thus individual standards could not be used. Standard curves were constructed for each of five selected peaks of the Aroclor 1254 chromatogram by plotting peak height vs quantity of PCB injected onto the column. Peaks quantitated (see Fig. 1) were 1, 4, 5, 8, and 10.

The meaning of "ppm" for a sample containing unaltered Aroclor 1254 is straightforward, but once the PCB composition is altered, "ppm" loses its meaning. Also, "ppm" for a single peak is meaningless as to conventional usage. Here, \underline{X} ppm of PCB as determined by peak \underline{Y} simply means that \underline{X} ppm of standard (unaltered) PCB must be in the sample to furnish the same amount of material that makes up peak \underline{Y} as is present in the sample.

PCB's in soil samples were quantitated by direct comparison to Aroclor 1254 standards. PCB's in carrot samples were quantitated by first quantitating one sample of carrot extract by direct comparison to Aroclor 1254 standard and then using the sample as a secondary standard. No corrections for background, as determined from control samples, were necessary.

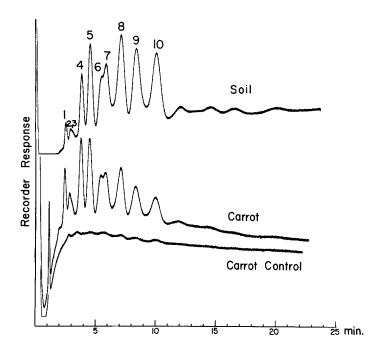


Fig. 1--Electron-capture gas chromatogram of extractives from 40 μg of field-treated soil, 400 μg of carrot root grown in field-treated soil, and 400 μg of carrot root grown in untreated field soil.

Results and Discussion

Quantitation of the PCB residues in soil using each of five selected gas chromatographic peaks (see Fig. 1) gave the results in Table I.

Table I. Aroclor 1254 Residues in Field-treated Soil.

	2/	Gas Chromatographic Peak Used						
	Date sampled ^{a/}	1	4	5	8	10		
Plot	(1972)	ppm ^b /						
A	Jan. 18	79	83	84	85	85		
	Aug. 15	79	86	88	91	94		
	Oct. 11	75	79	82	92	91		
	Nov. 22	67	73	75	85	89		
В	Jan. 18	53	55	56	5 7	59		
	Aug. 15	59	62	64	67	69		
	Oct. 11	39	49	50	60	61		
	Nov. 22	44	52	53	60	63		
С	Jan. 18	97	103	104	104	104		
	Jul. 26	74	80	82	84	85		
	Oct. 11	76	89	89	101	100		
	Nov. 22	74	82	85	91	93		
D	Jan. 18	83	89	88	94	94		
	Jul. 26	58	63	65	67	69		
	Oct. 11	66	74	77	85	84		
	Nov. 22	61	70	73	80	82		

 $[\]frac{a}{1}$ Soil treated on Dec. 20, 1971, with 100 ppm.

If the Aroclor 1254 recovered from the soil is unchanged in composition, then the ppm value for a sample is independent of the quantitating gas chromatographic peak. One month after soil application the PCB residue as quantitated by each of five chromatographic peaks is essentially the same. However, the residue as quantitated by peak 10 is 8 ± 2 ppm greater than by peak 1 indicating that a slight alteration in the relative amounts of PCB isomers has occurred. This difference increased to 12 ± 2 ppm after about $7\frac{1}{2}$ months, and after 10 and 11 months was 20 ± 4 and 20 ± 2 ppm, respectively. The lesser chlorinated biphenyls represented by peak 1 disappeared from the soil faster than the greater chlorinated biphenyls. This trend is seen to a lesser degree by comparing peak 10 with peaks 4, 5, and 8.

Although relative changes in composition were demonstrated, the PCB residue represented by peak 10 did not appear to diminish with time. Residue variations of peak 10 determined for a given plot are attributed to irregularities in the plot resulting from uneven application and subsequent incomplete mixing of the treated surface soil into the lower layers (TAYLOR et al. 1971). If the concentration of peak 10 is unchanged over the 11-month period studied, the concentration of peak 1 in the soil decreased by 25±4% over the same period.

Expressed as ppm equivalent of Aroclor 1254 unaltered in composition. Dry soil. Average of duplicate samples.

Table II. Aroclor 1254 Residues in Carrot Roots Grown in Field-treated Soil.

		Gas Chromatographic Peak Used						
	Date sampled ^a /	1	4	5	8	10		
Plot	(1972)	ppm ^b						
A	Oct. 11	30	16	12	6.6	3.6		
	Nov. 20	21	12	7.2	5.5	3.1		
В	Oct. 11	22	12	8.7	5.3	2.7		
	Nov. 20	14	7 . 5	5.5	3.7	2.0		
С	Oct. 11	42	22	16	8.7	4.4		
	Nov. 20	22	13	8.7	6.0	3.1		
D	Oct. 11	30	16	12	7.0	3.7		
	Nov. 20	15	9.2	6.7	4.6	2.6		

Carrots seeded on July 31, 1972.

Comparison of the data for carrot roots given in Table II for the two sampling dates show that the "ppm" residue level in the November sample decreased to 66±10% of that of the October sample. However, since the average weights of the October and November carrots were 21 g and 62 g, respectively, the total quantity of PCB per carrot approximately doubled during the 40-day sampling interval. The lesser chlorinated biphenyls are clearly translocated to a greater degree from the soil into the carrot root. The ratio of the "ppm" values of peak 1:peak 10, peak 4: peak 10, peak 5:peak 10, and peak 8:peak 10 are 8.6±0.7, 4.6±0.3, 3.3 ± 0.2 , and 1.9 ± 0.1 , respectively, for October samples and 6.7 ± 0.6 , 3.9 ± 0.3 , 2.6 ± 0.2 , and 1.9 ± 0.1 , respectively, for November samples. Thus, material composing peak 1 was absorbed at seven to eight times the rate of that from peak 10. This information is quite important if the lesser chlorinated biphenyls are demonstrated to be the more toxic compounds of the PCB mixtures. Little is known concerning the effect of degree of chlorination on lethality for mammals, although toxicity probably increases with the degree of chlorination (HAMMOND and NISBET 1972). Since different batches or sources of PCB's of similar degree of chlorination seem to vary as to potency, interpretation and comparison of toxicological studies in the literature are difficult.

To determine the distribution of the PCB residues in the carrot root, peel and peeled carrot were analyzed separately. Residue levels in the peel for peaks 1, 4, 5, 8, and 10 were 106, 65, 47, 33, and 19 ppm, respectively. The corresponding values for the peeled carrot were 0.55, 0.32, 0.23, 0.15, and 0.09 ppm, respectively. Thus, the carrot peel, comprising 14% of the carrot weight, contained 97% of the PCB residues; this situation has often been observed for DDT and other organochlorine compounds in soil in which carrots are grown.

Expressed as ppm equivalent of Aroclor 1254 unaltered in composition. Fresh weight of carrot root. Average of duplicate samples. Corrected for PCB's theoretically lost due to extract unrecovered from carrot pulp filter cake.

Calculation of the percentages for the various peaks present in carrot roots with respect to the surrounding soil for peaks 1, 4, 5, 8, and 10 gave 50 ± 8 , 23 ± 2 , 17 ± 1 , 8.2 ± 0.7 , and $4.3\pm0.2\%$, respectively, for October samples and 30 ± 3 , 15 ± 2 , 9.9 ± 0.6 , 6.3 ± 0.3 , and $3.3\pm0.2\%$, respectively, for November samples. Thus, the residue level of peak 1 in one gram of carrot root is 30-50% that found in an equal weight of surrounding soil, while the residue of peak 10 in carrots is only 3-4% that of the surrounding soil. Greater absorption of residues would be expected from soil containing PCB's such as Aroclor 1221 which has a larger proportion of lesser chlorinated biphenyls.

Summary

The change in composition of Aroclor 1254 in soil was evident over an eleven-month period. Dissipation appeared to parallel the degree of chlorination. The lesser chlorinated biphenyls were slowly dissipated while the more highly chlorinated biphenyls were not appreciably affected. PCB's were absorbed by carrot roots; increasing translocation was associated with decreasing biphenyl chlorination. Since 97% of the residue was found in the peel, very little translocation occurred in the plant tissue.

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References

FISHBEIN, L., J. Chromatog. 68, 345(1972).

GUSTAFSON, C. G., Environ. Sci. Technol. 4, 814(1970).

HAMMOND, P. B., and I.C.T. NISBET, Environ. Res. 5, 249(1972).

HERMANSON, H. P., L. D. ANDERSON, and F. A. GUNTHER, J. Econ. Entomol. 63, 1651(1970).

LICHTENSTEIN, E. P., J. Agr. Food Chem. 7, 430(1959).

______, and K. R. SCHULZ, <u>Ibid</u>. <u>13</u>, 57(1965a).

G. R. MYRDAL, and K. R. SCHULZ, <u>Ibid</u>. <u>13</u>, 126(1965b).

MILLS, P. A., J. H. ONLEY, and R. A. GAITHER, J. Assoc. Offic. Anal. Chemists 46, 186(1963).

PEAKALL, D. B., Residue Rev. 44, 1(1972).

REYNOLDS, L. M., Bull. Environ. Contam. Toxicol. 4, 128(1969).

______ Residue Rev. 34, 27(1971).

SAHA, J. G., B. BHAVARAJU, Y. W. LEE, and R. L. RANDELL, J. Agr.

SAHA, J. G., B. BHAVARAJU, Y. W. LEE, and R. L. RANDELL, J. Agr. Food Chem. <u>17</u>, 877(1969).

SCHUPAN, W., Z. \overline{Pf} lanzenkr. Pflanzenpathol. Pflanzenschutz $\underline{67}$, 340(1960).

SELIKOFF I. J., ed., Environ. Res. 5, 249(1972).

TAYLOR, A. W., H. P. FREEMAN, and W. M. EDWARDS, J. Agr. Food Chem. 19, 832(1971).